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National Symposium on Polymers in the Service of Man

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June 9-11,
1980

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Industrial and Engineering Chemistry
American Chemical Society

Robert S. Shane
General Chairman

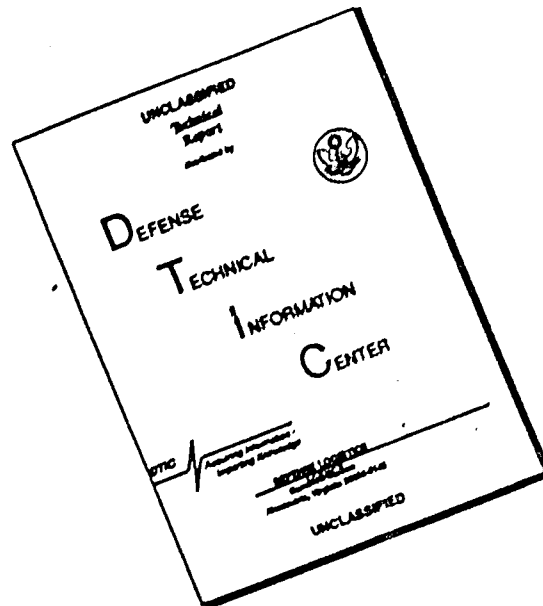
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Division of Industrial and Engineering Chemistry
American Chemical Society

SYMPOSIUM PROCEEDINGS (Available Papers)

POLYMERS IN THE SERVICE OF MAN

Honoring the Eighty-Fifth Birthday of Dr. Herman F. Mark

FINAL

AFOSR-80-0222

June 9 - 11, 1980

Carnegie Institution of Washington

1530 P Street, N.W.

Washington, D.C.

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TABLE OF CONTENTS

	<u>PAGE</u>
SESSION I -- <u>OVERVIEW</u>	
WELCOME AND INTRODUCTORY REMARKS, Robert S. Shane, General Chairman	
POLYMER SCIENTISTS RESPOND TO THE ENERGY PROBLEM, James D. D'Ianni	1
POLYMER SCIENCE IN EUROPE AND JAPAN, Charles G. Overberger	5
POLYMER DEVELOPMENT IN THE UNITED STATES, William J. Bailey	6
REMARKS, Herman F. Mark, Guest of Honor and Honorary Chairman	7
SESSION II -- <u>ENGINEERING PLASTICS</u> , Arthur M. Bueche, Session Chairman	
DEFINITION AND DESCRIPTION OF ENGINEERING PLASTICS BUSINESS, Glen A. Thommes	8
TRANSPORTATION AND ENGINEERING PLASTICS, Philip Weiss	13
GRAMS TO TONS (PLASTICS IN COMMUNICATIONS), L. Donald Loan	16
DURABLE CONSUMER GOODS AND ENGINEERING PLASTICS, Ralph S. Hagan	18
THE FUTURE OF ENGINEERING PLASTICS, Frank N. Kelley	21
SESSION III -- <u>CONVENTIONAL FIBERS</u> , Frans I.M. van Haaren, Session Chairman	
NEW HORIZONS FOR CELLULOSICS, Herbert L. Hergert	27
MODIFICATION OF FIBERS BY RADIATION GRAFTING, Vivian T. Stannett	32
FORTY YEARS OF MELT SPINNING, Frank S. Riordan, Jr. and James H. Saunders	35
RECENT DEVELOPMENTS IN THE OPTIMIZATION OF A MELT SPINNING PROCESS, Dusan C. Prevorsek and Young D. Kwon	44
SESSION IV -- <u>HIGH PERFORMANCE FIBERS</u> , David Tanner, Session Chairman	53
CARBON FIBERS, Roger Bacon	54
EXTENDED CHAIN AROMATIC POLYAMIDES, James A. Fitzgerald	58
POLYAMIDE-HYDRAZIDE AND COPOLYHYDRAZIDE FIBERS, W. Bruce Black	70
FIBERS FROM ANISOTROPIC MELTS, Donald R. Wilson and R. Sidney Jones	78
PROCESSING OF HIGH STRENGTH, HIGH TEMPERATURE POLYMERS, Thaddeus E. Helminiak	86
INORGANIC ALUMINA FIBERS FOR REINFORCEMENT OF METAL CASTINGS, Ashok K. Dhingra	88

SESSION V	--	<u>COMPOSITES</u> , John A. Parker, Session Chairman	
		PLASTIC AIRPLANES, Michael J. Salkind	124
		CARBON-FIBER TECHNOLOGY, C. Frederick Hansen and John A. Parker	125
		ADVANCED RESIN SYSTEMS FOR GRAPHITE EPOXY COMPOSITES. William J. Gilwee and A. Jayarajan	131
		IMPROVING THE FRACTURE RESISTANCE OF COMPOSITE LAMINATES, Frank W. Crossman	136
		ADVANCED COMPOSITES FOR AUTOMOTIVE APPLICATION, C.L. Hamermesh	137
		SPATIAL DISTRIBUTION OF VOLATILE COMPOUNDS IN GRAPHITE COMPOSITES, Michael A. Grayson, Clarence J. Wolf and Demetrius A. Kourtidis	141
SESSION VI	--	<u>COATINGS</u> , R. Dowbenko, Session Chairman	
		TSCA AND THE PAINT AND COATINGS INDUSTRY, Douglas G. Bannerman	148
		COATINGS FROM ACRYLIC POLYMERS, Werner S. Zimmt	152
		ADVANCES IN LATEX TECHNOLOGY, D.R. Bassett and Kenneth L. Hoy	156
		CROSS-LINKING AGENTS FOR WATER-BORNE AND HIGH SOLIDS COATINGS, Werner J. Blank	162
		RECENT DEVELOPMENTS IN OXIDATIVE POLYMERIZATION, William D. Emmons	167
		FLUORINATED POLYMERS AND THEIR APPLICATIONS, James R. Griffith	173
		RADIATION CURABLE COATINGS, Vincent D. McGinniss	175
SYMPOSIUM LUNCHEON	--	Edward G. Jefferson Speaker Capital Hilton Hotel, Wednesday, June 11, 1980	
		OUR DEBT TO THE POLYMER PIONEERS, Edward G. Jefferson	181

POLYMER SCIENTISTS RESPOND TO THE ENERGY PROBLEM

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ABSTRACT

The polymer industries have been faced with higher energy and materials costs since the abrupt increase in the world petroleum price in 1973. It was suddenly realized that the supply of petroleum was not unlimited, and serious efforts must be given to reducing the cost of energy and to the timely development of alternate energy sources. We will focus on the transportation market, which consumes 25 per cent of the total energy in the U.S.A., and review the impact of energy problems on rubber and other polymers used in the transportation field.

We will summarize progress in natural and synthetic rubbers as well as plastics, and the effects of the energy outlook on their development, production, and use. Changes in tires and other polymer products, and the impact of new standards of performance on the automobile, will be examined. Finally, we will attempt to assess future problems of the rubber and related polymer industries and how they can best adapt to the limitations imposed by higher energy costs.

BACKGROUND

Energy and materials costs in the polymer and automotive industries rose rapidly in 1973 with the abrupt increase in the world petroleum price. There was the sudden realization that the supply of petroleum was not unlimited, and that serious consideration must be given to the cost of energy and to the timely development of alternate energy sources. Our attention in this paper is focused mainly on the transportation market, since this is of primary importance to the rubber industry, with which I am most familiar. However, transportation consumes only 25% of the total energy in the U.S.A., with 42% consumed by industry and 33% by residential/commercial customers. In spite of future shortages looming on the horizon, the U.S. petroleum industry supplied oil products in 1979 at the rate of 18.9 million barrels/day, nearly half of which was imported. The Petroleum Industry Research Foundation has forecast a decline in oil demand to 17.8 million barrels a day in 1990.

We will examine natural and synthetic rubbers and other polymers, and the effects of the energy outlook on their production and use. We will look at changes in tires and other polymer products, and changes in automobiles to conform to new standards of performance. Finally, we will take a look at the over-all energy picture in an attempt to anticipate future problems of the polymer industry, and the responses of polymer scientists and engineers to these challenges.

NATURAL RUBBER

The energy outlook is generally favorable to

natural rubber since its production occurs by photosynthesis, a non-polluting source of solar energy. Although availability of land for natural rubber production is adequate today, expanded production may be limited by the need to increase production of food crops.

Since natural rubber is rather labor intensive, its costs will rise because of the expected demand by workers for an increasing standard of living. Costs for fertilizers and other required chemicals, land, and transportation will also increase.

Offsetting at least a portion of these higher costs will be the continuing increase in productivity on rubber plantations. This has come about through improvements in breeding, selection, grafting, tapping and yield stimulation, and by replanting. The average annual yield from Malaysian rubber plantations, for example, increased from about 500 pounds per acre in 1950 to 1,350 pounds in 1975. An average yield of 2,000 pounds is obtainable, growers believe, and experimental plantings have yielded up to 6,000 pounds. A ready market exists for all the natural rubber that can be produced today and in the near future. Goodyear has announced expansion plans costing \$6 million in Sumatra and \$10 million in Brazil, the latter due to successful efforts to control the South American leaf blight disease. The results have been successful enough to encourage the Brazilian government to plan a program for greatly increased production. Other companies have also announced plans to increase the production of natural rubber.

Guayule, another source of natural cis-1,4 polyisoprene, has once again come into the picture as a possible source of natural rubber to augment the production from the *Hevea brasiliensis* tree. In Saltillo, Mexico, the Mexican government operates a pilot processing plant based on the harvesting of wild guayule shrubs. Goodyear has an experimental planting at Litchfield Park, Arizona, and has built winter radial tires of guayule which passed Department of Transportation's high speed and endurance tests. The U.S. Government has approved the National Latex Act which is to provide \$30 million for the study and development of guayule in the southwestern part of the country in the period 1980-1983, but funds have not yet been appropriated.

Forecasts for rubber production and consumption indicate a growing market for both natural and synthetic rubbers. Natural rubber is a renewable resource and has outstanding physical properties, such as high green strength and building tack, high resilience and low heat buildup. Larger amounts of natural rubber will be needed in the future. However, the rapid development of synthetic rubber types continues to expand the market for special elastomers and results in their taking over a larger percentage of the market.

In the U.S.A., the natural rubber share of total rubber consumption has increased from 21.6% in 1971 to 23.9% in 1978, with radial tires accounting for much of the increase. A radial auto tire can require twice as much natural rubber as a conventional tire, and some radial truck tires use three times more natural rubber.

Natural rubber experts believe that natural rubber could regain a 40% share of world markets by 1985, but synthetic rubber proponents suggest that the natural rubber world share could drop below 30%. However, actual sales of natural rubber are expected to expand at the rate of 4%/year through 1985 as the demand for all rubbers continues to increase. Speaking at the German DKG Jubiläumstagung Kautschuk, Dr. Leonard Mullins said that the natural rubber industry "will remain for the foreseeable future the cheapest source of rubber elasticity".

SYNTHETIC RUBBER

The synthetic rubber industry, as well as the polymer industry generally, has felt the impact of higher monomer costs for petroleum-derived butadiene, styrene, acrylonitrile, ethylene, propylene, isobutylene, isoprene and other monomers during the past seven years. Further increases can be expected in the next five years, although at a slower rate. Steam crackers will supply larger amounts of the major monomers.

Supplies of monomers for synthetic rubber appear to be adequate until at least 1985, although costs will continue to rise because of increased feed costs, manpower and energy costs, and capital costs for new facilities, as well as added expenses for health and environmental reasons. D. H. Francis of Goodyear reported rapidly escalating costs for energy in the production of SBR and solution polybutadiene, and still higher costs in the future in spite of measures to reduce energy requirements. For example, the energy costs in 1970 to produce a pound of emulsion SBR was 0.17¢, which rose to 1.1¢ in 1977 and will rise to at least 3.0¢ by 1990.

The impact of increased energy costs has also stimulated work on new forms of synthetic rubber which require less energy to process into the final rubber product. They include carbon black masterbatches and new forms such as crumb, easily broken bales, powder and liquid forms.

Thermoplastic elastomers can be injection molded or otherwise treated as thermoplastics. Liquid types such as the urethanes have developed new markets through the use of the LDM (reaction injection molding) processing techniques.

Synthetic polyisoprene will continue to play an important role even though it competes directly with natural rubber. The improvement in green strength of SBR and polyisoprene will make them more competitive with natural rubber in tires.

COMPOUNDING AND PROCESSING OF RUBBERS

The rubber chemist continues to search for scorch retarders and safer accelerators so that rubber stocks can be vulcanized more quickly at higher temperatures. Continuing advances will be made in more efficient vulcanization systems to reduce energy costs.

Now, less energy-intensive processing techniques for rubber stocks are being thoroughly considered. Many rubber products are now made by injection molding to reduce the time and energy costs involved in curing.

Substantially less energy is required to mix powdered rubber compounds than bale rubber compounds. Powdered rubbers, as compared to bale rubbers, present maximum surface area for incorporation of the compounding ingredients and thus require decreased power consumption and less mixing time to reach optimum dispersion. If the carbon black is masterbatched with the powdered rubber, greater energy savings are possible; but the additional energy required to produce the masterbatch must be considered in the total energy equation.

Even larger energy savings should result from the use of powdered rubber by completely eliminating the banbury or the mill in favor of continuous processing equipment such as used for processing thermoplastics. Processing trials have demonstrated the feasibility of processing powdered rubber compounds to produce an extrudate suitable for subsequent fabrication or direct cure.

Another study on energy requirements by T. E. Rogers and W. O. Sasamann of Goodyear showed that LDM urethane slab stock requires one-third the energy

which is needed to produce an equivalent quantity of vulcanized rubber slab stock. "Cold" or HR molded urethane foam can be made with only one-fifth the energy required for an equivalent quantity of "hot" urethane foam.

CHANGES IN THE AUTOMOBILE TIRE

The emphasis today is on smaller tires for lighter weight vehicles, longer wearing tires, tires with less rolling resistance to improve gasoline mileage, and the modification or elimination of the spare tire and wheel to reduce weight and save space. The downsizing of tires is related to the reduction in weight of the newer cars. The increase in tire mileage is a continuation of the long term efforts of the rubber industry to provide constantly increasing life as we have progressed from the bias to the belted-bias and, finally, to the radial type construction which is rapidly becoming the standard tire today.

Radial truck tires are also rising rapidly in popularity in the U.S.A. because they "last longer, run cooler and provide better fuel mileage than bias-ply truck tires because of reduced rolling resistance", according to a recent Goodyear announcement. Radials captured about 18% of the market last year; but by 1983, it is expected that more than half the tires on new trucks, and almost 40% of truck tires sold in the replacement market, will be radials.

The automobile tire market will grow more slowly in the future because of such factors as reduced speed limits and delayed purchase of longer wearing replacement tires.

Gas-saving tires save energy because their reduced rolling resistance permits more miles per gallon of gasoline to be achieved. Goodyear has developed the so-called Elliptic tire which cuts rolling resistance up to 34% compared to conventional radials and puts up to 25 more miles in each tank full of gas.

Other rubber companies all over the world are also working on new designs for gas-saving tires.

The spare tire is a target for energy saving because it and the accompanying wheel represent considerable weight and space in the vehicle. One solution is the use of mini spares or crutch spares. Another is to provide a protective device within the tire upon which the car can ride when the tire is deflated. A more recent development is the Goodyear flat-proof tire which has the ability to maintain its load bearing shape even with a one-foot section removed.

Other major rubber companies have also been very active in the development of tires with run-flat capabilities.

Cast urethane pneumatic tires have recently enjoyed a revived interest as a result of the activities of the Polyair Company, Kittsee, Austria, and a joint venture with B. F. Goodrich and others. Many other rubber companies have already expressed interest in cast urethane tires including Goodyear with work in the late 50's and early 60's and Firestone in 1970. Material costs for the urethane tires are substantially higher than for the conventional tire, but these costs may be partially offset by processing, energy, capital investment and weight advantages. Initial markets being studied include small industrial tires and agricultural tires.

Still another possibility for the production of certain types of tires with low energy output is the injection molding of thermoplastic elastomers, such as PBT (polybutylene terephthalate), SBS block polymers, and TPU (thermoplastic urethane).

EFFECT OF ENERGY OUTLOOK ON AUTOMOBILES

The automotive industry must lower the average weight of its vehicles in order to attain a fleet average of 20 miles per gallon of gasoline by 1980 and 27.5 miles per gallon by 1985. If the target is to be reached, the average American car must lose about 1,200 pounds.

Substantial progress has already been made in reducing the weight of the automobile by use of high strength alloy steel and aluminum. For example, in the Chrysler Omni/Horizon the outer hood panel of high strength steel weighs 13% less than a panel of conventional low-carbon steel. General Motors is working with a high strength low-alloy steel as a wheel material which could reduce wheel weight as much as 25%.

Aluminum is continuing to make deep inroads into the automotive market. According to some industry predictions, the average 1980 model will contain up to 200 pounds of the metal, a figure which could rise to 400 pounds by 1985.

In 1976 a study was made by International Research and Technology, Inc., under contract to the Environmental Protection Agency, on the weight and materials that would be used to manufacture automobiles in 1980 and 1990. The 1980 composite car, according to this study, will contain 144 pounds of rubber and 188 pounds of plastic polymers, or 11.8% of the total weight of the vehicle. The composite 1990 car will contain 128 pounds of rubber and 231 pounds of plastic polymers, or 14.2% of the vehicle weight.

In another study by DeBell and Richardson, it was noted that plastics consumption in domestic autos and other motor vehicle applications amounted to 1.6 billion pounds in 1976, a figure which is expected to rise to 2.9 billion pounds by 1980. By 1985 average consumption of plastics could rise to 350 pounds per car. In another estimate the average 1978 U.S. car is said to employ around 180 pounds of plastics.

The importance of plastics to the automotive industry has been well stated by Robert M. Gerrity, General Manager of Ford Motor Company's Plastic, Paint and Vinyl Division, and I quote, "The challenge brought by the revolution in the role of plastics is to step up to a dramatic materials change and to make the shift to plastics as expeditious and orderly as possible. Not since the Movie 'The Graduate' -- when a friend put his arm around young Dustin Hoffman and whispered in his ear, 'Plastics, my boy' -- has either the academic community or the automobile industry had such an opportunity." This statement can be expanded to include the polymer industry, which also has an exceptional opportunity to expand its application in the automotive industry.

Although the estimates from different sources vary as to amounts and types, there is no question that plastics will play a major role in the weight-saving war being waged by the automotive companies.

The following materials were highlighted at a 1978 Chemical Marketing Research Association meeting in Detroit: Polypropylene, high density polyethylene, nylon, polybutylene terephthalate polyester, sheet molding compound, polycarbonate, ABS, and polyurethanes, especially for automotive exterior parts using RIM technology.

