The British Plastics Federation
Reinforced Plastics Group

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Sixth International Reinforced Plastics Conference

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PLASTICS TECHNICAL EVALUATION CENTER
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The Royal Garden Hotel

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Sixth International Reinforced Plastics Conference

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13-15 November 1968

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The British Plastics Federation
Reinforced Plastics Group

The BRITISH PLASTICS FEDERATION is the representative body of the Plastics Industry. It co-ordinates the efforts of its members to expand trade, both at home and overseas, by providing a forum in which technical standards for plastics are prepared and other matters of technical and commercial interest discussed. It also advises Government Departments on matters relating to plastics.

The activities of the British Plastics Federation are undertaken by twelve groups, each dealing with a specific aspect of the plastics industry. A group for Reinforced Plastics was established in 1958.

Reinforced Plastics have achieved prominence as strong lightweight materials with unique moulding characteristics and properties which clearly distinguish them from other plastics. The British Plastics Federation, as early as 1952, set up a technical committee on glass fibre and asbestos reinforced plastics to cater for the problems of this new industry. As the industry expanded, the committee grew until it necessitated the formation of a group.

The aim of the REINFORCED PLASTICS GROUP is to promote in every way the interests of the industry:

1. By tackling technical and commercial problems associated with raw materials, fabrication and machinery.

2. By co-operating with outside agencies (e.g. Government Departments and other organisations) in the use of reinforced plastics.

3. By establishing and maintaining good relations with the press to promote an adequate supply of informed publicity.

4. By the encouragement of research to widen the knowledge of the behaviour of reinforced plastics and to establish design criteria.

Any British manufacturer concerned with Reinforced Plastics is eligible for membership. The Group includes over seventy moulders, synthetic resin, asbestos, glass fibre and ancillary materials suppliers, and machinery manufacturers.

The technical work of the Group is undertaken by the Technical Committee to which all members of the Group are entitled to send representatives. Thus it is a committee fully representative of the various elements that make up the Reinforced Plastics Industry. The Technical Committee appoints sub-committees to deal with specific matters and currently topics such as specifications for laminates, methods of testing, design data, reinforcing fillers, dough moulding compounds and fire performance are being studied. In all its technical work the Group is aided by co-opted representatives from appropriate Government Departments and other authorities. The Group gives assistance to the British Standards Institution and to other official bodies in the preparation of standards or codes of practice.

The Group Technical Committee organises biennially an International Conference on Reinforced Plastics which has become recognised throughout the world for its contribution to progress in the Industry. On other occasions informed discussion meetings are held for Group members only.

Membership of the Reinforced Plastics Group of the British Plastics Federation provides the opportunity:

1. To have access to the full resources and share in the activities of the British Plastics Federation, and its publicity and opportunities for business.

2. To share in the combined knowledge of the members of the group.

3. To contribute to the preparation of standards and design data for the Industry through which public confidence in reinforced plastics can be upheld.

4. To join with the rest of the industry to expand trade in Reinforced Plastics.

5. To attend the various technical functions of the group.

6. To belong to the only National trade association concerned with Reinforced Plastics.

Programme

WEDNESDAY 13 NOVEMBER

9.00 a.m. Opening of the Conference.—*J. E. Swainson, Permali Ltd.*, Chairman of the Reinforced Plastics Group.
Conference Chairman—*S. R. Badley, BP Chemical (U.K.) Ltd.*

Session 1
Applications—Building, Transport, Engineering (Mechanical, Electrical and Chemical).

Pl-26232 Paper 1
Container testing and use of plastics in containers—*H. F. MacSwiney* and *E. R. Copage, Military Engineering Experimental Establishment.* — 01

Pl-26233 Paper 2
Unsaturated polyester resins in the building industry— *W. Kloeker, Farbenfabriken Bayer AG,* Germany. — 02

Pl-26234 Paper 3
Glass fibre reinforced plastics in building—present situation in Italy and needs for further development—*G. de Luca, R. Fulgini, Vetreria Italiana,* Balzaretti Modigliani, Italy. — 03

Discussion.

Coffee.

Pl-26235 Paper 4
Utilisation of organic fibres produced from sugarcane residue (Bagasse) in the moulding and the manufacture of reinforced plastics products—*R. Botz, R. Botz & Assoc. Inc.*, Puerto Rico. — 04

Pl-26236 Paper 5
Uni-directional glass fibre loops for electrical application—*W. A. Tillott* and *D. J. Meadows, GEC-AEI Engineering Ltd.* — 05

Pl-26237 Paper 6
Development of the pultrusion processes—*G. Kannebley, Grillo-Werke Aktiengesellschaft,* Germany. — 06

Discussion.

Lunch.

Session 2
Overseas Reports
This Session will include summaries and pictorial presentations of reports to be included in the bound volume of papers from the following countries:

Czechoslovakia
Holland
Israel
Italy
United States of America
West Germany
United Kingdom

Further contributions to this Session are being arranged and intending delegates from countries not included above who wish to make a contribution on behalf of their national industry should contact Mr. J. D. H. Pugh at the Federation.

5.30 p.m. Session Ends.

THURSDAY 14 NOVEMBER

9.00 a.m. Session 3
Product Development and Processes

PI-26238 Paper 7
The Vanadium-accelerator for unsaturated polyester resins—*S. Abrahami* and *R. Wachs*, *Makteshim Chemical Works* Ltd., Beersheva, Israel. -07

PI-26239 Paper 8
Long term water immersion tests on cured unsaturated polyester casts and laminates—*H. Williams*, *BP Chemicals (U.K.) Ltd.* -08

PI-26240 Paper 9
The study of the polymerization of a resin by means of a dilatometer—*J. Durand*, *Societe du Verra Textile*, Chambery, France. -09

PI-26241 Paper 10
Various organic/inorganic composites and the effect of silane coupling agents on their properties—*L.P. Ziemianski*, *Union Carbide Corp.*, New York, U.S.A. -10

PI-26242 Paper 11
A review of D.M.C. technical knowledge, its application and process in the field of glass reinforced plastics—*F. Parker*, *BIP (Chemicals) Ltd.* -11

9.50 a.m. Discussion

Coffee

PI-26243 Paper 12
The reinforcement of thermoplastics matrices with fibres—*J. H. Davis*, *Imperial Chemical Industries Ltd.*, Plastics Division. -12

PI-26244 Paper 13
Advances in glass fibre fabrics for plastics reinforcements—*Chas. E. Knox*, *Uniglass Industries*, United Merchants, New York, U.S.A. -13

PI-26245 Paper 14
Application of wire sheet in reinforced plastics—*H. D. de Pauw Gerlings* and *R. H. Stretton*, *National Standard Co. Ltd.* -14

PI-26246 Paper 15
Preimpregnated glass mats—*E. R. Huband*, *Turner Bros.*, *Asbestos Co. Ltd.* -15

Discussion.

Lunch

2.45 p.m. Session 4
Marketing and Promotion

Paper 16
The philosophy of marketing—*R. Collischon*, *The Institute of Marketing.*

Paper 17
The principles and practice of managing with particular reference to small companies and how these techniques can be satisfactorily used in a small organisation—*A. E. B. Perrigo*, *Small Business Centre*, University of Aston, Birmingham.

3.15 p.m. Tea.

3.45 p.m. Paper 18
Marketing of reinforced plastics—*E. Shankleman*, *Marketing and Economic Research Ltd.*
(A fuller version of the paper will be available as a loose insert.)

PI-26247

Paper 19
The development, production and sale of a reinforced plastics hot water storage cistern— —16
R. A. Richardson, Osma Plastics Limited.

Discussion

Session Ends

Conference Dinner—Guest Speaker, *Sir Edwin Leather.*

FRIDAY 15 NOVEMBER

Session 5
Research, Development and Testing.

Paper 20
PI-26248 Carbon fibres as high modulus reinforcements—*J. J. Stobo, L. M. Fitzgerald* and *D. R. Lovell,* —17
Morganite Research & Development Ltd.

Paper 21
PI-26249 Measurement of Mechanical properties at temperatures down to 4·2°K—*D. Evans, J. T. Morgan,* —18
R. Sheldon and *G. B. Stapleton, Science Research Council, Rutherford High Energy Lab.*

Paper 22
PI-26250 The determination of allowable wall stress for glass reinforced plastics pipe by measurement —19
of elastic deformation—*H. M. Schwencke, A. W. de Ruyter van Steveninck, Shell Plastics Laboratory,* Delft, Holland.

Discussion

Coffee

Paper 23
PI-26251 The wetting of glass fibres by polyester resins—*R. H. Peters, E. F. T. White* and *G. Inverarity,* —20
University of Manchester Institute of Science and Technology.

Paper 24
PI 26252 Investigations on the possibility of application of thick glass fibre for the manufacture of —21
high strength glass reinforced plastics—*E. F. Zelenski, A. Kogan, I. Petrova, A. M. Cuperman* and *G. C. Andreyevskaya, Institute of Chemical Physics,* Moscow, U.S.S.R.

Paper 25
PI-26253 The adhesion of certain polymers to glass fibres surfaces—*G. D. Andreavska, U. A.* —22
Gorgatkina and *V. G. Ivanova-Mumjieva, Institute of Chemical Physics,* Moscow, U.S.S.R.

Paper 26
PI-26254 Glass rods for reinforcements of plastics—*V. A. Ryabov* and *D. Fedoseev, Institute of Chemical* —23
Physics, Moscow, U.S.S.R.

Paper 27
PI-26255 The progressive nature of fatigue damage in glass reinforced plastics—*T. R. Smith,* and —24
M. J. Owen, Dept. of Mechanical Engineering, University of Nottingham.

Directing research in reinforced plastics—*N. G. MacCleod, Imperial Chemical Industries Ltd.*

Closing address—*J. E. Swainson,* Chairman, *Reinforced Plastics Group.*

Conference Ends.

Sixth International Reinforced Plastics Conference 1968

Delegates wishing to participate in the "Discussion Sessions" following the presentation of papers, will find a printed Question Form following each paper in this book. This will enable Delegates to present their questions well in advance, and also will enable delegates to be more readily prepared when they are called upon to put forward their questions.
The blue Question Forms should be submitted, either to Mr. J. D. H. Pugh, British Plastics Federation, 47 Piccadilly, London, W.1, prior to the Conference, or to Mr. Pugh or other Members of the Conference Staff on duty at the Royal Garden Hotel. Delegates returning their Question Forms at the Conference are requested to do so not later than the beginning of the Session which precedes the Session in which they wish to participate.

Container testing and use of plastics in containers 1

H. F. MACSWINEY and E. R. COPAGE, Military Engineering Experimental Establishment

INTRODUCTION

In writing a paper on the testing of containers, the authors would be wrong if they did not declare their authority for writing the paper, clarify their source of information and indicate their own limitations. The authors are of the staff of the Military Engineering Experimental Establishment (MEXE), Christchurch, Hampshire, which is one of the research and development establishments of the Ministry of Defence. Their duties are associated with developing full-scale prototype equipment in the Bridging and Structure field, and freight containers come within this category. Their experience of the latter is limited to one year; however, MEXE have been testing containers since April 1966. From time to time the authors have both been co-opted members of the British Standards Institution Committee 163/2 on the testing and dimensioning of containers and representatives of the Working Group 'C' of the International Standards Organization (ISO) TC 104 on the related subject. The sources of information are those generally available through published technical literature, experience gained in testing of some 40 containers of 20 individual firms and attending technical committees. Certain firms have co-operated in giving information about their containers and an acknowledgment to them is included.

Finally, every endeavour has been made to verify the facts as far as possible. The opinions expressed are those of the authors and do not necessarily reflect the views of the organization for which they work or the professional bodies to which they belong.

The main points to be covered by the paper will be:

Part 1 A short history of the container revolution and the evolution of testing;

Part 2 A description of the types of containers currently being tested;

Part 3 & 4 British Standards tests and the way in which they are performed at ~~MEXE~~.

Part 5 Some aspects of the typical design and views on the materials in use;

Part 6 Some aspects of the container development and their requirement for testing.

PART 1 — HISTORY

The container and the testing of it is not a new concept. From the earliest days of the movement of goods from place to place there have developed rules for safety, product protection, Customs and Excise and handling. These rules have been as loose or as binding as deemed necessary by the parties concerned or by national or international bodies. The development of transport of one media has not always been in the best interests of the others, so also with the movement of freight within one media and where it has to be trans-shipped to an alternative. The influence of size, weight and shape is often dictated by cost and physical limitations and not by considerations of compatibility has resulted in trade and development being severely restricted. One notable example of this was the virtual strangulation of the development of the Hawaiian islands in the early 1950's by the conventional trans-shipment in cargo ships of all the materials required in that group of islands. Here, containerisation was a complete solution and, as such, was the forerunner of the thoughts on the Atlantic bridge, the Australia run, etc. and these are reflected in the shorter and more parochial European and national trade routes. These things do not just happen, they are the logical development of existing techniques, but for all that, they would not happen unless they were feasible, practicable, profitable and highly acceptable by the users.

By the end of the 1950's, three major operators and possibly many small ones had gained a great deal of experience, and it was from this experience that many other countries drew their first inspiration and individual nationals their first lesson in what was hailed as the revolution in transport methods. The adaptation of the cellular ship principles, developed by the United States, has been copied by most countries. From the revolution came many attempts at designing transfer systems in order to simplify the exchange between various forms of transport. Out of this requirement for various reasons came the more acceptable system of lifting from the top rather than the bottom or the ends. The top lift most readily met the requirement to stack on ships, in ships, on the quay and transfer between vehicles.

At this point, it is worth reflecting that a case was developing for international standards both of dimensions and for safety. In 1960, with this in view, the Engineering Equipment Users' Association submitted to the British Standards Institution a proposal on the interchangeability of freight containers between land, sea and air transport. Recognizing the international significance of this proposal, BSI set up a committee—MEE. 163 to consider the proposal within the United Kingdom but also submitted a proposal to the International Standards Organization (ISO). The first ISO meeting on freight containers' standards was held in New York in September 1961, where outline proposals were drafted. TC 104 is the current ISO technical committee charged with this responsibility, and BSI have endeavoured to ensure that its work in this field has been closely co-ordinated with ISO.

In the national sphere, BSI drew up a draft specification B/65/207 which was subsequently published as BS. 3951 and re-drafted in the light of subsequent ISO meetings, in particular, Moscow 1967 to the present BS. 3951 of 1967—'the Specification for Freight Containers,' and a further BS. 4228 on 'the Specification of Corner Fittings of Freight Containers'. The activities of BSI reflected the United Kingdom interest in containerisation. British Railways introduced the first liner trains in 1966 whilst Lloyd's Register of Shipping took an active part setting up the framework of their type approval scheme. The activities of the transport industry have not gone unobserved by the British Government who have been active in joining together the interested parties under the auspices of the Ministry of Technology. Out of the discussions emerged the freight container approval scheme under H.M. Factory Inspectorate of the Department of Employment and Productivity. When agreement on standards for containers had been reached, manufacturers were concerned to get their design prototypes tested.

Various organizations concerned with structural testing became actively engaged in building test rigs specifically for containers. In this, MEXE was fortunate to have a very large Bridge Test Rig, and therefore was one of the early participants. As early as April 1966, MEXE had carried out the range of tests prescribed at that time. Recommendations were put to British Standards from Industry and the test stations following the earlier and subsequent tests. Certain of the recommendations were agreed at ISO meetings and these formed the current British Standard. They are now being applied to those containers intended to travel from the United Kingdom to countries abroad.

PART 3 — TYPES OF CONTAINERS

From the most cursory observation of the shipping ways and the railways of the World, there has been little standardisation in size, weight and shape of container. With the advent of ISO containers a new concept in standard was achieved. The ISO Series 1 container is based on an 8 ft × 8 ft (2435 mm × 2435 mm) section of varying lengths while the ISO 2 container covers a variety of sections, lengths and ratings. The dimensions and ratings for type 1 and 2 are in Table 1. The British Standard type E is ISO type 2B.

TABLE 1

Actual dimensions, permissible tolerances and ratings

Freight container designation	Height				Width				Length				Rating tonnes*
	Tolerances mm	mm	Tolerances ft-in	in	Tolerances mm	mm	Tolerances ft-in	in	Tolerances mm	mm	Tolerances ft-in	in	
1A	2435	+3 −2	8	0 −3/16	2435	+3 −2	8	0 −3/16	12190	+2 −8	40	0 −3/8	30
1B	2435	+3 −2	8	0 −3/16	2435	+3 −2	8	0 −3/16	9125	0 −10	29' 11.25"	0 −3/8	25
1C	2435	+3 −2	8	0 −3/16	2435	+3 −2	8	0 −3/16	6055	+3 −3	19' 10.50"	0 −1/4	20
1D	2435	+3 −2	8	0 −3/16	2435	+3 −2	8	0 −3/16	2990	+1 −4	9' 9.75"	0 −3/16	10
1E	2435	+3 −2	8	0 −3/16	2435	+3 −2	8	0 −3/16	1965	+3 −2	6' 5.50"	0 −3/16	7
1F	2435	+3 −2	8	0 −3/16	2435	+3 −2	8	0 −3/16	1460	0 −3	4' 9.50"	0 −1/8	5
2A	2100	0 −5	6' 10.50"	+3/16 0	2300	0 −5	7' 6.50"	+3/16 0	2920	0 −5	9' 7	0 −3/16	7
2B	2100	0 −5	6' 10.50"	+3/16 0	2100	0 −5	6' 10.50"	+3/16 0	2400	0 −5	7' 10.50"	0 −3/16	7
2C	2100	0 −5	6' 10.50"	+3/16 0	2300	0 −5	7' 6.50"	+3/16 0	1450	0 −5	4' 9	+1/16 −1/8	7

* 1 tonne = 1000 kg = 2240 pounds (the difference of 1.6% can be neglected).

Within each of these specified dimensions and ratings there are or will be a container to carry out specific functions.

Type of container	Function
Non insulated	for general cargo, waterproofed
Lightly insulated	for perishable and to prevent cross infestation
Heavily insulated	for refrigerated cargo
Tankage	for bulk liquid
Open structures including collapsible	for cargo requiring no protection.

Within these definitions there will be containers designed to meet the requirements for a particular transporter or the produce being transported. Much will depend on the intended use of the container and the ability for it to be used fully on a return journey.

The proposed recommendations to ISO on the lightly, partially or normally insulated container will be:

Type 1A 43k cal/h°C 94 BTU/h°F

Type 1B 33k cal/h°C 72 BTU/h°F

Type 1C 23k cal/h°C 50 BTU/h°F

Type 1D 14k cal/h°C 30 BTU/h°F

At present there are no recommendations on refrigerated containers, but the manufacturers' quoted figure of 30 BTU/h °F for the type 1C would appear to be about the standard. This will, however, be a compromise between insulation and coolant plant capacity and will depend on the degree of refrigeration.

The facts and figures given in this summary are not intended to be complete, but are necessary to provide the background to the range of equipment likely to be requiring testing under the present and future regulations.

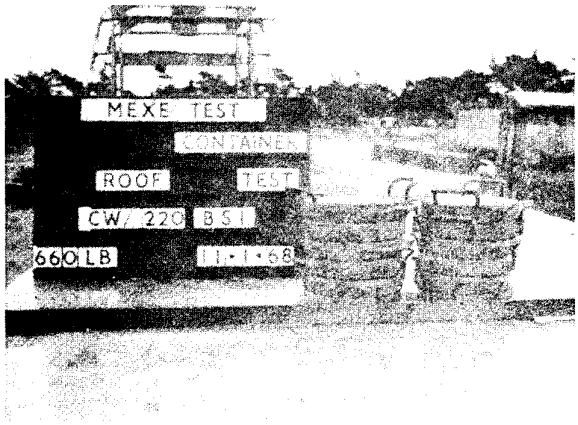
PART 3 — DETAILS OF TESTS

The authors would now like to introduce a brochure which is currently being used by them. It is in an extract from BS. 3951/67 and lays down the criteria for testing any of Series 1 type containers. The pictures in the brochure are those which will be described in Part 4 of the typical tests at MEXE.

MEXE carried out the full range of British Standard Tests to BS. 3951/67 on the 20 ft ISO Type 1C container. The strength tests to the requirements of Lloyd's Register of Shipping, and the ISO can also be covered. In addition to the standard tests, MEXE will undertake special advisory Tests as requested by manufacturers.

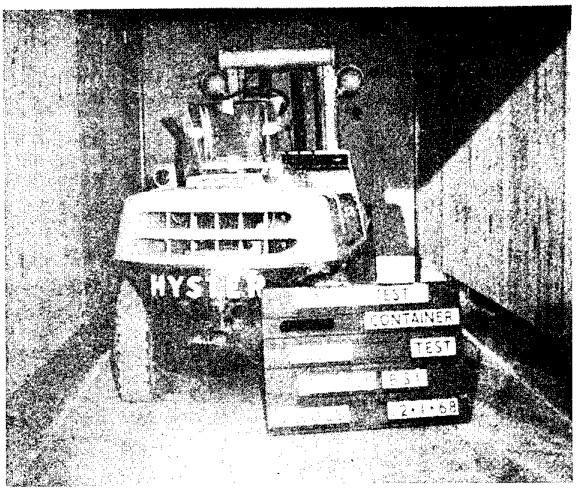
The Container Test Station has been set up at MEXE to provide a service to industry through the co-operation of the Ministry of Defence and the Ministry of Technology. The tests are carried out by a skilled staff trained in full scale structural testing and paid for by individual companies on a contractual basis.

This brochure described the nine tests laid down in BS. 3951/67 which operate at the date of this publication.



TEST NO. 1 Roof strength

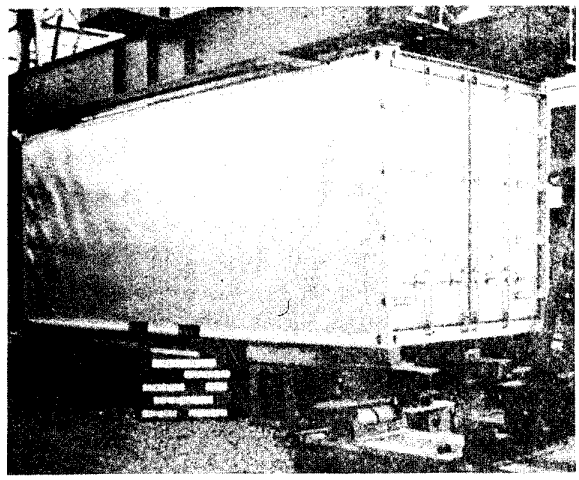
This procedure applies to all freight containers. A concentrated load of 300 kg (660 lb) shall be uniformly distributed over an area of 60 cm × 30 cm (2 ft × 1 ft) located so as to give the worst possible loading conditions on the container roof.



TEST NO. 2 Floor strength

An industrial truck loaded and of axle dimensions as follows shally be manoeuvred over the entire floor area of the freight container in a longitudinal direction.

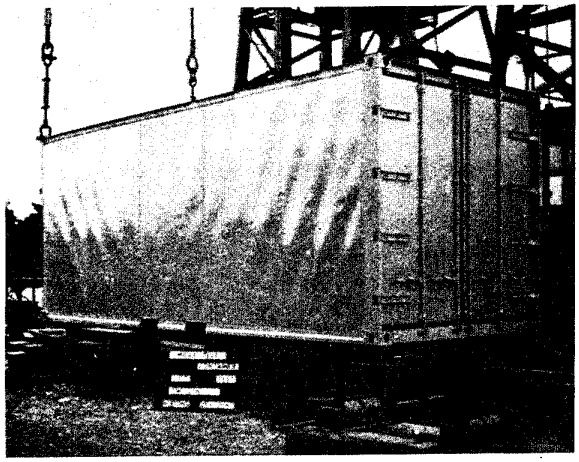
The specification of test load is to be an axle weight of not less than 5460 kg (12000 lb) including the weight of the truck, or 2730 kg (6000 lb) per wheel applied to a contact area not greater than 142 sq cm (22 sq in), assuming a wheel width of not less than 180 mm (7 in) and wheel centre of 760 mm (30 in).

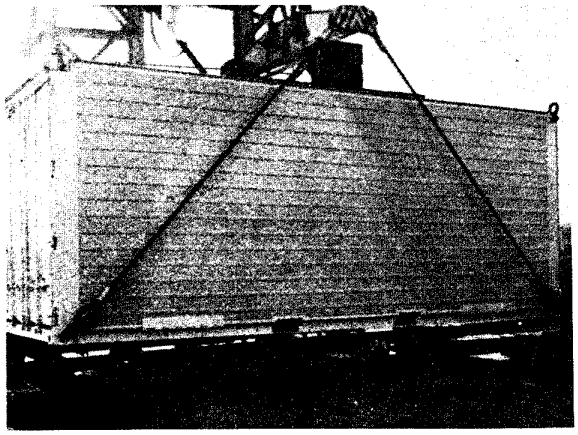


TEST NO. 3 Stacking

The freight container under test shall be placed on four level pads, one under each bottom corner fitting or equivalent corner structure. The pads shall be centralized under the fittings and be substantially of the same plan dimensions as the fitting. The container shall be loaded to 1.8 × R where R is the rated capacity of the container.

The container under test shall be subjected to a load of 9 × R applied through four pads of the same plan area as the corner fittings, and each containing a hole of the same dimensions and position as that in the bottom corner fittings. The load shall be equally divided among the four corner fittings. Each pad should be offset in the same direction by 25.4 mm (1 in) laterally and 38 mm ($1\frac{1}{2}$ in) longitudinally to give the worst conditions of loading.



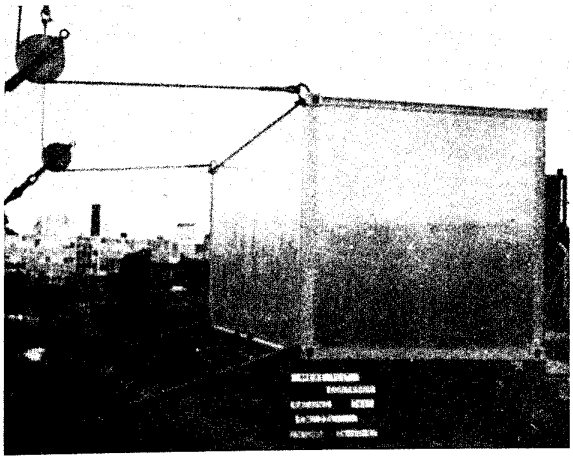


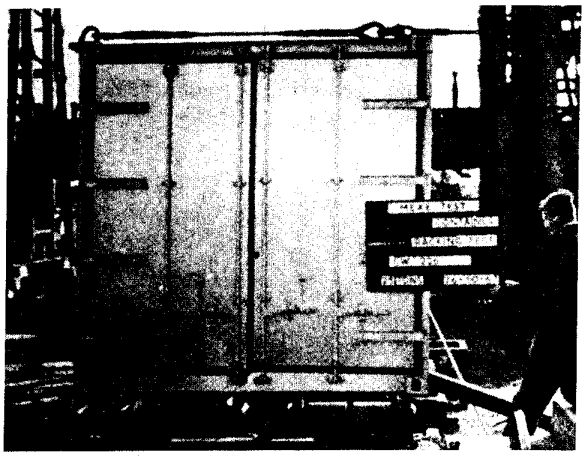
TEST NO. 4 Lifting

Procedure 1. The freight container under test shall be loaded to 2 × R and lifted vertically from all four top corners. After lifting, the container shall be suspended for not less than 5 min and then lowered to the ground.

Procedure 2. The container under test shall be loaded to 2 × R and carefully lifted from all four bottom corners in such a way that no noticeable acceleration or deceleration forces are applied. The lifting forces shall be applied using one spreader above the roof. The angle of the lifting force shall be 30° from the horizontal.

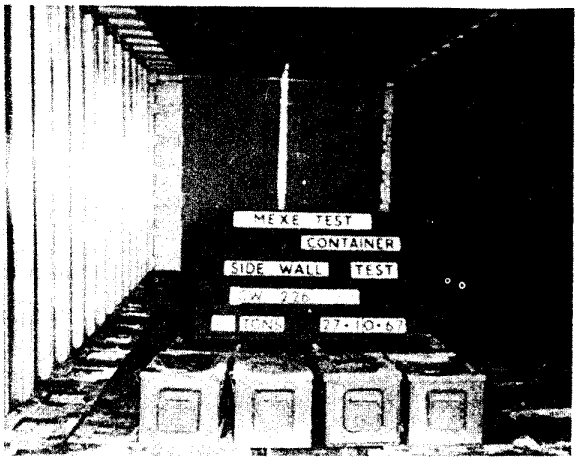
After lifting, the container shall be suspended for not less than 5 min and then lowered to the ground.





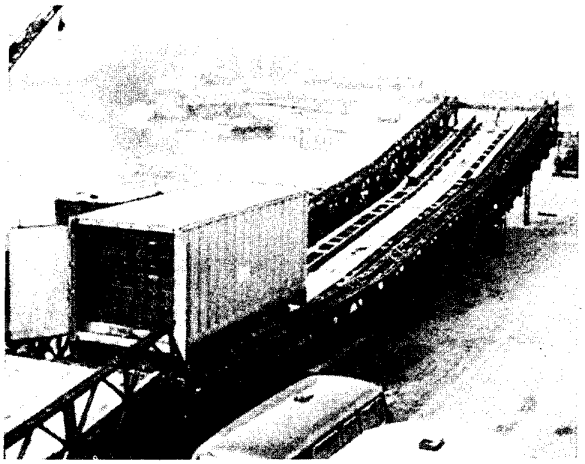
TEST NO. 5 Racking

The container under test shall be loaded to 1.25 × R, and shall be supported by pads underneath each bottom corner fitting, all the pads lying in the same horizontal plane. Equal forces shall be gradually applied to the two top corner fittings on one side of the container to put the top end rails into tension. Their line of action shall be horizontal and in the same plane as the ends of the container. The bottom of the container shall be restrained against horizontal movement by means of stops bearing against the sides of the bottom corner fittings. The magnitude of the applied forces shall be just sufficient to lift the bottom corner fittings on one side of the container clear of their supporting pads. The forces shall be removed gradually. The test shall be repeated putting the top end rails into compression.



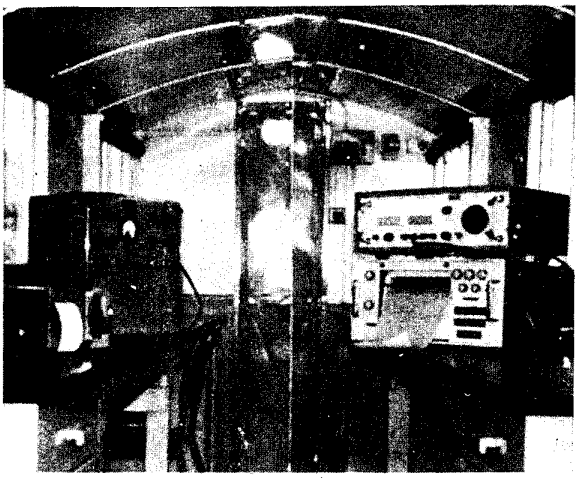
TEST NO. 6 Side wall strength

The freight container shall be loaded to 1.25 × R with material which as far as possible occupies the whole internal capacity. By suitable means the container shall be tilted to one side to an angle of 45°. If the side walls of the container differ in construction the test shall be repeated with the container tilted to the other side to an angle of 45°. The above procedure is also considered to be met if a side loading equivalent to 0.6 × P is applied by mechanical means. Where P is the pay load. P = R − T where P is pay load: R is the rating and T is the tare weight of an empty container.



TEST NO. 7 Restraint (dynamic)

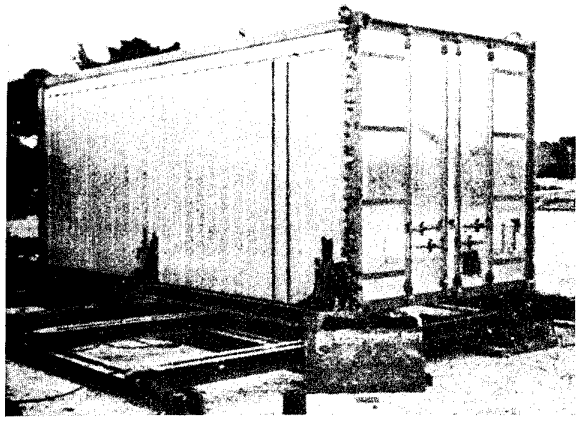
Procedure 1. The freight container, loaded to 1.25 × R with material which as far as possible occupies the whole internal capacity shall be accelerated or decelerated in a manner which will subject it to 2 g effective horizontally along its longitudinal axis at the securing points on or near the base. The duration of this deceleration shall be 100 milliseconds minimum.



TEST NO. 8 End wall strength (dynamic)

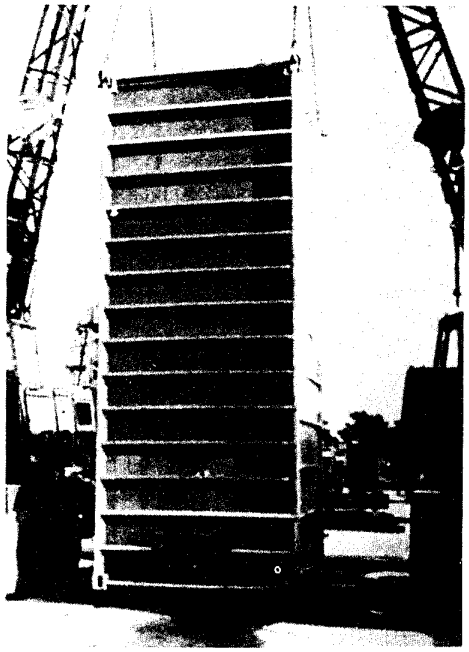
Procedure 1. The freight container shall be subjected to Procedure 1 of Test No. 7 Restraint, twice with it positioned so that the end doors are leading and twice with the end doors trailing in relation to the direction of motion, thus making a total of four checks.

Instrumentation: The deceleration is measured by two independent accelerometers of frequency response in the high range and low range. The results are recorded on a pen and an ultra violet paper recorder separately.



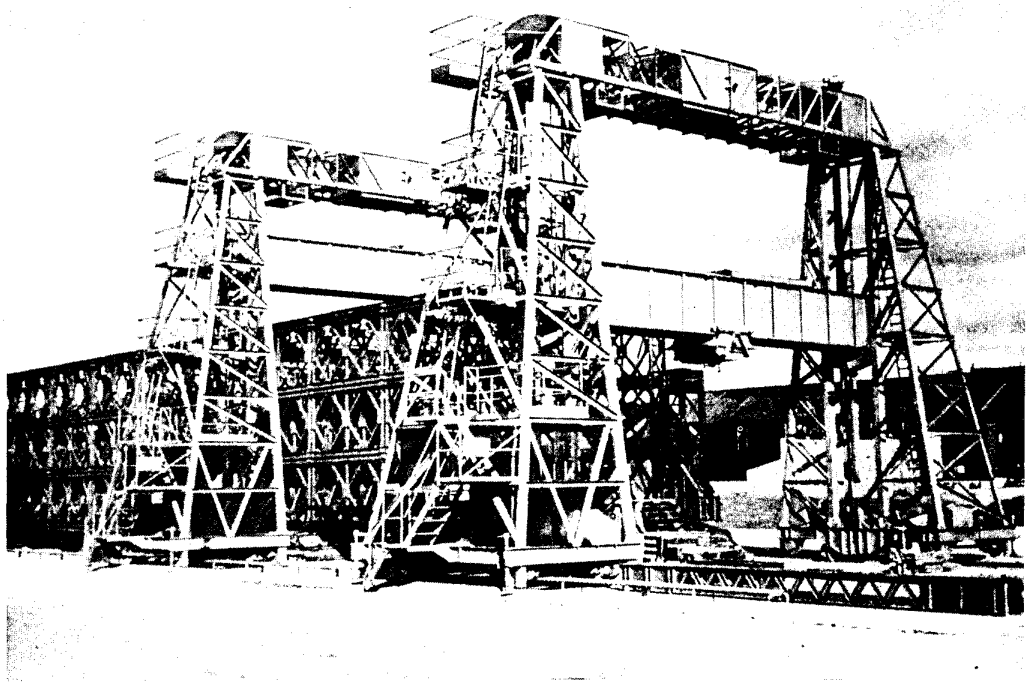
TEST NO. 7 Restraint (static)

Procedure 2. As an alternative, the following static test may be applied. The container under test, loaded as in Procedure 1, shall be longitudinally secured at the bottom corner fittings on one end, to rigid anchor points. A longitudinal force equal to 2.5 × R shall be applied through the bottom corner fittings at the other end first in compression and then in tension. The opposite end shall be tested in the same manner.



TEST NO. 8 End wall strength (static)

Procedure 2. As an alternative, the following static test may be applied. The freight container shall be loaded with a weight equal to 0.4 P using material which as far as possible occupies the whole internal capacity. By suitable means the container shall be lifted to hang vertically from one end so that the entire load is applied to the other end. After returning the container to the normal position, the procedure shall be repeated by lifting it from the opposite end.



MEXE Bridge Testing Rig

TEST NO. 9 Watertightness

After completion of tests Nos. 1-8, all joints and seams of the exterior surfaces of the freight container shall be sprayed at a rate not greater than 100 mm (4 in) per second with a jet of water from a nozzle 12.5 mm ($\frac{1}{2}$ in) inside diameter at a pressure corresponding to a head of 10 m (33 ft) of water. The nozzle shall be held at a distance of 1.5 m (5 ft) from the surface under test. The duration of the test shall be 15 min.

PART 4 — TYPICAL TEST ARRANGEMENTS USED IN MEXE

The preceding section lays down the standard and form of test to be carried out on the various parts of the container and was extracted from BS. 3951/67 with the permission of British Standards Institution. Each test had to be studied and a simple economic procedure developed. In testing as in other forms of engineering, time is a scarce commodity and now with the experience of two years of testing, the authors know what should and should not have been done. The error of using an equipment because it was available has led into sometimes cumbersome and more lengthy procedures. However, satisfactory tests have been developed and these are the ones that will be described.

Much discussion has been taking place on the acceptability of the parts of a container before and after test, the tolerance in production and after test and what constitutes (and here we quote from the British Standard) 'permanent deformation or abnormality which will make it unsuitable for use.' The definition has been found too open and loose in interpretation. Therefore a number of bodies have given guidance on these matters from which should result a more practical definition. From the point of view of the test, therefore, sufficient deflections and deformations are measured before, under load and afterwards in order to provide a comprehensive picture of the container's performance. The acceptance or rejection of a container can be agreed by the interested parties by relating the performance of the container to whichever set of criteria from which they should be judging.

Roof test

In the roof test, a concentrated load of 660 lb is placed on the roof of the container in a position which it is considered will give maximum stress.

Measurements are taken of the deflections of the roof before, during and after loading.

Floor test

This is a dynamic test requiring a prescribed Forklift truck of 12 000 lb front wheel axle of a particular track and wheel imprint size. The tests is carried out in two parts. Firstly, the truck traffics the whole floor and then later, it is driven over a level twin ramp onto hardwood blocks 22 in^2 of plan area in order to test the floor at two points selected to give the worst conditions of bending and shearing loading. Floor deflections before, during and after tests are measured.

Stacking test

The Bridge Test Rig at MEXE is capable of imparting loads up to 250 tonf and this is used to perform the stacking test. The container is placed on its four bottom corner castings resting on level pad supports. It is ballasted by rolling in a preformed single load on rollers uniformly distributing the weight to the floor. To protect the container, the floor is supported while ballasting and unballasting but not during the test. To simulate the underside of the superimposed container, two loaded spreader beams are placed across the top corner castings at each end of the container. A heavy girder is then added across the load spreader beams. Dummy bottom corner castings are placed between the two loading beams and the corner top castings. They are offset in the prescribed manner to simulate the eccentricity in a stack of containers. The load of 9R is built up in three stages. Prior to ballasting, floor deflection readings are taken and deflection readings are taken of each corner column in two directions at right angles. At each step in load, these readings are repeated and compared to the unloaded condition before and after test.

Lift test

This is a static test and performed by suspending the container on the Bridge Test Rig. In order not to impart a dynamic load, the container is lowered hydraulically from fixed strops attached to the container by two twist locks and two self locking hooks. As this is the heaviest load, the deflection of the floor is measured before ballasting in a similar manner to the stacking test, during the test and afterwards. In lifting from the bottom corners, care was taken in designing the corner attachments to conform to BS. 4228—'the Specification for Corner Fittings', which require the line of action of the lifting tackle to be at a maximum of $1\frac{1}{2}$ in from the face of the corner fittings. For the 40 ft container, the test load in the corners is 30 tonf and the 20 ft container, 20 tonf producing, 45 and 30 tonf/in moments respectively. Unless care is taken in the design of the bottom lift equipment, considerable damage can be occasioned to the container. The test is in all other respects similar to that for the top lift.

Racking test

The racking or deck lashing test is performed in an identical manner to that described in the British Standard. This test not only gives an indication of the performance under the deck lashing or racking load but is also able to give an indication of the torsion stiffness of the container. The horizontal pull from the top corner casting is first applied at the end wall which frees the bottom corner casting at about 3 tonf, then the pull is increased to 6.25 tonf. With the end wall supported by this pull, a similar pull is applied at the door end until that corner is free. While the container is suspended the diagonals of the door and end wall are measured against the unracked position. There are variations in this test to simulate practical conditions. One company requires that the water test be applied to the end doors to check their watertightness. Similarly, the air tightness of a refrigerated container could be tested under these conditions although this is not, as yet, a requirement. There is a proposal before ISO TC 104 to consider increasing the racking load to a horizontal pull of 12.5 tonf to conform to the expected working conditions on-board-ship where the container will be deck-mounted up to 4 high. The most severe condition was envisaged in BS. 4228 where this horizontal load could be as great as 15 tonf. The tests Stations will have to consider modifying their equipment some time in the future to apply this test.

Side wall test

Tilting the container weighing something between 25 and 37.5 ton, depending on the type, is not a practical proposition. The test is normally carried out with the container placed on its side on four corner castings; into it are placed layers of boxes evenly distributed over the side wall (this is now the floor). At the same time as the load is increased, the deflections of the side wall are taken and compared with those both before and after test.

The restraint and end wall strength tests

The tests to be applied are either dynamic or the static equivalent to the dynamic restraint and end wall strength. The criteria of the former and their qualitive analysis to produce the latter would form the subject of a paper itself. There is genuine concern over the criteria and there is still a great deal of discussion which will have to take place before the matter can be considered settled. What is in doubt here is not the British Standard but the interpretation of current practice. For example, the change in container transportation on close coupled freight liner trains as compared to current goods trains with the open coupling will, it is anticipated, reduce the present stringent operational loads and therefore the test loading.

At the time when the dynamic test load was being considered, there was little information available on the typical types of load which were currently being transported. A recent paper by the Imperial Chemical Industries Limited on the filling and emptying of containers shows typical loads being used in current transport practice; some of the loads were oil drums, carbon cartons and bags of fertilizers. Therefore, the choice

of a load composed of a number of steel ammunition boxes, is typical of many loads handled today as well as being a useful piece of test equipment.

Dynamic restraint test

Our aim in this test was to make the conditions as far as possible repeatable and uniform for all containers. Therefore, consideration had to be given to the performance of the load as a series of closely connected particles, and then as a homogeneous mass. To obtain uniformity steel boxes of a known surface friction are used which when stacked slide and do not interlock. The density is variable due to the filling but it is constant for one type of container. The energy imparted to the system and absorbed from the system is made as simple and as close to practice as possible. The imparted energy is that given by the mass moving a fixed distance down an inclined ramp, the absorption of that energy is carried out by the buffers and the mass of the structure supporting them. The buffers are the hydraulic variety of a known characteristic and performance currently used by the British Railways on goods wagons but not freight liner trains. The Test Rig is constructed from Bailey bridge. The container is mounted on a trolley with locking pins through the base of the two bottom corner fittings at the door end and with the end wall at the leading end of the trolley. The container is ballasted as already described with the load so arranged to be the full height of the wall under test. The trolley is mounted on a railway track and is winched up the sloping part of the ramp. Using a bomb release mechanism the trolley is allowed to run onto the pneumatic railway buffers. Trial runs are carried out to ensure contact of the load onto the end wall and then two sets of runs are carried out in order to obtain the prescribed deceleration in the horizontal plane. The test is repeated with the doors leading. Measurement are taken of the deceleration by attaching a decelerometer to the leading corner castings and obtaining a trace on two galvanometer paper recorders, one in the high and one in the low frequency range throughout the closure of the buffers. The container on the trolley is timed over the last 10 ft of travel and the deflection of the buffers is also recorded. The effect on the container is measured by deflection of the end wall both statically and dynamically, by the elongation of the bottom rail of the container and the tendency of the container to parallelogram by the movement by the movement of the side wall diagonals. In this way the end wall is tested and the side rails have an induced load placed upon them first in tension and then in compression because the fixing points to the trolley are retained throughout the test. The controversy aroused by this test has centred around the interpretation of the results and how they relate to the British Standard. In support of the controversy and this general arrangement of tests, the authors feel that, firstly, this is a practical test under practical conditions of the type of real life operations imposed on a container and secondly, that to obtain a uniform test for all containers, the energy imparted to and absorbed from the container should be the criteria and not acceleration or deceleration.

Static restraint test

The test needs little amplification from that already described in Part 3. The load is applied to both bottom rails simultaneously in order to place this in tension and then in compression. The measurements made are those of the elongation and compression of the bottom rail before, during and after tests.

Static end wall strength test

The test needs little amplification from that already described in Part 3. Measurements are taken of the deflection of the door and the end wall separately. The 20 ft container is a relatively simple test; however, for a 40 ft container, the sheer size of the container and the weight will present some difficulty. The present criticism of the test is that the static load falls well below those imposed by the dynamic test. This has been proved to be so by one manufacturer who took the dynamic door deflections and reproduced them statically by building up the load. This is a typical example where practical testing can help to correct test criteria.

Development of test facilities

The aim of any Test Station is to provide a technical service as economically as possible. The prescribed tests are generally expensive to perform and require purpose made equipment. They are expensive because the loads involved are often considerable and because the return on capital employed has to be high due to the uncertainty of the size of the container market and therefore the numbers to be tested. The proliferation of tests in number and complexity although appearing to be useful from the technical point of view would add considerably to the already high cost of testing. But of course, if in the future, additional tests were to be required then it would be necessary for the Test Stations to conform. MEXE are currently still with their first generation test equipment but foresee the time when these facilities will be extended to test the 30 ft and 40 ft container. There are at present a number of firms or companies both independent and privately owned who are setting up as test stations:

Ellis Research and Testing Laboratories Limited, Guildford.

British Railways, Derby.

Crane Fruehauf, Norfolk.

Marshall, Cambridge.

Each test station has interpreted the tests in a similar manner but has designed its test equipment somewhat differently. The exterior load application has been by hydraulic rams or jacks which make for speed of application. Internal test loads have varied from liquid to concrete and steel. Each have had their own problems and particular solutions. All other considerations being equal, the responsibility of a test station is to set a high technical standard at as low a cost as possible.

PART 5 — SOME ASPECTS OF THE TYPICAL DESIGN OF CONTAINERS

By the very nature of the International Freight Container certain aspects of its design have been made to conform. It has eight corner castings placed on the extremities and is of the strength and design laid down in BS. 4228, 'the Specification for Corner Fittings of Freight Containers', the British interpretation of the ISO agreement.

The British Standard makes a point that it in no way wishes to inhibit the design of containers generally and that if the corner fitting is part of the material of the structure of the container, it should conform to BS. 4228. Similarly the provisions of BS. 3951 covering the operational and test requirements of containers have to be met. From observations, containers are designed to give the maximum payload with the minimum tear weight consistent with the requirements of structural strength and produce protection, divided into categories which have been described in Part 3.

The designer of containers has had a full range of materials from which to choose and seems to have used them all at different times and various places in the container.

At the present time, there is very little information available which will lead one to decide the best materials for design. Such conditions as replacement costs, repairability and life of a container will eventually be available and it is by this sort of consideration as well as the structural strength of the material that the design will be dictated. In general terms, the corner fittings and main frame are in steel. The cladding of the walls vary on the insulation anticipated. For general cargoes, a thin aluminium alloy or steel skin on ribbing of a similar construction seems to be used. For lightly insulated containers plywood with a glass reinforced plastic or polyester coating is a likely candidate, and for heavily insulated or reinforced, a sandwich construction of GRP infilled with polyurethane foam is common. The roof conforms to the cargo protection required and is generally of a similar material to the walls but bonded to the roof cross members to reduce the chance of leaking rivet holes. The doors and the locking gear have been designed by a number of different firms not necessarily using the same material as the rest of the container. The floor has the two main functions of supporting the load and providing the level of insulation required. These are not always compatible particularly in the case of

the refrigerated container. Generally, there are floor bearers connected to the longitudinal rails upon which a variety of materials are placed to withstand the load. The typical materials used are plywood, hardwood, plywood coated with GRP, aluminium alloy extrusions, GRP by itself as in the refrigerated floor.

Container design in plastics

There are many uses for plastic materials in the manufacture of containers. They fall broadly into the categories of structural materials, insulators, adhesives and accessories. The latter term is included only to complete the catalogue.

Plastics in current use in Containers

Glass reinforced plastic (GRP)	a. In sheet as a structural member for walls, floors. b. Webbing between two sheets. c. Coating to plywood. d. Built in situ for walls.
Polyurethane foam	Insulation either expanded in situ between walls or preformed to a fixed density or k factor, then cut to shape and fitted between walls or supports
Polyurethane paint	a. Paint on plywood. b. Support for gritted flooring.
Polyvinyl chloride (PVC)	In the expanded condition as structural members between extruded aluminium sections.
Epoxy	Paint on plywood.
Neoprene (polychloroprene rubber)	As a preformed sealing fitted to doors, refrigeration air and liquid ducts.
Mastic	Sealing compound between aluminium and steel riveted sheeting and roof members.
Nylon bushes	Cathodic protection between Aluminium and steel joints.
Elastomer (derivatives)	Bonding of GRP walls and roof to the steel or aluminium alloy frame to impart strength.
Polystyrene	Insulation in standard framed construction

It includes such items as water stops in doors, plastic washers for cathodic protection and air seals for the refrigerated air supplies. The major problem when designing loaded structures in glass reinforced plastics is one of stiffness. The material can be amply strong in tension but it has so low a modulus of elasticity that it presents difficulties in parts like the floor. Once these have been overcome, it provides an ideal material in the insulated and refrigerated cargo containers. The container has a steel or aluminium alloy frame onto which in a more or less integral construction the box of the container is fitted. This frame consists of eight corner castings in the end frame connected by the top and bottom longitudinal rails with, if necessary, angle stiffeners in the corners and vertical rail supports. To this the insulated container is bonded by some flexible elastomer.

Designs

There appear to be two basic designs of the insulated refrigeration compartment, namely, the sandwich construction and the ribbed construction. The object of each is to provide a support for the insulation made from polyurethane foam or block polyestyrene. In the sandwich construction in the strength is usually provided by an inner and outer skin of glass reinforced plastic (GRP) or skins of plywood coated with GRP or a combination of both. The ribbed construction provides a framework which supports and separates a thin inner and outer metal skin between which the insulation is placed. The ribs themselves have to be made of a very low conductivity material; expanded PVC is one such material compressed between aluminium extruded sections. The ribbed construction has its own inherent strength due to the aluminium extrusions; if, however, the sandwich construction has to take the direct load, it needs reinforcing in various ways. Each manufacturer has their own particular method of providing this reinforcement. In general terms the additional stiffness required in a wall or a floor member is provided by inserting GRP webs of varying thickness bonded to the inner and outer skins, or in one particular case, steel bars are bonded into the structure; each has its own particular merit.

Fittings

In refrigerated containers, in order that the coolant can circulate, the floor is usually of the extruded alloy plank construction allowing for a free flow of cooland around the produce; in a similar way the walls of the container are normally heavier than the general cargo container requiring stronger hinges and locking gear. The strength and fixing of these must maintain the standards of thermal insulation with adequate air selas and resistance to the racking loads. In addition, depending on the type of refrigeration employed, provision has to be made for external air supply through an inlet/outlet duct of about 12 in dia; if the refrigeration plant is electrical and built in, pipe work is required through the structure or if the container is cooled by liquid CO_2, with the bottles inside the container, provision has to be made for recharging CO_2 bottles from the outside.

Manufacture of sandwich

The sandwich is made on a variety of principles. In one case it involves pressure after the resin has been impregnated into the fibre-glass combined with a vacuum process. In another, the inside of the container is constructed on a mould to give a seam-free finish onto which is built the strengthening ribs, the infiller and the outer skin. In some cases, the steel frame is able to transmit part of the external load to the container while in others, the steel frame and the container are separate to play their own structural part.

Insulation

A recent paper submitted to British Standards gives some useful guide lines to the material considered for insulated containers based on the proposals for the minimum internal dimensions of the different types.

The comments drawn from the Table show that polystyrene will give a heat loss in excess of that proposed to ISO and could be achieved by careful manufacture and reducing the internal dimensions to allow for 5 in of insulation but this would require a thermal efficiency of about 70%.

Polyurethane, however, is able to meet the proposals without much difficulty therefore allowing flexibility in manufacture.

Container	Stated max loss BTU's /hr	Polystyrene insulation Standard framed construction			Polyurethane insulation		
		4" all round 65% eff'cy BTU/hr/°F	5" all round 65% eff'cy BTU/hr/°F	5" all round eff'cy req'd to obtain minimum	Framed const'n 4" all round 65% eff'cy BTU/hr/°F	Sandwich construction 2½" all round 95% eff'cy BTU/hr/°F	Sandwich construction 4" all round 95% eff'cy BTU/hr/°F
1A	94	132	104	72%	83	91	57
1B	72	100	80	73%	64	70	44
1C	50	71	56	74%	45	49	30.8
1D	30	40	32	72%	25.4	28	17.4

Comment

Of the current range of heavily insulated or refrigerated containers passing through the Test Station, each has its own particular merits. Generally they impress one with their ability to withstand the loads imposed upon them and their general hygienic apperance, but they are somewhat heavier than the non-insulated container. It is in this field of weight and thickness of insulation where improvements must surely be made to reduce weight and increase internal dimensions.

Where failure has occured in the containers, it can be attributed to a lack of appreciation of the tests involved. Typical failures have been: cracking around the air ducts in the end end wall during the dynamic test; excessive deformation of the air-seals in the racking test; inadequate stiffness in the doors and the seals around the doors in the racking test and the lack of stiffness in the floor members in the floor and lift tests. Generally, however, plastics are one of the new materials for containers. They are acceptable and always look clean; they are readily repairable and should have a very considerable future.

PART 6 — SOME ASPECTS OF THE FUTURE USE OF CONTAINERS AND THE DEVELOPMENT OF TEST FACILITIES

In the field of rail transport, we in Britain have seen the development of the freight liner train. With this improved mode of transport, the forces imposed on the containers have been correspondingly reduced. If this type of transport were accepted for containers internationally, then the requirements for restraint and end wall strength could be reduced with a corresponding saving in cost in both material and manufacture. In the field of air transport, with the introduction of the 'Jumbo Jet' series of transport, a very light ISO type container would be a practical proposition. Coupled with this, the vacuum package process using a plastic membrane now used for air transport could be developed to hold the produce in these ISO air freight containers, thereby ensuring maximum produce protection and safety.

The present first generation containers with limited thermal protection is likely to give way to those with an increased amount of protection. Here the use of continuous strip plywood with the GRP finish would be a most useful material. Similarly, any material with reduced thermal conductivity and strength would have an advantage. One such is a balsawood infill between aluminium or galvanised steel sheeting.

The introduction of new materials should provide no difficulty to the test stations to perform the prescribed tests. The present range of tests are not affected by any particular material. The changes in types of container will need development in typical test loads and variation in accepted test procedures; for example, there is at this time no agreed method of overrating a tankage container. It would probably be uneconomical to keep a test load of specific density, for example a bentonite slurry available. Therefore, some mechanical means of overloading would be needed. Similarly for Airfreight the stacking test is unlikely to be necessary with the consequent alteration to test equipment and loading for that test.

The Refrigerated or Heavily insulated container, once it has been designated as such, will require a Heat gain or loss test. At present a thermal test station is being built with the financial assistance of the Ministry of Technology at Cambridge for the Shipowners Refrigeration Cargo Research Association (SRCRA).

Conclusion

In concluding a paper of this form which would appear to dwell only briefly upon those items of material interest to the Institute of Plastics, one should draw highlights of those things in which the Institute of Plastics would be particularly interested.

The container is basically a very large box which is there to provide the maximum amount of protection at the minimum cost and the minimum wastage of weight and space when transported between one media and another. There is room for development in all these spheres. The containers as designed at the present moment come from manufacturers of transport, shipping and a variety of general engineering backgrounds. Each of these have their traditional techniques. Each of these will wish to improve their cost efficiency and sell more containers. The container which satisfies the customer and always looks right will possibly be the one which will have that added draw where other technical considerations are no longer paramount. The cleanliness and the produce protection that can be produced by reinforced plastic containers should certainly lead to a wide use of this material.

The authors would like to thank those listed in the acknowledgments for their assistance either wittingly or unwittingly in providing certain information contained in this paper.

ACKNOWLEDGMENTS

1. British Standards Institution. BS.3951: 1967—Specification for Freight Containers and BS.4228: 1967—Specification for Corner Fittings for Freight Containers.
2. Mr G.Downis, M.I.M.H., Assoc.Inst.T. Paper presented to The Institute of Materials Handling, October 1967 on the Developments of Container Handling.
3. Imperial Chemical Industries Limited. Report No. HO/ODA/680001 on the Filling and Emptying of ISO Freight Containers.
4. Duramin Engineering (Lydney) Limited, Glos. Insulated Container Construction.
5. Viking Marine Containers Limited. Insulated Container Construction.
6. Bonallack & Sons Limited, Essex. Insulated Container Construction.
7. ConCargo Limited, Southampton. Insulated Container Construction.
8. Frigor Virborg, Denmark. Insulated Container Construction.

Sixth International Reinforced Plastics Conference

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Unsaturated polyester resins in the building industry 2

W. KLOEKER, Farbenfabriken Bayer AG, Germany

The major part of the unsaturated polyester resins produced in the Federal Republic of Germany (FRG) is used in the building industry. Extensive experience has been acquired in these applications over the years. This as well as new types of polyester resin and various new applications are the subject of this report.

1. GLASS FIBER REINFORCED, UNSATURATED POLYESTER RESINS (GRUP)

In the Federal Republic by far the largest quantity of UP-resins continues to be used in the form of GRUP in the building sector. Among the various GRUP articles it is the translucent, flat and corrugated glass fiber reinforced polyester sheets, e.g. for translucent roofings and balcony enclosures, which accounts for the highest quantitative share in sales. About 7 million square metres of these panels were produced in the FRG in 1967; this accounts for resin requirements of about 13 000 tons (metric). The knowledge about the behaviour of GRUP in exposure to weather and light is backed by many years of experience (about 15 years). Transparent moulded articles made from cured UP-resins are generally known to be subject after several years to a reduction of translucency due to yellowing. This yellowing under the influence of light is particularly the result of the short waves in the sun's spectrum (lower than 4000 Angstrom Units). Therefore very early use was made of so-called light-stabilized UP-resins for the manufacture of the above articles, i.e. resin incorporating an ultra-violet absorber. This absorber reduces to a minimum the processes of photochemical degradation, which in the cured UP-resin especially attack the aromatic and halogen-containing building blocks such as styrene, phthalic acids and their chlorination and bromation products as well as chlorinated paraffins. Normal grades of UP-resins are generally known to lend themselves considerably better to stabilization against the influences of light than flame-retardant types containing halogens. Unlike many other halogen-containing UP-resins, the flame-retardant, light-stabilized special type Leguval R F30 S*) based on Het Acid shows a fairly good outdoor behaviour with a relatively low tendency to yellow.

Thus, the structure of the resins plays an essential role. In the resins not made flame-retardant, it is the glycol types which in addition to the dicarbonic acids and the monomers required for copolymerization are the structural component exerting an interesting influence on the outdoor behaviour. The results obtained with UP-resins containing butandiol were quite successful. Articles moulded from such resins were among those which after more than 10 years of outdoor exposure had changed least. According to our experience, the chemical structure of a UP-resin is of greater significance for the outdoor behaviour than the level of cross-linking. Many a flexible resin had changed less after 10 years than highly cross-linked resins with higher heat distortion temperature. The statements above make it understandable that UP-resins containing a combination of monomer styrene/methyl-methacrylate in place of only styrene show a more favourable outdoor behaviour, especially lower tendency to yellow. Because of its low reactivity, the considerably higher vapur pressure of the methyl-methacrylate than of styrene, and the substantially higher price, UP resins containing only methacrylates have not so far been used in practice on a large scale.

Apart from the chemical structure, the tendency to yellow and general outdoor behaviour largely depend on the technique by which the UP-resin is processed. The type of cure to which it is subjected should be mentioned first in this connection.

UP-resins given optimum hot cure in the presence of peroxides show a more favourable behaviour than castings and glass fiber reinforced laminates cold-cured after the addition of accelerators. This difference can be largely compensated through heat-treatment (annealing) of the articles cured at room temperature. Annealing is to yield a 100% cure, which is practically obtained when performed correctly. In this heat-treatment the content of free styrene is reduced to about 0.1% by weight and the content of peroxide not consumed in curing to almost 0%. The determination of free styrene (residual styrene) and peroxides according to ALT (1) can be applied to ascertain the curing level (degree of cure) of UP-resins.

Annealed mouldings that have been cold-cured from UP-resins in any case retain the adverse effect of the accelerator on the colour shade and tendency to yellow. Emphasis must in this connection be placed on the tert. Amines (e.g. dimethylaniline) used in combination with benzoylperoxide, which may cause pronounced yellowing even in the presence of u.v. - absorbers. The discoloration caused by cobalt accelerators, e.g. the green cast, can be eliminated in various ways from transparent sheet and finishing coats. Specific UP-resins free from this greenish discoloration are offered on today's market.

Other sources of yellowing in GRP laminates are as follows:

The size and finish on the glass fibre, the binder of glass mat and inappropriate incorporation of the glass fibre products in the UP-resin.

The appropriate incorporation of the glass fibres and the cure of glass fibre reinforced polyester components is another factor of importance with regard to erosion in outdoor exposure. Today, the transparent corrugated sheets obtained through continuous production about 10 years ago show more or less pronounced marks of weathering and erosion on their surfaces. — At that time the corrugated sheets were produced without gelcoat. — We did not find any confirmation of the supposition that this process proceeds increasingly as a result of possible capillary effect of the exposed glass fibres (which in turn depends on the type of glass, the size and the finish) as soon as the very thin UP-resin film on the glass fibres cracks or separates under the influences of weather. Strength testing revealed that GRUP sheets and panels within the first years of outdoor exposure lost their original mechanical strength in the order of 20%. However, strength reduction in the years thereafter was only negligible.

The exposed, free glass fibres cause pronounced contamination, thereby reducing translucency. This is very important with green-houses. It is interesting to note that translucent corrugated sheets have proved a suitable roofing material for greenhouses. GOERDEN (2) reported in detail on the results obtained with such large-scale greenhouses. The lower translucency of GRUP as compared with glass may be of advantage within certain limits. It protects the plant from excessive sun radiation, saving the shading and thereby time and labour costs. It is self-evident that the high mechanical strength in conjunction with light specific weight of the GRUP panels and sheets allows a considerably more lightweight sub-structure and, also because of the lower repair costs, the construction and maintenance of such buildings at a considerably lower cost than conventional constructions.

In building constructions made in consistency with the material, GRUP corrugated sheet generally had its full serviceability after 10 years.

As the corrugated sheet of the more previous design is not cleaned by the rain, heavily contaminated roofs such as in industrial areas had to be cleaned with suitable agents in order to bring translucency back to an acceptable level.

* Leguval R is a registered trademark of Farbenfabriken Bayer AG, Leverkusen/Germany.

Attempts to improve the quality of corrugated sheet involved extensive tests aimed at reducing the tendency to yellowing, erosion and contamination through the brush or spray-application of transparent coatings based on aliphatic polyurethanes. Panels exposed to several years of outdoor exposure have not so far yielded the desired results. In many cases the polyurethane finish flaked partly or largely within the 2 years following application. Satisfactory adhesion could be obtained when the above polyurethane products were applied to the freshly produced panels not yet fully cured.

More promising are the results hitherto obtained with corrugated sheets that were provided with a gelcoat during production. We have developed a special UP-resin for this gelcoat. This gelcoat resin gives a better flow when applied in thin coats than standard types. After curing, it shows substantially higher flexibility and elongation at break in conjunction with good resistance to surface-swelling by styrene. It is light (UV)-stabilized. When developing this product, we drew on the good experience gained in many years of outdoor exposure with various Leguval types. The gelcoat quantities recommended for application are 100-200 g/m^2 with transparent, flat and corrugated sheet and 300-600 g/m^2 with all types of pigmented mouldings.

Drawn glass fibre reinforced polyester profiles were occasionally used as material for the manufacture of window-frames. Although GRUP profiles generally have higher strength and especially higher heat distortion temperature than e.g. PVC profiles, they have not so far been widely accepted in this application. One reason is their higher price as compared to conventional materials. On the other hand, whenever plastics window-frames are intended for use in building construction, those made of PVC (perhaps with wooden or steel insert) are preferred on account of their neater and smoother surface.

Profiles compression-moulded from prepregs (flow-mats) have a smoother surface and show fairly good outdoor resistance. The longitudinal strength of such profiles is lower than that of drawn profiles; however, they generally have higher transverse strength. It must be left for future to decide whether or not window-frames made of such profiles will eventually be accepted, e.g. in industrial building construction, especially in areas with a corrosive atmosphere where use of steel and aluminium would not be advisable.

Especially for the manufacture of curtain wall panels, e.g. sandwich constructions using suitable foams, it is of interest that among the panels compression-moulded from the same UP type it is those produced from prepregs which show substantially better outdoor resistance than those produced by wet compression moulding. Similar to the corrugated sheets, the wet-moulded panels generally revealed slight erosion within a few years. However, the panels remained fully serviceable. The glass fibres were exposed on the surface, thereby changing the appearance of the panels.* With the corresponding panels made of prepegs, such erosion was observed not at all or considerably later, and then to a smaller extent. Thousands of outdoor switch cabinets or cable junction cabinets for electricity and telephone are striking examples in the FRG of the good outdoor resistance of mouldings appropriately compression-moulded for prepregs. One reason of this superiority of parts made from prepreg material may be the higher compression-moulding pressure applied with this type of prepreg. This pressure yeilds a considerably closer surface.

Discolouration is in most cases due to the incorporation of unsuitable dyestuffs and pigments. Our experiments have revealed the following inorganic pigments to have satisfactory outdoor behaviour in UP-resins: titanium dioxide (rutile), chrome oxide green, hydrated chrome oxide green, iron oxide brown, iron oxide black, iron oxide yellow and iron oxide red as well as blue pigment with spinel structure (e.g. Light Blue 100). Results obtained with other types of blue pigment partly were far less satisfactory.

Another interesting application for glass fibre reinforced polyester resins is thin-wall pressureless pipes and ducts. In the Federal Republic, these have hitherto been used primarily in the chemical industry as piping for various types of chemicals and as sewers for sewage aggressive to concrete. Such pipe can be produced by two methods:

1. Centrifugal casting
2. Filament winding.

In centrifugal casting the glass mat and glass fabric is used as reinforcing material. The glass content ranges between 20% and 30%. On this pipe it is more difficult than on filament-wound pipe to obtain an interior gelcoat with optimum resistance to chemicals, because the gelcoat must be cured in the presence of air.

Filament-wound pipe can be made from both rovings and fabric ribbons (glass content: 50% to 70%). When rovings are used as reinforcement, one or more layers of glass mat or, to obtain optimum longitudinal strength, several layers of unidirectional glass fabric are normally placed between the layers of rovings. The first step in making filament-wound pipe is to apply the gelcoat onto the winding mandrel. In every case this gelcoat consists of a UP-resin with high resistance to chemicals, e.g. resins based on neopentyl glycol or bisphenol derivatives. In the Federal Republic these resins play a considerably greater part than the isophthalic resins. According to our results and experience, the above glycols (also in combination with orthophthalic acid) have a considerably stronger and more favourable influence on the resistance to chemicals than e.g. isophthalic acid in combination with the usual glycols (mono and oligo-ethylene and propylene glycols).

The resins normally used for the GRUP laminates are types which, although exhibiting higher resistance to chemicals and higher heat distortion temperature than standard types, are considerably less costly than the above special resins based on neopentyl glycol and bisphenol derivatives. To obtain the optimum mechanical strength data and resistance to chemicals, the GRUP pipes and ducts are principally annealed (about 10-15 hrs at 80° -100°C). In some cases the filament-wound GRUP pipes are provided, in addition to the gelcoat, with a liner made of a suitable thermoplastic, e.g. PVC or Perbunan C ^{R}†. GRUP pressure pipe, which has so far been used on a relatively small scale, is basically equipped with such liners to obtain a leakproof pipe with minimum wall thickness. It must be mentioned that composites based on thermoplastics and GRUP have recently gained increasing importance in the construction of apparatus and containers especially used in the chemical industry. The application of such composite materials was essentially encouraged by our developing a special UP-resin, which shows very good adhesion to PVC without requiring a solvent swelling the PVC surface, e.g. by tetrahydrofurane. This special resin‡ is directly applied to the PVC surface freed from dirt and fatty substances, with rovings, mat or glass fabric being placed on this resin coat. Apart from good adhesion to PVC, this resin excels by higher heat distortion temperature and chemical resistance. Smokestacks and piping made of approx. 2-6 mm PVC with GRUP outer sleeve, which are used for carrying vapours and liquids aggressive to UP-resin, were occasionally operated in continuous service at temperatures up to 100°C. Although the rigid PVC used had a heat distortion temperature of less than 80°C, the composite constructions have proved successful. When using such composite materials in engineering, consideration must be given to the different coefficients of thermal expansion of the thermoplastic and GRUP. Occasional stress cracking has occurred under unfavourable conditions and when the construction was inconsistent with the material.

Special patented techniques now also allow the production of

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* Note on panels produced by wet compression moulding: Better results are obtained with suitable glass fibre overlay mats or mats and thin fabrics made of saturated polyester fibres.

† Perbunan C ^{R} is a registered trademark of Farbenfabriken Bayer AG, Leverkusen/Germany.

‡ Leguval ^{R} W 35.

composite materials using other thermoplastics, e.g. polyethylene and polypropylene. It is equally possible to rubber-line heavy-duty GRUP containers and pipe. There already are several years of successful experience behind the use of such composite materials in the chemical industry. The development of special resins offering particularly good adhesion to polyethylene and polypropylene has so far been unsuccessful.

Although pipe made of GRUP and PVC + GRUP offer such advantages over those made of conventional materials (concrete or clay) as great lengths (6-16 m), minimum laying costs, high chemical and thermal resistance, this pipe has not yet been generally adopted in sewage technology because the authorities concerned still show great reserve in giving permission. GRUP type is flexible and subject to relatively ready deformation. Unlike the common rigid pipe, it is unsuitable for structural analysis. Methods of calculation have been devised whose results correspond fairly well with those obtained from field testing.

An essential characteristic of GRUP pipe is the possibility of indicating its modulus of elasticity as a function of the concentration and position of the glass fibres to be 120 000-220 000 kgf/cm^2 in tangential direction. On account of its low wall thickness (with filament-wound pipe this is about 5-6m for a diameter D = 600 mm, about 8-9 mm for D = 1000 mm and about 20 mm for D = 1650 mm), therefore, this pipe shows a soil behaviour basically differing from that of the rigid pipe. The high load-carrying capacity of the GRUP pipe is only obtained through the co-action of the buried pipe and the soil enclosing it. Extensive studies into the behaviour of this pipe in exposure to long-term static and dynamic load were started and will extend over another few years.

For 3½ years, for example, a GRUP pipe (D = 800 mm), which was so buried in a road carrying, heavy-duty lorry traffic so that its crown was covered with 95 cm soil, has been subjected to measurement of the change in diameter by means of a built-in dial gauge measuring to the nearest $^1/_{100}$ mm. Notwithstanding the initial deformation until stabilization in the soil, roughly 1.7 mm crown sag has occurred during this period, with last year accounting for 0.2 mm. Radial bending strengths (flexural strength in radial direction) of more than 3000 kgf/cm^2 can be attained with normal pipe. Considering the creep-rupture strengths and other influences on the plastics material and assuming the reduction to 30% of strength data in accelerated testing and a double safety factor results in a stress of 500 kgf/cm^2. This stress is never reached in service.

The tests conducted on pipes revealed that the pipe-wall will not buckle even under maximum load. This failure is prevented by the soil enclosing the pipe, because any outward evasion of the pipe-wall will be opposed by resistance forces of the soil.

Detailed test results as well as experience gained in the design of potential pipe joints, connections to central shafts and direction for the construction of GRUP shafts with and without concrete sleeve were published by KLOEKER and KAYSER (3).

Only limited use has so far been made of GRUP for load-carrying constructions in the Federal Republic. This is because of legal regulations according to which UP-resins are considered a new building material, and new building materials are basically subject to official permission. However, the authorities show great reserve in issuing such permits. Applications must be accompanied by results obtained through extensive studying as well as by opinions issued by Government-controlled test institutions. The applications last year permitted for the first time were vertical silos for feeds. Another structural application was a footbridge. However, this project could not be executed in GRUP, because the lengthy permission procedures did not allow completion on time; as the customer was unable to extend the deadline, the footbridge was made of conventional building materials. Fig. 1 illustrates the unsupported structure of an extension roof for a tanker filling station.

Directions for constructions in GRUP are currently being devised by the Arbeitsgemeinschaft Glasfaserverstärkte Kunststoffe' (working committee on glass fibre reinforced plastics). These directions are intended as a contribution to shortening and accelerating the procedure of obtaining official permission for the erection of GRUP constructions.

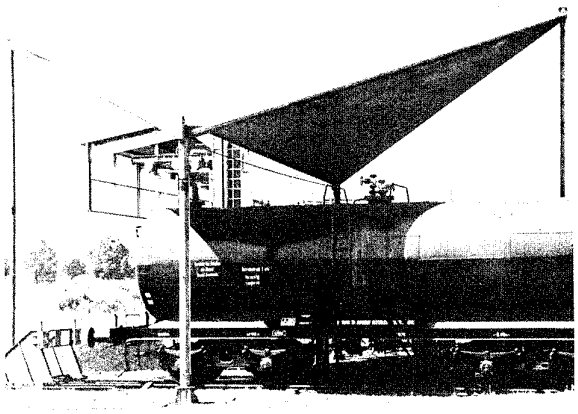

Fig. 1

Great importance has been gained in the FRG by glass fibre reinforced polyester coating applications on civil engineering structures especially made of steel-reinforced concrete. These GRUP applications satisfy the requirements posed for the rigid coating or insulation of such structures, i.e. pore-sealing effect, high chemical resistance, high mechanical strength, an elongation at break up to 2% to compensate crazing in the structure and, if necessary, good adhesion to the substrate. This is why such insulations have been applied successfully for quite some time in the construction of tunnels, shafts, channels, railway underpasses and civil defense structures as well as for lining water tanks and silos for chemicals that are made of brick-work or steel-reinforced concrete. Emphasis is placed in this connection on GRUP linings of swimming pools. The GRUP coat is generally applied by means of the dual feed fibre-resin depositing technique which in the form of a two-component mix simultaneously delivers glass fibres cut from rovings during the spraying cycle and the UP-resin to the surface to be coated. Only on small objects or particularly difficult places is the GRUP coat applied by the hand lay-up technique using glass mat.

More than 400 000 square metres have so far been coated with GRUP in the FRG. Both the material and the methods of application have proved successful in a great variety of uses. In sewage technology the material has gained importance in the protection of concrete pipe, sewers, water-carrying bridges, collectors, purification plants, gravitation tanks and similar structures from sewage aggressive to concrete. For this application we developed special UP-resins, which both meet the demands of the technique and satisfy the requirements posed for the material especially when used in the chemical industry. Let us first consider in this connection the UP-resins having structural viscosity, which were specially developed for the dual feed fibre resin spraying techniques. For the production of such resin we discontinued the use of highly disperse silicas some time ago, because these are known to have a disadvantageous effect on the properties of the cured UP-resins. We have since replaced the silicas by organic thixotropic agents of which only a fraction of the quantity of highly disperse silica must be added to the resin to obtain the same structural viscosity effect. This effect is achieved with additions of less than 1%. These types of resin readily permit the coating of vertical walls and overhead surfaces. Coating applications like these are produced with UP-resins that have better resistance to chemicals—especially to the basic substances, e.g. calcium hydroxide, normally contained in concrete—than the standard types.

Experience has been gained with the most previous coating applications over more than 7 years. The first coatings were partly made with UP standard resins. Not a single case of

separation or destruction has so far been noticed that would be due to hydrolysis of the UP resin base coat or finishing coat. Therefore, discussions on the susceptibility of UP coatings to saponification by the basic products in the concrete such as calcium hydroxide were more of theoretical nature and are in contrast to practical experience.

To achieve maximum safety for civil engineering structures expected to last for decades or even a century, the general trend nowadays is to produce the base and finishing coats from resins differing from that for the laminate, i.e. resins that excel by even higher chemical resistance, show better adhesion to concrete and without paraffin addition cure to yield a tack-free surface. These UP-resins include materials based on e.g. neopentyl glycol or bisphenol derivatives or special types modified with isocyanates. Such types are among the top products of the polyester industry.

Generally, a coating like this is built up as follows:

1. 1-2 prime coats, depending on the surface of the concrete to be coated
2. 1 or more glass fibre reinforced laminate plies, glass concentration about 25%-30% by weight
3. 1-2 non-reinforced finishing coats.

Giving the individual coats a different colour has proved to be an advantage. The overall thickness of the GRUP coating system normally ranges between 3 and 8 mm, depending on the mechanical and chemical exposure to be expected. GRUP coatings are tested for the absence of pinholes (pores) by means of high-voltage testers at voltages between 7000 and 20 000 volts.

Because of the different coefficients of expansion of GRUP laminates (20-40. 10^{-6}/°C) and concrete (10-14. 10^{-6}/oC), considerable stresses may occur at the interface between the two materials in some cases, especially where relatively high thermal differences must be expected; these stresses oppose the adhesion of a coating to the substrate. This lack of adhesion to the substrate is occasionally tolerated in such cases; the result is e.g. a GRUP container within a concrete container. Several joint designs have been elaborated and successfully tried out for compensating expansion and construction joints in non-monolythic structures of relatively large size.

2. POLYESTER-BASED CONCRETE

The application of unsaturated polyester resins in the form of polyester-based concrete, artificial stone (man-made-marble) and mortar in building construction has ever been on the increase. These materials, which are obtained through mixing dry gravel, sand and quartz flour (rock flour) with unsaturated polyester resins plus hardeners and accelerators, have the following advantages over ordinary concrete:

1. Faster setting
2. Higher mechanical strength data
3. Lower water absorption
4. Resistance to frost
5. Considerably higher resistance to various types of chemicals
6. Better adhesion to many other materials.

As early as after 24 hours after setting, polyester concrete has reached generally higher mechanical strength than highest-grade ordinary concrete after 28 days. Similar to ordinary concrete, the strength data substantially depend on the granulometric composition of the aggregate, degree of compaction and quantity and type of the binder. Within the range of resin-aggregate mixing ratios of from $^1/_{14}$ to $^1/_8$, polyester-based concrete has the properties compiled in Table 1.

The higher the content of aggregate the lower the shrinkage. The creep behaviour of polyester-concrete under long-term load depends on the temperature and the heat distortion temperature of the resin type incorporated. In the Federal Republic the major application for polyester-concrete currently is sewage technology. Within the temperature range up to about 30°C applicable to these used, the creep—even when standard types of polyester are incorporated—is low and comparable to that of ordinary concrete. It should be added that crushed prisms of polyester-based concrete with quartz aggregate almost exclusively show grain fracture, which indicates that the quartz particle is that material component within polyester concrete which has lowest strength. However, this requires that the quartz material is sufficiently dry and an effective bind with the polyester resin was ensured.

TABLE 1

Compressive strength as per DIN 1048 (cube 10 × 10 × 10 cm)	600 - 1,300 kgf/cm^2
Tensile strength in flexure as per DIN 1048 (prisms 70 × 15 × 10 cm	130 - 230 kgf/cm^2
Tensile strength	90 - 110 kgf/cm^2
Coefficient of linear expansion	15 - 20 × 10^{-6}/°C
Modulus of elasticity	150,000 - 300,000 kgf/cm^2
Coefficient of thermal conductivity	0,8 - 2,0 kcal/mh°C
Overall shrinkage	0,1 - 0,3%
Bulk density	2,2 - 2,4 metric tons/m^3
Water absorption	below 1% by weight
Abrasion resistance as per DIN 52108 (at 440 rev.)	7 - 11 m^3

Slabs and prisms made of polyester-based concrete can also be reinforced in a way similar to ordinary concrete. Optimum results are obtained with Tor steel. Especially where polyester-based concrete cannot be compacted sufficiently, care should be taken that the dry steel components are covered on all sides with a film of polyester resin. It may be advisable to coat the reinforcing steel components with a flexible type of polyester resin plus isocyanate addition prior to mounting. Such types of modified UP-resins have proved fairly suitable as a material protecting e.g. steel girders and containers from corrosion. (cf. Section 6, Thin-film coating applications).

According to our test results and experience, apparently, UP-resins used in polyester concrete and mortar exhibit higher chemical resistance than in glass fibre reinforced laminates or unfilled UP-resin-based coatings and cast slab. In our view this is because unfilled polyester-based coatings and laminates have a surface area that is large in comparison to thickness. In this case thickness of layer is about 0. 5-6 mm. In polyester-based concrete and mortar, the closely packed quartz particles ensure that the film of polyester resin between them, and thereby the resin surface subject to attack, is respectively very thin and small in comparison to the thickness of the polyester-based concrete, which may amount to about 5-200 mm. After a 1-year fill of 30% caustic soda solution, a UP standard resin based concrete pipe closed on one side showed almost no attack. Glass fibre reinforced laminates and unfilled cast slabs based on the same UP resin reveal extensive destruction under the same conditions. This is why we consider polyester-based concrete suitable for application even where coatings obtained with unfilled UP-resins and glass fibre reinforced laminates no longer appear adequate (cf. Section 4, Polyester-based concrete).

Similar to GRUP laminates, polyester concrete yields optimum properties when special UP-resins are incorporated and when the material is cured at room temperature and subsequently given thermal after-treatment(annealing). For example, large-sized tanks for the electroplating industry were constructed from polyester concrete.

Considerable importance has been gained by central sewage shafts made of polyester-based concrete for industrial operations as well as for communities and municipalities with sewage aggressive to ordinary concrete. Such shafts were previously made of brickwork and later on lined with ceramic tile or brick. The chemical industry frequently used milled granite slabs for these shafts. These slabs were jointed with

the help of chemical-resistant cements and mortars such as based on UP resins. While the cost of granite-made shafts was at 1800-2000 D-Mark/m^3, sewage shafts made of polyester-based concrete are nowadays delivered by special manufacturers at a cost of about 1000 D-Mark/m^3 free at building site. Such shafts are easy to provide with shut-off valves for the individual feed lines. — This is very difficult with shafts constructed from GRUP pipe; although polyester-based concrete costs about 4-8 times more than ordinary concrete in the Federal Republic, central sewage shafts made of polyester concrete offer economical advantages over shafts of conventional material.

Fig. 2 illustrates a sealing cap for the outlet of a central sewer to the Rhine river. This sealing cap was cast from polyester concrete as a single unit. As revealed by Fig. 3, this prefabricated polyester-based concrete unit is steel-reinforced. It has an overall weight of approx. 15 metric tons and a wall thickness of about 30 cm. The resin/aggregate mixture of the polyester concrete used for this unit was 1 to 13. The aggregate gradings selected in line with an ideal grading curve ranged from 40 microns to 30 mm particle size.

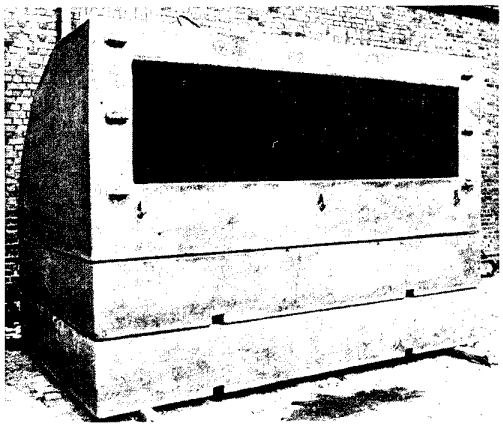

Fig. 2

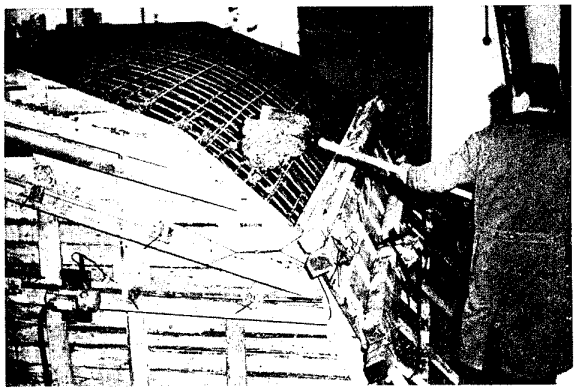

Fig. 3

The pot life was adjusted to about 7 hrs with the help of inhibitors. The mixing units available permitted the required quantity of polyester-based concrete to be poured, and to be compacted by means of external and internal vibrators, within $6\frac{1}{2}$ hrs. As the hardener and accelerator was added simultaneously to the required quantity of resin prior to operations, the cure of this building component set in all at once over the entire volume rather than stepwise. The member was left in the mould at a temperature of about 25°C over the weekend. After mould-release, it was found that the cracking which had been feared owing to the heavy steel reinforcement had not, in fact, occurred. The crazes on the surface were closed with a Leguval/Desmodur SL* based sealer (finished) after the mould release agent had been removed by sanding.

As far as we know, this cap was the biggest prefabricated component so far made from polyester-based concrete in Europe. Still greater importance for sewage technology has been gained by large-diameter pipe made of polyester concrete (diameter: 1000-3500 mm). Such pipe is manufactured by means of centrifugal casting. Although polyester-based concrete shows only low shrinkage, the manufacture of such large-diameter pipe free from cracking has presented difficulties for quite some time. Through the use of prestressed steel reinforcement, the manufacturing technique has been developed to a stage at which it ensures the manufacture of polyester-based concrete pipe with an accuracy coming very close to mechanical engineering. KLOKER and KAYSER (3) gave a detailed report on the manufacture of polyester concrete pipes. The chemical industry in many cases prefers poly ester-based concrete pipes to GRUP pipes. The latter are rigid and lend themselves to conventional structural analysis. As regards chemical resistance, they offer higher safety than GRUP pipes and cement-concrete pipes coated with polyester or epoxy resin. As compared with clay pipe, they have considerably higher strength and are less suceptible to breakage. Over composite pipe made of clay and cement concrete (3), they offer the advantage of consisting of the same material within and without, thereby excluding the problems occasionally arising with heterogeneous materials. They also allow greater effective length. Summing up the various properties results in both technological and, above all, economical advantages.

Fig. 4 illustrates the use of polyester concrete for machine foundations. In this application advantage is primarily taken of the short curing cycle and the high mechanical strength and also (in Fig. 5) of the high chemical resistance. Poly-

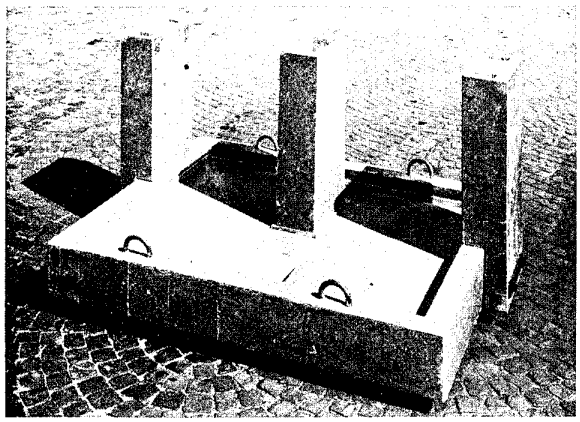

Fig. 4

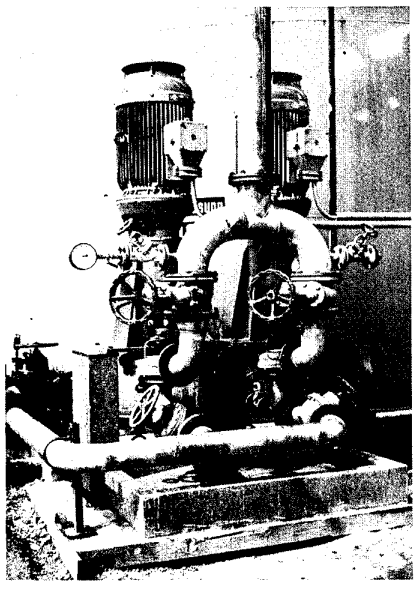

Fig. 5

* Desmodur R is a registered trademark of Farbenfabriken Bayer AG, Leverkusen/Germany.

ester-based concrete has also proved successful in the construction of connections from speedways to bridges. The reason why polyester-based concrete was preferred to epoxy-based concrete was the short setting time and the high mechanical strength the former material reaches as early as a few hours. The roads had only to be blocked for a very short time.

3. ARTIFICIAL STONES BASED ON UNSATURATED POLYESTER RESINS

An interesting new application for UP-resins is their use as binder for artificial stones (cast stones) and synthetic marble (man-made-marble). Artificial stones are building components made of pigmented polyester concrete with special decorative effects (e.g. terrazzo or marble character). They are used as wall tiles, curtain wall panels and elements, prefabricated building elements (of storey height, e.g. for entrance halls, offices, bathrooms, lavatories, etc.) as well as for monuments, plinths, window sills, table-tops, radiator tops and as structural elements for artwork. There are two methods for the manufacture of such stone:

On the one hand is the conventional method by which large slabs are cast and cut to panels with the help of the diamond saw. This method is preferably applied in the production of synthetic marble including marble chips up to a particle size of 200 mm in dia as aggregate. The panels are ground and mirror-finished in the familiar way. They have considerably better appearance than cement-bonded panels. Since the UP-resins used as binder are practically colourless, the colour shade of the 'binding mortar' can be adjusted through suitable pigmenting to that of the larger marble surface. Synthetic marble panels are primarily applied indoors.

On the other hand, there is the method that could be called 'casting-vibrating technique'. This technique provides for the polyester-based casting compound to be poured into suitable moulds to the thickness required for the building component. The method permits the manufacture of mouldings without special decorative effect, i.e. with a highly pigmented smooth or relief-patterned surface, as well as of mouldings having a special decorative effect, i.e. such mouldings as, while less pigmented, are given a special, interesting and very good appearance (resembling terrazzo or marble) through strewing e.g. quartz gravel or marble quarry over a gelcoat. The appearance of polyester-based cast panels having a smooth front and a sufficiently thick gelcoat can even be improved by means of polishing. Figs. 6 and 7 illustrate the application of two different polyester-based cast panels.

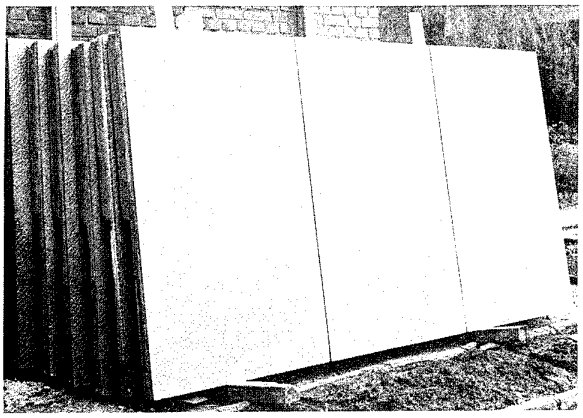

Fig. 6a

An important factor in the manufacture of cast stone is the type of the polyester resins used. The only material suitable for this application are light-fast, minimum-yellowing UP-resins having appropriate viscosity and curing properties. Where exposure to thermal load must be expected for the cast-stone structure, this must be taken into account through the use of UP-resins with increased heat distortion temperature. Special types of resin were developed for this application, and their outdoor behaviour was observed over many

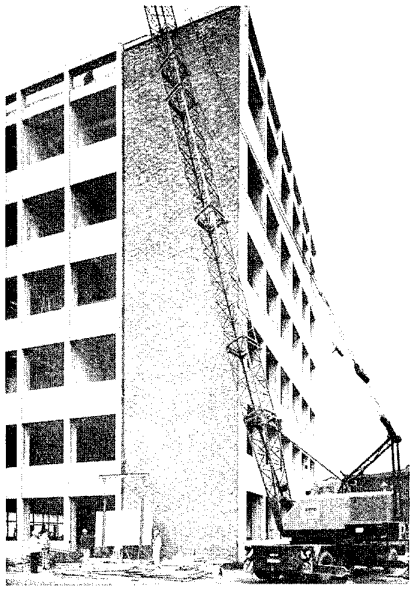

Fig. 6b

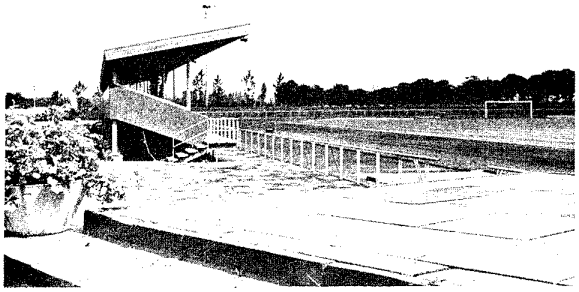

Fig. 7

years. It is interesting to note in this connection that substantially differing outdoor behaviour is shown by two UP-resins made from the same chemical-components but having different crosslinkage. The cast-stone panels that were made from the more crosslinked UP-resin revealed a clearly recognizable change of appearance as early as after short outdoor exposure. The originally blue pigmentated panels had adopted a greyish blue shade. In the case of unannealed panels, this may be due to the higher content of residual styrene.

What was earlier indicated for GRUP quite generally applies to the outdoor behaviour of cast-stone panels as well. With silicate-based aggregate, this can be pretreated with organic silicon compounds to improve the adhesion of the binder to the aggregate and the outdoor behaviour of the component. Only selected, absolutely dry aggregate should be used for making cast-stone.

The manufacture of a good polyester-based cast-stone requires adequate experience in every case.

4. POLYESTER-BASED MORTAR

Polyester-based mortar only differs from polyester-based concrete by the finer aggregate (up to 5 mm particle diameter) and a higher resin content (resin/aggregate mixing ratio: $\frac{1}{4}$ to $\frac{1}{8}$). In the Federal Republic polyester-based mortars have been used with great success for about 15 years in acid-proof constructions, i.e. ceramic tiles and bricks required to be resistant to chemicals are laid in polyester-based mortar. Its advantages over cement-based mortar are the

same as with Leguval-based concrete. Fig. 8 shows the lining of a 'beater', i.e. of a large-sized container in reinforced concrete for cellulose processing. About 7 years ago, this 'beater' was lined with ceramic tile laid in Leguval^{R}-mortar. The liner was subject to tremendous chemical exposure. Within a daily cycle various chemicals in aqueous solution were charged to the 'beater' at temperatures up to 50°C: caustic soda solution, chlorine or sodium hypochlorite solution, sulphuric acid, sodium bisulphate solution and dilute sulphurous acid. The pH changed from 12 to 1 in every case. The damage to and flaking of the ceramic tiles now observed was such that the 'beater' had to be repaired. The Leguval^{R}-mortar showed almost no indication of attack. In our view, this is a striking example of the good chemical resistance of polyester-based mortar.

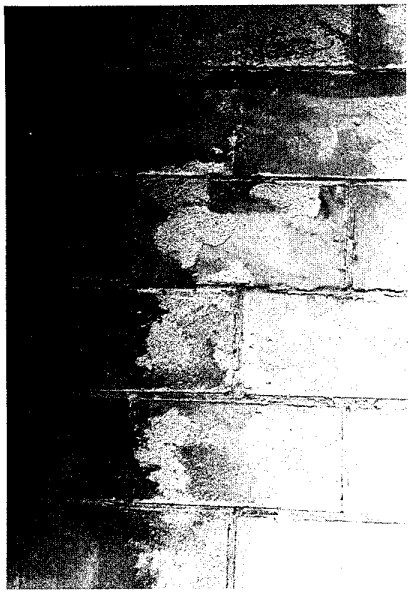

Fig. 8

Polyester-mortars were also used as coating material for the protection of sewers made from ordinary concrete. About 6 years ago the first stretch of by the 'Kubet-Technique' coated* concrete sewer was laid in Hanover (4). Good experience was also made with manually coated concrete pipes. To ensure perfect protection of the concrete even at the joints, the socket ends of the pipes are given an interior coat and the spigot ends an exterior one. With such coating application it is always an advantage first to apply a prime coat—most suitably based on an isocyanate-modified UP-resin—which is discussed in more detail below. With concrete pipe having a diameter of below 1000 mm no case of separation of the polyester-based mortar has so far been heard of, provided the coating was applied in consistency with the material.

For completeness' sake the 'plast-veneer-beton technique' should also be mentioned by which at first a polyester-resin coat 0.5-1 mm thick is applied to a special core provided with a release agent. The gelation of this coat is followed by the application of another polyester-resin coat and, as long as this has not yet been gelled, the mould is filled with ordinary concrete, as usual, and the concrete compacted by thorough vibration. This so-called 'wet-in-wet procedure' needing a special type of UP-resin, too, yields a satisfactory bond between the plastics coat and the concrete. The first pipes manufactured by this technique were laid in Würzburg in September 1964. (cf. KLOEKER and KAYSER (3)).

Great significance has been gained in the FRG by industrial flooring (made from polyester-based mortars). According to cautious estimates, more than 140 000 square metres polyester-based flooring was applied in the last 8 years in chemical plants, dairies, breweries, factory shops and storage sheds as well as on roads and bridges, etc. Initially, there was occasional failure on large surface areas due to flaking. We systematically studied this problem and developed a special washprimer. This washprimer is based on a combination of a flexible type of UP-resin with good adhesion strength and an oligoisocyanate compound. The viscosity of this combination is not particularly low. Nevertheless, the effect shown by this primer in the alternating temperature test was considerably better than that of very low-viscosity combinations of UP-resins and styrene. Cement concrete slabs that were coated after priming with polyester-based mortar (coat thickness: 1-2.5 cm) and exposed to an alternating temperature test applying a daily cycle of +60°C and −18°C revealed flaking within the first 3 months when primed with low-viscosity combinations of styrene and UP-resin. No damage was recognized after this period, when combinations of flexible Leguval^{R} resin and isocyanate were used. Severer test conditions were applied thereafter in such a way that after a cooling period of about 1 hr at room temperature the warm panels were placed into a water bath having a temperature of about 20°C for the period of about 2 hrs and then kept at −18°C in a freezing cabinet overnight. As no flaking was noticed even after 6 months, the test was discontinued and the primer put to large-scale field testing. Flooring obtained from polyester-based mortar was proved highly successful wherever applied over this primer appropriately and in consistency with the material. Flaking due to poor adhesion to the substrate has not since been noticed any longer. It should be added that it has proved a great advantage to seal the pores of polyester-based flooring with an unfilled UP-resin containing an isocyanate wherever such flooring is subject to wet exposure such as in chemical plants or breweries.

New applications of great interest in the building sector have materialized for our newly developed special UP-resin with high reactivity and chemical built-in amine accelerator. This resin, which has proved suitable for the formulation of surfacing compositions (fillers) with good shelf life, e.g. for car bodies, is quite useful for the formulation of prefabricated polyester-based mortars. Such products are said to have a shelf life of at least 6 months, and they have been found interesting materials both for industrial uses—e.g. high-speed repair, fastening of dowels and other holding fixtures in steel-reinforced concrete and brickwork, for force-transmitting adhesive bonds between prefabricated concrete components—and for the Do-it-yourself sector, e.g. in agriculture.

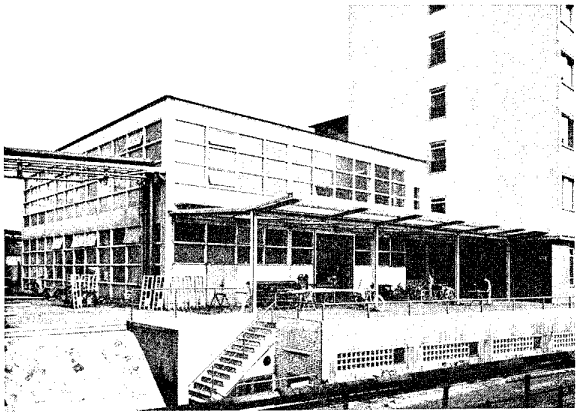

Fig. 9

The high reactivity and thorough cure of the special resin above even allows its application at temperatures below 0°C. Fig. 9 illustrates a repair shop building constructed from prefabricated concrete components between which force-transmitting adhesive bonds were obtained with this special Leguval^{R}-mortar at temperatures around −10°C. This building is now 6 years old and in the meantime has not given rise to any complaints. The same mortar was used in the force-transmitting connection between −5° and −23°C of the prefabricated reinforced concrete elements of a bridge in the Alps 3 years ago (see Fig. 10). A tensile strength of 100 kgf/cm^2 was specified. Preliminary tests revealed that the tensile strength in flexure of prisms 4 × 4 × 16 cm, which had been prepared and cured in a freezer at −18°C, had a tensile strength in flexure of 280 kgf/cm^2 after 3 days of storage at this temperature. The same compound cured at +20°C had

* cement

a strength of 300-320 kgf/cm^2. This bridge has not since revealed any negative effects.

In closing this section, mention should also be made of an experiment that has so far been successful: a bridge constructed from prefabricated components made of steel-reinforced concrete was provided with a Leguval/Desmodur^R primer and a topping about 3 cm thick based on mortar with a flexible type of UP-resin, instead of a copper foil (for insulation) and an asphalt topping 15 cm thick. This surface was sealed with the resin combination used for the primer, whose viscosity was reduced through the addition of styrene. The bridge was constructed under partly unfavourable conditions, but at temperatures above 0°C, early in 1965 (Fig. 11).

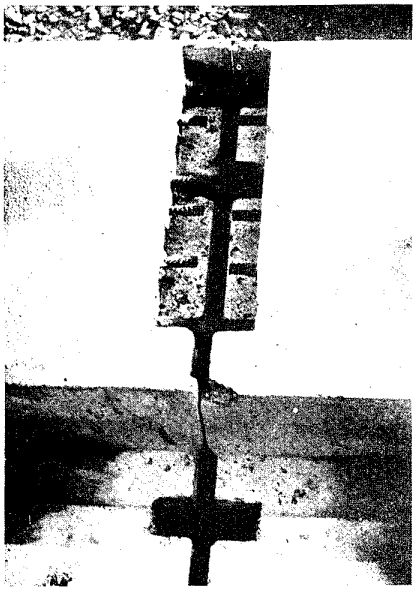

Fig. 10

Fig. 11

5. SEALING AND JOINT-FILLING COMPOSITIONS

UP-resins filled with e.g. quartz flour, slate flour (at a ratio of 1/1 to 1/3) were already used in the last decade for filling the joints of various types of sewers, especially stoneware sewers. For about 5 years the stoneware industry has supplied pipes and fittings of 100 to 200 mm nominal diameter with a sealing element consisting of special rubber and a centring fixture; the space between the sealing element and the socket end of the pipe was filled with a mixture of quartz flour and slate flour and a flexible type of UP-resin. This type of stoneware pipe is known as 'Steckmuffe L' (L-type socket-and-spigot pipe). Prior to joint-filling the socket end of the pipe is given a special prime coat, which ensures the outstanding adhesion of the polyester-based sealing compound to the stoneware. When smashing such socket ends, it is recognized that this adhesion frequently exceeds the inherent strength of the stoneware. Stoneware pipe with larger diameter (up to 700 mm) has also recently been lined with polyester-based sealing compounds instead of polyurethane products, which yields a slight taper of the socket inside. The spigot end of this large-diameter pipe is still coated with a polyurethane elastomer, e.g. Desmoflex^R*. This type of pipe seal is called 'Steckmuffe K' (K-type socket-and-spigot joint). Stoneware pipe fitted with the sealing element described above ensures high economy of laying, because it eliminates all the joint-sealing operations hitherto necessary at the construction site. The 'L-type socket-and-spigot pipes' with tapered spigot ends are coated with a lubricant and need only be slid into each other. As a result, laying operations are unaffected by weather. The described socket-and-spigot type stoneware pipe ensures leakproof and flexible sewers that meet all service requirements. The flexible pipe joints absorb any displacements possible.

Brief mention should also be made of a very interesting development within the range of the flexible types of UP-resin. This new material is the solution of a slightly reactive UP-resin in styrene, which can be hot or cold-cured by conventional methods and which, when cured, excels by an elongation at break at about 10 kgf/cm^2 tensile strength and 20-30 hardness units Shore A that is unusually high for UP-resins. Elongating the material by 100 percent only requires a low force (about 2 kgf). Like any other resin, the new development product can be loaded with fillers and be made thixotropic with appropriate additives. Because of its high elongation at break (about 200%) and its fairly favourable price in comparison with polysulphide and silicone, we consider this new type of UP-resin a binder for a versatile joint-filling and sealing composition for use in civil engineering and building construction work. After three years of outdoor exposure no reduction of flexibility was noticed for a road joint obtained with this product. Another remarkable property of the material is its very good adhesion to otherwise difficult substrates such as glass.

6. THIN-FILM COATINGS

Although UP-resins have for many years been used with good success in wood coating, especially in the furniture industry, the coating with general-purpose UP-resins of ordinary concrete and steel presented difficulties or did not yield the desired success. Either did the standard resins flake off because of their low flexibility, or the flexible types of UP-resin, though showing good adhesion, had insufficient resistance to corrosive media. These difficulties were overcome with the

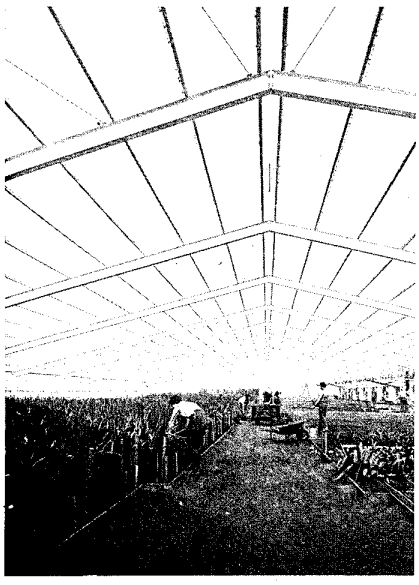

Fig. 12

* Desmoflex^R is a registered trademark of Farbenfabriken Bayer AG, Leverkusen.

help of UP-resin/isocyanate combinations, which proved quite successful even in the anti-corrosive finishing of steel. Fig. 12 shows a large-sized greenhouse whose steel structure was given a protective Leguval^{R}/Desmodur^{R} finish 8 years ago. The steel girders were cleaned by means of sand-blasting. Spots damaged through mechanical action do not reveal subsurface rusting of the finish. Similarly good results were obtained in finishing road tankers, bridge elements, etc. However, this coating system was not accepted on a large scale, because at least 3 components must be mixed at the construction site.

A new development product allows the application of a Leguval^{R}/Desmodur^{R} combination as a two-component material. A characteristic property of this isocyanate-modified UP-resin is its storage stability over a relatively long period of time when mixed with more Desmodur, even in the presence of a curing accelerator. Whereas normal UP-resins, when mixed with isocyanates, undergo heavy viscosity changes within from half an hour up to several days depending on the quantity of isocyanate added, and whereas this may even lead to gelation under specific conditions, there is practically no viscosity change with the newly developed product within several weeks after the addition of 20% Desmodur, appropriate storage provided.

The new product excels by outstanding adhesion even on critical substrates such as metal and glass. In the presence of air, it also cures to yield a tack-free surface without the addition of paraffin. This property and the surface hardness can be improved through an addition of Desmodur^{R}. Resistance to various types of chemicals, and especially to fuel oil, is very good. We therefore consider the product suitable for coating applications in general, and for the formulation of primers as well as finishing coats and sealing applications in particular. Through combination with suitable resins of the flexible type it is possible to obtain flexible and elastic products of good adhesion such as required for the formulation of primers used in steel coating.

7. EXPANDED MATERIALS BASED ON UNSATURATED POLYESTER RESINS (RIGID POLYESTER FOAM)

In closing, I would report on a new development that has made a stir under the designation 'Expandable Leguval^{R}'. This special UP-resin allows the manufacture of mouldings from expanded unsaturated polyester resin by a new and fairly uncomplicated technique.

For the manufacture of mouldings from 'rigid polyester foam' the moulder is required to add to the 'Expandable Leguval^{R}' a curing agent, as usual, as well as a newly developed blowing agent in proportions of 3% to 10%. The Leguval^{R} cure and the decomposition of the foaming reaction ranges between 30 secs and about 10 mins. It is thus considerably longer than with some other thermosetting foam systems. Mould release time is about 30 mins to 5 hrs, depending on the formulation of the foam and the moulding to be produced. In general, mouldings can be released after 1 hr. In foams extended with lightweight fillers—e.g. expanded clay, expanded glass and the like—the capacity of these fillers for heat absorption has a favourable effect on maximum temperature, mould release time and shrinkage. The 'Expandable Leguval^{R}' currently allows the production of foams with densities between about 120 and 250 kg/m^3—so-called 'heavy rigid foams'. The compressive strength of these foams results from the higher density and the stronger cell walls and is in the order of about 20 kgf/cm^2. As compared with the lightweight polystyrene and polyurethane foams, which have densities between 30 and 70 kg/m^3 and a coefficient of thermal conductivity in the order of 0.02 to 0.03, the rigid Leguval foam has a quite favourable coefficient of thermal conductivity ranging between 0.04 and 0.09. Being about 80%, the content of open cells is relatively high. However, this has a positive effect on sound attenuation. Understandably, water vapour permeability also is considerably higher than with the lightweight foams indicated above, which have about 90% closed cells. This increased water vapour permeability is highly appreciated in the building industry for the manufacture of 'breathing walls'. No decrease of the mechanical strength was noticed in the temperature/humidity test, i.e. after 16-day storage at +70°C and 95% R.H., and after 120-day storage at 50°C and 55% R.H.

As a result of the relatively long starting times, 'Expandable Leguval' lends itself favourably to the manufacture of building components from expanded clay, expanded glass beads or similar light-weight material. Such building components can be made, for example, by way of mixing the expanded clay with Expandable Leguval plus hardener (peroxyd) and blowing agent in a conventional mixer, filling this mixture into the mould, perhaps slightly compacting by means of vibration, closing the mould and allowing the material to expand and cure under slight pressure. It is conceivable that such a procedure can also be carried out at the building site. No complicated and expensive equipment is required, but devices generally available in the concrete industry will do. Another uncomplicated method is to first fill the mould partly or entirely—this depends on mould dimensions—with expanded clay or expanded glass beads and then to pour the mix consisting of expandable Leguval plus peroxide plus blowing agent over the expanded clay. The mixture will sink to the bottom, gradually foam-filling the cavities between the expanded clay beads from below under slight pressure. Continuous application from two-component pouring equipment is also possible. Table 2 represents the properties of such lightweight fillers bound with rigid Leguval^{R}-foam.

We think it worth mentioning in this connection that it is possible to manufacture sandwich elements in one single operation from e.g. GRUP, plasterboard, asbestos-dement and other materials.

We see potential applications for the rigid Leguval foam wherever higher strength and higher water vapour permeability is required, apart from good heat insulation, than generally obtainable with the so-called lightweight rigid foams based on polyurethane, polystyrene, phenolic resin and

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* Moltopren^{R} is a registered trademark of Farbenfabriken Bayer AG, Leverkusen/Germany.

TABLE 2

Mechanical strength data of rigid Leguval foam incorporating fillers

	Filler	expanded glass	expanded clay
Density	kgf/m^3	300 - 400	400 - 600
Compressive strength	kgf/cm^2	15 - 30	35 - 45
Modulus of elasticity from compressive strength	kgf/cm^2	2500	2300 - 3300
Flexural strength	kgf/cm^2	10 - 20	20 - 25
Modulus of elasticity from flexural strength	kgf/cm^2	3000 - 6000	5000 - 9000
Thermal conductivity kcal. m^{-1}. hr^{-1}. °C^{-1}		0.07 - 0.14	
Water vapour permeability	gf/m^2. day	20 - 30	

urea formaldehyde resin, which have densities below 100 kgf/m^2. Wherever emphasis is placed on thermal insulation and strength is of secondary or no importance, these lightweight foams—especially Moltopren R*—should be preferred.

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Sixth International Reinforced Plastics Conference

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Glass fibre reinforced plastics in building – present situation in Italy and needs for further development

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DISTRIBUTION AND ANALYSIS OF THE MARKET

The Italian glass fibres reinforced plastics production for 1967 can be estimated at about 21 000 tons. The 54.75%, that is 11 500 tons, has been absorbed by the building field, both as corrugated and flat translucent sheets and as curtain walls, cladding panels, partition walls, pre-fabricated roofs, cottages, sanitary fittings, concrete forms, swimming-pools, etc.

As information, we point out that FRP in the building represent about 5% of all the plastic materials used in this field. The distribution is according to the principal application groups or better according to the principal functions at present fulfilled by FRP in buildings.

The first group is essentially constituted by roofs, spires, domes realized by pre-fabricated elements. The second group comprehends both the flat and corrugated translucent sheets for which the bearing function is generally fulfilled by metallic structures, cladding, curtain and partition walls, supported by a frame. The applications where FRP have a finishing function (doors, door and window frames, one piece baths, swimming-pools, etc.) belong to the third group. Lastly, the fourth group comprehends essentially the concrete forms, both those used for concrete poured in loco and those utilized to produce prefabricated concrete elements.

As the Italian building industry is still feeling the consequences of an unfavourable situation began in 1962-63, probably to analyse now the reinforced plastics rôle in this particular and important field of our economy could appear out of place.

However, the most important possibility for the reinforced plastics market arises just from the deficit of buildings that has been becoming increasingly remarkable, as well as from the present transformation of the construction techniques and the development of the engineering design.

The present FRP situation in the building is reported in the table 1, where the tonnage and per cent distribution concerning 1967 is specified.

TABLE 1

Principal FRP applications in the building—relative tonnage and per cent distribution for 1967

	1967	
	Tons	%
Bearing structures		
Domes, spires, vaults, etc.; composite structures with reinforced concrete, steel, etc.	200	1.75
Secondary structures		
Sheets for industrial and civil buildings	10 000	87
Cladding panels, curtain and partition walls	650	5.5
Finishing structures		
(Doors, window and door frames, swimming-pools linings, sanitary, facing materials, gutters, etc.)	400	3.5
Building yard equipment		
(Concrete forms, barrack, tools shelters, etc.)	250	2.25
Total	11 500	100.00

APPLICATIONS

Now we are going to illustrate, through a brief analysis of the solved problems, some of the most representative applications of glass fibres reinforced plastics in the building field, pointing out the principal functions they have fulfilled.

FRP ADVANTAGES

The illustrated applications are a good example both of what is at present realized in Italy, and of the fundamental concepts on which the use of FRP seems to tend.

In order to point out better the future FRP position in the building and their great possibilities in this very important application field, it is necessary to consider the favourable valuation from those who act in the building field (designers, structures manufacturers, pre-fabricators, contractors) as regards the main qualities of FRP that distinguish them from the other plastic materials and from the traditional ones.

1. The first factor of valuation is represented by the variety of fabrication methods. For each level of production it is possible to select the more suitable process, in order to realize economically both a few building elements and an industrial series.
2. Another interesting factor is the technology of FRP, that allows the easy fabrication of complex shapes, with local and gradual variations of the thickness and with the possibility of inserting, during the moulding, sections or structural shapes to get higher resistance and stiffness specific zones.
3. Two other great factors in selecting FRP are their resistance/weight and modulus/weight ratios. The former, which is very high, allows the use of light sections with the consequent benefits in lightening the bearing structures, in reducing the expenses of transport and erection and in cutting down the material expenses. The second ratio, that on the contrary is very low, being comparable with the one of wood and granite, has a remarkable significance in acoustics. If with this ratio we consider the low coefficient of thermal conductivity of FRP, it is easily comprehensible as these materials are greatly considered for the particular comforts they offer.
4. Glass fibres reinforced plastics are the unique materials truly structural having the characteristics of translucency. On the other hand, by means of a right formulation of the resin, structures both with high transparency and quite opaque and with any colouring can be obtained.
5. Owing to their particular nature, FRP present no corrosion and on the other hand they are resistant to the most chemical agent.
6. The most important factor, which is highly discriminative in valueing a structure for the building concerns the number of intervention the structure needs, once erected. Fibre glass reinforced plastics, with colours incorporated, resistant to impact and corrosion, really need limited or no maintenance and this is well considered by the contractors.

NEEDS FOR FURTHER DEVELOPMENTS

These characteristics are today well known to the designers, even if more diffusion of informations and better communications between the designer and the manufacturers are necessary.

The over-simplified solutions tending to turn out in FRP designs conceived and developed for other materials, have been

completely neglected and at present engineers design rationally in function of FRP, considering all their aspects and conceiving new structures that takes in consideration all properties of FRP, included their limitations. The structures resistant by shape and those pre-stressed are a good example of the basic concept of the designer to reduce and sometimes to take advantage of the material elasticity.

Of course, for a really industrial development of FRP in the building, it is necessary to solve some problems, that is: the building elements normalization, the production cycles rationalization, which is bound to the building elements normalization too, the interpretation of the tests results, especially for fire and to ageing, the normalization of the tests methods themselves, and lastly the establishment of research institutes to orient the builders and those who act in this field and to select the quality.

Now, the matters that more often come out in valueing the glass fibres reinforced plastics in the building concern essentially the cost, the combustible nature of materials and the behaviour to ageing.

The matter of cost, that is susceptible of considerable reductions with the expansion of the raw materials, the rationalization of the production methods of FRP and the right valuation of the materials to be used and of thickness to be adopted, is often wrongly presented.

On the ground of the present costs too, it is necessary not to value the pure cost of the FRP structures, but its relation as regards the performances guaranteed by FRP (rapid erection, lower cost of the supporting structures, possibility of industrializing some processing phases and over all durability and reduction of the maintenance expenses.)

The matter of the fire resistance of glass fibres reinforced plastic is, one can say, merely psychological; it can be solved essentially on the level of the greatest operators in the building field and especially of the Insurance Companies, by properly interpreting the functions of each structure, estimating the FRP qualities and fixing precise specifications.

First of all it is necessary to specify that the fire behaviour of FRP is quite different from that of other plastics materials. During the combustion there is no dripping as in the case of thermoplastics. On the other hand, the fibre glass reinforcement is not altered and, together with the carbonized layer, acts as a protection for the layers below. This has been particularly pointed out during some fires where some FRP tanks for the fuels transport have been involved. During these fires, the metal structures appeared twisted and in some cases melted, while the FRP tanks, also with some millimetre of surface carbonized, has withstood maintaining intact the content. For better valueing this behaviour it is necessary to establish some tests duly developed for FRP, examining the structures under their real dimensions and specific condition of use. In this way the Reinforced Plastic Group of M. E. C. is acting.

The main existing methods to estimate the building materials have been examined, both as regards the fire reaction (inflammability, fire spreading, fumes development, etc.) and the fire resistance, as preservation of the functions fulfilled when the structure is placed in an oven heated following a normalized curve temperature/time.

Successively, it has to establish the most suitable methods for the FRP valuation. As information, we report the results of some tests carried out in Italy by the Anti-Fire General Direction of the Home Ministry, in conformity with the circular 91 of September 14/1961 concerning the safety rules for the protection against the fire of steel structure buildings for civil use.

These tests, carried out on sandwich structure having an eraclit core, thickness 63-64 mm, allowed the homologation of the structure as constructive element for class 45 buildings. This means that the structure withstood in the oven for over 45 minutes, maintaining its function, and this is certainly a very good result.

As regards the fire reaction of the structures (inflammability, flame spreading, fumes development, etc.) we can say that at present it is possible to formulate particular resins allowing to meet the minimum requirements for their use in the building. For these tests too we are trying to establish efficient methods to control clearly the FRP behaviour.

As regards the ageing behaviour, various tests have been carried out following various processes, among them the most followed are:

1. The treatment in boiling water for a certain number of hours (particularly for sheets).
2. The freezing test, consisting in examining a panel after 20 cycles respectively at temperatures of −20°C and +40°C, in air with an humidity rate of 90%. Each cycle is effected in 12 hours (6 at the lower temperature and 6 at the higher one).
3. The exposure to particular artificial conditions.

The exposure of FRP to a combination too of these conditions has given always satisfactory results. However, the chief problem consists in having yet no possibility to establish a comparative term with the natural ageing. This causes the difficulties sometimes met by the manufacturers of FRP structures in guaranteeing the durability of the structures themselves, by proving it. Fortunately, the FRP buildings realized in Italy for about 10 years and for a longer time abroad represent the first comparative terms.

On examining these buildings, even if in particular heavy atmosphere of industrial zones, we have verified the complete resistance of FRP, unlike other materials that on the contrary required numerous maintenance interventions or directly the replacement. Also for this particular problem, the Reinforced Plastics Group of M. E. C. is examining the possibility of conceiving an efficient valuation method to give the most precise idea on the behaviour in the time. However we are promoting a programme of tests for examining the structures erected for year in order to get useful information to establish their behaviour in the time and to establish comparative terms with the accelerated tests.

CONCLUSIONS

We have just considered the present FRP situation in the Italian building, their main applications and also the problems to be solved for a complete development in this field.

We have also considered the main characteristics took into consideration by the manufacturers on estimating the glass fibres reinforced plastics, and the trends in designing by using FRP.

The FRP characteristics today are well known and we have seen that the most specific applications are based on three essential concepts, all tending to balance the material elasticity and to take advantages of their important characteristics:

(a) Fabrication of composite structures, mainly sandwich structures.

(b) Fabrication of resistant structures by shape.

(c) Construction of pre-stressed structures.

As regards forecasts for the immediate future, we can say that the development of fibres glass reinforced plastics will occur chiefly in the industrial, school, hospital and commercial building, where there are problems whose resolution often is apart from the cost, while as to the residential building, other economic, organizing, and regulations factors have to be overcome before a rather interesting development can be achieved.

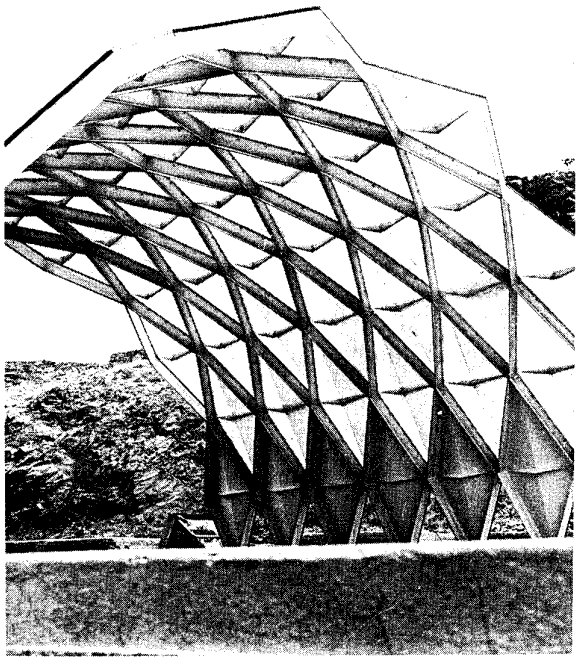


Fig. 1 This construction has been designed for a sulphur mine to provide a shelter for the production equipment. As these equipments have often to be removed, the problem was to realize a shelter construction easy to disassemble and unaffected by the sulphurous fumes developing from the numerous fumaroles of the mining area and from the material itself, under high moisture conditions. The choice of FRP resulted the only and really efficient solution.

The construction is a 240 m^2 vault, 24 m long and 10 m wide. The two ends have left open to allow the trolley enter. The polyester elements, which have a different degree of transparency, weigh 14 kg each and are 120 × 120 cm. They are connected by stainless steel bolts. The structure is joined to the foundation by means of a zinco-plated steel section, capable of absorbing the elastic movements of the structure. (By courtesy of Arch. R. Piano)

Fig. 2 This illustration concerns one of several constructions of an industrial building realized in Genoa. The construction here represented measures 60 × 40 m. The transparent reinforced polyester elements are square base pyramidal units measuring 2.5 × 2.5 m, 0.25 m high, and are constituted by a double shell whose upper membrane has a thickness of 3 mm and the lower one of 2 mm. (By courtesy of Arch. R. Piano)

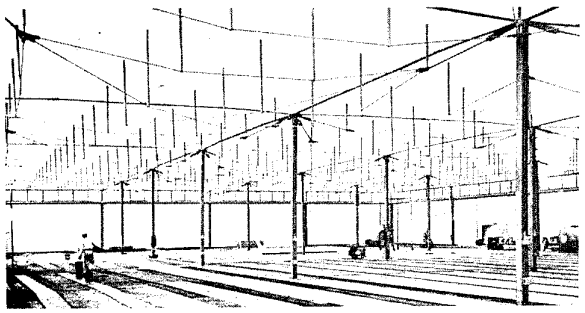


Fig. 3 The interior of the same construction. It is a matter of a pre-stressed structure whose stresses are supported in the upper part by the polyester elements and in the lower part by a steel cable net in tension. Tensions are discharged along the construction perimeter. The tension of the cable net is transmitted to the polyester elements through steel struts connected by bolts. The FRP elements constituting the external covering surface become so prestressed. Though the polyester surfaces are very thin, it becomes sufficiently stiff, uniformly distributing the tensions in every section of the elements. (By courtesy of Arch. R. Piano)

Fig. 4 Detail of the covering. The compression stress of the bolt on the polyester element is discharged by a steel plate. The polyester elements are connected each others by strips of mat impregnated with polyester resin. (By courtesy of Arch. R. Piano)

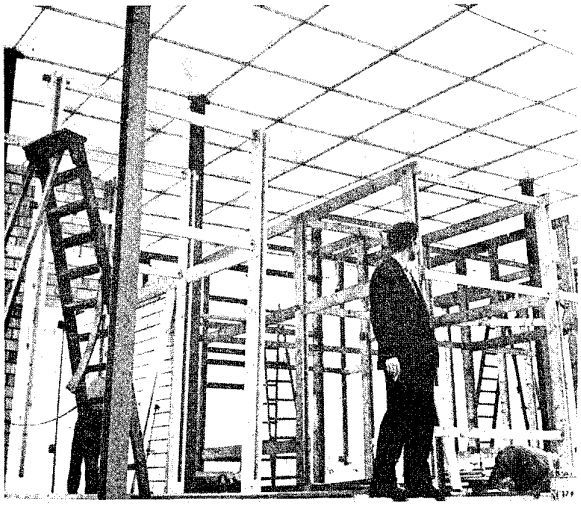


Fig. 5 The elements forming the covering of this construction are translucent square based pyramidal units measuring 1.20 × 1.20 m, 0.60 high and weighing 10 kg. (By courtesy of Arch. R. Piano)

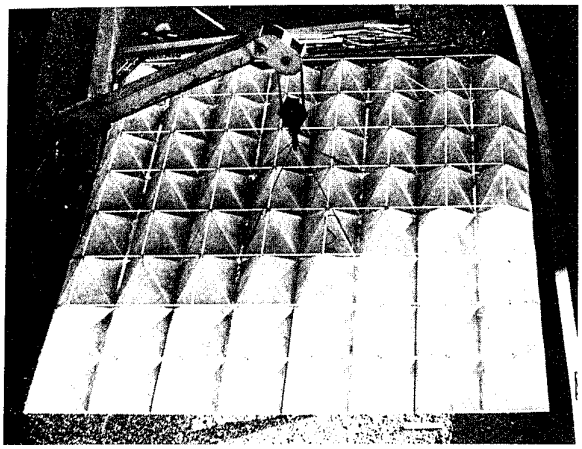


Fig. 6 As you can see in this illustration concerning another construction obtained with the same elements, the units are pre-assembled and then mounted in loco. The elements forming the structure are essentially two: the pyramidal unit and a grid of metallic tubes jointed to each other and to the pyramids by means of steel connectors. The polyester elements has a structural and covering function at a time, while the grid has the function to transmit the structure stresses to the tops of the pyramids. Each element is jointed to the other by bolts. The water-proofing is assured by elastic sections pressed by the bolts. (By courtesy of Arch. R. Piano)

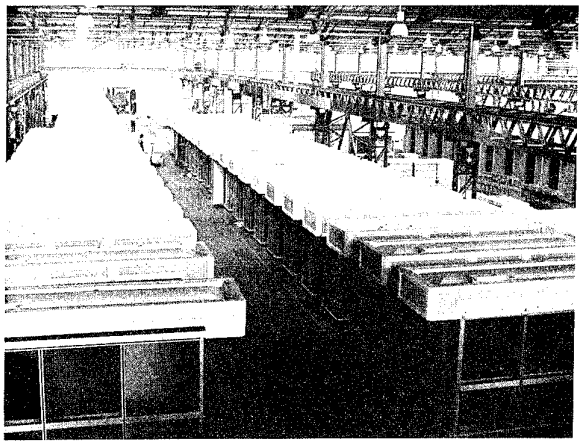


Fig. 7 Set of kiosks built up for AGIP. The covering structure has been realized in 5 parts. (By courtesy of Arch. R. Piano)

Fig. 8 This covering structure has been realized for a set of kiosks built up for Gulf. The covering with a surface of 25 m^2 has been moulded in one piece without stiffness frame but only with a joining frame. (By courtesy of Nuovo Pignone S.p.A.)

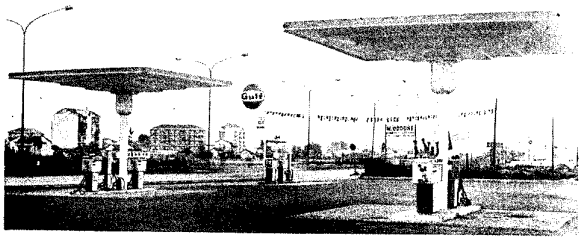


Fig. 9 Other covering elements designed for some filling stations of Gulf. The covering structures, supported only by the central column, is constituted by a simple laminate with thickness of about 5 mm. In the inside of the laminate cardboard tubes have been inserted, with the only function to increase the moment of inertia of the section. The structure has been tested under a uniformly distributed load of 7 tons, constituted of water. The test has not been carried out under higher loads, as the maximum capacity of the concavity is of 7000 litres. The drain of the rain waters takes place through the central column. At the sides the flashing lamp housings have been provided. (By courtesy of I.C.S. S.p.A.)

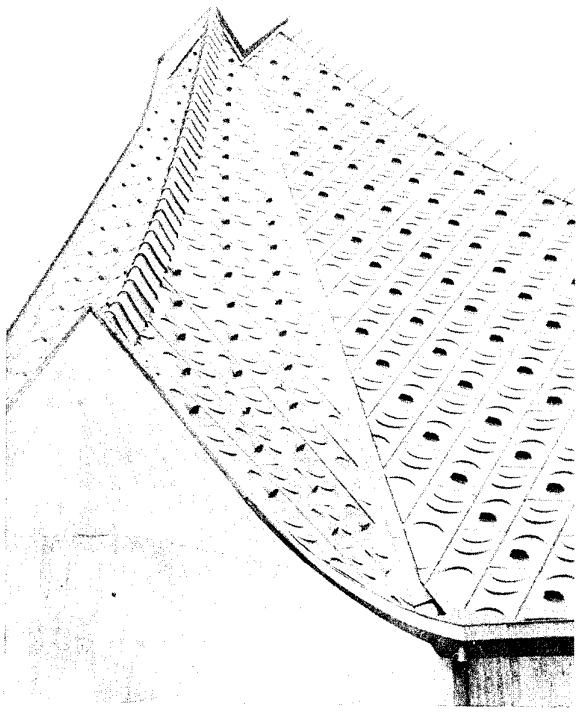


Fig. 10 The covering of this church, built up in a new quarter of Milan, is realized with FRP elements 2.40 m long, 1.20 m wide and 5 cm thick. The frp laminates have a thickness of 3 mm. The core is constituted by expanded polyurethane. The elements are stiffened by three ribs const tuting also decorative elements. Each element has also a slit used for passing the light in the interior. The edges of the panel present special joining edges by which the connection is effected. (By courtesy of Arch. A. Arrighetti)

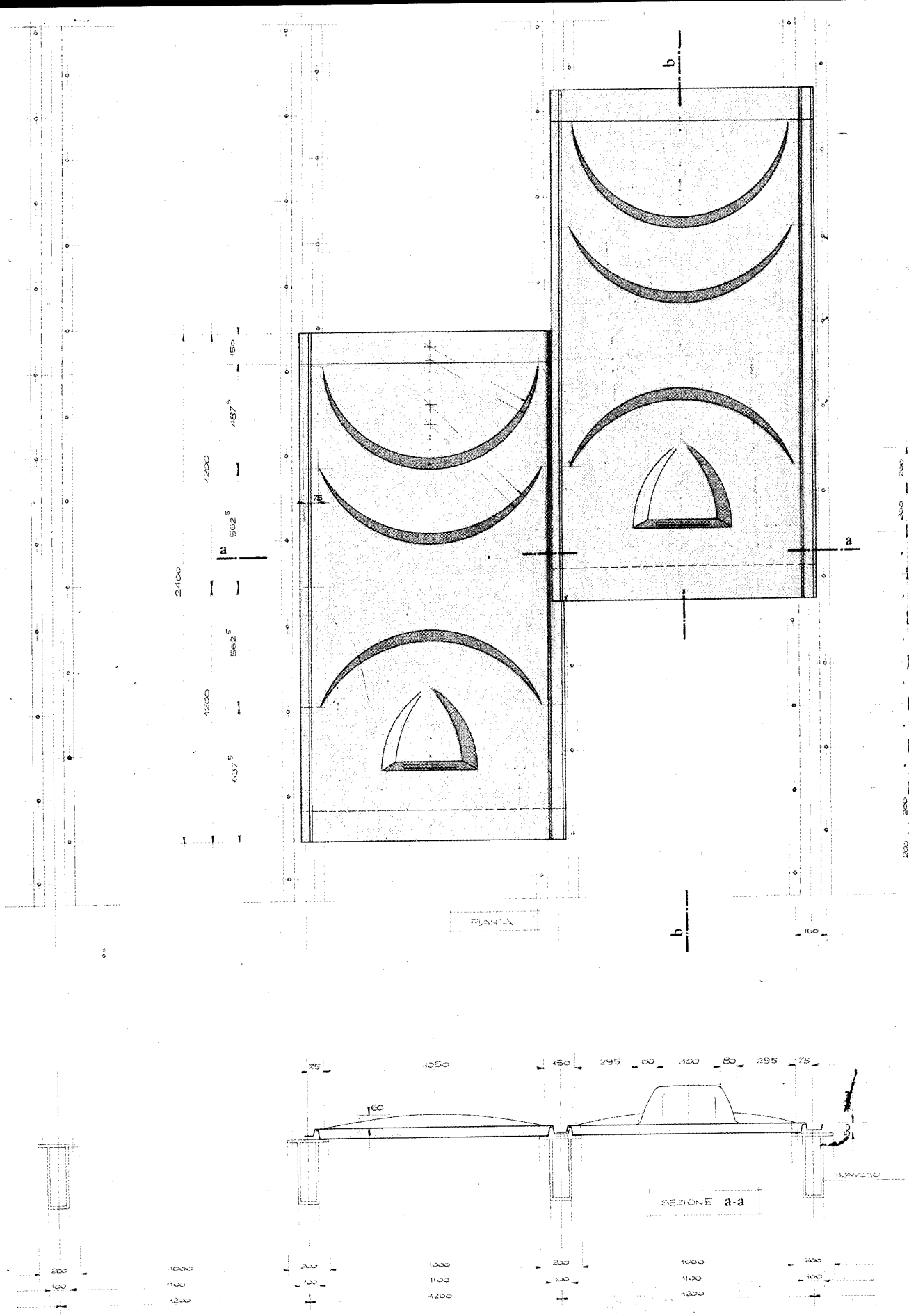
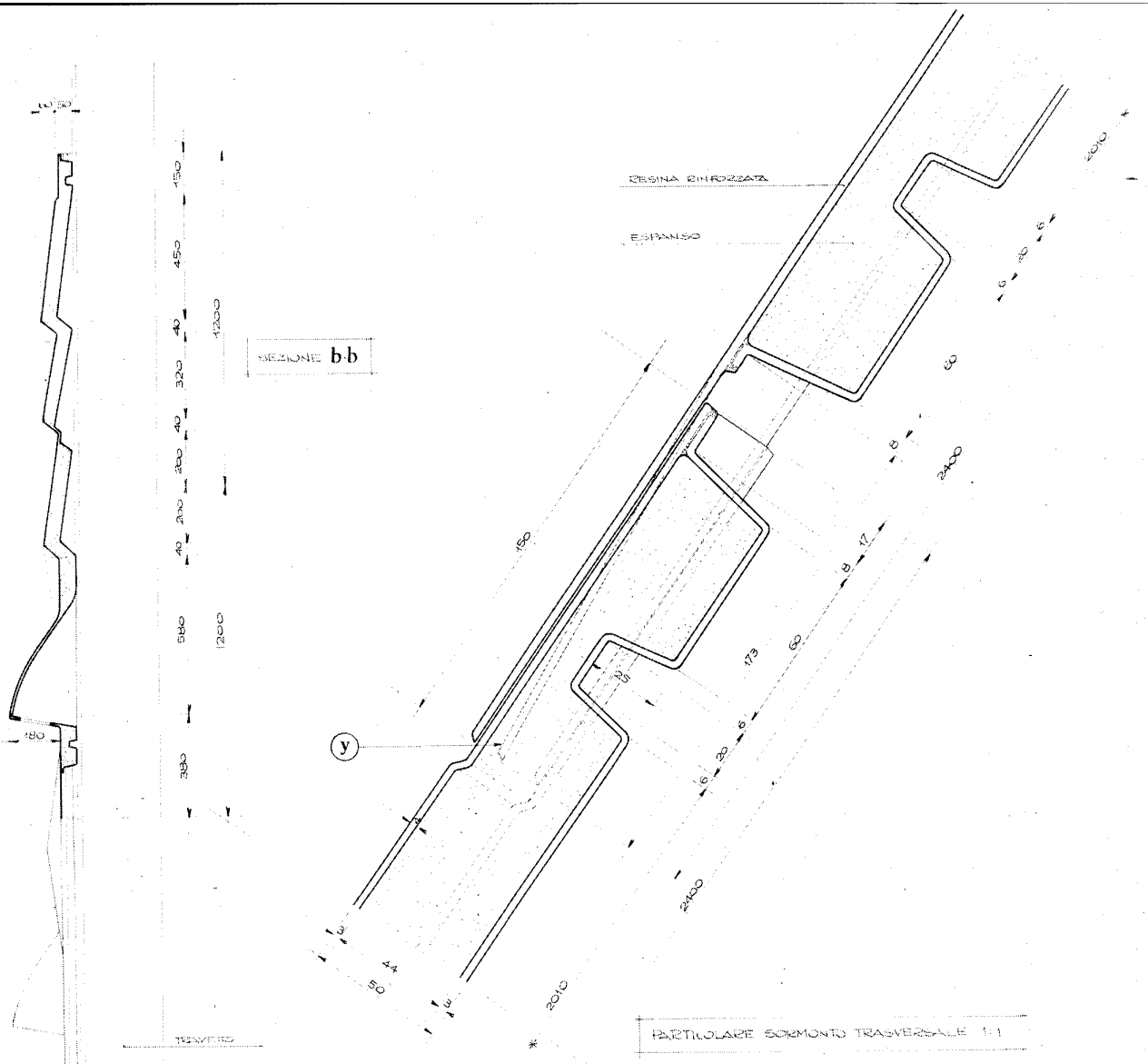


Fig. 11 Drawing illustrating the covering FRP elements in detail. (By courtesy of Arch. A. Arrighetti)



(y) NELLO STAMPAGGIO TENER CONTO DI UNA INCLINAZIONE DEL SOGMONTO PER LA FORZENTURA DURANTE LA POSA

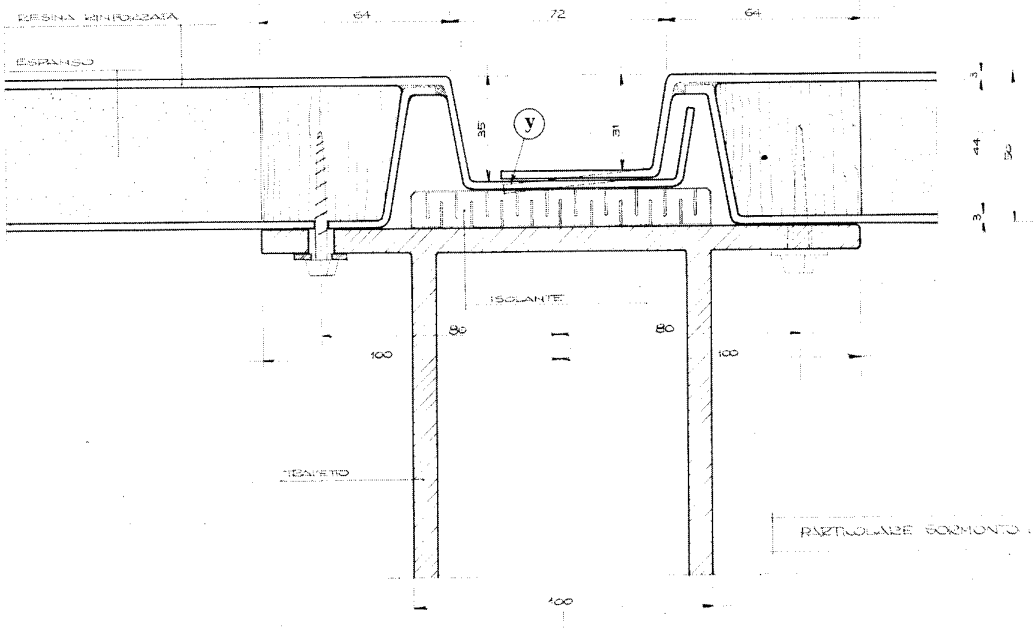


Fig. 12 This illustration concerns a part of the hospital for the Somaliland police in Mogadiscio and precisely the 'Surgery Department'. The hospital is composed of ten pre-fabricated pavilions delivered and assembled by an Italian firm.

The specifications of the contract prescribed to consider particularly the problems concerning the humidity that is very high (90-95%), the temperature, whose average in the year is 28-30°C, monsoons blowing in opposite directions during two different periods, and termites.

The modular dimension assumed in the horizontal direction has been 10 M (M = 10 cm), while in the vertical direction 6 M, 10 M, 12 M, 14 M, 20 M, 26 M and 30 M. The outside and inside walls are constituted with FRP 'sandwich' panels, 60 mm thick obtained by matched die moulding. (By courtesy of Serena Prefabbricati Edilplast)

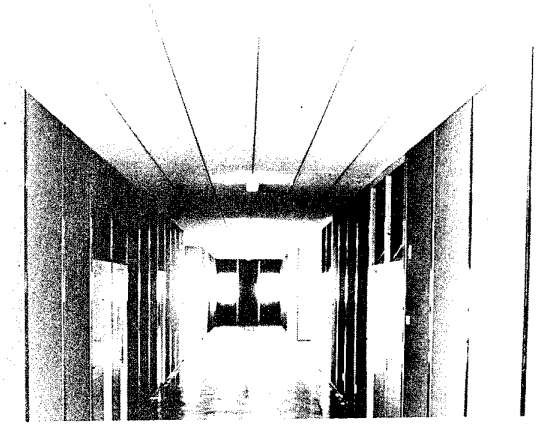


Fig. 13 Corridor of the 'Medicine Department'. The walls, constituted by the above said FRP panels, are painted with water paint. (By courtesy of Serena Prefabbricati Edilplast)

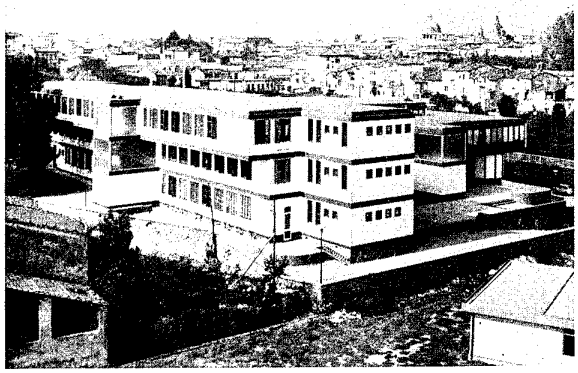


Fig. 14 A three floor pre-fabricated school formed by 24 normal rooms, 5 special rooms, a gymnasium and a covered swimming-pool, besides all services. The useful surface is of 6200 m^2. The outside walls consist of a shell in granular marble bonded with polyester resin and reinforced with glass fibres mat. The insulating core is in expanded polyurethane. The horizontal elements of the structure have as modulus 12 M (M = 10 cm). The standard height is 30 M, increasable by inserting two special elements of 6 M and 12 M. (By courtesy of E. I. Fratelli Bortolaso)

Fig. 15 The basic panel of this industrial building, particularly designed for the prefabrication of residential buildings, is the one below, whose dimensions are those of an outside wall for normal room (3.67 × 2.9 m).

The upper panel, even if it has the same composition of the previous one, is a variant of the same, having a different height and the window-space completed by a grate. In this particular case, in order to prevent the action from the environment moisture and acid fumes, the panels have been assembled in the internal part of the piers, so hiding the panel metallic frame.

The panel consists of mat reinforced laminates with expanded polyurethane as core (about 60 mm). The perimetrical metal framework allows to assemble the panel without using bearing structures or to insert the panel in the bearing structures. (By courtesy of I.C.S. s.p.A.)

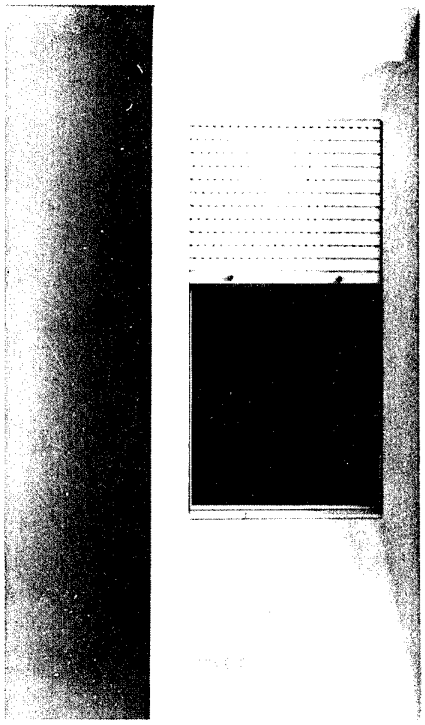


Fig. 16 The cladding wall, designed for the Instituto Autonomo Case Popolari in Milan, consists of an internal FRP face, insulated with a 30 mm thick mineral wool board and with an anti-condense barrier. This face is formed to constitute the rabbet of the window frame, equally in fibres glass reinforced plastics. The internal face should be realized with vertical panels (from floor to ceiling) of plaster and pearlite. The whole wall measured 3.4 × 3.2 metres and weighs about 80 kg. (By courtesy of Arch. M. Scheichenbauer)

Fig. 17 Holidays village. The cottages have been realized hundreds of exemplars for the account of Touring Club and have been installed in the more various climate. They have won the prize 'Compasso d'oro' for 1967. The walls, the roof, the door are entirely in glass fibres reinforced plastics with expanded polyurethane as a core and without other auxiliary structures. (By courtesy of I.C.S. S.p.A.)

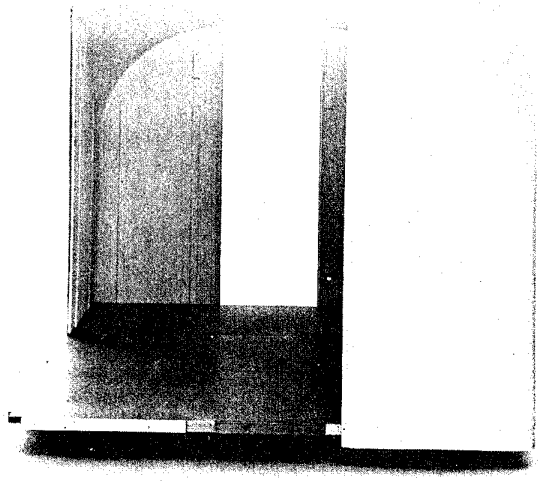


Fig. 18 Assembling phase of the walls to the floor. (By courtesy of I.C.S. S.p.A.)

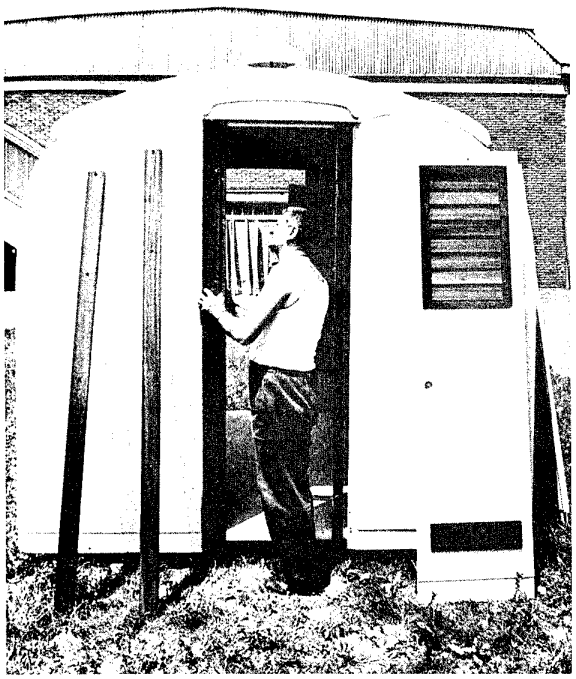


Fig. 19 Walls are gained by a mahogany structural shape painted with polyester. The structural shape is bolted with 4 double cheese brass bolts. The upper bolts of the structural shapes locked the roof that forms rabbet with the walls. The lower edge of the walls is fixed to the floor and by means of a plate, to the platform below. (By courtesy of I.C.S. S.P.A.)

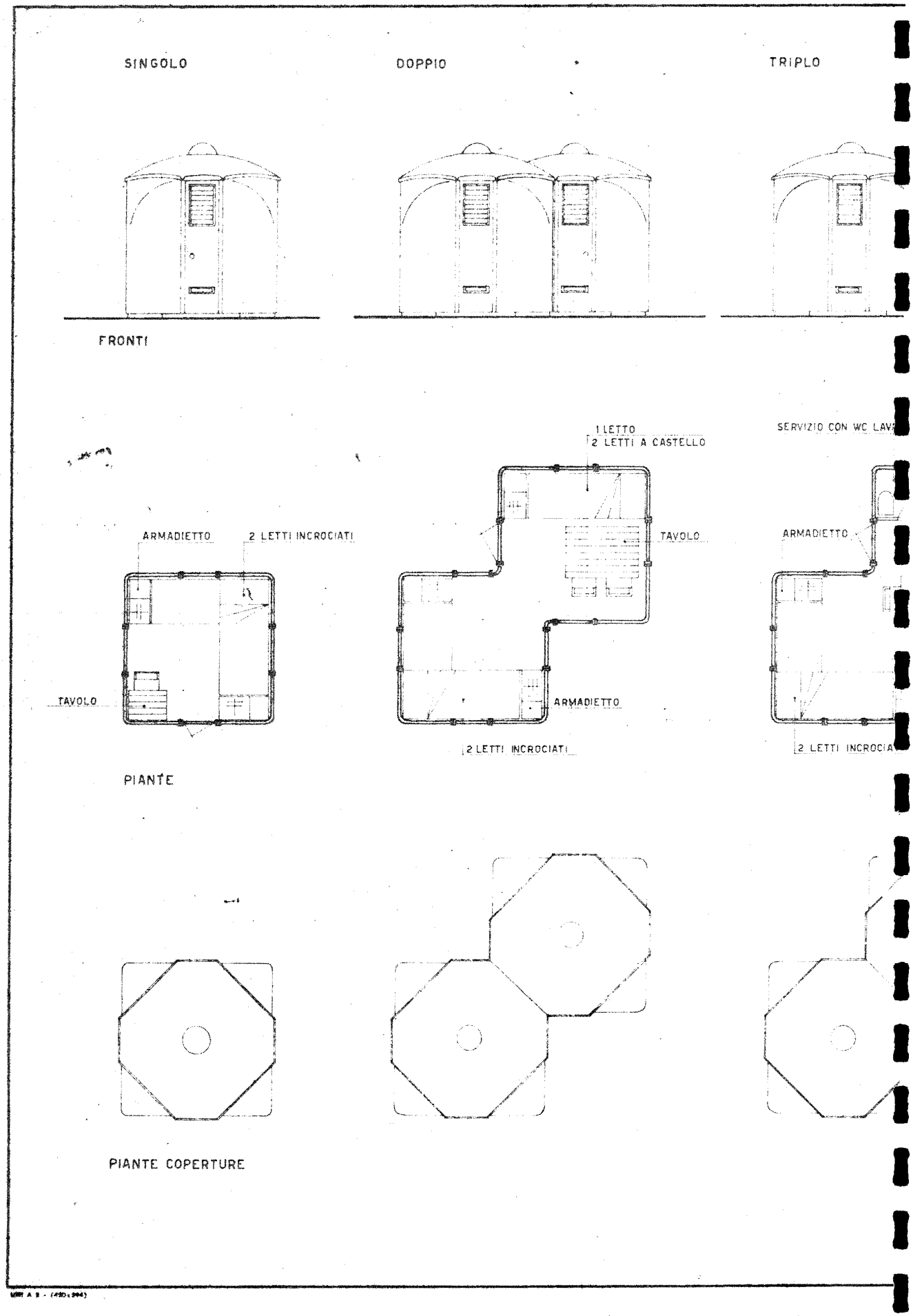
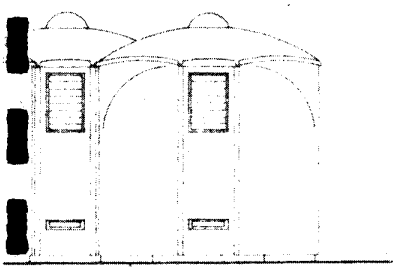
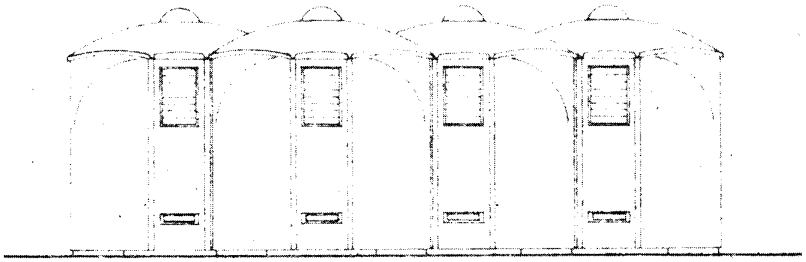


Fig. 20 Drawing presenting the different possibilities of assembling the basic units. (By courtesy of I.C.S. S.p.A.)

COMPOSTO (5 TETTI)



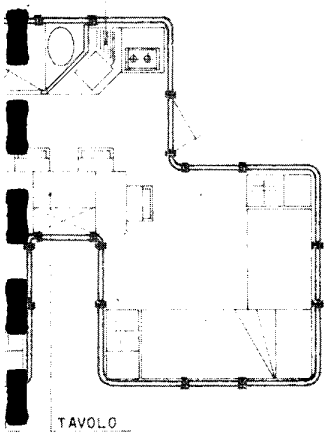


SERVIZIO CON W.C. LAVABO E DOCCIA

CUCINA LAVELLO FRIGORIFERO

2 LETTI INCROCIATI

DOCCIA CUCINA LAVELLO FRIGORIFERO



TAVOLO

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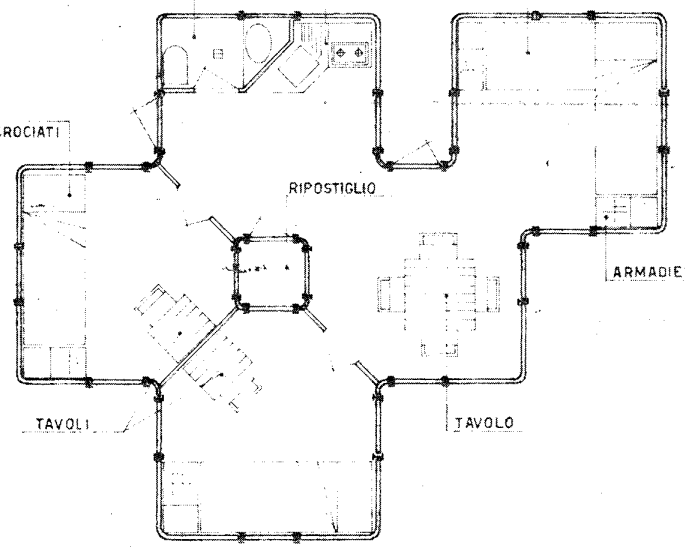

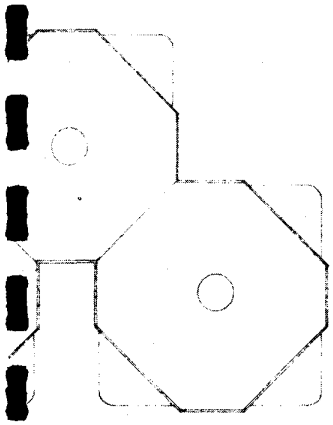

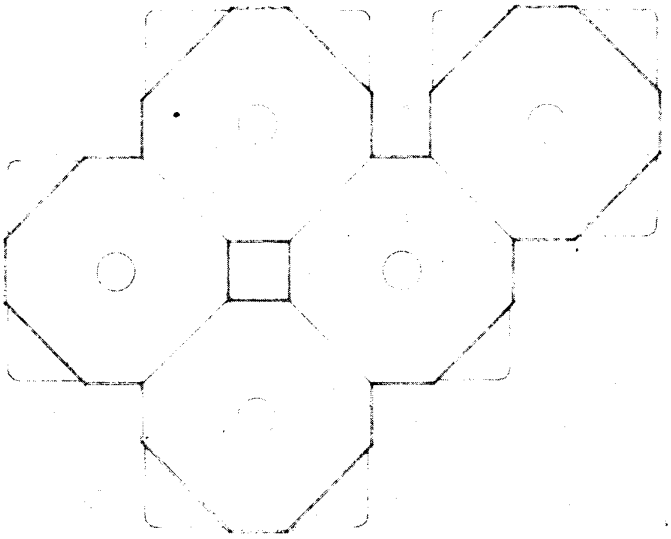

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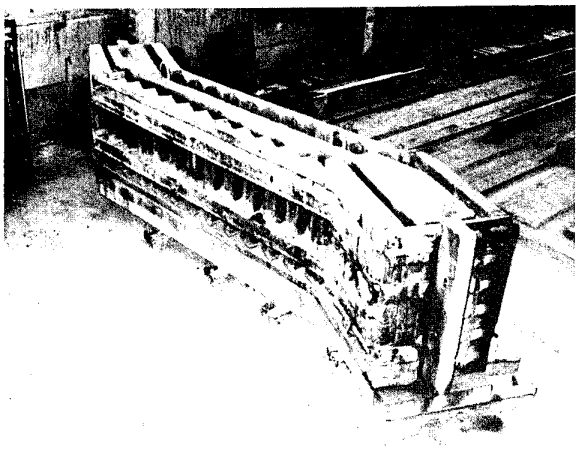

Fig. 21 FRP concrete form allowing the simultaneous pouring of two flights of 11 stairs with the relative landings. The main characteristic of this concrete form is the possibility of being installed on benches at very high vibration frequency. Other characteristics are:surface smoothness that allows to get pieces with no porosity; lightness that is important for the internal displacement and the dismantlement; the possibility of dismantling without using releasing agents. (By courtesy of Selip S.p.A.)

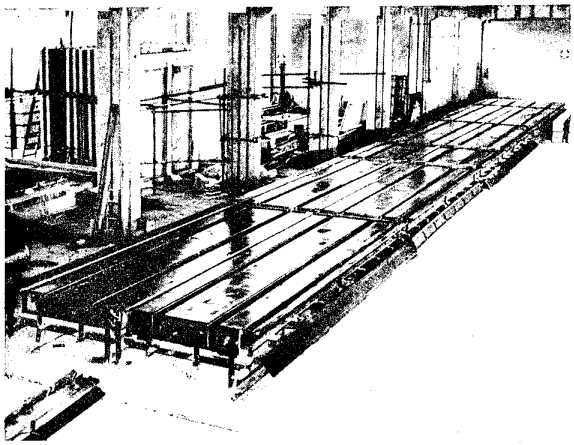

Fig. 22 Mould for floor consisting of ribbed elements 3 × 3.75 metres. (By courtesy of Selip S.p.A.)

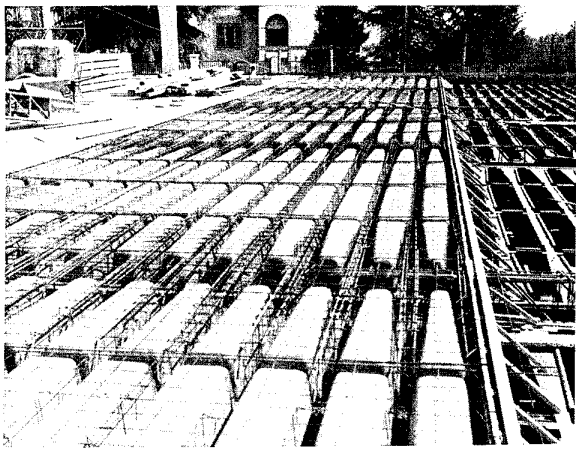

Fig. 23 Moulds for the hollow honeycomb type of concrete floor. (By courtesy of Impresa Edile Lodovico Maino)

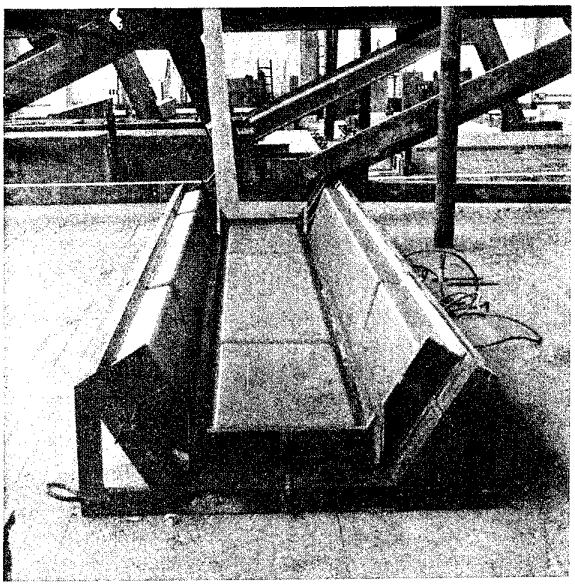

Fig. 24 FRP and iron mould for valley concrete elements. (By courtesy of Impresa Edile Lodovico Maino)

Sixth International Reinforced Plastics Conference

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Utilisation of organic fibres produced from sugar cane residue (Bagasse) in the moulding and manufacture of reinforced plastics products

R. BOTZ & Assoc. Inc., Puerto Rico

INTRODUCTION

The key to the continued growth and development of the reinforced plastics industry is, in a single word, economics. So long as RP is in a competitive position, growth will follow, as will profits. As self-evident as this basic truism might seem on the surface, a tour of the economic junk yards of world industry will also make it evident that this simple precept is not universally followed. The world coal industry is a good example. The details of a better mouse trap may make interesting reading, but the economic feasibility of the better mouse trap resolves the ending of the story.

The two main factors relating to maintaining a competitive position for the RP industry are material cost and manufacturing technique, the latter having a direct effect on labour cost.

This paper deals with research and experimental work motivated by the need for further reduction in material cost, and is dedicated to improving the RP competitive stance.

The author seeks to review some seven years of extensive research resulting in the successful utilization of processed sugar cane fibers as reinforcing fibers in reinforced polyester molding formulations. Patent technicalities prevent total disclosure now. However, the information which is related here should be of interest and of value to the industry. The results so far, which are positive, are believed to be only a first step in an area of vast potential.

REINFORCING FIBERS, PAST AND PRESENT

The history of the early development of the new composite material made up of glass fibers and polyester resin should be common knowledge in the industry, and need not be reviewed here.

Glass fibers were a natural reinforcement for the newly developed resins, and what was more important, they were available along with technological information resulting from past applications of spun glass in other fields of endeavor. Great credit is due the glass fiber industry for its pathfinding research and the RP technology it produced.

Following the first giant step of the industry upon the firm ground of the glass fiber and polyester partnership, came the experimental work with the less glamorous, but possible low cost fiber substitutes. They included sisal, cotton, jute, asbestos, and synthetic fibers. Sisal and asbestos appear to have received the most attention with the best results. Research work continues with asbestos fibers, but it is directed in the area of further sophistication of present asbestos uses, which do not reflect volume applications through high percentage content.

Sisal has attracted a great deal of attention. Mr D. MacCarvill submitted a learned paper, 'Sisal as a Plastics Reinforcement Medium' to the Third International Reinforcement Plastics Conference. Mr MacCarvill stressed the point that rising material costs, i.e. cost of glass fibers, dictated a long look at natural fibers, or other substitutes. For those interested in a comprehensive review of work conducted with sisal fibres, Mr MacCarvill's paper is an excellent source. The author cites sisal fibers and Mr MacCarvill's paper for two reasons:

1. Sisal and the experimental work conducted in that area are closely akin to the work conducted by the author in the area of sugar cane fibers.
2. Inasmuch as the physical factors resulting from the introduction of sugar cane fibers as a reinforcing agent for polyester molding formulations are closer to the results obtained with sisal than with more costly glass fibers, sisal fibers become the most likely natural fiber upon which to base comparisons.

Following, and along with, the development work dedicated to the above-mentioned fibers, the glass fiber industry continued to improve their product, giving the RP industry a vast range of possible end products. The only limitation reached with glass appears to be in the area of continued cost reduction. As a result, there still remains a very large and untapped market for a low cost RP composite material where high strength characteristics are not paramount.

With regard to cost factors, it must be noted that sisal fibers also have a built-in cost bottom which results from the source of supply, total world plantings and the success of the crop, harvest costs, world-wide appreciation of land value, water supply, processing costs and transportation costs. Not only do these factors serve to limit the amount of cost reduction possible, but they also dictate serious price fluctuations in the market place, such fluctuations being evident in the past few years. As will be noted later, these built-in cost bottom limitations and fluctutation factors are not as evident in the production of sugar cane fiber for use in RP manufacture. So it would appear that a 'market gap' does exist in the industry and this gap has provided the incentive for the author's interest in sugar cane fiber.

There has also been a great interest shown in recent years for the exotic and highly sophisticated new fibers such as carbon, graphite, boron, ceramic fibers and whiskers (Crystalline refractory oxides). These new exciting frontiers in reinforcing fibers present a valued addition to the overall range of the RP spectrum, but do not relate to the author's work, as they are mainly marketed as specialty fibers with premium prices to match their usefulness.

Based on the above, it is the author's opinion that there is a great need in the RP industry for a low cost reinforcing fiber, with a stable price factor, and that sugar cane fibers, properly processed, can fill that need.

RESUME: SUGAR CANE RESIDUE UTILIZATION PROJECTS

Bagasse originally referred to the refuse of plants and is now generally used to describe the fibrous residue resulting from the crushing of sugar cane in the cane grinding process.

The attempts at utilization of bagasse date back to 1838, but the first experimental manufacture of paper from this raw material took place about 1844. The records are not clear. Bagasse was mentioned as a papermaking material in patents of the 1840's and 1850's. In 1856, Henry Lowe of Baltimore, Maryland, produced a reasonable bagasse paper upon which The *Baltimore Advocate* was printed. These early experiments in the manufacture of paper from bagasse all failed as a matter of economics. Experiments continuing to the present date indicate that there are still problems to be solved prior to the profitable manufacture of quality grade paper of 100% bagasse.

In the early 1900's interest developed in manufacturing fiber board from bagasse. These enterprises have not been profitable, but a continued interest in fiber board manufacture is noted. With the exception of the bagasse board plants which produce their product in an economical environment which protects them from open competition with wood particle board, none has been a real success.

The history of this interesting raw material is rather depressing in that so many failures are reported and so few successes. The basic use for bagasse remains as a fuel for the sugar mill. Although mill bagasse is 50% water, requires close supervision and frequent cleaning of furnaces, burning is still the most economical means of disposing of the material.

There is one success resulting from the efforts of the Celotex Corporation. In 1920 a group headed by Mr B. G. Darhlbert organized the Celotex Corporation to manufacture a low density board made from sugar cane fiber. This single enterprise stands out as the only commercial group to operate profitably over an extended period of time through the utilization of bagasse. Celotex is still in business, manufacturing celotex board, refrigeration insulation, acoustic material, and flat stock of varying density.

In spite of these many failures, the fact remains that bagasse represents an attractive raw material if put to the proper use. It is produced in such a variety of geographical locations that the problem of long hauls to the market place is eliminated. The raw material is the result of a voluminous annual crop, and has the great advantage over other agricultural residues in that the costs of collecting, transporting, and crushing at a central location (the sugar mill) are all charged to sugar manufacture. In the case of a sugar mill burning its entire output of bagasse for fuel, the bagasse assumes a value at the mill of about $6.00 per dry ton. This cost is arrived at through the computation of costs for a substitute fuel and will vary somewhat in different locations.

The secret to profitable utilization of this plentiful and low cost raw material must, then, lie in the upgrading of the finished product to compensate for the additional costs of processing the bagasse into a usable product. Processing the bagasse into a marketable fiber for reinforcement uses in RP manufacture allows enough margin to compensate for the processing costs involved.

SUGAR CANE FIBERS: THE NATURE OF THE MATERIAL

The overshadowing obstacle in any sugar cane utilization research project is the lack of reliable information pertaining to this raw material, and the vast amount of misinformation which has been circulated by word of mouth or publication. This phenomenon is the result of well taken, but diverse opinions, which simply do not hold up under the light of intensive investigation. The author, after seven years of investigation, is somewhat in sympathy with other investigators; while disagreeing with them, he is not in total agreement with himself on some matters of technology involved. This conundrum appears to be the 'nature of the beast' and has appreciably decimated the ranks of those who would attempt to utilize the material.

There seems some common agreement that sugar cane residue is organic in nature, and there the agreement ends. Faced with the lack of reliable information dealing with this raw material, the author decided to forego precise technical knowledge of just what he was working with, conduct basic research in the direction of finding a grade of cane fiber which worked as a resin reinforcement, and then backtrack as success or failure dictated. This modus operandi, as unscientific as it might appear, was successful in that it produced results.

Once the sugar cane goes through the grinding mills, there remains a fibrous residue which in physical appearance resembles shredded corn stalks. The size of these bits and pieces of ground up cane (bagasse) depends on the efficiency of the grinding mill. The goal is to grind and press as much sugar as possible out of the cane. Therefore, most of the progressive mills produce a fairly consistent bagasse with large bits of about two to three inches long and the rest graded down to bits in the dust classification. These bits and pieces of ground up cane are made up of two distinct materials, and a third classification which is not so distinct. First there are the tough, but soft fibers from the outer periphery of the cane stalk, and then a pithy, low density material called pith, which comes from the core of the stalk. In between is a mixture of low density fibers which is all but inseparable from the pith. These fibers are found between the outer periphery wall of the cane stalk and the pithy core of the stalk. The outer fibers make up about 50% of the total usable dry cane refuse material, the pith about 40%; the remaining 10% is soft fibers and pith combined. The fibers from the outer periphery of the cane stalk are fine, strong, and flexible when properly treated and stripped of the pith material.

The chemical analysis of the overall material will vary from one geographic area to another, but in molding tests made with fibers from Louisiana, Texas, Puerto Rico and St. Kitts, no meaningful difference was noted in the end results.

The typical breakdown of dry bagasse results in the percentage content in Table 1 below:

TABLE 1

Chemical properties of dry bagasse by percentages

Cellulose	40.00
Gums (vylan, Arabian, Galactan)	24.00
Protein	1.80
Sugar, Sucrose	14.00
Sugar, Glucose	1.40
Acids	0.40
Fat and Wax	0.60
Ash	2.40
Lignin	15.00
Silica	Varies

with field conditions during time of harvest.

An analysis of bagasse reduced to fibers of 1 to 1.5 mm in length reveals the content percentages in table II below:

TABLE II

Analysis of bagasse fibers

	Percent
Ash	1.39-1.64
Water Solubles, cold	1.94-2.54
Water Solubles, hot	3.86-4.57
Dilute alkali extract	33.9 -38.8
Alcoholic benzene extract	2.69-2.83
Pentosan	26.19-27.53
Lignin	18.63-21.81
Oil	0.33-0.35
Alpha cellulose	34.72-37.23
Beta cellulose	4.97-7.12
Delta cellulose	5.79-8.22

Additional study of the raw material indicates that while the cane from the field contains about 14% sucrose, about 3% of this sucrose will remain in the bagasse following the grinding process. This 3% figure will also vary from mill to mill, depending on the efficiency of the mill. Bagasse fiber is similar to cotton and wood fibers in that it has a spiral structure, but cane fiber has a thickness of approximately 0.018 mm which compared to Douglas and Balsam Fir fibers indicates that cane fibers are about four times as slender as those wood fibers. In a second comparison with wood fibers, cane fibers contain more ash and parenchyme, and less lignin and cellulose.

THE FIBERS PRODUCED FROM SUGAR CANE

The first problem involved in processing mill bagasse into a usable fiber for RP purposes was quite evident from the start. Mill bagasse, a mixture of pith and fiber, was dirty and carried soil from the fields. It would have to be cleaned. The fibers would have to be separated from the pith and dirt without compromising the integrity of the fibers. This indicated a hydro-mechanical operation with the conventional

hammer mill eliminated because of the harsh mechanical action of a hammermill.

The first work commenced at Houma, Louisiana in 1961 where an experimental mill was put together from junk yard parts which more or less indicated what was truly needed, but it did not provide usable fiber. A second mill was constructed from similar parts and was partially success in separating the fibers from the pith, but the problem of dirt remained. However, the fibers produced in this second machine were washed by hand, and were used in experimental molding work at the Gisholt Plastics Division in Madison, Wisconsin in 1962. The results were promising, but indicated a need to return to the chemical aspects of bagasse. These early experiments indicated that the cane fibers were regaining moisture from the atmosphere during shipment in the range of 14% to 16% moisture content, which in turn inhibited the curing cycle. It was also noted that even with an added amount of mold release, there remained a problem of releasing the molded part from the steel die. The problem of moisture control was found to be interrelated with the nature of the overall bagasse and the pith content of bagasse. Tests indicated that fibers well stripped of pith cells would still absorb five times their weight of water, while the pith cells absorbed as much as thirty times their own weight. It was resolved that the fibers, even though totally stripped of pith cells, would still have to be chemically treated to prevent the regain of moisture in the dry product. In regard to the mold release problem, it was anticipated from the start that the remaining sugar in the bagasse (about 2% after milling) could cause a problem in this area, and it did.

These early tests dictated that a uniformly clean fiber be produced, free of pith and sugar, and chemically treated to make the fiber moisture resistant during transit and storage. Facilities were not available for the type of research needed to solve these problems at Houma, Louisiana, therefore arrangements were made to move project headquarters to San Juan, Puerto Rico in 1963. Through the cooperation of the Puerto Rico Development Administration (Fomento), laboratory facilities were made available for the completion of the investigation.

As already mentioned, patent applications, now pending, restrict the publication of details of the actual hydro-chemical-mechanical process finally developed to produce a suitable fiber. However, the many problems were overcome, and recent tests with production size machines support the premise of economic feasibility.

An interesting sidelight into this program of investigation stems from the fact that a considerable amount of attrition takes place in the processing of bagasse into clean fibers. As a result of this attrition, a considerable amount of clean material, too fine to classify as fiber, was manufactured. In an effort to put this material back in the profit column, the material was further reduced to a microfine flour which in turn was successfully used as a substitute for wood flour filler in phenolic compounds. Details of this work will not be reported here, as it related to another area of plastic manufacture.

The fibers can be produced in a variety of lengths from one quarter of an inch to five inches, and the degree of fiber fineness can be regulated between 400 denier to well below 200 denier. In comparison, the average fiber fineness of sisal fiber is 300 to 400 denier. The fiber is a light yellow color which comes from the lignin content of the bagasse. Bleaching experiments suggest that a fiber of a translucent nature can be produced. Although the most comprehensive physical tests have been conducted with premix formulations, some work has been done with these fibers formed into mats and the results were promising. The forming of these cane fibers into mats for other than premix moulding will require a complete new series of investigations and this work is scheduled for the later part of this year.

In another area of inquiry, it has been determined that cane fibers, prior to chemical treatment to make them moisture resistant, lend themselves readily to absorbing chemicals and resins which in turn add tensile strength to the fibers. This inquiry is in progress and results so far indicate that it is economically feasible to treat these fibers chemically, and that the resulting flexural strengths in the RP end product will approach the 12 000 PSI mark.

In summary, a practical system does exist for the manufacture of a reinforcing fiber suitable for RP premix applications from sugar cane residue. Further research should open the door to other RP applications.

MIXING TECHNOLOGY FOR RP PREMIX FORMULATIONS

There is a cardinal rule which regulates the success or failure of most research projects dedicated to progress or change within a given industry. This rule has particular application when one seeks to introduce a substitute material into an established manufacturing process. No one in particular formulated the rule. The rule stems from experience, and it dictates that a change in established industrial procedure must be unobtrusive, while a substitute for an established material must be capable of being introduced without undue change in the established manufacturing process. The rule stymies progress but is based on the hard premise that industrial change requires cash outlay, and though there are exceptions, it is best to try to comply.

The author has had this rule in mind from the beginning and is of the opinion that with reference to the handling, mixing and molding of a given premix formulation, with cane fiber as a substitute for sisal or glass fiber, no diversion from the regular routine or equipment is necessary. When a standard premix mixer is used in wetting out the fibers, the same normal tolerance between mixing blades and mixing chamber should be used with cane fiber as with sisal fiber. In some cases, this tolerance has been increased for glass-premix applications to avoid the breakdown of the glass fibers. Cane fibers will not break down during the mixing operation, and to achieve top efficiency, normal tolerance should be maintained. Where extrusion of the material is preferred, following the mixing operation, a premix of cane fiber will extrude in the same manner as a premix formulation with sisal or glass fiber reinforcement.

In summary, the cane fibers can be introduced as a substitute for other fibers in the premix operation without changes in present technology. Research now being conducted to expand the use of these fibers into other areas of RP application will also follow this general precept.

PHYSICAL PROPERTIES OF CANE FIBER PREMIX FORMULATIONS

Molding tests were conducted at the Reichhold Polyester Molding Laboratories at Detroit, Michigan, between June, 1965 and January, 1968. The results of these laboratory tests varied in that a variety of fiber sizes and pre-mix formulations were investigated to determine the most practical grade of cane fiber and formulation. The physical properties reported are deemed to be conservative by the author. The testing program will continue; however, the results of the test work conducted from 1965 to 1968, and divided in Series One and Two, are reported as follows:

The object of these tests was to determine the handling characteristics and physical properties of premix formulations reinforced with sugar cane fibers, and then to compare the results with these same premix formulations reinforced with sisal fibers.

In Test Series One, both the control mix with sisal fiber and the test mix with cane fiber contained 10% by weight of the respective fibers, as well as 5% by weight of 7T-5 asbestos.

In Test Series Two, the 10% by weight factor of the respective fibers was maintained in both the control and test formulations, but the 5% by weight of 7T-5 asbestos was not added to the cane fiber test formula. This elimination of the asbestos from the cane fiber test formulation allowed for a comparison with the sisal fiber control formulation which included 5% asbestos.

With the exception of the elimination of asbestos as explained above, the tests were conducted under uniform conditions and with respect to disciplined laboratory procedure. The standard formula for the comparative tests was arrived at following preliminary experimentations to determine the most

economical cost factors as opposed to greater strength factors. It has been mentioned that some experimental work has been accomplished with the cane fiber being formed into mats. In this work, the formulation contained 50% cane fiber, 30% resin, and the balance made up of mineral filler, pigment, and catalyst. The author sees no restrictions on the variety of formulations possible nor on the variety of applications possible as a result of the experimental work accomplished so far.

Puerto Rican cane fiber processed through the laboratory pilot system in Puerto Rico was used in Test Series One.

Puerto Rican cane fiber processed through production size machines at laboratories on the premises of the equipment suppliers at five locations in the United States was used in Test Series Two.

The logistics of moving some 32 000 pounds of raw bagasse, in bulk, from Puerto Rico to the mainland test locations presented problems, one of which stemmed from a United States Department of Agriculture regulation which required that all bagasse moving from Puerto Rico to the mainland be sterilized prior to shipment. In order to comply with this regulation, the van had to be plumbed for live steam distribution prior to loading in bulk. Upon completion of loading the van, live super-heated steam was connected and the load declared sterilized by the inspector after twelve hours of continuous steam application.

Heat in any form is not a normal phase of the processing system until the final drying phase, and just what effect this extended exposure to intense heat had on the fiber end-product is open to speculation. This point can only be resolved once production starts without the steam application. The problem will not be present in normal processing as the fibers will be sterilized during the drying process; however, we must try to evaluate the effect on test results. One visible change came about in the color of the fiber end-product. The steamed fibers were of a light tan color as compared to the normal off-yellow color. It is possible that this discoloration resulted from the activation of the lignins by the heat of the steam. It was also noticed that, when dried, these fibers were slightly stiffer than the more flexible fibers produced in the pilot operation. Also noted was a decided breakdown in fiber bundles prior to passing through the mechanical process designed to break up these fiber bundles, and it is suspected that some fiber integrity was lost as a result of the steam sterilization. Test results from Series Two show a small decrease in flexural strength where the steamed fibers were used. If, indeed, the steam treatment was the cause of this loss in strength, the results cited below establish that it was not a critical loss.

Test Series One and Two Standard Formulation

	% by weight
Resin at 1.9% BPO Paste	27.5
ASP-400 (Clay)	43.0
Snowflake ($CaCO_3$)	13.0
Zinc Stearate	1.5
7T-5 Asbestos	5.0
Fiber (sisal or cane)	10.0
	100.0

Test Results of Control Formulation with Sisal Fibers

Flexural Modulur $\times 10^5$	14.2×10^5
Flexural Strength, psi	5950
Izod Impact (notched)	1.68

Sisal went into resin mix creating a homogeneous mix in ten minutes time through the use of a Sigma premix mixer. Good extrusion, good in-mold flow, and good cure at 300°F with a closed time of two minutes. No fiber breakdown during mixing operation.

Test Results of Test Formulation with Cane Fibers Test Series One*

Flexural Modulus $\times 10^5$	13.4×10^5
Flexural Strength, psi	5300
Izod Impact (notched)	385

*This test formulation included 5% by weight of 7T-5 asbestos

Cane fibers went into resin mix creating a homogeneous mix in *six* minutes time through the use of a Sigma premix mixer. Good extrusion, good in-mold flow, and cure at 300°F with a closed time of two minutes. Cane fibers soft and flexible, show no sign of breakdown in mixing process, and are of off-yellow color.

Test Results of Test Formulation with Cane Fibers Test Series Two†

Flexural Modulus $\times 10^5$	11.0×10^5
Flexural Strength, psi	5030
Izod impact (notched)	1.32

†This test formulation did not include any asbestos.

Cane fibers went into resin mix creating a homogeneous mix in *ten* minutes time through the use of a Sigma premix mixer. Good extrusion, good in-mold flow, and cure at *250*°F with a closed time of two minutes. Some 'pre-jell' spots noted in molding this same formulation at 300°F. Cane fibers were not as soft and flexible as cane fibers used in Test Series One, and ten minutes of mixing was required for this mix as compared with six minutes in Test Series One. The fibers were also noted to be of a light tan color as compared to the normal light yellow color. Both variations in formula behavior may have resulted from steam application when bagasse was sterilized.

ADVANTAGES AND DISADVANTAGES OF CANE FIBER

The years of research and the results of the laboratory moulding tests are impressive, but until commercial production of cane fibers for RP use is achieved and extensive experience is reported by the users based on overall molding results, the actual advantages and disadvantages of cane fiber will not be known. This may be an overly candid evaluation, however, it is based on experience gained while observing the introduction of other new materials to the RP industry.

At the present time, the author considers it prudent to maintain a conservative tone in reporting advantages through the use of cane fiber as a substitute for sisal fiber from a physical properties point of view.

Test results show cane fiber to be about on an even par with sisal fiber in most regards, with sisal showing a small lead in flexural strength and impact characteristics. Cane fiber appears to mix more readily because of its flexibility. The softness of the cane fiber appears to give a better surface finish to the molded article. The cane fibers also lend themselves to a cleaner cutting of the shearing edge of the molding tool than do sisal or glass fibers.

The advantages or disadvantages of cane fiber in a premix application are not dramatic enough from a technological point of view to balance the scales one way or the other. Economics and marketing will ultimately resolve the question

of advantage or disadvantage. Having considered the matter of economic feasilibity from many points of view, the author is very optimistic that once assured delivery is achieved through commercial production, a stable and somewhat lower cost on the cane fiber price tag will point up the most meaningful advantage to the potential buyer, other factors being reasonably equal.

This project has reached the point of diminishing returns with regards to continued laboratory research. Those problems which remain constitute production problems, and they will only be resolved through production attempts on a commercial scale. Option agreements are now in force with a major sugar central in Puerto Rico, and a major U.S. chemical manufacturer, which agreements show promise of commercial production in 1969. Secondary options are in the offing, should the primary options not be exercised. This sort of detail is not usually included in a paper of this nature, however, the information is advanced in anticipation of curiosity about production plans.

ACKNOWLEDGMENTS

The author acknowledges a great deal of assistance from individuals and organizations in this project, however, the work extends over such a long period of time that individual citations are not practical.

Sixth International Reinforced Plastics Conference

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Uni - directional glass fibre loops for electrical application 5

W. A. TILLOTT and D. J. MEADOWS, GEC-AEI Engineering Ltd

UNIDIRECTIONAL GLASS FIBRE LOOPS FOR ELECTRICAL APPLICATIONS

The heavy electrical power industry has a requirement for long, very strong electrically insulating rods for actuating switches and clamping transformer coils. Unidirectional glassfibre reinforced thermosetting materials are an obvious choice for this application because of their intrinsically high strength and electrical properties. However, unidirectional glass reinforced epoxy rods proved unsuitable because of the problems of securing the rods to the equipment.

Loops manufactured by winding unidirectional glass reinforced pre-impregnated tape around a mould, then pressing and curing, have proved to be a satisfactory solution. It was found that pre-tensioning the loops before curing so that the fibres are approximately evenly tensioned was essential to give good quality loops. Correctly designed loops have strength of the loop and a series of experiments were undertaken to determine these parameters. From the results obtained, loops can be designed with breaking loads from 2-100 tons over the temperature range of 20°C-100°C.

Other applications for loops are being considered, such as stator end winding clamps, and encapsulated tension members for transmission lines.

1. INTRODUCTION

To meet the requirements within our Company for long, lightweight, electrically insulating rods for actuating switches in air blast switchgear, and for clamping transformer coils, the use of unidirectional glass fibre reinforced plastic materials was an obvious choice. As is well known, these materials possess extremely high intrinsic strengths when stressed in the direction of the fibres. Unfortunately, the Achilles heel of this type of material is that it is difficult to 'grip' or terminate successfully, so that the full tensile strength can be realised without the member failing prematurely by other means. For example, if such a tension member is 'gripped' or terminated by means of a threaded coupling or a simple shackle and pin arrangement, premature failure by thread-shear in the first case, and by bolt hole shear in the second case, will occur at stresses considerably below the intrinsic tensile strength of the material.

With this knowledge in mind, it was considered that if this type of material was to be used successfully as a tension-member, then either improved gripping/terminations would have to be developed, or alternatively modifications to the form of the unidirectional glass fibre reinforced plastic material would have to be made. Since another manufacturer had already adopted the first approach and had developed and patented[1] the use of crimped-on aluminium bronze end fittings for polyester/unidirectional glass rods, the alternative approach was adopted. This was done because it was considered that the mass of metal in the crimped-on end fittings of this type of rod would upset the electrical design characteristics of the air blast switchgear. Thus, we had to consider various ways and means of producing a satisfactory form of a unidirectional glass fibre laminate for use as an insulating tension-member.

First attempts at this were based on the use of a bar[2] cut from an epoxide/unidirectional glass fabric laminate, with the ends of the laminate increased in thickness by interleaving layers of the unidirectional glass fabric laid at 90° to the fibre direction of the main reinforcement. By this means, it was expected that the bolt hole shear of the bar would be greatly improved, so that when the bar was tensioned by means of a simple pin and shackle device, failure would occur in tension in the body of the bar and not at the ends in bolt hole shear. However, in practice this was found not to be so as the bars still failed at the holes in shear, at values of only 25 500 lbf/in^2, compared to an expected tensile failure in the order of 90 000 lbf/in^2.

It was then considered that a tension-member in the form of a simple loop design might prove to be suitable for our requirements, for the following reasons:-

(a) The tensile load can be easily and simply applied by means of suitable pins and shackles passing through the ends of the loop.

(b) With this type of end-fitting the mass of metal is kept to a minimum which satisfied the stringent electrical requirements.

(c) It was thought that if the loops were suitably designed then failure would occur much closer to the intrinsic tensile strength of the unidirectional material, than that achieved with the laminated tie bar mentioned previously.

Work was therefore initiated in our laboratories to investigate the possibilities of developing and manufacturing a simple high strength tension loop, which would satisfy our requirements.

It was found that by simply winding a number of turns of a commercially available pre-impregnated unidirectional non-woven glass tape around a simple tool, tensioning the wound tape and then pressing and heat curing at a suitable temperature to cure the thermosetting resin, lightweight, extremely strong tension-members could be obtained. Such loops if correctly designed, can possess strengths approaching the ultimate strength of the material, i.e. approximately 120 000 lbf/in^2.

2. MANUFACTURE OF UNIDIRECTIONAL GLASS FIBRE LOOPS

The manufacture of these loops developed and now patented[3] by our Company is in essence an extremely simple process. Basically, a loop is formed by winding a number of turns of a pre-impregnated unidirectional glass fibre banding tape around a metal centre piece, secured between metal side plates, thus forming a 'slot' for the tape. The centre member, which controls the internal dimensions of the loop must therefore be of the correct thickness and profile for each specific design of loop. This member is usually made in two sections, such that the 'as-wound' tape may be tensioned or stretched on the tool by mechanically forcing the two sections apart.

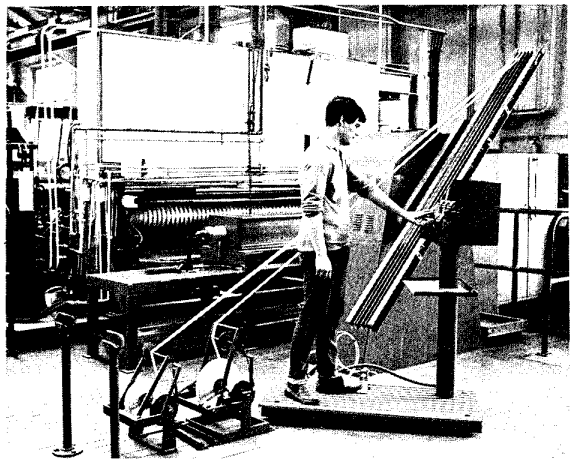


Fig. 1

The required number of turns of the unidirectional glass tape are wound into the formed slot preferably under a controlled tension, as shown in Fig. 1. Alternatively, the tape may be wound on the tool by hand and tensioned on the tool after winding. The wound tape is then wrapped with one turn of a

shrinkable plastic release film, (such as certain types of Polyester film) and secured to itself with a small length of a suitable pressure sensitive self-adhesive tape. The 'as-wound' loop is then tensioned, if required, by forcing the two portions of the centre member apart by a pre-set amount. This is usually done by suitable mechanical means which are attached externally to the tool for this purpose. A metal spacing piece of the correct dimensions is then inserted into the gap so produced in the centre member and the stretching tackle removed from the tool. After tensioning, steel pressing bars are fitted along the limbs between the tool side plates and the complete tool lifted into a steam-heated press for pressing and curing.

The wound loops are consolidated by applying a nominal pressure in the order of 100-150 lbf/in^2 to the pressing bars, although it has been found that the pressure used is not critical. Simultaneously, the tool is heated and maintained at 150°-160°C under pressure for one hour, (dependent on the loop thickness) in order to cure the thermosetting resin in the loop. For convenience, in production it is our practice to press to 'stops' i.e. pressing bars of the correct size are used, so that when pressed flush to the edges of the tool side plates the limb thickness dimension of the moulded loop is correct. After curing, the tool is cooled down in the press, before dismantling, to remove the moulded loop from the centre member.

After removal, the loop is carefully fettled to clear all traces of 'flash', and all loops are proof tested in tension by checking their load/extension characteristics up to a certain value of tensile load, as specified by the customer.

It should be noted that since the introduction of this process in 1964, improvements in productivity have been made. For example, by the use of 'multi-deck' tools (See Fig. 2.) a number of wound loops can be pressed simultaneously. In addition, by careful tool design, it is possible to cater for a range of lengths and widths of loops having a common end radius on a single tool.

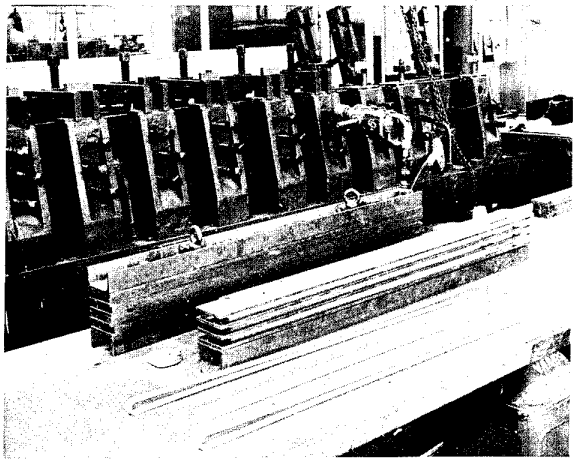


Fig. 2

By use of the basic method described above and a variety of suitable tools, loops have been made in the range of dimensions as follows:-

Length	6" to 15' 0"
Limb Width	$\frac{1}{4}$" to 4" inclusive
Limb Thickness	$\frac{3}{32}$" to $\frac{13}{16}$" inclusive
International end radius	$\frac{1}{4}$" to 2"

3. DESIGN CONSIDERATION

In order to design loops to carry loads safely for a minimum period of 20 years the probable areas of failure must be known. The failure stress may depend on the width of the loop, the thickness, length, end radius, initial tension of the tape, environmental conditions, ambient temperature and creep factor. To limit the cost of the investigation, it was decided to use 12" long loops in the testing and evaluation experiments.

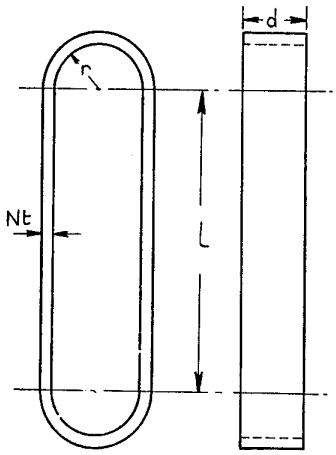
As non-extending tools were cheaper than extending tools the first question to be answered was the necessity for having extending tools for 12" loops. As stated previously, it had been found necessary to use extending tools for loops from 3 ft to 13 ft long to pre-tension the wound tape. Hence, 12" long test loops were wound with initial tape tensions of 10 lbf, 20 lbf, and 40 lbf, corresponding to loosely wound loops, hand wound loops which were subsequently extended, and tight machine wound loops. These were tested to destruction. The results indicated that there was little difference between the 20 lbf and 40 lbf tensioned tape and it was agreed that the cheaper non-extending type of tool could be used and the question of initial tape tension ignored as a factor in determining the failure stress of a loop in the test programme.

Thus, the failure stress of a loop S can be expressed simply as:-

$$S = f_1(d, Nt, l, r, S_u, K, \tau)$$

where

d = width of loop
N = number of turns of tape
t = pressed thickness of tape
l = length between centres
r = internal end radius
S_u = ultimate failure stress of the tape in loop form
N_t = limb thickness of loop
K = environmental conditions
τ = time under stress



For the purpose of this investigation: K was taken to be 1 for air at an ambient of 23°C, and correction factors for other environmental conditions have been determined. For example, the effect on failure stress against elevated temperature up to 155°C is shown in Fig. 3.

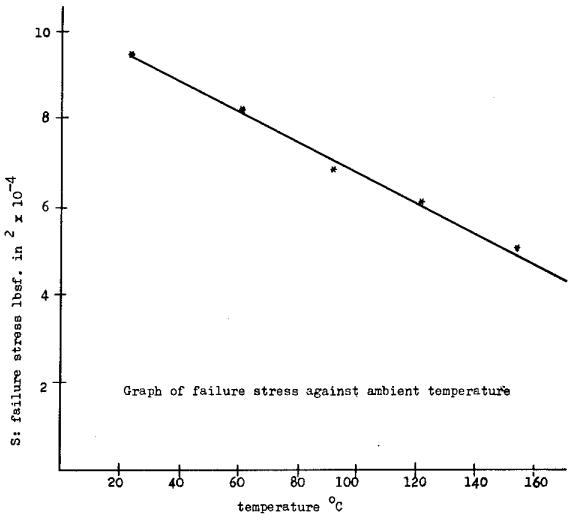


Fig. 3

The effects of immersion in hot transformer oil at 105°C, and exposure to the discharge products of SF_6 at room temperature were also required and have been determined; the results indicating a 3% reduction in failure stress after 18 months in transformer oil at 105°C, and a reduction of 20% after 10 months exposure to the discharge products of SF_6.

The relevance of accelerated creep and stress rupture (static fatigue) tests with respect to factor τ (time under stress) have been considered. Accordingly, loops have been continuoulsy loaded at stresses ranging from 35 to 60% of expected failure stress at room temperature until failure has occured; measurements of creep (extension) being taken throughout the test period. The results obtained indicated that the total creep strain at all stress levels was very small (about 0.1%) and the stress rupture values obtained to date tend to indicate

that for a 20 year life expectancy continuous stress levels not greater than 25% of instantaneous failure stress can be tolerated. Thus, it was considered that for loops required to operate continuously at normal ambient temperatures in equipment with a life expectancy of 20 years then the minimum safety factor used should not be less than 4. For certain applications where the life expectancy was much less, loops have been used at working stresses up to 50% of the expected failure stress.

Thus, the failure stress S can now be expressed as a function of width, length, thickness, end radius and the ultimate strength of tape in loop form, as follows:-

$$S = f_2(d, Nt, l, r, S_u)$$

By keeping d and l constant a series of experiments were undertaken to find a relationship between S, S_u, Nt, and r. Accordingly, a large number of loops were made all $\frac{1}{2}$" wide and 12" long (i.e. keeping d and l constant) with internal radius r ranging from $\frac{1}{4}$" to 2" and with the number of turns N = 9, 21, 42, and 70. These values of N were chosen so that with a pressed tape thickness of t = 0.0117 the resultant limb thicknesses Nt would be $\frac{3}{32}$", $\frac{1}{4}$, $\frac{1}{2}$" and $\frac{13}{16}$" respectively. The loops were tested to failure in tension and the mean failure stress S (usually obtained from the mean of 9 results) of each dimension of loop plotted in Fig. 6. Analysis of the shape of the curves suggested that S and S_u were related by the following equation:-

$$S = S_u (1 - e^{-r/Y})$$

where Y = a factor governed by the initial slope of failure stress/internal radius curve, and related to limb thickness Nt.

Loops generally fail at their ends at a point close to the start of the radius i.e. in contact with the loading pin or mandrel, as shown in Fig. 4. Taking this fact into account it was assumed that the well-known friction equation for flexible ropes of negligible weight around a capstan was applicable to loops. If this was so, then:-

The maximum frictional force $F = S_u{}^{-\mu\theta}$

Where μ = coefficient of friction

θ = angle of contact

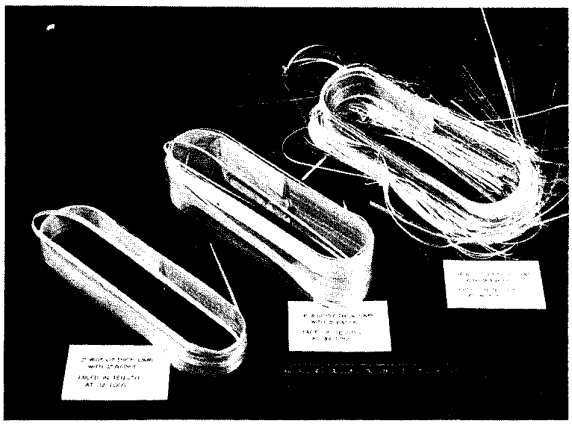


Fig. 4

The failure stress can then be expressed as $S = S_u(1 - e^{-\mu\theta})$ which can be re-written as $S = S_u(1 - e^{-r/Y})$.

By equating as simultaneous equations, a value of S_u of 115 000 lbf/in^2 was arrived at, and values of Y for different limb thicknesses Nt as shown in Fig. 5, were also obtained.

Hence, by substituting in the above final equation, values of failure stress S for loops of varying internal radius r and limb thickness Nt, were obtained. These theoretical values are drawn as curves in Fig. 6, and it can be seen that there is a good measure of agreement between primitive theory and experimental results.

The results have been re-written as a family of curves, as shown in Fig. 7, so that the failure load for any number of

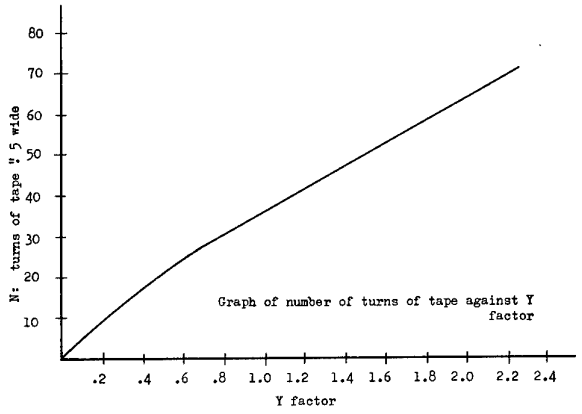


Fig. 5

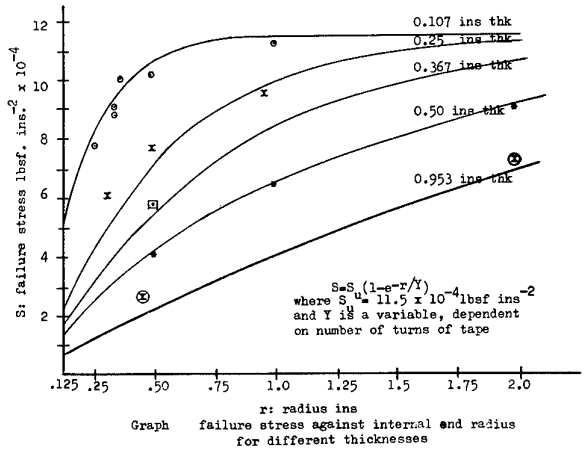


Fig. 6

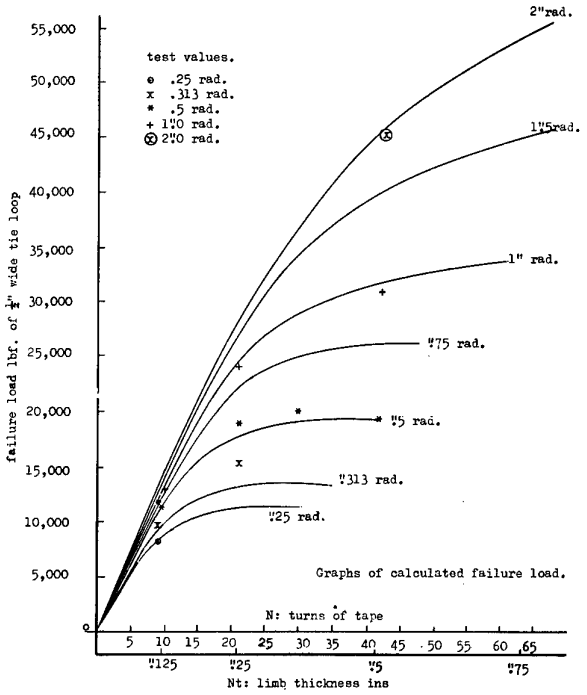


Fig. 7

turns of tape for the most common internal radii could be computed. Other curves have been calculated i.e. for $\frac{3}{4}$", $1\frac{1}{2}$", and 2" internal end radius, as required.

A closer examination of the curves in Fig. 7 particularly for the smaller end radii e.g. $\frac{1}{4}$", reveals that up to a certain number of turns, the loops fail linearly for increasing number

of turns, and thereafter when the radius to thickness ratio ($^{r}/_{Nt}$) is less than a certain value (approximately 2.8), the loops tend to fail at a constant load irrespective of the number of turns. The reason for this is that the relationship between the maximum pressure P on a surface of radius r under an applied tension T, is given by the well-known equation for curved structures of negligible thickness.

$$P_{max} = {}^{T}/_{r}$$

This equation can therefore apply to loops of small limb thickness, assuming the bearing pin is a perfect fit in the semi-circular end of the tie loop and does not bend or distort under tension. If P_{max} equals the crushing stress of the loop material, then the loop will break in compression at the mandrel.

The failure stress

$$S = \frac{T}{dNt}$$

and as T is a maximum prior to failure

$$S = P_{max} \frac{r}{dNt}.$$

Using the values from Fig. 6, failure stress S has been plotted against the radius to thickness ratio ($^{r}/_{Nt}$). The results shown in Fig. 8 confirm that linear relationships exist and that P_{max} has two values, viz.,

(a) 3.3×10^4 lbf/in^2 when $^{r}/_{Nt}$ is less than 2.8

(b) 0.25×10^4 lbf/in^2 when $^{r}/_{Nt}$ is greater than 2.8.

Thus, when the ratio $^{r}/_{Nt}$ is less than 2.8, loops fail by compression at the pin and when $^{r}/_{Nt}$ is greater than 2.8, the compressure P_{max} induced in the circular end of the loop is too low to exceed the material crushing strength and hence loops will fail in tension. Compression failures obviously must occur at the loop ends against the pin but tension failures, as stated previously, also occur at the ends because simple theory does not account for the complex stress situation in the ends of the loop.

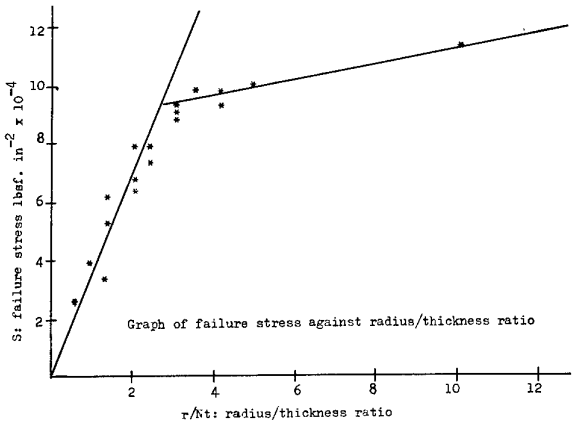


Fig. 8

The two remaining parameters which had to be determined, were the effects of length and width d. It was expected that the failure stress for any loop with all other factors constant, would be independent of length. Loops 6", 12", 33" and 13 ft long have been manufactured and within the accuracy of the experiments this has been found to be so. The standard deviation of failure stress for nine samples being of the order of 5%.

The effects of width d has been investigated by manufacturing $^{1}/_{2}$", 1", 2" and 4" wide loops with 9, 21 and 42 turns of tape and testing these to destruction. It was considered that the theoretical maximum failure stress for these loops could be calculated from the following expression:-

$$S = S_h \cdot 2d.$$

Where

S_h = failure stress of appropriate $^{1}/_{2}$" wide loop of similar end radius and limb thickness, as obtained from Fig. 6.

d = limb width of loop.

The experimental failure stress values obtained have therefore been calculated as a percentage of the theoretical stress, for loops of each width and limb thickness and a series of correction factor curves drawn. These are shown in Fig. 9.

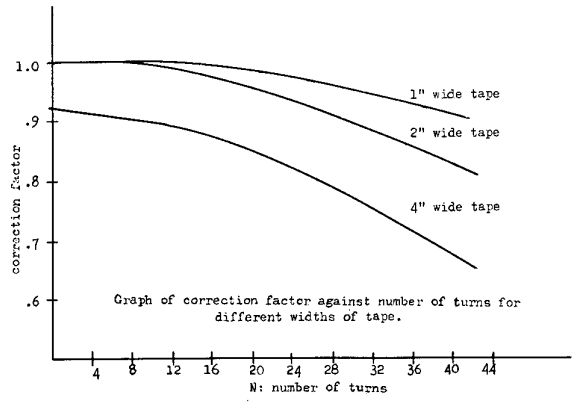


Fig. 9

In addition, some loops have been dynamically tested in tension at the C.E.G.B. National Tower Testing Station and the results obtained indicate that the dynamic failure stress is 85% of the static failure stress.

The relationship between Young's Modulus and thickness of the loop has also been determined as this information was required for the detailed design of the extending type of tools.

Thus, using all the above information it is now possible to design loops with failure loads in the range 2-100 tonf with confidence.

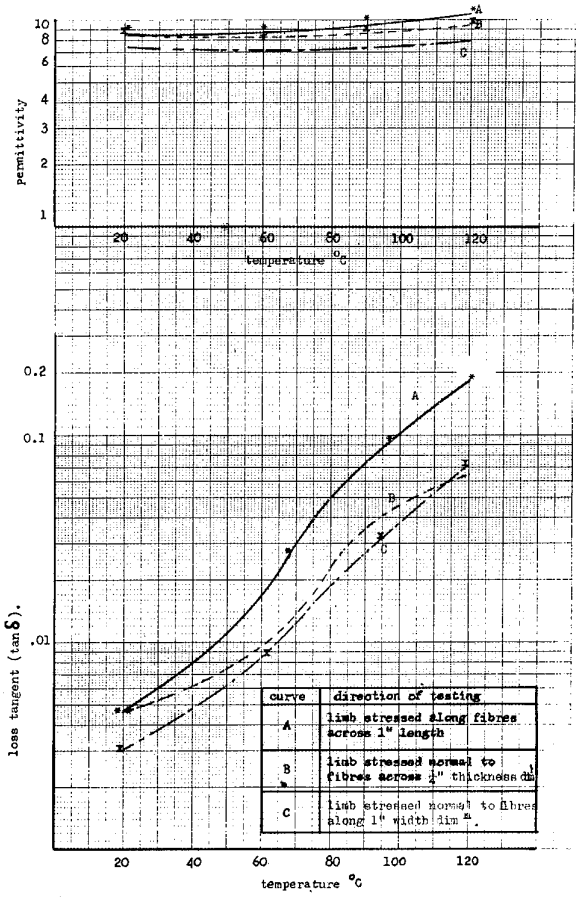


Fig. 10

4. ELECTRICAL PROPERTIES

Typical values of dielectric loss tangent/permittivity, discharge inception, electric strength and comparative tracking index measured along the fibres and normal to the fibre direction on production loops are given in Figs. 10 and 11. The dielectric loss/permittivity measurements were carried out over the temperature range 20°C-120°C. Thus, it was seen that the electrical properties of a loop depended to some extent on whether the voltage is applied along or across the fibres. This was particularly true in the case of track resistance, and it is for this reason that electrically stressed loops cannot be used out of doors, for mechanical linkages, without some form of external cladding. It is unfortunate that the worst electrical properties are obtained along the fibre direction as this is the direction of the highest mechanical strengths, and hence as always some compromise in properties has to be made.

Property	DIRECTION OF TESTING		
	Along Fibres	Normal to Fibres	
	Tested along 1" length	Tested through $\frac{1}{4}$" thickness	Tested through 1" width
Electric Strength in oil at 90°C	80 kV/in= 80v/mil	$\geq 22.5^{+}$ kV = ≥ 90 v/mil	$> 75^{+}$
Discharge Characteristics Inception Voltage V_i	> 20 kV *	> 15 kV *	> 20 kV *
Track Resistance C.T.I. to B.S. 3781	325	> 700	-

Notes:
+ Denotes flash-over occurred
* Maximum voltage obtainable with particular test apparatus, and for size of samples tested.

Fig. 11 Typical Electrical Properties of Loops with limbs $\frac{1}{4}$" thick × 1" wide

5. OTHER AND FUTURE APPLICATIONS

Apart from the previously mentioned main uses of loops for actuating switches in air blast switchgear and for clamping transformer coils together, other applications such as operating rods for railway pantographs, the bracing of stator end windings of large turbo-alternators are being developed and considered, both within and outside the Company.

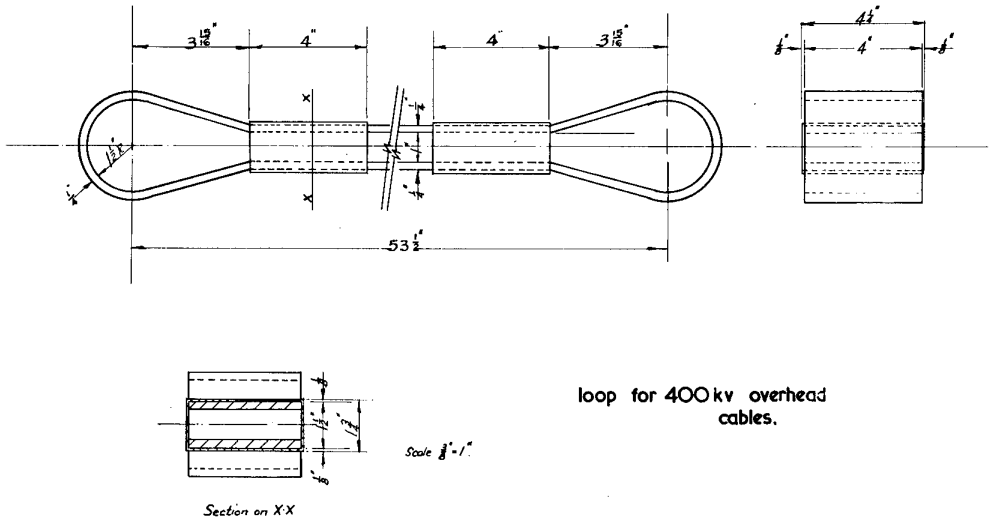
One other possible major application, actively being considered at the moment, is the use of these loops when encapsulated under tension in special track resistant epoxide resins, as tension members on overhead transmission lines, instead of the conventional system. The standard C.E.G.B. loading for this application demands loops capable of withstanding loads ranging from 5 to 40 tonf and satisfactory samples for working at the lower end of this range have been made. Suitable parallel sided loops capable of withstanding loads at the higher end of the range can of course be used, but because these loops must of necessity possess fairly large end radii, i.e. at least $1\frac{1}{2}$", the volume of space between the limbs is high and hence the cost of encapsulation with epoxide resin and the weight of the finished component are also high. In attempts to overcome these disadvantages, experimental loops in the form of a 'dog's bone' shape (see Fig. 12) with the parallel limbs drawn together to form a single central limb but still retaining the required large end radii, have been shown to possess approximately 95% of the strength of a similar sized parallel sided loop. Development work and acceptance trials on this and other projects are still in hand, and the future for tie-loops looks promising.

6. APPRECIATION

The authors wish to thank GEC-AEI Engineering Limited for permission to publish this paper, Mr H. C. Hamilton who carried out the experimental work and Mr C. S. Clemson who provided Fig. 8.

7. REFERENCES

1. British Patent 816 926. Method of attaching fittings to rods or tubes of resin bonded fibre and fittings attached to such rods or tubes.
2. British Patent 996 561. Improvements related to the manufacture of laminated insulating rods.
3. British Patent 998 391. The manufacture of insulating rods.



loop for 400 kv overhead cables.

Fig. 12

Sixth International Reinforced Plastics Conference

PAPER NO.

NAME

COMPANY

QUESTION

SIGNED

DATE

Development of the pultrusion processes

6

G. KANNEBLEY, Grillo-Werke Aktiengesellschaft, Germany

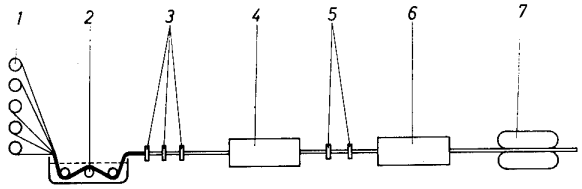
HISTORY

The pull-trusion process is the oldest one of the technical processes nowadays used for a continuous production of glassfibre reinforced polyester articles. Already in 1951, the first patent application (1) became popular in the USA describing the production of fishing-rods. During the following 15 years, a number of further patents were published (2-10) dealing with this technical process and mainly concerning devices by which the process should become improved or its range of usage become enlarged.

The special literature however as well as the programme of technical congresses about fibre reinforced plastics have a rather little publication regarding this technical process. With regard to the very early development of this process it can only be concluded that either technical difficulties prevented from a more popular application or that for this kind of products there had not been a ready market allowing the economic operation of a continuous production. The experience of the last years has shown that these two factors partly influence each other; by the technical improvement and the increasing variety of shaping further possibilities of application could be achieved so that the percentage of pull-truded products made from glassfibre reinforced polyester has considerably increased and now justifies an economic production.

TECHNICAL PROCESS

The first developed machines are horizontally operated by exclusively using rovings as reinforcing material. For the production of very simple profiles, mainly round bars up to 20 mm diam. these plants are still successfully used nowadays.



1 Roving spools
2 Impregnation - section
3 Forming - device
4 Heating - device (Orificeland)
5 Forming - device
6 Curing - section
7 Puller mechanism

Fig. 1 Horizontally operating pull-trusion equipment

Such a type of machine is schematically shown by illustration No. 1. The reinforcing material being on a coil grate at first runs through an impregnating bath provided with several guides, then through a stripping mechanism removing excesses of resin and then enters into the shaping nozzles; after leaving these nozzles the first hardening zone is passed, afterwards it is once more drawn through shaping nozzles and finally completely hardened in a further hardening zone. The hereby extruded rope is drawn off by a stripe draw-off device and then (not shown in the illustration) cut to the required lengths. Variation in this type of plant can be made either regarding the number of shaping nozzles and hardening zones or regarding the kind of the used heating, e.g. fluid rotary heating, radiant panel heating, or high frequency heating. The use of this process is however limited to light profiles with simple section shapes. For stronger profiles, the unobjectable conduct and shaping of the heavy, resin-impregnated fibre rope causes a lot of difficulties. A fall of the glassfibre distribution, vertical to the pulling axis can also occur, if it is not produced with the highest possible glass contents which is often uneconomic and by no means always necessary.

The using of other reinforcing materials besides rovings in the horizontally working method is also critical as it requires great effort to fix mat or fabric ropes in the desired position. Finally, the production of sealed profiles (hollow section), is rather impossible as the long cores which are necessary for the exact forming of the inside shape of the profiles and which can only be fixed at one end, cannot be held exactly in the horizontal position.

The limited possibilities of usage of the horizontal machines have finally led to the development of those with a vertically working method. Apart from the working direction, these machines have that advantage compared with the horizontally working ones that the fibre impregnating mechanism is concentricly situated around the form entrance by which the feeding of the reinforcing material and its exact lead (important when using mats or fabrics) becomes very easy. The main characteristic of this type of machine however, schematically shown by illustration No. 2, is the use of only one long enough and heated shaping nozzle where shaping and hardening are effected at the same time.

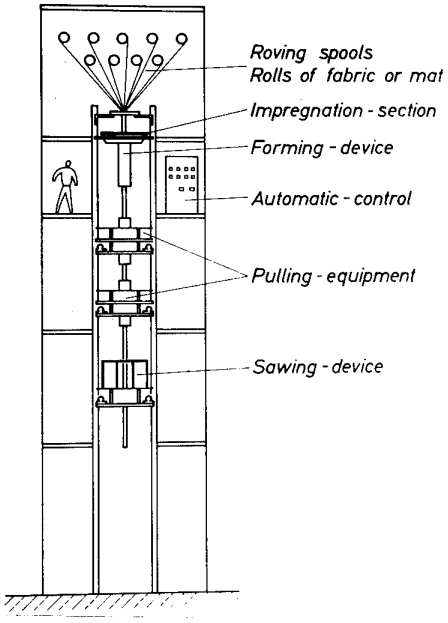


Fig. 2 Vertically operating pull-trusion equipment

For the production of open and hollow profiles with difficult sections this working method is unalterable. Naturally, hereby substantially higher frictional resistance in the mold have to be overcome than when using short nozzles, so that here the puller mechanism known from the treatment of thermoplastics cannot be used.

The working speed of such plants depends on the length of the nozzle wherein the curing up to the form-stability has to be effected. The working speed is limited because of the shrinkage occuring by the hardening and the frictional resistance growing with the increasing length of the mold. The working speed amounts to 0.2-1.5 m/min depending on the difficulties and wall thickness of the profile section. As the economy is destined by the capacity in the time unit, two or more profiles are truded on the plant at the same time. For simple profile sections, proposals for the forming of the clamps of the puller mechanism were already made in one of the former patent documents (4). Some examples are shown in illustration No. 3.

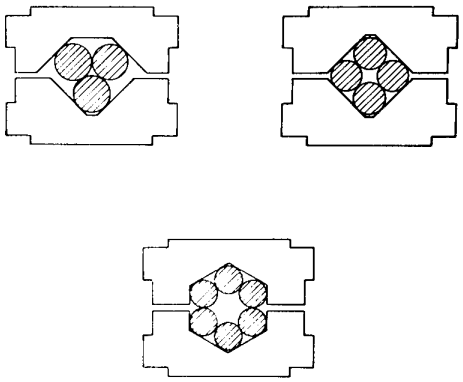


Fig. 3 Clamps of puller mechanism

This provision is not limited to profiles with the same section; eventually very different profiles can be truded at the same time when the clamps are formed correspondingly, provided that the production can be effected with the same drawing-speed. Illustration No. 4 shows a selection of special profiles produced on the above described machine.

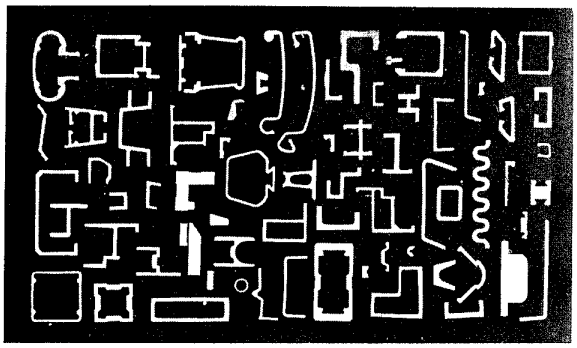


Fig. 4 Selection of special profiles made by the pull-trusion process

As one can see, a remarkable number of interesting applications regarding the variety of forming as well as the variation of wall thickness could be achieved. It goes without saying that apart from that conventional profiles like angles, T-, Z-, U-, and double-T-profiles in different dimensions and wall thicknesses are produced.

PROPERTIES

In contrary to all other continuous working methods, with the pull-trusion process no films are applied as cover- or wrapper films. The frictional resistances mainly occuring in the range of the nozzle when passing the machine have to be taken up by the hardened profile rope. Therefore a substantial part of the reinforcing material has to be put in as an endless fibre rope.

This kind of reinforcement is for the benefit of the usage of the profiles, as they are mainly stressed regarding flexure and tension. The endless reinforcement threads are lying under tension in the laminate and grant a very high tensile strength to the profiles, provided that the elongation of the applied resins is higher than that of the glassfibre the mainly used type of which is ES9 where the percentage amounts to 2 p.c. For laminates with not too low glass contents of tensile stress, the following simple relation is valid regarding the tensile strength.

$$\sigma_B \approx \psi . \sigma_{BG}$$

ψ means the volume content of glass and σ_{BG} means the tensile strength of the glassfibre which amounts to 140 kgs/mm^2. Theoretically, tensile strength of 70 kgs/mm^2 at a glass content of 50 p.c. which is technically absolutely representable, can be achieved if the following two conditions are fulfilled:

1. All glassfibres are without interruption running through the laminate straightly and in parallel direction.
2. No pin holes are existing and there is a complete adherence between the resin and the glassfibres.

Both suppositions are under normal conditions not very easy to fulfill. Even if the fibre rope which under certain circumstances exists of a few 100 rovings, is very carefully led, a bucking and with it an interruption of some fibres cannot be avoided, especially when entering the nozzle. Also the supposition for a perfect adherence between the glass fibre and the resin is not granted inspite of the constantly improved adhesives. The theoretic tensile strength therefore can at the best be achieved for round bars with a small diameter.

As real tensile stresses in the finished product are rather seldom and as there are mainly at the same time stresses vertically to the main axis—especially with hollow sections—an improvement of the transversal strength is necessary which for the roving reinforcement amounts only to the strength of the pure resin (11). For this purpose, spun rovings resp. mat or fabric ropes are used. These additional reinforcing materials are inserted where a high stress is expected, examples for which are shown by illustrations No. 5 and 6. They demonstrate endpieces of profiles of which the glassfibre reinforcement was not impregnated. On the right hand of the photo, the profiles are shown in the section.

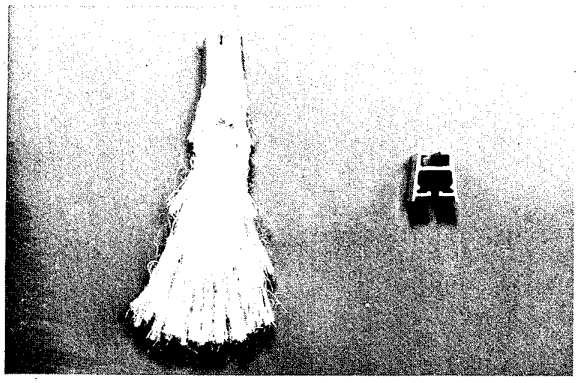


Fig. 5 Fixing profile for lighting units. Fabric reinforcement only in the transverse section

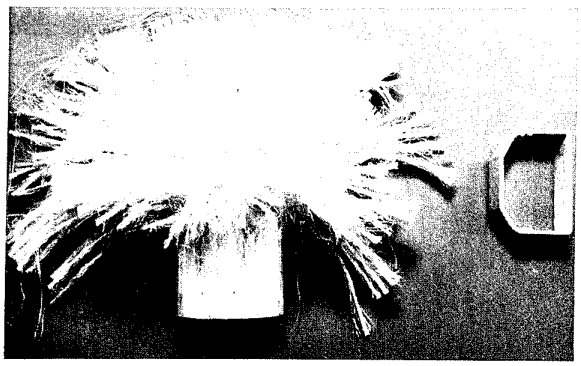


Fig. 6 Hollow profile with special fabric only in between the two noses

Only those fabrics can be used which do not bulge under the prevailing tensile stress and of which the wefts do not get shifted by the exceeding resin retained at the form entrance. Ripes of glassfibre mats need the fixing on a strengthened underground as they do not have an own sufficient tensile strength and even by using non-soluble adhesives break under the flowing pressure of the resin at the form entrance.

The different reinforcing materials as well as the changing volume relation in longitudinal and cross direction are forming a respectable variation of the mechanical properties. In the following table those maximum and minimum values are listed which are valid for the reinforcement constructions mainly used in praxis.

The symbols // resp. = are marking the values for the longitudinal resp. cross strength.

TABLE 1

Mechanical properties

Property	Test	Dimension	//	=
Gravity	DIN 53 479	g/cm³	1.7-1.9	1.7-1.9
Flexural strength	DIN 53 452	kp/mm²	20-50	5-10
Deflection	DIN 53 452	mm	1.1-1.5	—
Impact strength	DIN 53 453	mmkp/mm²	15-25	0.6-3.0
Compressive strength	DIN 53 454	kp/mm²	15-45	4-10
Tensile strength	DIN 53 455	kp/mm²	15-40	10-20
Flexural modulus		kp/mm²	1500-3000	500

The electrical properties except the discriptive strength do not show an important dependency on the stress and are listed in register 2.

TABLE 2

Electrical properties

Property	Test	Dimensions	
Track resistance	DIN 53 480	—	KA 3c/T5
Dielectric strength	DIN 53 481	KV mm	
Surface resistance	DIN 53 482	Ω	
Current-flow resistance	DIN 53 482	Ω.cm	
Dielectric constant	DIN 53 483	—	4.5-7.0
Power factor	DIN 53 483	tg δ	0.04
Arc resistance	DIN 53 484	—	80-120
Flame resistance	VDE 023/III	—	2-3

All the values in these tables are valid for profiles made from glassfibres of type E and styrol-containing polyester resins. The use of epoxide resins at present available and for this technical process necessary types requires such a slow working speed to reach the form stability that the machines becomes uneconomic. Therefore they have only been used in exceptional cases.

APPLICATION

The main application of truded profiles is in the field of the electrical industry and in the constructional branch as well as in the instrument construction industry and the general constructional engineering. The functions which especially the special profiles have to comply with are mostly known to the producer as detailed tests and eventually constructive alterations precede the end use. On the other hand, may applications of the so-called standard profiles such as angles, U-, Z-, and T-profiles remain unknown as these profiles are often distributed by the trade where the end use is very seldom followed up. Within this dissertation only a small selection of characteristic samples for application can be given. As far as it is the question where conventional material is used, its corrosion delicacy or insufficient isolating properties are the reason for the change of material. For the before mentioned reasons, in many cases FRP-profiles are used from the first, especially concerning the following examples of the building branch. Illustration No. 5, already dealt with when discussing the properties, shows a profile which serves for the fixing and suspension of long lighting units. Besides metal material, extruded phenol resin products were also replaced which are too strongly swelling when using them in damp rooms. A number of various profiles are applied for this purpose.

Of substantial importance are also supporters and coverings for conductor rails. An interesting example is shown by illustration No. 7.

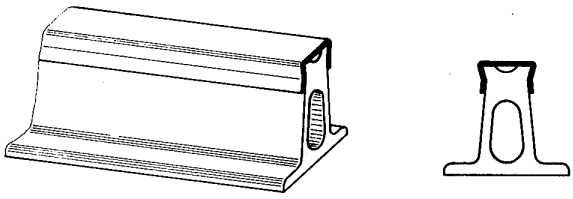


Fig. 7 Supporter for conductor rails with heating flue

The profile is provided with a flue for a heating wire as it is mainly used for crane ways in the open air and freezing is to be prevented.

Illustration No. 8 shows a fuse rail which is installed in depots of current distribution in public utilities. Here the use of FRP-profiles has enabled a very solid structure.

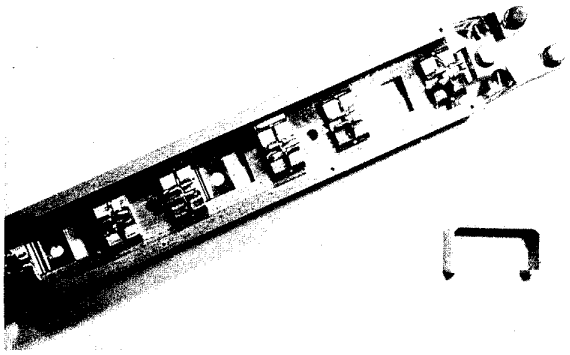


Fig. 8 Fuse rail

Low deflection and high corrosion stability was required of the roof beams which are necessary for large greenhouses. (Fig. 9).

In another case, profiles together with also continuously produced corrugated sheets are manufactured into separation walls for washing boxes which are more and more erected as hobby washing-boxes by the great mineral oil companies. Illustration No. 10 demonstrated such an installation.

Profiles are of increasing importance for sporting centres. Illustration No. 6 shown before represents a profile which is

used for the construction of football goals. Illustration No. 11 shows the fencing of a sports ground where the elasticity of the material is significantly exploited. Illustrations No. 12 and 13 show the application for the inside construction of indoor swimming halls and bathing cabins where without using wood or metal materials a profile system has been developed which permits a quick and clean assembly in combinations with wall elements to be prefabricated which means a substantial advantage besides the low weight and corrosion stability.

The use of stainless steel is the facade construction is attractive but also expensive. In addition hereto there exists a thermal conductivity between outside and inside caused by the metal. To avoid this and to retain at the same time the outer appearance of the stainless steel facade, a profile system has been developed, an example of which is shown by illustration No. 14.

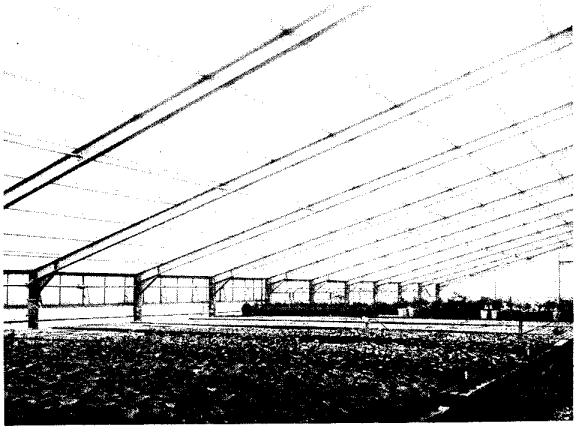


Fig. 9 Roof beams

Fig. 10 Separation walls in washing boxes

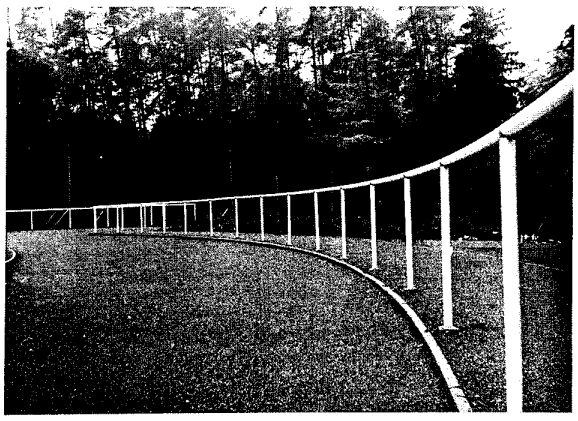


Fig. 11 Fencing of sports ground

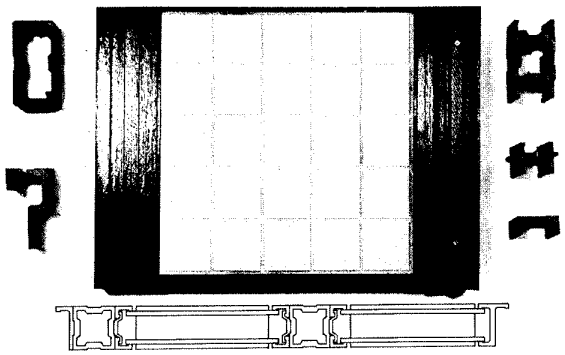


Fig. 12 Profile system for intersection walls

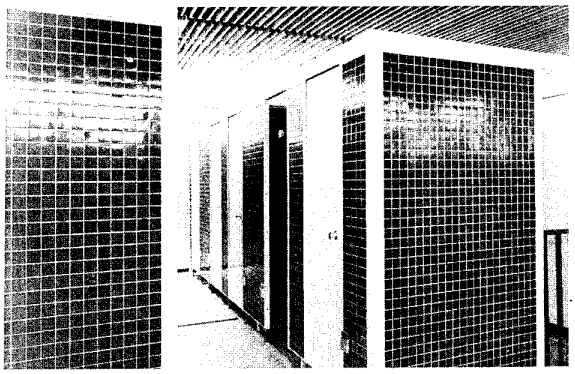


Fig. 13 Sanitary walls of an indoor swimming center

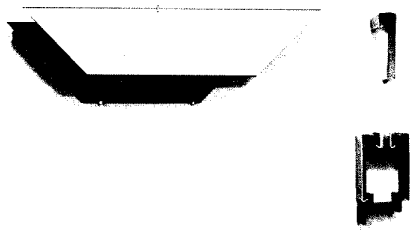


Fig. 14 Facade profile, FRP—refined steel

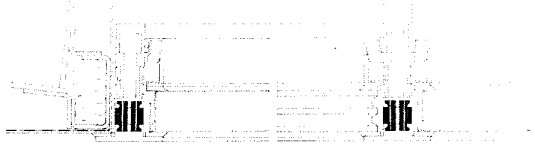


Fig. 15 Facade profile for the Hambourg television tower

The cramped stainless steel plate can be of small wall thickness and thus permits a competitive execution.