Urethane products for automobiles include seat cushions, instrument panel covers, protective knee pads, snap-on headliners and urethane covered steering wheels. For car exteriors RIM urethane parts include fenders for front and rear. If the RIM system is reinforced with glass fibers for higher modulus (GRIM), some possible applications are fenders, door panels and hoods. Some 1980 models of the Ford Motor Company will be equipped with such front fenders to reduce

weight, eliminate corrosion from salt exposure, and improve impact resistance.

Large amounts of FRP (glass fiber-reinforced plastics) are used in the automotive industry. Graphite fiber composites are being investigated, but are too expensive now. However, Ford Motor Company has demonstrated that, by using such composites as structural parts for the chassis and body as well as the power train, a prototype car weighing about 2,750 pounds can be built as compared to the 4,000 pound car with conventional materials.

Thermoplastic elastomers for automotive applications do not require vulcanization to develop properties characteristic of cured rubbers. They can be processed by high speed plastic techniques, such as injection molding, extrusion and blow molding. Moreover, scrap can be reground and reprocessed without difficulty. The principal types used today are the styrene-butadiene block copolymers, thermoplastic polyolefins, thermoplastic polyurethanes, and polyester copolymers.

An air spring made of rubber and aluminum will provide efficient and versatile suspension in light-weight vehicles. According to F. C. Melby of Goodyear, the air spring weighs less, requires less space, improves small car ride and handling with adjusted load capacity and controllable spring rate, and adds to safety with constant vehicle leveling.

Goodyear has also developed a "serpentine" drive belt system for automobiles that could reduce a car's weight about 100 pounds and increase gas mileage by as much as 0.5 miles per gallon. It features a single belt instead of the usual three to drive all under-the-hood accessories, and offers a possible engine space savings of almost an inch.

Another favorable aspect of the increased use of rubber and plastics in cars is the fact that larger amounts of adhesives will be needed. For example, the Goodyear Pliogrip system, which eliminated the need for shot blasting in structural bonding, is widely used in auto assembly for fiberglass parts. It cures in air with a water tight seal and, in some cases, gives plastic parts of greater strength than the steel they replace. The adhesive is used in fabricating tail gates, car tops, sun roofs, hoods, truck fenders and hood assemblies, and interior trim on automobiles.

Recreational vehicles and trucks, as well as passenger cars, will be under pressure to reduce weight and increase miles per gallon of gasoline. But the demand for heavy duty tires for trucks, buses, and other heavy equipment should continue to increase substantially to satisfy the needs of our growing economy. Production of truck tires in developing areas of the world will grow at even a faster rate than in this country so that rubber demands, especially natural rubber, will continue to grow at a faster rate than for passenger tires.

PROSPECTS FOR INDUSTRIAL RUBBER PRODUCTS

While the market for tires, especially passenger tires, will grow at a slower rate in the future, more substantial growth can be expected in industrial rubber products.

Conveyor belts, hose, and other rubber products will be needed in greater quantities for mining coal and other natural resources. Offshore oil rigs are a growing market for rubber in such applications as hose and belting, dock fenders, drive belts, gaskets, sea bocus, seals, and diaphragms. These products use such rubbers as SBR, polyisoprene, neoprene, nitrile rubbers, EPDM, and urethanes. According to the U.S. Department of Commerce, the use of oil field machinery is expected to increase at the rate of 8.5%, compounded annually from 1976 to 1985.

D. W. Holmes of Du Pont estimates the greatest

growth areas in the next decade will be in the non-automotive area. This includes rubber products for the containment and transportation of water, insulation of wire and cables, exterior trim and repair of automobiles, food protection, and in construction.

ALTERNATE SOURCES OF ENERGY FOR THE FUTURE

While there is no immediate danger of running out of current sources of energy, such as petroleum, the dramatic increase in price of petroleum in 1973 dramatized the fact that this fossil source will eventually diminish and continue to increase in cost. Other energy sources such as coal and nuclear power should be developed as rapidly as possible.

In the longer run, solar energy will become the ultimate source, and much attention has already been given to tapping this source of energy through the utilization of green plants, or biomass. Melvin Calvin of the University of California, Berkeley, has talked about "Green Factories" or the use of green plants as a source of energy. Certain plants such as Euphorbia lathyris contain substantial quantities of hydrocarbons in emulsion form which could serve as a replacement for petroleum. The yield and process of extraction must be improved if its cost is to be competitive with that of petroleum.

Alcohol obtained by the fermentation of sugar from sugar cane is being mixed with gasoline for use as a motor fuel in Brazil. A similar program at the University of Nebraska is studying the production of "gasohol" with alcohol produced from corn. Texaco has just announced it will start test marketing "gasohol" in selected areas, as a blend of 90% lead-free gasoline and 10% ethanol. The federal government is encouraging the use of "gasohol" by exempting it from the four-cents-a-gallon federal excise tax on gasoline. Still further down the road is the possibility of an energy system to produce hydrogen obtained by the photocytic splitting of water into hydrogen and oxygen. If a satisfactory catalyst for this photolysis can be developed, we would have a limitless supply of energy from water.

I am optimistic about the future as far as energy in the polymer industries is concerned. There may be short-term crises, but I agree with the findings in the report "Energy: The Next Twenty Years", sponsored by the Ford Foundation and prepared by Resources for the Future, Washington, D. C. It says there will be no future shortages or gaps in supply if U.S. energy policy and planning are improved and if prices are allowed to rise to a more appropriate level. Pricing at the world level is a better way of rationing available supplies than any artificial control system, in my opinion. Private enterprise will solve our energy supply problems, given the proper economic incentives.

A report to President Carter by the National Transportation Policy Study Commission indicates the automobile will overcome rising operating costs to remain the undisputed king of the road at least until the end of the century. There will be no shortages of fuel for transportation costs, provided we are willing to pay the increased costs. In 1975, the automobile accounted for 86% of intercity personal travel. By 2000 it will be 75 to 84%, depending on the rate of growth selected. Automobiles and airlines will retain their 98% market share of intercity passenger miles traveled.

Also encouraging is the recent Worldwatch Institute position paper by Christopher Flavin on "The Future of Synthetic Materials: The Petroleum Connection". He states that despite their nearly total reliance on oil and natural gas feedstocks, "synthetic materials really do have quite a bright future". He goes on to say, "There is a great

potential for synthetic materials to be used in various ways that actually save energy". Synthetic rubber, synthetic fibers and plastics currently require only 3% of the world's oil and natural gas - a figure that will rise to 6% in the 1990's - but they must depend on this raw material source. Coal is an alternate long-term but expensive source and Flavin finds few industry experts who view coal as "a cheap source of feedstocks for synthetics even after 2000".

In conclusion, the energy outlook is challenging the polymer industry to solve some serious problems in the next decade. I am optimistic that adequate sources of energy at affordable cost will be developed and that the polymer and automotive industries will continue to flourish for many years. The polymer industry can be proud of its contributions to the modern economy and will surely continue to play a significant role in improving the standard of living for everyone. Polymer scientists and engineers have worked hard and successfully in coping with the problems generated in the 70's, and will undoubtedly make major contributions to solving the difficult material and energy problems of the 80's.

POLYMER SCIENCE IN EUROPE AND JAPAN

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ABSTRACT

There is a large group of research centers primarily at universities, but industrial laboratories as well, carrying out research in basic polymer science. This lecture will attempt to present a few highlights of research activities in a number of universities in Europe and Japan.

A brief summary of statistics on centers of polymer science and engineering in Europe will be presented.

(Text was not provided for publication.)

POLYMER DEVELOPMENT IN THE UNITED STATES

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ABSTRACT:

Polymer science is alive and well in the United States. Our journals in the field of polymers are exceptionally strong and attract a very high number of papers by foreign authors. Foreign students and post-doctorates still come in large numbers to study polymer science in the U.S. The award of the Nobel Prize to Dr. Paul Flory for his work in polymer science gave great encouragement to the field. The establishment of new polymer institutes in polymer science and engineering in such schools as the University of Massachusetts, Case-Western Reserve, and the University of Akron complement such traditional centers as the Polytechnic Institute of New York and the College of Forestry in Syracuse. Our industrial firms still are the world's leaders in the production of polymers although our lead in this area is decreasing.

One of the very negative aspects in the polymer field in the U.S. has been the deemphasis of polymer chemistry. Most of the prestige chemistry departments in the U.S. have eliminated polymer chemistry from their curriculum and have no polymer chemist on their staff. While many of these universities have polymer programs in chemical engineering, material science, or separate institutes for polymer science, there is essentially no polymer chemistry available within the department of chemistry.

(Text was not provided for publication.)

REMARKS

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Thank you.

I'm sure you all understand that feelings of very warm gratitude, of deep appreciation are now uppermost in my mind. Together with the feeling of humility because you know and I know that much of what I have done was not done by me but by a large number of devoted and able collaborators and associates. Of course my gratitude is mainly due to Bob Shane and Eli Pearce, the chairmen of this meeting; to all the speakers; and to all of you who were so kind to come. I think our joint gratitude also is to our country because you look at this Symposium: its speakers, its chairmen, its topics. Anything of this kind could not be organized in any other country. In fact it could not even be organized in any combination of other countries. And so such a Symposium really is an unusual and invaluable birthday present. You know there are standard birthday presents. There are flowers, there is Scotch, there are cigars, there are wrist watches, there are all kinds of things. This is unique.

I have already a pilot planned run of such a Symposium in New York a few weeks ago, also organized by Eli Pearce and by Herbert Morawetz. It was a family affair. Now this is a national affair. I have only one birthday present which is equal in its uniqueness and that was when I was 80 years old and I went to Israel and we had a celebration of my 80th birthday. They gave me a forest. A forest which contains 80 trees in the domain of the Weitzman Institute. And of course they had planted those trees for that purpose. They're not very large, they're about that large. Last year I went there, my God. Oh well, they'll keep on growing even when there will be no birthdays for me any more and they will become larger and larger. And when I got this, when Ephraim Katchalski gave it to me he said, well at least this is a birthday present which you can't carry away. Well this is a birthday present which I can't carry away either. We all are benefiting by it.

Now the topic is Polymers in the Service of Man. And you realize that this is a very large subject. And in fact when the Symposium was organized it was realized that not all branches can be handled, not even in three days, probably it would take a week or more. And therefore what I would like to do in five minutes is to mention a few additional areas where polymers are extremely active and important in the service of man which are not included today, tomorrow and after tomorrow. And this is really whatever we have to do with bio-polymers with polymers directly interfering, helping, assisting, health, well-being of humanity of all of us; maybe some medical treatments and others. I have a few slides but in view of the time I think I could just as well tell you of what it is about. I think the most important areas in the assistance of polymeric materials in biology, in bio-engineering, in medicine; are two.

One is polymeric delivery systems of drugs because the tendency to enter this field successfully has actually sparked the synthesis of a large number of new

polymers; new polymers which eventually if put somewhere on the skin with a tape would deteriorate gradually, they would either decompose, they would be bio-degradable or they would be bio-erodable and permit the drug, liquid or fine powder to enter the body, our system, through the skin. Similar polymeric materials can be prepared in such a manner that they are bio-degradable, for instance any standard polyester which contains a few percent glycolite groups will degrade under atmospheric conditions. Packaging materials produced from such films would therefore automatically disappear within a few weeks just like paper or other natural polymers. Well you know a lot of work is being done and the elaborate and extensive research on bio-degradable and bio-erodable polymers is another big area of service to medical treatments.

Another field which I wanted to mention has more to do with bio-engineering, if you want to call it that way, particularly with the industry of fermentation. These are the immobilized enzymes. Again some 25 years ago when Ephraim Katchalski worked at our Institute, Charlie Overberger and Murray Goodman at that time were anxious to produce synthetic polymeric materials with pendant reactive groups, so that one could use synthetic polymeric materials as drugs. And if the polymer chain would somehow see to it that the active material gets in the right place in the system. Well when Ephraim Katchalski was there he said well that's very nice and that's very interesting but why don't we try to combine enzymes with synthetic polymers rather to replace them by synthetic polymers. And really that was the origin of his work immobilizing polymers. McLaren was at that time at the Institute. He worked among the same lines and as you know this is today a big industry. Besides of the fact that it is a very interesting research area, it's a big industry. The fermentation industry in many instances now utilizes the success immobilized enzymes or immobilized other biologically active substances. So this is another branch a special Symposium probably would be needed in order to bring our attention to all its present ramifications and to its present success.

So this is really; those are the remarks. I would like to conclude these remarks again by expressing my deep appreciation, my warm gratitude to all those who have helped the Symposium to start and to all those who will help it today, tomorrow and after tomorrow to succeed.

Thank you very much.

DEFINITION AND DESCRIPTION OF ENGINEERING PLASTICS BUSINESS

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ABSTRACT

Engineering plastics are those high performance resins which tend to replace nonplastics materials, often metal, in durable goods.

Several factors have had major influence on the historical development of these materials and on their use. The history will be briefly traced but major emphasis will be placed on the factors driving the growth of engineering plastics in today's climate. For example, the tight energy supply; engineering plastics require less energy than metals to produce, and also often save energy in their end uses. A second factor is a favorable cost position vs. die cast metals. Another factor is the broad range of materials available today, each with unique combinations of properties. Finally, designers have demonstrated increasing ability to use the special properties of engineering plastics to eliminate parts, save costs, and provide durable goods products that are unique.

All of these factors contribute to a healthy business climate for engineering plastics, now and in the future.

TEXT

This paper presents an overview of the engineering plastics business and an understanding of how it fits into the total plastics industry spectrum. Other session papers will review the application of engineering plastics in transportation, information technology, communications, electronics, and durable consumer goods.

Most of the examples I use are from the Du Pont Company. I think you'll agree we are all more comfortable discussing products directly related to our own experience.

To effectively accomplish my task, let's begin with a definition of engineering plastics.

The definition used by George P. Foy of the Chemical Business Development Company at an ACS engineering plastics symposium back in 1969 remains about the best one I know. As Mr. Foy put it, "Engineering plastics are those which possess physical properties enabling them to perform for prolonged use in structural applications, over a wide-temperature range, under mechanical stress, and in difficult chemical and physical environments." After 11 years, I think that's still an effective general definition.

Types of Plastics (Examples)

Specialty Plastics

Fluoropolymers ■ Polyimides ■ Polyaramids

Engineering Plastics

Nylon ■ Polycarbonates ■ Acetal Resins

Intermediate Plastics

ABS ■ Acrylics

Commodity Plastics

PVC ■ Polyethylene ■ Polystyrene ■ Polypropylene

Fig. 1.

Figure 1 gives you a feel as to where engineering plastics fit in the total spectrum of polymers utilized in the plastics industry from a volume/selling price standpoint.

At the top are the low volume (1M-20M lbs/yr), high cost (\$5-\$40/lb) ultrahigh performance materials -- such as fluoropolymers and high-temperature aromatic polyimides and aramids -- frequently referred to as "specialty polymers." These resins have special characteristics such as outstanding electrical resistance, chemical inertness, and high-temperature strength. Most are expensive to produce, but because of high value-in-use can command a premium selling price.

Next come the engineering plastics with selling prices in the \$1-\$2 per pound range and annual volumes of ten to several hundred million pounds.

I've then listed what I call the "intermediate" plastics -- ABS and acrylics. These products cannot be totally classified as either engineering plastics or commodity resins since they exhibit characteristics of both groups. Selling prices are in the \$0.50-\$1 per pound range and volumes exceed one billion pounds per year.

Finally, we have the least expensive, but high volume "commodity" resins, ranging from \$0.35-\$0.50 per pound. Sales of individual polymers in this category range from 500 million on the low side to over ten billion pounds per year on the high end.

Engineering Plastics

- Nylon
- Polycarbonates
- Modified Polyphenylene Oxide
- Acetal Resins
- Polyesters
- Polysulfone
- Polyphenylene Sulfide

Fig. 2.

While commodity-type polymers offer distinct cost advantages, engineering plastics, such as those listed in Figure 2, generally offer advantages in rigidity, impact and abrasion resistance, high-temperature strength, dimensional stability, and chemical resistance. Frequently, it's an improved balance of these properties that makes them useful in engineering applications where components are redesigned to take advantage of the special combination of properties that each engineering plastic has.

This group of polymers has been replacing and extending the use of metals, wood, ceramics, and other structural materials at a significant rate for the past 25 years. They have grown at 21 percent per year over that period, and a growth of 10 - 12 percent per year is projected to continue. By contrast, the principal metals with which they compete are expected to grow at about two percent per year. Priced from between \$1 to \$2 per pound, approximately 800 million pounds of engineering plastics were sold last year.

Non-Ferrous Metal Castings vs. Engineering Plastics 1960-1986

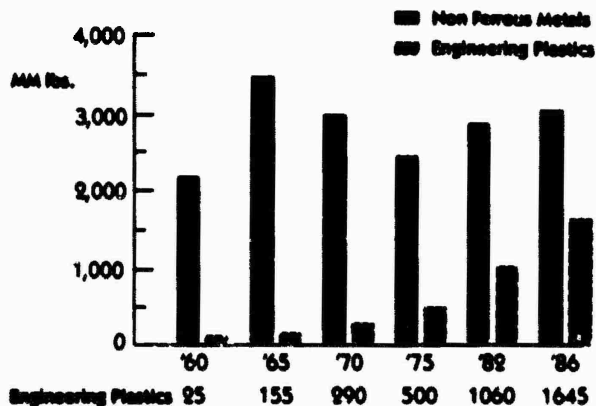


Fig. 3.

Figure 3 shows the growth of engineering plastics and nonferrous metal castings since 1960. Plastics have grown from two percent of the market in 1960 to about 25 percent today, and we project that engineering plastics will account for more than one-third of the market by 1985.

Hydrocarbon Feedstocks and Energy Cost Index 1969-1979

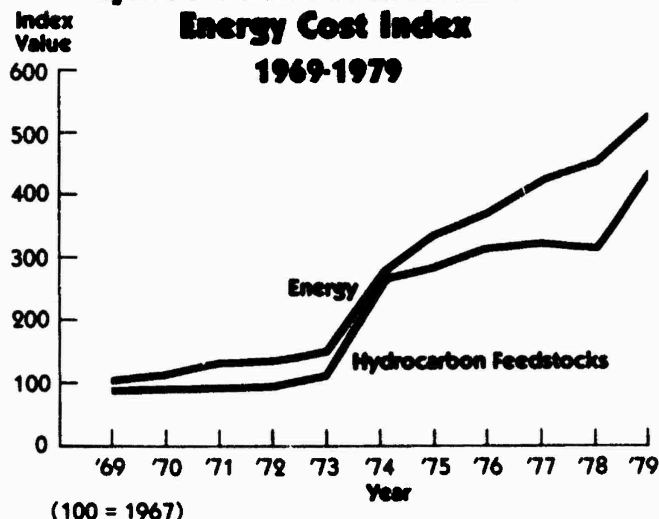


Fig. 4.

One major reason for the growth of the plastics business in general, and engineering plastics in particular, is the soaring price of energy. Figure 4 graphically portrays what has happened to energy and hydrocarbon feedstock costs over the past ten years. We project this trend will continue for the next decade as demand for available fuel resources continues to grow.

It's interesting to note that at the 1969 symposium, which I mentioned at the outset, the speakers made no mention of the effect of energy costs on engineering plastics. But how could they have known then of the oil embargo that was to come four years later? The point is that the external environment, over which we have little or no control, is a major factor in the development of our industry. We have to be sensitive to that environment in the area of research and development, as well as from a marketing point of view.

It's obvious that the current environment, given its energy implications, is having a significant impact on the plastics industry. That's because plastics differ from most other major materials in that they not only require energy to process the raw materials into finished product, but also require a form of energy (petroleum products) as raw materials. Despite this, energy analyses show that plastics are one of the most efficient uses of oil and natural gas. In many cases, the total quantity of the energy required to make plastic products is less than the total energy required to make the same products of nonplastic material.

Energy Requirement

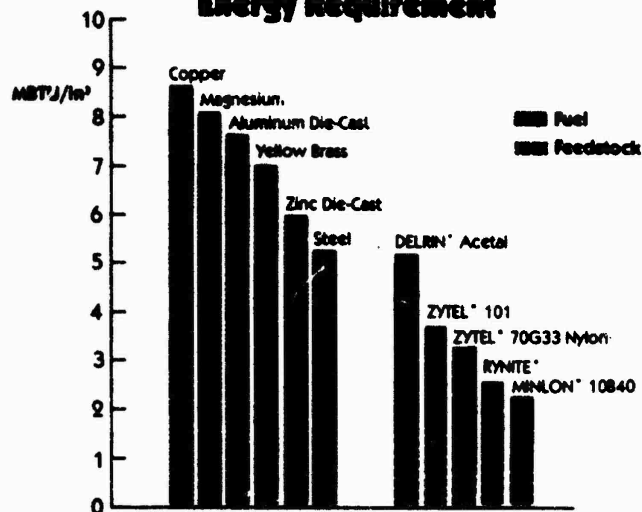


Fig. 5.

Figure 5 compares the total energy requirement per unit volume of material for representative Du Pont engineering plastics with competitive metals. The data is reported in thousands of equivalent BTU's per cubic inch.

The polymers I have chosen include: Delrin® acetal resin, an unfilled and a glass reinforced Zytel® nylon polymer, our recently commercialized PET polyester, Rynite®, and a grade of mineral reinforced nylon, Minlon® 108 40.

In the case of the metals, we measured the energy required to take the metal from its ore state to an ingot. For the plastics, we took the thermal value of the feedstocks used as raw materials plus the energy required to convert the feedstock into resin pellets.

It is readily apparent that the total energy required to make a unit volume of plastic is significantly less than for comparable metals. If we were to add to this the energy required to fabricate metals or plastics into finished parts, the energy differences would be even more striking.

In comparison to other materials, then, engineering plastics consume less energy in material production, part fabrication, and, by virtue of their high strength-to-weight ratio, in end-use performance.

A good example of where these concepts are being put into practice is in the automobile industry. It is estimated that there are almost 200 pounds of plastic in the average U.S. built 1979 car. A substantial fraction of this is the result of an intensive program by automobile manufacturers to improve gasoline mileage performance through weight reduction.

Engineering plastics are increasingly being substituted for heavier metal components because of all-around performance advantages. The plastics' great strength-to-weight characteristic is an added bonus. This "light-weighting" program has a "cascade" effect. Weight reductions in automobile peripheral components by substitution of plastics permit use of lower horsepower, lighter engines, and more efficient transmissions and drive trains.

For every 400 pounds of "light-weighting" the average car will increase its gas mileage by one mile per gallon (MPG).

Based on estimates of the plastics light-weighting in all cars presently on the road, the total annual energy savings in fuel consumption is 80.5 trillion BTU's, or the equivalent of 14 million barrels of crude oil.

Energy Requirements for Fender Liner*

	Steel	Aluminum	Plastic
Weight (lbs.)	13	5	6
Gasoline, Energy Equivalent, Gallons:			
To Produce	3	6	2
To Transport	11	4	5
Total	14	10	7

*General Motors Study

Fig. 6.

A more specific example of engineering plastics' lower energy need in actual use is illustrated by a General Motors study of the energy required to produce and transport a typical automotive part -- a fender liner -- made of different materials. The results of this study are most enlightening. (See Figure 6)

As you can see, the steel liner requires the most total energy to produce and transport, while the plastic part requires the least. Although the aluminum liner weighs less, the energy required to produce the aluminum more than offsets its weight savings, making the plastic fender liner the most energy efficient.

The point is that with energy cost increases propelling the growth and development of the engineering plastics business, our industry is clearly impacted by external influences. The development of engineering plastics technology, then, is really an evolutionary process, pulled along by evermore demanding needs in the marketplace.

Let's take a look at how this evolution has brought the industry to where it is today.

The early engineering plastics resulted from extensions of polymer technology in other fields. Nylon, for instance, was originally commercialized as a textile fiber. ABS was an outgrowth of the rubber industry. Initial market development centered on end-uses where the engineering plastic could be directly substituted for metals. As acceptance and use grew, there was continued feedback from the marketplace for resin modification to meet new product development needs. From this effort new families of engineering resins have evolved. But, more importantly, thousands of modifications have been commercialized.

ENGINEERING PLASTICS TECHNOLOGY EVOLUTION

- Basic Families
- Copolymers
- Melt Blends
- Additives
- Fillers
- Reinforcement

Fig. 7.

The technology for this evolutionary process of product modification is both fascinating and diverse. Figure 7 shows the components of that evolution: basic families, copolymers, melt blends, additives, fillers, and reinforcement. It is impossible for me to adequately cover this broad spectrum, but, hopefully, a few examples will give you a feel for the

many "levers" the polymer chemist can pull to tailor his engineering plastic to meet a specific product need.

BASIC FAMILIES - First, well over 90 percent of the engineering plastic annual sales volume falls within five basic engineering plastics families. These are:

- Nylon
- Polycarbonates
- Modified Polyphenylene Oxide
- Acetal resins
- Polyesters

Other, lower volume, engineering plastics include polysulfone and polyphenylene sulfide.

COPOLYMERS - The cost of commercializing a new polymer family is high and the time span from laboratory to commercial production is long. So, the natural trend of the polymer chemist is to modify the resins within a family to meet new customer needs. Major property changes can be effected by introduction of comonomers, usually of the same generic family. A highly crystalline, high-melting 66 nylon, for example, can be transformed into a soft, amorphous, low-melting polymer by copolymerization with caprolactam or a different dicarboxylic acid.

MELT BLENDS - Melt blending, via extrusion, of two different homopolymers within the same family or of different families has been successfully used to modify resin properties. Probably the most successful application of this technology is the blending of styrene with polyphenylene oxide, which has resulted in a large family of plastics with a wide range of properties.

However, mixtures which are molecularly intimate are limited. What can the polymer chemist do with those components which, by their nature, are not molecularly compatible?

The answer is compatibilization, whereby polymer chemists are able to form a chemical bridge between two incompatible polymers. The result is a product that is superior to either of the original two.

The most familiar example of compatibilization is the impact styrenes where, by use of a grafting technique, styrene is polymerized around rubber. The result is a combination of properties in the pure crystalline styrene and the rubber that is unavailable in their original form.

Compatibilization promises to be a fruitful area for future polymer research.

ADDITIVES - The use of additives offers the broadest spectrum for polymer modification. It includes:

- dyes and pigments
- stabilizers (such as antioxidants, hydrolytic, thermal and ultraviolet)
- flame retardants
- plasticizers
- fast-molding additives (such as nucleants and lubricants)

FILLERS - The effect of fillers is similar to that of additives. Fillers usually consist of mineral or fiber added in concentrations of 10 to 30 percent. They are added to make a stiffer, more metal-like product. Unfortunately, they usually result in a less tough, more brittle product.

REINFORCEMENT - Polymer scientists found a way to retain most of the toughness of the unreinforced plastic while attaining higher stiffness of filled compositions by chemically treating the surface of the filler so it reacts with the polymer molecules. This technology is called resin reinforcement.

For example, Du Pont's 43 percent glass-reinforced Zytel® nylon has a modulus of 1.6M psi at 23°C. This can be compared to a modulus of 0.4M psi for the unreinforced 66 nylon base resin. In this case, reinforcement yields a fourfold improvement in stiffness and, as measured by notched Izod, toughness increases from one foot-pound to over two foot-pounds per inch of notch.

As we review this technology evolution, it's interesting to measure our progress against two major physical properties important in engineering plastics: stiffness and heat resistance. The next two figures give a visual chronology of the products which have been commercialized as measured in terms of these two properties.

Flex Modulus vs. Act Commercialization Date

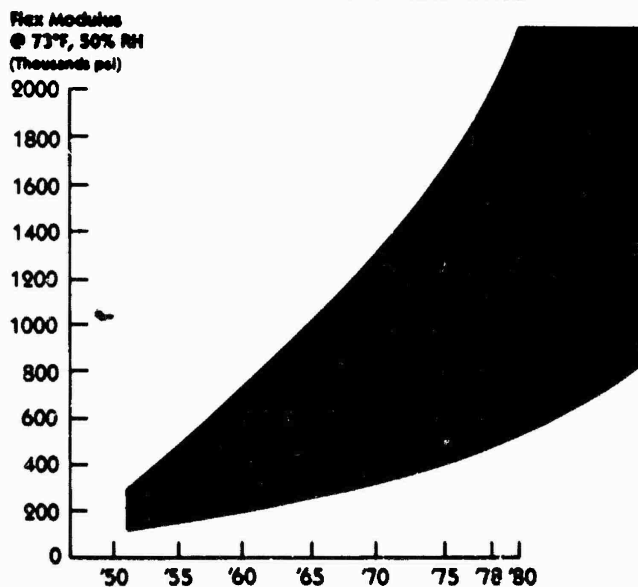


Fig. 8.

Figure 8 shows a comparison of the flex modulus of various engineering plastics with their dates of commercialization. At the bottom and to the left are the unreinforced basic resins. The first significant modulus increase occurred in 1970 with the commercialization of a 33 percent glass-reinforced nylon. In succeeding years, stiffer and stiffer materials have been developed to meet the needs of the designer. A 43 percent glass-reinforced 612 nylon was introduced in 1975 and a 30 percent glass-reinforced polyethylene terephthalate was marketed in 1979.

This trend has continued with the recent Du Pont introduction of a 45 percent glass-reinforced PET composition with a modulus of 2M psi at 23°C. This new Rynite® has a modulus 10 times higher than was available in engineering plastics of the 1950's.

Heat Deflection Temperature at 264 psi

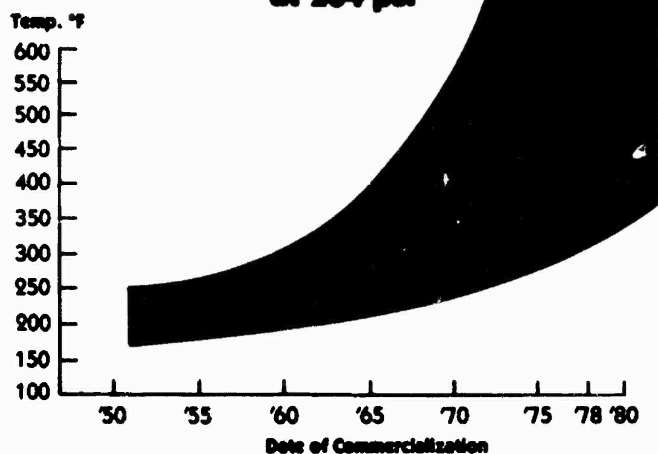


Fig. 9.

Another very important property in many applications is heat resistance. Plotting the heat deflection temperatures of various engineering plastics against their dates of commercialization, as shown in Figure 9, again reveals steady improvement in properties. Glass-reinforced plastics have heat distortion temperatures that are generally twice those of the unreinforced resins which were available 25 years ago.

The development of new plastics based on the technologies I've discussed with you today has greatly expanded the use of engineering plastics in virtually every segment of industry. In the automotive field, we find these new engineering plastics used in engines, transmissions, cooling and fuel systems, steering and suspension components, electrical parts, accessories, and a variety of interior and exterior body parts.

We also see these plastics used in industrial products, such as small gas engines, appliance parts, electrical and electronic components, and consumer items such as sporting goods and power tools. These new engineering materials are contributing to the evolution of end-use products and applications which were never before possible.

As you can see, engineering plastics are continually evolving as basic engineering materials. More designers are "thinking plastics" first because of their high-performance capabilities and strength, and because their multifunctional design and low-cost assembly capabilities lead to production cost savings.

Engineering plastics continue to make inroads into traditional metal markets, but they no longer are considered merely as low-cost, low-quality replacements or alternatives. Today they bring new dimensions in value to parts production. As you will see by some of the other presentations being given here today, engineering plastics have come of age.

4/24/80

TRANSPORTATION AND ENGINEERING PLASTICS

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ABSTRACT

Engineering plastics, such as thermoplastic polyesters, filled nylons, polycarbonate and sheet molding compounds, are used in the automotive industry. Specific applications including processing methods will be presented. For effective utilization of engineering plastics, there must be a balance between properties (physical, chemical, etc.), rapid processing, environmental and safety considerations and cost advantages over components fabricated from steel, aluminum and other polymeric materials. Selection of an engineering plastic for a given application, particularly for the exterior of the automobile, must also be impact resistant and provide the required surface characteristics for painting. While engineering plastics are of importance in reducing the weight of the automobile, the presentation will stress the competition between available materials for a given application.

IN SELECTING POLYMERS FOR AUTOMOTIVE APPLICATIONS, it is necessary to consider physical and chemical properties, weight, durability under environmental extremes, aging, safety, ease of recycling, energy-absorbing properties, appearance, and materials and processing costs. For automotive interior applications, special attention must be given to flammability resistance requirements as outlined in the Motor Vehicle Safety Standard (MVSS 302). Polymers for exterior applications must also be impact resistant. For underhood applications, in close proximity to the engine, polymers should have long-term resistance to heat and/or oils. Automotive polymers need to be processed rapidly in order to meet the high volume production of vehicles. The polymers must respond to and perform satisfactorily under varying environmental conditions including extremes in temperature (-40 to 121°C and in some underhood areas to 150°C). Table I lists the maximum service temperature for some automotive plastics. Automotive polymers must also survive humidity conditions and vibrations associated with in-service performance.

Plastics usage has been climbing steadily (1,2)* (Table II). The 1979 automobile used 90 kgs of plastics/car to fabricate more than 500 plastic parts. This weight includes 19 kgs or 21% of engineering plastics such as polyamides, saturated polyesters, polycarbonate and unsaturated polyesters in sheet molding compounds. Table III lists some of the engineering and other commercial plastics used and some representative applications.

*Numbers in parentheses designate References at end of paper.

Although cost is a factor in any industrial product, improved performance, durability, and safety are of major importance in material selection. In automotive applications, price comparisons must be made on a volume basis, and when this is done, many plastics (e.g., poly(vinyl chloride), acrylonitrile-butadiene-styrene terpolymer (ABS), polyethylene, and polypropylene) become realistic candidates. Additional advantages of plastics include lower tooling and finishing costs. This is so because complex shapes can be fabricated in a single operation. The development of the injection molding machine, in 1936, was of major importance to the automotive industry in that it provided a very rapid method for fabricating high volume automotive parts. For example, in 1970, the automotive industry used 165×10^6 kg of polymeric materials to manufacture injection molded plastic parts. Typical products include grilles, instrument panels, fender extensions, fender liners, lamp housings, bezels, and inner door panels. Improvements in injection molding (e.g., reciprocating screws and process control aids) further contributed to rapid processing of plastics. Other polymer processing methods used by the transportation industry include calendaring, extrusion, vacuum forming, compression molding, blow molding, and plastics stamping. For example, front-end retainers are fabricated by stamping a sheet of 40% glass-reinforced polypropylene. The part made in one operation in a conventional metal stamping press covers the entire front end of the automobile from headlamp to headlamp.

Improved physical and mechanical properties in plastics must still be attained if plastic compositions are to meet structural application requirements. Due to climatic conditions, automobiles must endure extremes of temperature (-40 to 121°C), and, yet, materials must maintain a reasonable modulus of elasticity, even at elevated temperatures. For example, the modulus of elasticity for nylon is 3450 MPa at -40°, 2070 MPa at 10°C, and 690 MPa at 49°C, but it falls off to 414 MPa at 121°C.

Rapid decrease in modulus with increasing temperature is characteristic of most thermoplastics and therefore limits their use for structural automotive applications. The modulus may be increased by using engineering plastics and/or reinforcing the polymer with fillers (e.g., glass, clay, silica, etc.); reinforcement imparts dimensional stability to the finished article. Dimensional instability is manifested by warping and distortion of the plastic part due to softening and excessive expansion when exposed to heat and also by cracking due to brittleness and shrinkage on exposure to cold temperatures. Glass, for example, improves the dimensional stability by increasing stiffness and decreasing the coefficient of thermal expansion in comparison to the nonreinforced plastic. Glass-reinforced polyesters (30% glass) approach the requirements for structural applications in that their flexural modulus is 5520 MPa at 21°C and only drops to 490 MPa at 121°C. Sheet molding compound (SMC), prepared as a preform by combining chopped glass fiber and polyester resin, is also used for manufacturing automotive plastic parts. It is conveniently handled as a tacky material for subsequent processing by compression molding. SMC is used for making automotive front ends, valance panels, and hoods in limited production. The part is fabricated as one piece in one operation and therefore represents a cost advantage when compared to multiple metal stamping operations and final assembly by joining many metal parts. Manufacturing costs would be greatly reduced if sheet molding compounds could be processed rapidly. Some progress has been made in fabricating glass-reinforced plastics by injection molding. Successful applications include lamp housings, radiator fans, fuel pump components, shift

consoles, and fender liners. Due to the presence of glass fibers, injection molding techniques must be modified to insure minimum damage to the glass fibers during processing.

Thermoplastic polyesters (e.g., polybutylene terephthalate) (3) are versatile engineering plastics. They have outstanding dielectric characteristics, good mechanical properties, high chemical resistance, and can be readily injection molded. Typical automotive applications include headlamp housing - fender extension, rear window louver, distributor cap for high energy ignition system, rear-end panel, and connectors for electrical devices. Compounding of injection molding grades of nylon with treated mineral fillers (e.g., silica) increases stiffness and reduces costs associated with plastic reinforcement (4). Mineral filled nylons are also less prone to develop sink marks (surface imperfections) on surfaces backed by ribs. To achieve effective reinforcement, the fillers are treated with coupling agents.

As noted in the few examples above, engineering plastics, such as thermoplastic polyesters, filled nylons, polycarbonate and sheet molding compounds, are used in the automotive industry. For effective utilization of engineering plastics, there is a need to optimize the structure-processing-property relationships for automotive exterior applications. Environmental, safety and cost advantages over components fabricated from steel, aluminum and other polymeric materials must also be considered. While engineering plastics have good impact resistance and are of importance in reducing the weight of the modern automobile, they are in strong competition with other available materials for specific applications.