The profile system demonstrated by illustration No. 15 has also been developed for a facade covering and serves for the interruption of the thermal conductivity of the aluminium. In addition to that the FRP-bars put in take up a certain amount of the load of the inside covering. The system was used for the first time for the construction of the new Hambourg television tower for the covering of the restaurant and working platform.

The last illustration No. 16 demonstrates that it is also possible to produce profiles which have inspite of a high glass percentage still enough light transmission to enable a sufficient lighting of rooms lying behind. Here it is the question of a profile for roll doors, which are produced up to a width of 25 m for industry- and hall-doors of e.g. aeroplane-, train-, or bus-sheds. On the right hand of the illustration the vertical section is shown to demonstrate the mechanism.

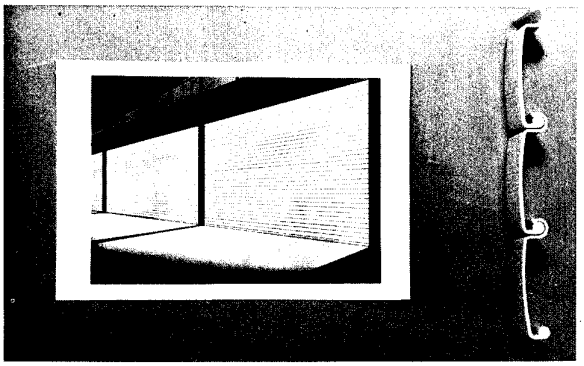


Fig. 16 Profile for roll doors

TREATMENT

Apart from a few exceptions, the profiles have to be treated before they can be used. Because of the relatively high glass content and the orientation of the reinforcing fibres, several recommendations have to be observed to avoid failures. The profiles can be sawn—if only a few cuts are necessary—by a usual iron saw. When using band saws, the cutting speed should be 1000-1500 m/min. One can use the same saw-blades like for the treatment of hard paper. For disk saws, diamond-tipped steel blades have proved to be the best. The minimum peripheral speed should be 1500 m/min, for higher wall thicknesses 2000-3500 m/min. Corundum- or silicon carbide blades can be used, but the plane of section does not become that smooth. The diamond-tipped saw-blades have to be cooled by water, for the other blades it is recommended.

Besides sawing, boring and milling are the most important processes of the treatment. In both cases, hard metal tools are used, where cutting speeds of 150-250 m/min are suitable. The feeding speed depends to a high degree from the wall thickness and amounts to 30-300 mm/min. When boring and milling it should be cooled by water, too.

Punching is not always possible and required a certain structure of fibre reinforcement. If this is taken into consideration, it has to be watched that the tools are made from hardened steel and that the plane to be punched has a good rest. A heating of the work piece to 120-150°C can be suitable. For further treatments such as sand blasting, filing, grinding, and polishing the usual steel treatment tools can also be used.

The profiles can be connected with each other or with other parts made from the same or a different material by sticking, screwing, or riveting eventually by a combination of the before mentioned methods. For sticking, adhesives on polyester- or epoxide resin basis are the best. When the profiles are screwed or riveted additional to the sticking—which is sometimes recommended—only through-passing screws (machine screws) should be used.

For riveting, it has to be watched that large washers are put in and that the rivet cannot beat out the rivet hole. The cut in of threads and the use of self-cutting screws is not recommended. The so-called sheet iron screws should only be used where no dynamic stresses are expected.

The profiles can easily be varnished—even without any preparatory treatment—when the procedure corresponds with the technical level.

PROSPECTS

The development of a process for production of pull-truded profiles started nearly 20 years ago, has had a substantial progress especially during the last 5 years. The hereby reached large variation in shaping and structure of the profiles has enabled interesting applications. The production has therefore become economic and the product competitive. Because of the good mechanical, electrical, and chemical properties it can be expected that the enormous experience gained in the last few years will enable further applications of the product. If beyond that it will be possible to solve still existing problems concerning the power feed at loaded constructions and to enable a further improvement of the quality of surface, additional fields of usage are to make accessible for which the material almost presents itself. It is to be hoped that it can soon be reported about the success of these efforts.

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Sixth International Reinforced Plastics Conference

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The Vanaduim - accelerator for unsaturated polyester resins

7

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INTRODUCTION

The use of vanadium accelerator for curing of unsaturated polyester resins is comparatively new (1, 2). Its advantages over other accelerators are: smaller quantities of accelerator are needed (4, 5, 10); improvement in colour of the cast material (4, 6, 8, 9); improved mechanical properties, especially HDT (10); firmer hardening of the product, even without post-curing (10); the use of a wide range of peroxides (5, 6) and hydroperoxides (3, 4), particularly Cumene Hydroperoxide, which is less expensive than other peroxides. With a vanadium accelerator it is possible to use monomers other than styrene, like triallylphosphate or acrylonitrile, for self-extinguishing compositions decreasing both the gel and cure time of the resin (9). The main problem with this accelerator is in the difficulty to control the very reactive oxidation-reduction system of vanadium and peroxide. The use of this system gives a very short gel time and the curing is accompanied by an appreciable exothermic effect (5).

After receiving several requests for a system that would shorten the work cycle, we decided to prepare an accelerator on a vanadium basis. After a considerable amount of work we eventually developed a stable accelerator that could be used in pre-accelerated polyester compositions. We also found the suitable ratio for a combination of vanadium with cobalt that helps to control the oxidation-reduction system and consequently makes it possible to apply the accelerator in field work. Finally, a fast curing resin system was developed, whereby we were able to reduce the curing time without decreasing the gel time, thus shortening the work cycle and permitting better use of the moulds.

EXPERIMENTAL AND DISCUSSION

We used in these experiments a resin made of 1 mole fumaric acid + 1 mole phthalic anhydride + 2.1 moles propylene glycol. We mixed 70 parts of the condensation product with 30 parts of styrene, adding 130 ppm of hydroquinone and 25 ppm of TBC as inhibitors. The curing agents in these experiments were:

(a) Vanadium accelerator — a solution of a vanadium compound having a concentration of 0.5% in vanadium metal (a product of Makhteshim);

(b) Cobalt accelerator — a solution of cobalt octoate with a concentration of 6% in cobalt metal (commercial product);

(c) Catalysts — MEKP, Cyclohexanone peroxide, Cumene hydroperoxide and Trigonix X-11 (commercial, products).

Unless otherwise stated, all experiments were done by casting the polyester resin in a Petri dish. A reading of 30-40 in the Barkol 934 meter was considered as an indication of full cure.

1. Preparation of the Accelerator

The vanadium accelerator was prepared by reacting V_2O_5 with a strongly reducing agent in the presence of a solvent. The resulting compound and complex materials of vanadium were of a valence less than 5. In the course of these experiments we found that this particular accelerator performs better with Cumene hydroperoxide than do other vanadium accelerators that are commercially available. The reproducibility and stability of the accelerator were checked by curing a resin at a constant temperature, and measuring the gel time, within a ±1 minutes accuracy. We have now had three years' experience with this material, and its stability and reactivity did not change during this period.

2. The vanadium accelerator as compared to a cobalt accelerator

TABLE 1

Quantities: Catalyst 2%, Accelerator 0.2% (V 10 ppm or Co 120 ppm) Temperature: 27.5°C

Catalyst	Accelerator	Gel-time, minutes	Barcol reading after 75 mins. 935	934
Cumene hydroperoxide	V	9	– –	50
Cyclohexanone peroxide	V	17.5	–	20
Trigonox X-11	V	19.5	80	–
MEKP	V	21.5	–	45
MEKP	Co	14.5	80	
Cyclohexanone peroxide	Co	20	70	
Trigonox X-11	Co	50	0	
Cumene hydroperoxide	Co	1300	0	

Table 1 illustrates the activity of the vanadium accelerator as compared to a conventional cobalt accelerator, and using the same catalysts. The system vanadium-MEKP gave reasonable gel-times and fast curing. The colour of the casts were better than in the cobalt-MEKP system, but there were more intense inner stresses and a tendency to crack. With Cyclohexanone peroxide, no great differences were noted in the gel-time, but the curing with the vanadium accelerator was faster. Almost water-white castings were obtained with this system, but here, too, there was a tendency to crack. Trigonox X-11 is a catalyst not defined by the manufacturer. It seems to be a combination of more than one catalyst and we mention it here only because of the almost complete absence of colour it gave with the vanadium accelerator, especially in thin coatings on white surfaces.

Cumene hydroperoxide seems to be the catalyst of most interest. Its activity with cobalt is too slow, and with vanadium very fast, but as fast as it is, and in spite of the high exotherm it causes, there is no tendency to crack. This advantage could possibly lead to the curing of large-size castings.

The activity of this catalyst gave us the idea of mixing the two accelerators to achieve better control of the system; in other words, to shorten the gel time, and still obtain a fast cure.

3. The System Vanadium-Cumene Hydroperoxide

From Fig. 1 it is obvious that there is no advantage in working with a concentration higher than 50 ppm vanadium accelerator. This disadvantage of small concentrations is the high sensitivity of the system, which makes the application impractical. The same applies when higher and lower concentrations of catalysts are used.

Fig. 2 also shows the sensitivity of the system, especially at higher temperatures. The slopes of the curves in the two figures indicate that the system would be of little practical interest. Nevertheless, we would point out that in every case, after about two hours, full curing is effected even at low temperatures and with low concentrations of accelerator and catalyst. This is of considerable advantage for places of rather cold climate.

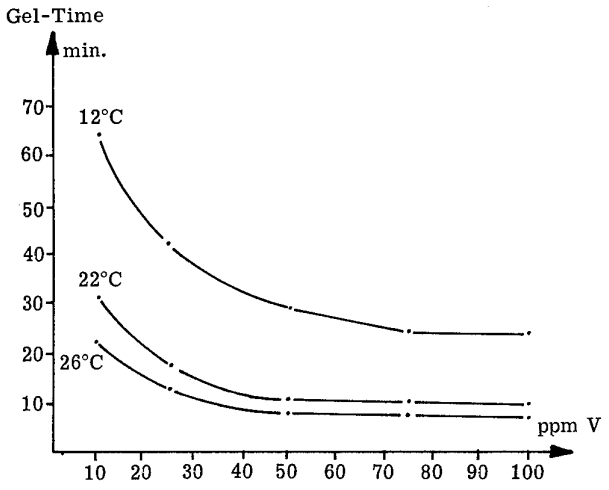

Fig. 1 1% Cumene hydroperoxide

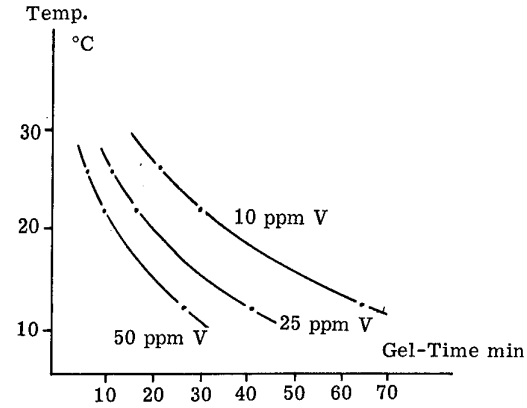

Fig. 2 1% Cumene hydroperoxide

4. Combination of vanadium with cobalt

Fig. 3 summarizes the experiments in which we looked for a suitable working relation between the amount of vanadium and cobalt compounds with cumene hydroperoxide as a catalyst.

To our surprise, when experimenting with a ratio of 1 : 1 vanadium to cobalt in the accelerator, and by changing only the concentration of the cumene hydroperoxide catalyst concentration, we obtained a straight line, with a slope indicating the possibility of suitable working conditions. All subsequent experiments were carried out with this accelerator, which is now referred to as accelerator 'S'.

5. Practical examples

Fig. 4 summarizes the experiments carried out in industry. We worked generally with constant concentrations of accelerator 'S' changing only the amount of cumene hydroperoxide catalyst.

The experiments in industry were done by using the hand lay up technique, producing a variety of laminates ranging from lamp shades, corrugated sheets to vehicle structures. We were requested to produce gel times of 20-40 minutes, at ambient temperatures ranging between 19-38°C. In all cases, full curing was obtained after no more than three hours at these temperatures. Parallelly, we worked on the same laminates using the Cobalt-MEKP system, but with the given gel-time as stated above, full curing was effected only after 12-24 hours.

From the figures it can be clearly seen how sensitive the accelerator is, even with the presence of cobalt and especially in concentrations of lower than 25 ppm.

The finished laminates prepared with the two systems were

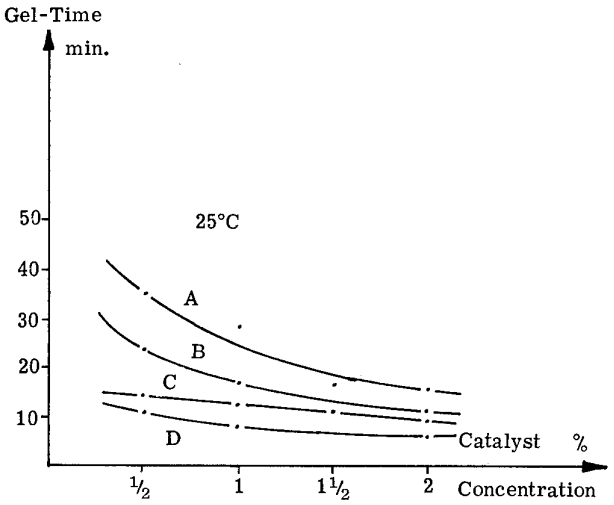

Fig. 3 Catalyst: Cumene hydroperoxide

(a) Accelerator V 50 ppm/Co 150 ppm
(b) Accelerator V 50 ppm/Co 100 ppm
(c) Accelerator V 50 ppm/Co 50 ppm
(d) Accelerator V 50 ppm/Co 0 ppm

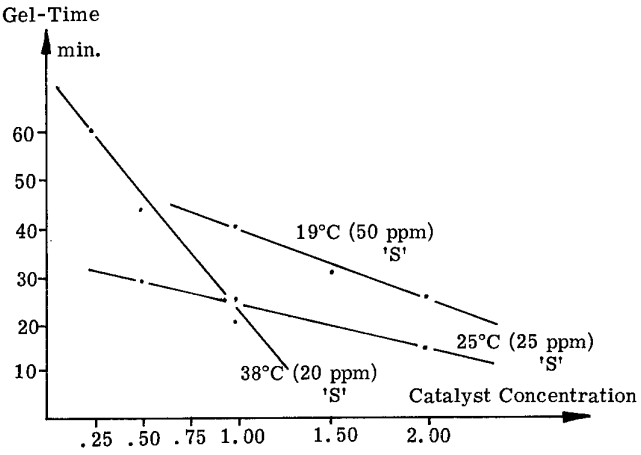

Fig. 4

tested for tensile strength; no significant differences were noted, but there is a tendency for higher values of tensile strength in the laminates produced with the vanadium system.

6. Post curing

The vanadium accelerator has another advantage. A major problem in the car-body industry is the deformation of the finished car-bodies after curing, painting and drying. In the production of vehicles, the bodies that were cured with the cobalt-MEKP system, then painted and dryed in an oven at a temperature of 80°C, became slightly deformed, causing many difficulties in the assembly line.

TABLE 2

Curing System Catalyst	Accelerator	Deformation after 80°C
1% MEKP	Co 120 ppm	4.5%
2% MEKP	Co 120 ppm + V 10 ppm	1.8%
1% Cumene hydroperoxide	V 25 ppm + Co 25 ppm	0.9%

Table No. 2 summarizes our experiments with the same car model, using the vanadium accelerator.

Following the established regime of the workshop no deformation occurred when the laminates were removed from the mould after 4 hours and left at room temperature for 48 hours, before post-curing in an oven at a temperature of 80°C for 2 hours. From the table it can be seen that whenever our vanadium accelerator was used, (even in conjunction with cobalt), curing is effected in a much shorter time than 48 hours, and therefore no serious deformation did occur, even if the finished car-bodies are heated to 80°C for a short time after completion. This proves that there is no need for post-curing when using the vanadium accelerator-cumene hydroperoxide system.

7. Pre-acceleration of Polyester with Vanadium accelerator

In the course of our experiments we found that it is possible to pre-accelerate a polyester resin by using our accelerator 'S' stabilized with a copper salt. We also found that the container has a large influence on the stability of the pre-accelerated polyester, and that the best one to use is a commercial container, coated inside with a phenolic-resin-based lacquer. The results of the experiments are summarized in Table No. 3. We pre-accelerated the resin with 50 ppm accelerator 'S' and the gel time was measured by using 1% cumene hydroperoxide.

TABLE 3

Gel-time		Room Temp. Tests			
Time, days	(min.) 30°C	Room temp. °C	Gel-time minutes	Barcol 934 after 60 minutes	Viscosity cp 25°C
0	12	18	26.5	40-45	950
7	12	18	26	40-45	—
11	12	19	23-5	40-45	—
14	12.5	17	27.5	40-45	—
18	12	17	26	40-45	970
21	12.5	12	30	40-45	—
25	13	18.5	24.5	40-45	—
28	13.5	17	29	40-45	—
32	13	16.5	32.5	40-45	1000
38	13	13	48	40-45	—
49	13	16	39	40-45	1010
69	13	16	32	40-45	1100
81	14	14	42	40-45	—
85	14	19.5	25	40-45	1160

From the table it can be seen that there is a small drift in the gel-time during the first two months, after which time it begins to decrease. This is especially noticeable at lower temperatures; it has no significance at higher temperatures. The increase in the viscosity of the resin proves, too, that there are no significant changes in the polyester after three months. In all cases, we got a full cure of the cast after an hour. We would like to mention, however, that after about 50 days the resin shows a tendency to gel at the resin air interface, but only on the container wall.

8. Influence of polyester components and stabilization systems

During our different applications with the vanadium accelerator system as compared to other systems, we noted several points which should be mentioned here.

(a) The considerable influence of stabilizers and retarders on different curing systems at room temperature are well known. However, we found that the addition of TBC which has a considerable influence on the drift when using the Co-MEKP and Bz_2O_2-DMA systems, does not bear any influence on the vanadium-cumene hydroperoxide system, whereas hydroquinone has the same influence on all types of curing systems.

(b) The presence of TPP in the resin has a considerable influence on the Co-MEKP and cyclonox systems, but not on the vanadium-cumene and Bz_2O_2-DMA systems.

(c) An excess of glycol in the resin increases the gel time in all systems except the vanadium-cumene system.

(d) The type of glycol influences other systems; (the Bz_2O_2-DMA system being expecially sensitive to the type and reactivity of the glycol). However, the vanadium-cumene system is not affected.

(e) The use of isophtalic acid instead of phthalic anhydride in a resin composition influences the gel time in all systems including the vanadium-cumene hydroperoxide system. The Bz_2O_2-DMA system is especially sensitive.

SUMMARY

The advantages of accelerator 'S' may be summarized as follows:-

1. It offers efficient performance with practically any commercial catalyst over a wide range of conditions.
2. Practically no discoloration of the castings is taking place.
3. There is no tendency of the castings to developing cracks or faults, despite the rapid cure.
4. It offers the possibility of working at low ambient temperatures.
5. Concentrations of both accelerator and catalyst are smaller than with conventional systems.
6. Easy control of the system is possible by admixture of cobalt accelerator.
7. The work-cycle is decreased considerably in low temperature lamination as a result of shorter cure-out time. The shortened cure-out of the laminates is achieved while maintaining gel-times that are conventional in the art.
8. No post-cure at elevated temperatures is required with this system.
9. Pre-acceleration of the resin is possible, with shelf-life of at least 4 months at a medium temperature of 20°C.
10. The 'S' accelerator-cumene hydroperoxide system is less sensitive than other systems to variations in polyester composition, as well as to the type of stabilization additives of the resin.

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Long term water immersion tests on cured unsaturated polyester casts and laminates

8

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INTRODUCTION

The long term resistance of polyester cast resins and chopped strand glass/polyester laminates to water immersion has been examined.

The resins included were commercially available orthophthalic resins, isophthalic resins and an acetylated orthophthalic polyester resin.

The effect of curing conditions and variation in the type of glass used in the laminates was also examined.

The testing included the measurement of water absorption and physical properties such as flexural strength, tensile strength, Young's Modulus in flexure and tension, and Barcol hardness of casts and laminates after various periods of immersion in distilled water.

EXPERIMENTAL

The following resins were evaluated:-

(a) Resin A is an orthophtahlic/maleic polyester acetylated with acetic anhydride to produce a low molecular weight product. It is approved to BS. 3532 Type A, DTD. 5537, and DTD. 5549 Class MA/EA.

(b) This is a general purpose orthophthalic/maleic polyester resin with good mechanical properties, and complies with BS. 3532, Type B.

(c) An isophthalic/maleic polyester resin with very good chemical resistance and mechanical properties. Complies with BS. 3532, Type C and DTD. 5537 Class MC/BC.

PREPARATION OF RESIN CASTS AND LAMINATES

Resin casts and CSM laminates were prepared to the following formulation:-

Resin	100 pts by weight
Catalyst 60% methylethyl ketone peroxide	2 pts by weight
Promoter cobalt soap 0.6% Co	1 pts by weight

Cast resin was prepared as laid down in BS. 3532 Appendix 0.

Laminates were prepared by the hand lay up process, each laminate consisting of 3 plies of $1\frac{1}{2}$ oz/sq ft CSM with a glass : resin ratio of 1 : 2. Two types of glass were used in the preparation of laminates:

(a) FGE 2000

(b) HPE 2000

The curing cycles for cast resin and laminates were as follows:-

1. 24 hrs at room temperature and 2 hrs post stoving at 120°C.

2. 6 days at room temperature.

The casts and laminates were cut to specimen size, using a fine grinding wheel. The specimen edges were not polished or sealed.

TEST PROGRAMME

1. Control tests were carried out initially.

2. Specimens were immersed in distilled water at 23°C for a total period of 1 year. After immersion times of 1 day, 1 week, 1 month and monthly up to 12 months, specimens were removed from the water, wiped dry and tested. The following tests were carried out:

On cast resins	**Method**
Crossbreak strength	BS. 2782 304B
Young's modulus in flexure	ASTM. 790-61
Barcol hardness number	—
Water absorption	BS. 2782 502F
Water leaching	BS. 2782 502G
On CSM laminate	
Izod impact strength (1 in notch)	BS. 2782 306A
On CSM laminate	
Izod impact strength (1 in notch)	BS. 2782 306A
Crossbreak strength with deflection to break	BS. 2782 304B
Tensile strength with percentage elongation to break	BS. 2782 301C
Young's modulus in flexure	ASTM. 790-61
Young's modulus in tension	BS. 2782 301C
Water absorption	BS. 2782 502F
Water leaching	BS. 2782 502G

3. Cast resin water absorption specimens were immersed in distilled water at 40°C and at 60°C. After immersion times of 1 day, 1 week, 1 month and monthly up to 12 months the specimens were removed and their water absorption measured.

The results of these tests are given in the following Tables.

ABBREVIATIONS

C. B. S.	- Crossbreak strength or flexural strength
Defln.	- Deflection at Crossbreak strength
Y. M. in C. B.	- Young's modulus in flexure
T/S	- Tensile strength
E%	- Percentage elongation at ultimate tensile strength
Y. M. in T.	- Young's modulus in tension
I. S.	- Izod impact strength (1 in notch)
B. H.	- Barcol hardness number
W. A.	- Water absorption
R. T.	- Room temperature

TABLES

Cast Resin

Cure: 24 hrs at room temperature + 2 hrs at 120°C

Table 1/1 0-4 months immersion in water at 23°C
Table 1/2 5-12 months immersion in water at 23°C

Cure: 6 days at room temperature

Table 2/1 0-4 months immersion in water at 23°C
Table 2/2 5-12 months immersion in water at 23°C

Cure: 24 hrs at room temperature + 2 hrs at 120°C

Table 7/1 0-5 months immersion in water at 40°C
Table 7/2 7-12 months immersion in water at 40°C

Table 8/1 0-6 months immersion in water at 60°C
Table 8/2 7-12 months immersion in water at 60°C

Laminates

FGE 2000 CSM
Cure: 24 hrs at room temperature + 2 hrs at 120°C

Table 3/1 0-4 months immersion in water at 23°C
Table 3/2 5-12 months immersion in water at 23°C

Cure: 6 days at room temperature

Table 4/1 0-4 months immersion in water at 23°C
Table 4/2 5-12 months immersion in water at 23°C

HPE 2000 CSM
Cure: 24 hrs at room temperature + 2 hrs at 120°C

Table 5/1 0-4 months immersion in water at 23°C
Table 5/2 5-12 months immersion in water at 23°C

Cure: 6 days at room temperature

Table 6/1 0-4 months immersion in water at 23°C
Table 6/2 5-12 months immersion in water at 23°C

TABLE 1/1

4 months water immersion at 23°C—resin casts cured at R.T. and poststoved

Resin	Test	Control	Immersion Time						
			1 day	1 week	2 weeks	1 month	2 months	3 months	4 months
A	C.B.S. (psi)	16690	16630	12500	13360	8880	11780	10490	9240
	Y.M. in C.B. x 10^5 (psi)	4.34	4.81	4.31	4.4	4.5	4.0	4.37	3.79
	B.H.	47.8	45.8	44.5	42.2	40.2	35.7	35.5	39
	W.A. (mg)	13.4	16.5	47.6	71.2	106.4	161.5	186.4	207
	Leaching (mg)	Nil						19.9	
B	C.B.S. (psi)	14940	18130	16860	13100	13180	11490	11440	13380
	Y.M. in C.B. x 10^5 (psi)	5.28	5.77	5.15	5.46	5.38	5.05	5.37	5.12
	B.H.	51.5	49.2	48.2	46.8	47.2	44.8	45.5	46
	W.A. (mg)	17.5	18.4	49.8	70.1	97.9	131.5	142.2	148
	Leaching (mg)	Nil						29.7	
C	C.B.S. (psi)	15375	13840	11110	10700	10310	10190	9460	11660
	Y.M. in C.B. x 10^5 (psi)	5.02	4.87	4.8	4.92	5.04	5.03	5.36	5.08
	B.H.	50.8	46.8	46.5	46.3	47.0	45.5	47.0	47.0
	W.A. (mg)	26.4	22.2	64.4	87.0	108.3	122.5	125.5	127.3
	Leaching (mg)	1.1						28.8	

TABLE 1/2

12 months water immersion at 23°C—resin casts cured at R. T. and Poststoved

Resin	Test	Immersion Time							
		5 months	6 months	7 months	8 months	9 months	10 months	11 months	12 months
A	C.B.S. (psi)	10640	8700	9940	7950	9160	8310	8250	8950
	$Y.M._5$ in C.B. x 10^5 (psi)	2.9	3.72	4.08	3.42	2.94	2.83	2.71	2.93
	B.H.	34.0	28.0	30.0	31.7	27.0	29.0	29.5	24
	W.A. (mg)	225.2	232.9	243.7	251.7	256.8	262.6	286.1	275.5
	Leaching (mg)		19.7						
B	C.B.S. (psi)	13680	12300	13500	12040	10620	11560	10700	11570
	$Y.M._5$ in C.B. x 10^5 (psi)	4.62	4.72	4.49	4.9	4.61	3.39	4.86	4.84
	B.H.	45.0	42.0	42.5	42.5	38.0	44.0	42.0	40.0
	W.A. (mg)	153.7	155.6	156.6	158.7	160.2	160.8	173.4	162.4
	Leaching (mg)		27.5						
C	C.B.S. (psi)	9590	11740	11850	10920	11750	10380	10670	9770
	$Y.M._5$ in C.B. x 10^5 (psi)	4.53	4.66	5.19	4.82	4.48	4.56	5.0	4.95
	B.H.	45.0	43.0	42.6	41.8	40.0	45.0	44.0	44.0
	W.A. (mg)	128.5	129.1	129.6	131.1	131.3	132.0	134.6	132.0
	Leaching (mg)		28.5						

TABLE 2/1

4 months water immersion at 23°C—casts cured at R. T. for 6 days

Resin	Test	Control	Immersion Time						
			1 day	1 week	2 weeks	1 month	2 months	3 months	4 months
A	C.B.S. (psi)	9990	11220	13240	12800	13490	10369	9620	8600
	Y.M. in C.B. x10^5 (psi)	2.59	3.09	4.03	3.54	3.73	3.71	3.25	3.21
	B.H.	30.5	32.2	39.3	35.3	37.0	35.0	34.0	34.0
	W.A. (mg)	15.1	13.1	47.8	73.9	112.1	159.8	184.5	195.4
	Leaching (mg)	Nil						60.2	
B	C.B.S. (psi)	11960	9600	11060	8990	11340	12040	9980	9690
	Y.M. in C.B. x10^5 (psi)	3.27	3.63	4.72	4.56	4.68	4.85	4.62	4.85
	B.H.	36.5	35.5	41.7	42.5	42.5	41.0	42.0	43.0
	W.A. (mg)	16.8	15.3	48.4	73.3	100.2	126.8	136.5	141.6
	Leaching (mg)	Nil						52.0	
C	C.B.S. (psi)	9760	8480	7140	8206	8815	7510	7130	9160
	Y.M. in C.B. x10^5 (psi)	2.8	3.11	4.06	4.08	4.28	4.65	4.49	4.52
	B.H.	28.5	28.3	33.5	36.3	39.3	38.6	42.6	42.0
	W.A. (mg)	22.8	18.1	54.1	74.7	96.2	114.9	122.4	126.6
	Leaching (mg)	0.3						49.1	

TABLE 2/2

12 months water immersion at 23°C—casts cured 6 days at R. T.

Resin	Test	Immersion Time							
		5 months	6 months	7 months	8 months	9 months	10 months	11 months	12 months
A	C.B.S. (psi)	10420	8380	8270	8600	4350	9440	8440	7276
	Y.M.in C.B.x10^5 (psi)	3.01	3.06	2.82	2.87	2.43	2.97	2.5	2.86
	B.H.	28.0	30.0	25.0	26.0	25.0	23.0	22.0	16.0
	W.A. (mg)	209.5	217.6	227.6	231.7	237.4	242.4	231.3	256.1
	Leaching (mg)		66.6						
B	C.B.S (psi)	9430	10140	9610	9800	9870	10480	9250	7990
	Y.M.in C.B.x10^5 (psi)	5.09	5.05	4.49	4.67	3.87	3.63	4.25	4.58
	B.H.	37.5	39.0	37.0	37.8	40.0	38.0	39.0	35.0
	W.A. (mg)	145.4	143.4	146.6	148.3	149.4	150.9	151.9	152.8
	Leaching (mg)		63.2						
C	C.B.S. (psi)	8200	9850	8700	7200	7890	9090	7230	9620
	Y.M.in C.B.x10^5 (psi)	4.36	4.14	4.67	4.4	3.91	4.16	4.49	4.39
	B.H.	37.5	38.0	39.0	38.0	39.0	38.0	39.0	34.0
	W.A. (mg)	130.6	132.8	136.7	138.7	140.0	143.1	144.7	147.6
	Leaching (mg)		55.5						

TABLE 3/1

4 months water immersion at 23°C—FGE. 2000 CSM laminates cured at R. T. and poststoved

Resin	Test	Control	Immersion Time						
			1 day	1 week	2 weeks	1 month	2 months	3 months	4 months
A	I.S. (ft.lbs)	16.7	15.9	15.5	14.0	12.9	13.1	12.1	12.1
	C.B.S.(psi)	27600	27210	25450	20200	24640	21975	23000	21540
	Defln.(ins)	0.41	0.38	0.30	0.30	0.30	0.22	0.29	0.23
	T/S (psi)	19070	17035	16730	15960	16335	15130	15930	14230
	E %	2.0	1.97	1.81	1.77	1.57	1.74	1.64	1.51
	Y.M.in C.B. x 10^6 (psi)	1.21	1.12	1.02	1.05	0.94	0.89	1.0	0.94
	Y.M.in T x 10^6 (psi)	1.23	1.16	1.14	1.00	1.03	1.14	1.11	1.23
	W.A. (mg)	22.9	16.2	42.8	62.2	89.2	123.2	147.9	164.1
	Leaching (mg)	1.8						28.8	
B	I.S. (ft.lbs)	16.6	13.1	14.8	15.9	13.3	12.7	12.8	12.4
	C.B.S. (psi)	28700	22950	24025	24700	25750	22700	23225	22400
	Defln. (ins)	0.35	0.29	0.32	0.21	0.30	0.22	0.23	0.19
	T/S (psi)	15400	15565	15980	14780	16070	13950	14820	12500
	E %	1.56	1.69	1.94	1.70	1.69	1.75	1.39	1.41
	Y.M.in C.B. x 10^6 (psi)	0.96	0.93	0.95	0.88	0.95	0.86	0.87	0.77
	Y.M.in T. x 10^6 (psi)	1.26	1.27	1.26	1.34	1.14	1.20	1.21	1.30
	W.A. (mg)	28.8	21.5	71.4	95.2	113.2	131.7	145.4	153.9
	Leaching (mg)	0.7						39.2	
C	I.S. (ft./lbs)	16.6	16.3	14.5	13.3	13.6	13.3	13.6	11.8
	C.B.S. (psi)	28200	26800	30250	28075	26200	26775	25575	24530
	Defln. (ins)	0.36	0.32	0.31	0.26	0.29	0.23	0.27	0.25
	T/S (psi)	13530	15135	15500	13410	14900	13880	14900	14340
	E %	1.64	1.64	1.61	1.54	1.39	1.38	1.60	1.68
	Y.M.in C.B. x 10^6 (psi)	0.99	0.99	1.04	1.03	0.91	0.92	1.10	0.96
	Y.M.in T x 10^6 (psi)	1.28	1.07	1.24	1.26	1.23	1.42	1.27	1.31
	W.A. (mg)	22.9	19.2	50.6	74.4	105.7	131.4	145.2	148.8
	Leaching (mg)	1.5						25.6	

TABLE 3/2

12 months water immersion at 23°C—FGE. 2000 CSM laminates cured at R. T. and poststoved

Resin	Test	Immersion Time							
		5 months	6 months	7 months	8 months	9 months	10 months	11 months	12 months
A	I.S.(ft.lbs)	10.5	12.0	12.1	11.1	11.0	11.1	9.7	11.2
	C.B.S. (psi)	21300	21850	19940	20000	22430	16420	24380	20600
	Defln. (ins)	0.17	0.23	0.17	0.18	0.20	0.22	0.23	0.21
	T/S (psi)	12350	13170	11800	12830	11200	12970	10350	11580
	E %	1.33	1.53	1.45	1.56	1.28	1.39	0.8	1.41
	Y.M.in C.B. x10^6 (psi)	0.87	0.91	1.13	0.90	0.84	0.82	1.06	0.76
	Y.M.in T. x10^6 (psi)	0.93	1.18	1.03	1.06	0.97	1.06	0.87	0.91
	W.A. (mg)	179.2	191.1	202.5	216.0	227.4	239.0	250	262.4
	Leaching (mg)		19.1						45.7
B	I.S. (ft.lbs)	11.8	12.0	11.2	12.0	11.1	11.3	11.9	12.7
	C.B.S. (psi)	22900	21350	21775	20625	20260	15780	19370	26900
	Defln. (ins)	0.22	0.20	0.19	0.19	0.23	0.23	0.22	0.21
	T/S (psi)	11650	15640	13240	13500	11700	13750	11520	10880
	E %	1.50	1.55	1.36	1.34	1.46	1.35	1.42	1.04
	Y.M.in C.B. x10^6 (psi)	0.85	0.92	0.93	0.93	0.79	0.88	0.83	1.02
	Y.M.in T. x10^6 (psi)	1.20	1.24	1.13	1.01	1.08	1.22	1.04	1.05
	W.A. (mg)	156.2	155.4	153.8	157.1	173.7	163.8	172.1	182.1
	Leaching (mg)		32.8						44.7
C	I.S. (ft./lbs)	12.9	12.6	12.8	13.0	11.3	12.2	12.2	12.6
	C.B.S. (psi)	24600	25900	23800	25375	29610	23550	24330	24530
	Defln. (ins)	0.20	0.26	0.23	0.19	0.25	0.23	0.24	0.25
	T/S (psi)	14700	13090	11520	13800	14220	12920	13910	12940
	E %	1.46	1.38	1.21	1.32	1.32	1.30	1.53	1.39
	Y.M.in C.B. x10^6 (psi)	0.93	1.03	0.83	1.08	0.84	0.81	0.83	0.93
	Y.M.in T. x10^6 (psi)	1.37	1.24	1.14	1.08	1.20	1.31	0.65	1.40
	W.A. (mg)	146.0	138.7	135.4	132.1	131.4	132.2	138.1	138.0
	Leaching (mg)		2.4						28.7

TABLE 4/1

4 months water immersion at 23°C—FGE. 2000 CSM laminates cured 6 days at R. T.

Resin	Test	Immersion Time							
		Control	1 day	7 days	2 weeks	1 month	2 months	3 months	4 months
A	I.S. (ft.lb)	13.9	13.4	12.3	12.1	11.3	10.6	10.7	10.2
	C.B.S. (psi)	24100	23010	24330	21360	18650	18260	17030	17450
	Defln. (ins)	0.33	0.26	0.24	0.26	0.26	0.16	0.18	0.19
	T/S (psi)	15070	12570	12175	13400	12655	12480	13070	10570
	E %	1.71	1.75	1.93	1.99	1.79	1.59	1.40	1.44
	Y.M.in C.B. x 10^6 (psi)	0.79	0.81	0.71	0.61	0.65	0.64	0.71	0.62
	Y.M. in T x10^6 (psi)	0.87	1.08	1.20	0.87	1.07	0.96	0.84	0.73
	W.A. (mg)	20.7	11.9	48.4	71.5	105.1	143.5	161.2	174.4
	Leaching (mg)	2.7						68.4	
B	I.S. (ft.lb)	14.6	13.6	13.2	12.9	12.3	12.1	12.0	12.3
	C.B.S. (psi)	24200	22600	20990	21340	21500	20540	20580	18640
	Defln. (ins)	0.33	0.24	0.24	0.25	0.29	0.28	0.23	0.21
	T/S (psi)	16150	14135	9675	11600	9840	11360	10400	10160
	E %	1.82	1.76	1.58	1.72	1.25	1.63	1.23	1.38
	Y.M.in C.B. x10^6 (psi)	0.66	0.74	0.67	0.70	0.78	0.76	0.96	0.63
	Y.M. in T x10^6 (psi)	1.13	0.93	1.24	1.33	1.15	1.08	0.94	1.34
	W.A. (mg)	47.1	34.9	85.1	107.6	147.5	180.0	187.8	186.7
	Leaching (mg)	5.8						100.7	
C	I.S. (ft.lb)	14.9	14.2	14.8	13.7	14.6	13.1	12.9	11.0
	C.B.S. (psi)	26330	25830	26850	28250	28420	29570	22650	32380
	Defln. (ins)	0.31	0.36	0.44	0.33	0.25	0.28	0.26	0.28
	T/S (psi)	16335	13335	12330	12050	12455	13715	13380	13600
	E %	2.02	1.81	1.71	1.69	1.53	1.46	1.47	1.35
	Y.M.in C.B. x10^6 (psi)	0.82	0.86	0.99	0.90	1.05	1.04	0.85	0.80
	Y.M. in T x10^6 (psi)	0.95	0.93	1.04	1.17	1.27	1.21	1.33	1.30
	W.A. (mg)	35.6	28.1	89.7	97.3	116.7	138.7	135.5	122.9
	Leaching (mg)	12.0						70.6	

TABLE 4/2

12 months water immersion at 23°C—FGE. 2000 CSM laminates cured 6 days at R. T.

Resin	Test	Immersion Time							
		5 months	6 months	7 months	8 months	9 months	10 months	11 months	12 months
A	I.S. (ft.lb)	10.3	9.5	10.3	7.8	8.2	9.0	9.3	10.7
	C.B.S. (psi)	18450	16590	15540	19280	14760	17810	14060	17230
	Defln. (ins)	0.20	0.17	0.19	0.21	0.19	-	0.20	-
	T/S (psi)	10360	9730	8995	10780	8200	10420	10220	10250
	E %	1.42	1.21	1.07	1.15	1.14	1.17	1.32	1.39
	Y.M.in C.B. x10^6 (psi)	0.65	0.76	0.66	0.69	0.53	0.60	0.66	0.77
	Y.M.in T. x10^6 (psi)	0.79	0.79	0.89	0.91	0.90	0.74	0.76	0.83
	W.A. (mg)	184.5	190.6	199.6	206.1	202.7	214.4	219.4	229.6
	Leaching (mg)								122.6
B	I.S. (ft.lb)	12.1	11.6	11.9	13.3	11.2	11.1	11.0	10.3
	C.B.S. (psi)	20530	19125	18210	19910	16526	15940	13740	17520
	Defln. (ins)	0.24	0.23	0.27	0.25	0.22	-	0.25	-
	T/S (psi)	10500	10920	9690	9513	9520	10170	10240	10720
	E %	1.38	1.40	1.26	1.17	1.27	1.32	1.16	1.19
	Y.M.in C.B. x10^6 (psi)	0.60	0.70	0.62	0.54	0.55	0.86	0.77	0.70
	Y.M.in T. x10^6 (psi)	1.05	1.28	1.11	1.04	1.19	1.26	0.79	1.40
	W.A. (mg)	185.6	145.1	128.3	123.0	132.2	122.6	119.8	121.5
	Leaching (mg)								103.1
C	I.S. (ft.lb)	11.2	12.0	11.8	12.3	10.5	11.5	11.8	12.2
	C.B.S. (psi)	27700	27140	23325	26610	22780	25430	22800	24080
	Defln. (ins)	0.31	0.24	0.28	0.23	0.22	0.29	0.25	-
	T/S (psi)	12280	13680	12580	12400	10050	12270	10480	11520
	E %	1.46	1.33	1.28	1.15	1.40	1.32	1.10	1.23
	Y.M.in C.B. x10^6 (psi)	1.00	1.20	0.69	0.95	0.78	0.84	0.87	-
	Y.M.in T. x10^6 (psi)	1.00	1.16	1.07	1.19	1.27	1.22	1.30	1.20
	W.A. (mg)	127.6	117.4	112.6	105.6	99.4	115.7	118.0	128.5
	Leaching (mg)								69.9

TABLE 5/1

4 months water immersion at 23°C—HPE. 2000 CSM laminates cured at R. T. and poststoved

Resin	Test		Immersion Time						
		Control	1 day	7 days	2 weeks	1 month	2 months	3 months	4 months
A	I.S. (ft.lb)	15.2	16.6	15.0	14.5	14.0	13.5	12.8	12.8
	C.B.S. (psi)	29180	23300	26150	25360	24300	24490	22290	21130
	Defln. (ins)	0.33	0.31	0.30	0.33	0.29	0.30	0.22	0.22
	T/S (psi)	15900	14900	14570	14970	14630	11320	13710	12250
	E %	1.66	1.63	1.62	1.63	1.37	1.30	1.48	1.49
	Y.M.in C.B. x10^6 (psi)	1.05	0.92	1.03	1.00	0.99	0.90	0.90	0.95
	Y.M. in T. x10^6 (psi)	1.15	1.23	1.13	1.17	1.05	1.08	0.88	1.06
	W.A. (mg)	25.2	23.6	49.2	70.4	98.1	127.6	149.4	162.2
	Leaching (mg)	3.1						36.7	
B	I.S. (ft.lb)	17.7	16.2	17.3	15.9	16.2	15.2	14.6	14.7
	C.B.S. (psi)	30600	27160	24980	25675	26250	25180	22340	24250
	Defln. (ins)	0.34	0.33	0.32	0.30	0.30	0.31	0.19	0.21
	T/S (psi)	13950	11650	11070	12670	11890	11750	9830	11500
	E %	2.03	1.51	1.61	1.59	1.36	1.31	1.35	1.39
	Y.M.in C.B. x10^6 (psi)	1.14	1.14	1.19	1.13	0.95	1.20	1.03	1.01
	Y.M.in T. x10^6 (psi)	1.07	1.19	1.07	1.21	1.13	1.23	0.99	1.09
	W.A. (mg)	30.8	28.6	75.7	99.4	124.7	134.6	141.2	145.5
	Leaching (mg)	4.0						42.9	
C	I.S. (ft.lb)	15.3	14.6	13.7	14.6	14.2	15.0	15.0	13.3
	C.B.S. (psi)	26400	24260	22360	24990	24850	24850	25950	23690
	Defln. (ins)	0.35	0.31	0.29	0.33	0.31	0.30	0.22	0.20
	T/S (psi)	11130	11680	11900	10315	11350	10450	10410	11790
	E %	1.55	1.54	1.53	1.37	1.27	1.41	1.49	1.53
	Y.M.in C.B. x10^6 (psi)	0.87	0.93	0.95	0.99	0.96	1.39	0.79	0.91
	Y.M.in T. x10^6 (psi)	1.01	1.06	1.25	1.15	1.15	1.24	1.14	1.27
	W.A. (mg)	23.6	19.1	46.6	68.5	91.0	108.5	121.1	125.0
	Leaching (mg)	5.0						22.5	

TABLE 5/2

12 months water immersion at 23°C—HPE. 2000 CSM laminates cured at R. T. and poststoved

Resin	Test	Immersion Time							
		5 months	6 months	7 months	8 months	9 months	10 months	11 months	12 months
A	I.S. (ft.lb)	12.6	12.3	13.0	11.5	11.5	10.8	10.2	12.5
	C.B.S. (psi)	19840	21730	21350	22010	19540	20090	20840	20160
	Defln. (ins)	0.21	0.21	0.20	0.20	0.20	0.21	0.18	0.17
	T/S (psi)	14950	11200	12950	11680	11570	11070	12000	11100
	E %	1.48	1.16	1.39	1.25	1.21	1.31	1.32	1.11
	Y.M.in C.B. x10^6 (psi)	0.92	0.63	0.85	0.94	0.85	0.83	0.78	0.86
	Y.M.in T. x10^6 (psi)	0.84	0.93	1.08	0.93	1.13	0.77	0.93	0.96
	W.A. (mg)	174.2	182.8	197.6	206.4	206.4	225.7	220.8	243.5
	Leaching (mg)		27.1						51.9
B	I.S.(ft.lb)	13.0	13.3	11.4	12.4	13.4	13.6	13.2	12.7
	C.B.S.(psi)	21740	23730	22840	22650	22100	24710	21680	25170
	Defln.(ins)	0.20	0.21	0.19	0.20	0.21	0.21	0.21	0.20
	T/S (psi)	12080	10630	11980	12730	9960	10580	11410	10440
	E %	1.44	1.14	1.41	1.39	1.63	0.97	1.40	1.28
	Y.M.in C.B. x10^6 (psi)	0.90	0.90	1.16	0.96	0.92	0.97	1.01	0.91
	Y.M.in T. x10^6 (psi)	1.14	1.12	1.27	1.04	1.16	1.15	9.4	10.4
	W.A. (mg)	154.7	156.2	163.1	165.2	149.8	165.9	153.4	166.5
	Leaching (mg)		30.1						49.4
C	I.S.(ft.lb)	13.6	12.8	12.2	12.1	11.4	11.4	11.0	11.1
	C.B.S.(psi)	25590	22180	24680	23080	20440	25300	24710	23980
	Defln. (ins)	0.2	0.2	0.27	0.17	0.17	0.18	0.16	0.17
	T/S (psi)	10630	9840	10490	12270	11600	9670	11700	9880
	E %	1.41	1.17	1.36	1.2	1.31	1.18	1.3	1.25
	Y.M.in C.B. x10^6 (psi)	1.18	0.77	0.88	0.95	0.82	0.75	0.77	0.81
	Y.M.in T. x10^6 (psi)	1.09	1.21	1.23	1.13	1.11	1.24	1.46	1.12
	W.A. (mg)	131.3	134.5	139.2	149.8	141.2	158.9	158.0	170.7
	Leaching (mg)		19.2						18.3

TABLE 6/1

4 months water immersion at 23°C—HPE. 2000 CSM laminates cured 6 days at R. T.

Resin	Test	Immersion Time							
		Control	1 day	1 week	2 weeks	1 month	2 months	3 months	4 months
A	I.S. (ft.lb)	17.5	14.4	15.4	16.8	17.0	14.9	14.6	12.9
	C.B.S. (psi)	23400	21790	19850	18246	20700	18700	16280	17030
	Defln. (ins)	0.34	0.31	0.31	0.26	0.29	0.2	0.22	0.26
	T/S (psi)	15100	13670	10550	11700	10720	10160	11080	10930
	E %	2.34	2.19	1.76	1.81	1.61	1.17	1.56	1.5
	Y.M.in C.B. x10^6 (psi)	0.81	0.79	0.67	0.73	0.72	0.59	0.59	0.8
	Y.M. in T. x10^6 (psi)	1.04	0.87	1.1	0.98	1.02	1.02	0.92	0.96
	W.A. (mg)	21.5	14.8	44.9	70.6	102.6	135.1	158.7	172.9
	Leaching (mg)	4.7						79.0	
B	I.S. (ft.lb)	19.9	16.4	16.0	17.5	17.8	14.8	13.7	15.7
	C.B.S. (psi)	21000	24830	21900	22410	25410	20900	20600	20940
	Defln. (ins)	0.21	0.31	0.23	0.25	0.29	0.18	0.21	0.23
	T/S (psi)	15835	11360	10040	11070	10770	7500	11320	11180
	E %	2.22	1.77	1.45	1.42	1.44	1.11	1.42	1.54
	Y.M.in C.B. x10^6 (psi)	0.71	0.79	0.72	0.66	0.87	0.88	0.93	0.82
	Y.M.in T. x10^6 (psi)	0.91	0.83	0.19	1.08	1.07	1.09	1.1	1.15
	W.A. (mg)	37.9	28.8	66.3	93.1	140.6	168.0	185.6	183.5
	Leaching (mg)	7.2						70.6	
C	I.S. (ft.lb)	16.6	14.6	15.0	14.6	14.6	13.0	13.6	12.9
	C.B.S. (psi)	24800	24390	24825	27930	26530	23600	21440	26750
	Defln. (ins)	0.3	0.32	0.22	0.32	0.3	0.22	0.21	0.22
	T/S (psi)	11630	14050	12570	11180	12800	11270	12450	12550
	E %	1.92	1.89	1.63	1.41	1.58	1.39	1.35	1.32
	Y.M.in C.B. x10^6 (psi)	0.86	0.78	0.98	0.93	1.07	0.97	0.96	1.1
	Y.M.in T. x10^6 (psi)	0.8	0.87	1.06	0.99	1.08	1.17	1.1	1.1
	W.A. (mg)	35.3	36.8	75.7	104.1	121.1	127.1	133.1	136.3
	Leaching (mg)	6.4						58.0	

TABLE 6/2

12 months water immersion at 23°C—HPE. 2000 CSM laminates cured 6 days at R. T.

Resin	Test	Immersion Time							
		5 months	6 months	7 months	8 months	9 months	10 months	11 months	12 months
A	I.S. (ft.lb)	13.1	13.5	13.0	12.7	13.4	11.7	12.3	11.0
	C.B.S. (psi)	17025	18540	16250	16975	18110	15150	15080	14390
	Defln. (ins)	0.25	0.16	0.185	0.21	0.19	0.2	0.2	0.2
	T/S (psi)	10190	9810	9260	9660	8710	8400	11270	11800
	E %	1.36	1.34	1.32	1.09	1.04	1.14	1.29	1.33
	Y.M.in C.B. $x10^6$ (psi)	0.67	0.78	0.61	0.71	0.65	0.64	0.78	0.65
	Y.M. in T. $x10^6$ (psi)	0.98	0.98	0.87	0.96	0.97	0.98	0.98	0.95
	W.A. (mg)	183.4	196.0	203.6	213.4	219.4	221.9	230.3	234.3
	Leaching (mg)		101.5						131.0
B	I.S. (ft.lb)	14.1	15.3	14.94	14.1	15.1	15.1	15.0	12.7
	C.B.S. (psi)	19825	19560	20190	21685	19230	21030	21590	19430
	Defln. (ins)	0.18	0.2	0.23	0.21	0.22	0.17	0.25	0.18
	T/S (psi)	12000	10970	10540	11680	8280	8650	10000	9540
	E %	1.21	1.39	1.58	1.32	1.1	1.01	1.15	1.22
	Y.M.in C.B. $x10^6$ (psi)	0.87	0.97	0.72	0.86	0.75	0.8	0.99	0.93
	Y.M.in T. $x10^6$ (psi)	1.0	1.14	0.99	1.2	1.1	1.1	0.91	1.08
	W.A. (mg)	151.8	147.0	120.3	100.0	110.7	106.3	100.1	104.7
	Leaching (mg)		78.5						97.8
C	I.S. (ft.lb)	11.7	12.9	12.0	12.0	11.8	13.4	11.5	12.0
	C.B.S. (psi)	24825	23840	21890	22155	24660	22480	26100	22730
	Defln. (ins)	0.21	0.22	0.19	0.19	0.21	0.24	0.27	0.22
	T/S (psi)	12800	10280	11620	11920	10930	12930	11360	10920
	E %	1.43	1.19	1.47	1.1	1.04	1.05	1.14	0.91
	Y.M.in C.B. $x10^6$(psi)	1.01	0.98	0.72	0.96	0.91	0.99	1.12	1.93
	Y.M.in T. $x10^6$ (psi)	1.25	1.29	1.09	1.19	1.13	1.01	1.14	1.09
	W.A. (mg)	131.3	139.4	136.2	117.4	128.0	126.9	119.5	126.5
	Leaching (mg)		62.8						76.7

TABLE 7/1

5 months water immersion at 40°C—cast resin cured at R. T. and poststoved

Resin	Test	Immersion Time at 40°C.							
		1 day	1 week	2 weeks	1 month	2 months	3 months	4 months	5 months
A	W.A.(mg)	24.7	71.5	92.3	147	187.1	214.9	229.4	250
B	W.A.(mg)	31.4	79.0	102.1	137.7	149.5	155.7	158.8	154.1
C	W.A.(mg)	33.7	78.3	91.4	101.5	102.7	102.7	102.0	105.0

TABLE 7/2

12 months water immersion at 40°C—cast resin cured at R. T. and poststoved

Resin	Test	Immersion Time at 40°C.					
		7 months	8 months	9 months	10 months	11 months	12 months
A	W.A.(mg)	307.6	302.1	323.6	335.9	344.9	275.7
B	W.A.(mg)	165.8	162.4	164.0	189.7	200	181.8
C	W.A.(mg)	109.6	107.7	108.1	108.6	109	116.2

TABLE 8/1

6 months water immersion at 60°C—cast resin cured at R. T. and poststoved

Resin	Test	Immersion Time at 60°C.							
		1 day	1 week	2 weeks	1 month	2 months	4 months	5 months	6 months
A	W.A.(mg)	39.5	188.3	228.3	298.5	303.0	66.0	Casts Disintegrating	
B	W.A.(mg)	43.9	151.3	168.9	171.4	188.7	215.8	216.5	243.2
C	W.A.(mg)	44.7	104.1	104.7	109.9	112.3	120.2	124.5	125.7

TABLE 8/2

12 months water immersion at 60°C—cast resin cured at R. T. and poststoved

Resin	Test	Immersion Time at 60°C.					
		7 months	8 months	9 months	10 months	11 months	12 months
A	WA.(mg)	-------- Casts disintegrated at 4 months ----------					
B	W.A.(mg)	264.1	275.2	300.8	321.8	304.6	223.6
C	W.A.(mg)	131.0	133.7	138.6	143.2	147.9	136.7

DISCUSSION

Cast Resin

Water absorption at 23°C

During the first week the acetylated resin A had the lowest rate of water absorption, while the isophthalic resin C had the highest rate of water absorption. Thereafter, and particularly after one month, the absorptions increased steadily but resin A increased at a much faster rate than B and C. Eventually, after 12 months immersion, the total water absorbed by resin A was double that of C and about 70% more than B.

Water absorption at 40°C

After one day the water absorption of the three resins was similar, and this was maintained for two weeks. Thereafter the absorption rates diverged, that of A being much higher than the other two resins. After 12 months immersion the picture was much the same as that at 23°C except that resin A had leached badly, whereas B and C had not. It should also be noted that the isophthalic resin C appeared to have reached equilibrium and ceased to take up water after one month.

Water absorption at 60°C

Again the one day figure was similar for the three resins. The rate of water uptake, however, was high for all resins during the first week. After one week the rates began to diverge, A was very high, B low and C had reached a very low rate of water uptake. After two months the acetylated resin A had leached badly and tests had to be discontinued after four months owing to disintegration of the casts. Leaching did not appear to occur with resin B until some 10-11 months had elapsed. The isophthalic resin C continued with a very low rate of water uptake for the 12 months.

Barcol hardness after water immersion at 23°C

Although the test results are somewhat erratic, they show in a dramatic way the poor performance of the acetylated resin A compared with B and C. The test, of course, is a measure of the surface hardness of the cast material and would show more quickly than say the bulk flexural strength the effect of a particular environment on the resin surface.

It is also noticeable that casts cured at room temperature and without a post-stoving showed an increase in Barcol hardness after one week's immersion, suggesting an advancement in cure, although immersed in water.

Crossbreak strength after water immersion at 23°C

This test did not show any dramatic change in the strengths of the three resins during the 12 months immersion at 23°C. All resins decreased slightly in flexural strength, resin A more than B or C.

The flexural modulus of the three resins, however, showed resin A to be much more affected by immersion than either B or C.

Laminates

Water absorption at 23°C

A similar pattern emerged with laminates as with cast resins. The initial water absorption of laminates from the acetylated resin A was low, and its rate of water absorption slower than that of laminates from the non-acetylated resins B and C. After one month, however, the water absorption of A increased at a higher rate than that of B and C until after 12 months it had absorbed nearly twice as much water as B or C.

Crossbreak strength of laminates

It can be seen that after immersion in water for 12 months at 23°C all laminates retained a good proportion of their initial crossbreak strengths. There is some evidence that resin A with HPE glass produced a laminate which, after 12 months immersion, retained less of its initial strength than was the case with resins B and C.

Results of flexural modulus tests on the laminates were extremely erratic. About the most that can be said is that, bearing in mind the variable density of reinforcement obtained with mat, the modulus of each laminate was fairly well maintained over the period of immersion.

Tensile strength and modulus in tension

This test also indicated that laminates from the three resins retained a good proportion of their initial strengths.

The most striking aspect of this work is the fact that a resin which in cast form gives a low 24 hour water absorption figure may not be suitable for long term immersion. There has grown up in the industry rather too pedantic an emphasis on the performance of a resin after 24 hours water immersion. In fact, this work shows that observations of water absorption should be made for extended periods, particularly when carried out at room temperature. In the cases under review it appears that immersion at 23°C for one to two months is necessary before a clear pattern emerges. At 40°C a somewhat shorter time approaching one month is necessary, whilst immersion at 60°C appears to give a sensible picture after one week.

There is a significant difference between the figures obtained for leaching from both casts and laminates depending on the method of curing. Where only room temperature curing for 6 days was used after 6 months leaching was about double that for post-stoved material, although the figure could not be called excessive.

Tests on laminates gave rise to a much wider scatter of results than tests on casts as would be expected from the type of reinforcement used. Environmental tests on cast resin, therefore, are recommended in order to furnish comparative figures for resins. The testing of laminates, however, should be included since ultimately this will be the form of use.

Acetylation of free hydroxyl groups in polyester A has given a product which, at the same concentration in styrene as resin B, has a lower viscosity. However, although the 24 hour water absorption figure is low subsequent experience is not so favourable with some evidence that hydrolysis takes place to form acetic acid.

The superior performance of the isophthalic resin compared with the orthophthalic resins should be noted by those who have applications involving long-term water immersion for their products.

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The study of the polymerization of a resin by means of a dilatometer

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1. SCOPE

We propose to study the evolution of the copolymerisation reaction of an epoxy resin, as a function of the thermal conditions.

We know that a copolymerisation reaction usually goes with a shrinkage of the volume of the resin.

The principle of the method we are going to describe, therefore consists in comparing the dimensional variations, function of the temperature, of a non stabilized resin test-specimen, with those of the same test-specimen after cure.

We will attempt to find the rules that must be followed to obtain a complete stability of the resin.

2. PRINCIPLE OF THE DILATOMETER

The ADAMEL DHT 60 dilatometer used for this study is of the 'real dilatation' type and comprises:

- a double-wall circular oven, with a variable temperature in the range: room temperature + 400°C,
- an optical device for detecting and amplifying the dilatations (Chevenard tripod),
- an apparatus for recording the parameter dilatation and the factors temperature or time. (Appendix I).

The test-specimen to be used is 50 mm long; its maximum section is 5 × 5 mm. It is set in the silica specimen holder, one of its ends being in contact with the reference side of the specimen holder, the other with a silica push-piece. The latter is mobile inside the specimen holder and exerts a pressure of a few grammes against the test-specimen.

The test-specimen with the holder are put into the oven and the dimensional variations of the former are transmitted by the push-piece to a tripod, standing on two sharp edges and being able of a roational movement. The tripod bears a mirror for reflecting a beam of light onto a 'photo-resistive' cell, which transcribes the movements of the beam of light on a drum recorder and hence the dimensional variations of the test-specimen.

The drum-recorder can be made to rotate:

- either by bringing it under control of a potentiometer, itself controlled by a thermocouple placed inside the oven near the test-specimen,
- or by means of a synchronous motor, in relation with time.

Two successive amplifications, going out from the Chevenard tripod and from the photoresistive cell allow amplification coefficients ranging from 50 to 1530 for the dilatation parameter. This apparatus therefore allows to measure a lengthening of about one micron of the test specimen, since, for a maximum amplification, the pen of the recorder will move over more than one millimeter.

The curve representing the dimensional variations in relation with the temperature (Appendix II) will be obtained by driving the drum-recorder through the medium of the potentiometer. The curve shows the coefficient of dilatation α_i of the material near a given temperature θ_A.

This coefficient is equal to the slope of the tangent of the curve at a point corresponding to θ_A.

3. USE OF THE DILATOMETER

A resin test-specimen previously treated in a drying oven under strictly definite conditions of time and temperature is submitted in the dilatometer to a first heating at a constant rate of 1°C per minute up to a maximum value θ°C

If we admit that the initial state of copolymerisation was incomplete, this process in the dilatometer allows the propagation of the copolymerisation reaction together with shrinking. (Appendix III).

The dilatometer detects these dimensional variations, which is shown by the curve $\Delta 1 = f$ (temperature) curve 1.

Various points of transformation indicate the successive stages of the phenomenon.

Segment AB: The test-specimen being rigid, we have the usual thermal dilatation.

Segment BC: for a temperature which corresponds to the abscissa of B, we find a point of transformation and a decreasing of ΔI down to C where there is a new point of transformation. This decreasing of $\Delta 1$ in the BC section of the curve means a shrinkage, the origin of which is in a copolymerisation reaction having preceeded the thermal dilatation of the material.

Segment CD: a state of equilibrium is reached between the shrinkage due to the chemical reaction and the thermal dilatation. It is materialized by the section CD parallel to the axis of temperatures which also corresponds to a slowing down of the complementary reaction.

Segment DE: Once the complementary reaction is over the thermal dilatation becomes more important than the shrinkage which progressively tends towards zero from D on.

Point E corresponds to the end of the thermal process and to the beginning of cooling down which is shown by curve 1^1. The complementary chemical reaction which could be observed during the thermal process being an irreversible phenomenon having modified the structure of the material, the way of cooling down will represent a reaction to heat of a totaly different substance. We discover that ED is the only remaining section. This section corresponds to the thermal dilatation of a material having already reached this new state.

After cooling down to room temperature (20°C) the primitive displacement appearing on the axis of dilatation represents the total shrinkage due to the complementary reaction.

If taking this new origin as a starting point, we study the scale of temperatures as we did previously, the resulting curve (2) will practically correspond to the curve which represents the cooling.

This curve (2) could be different and show other numerous points of transformation. It must be stated however that the amplitudes of these new phenomena would in most cases be of little importance compared to those of curve (1). If it were not so, such an evidence would show a new complementary reaction, in so far that the preceeding thermal treatment would not have completely finished off the copolymerisation, and therefore stabilized the material.

The shrinkage as shown on curves 1 and 2, is a first element of comparison between two resin test-specimens, completely and incompletely stabilized.

This shrinkage gives a general information but does not allow to follow the reaction.

On the other hand the difference in slope of the segments AB, BC, CD and DE, allows to think that this shrinkage has been gradual with a maximum for a given temperature.

But we have said that the curve $\alpha i = f$ (temperature) (αi being the dilatation coefficient for a θi temperature) is the curve representing the differential coefficient of $\Delta 1 = f$ (temperature) to the temperature θ.

Besides, since the temperature θ is a linear function of time, it can be shown that instantaneous dilatation coefficient and shrinkage speed are proportional.

We will later on compare the shrinkage speeds for each temperature (Appendix V). The dotted curve Vi_1 represents the thermal evolution speed of the material to which is added the evolution speed of the complementary chemical reaction.

The curve Vi_2 in full line represents the thermal evolution speed of the stabilized material.

If for each temperature we study the difference $(Vi_2 - Vi_1)$ between the speeds, we practically eliminate the thermal evolution parameter only to keep the complementary reaction.

We thus obtain the curve $(Vi_2 - Vi_1)$ as a function of temperature. (Appendix V).

This curve gives us three further informations:

- The abscissa of the maximum corresponds to the temperature of the highest shrinkage speed.
- The ordinate of the maximum indicates the highest shrinkage speed.
- The time of reaction can also be determined since it corresponds to the time necessary for the investigation of the temperature range lying between the two points of a zero ordinate in the curve $Vi_2 - Vi_1$.

In the given instance we have:

- Maximum reaction temperature: 80°C.
- Shrinkage speed: 51.10^{-3} mm/h (for an initial length of 1 mm).
- Total reaction time: about 1 hour.

4. USE OF THE DILATOMETRIC METHOD

As an example we will use the method for studying the copolymerisation reaction of an epoxy resin.

The system includes:

- an epoxy resin: CY 207 by CIBA,
- a hardener: HT 972 by CIBA (diaminophenylmethane).

The copolymerisation can be divided into two phases:

1. The pretreatment, from the liquid resin to the resin incompletely polymerised material. In the course of this transformation, the couple time/temperature must be strictly controlled.
2. The study proper making it possible to follow the evolution of the copolymerisation until the material becomes stable.

It is obvious that the second phase must be as important as possible so that the greater part of the reaction can be observed. It is necessary to say first that:

If test-specimens are incompletely copolymerized following different time-temperature couples, and if we draw the curves $\Delta 1 = f$ (temperature) for each test-specimen, a group of curves (appendix VII) is obtained, showing points of transformation corresponding to given temperatures as long as the test-sample has been pretreated at less than 85°C. This is what we can find on curves 2, 3, 4 and 5.

The reproductibility of these points of transformation seems to show that the latter are characteristic of this resin system. These points are as follows:

- 65°C: temperature at the beginning of the reaction.
- 85°C: temperature of the reaction at its maximum.
- 130°C: temperature at the end of the reaction.

Remark

If the pretreatment was done at temperatures beyond 85°C, the curves $\Delta 1 = f$ (temperature) have a particular aspect (please refer to Appendix XVII).

We can see that, after the first heating cycle the movement of which follows the curve 1, the following cycles (of which we have displaced the ordinates in Appendix XVII so as to make reading easier) all take the aspect of a loop. Everything seems to happen as if there appeared a reversible transformation temperature of the resin system.

Taking into account the proceeding results, whole series of test-specimens at different stages of cross-linking will be made. To this purpose, they will be put into an oven at the previously given characteristic temperatures for increasing lengths of time (in our example from 1.5 h to 48 h).

For each time temperature couple, we draw the curves $\Delta 1 = f$ (temperature), from which we obtain the bell shaped curves representing the difference of speeds as a function of temperature (Appendix VIII — for a pretreatment temperature of 65°, times varying from 3 to 48 h). (Appendix IX — pretreatment temperature 85°C).

These curves present an interest since:

- The ordinate of each peak represents a shrinkage speed and therefore a rate of evolution of the phenomenon.
- The total shrinkage due to the complementary reaction is represented by the surface between the curve and the θ axis.

As a matter of fact, if we draw the group of curves representing the shrinkage of the material as a function of the temperature of pretreatment during the complementary reaction of copolymerization and the group of curves representing the shrinkage speed also as a function of the temperature of pretreatment, we obtain two groups of superimposable curves (Appendix XII: shrinkage = f (temperature of pretreatment), (Appendix XIII: shrinkage speed = f (temperature of pretreatment).

We therefore admit that the speed of the evolution of shrinkage constitutes a quantitative reference of the complementary copolymerisation reaction.

If we analyse these curves representing the shrinkage speed, we discover that:

1. With temperatures of pretreatment ranging from between 50 and 75°C, the rate of crosslinking increases with time and temperature, which seems to be logical.
2. With temperatures of pretreatment ranging from between 75 and 85°C we obtain optimal copolymerisation values and we discover that the time of treatment inside this range of temperature has an effect on the rate of cross-linking.

   Besides, we can observe an 'h_0' level of residual under polymerisation.
3. With temperatures of pretreatment ranging from between 85 and 160°C, the rate of copolymerisation decreases with the temperature but improves with time.

If going out from the preceeding curves we draw the curves representing the shrinkage speed as a function of the time of pretreatment at a constant temperature (Appendix XIV), we discover two important points:

1. One single temperature cannot lead to a complete polymerisation whatever the heating time.

   This result implies therefore the using of copolymerisation cycles constituted by the juxtaposition of several time-temperature cycles.
2. An initial treatment temperature which is too high has an unfavorable effect on the phenomenon which we have been studying.

AN APPLICATION OF THE DILATOMETRIC METHOD TO A REINFORCED PLASTIC STRUCTURE

As an example we wish to give an instance of how to apply the dilatometric method to a strictly industrial realisation.

The problem had be termed as follows:

A working structure constituting the vital part of a given system is made of:

- a parallel unidirectionnal roving reinforcement,
- and an epoxy resin matrix.

It had not been possible to go beyond 90°C for the copolymerization of a first model of the structure. It had therefore been decided to copolymerize for 16 hours at a constant temperature of 90°C (we will call this the A stage in the example to come).

A second structure being however under study, this limit set to the temperature could be hoped to disappear.

The two following questions have therefore been asked:

(a) How to find a time T of a complementary thermal treatment at a temperature of 90°C which would allow to finish up the initial state of copolymerization.

(b) How to find an optimum copolymerization by modifying if necessary the time temperature couple.

Delamination tests are made at each stage. They make it possible to determine the influence of the modifications in the various stages of copolymerization over the mechanical resistance of the material.

We have seen in the preceeding study that for a given temperature the dimensional stability and therefore the rate of copolymerization increases as a function of time up to an asymptotical value of upon this temperature.

The time is generally about 48 hours. We have therefore from the start taken a total length of 48 hours for the thermal treatment of this material.

The initial treatment was made to last 16 hours at 90°C. We have done two subsequent treatments:

B = 8 hours at 90°C representing a total of 24 hours.

C = 32 hours at 90°C representing a total of 48 hours.

Dilatometric tests similar to those of stage A have been performed for each of these two stages.

The results are given in Appendix XIX.

These two curves practically correspond to curve A. We can therefore admit that, whatever the time, a complementary treatment at 90°C will not noticeably improve the rate of copolymerization in the material.

We had to answer the second question which had been asked, that is to say finding the best state of polymerization.

To do this we treated the fourth test-specimen by using the informations we gathered when studying the material at the initial stage A: 30 minutes at 110°C + 1 hour at 125°C. (These two temperatures represent the abscissas of the two peaks).

Although the initial under-cure was not very important, we nevertheless wanted to obtain a better stability with an appropriate treatment.

The results obtained at this stage can be read from curve D in Appendix XIX.

It can be seen that this curve practically corresponds to the temperature axis which means a state of almost total stability.

It must be pointed out that the dilatometric curves in Appendix XIX have been obtained from test specimens taken off the reinforced plastics under study. These test-specimens have the shape of 50 × 5 × 3 mm parallelipipeds. The reinforcement is perpendicular to the greater dimension. The variations in length of the test specimen were measured along the greater dimension.

A test showing the delaminating strength of the material has been performed at each stage as a complement to the dilatometric study.

For each of the various stages A, B, C, D, 40 6.5 × 17 mm test-specimens have therefore been made and tested after diverse preliminary conditionings:

- 10 test-specimens tested after 88 h at 20°C and 65% relative humidity,
- 10 test-specimens tested after 2 h in boiling water,
- 10 test-specimens tested after 200 h in air at 70°C and 95% relative humidity.

In the last two cases the test-specimens had been cooled d down in the atmosphere of the laboratory for 1 h before the tests. All the delaminating test results are given in the table shown in Appendix XXI.

It is to be noticed that the copolymerization cycle as determined by the dilatometric method (last line of Table XXI), produces a laminate the ageing properties of which in hot and damp atmosphere is very much improved.

Besides, the initial laminate being very little under cured, this example puts the stress on the importance of the rate of cross-linkings of the matrix for the behaviour in time of the reinforced plastic.

5. CONCLUSION

It has not been our purpose to make a basic study on copolymerisation, but much rather a practical investigation giving precise informations on the state of the resin system in relation with its thermal past and its nature.

The dilatometric study we have just been talking about, has shown that it is necessary to be careful in determining the thermal cycles of copolymerisation and that

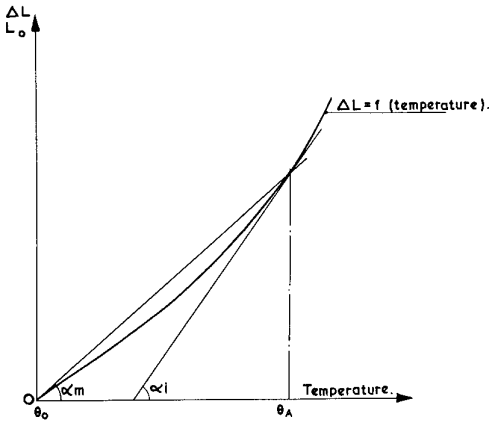
1. One single temperature cannot give a satisfactory state of copolymerisation. Besides, it is necessary to determine the couples time-temperature in order to obtain a complete stability of the material.
2. A certain temperature (85°C in our example) must not be exceeded during the first part of the hardening cycle.
3. The successive temperatures of the cycle must not be chosen too high either, as the higher temperatures do not, on the contrary, lead to a greater stability of the material.
4. It is possible by reading the curves of dilatation to determine the couples time-temperature which define a curing cycle. To do this, it is only a matter of submitting the resin to a first arbitrary time-temperature couple which brings the resin system to the solid state (please refer again to paragraph 2 above). Considering the resin of the test sample thus obtained, we will draw the dilatometric curve $\Delta l = f$ (temperature) and the 'bell-shaped' curve as represented in appendix V.

   The latter curve makes it possible to determine the temperature and the time of the second phase of the copolymerisation cycle. A polymerized test-specimen is then prepared according to the two phases determined above and the dilatometric study of a similar type will make it possible to determine the third phase of the copolymerisation cycle, should this third phase be necessary. The cycle thus determined is certainly not the only one that can be used but the advantage of the method is that it systematically leads to a technically acceptable cycle.

   Moreover, the dilatometric method is applicable in most cases, not only to the resin but also to the laminate.

   The dilatometric method must therefore bring an aid to the manufacturer in his choice of a manufacturing process of a laminate in enabling him to determine if necessary and to control the quality under the angle of the polymerisation of the reinforced plastic. Now, it is well known that the characteristics of the reinforced plastics have a close link to the nature and the state of the resin system it is constituted with.

   This dilatometric study is far from being finished and numerous questions still arise; our purpose was to briefly state the principles which might bring a solution to certain technical problems which we come against in the laboratories and in the manufacturing plant



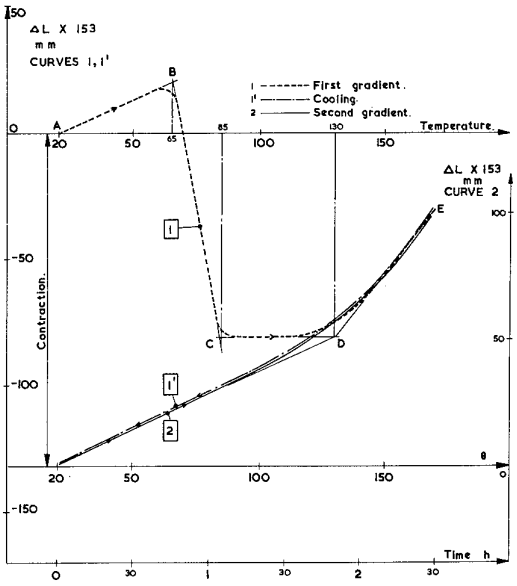
Curve $\Delta L = f$ (temperature.)

θ_A: Given temperature.

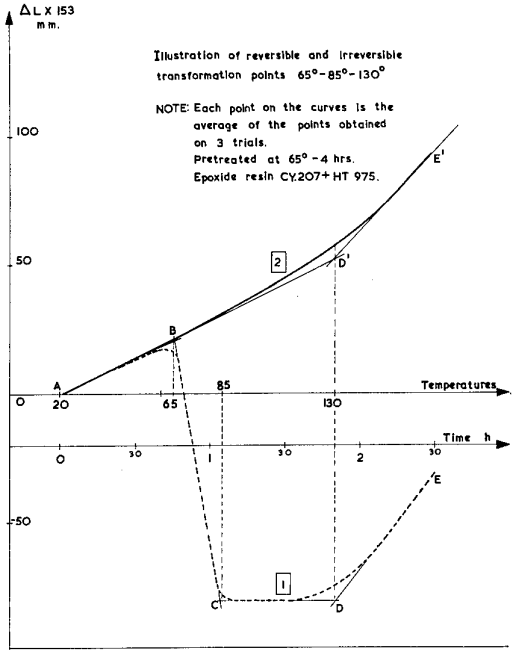
α_i: Coefficient of instantaneous linear expansion derived from θ_A °C

α_m: Coefficient of linear expansion average between θ_0 °C and θ_A °C.

APPENDIX I



APPENDIX II



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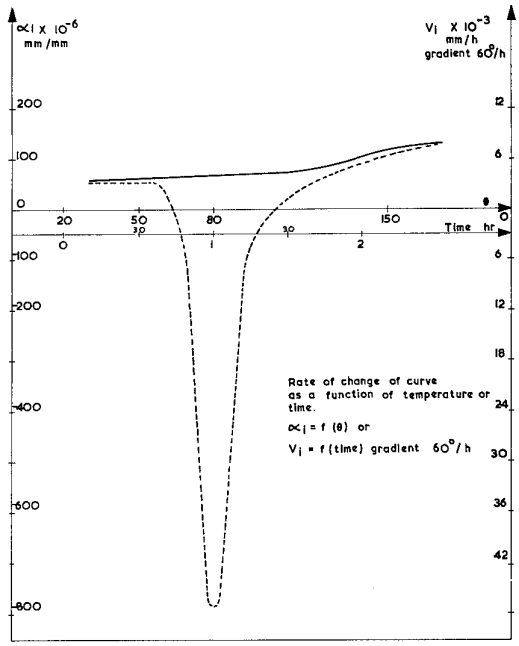

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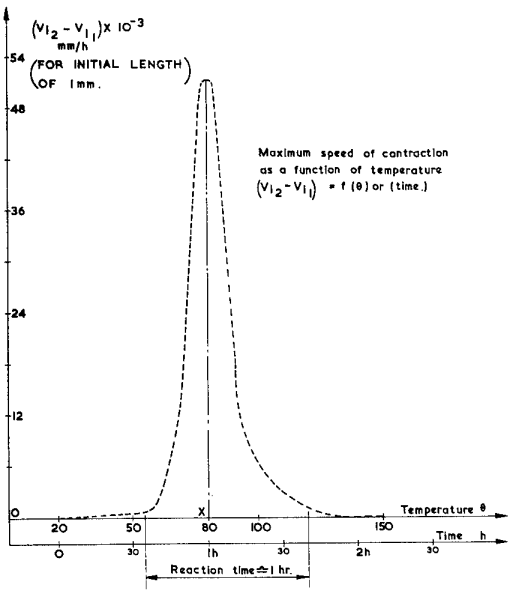

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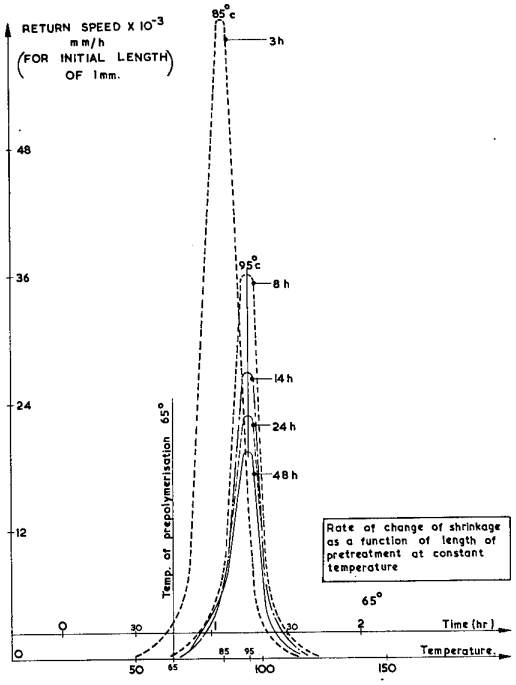

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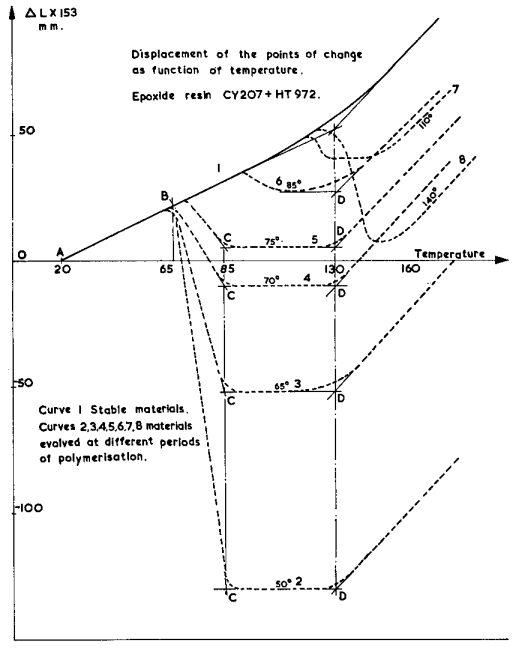

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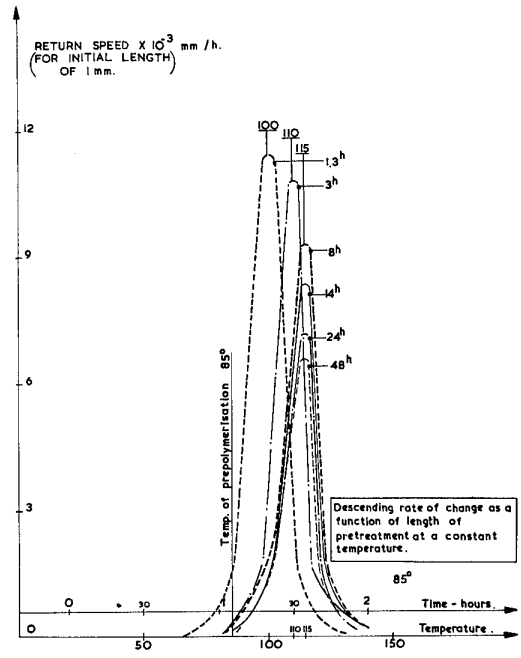
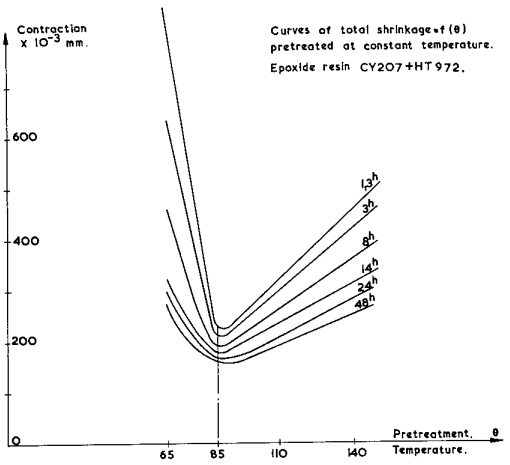


APPENDIX IX



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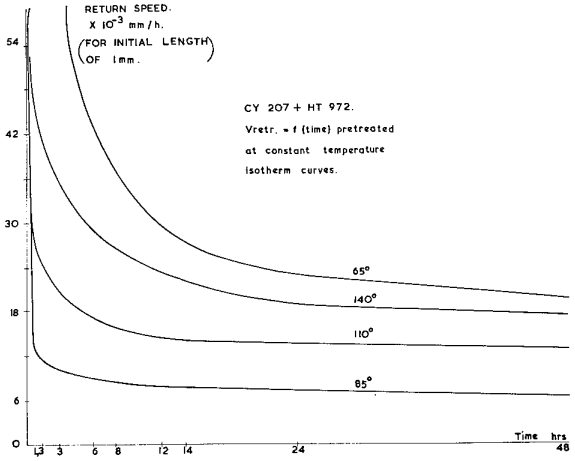
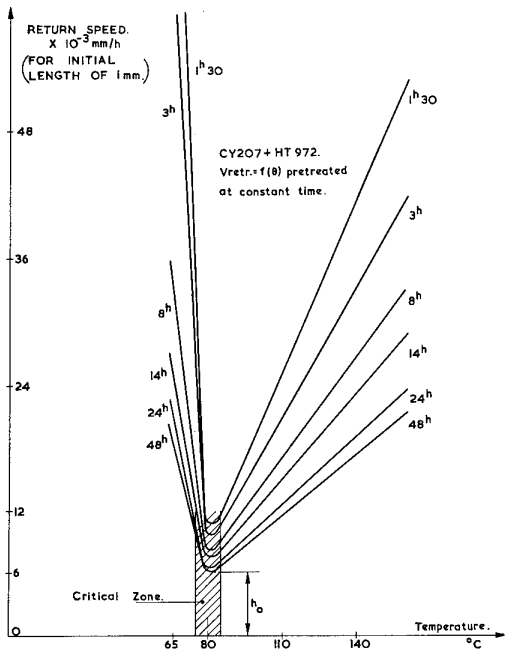
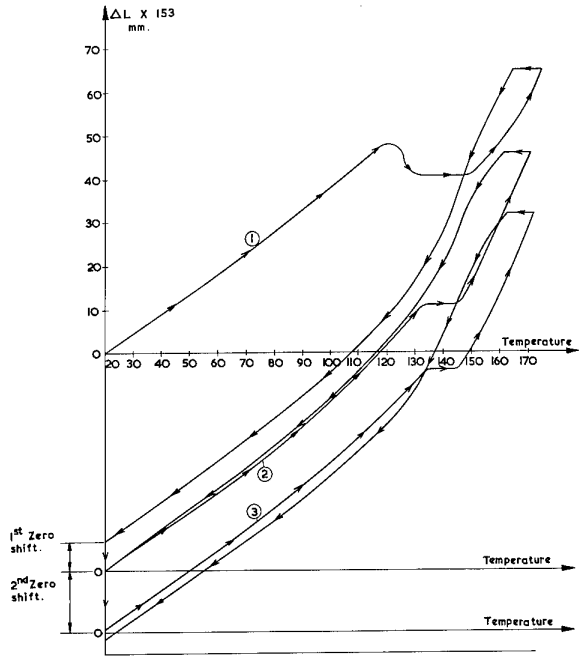


APPENDIX XIV

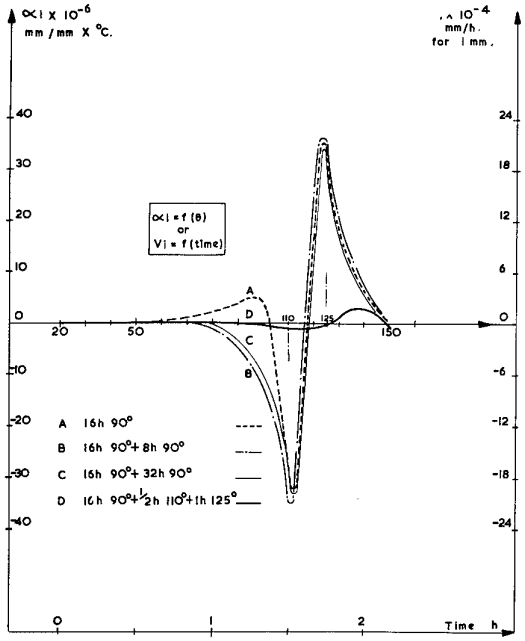


APPENDIX XIII

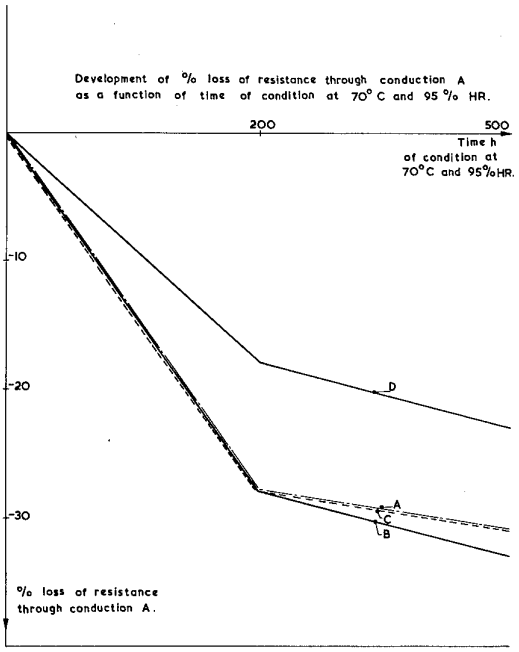


Expansion curves $\Delta L = f(\theta)$ showing a phenomenon under residual polymerisation under reversible and stable polymerisation.

APPENDIX XVII



APPENDIX XIX



APPENDIX XX

APPENDIX XXI

Rate of Polymerization — Delaminating Test

Conditioning / Complementary curing	A	D (2 h boiling water)		200 h air 70°C 95% R.H.		500 h air 70°C 95% R.H.		
	hbar	hbar	Variation % of compared to A cond.	hbar	Variation % of compared to A cond.	hbar	Variation % of compared to A cond	Weight % of reinforcement
Stage A	6.1	6.0	—2%	4.4	—28%	4.2	—31%	69
T = 0	S = 0.2	S = 0.2		S = 0.2		S = 0.2		
Stage B	6.0	5.8	—3%	4.3	—28%	4.0	—33%	69
T_1 = 8 h θ = 90°C	S = 0.1	S = 0.1		S = 0.1		S = 0.1		
Stage C	6.1	5 9	—3%	4.4	—28%	4.2	—31%	69
T_2 = 32 h θ = 90°C	S = 0.20	S = 0.1		S = 0.3		S = 0.10		
Stage D	6.1	5 9	—3%	5.0	—18%	4.7	—23%	70
T_3 = 30 mn st 110°C + 1 h at 125°C	S = 0.08	S = 0.08		S = 0.2		S = 0.1		

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Various organic/inorganic composites and the effect of silane coupling agents on their properties

L. P. ZIEMIANSKI, Union Carbide Corporation, New York, USA

INTRODUCTION

Silane coupling or keying agents have been known since the mid-forties for their use on glass fibers in reinforced plastics composites. Their well documented contribution is to impart significantly improved strength properties to the composite, especially in adverse environments.

An illustration of this up-graded performance is shown in Figure 1. Here polyester resin composites reinforced with glass fibers finished with methacrylate silate retain about 45% of their original flexural strength after 1000 hours exposure to boiling water.

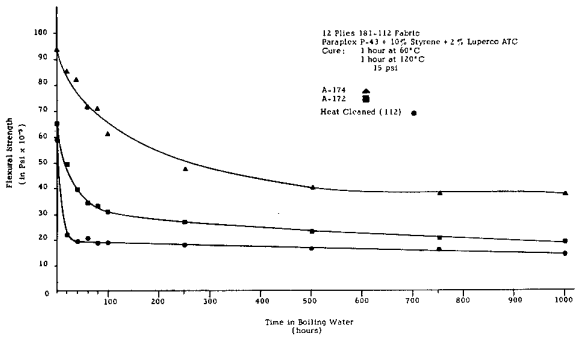


Fig. 1

More recently, a variety of other non-glass fiber composite materials have become important commercially. Among these are such composites as sand filled epoxy concrete patching compounds, phenolic bonded alumina grinding wheels, clay filled ethylene-propylene terpolymer[1,2] wire and cable coating compounds or aluminum metal filled epoxy molding tools and fixtures.

These composites all involve particulate mineral or metal fillers and thermoplastic, thermosetting or elastomeric polymers.

This paper deals with the evaluation of silane coupling agents in various non-glass fiber, filled polymers. The effect of the coupling agents either pre-applied to the filler or added directly to the polymer while compounding was observed in physical and electrical tests.

DISCUSSION

Table 1 lists the chemical composition of the silane coupling agents employed in this paper. Although various hydrolyzable groups such as OH, Cl, OAc or NR_2 may be used, the most common commercial coupling agents employ an alkoxy group. This group is hydrolyzed either in the application solvent medium or by surface moisture commonly present on filler or substrate surfaces. A siloxane is formed in this way on the substrate surface.

It is believed subsequent co-reaction with suitable organic polymers completes the coupling or keying action from the use of organo functional silane.

A Filled Thermoplastic Composites

Large volume, filled thermoplastic applications exist in such end uses as wire and cable coating compounds, floor tile, pipe, gutters, down spouts, and house siding. In these systems, economics play a major role. Coupling agents are recommended in those specific applications demanding optimum physical and/or electrical properties.

The following describes the evaluation of two filled thermoplastic polymers of current interest for the effect silane coupling agents have on their physical and electrical properties.

TABLE 1

Coupling Agent Reference Commercial Silane Coupling Agents

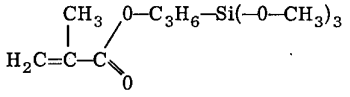
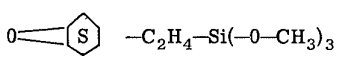
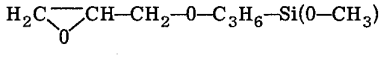
Union Carbide Designation	Nomenclature	Formula	Minimum Surface Area Coverage m^2/g
A-172	Vinyl-tris(beta-methoxy-ethoxy) silane	$H_2C{=}CH{-}Si(-O-C_2H_4-O-CH_3)_3$	278
A-174	*gamma*-Methacryloxypropyl-trimethoxysilane		314
A-1100	*gamma*-Amino-propyltri-ethoxy-silane	$H_2N-C_3H_6-Si(-O-C_2H_5)_3$	353
A-1120	N-Amino ethyl *gamma*-aminopropyltrimethoxy silane	$H_2NC_2H_4NH(CH_2)_3Si(OCH_3)_3$	351
A-186	beta-(3, 4-Epoxy-cyclo-hexyl) ethyltrimethoxy silane		317
A-187	gamma-Glycidoxypropyl-trimethoxy silane		
A-189	gamma-mercaptopropyl-	$HSCH_2CH_2CH_2Si(OCH_3)_3$	398

TABLE 2

Type	Composition	Supplier
Cab-O-Lite P-1	Calcium Silicate	Cabot Corp.
Iceberg	Calcined Clay	Burgess Pigment Co.
No. 40	Hydrated Clay	Burgess Pigment Co.
Atomite	Calcium Carbonate	Thompson, Weiman and Co.
Aluminium Powder	—	Various
Steel Wire	$\frac{1}{2}$ inch long, 6 mil diameter brass coated	National Standard Co.
Whitex Clay	Calcined Clay	Freeport-Kaolin Co.
Hi Sil 233	Silica	PPG Industries
Silene D	Silica	PPG Industries
Suprex	Hydrated Clay	J. M. Huber Corp
181-112	'E'-glass	Hess, Goldsmith Co.

TABLE 3

Polymer Reference

Type	Supplier
Hercoflat 1200 Nat Polypropylene	Hercules, Inc.
Styrene-acrylonitrile	Union Carbide Corp.
PVC-Bakelite QYTQ-7	Union Carbide Corp.
Epoxy ERL — 2774	Union Carbide Corp.
Hardener 4, 4′ methylene dianiline	Allied Chemical
Polyester Paraplex P-43	Rohm and Haas
Ethylene Propylene Terpolymer 3509	Enjay Chemical Corp.
Styrene butadiene SBR-1502	General Tire and Rubber Co.
Polyurethane (polyester base)	

1. *Polypropylene*

Polypropylene is attractive among polyolefins because of low cost, strength and low density properties.

In this work a theoretical mono molecular layer of various silane coupling agents was pre-applied to the filler surface and then the filler blended with polypropylene powder. This mixture was passed through an extruder/compounder and molded into test plaques.

Table 4 shows vinyl silane, A-172 in the calcium silicate ('Cab-O-Lite') filled system improved initial and wet flexural or tensile properties between 20-30 percent over a control containing no silane.

Calcined kaolin clay, 'Iceberg', containing systems responded to amino silane, A-1100 treatment with 10-15% improvement.

The best results of this series involved the No. 40 clay and amino silane. Improvements of about 50% over the control were evident in initial, wet, and 94°C flexural and tensile tests.

Electrical Testing

Dielectric constant, dissipation factor and volume resistivity measurements were conducted on the filled polypropylene composites and are listed in Table 4.

In general the initial electrical properties were not significantly affected when coupling agents were added. However, coupling agents are very effective in maintaining good electrical properties when the composites are subjected to water soaking at room temperature or 50°C.

2 *Polyvinyl Chloride*

Calcium carbonate, 'Atomite,' is a widely used filler in PVC applications such as gasket products, calendered goods, and wire and cable coatings because it is inexpensive and available over a wide particle size range. It is a non siliceous surface, however, and a more limited effect with silane coupling agents is expected compared to siliceous surfaces.

Table 5 shows a significant improvement in tensile and tear strength occurs with the addition of 1.0 PHR of A-1100 to the system. Tensile undergoes a 24% decrease with the addition of filler, but one-half of this loss is regained with A-1100. In regard to tear strength, actually more than 100% recovery is obtained with A-1100, and 0.25 PHR A-1100 is as effective as 1.0 PHR.

B Filled Thermosetting Composites

Many clay, silica, calcium carbonate, talc or silicate filler thermosetting resin applications such as molding or pre-mix compounds are common. Silane coupling agents hold a place in premium formulations with specific strength or electrical requirements in adverse environments.

Metal fillers or reinforcements in polymers contribute valuable improvements in strength, machineability or conductivity properties to the composite.

The following two evaluations illustrate the effect of silanes with metals as the polymer fillers. In these cases, the silane probably hydrolyses in the moisture contained in the surface oxide layers to produce the improvements noted.

TABLE 4

Effect of Silane Coupling Agents on the Electrical and Physical Properties of Filled Polypropylene[1]

Filler/Silane	Wt. %[2]	Flexural psi × 10^{-3}			Tensile psi × 10^{-3}			Dielectric Constant 1000 cycles/sec.			Dissipation Factor 1000 cycles/sec.			Volume Resistivity OHM/CM		
		Dry	Wet[4]	94°C	Dry	Wet[4]	94°C	Dry	Wet[3]	Wet[4]	Dry	Wet[3]	Wet[4]	Dry	Wet[3]	Wet[4]
Cab-O-Lite																
Control (no silane)		6.7	5.5	2.5	3.2	2.9	1.5	2.41	2.92	2.88	.004	.005	.06	10^{15}	10^{15}	10^{15}
A-1100	0.7	6.7	5.9	2.3	3.4	3.1	1.4	2.59	2.75	2.85	.006	004	.04	10^{15}	10^{15}	10^{14}
A-172	0.9	8.0	7.0	2.8	3.9	3.9	1.8	2.38	2.48	2.64	.002	.001	.003	10^{16}	10^{16}	10^{15}
A-174	0.8	7.4	6.6	2.7	3.8	3.6	1.6	2.43	2.85	2.78	.002	.002	.003	10^{16}	10^{16}	10^{15}
Iceberg Clay																
Control (no silane)		7.3	6.1	3.2	3.4	3.4	1 7	2.49	2.56	2.57	.002	.001	.02	10^{15}	10^{15}	10^{15}
A-1100	1.5	8.1	7.6	2.9	3.9	3.9	1.8	2.66	2.66	2.74	.002	.002	.004	10^{15}	10^{15}	10^{15}
A-172	1.9	7.5	6.4	3.2	3.7	3.4	1.9	2.56	2.59	2.63	.002	.001	.002	10^{15}	10^{15}	10^{15}
A-174	1.7	7.7	6.9	3.2	3.8	3.6	1.9	2.50	2.67	2.66	.002	.001	.002	10^{16}	10^{15}	10^{15}
No. 40 Clay																
Control (no silane)		4.6	4.4	1.8	2.5	2.1	1.2	2.77	3.00	3.67	.007	.02	.05	10^{15}	10^{15}	10^{13}
A-1100	2.0	7.1	6.6	2.7	3.6	3.5	1.7	2.79	2.76	3.01	.01	.01	.03	10^{15}	10^{15}	10^{15}
A-172	2.5	6.6	6.6	2.7	3.3	3.2	1.6	2.66	2.67	2.99	.002	.007	.03	10^{16}	10^{16}	10^{15}
A-174	2.2	7.0	6.5	2.8	3.4	3.3	1.6	2.79	2.61	2.92	.003	.005	.02	10^{16}	10^{16}	10^{15}

1 All composites contain 50 wt. % filler

2 Silane loading is based on filler weight

3 16 hours in 24°C H_2O

4 16 hours in 50°C H_2O

TABLE 5

Effect of Amino Silane, A-1100, on the Physical Properties of Filled Polyvinylchloride

Base Formulation	PHR
BAKELITE QYTQ-7	100
Flexol DOP	50
Dyphos	2
DS-207	1

Filler/Silane Addition	1	2	3	4	5
Atomite phr	0	50	50	50	50
A-1100 phr	0	0	0.25	0.5	1.0
Tensile psi	3011	2267	2482	2557	2652
Tear lbs./inch	545	521	604	598	596
Elongation	284	233	229	228	220

1. *Epoxy*

Table 6 shows the significant flexural strength improvement possible in aluminium powder filled epoxy resin when the metal is coated with a solution of epoxy resin containing silane coupling agent.

The most effective silane and concentration was one wt.% A-186 based on resin. This produced an average 100% improvement over the control initially and 535% after 72 hours boiling water immersion.

2. *Polyester*

Table 7 shows the effect of coupling agent in a brass coated, steel wire filled polyester composite. 30 wt.% steel wire was incorporated into a general purpose polyester containing 1 wt.% A-174 based on resin. A 45% improvement in initial tensile strength and 15% after exposure to a two-hour boiling water immersion is evident in the system containing the coupling agent.

TABLE 6

Effect of Silane Coupling Agents on the Flexural Strength of Aluminum Powder Filled Epoxy Resin

Wt.%	Type Silane	Flexural Strength psi Dry	H_2O Boil 72 Hour
none		1934	357
none		1670	628
none		1609	564
1.0	A-186	3478	3280
1.0	A-187	2463	2362
1.0	A-1100	2314	2060
2.0	A-186	2702	2510
2.0	A-187	1984	1908
2.0	A-1100	2444	2364

Composites were prepared by treating the aluminum powder (325 mesh) with a dilute solvent solution of ERL-2774 resin and amine hardener (4, 4^1 methylene dianiline).

In the cases where a silane was added, 1 or 2 wt.% (based on about 5% resin) were dissolved in the resin prior to treating the aluminum powder.

After drying the aluminum was packed in molds and cured for 2 hours at 150°C.

Flexural specimens $\frac{1}{2}$" × 4" × $\frac{1}{8}$" were cut from the moldings and tested initially and after exposure to 72 hours immersion in boiling water.

TABLE 7

Effect of Methacrylate Silane on the Tensile Strength of Polyester Filled with Steel Wire

Formulation	
Paraplex p-43	20.0 grams
Styrene Monomer	2.3 grams
Luperco ATC	0.4 grams
Brass Coated Steel Wire	10.0 grams
A-174 Silane	0.2 grams

System	Tensile Strength psi Dry	2 Hour H_2O Boil
Control (no silane)	4140	4520
1 wt.% A-174	6000	5330

Composites were prepared by charging the above formulation into tensile molds and press curing 1 hour at 60°C followed by 2 hour at 120°C.

A-174, when added, was dissolved in resin, styrene, and catalyst prior to introduction of the steel wire.

C Filled Elastomer Composites

The demonstrated effect of silane coupling agents in improving the properties of thermosetting and thermoplastic polymer composites makes them logical choices for mineral filled elastomers.

Two specific applications suggest themselves. The first concerns white formulations which preclude the use of a reinforcing filler like carbon black. The second involves the demand for long term electrical properties as in clay filled ethylene-propylene terpolymer.

TABLE 8

Effect of Silane Coupling Agents on the Physical Properties of a Calcined Clay Filled Ethylene Propylene Terpolymer System

Formulation	
Enjay EPT 3509	100 pts.
Whitex Clay	100 pts.
Flexon 580	40 pts.
Zinc Oxide	5 pts.
Stearic Acid	1 pt.
Sulfur	1.5 pts.
TMTD	1.5 pts.
MBT	0.5 pt.
Silane	As shown
Cure	30 Minutes at 160°C

Silane	Control	A-172		A-1100		A-189	
PHR		1	5	1	5	1	5
Hardness (Shore A)	64	66	65	69	67	67	67
Elongation %	483	460	420	295	425	360	390
Tensile (psi)	441	620	671	1152	1138	963	1145
Set at Break %	21	15	15	5	10	10	20
Tear (lb/in)	51	69	77	94	123	94	139
300% Modulus (psi)	325	529	610	—	922	914	948

The use of mineral fillers in both applications degrades the strength and long term electrical properties. Coupling agents enable the system to regain these properties.

The following describes three filled elastomer polymers to illustrate the improvements in physical properties possible with coupling agents.

1. *Ethylene Propylene Terpolymer*

Tables 8 and 9 show the effect of various silane coupling agent additions to sulfur cured EPT formulations containing calcined clay, or silica fillers. Three coupling agents comprising three different organofunctional groups are considered.

In general, tensile, modulus, hardness and tear increase while elongation decreases. These effects suggest an increased state of cure brought about by improved polymer /filler interaction capabilities with systems containing silane coupling agents.

As may be expected, the fillers evaluated respond differently to silane coupling agents. In this series, the silica filler ranks above the calcined clay.

Present commercial wire and cable coating applications require filler incorporation for improved compound hardness, abrasion and cut-through resistance. At the same time strength and electrical properties of the polymer are degraded because of the incorporation of the inorganic surfaces. These surfaces provide sites for degradation if they are not an intimate part of the polymer especially when operating in humid environments.

TABLE 9

Effect of Silane Coupling Agents on the Physical Properties of a Silica Filled Ethylene Propylene Terpolymer System

Same Formulation and Cure as Table 8 except filler is now Hi Sil 233

Silane	Control	A-172		A-1100		A-189	
PHR		1	5	1	5	1	5
Hardness (Shore A)	70	70	70	71	68	71	71
Elongation %	740	858	1100	745	800	740	613
Tensile (psi)	2182	2340	1571	2670	2874	2928	2976
Set at Break %	50	70	140	45	45	25	45
Tear (lb/in)		—	—	—	—	—	—
300% Modulus	347	360	270	528	522	658	992

2. *Styrene-Butadiene*

Tables 10 and 11 show the effect of various silane coupling agent additions to a sulfur cured SBR formulation containing calcined clay and silica.

As in the EPT systems, a similar polymer/filler interaction is apparent. A-189, mercapto silane is particularly effective in the silica filled system and clay filled system.

3. *Polyurethane*

The effect of silanes in a hydrated clay filled polyurethane is illustrated in Table 12. Tensiles are improved with each silane evaluated. The best improvement, 61% over the control, was achieved with 1.0 PHR A-1100.

TABLE 10

Effect of Silane Coupling Agents on the Physical Properties of a Calcined Clay Filled Styrene Butadiene Rubber System

General Tire SBR 1502	100 parts
Whitex Clay	100 parts
Zinc Oxide	5 parts
Stearic Acid	2 parts
Picco N.100	10 parts
Agerite Stalite	1 part
Sulfur	2 parts
Altax	1.5 parts
Cumate	0.25 parts
Silane	As shown

Silane	Control	A-172		A-1100		A-189	
PHR		1	5	1	5	1	5
Hardness (Shore A)	66	63	65	67	69	67	69
Elongation %	568	640	520	438	468	305	293
Tensile (psi)	1003	953	912	1003	855	1177	1187
Tear (lb/in)	77	116	152	108	91	113	124
Set at Break %	24	24	20	15	26	5	8
300% Modulus (psi)	470	573	764	853	686		1164

TABLE 11

Effect of Silane Coupling Agents on the Physical Properties of a Silica Filled Styrene Butadiene Rubber System

Same Formulation and Cure as Table 10 except filler is now Silene D

Silane	Control	A-172		A-1100		A-189	
PHR		1	5	1	5	1	5
Hardness (Shore A)	70	70	73	70	76	70	73
Elongation %	567	423	293	400	275	383	393
Tensile (psi)	1274	1409	2025	1637	2006	1500	2037
Tear (lb/in)	222	238	268	238	264	237	197
Set at Break %	10	10	5	5	5	5	15
300% Modulus (psi)	976		1251		1493	1416	1578

COMPOSITE PREPARATION

I. POLYPROPYLENE

A Treatment of Fillers

Sufficient amounts of A-172, A-174, A-186, A-187, A-1100 silanes were applied to 'Cab-O-Lite' P-1, No. 40 clay, and Iceberg clay to coat the particle with a mono molecular layer. Treatments were conducted in a Twin Shell Blender.

The filler/coupling agent mixtures were allowed to tumble for one hour. The treated filler was then heat set five hours at 120°C.

TABLE 12

Effect of Silane Coupling Agents on the Physical Properties of a Hydrated Clay Filled Polyurethane System

Formulation						
Polyurethane (Polyester Type)	100 phr					
Suprex Clay	100 phr					
Silane	0.5 phr					
Silane	Control	A-186	A-187	A-189	A-1100	A-1100*	A-1120
Hardness-A	88	93	91	93	87	80	93
Tensile (psi)	2870	3670	3940	3700	3960	4610	4300
Elongation (%)	120	80	80	100	150	100	80
Tear (lb/in)	650	560	540	580	570	550	500
Set at Break (%)	20	5	5	10	20	10	10

* 1.0 phr

B Composite Fabrication

1. *Formulation*

Filler 50 wt.%

Resin 50 wt.%

These blends were tumbled on a jar mill for one hour oven dry at 120°C.

2. *Extrusion and Molding*

The polypropylene/filler was extruded in an Egar Extruder/Compounder set at 215°C in all four zones. A uniform eight minute dwell time in the extruder was selected to insure complete melt and uniform heat. 250 gram charges were extruded and compression molded five minutes in a press pre-heated to 215°C. An 8' × 8" × 1/8" compression mold was used with Mylar film as a release.

After the molding cycle, the test plaques were cooled under pressure before removing from press.

3. *Testing*

The above composites were tested according to the following ASTM specifications:

Flexural Strength	D-790
Tensile Strength	D-628
Dielectric Constant	D-150
Dissipation Factor	D-150
Volume Resistivity	D-257

II. POLYVINYL CHLORIDE

The formulations were milled and molded into 20 mil plaques for tensile and elongation tests and into 75 mil plaques for tear strength tests.

Unlike the polypropylene composites, the calcium carbonate filler in PVC was not pre-treated. The A-1100 silane addition was made during the milling operation.

III. EPOXY

325 mesh aluminum powder was treated with a dilute solvent solution of epoxy resin and hardener.

When silane was added, 1, or 2 wt.% based on resin was dissolved in the resin prior to treatment of the aluminum.

After drying to desolvate, the treated aluminum was packed in molds and cured two hours at 150°C.

Flexural specimens 1/2" × 4" × 1/8" were cut from cured moldings and tested initially and after exposure to 72 hours immersion in boiling water.

IV. POLYESTER

A formulation consisting of 'Paraplex' P-43, styrene and catalyst was filled with 30 wt.% brass coated, steel wires. The A-174, when added, was dissloved in the resin-styrene mixture prior to introduction of the steel wire.

The mixture was charged into a tensile mold and cured in a press under pressure for one hour at 60°C followed by two hours at 120°C.

Tensile tests were carried out initially and after immersion for two hours in boiling water.

V. ETHYLENE-PROPYLENE TERPOLYMER

200 gram batches of each formulation were milled on a two-roll 6" × 13" rubber mill. The front roll was kept cold while the rear roll was at 70°C. The addition order for this system was as follows:

Material	Accumulative Time (Minutes) on Mill
EPT 3509	0
1/2 Filler	2
Silane, when used	4
Zinc oxide	5
Stearic acid	5
'Flexon' 580	5
1/2 Filler	7
Sulfur	15
TMTD Accelerator	18
MBT Accelerator	18
Complete cycle	20

After milling the mix is divided into four parts and cured in an ASTM 4 cavity mold for 30 minutes at 160°C and 50 000 psi, three mil Mylar film is used as a mold release. Upon completion of cure, the specimens are removed from the molds and allowed to cool at ambient temperatures before cutting and testing.

VI. SBR

The same batch size and equipment were used as in the EPT compounding. Both rolls were cold, however. The addition order for this system followes:

Material	Accumulative Time (Minutes) on Mill
SBR	0
1/2 Filler	1
Silane, when used	1
Zinc oxide	4
Stearic Acid	4
1/2 Filler	5
Altax	10
Cumate	10
Sulfur	15
Agerite Stalite	17
Picco N-100	18
Complete Cycle	20

After milling the batch is processed for testing as the procedure described for EPT.

VII. POLYURETHANE

Equipment for milling time is the same as for the EPT and SBR. The addition order for this system follows:

Material	Accumulative Time (Minutes) on Mill
Band polyurethane on rolls at 120°C	0
Filler	1
Silane	6
Cool rolls to 75°C and mix	8
Sheet compound off rolls	10
Pass compound through rolls 5X	12

After milling, the compound is placed in a four cavity ASTM mold and cured five minutes at 175°C and 50 tons platen pressure.

CONCLUSIONS

Silane coupling agents improve the performance of filled thermoplastics, thermosetting, and elastomer polymer composites.

In polypropylene, the improvement with the amino silane, A-1100 on a hydrated clay surface is about 50% in flexural and tensile strength.

In epoxy resin filled with aluminum powder, epoxy silane A-186 gives about 100% flexural strength improvement over a control initially and 535% after 72 hours immersion in boiling water.

In hydrated clay filled polyurethane A-1100 improves tensile strength 61% over a control.

Silane coupling agents have the potential to interact with many polymers and fillers. They may be used to create a balance of properties in a given composite and in this way serve as useful formulating tools.

Although no effort was made to optimize the formulations for a given application, from the trends better judgements can be made as to optimum final formulations.

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A review of DMC technical knowledge, its application and process in the field of glass reinforced plastics

11

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1. INTRODUCTION

DMC's have been in use in this country now for the last eight years and have now become well established as an important part of the G.R.P. industry. It is useful, therefore, at this point of time, to review these materials and try to assess their scope. It is the purpose of this Paper therefore to describe the different types of DMC's now available, together with their properties and use, and to present some new long term performance data on resistance to weathering and elevated temperatures. Much greater knowledge of the performance of DMC mouldings that is now available and will enable the scope for DMC to be widened and present and future fields of applications are indicated. However before reviewing this technology it is useful to consider what is the precise role of DMC within the whole field of glass fibre reinforced polyester materials in relation both to the process for manufacturing the moulding and the properties of the product.

For the scope of this Paper the term G.R.P. will be limited to glass reinforced polyesters.

2. COMPARISON OF PROCESSES FOR PRODUCING G.R.P. PARTS

The advantageous properties obtained by marrying glass fibre with polyester resin are well known and there is often a tendency to attribute the choice of these materials for a particular application exclusively to these properties, e.g. strength. While this may be so with some applications it is not often an overriding reason for the choice; there are nearly always other materials that will equally well provide a particular property. There are in fact three main factors to be considered when choosing a material for an application; they are performance, cost and the available process for fabrication. In fact, the last of these factors is more often than not the deciding factor in selection of materials and this is especially so with plastics.

An example of this is a machine guard which can be produced either in sheet metal or G.R.P. If it is required in large numbers then sheet metal pressings will usually be cheaper because both raw materials and processing costs are lower than G.R.P. But if the numbers required are small then different and much more costly fabrication methods will probably have to be used if sheet metal is still to be the raw material. Under these conditions G.R.P. often becomes competitive because the available fabricating process, i.e. hand lay-up, for this material gives a lower production cost in this instance.

In the light of this, it is not surprising to reflect that the rapid acceptance of G.R.P. when it was first introduced was almost certainly due mainly to the process of hand lay-up which was cheap to set up, simple, required little skill or experience and, perhaps most important, could be used for very limited production runs.

Since the advent of G.R.P. and the hand lay-up process, other methods of fabrication have been introduced but the hand lay-up process still dominates the industry. It is interesting to note that, excepting roofing sheeting, the main fields of application of G.R.P. laminates, namely boats, transport and chemical plant are all ones which are peculiarly suited to the hand lay-up process in that the number of parts required is relatively small and a simple and cheap process of fabrication is therefore essential. The hand lay-up process is in fact one which will continue to be eminently suitable for fabricating products such as boats but it seems very likely that the growth of G.R.P. will largely be restricted to these kinds of applications while the hand lay-up process continues to dominate the industry.