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Table I - Service Temperature (Maximum) for Some Automotive Plastics

	Service Temperature (Max.) °C
<u>Thermoplastic</u>	
Poly(methyl methacrylate)	87
Nylon	150
Polyethylene (L. D.)	95
Polyethylene (H. D.)	120
Polypropylene	140
Polyester	160
Acrylonitrile-butadiene-styrene (ABS)	95
Acetal	120
Poly(vinyl chloride)	85
<u>Thermoset</u>	
Phenolic	232
Urea-formaldehyde	120
Reinforced polyester	175
Polyurethane foam	100 - 150*
Epoxy	150

*Depends on type of foam (open or closed cell), flexible or rigid, and density.

Table II - Growth of Plastics in Automotive Applications

Year	kg/Car
1940	1.8
1950	4.1
1960	10.1
1970	45.4
1974	67.7
1979	90

Table III - Plastic Applications

Plastic	Applications
Acrylonitrile-butadiene-styrene (ABS)	Instrument cluster, heater ducts, air conditioner housing, grille.
Unsaturated Polyesters (Glass Reinforced)*	Lamp housings, front end assembly, fender extension.
Polyamide (Nylon)*	Canister for emission control, exterior trim clips, fender extension, steering column, bearings and bushings, brake-linkage support, tie rod bearing, seat belts, carpet.
Saturated Polyesters*	Seat belt assembly, windshield washer container, tire cord, ignition distributor assembly.
Polycarbonate*	Rear lamp assemblies, air conditioner outlet deflector retainer.
Polypropylene	Glove box, fan shroud, accelerator pedal, electrical connectors, radio grille, inner door panels, battery case, fender apron.
Poly(vinyl chloride) (PVC)	Upholstery, safety-pad, headliner, sun visor, wire insulation, roof covering.
Polyurethane	Seating, visor, headliner, safety-pad, arm rests, air cleaner filter element.

*Engineering Plastics

GRAMS TO TONS
(Plastics in Communications)

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ABSTRACT

As in many other industries, the use of polymers in the communications industry has increased year by year in a very dramatic way. Although most of these polymeric materials are used in what one might call bulk applications such as wire insulation and plastic equipment housings increasing amounts are being used in much more specific and perhaps demanding applications. A spectrum of these applications together with a snapshot view of the most important chemical requirements in each case is presented. At one end of the spectrum we must consider polymers used in quite small amounts in applications where many thousands of dollars worth of equipment would be sacrificed should a polymeric material perform inadequately. For example the preparation of masks for integrated circuit manufacture depends critically on the ability to write and develop 1 μ m patterns in a suitable polymer film. From such high technology low volume usages we may pass through intermediate applications to the very high volume usage in products such as wire and cable where longevity and in some cases, such as ocean cable, very low electrical loss are of paramount importance.

1. BACKGROUND

THE COMMUNICATIONS INDUSTRY currently uses in excess of 250 million pounds of plastics materials each year. While this volume is impressive it is not nearly as interesting as the wide variety of ways in which these polymers are used. Although most of this huge volume is used in what might be called bulk applications such as cable insulation and jacket and equipment housing, significant applications exist where extremely expensive equipment depends for its proper functioning or for its manufacture upon small amounts of carefully synthesized plastic materials. This paper will attempt to highlight some of the total range of applications, hence the title Grams to Tons.

2. POLYMERIC RESIST MATERIALS (1*)

Like so many others the communications industry has become very dependent upon microprocessor chips to efficiently do its business. Current technology calls for 1 μ m scale patterns on these chips and their manufacture depends critically upon reliable inscription of patterns upon substrates. Polymeric resists are used commonly for this purpose either applied directly to the silicon substrate or to prepare a mask, they may respond to uv, electron, or X-ray irradiation. In each case the aim is to sufficiently modify certain areas of a polymer film so that a well defined pattern may be developed in it by solvent, plasma, or vapor development.

Solution development is perhaps most common and for this to be efficient the polymer must be sufficiently crosslinked or degraded to substantially change its solubility. Crosslinking leads to negative resists

(e.g., partially cyclized polyisoprene with a diazide crosslinking agent) while degradation provides positive resists (e.g., poly(methyl methacrylate) or aliphatic sulfones).

3. COATINGS FOR GLASS-FIBERS(2)

Glass is obviously the transmission medium of the future and the communications industry is dedicated to its rapid continuing introduction into the communications network. Following the spectacular success of the materials community in producing fibers of very low loss the incorporation of fibers into cables imposes two further requirements, high fiber strength and low loss in cabled fibers.

For efficient cable production fiber strengths of the order of 10^5 psi are required. Although this is only around one tenth the strength of unflawed fiber it is difficult to achieve consistently over kilometer lengths. Surface flaws greater than 0.8 μ m must be completely avoided and this requires extraordinary care during fiber drawing. The fiber surface must then be protected by the application of a polymer film immediately following drawing. To avoid damage to the fiber during application the applied material should be of very low viscosity and thus uv curable materials such as epoxy-acrylates and urethane acrylates are attractive as also are thermally curable polysiloxanes using a poly-functional silane curing agent. Some hot melt elastomers, notably copolymers of ethylene and vinyl acetate, have also been utilized.

The finished films must serve the protective function mentioned but also ideally have low modulus to minimize the small scale bending of the fiber when it contacts a hard substrate such as a spool. Even small protuberances of the order of 1 μ m if impressed on the fiber will cause increased loss. In some cases, where a good low modulus coating lacks adequate abrasion resistance, a second hard extruded coat such as nylon may also be employed.

4. POLY(PHENYLENE SULFIDE)(3)

Thermosetting materials are often used in applications requiring very good dimensional tolerance during thermal bonding. For this reason among others a glass reinforced diallyl phthalate resin was initially chosen as an insulator in a specific circuit board connector for electronic offices. However, problems appeared during production in meeting tolerances, and controlling dimensions, and in shipping where parts were frequently broken.

Following extensive study a switch was made to a thermoplastic, poly(phenylene sulfide) (PPS) and as a result performance and cost advantages have been obtained. As a result of this success a number of applications using thermosetting materials have been reviewed and because of reduced scrap during molding and general processing advantages it has been found economical to replace the cheaper (per lb.) thermoset by PPS.

5. ABS(4)

Acrylonitrile-butadiene-styrene is the most widely used molding plastic in the Bell System. Its position results from excellent impact properties and modest cost. One major use is in telephone housings. Inevitably with use housings become scratched or otherwise disfigured and must be replaced. The old sets are returned to telephone companies and hence

* Numbers in parentheses designate References at end of paper

to Western Electric where recoverable housings are buffed or otherwise renovated. Some, however, are too badly damaged and must be scrapped. However, these scrapped housings still represent a valuable materials resource and recent efforts have led to a significant reclaiming operation.

Returned housings may have labels attached, and contain cotton-wool and brass or metal screws which must all be removed. The housings are first ground and the plastic cleaned by an air floatation process to provide material with impact strength almost equal to that of virgin. Due to the mixed colors of the input housings this recovered material may not be used for new housings but may be used in a variety of other applications. For applications where fire retardancy is required a blend with PVC and added iron oxide has been developed.

6. PVC(5)

Poly(vinyl chloride) is one of the major plastics used by the Bell System. Although its main uses are in wire insulation, cable jacket, and buried conduit, it is also used in a variety of molded applications where fire-retardance is required. With so much of this material in current use, its effective lifetime in each application is of great importance to the continued successful operation of the network. Two major degradation paths must be considered. In the applications where flexible, plasticized PVC is used, loss of plasticizer by volatilization may lead to embrittlement and failure and studies of this process have led to the selection of plasticizers carefully matched to the planned use. However, for this audience recent work directed to the study of chemical degradation -- and stabilization -- is perhaps of more interest.

PVC degrades by loss of hydrogen chloride to give conjugated sequences of double bonds which initially cause discoloration and finally loss of mechanical properties. The exact mechanism of this degradation has long puzzled chemists, and still does, but it is clear that the stability of PVC is less than that expected of the text book structure. This fact has led to the speculation that unstable groups are formed during polymerization and recent work at Bell Laboratories has been directed to the elucidation of the molecular structure in as detailed a way as possible. The prime tool has been ^{13}C NMR allied with mild, non-structure deforming, reduction of the PVC to polyethylene. In this way a variety of irregularities have been found and their concentrations measured. Similarly end group structure has been studied.

Interestingly, these studies have led also to an enormous increase in our knowledge of the polymerization mechanism. Primarily, perhaps, to an understanding of the role of head to head addition and also to the part played by chlorine atoms in transfer.

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DURABLE CONSUMER GOODS AND ENGINEERING PLASTICS

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ABSTRACT

Technology in engineered plastics has undergone a revolution over the past 20 years. Application of this technology in consumer durable goods has also revolutionized this industry in a visible and tangible way. This includes affordable products over a broader consumer market base, upgrading of real and perceived quality and in many cases new products which have improved the quality of life. The unique properties and processability of plastics over other materials have made this possible.

The growth of plastics can be attributed to technological advances in engineered polymeric materials, technological advances in fabrication processes and the impact of business and marketplace driving forces. Future growth will depend upon a creative design/materials/process systems approach.

OVER THE PAST 60 YEARS the plastics industry has undergone a tremendous growth and evolution: from billiard balls to dishwasher tubs; from decorative ornaments to electric coffee makers; from pyroxylin to polypropylene. This explosive growth has resulted from invention of new materials, the modification of existing materials, the invention of new processes and the modification of existing processes. In the consumer products sector, above all, this growth has come from the creative coupling of the technological advances with designs and manufacturing methods to produce a product which fulfilled a need - formed plastic refrigerator doors adding significant storage space, urethane foam insulation to expand interior storage space and reduce energy consumption, plastic washer and dishwasher pumps to improve efficiency and improve product durability, plastic air conditioner fans for improved air flow and reduced noise, a myriad of portable housewares which without plastics could never have been made.

Plastics have also made it possible to mass produce affordable consumer products for a broader consumer base. Handcrafted, wood radio and television cabinets have given way to plastic cabinets. Many of the electrical and electronic components in these products are insulated with modern day plastics materials. Who ever would have thought a decade ago that today we would have electric irons which are predominately made of plastic.

Certainly our quality of life has been greatly improved by the vast array of polymers that have been invented. Over the past 30 years this has been dominated by technological advances in engineered plastics: the impact modification and improved chemical resistance of styrenics, acrylics, polycarbonates, polysulfides, polysulfones, polyphenylene oxides, polyimides and others.

Today with the coupling of chemistry, molecular architecture and the blending of dissimilar polymers, as well as the incorporation of additives and reinforcements, there is almost a limitless number of plastics materials available for the manufacture of consumer durable goods. Variations on tailored materials based on styrenic polymers provide consumers with a multitude of products: functional parts such as refrigerator inner liners, crisper trays and pans; esthetically appealing, affordable, and durable luggage; affordable household furniture which replicates expensive wood pieces; modern furniture which has unique, appealing characteristics all its own.

Engineering plastics such as polycarbonate have made possible such diverse applications as: telephone dials - lightweight, non-corrosive outdoor air conditioner housings and grilles - housewares parts - and snowmobile housings. The many derivatives of nylon chemistry are used in consumer products ranging from cams, gears, and connectors to buckets for trash compactors. Thermoplastic polyesters range in applications from television tuner components to chain saw housings. Each new class of materials has brought a unique set of characteristics for the designer to work with and each has found market niches which fit these characteristics.

More recent research and development on high temperature thermoplastics and innovations in processing technology for older thermosetting materials have expanded applications to higher temperature, more structural applications such as microwave oven doors and internal components, air conditioner barrier and base pans integrated into one functional part, thermal breaks and decorative components for electric ranges, lawn mower housings and even furnace components. As the impact of rising energy costs and shortages intensifies, the replacement of metal castings is occurring in a multitude of products.

As fantastic as this explosion of plastics applications may be, the road from basic science to tangible useful products is a tortuous one and, in detail, requires a tremendous amount of creativity, technical development, resources, business commitment and perseverance.

By way of example, the route from the elegant scientific work of Drs. Ziegler and Natta on stereospecific catalysts which turned an amorphous grease into the rigid and useful semi-crystalline polymer, polypropylene, in 1954 to applications in the 1970's such as molded one piece dishwasher tubs and modern spray and steam iron housings is filled with technological innovations and engineering development.

Much creative technical work was required for the development of stabilizers to prevent material degradation by oxidation. This was followed by further scientific insights on solubility and diffusion that were essential for the development of specific stabilizer systems which were not extracted by polar and non polar solvents, e.g., hot water, food oils and plasticizers.

The technology of block copolymerization made possible ethylene-propylene block copolymers to achieve the desired balance of properties for applications requiring high ductility and rigidity. The technology of modifying the polymer with reinforcing mineral fillers was superimposed on all this to achieve the necessary reduction in mold shrinkage and dimensional stability for high volume, reproducible fabrication of these consumer product components.

The technology of injection molding, in one shot, a 12 pound complex shape such as a dishwasher tub involved characterization or rheological behavior, understanding and translation to mold filling and a major engineering effort in fabrication equipment and tool design.

Dr. Allan Hay's basic work on oxidative coupling in 1956 resulted in a new high temperature glassy polymer - polyphenylene oxide. Today this basic chemistry has made possible molded television cabinets which are attractive, resistant to breakage and provide fire retardancy for this electrical enclosure. Along the way to achieving this consumer product application, the technology of polymer alloying played a key role in modifying the polymer so that it could be an injection moldable plastic - Noryl[®].

Additives were developed to facilitate flow, enhance toughness and provide oxidative stability. Refinement in alloying technology produced the specific balance of properties required for thin wall television cabinets. In addition, in order to make this application a commercial reality, runnerless injection molding technology was employed in order to fill the mold in the fast cycles required for this high volume application and to produce abuse-resistant and esthetically acceptable and reproducible parts.

When viewed on an historical macro scale, over the past 60 years, the application of plastics technology has moved at a very rapid, almost explosive pace. Once pioneered by people like Dr. Mark, the field has been moving as it should considering that we have been very early on the learning curve.

As we look to the future, and on a micro scale - the immediate future, our economy is faced with some major and significant challenges. Key driving forces which will impact significantly on consumer durable goods are:

- . A resource limited environment - limited energy, limited materials, limited capital.
- . Inflation.
- . Trends for increased regulation and a growing public sector.

If we are to maintain a high standard of living and continue to have viable consumer products businesses, technology will be significantly challenged to move more deterministically and faster, if we are to meet these objectives without significantly reducing our quality of life.

These driving forces have created an urgent need for greatly improved productivity, a better focus for applied science to address these needs and a better coupling of scientific advances with engineering application. Plastics technology is certainly a fertile ground for accomplishing this.

We still need crystalline polymers with their many advantages which are not limited by high shrinkage and warping in large parts. Creative technology beyond the limited concept of simply adding fillers is required to see the full potential of this type of polymer realized.

We need filled and reinforced plastics with high strength/weight ratios that do not lose the inherently attractive surface finish of the base polymer.

From a design viewpoint, advances are beginning and need to be accelerated in the fundamental understanding of polymer properties and how they relate to engineering performance. Computers have revolutionized the opportunity to accomplish comprehensive finite element analyses of complex shapes and structures. The methods demand accurate and relevant property inputs.

Though there are many challenges in materials technology to achieve preferred or improved property balances, the major impact will probably be achieved through a systems approach which better integrates design, material, process, equipment and control - the multiple technologies essential for viable commercial applications.

In the consumer products arena where high volume, high quality, low margins and value received are the by-words, we must address fabrication processes in a more disciplined way to generate the output required to meet productivity needs.

Computer analyses of polymer flow into molds and of heat transfer during molding are beginning to emerge. Future applications development may well start with interactive graphics for part design, computer aided design of molds and direct programming of numerically controlled equipment which will automatically machine the molds.

New technologies in microprocessors and other electronics are leading to sophisticated, on line, closed loop controls for improved process efficiency. It is now almost routine to have pressure transducers in molds to monitor and/or feed back cavity pressure for adaptive control to produce high quality plastic parts.

We face major technical challenges in plastic fabrication process automation. We have rested far too long on the laurels of the inherent processing advantages of plastics. We now need to apply technology to automate these processes and creativity to develop new processes which are much faster and less energy intensive.

As we look to the future, in facing these challenges, it is apparent that polymer science must couple better with other emerging sciences and technologies. Science must couple more closely with engineering needs and above all engineering must be aware of, relate to and creatively approach what will be the future wants and needs of the consumer.

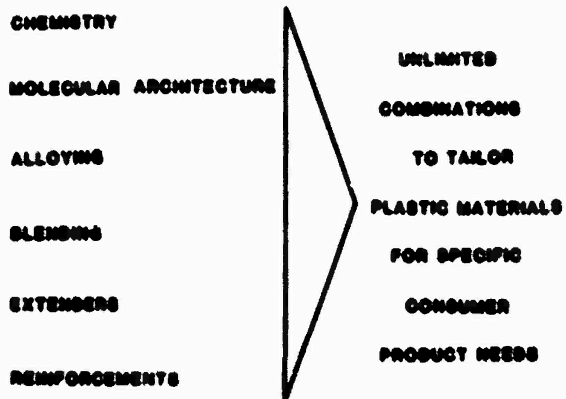


Figure 1

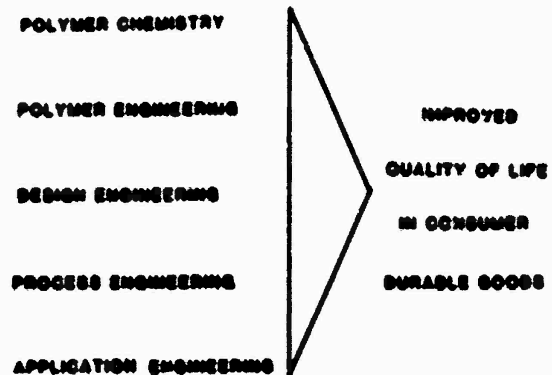


Figure 3

PLASTICS IN CONSUMER DURABLE GOODS

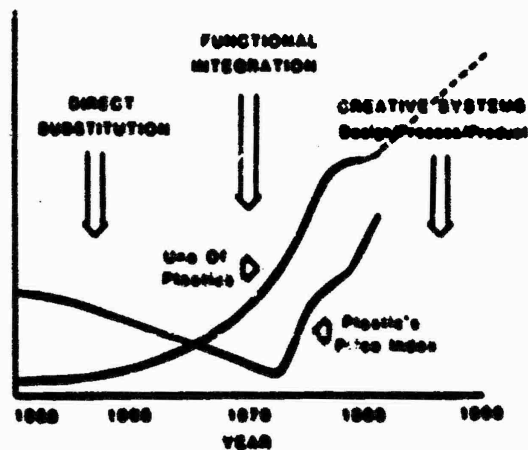


Figure 2

THE FUTURE OF ENGINEERING PLASTICS

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ABSTRACT

Forecasts of the wider use of polymers as engineering materials in structures are examined in light of trend extrapolations as well as the constraints imposed by shrinking supplies of materials, capital and energy. A favorable projection emerges related to the opportunities generated by needs for light-weight materials in transportation and other energy-dominated fields. Some major deficiencies in design know-how on the optimum use of plastics and resin-based composites are described, which may produce a large damping effect on optimistic projections. In addition, several new developments in polymer structures specifically designed for processability and engineering use, including "molecular composites", are discussed.

THE GROWTH OF PLASTICS in this century, and in particular during the past forty years, has been so phenomenal that our era may indeed be viewed as the "Age of Plastics" (1)*. Forecasters often extrapolate trend data and make projections with questionable expectations, whether optimistic or pessimistic in character. Figure 1 shows a typical extrapolation for a number of materials in terms of world production (2). Much of the forecasting literature concerning plastics and plastic-based composite materials has this character. In our examination of the future of engineering plastics, we will not project the rates of growth or decline of plastic materials consumption into the next century as others have done already (3, 4). We will, however, look to future possibilities, and illuminate what might be the key requirements for advancement or decline in the continued application of this important materials class. Restricting ourselves to engineering plastics will imply that performance criteria in engineering design are heavily weighted considerations with material costs, processing ease, quality control and durability as additional important factors.

This paper will stress what is not well known rather than enumerate what has been accomplished. We will focus upon the emerging fragments of a scientific basis for

*Numbers in parentheses designate References at end of paper.

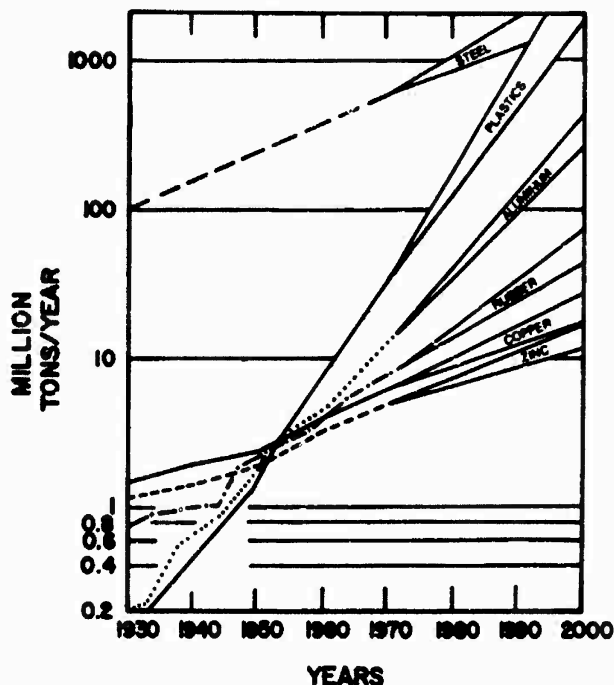


Fig. 1. - World production forecasts²

potentially spectacular advancements, and assess the deficiencies which are constraining transition of knowledge to practice.

TECHNOLOGY FORECASTING

To broadly view technology forecasting for a moment, one may recognize the following approaches as traditional:

- Intuitive - Polling of experts on their views.
- Trend Extrapolation - Graphical methods using historical data.
- Trend Correlation Analysis - Examination of several trends in closely allied areas.
- Analogy - Use of examples with documented trends in fields which have similar characteristics.
- Logic Trees - A decision path approach which examines key branch points for yes-no possibilities leading to future directions.

The approach which we will use employs a combination of features from several of the above, but introduces the concept of trend deviations due to imposed constraints (such as government regulations) and the positive influence of other technologies, which are themselves experiencing strong growth. In the one case, a constraint depresses growth, while possible influences by related technologies present opportunities for acceleration. Figure 2 is a schematic representation of a growth curve which is influenced by both negative and positive factors in sequence.

Opportunities for rapid growth and change in current polymer consumption trends are provided by potentially "intersecting technologies". The term is meant to identify those important technological areas which are

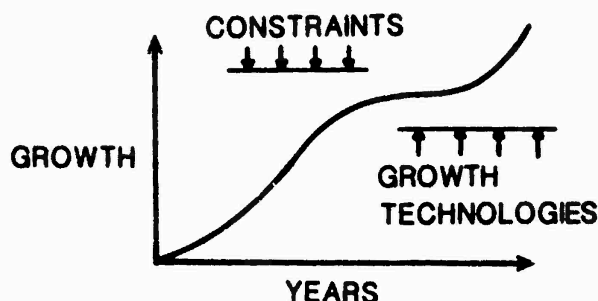


Fig. 2. - Schematic growth curve reactions

experiencing rapid growth and change and which have the likelihood of broadly influencing other trends through advantageous coupling. An example of such an area is microelectronics technology, currently in a very favorable growth climate which is likely to continue for some time.

The following listing of various constraints and opportunities is suggested for inspection with regard to their influence on any trend projections to be made concerning polymeric materials.

CONSTRAINTS - (1) Diminishing petroleum supplies and their control by international cartels. This is mainly an energy constraint, but has some implications for periodic variances in feedstock supply.

(2) Shortages of capital available for replacement of equipment and facilities as well as new ventures. This constraint is strongly linked to the high cost of energy.

(3) Government policies and regulatory laws which add to costs, but do not increase productivity. Environmental and safety regulations as well as product liability judgments impact chemically based technologies as severely as any in the nation, adding to the risk of new ventures.

(4) Materials shortages and foreign dependence. A specific example would be chromium which is crucial to the chemical industry through its use in stainless steel, but which must be obtained from a very few foreign suppliers, principally South Africa and the Soviet Union.

(5) Societal priorities for applications of federal funds. In particular, the allocation of funds for direct human needs such as health, education and welfare have modified funding patterns where engineering research and technology funding has existed (e.g., DOD, NASA, NSF).

OPPORTUNITIES - (1) Microelectronics developments in sensing, control, computation and display are generating polymer needs and applications of a direct nature in the construction of electronic systems, as well as benefitting polymer technologies which employ these functions (e.g., on-line process controls).

(2) Composite materials employing polymers as the continuous matrix as well as the dispersed phase. Advanced fiber-reinforced plastic is an example of a material seeing expanded use as a metal replacement in aircraft, automobiles, and a variety of structural applications.

(3) Adhesive bonded structures formed through low-cost manufacturing processes for bonding metals, plastics and composites.

(4) Biomedical applications. Some as structural aids and prostheses, others for highly specific replacement functions.

(5) Genetic engineering as may be applied to renewable resources (e.g., increased yield of natural polyisoprene from guayule plants in southwest U.S. and Mexico).

(6) Computer-aided design and manufacturing (CAD/CAM). Air Force and NASA sponsored programs are underway in the U.S., but are small compared with broad nationally supported efforts in Europe and Japan. The programs are closely-linked to productivity and efficiency goals of the sponsoring nations.

(7) Laser applications to precision engineering and manufacturing.

The lists above are illustrative and may be extended; however, the recognition of parallel trends in other technologies and their implications should be apparent.

ENGINEERING PLASTICS AND COMPUTERS

While a variety of exploding technologies can be considered important with respect to their possible impact on future engineering trends for the application of plastics, one of the most pervasive is the increased availability of devices based on microelectronics. The annual increase in electronic functions is shown in Figure 3, with some projections for the future. The last two decades have brought an era of "computational plenty". The significance of this enormous development is that it is characterized by miniaturization and cost reduction. This trend is compatible with the constraints listed earlier since the directions are to use less energy and materials rather than more. Society approves of microelectronics, in general, and is likely to promote growth rather than restrain it. Electronic industries are believed to be clean and non-polluting, and the man on the street has first-hand knowledge of microelectronic benefits in his automobile, wristwatch, television games and a host of consumer appliances.

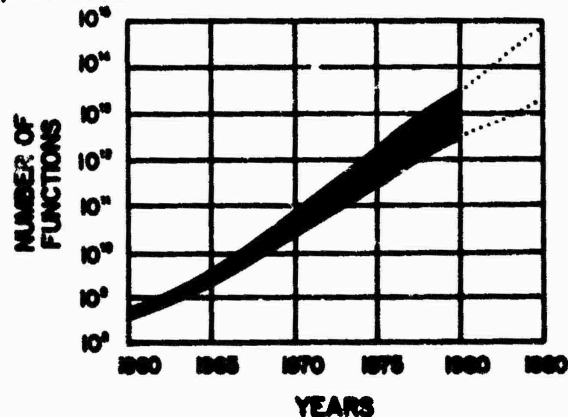


Fig. 3. - Annual utilization of electronic functions worldwide

Favorable coupling of developments in sensors, control systems, microcomputers and large capacity computational networks with technology in other fields, such as manufacturing, is expected to provide impetus for growth, as well as improved efficiency.

To apply this clear opportunity to the advantage of polymer applications we may examine current deficiencies which might be filled. A number of studies by various government agencies conducted in the past several years (5, 6, 7) have pointed out the necessity of extending the knowledge-base for materials science and engineering. The need for knowledge is specifically related to applications where performance is important, and trade-offs incorporating other factors such as cost, safety and producibility are considered. Engineering plastics and resin-matrix composite materials fit the categorization of needs and opportunities very well.

ENGINEERING OF AND WITH PLASTICS

A principal focus of the discussion which follows is engineering with plastics, considering the vast array of current and potential "engineering" plastics available. Those opportunities which have arisen in the past to substitute polymers for other materials for a perceived advantage, and which have been especially disappointing, point up the gaps in engineering know-how.

PROCESSING - There is very little doubt that there will be continuation of the trend to introduce parts made of plastics and resin-based composite materials in place of metals in engineering applications. Other papers in this symposium deal with a number of the important opportunities more specifically. The relative ease with which polymers may be shaped and fabricated has been an attribute which has ranked higher, as a motivation for expanded use, than any other factor. When applications have not demanded high performance, it has been quite possible to accept the properties of the material as they result from the processing sequence, with little attention to optimization except for costs and rapid throughput. In more sophisticated applications the lack of understanding of processing effects on the polymer have led to severe problems in design, quality control, durability in use, and ultimately cost. More recently, however, an important trend is developing which recognizes the importance of polymer processing, not only for optimization of the materials processing cycle, but in the creation of new materials with unusually good properties.

A major opportunity for the future of engineering plastics is presented by coupling the advancements in on-line process control technology, based on microelectronics, with shaping and conversion processes in both reactive and non-reactive systems. The deficiencies, at present, are not in the hardware, but in sufficient understanding to create the requisite software. There is growing use of closed-loop process control systems upstream of polymer forming operations in the monomer and polymerization reaction cycles, but few comparable examples may be found in the subsequent operations.

An impressive example of the integration of mini-micro computer process control with extrusion machinery is shown in Figure 4. An experimental extruder is running at the University of Bradford in the U.K. under full adaptive control and is being used as the basis for development of a commercial system (8, 9). This advance in process technology for polymers is important to the future of

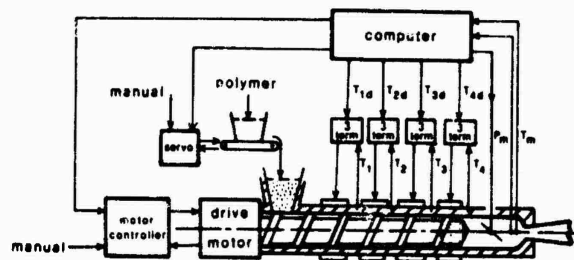


Fig. 4. - Experimental extruder with full adaptive control

engineering plastics since ultimately it may incorporate a control logic based on fundamental material-process interrelationships. Each step in the sequence, including the final product output, with the effects of processing history understood and monitored, could be controlled if there were a scientific basis available. Shaping of crack-resistant plastic cups or bottles utilizing a knowledge of favorable flow orientation is an example of a non-reactive, amorphous polymer sequence. More fully ordered and perhaps semicrystalline polymers, widely used in consumer items, rely to various extents on the development of an optimum morphology. Perhaps the most challenging area for the development of new basic knowledge concerns reactive processing, which exhibits a continuously changing molecular and, possibly, morphological structure during the process cycle. Thermosetting resins used as matrix materials in fiber-reinforced composites and high performance structural adhesives are examples of important applications where processing effects are poorly understood.

STRUCTURAL MECHANICS - As plastics invade the territory of other materials, most notably metals, the need for design data as well as design methodologies becomes more apparent. Many of the projections of accelerated use of engineering plastics, including advanced composites, fail to take account of the lack of confidence which exists in using these materials in critical components. The training of design engineers is severely limited in the application of polymeric materials, and each time a new design incorporates their use, the potential for initial failure is high. Through the years, the frequency of disappointment with plastic materials has led to unwarranted conservatism and misleading information regarding engineering plastics. Occasional failures have not been the fault of the material, as such, but of the design, in which designers have attempted to use methods based on experience with metal structures. While there is a growing body of knowledge in polymer mechanics, providing stress, deformation and fracture laws, the transition of this knowledge to the designer's desk is strongly inhibited. Since engineering plastics, used in bulk form or reinforced, exhibit complex behaviors including time-dependence, anisotropy, and non-linear response, the mathematical tools required are more advanced than those normally used in the design community.

Once again, an opportunity exists through large capacity, high-speed computational equipment which is growing in numbers and

availability. Efficient finite element and finite difference programs are being evolved which may accept complicated material descriptions applied to structural analysis. Through large-scale integration of micro-electronic functions, entire design manuals and catalogs of information may be incorporated into a single plug-in module attached to a desk calculator. In principle, a design engineer may operate advanced programs with little requirement for detailed understanding of their composition, if the necessary input information is available and limitations of application are followed strictly.

A recent example of an unusual application of advanced engineering plastics may be found in a program by the Charles Stark Draper Laboratories (10) to produce a low cost molded inertial guidance gyro. The plastic precision molded parts are expected to bring the unit price down to the range acceptable for commercial small aircraft, boats and farm machinery. Tolerances are extremely critical and long-term creep is a critical design factor. Reinforced polyphenylene sulfide is the current material of choice, but the major uncertainties lie in the materials characterization for both process control and engineering design. Figure 5 shows the overall design and Figure 6 is a photo of the various molded plastic parts. Finite element modeling of the

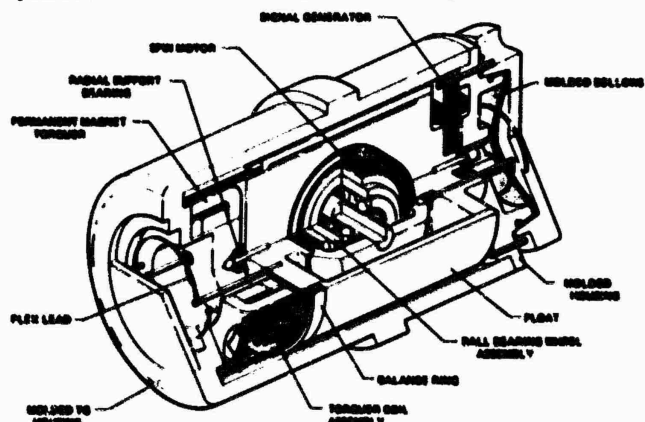


Fig. 5. - Draper Laboratory low cost precision molded gyro

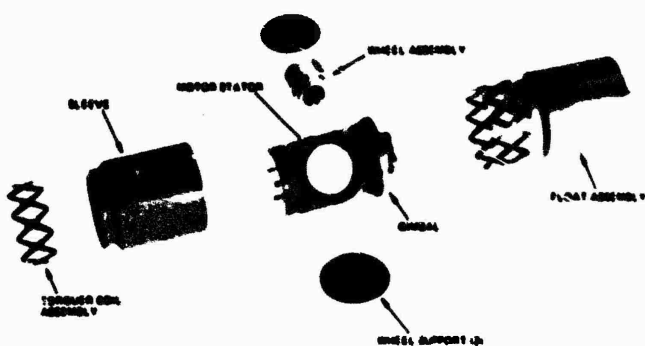


Fig. 6. - Precision molded gyro parts

structure in its dynamic and static operational modes is being undertaken recognizing existing uncertainties. Figure 7 illustrates a 3-D finite element representation of part of the gyro structure.

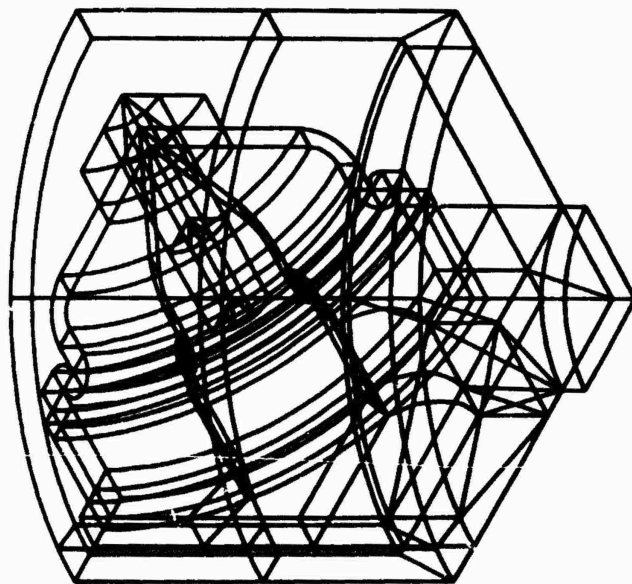


Fig. 7. - 3-D finite element model for Gimbal and float package

MACROMOLECULAR ENGINEERING - Polymer synthetic methods are becoming quite advanced in their capability to "engineer" the molecular structure to produce backbone sequences from various monomers, chain branching, blocks, grafts, length distributions and functionalization. To some extent synthetic chemistry has outstripped our ability to use its products. This situation is basically true in the commodity polymer market, where the polyethylenes, PVC, ABS, polystyrene, polypropylene, etc., are firmly established. In the categories of engineering and specialty polymers quite the opposite is the case. Polymer structures may be manipulated at the molecular, supermolecular and microphase levels to produce rheological behavior "tuned" to the most convenient processing cycles, and mechanical properties optimized for specific design applications.

As structure-property relationships become refined with reliable mathematical descriptions, the possibility exists for incorporating them in a format for accession and display in an interactive computer graphics system. Molecular structures may be designed on the cathode ray tube, their flow characteristics, fundamental parameters (such as glass transition temperature) and bulk properties estimated. Optimization of structure may be accomplished before synthesis is actually attempted in the laboratory. Efficient synthetic sequences and options may be selected as well. Many of these possibilities exist today, in principle, with hardware and some software available. However, systematic examination of relationships available for first-order effects has not been done nor has information been transposed to a unifying format which would allow this step. In addition to molecular design, compositional design for blends, composites and laminates will

become automated procedures as the knowledge gained from fundamental studies is validated. This is not to say that computerized data banks and empirical correlations are not being evolved today. There are several examples of such efforts. A corollary in the metallurgical community is computerized alloy design, which is making significant strides in recent years.