The chief disadvantages of the hand lay-up process are its limited production capacity and high production costs. The industry has therefore long looked for a suitable method for the mass production of G.R.P. parts which will enable it to compete in fields requiring large numbers of mouldings and thus achieve an expansion of a much greater order than heretofore. At the present time three possible processes exist, they are:-

1. Preform matched metal moulding.
2. Cold press moulding.
3. Press moulding using DMC or prepreg.

The following Sections of this Paper consider the merits of these processes for mass production, the chief essentials of which are fast and cheap production and minimal requirements for skill, and compares them with the hand lay-up process.

There are also of course several processes, such as pultrusion and those for the continuous manufacture of roofing sheet, which are mass production processes but these have been omitted from this Paper on account of their specialised and limited character.

2.1 Hand lay-up process

Briefly, the hand lay-up process consists of the following operations.

(a) Measuring and blending the polyester resin with catalysts, accelerators, pigments and fillers.

(b) Treating the mould with a parting agent.

(c) Tailoring the glass reinforcement to the mould.

(d) Moudling—combining the glass and resin mix.

(e) Curing.

(f) Finishing, i.e. trimming off excess.

There are several undesirable features of this process when it is considered in relation to a suitable method for mass production.

1. The fabricator has to combine the raw materials himself in small batches instead of having a fully compounded material supplied. This is time consuming and expensive and is a potential source of error.
2. Production rate is very slow.
3. The shape of parts which can be produced is limited.
4. There is a high dependency on the skill of the moulder.

Table 1 gives details of the pertinent features of this process compared with preform match metal moulding, cold press moulding and DMC and Prepreg moulding.

2.2 Preform matched metal moulding process

This process involves first making a glass fibre preform which is then moulded in a press with the resin mix. Like the hand lay-up process, the moulder has himself to blend the various raw materials making up the resin mix.

While it is a considerably faster process than hand lay-up the press cycles of usually only a few minutes, the fabricator is still involved with procedures outside the essential moulding process. What is more an additional process, i.e. that of making the preform, has been introduced so that the labour costs are not as low as might first be expected from the very much faster moulding times. Like all press moulding processes the capital outlay for the mould and the press is very high but this process requires additional outlay for a preform machine and oven could be up to £10 000. Glass mat can some-times be used in place of preform where a very simple

TABLE 1

Comparison of process for manufacturing G.R.P. parts

	Hand Lay-up	Preform Matched Metal Moulding	Cold Press Moulding	DMC Moulding	Prepreg Moulding
Raw material supplied fully compounded	No	No	No	Yes	Yes
Capital outlay required	Very low	Very high	Low	Very high	Very high
Skill required:					
(a) for setting up	Moderate	Moderate	Moderate	Fairly high	Fairly high
(b) for production	Moderate	Moderate	Moderate	Very little	Very little
Production rate for $\frac{1}{8}$" section (parts/mould/day)*	2-4	160	40	320	320
Production rate (parts/man/hour)†	1 (4 moulds)	10 (1 mould)	10 (2 moulds)	160 (4 moulds)	160 (4 moulds)
Limitation on size of moulding	Unlimited	Limited to size of press	Limited to size of press	Limited to size of press	Limited to size of press
Limitation on Complexity of moulding	Limited	Simple shapes only	Simple shapes only	Virtually unlimited	Few limitations
Dimensional Accuracy of part produced	Poor	Very good	Fair	Very good	Very good
Total material cost (d/lb) approx. ‡	30	30	30	30-33	30-42

Key to Table 1.

* Assuming a moderate size moulding of $\frac{1}{8}$" section throughout and an 8 hour working day.
† This figure takes into account time spent on all parts of process and the lower figure allows for the possibility of using a multiplicity mould.
‡ General purpose materials and including costs of auxillary materials such as fillers, pitments, catalysts, parting agents etc.

shaped part is being made and this reduces the capital outlay and labour costs.

Two important disadvantages of this process are the severe limitations it imposes on the design of the moulding and a considerable amount of skill and experience that is required to operate it. These last two factors may well be the chief reasons why after a decade the preform match metal moulding process still does not feature very largely in the G.R.P. industry.

2.3 Cold press moulding

Cold press moulding is a fairly new process which is attracting a great deal of interest because unlike the matched metal moulding process the equipment required costs only a few hundred pounds. It is nevertheless capable of a moderately fast rate of production and the labour costs are low but the fabricator has still to blend the raw materials and the process is limited to parts of relatively simple shape.

It is perhaps a little early to predict the potential of this process but the very low capital cost involved and the low labour costs will probably result in it being used very extensively for medium sized production runs which cannot justify the very large capital outlay necessary for hot press mouldings. There is little doubt that this process is capable of doing nearly all that the preform matched moulding process can do, albeit at a somewhat lower production rate.

2.4 DMC and prepreg moulding

Unlike any of the processes so far described for making G.R.P. parts, the process for making mouldings of DMC or Prepreg uses a fully compounded material and is very fast, the labour costs are therefore minimal. Equally important, the skill required by the moulder is very small. Thus DMC and Prepreg offer the essential features of a mass production process. There are very few limitations to the design of the part made and the size of the mouldings is only limited by the availability of a suitable press.

These comments apply almost equally to both DMC's and Prepregs which, compositionally, are similar materials. The essential differences between Prepreg and DMC are that the former is more expansive, rather more limited in the complexity of the moulding which it can make satisfactorily and has higher strength than a DMC. The two materials are really complimentary and Prepregs tend largely to be used where the strength of a DMC is not adequate.

It will be seen from this comparison of different processes for G.R.P. moulding that, where the volume of production justifies the capital outlay involved, DMC's and Prepregs alone provide the basic requirements for mass production of G.R.P. components. However, although it has already been argued that the process of fabrication most often dictates the choice of material, this of course is not to say that the performance of the moulding is unimportant and this aspect of comparison is now considered.

3. COMPARISON OF THE PROPERTIES OF G.R.P. MOULDINGS PRODUCED BY DIFFERENT PROCESSES

The electrical properties of G.R.P. parts are generally very good. They have been extensively reported and, as the electrical performance of G.R.P. parts produced by laminating or from DMC and Prepreg are very similar, it is not proposed to discuss these further here but rather to concentrate largely on the mechanical properties which do differ considerably.

It is difficult to define the mechanical properties of G.R.P. within narrow limits and thus permit critical comparison because the composition of polyester glass fibre laminates, Prepregs and DMC's can be varied so widely. For the purpose of this Paper therefore the general composition of each is defined as follows and typical mechanical properties for each are shown in Table 2.

Hand lay-up laminates - General purpose resin, chopped strand mat, 25-30% glass content.

Matched metal moulded laminates	- General purpose resin, chopped strand reinforcement, 35% glass content.
Cold press moulded laminates	- Continuous filament mat, 20% glass content.
DMC mouldings	- General purpose grade, chopped glass strands, 20% glass content.
Prepreg mouldings	- General purpose grade, chopped strand mat, 25% glass content.

TABLE 2

Comparison of mechanical strength

	Laminates				
	Hand Lay-up	Hot press moulded	Cold press moulded	DMC	Prepreg
Flexural strength ($lb/in^2 \times 10^3$)	22 000	28 000	20 000	18 000	20 000
Tensile strength ($lb/in^2 \times 10^3$)	15 000	18 000	8 000	8 000	13 000
Impact strength (ft lb/in)	15	20	—	5	10
Flexural modulus ($lb/in^2 \times 10^6$)	1.3	1.4	—	1.1	1.3
Compressive strength ($lb/in^2 \times 10^3$)	22 000	24 000	—	26 000	

It is clearly seen in Table 2 that DMC mouldings have lower flexural and tensile strengths than all but the cold press moulded laminates. Tensile and impact strengths exhibit the greatest differences so that the impact strength of a DMC is about one third of a hand lay-up laminate. Prepregs, although not quite as good as hand lay-up laminates, are significantly better especially with respect to tensile strength. It follows therefore that Prepreg is the only choice for the mass production of G.R.P. parts where maximum strength is needed.

Relative to other G.R.P. materials, the strength of DMC is undoubtedly its weakest feature and although DMC's are available with higher glass contents, the improvement in strength obtained is relatively small (see Table 4). Appreciation of this has recently lead to a process whereby the DMC is reinforced with a layer of continuous strand mat. This involves no more than placing a layer of the mat in the mould with the charge of DMC on top and moulding in the usual way. The DMC impregnates the mat and gives a moulding with a highly reinforced surface. The improvement in strength obtained, even with only thin layers of mat, is such that a cheaper low glass content DMC can be used. This process is still being fully evaluated but, as an illustration of the improvement obtained, comparative flexural strengths are given in Table 3 for $\frac{1}{8}$" panels produced with and without the mat reinforcement.

TABLE 3

	Flexural strength (lb/in^2)	Tensile strength (lb/in^2)	Total cost of moulding d/lb
Low glass content DMC without mat reinforcement	11 000	4 500	30
with $\frac{1}{2}$ oz/sq ft of mat reinforcement	23 000	6 100	31.5
with 1 oz/sq ft of mat reinforcement	30 000	6 700	33

It can be seen that this improvement in strength is provided at only a small cost increase so that such composite mouldings can be produced at a similar raw material cost to other G.R.P. processes whilst retaining all the advantages of a mass production material. Another important advantage of this composite is its usefulness for mouldings which are to be painted. Painting of glass fibre reinforced laminates presents problems caused by pin holes in the surface and fibre pattern and these can only be overcome by careful and expensive preparation of the surface prior to applying the paint finish. DMC mouldings do not suffer from these defects. Thus a DMC moulding can be reinforced with mat on one side to provide additional strength while leaving the other surface suitable for painting.

Two further properties of DMC mouldings which are worth comparison are self extinguishing properties and arc resistance. It is only very recently that resins have become available from which laminates can be made which meet B.S. 476 Class I flammability requirements. The use of conventional means of providing self extinguishing properties, by using chlorinated polyester resin or chlorinated additives with antimony oxide is not usually adequate and the specification can only be satisfied by using other self extinguishing fillers in addition to these. The amount of fillers used is of course limited by the viscosity which is acceptable for the moulding process whether it is hand lay-up or hot or cold press moulding.

This consideration does not apply to DMC where it is usual and desirable to employ high filler loadings. It is therefore relatively easy and cheap to formulate DMC's to meet a Class I flammability requirement. The availability of such materials could lead to an important expansion of the use of DMC in the building industry.

Recent years have seen an important growth in the demand for materials of high resistance to power arcs for applications such as electrical contactors and circuit breakers. Although polyester glass fibre laminates are generally described as having good arc resistance they cannot normally provide the very high level of performance required by these applications which are almost exclusively satisfied by special grades of DMC. This topic is discussed in more detail later in this Paper.

Grades of Prepreg have not so far been developed which meet Class I flammability requirements or which have high arc resistance but such developments are technically feasible.

4. DOUGH MOULDING COMPOUNDS

4.1 General purpose DMC's

The earliest DMC's were crude mixtures of the three essen-

tial constituents, namely polyester resin, glass fibre and finally powdered inert filler. They had poor storage life and as a consequence of their failure to flow homogeneously when moulded, the mouldings produced from them suffered from surface and internal cracks, poor surface finish and weak fibre starved areas. Much of the earlier development work was therefore directed towards improving the moulding characteristics and more sophisticated materials are now available. These improvements were largely achieved by better choice of fillers and modifications of the resin system to control its viscosity. The use of improved catalysts and inhibitors enabled the storage life to be extended so that nowadays a storage life of up to 6 months at 20°C is commonplace.

Nearly all general purpose DMC's now used are reinforced with glass fibre. In earlier years the very high cost of DMC's and particularly the glass fibre used in them, led to the development of grades using cheap glass fibre as an exclusive or part replacement for the glass reinforcement. This gave an appreciably cheaper product, albeit at the expense of lower strength, higher water absorption and poor electrical properties and surface finish. However, price reductions over the years have narrowed the gap in price of the glass and sisal reinforced DMC's so that the proportion of sisal reinforced DMC's now used is small.

One of the undesirable features of DMC is its physical form. They are tacky dough like masses which are not easy to handle but, unfortunately, attempts to make the material drier usually makes its manufacture more difficult, and the glass fibre reinforcement, and consequently strength, are thereby degraded. One answer to this problem has been the development of DMC's in extruded rope form although this too can only be done at the expense of some reduction in strength. Nevertheless the extruded grades are usually slightly cheaper and a very substantial proportion of DMC is now used in this form.

The most widely used general purpose DMC's contain about 20% of glass fibre. Grades with higher glass content (about 30%) have been developed to provide higher strength but unfortunately the strength is not improved in direct proportion to the amount of glass used (see Table 4).

More recent developments have provided some special grades of DMC's and these, together with the self extinguishing types, are discussed below:

4.2 Self extinguishing DMC's

The high filler loading of a DMC makes it easier to provide good self extinguishing properties than it is with polyester glass fibre laminates. Chlorinated polyester resins with antimony oxide were the first used self extinguishing agents and later chlorinated additives of various kinds have been used as well. While these all give good self extinguishing properties, halogenated compounds often reduce the track resistance of a DMC and some of the other electrical properties can be significantly degraded on exposure to elevated temperatures. For these reasons other more inert self extinguishing agents such as alumina have come into wider use.

4.3 Nil shrinkage DMC's

The shrinkage that occurs when DMC is moulded is very small, usually about 0.2%. Fairly recently, DMC's have been introduced which do not shrink at all when they are moulded. This has been done by a modification of the resin system although the mechanism is not clearly understood. It does seem

TABLE 4

Typical values for the physical properties of general purpose DMC's

	General purpose DMC	Extruded DMC	High glass content DMC	Units
Glass content	approx. 20%	approx. 15%	approx. 30%	
Specific gravity	1.8	1.7	1.7	
Flexural strength	18 000	13 000	21 000	lb/in^2
Tensile strength	8 000	7 000	9 000	lb/in^2
Impact strength (Izod, notched)	5	3	8	ft lb/in
Flexural modulus	1.1×10^6	1.0×10^6	1.3×10^6	lb/in^2
Compressive strength	26 000	24 000	28 000	lb/in^2
Surface resistivity (after 24 hours water immersion	15	14	15	$\log_{10}$ohms
Volume resistivity	15	15	15	$\log_{10}$ohms. cm
Electric strength at 90°C	200	250	200	volts/mil
Arc resistance (ASTM D495)	130	130	110	secs
Comparative tacking index	>600	>600	>600	volts
Water absorption (24 hrs @ 23°C)	15	20	20	mg
Mould shrinkage	0.15	0.3	0.1	%

TABLE 5

	General purpose DMC	Nil shrinkage DMC
Coefficient of linear expansion (average between 20-150°C)	18.5×10^{-6}/°C	8.5×10^{-6}/°C

likely however that changes in the coefficient of expansion of the DMC are partly responsible for eliminating the shrinkage.

While a reduction of the mould shrinkage has no value per se, in that whatever the shrinkage is, it can be allowed for in the design of the mould, certain useful advantages can accrue from this characteristic. They are improved surface finish and freedom from warping of the moulding.

It should be realised that the low shrinkage of a glass reinforced polyester resin composition is due entirely to the presence of the glass fibre, without which the shrinkage of a normal DMC would be about 1.5%. It follows that if any orientation of the fibre occurs during moulding the shrinkage can vary in different directions. Normally where this does occur the difference is dimensionally too small to be important but it can be sufficient to cause warping of the shape of the moulding. Clearly, reduction of the shrinkage of the resin will reduce or eliminate this defect and allow parts of greater accuracy to be made.

Equally, greater shrinkage occurs locally between fibres or bundles of fibre on the surface and this is the cause of fibre pattern developing on the surface of a moulding. Again, reduced shrinkage will eliminate or reduce this and give a smoother surface finish and this is particularly valuable if the moulding is to be painted.

Nil shrinkage DMC's are now available in both the normal dough form and also as extruded rope. Their physical properties are in most respects very similar to the general purpose grades. One problem with this class of DMC is that they cannot be pigmented satisfactorily at present.

4.4 Arc resistant DMC's

The last few years have seen an important growth in the demand for materials with improved arc resistance for applications such as electrical contactors. Conditions imposed on the material in such components are very severe as they are tested at 8 times their normal current loading. The component must not only resist the arc formed during breaking of the contacts, without forming a conducting path, but must also not catch fire or erode excessively. The material should also be capable of quenching the arc.

A considerable amount of development work has been done to provide materials to meet these requirements. The earliest successful materials employed hydrated alumina filler which was particularly successful in achieving the required performance. Later other fillers were found which gave similar results and a range of arc resistant DMC's is now available.

Development of these materials has proved unusually difficult as no suitable method of testing of the performance of the material was available. It was and is the usual practice to test performance of the material on the actual contactor rather than rely on any arbitrary designed test on a specimen of the material. However testing of a 250 amp/440 volt contactor for example requires a source of power capable of supplying 2000 amps at 440 volts and such test facilities are not usually available to raw material manufacturers.

The only existing arc resistance test was the A.S.T.M. one (D. 495) but this is a high voltage test using only a few milliamps of current and it can give very misleading indications of the performance of a material which is to be subjected conversely to high current/low voltage arcs. Of necessity therefore B.I.P. developed their own test method which, although not creating as severe conditions as apply in contactor tests, did provide a power arc test which was proved to be capable of selecting materials with adequate performance for these kinds of applications.

The apparatus for this test is shown in Fig. 1 and basically consists of two copper strip electrodes the ends of which are placed against the surface of the test specimen, the gap between the electrodes being set at $\frac{1}{4}$". The electrodes are connected to a source of 220 volts D.C. (18-12 volt accumulators) by means of a contactor and the current in this circuit is limited to 100 amps by a 2.2 ohm. non-inductive resistance. The electrodes are bridged with a piece of fine fuse wire so that when the contactor is closed the fuse blows and initiates an arc between the electrodes. The arc is allowed to burn for 1 second after which the current is switched off, although the arc may be extinguished in a shorter time than this by virtue of the quenching properties of the material. One second after breaking the circuit the full battery voltage is re-applied across the electrodes so that if the insulation resistance of the material has been appreciably reduced then the arc will restrike. If restrike does occur this is taken to be a criterion of failure of the insulation.

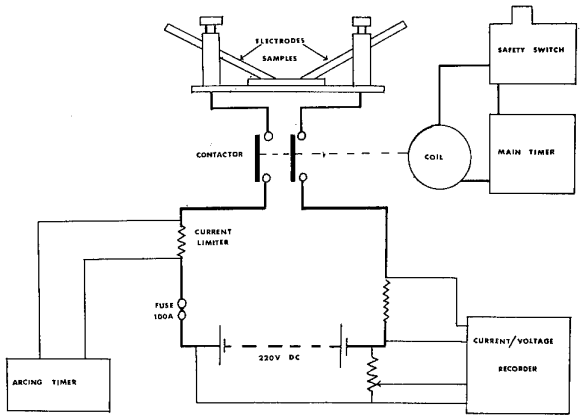


Fig. 1 Sketch of BIP arc testing apparatus

An ultraviolet recorder is employed to display the voltage and current characteristics of the arc and also can be used to monitor the insulation resistance between the electrodes. Accurate time measuring equipment is used to determine the time taken for the material to quench the arc.

The test usually consists of successively applying the arc up to 10 times to the same spot on the surface of the test specimen and the material is judged to have unsatisfactory arc resistance if restrike occurs after 10 or less applications. The quenching performance of the material is noted on each application of the arc and this gives additional information on the performance of the material.

It should be appreciated that the prime need to provide the highest possible arc resistance imposes limitations on the formulation of the DMC so that the strength and moulding performance of this class of DMC is not generally as good as the best general purpose materials. For example, it has been found that the glass fibre has a deleterious effect on the arc resistance of a DMC and therefore the best arc resistance materials have glass contents of only about 10%. There is however considerable variation in the composition and physical properties of different arc resistant DMC's and it is difficult to generalise but some indication of the general level of properties is given in Table 6.

A very recently introduced DMC (C in Table 6) is an exception to these general comments on strength and particularly mouldability. Unlike other arc resistant DMC's, its moulding performance is similar to the general purpose materials. In particular, heavy section mouldings can be moulded without any internal voids and the availability of this material will undoubtedly extend the application of arc resistant DMC's.

4.5 Resistance to outdoor exposure

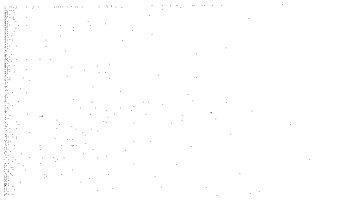
Information is now available on the resistance of general purpose DMC mouldings to natural weathering. Tests have been

TABLE 6

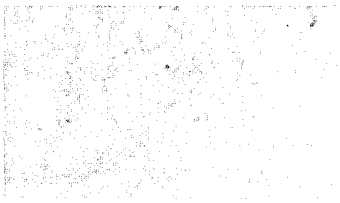
Mechanical properties of arc resistant DMC's

	Material A	Material B	Material C
Flexural strength (lb/in^2)	15 000	11 000	14 000
Tensile strength (lb/in^2)	5 000	4 500	6 000
Impact strength (ft lb/in)	3	3	4

carried out over a five year period in the severe conditions imposed by a highly poluted and industrial atmosphere. The results, which are summarised in Table 7, showed that most physical properties are substantially unaffected by this treatment. The only marked effect of weathering was on the surface appearance of the specimens which suffered fading of the colour and erosion of the surface (Fig. 2). This effect was undoubtedly responsible for the lowering of the surface resistivity after water immersion.



unexposed specimen
(×35 magnification)



after 5 years weathering
(×35 magnification)

Fig. 2 Effect of 5 years weathering on surface appearance

It is particularly interesting to note that the self extinguishing properties of self extinguishing grades are unaffected.

A number of different DMC formulations were included in this series of tests but the results showed no substantial differences between then.

TABLE 7

Effect of 5 years Natural Weathering on physical properties of DMC

Flexural Strength	No significant change
Electric Strength	No significant change
Volume Resistivity	No significant change
Surface Resistivity (after 24 hrs immersion in water)	15.7 $\log_{10}$ohms reduced to 11.9 $\log_{10}$ohms
Arc Resistance (ASTM D. 495)	Unaffected
Self extinguishing performance	Unaffected

4.6 Heat resistance

It should be immediately appreciated that the topic of heat resistance is inevitably very involved and a satisfactory understanding of the behaviour of materials at elevated temperatures needs to take account of a large number of factors. The work necessary to provide an adequate amount of data is considerable but cannot be avoided if designers are to be encouraged to use materials at high operating temperatures. Statements such as 'suitable for continuous use at 150°C' have no validity unless they can be backed up with adequate long term test data and the criteria defined.

It is not intended to present here all the information now available on the heat resistance of DMC but only to present sufficient to illustrate that adequate information is now available to define the maximum operating temperatures for DMC and thus to define the maximum operating temperatures for DMC and thus encourage the use of DMC for applications requiring heat resistance.

Morgan and Sturman in their Paper at the 1966 Reinforced Plastics Conference (Assessment of the Heat Resistance of Polyester DMC's) described the effects of long term thermal degradation on the mechanical properties of DMC and showed that the deterioration of strength that occurs on stoving at elevated temperatures is related to the weight loss and that, within reasonable temperature limits, this was independent of the stoving temperatures. From this they were able to predict the long term life of DMC at elevated temperatures based on shorter term tests at higher temperatures. Since then stoving tests of up to 25 000 hours (3 years) duration have been completed and the results show that their method was valid although their predictions were, as they suspected, rather pessimistic. Electrical tests after similar levels of thermal degradation have also been carried out and give a more complete picture of the overall thermal endurance of the material.

Fig. 3 shows the weight loss that occurs at 120, 140 and 160°C up to 25 000 hours. Although the weight losses are relatively high at the higher temperature, the effect on flexural strength (Fig. 4) and flexural modulus (Fig. 5) is not nearly as great as might have been expected, about 85% of the flexural strength and modulus being retained after 25 000 hours at 120°C and about 35-45% after 15 000 hours at 160°C.

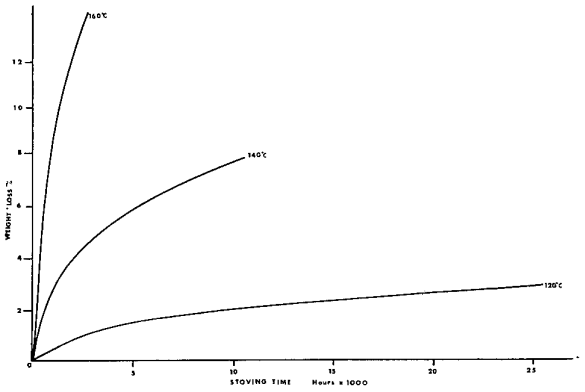


Fig. 3 Weight loss on stoving at various temperatures

Flexural strength and modulus after heat ageing were measured at room temperature for these tests and thus these results indicate the amount of permanent degradation that the material has suffered. Information on the strength at the test temperature is at least equally important and this information is shown in Fig. 6.

It will be seen from this graph that the immediate effect (albeit a reversible one) of heating the DMC to an elevated temperature is to lower the strength to a degree much greater

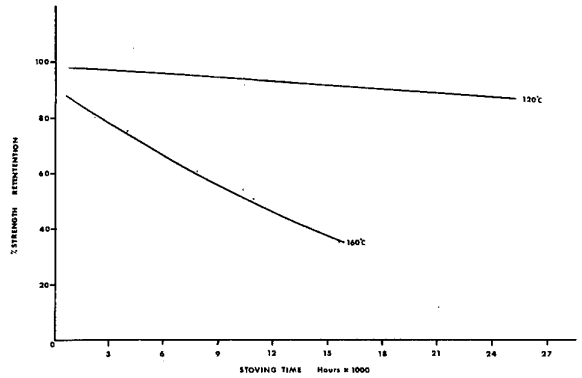


Fig. 4 Flexural strength at room temperature after heat ageing at 120°C and 160°C

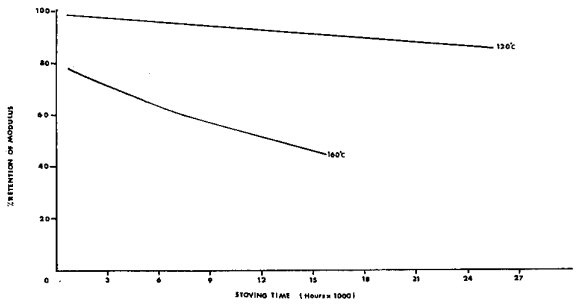


Fig. 5 Flexural modulus at room temperature after heat ageing at 120°C and 160°C

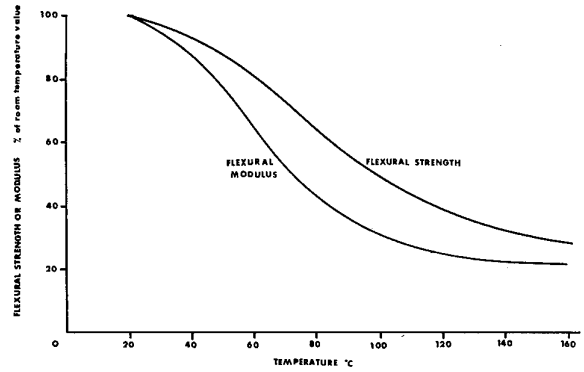


Fig. 6 Flexural strength and modulus at elevated temperatures

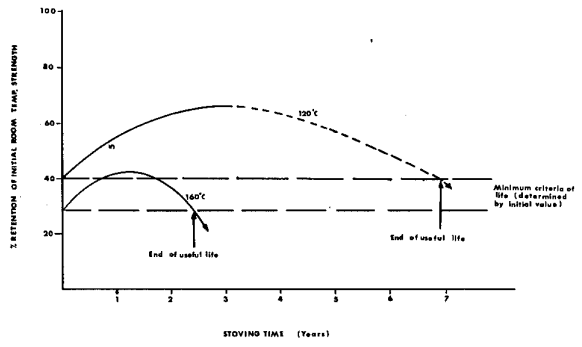


Fig. 7 Schematic representation of the behaviour of mechanical properties at elevated temperatures illustrating initial thermal effect and long term degradation

than that achieved by many thousands of hours of stoving. It has however been found that the thermoplasticity of the material is markedly reduced as the material is heat aged and when the change of strength after stoving is examined at the test temperature is is found that this improves over a very long period of time before degradation of the material finally causes a diminution of the strength (see Table 8 and Fig. 7).

TABLE 8

Flexural strength and modulus at elevated temperatures after stoving

	% Retention of initial room temperature value	
Stoving treatment	Flexural strength	Flexural modulus
0	40	32
2 years at 120°C	42	40
3 years at 120°C	66	69

In the final analysis it is found that:

(a) After heat ageing the hot strength eventually closely approaches the room temperature strength value.

(b) The hot strength after heat ageing does not fall below the intial value (before heat ageing) until several years have elapsed .

The conclusion drawn from these observations is that, within the temperatures for which results have been obtained, operating temperatures will be limited as much by the intial hot strength of the material as its long term degradation.

Electric strength and insulation resistance tests after heat ageing have also given good results (Table 9) It was feared that high weight losses after stoving, while not substantially affecting the dry electrical performance, might cause degradation of the electrical properties if the treated specimens were allowed to pick up moisture. However, conditioning them at 75% relative humidity until equilibrium was reached, affected very little change.

The availability of this data on heat resistance now makes it possible to indicate realistic maximum operating temperatures for DMC components providing the acceptable criteria (e.g. required life, pertinent properties and minimum values) are defined. Very generally speaking, and within the limites imposed by many electrical applications, DMC can be considered to be satisfactory for many years use at temperatures up to 140°C and somewhat higher temperatures could be considered for short times.

4. 8 Application of DMC

There are four features of a DMC moulding which distinghish it from many other plastics materials; they are its electrical performance, strength, heat resistance and dimensional stability. Originally it was considered that strength would be its most attractive feature but this property has not so far been the chief justification for the use of DMC in many applications. Early use of DMC was chiefly for electrical insulation of various kinds and it is still true today that the greatest number of applications, though not tonnage, is in this field. Fig. 8 shows an excellent recent example of DMC used for the insulation and body of an electric drill. Although strength is an advantage in some of these applications the choice of DMC has usually been made either on the basis of the materials superior electrical properties (compared with for example phenolics or ureas), particularly under adverse environmental conditions, or its dimensional stability. Indeed the excellent dimensional stability of DMC with ageing or when subjected to heat or high humidity has often been the sole reason for choosing this material. It is not therefore surprising that

TABLE 9

Effect of stoving on electric strength and insulation resistance

	Electric strength (V/mil)		Insulation resistance (megohms)	
Stoving treatment	Dry	After 75% relative humidity conditioning	Dry	After humidity conditioning
Stoved to weight loss of 8.5%*	340	280	$>10^8$	$>10^8$

* Equivalent to 800 hours heat treatment at 160°C or 14 000 hours at 140°C or about 10 years at 120°C.

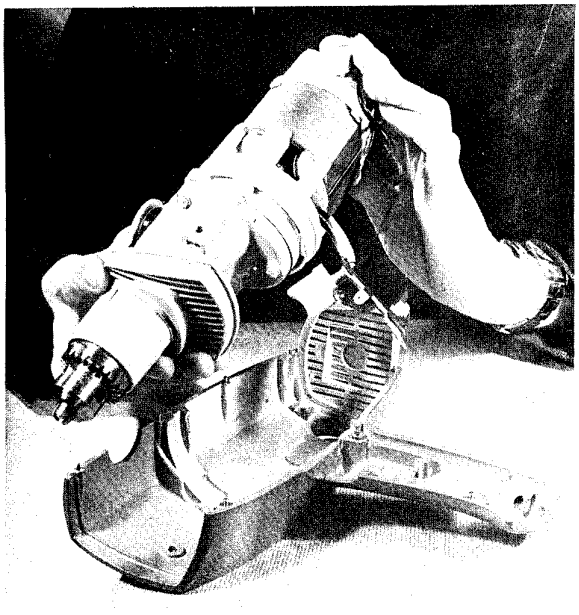


Fig. 8 Electric drill moulded by Arcoy Products Limited showing DMC components supporting the armature and field core and the painted DMC outer case

electrical components are a major outlet for DMC and there is still considerable room for expansion in this field particularly for higher voltage equipment. Until recently, DMC tended to be restricted to low voltage insulation; with increased experience, designers are beginning to extend the use of DMC to higher voltage equipment such as the 11KV bushing illustrated in Figure 9. The special arc resistant materials are also finding an increasing use for exacting electrical components.

The electronics industry represents another field for expansion of the use of DMC. Although a few applications already exist, exploitation is restricted by the form of the material as the parts are usually quite small and the problem of weighing out very small mould charges of DMC is a serious one. The advent of equipment for injection moulding of thermosets may well overcome this hurdle.

As stated, unlike electrical performance and dimensional

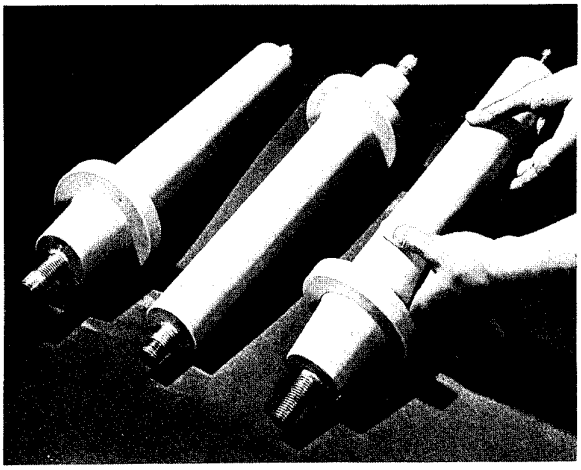


Fig. 9 11 KV bushings moulded by Mawson Taylor Ltd.

stability, full advantage has not so far been taken of the strength and heat resistance of DMC.

While the strength of a DMC does not compete with that for G.R.P. laminates it is often quite adequate for many applications and, as has been argued in the first part of this Paper, it does offer the means for mass production of G.R.P. mouldings. Where the normal level of strength of a DMC is insufficient, reinforcement with glass mat has now provided a means substantially to upgrade the strength of the products. As a consequence, applications such as protective cases for instruments and other shell mouldings have now become suitable applications for DMC. The ease of painting DMC will undoubtedly make this a fruitful area of growth within the next few years.

Possibly the most important advantage of thermosets compared with the thermoplastics is their superior heat resistance and yet designers have failed to take full advantage of this property. In the absence of adequate data, this is not surprising. Now, that long term heat resistance data is available this situation can be rectified and new applications, for example in the electrical machinery field, can be expected to develop which will fully utilise this property.

ACKNOWLEDGEMENTS

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The reinforcement of thermoplastic matrices with fibres 12

J. H. DAVIS, Imperial Chemical Industries Ltd., Plastics Division

INTRODUCTION

For many years glass fibres have been used in conjunction with polyester and epoxy resins for the fabrication of strong materials, now often called simply 'GRP'. The fibres are made available in a variety of forms, corresponding to the type of fabrication process preferred.

(a) Continuous rovings for winding

(b) Woven cloth
(c) Mats } for laminating

(d) Chopped fibres for doughs.

The preferred fabrication method largely governs the concentration and orientation of the glass fibres in the composite and hence dictates the strength of the final moulding. Furthermore, the easy impregnation of the fibres with liquid resins means that a minimum of damage is caused to them, so that they retain their full length and large measure of their strength. In general, however, the labour content for fabrication is high, so that costs have stayed high.

More recently the use of glass and other fibrous fillers in thermoplastics, as very successful commercial products, has steadily increased. These composites cannot at present draw upon the strength of the glass as fully as do traditional GRP composites, but useful properties can be obtained. They do however have the great advantage of ease of fabrication by those injection moulding processes used for the parent thermoplastics, thus making them suitable for high speed fabrication. It is the purpose of this paper to examine the fabrication processes currently used, to discover the limitations they impose, to see what proportion of the strength of the glass is being utilised and why.

BASIC PROBLEM OF REINFORCED THERMOPLASTICS

Dispersing glass fibres into thermoplastics is clearly more difficult than impregnating them with liquid resins and this difficulty highlights a basic problem with thermoplastics composites. The better the fibres are dispersed in the matrix, the more they become broken to short lengths: the longer the fibres that are retained in the final moulding, the worse the dispersion. The reason for this is straightforward; the two components must be mixed at elevated temperature so that the thermoplastic is softened and capable of flow under pressure. The viscosity, however, is still extremely high compared with the liquid thermosetting resins used for GRP, and considerable work must be done on the glass fibres and the viscous thermoplastic to get them to mix. This processing inevitably breaks and damages the fibres. We will therefore consider these compounding processes in more detail.

PROCESSES USED FOR COMPOUNDING GLASS FIBRES AND THERMOPLASTICS

Figure 1 shows diagramatically the essential parts of an extruder, the equipment usually employed for the compounding process. Polymer in the form of granules may be pre-blended with fibres by tumbling, and the mixture fed to the machine. Granules and fibres are picked up by the screw, the polymer softened in the heated barrel and mixed with the fibres, both then being passed forward to the die. By suitable design of screw a good mixing action occurs before the viscous mix is extruded as a 'lace' or 'worm', to be subsequently cooled and cut to granules once more.

These granules, now containing well dispersed glass fibres, may be fed to an injection moulding machine, as shown diagramatically in Figure 2, so that finished components may be fabricated.

Once again the granules pass via a hopper to the heated barrel, where they soften and are forced via a nozzle to the cool, split mould into which the viscous composite is injected. The material freezes to the required shape, the tool opens, the piece is ejected and the cycle continued

LIMITATIONS IMPOSED BY THESE PROCESSES

The main factors determining the properties of the composites may be listed as follows:-

(a) Fibre concentration

(b) Fibre length/adhesion to matrix

(c) Fibre orientation

The fabrication processes described above impose limitations on all three:-

1. The processes of extrusion-compounding and injection moulding, set a limit to the concentration of fibres that can be incorporated if the equipment is to work smoothly. The top practical limit is about 45 to 50% by weight i.e. about 25% by volume.
2. These processes are severe on the glass if a good dispersion is to be obtained, and in practice the average fibre length is about 0.010 to 0.020 inch, i.e. a length to diameter ratio (aspect ratio) of 25-50. This low aspect ratio makes matrix/fibre 'adhesion' of particular importance.
3. The moulding process-injecting a viscous fluid into a mould cavity-can cause an orientation of fibres which is retained in the final moulding. Mould design (and more particularly the arrangement of runners and gates into the cavity), can therefore greatly affect the properties of composites.

In our work we have used as far as possible standard moulded bars, which are end-gated and give a degree of orientation, properties being measured along the bar; we shall return to this point later.

Figure 3 is a diagramatic representation of the GRP field, showing the order of modulus in tension to be expected for different forms and concentrations of glass fibre in polyester resin. In terms of what has just been discussed we can pinpoint the sort of area that reinforced thermoplastics may be expected to occupy. Although the concentration of glass that can be achieved is low and the orientation of the glass is slight (corresponding more to a moulding from glass mat than from wound glass rovings), nevertheless the increase of strength of the thermoplastics matrix may be several fold, and reinforcement is therefore well worth while.

PROPERTIES OF THERMOPLASTIC COMPOSITES

With these several variables in mind we may pass to a consideration of properties of different reinforced thermoplastics. It must be stressed at the outset that the properties of thermoplastics themselves are complex and still being elucidated. They are extremely temperature and time dependent materials, so that any study in depth of composites based on them must be even more complex. In this paper we shall therefore limit discussion to quite simple properties namely, modulus in flexure, tensile or yield stress and impact strength.

Figure 4 shows the effect of fibre length on the tensile strength of polypropylene, a polymer which has poor affinity for glass so that increase of fibre length greatly improves the strength.

It has been convenient in experimental work to produce composites by two different mixing processes, namely by direct moulding and by Banbury mixing, giving materials with two different average fibre lengths. Thus, direct moulding of a blend of polymer and glass fibres breaks the glass to an average length of about 0.025 inch, compared with the more severe treatment in a Banbury mixer which reduces the glass to an average length of about 0.007 inch. Consequently diagrams are labelled appropriately with these two processes and it should be understood that they correspond in practice to 'long' and 'short' fibres respectively.

Figure 5 emphasises this point. The graph shows that flexural modulus over the practical range of cencentrations is largely independent of fibre length, whereas (as seen from Figure 6), tensile strength is sharply dependent on fibre length.

Figure 7 shows two types of impact test—Charpy, notched and unnotched. The lower graphs represent the notched test (employing a notch radius of 0.010 in.), which is really a crack propagation test; energy to break is sharply improved as fibre length increases, presumably because the crack propagation is more impeded by the more tortuous path it must follow. The unnotched test, shown in the upper graph, is however much more dependent upon concentration than on fibre length. It will be noted that the strength falls off as the concentration of fibres is raised and it must be supposed that this type of impact test is measuring the resistance of the material to crack initiation rather than to crack propagation. As fibres are added, cracks are more easily initiated because the discontinuities caused in the matrix by the fibres act to concentrate stresses and the thermoplastic may be changed in effect from tough to brittle. However, the balance of these two types of behaviour (crack initiation and crack stopping) will depend upon the particular polymer under consideration so that with some thermoplastics the fibres may act mainly as crack stoppers rather than crack initiators.

Nylon/glass composites derive much more strength from the glass than polypropylene/glass composites, but it is found that similar principles apply to both when the effect of concentration and fibre length are investigated. Figure 8 compares the tensile strength of three compositers to illustrate the point in more detail. Glass-filled nylon is clearly manifesting more of the strength of the glass than glass-filled polypropylene. The third composition, (polypropylene containing talc) shows a loss of tensile strength with addition of filler, which, evidently because of its poor affinity for polypropylene, merely acts to 'make holes' in the matrix. We conclude that the adhesion of glass to nylon is much better than glass to polypropylene. This conclusion is supported by the chemistry of the materials and by practical experiments of casting the polymers on to plain glass surfaces—nylon sticks, polypropylene does not.

Thus, as may be expected with these short fibre lengths, the degree of adhesion is extremely important. The effect is not however shown by properties involving low strains, e.g. modulus at low strain and thermal expansion, but is shown by high strain tests such as tensile strength or modulus measured at higher strains.

GLASS FINISHES

Over the years considerable improvement in the performance of glass-filled polyester and epoxy resins has been achieved by the prior treatment of the glass fibres with special coupling agents, usually silane or chrome based. These have not proved so successful with thermoplastics. One basic difficulty has been that glass manufacturers are not normally set up to carry out thermoplastics processing (and the equipment involved is very expensive), whereas the thermoplastics manufacturer has little knowledge of glass techniques and has no wich to start spinning glass fibres for experimental purposes. Published work in this field (Ref. 1) has often been based on laminates made from woven glass cloth either with thermoplastics films or with thermoplastic laid down from solution. By either method the product is very different from the final composite produced from an injection moulding machine. When a glass manufacturer produces a glass fibre with a special finish designed for a special thermoplastic he is rarely in a position to disclose what the coupling agent is. One supposes that it is a variation upon the particular silanes which have worked well for polyesters, but these silanes may be quite unsuitable for thermoplastics and may indeed be decomposed at processing temperatures (Ref. 2).

If new and quite different coupling agents are to be found, and if this field is to be explored scientifically and not remain completely empirical, close cooperation between glass fibre and thermoplastics manufacture will be essential.

ORIENTATION

Figure 9 shows a photo micrograph of a microtome section of glass-filled nylon. The orientation of the fibres can be seen, and except for an area of turbulence in the centre, they are clearly in sympathy with the flow direction during moulding.

It has been shown by Kelly (Ref. 3) and others that the strength of a fibre is only manifested in the direction in which the fibre points. If the fibres are aligned the full available strength of the fibres may be realised in the composite (corresponding to an orientation factor of 1.0), but if the fibres are not aligned, only a proportion of this strength can be realised and the factor is lowered. Theoretical considerations show that if fibres are completely random, a factor of 0.17 (instead of 1.0) must be applied, whereas when fibres are random in a plane (as in a mat-based laminate for example), a factor of 0.33 is applicable.

We have no means of assessing accurately the degree of glass fibre orientation in a moulding. For experimental work we use standard injection upon the flow patterns as the viscous molten polymer passes through the 'grating' arrangements and mould cavity. Because the fibres are short compared with the thickness of the moulded section, they may point in any direction in the final moulding but will tend to orient in the direction of flow, i.e. in the plane.

The orientation of the fibres can be seen from a photograph but, unfortunately, the degree of orientation cannot be measured; no numerical index can be deduced. A rough numerical estimate of orientation can however be deduced by other methods as follows:-

The improvement of modulus with glass fibre content of most thermoplastics is remarkably similar, as shown in Figure 10, and this allows one to deduce the extent to which the modulus of the glass has been utilised. Since the lines in Figure 10, corresponding to the augmentation of modulus with glass content, run essentially parallel, it may be argued that the degree of stiffening with concentration is independent of the matrix and is a function only of the glass, and hence the orientation of the glass fibres. Calculation of the proportion of the glass modulus being utilised gives an orientation factor of 0.4. Thus a fair degree of orientation is occurring in the test specimens used, as seen in Figure 9, and as is to be expected in an end-gated test bar. If this orientation factor of 0.4 is applied to the tensile strength results shown in Figure 11, one may conclude that in glass-filled nylon some 80% of the available tensile strength of the glass is being realised whereas in glass-filled polypropylene only about 30% of the glass strength is utilised; other polymers usually lie between these two extremes.

REINFORCEMENTS OTHER THAN GLASS

Much publicity has been given recently to synthetic filaments and whiskers which may have very high modulus and good strength. Unfortunately the cost of these materials is still far too high to permit their use as reinforcements for the large tonnage applications normally visualised for the common thermoplastics. They may find use however with high temperature resistant thermoplastics for specialised applications. On the other hand, asbestos fibres, which have been described as 'the poor man's whisker', have been used in thermoplastics, for example in popypropylene for automotive

applications. The work that we have done in this field suggests that the basic principles deduced for glass fibres, are applicable to other fibres (whether natural or synthetic, organic or inorganic) if due allowance is made for the different strengths of the fibres themselves.

CONCLUSION AND FUTURE PROSPECTS

It may be concluded that the simple properties of reinforced thermoplastics, containing as these composites must, quite low aspect ratio fibres, do not contradict the general principles advanced in published work on GRP and metal composites.

The way to improve thermoplastics composites for the future is clear in theory if more difficult in practice.

(a) Achieve a good bond between matrix and filler.

(b) Achieve longer, well dispersed fibres.

(c) Evolve high performance fibres at an economic price.

All these approaches are receiving attention and should bring steady improvement.

REFERENCES

1. The effect of silane coupling agents in improving the properties of filled or reinforced thermoplastics. Sherman and Marsden S.P.E. 21st Annual Conf. 1965.
2. Temperature effect in coupling thermoplastics to silane-treated glass-Plueddemann. Mod. Pl. Aug. 1966, p. 131.
3. The principles of fibre reinforcement of Metals. Kelly and Davies. Metallurgical Reviews 1965. Vol. 10. No. 37.

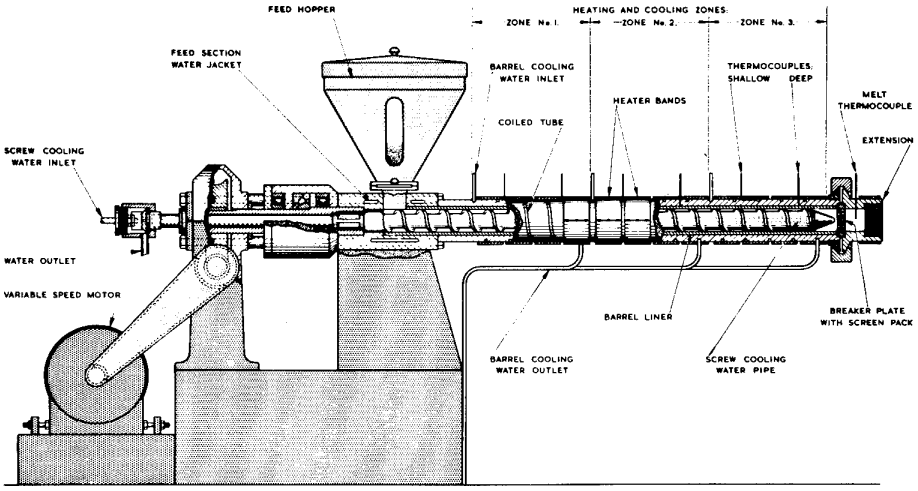


Fig. 1 Typical Single-Screw Extruder for Polythene

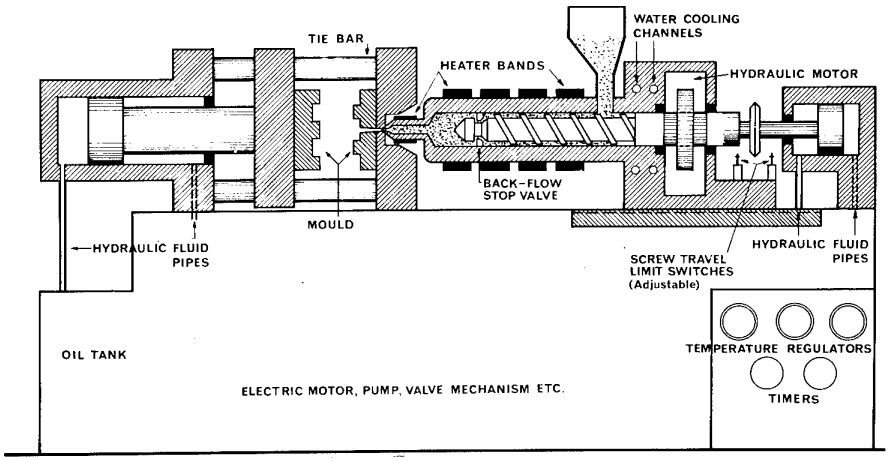


Fig. 2

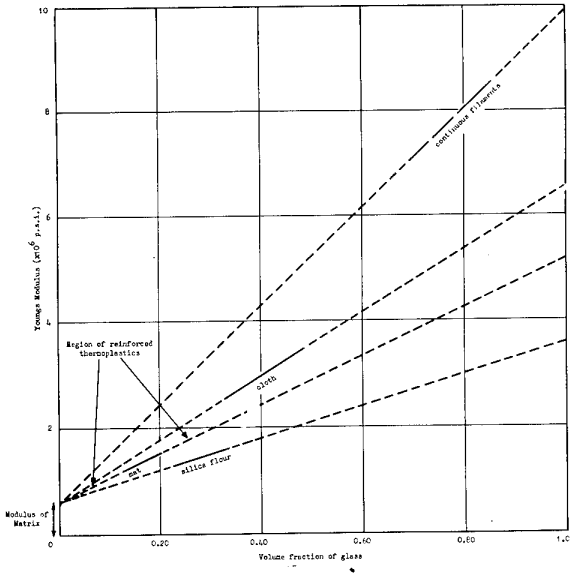


Fig. 3 Composite Modulus Against Volume Fraction

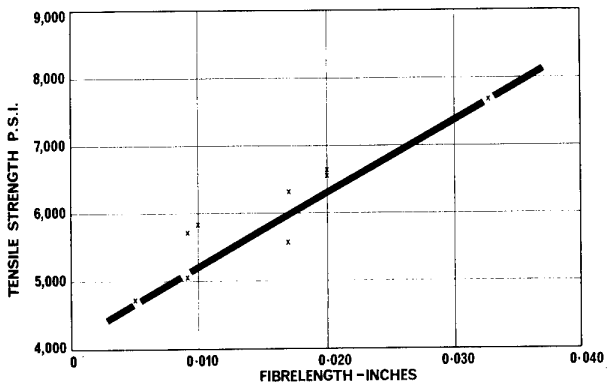
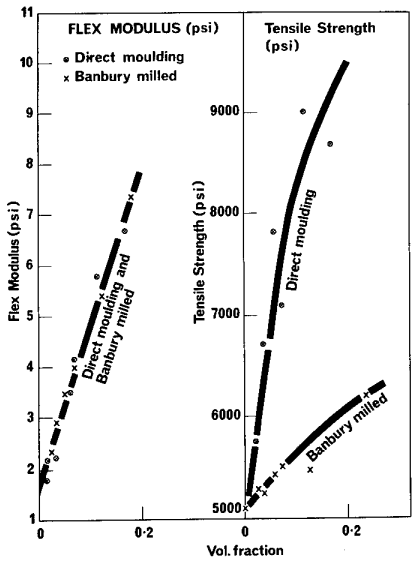


Fig. 4 Tensile Strength Against Fibre Length for Glass Filled Polypropylene



Figs. 5 & 6 Polypropylene and Glass

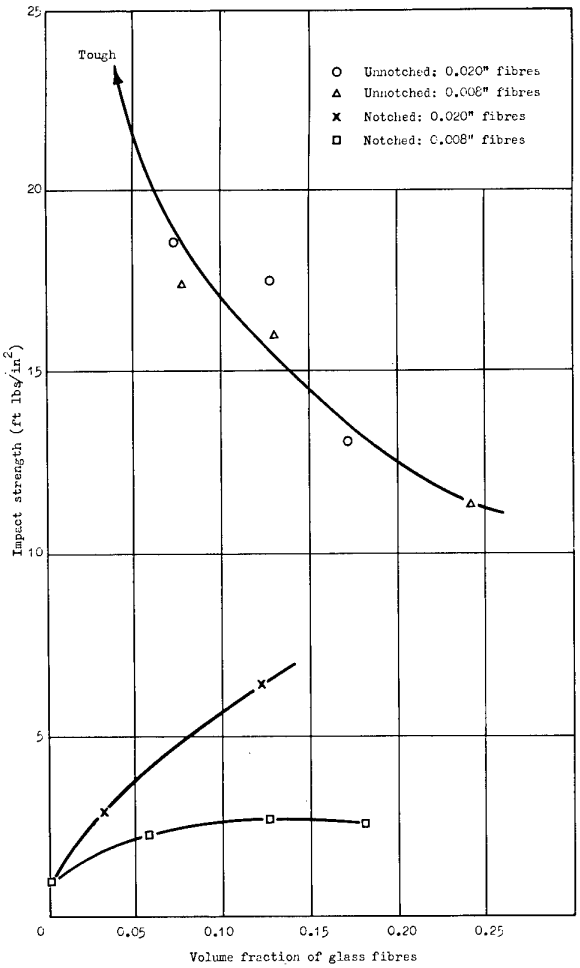


Fig. 7 Polypropylene/Glass Fibres — Charpy Impact

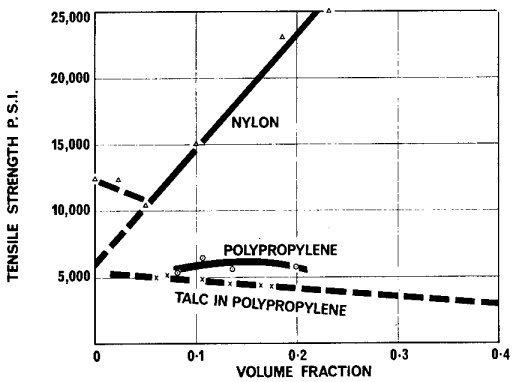


Fig. 8 Tensile Strength Against Volume Fraction of 0.010" Glass Fibres

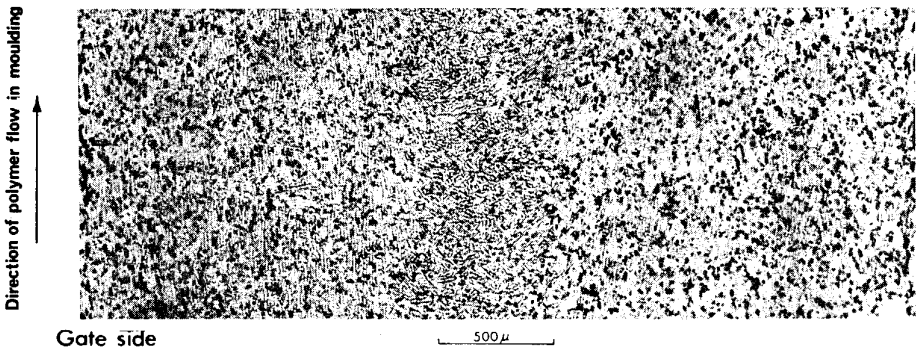


Fig. 9 Orientation of Glass Fibres in Glass Filled Nylon

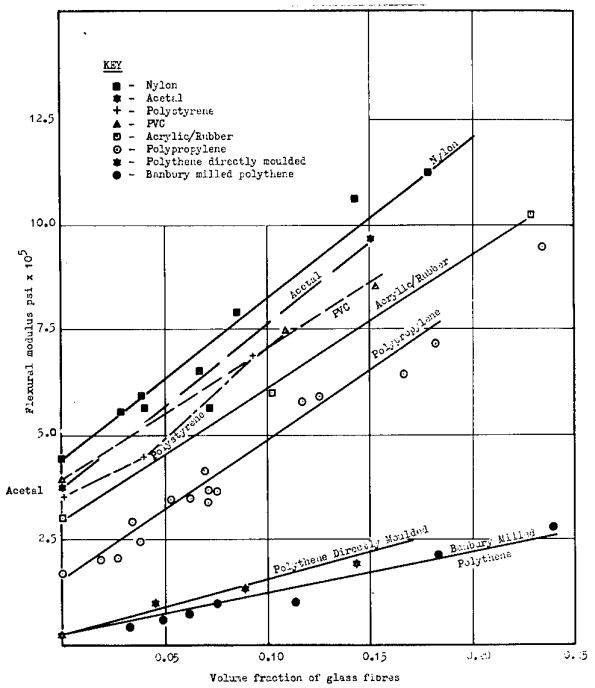


Fig. 10 Flexural Modulus of Various Polymers Containing Glass Fibres

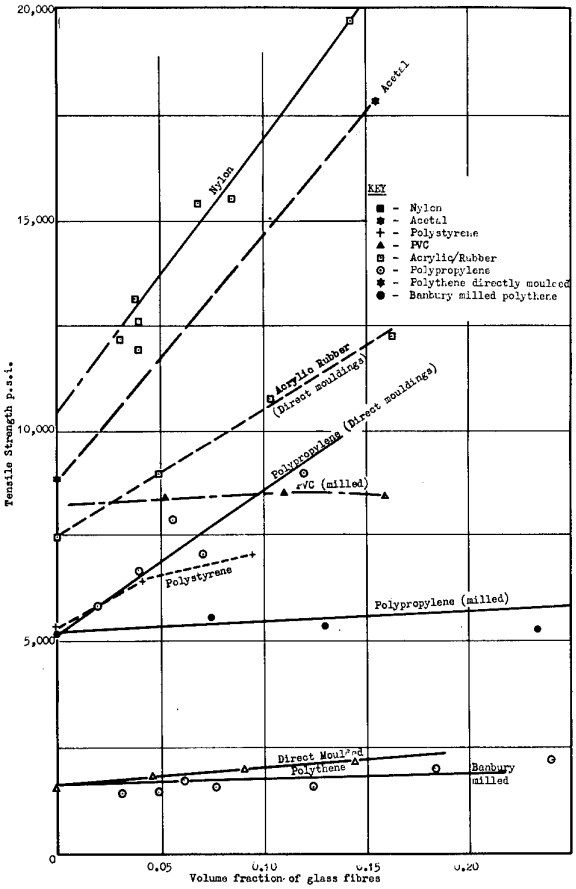


Fig. 11 Tensile Strength of Various Polymers Containing Glass Fibres

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Advances in glass fibre fabrics for plastics reinforcements

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ABSTRACT

Technical conferences relative to reinforced plastics in recent years have primarily stressed the role of coupling agents on the performance of woven glass fiber fabrics. Overlooked has been the technological advances of the fabric itself, including developments in glass composition, filament diameters and the influence of weave geometry on the properties of fabric reinforced composites.

Although borosilicate 'E' glass is the most widely used glass fiber in composites, other glass formulations such as 'S' glass fibers and 'D' glass fibers have found use as reinforcement.

Fiber drawing technology has resulted in a capability of producing large bundles of conventional glass filament diameters or fine bundles of ultra-fine filament diameters. The influence of fine filaments such as DE and B on glass fabric reinforced composite properties is discussed and compared with conventional E and G filaments.

New glass fiber compositions and filament diameters have led to an expanded fabric design capability. Properties and potential uses of these new fabrics designs will also be discussed.

INTRODUCTION

Performance characteristics of composites are dependent on the properties of the materials comprising the composite and the process by which they are combined. This is particularly true of fiber reinforced composites where the mechanical strengths are dependent on the type, amount and orientation of the fiber and the chemical properties are dependent on the resin matrix. The role of each material's contribution to the ultimate performance of the composite has been studied in depth in order to aid in stress analysis and design.

In the past decade, textile glass fiber production in the United States has grown markedly with additional growth forecast for the next decade. Reinforced plastics has accounted for a large part of this growth as the result of performance of composites in various products and economical factors.

Properties of glass fiber which have contributed to the growth are as follows:

1. High tensile strength and impact strength to give maximum strength-to-weight ratios.
2. High dimensional stability with a maximum elongation of 3% and perfect recovery.
3. High thermal endurance gives non-burning characteristics by the inorganic nature of the glass composition plus an excellent degree of strength retention at elevated temperatures.
4. Excellent electrical properties resulting from hydrophobic character of glass plus resistance to thermal degradation.
5. Excellent moisture resistance resulting in resistance to swell, stretch, degradation or chemical interaction in highly humid atmospheres.
6. Excellent chemical resistance to most chemicals and microbiological degradation, although hydrofluoric acid, hot phosphoric and strong alkali will attack and degrade the fibers.
7. Flexibility of glass fibers is considered low, although fine filament glass fibers have excellent flexibility.

Woven fabrics are a versatile fiber form for fabrication of reinforced plastic composites because of their ease of cutting, draping and handling during laminating, wetting with the resin and control of reinforcement-to-resin ratios. As each new application for glass fabric emerged, the need for improved material and composite technology was inadequate to meet the challenge, so it was necessary to expand the range of glass fabric beyond those available on existing specifications.

Uniglass Industries has met this challenge by working closely with the basic fiber producers in the evaluation of new glass compositions and filament sizes, as well as adapting existing glass fibers to fabric design studies and composite evaluation containing one or more fabrics. In conjunction with these studies on basic fibers and fabrics, the development of improved fabric finishes continued so as to obtain ultimate fabric reinforcement systems.

FABRIC VARIATIONS

Fabric characteristics are controlled by fiber properties, fabric count, yarn construction and weave pattern. The fabric count is the number of ends or picks per inch (2.5 cm) in the warp and weft respectively and controls fabric cover (degree of closeness of yarn). Fabric count is limited by the yarn construction and weave pattern. Fabric count plus yarn construction determines physical properties of the fabric, such as weight, thickness and breaking strength.

When fabric count and yarn construction in both warp and weft are comparable, the fabric is bidirectional. Composites containing bidirectional fabrics exhibit properties along the axis coinciding with the warp and weft. A high count of heavy yarn in one direction combined with a low count of light yarn in the perpendicular direction yields a unidirectional fabric with maximum properties along the axis corresponding to the direction of maximum yarn loading.

There are three basic weave patters–plain, twill, and satin (Figure 1). Plain weave is the most stable, gives the best cover and is best suited to flat composites with curvature suitable for the limited drapability of stable plain weaves unless the fabric is open so the yarns are free to move for curvature conformance. It gives lowest strength contribution to composites of all the weave patterns. The twill weave (1 × 3 broken twill or crowfoot is most common) has better drape characteristics than plain weave because it has fewer yarn interlacings making it more pliable. Twill weaves give higher composite properties than plain weaves. Satin weave (usually 8-shaft) is most pliable, drapes and molds readily and gives excellent composite properties.

Several of these variables of fabric constructions will be discussed in more detail in subsequent sections of this paper.

GLASS COMPOSITION

The glass fiber industry was built primarily on E-glass fibers, the composition of which is given in Table 1. For improved chemical resistance, A-glass and C-glass fibers were developed, but find use mainly in chopped strand mat rather than in woven fabrics. Compositions of both A-glass and C-glass are included for comparative information. The need for glass fibers with higher strength, higher modulus, improved electrical properties, etc. resulted in the development of a series of glass fibers of varying compositions as described in Table 1. The nomenclature of these glass fiber compositions are as follows:

A High Alkali Grade

C Chemical Grade

E Electrical Grade

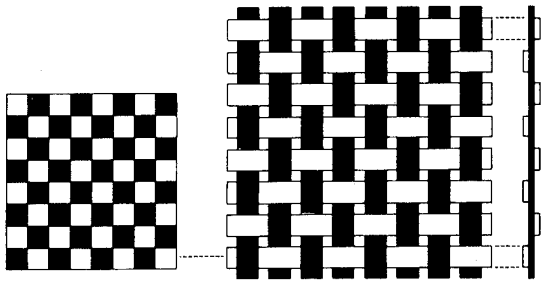

Fig. 1a Plain Weave

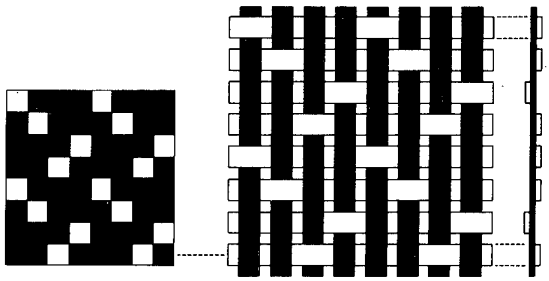

Fig. 1b 1 × 3 Broken Twill-Warp Face
(Crowfoot Satin)

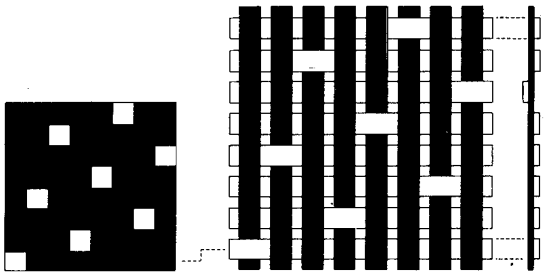

Fig. 1c 8-Shaft Satin Weave-Warp Face

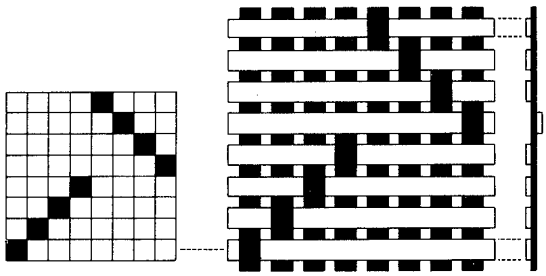

Fig. 1d Special Balanced 8-Shaft Satin Weave

S High Strength Grade

M High Modulus Grade

D Low Dielectric Grade

Properties of these compositions in fiber form are listed in Table 2. In addition to the above referenced compositions, research continues to be directed toward the development of high modulus and high strength fibers.

Since most of the glass fibers are drawn as 150's yarn, fabric studies were conducted primarily on the E-glass 1581 fabric construction as composite reinforcement. The data obtained from this study is compiled in Table 3. All data, unless otherwise indicated, was obtained from the Langley Processing Division, Uniglass Industries on press-cured laminates using cure cycles recommended by the resin producer. All tests were conducted in accordance with A.S.T.M. or Federal Standard Test Methods.

From this data it can be seen that both S-glass fabric and M-glass fabric give stronger laminates than E-glass fabric, with the higher modulus of the M-glass fiber being transferred to the composite to give the highest modulus values. Wet strength retention improvements can be realized by selection of a finish to give better adhesion of the resin to the glass surface, although there has been little reported in the literature on studies of the surface character of the newer compositions in order to determine the best chemical finish for optimum performance of the fiber in a composite.

While the D-glass fabric did not yield a particularly strong composite, even with the high performance 901 (HTS) binder, the electrical properties are more desirable than any of the others.

Economic considerations in the manufacture of both S-glass and M-glass fibers have limited development of uses for these materials. Owens-Corning Fiberglas Corp. has recently introduced a commerical grade of S-glass which could make the improved composite properties plus the economics more attractive. The potential field of interest for D-glass fabric is in rigid electrical insulation, such as printed circuitry, to take advantage of the electrical properties, but exploitation has been hampered by high material costs.

FILAMENT DIAMETERS

Glass fiber is available in a variety of filament diameters and yarn sizes as indicated in Table 4. Widespread examination of 1581 fabric using a variety of E-glass filament diameters as reinforcement has been conducted and a synopsis of the data is presented in Table 5A (polyester) and Table 5B (epoxy).

When evaluating plied yarns in the polyester composite study, filament diameter has little effect except in the ultra-fine B filament where a slight improvement in all properties except wet compression was notice. Unplied yarn fabrics in polyester composites show an improvement over the plied yarn fabrics, with the fine filament DE7581 fabric showing a noticeable improvement to give the highest properties of all fabric possibilities.

TABLE 1

Glass Fiber Compositions

	A-Glass	C-Glass	E-Glass	S-Glass	M-Glass
SiO_2	72.0	64.6	54.3	64.2	53.7
Al_2O_3	0.6	4.1	15.2	24.8	–
Fe_2O_3	–	–		0.21	0.5
CaO	10.0	13.4	17.3	0.01	12.9
MgO	2.5	3.3	4.7	10.27	9.0
Na_2O	14.2	7.9	0.6	0.27	–
K_2O	–	1.7		–	–
B_2O_3	–	4.7	0.8	0.01	–
BaO	–	0.9	–	–	–
LiO_2	–	–	–	–	3.0
BeO	–	–	–	–	8.0
TiO_2	–	–	–	–	8.0
ZrO_2	–	–	–	–	2.0
CeO_2	–	–	–	–	3.0

TABLE 2

Properties of Glass Fiber Compositions

	A-Glass	C-Glass	E-Glass	S-Glass	M-Glass	D-Glass
Specific Gravity	–	2.49	2.54	2.49	2.89	2.16
Tensile Strength, psi						
70° 50% RH		500 000	500 000	650 000	500 000	350 000
600°F		–	425 000	600 000	390 000	–
1000°F		–	250 000	350 000	185 000	–
Modulus of Elasticity	10.0×10^6	10.0×10^6	10.5×10^6	12.4×10^6	16.4×10^6	7.5×10^6
Dielectric Constant		6.79	6.11	5.6	–	3.8

TABLE 3

Glass Fiber Compositions in Epoxy Resin Composites

Fabric Construction				
Fabric No.	E1581	S1581	YM31A(1)	5681(2)
Count	57 × 54	57 × 54	57 × 54	57 × 54
WARP yarn	ECG 150 1/2	SCG 150 1/2	MCG 150 1/2	DCG 150 1/2
Weft yarn	ECG 150 1/2	SCG 150 1/2	MCG 150 1/2	DCG 150 1/2
Weave	Satin	Satin	Satin	Satin
Composite Strengths				
Flexural Strength				
Dry	88 600	87 100	89 800	60 400
2-Hr Boil	87 300	81 900	79 300	59 300
Flexural Modulus				
Dry	3.78×10^6	3.79×10^6	5.00×10^6	3.03×10^6
2-Hr Boil	3.61×10^6	3.86×10^6	4.79×10^6	3.07×10^6
Compressive Strength				
Dry	64 800	56 400	61 000	59 100
2-Hr Boil	61 200	50 000	46 700	61 000
Tensile Strength				
Dry	60 000	61 400	64 500	41 300
2-Hr Boil	60 500	61 500	62 100	40 500
Electrical Properties				
Dielectric Constant	4.99	—	5.47	3.83
Power Factor	0.0151	—	0.0154	0.0174

(1) Properties of High Modulus Reinforced Plastics, G. P. Peterson SPE Journal, Jan 1961, Page 57.

(2) Treated with Owens-Corning Fiberglas Corp. No. 901 (HTS) epoxy resin compatable yarn binder; no finish treatment after weaving.

TABLE 4

Glass Fiber Description

Filament Designation	Basic strand	Filaments per strand	Filament diameter (in.)
B	450	408	0.00012
B	150	1224	0.00012
D	1800	51	0.00021
D	900	102	0.00021
D	450	204	0.00021
DE	150	408	0.00025
DE	75	816	0.00025
E	225	204	0.00029
G	150	204	0.00036
G	75	408	0.00036
G	37	816	0.00036
K	75	204	0.00051

TABLE 5A

Influence of Filament Diameter on Polyester Resin Composites

Style	181	1581	DE 1581	1281	G7581	DE 7581
Count	57 × 54	57 × 54	57 × 54	57 × 54	57 × 54	57 × 54
Warp yarn	ECE 225 1/3	ECG 150 1/2	ECDE 150 1/2	ECB 150 1/2	ECG 75 1/0	ECDE 75 1/0
Weft yarn	ECE 225 1/3	ECG 150 1/2	ECDE 150 1/2	ECB 150 1/2	ECG 75 1/0	ECDE 75 1/0
Weave	Satin	Satin	Satin	Satin	Satin	Satin
Flexural Strength						
Dry	77 100	77 000	77 400	81 400	77 600	83 100
Wet	59 200	56 500	60 000	66 300	60 700	65 500
Flexural Modulus						
Dry	3.37×10^6	3.36×10^6	—	3.36×10^6	3.45×10^6	3.58×10^6
Wet	3.16×10^6		—	$3\ 37 \times 10^6$	3.18×10^6	3.27×10^6
Compressive Strength						
Dry	48 300	50 600	50 500	54 200	54 700	56 800
Wet	40 000	43 000	38 600	38 100	40 100	43 500
Tensile Strength						
Dry	50 300	53 700	49 600	59 100	55 800	66 100
Wet	49 800	52 100	47 200	59 900	55 800	62 600

TABLE 5B

Influence of Filament Diameter on Epoxy Resin Composites

Style		181	1581	1281	G 7581	DE 7581	B 7581
Count		57 × 54	57 × 54	57 × 54	57 × 54	57 × 54	57 × 54
Warp yarn		ECE 225 1/3	ECG 150 1/2	ECB 150 1/2	ECG 75 1/0	ECDE 75 1/0	ECB 75 1/0
Weft yarn		ECE 225 1/3	ECG 150 1/2	ECB 150 1/2	ECG 75 1/0	ECDE 75 1/0	ECB 75 1/0
Weave		Satin	Satin	Satin	Satin	Satin	Satin
Flexural Strength	Dry	93 000	88 600	92 400	92 600	94 900	101 000
	Wet	92 100	87 300	87 900	90 300	91 900	99 400
Flexural Modulus	Dry	3.88×10^6	3.78×10^6	4.06×10^6	3.78×10^6	3.90×10^6	4.02×10^6
	Wet	3.81×10^6	3.61×10^6	3.61×10^6	3.73×10^6	3.82×10^6	3.94×10^6
Compressive Strength	Dry	58 100	64 800	64 900	76 700	67 700	69 900
	Wet	56 900	61 200	62 800	73 500	62 600	64 700
Tensile Strength	Dry	60 000	60 000	64 800	64 200	66 300	69 400
	Wet	61 100	60 500	59 700	60 600	63 900	61 700

A slightly different picture emerges from the study of filament diameter effects in epoxy resin composites shown in Table 5B. All plied yarn fabrics, regardless of filament diameter, yield comparable laminate properties, although Style 1281 containing B filament yarn shows a slight improvement in modulus and would show an increase in fatigue life. Again, the unplied yarn fabrics show an overall improvement over the plied yarn fabrics, with the finer filaments showing higher flexural strengths, modulus and tensile strengths while the coarser filaments show higher compressive strengths. The plied yarn vs. unplied yarn phenomena also exists in S-glass fabrics as shown in Table 5C where the unplied yarn fabric gives markedly higher composite strengths.

The reason for this difference has never been explained, although the parallel alignment of filaments in unplied yarn exposes more surface area for improved glass-to-resin bonding. This can be substantiated by the observation that the fabric finish can more than offset the effect of the filament geometry will be discussed in a later section of this paper.

WEAVE PATTERN

General observations on the effects of weave pattern were discussed in the 'Fabric Variation' section. As indicated, the handling characteristics are determined by the amount of yarn and weave pattern present in the fabric construction. If the weave patter is too tight, the fabric will not accept resin resulting in a very weak composite. If the weave pattern is too open or loose, the fabric does not contain sufficient fiber to develop ultimate strengths and will be difficult to handle tending to distort resulting in an inability to align fiber with preferred strength axis.

Generally, the longer the float (the portion of a warp or filling yarn that extends unbound over two or more weft or warp

yarns), the higher the composite strengths. The transition from plain weave (Figure 1a) style 116 to crowfoot weave (Figure 1b) style 120 results in increased mechanical properties as shown by the data in Table 6A. Both are 3-ounce fabrics in a 60 × 58 count using ECD 450 1/2 yarn. The same observation exists in the transition from the plain weave 1528 fabric to the crowfoot 3528 fabric. The lower strengths of these latter 6-ounce fabrics compared to the lighter 3-ounce fabrics results from the heavier ECG 150 1/2 yarn not accepting and being thoroughly encapsulated as the finer yarns. This is the reason for the rule of thumb that heavier fabrics tend to give lower composite properties.

Structural epoxy resin composites show the same increase in mechanical strengths as a function of weave pattern shown by the data in Table 6B by comparing 7581 in an 8-shaft satin weave (Figure 1c) with the same fabric in a balanced weave pattern with shorter floats (Figure 1d).

Thus by changing the manner of interlacing warp and filling yarns, composite strengths can be increased or decreased to assist in meeting design criteria.

TABLE 5C

Plied vs. Unplied S-glass Fabrics in Epoxy Composites

Style		S1581	S7581
Yarn		SCG 150 1/2	SCG 75 1/0
Flexural Strength	Dry	87 100	116 000
	Wet	81 900	108 200
Flexural Modulus	Dry	3.79×10^6	5.21×10^6
	Wet	3.86×10^6	5.25×10^6
Compressive Strength	Dry	56 400	73 900
	Wet	50 000	68 300
Tensile Strength	Dry	61 400	86 400
	Wet	61 500	83 200

FABRIC DESIGN

The large number of basic fiber strands available resulting in numerous unplied and plied yarn combinations plus the possible combinations of fabric counts and several basic weave patterns leads to a potentially infinite number of glass fabric constructions. However, many combinations can be eliminted by economic factors or by end-use performance. Of the 200 or so glass fabrics available to industry, only a handful are used in the reinforced plastics industry because of limitations imposed by government and resulting industry specifications, many of which are obsolete for present needs. Fabrics are selected on the basis of per ply thickness combination, strength requirements of the composite, economics, adaptability to fabricating techniques, etc. With the recent

TABLE 6B

Weave Pattern Variable on Epoxy Composites

Style		16-317	7581
Flexural Strength	Dry	86 100	102 000
	Wet	82 700	95 900
Flexural Modulus	Dry	4.52×10^6	4.28×10^6
	Wet	4.40×10^6	4.09×10^6
Compressive Strength	Dry	54 900	67 600
	Wet	54 000	65 400
Tensile Strength	Dry	67 600	77 100
	Wet	65 400	68 700

advances in the technology covered in this presentation, it is now possible to use fabric design to select a woven reinforcement system to maintain a performance level while reducing material and fabricating costs. This concept leads to great design potential requiring knowledge of both materials and processes. An illustration of this concept is given in Table 7 where fabric 287 gives the same performance as 120 fabric with 10 less plies of fabric with a resultant cost savings in both material and fabrication. This came about by a yarn substitution only in the fabric design.

TABLE 7

Fabric Design Effect on Epoxy Composites

Style		120	16-287
Plies		36	26
Flexural Strength	Dry	82 000	79 400
	Wet	71 400	75 000
Flexural Modulus	Dry	4.17×10^6	4.13×10^6
	Wet	4.08×10^6	3.74×10^6
Compressive Strength	Dry	58 700	55 100
	Wet	52 400	55 500
Tensile Strength	Dry	58 700	55 100
	Wet	52 400	55 500

Yarn distribution plays a major part in fabric design and resultant composite performance, since strength is a function of reinforcement. A balanced fabric in which yarn distribution is equal in warp and filling directions will have comparable properties in those directions, but not necessarily equal. If the yarn is woven primarily in one direction as in unidirectional fabrics, the composite strengths will be greatest in the direction corresponding to the greatest concentration of yarn. This is illustrated by the data listed in Table 8.

TABLE 6A

Weave Pattern Variable on Polyester Composites

Style		116	120	1528	3528
Flexural Strength	Dry	66 100	71 900	56 400	64 600
	Wet	52 300	56 500	48 400	54 600
Flexural Modulus	Dry	3.32×10^6	3.36×10^6	3.30×10^6	3.89×10^6
	Wet	3.09×10^6	3.09×10^6	3.20×10^6	3.56×10^6
Compressive Strength	Dry	49 400	51 300	36 600	47 600
	Wet	35 300	34 500	28 700	35 600
Tensile Strength	Dry	51 400	54 100	45 900	53 300
	Wet	51 400	51 900	45 700	50 200

TABLE 8

Yarn Distribution in Fabric

Test Direction		Warp	Weft	Warp	Weft
% of Yarn		52	48	90	10
Flexural Strength	Dry	84 200	78 200	95 000	23 300
	Wet	75 500	68 500	87 400	24 100
Flexural Modulus	Dry	4.02×10^6	3.65×10^6	4.95×10^6	2.47×10^6
	Wet	3.87×10^6	3.41×10^6	4.80×10^6	1.46×10^6
Compressive Strength	Dry	62 700	63 400	64 500	28 900
	Wet	51 800	54 500	51 100	23 600
Tensile Strength	Dry	57 900	54 900	94 000	12 100
	Wet	55 700	50 200	91 600	11 700

FINISH

Although this paper is primarily concerned with fabric variations, it is difficult to avoid comments on the effects of finish as a fabric variable. It has previously been shown that optimum strengths can be obtained by selection of glass fiber composition, and fabric construction as dictated by yarn count, yarn construction (plied vs. unplied), and weave pattern.

Some of these fabric improvements can be offset by finish selection. Composite data presented herein has been based primarily on Volan A finished fabric. This led to the obvious inquiry as to the effect of high performance finishes on these same fabrics.

In lightweight fabrics, such as style 120, an increase of 20% in composite strengths can be realized by selection of a high performance finish such as UM665 (Table 9). Although the increase in strengths is not as pronounced in the 1581-type satin weaves shown in Table 9, an increase does exist. However, the increase in strength caused by finish is striking when the comparison is made in the unplied satin weaves such as DE 7581 or B7581 fabrics (Table 9). An interesting observation can be made here in that Volan A finish gives better performance with B7581 than with DE 7581. The reverse effect occurs with UM670 finish where DE 7581 outperforms B7581. It has already been noted that 'S'-glass fabrics give stronger composite than E-glass fabrics. What then, will be the effect of finishes for added composite performance. The 901 (HTS) finish on S-glass fabrics gives the highest composite data to date, but the fabric has not found widespread use because of economics and limitations in adoptability to fabricating techniques. It is of interest to note, however, that S-glass fabrics with UM670 finish gives flexural and compressive strengths comparable to the 901 finish while modulus is higher and tensile, as expected, is lower (since the 901 treatment was designed to compliment the high strength glass composition to give a system of ultimate tensile strength). In most applications the properties available with DE 7581-UM670 or S7581-UM670 are more than adequate for high performance structural parts, especially for primary aircraft structure.

There is an added advantage to the UM670 finish in its influence at elevated temperatures. After 48 hrs at 420°F, UM670 finished fabric-epoxy composites retain approximately 60% of the original strength whereas Volan A shows only 48% retention after $\frac{1}{2}$ hr at 420°F.

FABRIC ORIENTATION

As seen above, fabric construction influences the composite design by yarn distribution. Although fabric is a two dimensional plane geometrically, fabric orientation leads to more isometric distribution of fiber. This alters the strength along the various axis, but affords load bearing characteristics in any predetermined direction.

Bidirectional satin weave fabric gives excellent composite properties in both the 0° and 90° directions. Unidirectional fabrics give maximum strength in the 0° and minimum strength in the 90° direction. Cross-plying unidirectional fabric gives excellent bi-directional properties, sometimes higher than can be obtained by the birdirectional satin weave fabrics (see Table 10). Cross-plying of satin weaves at 0°-90° and at 0°-45°-90° is common practice and data on strengths on this effect is also included in Table 10.

Often it is desired to increase the strength of a bidirectionally reinforced composite along a given axis; this is accomplished by adding a unidirectional fabric to a bidirectional layup. This improves 0° properties noticeably.

CONCLUSION

During the past few years, the combined efforts of the yarn producer, the weaver and the fabricator has lead to developments in fabric reinforcements which open new potentials for fabric-resin composites. New glass fiber compositions give promise to stronger composites or composites with improved electrical properties. New filaments lead to more flexible fabrics for improved fatigue life. Improvements in fabric design and finish technology have raised composite design limits which is leading to a review of existing specification policies.

Thus the strengths published in existing specifications can be doubled by selecting fabrics using guidelines outlined herein. Thus, the strongest composite for bidirectional structural applications can be made using DE 7581 UM670 fabric. Slight improvements in modulus and tensile strength can be realized by using S7581-UM670 fabric Unidirectional fabrics can be added for increased strength along a given load axis. High load bearing capability with their laminates such as in honeycomb sandwich facings, can be achieved without weight penalties by fabric-finished system based on fiber selection, fabric construction and finish performance.

As engineering technology of composite components joins with material technology of glass fibers and fabrics, the forecast growth of the industry can be realized.

TABLE 9

Glass Fabric Finish Comparison in Epoxy Composites

Fabric	120	120	1581	1581	7581	7581	B7581	B7581	S1581	S7581	S7581
Finish	Volan	UM665	Volan	UM670	Volan	UM670	Volan	UM670	Volan	Volan	UM670
Flexural Strength											
Dry	82 000	105 000	88 600	90 100	94 900	114 500	101 000	103 700	84 800	120 000	116 000
Wet	71 400	101 300	87 300	89 200	91 900	109 200	99 400	99 500	65 500	78 000	108 200
Flexural Modulus											
Dry	4.17×10^6	4.60×10^6	3.78×10^6	4.02×10^6	3.90×10^6	4.09×10^6	4.02×10^6	4.15×10^6	3.10×10^6	4.18×10^6	5.21×10^6
Wet	4.08×10^6	4.42×10^6	3.61×10^6	4.03×10^6	3.82×10^6	$4\ 02 \times 10^6$	3.94×10^6	4.05×10^6	4.20×10^6	4.33×10^6	5.25×10^6
Compressive Strength											
Dry	62 300	77 400	64 800	74 600	67 700	77 000	69 900	74 100	61 300	55 800	73 900
Wet	52 000	74 200	61 200	70 000	62 600	76 900	64 700	67 100	40 300	30 000	68 300
Tensile Strength											
Dry	58 700	73 400	60 000	67 500	66 300	80 700	69 400	72 800	70 600	87 500	86 400
Wet	52 400	68 100	60 500	63 500	63 900	78 200	61 700	69 500	64 600	80 000	83 200

TABLE 10

Fabric Orientation

Style	7581	7581	7575	7575
Angle	0°	0°-90°-45°	0°	0°-90°
Flexural Strength (0°)	107 700	91 800	166 800	114 400
Flexural Modulus (0°)	4.30×10^6	3.83×10^6	5.9×10^6	$3.97 \times .10^6$

Sixth International Reinforced Plastics Conference

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Application of wire sheet in reinforced plastics

H. D. de PAUW GERLINGS and R. H. STRETTON, National Standard Co. Ltd.

Wire sheet is already known in the reinforced plastics industry as a high strength material which has certain properties giving it an advantage over others. The conception of wire sheet and the technique for manufacturing comes from Dr F. F. Jaray of Worcester, who has licenced National-Standard Company of Kidderminster to develop and market it.

Wire sheet offers the fabricator high speed easy moulding, higher fatigue strength and longer life in the finished laminate, also higher design strengths and moduli compared with glass fibre reinforced laminates. This is partly due to the nature of wire sheet which makes for easy wetting out and the avoidance of air inclusions or voids.

A comparison between laminates made with wire sheet and those made with unidirectional glass fibre rovings is shown in Table 1. The glass fibre tape and roving laminates were made by winding under a tension of about 2 kgf(5 lbf) per roving. The wire sheet laminates were produced using only a low pressure without any tension.

Note that in each of the types of reinforcement used in the samples for Table 1, the reinforcement percentage by weight was kept the same, this means that in the case of the wire sheet laminate the volume of wire sheet included is very low; this explaines the low strength and modulus figures for the wire sheet laminate compared with what one would expect from the high strength and modulus of the wire fibre.

TABLE 1

		Wire sheet	Unidirectional Tape	Unidirectional Rovings
Tensile strength	kgf/mm²	68.5	60.8	55.0
	× 10³ lbf/in²	97.4	86.4	78.2
Tensile modulus	kgf/mm²	5730	2700	2060
	× 10⁶ lbf/in²	8.15	3.84	2.93
Flexural strength	kgf/mm²	87.6	75.0	68.0
	× 10³ lbf/in²	124.5	106.5	95.2
Flexural modulus	kgf/mm²	4030	2580	2040
	× 10⁶ lbf/in²	5.73	3.67	2.90
Reinforcement by weight	%	59.5	59.5	59.5

Experience has shown that the design strength of a wire sheet reinforced laminate can be taken as 40% of the ultimate tensile strength; in the case of glass reinforced laminates 25% is probably the best figure quoted and, in many instances, the design strength may be 15% or less. Table 2 compares specific design strengths of each type of laminate and Table 3 compares specific moduli. It is further important to appreciate that the very good performance figures shown for glass fibre laminates can only be achieved by tensioning the fibres—no such tensioning technique is necessary with wire sheet. This means that the typical strengths quoted can be obtained using ordinary laminating techniques such as pressure bag, vacuum bag, or simple match tools in a press; extremely low pressures are sufficient to achieve a good quality high strength laminate. It is even possible to use wire sheet in hand lay-up contact moulding in certain circumstances. Utilisation of the strength of wire sheet is not limited to the winding of high performance pipes and other vessels.

After carrying out this initial series of tests it was evident that as a next step, wire sheet used in conjunction with other reinforcing materials should be investigated. Therefore, composite laminates based on wire sheet, glass fibre mat and asbestos mat, were tested and comparisons made with similar

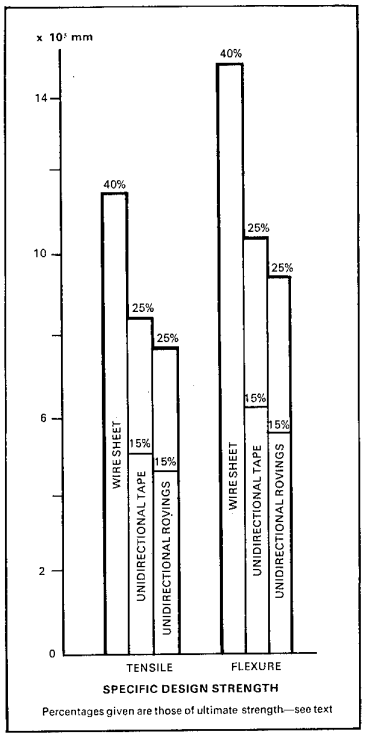


TABLE 2

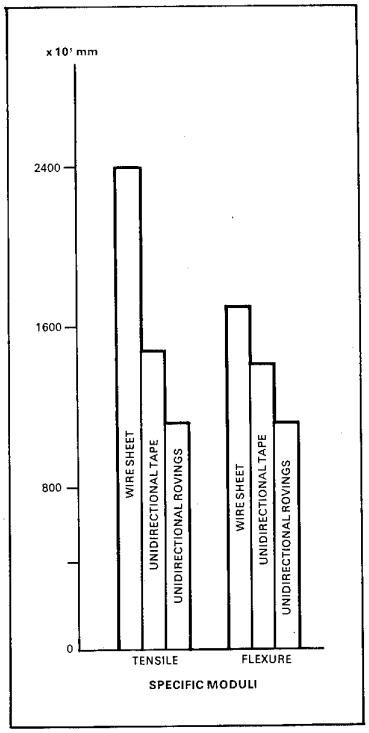


TABLE 3

laminates without the wire sheet reinforcement and, in some cases, with woven glass rovings instead of wire sheet. Over 2000 samples were tested and the results of these tests have shown that at equal or lower weight the rigidity of laminates containing wire sheet can be up to twice as great, and also have better flexural and tensile strengths. In addition to these factors, the composite laminates containing wire sheet proved two very important features, first no delamination or inter-laminar shear occurs, whereas glass fibre laminates are liable to start to delaminate at 50 to 55% of their short time ultimate strength; this confirms the very high design strength possible by using wire sheet. Secondly, under abnormal flexural loading laminates containing wire sheet will not rupture completely; the laminate remains intact and still supports a considerable load. The wires in the laminate are only deformed.

In Tables 4-7 the performance of the types of laminates just described are compared. The first two tables apply to sandwich type laminates with cross ply wire sheet and glass fibre or asbestos mat as the core material. In the second two tables comparison is made with unbalanced composite laminates with cross ply wire sheet on one side only, or with an uneven number of layers of wire sheet in each direction. Such laminates are commonly used in structure where the forces are acting in one direction more than the other, for example, in cylindrical pressure vessels. These tables again demonstrate:-

(1) Wire sheet laminates have higher physical properties than woven roving laminates

(2) Many wire sheet laminates have higher specific properties than woven roving laminates.

It must be stressed that these comparisons concern only the ultimate short time properties and that a comparison based on design properties, where one has to bring into account yield point, cyclic fatigue strength loading and static loading, will show that laminates based on wire sheet give a very much better performance.

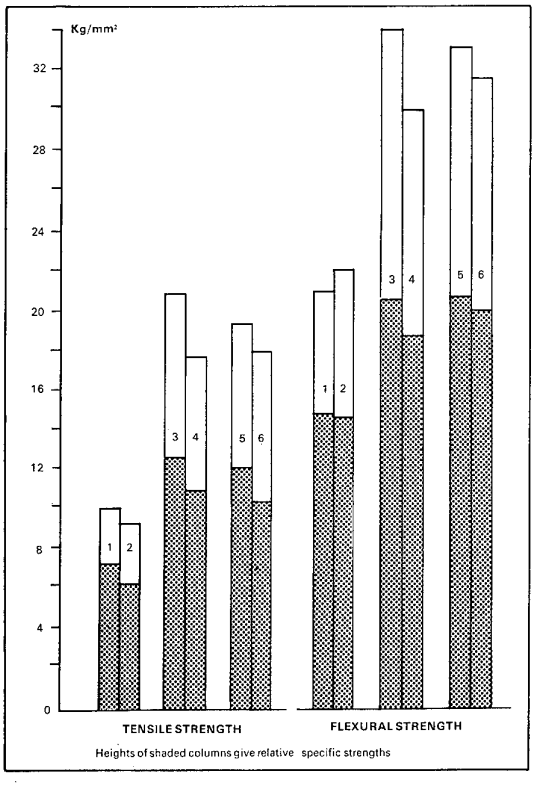


TABLE 4

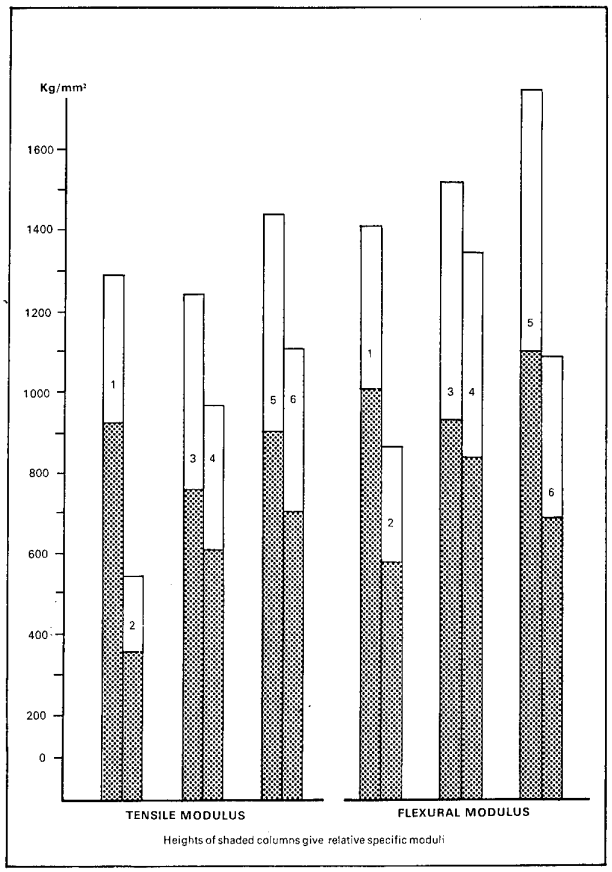


TABLE 5

No.	Composition	Thickness mm	% reinforcement by weight
1	N — cross 30 — 4N — cross WS 30 — N	5.3	37
2	N — WR — 3N —WR — N	4.8	33
3	cross WS 30 — 2 × 300 M — cross WS 30	3.6	41
4	WR — 2 × 300 M — WR	3.1	45
5	cross WS 30 — 450 M — 2N — — 450 M — cross WS 30	4.7	41
6	300 M — WR — 450 M — WR — 300 M — WR	5.1	44

Key for Tables 4 & 5

N = Noramite asbestos mat, 150 gr/m².

Cross WS 30 = two layers Wire Sheet 30 wires/inch, cross plied.

WR = Woven Rovings 820 gr/m².

300 M = Glass fibre mat 300 gr/m².

450 M = Glass fibre mat 450 gr/m².

SANDWICH LAMINATES FOR FLOORS

The performance of laminates just demonstrated show that they offer important advantages where products are repeatedly heavily loaded and great danger exists of permanent deformation. The engineering department of Aladna Gerlings NV, who were looking for stronger and cheaper designs for their refrigerated railway wagon floors, decided that wire sheet could be used with advantage. The floors have to withstand

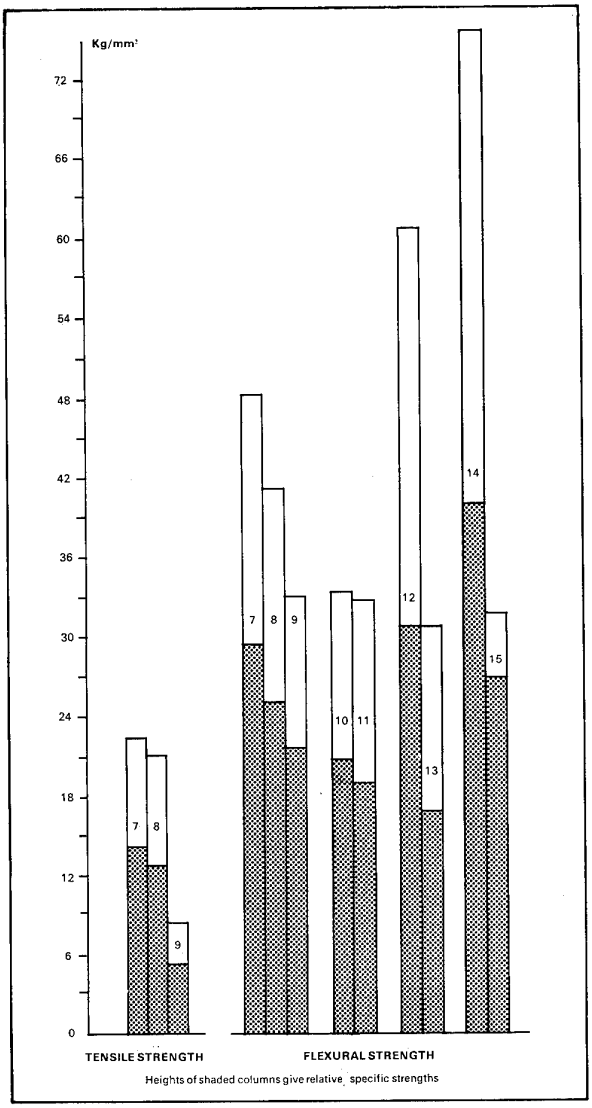


TABLE 6

No.	Composition	Thickness % mm	Reinforcement by weight
7	2 × 450M — cross WS 40	2.45	49
8	2 × 450M — cross WS 30	2.65	43
9	2 × 450M — woven rovings	3.0	38
10	2 × N — 2 × WR 1 — WL 1 — 2 × WR 1	4.4	37.5
11	2 × N — R1 — L1 — 2 × R1 — L1 × 2R1	4.1	53
12	300M — WR 3 — 2 × 450M — W3	2.7	57
13	2 × R2 — 450 M — 4 × R2 — 450M — 2 × R2	6.1	62
14	2 × WR 2 — 2 × 300 M — WL 2 — WR2	3.2	54
15	2N — 2 × R3 — L3 — 2 × R3	3.8	58

Key for Tables 6 & 7

450M = glass fibre mat 450 gr/m².

300M = glass fibre mat 300 gr/m².

N = Noramite asbestos mat 150 gr/m².

WS40 = 2 layers Wire Sheet 40 wires/inch.

WS30 = 2 layers Wire Sheet 30 wires/inch.

Woven rovings = woven rovings 820 gr/m².

WR1 = Wire Sheet 30 wires/inch in hoop direction.

WL1 = Wire Sheet 30 wires/inch in axial direction.

WR2 = Wire Sheet 40 wires/inch in hoop direction.

WL2 = Wire Sheet 40 wires/inch in axial direction.

WR3 = Wire Sheet 60 wires/inch in hoop direction.

R1 = Unidirectional Rovings 560 gr/m² in hoop direction.

L1 = Unidirectional Rovings 750 gr/m² in axial direction.

R2 = Unidirectional Rovings 750 gr/m² in hoop direction.

L2 = Unidirectional Rovings 750 gr/m² in axial direction.

R3 = Unidirectional Rovings 700 gr/m² in hoop direction.

L3 = Unidirectional Rovings 700 gr/m² in axial direction.

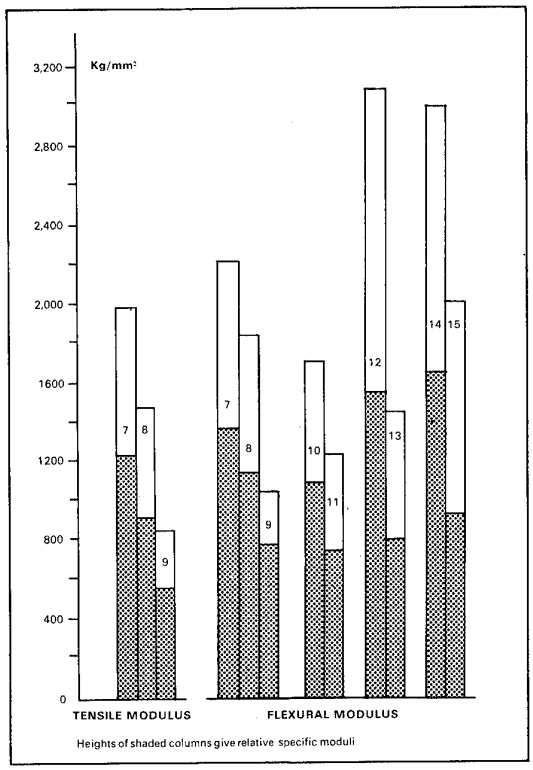
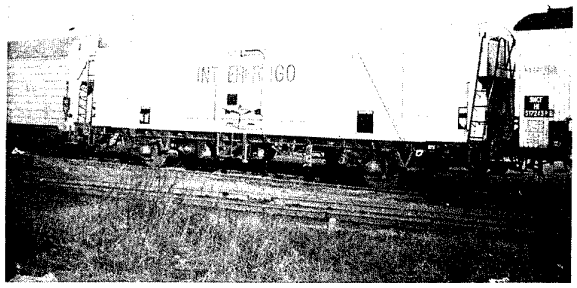


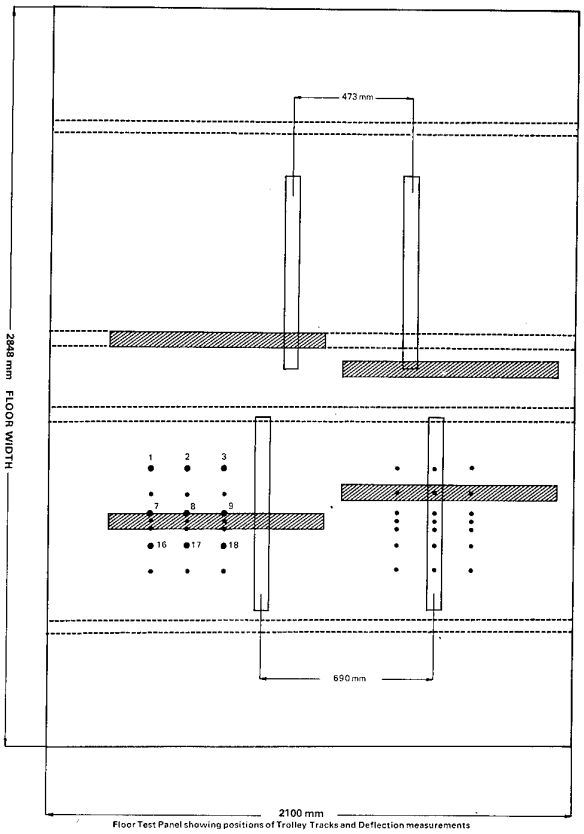
TABLE 7

severe loading whilst maintaining the maximum possible stiffness and strength; this must be achieved at the lowest possible weight. Experience in the past with over 600 such floors made of glass reinforced plastics, enabled them to design a new floor composition based on wire sheet which did give a considerable saving in weight and price.

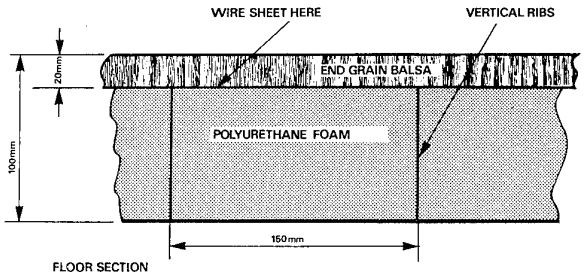
In principal, these floors now consist of a double sandwich construction, the main core consisting of polyurethane foam with a density of 35 to 40 kg/m³ (2.2 to 2.5 lb/ft³), the skin at the top, which has to withstand the severe trolley wheel loading, is designed again as a thin sandwich structure, this time using endgrain balsa wood as a core material—wire sheet reinforces the lower skin; previously the upper surface of the floor had been solid reinforced plastics. The skin at the under side of the floor, which is very little loaded, is a thin glass reinforced plastic composition; Noramite—asbestos fibre—is also used near the surfaces as a moisture barrier.



Complete refrigerated rail wagon



Floor Test Panel showing positions of Trolley Tracks and Deflection measurements



FLOOR SECTION

Chassis reinforcement crosswise is eliminated, the whole floor being supported by only four longitidinal beams; because of this there is a requirement for great strength across the width of the floor. The lower sandwich layer is reinforced with vertical plastic ribs at intervals running at right angles to the beams of the chassis so that these form a type of 'I' beam in reinforced plastic. Testing of a great number of floor parts, and experience in practice with floors of different constructions, has shown that this principle of construction gives the best results. Floors without these vertical ribs have failed after several years, or use has had to be made of a polyurethane foam of great density making the floors heavier and more expensive than was desired.

As a final proving test, floors have to withstand, for one hundred hours, a loading of 1200 kg applied by means of a hard rubber covered steel wheel with a diameter of 250 mm and a width of 80 mm. This wheel runs over the surface at a speed of 3 km/hour and is accelerated and braked at the end of each run. The number of cycles per hour is about 12. At the end of this test, the floors may not show a deflection greater than 1.0 mm.

INITIAL TESTING

Two types of short time initial tests are done on floor parts enabling one to predict the behaviour of a floor in the 100 hour test. Experimental results during the past years have given the necessary data for this prediction.

Load	1	2	3	7	8	9	16	17	18
550 A	0.08	0.06	0.16	0.09	0.01	0.10	0.14	0.04	0.17
B	0.00	0.14	0.04	0.00	0.09	0.11	0.00	0.23	0.08
700 A	0.16	0.13	0.08	0.25	0.23	0.55	0.12	0.10	0.12
B	0.10	0.13	0.00	0.03	0.07	0.09	0.01	0.12	0.03
900 A	0.29	0.29	0.16	0.35	0.29	0.58	0.30	0.16	0.38
B	0.14	0.14	0.12	0.05	0.02	0.02	0.03	0.01	0.05
1200 A	0.30	0.29	0.25	0.66	0.38	0.65	0.60	0.19	0.42
B	0.04	0.24	0.06	0.07	0.01	0.01	0.06	0.12	0.06

Initially flexural tests are run on the topside skin of the polyurethane sandwich construction. These flexural tests are done at different distances between the ribs. These distances are the same as the ones between the ribs which are found in the polyurethane foam. Secondly, a short time but more severe loaded wheel rolling test is carried out on a flat panel of 2.88 × 2.20 m, which is the same as the floor in its composition and construction, but without the built up edges that are on the proper floor. This panel is mounted on static steel beams similar to the ones of the chassis of the wagon. A small trolley with four hard rubber covered wheels is loaded successively with steel sheets in such a way that a load is obtained of 550, 700, 900 and 1200 kg per wheel. The trolley is rolled over the panel 50 times at each load. Deflection is measured directly after finishing the 50 runs and 10 minutes afterwards. These deflections are measured on specific points over which the wheel has passed.

The accompanying diagram shows a plan of the test panel, the position of the four longitudinal supporting chassis members and the points at which deflection is measured. The trolley is wheeled backwards and forwards over the floor at two posi-

tions—the one being parallel to the axis of the floor, the other at right angles; the positions of the tracks of the four wheels in each case is also shown. The table below shows actual figures recorded at some of the points on the test panel where measurements are taken. The figures given show the permanent set or remaining deflection after ten minutes has been allowed for the panel to recover.

PERMANENT DEFLECTION IN MM AT SPECIFIC POINTS ON TEST PANEL

Panel A has a solid reinforced plastic top skin 9 mm thick and the total weight of the panel is 259 kg.

Panel B has a sandwich top skin having wire sheet on the lower surface and is 20 mm thich. Total panel weight 147 kg.

One can see that is spite of panel B being very much lighter and hence cheaper, the deflections ten minutes after the load has been removed are very much less than for panel A. It should also be noted that the vertical ribs between the blocks of polyurethane were 100 mm apart for panel A and 150 mm apart for panel B.

To select the best sandwich for the upper skin of the floor, a series of tests were made on different compositions including the original solid reinforced plastic skin. Results of flexural tests for typical sandwiches are shown in the load-deflection Figure 1. All laminates were tested with a distance between the supports of 150 mm and brief details of the sandwiches are given below. The quantities of materials were chosen so that all constructions would be no more expensive than the all glass fibre reinforced panel (No. 7).

No.	Total panel thickness mm	Core material	Skin compositions Top	Bottom
1	15	Balsa	Wire sheet	Wire sheet
2	20	Balsa	Glass fibre	Wire sheet
3	15	Balsa	Glass fibre	Wire sheet
4	15	Plywood	Glass fibre	Wire sheet
5	15	Balsa	Glass fibre	Glass fibre
6	10	Balsa	Wire sheet	Wire sheet
7	12.5	Plywood	Glass fibre	Wire sheet
8	9	—Solid glass reinforced plastics—		

REFRIGERATED RAIL WAGON FLOORS

As a result of all this test work, it was decided to use the double sandwich construction containing wire sheet for the floors of 400 refrigerated rail wagons under construction for Interfrigo. The floors are being made by Fibrorensina at Turin and A.M.I.P. at Adria, the complete wagons are being built by Officine Mecaniche Ferrovaire Pistoiesi at Pistoia, Italy. The main dimensions of the floors are as follows:

Length:	12½ m	41 ft
Width:	2.88 m	9.4 ft
Thickness:	100 mm	3.9 in
Weight:	856 kg	1887 lb

(including all steel attachment inserts).

The weight of the floors made in the past was over 1000 kg, so that it was possible to bring the weight down by at least 144 kg, or about 15% from which can be judged the saving in cost of materials as well as in weight. In this project a total of 340 000 kg of raw material and about 28 000 square metres (300 000 square feet) of wire sheet is used. The whole of the development, design, planning of manufacture and control is done by the Engineering Department of Aladna Gerlings.

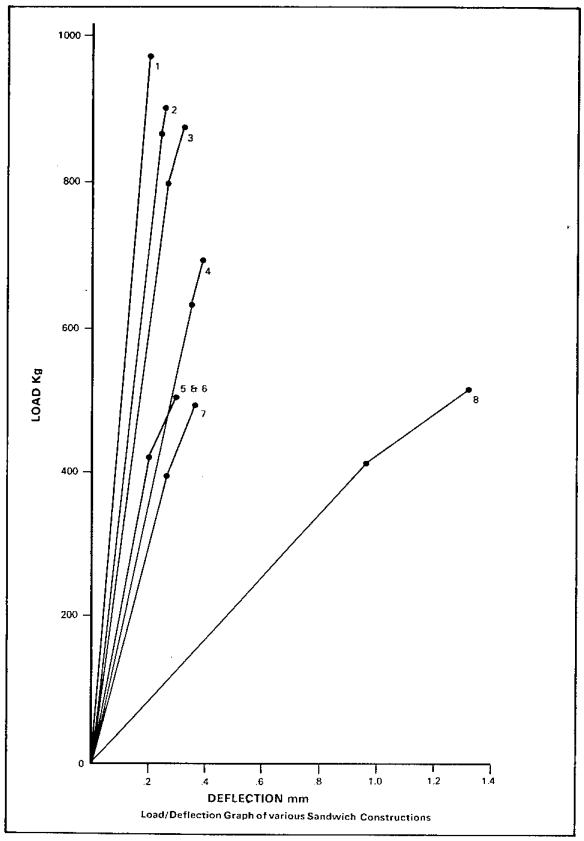
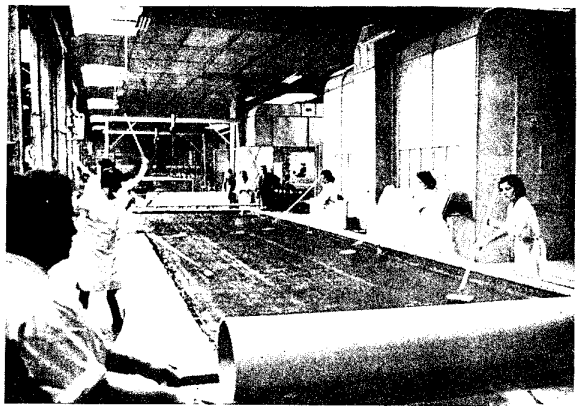


Fig. 1



Rail wagon floor under construction

Similar floor constructions will be used now in other refrigerated freight containers being manufactured in Europe—it is hoped that this new conception will be adopted in the U.K. in the near future. Laminates based on the top skin sandwich construction will be used for airfreight pallets, railway and motor-coach floors.

PIPES

At the time of writing this paper a project is well in hand involving the manufacture and testing of pipes reinforced with wire sheet. Details of the results of these tests and the method of construction of the pipes will be given at the conference together with relevant pictures.

OTHER APPLICATIONS FOR WIRE SHEET

A big outlet for wire sheet composite laminates is in the construction of road—and railway tankers. An important conti-

nental road tank vehicle manufacturer has started to develop and set up the production of this type of tank. It concerns the manufacturing of 37 000 litre (8000 imperial gallons) road tankers without any chassis, the wheel bogies are attached direct to the tank. Experience in the past has shown that due to low fatigue strength, even with filament wound products, reinforced plastics tanks fail or have to be made so thick and heavy that they are no longer competitive with those constructed of aluminium and stainless steel. This is especially true in cases where a chassis is used. Preliminary tests have shown that wire sheet compositions result in a somewhat lower weight in comparison with aluminium and they are competitive in price; to this must be added the great security against a complete rupture given by the wire sheet in the case of a road accident, and superior resistance to many chemicals.

Due to the forces acting on such a tank, and due to the fact that a 37 000 litre road-tanker has about 12 closed compartments, the volume of each of which must be accurate to within one litre; a special manufacturing technique and winding machine is being developed and made by Aladna-Gerlings.

Other similar products which will be made using wire sheet composite laminates and which are already in an advanced stage are:

1. Pressure tanks for bulk transport of powdered products like cement.
2. Freight transport tanks for bulk transport of liquids and products in powder form.
3. Buried oil storage tanks of large capacity and big sewer pipes.

   In the last two cases it is of the greatest importance to use a laminate which:

   (a) has sufficient strength and rigidity against earth load and traffic, and

   (b) does not rupture completely if it fails for some reason or other and the liquid inside seep through to the earth.

4. Big storage tanks

   In this case it will be possible to spray a rather thick layer of cheap chopped glass fibre on a rotating mandrel and then wind on only two or three layers of wire sheet. This will give equal stiffness and strength as glass reinforced tanks made by winding and will bring down the price of these tanks considerably.

Other specifications besides those already mentioned, where wire sheet could be used with great benefit are:

In the first place, Highway guardrail—several attempts in the U.S. and Europe were made to have them made of reinforced plastics; the strength and modulus even of unidirectional glass rovings was too low, this has been the reason why reinforced plastics have not given the results required; the main strength and stiffness must be in one direction. It is proved that wire sheet in combination with glass mat offers extreme high stiffness and strength, much higher than obtainable with glass fibres along.

Street and highway lighting columns are another outlet, especially the highway ones, as the loading of those by wind and other weather conditions is extremely high, reinforced plastics were not able to give sufficient strength and stiffness at an economical price.

There is a strong development all over Europe to cover large swimming pools complete with roofs made of reinforced plastics; the roof must be self-supporting over great spans. Here wire sheet may solve the problems encountered and make it possible to use reinforced plastics economically. Large segments for roofs, such as already made in the U.S. and Italy, covering great sport palaces or other buildings will be an outlet, and avoid expensive and complicated supporting structures to a far greater extent than now. In these cases, again the higher stiffness given by the wire sheet, is of greatest importance.

BOAT BUILDING

Nowadays large structures under development pose many big problems by way of fatigue strength and stiffness. There is certainly an outlet here for wire sheet, as this material is offering important advantages for local reinforcement in highly loaded areas.

MISCELLANEOUS

Cantilever arm mechanisms for elevating workmen to overhead power lines, etc.

Monocoque reinforced plastic cars for ski lifts; the development of these by winding is already in hand.

Snow and water skis, here again there is a great problem with stiffness and fatigue strength; to achieve this with glass fibre involves expensive techniques.

Propane and butane gas bottles, the development of these in reinforced plastics was successful except for one important point—heat transmission. Glass reinforcement was too good an insulator to overcome this problem and, therefore, development was stopped.

In general, one can say that wire sheet in combination with other existing reinforcements will make it possible to design reinforced plastics products which could not be made before. This was due to the lack of certain characteristics in available reinforcements, or because they were too expensive.

ACKNOWLEDGEMENT

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Preimpregnated glass mats

E. R. HUBAND, Turner Bros., Asbestos Co. Ltd.

INTRODUCTION

A demand has arisen in the last five years in this country for glass/polyester materials which can be moulded at fast production rates. The rather low production rates for hand lay up techniques fall short of today's modern high speed production requirements and this has led to a reduction in the use of these techniques for small and medium size mouldings. Mouldings from dough moulding compounds (D.M.C.) can of course be produced at high rates of production but they possess rather low physical properties. It is not surprising that moulders and fabricators have turned to preimpregnated glass polyester systems which possess both high strength, and can be moulded at high rates of production.

Estimated production figures for this country show that some 1 to 1.5 million pounds weight of preimpregnated glass mat is being used by moulders, embracing a variety of products, and that by 1970, this figure could be well in excess of five million pounds weight per year.

This paper covers some aspects of the chemistry of preimpregnated chopped strand mats. The ways in which this material can be used are discussed and illustrated, and evidence is presented to show that polyester prepregs are worthy of a high place in the already long list of well established polymeric materials.

1. POLYESTER RESINS

The first polyester product was probably that reported by Berzelius in 1847, he obtained this by the reaction of Tartaric acid with Glycerol.

Later in 1863, Lorenzo (Ref. 1) reported a polyethylene succinate produced by heating ethylene glycol with succinic acid. Vorlander (Ref. 2) in 1894 investigated glycol maleates, and later, in 1904, Blaise and Marcilly produced a polyester from hydroxy pivalic.

In 1916, reaction products from phthalic anhydride and glycerol became commercially available as finishes for wood and metal. Later in 1927 Kienle reacted fatty acids with polyols to improve their drying characteristics. He is credited with the word ALKYD (from alcohol and acid).

Throughout the thirties considerable work was carried out in the polyester field by such workers as Bradley, Krope and Ellis (Ref. 3). The work of Ellis, however is probably the most important as it was he who showed that in the presence of an unsaturated monomer, polyester resins could be made to cure at greatly increased speeds.

With the advent of the Second World War, considerably more interest was shown in polyesters, and in 1942 the United States Rubber Company reinforced polyester resins with glass fibres. Throughout the forties and into the fifties development work was intensified on new catalysts systems, filler to reduce warping and shrinkage, and also pigment systems which would not effect the curing characteristics of the resin. During this period the consumption of polyester resins had rapidly been increasing. In the United States alone from 1952 to 1962, the annual consumption rose from 20 million to 190 million pounds.

During the latter half of the fifties preimpregnated chopped strand mats began to appear on the commercial market.

There are now some six or eight large scale producers in this country. New developments are being carried out to produce more consistent, higher strength, and faster curing products. The last 12 months have shown that this material is finding large users in the 'containerisation' field. Its other uses are wide spread, and increasing, particularly in the automotive industry where the need is for high production rates coupled with cheap, easy to use materials.

2. STRUCTURE OF UN-SATURATED POLYESTERS

In general the polyester chain comprises three basic types of structural units.

1. Saturated acids
2. Un-saturated acids
3. Glycols

A general purpose polyester consists of phthalic as the saturated acid, maleic as the un-saturated, and propylene glycol. The ratio of these components determines the physical properties of the polyester resin. The use of Adipic or Sebacia as the saturated acid component gives the so called 'flexible' resins. A degree of aromaticity within the chain or the presence of certain cyclic components in either acid, or glycol, tend to give rigid cured products.

'The reactivity' of a resin system is determined by the ratio of saturated and unsaturated components in the system, which influences the degree of cross linking in the cured state.

The type of *glycol* used affects the chemical resistance, solubility and impact resistance, of the cured resin.

Molecular weight and chain length influence heat distortion point, chemical resistance, and hardness of the cured produet.

Industry over the years has developed a demand for low viscosity resin systems for various reasons, such as faster rates of wetting of the glass fibre surface, quicker removal of entrapped air and better filling of the mould cavities, and these are available commercially. They are produced by limiting the molecular weight by addition of chain stoppers during the initial condensation reaction. Addition of styrene monomer to lower the viscosity is bad practice, as this leads to greater shrinkage, and high peak exotherms when curing. Changing the ratio of monomer to polyester can also effect the final properties of the cured product adversely.

More rigid chains can be produced by substituting part of the propylene glycol with hydrogenated Bisphenol A. This gives increased flexural strength in laminates.

High tensile strengths can be produced by mixture of propylene glycol and diethylene glycol at molar ratios of 40 : 60.

Flame retardant polyesters can be produced by using chlorendic anhydride, commonly known H.E.T. acid, as the saturated acid component. Modification of the monomer can also result in an improvement in flame retardant properties. The following monomers have been suggested

2.5 Dichlorostyrene (Ref. 4)

Vinylchloroacetate or vinyltrichloroacetate (Ref. 5)

Diallylbenzenephosphonate and dimethylbenzene phosphonate (Ref. 6)

have been reported to give excellent fire retardant properties. More will be said later in this paper on fire retardant systems.

3. COMPOSITION OF PREIMPREGNATED GLASS MAT

In general a preimpregnated glass mat is made up of four components:

a resin system

a filler system which includes pigments and colouring matter

a catalyst system

a reinforcing agent

The resin system and all the additives in the resin may be considered purely as a 'paint to which is added the glass to

produce a tougher and more dimensionally stable product. Let us consider these components in more detail.

3.1 Glass mat

The glass mats used in prepregs may be subdivided into three groups:

chopped strand mat

mechanically bound mats (needled mats)

continuous strand mats.

Their properties are illustrated in Table 1.

3.2 Fillers

Fillers are used in glass/polyester systems for two main reasons:

(a) They reduce costs, and filler/resin ratios of the order of 50 : 50 and 60 : 40 are not uncommon, and can be tolerated if the fillers are low oil absorption types, which do not produce excessive increases in viscosity.

(b) They reduce the amount of heat generated during cure of a moulding, and therefore reduce shrinkage and warping. The shrinkage of a filled system is that of the unfilled resin multiplied by the volume fraction of the unfilled resin in the system.

Many fillers are available for incorporation in prepregs, Including sulphates of alkaline earths, silicates, and carbonates of alkaline earths. These could also be further subdivided into natural fillers and fillers produced by chemical precipitation.

The following properties are required in fillers for preimpregnated glass mat systems:

Low oil absorption

Easy dispersion in the resin system

Low cost.

Particle size distribution between 1-15 microns with a mean statistical diameter of 2-5 microns.

Low specific gravity

Chemical purity, and free from heavy metal ions

Low solubility in water to maintain low water absorption in the laminate.

3.2.1 Improvement of appearance

Fillers in preimpregnated glass mat reduce the tendency to surface 'crazing' of moulded parts. This is due to the reduction of heat developed at the exotherm stage, as the material cures. The consequent reduction in shrinkage reduces the strain which causes surface, and internal defects.

The surface appearance of moulded parts is also improved because fillers impart opacity, thus improving the tinctorial strengths of the pigments used.

3.2.2 Effect of fillers on curing characteristics

It is known that all mineral fillers have an effect upon the curing characteristics of a resin system. Because of the diluting effect, most fillers reduce the peak exotherm and therefore increase the gel time of a resin system. Some fillers accelerate or retard the rate of cure by affecting the catalyst system. This is usually due to the presence of impurities in the filler or surface treatments. It is preferable in impregnated glass mat materials to use non-absorbent fillers i.e. those that are crystalline and possess a low specific surface.

3.2.3 Properties of pigments

These can be considered under the heading of fillers. Pigments should possess heat, light and chemical stability. They should not affect the gel characteristics of the resin system, or the shelf life characteristics of preimpregnated mat systems. Copper phthalocyanine and chlorinated phthalocyanine, carbon blacks and some azo pigments are not considered suitable for prepreg systems.

In general it has been found that inorganic pigments, with the exception of the iron oxide type, have least effect upon the curing characteristics of the resin system. Pigments are usually supplied predispersed in a carrier such as dibutyl phthalate, in order to facilitate dispersion in the polyester resin mix, and obtain maximum shade and strength. Soluble organic dyestuffs may be used provided that their effect upon the cure time has been shown to be negligible. If the system contains carbon black as a pigment, the effect is to retard the cure unless special catalyst systems are employed.

3.3 The resin system

3.3.1 Rate and extent of gellation

A typical preimpregnated glass mat material consists of a glass mat that has been impregnated with a filled polyester resin mix-containing a catalyst system and in which the

TABLE 1

Properties and types of glass mat used in polyester prepregs

Type of mat	Method of manufacture	Binder	Finish on glass fibre	Properties and uses
Chopped strand	Random deposition of 2" fibre	Emulsion	Chrome or silane or mixed	Good drape properties. Hand lay-up process. Subdued fibre pattern.
Chopped strand	Random deposition of 2" fibres	Powder (soluble)	Usually silane or chrome/silane	Hand lay-up where improved mat strength is required. Better water resistance. Matched die metal moulding. Continuous impregnation.
		Powder (insoluble)	Usually silane	Matched die moulding. Poor drape properties. Continuous impregnation process. High grade translucent laminates. No washing of the fibres during pressing.
'Mechanical'	Random deposition of fibres onto a packing tissue (usually glass)	Fibre 'needled' through the base tissue	Chrome or silane	Limited useage. Matched die metal moulding. Vacuum bag (or pressure) application. Continuous impregnation. Good dimensional stability.
'Swirl mat'	Continuous fibre deposition onto a moving conveyor	Nil (powder or emulsion sometimes used)	Usually silane	Good strength. Very good dimensional stability on moulding. Matched die metal moulding. Can be deformed to mould contour. Continuous impregnation.

resin has been allowed to attain a highly viscous state. The mat should be non-tacky and easy to handle. To obtain this highly viscous non-tacky state, without resorting to the free radical polymerisation reaction, use is made of metal oxides, usually from group IIA, e.g. Calcium or Magnesium. Other substances have been used such as Zinc Oxide, Aluminium Oxide, Aluminium hydroxide and Stannous Chloride. It is the usual practice to use Magnesium Oxide as the agent to bring about gellation of the filled polyester, impregnated glass mat, and it is interesting to consider the various reactions that theoretically possible to bring about this change. They are:

(a) HOOC — COOH + MgO → HOOC — COO Mg OH
polyester molecule

(b) HOOC — COO Mg OH + HOOC — COOH →
HOCC — MgOOC — COOH + H_2O

(c) HOOC — COO Mg OH + HO Mg OOC — COOH →
HOOC — COO Mg — O — Mg — COO — COOH + H_2O

(d) HOOC — COO Mg OH + HO Mg OOC — COOH →
HOOC — COO Mg OOC — COOH + $Mg(OH)_2$

(e) HOOC — COO Mg OH + MgO →
HO Mg OOC — COO Mg OH

The viscosity of the magnesium basic salts of the polyester is not much greater than that of the polyester resin in styrene, and thus any increase that occurs in viscosity is due to joining of polyester chains via magnesium oxide (Ref. 7).

It is reasonable to assume that the heterogeneous reaction (a)—the reaction of MgO and polyester—is slow, compared with the other reactions which are homogenous as the components are soluble in styrene. This explains the fact, as shown in Fig. 1, that the slope of the viscosity/time graph increases with increasing magnesium oxide concentration. In other words, the basic magnesium salts of the polyester react faster with the end carboxyl group of another polyester chain, than does magnesium oxide itself.

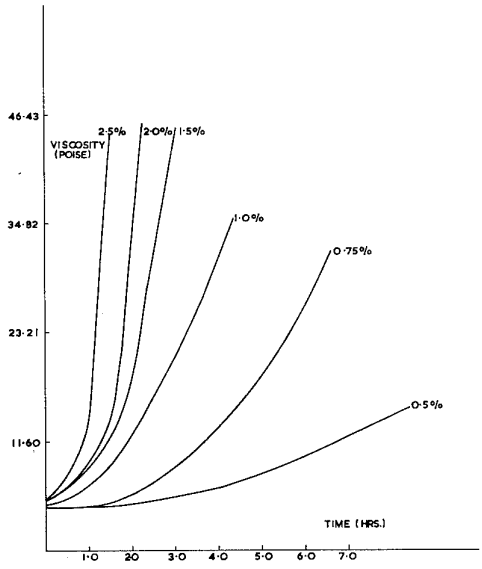

Fig. 1 Effect of concentration of magnesium oxide on the rate of gelation of a polyester resin (acid value 27)

It is doubtful whether reaction (c) would take place since after the addition of magnesium oxide in an amount greater than that necessary to take (e) to completion, the amount of magnesium combined with the polyester was found to correspond to a single magnesium atom bridging two polyester chains. Further it is also unlikely that reaction (d) would take place due to the improbability of randomly moving long chains assuming the required orientation and proximity of the—MgOH ends to allow reaction to take place. If reaction (a) was faster than that of reaction (b) then reaction (e) would become significant and the viscosity of the polyester would not attain a high value.

Provided that sufficient magnesium oxide is present to link each polyester chain (an amount dependent upon the acid value of the resin) and assuming that the basic salts of the polyester do react with carboxylic acid groups then a very high viscosity is possible i.e. reaction (b).

Magnesium hydroxide has been suggested as a possible gelling agent, but as Fig. (2) shows it is not as effective as magnesium oxide.

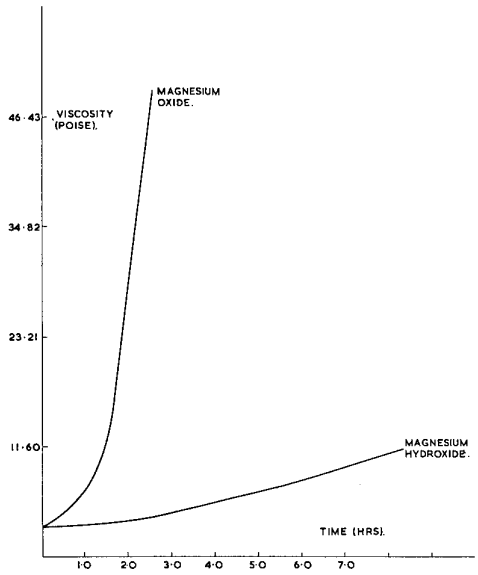

Fig. 2 Rate of gelation of a polyester resin (acid value 27) with magnesium oxide, and magnesium hydroxide at a concentration of 2%.

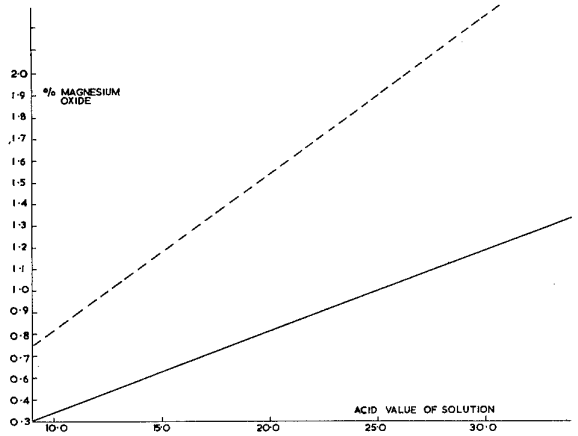

Fig. 3 % theoretical amount of M_3O necessary to give 1 polyester molecule. % theoretical amount of M_3O necessary to give Mg basic salt of polyester. % MgO (based on resin) 1. 2%

Fig. 3 compares the theoretical amount of magnesium oxide necessary to join all the polyester chains and yield one long chain, with the amount necessary to yield the magnesium polyester basic salt with — MgOH at each end of the chains. It is assumed here that all the end groups of the polyester are carboxylic and that none are glycol fragments. The correct amount of magnesium oxide to use must fall between these two lines, and depends upon the acid value of the resin system.

Other gelling agents can be used e.g. Aluminium Dioctoate. This will gell polyester systems, but not sufficiently to produce a 'tack-free' product. The use of aluminium dioctoate can bring about an increase in the water resistance of the final laminate. Anhydrous stannouse chloride will also gell polyester resins and the resulting gelled material is clear, but the extent of gellation is much inferior to that obtained using magnesium oxide.

zinc oxide also shows weak gelling properties but does not dissolve fully, and produces an opaque product. Aluminium chloride and silicon tetrachloride, have been tried and shown to produce no increase in the viscosity of polyester systems.

Amines failed to bring about gellation and the oxides of less basic metals are also ineffective. To date it would seem that the best gelling agent is magnesium oxide.

Magnesium oxide gelled polyester impregnated glass mat materials, in which the polyester chains have been linked to such an extent that the melt viscosity is extremely high will not give adequate flow on moulding. The effect is similar to phenolic resin impregnated materials which have been over-aged or over precured. The effect is irreversible and the material passes straight from the highly gelled to the completely crosslinked cured state on heating. The polyester chains are so long and entwined that the application of heat cannot 'unfreeze' them. Materials in this state of overgellation have occasionally found their way into moulding shops and tended to give prepreg a bad name. Only a basic understanding of the MgO/polyester reaction and methods of controlling it can give a guarantee against this sort of occurence. It is now possible to control flow properties and extend shelf life predictions as a result of such an understanding.

3.4 Curing characteristics of varous resin systems

Much information has been published with regards to the curing characteristics of polyester resins. These have usually been concerned with D.M.Cs, and hand lay up processes, but basically the same principles apply to resin in preimpregnated mats.

The shelf life of preimpregnated glass mats should be long enough to enable material to be transported to the moulder and stocked by him for a reasonable time, without significant change in mouldability. The 'shelf life' will of course depend upon the temperature of storage. It is controlled by the use of inhibitors added to the resin/filler mix, and most manufacturers of preimpregnated glass mats closely guard the inhibitor used in their own particular system. Inhibitors can be divided into two groups, namely true inhibitors and retarders.

3.4.1 Inhibitors

These react with and destroy free radicals from the catalyst system, or they neutralise active polymer growth centres. Only after the stabilising inhibitor has been decomposed completely does polymerisation of the resin system proceed in the normal way. Thus a certain amount of catalyst is 'wasted' when used in conjunction with these inhibitors. Inhibitors of this type are phenols, di or polyhydroxyphenols, aromatic amines, particularly p-phenylene diamine, benzaldehyde, ascorbic acid, hydroquinone, and some sulphur compounds. All have the property of accepting electrons from free radicals. Increase in temperature will of course increase the rate of degradation of the catalyst system, which in turn will use up the inhibitor faster, so that the effect of increasing storage temperature even with inhibitors present is to reduce the shelf life of the polyester system.

3.4.2 Retarders

These are compounds which cause stabilisation of the resin at ambient temperature and will modify the rate of cure at elevated temperature. To this class of retarder belong such compounds as substituted p-benzoquinones, quaternary ammonium salts, and salts of substituted hydrazines. The use of retarders causes a delay in the action between catalyst free radicals and the polyester chains.

Flory (Ref. 8) states that if a substance is added to the monomer, which reacts with free radicals to yield either a non-radical product or a radical with such low reactivity that the growth of chains in suppressed, then the substance is an inhibitor. Alternatively if its action is less efficient, so that the rate of polymerisation and degree of polymerization is reduced without total suppression of the reaction then the substance is referred to as a retarder.

The effectiveness of a retarder is governed by its solubility in the resin system. Retarders in preimpregnated glass mat systems are effective in the range of 0.005—0.15% concentration by weight. Fig. 4, 5 and 6 show the effect of retarders —a quaternary ammonium salt and phenylhydrazine, and an inhibitor,—hydroquinone on a medium reactivity resin system, catalysed with t-butyl perbenzoate at 176°C.

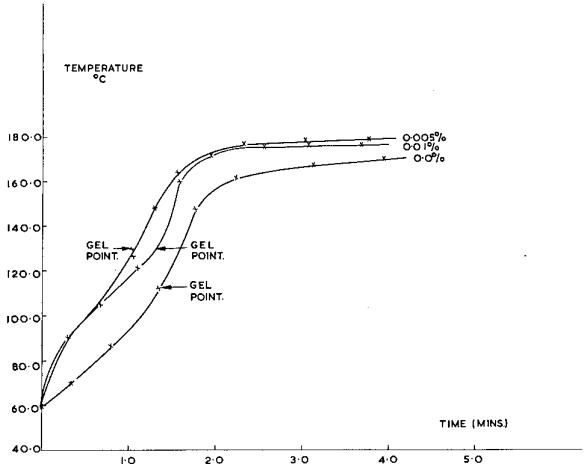

Fig. 4 Effect of cetyl trimethyl ammonium bromide on the rate of cure of a medium reactivity resin. Catalysed with t-Butyl Perbenzoate. Temp 176°C.

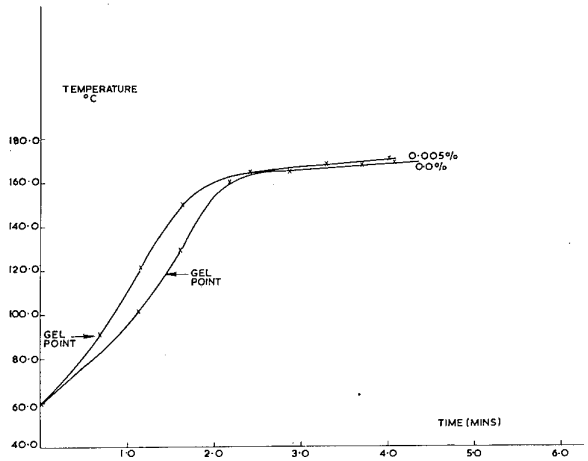

Fig. 5 Effect of phenylhydrazine on the cure rate of a medium reactivity resin catalysed with t-Butyl perbenzoate at 176°C

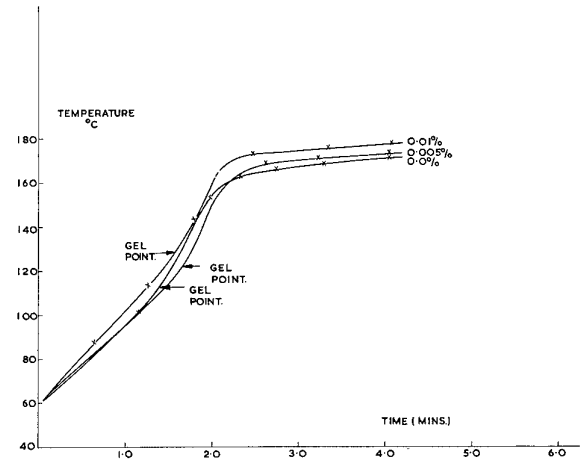

Fig. 6 Effect of Hydroquinone on the cure rate of a medium reactivity resin catalysed with t Butyl Perbenzorate at 176°C

In the case of the phenylhydrazine, a greatly reduced gel-time is obtained but the effect on cure time is negligible. The quaternary ammonium compound on the other hand displays

a dual role, acting both as an inhibitor and an accelerator. It increases shelf life slightly and also increases the temperature at which gellation occurs, thus behaving as a normal inhibitor. The inhibition effect however is off-set by an increase in polymerisation once the critical temperature is reached, so that the overall gel-time is not affected.

Hydroquinone will give a prolonged shelf life in glass fibre/polyester systems and is essentially an inhibitor. With hydro-hydroquinone an increase in the gel temperature is obtained and also an increase in the gel-time. This inhibition effect makes hydroquinone unsuitable for use in preimpregnated glass mats. It is therefore important, when selecting an inhibitor for a preimpregnated glass mat system to give good shelf life, that the effect of the inhibitor upon the curing characteristics of the particular resins system is taken into account.

3. 4. 5 Catalyst system

The catalyst system used in preimpregnated glass mat systems are of the free radical types. These catalysts decompose at a weak bond between two atoms under the influence of heat, and split up into two or more parts, each containing a free electron.

Each part is known as a free radical and is a highly reactive chemical entity due to its high internal energy. A free radical will remove a single electron or a group of electrons from other molecules, or add onto an unsaturated group and in doing so, the internal energy of the free radical is destroyed.

The following general points apply to catalyst systems for polyester resins.

1. The critical temperature of a catalyst is the temperature at which free radicals are rapidly produced as a result of thermal decomposition.
2. The chemical composition of the catalyst determines the critical temperature, and also the rate at which free radicals are produced.
3. The higher the concentration of free radicals the greater the rate of reaction for a given polyester resin.
4. For a given catalyst system, a higher moulding temperature will produce more free radicals, so that the polymerisation reaction is faster, and therefore the cure time shorter.
5. The gel point is dependent on the catalyst system, and also its concentration.
6. Above the critical temperature of the catalyst very rapid curing occurs. Slow cures result when the moulding temperature is near the critical temperature.

The temperature/time curve as shown in Fig. 7, is typical for polyester/catalyst systems. AB is the initial heating curve of the resin/catalyst system. BC is the rapid temperature rise due to the heat given out as the polyester resin polymerises and cures. Point B denotes the gel point of the resin system, and is dependent on the type and concentration of the catalyst. The maximum temperature obtained (point C) is usually higher than the heating bath temperature (T3).

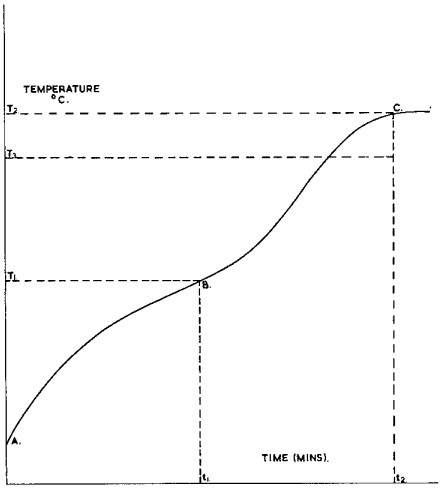

Fig. 7 General curve for a catalysed polyester resin system.

The peak exotherm is given by (T2 − T1), the time (t2 − t1) is the cure time for a particular resin/catalyst system and is directly related to the moulding conditions.

Let us consider three types of polyester resins, namely a high, medium and low reactivity resin. The differences in reactivity have a pronounced effect upon the flow properties (Figs. 8, 9, 10) and this is independent of the catalyst type used.

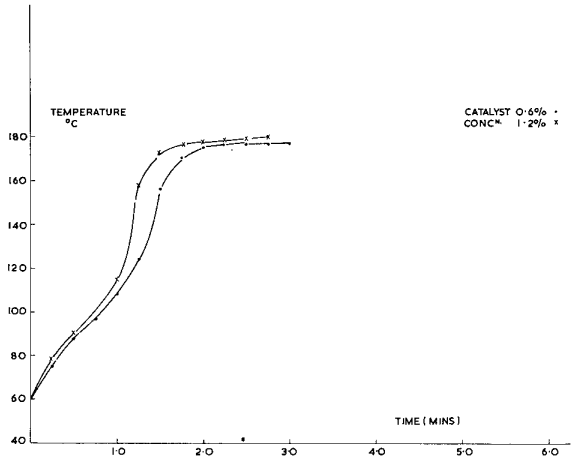

Fig. 8 Effect of t-butyl perbenzoate concn. on a high reactivity resin at 176°C

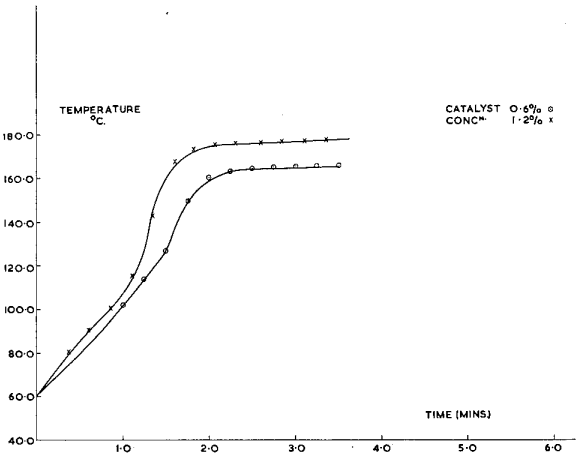

Fig. 9 Effect of t-Butyl Perbenzoate concn. on a medium reactivity resin at 176°C.

The initial rate of heating is similar for all resins up to the gel point since this is controlled by the thermal conductivity and specific heat of the polyester resin. A high reactivity resin will gel faster than a low reactivity resin because there are more unsaturated double bonds available. The rate of reaction is directly proportional to the concentration of reactive groups. Each type of resin system gives out an amount of heat which is proportional to the number of bonds formed on curing, and since a high reactivity resin reacts the fastest, the heat has less time to be dissipated to the environment, so that a higher temperature rise occurs for a medium or low reactivity resin.

The ability of the glass fibre polyester system to flow, and follow the contours of the mould is dependent on the temperature at the gel point. The longer the time taken to reach the gel point, the greater the flow. The low reactivity resin has a longer gel time than either the medium or high reactivity resin and therefore will have greater flow properties. The medium, or low reactivity resin systems are therefore, better for deep draw moulding rather than a high reactivity system.

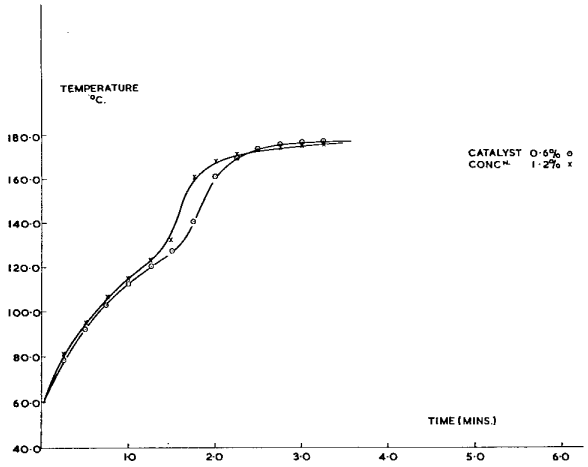

Fig. 10 Effect of t-butyl perbenzoate concn. on a low reactivity resin at 176°C.

After the gel point the resin will not flow because now it has become one large polymer network. However there is still some unsaturation present, which permits further polymerisation until complete cure is obtained. The resin has cured when no further reaction takes place; this is indicated for all practical purposes by the point of the maximum temperature on the graph.

The moulding temperature available will determine the type of catalyst to be used in a preimpregnated glass mat system and the prepreg manufacturers will take this into account and may even need to use specific catalysts for particular applications.

I Benzoyl peroxide

Benzoyl peroxide has a critical temperature of 50°C and is a very rapid curing catalyst. When used with a high reactivity resin system at 130°C the gel time is very short, so that little or no flow occurs. The very rapid cure produces a high peak exotherm temperature which is undesirable, since a high internal energy result in the final moulding. This in turn leads to shrinkage, warping, surface cracking and crazing and fibre pattern.

Benzoyl peroxide would be considered suitable for a non-flowing grade for use at temperatures up to 130°C. It is not considered suitable for higher moulding temperatures.

II t-Butyl-percrotonate

t-Butyl-percrotonate has a critical temperature of 90°C, and is suitable for moulding at temperatures of 130-150°C. The gel time is long, and is virtually independent of catalyst concentration and reactivity of the resin system. High flowing grades of preimpregnated/glass mat can therefore be produced from the catalyst. Such materials are suitable for deep-draw mouldings. Percrotonate will allow greater control over the flow and moulding characteristics of the glass fibre/resin systems, since the concentration of catalyst does not have a pronounced effect upon the cure time. Thus the gradual loss of catalyst activity with time in storage, has little effect on moulding characteristics.

III t-Butyl-perbenzoate

t-Butyl-perbenzoate has a critical temperature of 130°C, which restricts its use to moulding temperature of 150-180°C. Within this range it is a very rapid curing catalyst. Gel time for most resin systems are short and difficulty can be experienced in producing a high flowing grade. The peak exotherm does not normally reach the moulding temperature so that the internal energy of the moulding is at a minimum which gives strain free mouldings. Other catalyst systems can be used in preimpregnated/glass mats such as dicumyl peroxide, t-butyl peroctoate, t-butyl perisononanoate, and 2.4 dichloro benzoyl peroxide. These do not offer any general advantages over the systems mentioned previously and are only used for special applications. It can be seen, then, that by use of the right catalyst system, grades of preimpregnated glass mat can be produced to mould at temperatures within the range of 130° to 180°C.

3.4.4 Unsaturated monomers

I would now like to discuss briefly the use of different monomers which can be used in preimpregnated glass mat systems. The fact that unsaturated vinyl monomers such as styrene could be copolymerised with polyester resins has been known for some time (Ref. 9, 10, 11, 12, 13). Styrene monomer is the most common monomer used in preimpregnated glass mat systems as it is both readily available and cheap. Its action is twofold, it is a solvent for the unsaturated polyester resin and it also copolymerises with the polyester resin. The styrene monomer concentration affects the physical properties of the cured laminate, and for an optimum polyester system it is desirable that the ratio of monomer to double bonds is about 1 : 1 (Ref. 14). For a general purpose polyester resin having a ratio of maleic anhydride to phthalic anhydride of 1 : 1 usually 20% by weight of styrene is required for equimolarity. Increase in the styrene content beyond this level results in a deterioration in the strength properties of the resin.

Diallyl Phthalate

Diallyl phthalate is a colourless, high boiling liquid which has the ability to react with both unsaturated monomers and resins. Because of its low volatility and long shelf life it can be used in preimpregnated glass mat systems to impart longer shelf life, less shrinkage and slower cure. It also improves resistance to solvents and heat and gives a higher rigidity to the cured product.

Methyl Methacrylate

Methyl methacrylate can be used in conjunction with styrene in the polyester system. The final laminates have been found to possess good translucency and colour retention during weathering. Disadvantages of using methyl methacrylate are its low boiling point when compared to styrene, and greater volume shrinkage on curing.

4. FLAME RETARDANCY

Within the last few years a greater need has arisen for polyester/glass mat systems that are either flame retardant or self extinguishing, especially in the building industry, and for mouldings associated with the electrical industry. Self extinguishing grades are materials that in the cured state do not continue to burn after withdrawal of a small flame. The methods of reducing the burning rate of glass fibre/polyester laminates can be brought about in three ways.

4.1 Addition of inorganic fillers

The most widely used of the inorganic filler to impart flame proofing is Antimony Oxide. It is however expensive and has a high density. It also imparts opacity and increases the softness of the laminate. When antimony oxide is added to a prepreg system in conjunction with a chlorinated organic compound, it reacts during combustion to produce antimony trichloride which has the effect of 'poisoning' the flame.

Many other inorganic compounds have been reported to the effective fire retardants. These are aluminium hydroxide, zinc borate, calcium borate, sodium silicate, ammonium sulphate, zinc oxide, calcium sulphate, ammonium bromide, aluminium chloride, talc and ammonium borate.

4.2 Addition of organic compounds

Chlorinated paraffins are probably the most widely used as flame retardants. Their action as flame retardants is due to 'blanketing' effect of the flame by release of chlorine at the high flame temperatures. It is normally used conjunction with Antimony Oxide.

The use of Dibromostyrene (Ref. 15) or dichlorostyrene (Ref. 16) have been reported to improve the flame retardancy in polyester resins when used as the cross linking monomer, either with styrene or along. The dichloro compound is not considered to be as effective as the dibromo compound. To achieve good self-extinguishing properties in polyester resins

it has been found that 30% of aromatically bound chlorine is necessary. Pentabromotoluene has been claimed to be a very effective flame-retardant, because of its high Bromine content (82%) (Ref. 17, 18). It has also been shown that self extinguishing polyester resins can be obtained by introducing polytrifluorochloroethylene and antimony oxide into the resin (Ref. 19). Improvements can also be brought about by the use of organo-metallic compounds of the type (RO)n M where M is boron, silicon, titanium, tin, lead, arsenic, bismuth R is a vicinal dihaloalkyl group.

4.3 Modification of the resin system

Polyester resins possessing good flame retardant properties have been developed with chlorinated phthalic acids in the polyester chain. The use of H.E.T. acid (Chlorendic anhydride) Ref. 20 is one such example.

Another compound chloran T.M. or 2. 3. dicarboxy 5. 8. endomethylene 5. 6. 7. 8. 9. 9. hexachloro 1. 2. 3. 4. 4a. 5. 8. 8a. octahydronaphthalene anhydride is also commercially available for use as the saturated acid component in polyester systems as a means of incorporating chlorine into the polyester chain.

Slagel, Shulman and Young (Ref. 21) claim polyesters based on 2. 3. Bis (ethylene carboxy) 1. 4. 5. 6. 7. 7. hexachlorobicyclo (2. 2. 1.)-5-Heptene as the unsaturated acid component.

Combinations of the various types of compounds described above, can be used, but when dealing with modified polyester resin systems the effect on the rate of gellation with magnesium oxide must be determined before these compounds are incorporated into a preimpregnated glass mat system.

5. MOULDING CONDITIONS

The advantages to be gained from using a preimpregnated glass mat material, based on a polyester resin, over most other thermosetting materials are:

1. Easy flow
2. Comparatively low moulding pressures
3. Rapid cure
4. No evolution of gaseous products.

Although moulds, presses and moulding conditions for D.M.C's are applicable to prepregs, the highest quality mouldings are produced on moulds designed especially for preimpregnated glass mats.

5.1 Moulding temperatures and times

Prepregs can be cured at temperatures in excess of 120°C (250°F), but it is recommended that for most applications the temperature range should be between 130°C (265°F) and 150°C (302°F). An accurate temperature guide cannot be given since deep draw and complicated mouldings, where high flow is required, usually require lower temperatures to ensure complete filling of moulds. High temperatures and higher pressures will produce a better surface finish. On simple shapes, where fast cycling is required, temperatures of 160° (320°F) to 170° (357°F) may be employed.

It is normal practice to maintain both punch and die at the same temperature, but in some cases small temperature differences between the male and female tool may be employed. In this case the moulding will be retained on the half of the tool which is at the lowest temperature. The cure time will vary with the shape and thickness of the moulding.

Where thick section mouldings are involved and also where dimensional accuracy is of importance, completion of the cure in the mould is recommended. A cure time in excess of the recommended minimum should not affect the properties of the mouldings. Post stoving of a prepreg should not affect the physical properties, but prolonged heating at elevated temperatures after cure could affect the physical properties and also in some cases lead to blisters being developed on the surface.

5.2 Moulding pressures

Since, in a preimpregnated mat no volatiles are liberated, comparatively low moulding pressures can be employed.

Mats can be moulded at pressures as low as 200 p.s.i. for a simple shape, but for mouldings that are complicated, or mouldings with deep draw sections, higher pressures are recommended. The design of the mould to some extent will govern the pressure required to produce mouldings. An open flash mould will in general required a lower pressure than a semipositive mould. A higher pressure than required can lead to difficulties due to excess 'flashing' especially down ejector pin bushes.

5.3 Press operation

Because preimpregnated glass mats are fast curing, fast operating presses are required. Any delay during press closure can result in some precure of the material which is in contact with the mould taking place. This restricts the flow of the material and results in short or oversize mouldings, particularly when high moulding temperatures are involved. It is not necessary to breathe the press during mould- since no gaseous by-products are evolved. Presses with fast initial closing speeds are recommended, but a slow closure over the final stage is preferred, as this prevents air from being trapped in the mould, and also aids the flow into 'blind cavities'. The initial press closure should be complete after 6. 8 secs in order to minimise precure, slow closure over the last $\frac{3}{4}$" (19 mm) to $\frac{1}{4}$" (6. 4 mm) of travel is recommended since this assists the production of strong dense parts and prevents excessive flash and can often compensate for a loose or worn mould.

5.4 Mould loading

The charge for the mould can either be preweighed or cut to the required shape using a template. It is desirable, which ever method is adopted, to cover at least 70% of the mould surface. In cases where deep draws are concerned, it may not be possible to cover 70% of the mould surface. In these cases as large an area as possible should be covered by the charge. On simple mouldings, with shallow draws, up to 95% of the mould surface can often be covered. The mould should never be loaded with two separate charges of material, since this causes weak areas at the junction of the two charges. This is known as a 'weld-line'. It is also an advantage to keep the shape of the charge as simple as possible, in order to eliminate flow lines. For large flat or simple curved areas it is not recommended to make up charge weight by the addition of small pieces, since this can lead to blistering, flow lines and fibre pattern on the surface.

5.5 Extraction and the use of cooling jigs

It is normal practice to include a mould release agent in the preimpregnated glass mat, usually zinc Stearate. It is however advisable to apply extra mould release agent to a new tool, or one that has been out of service for some time. Suitable release agents for this purpose are Carnauba Was or Stearic Acid dissolved in either Xylene or toluene. For deep draw mouldings, with almost vertical wall sections it is sometimes necessary to apply mould release agent after every lift. Extraction of mouldings is normally carried out by means of ejector pins, although in many cases the use of compressed air is very effective.

For flat mouldings or channel sectioned mouldings it is sometimes desirable to jig-cool to alleviate the strains that are built in during normal cooling. To some extent warping and shrinkage can be avoided at the formulation stage by suitable choice of catalyst and resin.

6. PROPERTIES OF PREIMPREGNATED GLASS MATS

It is normal practice to supply prepregs with glass contents varying from $17\frac{1}{2}$% to $33\frac{1}{3}$%. The materials is supplied in roll form, interleaved with polyethylene film, and the roll wrapped in a suitable material such as regenerated cellulose to minimise the loss of styrene on storage. The preimpregnated glass mat as supplied to the customer is easy to handle, and can be cut with either knife or scissors. The polyethylene film ensures freedom from contamination before use and is removed prior to moulding.

Mouldings produced from a preimpregnated mat have the following properties:

1. Good mechanical strength
2. Good electrical properties
3. Excellent dimensional stability
4. Good water resistance
5. Good heat resistance

Tables 2 and 3 compare the properties of low, medium and high glass content prepregs.

It can be seen from these results that high strength, tough dimensionally stable products can be obtained. Table 4 and 5 show comparative values for D.M.C's.

6.1 Heat, water and chemical resistance

Preimpregnated glass mats in general have good heat resistance and when tested at room temperature, after stoving at 150°C for 100 hours show a strength retention of 50%.

Where strength is not of the utmost importance mouldings may be safely used at temperatures of 150°C and a temperature of 200°C may be tolerated for short periods of time.

Weathering tests have shown that although the surface appearance may be impaired, fade, and loss of colour may take place. In general the loss of mechanical properties is only slight.

The effect of water immersion on the mechanical properties is relatively small.

For resistance to boiling water it is desirable to formulate the prepreg with resin systems based on Bisphenol A, hydrogenated Bisphenol A, or Isophthalic acid.

Prepreg mouldings are only slightly affected by aromatic and aliphatic solvents, mineral oils, alcohols and petroleum spirit. They are attacked by chlorinated hydrocarbons, ketones and esters. Resistance to dilute acids is fairly good, but degradation occurs under strong alkaline conditions.

TABLE 2

Physical test results of high, medium and low glass content grade prepregs

Property	Type		
	Low glass content	Medium glass content	High glass content
Tensile strength			
p.s.i.	8 000-10 000	10 000-12 000	13 000-15 000
Kg/cm^2	560-700	700-840	900-1052
Tensile modulus			
p.s.i.	$1.5\text{-}1.6 \times 10^6$	$1.6\text{-}1.7 \times 10^6$	$1.7\text{-}1.8 \times 10^6$
Kg/cm^2	$1.05\text{-}1.1 \times 10^5$	$1.1\text{-}1.2 \times 10^5$	$1.2\text{-}1.5 \times 10^5$
Cross breaking strength			
p.s.i.	18 000-22 000	24 000-26 000	28 000-30 000
Kg/cm^2	1 250-1 550	1 650-1 800	1 950-2 100
Flexural modulus			
p.s.i.	$1.5\text{-}1.6 \times 10^6$	$1.5\text{-}1.6 \times 10^6$	$1.5\text{-}1.6 \times 10^6$
Kg/cm^2	$1.05\text{-}1.1 \times 10^5$	$1.05\text{-}1.1 \times 10^5$	$1.05\text{-}1.1 \times 10^5$
Shear strength			
p.s.i.	10 000-12 000	10 000-12 000	12 000-14 000
Kg/cm^2	700-840	700-840	840-980
Impact strength			
ft lb/in	6-7	6-7	6-7
Water absorption			
mgms	22	22	22
Barcol hardness	58	57	58
Specific gravity	1.74 ± 0.01	1.77 ± 0.04	1.80 ± 0.03

TABLE 3

Electrical properties of high, medium and low glass content grade prepregs

Properties	Type		
	Low glass content	Medium glass content	High glass content
Insulation resistance ohms	$1.0\text{-}1.2 \times 10^{13}$	7.0×10^{12}	6.0×10^{12}
Electrical strength in water	withstood 3 KV	withstood 3 KV	withstood 3 KV
Electrical strength in oil V/mm	180	180	180
Surface resistivity $\log_{10}$ ohms	15.0	15.0	15.0
Volume resistivity $\log_{10}$ ohms cms	15.0	15.0	15.0

TABLE 4

Physical test results for two types of dough moulding compounds

Reinforcement	Glass/sisal	Glass
Form	Fibrous dough	Extruded rope
Property		
Tensile strength		
p.s.i.	4 000-8 000	6 000-10 000
Kg/cm^2	280-500	420-700
Flexural strength		
p.s.i.	10 000-16 000	10 000-16 000
Kg/cm^2	700-1 120	700-1 120
Flexural modulus		
p.s.i.	$1.0-1.4 \times 10^6$	1.0×10^6
Kg/cm^2	$0.7-1.0 \times 10^5$	0.7×10^5
Impact strength ft lb $\frac{1}{2}$ in notch	2.0-3.5	1.0-2.0
Specific gravity	1.9	1.70
Water absorption 24 hrs at 23°C (73°C)	10-170 mgs	12-25 mgs

TABLE 5

Electrical properties of two types of dough moulding compounds

Reinforcement	Glass/sisal	Glass
Form	Fibrous dough	Extruded rope
Property		
Electrical strength 20 sec value at 90°C (194°F)		
V/mil	100-150	200-300
KV/mm	4.00-10	8.0-12.0
Volume resistivity log 10 ohms cm	13-15	14-16
Surface resistivity (after 24 hrs immersion in water at 23°C) log 10 ohms	7-10	12-15
Power factor at 10^6 cycles/sec	0.015-0.02	0.008-0.012
Permittivity at 10^6 cycles/sec	5.0-6.0	4.0-4.5

For improved chemical resistance it is usual to use a 'silica' filler in conjunction with an isophthalic resin system.

7. APPLICATIONS

Preimpregnated glass mat is the logical development of a Dough Moulding Compound. So much so that these materials are often referred to as sheet moulding compounds. By control of the material at the manufacturing stage the customer is assured of a constant glass/resin ratio in his mouldings. This means that consistant mouldings can be produced, simply, at high production rates.

The uses are numerous and varied, some of these include automotive parts i.e. facia panels, gearbox covers, fan-cowlings, battery box holders, bonnets and roof bracing struts. Welding masks and safety helmets have been successfully moulded from prepregs. Other applications include electric light fitments, chair shells, lawn mower covers, typewriter covers, engine cowlings. Within recent months considerable interest has developed in the use of prepregs in the container field by facing plywood. Future expansion will occur in the automotive trade where the use of prepregs is expected to increase considerably over the next few years.

Interest is also shown in the building industry for cladding outside walls of buildings and interior decoration. The building regulations will govern the type of prepreg that can be made available to this industry.

In the few short years that prepregs have been available to the general consumer, considerable advances have been made in the quality and range of materials on offer. The prospects for further penentration of markets now held by traditional materials are excellent and useage of prepregs is expected to increase considerably over the next few years.

In concluding I would like to thank the Directors of Turner Brothers Asbestos for permission to publish this paper and my colleagues in the Moulding Materials and Physics Research Departments for their help in its preparation.

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PAPER NO.

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The philosophy of marketing

R. COLLISCHON, The Institute of Marketing

In the History of commerce, marketing has only recently emerged as a preoccupation of top management, and in the process a certain amount of confusion has arisen about the meaning of the term.

To some it represents no more than a new and impressive name for existing sales management and sales activity; to others it implies at best an enlargement of the area in which sales planners will have an influence in future. In a third and more perceptive group marketing is recognized as involving a fundamentally altered attitude of mind among businessmen, bringing in its train a whole array of new techniques to be applied in consequence.

TODAY'S NEEDS

The essentials of the marketing idea, and its practice, have of course been understood since time immemorial, but its progress to a place of dominant concern in the minds of businessmen has been impeded by tradition of another kind. This is the tradition of proud over-emphasis laid by producers upon the significance of the particular goods they choose to make; it is a tradition derived from generations of success as pioneers of industrial production in a former era; a tradition tending to disregard the circumstances in which production is undertaken today, and of the changing needs and nature of the society that consumes it.

It has been easier, and until recent times apparently more rewarding, to concentrate on how to make things than to study what makes poeple want things. A great wealth of ingenuity has been focused on the production side of industry and commerce; and powerful groupings have taken shape, to maintain and give weight to particular production interests.

Product-consciousness (and the dust and uproar of the battle between employers and employed in production) has tended to obscure the interest of the third group deeply involved in the whole process—namely, the consumers of the production, that unorganized element in the community whose money supports production and provides its wages and profits.

Adam Smith's 18th-century dictum has been neglected at great cost, but its relevance remains as topical as today: 'Consumption is the sole end of all production, and the interest of the producer ought to be attended to only so far as it may be necessary for promoting that of the consumer'.

There could hardly be a better text to show where the emphasis in production should lie, and the marketing concept, in its essence, is concerned with precisely that shift of emphasis from interest in production to interest in consumption. Marketing is concerned with people first and their need for satisfactions, and only thereafter with organization and production to meet that need. Having made this fundamental change in their approach to business, a number of organizations have achieved a dazzling success and prosperity, often on an international scale.

The impact of modern marketing approaches and methods has echoed around the commercial world, and tradition-encumbered producers are now increasingly confronted by competition of a new and compelling kind. Indeed, technolcgy has greatly enlarged the capacity to produce, but the cost of failure to dispose of production has grown to disastrous proportions in money and waste, and it has become sensible to think in terms of how production may be disposed of, before production is started.

PANOPLY OF SKILLS

This is what marketing is about. It starts with the consumer and his needs, actual or potential. It sees the beginning of wisdom in the skilled, organized and continuous application of marketing research, in which a whole panoply of skills is now available, based on every scientific discipline from mathematics and statistics to sociology and the study of behaviour. Marketing asks, what can we sell? and then, and then only, how can we make it?

Once the nature and extent of demand, actual or implied, has been verified (as closely as ingenuity, effort and treasure will allow) everything that a marketing organization has in the way of imagination, flair and skill in planning design and production is then coordinated and directed to the profitable satisfaction of that demand. The whole organization is directed to this sole end, and the coordinator of all its efforts is marketing management.

AFTER RESEARCH

A product or service is developed in the light of market research and meticulously calculated probability. Now, if the need for the product is to be met efficiently, and if many are to be satisfied, that product or service must be made known in terms that are meaningful and reassuring to the consumer and that show what benefits there are on offer for him. This process of communication between producer and consumer is accomplished via all or a combination of today's many communication media.

After research, advertising is brought to bear in marketing operations. It is communication with the consumer, and it includes sales promotion and public relations activity.

The third power harnessed to marketing operations is that of the company sales force, specialized in the business of informing, reassuring, advising and servicing the distributors of goods and services; and at the end of the distribution chain there is the consumer, with whom the whole marketing process began.

Here is the arbiter of fortune in business, whose response to proffered satisfactions is the acid test of all the research, product development, creativity, marketing planning, advertising, sales and distribution effort that have gone before. It pays to be in touch with the consumer, to study his needs both actual and potential, and to understand his role in the processes of business.

To outline marketing in this way is not to overcome the problem of communicating its significance universally. Marketing is a large term, large in the sense that industry is; and it is common knowledge that industry means something different to the man in the boardroom and to the man on the shop floor.

Communication can be seen near the very core of contemporary problems in business when those engaged in production, in industry, in marketing do not share a common understanding of these activities and of their purpose in the life of the community.

If, however, for communication's sake, we stay within the familiar terminology of more trade and more employment, these are widely recognized as the purposes underlying industrial activity. Effective trading can be seen to have four main components:-

1. Ideas
2. Marketing skill, to gauge the acceptibility of ideas. Can the eventual product or service be sold at a profit?
3. Money, to put behind the development and exploitation of salable ideas.
4. Capacity, to produce salable products and services.

Selling is another term familiar enough in industry. In America years ago Red Motley used to point out that nothing happens until you sell something. Marketing extends this somewhat. It suggests that nothing will happen until we think in terms of selling something, and that what get sold are not goods but benefits.

Just as production, or money, are not ends in themselves but means to an end, so also are products and services. They do not sell because they are products or services but because of the benefits which are conveyed to the consumer or user when they are sold to him.

CONSUMER DECIDES

In a free society, all the users—the Mr and Mrs Jones, the customers—have the right to say I will buy or I will not buy and, having bought once, to say: I will (or will not) buy again. In this very real sense the consumer or user decides the destinies of individual companies and ultimately controls the levels of trade and employment.

With consumption seen as the sole end of production, and with the role of the consumer as beneficiary and motivator rightly appreciated, the logical attitude to be adopted by producers readily emerges. It is one of the principal ideas inspiring successful managers today.

Charles E. St. Thomas defines it in a celebrated phrase: 'The marketing approach is a way of managing a business so that each critical business decision, whether made by the marketing people, engineering people, manufacturing people or financial people or people in any other activity of the business, is made with the full, firm knowledge of the impact of the decision on the customer'.

There is within this porposition the clear implication that everyone associated with production, every single individual in a company, is implicated in the marketing process, and that includes the telephonist, the accountant, the sales and service department and the board of directors. The history of trade and employment is full of casualties among companies devoted to a narrower view of the purposes of production. To the consumer not even price is decisive. It is on the sum of benefits provided that his verdict is given.

Here is almost a philosophy of business, acceptable even to those motivated only by enlightened self interest. In this sense, a marketing operation is an undertaking meaningful for all concerned, for the worker at the bench, for the managers of enterprise and for the consumers, because it does much to ensure that production will be disposed of efficiently, economically and thus profitably.

If more goods are bought by more people, the economies of large scale production are encouraged; if the goods are wanted goods and can be bought at less cost, a rise in standards of living is the result. Industry is sorely need of a common objective. The marketing approach makes it possible for industry to play a socially constructive role, to thrive in its service to the community, to raise standards of living, and to merit the rewards it receives—from the consumers.

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The principles and practice of managing with particular reference to small companies, and how these techniques can be satisfactorily used in a small organisation

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A. E. B. PERRIGO, Small Business Centre, University of Aston, Birmingham

1. THE PURPOSE OR PRIME FUNCTIONS OF MANAGEMENT

A common feature of many companies—and this is particularly so of the smaller company—is that management is so preoccupied with the events of the day that it gives little or no time to the conscious planning and shaping of its future, and usually insufficient time to assessment of performance in the present.

It is almost a vicious circle. The less management gave thought in its yesterdays to its needs of today, the more likely is it to carry routine burdens and live from crisis to crisis today and, in consequence, the less likely is it to sit back for a while today and determine what it should be doing now in preparation for its tomorrows.

And yet this hard, cold, detached look at itself, its strengths and weaknesses, and its potential market of tomorrow, is essential if, when tomorrow arrives, its task is then to be as easy and fruitful as management can make it.

As one who, until recently, was the managing director of a company in a rapidly changing industry, I appreciate the tremendous day-to-day routine pressures on top management—pressures which tend to prevent it from giving adequate thought to the future—and I sympathise with management in its difficulties in trying to set aside time to ensure that, in the terms of our national summer game, it will be 'batting on a better wicket' in future than it is at present.

The importance of this will be appreciated when one pauses to realise that, no matter how efficiently a company may produce a product, it will (again in cricket parlance) be batting on a sticky wicket if the outside world no longer requires the product, or if management does not know how or where, or at what price to sell it.

On the other hand, if there is a market for its product, and it knows how to promote its sale, the company will still be in trouble if its production efficiency is significantly below that of its competitors.

From the above it will be clear that the function of top management is to secure balance—balance of resources with sales, balance of effort between the routine needs of today and the probable requirements of tomorrow, balance of effort between design of product, production, marketing, and service of the product.

It has been said that the most important nut on an aeroplane is the loose one. Similarly, in business, the most important part of the business is that which is receiving insufficient attention and consideration—and, therefore, a paramount function of the chief executive is frequently to be scanning his organisation to ascertain what aspects of the business are receiving insufficient attention, and then to take the necessary steps to remedy the situation.

2. DETERMINATION OF OBJECTIVES AND ORGANISING TO ACHIEVE THEM

Following his assessment, the general- or owner-manager should define the specific objectives to regain balance within the company, or to bring the resources of the company in balance with the potential demand for the company's services or products. He should then agree with his subordinates the specific tasks which each should undertake to attain these objectives and follow this up with regular assessment together of achievement.

3. THE IMPORTANCE OF MARKETING AND FORECASTING

However, the general manager needs to know what that potential market is. Unfortunately, only too often, he does not know sufficient about the market available to him and, in consequence, cannot forecast with any reliability the potential demand for the company's products or services. Without this corner-stone of information, he is operating in the dark.

One cannot therefore stress too heavily the importance of marketing—to the general manager at least as much as to the sales manager—and I therefore commend to you all that my fellow speakers Mr Collischon and Mr Shanklemann have to say to you on this subject.

4. TOOLS OF MANAGEMENT

From the title of this paper, you will note that I have been asked to touch upon the principles and practices of managing with particular reference to small companies. It may therefore be helpful to this end if we consider those problems which have been found to be most common in the smaller firm, and discuss those techniques which have proved most helpful in overcoming them.

Inadequate financial control

In many small businesses there is a confusion in understanding regarding profit and cash. During periods of growth, profit may be used up in increasing the possessions of the company to meet the requirements of increased inventory or work-in-progress, or accounts receivable from customers. Thus, profit results in increase in possessions of the company, rather than increase in cash.

Many firms have not appreciated this and this had led them into the errors of 'over-trading'. Many bankruptcies and liquidations have occurred as a result of this situation. In such circumstances, firms have had all their available funds in stocks of goods and no money is available to meet the needs of current wages and expenses.

Cash flow forecast. To avoid such a situation, budgeting future financial requirements is highly desirable, and a Cash Flow Forecast, on the lines of Appendix 1, is invaluable.

This should agree with budget statements, where developed, and is of immense value for ascertaining that cash will be available in accord with plan, to meet envisaged future requirements. Furthermore, it is of great help when approaching the bank manager for short-term overdraft facilities or, where the indication is that the capital requirement is of longer term, appropriate sources for the loan of such capital.

Concerning this simple Cash Flow Forecast, it should be mentioned that, when a change in a balance level represents a flow of cash out of the company (e.g. an increase in the level of Accounts Receivable or a decrease in Accounts Payable) it should be negative—i.e., bracketed—as illustrated.

1. Current assets to current liabilities. This ratio should always be higher than 1 : 1 and firms frequently aim for 3 : 2 or even 2 : 1. Where the ratio is around 1 : 1, it indicates that further funds are likely to have to be obtained from the shareholders, or in the form of loan capital from other sources. Otherwise, there is a possibility that the time may arrive when fixed assets have to be sold in order to meet liabilities as they fall due.

2. Liquid assets to current liabilities. This ratio is concerned with assets which can shortly be turned into cash, since liquid assets include cash and such other items as amounts due from customers. It will vary with the type of business and suppliers' terms of sale, but a healthy company should aim to keep it near 1 : 1.

   Stocks of raw materials, work-in-progress and finished goods are regarded as current assets rather than liquid assets, since they represent money which may be locked up for considerable periods, or only converted to money quickly at a heavy loss.

3. Accounts receivable to sales turnover. This ratio is frequently expressed in number of days' billings, thus

   If annual sales = £1 000 000
   and outstanding accounts = £150 000

   $$\text{then days' billings} = \frac{150 \times \text{No. of days in year}}{1\,000\,000}$$

   $$= \frac{150\,000 \times 365}{1\,000\,000}$$

   $$= 54.75$$

   The ratio which would be considered reasonable would depend upon the nature of the business and the credit terms allowed. In the plastics industry, for example, where terms of credit are 30 days, a small business should expect to bring the figure to around 45 days.

4. Inventory (or stock) turnover per year. This ratio is determined by dividing the materials used per annum by the average stock value held. Again, this ratio varies from industry to industry but the small firm in the plastics industry is doing well if it achieves 4 or 5 times per year.

5. Return on capital. This is the net profit before tax divided by all the capital employed in the business. Since return on capital comprises:

   (Percentage profit on sales) × (Ratio of sales per annum to capital employed)

   these subsidiary indices are also worth reviewing.

   For example, a firm which made a net profit of £12 000 on a sales turnover of £100 000 using a total capital of £70 000, would have the following ratios:

   (a) Return on capital $\frac{12\,000}{70\,000} = 17.2$ per cent

   (b) Return on sales $\frac{12\,000}{100\,000} = 12.0$ per cent

   (c) Ratio of sales per annum to capital employed (i.e. capital turnover)

   $$= \frac{100\,000}{70\,000} = 1.42$$

   i.e. Return on capital = 12.0 per cent × 1.42 = 17.2 per cent.

   These indices are of particular value where a company has been increasing, or merely sustaining, its profit by injecting further capital in the business, to counteract lower return on sales or rate of turnover of capital, without recognising the realities of its situation.

The above simple ratios are of great value for comparing the trend of results of the company, from year to year, or of effecting inter-company comparisons, and an extremely useful indication as to the financial soundness of the business.

Routine pressures on management

In many small organisations, duties and responsibilities of management and their staff have, like Topsy, 'just growed'. Certain duties, because the owner-manager did them when the company was smaller have become hallowed in status far beyond their significance to the company, and other duties which are of more importance are carried out by 'Nellie', simply because she or her predecessor happened to be most free to undertake them when they were introduced.

Often, re-assessing the duties of management and its assistants, and then rationalising and re-grouping of these activities, considerably relieves the routine pressures of top management, and also improves the morale of its subordinates; not necessarily involving extra staff.

Such reorganisation, contrary to the unfounded fears of the small owner manager, need not add to the overheads of the company. Where it does do so, the overall financial benefits derived are usually greater than the cost incurred.

Costing information

Many companies have a dearth of simple costing information upon which to base sound decisions on performance, pricing, or selection of orders of greatest value to the company. Sometimes, on the other hand, such information is being gathered, but is not processed and presented well enough to top management to have any real meaning.

In consequence, such firms are not likely to know what product mix is in their interests. They use sales turnover as their sole criterion of performance and go out for all orders, irrespective of the actual profitability of each of them and—particularly in the crisis times—quoting as sharply as possible to obtain them, and sometimes giving the firm's assets away in the process. It is not surprising, in such circumstances, that profit at the end of the year seems to bear no relationship with sales turnover, and appears unrelated to the total volume of the product mix.

If the company is to gain control of its destiny in such circumstances, it must take a marginal costing approach to its problems. This technique enables it to predict with reasonable reliability the profit which it will actually obtain from its sales volume for any product mix, to decide which types of orders or items in its product range it is in the company's interests to develop, and also those from which it would be financially desirable to disengage.

Now, in simple terms, the profit which a company makes is the sales income less (a) the direct (marginal) costs involved in producing and distributing the products (i.e., those which vary directly with volume) and (b) those expenses incurred in the company (fixed expenses) which are independent—within normal fluctuations of activity—of the sales or production volume of the plant.

Thus, knowing these marginal costs of each of the products, the sales prices and sales volume of each, and the fixed expenses of the company, it is possible

(a) to predict profit for any sales-mix

(b) to ascertain which product mix is in the company's interest and

(c) the real value of different orders to the company, in terms of profitability rather than sales volume.

This information assists the company to maximise its profit for any given sales turnover. This is most important, since too many firms indiscriminately pursue sales volume, without the necessary selectivity of orders to ensure profitability.

The following simple example reveals the importance of selectivity of orders, and I trust those of you who are already well aware of the techniques and advantages of marginal costing will bear with us for the benefit of those who may not yet realise the value of this powerful tool for profit planning purposes.

A small company produced three items in its product range. Although its sales turnover in successive years increased from £150 000 to £180 000, the profit had actually and unexpectedly reduced from £18 500 to £17 000.

It sought advice as to the reason for this and the steps which it should take to reverse the trend. An analysis was made of the direct costs involved in each product (i.e., those which directly varied with volume, such as materials, direct wages, etc.) and the fixed costs incurred by the company. In round figures, this revealed the following.

This information was of considerable value to the company and, henceforth, it changed its sales and pricing policy to aim at maximising gross margin, and the salesmen sought orders on this basis. The result was that, the following year, although

	Figures in £000's							
	Year x Product				Year x + 1 Product			
	A	B	C	Total	A	B	C	Total
Sales income	70	30	50	150	50	75	55	180
Direct costs	31.5	24	35	90.5	22.5	60	38.5	121.0
Gross margin	38.5	6	15	59.5	27.5	15	16.5	59.0
Fixed expenses				41.0				42.0
Profit				18.5				17.0

sales dropped in total to £155 000, the company made a profit of £22 000.

The above illustrates how marginal costing can be used for sound price fixing and the selection of that type of business which is of most value to the company. This is of particular importance in such industries as Plastics, where the same products may be produced by labour intensive or capital intensive means and a company should be endeavouring to select orders of those volumes for which its own productive resources and methods are competitively suited.

Production planning and control

Another important formal tool of management (which supplants the age-long practice of leaving it to the foremen to programme production as best he can through the shop) is production planning and control. It is of as great value to the sales manager as to the production function. The sales manager wants to know with reliability what delivery dates he can quote customers on potential orders. Since, unhappily, manufacturers' schedules are not always adhered to, he will also want to know as soon as possible when delivery is likely to be late, and by how much, so that he can inform his customer and not have the latter angrily asking him what has happened when the promised delivery date has passed. The customer has his own programme to keep, and a communication before delivery is due is often accepted with good grace, but the same information extracted by an annoyed customer after the promised delivery date is most likely to be considered, at best, as an excuse and not an explanation. Remember always that you are selling a service to the customer and not just a product at a price.

It would be inappropriate here to describe the detailed procedures of planning and control, but it may be worthwhile listing the main responsibilities of a production planning officer. They are as follows, the relative importance of each depending upon the nature of the product and business.

1. Receiving from the sales department information on orders for execution.
2. Conditioning this information into a form suitable for passing to the production shops for execution.
3. Expressing this order load in terms of shop-floor loading.
4. Preparing a production programme in accordance with this order load and production resources available, to meet as far as possible the requirements of the sales and production departments.
5. Providing the sales department with reliable information upon which it can base promises to deliver the various products within the range offered.
6. Determining the time required for the various production operations or cycles, and improving methods in co-operation with the production department.
7. Ascertaining how far production equipment can meet production and sales needs, and therefrom discovering possible bottlenecks.
8. Calculating the performance of the production resources for each production period, and reporting thereon to management.
9. Keeping the sales manager informed of the progress of orders in all cases where they are falling behind schedule.

Effective production planning and control results in greater support for the sales department, greater utilisation of productive resources and, because of shorter delivery periods and reduced work-in-progress, less money tied in inventory.

Budgetary control

The tool of management of which most effectively facilitates delegation—and which is essential if management is to relieve itself at each level of as much pressure as possible—is budgetary control.

It starts with the budget, which should be the servant, and not the master, of management and staff. This needs to be based upon forecasts as to the levels of activity that are anticipated during the forward period under consideration.

The corner-stone of these forecasts is the sales forecast, which depends upon the market information available to, and utilised, by the company. The paramount importance of this information cannot be stressed too highly and I am happy to think that my two fellow-speakers are engaging themselves exclusively on this subject.

The budget itself is really a statement by management of its anticipated activities and intent during the forthcoming period, and the part which it expects various individuals to play in this co-ordinated whole. It is expressed in the common denominator of money.

The pattern should coincide with the pattern of individual executive responsibility, right down to the chargehand on the plant, and each person should have been actively brought into the dialogue regarding the forecast of performance of his particular parish. This involvement is essential if each is to strive to attain his target.

Each person involved should be provided with the budget information regarding his own sphere of responsibility, and of actual performance as the period progresses. Both of these elements of information should be progressively consolidated, so that they coincide with the areas of responsibility of individuals in successive senior levels of management.

At each stage of consolidation, the information should be provided in more focused form. Otherwise, at the upper levels of management, there would be such a welter of detailed information that the executives who received it would find it difficult to see the wood for the trees.

Once information is presented in this focused form, a senior executive should be able to see which areas under his command required investigation. He should then call for more detailed information from the subordinates responsible for the area concerned. This scrutinising process might go right down to the level of the charge-hand and the direct operator.

In a really healthy organisation, each level of co-ordination or supervision, right down to the charge-hand, will be encouraged to appreciate the value of information it receives. Furthermore, each level will have been trained to scrutinize the control statements carefully, read their inner meaning, and decide how best to remedy any shortcomings.

If the team is a good one, each co-ordinator will approach his direct senior voluntarily and explain the reasons why

significant departure of the performance figures from budget, so far as his own area of activities is concerned, and the remedial action he proposes taking.

A great deal of initiative will be lost to the group if the organisation works the other way, and seniors 'police' their direct subordinates with the information instead of training them to study their own control data and use their own initiative in deciding what remedial action should be taken. Furthermore, the subordinates will have less opportunity to develop creative abilities. Interpretation of data covering the area of his responsibilities and determination of appropriate correctives are essential parts of every executive's training and development. By exercising these critical skills he can also help to reduce the pressure on successively senior levels of management.

The most important management control statement is that prepared for the chief executive as an overall operating summary. In commercial and industrial organisations this is usually in the form of a summarised profit and loss statement, generally prepared monthly. In most well-run organisations this is available within, say, two or three days after the end of the period to which it refers. A typical statement would be headed by income earned; i.e., net sales billed. From this would be subtracted the direct cost of net sales billed to give the contribution to gross margin, often termed gross profit.

The expenses would then be listed under the main headings (i.e., Factory sales, Engineering, Accounting and Administrative) and the subtraction of their total from the gross margin would give the income earned during the period, or, in other words, the month's contribution to profit.

A suitable format for such a summary is shown in Appendix 2.

Generally, to facilitate comparison between performance and target, the actual figures for the month, and the cumulative total for the financial year to date, are accompanied by the corresponding budget figures.

This summary statement can be most useful to the chief executive, since it will enable him to discover the weak areas in his business.

It will be noted that each entry in this summary statement coincides with the sphere of responsibility of one of the executives directly responsible to the chief executive. In the small firm, of course, one executive may be responsible for several areas of performance, but it is helpful to him to know which hat he should be wearing, and for what areas of activity he is directly responsible, when scrutinizing the results from different areas of activity.

4. THE SMALLER BUSINESS AND INCENTIVE TO IMPROVE

It will not be surprising if some of you, particularly those running smaller businesses, say 'The above techniques are all very well, but what good would they be to me. They would be costly to introduce and would only add overheads to my business'.

It is an understandable reaction if one cannot see the potential in one's business, since we all rarely buy anything if we can only see the cost and not the benefit available to us.

Thus, the small firm (which frequently knows far more about the product and its production, than it does about the market for its product, or about its costs, or about the most effective administrative procedures for running such a business) has gradually to become enlightened as to its potential and, at each stage of enlightenment, it begins the more to see the financial benefit which it could obtain through the employment of further techniques.

It may start with simple costing. Costing shows it the rewards that are open to it through better production flow. Simple production planning and control procedures are then likely to be introduced, and these quickly reveal the rewards to be obtained from planning on a wider scale—i.e. management planning, in the form of budgetary control. Budgetary Control is seen to need to start at the sales forecast, and this leads to greater emphasis on marketing.

With the small company, all the above procedures can be simple. In fact they need to be for economic reasons. For example, the young cost control person may be trained to undertake responsibility for production planning and control. In the very small firm, under guidance, he may also undertake the market research.

Probably one of the vital things which differentiates the small firm from the larger firm, is its greater reluctance to obtain external advice as to its potential and how to achieve it. I therefore hope that on leaving this meeting you will ask yourself 'do I know the potential of my company and, if not, am I taking any steps to find out, so that I may have incentive to develop in the most fruitful directions'.

APPENDIX 1

Cash flow forecast
Years x, x + 1, x + 2 (stated in £000's)

	Year x						
	1st qtr.	2nd qtr.	3rd qtr.	4th qtr.	Year	Year x + 1	Year x + 2
Cash source (Disposition)							
Net income	25	20	19	24	88	93	100
Provision for depreciation and amortization	6	4	4	6	20	22	28
Provision for taxes on income	20	16	14	18	68	72	78
Income tax payments	(32)	—	(32)	—	(64)	(68)	(72)
Acquisition of fixed assets	(2)	(8)	(10)	(1)	(21)	(22)	(60)
Dividends payments	(28.5)	—	—	—	(28.5)	(32.0)	(39.0)
Long-term debt, principal payments	—	(6)	—	(6)	(12)	(12)	(12)
Accounts and notes receivable	(8)	2	1	(5)	(10)	(6)	(12)
Inventories	4	(5)	(4)	2	(3)	(5)	(8)
Accounts payable	(2)	4	2	1	5	3	4
Accrued expenses	3	1	(6)	2	—	—	—
Other							
Acquisition of licenses	—	—	(15)	—	(15)	(16)	(17)
Change in cash	(14.5)	28	(27)	41	27.5	29	(10)
Beginning balance	(18)	(32.5)	(4.5)	(31.5)	(18)	9.5	38.5
Ending balance	(32.5)	(4.5)	(31.5)	9.5	9.5	38.5	28.5

APPENDIX 2

Specimen monthly operating summary

	Month ending 31st July Year 1968			
	Actual	Budget	Actual cumulative	Budget cumulative
Net sales billed	11 000	10 500	77 000	80 000
Direct cost of net sales billed				
Cost of materials	3 950	3 900	29 000	30 000
Variable labour content	2 150	2 050	14 500	15 000
Variable overheads content	700	660	4 900	5 000
Total	6 800	6 610	48 400	50 000
Gross margin	4 200	3 890	28 600	30 000
Fixed expenses				
Factory	1 280	1 270	8 900	9 000
Selling	750	720	5 100	5 000
Technical and/or engineering	210	210	1 550	1 500
Accounting	270	280	1 950	2 000
Administrative	650	640	4 450	4 500
Total expenses	3 160	3 120	21 950	22 000
Contribution to profit	1 040	770	6 650	8 000

Sixth International Reinforced Plastics Conference

PAPER NO.

NAME

COMPANY

QUESTION

SIGNED

DATE

Marketing of reinforced plastics

18

ERIC SHANKLEMAN, Marketing and Economic Research Limited,

The paper considers to what extent the custom moulder in particular, providing a service to other industries, can use the processes of marketing normally adopted in other industries. The GRP moulder very often, for example, assumes that in a service industry you cannot advertise; that the scope for personal selling is limited; that essentially he is an order taker rather than an order creator. These assumptions are questioned in this paper. It considers the sort of selling organisation that even a small company can adopt in order to manage its business rather than be managed by it. It shows the sort of research that can be done and how rudimentary forecasting can be undertaken if only to determine the way in which forces react on the GRP business. The paper stresses the need to understand one's market, which in many cases boils down to the composition of a local market. It also considers the extent to which the disadvantages as well as the advantages of GRP determine the product policy that moulders should adopt; this product policy should be an essential element in a marketing operation.

Sixth International Reinforced Plastics Conference

PAPER NO.

NAME

COMPANY

QUESTION

SIGNED

DATE

The development, production and sale of a reinforced plastics hot water storage cistern

R. A. RICHARDSON, Osma Plastics Limited

1. FINANCIAL CONTROL

Most successful Companies have taken many years to develop a good secure platform from which to operate. In a substantial growth market the platform should be more like a spring board, to bend according to the specific need of the occasion.

We at Osma, have cemented a marriage between Marketing and Strict Financial Control positioned on a proven Management springboard.

Referring to Mr A. E. B. Perrigo's paper on small businesses, most of the points brought forward also apply to larger businesses. The only real difference being that in a small company, the managing director in most cases is involved in some preparation of the detail and then has the problem of taking action. The detail, rather than conclusions, perhaps is uppermost in his mind.

In larger companies, specialist people are employed to prepare the data and management, without being bogged down with detail, can see a picture on which to act.

In Osma, using marketing surveys and intelligence, we prepare a realistic five-year sales forecast in detail down to individual products. In a market such as ours, which is expanding at a fast rate, we have the opportunity of making an overall reduction to the year's sales forecast so as to give us plenty of slack for manoeuvreability.

Budgets are prepared for capital expenditure, changes in the elements of working capital, turnover and expenses. These budgets are broken down to individual departments, based on the information presented by the managers of those departments. The budgeting profit is thrown up, return on capital employed and all the other results that are so necessary.

In fact, we prepare budgets for five year periods. In the first years, one would expect to be reasonably accurate while the later years will obviously be less accurate. Nevertheless, Management is provided with the picture and guide lines on which to work.

Future additional capital required or additional factory capacities, extra storage and distribution facilities, increases in sales force, are all shown up well in advance for planned action to be taken. In throwing back these points to the sales forecasts, adjustments may have to be made, e.g. if the market will take a certain level of sales but storage or manufacturing capacity is not available, the market will have to go short and the sales figures adjusted downwards accordingly.

One finds that the first budget figures are certainly not the final ones. With adjustments and manipulations, the exercise in part is possibly carried out three or four times. Once the scheme has been in operation for a number of years, the whole operation obviously becomes easier as the forecast becomes an extension in time.

Above all, it must be borne in mind that budgets represent an evaluation of the intentions of management based on careful estimates of all the foreseeable factors. While budgets provide a means of control and measurement, it is essential that sufficient flexibility is maintained to allow for changes of circumstances. Rigidity must be avoided.

Results are compared with the budget month by month and reasons for deviations from the budget carefully examined. Any necessary corrective action must be taken.

Further control is provided by standard costing. Pre-determined costs are ascertained relating to material, labour and the various overheads. Actual costs incurred are compared with the standards as work proceeds. The differences between the two—variances— are analysed by 'reasons' so that inefficiencies are quickly brought to light and appropriate action taken.

With this setting of planned growth, with market knowledge and strict financial control, Osma introduced their hot water cylinder on to the market.

2. NEW REINFORCED PLASTICS PRODUCTS

We have three ways of approaching the introduction of new business in our Reinforced Plastics Factory.

One approach is in conjunction with the Osma Marketing Organisation, who are constantly on the look-out for new products to add to their range.

The second approach is through the factory's own product development section who wish to extend and improve existing ranges of products in addition to looking for new ones, with a definite bias to reinforced plastics.

The third is by custom moulding. It might be pertinent to say that we have spend a small forture on design staff, experimental work, specialist sales force, etc. to obtain custom moulding business. Whilst the potential is obviously fantastic and we have been told this by everybody during the last five years, just nobody has woken up to it especially those who are giving out the work. Quite naturally, this type of business now has relatively little importance in our company and we have substantially cut back our efforts in this direction.

Reinforced plastics have a future but the only sure way of enjoying this is perhaps by putting down tools for your own products. This may put up the initial capital expense but at least you have some control on the sales effort necessary for success.

It is important to make sure that if you are going to make a product in reinforced plastics, no other plastics material will do a better job. Ultimately, the right material for the product will have the sales edge.

The original concept of making a Plastics Hot Water Cylinder has now been lost, the idea had been around for a considerable period of time. We were the largest suppliers of Plastics Cold Water Cisterns in the market and a Cylinder looked an obvious addition.

At that time, we had brought to our attention a Bisphenol Resin which had been successfully used in the moulding of plastics radiators for autombiles in the U.S.A. Because of the fluctuating pressure and heat encountered in this application, we carried out some initial material evaluation tests. These proved positive and with the confidence of having found an acceptable material, we organised a Market Survey prior to Production Development.

3. PRODUCTION DEVELOPMENT

1. Appraisal of available materials.
2. Tests for heat resistance, strength retention etc. with ordinary cisterns moulded in bisphenol resin when subjected to boiling and alternately hot/cold cycles.
3. Design of prototype tool for environmental tests. (Initial tool was .075 thick, plain hemispherical end and centre joggle. Joggle was cut off alternate mouldings and offered up in pairs to form cylinder).
4. Prototype mouldings had plastic bosses, compression moulded in bisphenol based DMC. All were female 1 in BSP and $2\frac{1}{4}$ in BSP and had shaped shoulder to conform with the curvature of the cylinder. These were attached by an epoxy resin adhesive after preparing jointing surfaces by grit blasting.

   Evaluation of adhesive and method was necessary:

(a) to ensure that on tightening pipe to boss the bond was not sheared.

(b) to ensure that tapered thread fitting would not split boss.

5. Samples from prototype mould put on life test and the following lessons were learned:

(a) Idea and materials basically satisfactory.

(b) .075 thickness gave sufficient tensile strength to resist pressure, but not enough rigidity to withstand handling.

(c) Plastic bosses were generally satisfactory but could be dislodged with a blow which applied tensile rather than shear force to adhesive.

6. Tool re-cut to give .100 thickness. Also second tool laid down for second half—still plain hemispherical ends—to avoid necessity of cutting off joggle, etc.

7. Further tests showed:

(a) .100 good for rigidity and ample safety factor for stresses exerted by working head.

(b) Costs of moulding and particularly of attaching plastic bosses makes them more expensive than metal.

8. Development of metal bosses instituted. It was necessary to trace suitable material to avoid electrolytic action and de-zincification. Various yellow metal alloys and others evaluated before suitable components and materials were found.

9. Problem of getting metal bosses to readily conform to curved metal surface prompted localised re-design of cylinder. Flat for immersion heater boss introduced, but flats on sides not practicable because of limitation of variations of boss positions and the fact that the flats would have to be carried through to cut-off area making central joint difficutl.

10. Top tool re-cut to include immersion heater flat. At same time, development put in hand to develop free standing base.

11. Mouldings put into production at this stage.

The following points needed development:

(a) Accurate method of producing preform screens, particularly important where high glass content is combined with minimum draft angle.

(b) Method of retaining mix on tool during closure.

(c) Controlling gel-cure characteristics of bisphenol resin used—which are quite dissimilar to conventional polyesters.

(d) Method of control of glass reinforcement to give consistent results with respect to mechanical strength.

(e) Release of moulding from tool.

(f) Method of obtaining consistent results in making glue line.

(g) Development of all equipment for stages of assembly.

12. Anticipated stages of future production development:

(a) Speed up of press cycle—aggravated at the present time by characteristics of bisphenol resin.

(b) Development of other suitable raw materials to make product more competitive—since outset glass has gone up 4d. per lb.

Surfacing tissue by 15%
filler by 15%
resin by 15%
} devaluation

(c) Simplification and automation of assembly stages.

4. PRODUCT TESTING

Earlier Production Development in conjunction with our Research and Development Department had established:

the material
method of manufacture
design criteria

which enabled a final decision to be made on the manufacture of the production tool.

The Production Testing Department had now to evaluate the long term function of the cylinders under practical conditions. They had to prepare a specification which would enable consistent quality control procedures to be introduced once the cylinders were in production.

The parameters of design had been established to meet the Grade 3 requirement of B.S. 699: 1967 (Copper Direct Cylinders for Domestic Purposes).

The initial requirement for cylinders was that they would operate at a maximum working head of 30 ft (13.5 p.s.i.). Two Rigs were devised. The first designed to operate under a 30 ft head at a consistent temperature of 95°C. The other also operating under 30 ft head but tested at extremes of temperature change. The water was raised to boiling (119°C at 13.5 p.s.i.) (20 minute period), then continued to boil for 2 hours 40 minutes. A Solenoid valve operated to discharge the boiling water and replace with cold water via the cold feed connection. The cycle was then repeated. Both tests were continuously carried out over a total period of 21 months.

As the results of these tests would of necessity be protracted, a third test rig was run in tandem to give accelerated results. This consisted of a 2-cylinder station with facilities to produce boiling conditions and variations on head pressures. Cylinders on this rig were tested to destruction by increasing the head pressure well in excess of the recommended working head and carefully noting the areas of failure.

After each test programme, consultations took place with the Production Unit which resulted in additional prototypes being produced incorporating agreed recommendations. Development was continued until the all-round performance had a substantially high safety factor over the maximum British Standard requirements.

The destruction test programme also confirmed the most successful method of bonding the two mouldings together. During this programme, complete evaluation of adhesives under shear and tensile stress was carried out.

A stage was reached in the production evaluation when we were in a position to supply the British Waterworks Association with sufficient cylinders to enable field tests to be carried out. This approving body had from a very early date been consulted on this project. We were advised that results from these field tests would not be expected for at least 6 months and the energies of the department were concentrated on the evaluation of an indirect type of cylinder.

Although it had been established that G.R.P. had good insulating properties and that the user could reduce the thickness of an insulating jacket required on the outside, this property prevented us using G.R.P. as annulars as its heat exchange properties were minimal.

After some further development work, we decided on using the standard copper annulars which were equal to the minimum requirements of BS 1566, Part 1, 1966.

It is past history that we obtained approval of the British Waterworks Association of our Hot Water Cylinder but as with all product testing, this was not the end. We are still carrying out extensive test programmes to establish alternative designs, improve methods of manufacture and greater flexibility in the range.

5. MARKET SURVEY

When plastics Hot Water Cylinders were proposed as a new Product, we decided to investigate with a Market Survey. This was carried out on a National basis to find out:

The overall size of the market.

Division into size and capacity.

Breakdown into direct and indirect units.

Details of Competitors.

Geographical area of operation of competitors.

Price and discount structure.

Special requirements of Merchants and Plumbers, etc.

We were also very fortunate in having a good relationship with some of our competitors and were able to obtain from them their assessment of the market which generally coincided with the survey.

In carrying out this survey, we contacted all the specifying authorities, local water undertakings, builders, plumbers and merchants, etc. The results of the survey showed that the market was very large and that we could introduce a nominal range of sizes and still be effective. The largest demand was for 28 gallon Direct and Indirect, followed by 25 gallon Direct and Indirect.

The survey was very encouraging and approval was given for the factory to commence development work on this project. Major merchants concerned with distributing Hot Water Cylinders, kept us informed on the fluctuating market price of Copper Cylinders. Likewise our large National Sales Force was able to advise on the net prices being paid by Plumbers.

During the period when field trials were being carried out by the British Waterworks Association, the Marketing Department finalised their

Technical Details
Sales Literature
Price Lists
Press Release

and had organised their sales plan for the most effective marketing of this product.

At this time, due to the Rhodesian crisis, copper prices were continually going upwards, making the proposed cylinder more attractive and there was obvious pressure on all sides to accelerate the launching date.

The technical detail of the Product was prepared by the Research and Development Department and this was fed through to the Sales Force for early digestion. The technical detail included not only material technicalities but perhaps more important, plumbing technicalities on cylinders in general. It is of prime importance that the salesman knows the plumbing detail behind a plumbing product.

6. THE LAUNCH

We timed the official launch to coincide with the International Building Exhibition at Olympia in November last. We featured 28 gallon Direct Cylinder fully connected, in continuous working order throughout the 15 days of the Exhibition. This led to considerable interest in sales.

Several weeks previously, all trade and technical journals had received comprehensive details and photographs for publication which was widespread.

This product was launched in line with the general Osma pattern. All Builders' and Plumbers' Merchants in the United Kingdom were advised by mail of technical details and British Waterworks Association acceptance. A comprehensive leaflet was produced giving technical facts, dimensions, etc. Secondly, all Local Authorities were sent similar information.

Thirdly, the Osma Sales Force was briefed and each member received a sample Cylinder and personal interviews were arranged with the leading potential users, i.e. large Plumbing Contractors, Housing Developers, Architects, Local Authorities, etc.

A continuous programme was introduced whereby the individual permission of Local Authorities throughout the country was sought for the use of the Osma Cylinder within their area. Evening lectures were given by the Company to specially invited audiences likely to be concerned with the introduction and continual use of the Cylinders in conjunction with local Plumbers' Merchants Stockists. Short day-time lectures were also given to certain individual Contractors, Registered Plumbers' Association Sections, Clerk of Works Committees, etc.

Progressive Merchants throughout the country generally placed initial orders for one half-dozen Cylinders prior to holding large stocks on a repeat basis.

7. DEVELOPING SALES

Because of the hard water experienced in certain parts of the country and the ever increasing demand for central heating, pressure was put on the Company by users and Merchants for an Indirect version and this became the next introduction.

Similarly, in line with market research findings, the second biggest demand was found to be for the 25 gallon size and the automatic introduction of direct and indirect versions soon followed.

Local Electricity Boards were keen to promote night storage heating which is only really efficient with a large capacity container and in conjunction with the Eastern Electricity Board, a 53 gallon Cylinder was successfully marketed for this application.

Sales/Technical development continues to meet the demand for cheaper versions, higher pressure requirements, combination tanks, etc. etc.

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Carbon fibres as high modulus reinforcements

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ABSTRACT

Carbon in the form of filaments can be produced with consistently high strength and stiffness and with low density. This makes it suitable for reinforcing plastics to provide a light structural material with greater specific stiffness than any existing metal or composite.

The structure and properties of two types of high modulus carbon fibres, already in production in tonnage quantities are described and some results of tests on epoxy resin/carbon fibre composites are reported with special reference to interlaminar shear strength and fatigue.

1. INTRODUCTION

High Modulus Carbon Fibres are produced by a number of manufacturers each of which have their own range of types. These fibres can be produced by thermal degradation of synthetic fibrous raw materials—chiefly cellulose (rayon) and polyacrylonitrile (P.A.N.).

These two raw materials give carbon fibres of somewhat different density and breaking strain.

Morganite Research and Development Limited manufacture two types of the P.A.N.—based carbon fibre material. Type I (High Modulus) is a material with a very high Young's Modulus (60 million p.s.i.) and Type II (High Strength) a material of medium modulus but very high strength (400 000 p.s.i.). The properties are shown in detail in Tables 1 and 2 and represent materials with twice the modulus or four times the strength of mild steel at a density only one quarter as great.

TABLE 1

Specification and batch mean properties of Type I (High Modulus) fibres 39" long

	Batch mean of fibre property		
	Strength thousand psi	Modulus millions psi	Diameter micrometers
Specification	greater than 200	greater than 50	6-8
Mean of 51 batches	246	60.78	7.8
Minimum value	196	43.9	7.0
Maximum value	296	68.3	9.7
Standard deviation	23	4.1	0.33
Coefficient of variation	9.5%	6.7%	4.3%

Density 2 grm/ml 0.072 lb/cu in

Average specific strength 123 000 p.s.i. 3.41×10^6 ins

Average specific modulus 30.39×10^6 p.s.i. 8.45×10^8 ins

Breaking strain (strength/modulus) = 0.41%

However, these properties are useful only when the fibres are used to reinforce a matrix material which could be resin, metal or ceramic. Such a matrix allows the fibres to be ordered in the desired pattern and directions and transmits loads to and between the fibres. At ordinary temperatures, resins are the normal matrices and epoxy or polyester resins are commonly used, although other types are selected for particular applications. Epoxy resins have found widespread applications in the aerospace industry.

The most important design parameter for carbon fibre—resin composites is the ratio of the modulus of elasticity, E, a measure of stiffness, to the specific gravity or density i.e. the specific modulus. For most conventional structural materials such as wood, glass and the majority of metals and alloys, this parameter is around 3.9×10^6 p.s.i. (i.e. 1×10^8 inches) Glass fibre—resin composites are no better than metals with respect to specific modulus. Fig. 1 shows the relationship between the specific strength and the specific modulus of a variety of constructional materials.

TABLE 2

Specification and batch mean properties of Type II (High Strength) fibres 39" long

	Batch mean of fibre property		
	Strength thousands psi	Modulus millions psi	Diameter micrometer
Specification	greater than 350	34-40	7-9
Mean of 19 batches	401	37.6	8.1
Minimum value	344	34.0	7.6
Maximum value	462	40.7	8.6
Standard deviation	30.8	1.8	0.2
Coefficient of variation	7.7%	4.9%	2.9%

Density 1.74 grm/ml 0.063 lb/cu in

Average specific strength 231 000 psi 6.4×10^6 ins

Average specific modulus 21.6×10^6 psi 5.98×10^8 ins

Breaking strain = 1.07%

A second important design feature of composite materials is the ratio of their strength to modulus i.e. their strain at fracture. To make full use of the potential of the material its maximum strength should be reached before its extension becomes unacceptable for the component under consideration. For example, although glass fibres may be stronger than carbon fibres they require much less load to reach a given extension. Their useable strength may, therefore, be lower than that of the weaker but stiffer carbon fibres.

For unidirectional fibre composites the tensile strength and modulus of the composite are theoretically proportional to the volume of the reinforcing fibres. However, factors such as the degree of orientation of the fibres, their length to diameter ratio and the degree of adhesion between the fibres and the matrix can all cause departure from the theory. The adhesion is perhaps the most important factor to be considered since it largely controls not only the shear and torsional properties of the composite but also the propagation of cracks through it. The matrix-fibre bonding is possibly of even greater importance in the design of those composites in which many of the fibres are at large angles to the direction of stress.

2. FORMS OF CARBON FIBRES

Morganite Research and Development Limited produce the two types of carbon fibre mentioned above in three different forms.

2.1 Short lengths

The fibre was first produced as 39" lengths because of the existence of plant which could be quickly modified to produce such material. Fig. 2 shows a photograph of this material and it will be noted that a very high degree of straightness of the individual fibre bundles has been achieved. This makes for easy incorporation into resin when manufacturing composites. Table 3 shows the variation in the weight per unit length of this 39" material.

TABLE 3

Variation of weight per unit length (grm/m) for Type I and II fibres

	Minimum	Maximum	Mean
Type I High Modulus	0.84	1.02	0.91
Type II High Strength	0.89	0.98	0.92

Coefficient of variation

between samples from same tow 0.7%

between tows within one batch 1.7%

between batches 7.5%

0.91 grm/m = 1 ounce per 100 feet approx.

This form of fibre can also be supplied chopped to between $\frac{1}{4}$ and $1\frac{1}{2}$" long. It has been found desirable when supplying chopped lengths for the tows to be treated with a small quantity of resin before chopping, otherwise the individual filaments are difficult to incorporate into a resin.

2.2 Long lengths

Short lengths are of restricted use, and for commercial applications, lengths of at least several hundred and, preferably, several thousand feet are required. Methods of manufacturing such lengths of continuous filament tow have been developed and at present material is available in lengths up to 1000 ft. Fig. 3 shows a photograph of a reel of long length carbon fibre.

Both the short length and the long length material is made in the form of a tow containing 10 000 filaments. Each filament is about 8 microns or 0.3×10^{-3} inches diameter. It has been found possible to make pre-preg sheet from this 10 000 filament tow with a thickness after moulding of 0.005" although material of twice this thickness is more easily manufactured.

2.3 Spun yarn

A method of producing a yarn which is thinner than the 10 000 filament tow has been developed by the Shirley Institute (the Cotton, Silk,and Man-Made Fibres Research Association) under a Ministry of Technology contract. This can be supplied in lengths of several thousand feet. From the 39" lengths they produce a spun yarn with a staple length of about $\frac{3}{4}$" already impregnated with a suitable amount of resin. The yarn can be produced in various weights representing different diameters and with a breaking strength sufficient for winding the material on to a mandrel. Fig. 4 shows a photograph of this spun yarn.

3. PROPERTIES OF HIGH MODULUS CARBON FIBRE

To date, the majority of information on the properties of fibre has been obtained from short length material. More information on the properties of filament wound composites made from long length material will be available for presentation at the conference.

3.1 Sampling and testing

Forty individual filaments were tested for each 26 lb of short length material produced. Since the material is in the form of 39" long bundles or tows of 10 000 individual filaments and 25 lb is about 12 000 such tows, this represents a sampling rate of about 1 in 3 000 000. The average properties of 51 batches of Type I (High Modulus) material are shown in Table 1 and the average for 19 batches of Type II (High Strength) material in Table 2. The variation of properties within one batch for Type I (High Modulus) fibre is illustrated in Figs. 5, 6 and 7. From the original data it can be calculated that the coefficient of variation within one batch for each property is within the following range of values.

Tensile Strength 26-30%
Young's Modulus 9-11%
Diameter 6- 8%

Fig. 8 relates the coefficient of variation to the number of filaments tested and indicates that even at a sampling rate of 1 in 3 000 000 the mean strength is measured to an accuracy of 10% with more than 96% confidence; the Young's Modulus is measured to an accuracy of 5% with more than 99% confidence; and the diameter is measured to an accuracy of 3% with 99% confidence. These accuracies are adequate for such a material.

However, sampling must be representative of the whole batch and to achieve this the following scheme was adopted. From the batch of 12 000 tows, 9 are selected from the positions shown in Fig. 9a. 6" lengths are cut from each of these tows at different distances from one end as illustrated in Fig. 9b. From each of these 9 lengths, 6 filaments are withdrawn, 3 from the outside of a tow and 3 from the inside, and mounted on cards for testing. Fig. 10 shows this procedure. Allowing for some filaments being broken during mounting at least 40, and generally 50, are available for the measurement of diameter and breaking weight from which tensile strength and Young's Modulus can be calculated. Figs. 11, 12 and 13 show this process.

This procedure has two disadvantages—it is expensive because of the time it takes and there is a chance that a biased result, especially for tensile strength, could be obtained because more of the weak filaments were broken during mounting does not preferentially select the stronger filaments for testing. The statistical distribution of the strength of the filaments is normal (1). Two alternative methods have also been developed which test a whole 10 000 filament tow. These have been compared with single filament tests and give equally good results for about one-third of the expense.

3.2 Test results

Figs. 5, 6 and 7 related to the spread of properties within one batch. Between batches there is a smaller spread as shown by the coefficients of variation in Tables 2 and 3. Figs. 14, 15 and 16 show the overall properties of the Type I (High Modulus) fibres produced as 39" lengths.

3.3 Possibilities for improvement

Since the modulus of a graphite crystal in the 'a' direction is about 140 million p.s.i. and fibres with a modulus of about 100 million p.s.i. have been reported already there is little room for improvement in modulus properties.

The ideal strength of fibres is one-tenth of the modulus of elasticity, E/10, that is, about 6 million p.s.i. at present. Since they are polycrystalline and porous they will never achieve this degree of perfection but it does seem reasonable that E/50 might be achieved if our understanding of the causes of defects were better. The present Type I fibres give about E/200 and Type II about E/100 strengths. Thus average strengths of 1 000 000 p.s.i. provide a reasonable target for future development work giving a breaking strain of 1.6% for a material of 60 million p.s.i. modulus (or 1% for 100 million).

4. RELATION BETWEEN PROPERTIES AND STRUCTURE

4.1 Elastic modulus

Watt, Phillips and Johnson (2) were the first to show that the degree of axial alignment of the graphite basal planes in a bundle of fibres could be related to the average axial elastic modulus measured in the tensile test. Joiner (3), in our laboratories, has confirmed the broad shape of this relation-

ship. Both sets of data are shown in Fig. 17, where the modulus is plotted against the angle of fibre tilt with respect to the X-ray beam at which the basal plane Bragg reflection reaches half its peak intensity. This is a measure of the spread of basal plane orientations; in a perfectly aligned graphite fibre this angle would be zero.

Brydges (4) has attempted to predict fibre moduli using published elastic constants for the graphite crystal and these orientation data. He predicts two curves shown in Fig. 18, the lower bound when the assumption is that each crystal reaches homogenous stress and the upper bound for the homogeneous strain condition. The observed curves fall between these bounds, but are somewhat closer to the lower bound at larger misorientations and move towards the upper bound as orientation improves.

The modulus of these fibres can, therefore, be satisfactorily explained by simple reasoning based on the degree of alignment of their graphite crystals obtained from X-ray defraction data. No comparable success has attended efforts to explain fracture strength since, as would be expected, it is a more structure-sensitive property. Before discussing strength, it is necessary to describe what is known about the fine structure of the fibres.

4.2 Fine structures

Johnson and Watt (5) and Badami, Joiner and Jones (6) have contributed to the literature on the fine structure as revealed by thin film electron microscopy. Their agreed findings are schematically summarised in Fig. 19. Fig. 20 is a striking electron photo micrograph of the cut end of a high modulus fibre in which the small graphite crystals which are in the correct orientation to diffract are shown in dark contrast. The fibrils made up of these small crystals are also clearly shown.

These results show that the graphite crystals are arranged, apparently at random apart from the requirements that their 'a' axes should be less than 10° from the fibre axis, in polycrystalline fibrils between 250 and 1000 Angstroms thick and of unknown length. These fibrils are almost certainly remnants of the original polymer fibre.

4.3 Strength

The strength of individual fibres within a tow have a coefficient of variations up to 30%; the average strength of fifty fibres varies with the testing gauge length in the way shown in Fig. 21 (7). This behaviour is characteristic of a material containing flaws or defects of varying severity and at random axial positions, at which fracture originates. Evidently, from Fig. 21, the complete spectrum of severity of defects is not included in 20 cm of fibre.

We do not positively know what these defects are but, in view of the fibrillar nature of the structure, it is tempting to 'blame' the fibril-fibril junctions.

5. PROPERTIES OF CARBON FIBRE/EPOXY RESIN COMPOSITES

Various resins can be used as matrices and reinforced with carbon fibre but because of the interest of the aerospace industries the majority of the work has so far been carried out with epoxy resins. The chief problem is associated with the difficulty of handling thousands of very fine filaments. There is a problem in maintaining alignment and a tendency to damage due to mutual abrasion particularly if the fibres are not properly wetted by the resin. Composites have been made by wet lay-up techniques and by manufacturing pre-pregs, as well as by filament winding.

The following sections describe test methods and comment on some of the properties of particular interest.

Table 4 gives a collection of results from a variety of sources. More recent results will be presented at the Conference.

5.1 Specimen preparation and test methods

Test specimens have been made in the form of moulded bars and N.O.L. rings.

For flexural and impact tests a leaky mould technique is used to make bars 3.7" × 0.5" × 0.083" from preimpregnated tows.

For interlaminar shear strength tests similar bars 0.62" × 0.5" × 0.1" are used.

For tensile tests on composite bars a specimen of the shape shown in Fig. 22 is used.

Tests for interlaminar shear strength and flexural strength are normally made by a three point bend method using a distance between supports of 0.57" for interlaminar shear and 2.5" for flexural strength, giving length thickness ratios of approximately 6 and 30 respectively.

It is appreciated that a four point bend method is more satisfactory but for the comparative tests normally required, the simpler method is adequate.

N.O.L. ring specimens are produced and tested by internal hydraulic pressure for tensile strength in the machine shown in Fig. 23.

5.2 Interlaminar shear strength and impact strength

The first carbon fibres which were produced had poor adhesion when incorporated into resins, especially the Type I (High Modulus) variety. A number of surface treatments for the fibres have been developed (8, 9 and 10) which have the effect of improving the interlaminar shear strength (I.L.S.S.). It is possible to increase the interlaminar shear strength of Type I (High Modulus) fibre from between 2500 and 4000 p.s.i. to over 8000 p.s.i.; and Type II (High Strength) fibre from 5000 to 7000 p.s.i. up to over 11 000 p.s.i. The actual numeri-

TABLE 4

Results of tests on composites

Company	A		B	M.R.D.	
Reinforcement	Type I	Type I	Type II	Type I	Type II
Specific gravity	1.66	1.72	1.62	1.6	1.5
Volume % fibre	50	?	?	50	50
Resin	3M-PR-279		E-798	Epikote 828	
Flexural strength (psi)	107 200	113 000	322 000	104 000	150 000
Flexural Mod. ($\times 10^{-6}$ psi)	34.6	29.4	22.9	24	15
I.L.S.S.	4000 (untreated)	4400 (untreated)	11 400 (untreated)	8000 (treated)	11 000 (treated)
Impact (ft lb/in)	—	—	—	12 (treated)	12 (treated)
Tensile strength (psi)	—	—	—	130 000	180 000
Tensile mod. ($\times 10^{-6}$ psi)				30	20

TABLE 5

Fatigue test results on fan blade

by Dowty Rotol Limited
50% v/v Type I fibre in epoxy resin (untreated fibre)

Note:- In none of the cases quoted has actual failure occurred.

(a) **Oscillatory Bending**

Specimen No. 1 — ± 10 000 p.s.i. for 100 × 10^6 cycles followed by
± 15 000 p.s.i. for 100 × 10^6 cycles

Specimen No. 2 — ± 10 000 p.s.i. for 100 × 10^6 cycles followed by
± 12 000 p.s.i. for 145 × 10^6 cycles

Specimen No. 3 — ± 17 000 p.s.i. for 120 × 10^6 cycles

(b) **Steady Tensile Force and Bending with Oscillatory Bending**

Specimen No. 1 — Steady tensile force — 1260 lbs
Steady bending maximum tensile fibre stress — 15 600 p.s.i.
Oscillatory bending ± 5200 p.s.i.
Cycles applied 50 × 10^6

Specimen No. 1 — Steady tensile force — 1100 lbs
Steady bending maximum tensile fibre stress — 13 200 p.s.i.
Oscillatory bending stress ± 4850 p.s.i.
Cycles applied 33 × 10^6

This represents very approximately twice the life of a corresponding glass fibre reinforced plastic blade for the same drop in stiffness which is the criterion used in lieu of complete break-up for all blade testing for gas turbine engines.

The C.R.P. blade is 25% lighter and three times the flexural stiffness of a corresponding glass fibre reinforced blade.

cal results obtained depend on the resin and the method of test but under standardised conditions results can be compared. The treatment now in use in our process does not affect the mechanical properties of the fibre or contaminate its surface. Fig. 24 shows values of I.L.S.S. of Type I and Type II fibres both in the untreated condition and after surface treatment. Also shown is the curve of modulus against I.L.S.S. from reference 9 for a variety of fibres of different origin. The tendency, which Fig. 24 reveals for high modulus fibres to have inherently less resistance to interlaminar shear than low modulus fibres must imply that the graphite orientation in some way affects bonding to the resin. The mechanism of this is obscure but there are two schools of thought.

(a) A chemical species of some kind is present at the interface and is more effective in promoting bonding in fibres of poor orientation.

(b) The surface is rougher in the poorly oriented fibres and so mechanical keying of fibre to resin is better.

As interlaminar shear strength improves, so for a given resin system impact energy at fracture decreases; this is interpreted by Blakelock (11) as a straightforward consequence of the resin-fibre bond strength. With a strong bond, fracture in a fibre will tend to propagate transversely through the resin to the neighbouring fibre and the stress concentration at the tip of the crack may be sufficient to fracture it leading eventually to brittle failure. With a weak bond the fracture path will tend to follow interfaces, and so be longer and thus dissipate more energy in a fibrous type of failure. Fig. 25 shows specimens of low and high I.L.S.S. after fracture.

5.3 Fatigue strength

Components reinforced with carbon fibres have a fatigue resistance superior to that of glass fibre reinforced plastics and a high damping factor. McCarthy (12) has tested a fan blade containing 50% V/V of Type I fibre and obtained the results shown in Table 5. These tests are still in progress.

5.4 Friction and wear properties

The incorporation of fairly small proportions of carbon fibre in a wide variety of resin matrices has the effect of reducing the wear rate against steel or other surfaces by orders of magnitude (13, 14) and also reduces the coefficient of friction to a value of about 0.3 irrespective of the original value for unreinforced resin.

5.5 Effect of using yarn as reinforcement

The use of the spun yarn for the manufacture of composites is just beginning to be investigated. In general it appears that the mechanical properties of composites made with spun yarn are somewhat lower, perhaps up to 25% in most properties, compared with the composites made of continuous filament material. Further details of these results will also be given at the Conference.

6. CONCLUSIONS

A new structural material has been sought for some time, which combines light weight with greater stiffness than can be achieved with any existing material. Carbon fibres provide a reinforcement for resins which meets this demand.

During 1967 carbon fibre of high quality was produced in tonnage quantities of short lengths with consistent and reproducible properties. It is now being produced in longer lengths as continuous filament tow and spun yarn which are suitable for the manufacture of pre-preg sheet and tape and for filament winding.

It has been found that when these fibres are incorporated into resin matrices the properties of the fibre and resin combine in the predicted manner to give composites with the expected qualities.