NEW CONCEPTS FOR ENGINEERING POLYMERS - Unified approaches which blend a detailed knowledge of macromolecular design with synthetic methods to achieve new materials having advantages in processing and properties represent the forerunners of engineering plastics for the future. While it is not the purpose of this paper to catalog the many new and interesting advances in engineering polymers, two recent examples will be described for illustration.

Intramolecular cycloaddition reactions (IMC) have been proposed as a route to producing rigidized structures in initially fluid polymers, without cross-linking. Since reactions occur between adjacent functional groups on each polymer chain backbone, the process is not dependent on chain diffusion and flow. Polymers produced are linear, and the use temperature is not dependent on the cure temperature, as is true in thermosetting, 3-dimensional network polymers, such as epoxies. A schematic diagram of the IMC concept is shown in Figure 8. The method has

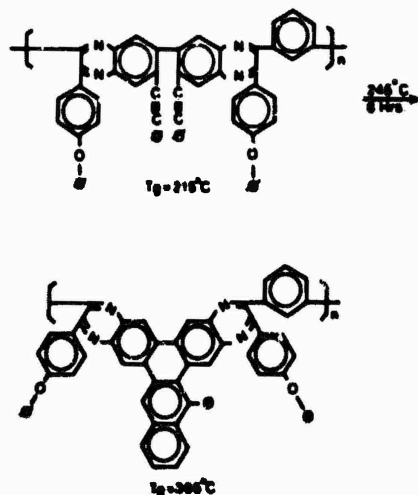
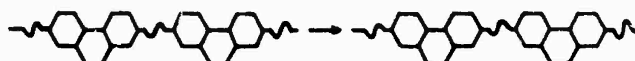


Fig. 8. - Intramolecular cycloaddition cure concept

been demonstrated for high temperature aromatic heterocyclic polymers with the adjacent reactive species being acetylenic structures (10). Reaction temperatures around 245°C were required and the glass transition temperature of the product was in excess of 365°C. Other reactions such as enyne cyclization are being explored for lower temperature curing cycles (12). There are distinct benefits to a structural resin which may be processed at moderate temperatures and retain its stiffness at much higher temperatures. The potential to provide thermosetting polymer

properties, with some of the thermoplastic processing characteristics, can have wide implications in composites and adhesively bonded structures.

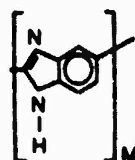
A second example, which is particularly attractive in its potential, is the true molecular composite. Rigid rod polymers dispersed in a chemically similar flexible polymer matrix provide an analog, at the molecular level, to short-fiber reinforced composites. Preliminary work has demonstrated the feasibility of these materials using a variety of para-catenated aromatic heterocyclic polymers (13). Unusually good film properties have been obtained from solvent stretched or water precipitated blends having 10% rod molecule concentrations. The following table shows the mechanical properties and composition of the combination PDIAB (poly p-phenylene diimidazobenzene) rod and AB-PBI (polybenzimidazole) matrix. Scanning electron micrographs of the matrix

AB-PBI PDIAB MOLECULAR COMPOSITE

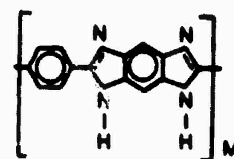
Wt. % Rod	Modulus (GPa)	Tensile Strength (MPa)	% Strain
0	1.6	128	118
10	10	316	14

(solvent stretched)

alone and the resultant composite are shown in Figure 9 for comparison. The structure of



AB-PBI



PDIAB



MATRIX



COMPOSITE

Fig. 9. - AB-PBI/PDIAB molecular composite

the blend clearly contains small ellipsoidal domains consisting of a composition of high rod concentration with a secondary dispersion in the unblended matrix. While much optimization of structure and processing methods remains to be done, this attempt to generate a remarkable new material from molecular design concepts stands as an example of the many untapped possibilities remaining for the future.

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Table 1

World Fiber Production, 1978
(millions of metric tons)

	<u>U.S.A.</u>	<u>World</u>
Cotton	2.4	13
Rayon and acetate	0.4	3.5
Synthetics	3.5	10.4

Source: Textile Economics Bureau

ABSTRACT

Although the study of the chemical nature of cellulose initiated the field of polymer science, and cellulose is the world's most abundant polymer, its use for production of man-made fibers, films and plastics declined until the late 1970's. There is now a resurgence of interest in this polymer as a substitute for oil-based products. Recent commercial fiber developments have centered on high wet modulus rayons with crimp or modified cross-sections to improve textile opacity and "hand," hollow rayon fibers for dialysis applications, and absorptive rayons modified by grafting or incorporation of carboxyl-containing polymers. Anisotropic solution properties offer future promise of improved strength properties of cellulose derivatives. New solvent systems are being studied to provide totally enclosed systems for regenerating cellulose without the effluent or emission problems experienced in the viscose or cuprammonium processes. The discovery of stoichiometric esterification systems could lead to expanded production of cellulose-based thermoplastics.

APPROXIMATELY SIXTY YEARS AGO, an infant science, high polymers, was in the process of being born. It arose out of the necessity to assist in the development of the growing man-made fibers and plastics industry of the early 1920's. Practical methods had been found to chemically convert cotton linters into filament rayon, cellulose acetate, cellophane and celluloid. Properties of these products needed improvement and a science was needed for guidance. Dr. Herman Mark, whom we are honoring today, helped usher in this new science by his basic investigations on the polymeric nature of cellulose.

The near explosive growth of the man-made synthetic fiber industry in the United States and Western Europe during the past decade tends to obscure the fact that almost two-thirds of worldwide textile production still depends upon cellulose in the form of cotton, rayon and cellulose acetate (Table 1).

Examination of fiber production data for the past thirty years does not suggest much actual displacement of cellulose by synthetics. What it does show is that much of the overall growth in western textile markets was achieved by the synthetics while growth in the use of cellulose has been modest.

Barring world catastrophe, population will continue to expand--especially in the developing nations. How will the textile needs be met of the four billions of new people who will be added to our planet during the next twenty-five years? At current levels of textile consumption, admittedly low in many parts of the world (Table II),

Table II

Estimated Per Capita Consumption
of Textile Fibers

1979

United States	28 Kg.
All Developed Countries	19 Kg.
Third World Nations	2 Kg.
Whole World	7 Kg.

an additional 25 million metric tons of annual fiber production will be needed by the end of this century. Can (or should) this new production be met by oil-based synthetics? The current escalation in price of chemical feedstocks (Fig. 1) suggests real future problems with this approach. To supply this future market with cotton would require tripling of the existing cotton-growing land base. This also seems unlikely in the face of competition for the same land base to provide the food that will be needed by the increased population. Man-made cellulosic fibers remain as a possible alternative for serious consideration (1,2)*. In this paper we wish to show that there is a more than adequate, long term raw material base for cellulosic fibers and plastics, there are interesting new products appearing on the market, and, finally, new technology is being developed that promises environmentally sound, cost-effective processes for converting cellulose into new types of fibers.

*Numbers in parentheses designate References at end of paper.

AVAILABILITY OF CELLULOSE

Almost all of the viscose rayon and a substantial part of cellulose acetate production throughout the world is now based on a purified form of wood pulp termed "chemical cellulose" or "dissolving pulp." The processes for manufacturing dissolving pulp are basically the same as those used for producing paper pulp except additional purification stages have been added to remove hemicelluloses such as xylan and mannan which would otherwise be present in paper pulp. In the case of the kraft process, this is achieved by pretreatment of wood chips with steam, water or dilute acid solutions at 160-175°C. prior to the alkaline pulping stage, i.e. prehydrolysis-kraft (3). No pretreatment is used in the acid bisulfite process, but a pressure, alkaline stage is inserted between the bleach stages. The latter removes hemicelluloses through conversion to isosaccharinic acids. An ambient sodium hydroxide extraction may also be used in either the acid bisulfite or prehydrolysis kraft process to produce wood pulp with 98.5% or higher cellulose content for the most demanding end uses such as acetate plastics or high tenacity rayon.

Corporate and government strategists concerned with future supplies of raw materials have tended to have different views of the future depending upon their biases. One view (4) of the dissolving pulp industry and its capability to supply increased amounts of product to substitute for oil-based fibers and plastics is that "capital costs are high, pollution control is costly, the raw material, cellulose, is in short supply....." The implication is a lack of commitment to meet environmental goals or provide adequate supplies of cellulose. This, of course, is contrary to fact. The dissolving pulp industry, at least in the United States, has developed technology to meet current federal standards. All sulfite and prehydrolysis-kraft mills have recovery systems to capture pulping effluent and secondary treatment systems to reduce B.O.D. to acceptable levels. Self-sufficiency in energy is being attained. The largest dissolving pulp mill in the United States obtains 78% of its energy from combustion of pulping waste and wood and bark residues. World capacity of this industry (6 million metric tons) is adequate to meet existing demands. If dissolving pulp demand were to grow greatly through establishment of new cellulosic fiber and plastics markets and there was appropriate economic incentive, some part of the world's existing 145 million metric ton paper pulp production capacity could be modified to produce dissolving pulp.

A second problem that continues to bother some futurists is whether there is adequate wood or related materials to base our future economy on renewable raw materials (5). Recent studies carried out for the National Academy of Sciences and the National Research Council by the Committee on Renewable Resources for Industrial Materials (CORRIM) showed that there is substantial material for further expansion of the pulp and paper industry through whole-tree utilization, increased fiber recycle, etc. (6). Beyond this, we have not even begun to tap the cellulose resource

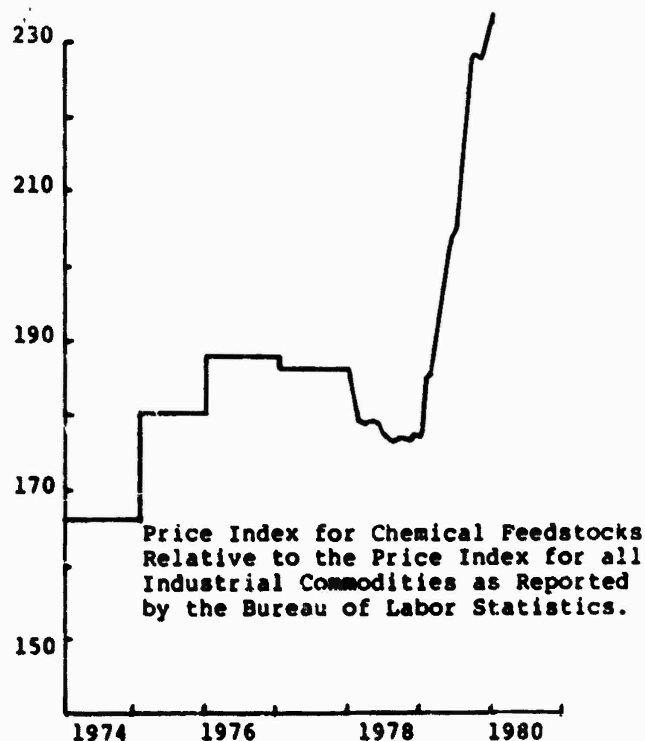


Fig. 1

present in the millions of tons of agriculture and forest residues still wasted each year. In the United States alone, sufficient cellulose could be produced each year from this source to supply all the needs of the world's textile and plastics industry (assuming availability of appropriate technology) if textiles and plastics were to be based only on cellulose! Conservative estimates (7,8) indicate the annual generation of 550 million metric tons of collectible agricultural and forest residues. If this material was to be "pulped" and combined with the cellulose present in the waste paper and board not currently used or recycled, 270 million metric tons of cellulose could be made available (calculation based on 45% cellulose in agricultural residues and 55% in waste paper/paperboard mixtures).

Going beyond this, there is an immense worldwide cellulose potential through intensive forestry (9). Production from the one billion hectares of forests in Europe, North America, Japan and the U.S.S.R. could be increased to 6 billion tons of dry mass, i.e. 2.5 billion tons of cellulose, through the application of intensive forestry, genetics and substitution with faster growing species. Third World forests (2 billion hectares) currently produce 650 million tons of dry mass at an efficiency that is only 5% of their potential, i.e. 13 billion tons of dry mass annually. Looking at the world as a whole, the total land suitable for forest growth (4 billion hectares) is potentially capable of producing 80 billion tons of dry biomass annually. This amount of material is 4 to 8 times the fuel equivalent of all the world's oil, gas and coal sources of energy. Based

on these considerations, it should be apparent that neither production facilities nor raw material availability are barriers to expanded future use of cellulose for fibers and plastics.

CURRENT PRODUCTS AND TECHNOLOGY

While the viscose process for producing rayon is very old, it has been updated to meet environmental requirements. Effluent streams containing by-product sodium sulfate are evaporated to yield detergent-grade salt cake. Zinc salts are recovered by basic precipitation or ion exchange for recycle in the process. Carbon disulfide is captured by condensation and the use of absorption towers for reuse. Oil independence is being achieved by substitution of coal-fired boilers. Sodium hydroxide and sulfuric acid usage has been reduced through the development of viscose compositions that are "leaner," i.e. contain a lower ratio of sodium hydroxide to cellulose. These achievements have been gained through modifications to existing plants.

Installation of newly designed equipment in a greenfield viscose installation permits a different approach (10). The new Maurer spinning machine has multiple acid and zinc washing troughs for the rayon tow with intermediary squeezing and flushing. A zinc free tow is delivered to the staple fiber cutter and a high zinc concentrated waste acid wash water to the spin bath circuit, thus making a separate zinc recovery unit unnecessary. Most of the carbon disulfide and hydrogen sulfide are captured in two process streams, one by direct condensation from degassing of the spin bath and the other by activated carbon treatment of exhaust gases from the stretching troughs and the first part of the washing machines.

Labor efficiencies have been obtained through use of modernized xanthation and viscose filtration equipment. The new Wonjin rayon staple fiber plant at Kyungi-do, Korea, for example, uses a continuous belt xanthator (CBX) unit designed by Chemtex. Maurer has a continuous xanthator based on a screw-extrusion principle which is reported to be working well in commercial practice but is more expensive than new, large (2000 Kg.) batch churns. Continuous filtration systems reduce waste through recycle of gels, particles, etc. These are principally of two types, screen with scrappers (Viscomatic) and particle beds (Funda, ChemMap).

Rayon product development has recently moved along two lines: modification of staple fibers for improved blends with synthetics (11) and development of highly absorbent products for hygienic and disposable end uses. The resurgence of interest in rayon and the impetus for bringing new types of rayon into the marketplace has been commented on in a variety of quarters (11-18). The most important reasons seem to be (a) the spiraling costs of naphtha and aromatics used in the manufacture of dimethylterphthalate for the competitive fiber, polyester, (b) environmental problems and escalating cost of cotton, and (c) promotion coupled with the new rayon product development. A whole new family of third generation rayons are now being marketed

to replace or supplement cotton in blends. This has been done by chemically crimping high wet modulus rayons through changes in the spin bath and stretch chemistry. Examples of these products are Avril II (Avtex), Hochmodule 333 (Lenzing) and Prima (ITT Rayonier Inc.). A polynosic fiber with micro crimp, Fiber C-311, has recently been test marketed in Japan (19). Other approaches are to change the external cross-section of the fiber to a "Y" shape for maximum light refraction (Avril III), or to produce a hollow rayon fiber simulating the cross-section of cotton, such as Courtaulds' Viloft (19). Regular rayons are also being modified to participate in the cotton blend market. An example of this is Kanebo's Lon-Bell Type H-L which has a change in tenacity and elongation to match that of cotton (20).

Applications in the nonwoven sector have been directed toward fibers with improved water absorbency. Courtaulds has recently introduced S.I.Fibre, a very high surface area product (15) for the tampon market which is probably an extension of Viloft technology. Other rayon producers, such as American Enka and Avtex, produce "alloy" rayons which are produced by addition of hydrophilic polymers to the spin dope. These polymers then become an integral part of the fiber. Although neither corporation has identified the precise materials being used, suitable polymers are partially carboxymethylated cellulose, polyacrylic acid and polyvinylpyrrolidone (22-23). While the primary application of alloy rayon fibers appears to be in feminine hygiene products, disposable wipes, etc., they may have future applications in textile blends. A more absorbent rayon should permit differing ratios of cellulosic to polyester or nylon than regular rayon.

Over the years there has been a substantial amount of research on chemical or radiation grafting of synthetic polymers to cellulose. Rayon graft copolymers have been produced by xanthation of grafted wood pulp, redox grafting of cellulose xanthate or grafting of rayon (14). The only product to reach the marketplace thus far is a graft copolymer of rayon and polyacrylonitrile produced in the Soviet Union under the name Mtylon. Much work has been devoted to studies of cross-linking in order to obtain better permanent press properties of cellulosic textile fibers. This work is now being directed to finding materials which do not contain formaldehyde. The latter shows a teratogenic response so it is likely to have severe limitations on its use in the workplace or in products.

Cellulose diacetate has been made for many years. Use in textiles was gradually displaced by synthetics, but large volumes continued to be produced for cigarette filters worldwide. Cellulose triacetate has been used in a variety of applications such as warp and circular knits, satin, terry, creped constructions and velvets. The recent fashion shift to the "disco" look and softer, more flowing clothes for women (11) has significantly increased demand for diacetate and triacetate in the United States. Various research studies have shown methods for reducing acetate's elongation, improvement in

tenacity, etc., but current interest in the fiber seems to be a consequence of its sheen and softness. One of the most interesting developments with regard to acetate does not relate to product changes but to manufacturing conditions. Earlier this year, Eastman Kodak announced (24) its intention to build a plant for making acetic anhydride from coal. Upon completion this process would completely divorce the cellulose acetate process from oil dependence.

While not a tonnage business and certainly not well publicized, there is another rayon/acetate "fiber" development that has great importance from a public welfare standpoint, e.g. hollow fibers for kidney dialysis. Most of the medical equipment used for this purpose is based on fine hollow cellulosic fibers extruded from cuprammonium solution by companies such as Enka A.G. (West Germany) and Asahi (Japan). Similar fibers can be made by the viscose process (25) but they generally contain minute quantities of zinc and sulfur compounds which can cause problems with blood chemistry. This field is particularly exciting because of the potential application of blood dialysis to sickle cell therapy and remission of schizophrenic mental problems. A much larger volume usage of hollow fine fibers is for water purification. In this instance, extruded cellulose acetate (26-27) or (experimentally) mixed ester carbamates (28) are usable. Cellulose esters are also formed into reverse osmosis or ultrafiltration membranes by evaporation of the solvent from a solution of an appropriate ester.