7. ACKNOWLEDGEMENTS

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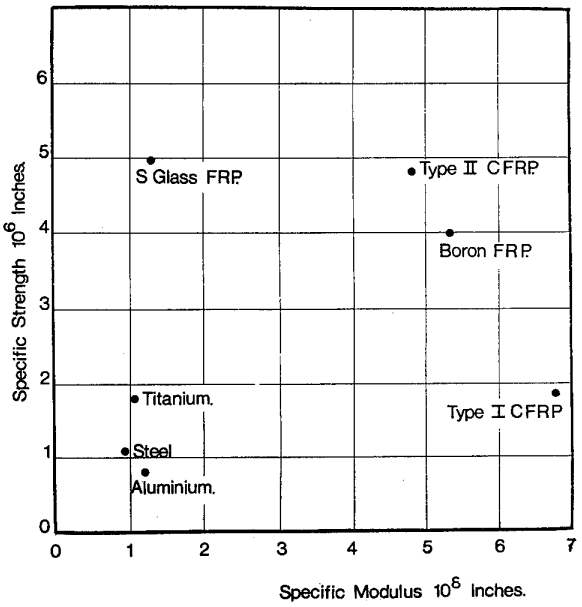


Fig. 1 Specific properties of composites

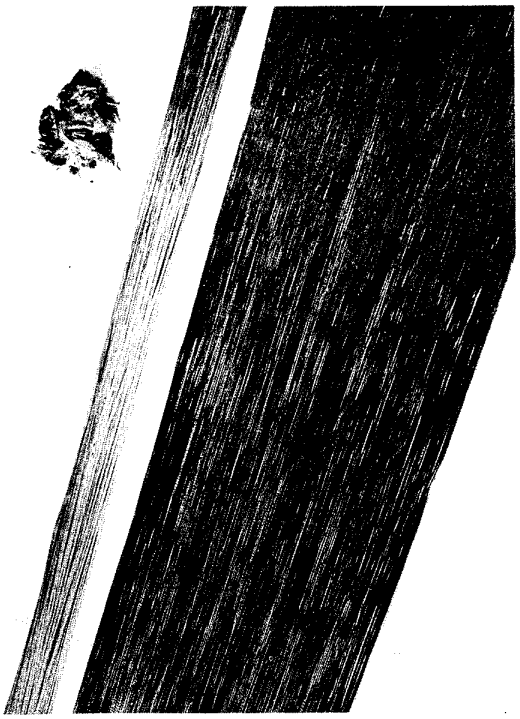


Fig. 2 Short length material and pre-preg sheet

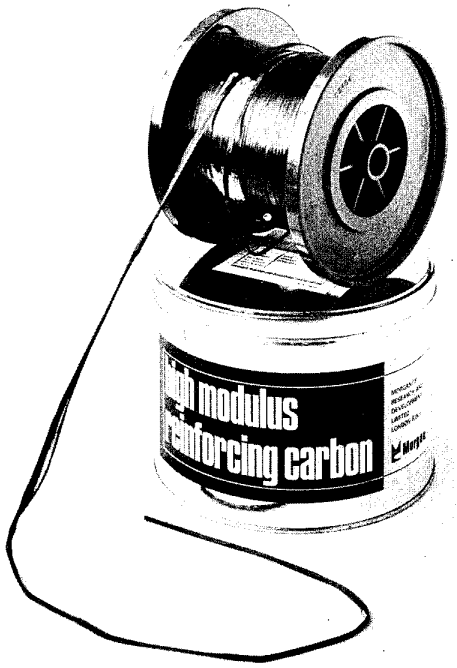


Fig. 3 Long length material

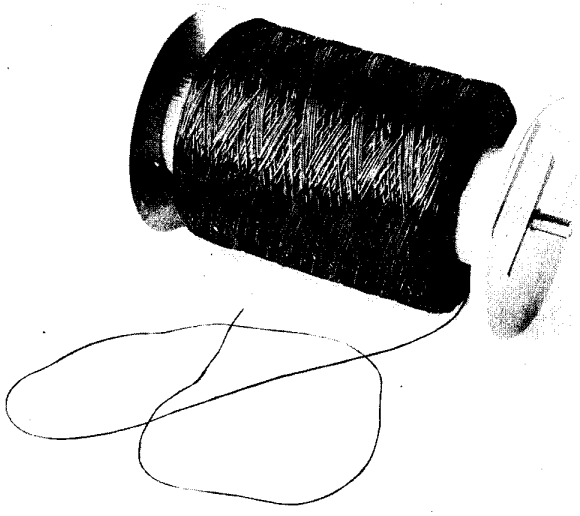


Fig. 4 Spun yarn

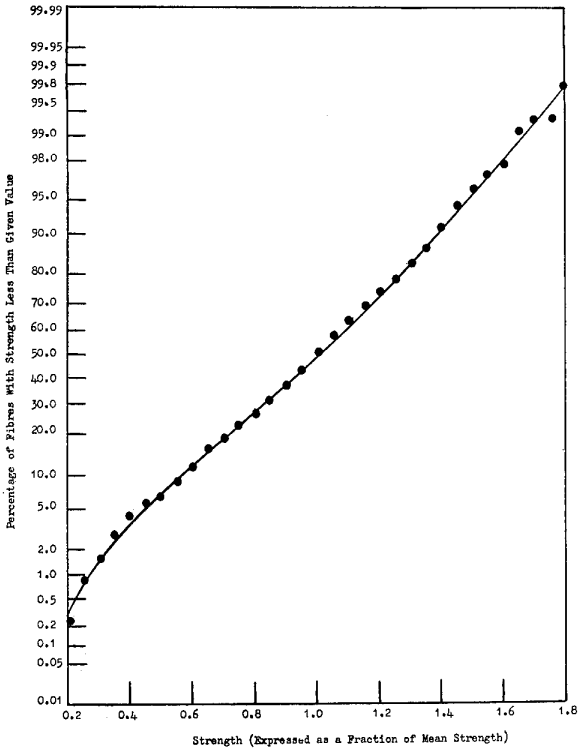


Fig. 5 Variation of strength within one batch

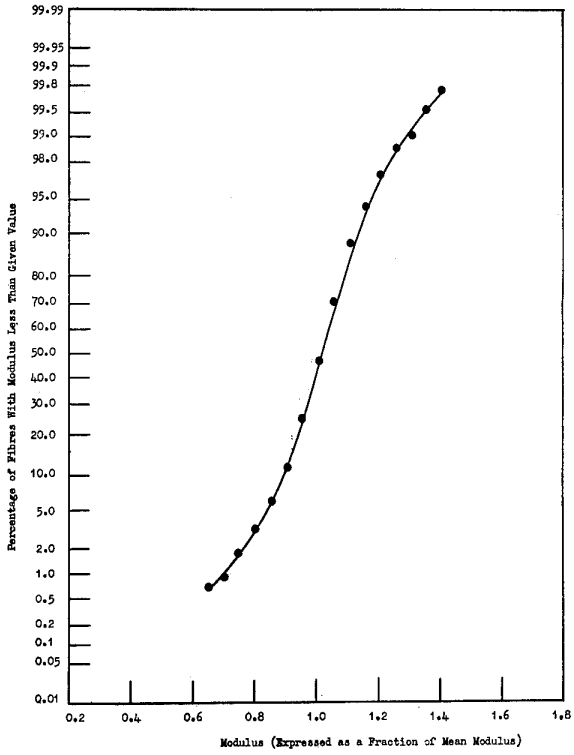


Fig. 6 Variation of modulus within one batch

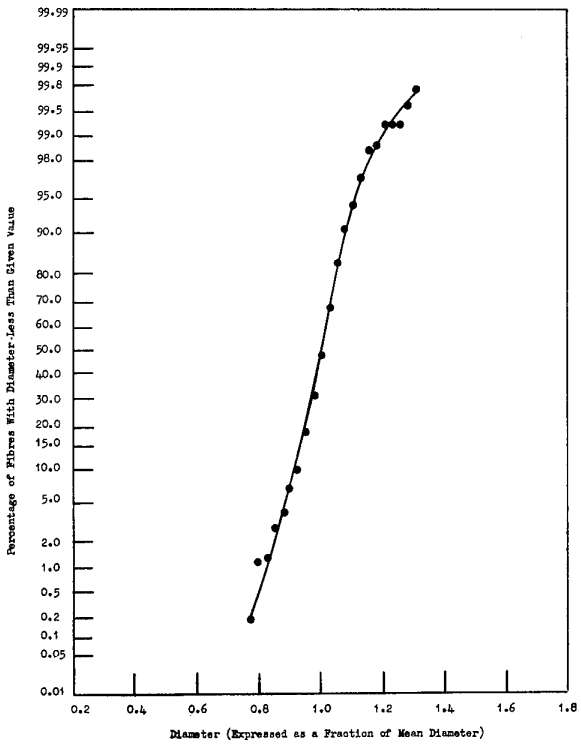


Fig. 7 Variation of diameter within one batch

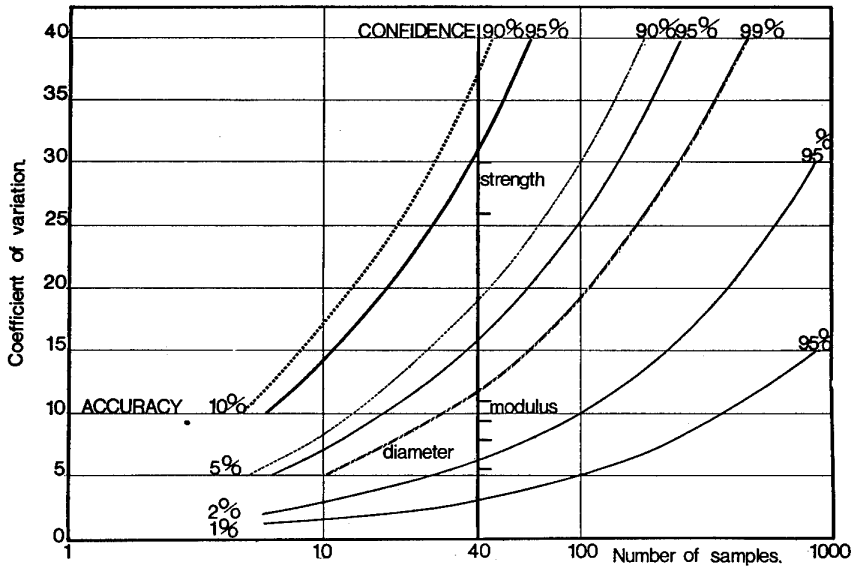
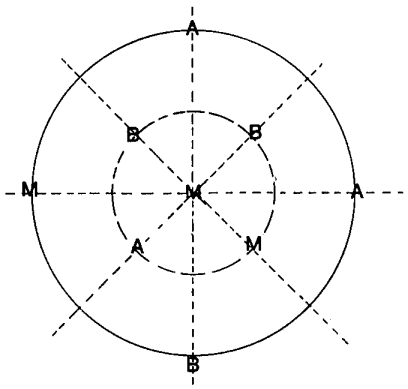


Fig. 8 Variation, confidence and accuracy related to a number of samples

(a) End view of bundle



(b) Side view

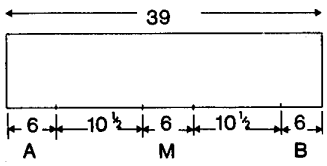


Fig. 9 Sampling scheme

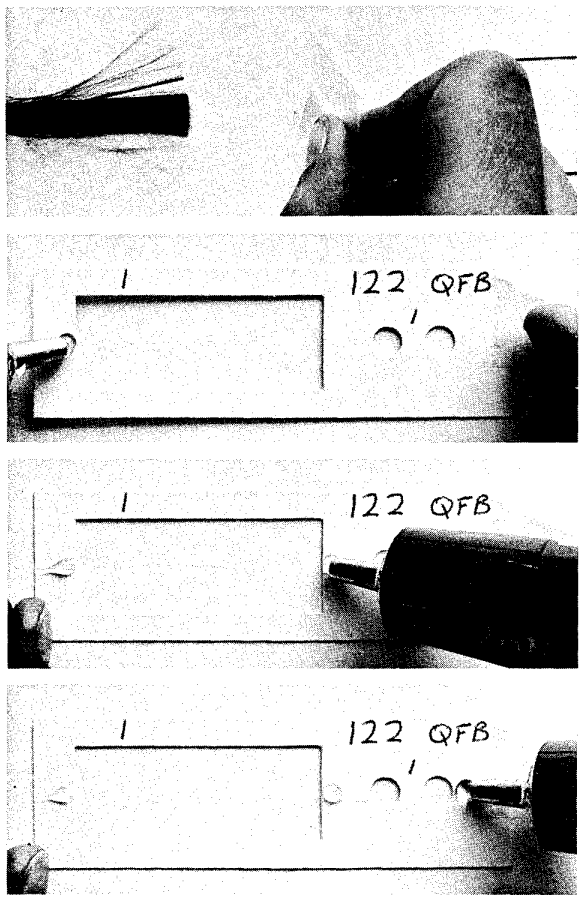


Fig. 10 Mounting filaments on cards

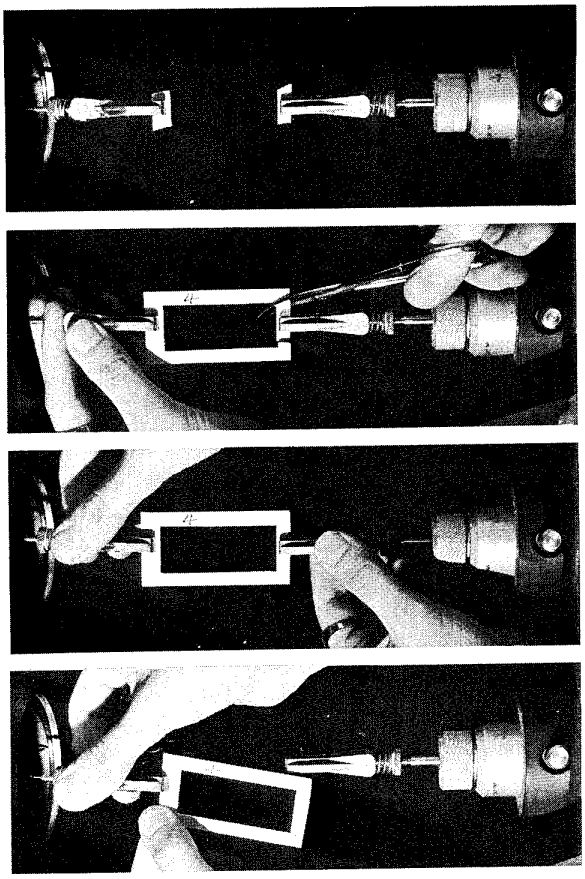


Fig. 11 Mounting cards in tensile testing m/c

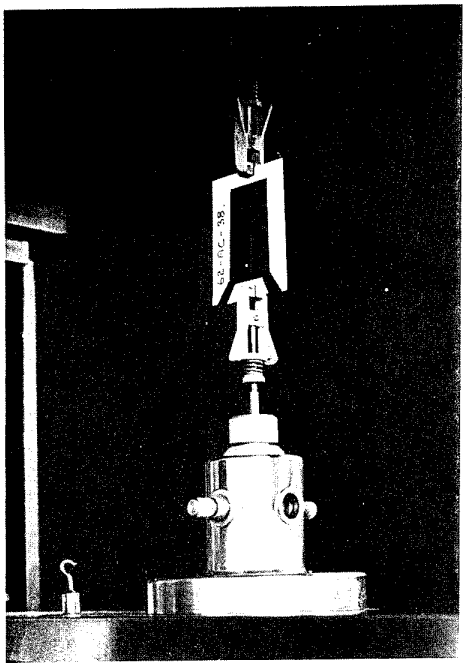


Fig. 12 Tensile test

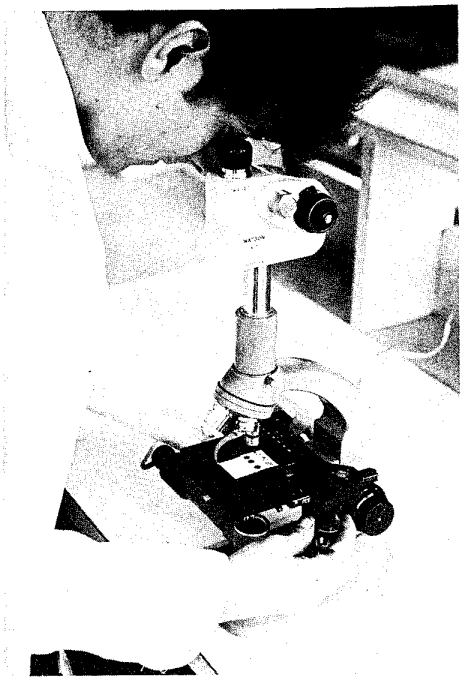


Fig. 13 Diameter measurement

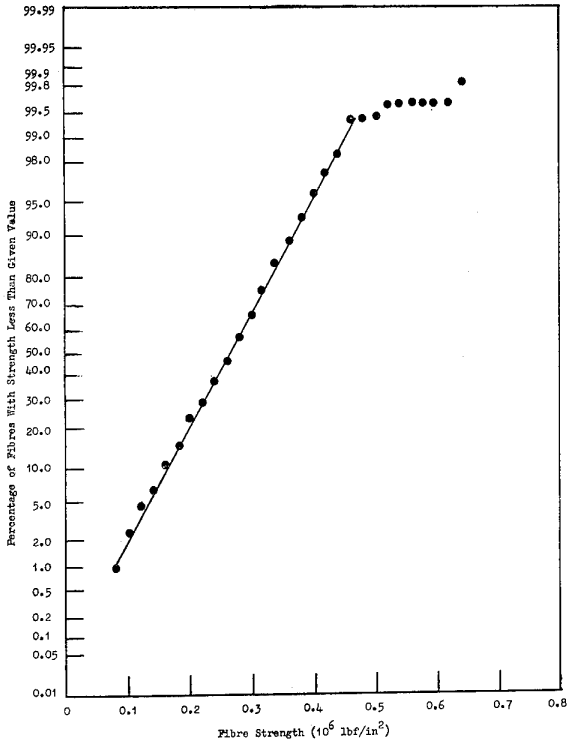


Fig. 14 Variation of strength of overall production of short lengths

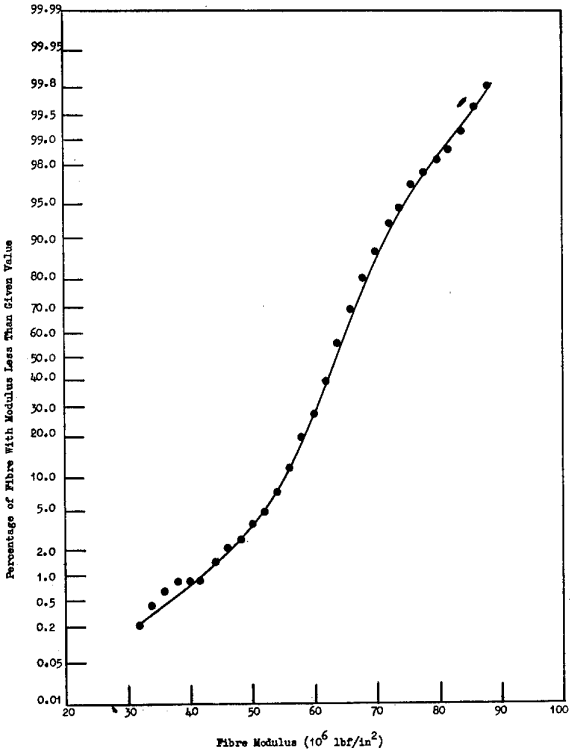


Fig. 15 Variation of modulus of overall production of short lengths

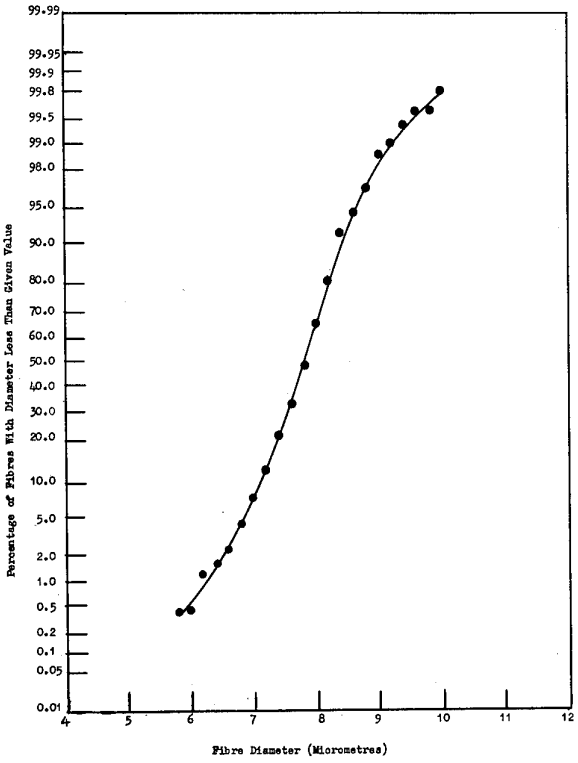


Fig. 16 Variation of diameter of overall production of short lengths

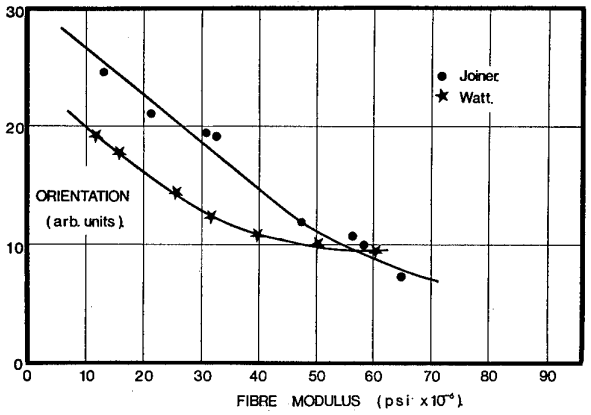


Fig. 17 Orientation and modulus measurement

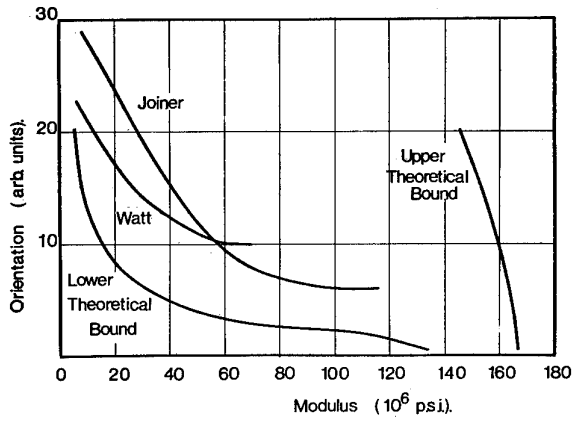


Fig. 18 Orientation and modulus calculated results

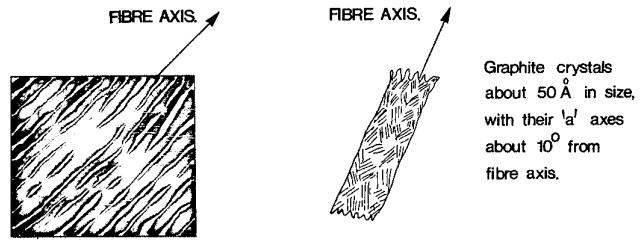


Fig. 19 Schematic representation of fine structure of filament

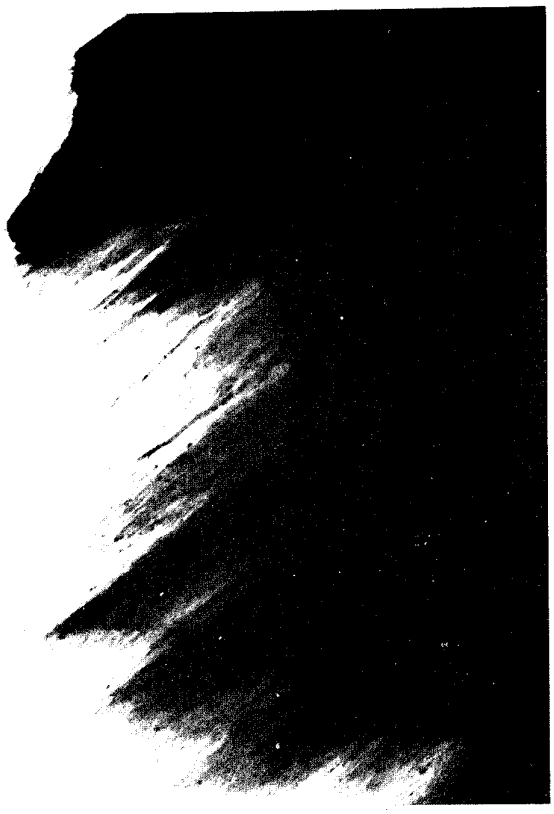


Fig. 20 Cut end of filament ×10 000

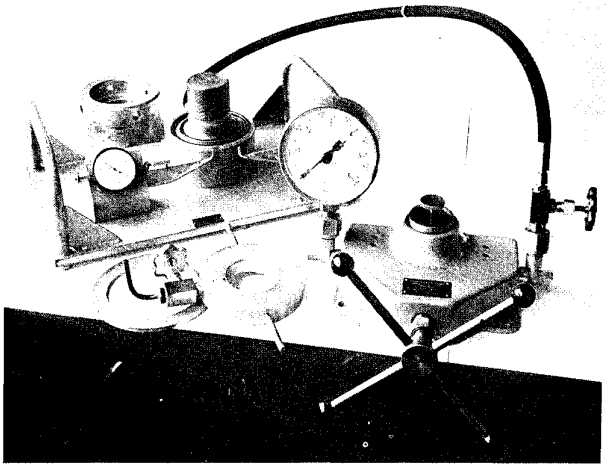


Fig. 23 N.O.L. ring apparatus for tensile strength

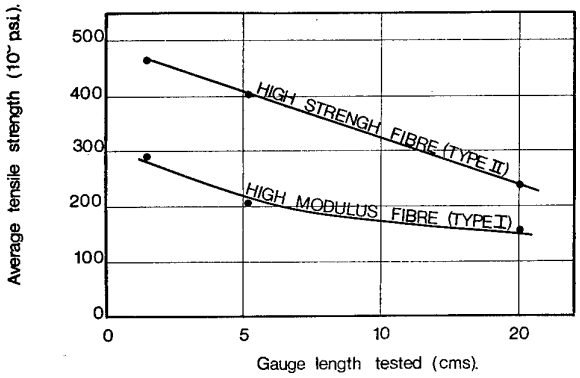


Fig. 21 Variation of measured strength with gauge length

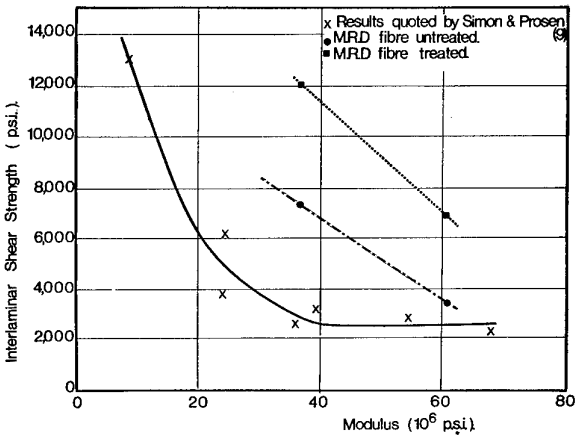


Fig. 24 Interlaminar shear strength and modulus relationship

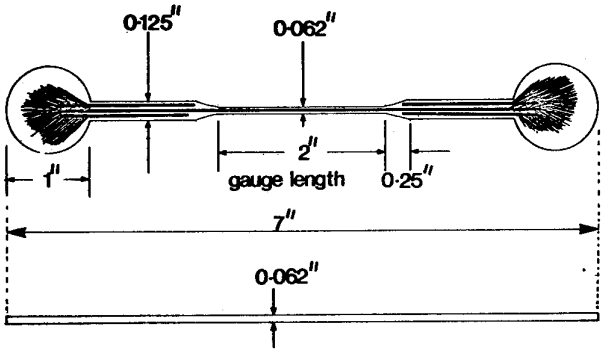


Fig. 22 **Tensile specimen** for composites

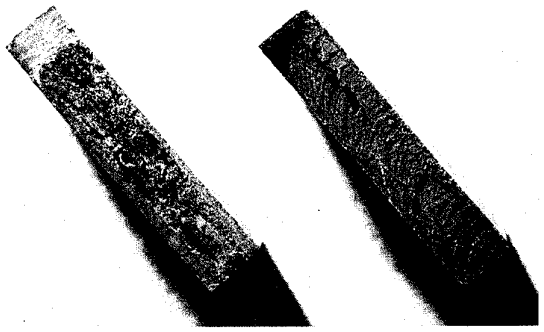


Fig. 25 Impact specimens

Sixth International Reinforced Plastics Conference

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Measurement of mechanical properties at tempertures down to 4.2°K

R. SHELDON, Science Research Council, Rutherford High Energy Laboratory

1. INTRODUCTION

Superconducting magnets and bubble chambers require that glass reinforced plastics should operate satisfactorily at the temperature of liquid helium (4.2°K or −269°C), an environment in which the knowledge of their mechanical properties is sparse. An evaluation of the effects of low temperature on the mechanical properties of these materials is required before the manufacture of large scale equipment may be undertaken.

2. MATERIALS

A number of conventional epoxy materials were examined in conjunction with various glass fibre arrangements. An unreinforced and a filled resin system were also included in the programme to aid analysis of the data.

2.1 Reinforcement

The following modes of reinforcement were examined:-

Unidirectional glass fibre*

Plain weave glass fabric

Satin weave glass fabric

Particulate filler†

2.2 Resins

Epoxy resins, representative of three basically different molecular structures were selected for examination, (Ref. 1).

Namely: Bisphenol A diglycidyl ether

Glycidyl amine

Epoxy Novalak

An acid anhydride (methyl nadic anhydride) and a primary aromatic diamine (diamino diphenyl methane) were chosen as curing agents for each of the above resins.

The methods of sample preparation are given in the appendix, together with details of the glass to resin ratios achieved.

An evaluation of the effects of various modes of glass reinforcement was undertaken using a common resin system (bisphenol A diepoxide cured with diamino diphenyl methane). Specimens were cut from the warp and weft directions of the panel and at an angle of 45° to these principal axes. Following this, a study of different resins was carried out. Specimens were cut at an angle of 45° to the principal axes of the plain weave glass fabric reinforced panels.

3. TEST EQUIPMENT

It is a fundamental requirement for the test specimen to be immersed in liquid helium at 4.2°K and to be coupled to a testing machine at a room temperature of approximately 300°K. The straining assembly which attaches the test specimen to the moving crosshead, has been designed to minimise heat conduction into the cryostat. This is shown diagramatically in figure 1. Figure 2 shows the general layout of the test facility. It was considered desirable to base the test equipment on a standard commercial testing machine of proven design. The basis of the test facility at the Rutherford Laboratory is an Instron‡ test machine, having an additional

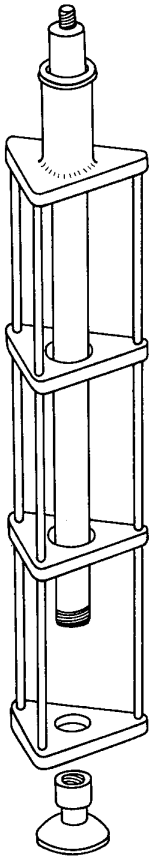


Fig. 1 Diagram of straining assembly

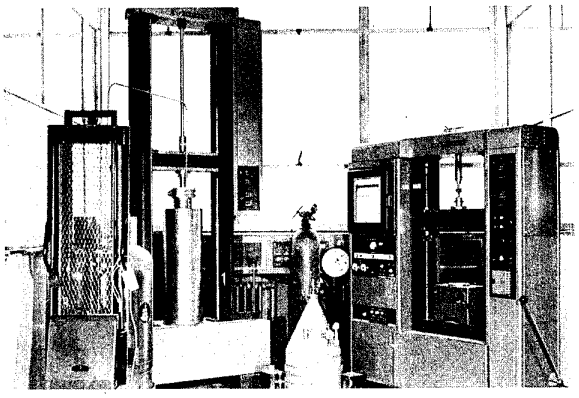


Fig. 2 General layout of test facility

width of 20 cm and an additional 107 cm of crosshead travel. (Ref. 2). The load may be accurately recorded up to 5000 kg, and the rate of crosshead travel may be varied in 13 increments from 50 cm/minute to 0.005 cm/minute. The downward motion of the crosshead applies the stress through the compression member of the straining assembly to the base of the specimen. This stress is transmitted through the specimen, via the tension member of the straining assembly to the load cell. The tension member is manufactured in three sections in order that the upper member may be removed to facilitate raising the crosshead to withdraw the assembly from

* Permaglass, XE 5 Permali Ltd., Bristol Road, Gloucester.
† Permacast Permali Ltd., Bristol Road, Gloucester.
‡ Model TTCM, Instron Ltd., High Wycombe, Bucks.

the cryostat. It is also possible to calibrate the load cell whilst the straining assembly and specimen are cooling, by removal of the upper tension member.

A substantial part of the cycle time in the test procedure is devoted to cooling the specimen from room temperature to 4.2°K, permitting a maximum of two tests per working day. An apparatus capable of accepting ten specimens in each cool-down and testing these consecutively has been designed. With this apparatus it will be possible to perform a maximum of ten tests per day, thus significantly reducing the cost per test. Full facilities are provided to recover helium gas during the test cycle.

4. SPECIMEN DESIGN AND PREPARATION

4.1 Flexural specimen

Test specimens were cut from the laminates using a diamond tipped cutting disc. A span to depth ratio of 16 in accordance with ASTM D 790-59T was adopted, but a specimen width of 6 mm was selected to simplify the problems associated with the design of the proposed multi-specimen testing assembly. The radius of the loading members was 3 mm. Results obtained at room temperature using this modified specimen were in good agreement with results obtained using a standard specimen.

4.2 Tensile specimen

The microtensile test specimen ASTM D 1708-59T was modified slightly to incorporate a taper grip, since previous work at 20° K has shown this to be the best method of gripping the specimen, (Refs. 3, 4). The specimens were trimmed to shape by a commercial cutting machine* using a template.

4.3 Interlaminar shear specimens

The mode of failure of the materials in the tensile tests at low temperatures, indicated a tendency for delamination. (Fig. 3). In order to investigate the changes in the strength of the interlaminar bond at low temperatures, the tensile test specimen was notched on opposite sides, to provide a shear area in which failure could occur. (Ref. 5). It was found in practice that the optimum shear length was equal to specimen width. This configuration was therefore adopted for this series of test. The various types of test specimen used are illustrated in Figure 4.

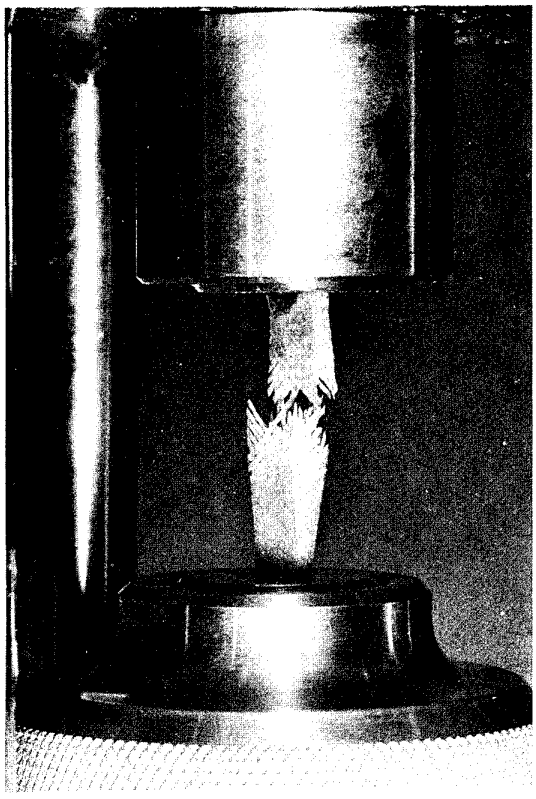


Fig. 3 Tensile specimen showing delamination which occurred on failure at 4.2°K

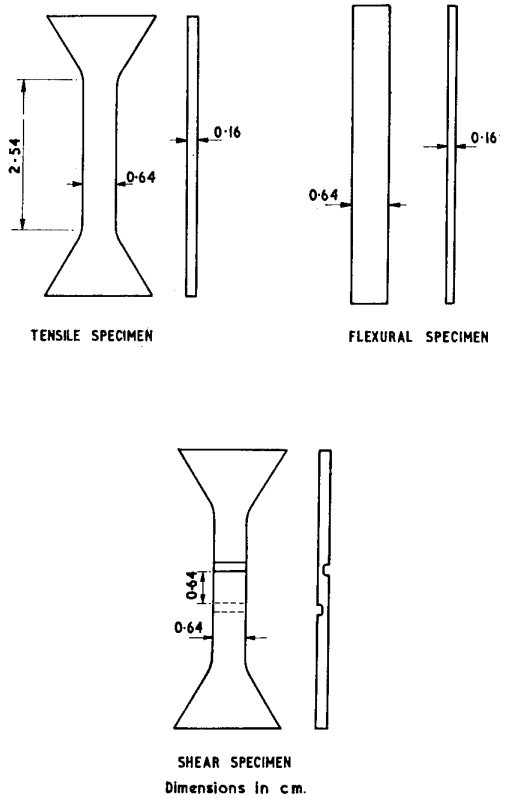


Fig. 4 Mechanical test specimens

5. EXPERIMENTAL

The precision of each test procedure was established at room temperature and at 4.2°K, using five replicates, the results being shown in the appendix, table IV. In order to reduce the number of tests at 4.2°K, most materials were tested in duplicate and the results accepted where agreement was within 10%, which was shown to approximate to two standard deviations.

The rate of crosshead motion for all tests was 0.05 cm/minute, which corresponds in the flexural test to a maximum strain rate of 0.007/minute, and in the tensile test to a strain rate of 0.02/minute.

A further feature of interest which was examined was the possibility of degradation of the glass/resin bond by the stresses set up by the rapid cooling of the specimen. The thermal expansion coefficients of the glass and epoxy resin are markedly different, and therefore cooling of the composite specimens may result in enhancement of stress at the glass/resin interface. It has previously been reported (refs. 3, 4) that the rate of cooling of glass reinforced specimens to 20° K had no observable effect on the mechanical properties of the material. This was borne out by an experiment involving repeated cycling of specimens of composite through a wide temperature range. Flexural test specimens were plunged alternately (for 15 minute periods) in liquid nitrogen and boiling water (ΔT = 296°C) for a period of six hours. It was shown that the flexural modulus at room temperature was decreased by 4% and the flexural strength was not significantly changed following this treatment. Data are presented in tables 1, 2, 3 and 4. Figure 5 shows the variation of flexural strength of a typical epoxy resin/glass fibre composite with temperature and figure 6 shows the changes in modulus with temperature.

* Tensilkut—Metallurgical Services, Betchworth, Surrey.

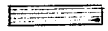
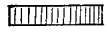
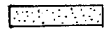
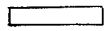
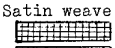
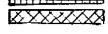
TABLE 1

Flexural properties at 4.2°K (specimens cut in the bias direction)

Hardener	Resin	Flexural Modulus (Kg/cm^2)	Flexural Strength (Kg/cm^2)	Deflection at Break (cms)
DDM	Epikote 828	2.2×10^5	7670	0.39
	CIBA 1020	2.5×10^5	6727	0.25
	CIBA LY558	2.4×10^5	6816	0.34
MNA	Epikote 828	2.4×10^5	7914	0.46
	CIBA 1020	2.6×10^5	7570	0.28
	CIBA LY558	2.4×10^5	6668	0.37

TABLE 2

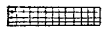
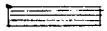
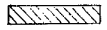
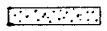
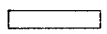
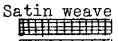
Flexural strengths Kgs/sq cm

Orientation of Filler	Room Temperature	4.2°K	Ratio 4.2°K : R.T.
	4.3×10^3	1.0×10^4	2.3
	2.7×10^3	7.7×10^3	2.9
	1.6×10^4	3.1×10^4	1.9
	1.5×10^3	6.1×10^3	4.1
	8.3×10^2	4.5×10^3	5.4
	1.4×10^3	2.5×10^3	1.8
	6.9×10^2 Range (4 to 12×10^2)	1.3×10^3 * Range (0.6 to 2.2)	1.9
Satin weave 	4.3×10^3	1.0×10^4	2.3
	2.6×10^3	7.0×10^3	2.7

*77°K

TABLE 3

1% secant moduli Kgs/sq cm

Orientation of Filler	Room Temperature	4.2°K	Ratio 4.2°K : R.T.
	1.9×10^5	3.0×10^5	1.6
	1.1×10^5	2.4×10^5	2.2
	4.6×10^5	5.6×10^5	1.2
	1.6×10^5	5.2×10^5	3.2
	1.6×10^5	4.5×10^5	2.8
	9.1×10^4	2.7×10^5	3.0
		1.6×10^5 *	1.8*
	3.1×10^4	7.4×10^4 *	2.4*
Satin weave 	1.9×10^5	3.1×10^5	1.6
	1.1×10^5	2.5×10^5	2.3

*77°K

TABLE 4

Deflection at break (cms)

Orientation of Filler	Room Temperature	4.2°K	Ratio 4.2°K : R.T.
	0.16	0.32	2
	0.65	0.41	0.63
	0.25	0.51	2
	0.07	0.07	1
	0.05	0.06	1.2
	0.11	0.08	0.7
		0.09 *	
	0.33	0.22 *	0.7
Satin weave			
	0.16	0.32	2
	0.82	0.32	0.4

*77°K

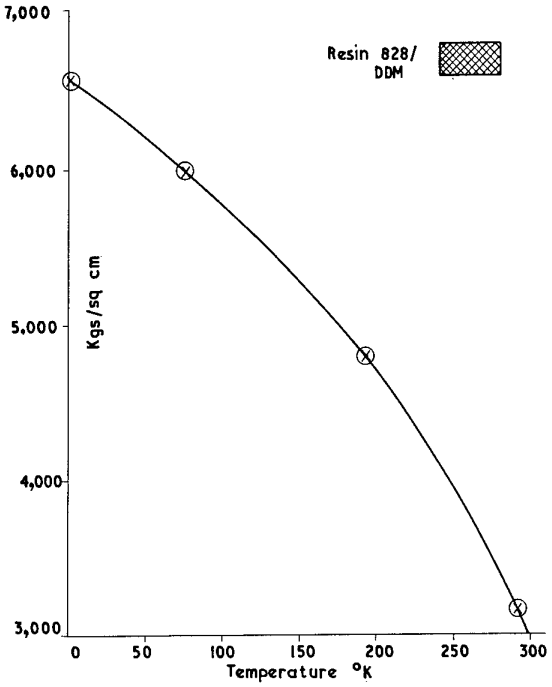


Fig. 5 Flexural strength against temperature

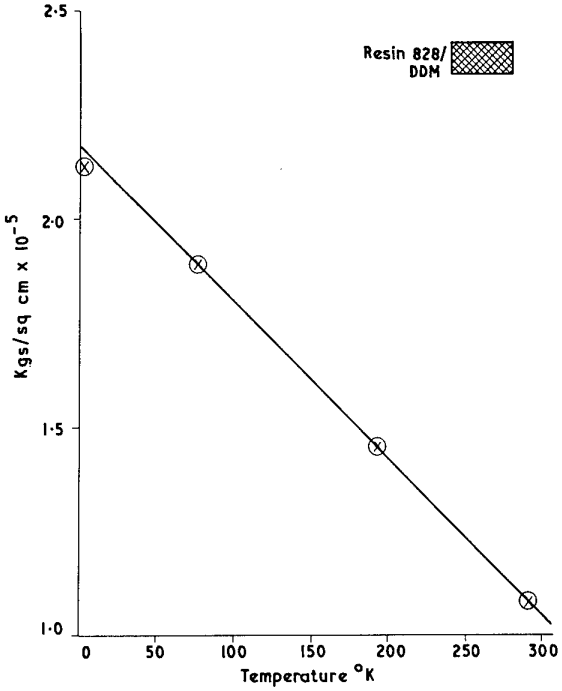


Fig. 6 1% secant modulus against temperature

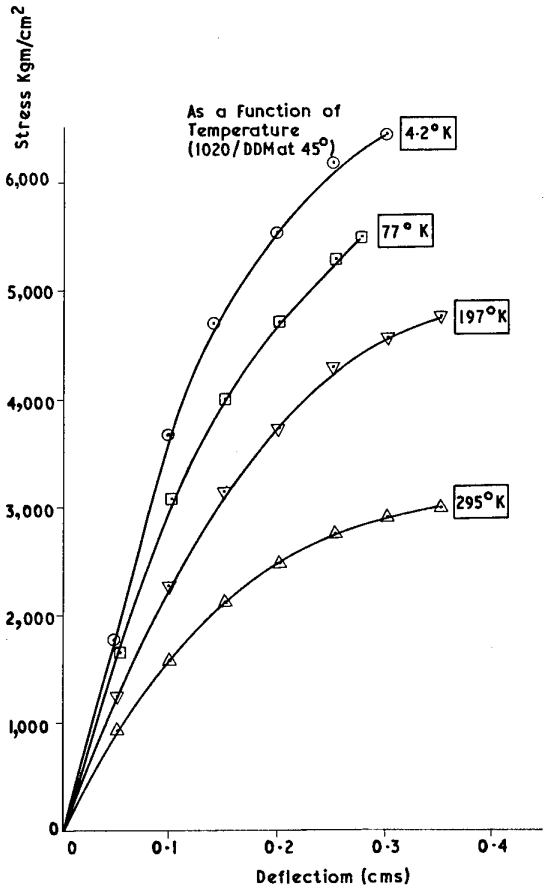


Fig. 7 Typical stress/strain curves. As a function of temperature (1020/DDM at 45°)

6. DISCUSSION

The cross-breaking strength of all materials tested at 4.2°K is nearly double that of their room temperature values. (Tables 1, 2 and 3). The interlaminar shear strengths do not increase so markedly with cooling and in most cases are very similar to the room temperature values. The fact that the shear strength does not increase in the same proportion as tensile strength has previously been suggested, (ref. 3) when severe gripping difficulties were experienced in tensile testing. The modulus of the specimens also increases, although the general shape of the stress/strain curve does not change significantly. A family of typical stress/strain curves for one composite at temperatures from 4.2°K to room temperature are shown in figure 7.

The change in modulus which occurs on cooling to 4.2°K is dependant upon the orientation of the reinforcing fibres. Specimens with longitudinal reinforcement show only a small increase in modulus, whereas specimens with reinforcement in the bias or transverse directions show a larger increase in modulus. (Table 3). The change in deflection necessary to break the specimen is also shown to be dependent upon fibre orientation. (Table 4). Specimens having longitudinal reinforcement will sustain a greater deflection at low temperatures than at ambient, whereas the reverse is nearly always

true for bias specimens. The results of this behaviour is that the difference in properties between the longitudinal and bias directions becomes smaller at low temperatures. This may be observed by comparing the data obtained at room temperature and at 4.2°K, reported in tables 2 and 3 and figure 8.

The mechanical properties of the laminates prepared from the six different resin systems were similar at room temperature and behaved similarly on cooling to 4.2°K. In general, systems cured with MNA showed greater deflection at break at 4.2°K and tended also to have higher flexural strengths than the systems cured with DDM. (Table 1). Bisphenol A resin system gave laminates having marginally higher flexural strengths and somewhat greater deflections at break.

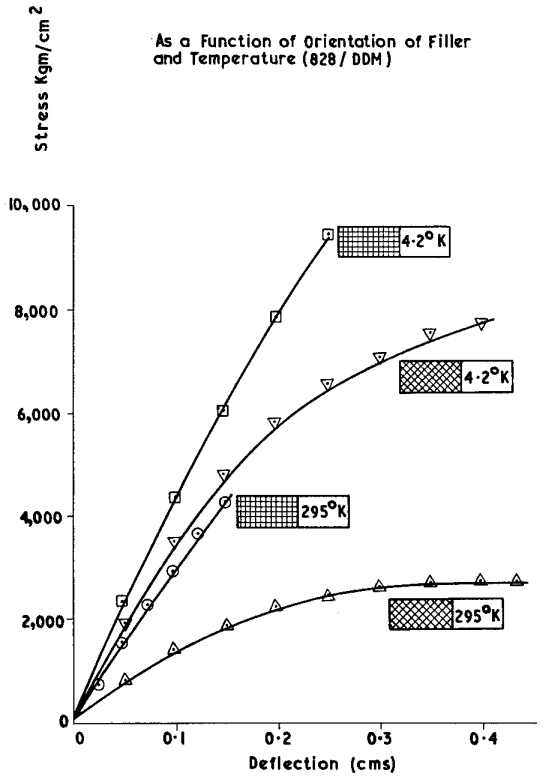


Fig. 8 Typical stress/strain curves. As a function of orientation of filler and temperature (828/DDM)

Finally, for non-reinforced epoxy resins or resins with particulate fillers, the increase in modulus on cooling is greater than the corresponding increase in flexural strength; whereas for glass fibre reinforced composites, the reverse applies.

7. CONCLUSIONS

The work described may be regarded as the precursor of a larger programme which is becoming increasingly important with the advances in technology of superconductors. At this stage the needs of design engineers dictate to a large extent the types of materials to be tested. In the first instance, it is desired to determine whether readily available materials are suitable for use at 4.2°K, rather than embark on a large programme to evaluate fully all plastics materials. However, if the impetus in cryogenic engineering is maintained, the need for plastics insulating materials will increase manyfold and it is hoped to expand the programme of testing accordingly.

8. ACKNOWLEDGEMENTS

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APPENDIX

1. Epoxy resins

TABLE 1

Resin	Manufacturer and Designation
Bisphenol A diglycidyl ether	Shell Epikote 828
Glycidyl Amine	CIBA X83/1020
Epoxy Novalak	CIBA LY 558

2. Crosslinking agents

TABLE 2

Type	Chemical name	Proportion of hardener per 100 parts of resin		
		Bisphenol A	Glycidyl Amine	Epoxy Novalak
Acid anhydride	5 methylendomethylene 1234 tetrahydrophthalic anhydride (MNA)	80*	110*	100*
Primary aromatic amine	Diamino diphenyl methane (DDM)	27	40	30

* plus 1 pphr of Benzyl dimethylamine

3. Preparation of Laminates

Each laminate was constructed from ten layers of glass fabric, using conventional hand lay-up techniques. In some cases elevated temperatures were used to ensure complete impregnation of the cloth. The substrate was a polished metal platen, which had been treated with a silicone release agent.* The top platen, (also silicone treated) was positioned after the final fabric layer had been impregnated, and the laminate pressed between stops, to give a nominal glass/resin ratio of 60/40. Following cure of the material at the specified temperature, a substantially void free laminate approximately 0.064" thick was produced. The axes of subsequent layers of fabric were parallel to those of the previous layer, but the warp and weft directions were randomised. In addition to these materials, a commercially available unidirectional glass/epoxy laminate was also included in the test programme. This was Permaglass† XE 5, the resin system being MY 750‡ and DDM.

* Releasil 14—Midland Silicones Ltd., Barry, Glamorgan.
† Permali Ltd., Bristol Road, Gloucester.
‡ CIBA (A.R.L.) Ltd. This material was regarded as equivalent to Epicote 828/DDM.

TABLE 3

Glass/Resin ratios (plain weave) by weight

Hardener \ Resin	Epikote 828 (Shell)	X83/1020 (CIBA)	LY 558 (CIBA)
MNA	59:41	58:42	58:42
DDM	60:40	55:45	58:42
Permaglass XE 5	80:20		

The glass/resin ratio for the laminates constructed from satin weave glass fabric was also nominally 60:40. Unreinforced materials were also included in the test for completeness. These were a cast resin system (Shell 828/DDM) and a silica filled resin.*

4. Replication

TABLE 4

(1) Flexural strength X83/1020 and DDM on the Bias at 4.2°K. Results in Kg/cm^2

Individual results	Mean	Standard deviation
6596	6727	273 (4.1%) S.D. (mean) 124 (1.8%)
7172		
6723		
6439		
6703		

* Permacast—Permali Ltd., Bristol Road, Gloucester. CT200/9010. 200 pphr silica flour.

TABLE 5

(ii) Interlaminar shear on the bias at 4.2°K. X83/1020 and DDM. Results in kg/cm^2

Individual results	Mean	Standard deviation
120		
135	128	8.4
139		(6.6%)
127		
121		

It would have been desirable to use specimens drawn from duplicate panels to check inter-panel replication. However, this was not always possible, and inter-panel replication was determined by using specimens drawn from four panels and found to be not significant.

5. **Cure schedules**

TABLE 6

Curing Agent	Resin	Cure time (mins)	Cure temp. (°C)	Post cure
	828	30	100	—
DDM	1020	120	100	2 hrs at 180°C
	LY 558	120	100	2 hrs at 180°C
	828	240	150	—
MNA	1020	180	80	1½ hrs at 130°C + 16 hrs at 180°C
	LY 558	120	100	2 hrs at 140°C + 8 hrs at 180°C

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The determination of allowable wall stress for glass reinforced plastics pipe by measurement of elastic deformation

H. M. SCHWENCKE and A. W. DE RUYTER VAN STEVENINCK, Shell Plastics Laboratory, Delft, Holland

1. INTRODUCTION

Glass-reinforced epoxy and polyester pipes, especially those made by the filament winding technique, are now becoming generally accepted. The material is no longer only of interest to those concerned with ballistics for military or space travel purposes.

This new development can be explained by a number of reasons: the high strength to weight ratio of glass reinforced or more specifically filament wound structures, the absence of corrosion problems, the high chemical resistance and the low level of creep (compared with thermoplastics); all these properties have paved the way to more-down-to-earth applications. Moreover, the possibility of applying the reinforcement in the direction of the major stresses, and the growing availability of commercial filament winding equipment have been factors responsible for an industry-wide interest. The combination of extremely strong glass fibres and a resin which acts as an adhesive to preserve the optimum fibre orientation, and at the same time as a stress transfer medium between the fibres, presents a unique set of properties, which places filament wound material in between conventional materials — e g. metals — and the thermoplastics. This is of great value in constructions for which a combination of the above mentioned properties is required, i.e. in (pressure) pipes and vessels.

If excellent properties were the only criterion, there would be no objection to complete acceptance; however, the rather high price per unit of weight, and a lack of knowledge of the long term properties, makes engineers hesitant, and holds back the development of the market.

In order to take care of the long term behaviour of filament wound structures, use has so far been made of rather arbitrary safety factors which are related to the short term bursting pressure of the structure. They are sometimes broken down into separate factors for inhomogeneity, anisotropy, creep, ageing etc. Such factors hardly ever take into account the resinous binder, the winding angle, the winding process, the cure cycle, the glass content and other variables which after all determine the quality of the final product.

We have two objections to safety factors which are related to the short term bursting strength of the type of material under consideration.

(1) Such a factor must be high for more security, which, however, makes the product unnecessarily expensive.

(2) It is basically wrong, because a phenomenon which only occurs once (bursting, delamination) is taken as the yardstick to describe working conditions which will be encountered many times.

In this context we now wish to postulate that GRP material (except in special applications such as rocket motor cases), should not be used under conditions of stress which cause irreversible deformations.

For the sake of simplicity the rest of this paper will only be devoted to pipe, although our conclusions are felt to have wider scope.

2. DEFORMATIONS AND THE FAILURE MECHANISM OF GRP PIPE

The measurement of deformations as such on GRP pipe is not new.

In 1962 Darwell and Hughes (1) measured deformations on filament wound structures but no conclusions concerning allowable stresses were drawn. Schaper and Schlehöfer (2) also conclude that bursting is not acceptable as the determining factor for long term use and they assume that a certain maximum allowable permanent deformation (0.1%) after pressurising a pipe to 1.5 times the working pressure can be taken as the yardstick. Although this could well be acceptable for one particular pipe, it still does not take into account the winding technique, the winding angle, glass-content and the resinous binder and is therefore not precise enough. From our own long term investigations it can be seen that for example variation in only the resin can produce enormous variation in the long term bursting strength of pipes having the same short term bursting pressures. In Table 1 the results

TABLE 1

Time until failure of a number of GRP pipes with different resin systems, when exposed under 60% of the short term bursting pressure in water of 20°C

Resin system	Average number of hours till bursting
'EPIKOTE' 828/DDM	1350
'EPIKOTE' 816/1PD	700
'EPIKOTE' 816/DTA	450
Isophthalic Polyester	100

are shown of a long term static pressure test. (It should be noted in this context that 60% of the short term bursting strength causes inelastic deformations and is therefore impermissible when longer term use is intended).

From studies carried out by Niederstadt (3), Broutman (4) and Puck (5), it can be concluded that there is little doubt that failure of a glass-reinforced resin structure starts with debonding at the glass-resin interface. Once this debonding phenomenon starts, less surface area will be available for a proper stress distribution, and this causes stress concentrations and hence further debonding etc. The macroscopic effect of this will be: creep i.e. increasing deformation at constant load (in other words a decreasing E modulus) and in most cases also an increasing permanent deformation when the load is released.

As only uses are considered in which pressure is applied during a longer period of time, such a snowball effect is absolutely intolerable. For this very reason we have chosen the occurrence of increasing deformations at constant load as the borderline between allowable and not allowable deformations or stresses.

We call this borderline the Ultimate Elastic Wall Stress (UEWS).

The practical aspects of the method, the results of the tests and the discussion will be presented in the subsequent sections of this paper.

3. EXPERIMENTAL

3.1 Preparation of the pipes

The pipes, having different winding angles, were prepared on a McClean-Anderson filament winding machine, type W2. The resin systems applied were 'EPIKOTE' 828/DDM and an isophthalic polyester (cured with benzoylperoxide); the reinforcement, provided with a silane type finish, was Silenka 1034 type: 10/400, G filaments

TABLE 2

Glass content and wall thickness of the single angle wound test specimens

Winding angle relative to the axis	Glass content % wt	Wall thickness mm (average)
47°	80.0	1.07
48°	81.0	1.09
50°	79.6	1.12
53°	80.7	1.20
54°30'	79.0	1.10
57	80.0	1.18
59	81.6	1.05
61	80.4	1.07

TABLE 3

Glass content and wall thickness of the dual angle wound test specimens
The diameter of all specimens is 50 mm

Winding angles relative to the axis		Glass content % wt	Wall thickness, mm
combination	equivalent		
30/70 30/70/30/70	48°45'	80.0	1.2
34/70 34/70/34/70	50°40'	80.1	1.2
38/37 38/70/38/70	52°39'	79.8	1.2

The glass contents and wall thicknesses of the single angle pipes are given in Table 2 (they were of the order of 80% and 1 mm respectively) and for the dual angle wound pipes in Table 3. The latter types were wound in two different ways, viz. two layers low angle — two layers high angle, and one layer low — one layer high — one low — one high angle, respectively. The glass content was also about 80% wt. The equivalent single angle can be calculated via the stress ratio in tangential and axial direction:

$$\frac{\sigma^t}{\sigma^a} = \frac{\sin^2\alpha_1 + \sin^2\alpha_2}{\cos^2\alpha_1 + \cos^2\alpha_2}.$$

All dual angle wound pipes were made with 'EPIKOTE' 828/DDM. Apart from these filament wound pipes a number of cloth wound pipes have been included In these pipes four layers of woven roving of 300 g/m^2 and four layers of woven roving of 550 g/m^2 were applied. The glass content was 46% wt, the wall thickness 4 mm and the diameter 110 mm. In this case, too, use was made of the 'EPIKOTE' 828/DDM system.

3.2 The method used for the deformation measurements

The principle of the measurement is as follows:

(a) axial deformation: changes in length of a certain part of the pipe are measured with a micrometer.

(b) tangential deformation: a small chain of special construction (see below) is slung round the pipe, the change in length caused by the tangential deformation is again measured with a micrometer.

Fig. 1 shows the equipment used for the measurement of the deformations. The set-up for the measurement is simple: the pipe provided with end-closures is filled with water and pressure is applied with compressed air via a valve, while the pressure is released via a second valve.

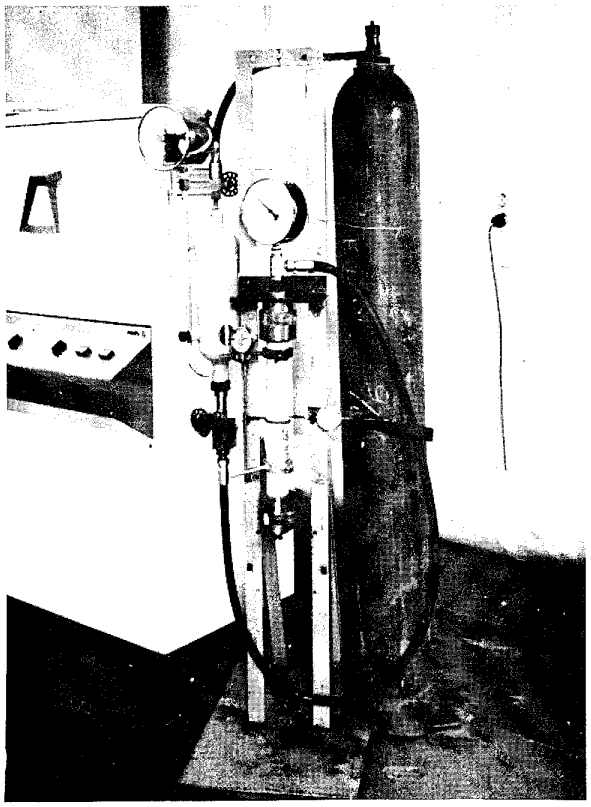


Fig. 1 Apparatus for determination of the deformations of G.R.P. pipes

The chain used for the tangential deformation is a normal commercial type provided with rollers of increased diameter so that the chain can move without friction between chain and pipe-wall.

With this equipment it has been found possible to determine, in a reproducible way, the deformation behaviour of various pipes.

The stress-strain curves, in the axial as well as in the tangential direction, for the various winding angles are presented in Figures 2 and 3.

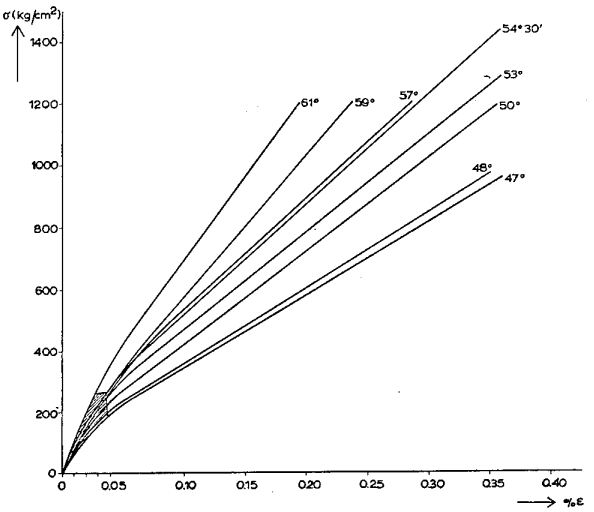


Fig. 2 Tangential deformation of G.R.E. pipes with winding angles from 47 to 61 degrees

It has been observed during the experiments that a certain pressure, creep — as an indication of irreversible changes — becomes visible rather suddenly. Although this incipient creep effect can be taken as the criterion for the determination of the UEWS, we have observed that the borderline be-

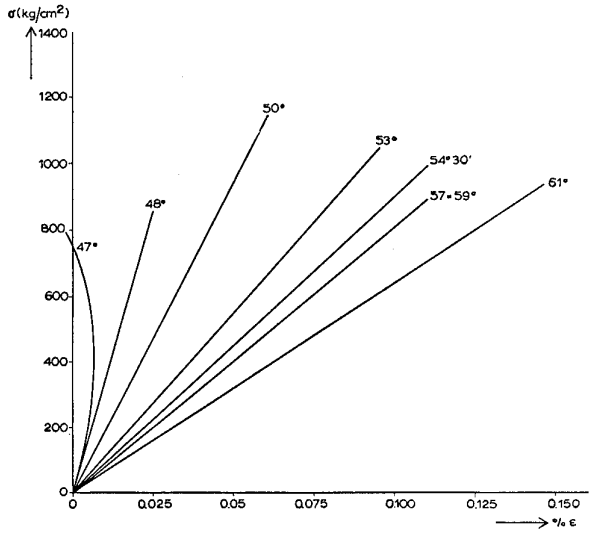


Fig. 3 Axial deformation of G.R.P. pipes with winding angles from 47 to 61 degrees

tween elastic and inelastic behaviour can more precisely be established by means of a cycle test. In our version, the pipe is pressurised up to a certain stress level which is believed to be still permissible i.e. below the UEWS. The deformations are then read off from the micrometers after 3 mins. and subsequently the pressure is released. Then after 3 min., when the micrometers have been read off at zero pressure, the procedure is repeated. After 10 cycles have been performed the pressure is increased (in our tests pressure steps of 10 atm. have been used). The cycle test is now carried out again, but at the new and higher stress-level and this procedure is repeated until the deformation at the 10th cycle is no longer equal to that at the first one. For easy reference, the correlation between pressure and wall stress for our test specimens is given in Table 4.

TABLE 4

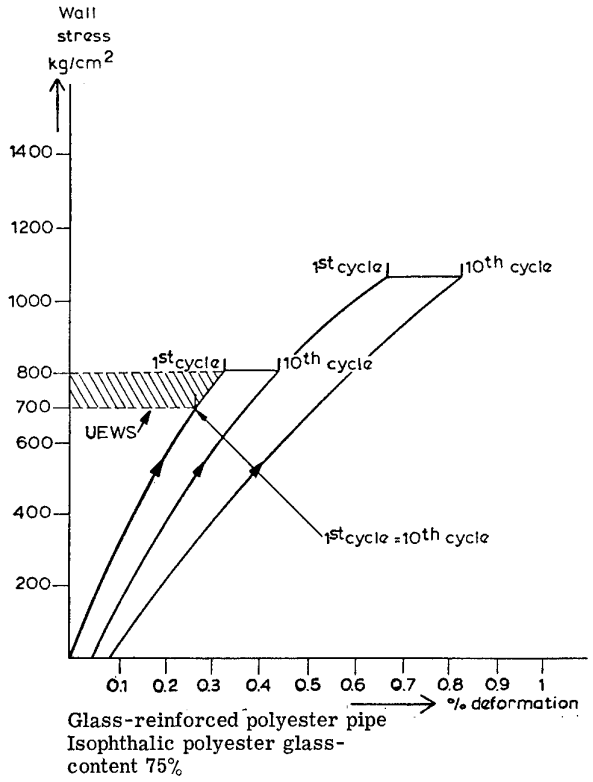
Correlation between pressure and resulting wall stress in GRP pipes with winding angles from 47-61 degrees
The diameter of all specimens is 50 mm

Pressure kg/cm²	Resulting wall stress in kg/cm² in GRP pipe with winding angle of							
	47°	48°	50°	53°	54°30'	57°	59°	61°
10	240	230	230	210	230	210	240	240
20	480	460	460	420	460	420	480	480
30	720	690	690	630	690	630	720	720
40	960	920	920	840	920	840	960	960
50	1200	1150	1150	1050	1150	1050	1200	1200
60	1440	1380	1380	1260	1380	1260	1440	1440

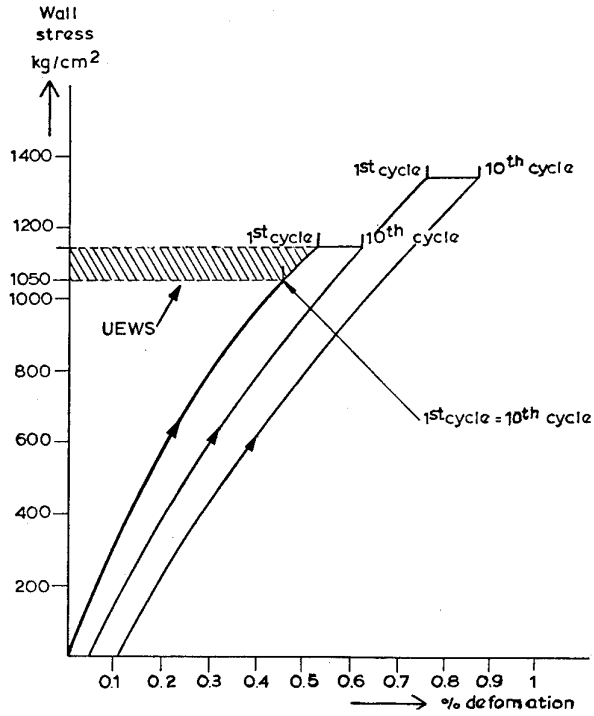
For the sake of security, the highest stress level at which the first cycle gives the same curve as the tenth cycle is taken as the UEWS. In Figure 4 a typical result is given of two pipes made in exactly the same way but differing in the resin. Three further typical results of pipes with winding angles of 47°, 50° 30' and 61° are shown in Figs. 5, 6 and 7.

3. 3 Constant pressure tests on GRP pipes loaded below and above the earlier established UEWS

In order to clarify the effect of stressing a filament wound pipe above the UEWS and to establish what happens when the pipe is stressed below this borderline, 16 hr constant pressure tests have been carried out for a number of pipes. For the sake of simplicity only three typical creep curves will be presented (Figs. 8, 9 and 10), the one for the optimum winding angle and two extremes, viz 47° and 61° (relative to the axis). For the pipe with the optimum winding angle the wall stresses applied were 1800 and 700 kg/cm² respectively; for the other



Glass-reinforced polyester pipe
Isophthalic polyester glass-content 75%



Glass-reinforced 'EPIKOTE' pipe
Resin 'EPIKOTE' 828/DDM
glass content 75%

Fig. 4 Tangential deformation of polyster and 'EPIKOTE' pipes with winding angles of 50°

two — which are much weaker in one direction, cf. Fig. 11 — these stresses amounted to 1150 and 450 kg/cm² respectively.

4. RESULTS AND DISCUSSION

Considering the deformation curves shown in Fig. 2 and 3, it is seen that with increasing winding angle the tangential deformations decrease (Fig. 2) and that at the same time the

axial deformations increase at a given wall stress. This can be explained by the fact that high winding angles give a high strength in the tangential direction and a lower strength in the axial direction. This will result in low tangential and high axial deformations at a certain wall stress, assuming that the pipe shows elastic behaviour.

It can also be seen that pipes wound with winding angles of 50° and lower produce very low axial deformations and even negative deformations are possible. For special occasions this can be an advantage; one has to bear in mind, however, that the allowable stresses are considerably lower, as also the UEWS is lower (Fig. 5) than at the optimum winding angle of 50° 45'.

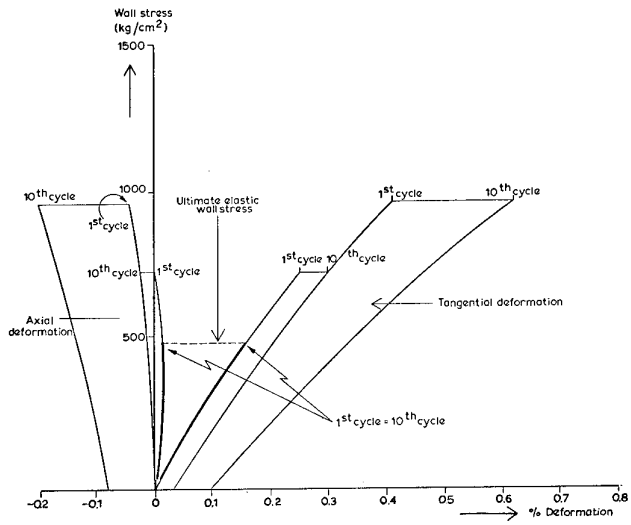


Fig. 5 Determination of the ultimate elastic wall stress of a G.R.E. pipe with a winding angle of 47°

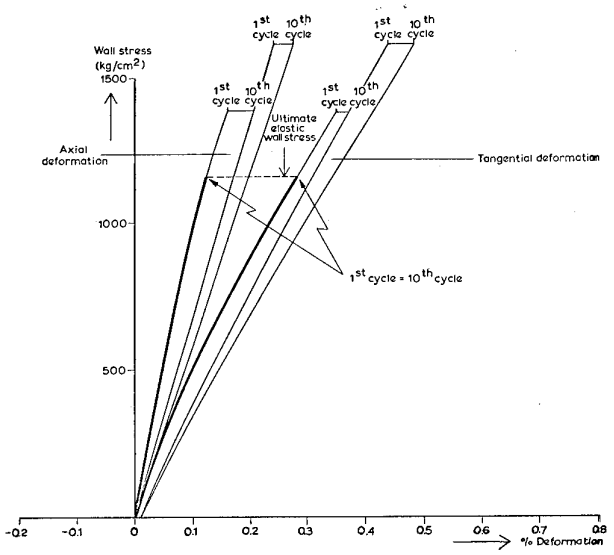


Fig. 6 Determination of the ultimate elastic wall stress of a G.R.E. pipe with a winding angle of 54°30'

The figures showing the results of the cycle tests (Figs. 4, 5, 6, 7) can be explained as follows: the fat lines (tangential as well as axial) give the deformations up to the ultimate elastic wall stress; the deformations are elastic up to this point, i.e. they follow exactly the same curves during the cycle test and there is no creep. At a certain pressure, as soon as the ultimate elastic wall stress is exceeded, creep becomes apparent as demonstrated by the horizontal line in the graph. At each cycle, one or both deformations show a slow but constant increase whereby the length of the horizontal line is the total creep during the 10 cycles.

Special attention has to be paid to Fig. 4 in which two different resin systems have been compared. In that case the glass content was somewhat lower, viz. 75%, while the pressure steps were only 5 atm. Only the tangential curves are given.

It can be seen that the UEWS of the isophtahlic polyester pipe is about 30% lower than that of the epoxy one, which might be attributed to the inferior adhesion between the glass and the polyester resin compared with the epoxy.

Figures 5, 6 and 7 are representative for the complete series. From the results obtained, it is again found that with winding angles which increase from 47 to 61 degrees, the amount of tangential deformation decreases. Also, the creep (i.e. the increasing deformation at constant load) decreases continuously (at a given wall stress). In addition, in the results of the cycle tests (as well as with the constant pressure tests, see below) a typical phenomenon that influences the deformation and creep behaviour of the pipes can be observed. It can be explained as follows: in a glass reinforced pipe the rovings will always tend to orientate according to the optimum winding angle of 54° 45', as in the case the direction of the maximum strength coincides with the direction of the load.

As soon as the resulting deformations have led to (destructive) delaminations (as in the case with inelastic deformations), this tendency of the rovings will show up in the stress/strain curves, depending on the degree of deviation between the angle of winding and the optimum winding angle.

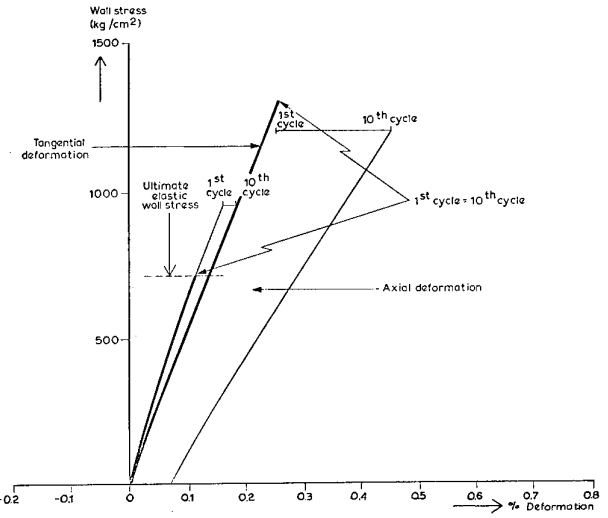


Fig. 7 Determination of the ultimate elastic wall stress of a G.R.E. pipe with a winding angle of 61°

(For the same reason a pipe with a winding angle of 47° shows enormous negative axial deformations after 16 hours when stressed beyond the UEWS, and a 61° wound pipe shows very large positive deformations (see Fig. 5 and 7, and 8 and 10 respectively). At winding angles with small deviations from the optimum winding angle, only very slowly increasing deformations will take place under the new conditions.)

The tests at constant pressure given in Fig. 8 to 10 show the following results: at wall stresses in the elastic area no increase in deformation occurs, while as soon as the wall stress lies beyond the elastic area, the corresponding deformations increase continuously, whereby an interruption of the test (even for one or more days) has no influence on the deformations, i.e. after the interruption the deformation versus time curve starts at about the final deformation values of the previous day. This indicates that deformation in the inelastic area is a constant and irreversible phenomenon which will sooner or later cause failure and hence is nearly always impermissible. On the other hand deformations are completely reversible when the wall stresses applied are well below the ultimate elastic wall stress, at least for the periods employed in this study.

The dual angle wound pipes which have been tested in the present investigation behave very much like the equivalent single angle wound pipes. Darwell and Hughes have found that such pipe has advantages in the event of combined pressure and bending; when only internal pressure is applied, no improvement of the UEWS is apparent. A lower UEWS is found

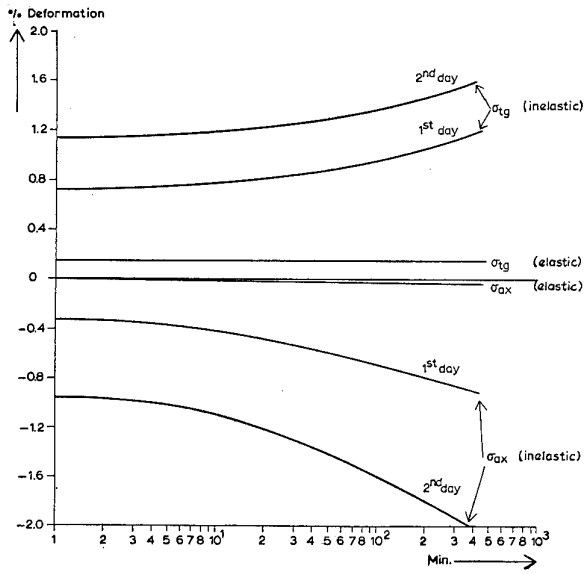


Fig. 8 Creep of a G.R.E. pipe loaded in and beyond the elastic area (winding angle 47°)

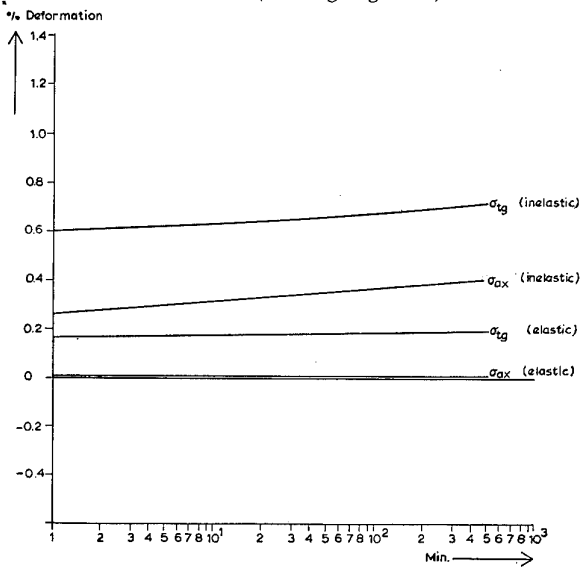


Fig. 9 Creep of a G.R.E. pipe loaded in and beyond the elastic area (winding angle 54°30')

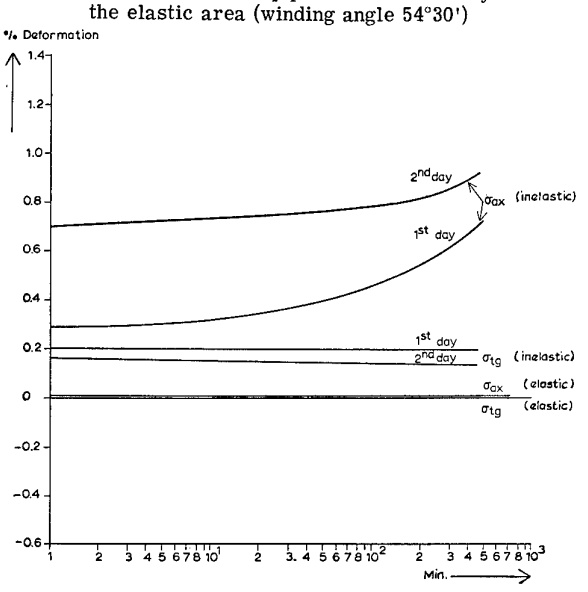


Fig. 10 Creep of a G.R.E. pipe loaded in and beyond the elastic area (winding angle 61°)

when the first half of the wall thickness is wound with a low angle followed by high angle winding. Rather soon delamination takes place between the two different layers. In this type of winding, the various layers must therefore be equally distributed over the wall thickness.

The UEWS has also been established for the cloth wound pipes; however, the spread in the results was rather high. The average value of four pipes for the UEWS is about 400 kg/cm^2 which is about $1/3$ of the UEWS of a filament wound pipe with a winding angle of 54°. The allowable wall stress will therefore also be considerably lower and this, combined with the fact that the raw material cost will be higher, will make this type of winding less attractive for pressure applications.

The results of the cycle tests are summarised in Figure 11 in which the UEWS is plotted against the winding angle. The optimum is clearly found at 54° 30' (or 54° 45' which is in fact the theoretical optimum).

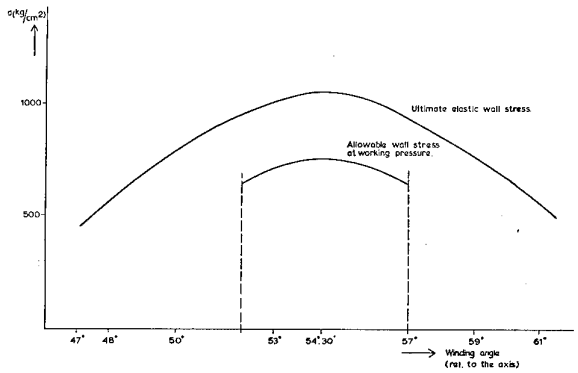


Fig. 11 Influence of winding angle on the ultimate elastic wall stress

We feel that for reasons of security (e.g. inhomogeneity of production, long term loading) the allowable wall stress at working pressure can be taken as one half to two thirds of the irreversible changes occur under these conditions, although it has to be pointed out that a greater degree of certainty can only be obtained by extending the duration of these tests. Work on this is in hand.

5. CONCLUSIONS

5.1 ~~In the present paper~~ a method is described for the determination of the highest wall stress to which a GRP filament wound pressure pipe may be subjected, called the ultimate elastic wall stress (UEWS). In this method the degree of creep — occurring when the pipe is loaded above its UEWS — is cumulatively registered over a number of pressure cycles.

5.2 Constant pressure tests at wall stresses below and above the UEWS for a longer period of time (16 hrs) indicate that below this limit no increase in deformation (creep) occurs; above it deformations increase continuously with time.

5.3 With a good degree of confidence it is felt that the working pressure of a filament wound pipe can be based on the UEWS; we propose that the operating wall stress should be from $1/2$ to $2/3$ of the UEWS.

5.4 The theoretically optimum winding angle of 54° 45' has in the present work been found to produce the highest UEWS.

5.5 The UEWS of an isophthalic polyester filament wound pipe has been found to be 30% lower, compared with an identical 'EPIKOTE' 828/DDM one.

5.6 Dual angle filament wound pipe have an UEWS similar to that of a comparable single angle pipe provided that the two types of layer are distributed homogeneously over the wall; cloth wound pipes appear to have a considerably lower UEWS.

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The wetting of glass fibres by polyester resins

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INTRODUCTION

Corrugated sheeting was one of the earliest products to be manufactured from glass fibre reinforced polyester resins; initially, a hand lay-up process was used which still survives today. In this process, a glass fibre mat is worked into the polyester resin which has been poured onto a sheet of cellulose. When the mat is thoroughly impregnated with resin a second cellulose sheet is laid on top and excess resin and air bubbles are squeezed out before transfer of the sandwich to a suitable mould for gelation and cure. Depending on the gelling characteristics of the catalysed resin, up to one hour may be available to ensure that impregnation is complete and that the fibre mat is evenly and completely wetted.

Economic and quality control considerations prompted the development of continuous laminating plant[1,2] which mechanised the hand lay-up process in such a way that the wetting out time available for impregnation with resin and expulsion of air from the mat was reduced to a few seconds. The process attempts to spread resin through the mat of fibres at a much higher rate than that in the hand lay-up technique where wetting occurs by the usual capillary forces. A result of this type of forced wetting can be that individual glass fibres or fibre bundles are not adequately wetted out. Any air trapped at the initial impregnation stage cannot escape later in the continuous process as gelation occurs within a few minutes.

Analogous situations may arise in other industrial processes such as the sizing of glass fibres, the lubrication and finishing of textile yarns and filaments, coating operations using a doctor blade or even in the brush application of paint. In all these processes, attempts are made to spread viscous liquids over the surface of solids at rates faster than those expected from consideration of the surface properties of the materials. It is often found that under these conditions inadequate wetting may occur even though under equilibrium conditions complete spreading is observed. These difficulties are enhanced if spreading is followed by evaporation of solvent, by gelation or polymerisation or by solidification of a melt.

It is necessary therefore to consider wetting as a dynamic process and not as is usually the case as a problem in thermodynamic equilibria. In many of these spreading processes, a true thermodynamic equilibrium can never be attained. Wetting normally refers to the displacement of air from the surface of a solid by a liquid; the usual criteria for unlimited spreading on high energy surfaces is that the contact angle should be zero, or for surfaces of low energy, such as polymers, that the surface tension of the liquid should be less than the critical surface tension of the solid[3].

However in a non-equilibrium process, it seems it is not the static contact angle that is important but rather the dynamic one between the solid and the advancing liquid front. As the wetting process in the production of reinforced plastics, particularly in continuous systems, is of paramount importance in determining the strength and optical properties, it seemed essential that some study should be made of this process in terms to ascertain the importance of dynamic contact angles and of the interfacial properties in relation to speed of wetting.

EXPERIMENTAL TECHNIQUES

Two possible experimental approaches could be adopted for the measurement of the changes of contact angle with speed of movement, namely by passage of the liquid over a solid surface or through a capillary tube, or by pulling a filament into the liquid. In this work the latter procedure has been employed since the method is experimentally convenient to use at high speeds (i.e. greater than 100 cm/min) and the use of glass fibres was relevant to the particular problem in hand. An apparatus was therefore developed capable of drawing a single filament into a liquid contained in a cell over a range of speeds from 0.05 cm/min to 60 000 cm/min. A block diagram is shown in Figure 1; details of the apparatus will appear elsewhere. The observation area was enclosed to prevent contamination and to allow liquid vapour equilibrium to be set up.

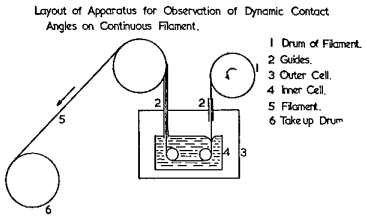

Fig. 1

The advancing three phase boundary was observed with a microscope and recorded photographically: measurements of the contact angle were made on the resulting negative with a simple goniometer system.

RESULTS AND DISCUSSION

The wetting of a fibre bundle or fibre mat by a liquid resin will be affected by a number of features among which are those thermodynamic factors concerned with the respective energies of the wetted and un-wetted surfaces which will determine the final equilibrium state and those kinetic factors which arise prior to the attainment of this equilibrium. In some situations, these kinetic factors in the wetting process may, temporarily at least overshadow the underlying equilibrium state. In a continuous industrial process in which the wetting of fibres or fibre bundles is an essential preliminary, it is with these latter kinetic factors that we are primarily concerned, since polymerisation or solidification of the wetting liquid may intervene before a true static wetting equilibrium has been reached.

In any equilibrium study of wetting, the contact angle has long been recognised as an essential factor in determining whether wetting will occur and also in determining the adhesion between liquid and solid[5]. In the absence of evidence to the contrary, the same importance of contact angle has been assumed in dynamic wetting processes.

The determination of contact angles on fibre-bundles is experimentally difficult since the roughness of the bundle surface and the geometry of the bundle interior substantially modify the observed contact angles[6]. Hence, since it is also impossible experimentally to maintain consistent bundle geometry, the simpler system of single glass filaments was studied, thereby avoiding the complications of capillary wetting.

In attempting to use the advancing contact angle as a diagnostic test for the ability of a single fibre to wet under dynamic conditions, it was decided to investigate the variation of the dynamic angle (ϕ) with interface velocity (V), liquid viscosity (η) and surface tension (γ), in order to assess the extent to which ϕ is a measure of wetting efficiency.

At the outset hand-drawn filaments of E glass were used; these were larger than commercial fibre glass having diameters of 100-200 μ. However these were not only easier to manipulate than the commercial product but had a known history, and could be kept clean and uncontaminated. However, these fibres did not behave in a reproducable fashion as shown by our inability to obtain consistent results over the

range of speeds used. The relationship between the dynamic liquid/glass-fibre contact angle ϕ and the velocity of the 'as drawn' fibre entering the interface is shown in Figure 2. Residual surface strain is known to affect the surface properties of solids[7] and it was thought that annealing of the fibres might reduce this effect as was indeed the case. Results obtained using fibres annealed at 650°C for 1 hour, cooled in a dessicator and conditioned at 65% r.h. are also shown in Figure 2. The experimental scatter is less than ±2° and the results are repeatable. Fibre diameter was not found to be an important parameter—at least up to $\frac{1}{16}$" diameter. The annealing process may relieve strain in the surface of the filament but also may result in a more efficient surface cleaning process or both. Hence for which ever reason applies, annealed fibres were used in most of the subsequent work.

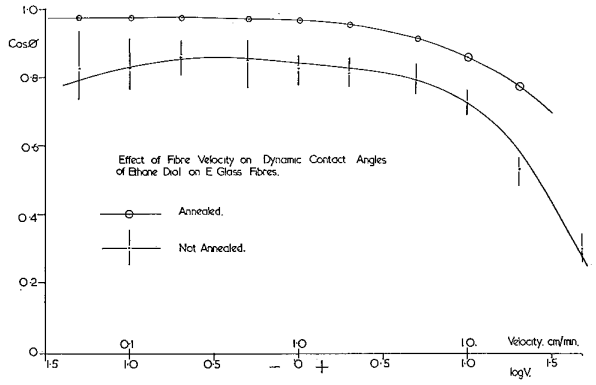

Fig. 2

Annealed fibres have almost zero dynamic contact angle which which increases less rapidly with increasing fibre velocity than does that for the 'as drawn' fibre, so that if dynamic contact angle alone is used as a criterion of wetting, then annealing improves the wetting process. The question of surface strain and structure has not been further investigated; rather attention has been devoted to establishing the effect of liquid parameters (viscosity and surface tension) on the rate of wetting of annealed glass fibres. The heterogenous surfaces were apparently produced by hand drawing as subsequent experiments on continuous filament did not show these wide variations.

Even for a liquid such as ethane diol which under static conditions wets glass making a zero contact angle, as the fibre speed is increased the advancing contact angle increases to high values—approaching 90°. Judged by equilibrium contact angles, such a value would predict that the liquid will not wet the glass. It appears therefore that the accepted relationships of contact angles and wetting are not applicable in the dynamic situation.

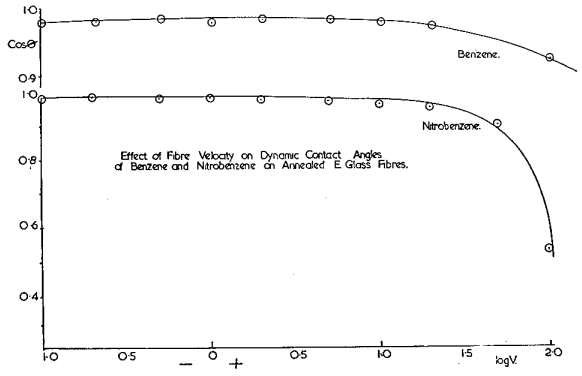

Fig. 3

Despite early measurements of advancing dynamic contact angles on a paraffin wax surface by Ablett in 1923[8], results of many authors have lead them to the belief that advancing contact angles are independent of velocity[4]. This is understandable for liquids of low viscosity; in Figure 3 are plotted the advancing contact angles for nitrobenzene and benzene on glass fibre surfaces. It may be noted that only above 50 cm/min in the case of nitrobenzene does the contact angle increase markedly; below this speed, the contact angle is substantially independent of velocity.

Experiments with liquids of higher viscosities but of substantially similar surface tensions show a very different picture. Figure 4 shows cos ϕ plotted against log (velocity) for a series of polymeric glycols. As the viscosity of the fluid increases, the increase in contact angle becomes apparent at lower speeds. Thus in the case of the polypropylene glycol (Dow, P4000) having a low shear viscosity at 25°C of 10.6 poise the angle has increased to 90° with a speed as low as 5 cm/min, while the dynamic contact angle approaches 180° at speeds in excess of 100 cm/min. The effect of viscosity may be taken into consideration by plotting cos ϕ against log ηV, as in Figure 5. It is seen that all the previous data fall onto a single master curve.

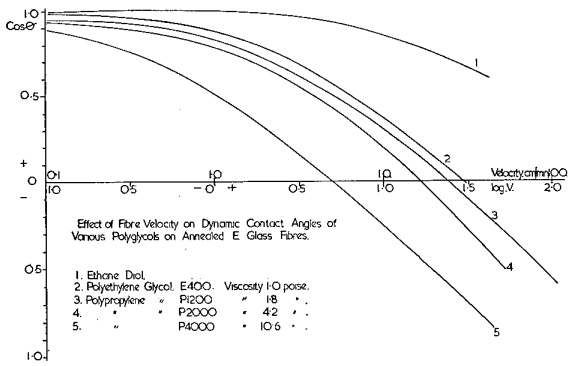

Fig. 4

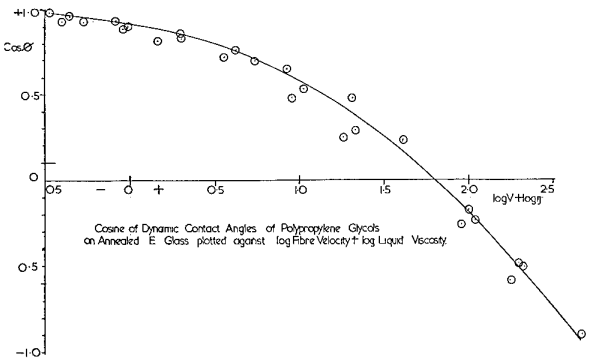

Fig. 5

This result indicates clearly that the effect we are observing is more a hydrodynamical one rather than a surface tension effect. In this connection too, it must be noted that whereas the viscosity of the liquids used can be very different, by a factor of 10 in this instance, it is not possible to modify the surface tension over such a range.

The effect of surface tension is more difficult to determine because liquids of similar viscosity but with systematic change in surface tension are not available. In an attempt to overcome this difficulty, attention was directed to solutions, where a change in solute concentration could markedly affect the viscosity but would produce little change in surface tension. This is particularly true for solutions of high polymers and to check the use of such solutions, dynamic contact angle measurements were made for a series of polystyrene in xylene solutions. The viscosity range was now 0.1 → 15 poise while the surface tension was very similar to the polyglycols discussed above. Again a master curve between cos ϕ and log ηV was obtained (Figure 6).

Glycerine-water solutions provide a similar viscosity range at a high surface tension, and again a master curve is obtained (Figure 7). It is remarkable that the three master curves presented, although obtained using liquids having very differ-

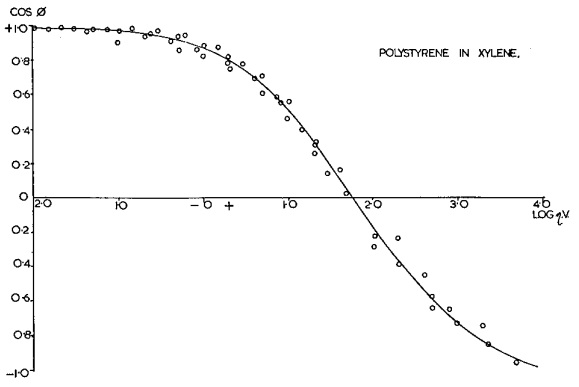

Fig. 6

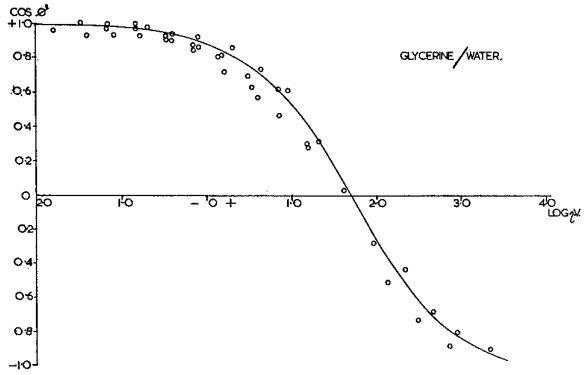

Fig. 7

ent surface tensions are almost identical. It is apparent therefore that the interfacial situation under dynamic conditions is hardly affected by the surface properties of the liquid. Hence to speed up wetting, it would seem that additions to the liquids used in the present system would be ineffective. This was confirmed experimentally.

A substantially similar master curve was also obtained for the wetting of an untreated E glass filament with a polyester resin. However, as might be expected the effect of surface finish on the glass gave somewhat different results.

Figure 8 shows that the contact angle at low speeds is somewhat greater for the coated filaments than for the untreated ones; this is hardly surprising since on sizing a lower energy surface is formed. At higher velocities, however, the treated fibres do appear not to change their dynamic contact angle with increasing velocity as rapidly as the untreated fibres. This may not indicate better wetting but more probably results from 'slippage' at the fibre surface—an effect noticed in other experiments using fibres of low surface energy, or it could be an effect of surface roughness as subsequent experiments showed that the surface of the sized filament was heterogeneous.

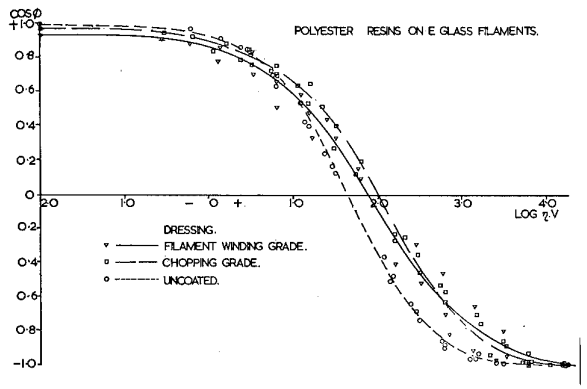

Fig. 8

At high fibre/liquid interface speeds when the dynamic contact angle is approaching 180°, it is apparent that wetting cannot occur by a normal spreading process. It is implicit in this statement that as the contact angle increases up to 180° the actual point of contact, i.e. the height of the meniscus, will extend further and further into the liquid. Substantiation of this point is shown in Figure 9 in which the meniscus height is plotted against cos ϕ. As the contact angle approaches 180° the depth of the meniscus below the free liquid surface (height = 0 in Figure 9) increases asymptotically. If these conditions persist then it is suggested that at some point the surface forces of the meniscus will no longer balance the hydrostatic forces and instability and collapse must occur. Figure 10 shows such collapse apparently occurring in the polyester resin E glass system. Such collapse may lead to encapsulation of air and highly intermittent wetting since once collapse has occurred, the meniscus will again be drawn down and the cycle will again begin. This irregular coating would normally spread to form an even coating; however, under the conditions of this experiment which is akin to filament winding, there is rapid loss of styrene where the filament emerges from the liquid and the irregularities remain. The irregularities take the form of droplets and are shown in Figure 11—again for the polyester resin E glass system. As far as experiments have been able to determine the glass between the droplets is free from polyester resin. Further evidence for the incomplete wetting was found using the polyester resin and E glass system when it was observed that at rest, and at low speeds, it was difficult to see the glass filament in the resin due to the matching of the refractive indices of the glass resin. However, at the high speeds the moving filament can be seen quite clearly suggesting that there is undisplaced air at the solid liquid interface.

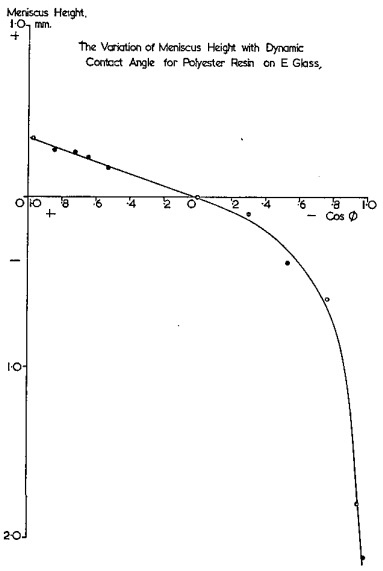

Fig. 9

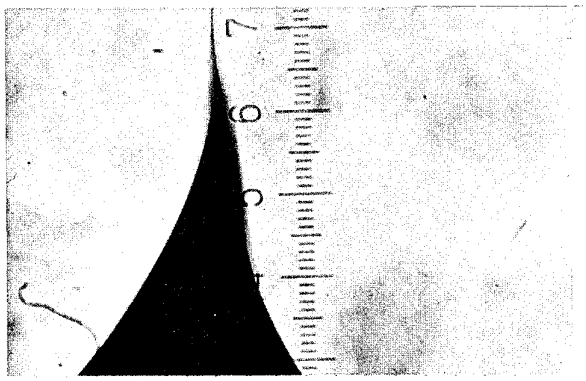

Fig. 10 Unstable meniscus for polyester resin on E glass at 2000 cm/mm

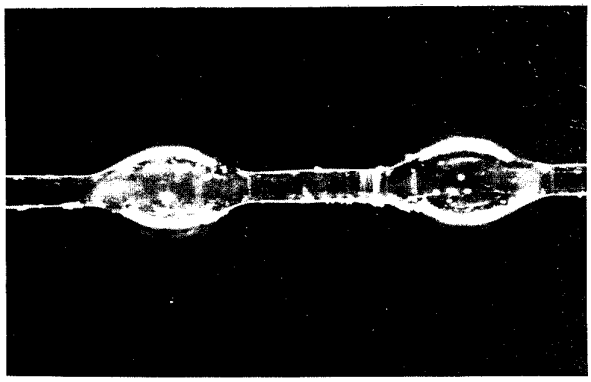

Fig. 11 Droplets of polyester resin on clean E glass

Droplet formation is known to occur when a solid is withdrawn from a liquid[9]. However, examination of the literature data shows that the solid is still wetted between the drops and does not exhibit uncoated areas as does the present system.

Evidence of droplet formation was found when Stereoscan photographs were taken of the experimental sized E glass filaments. Figure 12 shows a typical example with apparent uncoated areas between the remains of dried out size droplets.

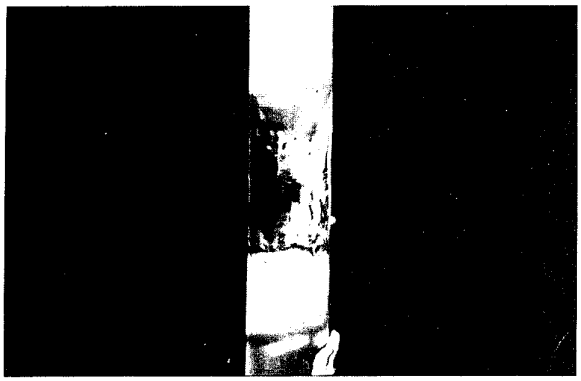

Fig. 12 Stereoscan photograph of experimental E glass filament after sizing

The areas between the droplets are identical to untreated filaments as far as can be ascertained from electron microscope photographs.

It is apparent from these results that the dynamics of the wetting process is more a question of hydrodynamics than of surface properties under conditions where a manufacturing process is attempting to spread liquid at a rate in excess of that dictated by surface tension. Contact angle itself is of little use in determining the breakdown of spreading wetting at high speeds; however, during the experiments with various polyester resins on E glass both treated and untreated, it was observed that droplet formation occurred at similar ηV values. Thus we have a means of determining a critical velocity for any particular resin above which intermittent wetting will occur. Indeed in the practical cases of continuous sheet production and filament winding, the speed of the process may be considerably affected by the inability of the wetting process to keep up with the machine conditions.

ACKNOWLEDGEMENTS

The authors wish to thank the Directors of British Industrial Plastics Ltd., and Turner Brothers Asbestos Co. Ltd., for financial assistance and leave of absence given to one of us (G.I.).

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Investigations on the possibility of application of thick glass fibers for the manufacture of high strength glass reinforced plastics

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ABSTRACT

The article below gives investigation results of glass filaments strength with the diameter from 7 to 100 microns; the above filaments having been produced at an industrial plant. Utilization efficiency of glass filaments initial strength in unidirectional glass-reinforced plastics is estimated. Manufacturing methods of nonwoven oriented glass-reinforced plastics on the basis of thick filaments are described and physical-mechanical and electrotechnical properties of such materials are given.

INTRODUCTION

At present, scope of world production of glass fibers and glass-reinforced plastics grows rapidly. However, present industrial manufacture of glass-reinforced plastics is based so far upon application of filaments of 6-12 microns diameter.

Evidently, alongside with the increase of a diameter production of glass fibers will go up and cost will go down; taking into account that in the world market prices of glass fibers go down much slower than those for the resins.

Application problem of large diameter glass fibers are becoming more and more urgent. (For example price for polyester resin went down from 1956 to 1966 from 0.9 dollar per pound to 0.16 dollar per pound whereas the price for chopped strand mat went down, for the same period, only from 0.8 dollar per pound to 0.46 dollar per pound /1/). Its solution will enable to reduce considerably price of glass fiber reinforced plastics and widen fields of their application in industry, agriculture and transport.

STRENGTH OF GLASS FIBERS

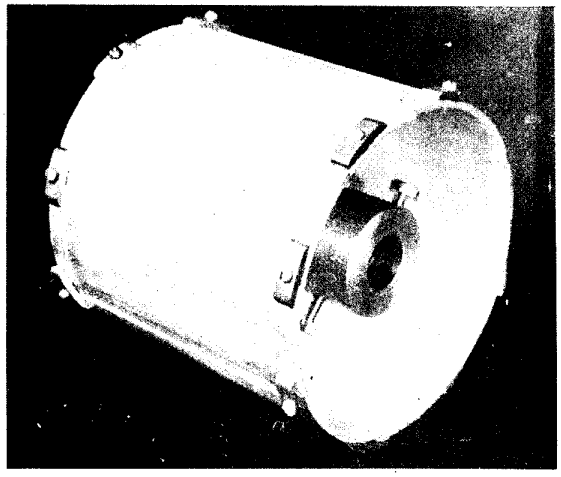
As it is known strength of ordinary bulk glass amounts only to 5-7 kg/mm sq and strength of glass fibers reaches 200-500 kg/mm sq /2, 3, 4/. Attempts to explain this difference by peculiarities of structure of glass fibers — orientation of 'molecular chains', formation of particularly strong bonds in surface layer, effect of specific formation conditions, were made by many investigators /2, 5, 6, 7/; but investigation of physical-mechanical properties and structure of glass fibers has convincingly shown identity of structure of bulk glasses and glass fibers /8, 9/. The most satisfactory explanation of high strength of glass fibers is based on the assumption of prevailing influence of defects on the glass surface upon glass strength as well as on random character of their distribution.

Assuming that bulk glass and glass fibers possess equal structure and equal nature of strength, increase in the strength of glass fibers compared to glass is explained by decrease of probable dangerous defects on the sample surface, being caused by reduction of its surface /10, 11/. (Conditions of spinning the fibers, temperature conditions of their manufacture, plays certain part but the influence of the above conditions upon strength of fibers shows up only in limited bounds).

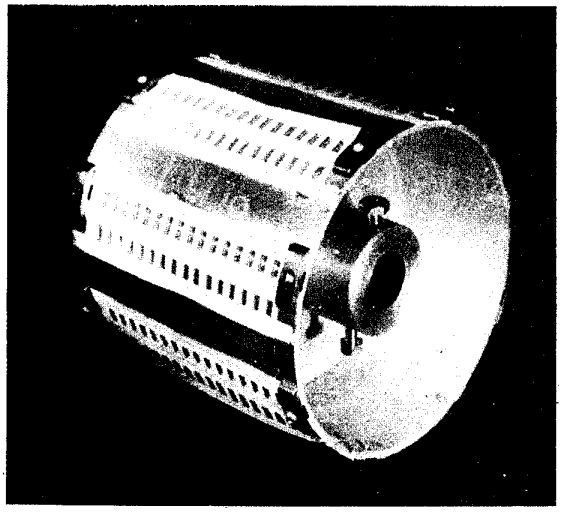
Various experimental data characterizing relation of glass fiber strength to their diameter during test under normal conditions, that is during their taking off the strand and during test in the air can be fitted well within the framework of these conceptions. Investigations results of the strength of glass and glass fibers produced and tested under conditions, excluding, to a certain extent, the possibility of their damage, do not contradict to those conceptions. Let us elaborate on these works.

W. Otto /12/ and G. Bartenev /13/ have found absence of pronounced relation of glass fibers strength to their diameter in the range of 5 to 18-20 microns. Strength of glass fibers produced by W. Thomas /14/ at laboratory plant from E-glass amounted to 380 kg/mm sq and was constant regardless of diameter in the investigated range from 7 to 20 microns. For the rods drawn under special conditions from E-glass N. Cameron /15/ has obtained bending strength values exceeding 210 kg/mm sq F. Vitman /16/ has obtained strength values (under central-symmetrical bending) up to 300 kg/mm sq at minimum scatter of individual values of strength by means of etching of glass sheets, the samples being stored and tested under conditions, that excluded possibility of their damage.

The data disclosed above convincingly confirm correctness



a



b

Fig. 1 Winding drum with longitudinal slots for obtaining undamaged glassfilament samples

(a) before the winding
(b) after the winding and sealing filaments into paper frames.

of conceptions on high initial strength of glass-solid samples as well as glass fibers.

In our investigations standard industrial 204 spinnerets apparatus was used, spinneret diameter being equal to 1.7 mm.

Manufacture of filaments from alumoborosilicate glass was carried out at spinneret plate temperature of 1180°C and the height of molten glass of 100 mm. Manufacture of fibers of various diameter was achieved only by the change of their drawing sped.

To exclude possibility of the damage of monofilaments during their contact with each other and the surface of wind-up device, special drum with longitudinal slots of 10 mm width was used (Fig. 1a). In all experiments glass filament was drawn from the same spinneret located in the centre of the spinneret plate. Filaments were sealed in paper testing frames straight on the drum (Fig. 1b). It enabled to obtain simultaneously series of samples under quite the same conditions. Tests were carried out for 3 hours, after filaments had been made, at room temperature and air humidity of 60-70%.

In parallel with the tests of undamaged filaments we measured strength of filaments by ordinary method — taking them off the strand after 7-10 days of their storing under ordinary conditions.

Fig. 2 shows results of the measurements. Each point is obtained by means of testing of 30-40 samples; variant factor amounts to 12-16% for undamaged filaments and to 25-30% for the filaments tested under ordinary method. Strength of undamaged filaments (curve 1) reaches 300-320 kg/mm sq with the diameter of 7-15 microns and goes down to relatively small extent when diameter goes up to 90 microns.

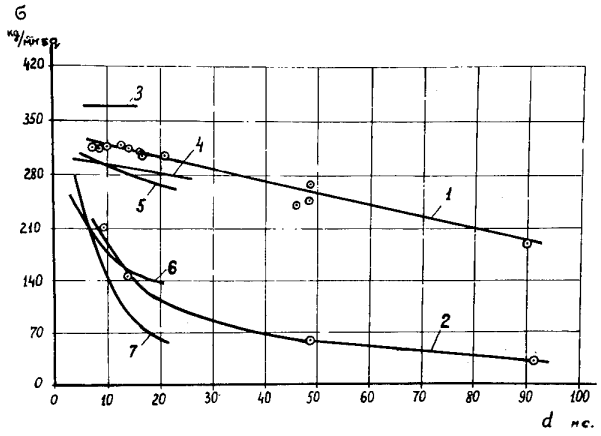


Fig. 2 The effect of glassfilaments diameter on their strength:

1. strength of undamaged filaments
2. strength of filaments tested at the ordinary conditions;
3. data obtained by W. Thomas,
4. by G. Bartenev,
5. by W. Otto,
6. by W. Otto,
7. by F. Anderegg-for filaments, tested at ordinary conditions.

When filaments are tested by ordinary methods their strength is considerably reduced showing up regular dependance upon the diameter, this phenomenon has been earlier described by many authors /2, 3, 4/.

UTILISATION OF GLASS FILAMENTS STRENGTH IN GLASS-REINFORCED PLASTICS

As it is known glass filaments with diameters from 3-5 up to 9-10 microns are used for the manufacture of woven fabric glass-reinforced plastics. This is caused by the fact that filaments of larger diameter are completely unsuitable for traditional textile processing due to their low flexibility and brittleness. It should be also noted that rewinding, twisting and weaving of thin filaments, used nowadays, not only complicate and make the technological process more expensive, but also lead to noticeable reduction of their strength.

Development of winding technology and other methods of making nonwoven glass-reinforced plastics with oriented distribution of strands (or filaments) has enabled to increase considerably utilization efficiency of reinforcing elements.

Table 1 compares tensile strength of woven fabric and some nonwoven oriented glass-reinforced plastics /18, 19/.

TABLE 1

Tensile strength of certain high performance glass-reinforced plastics*

Type of material	Tensile strength kg/mm sq
Unidirectional, 'high-mode'	170-180
Unidirectional materials on the basis of tapes, rovings and strands	140-170
Unidirectional, 'Scotchply' type 1002 v	110-130
90°-crossplied 'Scotchply' type 1002c (total bidirectional strength)	100-120
Woven fabric glassreinforced plastics (total strength of web and weft)	65-85

* Data given in the Table relate to glass-reinforced plastics on the basis of modified epoxy resins.

A. Burov and the authors of this paper /18, 20, 21/ have developed and investigated in laboratory conditions and checked up semi-industrially methods of manufacture of the so-called synthetic filament anizotropic materials (SFAM).

In the course of SFAM manufacture solution or melt of binder is applied directly on the surface of glass filaments at the moment of their drawing from the glass melt (to be more exact 1/30-1/100 second after filaments having been spinned).

The filaments, being drawn, covered with binder, are located in parallel with each other, with certain tension, forming nonwoven unidirectional laminate called 'plyglass' (in analogy to ordinary plywood).

Combining the process of filaments drawing with the applying of binder and orientation of filaments prevents the surface of filaments from mechanical damage as well as from the influence of atmospheric humidity. Removal of all the textile operation allows to use filaments of various diameters from 5-6 to 50-100 microns and higher. (Recently due to the use of glass fiber reinforced plastics in submergency apparatuses tendency of using thick glass filaments (more than 100 microns in diameter) has come into life /22/. This investigations were devoted mainly to increase compression strength and compression rigidity of the materials; nevertheless it indicates principal possibility to use thick filaments for high strength glass-reinforced plastics for various applications. Winding technology of making such articles are close in principle to that of SFAM).

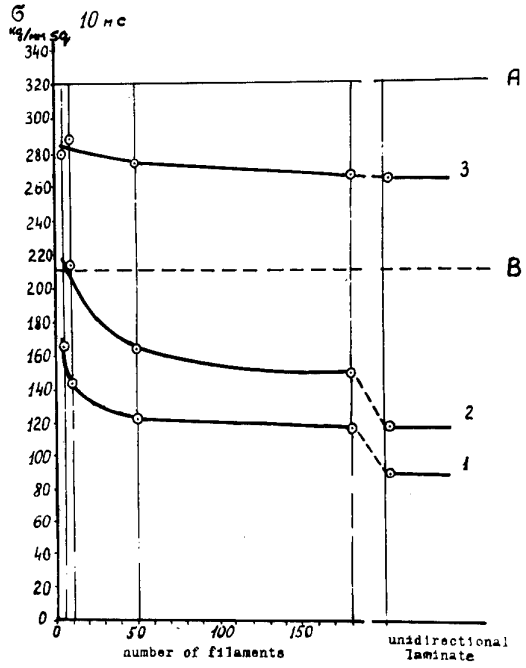
In order to estimate quantitatively the efficiency of maintaining initial strength of filaments of various diameters when applying binder in the course of their drawing, we have prepared samples consisting of different number of monofilaments – 180, 50, 10 and 5. The length of the part of such strands to be tested was equal to 100 mm. At the same time strength of unidirectional plyglasses (15 mm width, 0.3 mm thickness, testing length – 120 mm) was tested. Solution of epoxy binder was applied on the surface of the filaments by means of a special roll or applier in the course of drawing of the filaments and their wind-up (with a given pitch) on a rotating drum. Drying and solidification of strands and plyglasses were carried out straight on the drum.

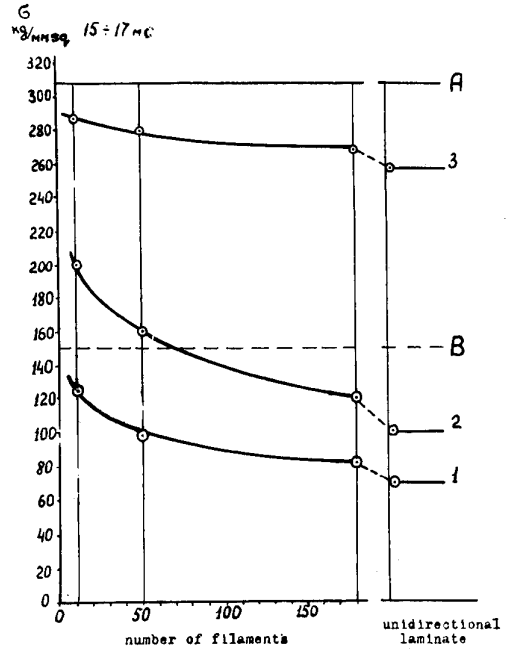
While calculating strength of filaments in the material, breaking load related to the total area of filaments cross-section; We also allowed for certain error in estimation of the strength during tensile tests due to bending deformations

arising in the course of the samples being unbent. Simple calculation shows that in case of the binder content up to 35% by weight and given thickness of samples, total error of that allowance does not exceed 3-5% .

The samples were made from the filaments of 9-10, 15-17 and 50 microns diameter. Epoxy resin ED-5 hardened by triethanolamine was used as binder. Content of binder amounted to 15-35% by volume. The samples were tested at the room temperature and air humidity of 60-70%.

Results of measurements shown on Fig. 3 represent mean values obtained during tests of 20-30 samples.





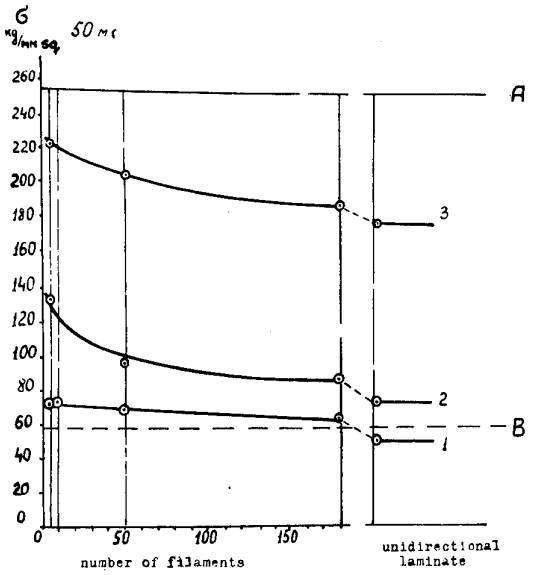


Fig. 3 The strength of filaments in strands:

(a) initial strength
(b) strength of filaments, tested at ordinary conditions;
1. strength of filaments in strands without the binder;
2. the same in strands with unsolidified binder;
3. the same on the epoxy resin ED-5 with triethanolamine as a hardener.

In case of the absence of the binder (curve 1) and when binder is not solidified (curve 2) one can notice regular reduction of strength of glass filaments with increase of their number in strand. It should be noted that maximum values of the filament strength, unprotected with a binder, are close to those of monofilaments measured under ordinary conditions; at the same time filaments measured under ordinary conditions; at the same time filaments covered with unsolidified resin possess higher strength.

As to the samples on the basis of solidified resin (curve 3) the strength of filaments in strands is getting near to the value of the initial strength of undamaged filaments.

When increasing the number of filaments and in testing the samples of plyglasses certain reduction of calculated strength of filaments shows up. This is caused by the influence of properties of a polymeric binder upon uniformity of tension distribution in reinforcing elements and simultaneous deformation of the whole system of filaments. (Great number of special investigations /18, 23/ have been devoted to the study of influence of mechanical properties and adhesion ability of polymeric binders upon characteristics of glass-reinforced plastics. This problem has not been touched upon in this paper).

Data obtained during testing of plyglasses on the basis of filaments with the diameters from 10 to 100 microns are summarized in Table 2.

As seen from Table 2 it is possible to utilize up to 75-85% of initial strength of filaments in plyglasses produced by the above method and to make high strength materials on the basis of filaments with diameter up to 100 microns. (R. Riabov /24/ has shown the possibility to use successfully filaments with diameter up to 135 microns, while making plyglass SFAM on the basis of sodium-calcium glass-filaments.

TABLE 2

The effect of alumoborosilicate glass-filaments diameter on the tensile strength of plyglasses on the basis of epoxy resin ED-5 with triethanolamine as a hardener

Diameter of filaments, microns	strength of filaments, kg/mm sq	Binders content, % by weight	Limit of strength of plyglasses kg/mm sq	Calculated strength of filaments in plyglasses kg/mm sq	Utilization of the initial strength, %
10	320	19,3	180	270	84
15	310	21,4	159	252	81
22	300	21,9	148	236	79
50	250	19,4	131	204	81
100	190	18,4	93	142	75

METHODS OF MANUFACTURE AND PROPERTIES OF SFAM ON THE BASIS OF GLASS-FILAMENTS OF VARIOUS DIAMETERS

Basic principles of making SFAM securing efficient utilization of high initial strength of filaments of various diameters were embodied in technology of production of these materials at industrial plants.

One of the methods is successfully used mainly for the manufacture of sheets. Plyglass in this case has the shape of square sheets 3 × 3 meters, thickness from 0.02 up to 0.35-0.45 mm with parallel or interperpendicular location of filaments. Preset anizotropy of mechanical characteristics in sheets is achieved in the course of plyglass winding or pressing plates from it. This method does not put practically any limitations on thickness of the filaments used and allows to produce together with high performance plyglass very thin (from 20 microns) crossplied electric insulation materials. Drawbacks of this method lie in interrupting of process and necessity of plyglass drying to remove solvent in special chambers.

The machines based on this method are shown on Fig. 4.

The second method allows to make unidirectional plyglass in the shape of a band of various width (at the existing plant width is 55 mm), and thickness of 0.30-0.45 mm suitable for subsequent pressing of articles of various profiles and for the manufacture of structural elements by winding technology. Filaments in the band are oriented along its axis under small 2°-5° angle to each other thus improving technological properties of the band without reducing mechanical characteristics of materials and articles produced from it.

Important advantage of this method lies in continuity of the method and possibility of making the band of unlimited length. The method includes drawing of filaments, applying of polymeric binder, orientation of filaments and drying of plyglass thus securing in one mechanized cycle the possibility of obtaining pre-impregnated material completely ready for processing into articles. This method puts certain limitations on the thickness of filaments used, however, as the experiments have shown, utilization of the filaments with the diameters up to 30-35 microns is quite possible. Continuous action plant is shown on Fig. 5.

Table 3 gives basic properties of sheet glass-reinforced plastics SFAM made on the basis alumoborosilicate filaments of various diameters.

As seen from the data given with increasing diameter of filaments by 5-7 times tensile, bending and high impact strength of reinforced plastics is reduced on the average by 20%. Compression strength of materials on the basis of filaments with 32-35 microns diameter goes up to some extent which corresponds to the data obtained by other authors.

Characteristics given in the table are not the optimum values of SFAM properties; for example, with ED6-R30 (on the basis of epoxy resin) tensile strength of 90°-crossplied structure

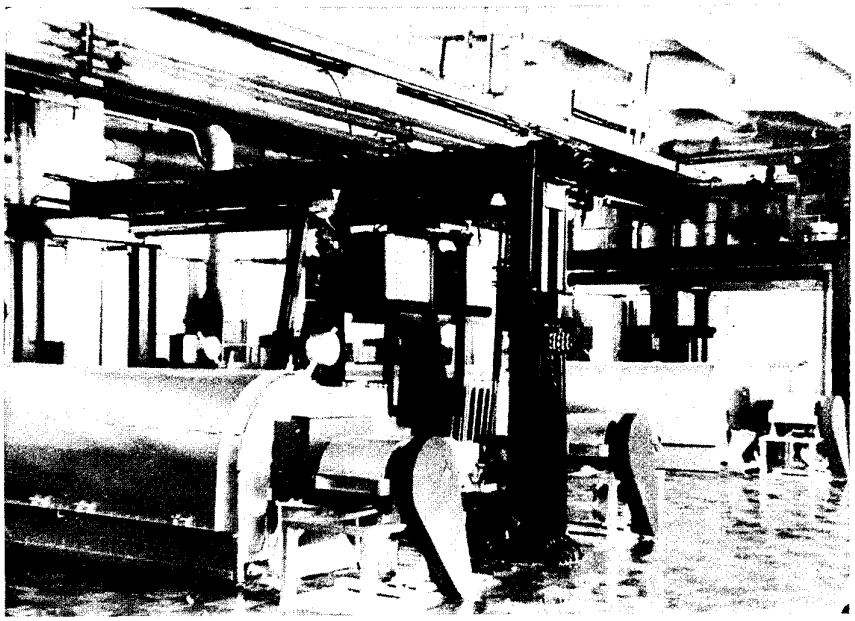


Fig. 4 Machines for plyglass manufacture (sheet plyglass)

TABLE 3

The effect of alumoborosilicate glassfilaments diameter on properties of sheet glassreinforced plastics SFAM with 90°-crossplied (1 : 1) structure on the basis of the epoxy-phenolic binder*

Diameter of filaments, microns	Binders content % by weight	Limit of strength, kg/cm sq			Specific high imp. viscosity kgcm/cm sq
		Tension	Compression	Bending	
5-7	20-25	4800	4400	7900	580
12-14		4700	4000	7500	500
16-17	25-30	4200	3750	7600	—
32-35		3800	4700	6700	460

Independent from diameter of filaments:

Specific volume resistance, om	3.10^{14}
Specific surface resistance, om cm	$3.5.10^{14}$
Tangent of dielectric losses	0,020
Dielectric permiability	5-6
Electrical strength, kv/mm	35-40
Heat resistance, °C (Martens	280-300

* data given in the Table shows up results obtained by testing of industrially produced materials.

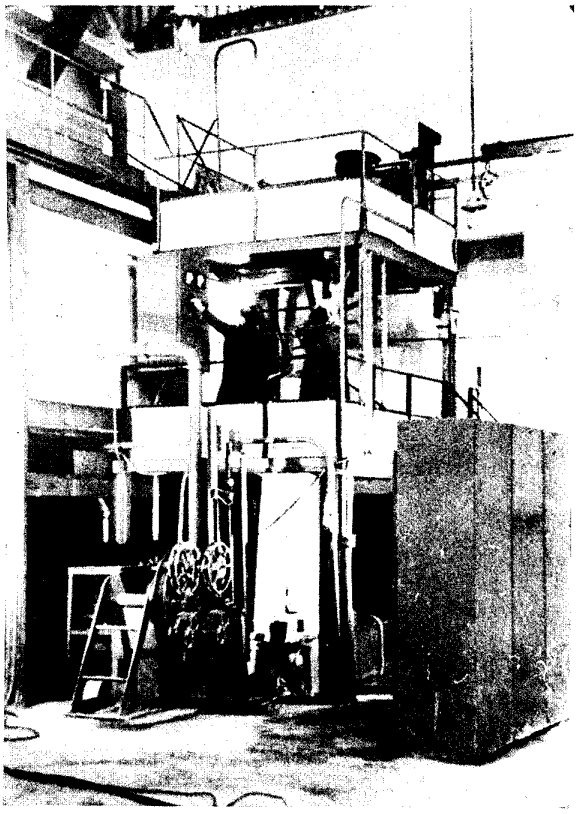


Fig. 5 Machine for continuous band plyglass manufacture.

sheet is in the order of 5600-6300 kg/cm sq. For unidirectional materials SFAM hardened straight on the wind-up mandrel, tensile strength reaches 18 000-19 500 kg/cm sq.

Properties of SFAM produced by both described methods, on the basis of the same glass-filaments and biner, are practically the same.

CONCLUSIONS

Investigations which have been carried out at the industrial plant shows that strength of undamaged glass-filaments is considerably higher than that of measured at ordinary conditions and depends relatively little on the diameter of filaments.

Applying of polimeric binders on the glass-filaments surface immediately after their spinning gives the opportunity to secure high initial strength of filaments of different diameter.

Manufacture methods of nonwoven oriented glass-reinforced plastics SFAM by using simultaneously spinning of filaments, applying of binders and orientation of filaments in the matrix makes possible to produce high performance glass-reinforced plastics on the basis of various in diameter filaments, including such thick filaments which are completely unsuitable for manufacturing ordinary yarns and woven fabrics.

The possibility of considerable raising the productivity in glass fibers manufacture and avoidance of all intermediate glass-filaments processing open prospects for decreasing of materials and articles prices and widening of their manufacture scope.

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The adhesion of certain polymers glass fibres surfaces

25

G. D. ANDREAVSKA, U. A. GORGATKINA, and V. G. IVANOVA-MUMJIEVA, Institute of Chemical Physics, Moscow, USSR

The physical and mechanical characteristics of reinforced plastics depend to a great extent on the resistance to bonding between the glass fibres and the resin. In general, volumetric (solid) samples are used for the determination of the degree of adhesion. But, because of their brittleness and low mechanical strength, these samples disintegrate, and the tests are made with a resin with a great power of adhesion. In addition, volumetric samples have to be carefully ground and polished to make them smooth. During this treatment the hard grains of grinding powder and the acid media of the polishing suspensions cause mechanical and chemical changes in the surface of the glass.

It is therefore more rational to determine the adhesion to the clean, smooth surface polished by the lustre of the glass fibres. Moreover, the glass fibres have great mechanical strength.

We developed this method of determining the adhesion-resistance with the aid of the shearing stress. The method is based on the following principles. Two thin metal wires (or glass fibres with diameters of 120 to 150 microns) are placed one exactly above the other by means of a special device. A small part of each wire is covered with a layer of the resin to be tested. A thin sample, 7 to 20 microns in diameter, of the glass fibre whose adhesion is to be tested, is stretched between these two wires. The wires are then placed in such a position that the glass fibre is completely immersed in the layer of resin, covering the wires, as shown in Fig. 1. This method of preparing the mounting ensures that a layer of the resin which is to be tested will form [1].

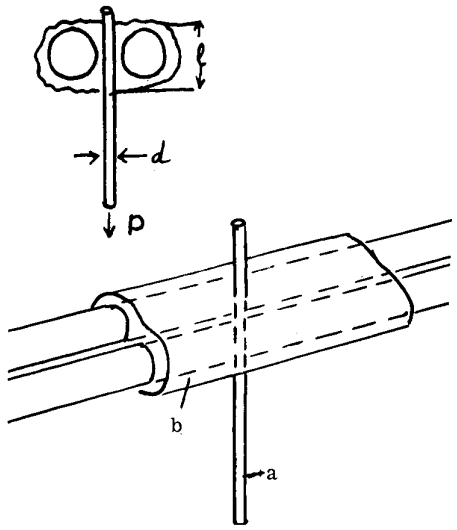

Fig. 1 Positioning of the glass fibre in the resin:

a glass fibre
b layer of resin covering the the metal wires (or thick glass fibres)
d diameter of the thin glass fibre
l length of the mounting

The sample is mounted in a frame of paper or thin metal foil so that the ends of the glass fibre are firmly fixed in it. The sample is left for about 20 hours in air and is then polymerized under conditions which are specific for the resin under test. When polymerization is complete the sample is slowly cooled. Then the length 'l' of the mounting and the diameter 'd' of the thin fibre are measured with a micrometer under a microscope. The surface area 's' of the mounting is found as the lateral surface area of the cylinder ($s = \pi\, dl$). The frame of the sample is clamped between the jaws of the rupture-test apparatus, and the load needed to tear the fibre loose from the layer of resin is measured. The adhesion-resistance τ_i is determined for each sample from the formula:

$$\tau_i = \frac{P}{S} = \frac{P}{\pi l}$$

where P is the shearing stress to be measured and S is the mounting surface. (The surface area of the mounting is of the order of 1.10^{-4} cm^2).

The figures for the adhesion-resistance τ_0 are calculated from the formula:

$$\tau_0 = \sum_{i=1}^{n} \frac{\tau_i}{n} + \Delta\tau$$

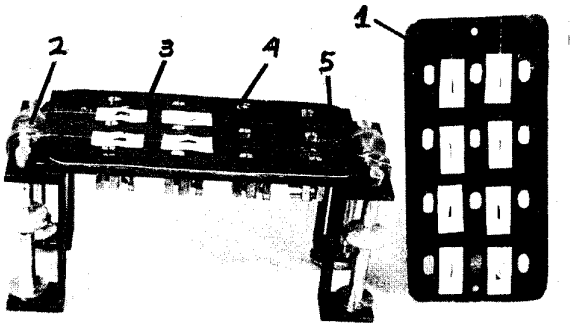

Fig. 2 Apparatus for preparing the samples for the tests in series:

1, 3 standard plate
2 small drums for stretching the thin glass fibres
4 small jaws for the metal wires
5 glass fibres

30 to 50 measurements being made. Here, $\Delta\tau$ is the correction made to account for the fact that among the adhesion-rupture samples there are to be found cohesion-rupture samples of fibre glass (Article [2] describes the method of calculation).

This method of determining adhesion is applicable not only to glass fibres but also to synthetic fibres and thin metal wires.

Since the determination of adhesion involves the preparation of a large number of samples, we evolved an apparatus with which it is possible to prepare about 100 samples in 6 hours [3].

Fig. 2 shows this apparatus. The results obtained by the method of determining the adhesion-resistance directly at the surfaces of the fibres are highly reproducible. Moreover, it produces conditions very close to those of the actual reinforced system. By this method we were able to demonstrate the influences on the adhesion [4] of various factors involved in formation and rupture of the mounting. For instance, Table 1 shows the influence E of the modification of the surfaces of the glass fibres on the adhesion of the bonding agents to the bases of epoxy resins. The results shown are the outcome of 40 to 50 measurements for each type of resin. The accuracy of measurement is about 5-8%.

It will be noted that the adhesion of the oiled samples is less than that of the unmodified samples, and that, on the other hand, special finishes improve adhesion.

It is generally assumed that the low mechanical strength of reinforced plastics based on silicone resins is due to their poor adhesion.

The results that we have obtained indicate that the adhesion of silicone resins depends on their structure, on the nature of the organic groups in the macromolecular chain. In certain cases the adhesion of silicone resins is comparable to that of phenol resins; that is, the adhesion is 250-290 kg/cm^2.

TABLE 1

Influence of the modification of the surfaces of glass fibres on the adhesion of the bonding agents to the bases of epoxy resins.

Resin	Modification of the surfaces of the fibres	kg/cm^2
epoxy (ED-5)	unmodified	348
	oiled	302
epoxy-thiocol (5% of thiocol	unmodified	390
	oiled	300
epoxy-aniline-phenol	unmodified	448
	oiled	373
epoxy-phenol	unmodified	376
	oiled	323
	with amino ethoxy silane	438
epoxy-polyester	unmodified	353
	oiled	244
	with amino ethoxy silane	406
	with vinyl ethoxy silane	392

Table 2 shows the influence of the structure of certain silicone resins, and of the type of solvent used, on the adhesion.

The results show the influence of the nature of the organic group on the adhesion of silicone resins. We thus observe the influence of the chemical affinity between the resin and the solvent on the adhesion.

We are carrying out experiments in our laboratory to determine the influence of the temperature, and of the method of applying the load, on the adhesion.

TABLE 2

Influence of the structure of the resin and of the type of solvent on the adhesion of silicone resins

Resin	Solvent	τ_0, kg/cm^2
poly-methyl poly-phenyl silicone	ethyl alcohol	320
	acetone	287
	toluene	219
	benzene	198
poly-methyl silicone	ethyl alcohol	257
	acetone	269
poly-phenyl silicone	ethyl alcohol	130
	acetone	137
	toluene	158

The measurements were made with a specially designed adhesion meter with which it was possible to determine the adhesion at temperature intervals between —180 and +300°C. It is possible with this apparatus to vary the speed of loading by three orders of magnitude (from 10 to 10 000).

Fig. 3 shows a general view of this adhesion meter. Ten samples were polymerized simultaneously in this apparatus.

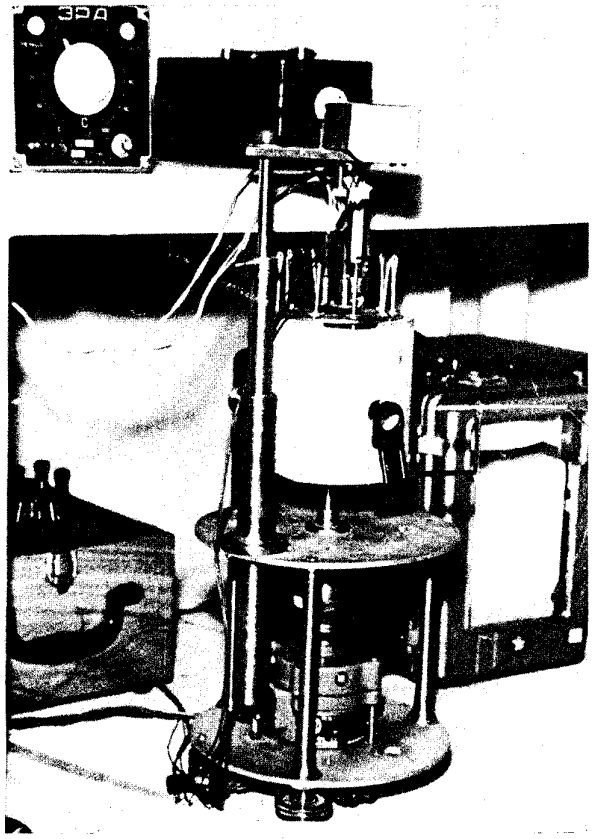

Fig. 3 General view of the adhesion meter

The force is measured by a strain gauge and the samples are tested in a single measuring apparatus.

Fig. 4 shows the relation between adhesion and test temperature for butvar-phenol resin and polyester resin. The speed of loading is 7 kg/cm^2/sec.

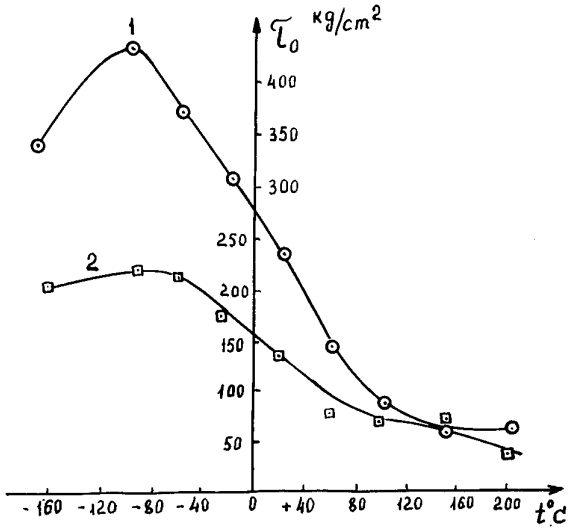

Fig. 4 Influence of temperature on the adhesion-resistance

1 butvar-phenol resin
2 polyester resin

It will be seen that the curve for the relation between adhesion and temperature has its maximum in the range of temperatures below zero, and that the temperatures for maximum

adhesion (t_{max}) are not the same as those for the vitreous transition (T_v) of these resins.

	t_{max}(°C)	T_v(°C)
Butvar-phenol resin	−100	~70
Polyester resin	−90	30-40

The explantion for the reduction in the adhesion at temperatures above zero may be the increase in the heat transfer due to the reduction in the adhesion at temperatures below zero (below t_{max}) is clearly the occurrance of tensions at the interface limit due to the different coefficients of expansion of glass and resin.

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Glass rods for reinforcements of plastics

26

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Glass plastic materials are distinguished by a wide range of technical characteristics and properties and therefore find wide application in various branches of technology. Most of the glass plastics are obtained from continuous glass fibers—thin rods combined with man-made resins. The type of glass and of the binding agent determines the properties of the glass plastic and the product manufacturing process.

Continuous glass fibers — rods for glass plastics — are obtained by the spinneret or ingot method. The rods are classified into several groups, depending on the field of application and the average diameter: (1) ultra-thin, up to 3μ used for the manufacture of glass pertinax (micarta); (2) thin, up to 12μ — for fiberglass; (3) coarse, up to 35μ, used in the manufacture of anisotropic materials. Elastic glass rods of 35 to 100μ have been tested under industrial conditions in the manufacture of structural glass plastics. Thick glass rods of 100 to 300μ have no application at present, but, in our opinion, can be used for reinforcement of plastics (1).

As a result of the consideration of the physicochemical characteristics of glass fibers and the methods for their manufacture as well as the experience of coating them with man-made resins (2, 3) it was found expedient to use elastic glass fibers for the manufacture of structural glass plastics.

The spinning of fibers from a glass melt proceeds at high temperatures, when many structural elements on the surface of the glass possess an increased reactivity and therefore readily enter into chemical reactions with various substances in the environment.

The surface layers of silica glass always differ from the glass melt in their properties and chemical composition, however the most important differences are due to the topochemical reactions in glass products with a developed surface.

The formation of stable coatings on the surface of glass fibre in the course of its extrusion is possible only in the presence of a chemical reaction between the coating and the glass surface with the resulting completion, so to speak, of the glass surface with new structural elements.

The properties of glass plastics depend not only on those of the glass fiber, but also on the topochemical reactions between the active groups of the glass and the reactive radicals of the resins. The chemical activity of the surface of a glass fiber is often the decisive factor for a uniform distribution of the coating and for the manufacture of high-quality glass plastics.

The entire process of obtaining reinforced plastics can be divided into several stages. Let us consider them briefly, in the appropriate sequence.

The diameter of the reinforcing glass fiber depends on the conditions of its spinning. In order to establish the relationship between the diameter of glass fibers and the spinning conditions, Poiseuille's formula can be used. Poiseuille's formula for the flow of viscous incompressible liquid is valid for an isothermal process, but if one takes into account the viscosity at the outlet cross section of the spinneret, its application yields satisfactory results /4/. The spinning conditions can be written in the dimensionless form

$$\frac{d}{D} = 0.176\sqrt{K} \qquad (1)$$

where $K = \frac{LpgD^2}{l\eta u}$ is the criterion determining the process.

Here d = fiber diameter, D = spinneret diameter, L = height of the glass melt layers, g = acceleration of gravity, l = length of the spinneret, U = extrusion rate, η = viscosity. The relationship (1) is illustrated in Fig. 1.

The process of cooling of glass fiber considerably affects such properties as strength and flexibility. This problem is considered in detail in the authors' work /5/.

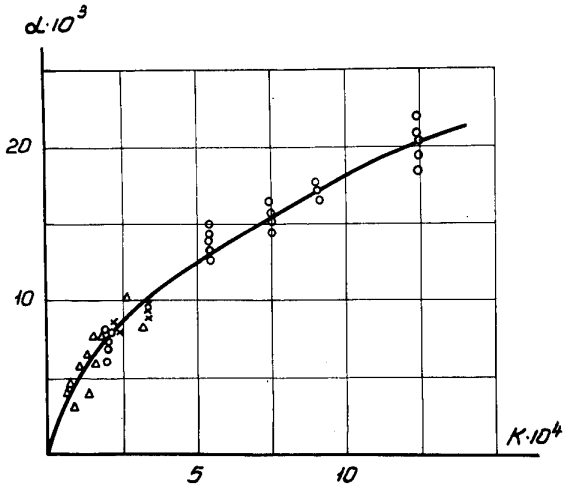

Fig. 1 Dependence of degree of elongation on criterion K in fiber spinning.

Reinforcement can be effected both with ordinary and metallized fibers. The metal can be applied to glass fiber by the so-called hot method, i.e. the drawing of continuous glass fiber through a layer of molten metal during spinning, when the surface of the fiber is juvenile. Our investigations of this method were based on the theory developed by B. V. Deryaguin /6/. If the metal forms a film entrained by the fiber, the thickness of the coating applied, h, is equal to /7/:

$$h = 2.64\ De \cdot r \qquad (2)$$

where r = fiber radius, $De = \frac{u\eta}{\sigma}$ = a dimensionless criterion (here σ = surface tension of the molten metal). If, however, no such film is formed, the constant in (2) is halved.

Strength is one of the principal characteristics of glass-fiber, and it can be analyzed on the basis of the statistical theory suggested by us, which takes into account the effect of surface and volume defects /8/.

Reinforcement of resins can be successfully done with elastic /9/ (dia 35-100μ) glass fibers. The method for obtaining oriented glass plastics with a nonwoven structure makes it possible to use elastic and thick glass fibers for the manufacture of structural materials; these fibers are much cheaper than thin fibers with an average diameter up to 12μ /10/. It is well known, however, that glass fibers cool at a high rate in the course of spinning. Under the same manufacturing conditions, the average diameter of elementary glass fiber will be the less, the higher the extrusion rate. This in turn, results in a higher cooling rate for smaller diameter ones. Therefore, the thinner the fiber, the better it retains the liquid structure and the higher its strength. In our case, the further from equilibria the system is, the stronger it will be. The time required for the equilibrium state to set in is determined by the time of Maxwell relaxation τ_*. Consequently, the condition for obtaining a considerable strength of glass fiber is

$$\tau_1 \ll \tau_* \qquad (3)$$

where τ_1 = cooling time.

In this connection it should be noted that the use of small-diameter spinnerets is inexpedient. Indeed, the rate of fiber extrusion from a smaller-diameter spinneret is much lower, and hence the characteristic cooling time is greater. Therefore, the spinning of high-strength glass fibers in the single-process manufacture of compositions should, as we believe, be done by the jet method /11/.

Tensile tests were performed on metallized glass fibers with

diameters from 22 to 78μ and a length of 10 to 100 mm. The glass used for fiber extrusion had an alkaline composition: SiO_2 — 71; CaO — 5.6; MgO — 4 0; Na_2O — 17; Al_2O_3 + Fe_2O_3 — 1. At least 50 specimens from each batch of monofibers were subjected to tensile testing.

The test specimens were prepared according to the conventional procedure, the fibers being pasted on paper frames. The tensile tests were carried out on a machine with a maximum load of 200 and 1000 g. The rate of load application was 60 mm/min.

Figure 2 demonstrates the dependence of the strength of metallized glass fiber on its diameter. As the glass fiber cylinder increases, its strength drops. The same Figure shows the test results for three specimens of different length: 10, 50 and 100 mm. The surface of the specimens is protected by a layer of zinc formed on the fiber in the course of extrusion within one thousandth of a second. The longer the specimen, the lower its strength.

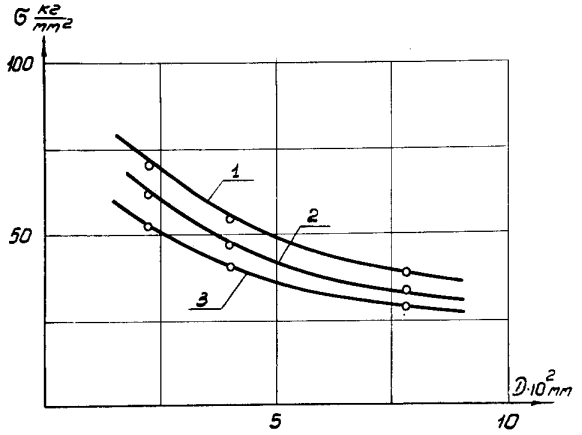

Fig. 2 Dependence of average strength of glass fiber on its diameter. 1 — specimen length (l) = 10 mm; 2 — l = 50 mm, 3 — l = 100 mm.

The results obtained fit well into the statistical scheme suggested in the work /12/. Glass fiber has surface and volume defects. The probability of specimen fracture owing to the surface and volume defects can be written down thus:

$$\Phi(\sigma) = P_1 e^{-\mu A F_1} + P_2 e^{-\nu V F_2} \qquad (4)$$

Here $P_1 + P_2 = \mu$ and ν = density of surface and volume defects, respectively; A and V = specimen surface and volume respectively; F_1 and F_2 = probability that the specimen will not be ruptured by stress σ in the presence of a single defect on the surface or in the volume, respectively.

If specimen I has a surface and volume greater than specimen II, all things being equal, it follows from (4) that

$$\Phi_1 > \Phi_2 \qquad (5)$$

In this connection, it is of interest to consider experimentally the problem of the effect of the dimensions of glass fiber on the shape of the curve of the integral distribution function Φ_1.

The coating of glass fiber with a layer of metal decreases the tensile strength of the glass fiber. This is evidently associated with the further approach of the glass structure towards equilibrium, which results in the weakening of the inequality (3). Figure 3 exhibits integral distribution functions in respect to the strength of metallized glass fiber 39.6μ in diameter.

Curve 1 — length 10 mm, curve 2 — 50 mm, curve 3 — 100 mm.

Figures 4 and 5 depict, respectively, the integral and differential distribution functions for glass fiber (dia. 20μ) and metallized glass fiber (dia. 29μ), i.e. the curves $\Phi(\sigma)$ and $\frac{d\Phi(\sigma)}{d\sigma}$ (curves 1 and 2), respectively. These figures distinctly show the displacement, on metallization, not only of the entire dis-

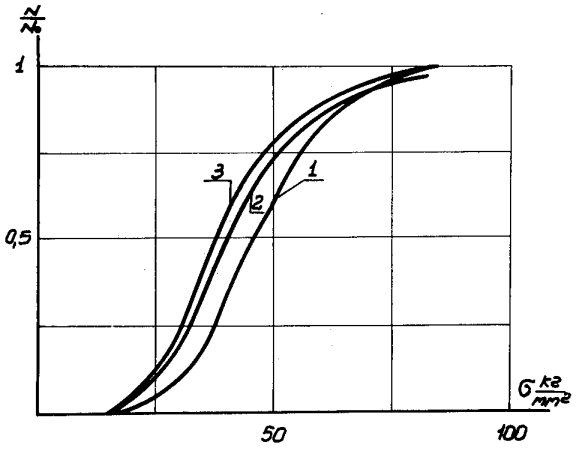

Fig. 3 Integral curves of strength distribution for glass fiber, 40 mm in diameter, of different lengths: 1 — l = 10 mm, 2 — l = 50 mm, 3 — l = 100 mm.

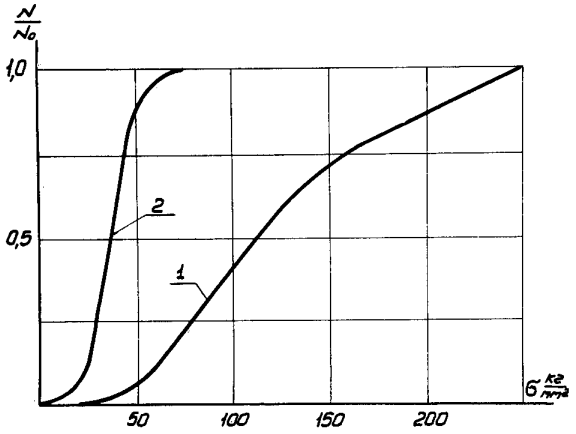

Fig. 4 Integral curves of strength distribution for glass fiber (1) and metallized glass fiber (2).

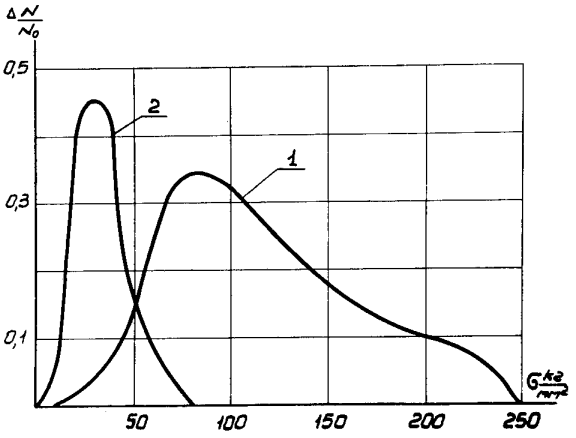

Fig. 5 Differential functions of strength distribution for glass fiber (1) and metallized glass fiber (2)

tribution curve but also of the most probable tensile strength of ordinary and metallized glass fiber.

If the strength of a glass fiber decreases on application of metal coating, it increases when resins are applied (which is done at considerably lower temperatures). In Fig. 6 we see the dependence of tensile strength for an unprotected fiber (line 1) and for a glass fiber coated with resin 3Δ — 5 (line 2). These results show that there is a linear relationship be-

tween the tensile strength of glass fiber and the inverse diameter.

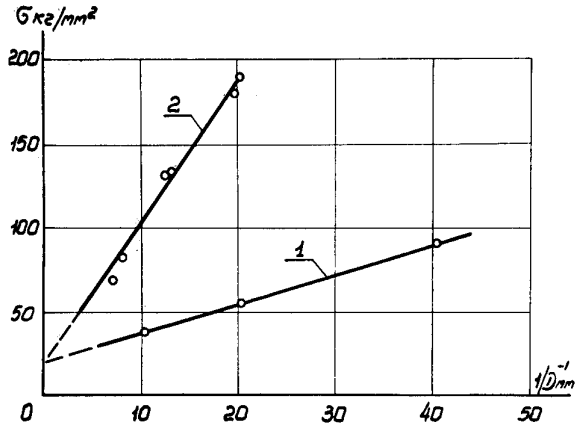

Fig. 6 Dependence of glass fiber strength on inverse diameter. 1 — unprotected fiber; 2 — fiber with epoxy resin coating.

Data concerning other coatings (varnish P-21, combined epoxyphenol resin ЗПф, polyester resin ПН — 1) can be found in work /9/. Different resins promote glass strengthening to a different extent. This should obviously be contributed not only to the different thickness of the coating applied. The thickness of the coating is determined by the physico-chemical properties of the coating material.

The strength of glass fiber products reveals a definite dependence on the strength of protected glass fiber. Figure 7 presents the relationship between the strength of glass veneer based on resin P-21 and that of the initial glass fibers protected by the same resin. Tensile specimens of glass veneer were tested on a machine with a specific load of 1000; 5000 and 10 000 kg. Ten specimens from each batch of glass veneer were tested. The width of the glass veneer specimens was 15 mm, the thickness about 1 mm. The distance between the clamps was 50 mm. For better gripping of the specimens, corrugated jaws built into the clamps. The rate of load application equalled 20 mm/min. It is a curious fact that the strength of glass veneer made of elastic fibers is less dependent on the glass fiber diameter than the strength of the elastic fibers themselves.

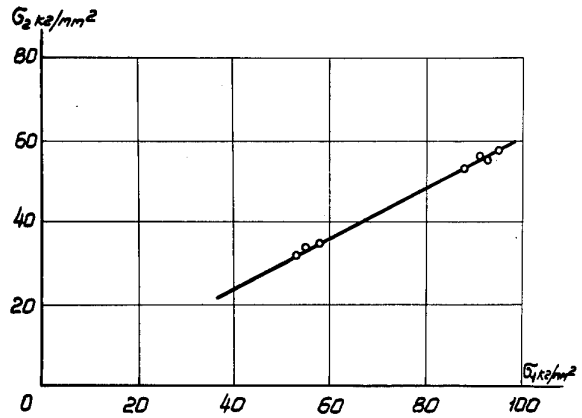

Fig. 7 Dependence of tensile strength of glass fiber (σ_2) on strength of initial glass fiber (σ_1).

Along with strength, flexibility is a very important characteristic of glass fiber /15/. The comparatively low flexibility of glass fibers is one of their substantial disadvantages. Thus, for instance, if thin fibers (up to 12 μ) can be used for textiles, coarser glass fibers (up to 35 μ) can be used only in the manufacture of felts and coarse canvasses. Elastic glass fibers (up to 100 μ) and thick glass fibers (up to 300 μ) cannot be used in the manufacture of certain articles because their low flexibility prevents them from withstanding the necessary loads in a stabilized elastic structure.

The flexibility of glass fibers is evidently determined not only by their mechanical strength, but also by other factors, in particular, by the nature of the formed or applied coatings on the surface of the glass fiber. Nevertheless, the profound relationship between the strength and flexibility of glass fiber is quite obvious.

Experimentally, glass fiber flexibility was studied in the following way. A glass fiber of definite diameter and length was clamped at one end. The deflection of the other end was measured. For each specimen diameter and length, 25 to 30 measurements were made. The dependence of the dimensionless sagitta (ratio of the sagitta to the length of the glass fiber — $\frac{\sigma}{l}$) on the diameter of the glass fiber is presented in Fig. 8 for L = 12 and L = 15 cm. Deflection measurements were also made at distances of 5 and 9 cm (for l = 12 cm) from the fixed end and 6 and 10 cm for l = 15. Therefore, each graph of Fig 8 includes three curves. For rod bending, it is possible to obtain the following relationship between the sagitta and the other values /13/

$$\delta(z) = \frac{g}{24ET} z^2(z - 4lz + 6l^2) \qquad (6)$$

where g = weight per unit length of rod, E = Young modulus, I = moment of inertia, z = distance from the fixed end to the measurement point. For z = l

$$\delta(l) = \frac{1}{8} \frac{gl^4}{ET} \qquad (7)$$

It was found from the experimental results that for each glass fiber the equation (6) coincided with high precision, but the results obtained differed drastically from theoretical ones in

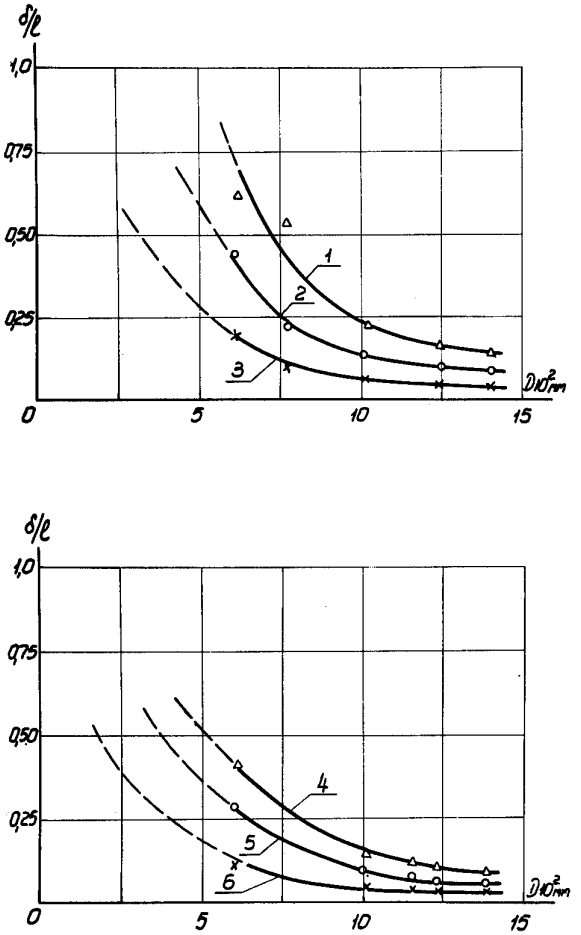

Fig. 8 Dependence of dimensionless seggita on diameter of glass rod (a) for length (l) = 15 cm, (b) l = 12 cm, 1 — 15 cm, 2 — 10 cm, 3 — 5 cm, 4 — 12 cm, 5 — 9 cm, 6 — 6 cm.

passing from one diameter to another. This cannot be explained by the applicability of equation (6) only to a weak deflection of rods. The main cause for the deviation is the change in the flexural and strength properties with the variation in the specimen length. Figure 9 illustrates the dependence of the dimensionless sagitta $\frac{\delta}{l}$ for l = 15, 12, 9 and 5 cm (the respective curves are 1, 2, 3, 4). The considerable scatter of the points on curve 1 in the region of 50 μ is explained by a different deflection mechanism. It would have seemed that curves 3 and 4 should be reflected by theory still more accurately.

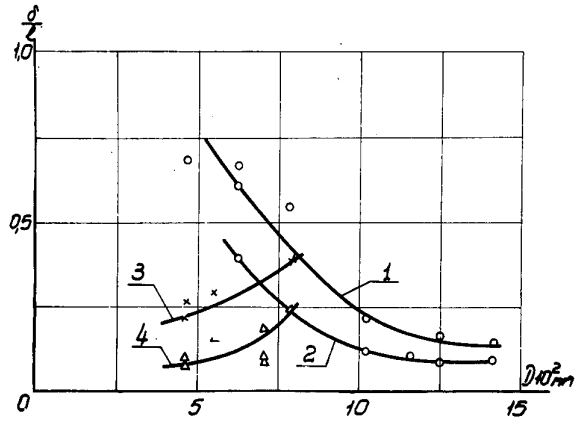

Fig. 9 Dependence of dimensionless saggita on diameter of glass fiber with different fiber length.

Equation (7) includes all the values measurable experimentally with the exception of the Young modulus E. Therefore it is natural to assume a definite relationship between the Young modulus and the specimen length.

Since $I = \frac{T_1}{64} d^4$, we obtain, instead of (2),

$$E = \frac{8l^4 pg}{d^2 \delta(l)} \qquad (8)$$

With the aid of this relation it is possible to calculate E.

It turned out that with the same specimen length smaller-diameter fibers have a larger Young modulus, which can be seen from the following data (l = 15)

E/125 / E/141	E/125/ /E/125	E/125/ E/117/	E/125/ E/102	E/125/ E/29/	E/125/ E/55/	E/125/ E/47/
1.18	1.00	0.99	0.96	0.80	0.82	0.63

Since the tensile stress σ is proportional to the Young modulus (according to Orovan's rule $\sigma_{theoz} \cong 0.2E$), it should be expected that, all other conditions being equal, larger-diameter specimens will have a lower strength, i.e. $\sigma \sim E \sim \frac{1}{d}$.

This is in good agreement with the works /12/ and can be explained by the presence of various defects on the surface.

At the same time the values of E calculated for specimens of different length but equal in diameter, are rather similar.

The surface layers of silica glass always differ from the glass melt in their properties but the difference becomes especially prominent as a result of topochemical reactions.

In investigating the mechanical properties of glass fibers by determining the limiting diameter D_1 of the loop which can be obtained by knotting, it was found that $\frac{D_1}{d}$ is a constant for fibers manufactured by the same process. Figure 10 displays the results obtained in these experiments (line 1 — glass fiber with organic coating; 2 — glass fiber without coating; 3 — glass fiber with zinc coating obtained at a temperature of 450 to 500°C).

It can be seen from this Figure that the constancy of the ratios $\frac{D_1}{d}$ is maintained for fibers with organic or inorganic coatings applied in the course of extrusion.

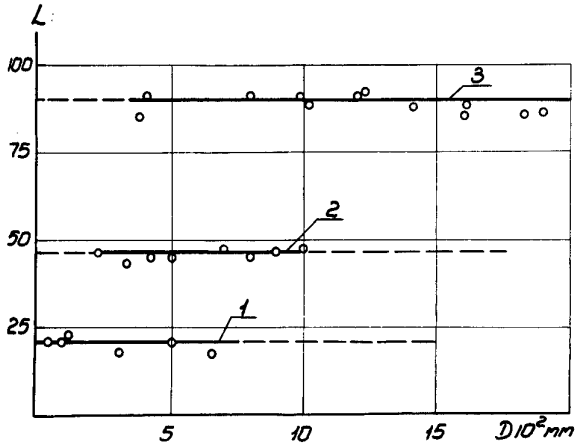

Fig. 10 Dependence of flexibility factor on fiber diameter 1 — glass fiber with organic coating, 2 — glass fiber without coating, 3 — glass fiber with metal coating.

It is known /17/ that the value of bending stresses σ in knotting a loop is expressed by the equation

$$\sigma \frac{P_1 R(1 - \cos \varphi)}{0,1 d^3} \qquad (9)$$

where P_1 = force applied to the loop end, R = loop radius, φ = angle between the loop diameter perpendicular to the force P_1 and the cross section in which the stresses are determined. The tensile stresses in the fiber are determined thus:

$$\sigma = \frac{4P_1}{\pi d^2} \qquad (10)$$

Since the ultimate bending and tensile stresses for glass are approximately equal, by equalizing equations (9) and (10) we find that the ratio $\frac{D_1}{d}$ is a constant (φ = 180°). The same dependence law is well obeyed by the results of the famous experiments of A. F. Ioffe on the bending of glass rods with the defective layer removed in solutions of hydrofluoric acid.

It should be noted that for high-strength glass fibers with a juvenile surface one can observe a special, 'explosive' nature of destruction on application of a load /16/.

The mechanism of this type of destruction might be visualized in the following manner, by analogy with the propagation pattern of a detonation wave in solid explosives. (The similarity is purely visual, of course). On gradual application of a load to a glass specimen, a potential deformation energy — an analogue of the chemical energy of explosive transformation — accumulates in it. When a certain critical stress is attained, destruction sets in at a certain point. From this point, a relief wave propagates in all directions at a velocity equal to sound velocity in glass. This wave is supported by the stored potential energy of deformation at spots which it has not reached yet. Behind the front of this wave (more precisely, at its front), the potential energy of elastic deformation converts to the surface energy of the crushed glass. The ambient medium (air) flows into the crushed glass and causes something like a local explosion which scatters the fragments in all directions and is accompanied by a characteristic shot-like sound.

As was shown by our investigations carried out at the State Research Institute of Glass and at the Institute of Physical Chemistry of the USSR Academy of Sciences, the method for the manufacture of oriented glass plastics with a nonwoven structure of glass fibers makes it possible to use elastic and thick fibers (35-300μ in diameter) for the manufacture of structural and insulating materials; these fibers are much cheaper than thin ones.

Some characteristics of glass plastics are summarized in the following Table.

Characteristics of plastics reinforced with glass rods

Resin	Maximum impact resilience kg cm/cm^2	Ultimate tensile strength kg/cm^2	Brinell hardness, kg/mm	Rod diameter, mm × 10^3
Phenol phormaldehyde	75	5700	20	50
Epoxy phenol	200	7500	24	50
Polyester	300	5000	28	50

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The progressive nature of fatigue damage in glass reinforced plastics

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University of Nottingham

GENERAL INTRODUCTION

As the technology of plastics develops, reinforced plastics as structural materials are becoming more intensively and extensively used. The majority of engineering structures are subjected to long term loading, of which at ambient temperature fatigue loading is probably more important than creep loading, and consequently designers required suitable long term properties of the materials they use.

Over the past twenty years, glass reinforced plastics have been evaluated for use in primary structures mainly in aircraft, space and deep submergence applications. The main emphasis for all this research has been placed on materials with high specific strength or modulus. A considerable body of conventional fatigue data has been accumulated for such materials, particularly in the United States (1, 2, 3)*. Relatively few data have been obtained for chopped strand mat/polyester resin laminates, although these materials are of considerable commercial importance in the United Kingdom. Indeed, the British Plastics Federation has twice (4, 5) drawn attention to the need for more data. A review of the fatigue and creep properties of reinforced plastics has been recently published by the Federation (6). In 1964, at the University of Nottingham, the authors commenced an investigation into the fatigue properties and failure mechanisms of glass reinforced plastics with particular reference to glass chopped strand mat/polyester resin laminates. The work was sponsored by a research grant from the Science Research Council and a postgraduate studentship provided by the Reinforced Plastics Group of the BPF.

This paper describes an investigation of the fatigue properties and failure mechanisms of glass reinforced plastics based mainly on 'E' glass chopped strand mat and orthophthalic acid polyester resins. It is divided into two sections, the first relating to conventional fatigue testing and the second describing the progressive nature of internal damage under both single and repeated loading. The first section discusses the effects on fatigue life of stress amplitude, mean stress, resin reactivity, glass content and fillers. From some of the work it has been possible to construct Master diagrams. The work has been extended to include the fatigue of resins, the distribution of fatigue lives for laminates and the fatigue of a glass roving reinforced epoxy laminate. The second section describes the progressive nature of debonding and an attempt has been made to produce S-N diagrams showing the various stages of damage for several types of laminates, and also to construct a Master diagram for the debonding stage in a chopped strand mat laminate. Full details of almost all the work are included in a PhD thesis submitted to the University of Nottingham (7).

PART 1. CONVENTIONAL FATIGUE RESULTS

(a) Introduction

The detailed results of the work on chopped strand mat laminates were privately circulated to members of the Reinforced Plastics Group of the Federation in June 1967 and were subsequently published by the Plastics Institute (8). The following paragraphs summarise the results of investigations into the effect of mean stress and stress amplitude, glass content and fillers on the fatigue performance of chopped strand mat/polyester resin laminates. The work has been extended to include investigations into the distribution of fatigue lives, the fatigue of resin specimens and the fatigue of a cross plied non woven glass roving reinforced epoxide laminate.

All the unfilled laminates were made with one of two typical orthophthalic acid polyester resins, which had differing reactivities, reinforced by 'E' glass chopped strand mat ($2oz/ft^2$). The formulations of the resins are given in table 1. The properties of all the unfilled laminates are presented in table 2. Axial fatigue tests were conducted on a variable speed (55-324c/min) fatigue machine which was designed specifically for reinforced plastics (9). The machine consists of five independent loading frames driven by a common hydraulic pulsator pump. The loading frames are of the direct-stress type and any combination of mean and alternating load can be obtained within the overall limits of ±6000 lbf. The fatigue tests have been conducted at 74 c/min to avoid any internal heating effects in the specimen.

TABLE 1

Composition of the orthophthalic resins

	Low Reactivity Resin (LR)	High Activity Resin (HR)
Maelic anhydride, Mol	1	2
Phthalic anhydride, Mol	2	1
Propylene glycol, Mol	3	3
Alkyd/styrene ratio	65/35	65/35
Hydroquinone % on Blended resin	0.008	0.008

(b) Mean stress and stress amplitude

Laminates of both resin types containing similar amounts of glass reinforcement were loaded in fatigue at five mean stress levels and also in zero tension loading. From these results S-N diagrams (stress amplitude (or maximum stress) plotted against the logarithm of the life) were produced. By cross plotting these diagrams, two Master diagrams, which show the stress amplitude plotted against the mean stress for given lives, were constructed and are shown in figures 1 and 2. This type of diagram is frequently used by design engineers. The main features of the results include the following points. The effect of resin composition on the fatigue life is small particularly at long lives. For short lives under tensile mean load conditions the low reactivity resin laminate is superior. However, the slight differences involved are most probably of no practical significance. When there have been insufficient test results to produce a Master diagram, it has been common practice amongst engineers to produce an approximation of the diagram, using the linear relationship.

$$\frac{S_A}{S_E} = 1 - \frac{S_M}{S_U}$$

where S_A and S_M are the stress amplitude and mean stress respectively and S_E is the fatigue strength at zero mean stress for a given life. S_U is the static ultimate strength of the material. This relationship is known as the Modified Goodman Law and is suitable for most common metals. However, Boller (10) has shown that his experimental results for reinforced plastics fall below this line, and has proposed the use of the alternative relationship

$$\frac{S_A}{S_E} = 1 - \frac{S_M}{S_C}$$

* Numbers in parentheses refer to the references at the end of the paper.

TABLE 2

Summary of laminate properties for polyester resin/chopped strand mat system

Test series	No. of laminates in series	Reinforcement type	Resin type	Glass content %	Coefficient of variation for glass content %	Tensile strength lbf/in^2	Coefficient of variation for tensile strength
A	7	C.S.M.	L.R.	33.29	4.08	17325	7.73
B	6	C.S.M.	H.R.	32.58	5.10	16215	9.32
C	3	C.S.M.	H.R.	29.68	6.16	12994	9.89
D	3	C.S.M.	H.R.	36.01	4.43	18852	7.22
E	5	C.S.M.	H.R.	32.67	3.36	16472	6.50
F	3	C.S.M.	H.R.	33.50	4.18	16545	7.03
G	3	C.S.M.	L.R.	33.99	3.69	17008	7.66
H	8	C.S.M.	H.R.	32.90	3.02	16530	6.94

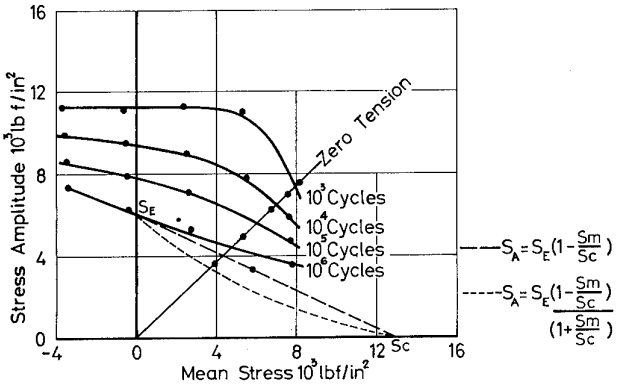

Fig. 1 Master diagram for chopped strand mat/low reactivity polyester resin laminates.

Cyclic speed 74 c/min; 20°C and 40-42% RH.

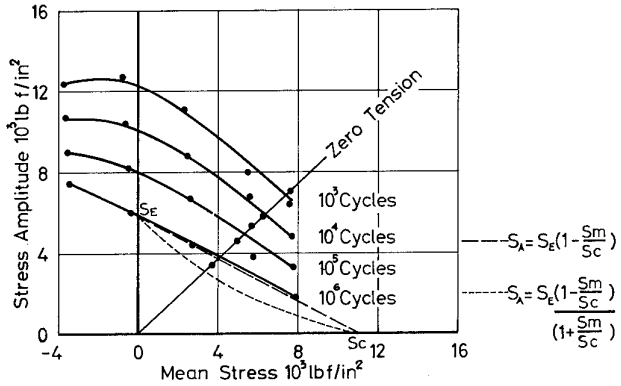

Fig. 2 Master diagram for chopped strand mat/high reactivity polyester resin laminates

Cyclic speed 74c/min; 20°C and 40-42 RH

where S_C is the stress rupture strength for the time corresponding to the cyclic endurance. However, some of Boller's results fall below this line.

Some of the results of this investigation fall below Boller's suggested relationship especially at 10^5 and 10^6 cycles. As a result of this it is proposed to offer an alternative relationship of the form

$$\frac{S_A}{S_E} = \frac{1 - \frac{S_M}{S_C}}{1 + \frac{S_M}{S_C}}$$ for tensile mean stresses only

This is a modification of a law proposed by J. O. Smith (11) for brittle cast irons, substituting the stress rupture strength in place of the tensile strength. All the data now fall above this line. The scatter of individual results making up the S-N diagrams is suppressed, but the use of this new relationship would appear to be sufficiently conservative to allow for scatter.

(c) **Glass content**

One of the variables which has a large effect on the tensile strength of laminates is the glass content. Results included in table 2 show that there is a relatively large change in strength for a small increment in glass content. However, the effect of the reinforcement content on the fatigue performance is very much smaller and almost negligible at long lives, for both zero-tension and fully reversed loading (see figures 3, 4). This is understandable for discontinuous glass reinforcements if it is the resin properties which are dominant at long lives. With increasing numbers of load cycles, internal damage commences and starts to propagate. (further discussion about this point can be found in part II). Increasing numbers of reinforcing fibres can no longer transfer load because of a breakdown in the glass resin bond, leading to an increasing load being placed on the resin. Since there are large numbers of crack nucleation sites, it is the resistance to crack propagation in the resin that becomes the important factor, if structural integrity of the laminate is to be maintained.

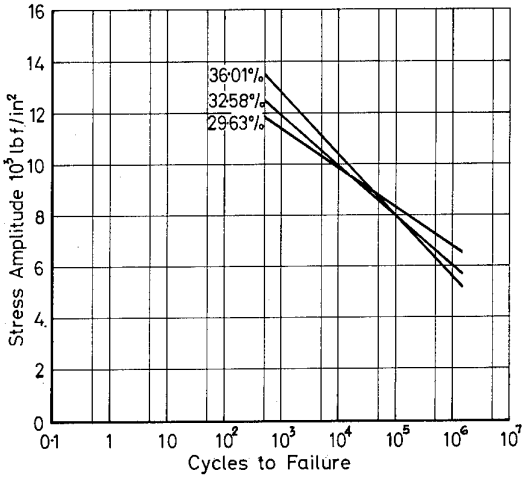

Fig. 3 The effect of glass content on the fatigue performance chopped strand mat/high reactivity polyester resin.

Zero mean stress; cyclic speed 74c/min; 20°C and 40-42% RH

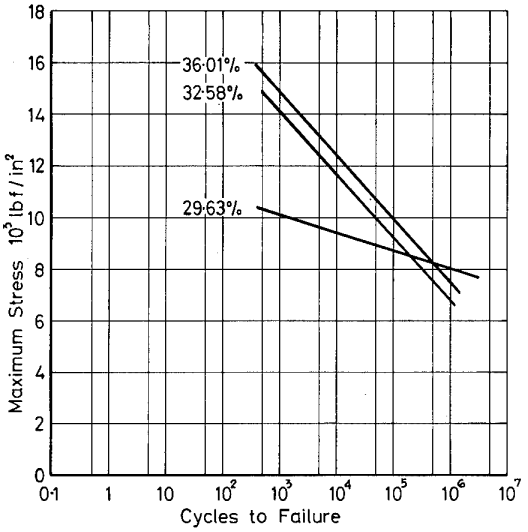

Fig. 4 The effect of glass content on the fatigue performance chopped strand/mat high reactivity polyester resin.

Zero-tension loading; cyclic speed 74c/min; 20°C and 40-42% RH

(d) Resin fatigue

Since the long term fatigue strength of laminates reinforced by short fibres are dependent on the resin, a limited investigation into the fatigue performance of both polyester resins was conducted. The results show that there was no noticeable difference between the high reactivity and low reactivity resins and also, by comparing maximum stress, that there was a negligible difference between fully reversed and zero-tension loading (see figure 5). These results agreed with those for the laminates in so far as there was only slight difference in conventional fatigue performance of both resin types. The results presented here are probably conservative due to the difficulty in testing these brittle resins. Failure usually originated from a surface scratch or subsurface defect, probably caused by the cutting and polishing processes, leading to premature failure. The values for the fatigue strengths of both resins, which were approximately 4400 lbf/in^2, were superior to the values of 3100 lbf/in^2 quoted by Carswell and Borwick (12) for polyester resins tested at 20 c/min.

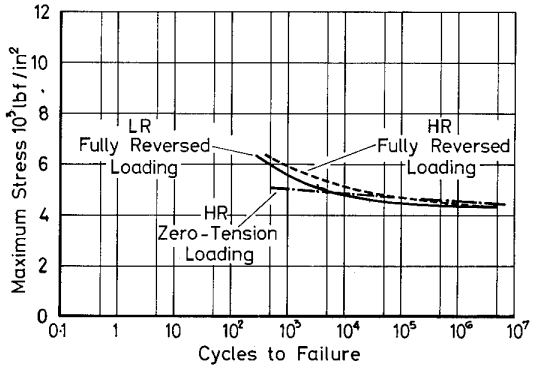

Fig. 5 S-N diagram for polyester resin

Cyclic speed 74c/min; 20°C and 40-42% RH

(e) Scatter

A preliminary series of fatigue tests designed to determine if there was any effect on fatigue life due to loading on any particular one of the frames of the fatigue machine had suggested that there was the possibility of a bimodal distribution of fatigue lives. Consequently a more thorough investigation was conducted using three groups of thirty specimens which were drawn by random selection from a stock of material.

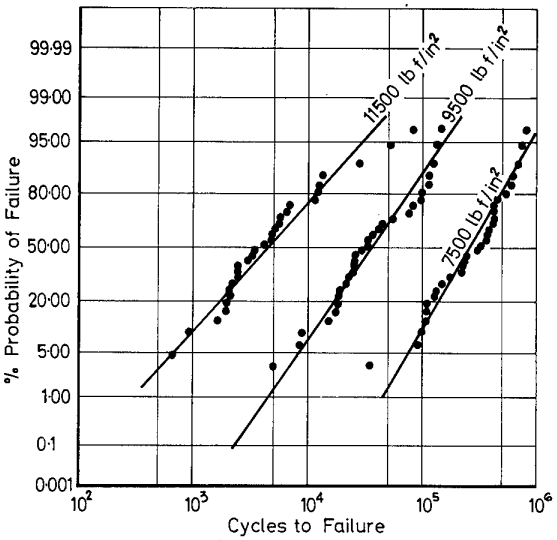

Fig. 6 The distribution of fatigue lives chopped strand mat/high reactivity polyester resin.

Zero mean stress; cyclic speed 74c/min; 20°C and 40-42% RH

Each group was tested at one of three stress amplitudes (7500, 9500 and 11 500 lbf/in^2) with zero mean stress. The results have been plotted on probability paper (figure 6) and it can be seen that the logarithms of the fatigue lives are reasonably normally distributed. One point of interest is that the variance of the lives is highest at the higher stress levels and lowest at the lower stress amplitudes. For metals, the converse is true. The coefficients of variations for the log life for all three stress amplitudes are indicated in table 3. The greater variances at the higher stress levels are probably due to the fact that reinforced plastics tend to show greater variations in ultimate tensile strength than metals.

TABLE 3

The coefficient of variation for fatigue life at three stress amplitudes

Stress amplitude lbf/in^2	Mean life cycles	Coefficient of Variation based on log life—%
11500	4460	13.6
9500	35420	8.5
7500	266900	6.1

(f) Fillers

Fillers are widely used in reinforced plastics for a variety of purposes, the most important of which are to reduce the cost of resin, to modify mechanical, chemical or electrical properties, as colouring pigments, to make resins thixotropic, to reduce the exotherm and for fire retardency. Although the effect of fillers on the static performance of glass reinforced plastics has been investigated, the effect on the fatigue properties has been almost completely neglected. In this limited programme, two model fillers, hessian cloth and glass beads have been used in conjunction with glass mat/polyester resin laminates.

The advantages of using hessian cloth are that its density is lower than that of resin or glass and that material costs are reduced. Glass beads may be used to improve the stiffness, insulation properties as well as the chemical resistance of laminates. Five sandwich-type hessian/glass mat laminates, which were of differing construction (see table 5) were made and supplied by the British Jute Trade Research Association. The properties of these laminates and those of two mat lami-

TABLE 4

Summary of laminate properties for polyester resin/chopped strand mat/filler systems

1. Glass bead content = 25.25% (by weight)
2. Glass bead content = 29.40% (by weight)

Test series	Resin type	Glass reinforcement type	Filler type	Glass mat content %	Tensile Strength lbf/in^2
H	H.R. polyester	2 oz/ft^2 C.S.M.—6 layers	Nil	32.90	16530
I	H.R. polyester	2 oz/ft^2 C.S.M.—6 layers	Ballotini (20% vol)	26.03[1]	15330
J	H.R. polyester	2 oz/ft^2 C.S.M.—6 layers	Ballotini (40% vol)	30.04[2]	17987
K	Polyester	Nil	Jute cloth—10 layers	0	6440
L	Polyester	1 oz/ft^2 C.S.M.—2 layers	Jute cloth—8 layers	6.70	7310
M	Polyester	1 oz/ft^2 C.S.M.—6 layers	Jute cloth—5 layers	16.60	9340
N	Polyester	1 oz/ft^2 C.S.M.—8 layers	Jute cloth—2 layers	27.90	12260
O	Polyester	1 oz/ft^2 C.S.M.—12 layers	Nil	33.00	18460

TABLE 5

Summary of laminate constructions and properties used to determine the onset of damage

Test series	Resin	Reinforcement	Ultimate Tensile strength lbf/in^2	Initial modulus 10^6 lbf/
P	H.R. polyester	1/4" chopped glass strands	7002	0.69
Q	Polyester	2" chopped strands	—	1.35
R	Isophthalic polyester	C.S.M. (2 oz/ft^2)	—	1.38
S	H.R. polyester	C.S.M. (2 oz/ft^2)	16545	1.41
T	Polyester	C.S.M. (1 1/2 oz/ft^2)	—	1.38
U	L.R. polyester	C.S.M. (2oz/ft^2)	17008	1.44
V	Polyester + 25% vinyl acetate	C.S.M. (1 1/2 oz/ft^2)	—	1.54
W	Epoxy (prepreg)	Marglass 116T/ P705/1032		3.77
X	H.R. polyester	Y227 glass cloth	55104	4.23
Y	Epoxy	Non-woven cross-plied glass rovings	61446	4.98
Z	H.R. polyester	Y221 glass cloth	75785	6.55

nates containing glass beads (BALLOTINI type 2429)* representing 20% and 40% of the resin volume, are shown in figure 7 for the hessian filled laminates and figure 8 for the glass beads filled laminates. Both sets of data show that the axial fatigue performance is reduced by the use of fillers. If the fatigue strengths of the hessian filled laminates are made dimensionless (using the ultimate tensile strength), then all the results fall within one scatter band and indicate that the fatigue strength at 10^6 cycles is between 35-45% of the ultimate tensile strength. Hessian core laminates might be expected to have good flexural fatigue strengths, because the outer layers of glass fibre will be taking the highest stress, and the inner layers of hessian will be only lightly stressed. Both types of laminates suffered internal damage, the laminates containing glass beads being particularly noticeable in suffering resin cracking earlier than the unfilled laminates. This may be due to the glass beads having a diameter larger than that of the glass fibres. Much smaller diameter beads

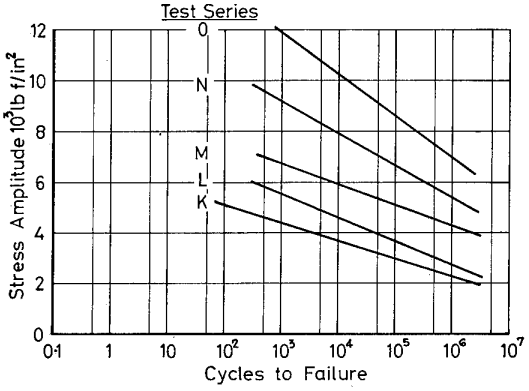

Fig. 7 S-N diagram showing the effect of hessian cloth.

Zero mean stress; cyclic speed 74c/min; 20°C and 40-42 RH

* Potter Bros. Inc., Carlstadt, New Jersey.

comparable with the fibre diameter, are now available and laminates containing these may not be so prone to resin cracking.

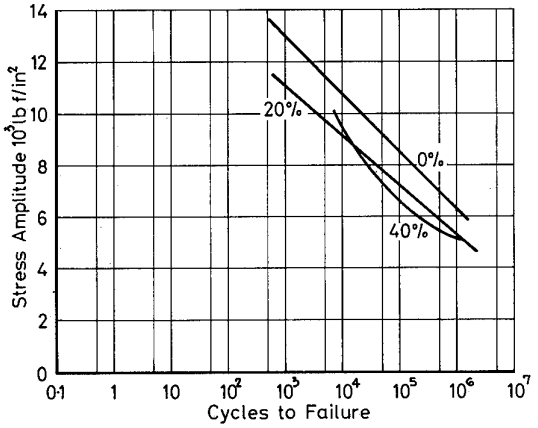

Fig. 8 S-N Diagram showing the effect of glass beads.

Zero mean stress; cyclic speed 74c/min; 20°C and 40-42 RH

(g) Permaglass XE6

Higher performance composites based on epoxide resins are important, particularly in the electrical industry because of their good combination of mechanical and electrical properties. Permaglass X* is a commercially available range of this type of composite, and the XE6 type is a cross-plied non-woven glass roving epoxide laminate in this series. Fatigue tests have been conducted on Permaglass XE6 laminates at four mean stress levels and zero-tension loading. The results of these tests are summarised as a Master Diagram in figure 9. At long lives all the individual S-N diagrams exhibited signs of becoming asymptotic to the life axis and therefore only a slight drop in the fatigue performance would be

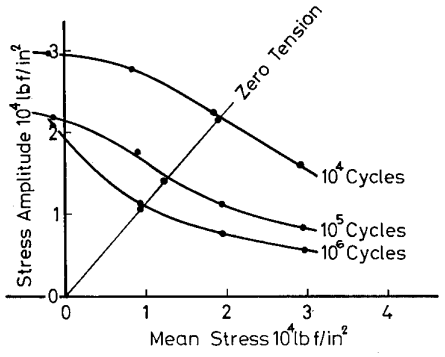

Fig. 9 Master diagram for Permaglass XE6.

Cyclic speed 74c/min; 20°C and 40-42% RH

expected at even longer lives. Although stress rupture tests were not conducted on this material, the results available indicate that both the Goodman Law and Boller's modification would give over-optimistic estimates of the fatigue performance. The fatigue performance of Permaglass XE6 is superior to the mat laminates and compares very favourably with results obtained by American workers (1).

A bar chart summarising the relationship between the tensile strength and the fatigue strength for all the types of laminate investigated is presented in figure 10.

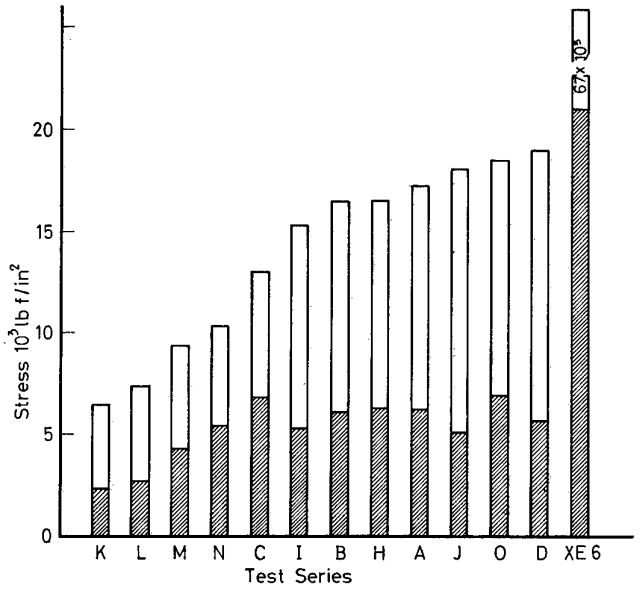

Fig. 10 Comparison of tensile strength with the fatigue strength at 10^6 cycles of load

Zero mean stress; cyclic speed 74c/min; 20°C and 40-42% RH

PART 2. THE PROGRESSIVE NATURE OF DAMAGE

The foregoing results were based on the conventional definition of fatigue failure i.e. complete separation of the specimens. However, it is well known that failure in glass reinforced plastics is progressive. A review of failure of reinforced plastics has been published by Owen and Dukes (14). For some applications incipient damage in laminates is unacceptable because of the loss of mechanical, electrical, thermal and chemical properties. An understanding of the failure processes in GRP is a necessary preliminary to the interpretation of the results of non-destructive test methods. Initial investigations were conducted using single applications of tensile load to produce damage. Subsequently attempts were made to produce S-N curves showing various stages of failure for different types of laminate subjected to various types of loading. Some of the initial investigations have been previously published (15) and these have been summarised here. The more recent work is reported in greater detail.

(a) The effect of damage on the initial modulus

At low stresses, the stress-strain relationship for a laminate is usually linear for a single application of load. As the load is increased the linearity is no longer maintained when the glass and resin commence to separate (debonding)(see figure 11). A 'knee' is produced in the stress-strain diagram and the tangent modulus is reduced. This breakdown occurs within strand groups and is associated with strands which are perpendicular to the direction of the load. Although laminates made from flexible resins do not have a well-defined knee in the stress-strain diagram, debonding still occurs. As the load is increased the debonding becomes more intense and, in randomly oriented reinforced materials, occurs along fibres at smaller angles to the loading. Further increases in the load produce failure processes which are dependent on the type of reinforcement. In fabric, woven roving, and chopped strand mat laminates, where there are resin rich areas between strands of filaments, debonding extends beyond the strand groups into the resin rich areas forming a resin crack (see figure 12). For some materials, this results in a further reduction in the tangent modulus and can be seen as a second knee in the stress-strain diagram. Debonding occurs back along fibres which cross a resin crack as in figure 13. This photograph was taken on the Cambridge Stereoscan electron microscope by Mr R. G. Rose of Nottingham University. In non-woven cross-plied laminates, the debonds commence to turn and propagate along the aligned fibres at the ply interface, producing a local form of delami-

* Permali Ltd., Bristol Road, Gloucester

nation. Further increases in load eventually lead to complete separation by strand failure.

A method of test was developed using single applications of tensile load to produce damage. The initial modulus at low stress levels was measured by means of a Tensometer Type E testing machine in conjunction with the Tensometer extensometer. No damage was observed at these low stress levels.

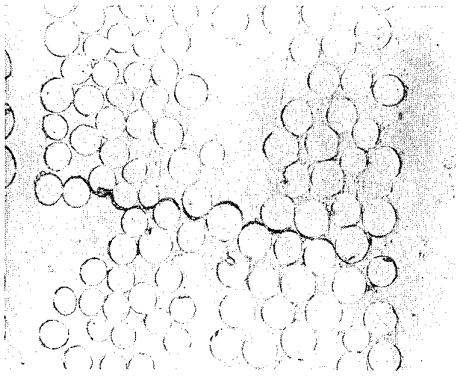

Fig. 11 Debonding occurring along fibres at right angles to the direction of loading. Single application of 6500 lbf/in^2. (× 600)

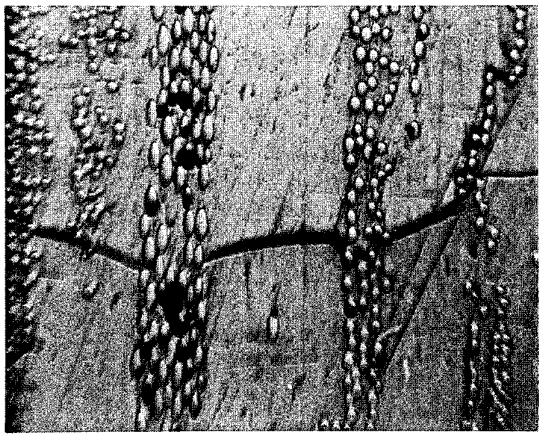

Fig. 12 Resin cracking occurring in the resin rich areas between strands of filaments. Single application of 13000 lbf/in^2. (× 160)

Fig. 13 Debonding occurring away from a resin crack traversing a fibre, which is aligned to the direction of loading. (× 1350)

The specimen was reloaded to a stress more likely to produce damage, unloaded and reloaded in order to determine a second value for the modulus. If damage had occurred at the higher stress level, then the second value of the modulus was lower than the original. Depending on the material under test, microscopic examination revealed that a certain value of the loss in modulus could be taken to indicate that debonding had commenced. A typical diagram is illustrated in figure 14.

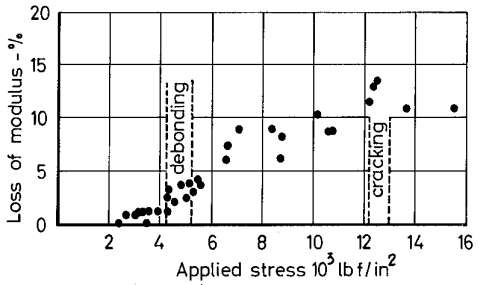

Fig. 14 Typical graph showing loss in modulus against the applied stress producing damage.

Chopped strand mat/low reactivity polyester resin.

A wide range of materials have been studied in this manner, A summary of the types of laminates used is given in table 5. It was previously noted (14) by the authors that for six types of laminate the relationship between the initial modulus and the nominal stress at the commencement of debonding was remarkably linear. The interpretation of this linear relationship was that debonding occurred within transverse filaments at a nominal laminate strain of approximately 0.3%. It was also noted that all these laminates and local (within s strand) volume concentrations of glass of 65-70%. This work has been extended to cover a wider range of laminates and the new results have been added as shown in figure 15. The majority of the new data is in close proximity to the previously drawn line, which represents 0.3% strain. However one fabric reinforced epoxy resin laminate, which was made from prepegs, is well removed from this line and suffered internal damage at a strain of less than 0.2%. The reason for this material to differ from the others in respect of debonding is not understood, but the fact that this was the only laminate made from prepegs may be of significance. It is thought that this type of test based on debonding behaviour could form the basis for quality control checks.

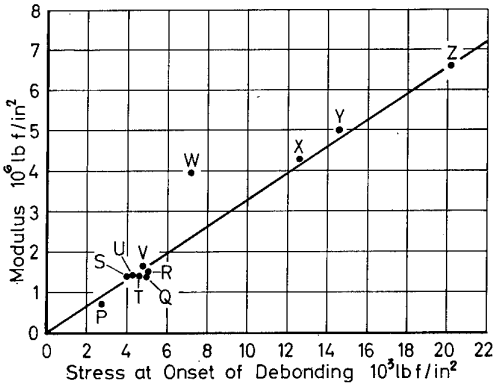

Fig. 15 Effect of modulus on the stress at the onset of debonding

For the chopped strand mat programme, it has been found difficult to correlate resin cracking with a loss in modulus. However, resin cracking was readily visible with the aid of a low powered microscope and this method was adopted to determine the onset of resin cracking. The results of the chopped strand mat programme indicated that there was a negligible difference between the debonding performance for both the high reactivity and low reactivity resin matrices. How-

ever, resin cracking occurred earlier in the high reactivity resin laminates.

(b) **The onset of fatigue damage**

Using a loss in modulus as a criterion of failure to indicate that debonding had occurred, a series of fatigue tests were conducted on one fabric and two chopped strand mat/polyester resin laminates and one cross-plied non-woven roving epoxy resin laminate. The mat laminates were subjected to fully reversed fatigue loading whereas the fabric and roving laminates were subjected to zero-tension loading. In addition resin cracking was detected optically in the glass mat laminates. The fatigue results for the mat laminates are presented in figures 16 and 17. There is negligible difference in debonding performance between the two different resin matrices, but resin cracking is delayed in the low reactivity resin laminate. This probably reflects the low reactivity resin having the greater strain to failure. The results for the two mat laminates are compared with the other two laminates on the basis of maximum strain in the load cycle (figure 18). Comparison in this manner is possible because the laminates are linearly elastic up to debonding. These results correlate reasonably well and emphasise the importance of the maximum strain in the fatigue cycle. It was suggested (15) that a single S-N line might represent the undamaged region for fatigue loading at any mean stress or strain, if the maximum strain in the load cycle was the most critical factor involved. Accordingly, further fatigue tests were conducted on the high reactivity polyester resin/chopped strand mat laminate at + 2000 and −3000 lbf/in^2 mean stress levels. For technical reasons, due to buckling under high compressive loads, or the stress range being less than that used in the modulus test, it was no longer possible to use a loss in modulus as a criterion of failure and it was necessary to determine when debonding had occurred, by careful optical examination. This was possible because the specimens were initially translucent. The results are presented in figures 19 and these show that the initial suggestion was incorrect. In general, debonding occurred at higher maximum stresses in conjunction with higher mean stress levels. The knee in the −3000 lbf/in^2 mean stress diagram is believed to be caused by a speed effect coupled with the higher stress amplitudes. For short lives, (up to 5000 cycles) tests were conducted on the Tensometer machine at 8 cycles/min and longer lives were conducted at 74 cycles/min on the fatigue machine. A Master diagram for debonding of this laminate series has been constructed and is presented in figure 20.

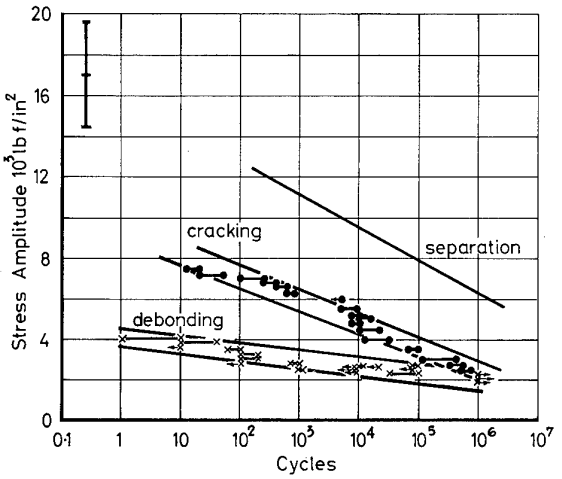

Fig. 16 S-N diagram showing the various stages of failure chopped strand mat/low reactivity polyester resin.

Zero mean stress; 20°C and 40-42 RH

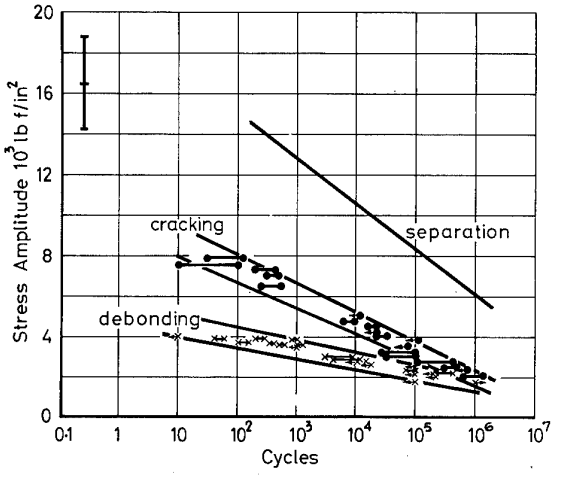

Fig. 17 S-N diagram showing the various stages of failure chopped strand mat/high reactivity polyester resin.

Zero mean stress; 20°C and 40-42% RH

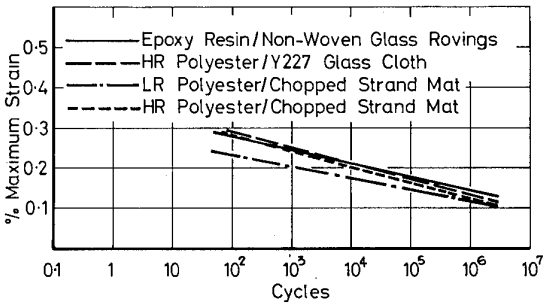

Fig. 18 Onset of damage compared on the basis of maximum strain in the cycle

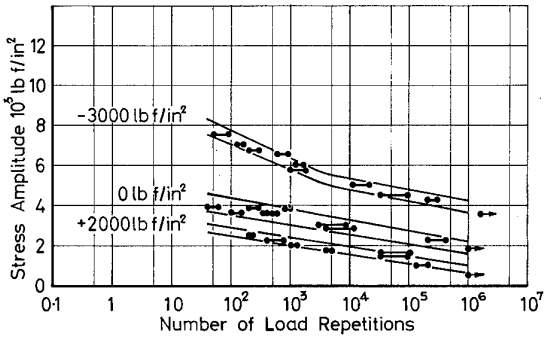

Fig. 19 The effect of mean stress on the onset of debonding chopped strand mat/high reactivity polyester resin. 20°C and 40-42% RH

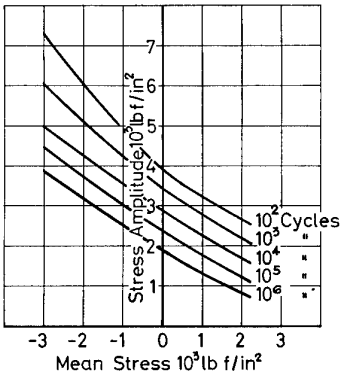

Fig. 20 Master diagram for the onset of damage.

Chopped strand mat/high reactivity polyester resin

TABLE 6

The effect of fatigue damage on the tensile strength of laminates

Test series	Ultimate tensile strength lbf/in^2	Standard deviation lbf/in^2	Tensile strength after debonding lbf/in^2	Standard deviation lbf/in^2	Tensile strength after resin cracking lbf/in^2	Standard deviation lbf/in^2
S	16545	1163	15712	1399	15438	916
U	17008	1302	17315	1221	16502	1156
Y	67696	4104	65052	4174		

(c) Design consideration

Debonding caused by fatigue loading has only a slight effect on the residual tensile strength of a laminate. Table 6 compares the residual tensile strength and standard deviations with those of undamaged material. This reduction in strength is statistically insignificant due to the relatively large amount of scatter in the data. For the mat laminates the residual strength after resin cracking due to fatigue loading, is only slightly reduced and for practical purposes insignificant.

Given adequate load determination and stress analysis it should be possible to design for stress levels which just avoid debonding. The choice of safety factors will then depend only on the accuracy of the load determination and stress analysis and not on the progressive damage behaviour of the material. There would be an adequate margin of safety against catastrophic failure due to accidental overloading. However, for some applications, the debonding criterion may be uneconomic and it may be possible to tolerate some debonding. This will be for the designer to decide. Resin cracking probably cannot be tolerated, except in rare cases.

Before concluding, the authors pose the following questions:

1. How much damage can be tolerated in structures?
2. Do present designs based on stiffness and deflection coupled with large factors of safety avoid debonding?
3. Is the use of the onset of debonding an acceptable design criterion both technically and economically?
4. What allowances must be made for the variation in quality?
5. Does proof testing of pressure vessels and other structures produce damage?

CONCLUSIONS

1. The fatigue properties of the low-reactivity polyester resin/mat laminates were slightly superior to those of the high reactivity polyester resin/mat laminates, although this superiority is not likely to be of practical use.
2. Both types of mat laminates have fatigue strengths of approximately ±6000 lbf/in^2 at 10^6 cycles, when loaded at 74 c/min at 20°C.
3. The Goodman Law would give unsafe prediction, and Boller's modification using stress rupture strength in place of the ultimate tensile strength of the material is more reliable. However, some data still remains below the line and a new relationship

$$\frac{S_A}{S_E} = \frac{1 - \frac{S_M}{S_C}}{1 + \frac{S_M}{S_C}}$$

has been proposed. This relationship is more conservative.

4. Glass content, over the range 29-36% by weight, has a considerable effect on the tensile strength but only a small effect on the long term fatigue strength.
5. The fatigue strength of both types of polyester resin is approximately 4400 lbf/in^2 both for zero-tension and fully reversed loading at 74 c/min at 20°C.
6. The distribution of fatigue lives for chopped strand mat laminates is approximately log-normal. The coefficient of variation, based on logarithmic values of fatigue life, is much lower at low stress amplitudes.
7. Fillers are detrimental to the fatigue strength of mat laminates.
8. Internal damage in laminates can be detected by means of a loss of modulus.
9. With the exception of one laminate, debonding occurred at a nominal strain of 0.3%. The exception exhibited debonding at 0.2% strain. The strain at debonding may be useful as a quality control test.
10. Fatigue damage is progressive and can be detected by a loss in modulus.
11. S-N curves have been presented for fatigue damage in four types of laminate. All these results correlate on the basis of maximum strain.
12. Mean stress in the fatigue cycle has an effect on the maximum stress that can be applied to produce damage. A Master diagram for debonding has been produced for one type of laminate.

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Overseas Reports

THE DEVELOPMENT OF REINFORCED PLASTICS IN CZECHOSLOVAKIA

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In the documents referring to the problems of the economic development of Czechoslovakia, the requests of application of plastics are getting more and more into the foreground.

Important branches of the Czechoslovak national economy, among them for example mechanical engineering and building industry, cannot exist without intensive application of plastics. The task of the mechanical engineering including electrical engineering, is not only to produce modern technical equipment for development and modernization of the production basis for industry and agriculture, to supply high-class consumption articles for enrichment of the home market, but also to ensure plenty of superior articles, by which Czechoslovakia would pay the necessary imports of goods from abroad. These tasks are beyond the powers of mechanical engineering in the classical sense.

The complexity of machines and demands for high parameters of efficiency, safety, hygiene and aesthetics of work, draw into the sphere of classical mechanical engineering, electronics, chemistry, as inseparable parts.

Relatively in volume small quantities of products of these branches, seemingly of smaller significance, enter into the products of mechanical engineering in a highly refined form, as integrated components of vital importance, without which a product of mechanical engineering cannot be realized at all, or at least not in such a quality, that would give hope for successful use in the international division of labour.

One of the representatives of the components of vital importance are reinforced plastics and products thereof.

Analogously, in the building industry, it is not possible to realize advanced methods in the industrial construction and civil housing without reinforced plastics. Reinforced plastics and first of all laminated glass recorded in the last 2-3 years a faster development of application in Czechoslovakia.

Decisive factors for a fast development of application of reinforced plastics were their significant technical and economic properties. From technical properties it is necessary to name first of all a high ratio of strength to weight, corrosion resistance, low thermal conductivity. From economic properties it is necessary to name, in comparison with products manufactured of traditional materials, first of all a reduction of hard work, decrease of actual costs. From the above indicated reasons just reinforced plastics made themselves useful in Czechoslovakia in particular in mechanical engineering and in building industry.

The contemporaneous consumption level of reinforced plastics products in Czechoslovakia and the prognosis of the development are shown in the survey (data in tons of finished products).

Branch	Year 1966 reality	1980 prognosis
Mechanical engineering including electrical engineering	920	10 000
Building industry	830	7 000
Agriculture	280	2 000
Other industries	770	3 000

In the contemporaneous time the centre of application of reinforced plastics is in a row of branches in mechanical engineering, e.g. in the production of track vehicles (bodywork of express wagons, parts of tramcars).

A bright sphere of application of reinforced plastics is in chemical engineering (pipelines for chemical plants, separators, centrifuges, pressurelss vessels).

Reinforced plastics find their application with the construction of machines and equipment for textile, agricultural food-stuff and cooling industries, further with the construction of machine-tools, electric rotative machines, transporting, compressed air-technical and irrigation equipment.

They have special function as elektro-insulats for high tension electrical art for their high resistance against difficult climatic influences, especially against humidity, for their high and persistent heat-resistance and stability (minimum 130°C), high dielectric parameters.

In the survey shown below there are data on consumption of reinforced plastics in selected branches of mechanical engineering and building industry (data in metre tons).

Branch	1966 reality	1980 prognosis
Equipment for water treatment	20	1800
High tension electrical art	230	500
Chemical equipment	50	800
Machine-tools	45	200
Food-stuff and cooling machines and equipment	50	400
Agricultural machines and tractors	150	500
Track-vehicles	600	1800
Road-vehicles	350	2000
Housing sanitary cabins	560	6500
Structural members, building units, insulation	280	900
Agricultural equipment	150	1500

Special attention deserves the production of various profile materials, the most remarkable application of which is in the form of torsion bars and laminated fishing rods.

Contemporaneous Czechoslovak speciality in the application of reinforced plastics, reaching by its importance over the border of the state, is the mantle of television transmitter Ještěd near Liberec, made of polyester resin laminated glass.

Among applications ranking with the world's top applications of reinforced plastics in Czechoslovakia it is possible to rank also separators, water clarifiers, water houses, electric locomotive shells. We are still owing to the applications as pressure and pressureless vessels, cisterns, containers, chimneys, pipelines etc.

Several words concerning the raw material base

In the next future reinforced plastics as construction material will be dependent on glass fibre as on the principal reinforcing component. Today, with the laminate structures, the top problem is the rigidity, which is not satisfactory for some applications, even though it can be compensated to a certain degree by a correct structural design. A satisfactory solving of this problem can be achieved by combination of reinforcing materials and by completing glass fibre with new types of reinforcement. In this connection probably the most interesting fibres are monocrystal fibres, synthetic fibres and a number of fibrous materials, which will be available in future years.

The contemporaneous situation of applications in Czechoslovakia is characterized by considerably developed applications, being often on the world's top (e.g. separators, water clarifiers, water houses), but at the same time the application of laminates for example in the mechanical engineering is not yet great enough and by the assortment realized touches only a fragment of possibilities of the branch (pressure vessels, cisterns, chimneys, containers, pipelines, anticorrosive coatings etc.).

Deficiency to be found from the research till to the realization of application are most strikingly shown.

(a) **in bonding materials**

Hereto it is necessary to say that in the home assortment, suitable types of resins with increased chemical and heat resistance are lacking in sufficient quantity, further high adhesive low viscous polyester resins, transparent polyester resins with guaranteed self extinguishing properties, commercially prepared elastificated resins for gelcoat layers, compounds of thixotropic low-viscous lamitane epoxide resins with higher heat resistance, special laminate phenolic resins with cold polymerization, fural laminate resins for high aggresive medium, special resins and varnishes with high dielectrical parameters.

(b) **in glass reinforcements**

Sufficient quantities of materials are concerned, e.g. veil covering mats for gelcoat layers, high quality mats of cut slivers, roving for technology of exact winding (with a reduced number of slivers and guaranteed continuous grain), two-sidedly felled glass, textile strips (ribbons) in various widths for winding from strips and relaminating of joints using hand-lay up method, pre-impregnated roving, mats of fabric for winding and molding practise, fabrics for electroinsulants with minimal hygroscopicity etc.

(c) **in auxiliary materials**

It is necessary to mention commercially supplied, fine granulated and dehydrated fillers on basis of glass ponder, quartz sand, chalk, kaolin etc.; reliable separators on basis of polyvinylalkohol and silicous in normal and aerosol finishing; styrene resistant cloths of durable elastomers for technology of vacuum and press forming by means of bag.

In the indicated enumeration there are some specialities, the consumption of which in this country cannot reach the quantity necessary for economic production. It is necessary to ensure their import, because the lack of these auxiliary materials would make impossible or endanger numerous progressive applications.

Several words concerning the ensurance of the raw material basis

The raw material basis in sufficient in Czechoslovakia. The surpluses in raw materials can be used for other purposes than for the production of reinforced plastics. (This prognosis is valid irrespective of the amount of the exported glass reinforcement).

Some chemical raw materials being imported are difficult to ensure till the year 1970, but the production equipment of the Society for chemical and metallurgical production (Spolek pro chemickou a hutní výrobu) belongs among the largest and most modern in the Central Europe and guarantees the covering of the needs considered.

Glass and products of glass will not make a problem after 1970, because a new plant for the production of glass fibre is being built actually.

Problem will remain with quality glass reinforced thermoplastics (e.g. polyamides), which have to be imported in view of the low quality of thermoplastics themselves.

Now I wish to mention the development of the processing basis

The mechanization and automation of processing reinforced plastics will enforce a centralization of the production of molded parts of reinforced plastics on the one hand with the producers of basic components of raw materials, on the other hand with the producers of the final industrial products. The centralization of production and its specialization will be limited first of all by the quantity of raw materials treated, furtherby the costs of realization of the production, by the costs of transport, by the possibility of production in series, by dimensions, by final use of molded pieces and by the price relations of raw materials in their processing by separate technologies.

With respect to the aspects mentioned, my opinion, concerning the development of the processing base, e.g. plants for production of glass laminates, is, that the processing plants of glass laminates are to be built almost exclusively with the producer of final industrial products and a specialized universal cooperative plant independently only in economically motivated cases (e.g. smaller products, electroinsulants etc.). In the case of mass production of normalized voluminous products (e.g. pipelines) it is possible to realize the production for example with the producer of glass fibre, eventually in an independent specialized plant.

The contemporaneous situation in the series production of verified applications in Czechoslovakia does not correspond with the state and tendencies in the world. With the mechanical engineering applications the production of laminates itself forms a part of the whole production process (production of steel reinforcements, production of moulds in a direct dependence on the final mechanical engineering product, moulds handling, completation operations).

There are no reasons for separating laminating plants for mechanical engineering plants, neither technical, nor economic ones, as acquisition costs of equipment for laminating plants in comparison with other mechanical engineering plants require relatively low investitions, whereas the cooperation of voluminous products of reinforced plastics is very expensive for the reason of transport. On the contrary, there exist following reasons for the connection with the affiliated mechanical engineering production:

(a) a possibility of optical access to the basic conception of mechanical engineering products of reinforced plastics in harmony with the demands for the structure to be technologic;

(b) complex equipment by basic models and moulds;

(c) a possibility of operative interference with the technologic order;

(d) a possibility of shifting employees, with whom symptoms of allergy against components of laminating materials appear in the course of their work in laminating plants. Abroad, an effort to create production complexes is clearly evident, first of all with the body engineering applications, in the chemical engineering, in light prefabrication in the building industry etc.

The processing bases in Czechoslovakia do not yet keep this conception in an economic extent.

In the technology of production of laminates hand lay-up method will predominate for a number of years according to my opinion, even though the production processes based on making use of machines and equipment will be coming into the foreground, as far as the economy of their application will render it possible. For completeness I wish to quote a survey of portions of separate technologies in the total processing of glass laminates including premixes in Czechoslovakia—the contemporaneous state and the prognosis of development (data in %).

Technology	1966 contemporaneous state	1980 prognosis
Hand lay-up	51.8	27.9
Machine spraying	17.2	26.2
Molding	13.4	14.4
Drawing	4.2	3.0
Premixes	10.0	12.9
Other Technologies	1.7	3.7
Total	100.0	100.0

A successful development of the branch has to be percieved in the sphere of the technical preparation of the production. The technical level of the inland laminate structures in comparison with foreign structures carries direct consequences of insufficient orientation and information of the leading technical factors in the deciding posts of our industry. Endeavours for cooperation in the most essential mechanical engineering applications do not form in a sufficient degree conditions for

the growth of the level of designers of the respective branch, not even assumptions of utilization of laminates as constructional materials.

In case of need there will be formed specialized constructional-development centres, e.g. for the branch of the body engineering technology, chemical equipment, mechanical engineering technology, chemical equipment, mechanical engineering technical elements etc. with enterprises, where maximum and complex asumptions for securing of the development of the given sphere (branch) of application.

In the sphere of the technological preparation it will be appropriate to solve the problems of production of the basic models and molds with utilization of voluminously constant and easily workable materials (special clays for modelling, used for example in USA, casting and ceramic materials, for example 'Stonex' of the company Dr Raschig from GFR (German Federative Republic), high voluminous rigid polyuretan foams etc.).

In the sphere of technological methods applied in the production (first of all in the series production), in comparison with foreign countries, method of hand laying up is used in absolutely predominant extent.

The technology of machine spraying of the compound occupies a much more notable position in the scope of processing in foreign countries, than in Czechoslovakia. At the same time it is necessary to consider that the parameters of strength of sprayed products limit in a certain degree the spheres of application, first of all to applications not pretentious for strength.

The completion of machine equipment of laminating plants should be aimed at the most modern machines in our country. The machine spraying of the compound should be given an advantage with all compositive structures, either in composition laminate-thermoplast, or in sandwiches laminate-foam.

In the sphere of mechanized laminating technologies, the exact winding is only a little developed in our country. This technology enables the production of most intricated applications, pressure vessels, cisterns, containers, pipe lines etc. Its use in the scope of the facts indicated and for glass laminates of typical assortment is absolutely inevitable.

Another progressive technology is the method of low-pressure and middle-pressure molding of laminates in matched-metal dies. This technology has a good tradition already in Czechoslovakia in the sphere of production of smaller products (molding of crash helmets, loud speakers, converings of lighting fixtures etc.). High prices of the necessary moulding tools, as well as a want of large surface moulding presses prevent brighter vindicating with large surface products. At the same time in fact, in foreign countries the greatest part of the application in bodywork is realized first of all by moulding in matched metal heated dies. The main problem in the series production and the securing of toolmaking.

In the branch of laminating technology also the production of surface reinforced glass fibre for the purpose of electro-insulation finds its place, as well as the production of metal-clad laminates for printed connections. The machine equipment being at the disposal actually, is not in sufficient level, especially for low temperatures in processing of epoxide resins, which is followed by prolongation of curing time and herewith also by decrease of impregnation velocity. This distress will be solved to a certain degree by a more appropriate machine equipment of the new plant.

As far as micaceous insulants are concerned, where glass fibre serves as reinforcement, the production is in contemporaneous time on the world's level in our country.

A supplement of both indicated basic productions in the branch of electro-insulants in the production of glass insulating sleeves. The quality of these insulants is not on the world's level, because the machine equipment is obsolete and from the point of view of the heat resistance unsuitable superficial varnishes are used.

The production of insulated conductors for winding and of special conductors for aircraft industry forms a separate group. In both cases the use of glass fibre as insulating material increases rapidly and it may be assumed it will be doubled in the next five years.

As for the extent, the use of glass insulants in Czechoslovakia is in the frontal post in the scope of the countries of the socialist camp, but it does not yet reach the world's level, especially in the width of assortment.

The state of utilization of compositive structures is not satisfactory. Two-layer combinations are concerned: thermoplastics-sprayed laminate reinforcement, of three-layer structure laminate-foam core-laminate, or thermoplastics-foam core-laminate. The combinations represent in contemporaneous time the principal constructive-technical directions in the vindication of plastics in mechanical engineering and engineering structures.

The development of more-layer combination assumes to have at disposal:

- large size plate thermoplastics with higher impact and heat-resistance (ABS);
- large surface machines for vacuum forming;
- high pressure spraying machines;
- appropriate foam materials (first of all rigid polyuretans);
- large capacity foaming equipment (high pressure, with exact dosing).

Problems of effectivity

The application of polyester glass laminates in a series of branches of the Czechoslovak national economy enables to achieve significant technico-economical contribution:

1. reduction of actual costs as a result of hard work reduction and saving of energy;
2. saving of conventional materials;
3. weight reduction of products and improvement of their functional parameters;
4. raising of aesthetic qualities of the product and herewith its sales-appeal.

Actual costs of products made of polyester glass laminates are regularly lower than of those made of conventional materials. The reason is a less hard work for the laminate products in comparison with the hard work for products of conventional materials, lower power engineering claims of technologies used in the production of glass laminates and lower costs for production equipment.

The less hard work for laminate products in comparison with the products of conventional materials are expressively documented by data from the branch of track vehicles, where the hard work for the product in the laminate execution drops roughly by 60% of original hard work (body work of electric locomotive 52 E Co-Co, SKODA WORKS, Plzeň, and face of the suburban transport unit EM 457, Wagon factory Tatra Studěnka).

Savings following from lower costs of production equipment for laminate products are proved by data from the production of body work of truck vehicles in branch enterprises Skoda Works Plzeň and CKD Prague.

For the production of four types of locomotives, one type of trolleybus and the security of production of increased number of trams produced in contemporaneous time in the branch enterprises mentioned, costs for production of laminate parts are assumed in total value of 6 millions Kčs.

Considering the alternative of metallic parts and the keeping of claims for technical and aesthetic level of the products it would be necessary to spend 15 times more for production equipment, i.e. 90 millions Kčs. At the same time it is necessary to consider that changes of claims for the finish of product with the metallic parts, which can be realized for high costs of reconstruction of the production equipment only, with the laminate products the realization is relatively easy, quick, and requires minimum costs.

The savings of conventional materials include first of all deep-drawing steel sheets, stainless steel, non-ferrous metals, wood. In a rough average the use of polyester glass laminates enables a saving of conventional materials in quantity of double till triple of the laminate products weight. The

savings are relatively significant, which is proved for example by data from the branch of the mechanical engineering, where for the period 1965-1970 savings of conventional materials are assumed in total of about 3015 metre tons, from which carbonaceous materials make 1 170 tons, stainless steel 1025 tons, lead 800 tons, aluminium 200 tons.

Similar savings are being achieved also in other branches of mechanical engineering production. It is justified to assume that the savings of actual costs will make minimum 30% of actual costs of the conventional execution in the all country average.

In foreign countries the permanent fall in prices of raw materials for reinforced plastics has but one meaning. The prices of glass laminated products are lower than of the products of brass, stainless steel and special alloys. They fluctuate on the level of aluminium and its alloys castings. When special claims are laid upon a product (corrosion resistance, low weight, electric resistance, translucence ect.), products can compete also with steel.

A contradiction in this development appeared in scope of recalculation of wholesale prices, valid in Czechoslovakia from the 1st January 1967; the relations between prices of basic raw materials and prices of substituted materials, first of all refined steel and non-ferrous metals, become substantially worse, which is in discord with the development in the whole world, and these tendencies should be gradually set in world's relations.

The significance of reinforced plastics deserves it and the development in the world confirms it.

In the conclusion I wish to recapitulate:

In the sphere of reinforced plastics application, first of all of polyester glass laminates, we achieved significant success and a number of applications is technically among the first in the world.

In Czechoslovakia we shall have to solve, of course, a number of problems, not only technical ones, and problems of application, but also of economic ones.

For example, we shall have to secure the production of cut glass reinforcement for premixes, putting into operation the technology of one stage drawing, the orientation of glass laminate production technology for the use of roving and mats in place of deficit glass sliver fabrics, adopting measures for perfect exploit of basic raw materials production capacities for the production of synthetic resins and auxiliary compounds.

By solving these problems Czechoslovakia will be placed in order of world's top in the application of reinforced plastics.

MARKET DEVELOPMENT FOR GLASSFIBER-REINFORCED PLASTICS IN THE FEDERAL REPUBLIC OF GERMANY DURING 1967

A. VON SEIDEL, Gevetex Textilglass-GMBH

In 1967 the production of glassfiber-reinforced plastics has increased from 36.000 ts in 1966 to 38.000 in 1967. As a result of the downward business trend during the last year that represents only a slight improvement of 6%. The distribution pattern is as follows:

Construction	16.200 ts	43%
Electrical	5.600 ts	15%
Tanks, Containers, Pipes	5.500 ts	14%
Industrial Housings and Appliances	5.000 ts	13%
Boats, Shipbuilding	2.700 ts	7%
Transportation	2.000 ts	5%
Miscellaneous	1.000 ts	3%
	38.000 ts	100%

Construction

Because of the business recession on the construction market there was a decrease in the tonnage of 200 ts as against the last year. Therefore the normally increasing demand of the building industry primary for corrugated sheets, panels, domes, skylights etc. stagnated.

Electrical

In consequence of the better conjunctural situation, the market expanded by 24% compared with 1966. In addition to that the production of molding compounds and prepregs mainly applied in the electrical industry increased further on.

Tanks, Containers, Pipes

The consumption has grown in 1967 by 10%. It is evident that the market of tanks and pipes is a slowly growing one with no unexpected developments. The construction of containers is still in its infancy but there were made many efforts in this direction by a number of greater companies. Good outlooks exist for products-pipe with the major applications being in the chemical and crude oil industries. Also sewage-pipes show greater sales opportunities.

Industrial Housing and Appliances

The tonnage increased by 4% as against 1966. In spite of this very interesting market there is still a small extention possible because of the difficulties for the RP-producer to canvass orders. Especially in this sector competitive materials are hard to displace because of their common use and the attitude of machine producers.

Boat- and Shipbuilding

The consumption has increased in 1967 by 42%. A number of companies expanded in such a manner, that one can speak of a production in series. In so far this market has had a satisfactory development and the percentage of RP in the boat- and shipbuilding-sector has certainly reached the same level as in other countries.

Transportation

The market extended by 11% compared with the preceding year. There exists not yet a production of RP motor-car bodies in a greater volume. Only some body parts are produced in an extensive number of pieces. Parts for commercial-vehicles and caravans responded to more support during the last year.

THE REINFORCED PLASTICS INDUSTRY IN THE NETHERLANDS

W. J. SCRIWANEK, Ferro (Holland) N.V.

From a raw material point of view it can be said that Holland is the paradise for the moulder of reinforced plastic products. Within a few hours driving from his plant he finds all he needs for his production and what is more, he can make a choice. Glass fibre is drawn in two factories. Polyester resins are made in four plants, epoxide resins in one. Catalysts and accelerators are produced locally, while furthermore a number of weaving looms and a plant specialised in the production of glass fibre mats are at his disposal.

Seen from this angle an estimated consumption of 3500 tons of polyester resin may seem rather small. Per capita consumption of reinforced plastic products in Holland is approx. 1 lb and this figure compares unfavourable indeed with countries like France, Germany, U.K. and others. One of the main reasons is that corrugated sheets are not as widely accepted in Holland as in other countries. This has an immediate effect on the per capita consumption figure. Although official statistics on consumption of reinforced plastics are not available—work is being done in this line—a total consumption of 3500 tons of resin is a fairly close estimate, as interviews with people in the trade learned me. Opinions on the distribution pattern are less unanimous. The following is believed to represent today's reality:

Corrugated sheet	22%
Building	15%
Transportation	6%
Boats	20%
Agriculture	17%
Tanks-Containers-Pipes	10%
Electrical	5%
Various	5%

A yearly growth between 15 and 18% is expected for the coming years, and this growth will certainly shuffle the distribution pattern, as the sheeting industry, agricultural, electrical and non corrosive applications will attribute most of it. Up till now epoxide resins are not widely used in reinforced applications but it is expected that non corrosive applications will have a positive influence on the consumption of these resins.

Reinforcements

Of all types of glass reinforcements approx. 52% goes to the processing industry in the form of roving. Glass fabrics—mainly woven roving— have a 8% share and are absorbed for the greater part by the boating and container industry. The remaining 40% glass reinforcements is supplied in the form of glass fibre mats to handlay-up moulders and the sheeting industry.

Processing techniques

The majority of the laminates are made by *handlay-up and spray up*.

Matched metal die moulding is done by some companies, making electrical and agricultural parts out of flow-mat type prepregs.

Cold press moulding is applied in some cases.

Autoclave and vacuum moulding with the more sophisticated prepregs is used for the production of aircraft parts.

Filament winding is gaining territory and although natural gas resources in Holland make it doubtfull that oil storage tanks will have a future in Holland, the non-corrosive field will certainly make this processing technique more important in the years to come.

The reinforced plastic industry in the Netherlands in organised in a sub-group of the Dutch plastics federation. Several working committees have been formed in this group, studying such problems as raw material specifications for boat-building, tanks for transport and storage of liquid hydrocarbons, training of labourers in reinforced plastics etc.

REINFORCED PLASTICS IN ISRAEL

A. EDEN, Su-Keet Ltd.

Introduction

Normalcy is a situation that seems to evade us in Israel, this throughout our very short history as a modern State. The last two years have been further from normal, even for us. 1965/66 found Israel in a deflation if not a virtual depression. This as a result of a change in government economic policy, aimed at cooling off the economy which had been running ahead under full steam for a number of years. By early 1967 the economy was beginning to turn around, and then we found ourselves faced by virtual destruction by our neighbors. Fortunately, we rose to the occasion, overcame our adversaries and continued our economic improvement. In the latter part of 1967 Israel devalued its currency following the devaluation of the pound sterling. The gyrations which took place as a result of these events did not leave the plastic industry in general and nor the reinforced plastic industry in particular, unaffected.

Overall, plastics picture

Despite Israel's rapid advancement and development in various fields, in terms of plastic application, Israel is down the list in consumption. There are many reasons for this. These range from conservatism of industry, in terms of acceptance of new materials and applications; the fact that many of the molders started from small shop operations and have failed to keep abreast of technological developments; the extreme price consciousness of the Israeli consumer who has tended to place less emphasis on quality than on price; and last but not least, the fact that Israeli industry sits behind very high protective tariff walls, both for raw material and finished product.

Consumption per capita in 1967 of all plastic materials was estimated at about 8 kilo per person which is relatively low but one must bear in mind that the packaging industry, one of the large consumers of plastics in the more advanced countries, is relatively undeveloped here. Allied to that has been the small shop type operation—which did not give the confidence nor know-how necessary to entering into more advanced engineering applications, architectural applications, etc., which has tended to hold back development.

Yet the picture is not as cloudy as one might assume. The Israeli plastics industry has shown a versatility and capability of grappling with technical problems which sometimes leads visitors and even ourselves, startled by the application results obtained.

Some 90% of the polymers used in Israel are thermoplastic, with the bulk of these being in non-engineering applications. There is an increased tendency to use plastic in agriculture and in building; mainly PVC and to a lesser extent, polyethylene. Both are manufactured locally as are urea and phenol formaldehyde molding compounds, and last but not least, polyester resin.

There was an economic turn around in the latter part of 1967, with all segments of the economy sharing in this. Aligned with this, has been an increased defense budget for very obvious reasons. More important, the Military have become aware of the necessity to develop home production of many of the items needed by them and previously purchased abroad. This is leading to better quality and productive facilities, to meet the demands of MIL specs. This of course, will have its effect on local industry. It will increase local quality and no doubt lead to export, due to better technology, more stringent controls and more know-how. Hence, the industry in general looks forward to a number of bright years in the immediate future.

GRP in Israel

The industry has established a reputation for itself, particularly so in the field of automotive applications but perhaps the most significant trend in the past few years is for its increased use in anti-corrosive applications.

By and large, the industry has remained static since the last report given at this forum and it would be difficult to pinpoint specific developments in any sphere, be it in terms of workmanship, diversity or in manufacturing techniques.

There has been some shake up in the industry. There are some 20 shops in the field today with two or three assuming major importance and thinking in terms of more mechanised methods of production. Basically, the bulk of Israel's production is done by hand lay up with some spray up being done and two firms with matched-metal presses in operation. There is further interest in the latter process as well as in filament winding, which still has not been introduced commercially.

The industry uses polyester resin in the main, with perhaps 5% epoxy being used in reinforced applications. Glass fibre reinforcement is being used, and of the glass fibre some 85-90% being mat. With increasing structural applications, cloth and woven roving is being used more and more and we believe this trend will continue into the future.

Applications

After a short summary of our position one should turn to the actual and specific fields in which GRP has found its place in Israel and to consider its advantages in terms of a country devoid of natural resources, devoid of an in tra-structure and technology built in the course of decades, devoid of trained personnel in the various fields of endeavor.

GRP was accepted in Israel because it gave latitude to designers and end users in fabricating products which were impossible to do or if possible, at very high cost. The versatility of the material, the lack of heavy capital investment necessary and last but not least, the various quality factors which make for its use throughout the world, made it an ideal material for us.

It would be presumptiousness for us to say that Israel has added new conceptions to GRP work in the world. On the other hand, there are quite a number of interesting applications and a wide variety of end products produced from this material which have not been done in other parts of the world, basically because of economics and possibly because other competitive materials are lacking in Israel. Most items are modifications of products produced abroad and hitherto, little or no pioneering or developmental work has been done in reinforced plastics.

Perhaps, since the industry is only 12 years old, one can say that we have come a long way and in Jewish tradition, the thirteenth year is the year of what we call 'barmitzvah' or 'confirmation', when one assumes the full responsibilities of adulthood. We in the GRP industry in Israel, are just about ready to enter this period in our development and perhaps we too, will, begin to bring forth the fruits of becoming of age. Reinforced plastics production probably has reached 1600 tons of finished products in the past year and on a per capita basis this is no small figure. We are doing better as an industry than the general plastic industry as compared to per capita consumption figures abroad.

Transportation

Due to the different characteristics of the economy, social structure, application and end usage differs from that in most countries. Sheeting and boating—one of the mainstays of the industry abroad, plays a very minor role, particularly boating. Yet, it is in this field that one might hope for a change with the establishment of a new firm, to develop an Israeli boat of radical design as well as to manufacture for export. On the other hand, Israel has achieved the reputation in GRP circles for its bold development and use of reinforced plastics in the automotive field, particularly in the Sabra and Sussita vehicles, which have been coming off production lines at the rate of 3000-4000 per year, for the past few years. With know-how and experience, various models have been produced and improvements made constantly.

One does feel though, that the impetus and drive has been lost due to lack of engineering development, investment in time and effort in developing new techniques, technology, etc. Yet the industry has shown the possibilities inherent in our materials for a small country and perhaps is a key to the satisfaction demand for industrial development in the less fortunate countries in the world, who for a variety of reasons seem to feel that auto assembly is a sign of coming of age.

Use is being made of GRP extensively by a Leyland motor vehicle assembly plant, manufacturing an all GRP cab and components for other models, not to speak of extensive use being made of the material in buses, both for front and rear ends, doors, seats, etc. Jeep bodies for the police are standard as are roofs for the Dechevaux model of Citroen. Side cars for motor cycles and scooters have virtually replaced metal ones and one might say these are standard.

In terms of tonnage, therefore, transportation is by far the largest and most developed user of FRP in Israel. Where and what the future holds for us, is difficult to say for the sole reason that interest in further development in this field seems to be waning rather than increasing.

One should mention that in the course of the last few years some 300 Class 420 sailboats have been produced. There are probably 100 3 to 5 meter speed boats also in use. As mentioned previously, new impetus is expected in the boating field.

Construction

The construction industry was the hardest hit by the deflation in the past few years and certainly has not come back to the position it held in 1965. There had been some breakthroughs in the use of sheeting for balcony enclosures, roofing and bathroom and shower dividers of various types, but sheeting still has not established itself on a large scale basis here.

Use of sheeting for agricultural greenhouses, still on an experimental basis does indicate advantages and there is hope that this will lead to wider acceptance in this as well as other applications. Yet, one wonders whether an integral GRP greenhouse would not be making more and better efficient use of the design characteristics available to us.

We saw the introduction of concrete pouring pans and these were becoming accepted but relatively little production has come forth because of the building slow down. Interior panels of various types, false ceilings, etc. have been made and have found acceptance and one believes that the use of our material will continue and increase if and when construction picks up.

Perhaps the most striking and in a way, interesting, constructional use of FRP in the past year, has been that of the Wimpy restaurant chain who have come to Israel. They have virtually used only GRP for their interior and exterior elements and have made their chain distinctive in format—decoratively and from point of view of cleanliness and maintenance. There is little doubt that this development will have fall out effects in the future. GRP has also found increased use as an exhibition material and one sees more of this from exhibition to exhibition. The Israeli pavilion at the Canadian Expo '67 unfortunately was not produced in Israel and therefore may not have lent the prestige and know-how we could have garnered, should this have been done here.

Some evaluation was done some years ago with FRP bathtubs and shower stalls but no conclusive results were obtained.

With further information obtained from the U.S. this past year as to increased interest and growth potential in this field there, our people are again beginning to think in terms of these for local use. Unfortunately, the building field is still in the doldrums and no real emphasis is being placed on this development at the moment. There is a feeling of great potential in this market for such units, both because of design advantages, as well as because of the interest in lowering building costs and the higher quality finish obtainable as a completely installed room.

Chemical food processing industries

The largest growth registered has been in the field of chemical and food processing, with GRP becoming a standard material.

Some two years ago an olive pickling plant with over 300 pickling vessels of a total capacity of 1000 cu meters was installed with great hesitation. The equipment has stood up so well that with the expansion of the plant this year, an additional 100 tanks have been made with complete confidence on the part of the client. Other olive pickling plants have also gone over to our material.

Five years ago tanks of only 1 cu meter were made and up to 2 years ago, the largest capacity tank produced was 12 cu meters. This year has seen the manufacture of a number of 70 cu meter tanks and there is belief that even larger units will be made in the future. These tanks are being used by the wine processors, fruit juice people and of course, over a wide range of chemical atmospheres under acid and alkaline conditions.

Tanks have been used for liquid ammonia on tractor-drawn equipment for agricultural use and last but not least, lab benches and laboratory hoods are becoming standard at the universities and research institutes.

Another large scale application has been in the marketing of bulk motor oils whereby the motor oil companies supply the larger consumers with bulk storage tanks of 1 ton capacity at their expense.

Composite laminates are becoming more common, particularly GRP, PVC and some experimental work has been done on polypropylene—GRP laminates as well. These are becoming more common and the marriage of these materials undoubtedly has been advantageous for all concerned.

Evaluation work is going ahead in the use of storage tanks and possible transport tanks for bulk milk—but it would be too early at this stage to intimate what the eventual results would be. The Health Authorities have given limited approval for

these tanks, based on data submitted to them from Health Authorities abroad and this will no doubt be a hurdle to overcome in the future. Yet if we can meet the stringent cleaning and heating cycles necessary, this too can become a major outlet in the future.

There is little doubt that the tremendous surge made by GRP in this field will continue, particularly so with a number of large scale chemical processing plants being contemplated and the increasing awareness of the advantages, utility and performance of our material. Tanks mounted on vehicles of all sorts are becoming known and performing satisfactorily and one assumes that this trend will also continue. There is every reason to assume that this field will shortly be one of the major consumers of our material, due to its excellent cost performance, experience in the past and to confidence on the part of the consumer and no less important, of the designer and producer of such equipment to the trade. There is a very optimistic mood prevailing with respect to this segment of the industry and serious contemplation is being given to filament winding processes for such type equipment.

General Products

The diversity of products that can fall in this category is very large indeed and one should of course mention the various types of chairs being made here and in particular, single out the fact that many of the new cinemas and theatres in Israel are using GRP chairs in their halls. Their performance and acceptance has been exceptional.

GRP plywood laminates are being used by industry for containers of all types by the industry and military, but this is still not a significant feature.

Lamp housings, telephone exchange housings and some electrical switch boxes have been made—not to speak of GRP cabinets for fire fighting equipment as standard by the national steamship lines.

Machine guards are being made for an international machinery company producing in Israel and protective helmets of GRP were given a push with the recent introduction of a mandatory helmet law for two-wheeled vehicles. The Public Works Department responsible for putting up signs on the major highways have used GRP for the past few years.

The material has also been used for air ducts, of various types, both for general industry where installation calling for over 1000 meters of duct with a one square metre chamber, has been installed as well as being used in aircraft components and lining of aircraft cargo hatches, etc.

Dough molding compounds

Polyester dough molding compounds have not been used in Israel to any extent, due in the main to the fact that no-one has undertaken local manufacture of these products here. It is probably due to lack of marketing and promotional acumen, rather than inherent characteristics of the material or lack of potential demand. On the other hand, shelf life problems associated with imported polyester DMC"s and Israeli Customs Administration's interpretation of the Brussels Classification of these materials as a composite, on which they levy a high duty, frightens off potential interest.

On the other hand, for special electrical applications DAP, epoxy, and phenolic molding compounds are being used and with increased interest in upgrading characteristics of technical components, there should be an increased use of these materials as they become better known and appreciated, for their technical capabilities.

Reinforced thermoplastics

Some mention should be made of the fact that there is the beginnings of interest and small scale use of reinforced thermoplastic molding materials, particularly glass reinforced nylon, polypropylene and Lexan. This is still in the infancy stage. One can anticipate growth as molders become more aware of their characteristics and overcome some of the fears associated with the use of glass reinforced materials in their equipment and molds.

Summary

There is little doubt that GRP has carved out a niche for itself in the Israel economy and that growth and development of the industry is assured at a higher level than the growth of the general economy. There is certainly larger potential for GRP in our estimation in a market such as ours, devoid of natural resources and an established industrial base, should our designers and engineers become more acquainted with the material and able to think in terms of their application. The major drawback to such developments is the fact that because of the smallness of the market people are very wary of investing the time and effort necessary in such development work, since they feel they will not be able to recover the costs invested in such development. Hence, as one stands in the ambivalent status of material offering tremendous advantage particularly for large scale constructions and the like, in a small country where long runs cannot be anticipated and yet, just by dint of this fact one cannot invest the necessary time and money for such development.

We do not believe this to be a unique problem for Israel but for many of the countries of our size and industrial development. Certainly, even more so for countries who have not reached the status we have. A solution of course is to turn to foreign countries and try and obtain the necessary know-how and this has been done but unfortunately, industry in the more advanced countries, thinking in the terms they are used to which is only normal, request very substantial down payments to grant such know-how which again almost obviates the possibility of undertaking such arrangements. I believe in many cases this is an unrealistic attitude, since many of these type items are not exportable over a long period of time, and sufficient legal guarantees can be arranged so that granting of such a know-how would not be detrimental to the interests of the licensor. It may very well work out the other way where items of interest could then be developed jointly between the two companies and in specific instances, prototype work could be done by the licensor which may have implications and application in his home country as well.
It is difficult to ask business and profit oriented managements and companies to adopt a policy which may be considered altruistic since the immediate returns in financial terms can be limited. Yet, one wonders if this is so in the long run as some of my friends in the industry can attest that the opposite is true.

I believe it is desirable and necessary both for technical and humanitarian purposes, that our industry seek out a method of cross-communication in the use and application of our technology between those who know and those who would like to know, for the mutual advantage of all people on the face of this globe.

STATUS OF REINFORCED PLASTICS IN ITALY

Elio Rial, Filiclair S.p.A.

Market distribution and analysis of the main fields

The year 1967 has been characterized by a rather satisfactory development in the reinforced plastics production in Italy, even if this increase compared with the year 1966 has been inferior to that recorded in the previous year.

In fact the Italian reinforced plastics production for 1967 can be valued at about 21 000 tons with an increase of about 14% in comparison with 1966, whereas the increase of 1966 was about 20% in comparison with 1965.

In table 1 we have reported the market distribution valued for 1968 and formulated on the ground of the first six year's months.

On the ground of the data specified in the table, we here survey the various application field of the Italian market.

Building

Actually the field of sheets in Italy is representing more and more low percentage of the whole reinforced plastic market and we are pleased to note that this is characteristic of every country having an advanced FRP industrial development. It denotes that glass fibres reinforced plastics are penetrating more and more successfully in the other application fields.

TABLE 1

Distribution of the reinforced plastics market in Italy—Forecasts for 1968

	1968	
	Forecast tonnage	Respective %
Building		
Translucent building panels	10700	44.6
Other applications	1700	7.0
Land transport		
Refrigerated truck bodies, railway refrigerator cars tanks	2700	11.25
Car bodies and other applications	400	1.7
Marine		
Boats	1200	5.0
Other applications	300	1.25
Chemical plant		
Tanks, ducts, pipes, chimneys, etc.	2200	9.15
Industrial items		
Housings, appliances, refrigerated display benches, moulds	1800	7.5
Consumer items		
Chairs, trays, helmets, etc.	1500	6.25
Electrical		
Laminates and premixes	1100	4.6
Miscellaneous	400	1.7
Total	24000	100.00

However it is always the greatest application field of the reinforced plastics in Italy and even the tonnage is increasing, owing to the higher standard of mechanical characteristics, translucency and ageing resistance achieved at present.

The other activities of the building field are grouped as 'other applications' that is: the buildings where the sandwich structures for internal partitions and face panels are used, the sanitary groups, the concrete forms, the swimming-pools, the different types of bungalows, the school pavilions, etc.