FUTURE PROCESSES

The primary disadvantage of rayon as made by the viscose process is the relatively high production cost, a little more than twice that of the cellulose starting material. Extrusion speeds are slow compared to melt-spun synthetics or dry-spun fibers, and capital costs of a new plant are significantly higher than a polyester fiber from flake plant. In spite of the improvements noted in preceding paragraphs, consumption of sodium hydroxide, sulfuric acid, carbon disulfide and zinc salts is inherent to the process. We have been maintaining (29-32) that it is imperative to develop a new, non-viscose system for producing regenerated cellulose fibers. Research on non-aqueous systems has now been initiated in a number of university and corporate laboratories. Major systems investigated to date are (a) dimethyl formamide-nitrogen tetroxide, (b) dimethyl sulfoxide-paraformaldehyde, (c) N-ethylpyridinium chloride melt or in DMF, (d) nycazine, (e) N-methylmorpholine N-oxide, and, most recently, (f) liquid ammonia-ammonium thiocyanate (33).

One or more of the above systems, particularly the cyclic amine oxides, show especially strong promise with continued research and development. American Enka has proceeded to the pilot phase of their Newcell process and will make a decision in 1981 on going commercial (14). Although Enka has not described their process publicly, recent Enka patents suggest that it is based on a high solids solution in an amine oxide. There is no reported reaction between an amine oxide

and cellulose, so it should be possible to effect total recycle of the solvent with relative ease. ITT Rayonier has indicated that it also has a proprietary system (different from those listed above) that it is currently studying (12).

Three years ago in a Fiber Society symposium (which incidentally contained a presentation by Dr. Mark on super high tenacity fibers), the author presented a lecture in which he noted that it should be possible to use molecularly ordered solutions to produce extremely strong cellulosic fibers. This same theme has more recently been reiterated by Braham Norwich (34). He states, "If we could do with cellulose what has been done to produce Kevlar, the textile market would really be revolutionized. So could tire cord." The net result has been a flurry of activity in university and, hopefully, though they have remained quiet so far, industry laboratories. The first symposium on liquid crystal formation in cellulose derivatives was held at the spring National Meeting of the American Chemical Society in Houston on March 24, 1980. Presentations ranged from Dr. Paul Flory's discussion of his theory of nematic phases in systems of rigid chain molecules to the commercial implications of anisotropic cellulose ether and ester solutions by Dr. A. B. Auerbach. Much enthusiasm for this newest of high polymer investigative fields was expressed by attendees. Perhaps anisotropic spinning will help us to redress the fact that for all too many years we have been taking individual fibers from wood with a native tenacity of 25-30 g./den. and going through an extensive set of chemical steps to produce textile fibers which have a strength of 4-5 g./den. at best.

Along with the new surge of interest in cellulose solvents and anisotropy, it should be pointed out that there is still another area of research that needs reviving. I refer to methods for preparation of cellulose esters and ethers using stoichiometric quantities of reagents. The basic methods for preparing cellulose acetate have not really changed for almost thirty years. Less expensive preparation methods would surely open up new markets, especially in thermoplastic applications. The same may be said for propyl cellulose which has fiber-forming potential by itself or in blends with synthetic polymers. The cellulose propyl and hydroxypropyl ethers, in particular, form liquid crystal systems quite readily, but current manufacturing procedures are relatively expensive because of by-product formation, non-homogeneous reactions, etc.

CONCLUSION

After a hiatus of more than twenty years there is now a new resurgence of interest in cellulose technology. There are immense amounts of raw material, perpetually renewed through the energy of the sun, provided we act as a good husbandman of this resource. New processing techniques have been found, but a significant expansion of research and development effort will surely be needed if we are to effectively convert nature's most abundant polymer to the fibers, films and plastics that we will need in the future.

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Contribution No. 198 from the Research Laboratories of ITT Rayonier Inc.

MODIFICATION OF FIBERS BY RADIATION GRAFTING

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ABSTRACT

The use of high energy radiation to effect the grafting of vinyl polymers to a polymeric backbone was one of the earliest applications of radiation to be explored. Grafting to textile fibers to impart useful or improved properties was emphasized from the beginning. Many of the ideas and approaches which are in vogue today were already investigated in the late nineteen fifties.

Both surface and bulk properties of the fibers can be modified by radiation grafting. Surface improvements which can be imparted by grafting include abrasion, anti-static properties, wettability and adhesion, water repellancy and crease resistance. Bulk properties, or deeper "ring" grafting can impart greater water sorption, flame retardancy and changes in the mechanical behaviour. The high order (orientation, crystallinity) of textile fibers make it more difficult to impart bulk property changes. Methods to overcome this problem which can lead to super-water absorbency and elasticity will be described. In addition, methods of localizing the grafting will be discussed.

RADIATION GRAFTING *per se* appears to have begun in earnest about the middle of 1936. Mesrobian and Ballantine at The Polytechnic Institute of Brooklyn and Brookhaven National Laboratory carried out some early, largely unpublished, work. W. Magat and Chapiro in Paris also did important pioneering work in the field. Neither of these two groups however appeared to have applied the technique in any detail to fibers. This was left to E. E. Magat (a cousin of the late Professor M. Magat) and David Tanner of the DuPont Co. who carried out extensive work mainly using the General Electric Company's newly developed resonance transformer electron accelerator. Their work was highly imaginative and extensive and largely applied to the modification of textile fibers by radiation grafting. Their work is described in an extensive U.S. Patent (1) which issued in 1963. This patent contains 36 examples, 48 of which concern fabrics and fibers, 2 fibrils and 6 with non-textile applications. This patent is a classic in the context of this presentation and should be studied by all interested in the field. It is appropriate at this point to quote verbatim from the patent.

"The process of the present invention is valuable in creating both surface and bulk effects upon shaped articles produced from synthetic organic condensation polymers. It may be employed upon textiles to affect softness, resilience, tendency to shrink, static propensity, resistance to holocasting, pilling, hydrophilicity, wickability and the like. It is useful in changing such properties as tenacity, elongation, modulus, creep, compliance ratio, work recovery, tensile recovery, decay of stress, wet properties, high-temperature properties, abrasion and wear resistance, moisture regain, flammability, hydrolytic stability, heat-setting

properties, boil-off shrinkage, dry-cleaning properties, heat stability, light durability, zero strength temperature, melting point, soilability, ease of soil removal, laundering properties, wash-wear properties, liveness, crease resistance, crease recovery, torsional properties, hysteresis properties, fiber friction, dyeability (depth, rate, permanence and uniformity), printability, washfastness of dyes or finishing treatments (resins, ultraviolet absorbers, etc.), handle and drape properties (stiffening or softening), heat-yellowing, snag resistance, elasticity, density, ease in textile processability, solubility (insolubilization or increase in solubility), bleachability, surface reactivity, delustering action, drying properties, fabric life, crimpability, stretchability, fabric stabilization, compressional resilience (rugs), thermal and electrical conductivity, transparency, light transmittance, air and water permeability, fabric comfort, felting, ion exchange properties, germicidal properties, adhesion, overall appearance and combinations of these as well as others."

It is clear that most of the ideas still being worked on were perceived in those, comparatively early, days. Unfortunately it was ahead of its time and the tremendous resurgence of interest and industrial use of radiation processing which has taken place since about 1975 has not in general involved the textile industry. Between the early days of the DuPont work and the present day, there has been considerable research interest but except for the Deering Milliken announcement in 1966 of a successful quasi-grafting process for imparting permanent press and soil release to polyester and cotton and their blends there has been only limited success. This process has apparently now been discontinued and to the knowledge of the author no other commercial textile grafting process is being practiced. There has been considerable activity both industrially, e.g., Staby International and academically, e.g., W. K. Walsh, N.C. State University, on the use of radiation to cure 100% reactive adhesive and coating compositions.

The reasons for the lack of any real industrial application of radiation grafting techniques is not really clear. Presumably the modifications introduced by radiation grafting are not, up to this time, sufficiently attractive to justify the attendant economic considerations. It is hoped in this paper to present some of the aspects and advantages of radiation grafting to fibers to, hopefully, rekindle interest in this important area of research and development.

LOCATION OF THE GRAFTING IN THE FIBER--It was recognized from the earliest days of radiation grafting to fibers that it would be important to locate the graft copolymer at the surfaces or in the bulk according to the application. If only surface changes are required it would be poor economics to graft throughout the fiber, in addition bulk grafting could, in principle, disturb other desirable properties of the fiber itself. In the case of bulk grafting it is also possible to leave the surface ungrafted if the original fiber surface needs preserving.

Radiation grafting lends itself well to changing the location of the reaction. Variables in the reaction conditions are easily controlled. The monomer can be allowed to penetrate the whole fiber or only given brief contact with the fiber before irradiating. These two approaches would tend to give bulk or surface grafting respectively. In the former case if the irradiation is carried out in air or in the presence of a bulky inhibitor in solution surface grafting can be essentially eliminated. The degree of swelling also will affect the location if a good swelling agent is incorporated with the monomer bulk grafting is highly favored. If the swelling is weak the surfaces only will be grafted. If the monomer is itself a good swelling agent it might be necessary to add a non-

solvent. The swelling method applies equally to both the direct and pre-irradiation techniques. Two examples of choice of location are illustrative.

Walsh and coworkers (2) grafted ethyl acrylate to cotton fabric to impart abrasion resistance. One technique involved padding the monomer in methanol solution onto the fabric which had previously been irradiated in air. This method clearly allows the monomer to penetrate inside the cotton fibers. In a second method the fabric was irradiated in ethyl acrylate vapor, here very little penetration of the monomer could occur. The abrasion resistance of the grafted fabrics clearly illustrated the differences between the two methods. The vapor phase surface grafting resulted in an improvement of four fold in abrasion resistance whereas the bulk grafting actually decreased the abrasion resistance by 50%. Both results were at a grafting level of 10% based on the weight of the cotton fabric.

The author and his colleagues (3, 4) have conducted somewhat similar studies on the grafting of flame retardant monomers to polyester fibers. Bulk grafting was accomplished by preswelling the polyester fibers in ethylene dichloride solution at 70°C for 0.5 hours then in a solution of the flame retardant monomer for 2 hours followed by irradiation. Surface grafting was accomplished by immersing the fibers in the monomer solution and irradiating immediately. The location of the graft copolymer was shown by the use of an X-ray microprobe technique (3,4,5). The flame retardancy was estimated using oxygen index (OI) measurements. The results are presented in Table I.

Table I. Effect Location of Grafting on the Flame Retardancy of Polyester Fibers

Monomer	Percent Grafted		O.I.	
	surface	bulk	surface	bulk
O (Control)	-	-	20.4	-
Vinyl bromide	18.8	18.8	23.5	26.3
Diethyl vinyl Phosphonate	21.0	16.0	24.3	27.6

It can be seen that, in contrast to the abrasion resistance bulk grafting is clearly superior to surface grafting as far as flame retardancy is concerned. An interesting side effect of the bulk grafting was the increase in the elongation of the polyester fibers even with small amounts of grafting. For example, only 2.9% of vinyl bromide increased the elongation by 2.4 times to 92%, this was accompanied by a small increase in the tenacity.

THERMAL PROPERTIES--Changes in the thermal properties of fibers can be introduced by radiation grafting. J.C.Arthur and his coworkers(6,7) as part of their detailed and pioneering work on the modification of cotton with radiation, studied styrene grafts. The grafted styrene was found to be mainly located within the growth layers of the cotton. The samples were found to be thermoplastic with a marked decrease in stiffness at about 100°C, the glass temperature of polystyrene. With 18% graft based on the weight of cotton the load at 1% elongation actually increased at 21°C from 12 gms. for the untreated to 24 gms. At 100°C the untreated had a load of 14 gms. whereas the grafted sample had dropped from 24 to 9 gms. Fabrics of such material should certainly be of interest for some practical applications.

In a very interesting paper by E. E. Magat and coworkers (8) a somewhat different temperature effect was achieved by grafting. Acrylic acid and maleic acid were grafted to nylon 6-6 fibers. The melting points and X-ray crystallinities were similar to those of the original nylon. This was ascribed to the idea that

the grafting presumably only takes place in the amorphous, accessible regions. Conversion of the grafted fibers to their sodium or calcium salts had, however, a dramatic increase in the melting temperatures although the nylon crystals themselves had the same melting point. Fiber melting temperatures up to 400°C were obtainable with the sodium salts and above 600°C with the calcium salts. These lead, of course, to greatly increased hole melting temperatures.

EFFECTS OF CRYSTALLINITY -- Most textile fibers are quite crystalline and this can effect considerably the properties of the grafted fibers. If, as is usually the case, radiation grafting is carried out directly on the fibers often only the amorphous, accessible regions contain the graft copolymer. Magat and coworkers (8) pointed this out when they found that their acid grafted nylons had similar elastic moduli, X-ray crystallinities and melting points to the ungrafted fibers. Work by the present author and his colleagues has repeatedly shown only modest effects on the tensile properties even with very substantial degrees of grafting. This was ascribed to the idea that the tensile behaviour depends largely on the degree of crystallinity and the morphology. This can be exploited practically since certain properties of the grafted side chains can be imparted to a fiber without grossly changing its tenacity, elongation and moduli. Fire retardancy, thermal properties and resistance to microorganisms would be good examples from among many. However, it is an obvious disadvantage if the grafting is aimed at changing the tensile properties such as the elongation and elasticity. Work in these laboratories has shown that at very high degrees of grafting, greater than several hundred percent in some cases, the crystallinity is greatly reduced. When an elastomer, such as polyethyl acrylate, is grafted the fibers develop rubber like elasticity although the fibers themselves retained their shape and general appearance. A method was developed whereby similar results could be achieved at rather modest grafting levels (9, 10, 11). With cellulose fibers, including cotton and rayon, it was found that the grafted polyethyl acrylate held the fibers intact in solvents for the cellulose which were nonsolvents for the elastomer. Concentrated zinc chloride is a good example. On removing the solvent, by washing for example, the cellulose recrystallized to a much lower extent enabling the elasticity to develop at much lower levels. A few results with rayon are given in Table II.

Table II. Effect of Decrystallizing on the Load-elongation Behaviour of Rayon Grafted with Polyethyl Acrylate

Percent Graft	Before ZnCl ₂ Treatment		After ZnCl ₂ Treatment	
	Tenacity	Elongation	Tenacity	Elongation
0	1.60g/d	26	1.55g/d	26
75	0.65	25	0.08	490
300	0.19	41	0.06	800

It can be seen that a 60-80 cellulose-polyethyl acrylate fiber has nearly 300% elongation. By changing the percent of grafting and the conditions of decrystallization a controlled and wide range of tensile properties could be achieved. The accompanying drop in tenacity is disappointing but expected. It is believed that this property can be increased, however, by adjusting the conditions of grafting. Radiation is peculiarly effective for this development since it creates radical grafting sites throughout the fiber. Similar results have been achieved with wool fibers but using thioglycolic acid, for example, to break

the cystine bonds as opposed to decrystallizing.

Water absorbency is another example of a fiber property which is substantially governed by the degree of crystallinity. Cellulose fibers, for example, grafted with polyacrylic acid only give modest increases in water sorbency although changing to the sodium salt does give a further increase. Decrystallization of the grafted fiber in a similar manner to the previous example leads to enormous increases in water sorbency and to "super slurping" fibers (12, 13, 14). Again, controlling the degree and the conditions of grafting can lead to a wide range of sorption characteristics.

Table III. Sorption of Water and Water Vapour
By Rayon Grafted With Acrylic Acid

Material	RH	Per cent water sorption at 25°C			
		25	50	75	100
(Control)		9.0	14.5	20.0	35.0
108% Graft		8.6	14.3	21.5	43.0
108% Graft		22.0	36.0	48.5	3,250*
(Decrystallized)					

*Measured by centrifugation procedure.

It is interesting that sorption is largely a lateral characteristic whereas elasticity is a longitudinal property. If grafting is limited to various depths of penetration of the fiber only a modest response to decrystallization is observed. This greatly reduces the elongation since the center of the fiber recrystallizes, restricting that property. However, in the case of water sorbency, although the overall sorbency may be decreased somewhat without bulk grafting it does give the possibility of developing super water sorbing cellulose fibers with differing degrees of strength which could have interesting commercial implications. Although the work to date has mainly been concerned with cellulose fibers there is no reason why both the elasticity and water sorbency properties could not also be extended to synthetic fibers. Some work in this direction has been initiated but much remains to be done.

In this brief review of radiation grafting to conventional fibers only a few highlights have been presented. There exists a large reservoir of knowledge of other aspects in the literature but clearly much further work is still needed.

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FORTY YEARS OF MELT SPINNING

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ABSTRACT

The age of truly synthetic textile fibers began in October 1939 with the commercial production of nylon in the Seaford (Delaware) plant of the DuPont Company. It is possibly not fully appreciated that to make nylon into textile yarns and fibers required the development of a totally new technology: melt spinning. Nylon was joined by polyester in the early '50's, and by polypropylene in the early '60's. World-wide capacity for these three fibers is close to 25 billion pounds per year, an increase of over 800 times the 30 million pound per year capacity of the Seaford plant. We suppose a latter day Rip Van Winkle who fell asleep in the Seaford plant in 1940 - how would he react if he awoke 40 years later and visited the melt spinning plants of 1980?

BACKGROUND

The era of truly synthetic fibers (contrasted to regenerated or modified cellulose-based fibers) began in October 1939 when the Seaford Delaware plant of the DuPont Company began commercial production of nylon. The public recognized that nylon was a new material, previously unknown. What was not widely recognized was the extent of the completely new technology required to make the nylon yarns.

Prior to nylon, man-made fibers meant viscose and acetate rayon. Viscose rayon is made by wet spinning: a viscose solution is extruded into a spin bath where the filaments are formed by coagulation. Acetate rayon is produced by dry spinning: a solvent solution of the cellulose acetate is extruded into hot air and the solvent evaporates, leaving the acetate filament.

Conversion from nylon polymer to filament was accomplished by a radical departure from either of these: the polymer was melted and extruded into air where the molten filaments solidified. The filaments were not usable in this form but had to be "drawn" or stretched which changed the polymer structure and resulted in the outstanding properties that characterize nylon.

The capacity of the Seaford nylon plant in 1939 was 30M pounds per year of filament yarn; staple did not appear until 1947. Nylon was joined by polyester in the early '50's and by polypropylene in the early '60's. Today melt spinning of these three polymers has reached a capacity of very nearly 25 billion pounds per year, an 800-fold growth in the 40 years. At present, ca. 80-85% of the world production of synthetic fibers is produced by melt spinning.

Attempting to specify the place in history that

anyone or anything will be accorded is always risky, but it would seem grossly unfair not to include melt spinning in any list of the most influential technologies developed in our century. It is our hope to provide a look at this technology at its birth and to show the advances made over these past four decades to bring it to its present state. We will deal primarily with filament yarns with only brief references to staple fiber or tow and none whatever to spinning webs for nonwovens. To distinguish the detailed differences among nylon, polyester and polypropylene melt spinning would violate the time constraints. Time available forces the pictures to be those of a wide-angle rather than a telephoto lens, mentioning advances with a brevity in no sense indicative of their importance.

The technology of today will be described in terms of equipment and processes which are for sale in the open market and by this exclusion of producer's proprietary technology the true state of the art may be somewhat understated. The differences are not believed to be of kind but of degree and are not such as to distort the picture seriously.