The analysis of this field points out that the most immediate development of glass fibres reinforced plastics will occur mainly in the school, hospital, commercial building while other technological and economic presuppositions shall be satisfied for a development in the residential building and, on the other hand, in Italy there is no precise rule regulating their use.

Land Transport

The realizations in this field, from 1966 to the present, have become more and more important and the increase percentage has been the most notable.

The construction of refrigerated truck bodies for food transport is undoubtedly favourable to FRP both for the reduced weight of the structures and the consequent greater possibility of load and for the coefficient of thermal insulation got by the sandwich panellings, that is very important for the frozen foods transport.

In 1967 over 300 railway refrigerator cars have been constructed in Italy, equivalent to over 1000 tons of reinforced plastics. A similar quantity of reinforced plastics has been absorbed by the refrigerated and not refrigerated truck bodies construction for the transport by road and by the tanks construction, always for the transport by road, of milk, bear, fruit, juices, wine and musts as well as of chemical products.

As regards the tanks for the transport by road of some chemical products considered dangerous, the development of glass fibres reinforced plastics is at present restrained by some legislative impediments that allow the transport of this products in metal tanks only.

The UNIONPLAST is carrying on an intense activity on this subject towards the competent Organs and we think that these impediments will be soon removed.

This will result in a considerable development of the tanks construction, for which some Italian firms are really well tooled.

Among the other applications we have included the bodies of some sporting cars, the bus roofings for the public conveyance etc.

Marine

This field comprehends boats, coverings for metallic and wooden boats, installations on board of ships and the other applications concerning the navy: pontoons, buoys, harbour, accomodations.

As regards the boats field, in 1967 over 8000 units have been constructed, of which about 5000 represented by outboard motor crafts.

The state of the other materials used for the boats construction may be so resumed: At present most of cruisers ranging from 14 to 30 metres are built in wood, while for larger dimensions the steel is used. Under 14 metres the prevalent trend is for the FRP boats. This trend will be more emphasized when the control from the Lloyd's Register is sempli-fied.

The other applications to be pointed out are: the applications on ships (hatches, port-holes, wind socks, shower and bath in one piece, refrigerator doors, closing panelling for decks and promenades) and some harbour accommodations (pontoons, rafts, anticorrosive coverings).

Chemical plant

The present consumption of the glass fibres reinforced plastics in the chemical industry may be regarded as satisfactory, considering that only a few years ago the reinforced plastics were used in this field for anticorrosive linings or coverings only.

Today, thanks to the better knowledge of the parameters concerning the structures design (coefficient of safety, chemical and temperature resistance, processing costs, etc.) and to plants working excellently for years, the installations in the reinforced plastics field have become usual and considering their potential uses, it is right to state that the fields of the Chemical and Food industry are destined to represent the most important field of application for glass fibres reinforced plastics in Italy.

The glass fibres reinforced plastics are able to solve the most dissimilar problems of the chemical industry and of industries dealing with chemical agents, with considerable saving.

The main applications, some of which we shall illustrate, include tanks for chemical products and oils, smoke flues, plating vats, filter plates, cyclones, tanks for processing and storage of wine, beer, fruit, juice, etc.

Industrial items

We have grouped in this field: housings for working and agricultural machines, some realizations effected for the household appliances, both with thermosetting materials: laminates, premixes and prepregs and reinforced thermoplastics; refrigerated display benches; moulds both for the reinforced plastics processing and the metal embossing, centrifugal pump housing, pieces of washing machines.

Consumer items

Among the applications that, for their destination, may be included in the consumer items field, the principal one concerns the furnishing pieces.

For these pieces, the consumer becomes familiar with the modern shapes, appreciating its colour brightness, the exellent surface finishing, the lightness, the ageing resistance.

On the other hand, the glass fibres reinforced plastics give to the furniture industry a series of intrinsic advantages that greatly help in lowering the production costs, considering that in this period the high labour costs have nearly obliged to give up particular wood processing.

The principal advantages of the glass fibres reinforced plastics are: incorporated colours, high mechanical resistances, spot resistance, lightness, design freedom, and possibility of easy realizing complex shapes.

The chief factor, from various points of view, concerns undoubtedly the shapes that these materials can take and that should be judged advanced and anyhow impossible to realize, following the traditional methods, as regards the costs.

Lastly, the greater rigidity and resistance of the furniture piece being connected to the shape (resistant structures by shape) cause the reduction of thickness with considerable economic and lightness advantages.

Other consumer items of a certain importance, representing a fair rate of the glass fibres reinforced plastics market in this field are: fishing-rods, water and snow ski, trays, helmets, statues, sledges.

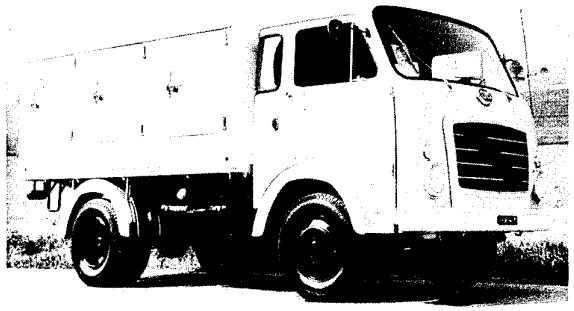


Fig. 1 Beginning from the transport field, we are showing one of the many refrigerated trucks realized in glass fibres reinforced plastics. The body is obtained by sandwich construction, by using expanded polyurethane as core.

Electrical

Also in this field the applications are very different and it is difficult to divide the applications. As specified in the table, the tonnage is referred to the use both of laminates and premixes or moulding compounds.

The main applications are: parts of transformers, motor, generators, switches and electrical units; shunting boxes; insulators, anti-arc diaphragms, spacer bars.

The application of the glass fibres reinforced plastics in the printed circuits, road lamps covers and bearing poles of the same is becoming more and more interesting. The production of road lamps covers tends increasingly towards the use of prepregs.

VETRORESINA

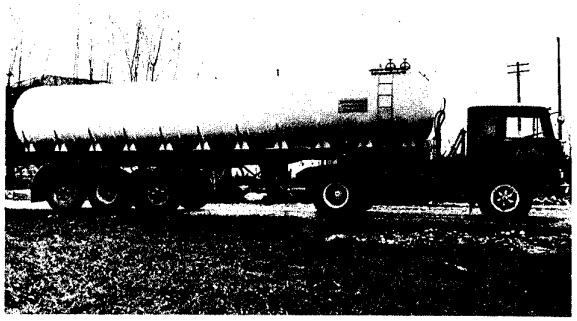


Fig. 2 Another interesting application in the transport field is represented by the tanks for the transport of liquid foodstuffs and chemical products. This tank is got by winding of roving and polyester resin. The same process has been utilized for storage tanks up to a capacity of 60.000 litres.

Forecasts

Before illustrating some of the principal FRP applications in the above considered fields, we wish to complete this outline with some forecasts concerning the development of the glass fibres reinforced plastics fields five years from now, as regards the market distribution.

In 1973 the glass fibres reinforced plastics production might be, according to sound market surveys, not less than 45000 tons or double approximately the present one.

The per cent market distribution, considering the principal application field, might be modified as follows:

Sheets	33-35%
Other applications in building	9-10%
Land transport	10-12%
Marine	7-8%
Chemical plant	10-12%
Consumer items	10-12%

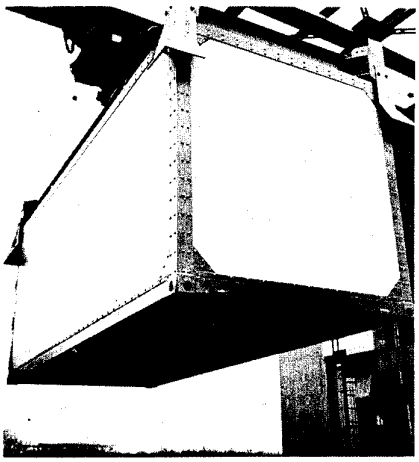


Fig. 3 A revolution in the transport field is due to containers. In Italy only a few prototypes have been realized in reinforced plastics, one of which is here presented. This is a container quite in conformity with ISO standards, realized with sandwich panels by a particular technique. The advantages obtainable by glass fibres reinforced plastics are numerous and many Italian firms are developing various designs in order to make the FRP containers more competitive.

Applications

The applications we are going to illustrate concern the principal Italian application fields, except the building one, about which another paper here presented shall relate more in detail.

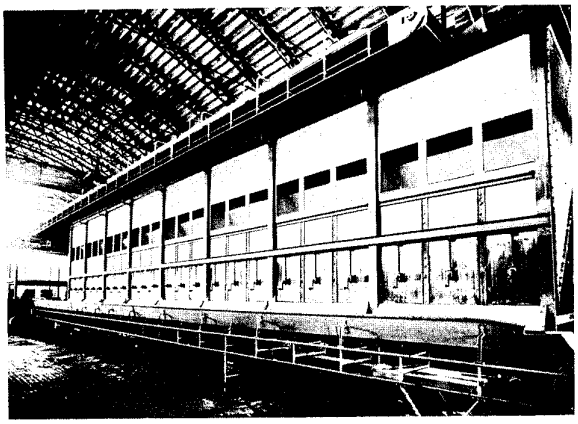


Fig. 4 This slide and the following two illustrate a plant for the olive processing, where the glass fibres reinforced plastics have appeared unequalled, owing to their nature, their chemical resistance and the particular surfaces smoothness. This figure presents a series of silos where olives undergo a first phase of ripening.

Fig. 5 Here the series of vats where olives are treated with a sodium solution for sweetening is shown.

Fig. 6 This is the group of tanks where the sodium solution necessary for the sweetening treatment is prepared and preserved.

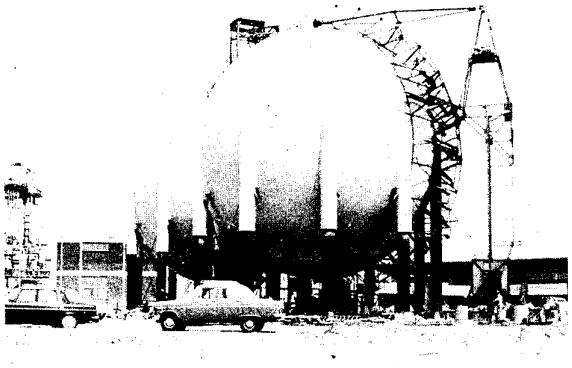


Fig. 7 This illustration represents two metallic tanks for liquid carbon dioxide (—30°C) covered by FRP elements and insulated by expanded polyurethane. The realization has been carried out in France by an Italian firm by using elements constructed in Italy. The covering has been effected in sectors. After the realization of a first sector, constituted by 10 FRP elements, expanded polyurethane has been injected in its interior, so to realize an insulation having density of 30-32 kg/m^3 and thickness of 12 cm. The external temperature range grom —10°C to +60°C. The subsequent sectors have been constructed in the same way. The whole covering of each tank required 20 sectors. The final operation is constituted by a sealing with bands of impregnated mat followed by the spray up of white highly reflecting gel coat. The average thickness of the covering is 3 mm of glass fibres reinforced plastics.

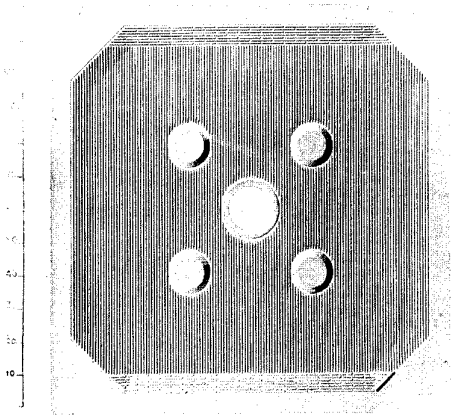


Fig. 8 This filter plate, side of 120 cm and weight of over a metric quintal, is matched-die moulded by using continuous mat.

Fig. 9 One of the most important applications of the glass reinforced plastics in the furnishing field is constituted by easy-chairs structures and tables. The pieces here presented show perfectly the reinforced plastics possibilities. This series has been got by hand lay-up, the one method to allow the realization of the considerable undercuts presented by the structures.

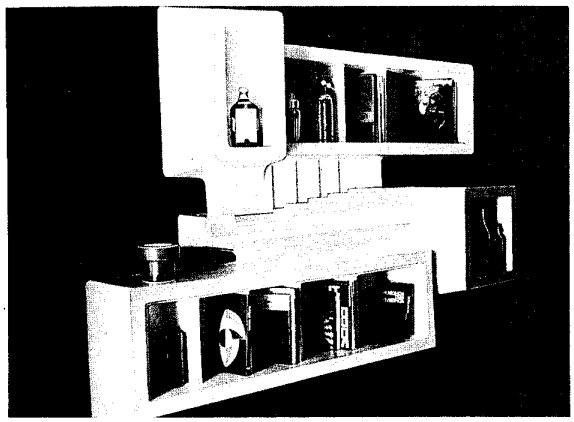


Fig. 10 This unit is formed by two parts realized in a FRP mould. This application points out the designer's idea to realize light and then cheaper structures, by exploiting the glass fibres reinforced plastics possibility to be moulded in any shape. In fact it is easy comprehensible as the numerouse recesses be as many stiffening elements.

MARKET DEVELOPMENT FOR GLASS FIBRE REINFORCED PLASTICS IN THE UNITED STATES OF AMERICA

J.D.MENTON, Owens-Corning Fiberglas, Europe SA.

Products made either partially or totally of glass fibre reinforced plastic reach into almost every phase of American life, i.e. sail boat, chemical tank, furniture, helicopter, air-conditioner, deep submergence rescue vehicle, skis, printed circuit board, corvette, patio panels, saturn rocket, bathroom.

In market after market from rocket ships to motor cars, from park benches to sky scrapers, from bathrooms to storage tanks and from pleasure boats to working tug boats, glass reinforced plastic is out performing and replacing traditional materials such as metal and wood.

Over the past twenty-five years glass reinforced plastics has grown from almost nothing to half-a-billion pound industry in the U.S. values at between one-half-and-three-quarters of a billion dollars annually. Its future promises to be even more spectacular.

In the next few minutes I would like to discuss with you the market by market growth of glass reinforced plastics in the United States. In the course of this talk I will answer such questions as 'what are the reasons for the growth of glass reinforced plastics in the U.S.'; 'what statistics are available to prove glass reinforced plastics success'; 'what specific markets have been most affected by glass reinforced plastics' and 'what are some of the newest, and most exciting applications that will have the greatest impact in these markets'.

Though statistics can get a bit boring, I think a few are in order to show how the glass reinforced plastics has grown in the U.S. in the past decade. In 1958 total consumption of glass reinforced plastics laminated in the U.S. was one-hundred and eighty-five million pounds. In 1967 that figure had jumped over two-hundred percent to five-hundred and sixty pounds. It is expected to reach six-hundred and ten million pounds in 1968. The source for these and other figures used in this paper is the Reinforced Plastics Division, The Society of the Plastics Industry.

It is estimated by industry experts that total glass reinforced plastics laminate consumption will grow at a compounded annual rate of seventeen per cent through 1975. It will pass the one-billion pound mark in 1971 or at the latest 1972. The steady increase in the consumption of glass reinforced plastics is proof of its value as a competitive engineering material. Especially appealing to end users are glass reinforced plastics high strength/weight ratio.

Products made of these materials are light weight and virtually unbreakable. Continued improvements are also being made in cost/performance relationships of glass reinforced plastics to other materials. While the cost trend for many other materials, notably metals, is upward, glass reinforced plastics cost trends are downward at a rate of five per cent a year. With cost/performance as the basic of its evaluation, the industry is confident that glass reinforced plastics materials will compete successfully against traditional materials.

Let's take a market-by-market look at glass reinforced plastics used in the United States.

Beginning with transportation, i.e. automobile, train, truck which ranks as the largest user of glass fibre plastics composites, roughly twelve per cent of the total.

Current consumption of glass reinforced plastics in transportation is one-hundred and fifteen million pounds annually, up three-hundred per cent over the thirty-million pounds consumed in 1958. This is about ten to twelve pounds per vehicle based on an estimated production of 9.5 million cars, trucks and other commercial vehicles. Some criticisms have been received through the years that glass reinforced plastics in the transportation industry is more promise than production. To some extent this has been true. The Corvette remains the single outstanding example of glass reinforced plastics' automotive accomplishments. However, there is plenty of new action which may mean glass reinforced plastics is ready to fulfill much of its long awaited promises. The projected growth rate of glass reinforced plastics in the transportation industry is a healthy fifteen per cent. By 1970 the transportation industry expects to use one-hundred and eighty-four million pounds of glass fibre reinforced plastics—by 1975 three-hundred and forty-five million pounds.

One industry expert speaking at the SPI reinforced plastics technical conference, recently predicted that volume for reinforced plastics U.S. transportation could multiply ten times in the next five years to a level of over one-billion pounds annually. He based his forecast on the growing trend in the auto industry towards producing smaller cars and different body types. As far as we know at present there are more than thirty known new applications of glass fibre plastics in 1968 U.S. cars. Among the most significant thermoset applications include:

1. The fender extender for Ford. This component is expected to be produced in quantities of two-hundred-thousand this year, highest volume of any glass reinforced plastics part ever specified.
2. Sixteen major body parts in the Ford Shelby GT 500, soon to be produced with a planned volume of nine-thousand units.
3. Chrysler Hardtop package tray.

4. The completely redesigned Corvette with an entire glass fibre plastic body for the fifteenth consecutive year.
5. Timer belt housing for the Pontiac Tempest.

We expect that about twenty-five million pounds of glass fibre/thermoplastics will go into the U.S. cars in 1968.

Among the new applications is the instrument panel in the Olds F-85 made from reinforced ABS. The crash pad retainer is made of reinforced polystyrene. The Chevrolet Corvette, the most famous car with a glass fibre reinforced plastic body is building up its glass reinforced plastics content inside. This year's completely redesigned Corvette has a glass fibre plastics instrument panel and seven parts on the steering column. The Pontiac Tempest has now fitted a reinforced polypropylene fan shroud. The Ford Galaxie with instrument panel cluster of reinforced styrene acrylonitrile.

General Motors is introducing glass fibre reinforced air-conditioner ducts to replace sisal reinforced ducts because glass fibre assurs greater heat and moisture stability.

The growing acceptance of glass fibre thermoplastics by the automotive industry is one of the brightest spots in the glass reinforced plastics future.

In 1965 auto manufacturers used 3.4 million pounds of glass fibre thermoplastics. The 1968 projection is for more than almost twenty-five million pounds. The industry looks for about forty-million pounds in autos in 1970 and 52.8 in 1972.

Glass fibre thermoplastics is a natural for the U.S. automotive industry which has a huge injection moulding capability. One manufacturer has more than two-hundred moulding machines in a single plant. New low-shrink premix polyester resins, in the thermoset area, is another development which boosts glass reinforced plastics stock among auto makers. Combined with new moulding techniques these resins produce glass reinforced plastics parts with a surface finish as smooth as steel when it comes from the mould. Sanding, putty rubbing and other normal glass reinforced plastics surface preparations are eliminated.

Another inovation is the one-piece 1968 Falcon fender extender made from these new resins and moulding techniques at a tooling cost saving of twenty-five per cent.

Not all the 1968 transportation advances of glass reinforced plastics are in automobiles. For example International Harvester is introducing a new front end truck design in glass reinforced plastics. White is planning production of five-thousand tilt cabs equipped with glass reinforced plastics panels. Glass reinforced plastic is making its mark in farm and garden vehicles. John Deere Company now uses a glass fibre hood as a prime feature in its Model 140 garden tractors. In rail transportation as many as one-thousand rail cars for Pacific Fruit Express will have glass fibre reinforced plastics liner panels. Glass reinforced plastics will also be used for front end housings for one-thousand new Chicago rapid transit cars made by St. Louis Car Company and the new Northwest Corridor transit cars by Budd Company.

The second one-hundred-million pound-plus market for glass reinforced plastics in the United States is Marine. It accounted for one-hundred and ten-million pounds in 1967 up from thirty-seven-million pounds in 1958. Boats are probably glass reinforced plastics best known in United States application. The light weight low-cost properties of the material is generally credited as one of the most important factors in the boating boom in the United States. It dominates the inboard, outboard and day-sailor categories and has a fast growing position in large yachts. About seventy-five per cent of the outboard boat hulls (4.5 million units) are glass fibre. Major advances have been made by this material in large inboard yachts with a projection of twenty-per cent penetration expected in 1967. Glass fibre-boat hulls are now being adopted for houseboats making this form of water recreation more popular than ever. According to a recent study houseboat sales are increasing from thirty-to-fifty per cent a year as more new models are being introduced. The sleeper in the boat business is the big yacht—pleasure craft of 40, 50 feet and longer. Although this constitutes a relatively small segment of the total pleasure boat market, it is beginning to grow rapidly as Chris-Craft, Pacemaker and others introduce glass fibre lines. Glass fibre was also used in about thirty per cent of all large yachts in 1967.

A new production process called 'unitized construction' for building large glass fibre yacht interiors has cut production costs and time substantially and promises to widen the market for large boats. Developed by Columbia Yacht Corporation and used in five of its models, unitized construction is basically the consolidation of dozens of individual component parts into a single glass fibre moulding. Parts which were once tediously made by bits and pieces are now all part of a single interior moulding. The growing acceptance of glass fibre in large yachts has led to its application in commercial fishing vessels which are now mostly metal or wood. Several models with hulls up to eighty-four feet are being made of glass fibre in South Africa and two firms in the U.S. are tooling up to make shrimp boats of similar size.

In the future you will see military vessels, work boats, fishing boats and cargo transports in glass fibre in lengths up to two-hundred feet. Already on the drawing board is a 146-foot fishing trawler. On the other end of the scale, glass fibre is beginning to penetrate the cartop boat market now dominated by aluminium. Another area for glass fibre in marine applications is underwater research vehicles. This includes the U.S. Navy's Moray, a 2-man crew submersible shaped like a torpedo. A glass fibre outer hull gives Moray its streamlining and also serves as a structural frame. The Woods Hole Oceanographic Institute's Alvin, a deep-diving research vehicle that located the H-Bomb off the coast of Spain has a protective skin of glass fibre which covers over four-hundred and fifty-square feet of wetted surface area.

The third largest market for glass fibre in the U.S. is the construction field. The 1967 consumption of glass fibre reinforced plastics in this area was one-hundred and five-million pounds, up twenty-one per cent above eighty-seven-million pounds in 1966. The increase in the use of glass fibre in construction is based largely on the acceptance of these materials for curtain wall panels and building structurals. More and more builders are turning to glass fibre in place of steel, aluminium and wood.

Glass fibre reinforced plastics has made possible the development of modular construction forms allowing dismantling, transportation and re-erection of buildings with relative ease. This was demonstrated after Expo '67 in Montreal, when many of the pavillions were taken down and successfully re-erected on other sites. Glass fibre is strong and completely weather-proof, yet also light in weight. Therefore, shipping modular units do not involve excessive costs. Moreover, the dimensional stability of glass fibre assures the architect and builder that any building in which they are used can be dismantled and re-erected without any great difficulties, even under radically different physical and climatic conditions. Some of the most successful building products and components made of glass fibre recently introduced in the U.S. include:

1. Bathroom components and modules.
2. Concrete forms and pouring pans for unusual sculptured concrete shapes.
3. Decorative panels.
4. Panelling.
5. Patio roofing.
6. Sandwich panels.
7. Shower stalls and receptacles.
8. Swimming pools.

Most of the glass fibre used in construction are replacements for metals such as steel or aluminium.

The appliance market up to now has been relatively small for glass fibre but it holds great promise. In 1967 close to twenty-million pounds of glass fibre were used in this area. This year about thirty-million pounds of glass fibre reinforced plastics are expected to be used by the appliance industry:- by 1970 up to fifty-million pounds.

Important recent developments include the introduction of a glass fibre base pan, bulkhead and scroll for an Amana portable room air-conditioner; and bulkhead for the Admiral air-

conditioner. The Amana air-conditioner rated at 5000 BTU is a small unit compared to the average of about 12 000 BTU. Yet a weight saving of six pounds was realised by a design permitting the use of glass fibre parts which weigh one pound and serve the same function as that served by twelve pounds of metal.

Design studies indicate that similar parts in 12 000 BTU units could replace forty-three pounds of metal with nineteen pounds of glass fibre. Potential market of three-and-one-half million units a year could utilize up to sixty-six-million pounds of glass fibre.

The first all glass reinforced refrigerated food cases for supermarkets has been introduced by the Nolin Manufacturing Co., Montgomery, Alabama. Considerable sales and future potential exists for glass fibre home humidifiers such as those made by Lau Blower Company.

More glass fibre is now in use and more is expected in water and detergent handling systems, such as dishwashers and home laundry equipment. One of the biggest appliance-industry uses of glass fibre thermoplastics to date is in a 1968 General Electric dishwasher—twenty-three injection moulded parts of glass fibre polypropylene in the pump and impeller sections. Glass fibre thermoplastics replaced aluminium die castings for most of the parts because of its detergent resistance and economy. Main reason for glass content is high temperature performance. Some parts are exposed to temperatures as high as 180°F.

Another major growth market for glass fibre is corrosion-resistant equipment, i.e. pipes, tanks and ducts. This industry is based upon a fact of nature—steel rusts.

In the petroleum industry alone it is estimated that corrosion damage to steel pipe costs the oil companies two-billion dollars annually. Glass fibre plastics pipe, tanks, ducts and other accessory equipment are a natural solution to the corrosion problem because glass fibre won't rust, corode, or contaminate and it is competitive with steel on a cost/performance basis.

Glass and resin producers are developing strong and more chemical resistant products for the corrosion market. Owens-Corning, for example, is currently working of a whole new grade of glass fibre called 'R' glass. This material offers a thirteen per cent improvement in filament strength over currently available 'E' glass fibre reinforcement. Weight loss tests show that 'R' glass resists a variety of chemicals far better than current reinforcements. This new glass is now being evaluated by manufacturers of corrosion resistant pipe and tanks and will be available in about twelve months.

The four-billion dollars spent each year for steel pipe and equipment is the potential market for glass fibre corrosion equipment and piping. The 1967 market of forty-one-million pounds is a tiny fraction of the market for pipes and tanks. To the present largest applications for glass fibre are chemical processing and crude oil industries. Glass fibre line-gathering pipe (seventy-million feet per year) now competes in price in sixty-seventy per cent of the industries needs, particularly where lined and coated steel is now used. In downhold tubing, about seventy-million feet of the one-hundred and thirty-million feet now used is a candidate for glass fibre.

The Wisconsin Gas Company has used glass fibre reinforced epoxy for rehabilitating existing gas mains since 1962. The company opens up the ends of lines and slides the pipe through the deteriorated cast iron mains.

As technology improves, target areas for glass fibre products are irrigation, sewer and drainage pipe.

Glass fibre tanks for underground gasoline storage at service stations and aboveground chemicals storage continue to gain acceptance. One leading company expects more than two-thousand-five-hundred of its gasoline tanks to be in the ground by the end of the year. In chemical tanks the development of a new high-strength laminate structure has enabled glass fibre to beat out steel for storage of a variety of corrosive chemicals. There were about two-hundred installations by the end of 1967.

The electrical industry, a relatively new market for glass reinforced plastics, will use more of these materials than any other industry in 1975. This forecast puts glass fibre for electrical applications at three-hundred-seventy-million pounds in 1975 out of a projected total glass fibre market of 1.9 billion pounds. Currently the electrical industry rates number five in total glass fibre volume at fifty-four-million pounds annually.

Glass fibre is now used for such electrical products as switchgear, industrial controls, telephone equipment, transformer components, connectors, electronic parts, printed circuits, computer parts, switch housings and pole-line hardware.

Among the latest outstanding applications is the Western Electric backboards. The change from aluminium to glass fibre for telephone switchgear backboards reduced production and materials costs and gave additional advantages of superior insulation, sound control and corrosion resistance. Change from wet process porcelain to glass fibre for Westinghouse Electric high voltage terminal blocks reduced part weight seventy-six per cent. Allan Bradley manual motor starter enclosure when changed to glass fibre produced on-off starter enclosure with moulded-in reliable grounding grid. These NEMA type 4 water-tight enclosures are suitable for insulations requiring water-proof or corrosion-proof enclosures.

The U.S. consumer market for glass fibre is hard to pin down because it is made up of so many pieces. In 1967 forty-five-million pounds of glass fibre plastics replaced some sixty-one-million pounds of metal products in items such as golf shafts, fishing rods, camping trailers, industrial and transportation seating.

New developments in use of premix and sheet moulding compound will facilitate glass fibre's penetration of two-piece and commercial type seating dominated up to now by materials such as melamine and moulded plywood. Glass fibre plastics will play an increasing role in aerospace and military applications, particularly in ordnance and aircraft. Aircraft components made of glass fibre have been and are seen continuing to increase at a rate of fifteen to twenty per cent a year.

For aircraft structural skin components, radomes, tail assemblies, elevator panels and landing gear doors, an increase of one-hundred per cent is seen in each of the next five years. Although present total is now quite small some large commercial airliners do make use of glass fibre on ten to fifteen per cent of their total skin area. For instance elements of the elevator and rudder of Boeings 737 are made of glass fibre. Also the Boeing 747 is reportedly slated for several applications of glass fibre. Glass fibre has been making tremendous inroads replacing metal in ordnance applications, artillery pieces and individual weapons. Barrels, tubes, breach mechanisms and the like are turning increasingly to the material. Many of the newer generation missiles, such as Polaris and Posiedon, make use of glass fibre where only metal would do before. For such applications as rocket motor cases and rocket motor nozzles, metals are never used.

To symbolise our industry I started this report with a look at glass fibre uses in conventional land vehicles, autos, trains, trucks, and ended with its use in outer space missiles. So too does the reinforced plastics industry in the U.S. start with its feet planted firmly on the ground developing its present wide based and diverse markets, but also looks to a promising future for a new and unknown world (markets) to conquer.

There seems little doubt that reinforced plastics volume leader among composite materials for many years in the U.S. shows no sign of running out of steam, or rather to bring this old phrase up to date, shows no sign of running out of liquid oxygen.

REINFORCED PLASTICS IN THE UNITED KINGDOM —A REVIEW

J. MOUNTFIELD, Market Development Manager,
Reinforcement Division, Fibreglass Limited

Reinforced plastics in the form of high-pressure phenolic mouldings have been in existence for many years—for the purpose of this review the term 'reinforced plastics' covers es-

sentially those materials moulded from resin mainly polyester and reinforcement such as fibrous glass.

Polyester resin was produced for the first time in the U.K. in 1946, woven glass cloth was already established but was expensive and the cheaper forms of reinforcement such as random type and continuous filament mats were developed to meet the growing demand. Cold curing resin systems were pioneered in this country but it was not until the early 1950's that resin and reinforcement became available in commercial quantities.

The new materials brought problems some of which are still with us today but critical studies show the basic materials to have achieved considerable improvement and the technology has certainly advanced.

Commercially—we are still looking for the big breakthrough, the success that is always 'imminent'.

The United Kingdom development and subsequent production was based almost entirely on the wet lay-up or contact moulding technique. Presses were not available and in the post-war years capital was difficult to obtain.

Much has been written about the early history of G.R.P. in the United Kingdom—it is sufficient to say that the development up to the 1960's was reasonable and despite the apparent rapid growth far from spectacular.

It was already evident that the major drawback to commercial advancement was the low production rate associated with the contact moulding process and that some degree of mechanisation was necessary. New fabricating methods were studied and continuous production on a large scale adopted by the sheeting manufacturers.

Up to 1961 there was some military requirement and the use of G.R.P. for secondary structures in aircraft was impressive. The number of firms with press capacity remained small and with the growing interest of the transport and marine fields hand moulding predominated.

By 1962 the consumption of reinforced plastics steadied at about 15 000 tons, an increase of roughly 10% over the previous year, the majority of which was glass reinforced polyester. The use of epoxides was moving slowly mainly in the electrical applications market and it was becoming evident that glass fibres would be used increasingly in conjunction with nylon and other thermoplastics. The cutback in the aircraft and military fields resulted in a severe reduction in the use of G.R.P. in those applications but transport and marine continued to expand.

1963 saw the general expansion in traditional markets with 1964 and 1965 showing interesting growth rate—there were signs that the long awaited breakthrough may have been achieved.

Pre-preg was enthusiastically welcomed and a big expansion was predicted for 1968.

Through 1966 the growth rate slowed significantly and this trend continued in 1967. The national economy and related difficulties was affecting all industry and forward planning had to be revised.

P.V.C. and G.R.P. translucent sheeting appeared to be settling in two distinct areas, the former strong in domestic applications with the latter maintaining and even increasing load in industrial markets.

Polyester consumption in major U.K. reinforced plastics markets (tons)

Year	Transport	Sheeting	Building	Marine	Chemical	Electrical	Misc.
1962	2200	2750	220	1100	550	550	?
1963	3230	3500	540	2020	880	675	?
1964	3200	3370	525	2970	1050	700	1600
1965	4800	4290	760	4600	1940	730	2400
1966	5200	4375	1000	4450	2450	850	1975
1967	5500	4850	1200	4950	2550	600	1925

These figures are based on what is considered to be the fair estimate of polyester tonnage consumed in each market as indicated. With the shifting emphasis away from strategic materials to general purpose certain specialist markets have become so small that they cannot be properly separated.

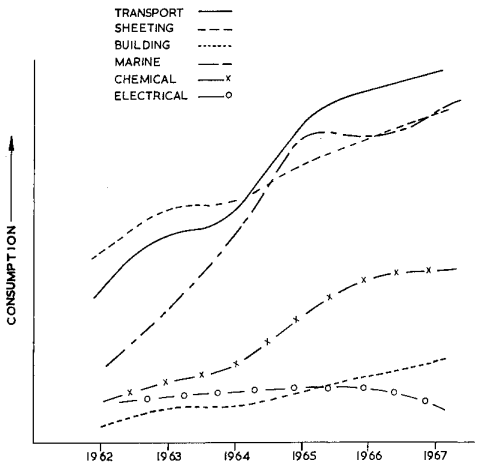


Fig. 1 Consumption trends in major United Kingdom reinforced plastics markets

Fig. 2 gives consumption of glass reinforced plastics in the U.K. together with predicted growth to 1975. It is interesting to note that growth pattern in both the U.S.A. and United Kingdom has been fairly similar in that lean periods have occurred around 1961 and appear likely around 1969. This suggested pattern in 1969 is arguable but the trends would seem to indicate this unless there are some new major areas of growth. In the U.K. this could be chemical plant and containers and in both countries reinforced thermoplastics.

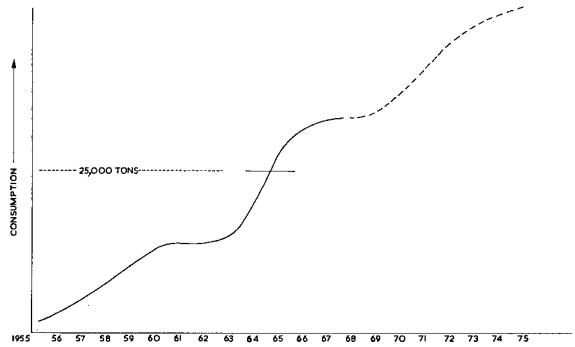


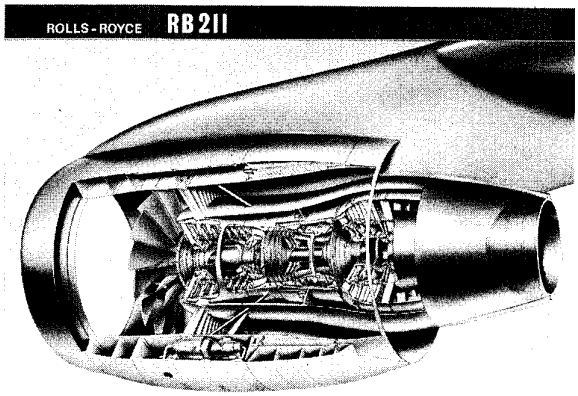
Fig. 2 Consumption of glass reinforced plastics and predicted growth to 1975 (United Kingdom)

A recent major accomplishment in the United Kingdom has been the invention at the Royal Aircraft Establishment Farnborough, of practical methods of producing high modulus, high strength carbon fibres. This work was reported in 1966 and has aroused world-wide interest. It has always been acknowledged that if fibre-reinforced plastics are to truly compete with metals then there would have to be a considerable increase in fibre stiffness to approximately five times that of 'E' glass. This has now been achieved and the problem of converting them into useful reinforced plastics being vigorously tackled by particular firms and authorities.

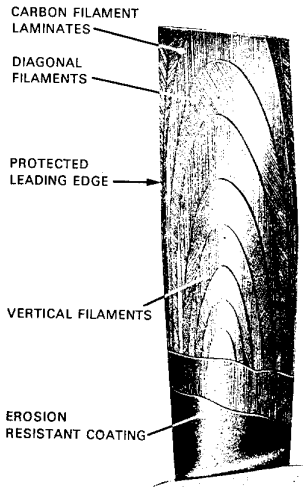
It has already been established that these carbon fibres are compatible with a wide range of thermosetting and thermoplastic matrices and that by employing suitable methods useful volumes of fibre can be incorporated. In such composites the specific stiffness and strength inherent in the fibre can be realised to a high degree. Additional work has shown that certain properties of carbon fibre plastics such as fatigue life in fluctuating tension, chemical inertness and low rate of wear could lead to a range of applications where they could become the preferred materials of construction.

It is expected that the considerable programme of research and development now organised will include the provision of carbon fibre reinforcement in various forms such as staple yarns, continuous fibre, felt, paper and other types.

The use of composite materials by Rolls-Royce Limited is based on research work started in the early 1950's and engine running since 1962. A result of this research is seen in their new material 'Hyfil', composed of carbon fibres in resin matrix, a composite that has been used extensively in their new RB 211 jet engine. The extensive engineering and manufacturing programmes for the use of composite materials in the RB 211 include the development and commercial service operation of fan blades of this material in the Rolls-Royce Conway engine. This operation commencing in July this year will amount to more than 100 000 hours of operating experience by the time the first RB 211 powered U.S. tri-jet airliners enter service.



The Rolls-Royce advanced technology Turbofan RB 211



Carbon fibre reinforced composite (hyfil) blade

Fig. 3 Carbon fibre reinforced composite (HYFIL) blade. (Courtesy Rolls-Royce Ltd.)

The U.K. moulding processes are similar to those in other countries with contact moulding still the most widely used. Excellent presses are now available and with the increasing popularity of pre-mix and pre-impregnated materials, mechanised production is steadily expanding. It is thought that pre-impregnated materials introduced during 1963 have made satisfactory if rather slow progress, the current consumption being estimated at about 1000 tons per annum. Study of the various applications indicates a steady growth rate over the next few years and it is interesting to note the increasing use of the material in engineering applications.

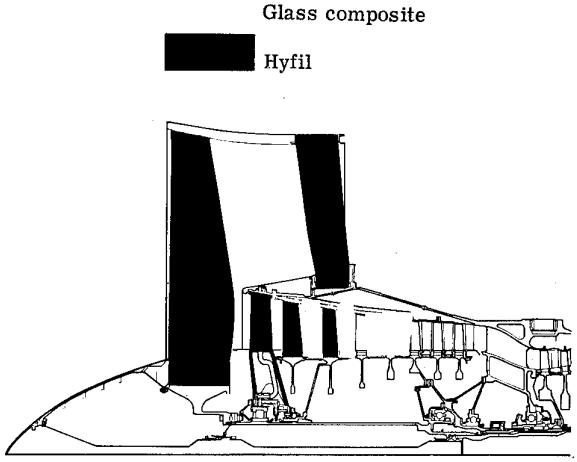
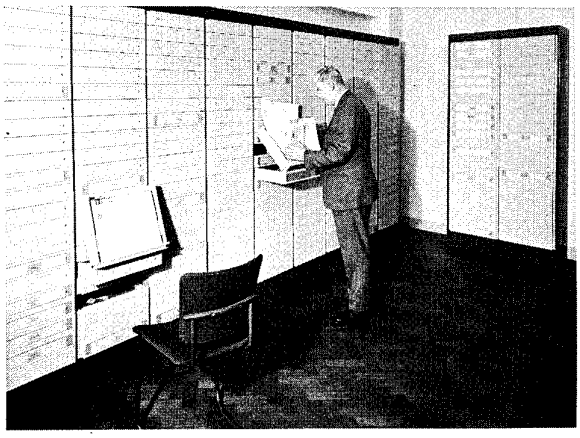
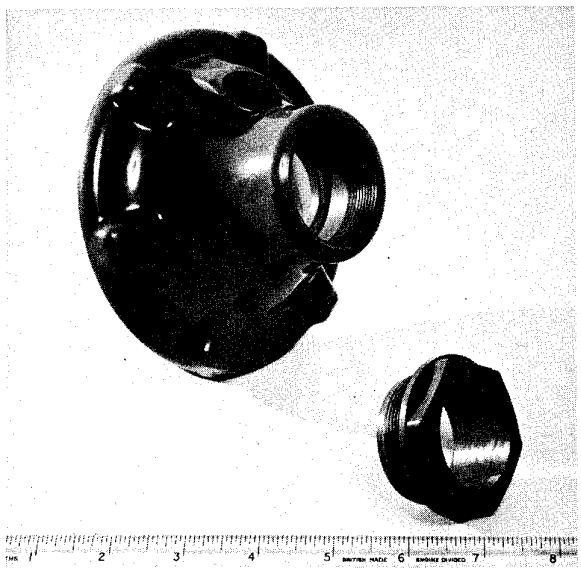


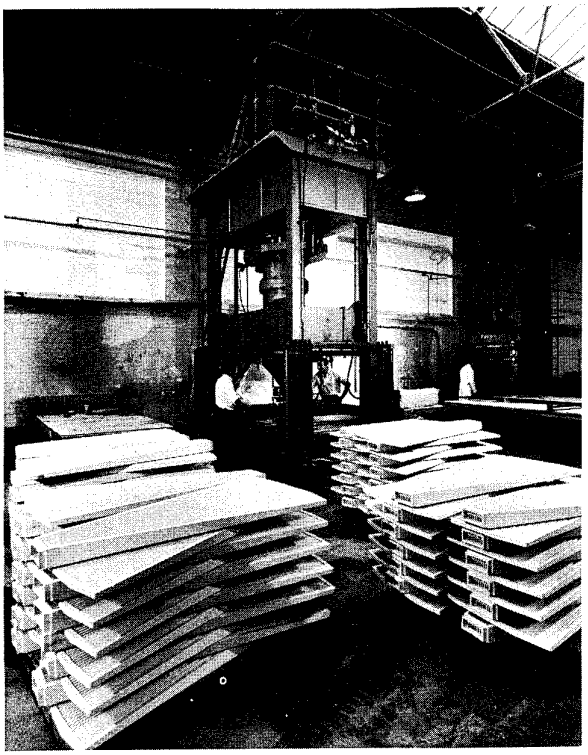
Fig. 4 shows section through single fan blade. (Courtesy Rolls-Royce Ltd.)



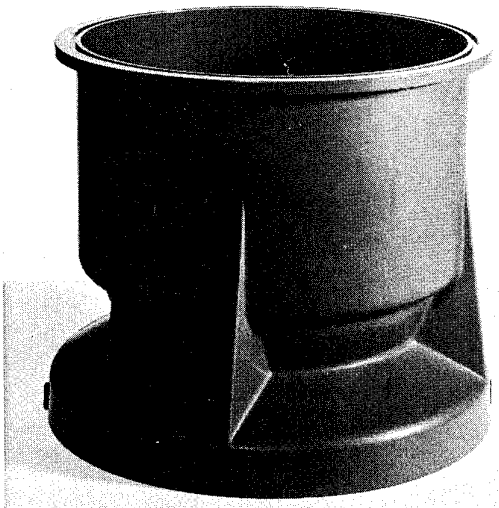
Part of the installation of some 4500 drawers manufactured in Flomat pre-impregnated chopped strand mat, specially designed by Ministry of Public Building and Works. (Courtesy Fothergill and Harvey Ltd.)



Cable gland bottom and gland nut with fine thread moulded in Flomat (Courtesy-Fothergill and Harvey Ltd.)

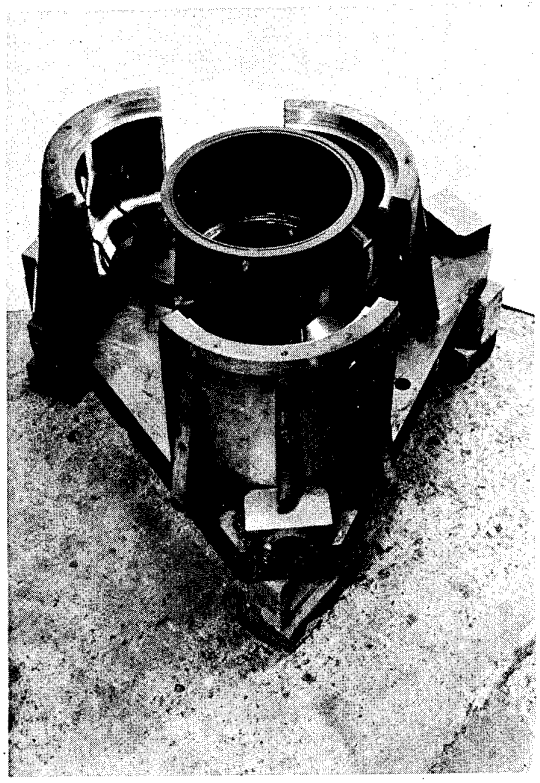


Polydisc filter mouldings and press shop at Bifort Engineering Ltd., showing 30° segments moulded in Flomat pre-preg.



The binnacle moulding removed from tool (Photographs, courtesy Fothergill and Harvey Ltd., illustrating various Flomat pre-preg applications.

An earlier process now being usefully employed and making notable progress is cold press moulding. This is the intermediate between the hand lay-up which is slow and pre-eminently suitable for the really large product and the fully mechanised hot press method. The press or rig can be relatively simple but the design of tools is most important. Moulds of reinforced plastic, faced concrete or similar are generally used and with considerable success. High glass reinforcement content is easily achieved and this process which permits the production of mouldings smooth on all surfaces is proving most economic for short and medium runs. With the availability of special resin systems and selected reinforcements this technique is being increasingly used. Glass chopped strand and continuous filament mats are the usual reinforcement with sisal, jute or asbestos incorporated into the lay-up to give greater bulk and stiffness. British rail has developed this production method to a satisfactory level and the g.r.p. seating illustrated was made by this process.



Compass binnacle moulding showing position in the three-way split female tool.

A wide range of reinforcement materials are manufactured and readily available. Where necessary these are produced to Ministry specifications and British Standards and meet all known requirements. Intensive development work has resulted in improved resin systems for both general and specialised applications. Advanced treatments for glass filament are under continuous review and search for the ideal goes on. In recent years the prices of raw materials has dropped steadily but it is unlikely that this trend can continue and any further significant savings may have to come from improved moulding techniques.

It should be noted that glass fibre is marketed in two glass compositions, electrical or 'E' and alkali or 'A' glass. The former is used for the major proportion of applications but 'A' reinforcement is still very much in evidence. This is perhaps mainly due to price advantage but of recent years the price differential has narrowed and if this trend continues it would be reasonable to assume that alkali glass reinforcement may eventually be withdrawn.

Other reinforcement materials include crocidolite and amosite asbestos fibres but despite the excellent properties claimed for these fibres there is no evidence of their making significant headway in current market applications.

At the time of preparing this review there were twelve firms competitively engaged in the marketing of reinforcement

materials in the U.K., four of these being U.K. producers of glass fibres and two firms supplying asbestos.

There are twelve companies actively supplying polyester resins and three major suppliers of epoxides.

There are no published figures for the total quantity of glass reinforcement consumed in the manufacture of reinforced plastics in any one year but private market research and statistics indicate a reliable estimate of approximately 11 000 tons for 1967, a significant percentage being imported. Of this total, chopped strand mats accounted for nearly 60% and rovings for all purposes approximately 20%. The use of woven roving continued to expand with chopped strand usage remaining fairly constant.

Reinforced plastics production—1967

Polyester resin	21 575 tons
Epoxides (estimated)	750 tons
Glass reinforcement	11 000 tons
Total (excluding other resin and reinforcement)	33 325 tons

APPLICATIONS

Marine

Reviewing the established markets using reinforced plastics in the United Kingdom, the boatbuilding industry is clearly one of the most satisfying, with the material fully accepted for a whole range of craft including dinghies, motor cruisers, yachts and lifeboats etc.

Despite the economic difficulties it has achieved an impressive growth rate and is expected to maintain reasonable expansion.

As in other countries the development of small boats was fairly rapid, particularly for pleasure craft but significant progress has followed in the areas of lifeboats and large hulls. Experience has been gained on the building of single piece moulded hulls in excess of 60 feet and it is now considered economically feasible to build larger vessels up to 200 feet.

Marked success has been evident in the building of large yachts and most of the firms act strictly in accordance with Lloyds Rules and there is no better guarantee of good workmanship. Investigation of Lloyds Register shows that 70% of yachts classed during 1966 were built in reinforced plastics. A number of U.K. firms whose names are world famous have in recent years built their popular ranges in G.R.P. and these yachts conforming to Lloyds 100A classification are not only exported but built under licence in other countries. Many firms export more than 60% of their annual production.

The reinforced plastics lifeboat was first developed in the U.K. by Watercraft in 1952 receiving Board of Trade approval some two years later. Since that first approval more than 5000 lifeboats have been build of that type. It is estimated that of all lifeboats carried by shipping, at least 75% are constructed in G.R.P. In addition to lifeboats, Harbour authorities throughout the world use large numbers of workboats and launches built in this country.

An interesting trend in the popularity of the reinforced plastics craft is revealed in statistics recently released and which cover boats of all types displayed at five of fourteen London Exhibitions. (Table 1)

An important development is the investigation by the Naval Department of the Ministry of Defence into the building of a glass reinforced plastics Ship. A design study was commissioned by the Navy Dept. for a vessel with a displacement of the order of 600 tons and an overall length of about 160 feet.

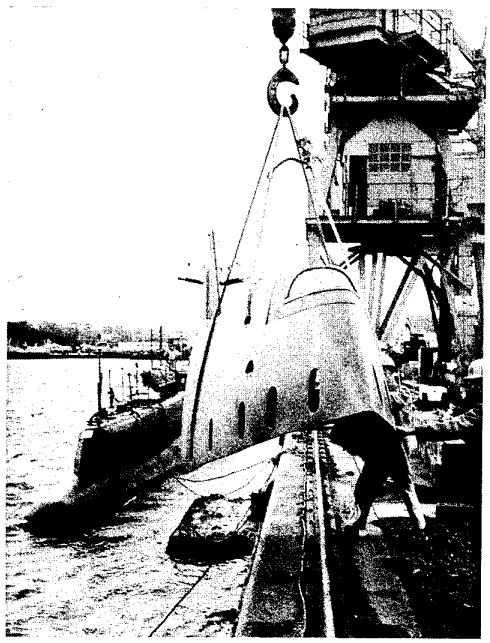
The consortia consisted of a shipbuilding form experienced in the building of small warships and a specialist engineering company with the knowledge and experience of the latest rein-

TABLE 1

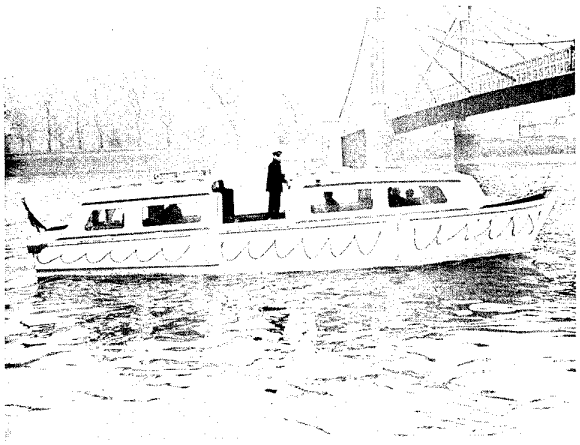
Construction materials

	1st show 1955	5th show 1959	10th show 1964	13th show 1967	14th show 1968
Timber	75 82.4%	239 69.1%	350 62.2%	232 34.6%	200 28.0%
Metal	5 5.5%	14 4.1%	17 2.8%	12 1.7%	13 1.8%
G.R.P.	4 4.4%	70 20.2%	172 30.5%	379 55.0%	430 60.1%
Others	7 7.7%	23 6.6%	24 2.5%	58 8.5%	72 10.1%
Total boats	91	346	563	671	715

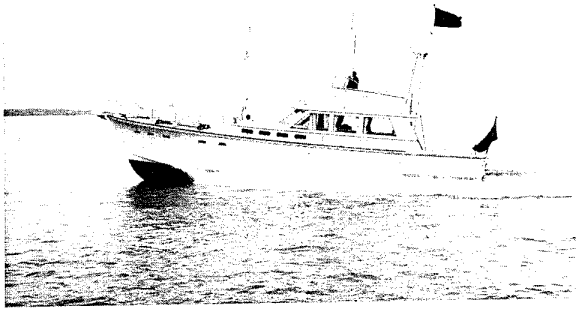
A view of the construction of the g.r.p. outer structure for the 'Oberon' Class Submerine. (Courtesy Ministry of Defence, Naval Dept. & B.R.P. Ltd.)



The aft end outer structure of the 'Oberon' Class Submarine moulded in g.r.p. (Courtesy Ministry of Defence, Naval Dept. & B.R.P. Ltd.)



One of the six luxury g.r.p. launches built by Watercraft Limited for use on the 'Queen Elizabeth 2'. (Courtesy Watercraft Ltd.)



The Hargrave 64 is built by Halmatic Ltd., and designed by one of the world's leading designers of high speed craft. The hull form is suitable for use as a fishing boat, patrol boat or luxury yacht. With suitable engine installation will give speeds up to 35 knots. (Courtesy Halmatic Ltd., Fibreglass Ltd.)

forced plastics materials and fabrication techniques. The work was co-ordinated and reports showed the project to be feasible.

A full size mid-ship section of the proposed vessel was built successfully and thoroughly tested. The maximum amount of information criteria and material properties has been extracted and this together with experience previously gained will be thoroughly and properly studied before plans are finalised on the possible construction of a complete hull.

It is of commercial as well as military importance and a new company was formed to exploit the possibilities in 'ship' construction.

This has rightfully been described as a pioneering story of advanced British technology applied to a traditional field and considerable interest is being shown by authorities in the United States and other countries. (Figs. 5-3).

Other Ministry of Defence Naval applications include submarine outer unpressurised structures, fins and battery boxes etc.

The most modern passenger afloat today is the new Cunarder 'Queen Elizabeth 2'—this great vessel brilliantly designed features many glass reinforced plastic applications. Outstanding among these are the twenty g.r.p. lifeboats and launches, the whole boat complement being of Watercraft design comprising two class A emergency boats, four class B motor launches, eight glass B lifeboats and six cruise launches capable of being used as lifeboats.

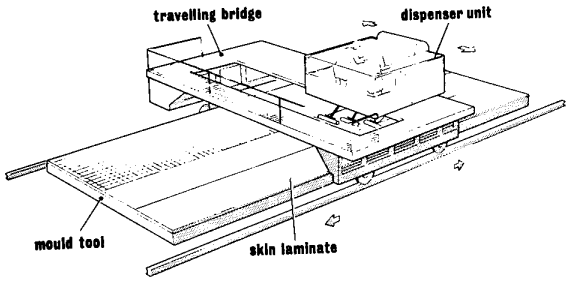


Fig. 5

Deck Construction

Resinated glass cloth is dispensed from a mechanised unit mounted on a travelling bridge spanning the full width of the tool.

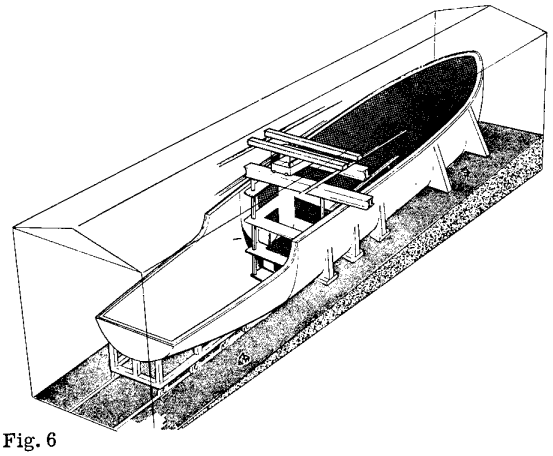


Fig. 6

Hull Construction

A travelling bridge is suspended within the hull mould from overhead rails: centrally positioned over the bridge on an independent rail is a mechanised cloth-dispensing unit. Resinated glass cloth is lowered from this unit onto the tool surface where consolidation takes place. Required laminate thickness and coverage is progressively built up.

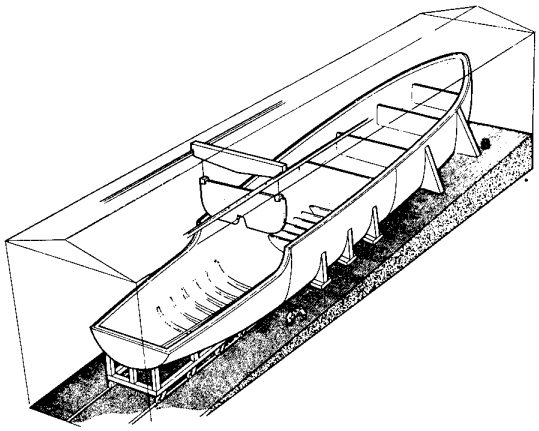


Fig. 7

Stage Assembly

Bulkheads and decks etc, prefabricated on panel tools, are positioned in the hull and the joints laid up.

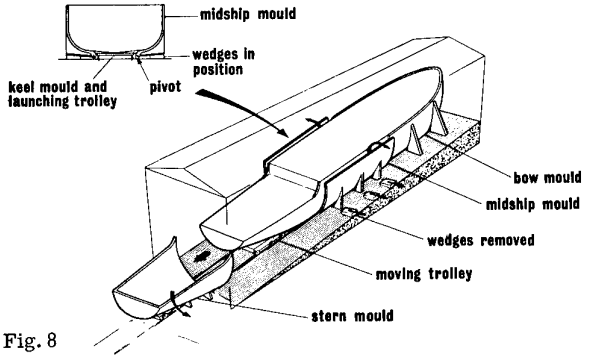


Fig. 8

The Lauch

The after end of the hull mould is removed, followed by the port and starboard midship sections, the bow mould remaining fixed. The bottom section of the midship mould serves as a launching trolley, thereafter being winched back into position and prepared for the next ship production.

(Figs. 5-8, courtesy Bristol-Thorneycroft, Ministry of Defence, Navy Dept.)

Containers

After several years of deliberation Container ships are now being built and it is confidently expected that, as in the U.S.A., reinforced plastics, mainly in conjunction with other materials such as plywood, will be used in fairly large quantities for the construction of refrigerated container units.

The U.K. containers are being built in accordance with British Standards and to the recommendations of the International Standards Organisation, and may also be approved by Lloyds Register. They provide a modern and highly efficient method of transportation combining high thermal efficiency with great strength and rigidity.

Certain non-standard all G.R.P. clad units have been in regular service for some time and these totalling several hundred have been used mainly for the transportation of perishable cargo. Reports on their performance show them to be most satisfactory.

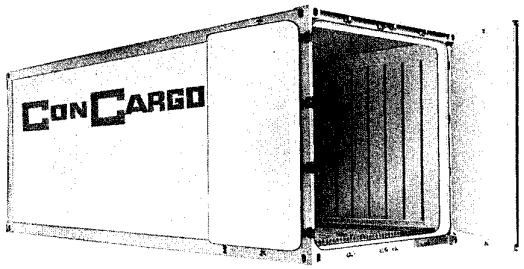
The latest approved designs incorporate rigid foam insulation core with glass reinforced polyester panelling bonded to the inner and outer surfaces. An alternative design features a plywood reinforcement to the outer G.R.P. skin, a central core of rigid foam insulant and with an inner skin of G.R.P.

It is clear that the plywood/reinforced plastics composite is a useful material not only for the refrigerated types in conjunction with a highly efficient insulation but it is now also being seriously considered for the construction of dry cargo container units where some degree of insulation value is necessary and also for the building of 'Dual purpose' units.

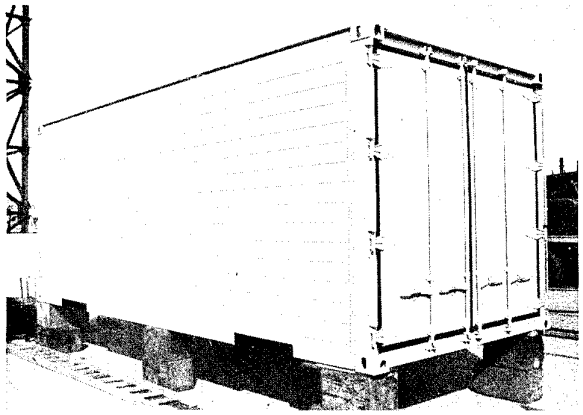
With containerisation becoming established for sea, rail and road and on a world-wide basis, the future for containers of all types must be excellent. In the United Kingdom the concept should create a demand for reinforced plastic/plywood composite panels to a significant degree which it is hoped will justify the intense engineering effort applied to this particular field. The potential depends to a large extent upon the system of container usage and ownership and the percentages of dry to refrigerated cargo units per ship. Some authorities suggest that insulated containers will acount for about one third of total requirements and on this basis and observing the limited life of the units a most satisfactory market should develop. Orders for several thousand G.R.P. clad units are now being completed and others are in negotiation.

British Rail and certain road transport units will build own containers and these will include tanks etc. which will conform to I.S.O. transport recommendations.

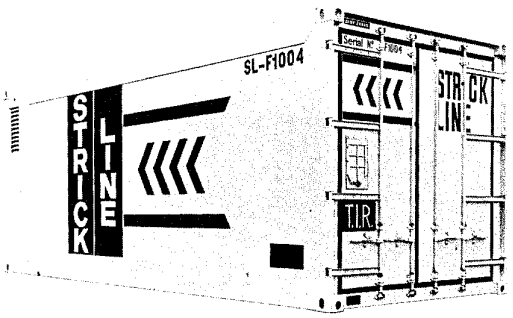
There exists a small demand for special air freight 'igloo' type containers and many of these are constructed in G.R.P.



G.R.P. Container by ConCargo Limited. (Courtesy ConCargo Ltd.)

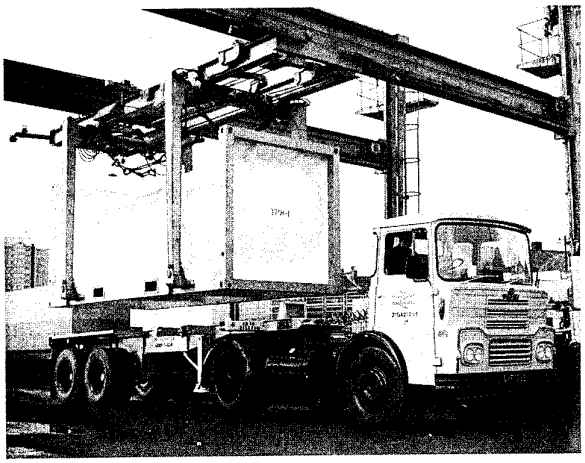


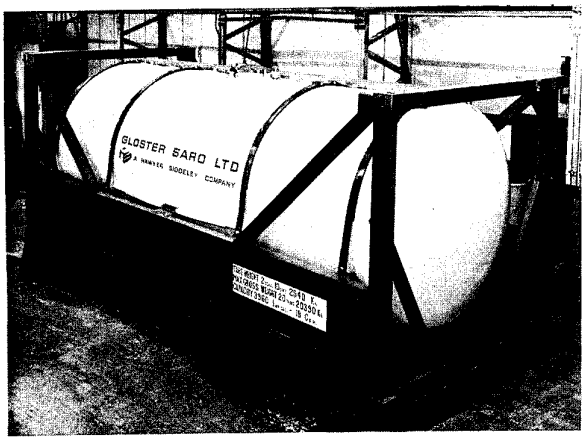
Standard reinforced plastic container by Watercraft Ltd. (Courtesy Watercraft Ltd.)



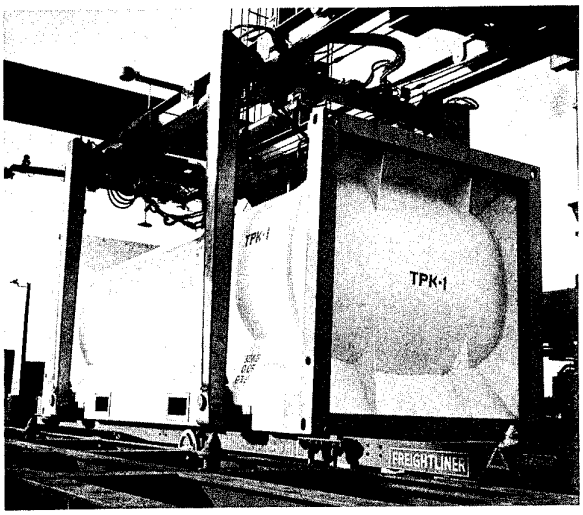
G.R.P. Container for Strick Line built by Duramin Eng. Co. Ltd. (Courtesy Duramin Eng. Co. (Lydney) Ltd.)

G.R.P. Container for the carrying of bananas. Built for Geest by Seaway Container Limited. (Courtesy Seaway Containers Ltd.)





The bulk liquid carrier filament wound in glass reinforced plastic by Gloster Saro Limited. The carrier has a 3960 gallon capacity, of the latest design and complies with I.S.O. specification. (Courtesy, Hawker Siddeley Group Limited)



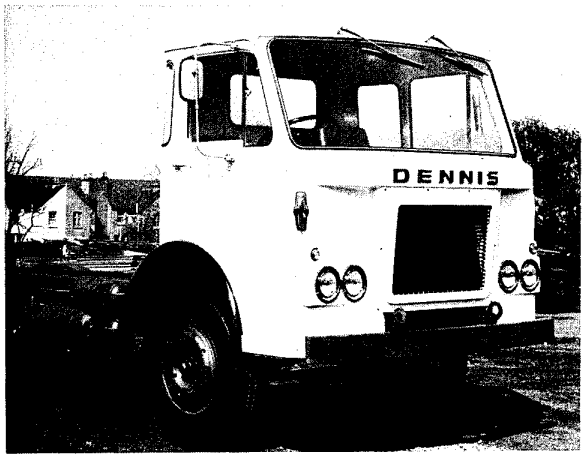
The container vessels manufactured by Gloster Saro Ltd. For Trafpak Limited in g.r.p. The vessels are of 3600 gallon capacity and of max-section. (Photographs, courtesy, British Rail Board and The Hawker Siddeley Group Limited)

Transport

This group covers all non-marine transport applications, and on a general basis is estimated to account annually for about one fifth of reinforced plastics consumption.

For this large potential market, the performance and properties of reinforced plastics have proved completely acceptable in many applications. They are used for the building of lorry cabs above a certain size, domes and other panels of passenger service vehicles etc. and to a limited extent in caravans.

Reinforced plastics are now almost a traditional material in the commercial vehicle market but these vehicles are becoming more competitive, costs are playing an increasingly important part and the g.r.p. cabs are known to be expensive. With the rationalisation of the vehicle industry the big specialist body builders are finding their markets reduced and they are clearly looking to capture some of the g.r.p. market to replace existing business.



The Dennis Bros. 'Pax V 15 tonner with glass reinforced plastic cab. (Courtesy, Dennis Bros. Ltd., Guildford)

The car market is still disappointing and with no major breakthrough in sight. It is agreed that this may come when plastics are accepted by the big car producing firms for the manufacturing and fabricating industries and the car body manufacturers for some years such acceptance is not expected in the foreseeable future. It has however been predicted that eventually steel sheet will be replaced in external body panels by moulded plastics although not necessarily by reinforced plastics as we know them today.

A certain amount of glass reinforced thermoplastic material is used in automotive components—this is a field with very large potential ranging from structural trim to replacing metal for engineering purposes.

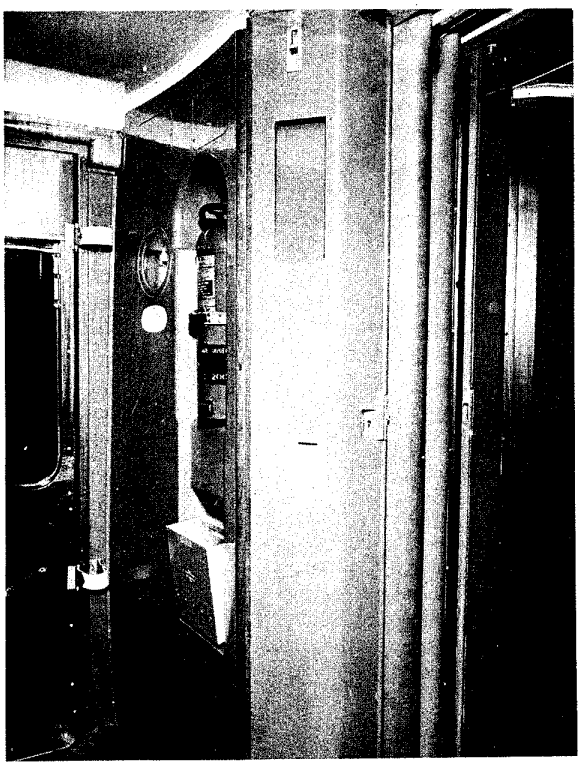
The other car firms also represent valuable markets. Of these Reliants have a most impressive growth record particularly in the three wheeler version and they claim to be the largest user of glass reinforced plastics in the European motor industry and second only to General Motors in the World. Building their first g.r.p. vehicle in 1957, Reliant produced 16 000 cars and commercial vehicles for home and export during 1967. In addition to exporting direct Reliant has established motor manufacturing industries in many countries. A large operation is now underway in Turkey where production beginning in January 1967 will reach 4000 vehicles by 1968.

Other outstanding firms also use reinforced plastics. Both Bond Cars and Lotus are renowned for their high performance cars which sell into specialised markets. The 'Lotus' service is world famous and the 'Europa' is a worthy addition.

These firms, with others producing 'specials' account for the bulk of reinforced plastics used in car bodies. It is not a large market and it is difficult to value in detail. Private surveys indicate that including ambulances, the value of g.r.p. used in the U.K. car market during 1967 to be roughly £1/4 million.

The 'Lotus Europa' (Courtesy, Lotus Cars Ltd.)

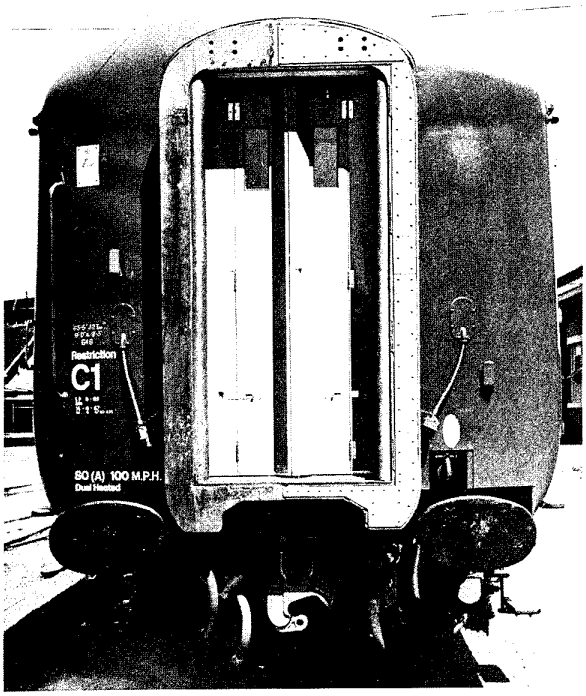
The nationalised railway system operated by British Rail Board has well controlled manufacturing facilities and a modern Development Unit recently opened at Derby. It is considered that of the United Kingdom industries using reinforced plastics British Rail is the one that has looked at the material most critically.



Glass reinforced plastics vestible end panel with fold-away end door of the same material in the open position. (Courtesy, British Rail Board).

The advantageous strength to weight ratio argument is easily refuted because the total weights are so enormous that any small saving from G.R.P. substitutional uses is negligable. However, now that attempts are being made to increase speed and tighten economics the power/weight ratio of vehicles is becoming increasingly important, and the assessment criteria of cost/performance now gives way to cost/performance/weight.

British Rail have been using G.R.P. items for about thirteen years and although many of these are quite simply three-dimensional space fillers more and more applications are now derived with function duties, including:



End view of Mk. 11A Coach showing the glass reinforced plastics doors in the closed position. (Courtesy, British Rail Board)

Glass reinforced plastic seating shells currently in use by British Rail. (Courtesy British Rail Board)

Coaches and locomotives— ergonomically designed seating with G.R.P. shells, doors, roof canopies, interior vehicle lining and in the vehicles of the future, streamlining nacelles and further into the future, interchangeable modules.

Freight vehicles—Containers must take pride of place although at the present time only 120 insulated G.R.P. containers are in regular service. Experiments are currently in hand to determine the practicability of G.R.P. faced plywood clad container units.

Rail tankers—To date although experimental units have been built in reinforced plastics no positive conclusions have been reached.

Civil, signal & telecommunications, electrical engineering— Buildings of various types are being developed over and above the obvious use of G.R.P. sheeting. Items such as duct work, cabinets and effluent troughs are currently in production with ideas being developed on components for bridge structures and overhead electrical supply.

It is suggested that the future for reinforced plastics in British Rail lies in applications in conjunction with other materials and that, for example, the lightweight coach of the future will be made from steel, alloy and plastics. Indeed the first study undertaken by the 'Advanced Projects Group' has been an examination of the new techniques and developments which are now available for the construction of a passenger train of an advanced kind. The result of these preliminary studies is a new concept of passenger train design, planned to give speeds on existing tracks up to 150 miles per hour. The design, now on the drawing board may well lead to the much greater use of G.R.P. by British Rail by the early 1970's.

The Hovercraft

An outstanding invention that sprang from the brain of one man, Christopher Cockerell.

Several of these craft are now in service and a new type, the 'HM 2' Series is a rigid sidewall version will all glass reinforced plastic hull moulded to Hovermarine design by Halmatic Limited.

The G.R.P. structure is derived from two main moulds, the hull and sidewalls and the deck and superstructure. For ease of production the mouldings from the latter are manufactured in several sections, comprising deck, superstructure, forward fan intakes, engine room covers and wheelhouse. The transverse frames which reinforce the hull shells and sidewalls are of sandwich construction with G.R.P. on either face of a 2" thick foam core.

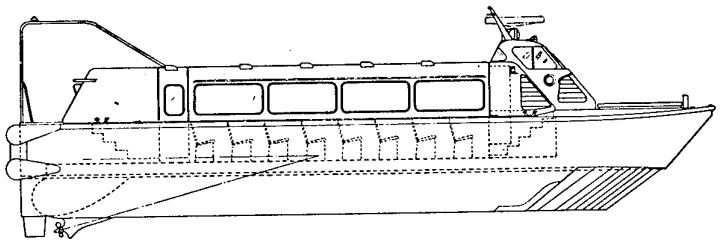
The first HM 2 passenger hovercraft is being operated by British Rail Seaspeed service across the Solent.

These vessels are being ordered in reasonable numbers and larger types are already being designed which it is reported will also be constructed mainly in reinforced plastics.

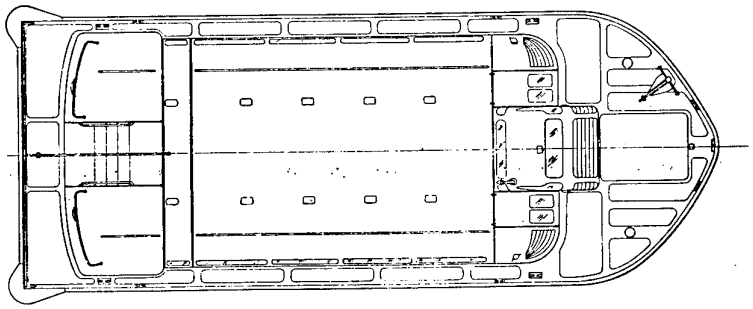
An excellent future is forecast for the rigid-sidewall all reinforced plastic craft, not only in the passenger service field but as Survey, Fire and Rescue and other special purpose vessels.

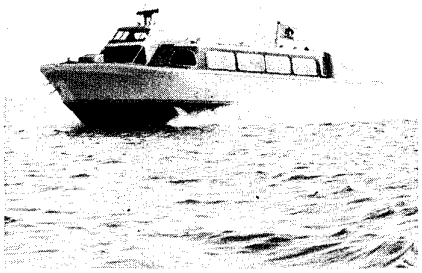
It has already been announced that Hovermarine will be operating a new Works to increase building rate of these fine crafts.

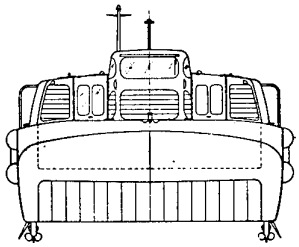
HM-2. Fire/rescue Hovercraft.



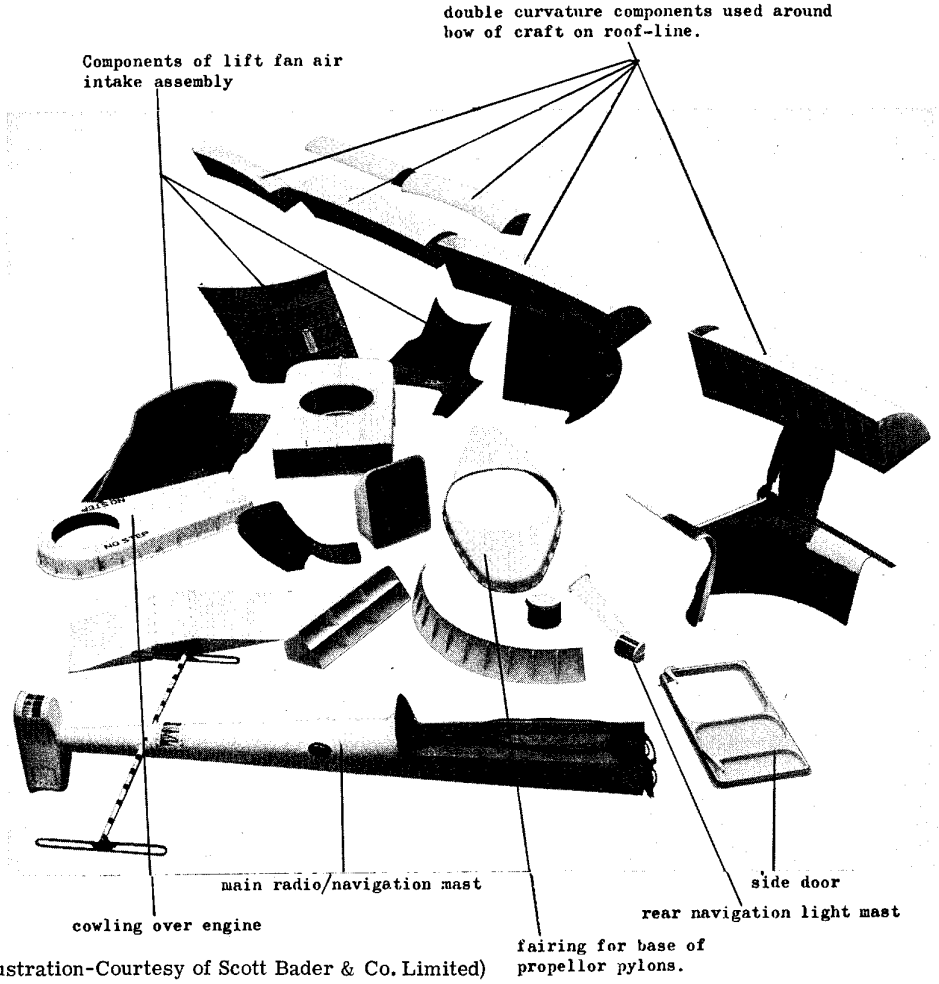
The first HM-2 rigid sidewall hovercraft built for British Rail seen on trials in the Solent. This craft is now in service in in British Rail's 'Seaspeed' service. (Courtesy British Rail Board.)







General arrangement of HM-2 60 Passenger Class Sidewall Hovercraft.



(Illustration-Courtesy of Scott Bader & Co. Limited)

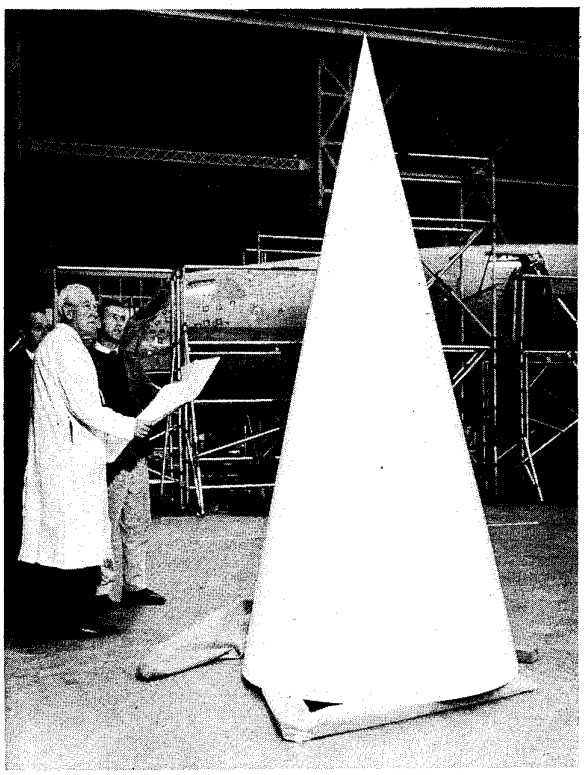
February this year saw the launching of the Mountbatten Class SR.N4—the world's largest Hovercraft. The SR.N4 has also been bought by British Rail for their 'Seaspeed' service between Dover and Boulogne. This craft has a number of interesting reinforced plastics applications including nose pods for the nacelles housing the No. 2 gearboxes at the top of the four propellor pylons and fairings for the bases. Some of the components are shown in this illustration.

Aircraft

In the past few years there has been little change in the uses of reinforced plastics in British Aircraft. Concentrating to an increased extent on civil aircraft the three main areas where they are employed are:

Radomes and dielectric panels.—The more exotic of these are epoxy resin laminate/glass-cloth honeycomb structures. Others are merely polyester resin glass-cloth panels or polyester laminate/Hycar foam sandwich structures.

Ducting.—The rigid ducts are polyester resin/glass-cloth or tape wound for air pressure ducts, fuel venting etc. Perhaps more interesting is the range of flexible ducts used for cabin air distribution and made from a flexible polyurethane resin, glass tape wound.



The 'Concorde' Radome made from glass reinforced epoxide resin by the vacuum/pressure, matched metal technique using a system developed by B.A.C. for the production of radomes for surface-to-air missile, Thunderbird. (Courtesy: British Aircraft Corporation).

Furnishings—These include cabin linings, hat racks, passenger service panels (rigid P.V.C. backed with polyester glass cloth for increased rigidity). In this group can be included electrical distribution panels, also an increasing range of secondary brackets made from pre-preg mat.

The United Kingdom aircraft industry has experienced troubled times and the use of reinforced plastics in aircraft during 1967 was small probably no more than 400 tons. Radomes are still the most important outlet in primary structures but secondary structure applications such as doors, wing tips etc. continue. A small amount of g.r.p. is used in glider construction, for the building of rocket nose cones and certain other highly specialised military projects.

The Concorde radome is the largest of its type ever built in Western Europe and possibly the largest in the world, the basic dimensions being 10 feet long with 5 feet diameter at the base. This radome carries one of the most rigorous specifications ever applied to a glass reinforced plastics component with exacting requirements covering mechanical strength necessary to withstand the stresses imposed by trans/supersonic flight and tolerances on wall thickness and consistency of glass/resin ratio necessary to ensure constant electrical transparancy.

Building and construction

A published report states that in 1965 the consumption of all plastics materials in U.K. construction totalled 173 500 tons and that of this amount reinforced plastics accounted for 7400 tons or about $4\frac{1}{4}\%$. It has been estimated that by 1975 the total usage of all plastics in this field will reach 560 000 tons with reinforced plastics increasing to about 20 000 tons or $3\frac{1}{2}\%$. This forecast is based on extensive market research and points to future trends rather than firm estimates of demand. Nevertheless the forecast is important particularly when considering the restrictions imposed by the Building Regulations and Codes of Practice.

Reinforced plastics can provide excellent performance characteristics even in present conventional design and despite the major problems of fire resistance—it is expected that significant progress can be achieved by the greater use of composites of reinforced plastics together with other materials noted for their good fire resistant properties.

Glass reinforced plastic sheeting is by far the largest growth material and it is claimed that approximately 36 000 000 square feet was sold during 1967. The outlet is principally in industrial building where the translucent sheet is used in conjunction with other cladding such as asbestos cement, coated sheet etc. The major portion of market demand is met by machine made sheeting.

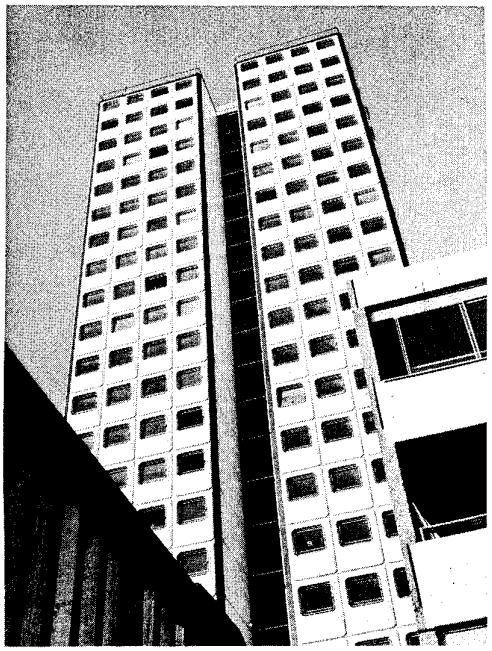
Resiform low-rise housing. (Courtesy, Wm. Old. Limited)

Resiform is a successful U.K. industrialised building system based on the use of g.r.p. modular load bearing panels and this system has received the all important N.B.A. appraisal certificate. The reinforced plastics wall unit weighs only 7% of the same area of brickwork or concrete panel and is fully insulated. Bathroom units are also produced by this system building.

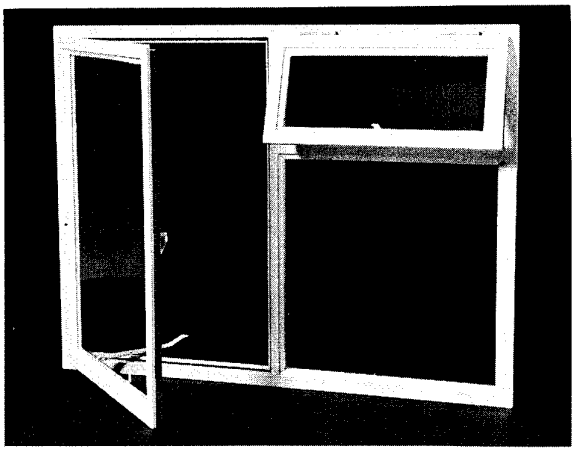
The Greater London Council has approved the use of g.r.p. cladding panels for their S.F.I. scheme and much has already been published on their form of construction. These well designed multi-storey blocks of flats are being observed with keen interest by building engineers throughout the world. The moulding firm concerned has recently installed a 1200 ton hot moulding press for the production of the panels at the production of rate 10 000 per annum.

There are other manufacturers of reinforced plastics building panels which are used successfully in local authority approved schemes, many of these being infill panels assembled to provide adequate fire resistance and thermal insulation. It is reasonable to assume that the use of g.r.p. cladding will steadily increase as long as costs are realistic and mandatory requirements can be met.

General g.r.p. building applications which can also be considered successful include roofing trim, restoration work on old buildings, shop fronts, huts and shelters, heart units, concrete formwork and permanent shuttering etc.



The greater London Council Project—the first block of flats nearing completion. (Courtesy G.L.C., B.R.P. Ltd)

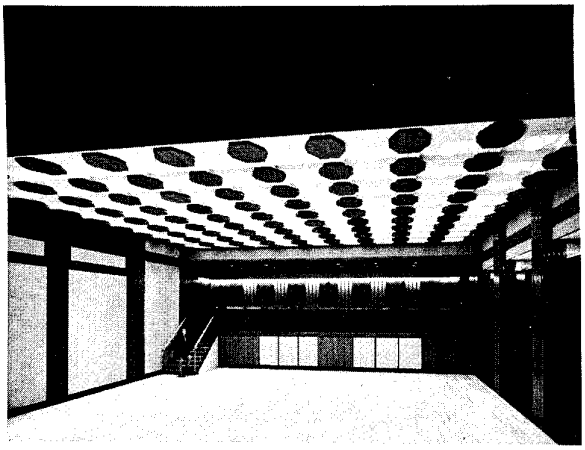


The I.C.I. Casement Window. (Courtesy, Building Development Group, I.C.I. Limited)

Plastic window frames have been made previously but a new I.C.I. Casement Window is now in production which is available in a range of sizes and with excellent weather resistance and dimensional stability. This is made from g.r.p. pre-impregnated sheet compound by hot press moulding method. The components of the window are straight pieces of the two different cross sections moulded in four different lengths, which when coupled by the separately moulded corner and T-pieces give a range of modular sizes. The design is outstanding and the window arousing considerable interest should have a very high market potential.

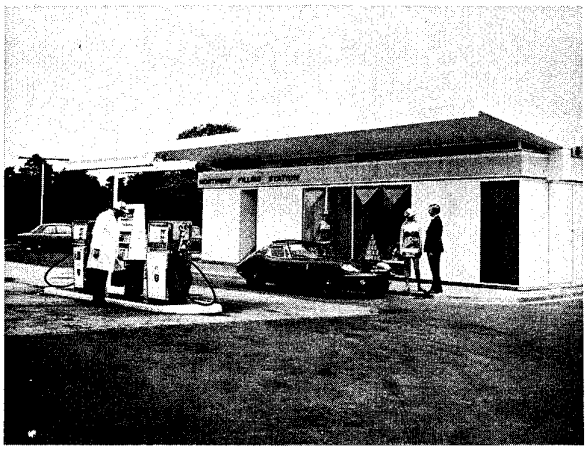
In sewerage and water drainage schemes we have underground concrete piping armoured with filament wound glass reinforced polyester which accounts for approximately 700 tons of g.r.p. annually. This well established technical development was the result of several years of experimental work with government and other research establishments.

The Building Research Station is currently evaluating and developing several interesting projects incorporating glass reinforcement materials.



Glass reinforced polyester Ceiling in Bank H.Q. (Courtesy, B.I.P. Chemicals Limited)

A most interesting feature of the Great Hall at Barclays Bank Head Offices in Lombard Street, London, is the 1610 sq ft suspended ceiling containing 81 coffered panels moulded in g.r.p. by Brensal Plastics Ltd. Using fire retardent polyester with class 1 spread of flame rating, this ceiling is lighter in weight and easier to fabricate than alternative materials with this rating. Total weight of panels 18 cwt about one fifth that of plaster. The ceiling is the underside of a 22 ton raked auditorium floor which can be raised or lowered in eight minutes. Seats for 270 people are permanently attached to the upper side of the structure.

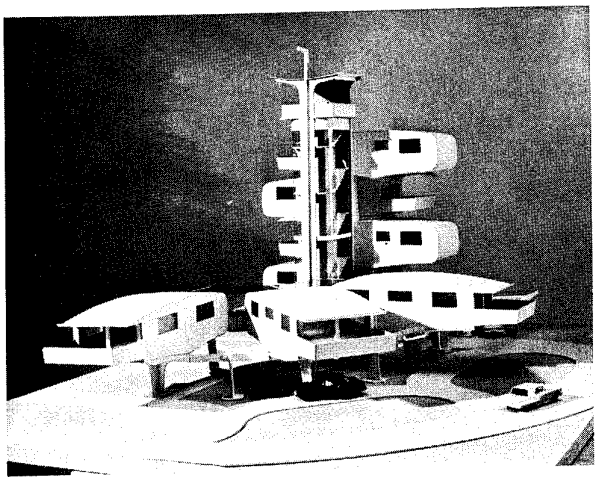


The B.P. Plastics Petrol Station. (Courtesy, Shell-Mex and B.P. Limited)

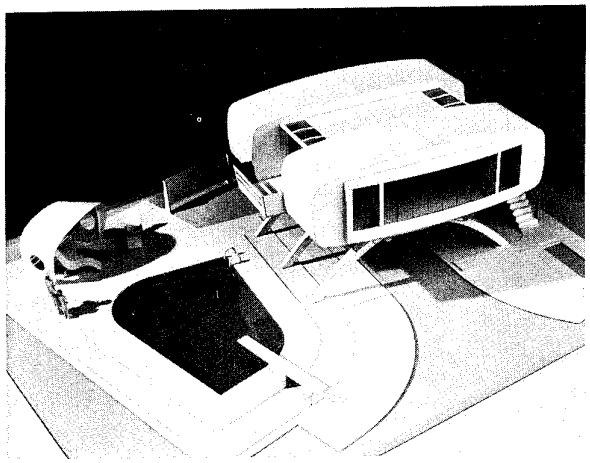
An all plastics petrol station, the first of its type in Europe was erected at Baldock on the A1. This will be evaluated to find out to what extent future petrol stations can be cheaper to build and maintain, erect, and be more attractive in appearance. This station was erected by six men in only six days. The building is designed to withstand steady winds of up to 63 m.p.h. and gusts of up to 120 m.p.h. Station was designed by Polyplan of Leicester to the requirements of B.P. Many features are in reinforced plastics including the wall panel retaining channel, wiring ducts, wall panel skips, interlocking tongues for wall panel skins, interlocking tongues for wall panels, external fillets, cold water tank, cladding of steel beam, roof modules skins, signing panels and pump island lighting.

G.R.P. Modular Buildings are being widely used in the U.K. They are used as Switch Rooms, Instrumentation and Control Rooms and as Sub Stations etc. They can be supplied with or

without insulated panels and can be factory assembled for delivery to prepared foundations. An interesting example is the electricity transformer stations which are made entirely of glass reinforced plastics and which are installed in Northumberland and the North Riding of Yorkshire by the N.E. Electricity Board. They can be erected in $2\frac{1}{2}$ hours and orders for 75 of these have been placed. Each station measures $14\frac{1}{2}$ feet by $12\frac{3}{4}$ feet by $8\frac{1}{2}$ feet high and is built of 12 panels which are bolted together. Any panel can be easily removed and replaced.



Flats of the future? A suggested new building design—service tower of light weight steel or aluminium girders supporting prefabricated reinforced plastic modules on the 'shell' principle. This method of construction offers dramatic new design possibilities for really tall buildings.

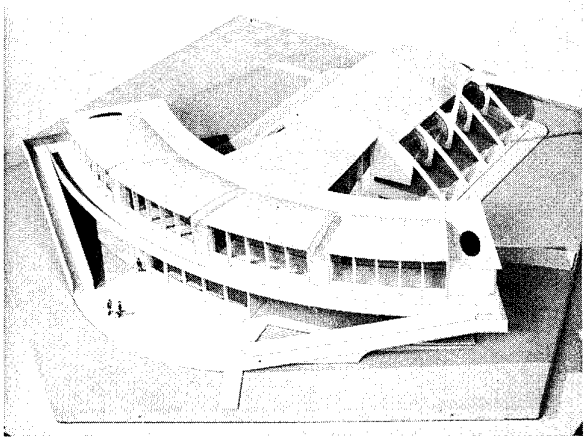


House of the future? Idea for prefabricated sectional home with two modules of shell structure from identical quarter moulding, bolted together to form the basic floor and roof structures. Flat glass reinforced panels and glass provide the other surfaces with corrugated translucent sheeting for the sun canopies and carport. The whole including swimming pool and garden furniture need never give any worry about excessive maintenance.

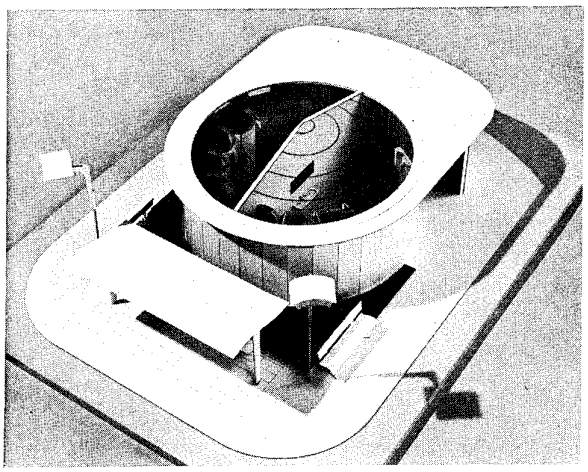
The Building and Construction industry is expected to provide a most important market for reinforced plastics but when trying to assess future trends and potentials many factors have to be considered. The Building Regulations demand certain standards but despite restrictions imposed it is reasoned that the use of g.r.p. in building will expand providing the material can be made more fire resistant and composite structures developed more economically. Imitative surfaces do not necessarily show any advantage.

Although much work has been done and some significant progress has been made, close scrutiny of the industry reveals that the true structural use of g.r.p. in building is still very much of a prototype nature and one-off uses predominate. Church Spires and Domes are interesting but not really big business. It has been suggested that the industry itself is too aligned to unchanging form and too dedicated to designing for conventional structures and materials. At the present time alternative materials are required to conform to ancient standards which in themselves can prevent the newer such as reinforced plastics being utilised to the best advantage. This is not implied criticism but an attempt to assess the potential realistically in the period covered by this review.

Perhaps therefore, it is wiser to suggest that reinforced plastics as we know them today and envisage them in the years ahead are most suitable for 'advanced building design and methods'—the Homes, the Offices and Schools of the Future could well be based on the sensible use of reinforced plastics.



School of the future? The school of the future as portrayed in this model makes extensive and imaginative use of Fibreglass Reinforced Plastics and glass. The roof sections, supported on a stressed FRP framework, form an immensely strong, light-weight weatherproof structure and panels can vary from translucent to opaque, while the walls are clad in a sandwich construction of pigmented reinforced plastics with a core of insulating material.



Island site? This model of an Island site combining bus station and public convenience emphasises the pleasing appearance and durability made possible by glass reinforced plastics. The translucent dome is highly resistant to vandal damage as are interior toilet fittings. Prefabricated FRP lavatory units and stalls and also hand wash basins are smart, hygenic and tough. Sliding doors of the same material are also a feature. The walls of the structure would be of double skinned FRP sandwich construction self-coloured to minimise maintenance.

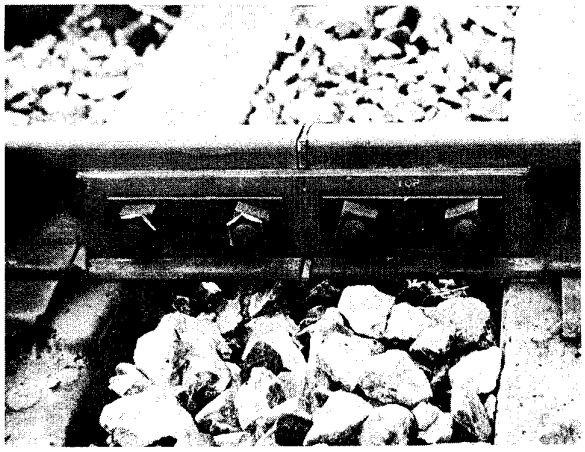
Electrical

This industry which has played such an important part in the development and application of reinforced plastics appears to have made significant change during the last few years. Accurate details of material consumption for 1967 are not yet available but it is suggested that whereas the polyester usage has dropped this has probably been matched by increased consumption of epoxides. The amount of moulding compounds used in this field is also difficult to estimate.

Although it is often claimed that the greatest outlet is in switchgear, reinforced plastics are used for a wide range of important projects in the electrical industry. These include Submarine Battery containers which, with a wall thickness of only $^{5}/_{32}$" withstand the ardous tests specified by the British Naval Authorities. G.R.P. not only provides increased shock resistance but many other advantages, weight reduction and added resistance to acid contaimination.

An outstanding development in glass reinforced plastics by Permali Ltd. is the large scale production of unidirectional glass fibre epoxy bonded high strength laminates. With a glass content of 75%, a flexural strength of 185 000 lbf/in^2 and a tensile strength of 100 000 lbf/in^2 are achieved. Typical applications for this material which possesses high mechanical strength and good dielectrical properties are Railway insulating Fishplates, moving contact lift plates on switchgear and as the core of resin insulated cross arms for overhead electrical transmission systems where this outstanding material provides the entire structural strength.

Underground E.H.T. Electrical Cable Joint Box. produced by hot press moulding techniques. (Courtesy Permali Ltd)



Railway insulating fishplates moulded from Permaglass-X. (Photograph courtesy Permali Limited)

Reinforced thermoplastics

Considerable success has been achieved with glass-fibre filled nylon with major areas of usage in power tool housing and telephone exchange components.

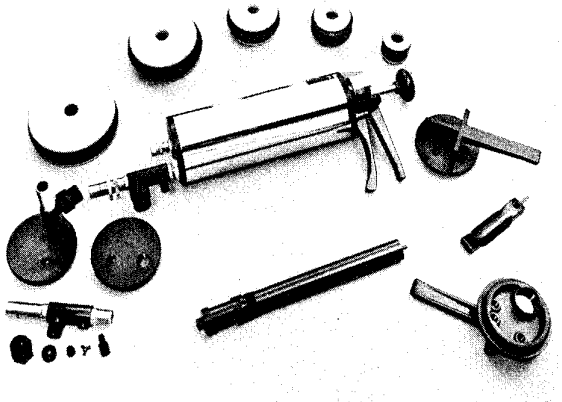
It is widely used throughout the electrical industry where it offers high strength, rigidity, creep resistance and high temperature resistance in addition to electrical insulation properties. Elsewhere it is used over a wide range of mechanical engineering applications. Among recent United Kingdom developments are the production of mouldings weighing approximately twenty pounds and also thin section electronic components with a wall thickness down to 0.008".

Development work continues on the reinforcement of other thermoplastic resin systems and no doubt a later review will cover the anticipated progress and market applications.

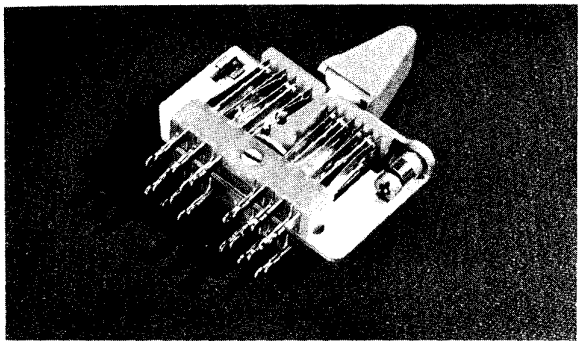
Until recently the conventional method of housing cable joints was by means of concrete containers. These have now been replaced by g.r.p. moulded boxes weighing only 15 lbs as compared to a concrete box with an approximate weight of 500 lbs.

The electrical supply industry requires high strength insulating vessels capable of operating in oil or air. Two examples of which are arc control chambers for rapid extinction of the arc and air pressure storage vessels capable of withstanding pressures in excess of 10 000 lbf/in^2. The filament winding technique has proved very successful as a means of fulfilling the required conditions and has the advantage of allowing metal inserts to be incorporated during the winding process, thus eliminating conventional fittings.

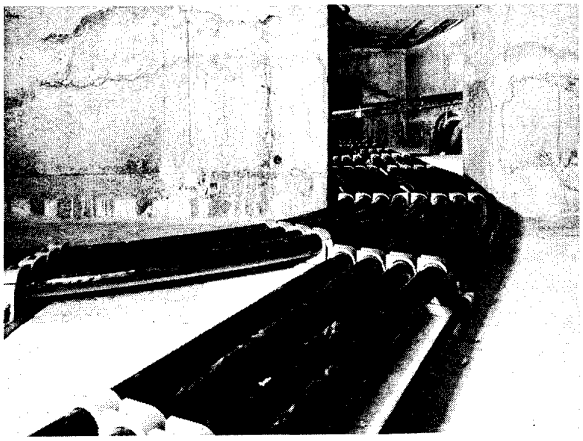
Domestic electrical meter boxes are made using dough moulding compounds of glass and resin and when fitted with a g.r.p. door provide a housing both mechanically and electrically strong.



The Hydraulic Water Ram in which the following components have been moulded from Maranyl A190 glass-filled nylon compound: Two end caps—non return valve body—bleed valve—spider and nut—trigger—pump body—compressor plates. (Acknowledgements, I.C.I. Ltd, Plastics Divn., Tatra Plastics Ltd. Hydraulic Water Ram Co. Ltd.)



Telephone miniature lever key with spring lifters moulded from Maranyl A190 glass filled nylon. (Acknowledgement: I.C.I. Ltd, Plastics Division, Plessey Telecommunications Group)



Some 40000 power cable supports made from Maranyl A190 Glass-filled nylon have been used to cleat over 17 000 yards of cable in the recently completed Blackwall Tunnel duplication under the Thames. (Acknowledgement: I.C.I. Plastics Division & Cablock Co. Ltd.)

Chemical

It has been estimated that approximately 2500 tons of polyester resin plus reinforcement were used in the chemical application field during 1967 indicating a strong and expanding market. It has proved difficult to give an accurate estimate of the reinforcement materials employed owing to the varied types of application and methods of use.

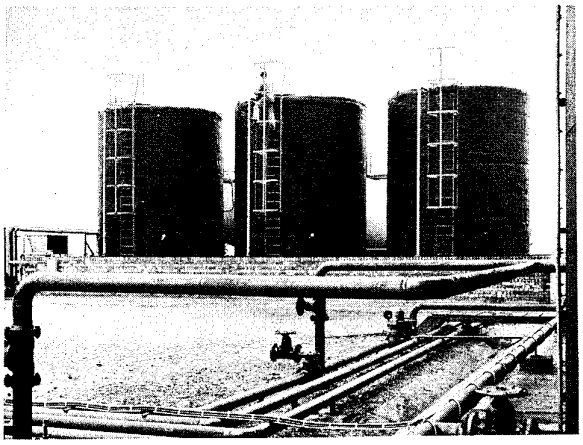
Reinforced plastics are being used regularly in the chemical and allied industries for such items as silos, pipe and ducting, tanks, vats, effluent disposal, chimneys, fume scrubbers, storage and mixing vessels, ancillary equipment and a certain amount of repair work.

Although the United Kingdom Processing Industry has to date been slow in applying the use of reinforced plastics it is encouraging to note that several of the larger companies are at last accepting them as a class of structural materials in their own right and that the true economic advantages of changing from the conventional materials are now being considered at the design stage.

The chemical industry is a major area where anticipated growth can be achieved and during the next few years we expect to see a realistic increase in the use of reinforced plastics as replacement for corrosion prone metallic structures.

A recent view of corrosion damage in the U.K. gives a cost of approximately £600 million annually and while corrosion is described as a natural phenomena it must be adequately resisted.

Glass reinforced plastics waterboxes are regularly being fabricated for modern Power Stations and are in use in places



Three g.r.p. tanks, each 13' diameter by 18' 2" high, (15 000 gallons) installed at Esso Agroservice, Warboys, Cambs. The tanks contain phosporic acid having a crystalisation point of 8°C. Designed and fabricated by Whessoe Ltd. (Acknowledgements: Whessoe Ltd. Applied Research & Eng. Co. Ltd.)

as far apart as Guyana and Cyprus. Many have been in successful service for up to eight years in the United Kingdom and more than three hundred waterboxes manufactured by C. F. Taylor (Plastics) Ltd. are currently being installed in one of the countries most modern Stations.

Miscellaneous

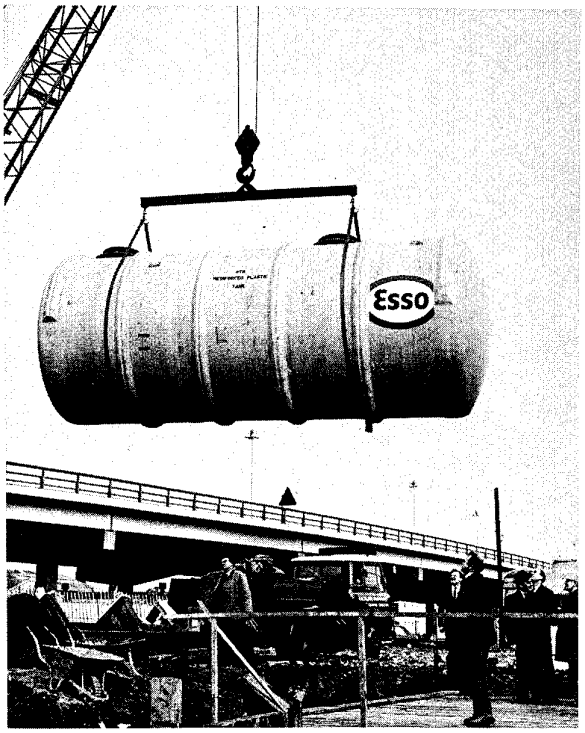
As a general assessment it has been estimated that approximately 6000 tons of glass reinforced polyester were used during 1967 to produce a wide range of general applications not covered in the detailed groups. It would be impossible to review the whole—it is therefore proposed to mention those which demonstrate the versatility of reinforced plastics:

Underwater research 'submarine'. (Courtesy W. and J. Tod Ltd. Lintott Engineering Ltd.)

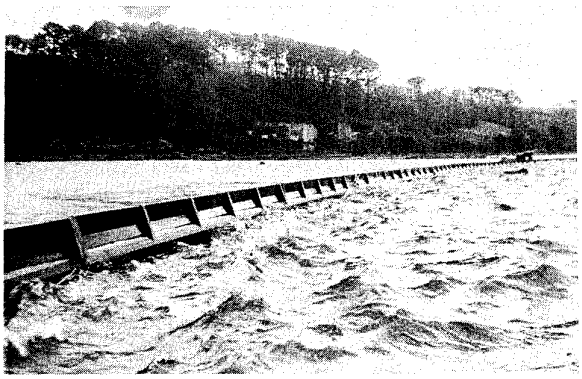
This two-man submarine is intended to cover all aspects of undersea work including seabed surveys, evaluating underwater mineral deposits, investigating undersea life and as a search and recovery vehicle. Apart from the steel pressurised crew chamber the rest of the structure is a glass reinforced plastics moulding, which houses the buoyancy tanks, air bottles, batteries and motor supports.

Osma Plastics who have been in production of cold water tanks since 1962 have produced more than a million g.r.p. tanks using the hot press moulding method. The smallest of ten gallon capacity weighs $4\frac{1}{2}$ lbs and has an hourly production rate of 28 by one operator. The 70 gallon tank weighs 21 lbs, production rate 20 per hour by two operators. Tank lids on single impression moulds are made at the rate of 42 per hour again by one operator. Also in regular production and approved by the major U.K. Water Boards are two sizes of hot water cylinders and their special water heating combinations which will be of prime use in industrial housing schemes schemes. Their extensive experience and advanced manufacturing ability enable this firm to produce industrial mouldings and sell them at a price of around 4/- lb finished moulding and even lower in certain cases. It has been stated that in 1967, the Osma production of reinforced plastics totalled some 1400 tons.

The Bristol Floating Boom designed for the protection of tidal estuaries, harbours and coastal waters against oil polution is fabricated in glass reinforced plastics. Each boom section comprises a 20' length of 10" diameter g.r.p. pipe, s sealed at each end to provide the buoyancy chamber and fitted with a 9" high ribbed fin and 12" ribbed skirt of laminated plywood. The boom was successfully tested at H.M. Dockyard. A typical example of usage was the installation of a 900' boom in the Helford River to protect oyster beds.



Underground petrol storage Tank. (Courtesy B.T.R. Reinforced Plastics Ltd.)



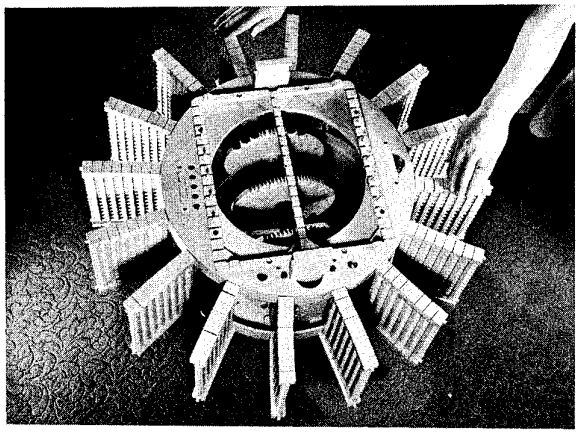
The Bristol Floating Boom. (Courtesy Bristol Aeroplane Plastics Ltd.)

B.T.R. Reinforced Plastics have successfully built a g.r.p. petrol tank for ESSO and which was installed at Kingston for evaluation. This tank has a capacity of 5000 gallons contained in two compartments of 3500 and 1500 gallons. Dimmensions— 19 feet long diameter 7 feet 6 inches. Weighing approximately 1800 lbs the tank was moulded in five sections using the contour spray method.

Aerial Support Tubes up to three feet in diameter and thirty-nine feet long-filament wound g.r.p. are giving excellent service. The wall thickness is a minimum for the strength resuirement and constant within a limit of 25 thousandths of an inch of the nominated wall thickness. The finish is designed for an estimated life of approximately 25 years.

Domestic oil fuel storage tanks are now under critical review and are expected to go into regular production. Comparative range of tests carried out against metal counterparts are most encouraging.

There are more than 140 components in this $28\frac{1}{2}$ inch diameter radar aerial coil assembly produced for Decca by Ferranti using Beetle dough moulding compound. Material chosen to provide dimensionally stable, mechanically strong mouldings with a low power factor.

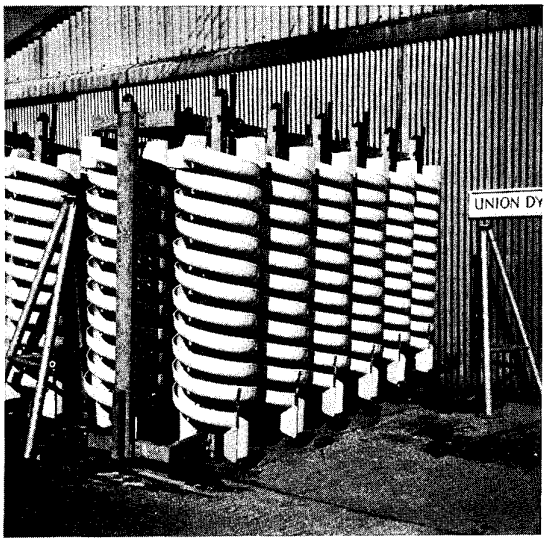


D.M.C. Radar Coil Assembly, (Courtesy Ferranti Ltd. B. I. P. Chemicals Ltd.)

Following several years of experimental work, Burton on Trent Corporation awarded a contract to Prodorite Ltd, to make glass reinforced troughs for installation in the Burton Sewerage Purification works. 30 feet long by 2 feet wide and three feet deep, the trough sections were joined together on site by Prodorite technicians, by bolting after coating the surfaces with an epoxy jointing compound. Altogether on site are more than 4000 feet of the g.r.p. troughing.

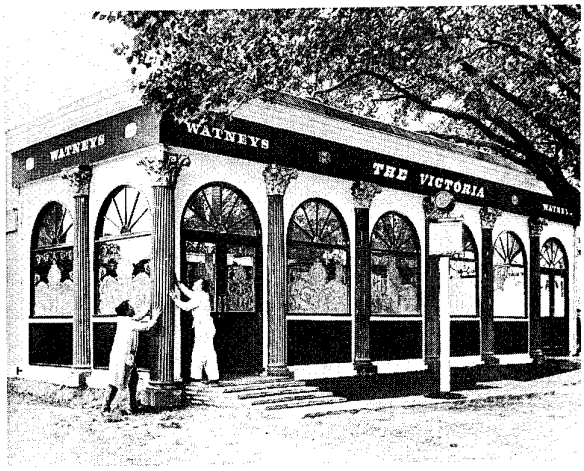
Glass Reinforced Plastics Troughs. (Courtesy British Industrial Plastics Ltd.)

At St. Ives Bay, Cornwall, a dredger owned by Coastal Prospecting Ltd. is scooping tin bearing sand from the sea floor. The g.r.p. spiral separators are installed on the dredger, enabling the sand to be dredged, partially concentrated and a large proportion of the waste discarded before the vessel returns to the shore treatment plant. The two feet diameter spirals are made by cutting and stretching a circular glass-fibre mould, giving one turn of the spiral. This then becomes the master mould and is used to make the remainder of the spirals. The light weight of g.r.p. permitting the separators to be installed on board means that fewer journies are made per ton of tin produced.



Glass Reinforced Spiral Separators. (Courtesy Union Dynamics Ltd and B.I.P. Chemicals Ltd.)

There are of course, many other important industrial applications including street furniture, silo's, trays, storage bins, observatory domes, fishing rods, swimming pools, road signs, motor cycle fairings, industrial trucks, battery boxes, bus shelters, sculpture and roofing ventilators to name but a few. Not to be overlooked in the elegant Victorian-styled public house which was built almost entirely of reinforced plastics and which is being sent to various parts of the world to promote exports at the Board of Trade exhibitions. Sixteen feet high with the main bar 48 feet by 40 feet, it can be erected and taken apart in ten days—thirsty work indeed!



In summary—The United Kingdom usage of reinforced plastics is relatively small and growth rate is likely to remain slow until the economic situation improves and other factors are resolved. Further mechanisation is necessary and processing technology and materials should improve. With mechanisation the use of pre-preg and D.M.C. will increase and a healthy growth rate can be predicted. It is expected that the use of reinforced plastics will continue to expand as a structural element in the construction field and will contribute to the building of trawlers and much larger marine craft.

There is obvious growth potential in chemical building and repair applications and this will be exploited. Reinforced thermoplastics present a challenge and useful potential in many spheres.

In addition to those examined, many of the major U.K. industries are looking critically into possible applications for reinforced plastics—and new engineering projects—in new markets, in addition to improved materials and techniques will be a deciding factor in determining the future growth.

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