The Seaford plant began nylon production using a spinning machine identified as Type 8. In this machine nylon polymer chips were stored under nitrogen pressure in a sealed hopper, from which they flowed by gravity to a pancake coil heated by a central Dowtherm system. The nitrogen pressure moved the molten polymer to a gear pump which forced the metered polymer stream through the sand-filled filter pack and the spinneret, all maintained at the desired temperature by the single Dowtherm system for the entire machine. The molten filaments were quenched by a cross-flow of ambient temperature air in a chimney with side panels to prevent outside air disturbances and the quenched filaments converged over a ceramic guide to form the single threadline per spinneret. Finish was applied by a kiss-roll and the threadline wound-up on a friction-driven spin bobbin at speeds of a few hundred yards per minute. Motive power came from a synchronous motor and was distributed via chain-driven line shafts with suitable gears to take off power for the bobbin drive rolls, feed wheels and metering pumps. Finish application rolls and the traverse drives for the windup were driven by separate small motors.

The spun yarn was then taken to another totally new machine, the drawtwister where it was stretched or "drawn", given twist for coherence and wound up on shipping packages containing one pound of yarn.

Let us look at what has happened to the major elements of the process in the past four decades. We will look through the eyes of a counterpart of Rip Van Winkle: an engineer in the Seaford plant who fell asleep in 1940 and who recently awakened and toured the melt spinning plants of 1980. What would he see and how would he feel?

We start with the first process step, melting the polymer.

MELTING POLYMER

The melting capacity of the 7" diameter pancake coil on the Type 8 machine was limited and maintaining the nitrogen atmosphere was both expensive and cumbersome.

These deficiencies were overcome by a new and improved design of spinning machine, which used atmospheric pressure steam to prevent oxidation of the polymer chips and replaced the pancake coil by finned grids which had a much larger heat transfer surface; Figure 1 shows typical grid design. Polymer chip feed to the melting grid was by gravity. The melting capacity was ca. five times greater so that multiple threadlines per spinneret were readily possible.

Instead of a central Dowtherm system for each machine with its one boiler piped to each spinning unit, this design used an integral, electrically heated Dowtherm boiler in each unit, eliminating the possibility of complete machine shut down because of boiler failure and making replacement of spinning units much simpler.

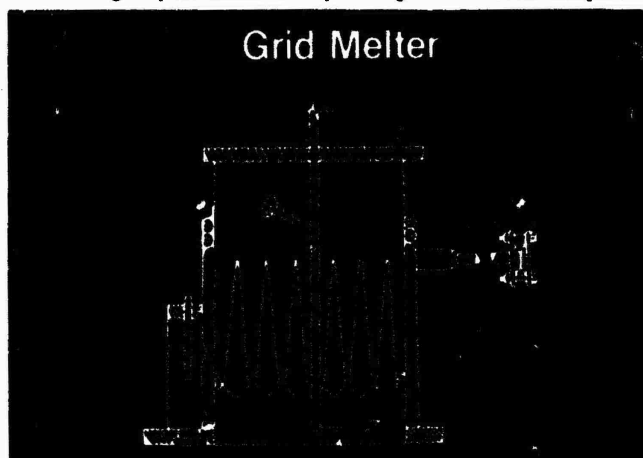


Fig. 1. - Typical grid melter for steam spinning

The next step forward was a truly major one: the DuPont development early in the '50's of a continuous polymerization system for nylon and coupling it directly to the spinning units to eliminate the use of polymer chips. Continuous polymerization was initially used for nylon tire yarn but has been expanded and is now used for nylon and polyester apparel, carpet and industrial filament yarns and for staple. It is not used for polypropylene. The capacity of a continuous polymerization - direct spinning machine can be as high as 150M pounds per year, five times the original capacity of the entire Seaford plant and a far cry from the 1-1.5M pounds per year capacity of the original Type 8 machines. Unfortunately a continuous polymerization train does not lend itself to being pictured on one slide.

Grid melting had a major defect: bridging of polymer over the annular spaces between the heating surfaces lowered the melt rate and led to erratic flow of polymer to the metering pump. The end result was yarn of variable denier. In the '60's grid melting was supplanted by extruders and today they are the standard process where scale and flexibility requirements argue against use of continuous polymerization and direct spinning. Extruders can be horizontal or vertical, vented or unvented, with capacities up to 12-15M pounds per year. Typical extruders are shown in Figures 2 and 3.

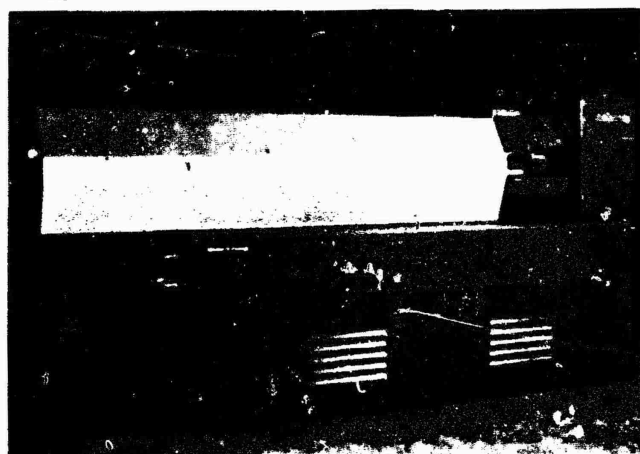


Fig. 2. - Modern horizontal extruder

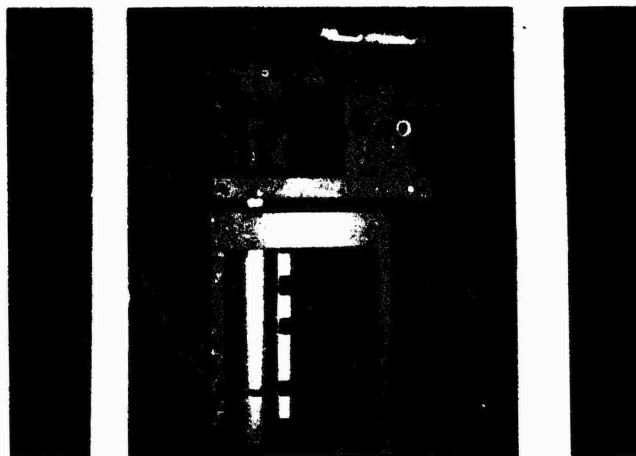


Fig. 3. - Modern vertical extruder

Our sleepy head would not be too surprised by grids or extruders, but the continuous polymerization trains he would find mind-bending.

SUPPLY MELTED POLYMER TO SPINNING UNITS

The Type 8 machine used the nitrogen pressure to move the melted polymer to the inlet of the meter pumps which pumped it through the filter pack and spinneret assembly. As the grid melters operated at atmospheric pressure a booster pump was placed beneath the finned grid to provide positive feed to the meter pump.

In continuous polymerization coupled to the spinning units, a large positive displacement pump takes the molten polymer and pumps it to the metering pumps of the spinning units.

The extruder, being a positive displacement device, provides the motive force to supply the polymer to the spinning units.

Our modern Rip would be impressed by the size of the transfer pumps on continuous systems but he would see no principles that were truly new and this part of the process he could accept easily.

PUMP PRECISELY METERED POLYMER STREAM THROUGH SPINNERETS

The molten polymer must be delivered to the spinneret in precisely metered amounts or the filaments will vary in size and produce final products unacceptable aesthetically or in performance.

The metering pump must discharge exact volumes of molten polymer per unit time, against pressures as high as 10,000 psi and at temperatures in the 300°C range - not an inconsiderable set of requirements.

Fortunately a firm technology basis was available from experience in the rayon industry and the high-precision gear pumps used at Seaford were a comparatively simple extension of previous practice. Each pump supplied one metered stream to each spinneret. After 40 years, metering pumps have become bigger with capability to supply as many as four metered streams and new materials have been used to make them last longer, but they have not had any quantum improvement in accuracy, a testimony to the very high quality of the original pumps. The metering gears are shown in Figure 4 and a typical pump in Figure 5.



Fig. 4.

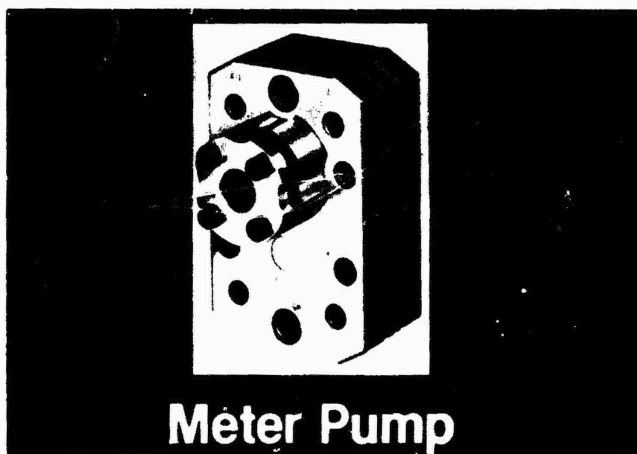


Fig. 5.

Polymer may contain catalyst residues, gel particles, precipitated additives, etc., all of which would clog the spinneret holes. Before the metered streams of molten polymer can be extruded through the capillaries of the spinneret, they must be filtered and subjected to fairly high shear to achieve melt homogeneity. Filtration and shear are accomplished in the pack assembly, consisting of the filtration/shear device attached directly to the distribution plate and spinneret.

At Seaford the pack was a cylindrical cavity approximately 1 1/2" in diameter by 1 1/1" high, filled with layers of different sizes of special sand, the finest on the bottom and the coarsest on top. Fine mesh screens in the bottom and top of the cavity retained the sand in place.

Today the layers of sand have been largely supplanted by specially designed screens and sintered metal. Pack designs must minimize the possibility of "stagnant spots" where polymer could be trapped and thermally degrade, increasing the pressure drop through the pack and shortening its life.

Packs have grown bigger and certainly better since Seaford, but their apparent simplicity man's subtleties still not completely mastered. Four decades have brought many answers but not all, and individual producers will differ rather widely in their perceptions of what constitutes the preferred pack design and composition.

The Seaford spinnerets were 316 stainless steel discs about 2" in diameter, 3/16" thick and with 13 round holes having the cross-section shown in Figure 6. The finish of the spinneret walls and face was primitive by today's standards. The demands

for increased productivity led to larger and larger spinnerets and instead of filaments with simple round cross-sections, much more complex shapes were spun; a few such cross-sections are shown in Figure 7. Today disc spinnerets are available with as many as 500 holes and rectangular shapes for staple with up to 4000 holes.

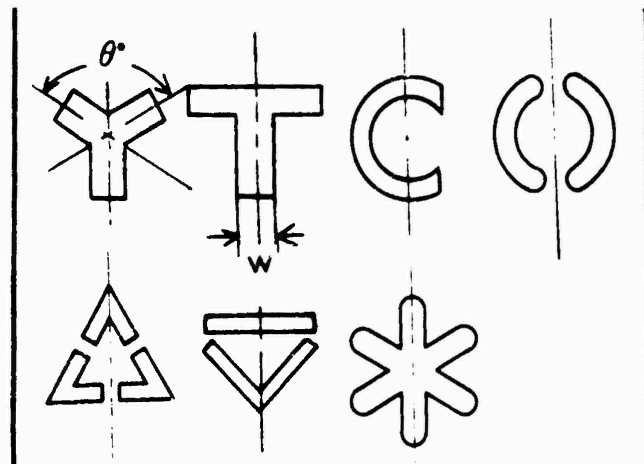


Fig. 6. - Representative non-round spinneret holes



Fig. 7. - Non-round holes in spinneret

Increased size and better methods of fabrication were accompanied by new metals, and after the austenitic 316 stainless came martensitic 430 stainless and most recently, the 17-4 precipitation hardening steels which give the corrosion resistance of a 316 steel plus much greater tensile strength and hardness; AISI 630 is illustrative of this class of steels.

Detailed specifications for spinnerets are jealously guarded proprietary information and commercial manufacturers normally make spinnerets for the different producers under stringent confidentiality agreements.

Our old timer would be impressed by the size and variety of the modern pumps, packs and spinnerets but he would find it easy to relate to them.

QUENCH FILAMENTS, COMBINE INTO THREADLINES AND APPLY FINISH

The 13 molten filaments from the first Seaford spinnerets were solidified by a stream of ambient temperature air flowing perpendicularly to them in a "chimney". The chimney was ca. 30" long and had a rectangular cross-section; the front was open. To insure laminar flow, proper volumes of air were fed to

each chimney through a distribution plate and fine-mesh screens at the back; the sides of the chimney prevented stray air currents from disturbing the filaments. At the bottom of the chimney the filaments were converged to form the threadline in the "v" formed by crossed ceramic pins, and this threadline passed to the floor below where finish was applied and it was wound up on the spin bobbins.

As succeeding generations of spinning machines went to higher speeds, a greater range of deniers per filament, greater numbers of filaments, and a variety of cross-sections, the design of chimneys changed to accommodate the new demands. Aerodynamics has been an invaluable source of technology for designing quenching systems with the necessary capabilities. Figure 8 shows a typical chimney installation of the 1950's, Figure 9 of the 1970's.



Fig. 8. - Typical quenching chimneys of 50's

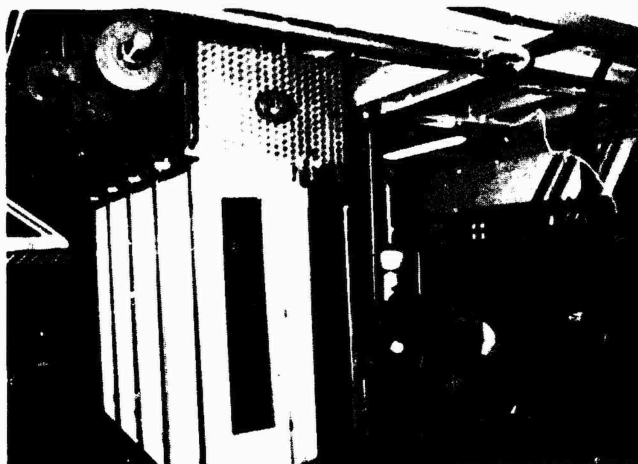


Fig. 9. - Typical quenching chimneys of 70's

Air is not the only quenching medium that has been used, nor is cross-flow the only quenching geometry. A good deal of information on design of quenching systems remains proprietary.

Threadline convergence is still done via ceramic pins arranged in a variety of ways, as well as by bringing the threadlines together in the grooves of a metered finish applicator or a finish roll.

Our modern day Rip would feel at home with the external appearance of the chimneys but the sophistication of the design details would be completely foreign to him.

After the individual filaments have been quenched and converged into a threadline, spin finish must be applied. Without a proper finish subsequent process-

ing by producer and customer would be essentially impossible in any realistic sense.

In the beginning, the function of a spin finish was to provide lubrication and cohesion. Without cohesion the yarn could not be wound into stable packages capable of being handled and transported within the plant, let alone to customers, and lubrication was necessary for the drawing operation as well as for customer processing steps. The finish was an oil-in-water emulsion applied by running the threadlines through a liquid film on a rotating roll partially immersed in the finish solution - the "kiss-roll".

Finish compositions were based on those which had been used on natural fibers and on rayon. They were mostly natural materials plus some fairly pedestrian chemicals. Typical components in the early years are shown in Figure 10.

TYPICAL FINISH COMPONENTS

1940's

NATURAL

Teaseed Oil
Lecithin
Mineral Oil
Neofat

SYNTHETIC

Triethanolamine
Boric Acid
Sorbitan Monolaurate
Diethylene Glycol

Fig. 10.

Finishes today must do much more than provide lubrication and cohesion; it is not unusual in some yarn end-uses for a spin finish to be able to satisfy as many as 50 processing needs of the producer plus the trade. Functions which may be required of today's finishes are shown in Figure 11.

FINISH FUNCTIONS

1980

Antioxidant

Antistatic

Bactericide

Chelating Agent

Coacervating Agent

Cabling Aid

Dyeing Aid

Dye Leveling Agent

Emulsifier

Fungicide

Fugitive Int

Humectant

Lubricant

Securing Aid

Softening Agent

Surfactant

Texturing Aid

Fig. 11.

Besides the roll applicator used in 1939 we have pin applicators by which metered amounts of finish are supplied to the yarn as it passes through the V-shape of the applicator; Figure 12 shows a typical installation.

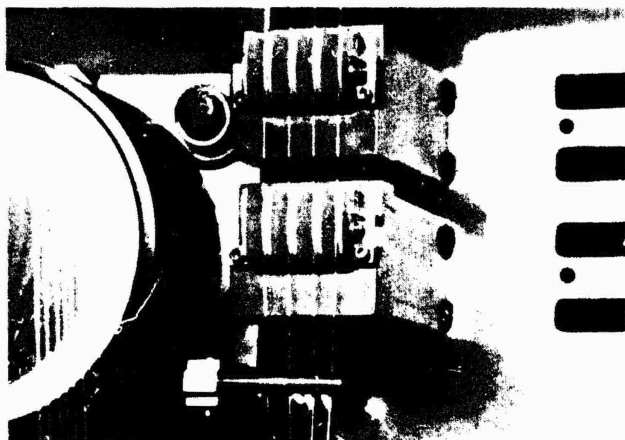


Fig. 12. - Metered finish applicators

A partial listing of the chemicals used for lubrication in today's finishes is shown in Figures 13 and 14. Note that these show some of the chemicals used for just one of the functions of finishes today.

MODERN FINISH CHEMICALS: LUBRICANTS

NATURAL

Waxes
Mono Di & Triglycerides (Vegetable)
Acetylated Monoglycerides
Hydrogenated Glycerides
Oxidized Triglycerides
Mineral Oil
Vegetable Oils, Glycerides & Fatty Acids

Fig. 13.

MODERN FINISH CHEMICALS: LUBRICANTS

SYNTHETIC

Silicones
Emulsifiable Polyethylenes
Trimethylol Ethane Tri-Esters
PEG 400-600 Mono & Diesters
Dialkyl Diesters (Adipates, Phthalates)
Hexadecyl Stearate
2-Ethyl Hexyl Stearate
Isopropyl Stearate

Fig. 14.

Another element in the increasing complexity of spin finishes is the need to insure that they do not pollute and, needless to say, they are carefully screened to insure dermatological and toxicological suitability.

Four decades have seen us advance from a largely empirical approach to the scientific compounding of compositions whose various moieties have been correlated with their effects in the finishes.

The materials, the methods of analysis and the complexity of the formulations would have our friend

shaking his head in wonder. Only the finish roll applicator would be familiar.

WINDUP AND DRAWING

At Seaford, after finish was applied to the threadline, it continued over two feed wheels or godets and then wound up on a bobbin; yarn speed was around 300-400 yards/min. The yarn was laid on the bobbin by a diminishing stroke traverse to form a bi-conical package because the finish was not cohesive enough to form a square package. Each bobbin had one cake of yarn. Figures 15 and 16 show views of the Seaford windup floor.

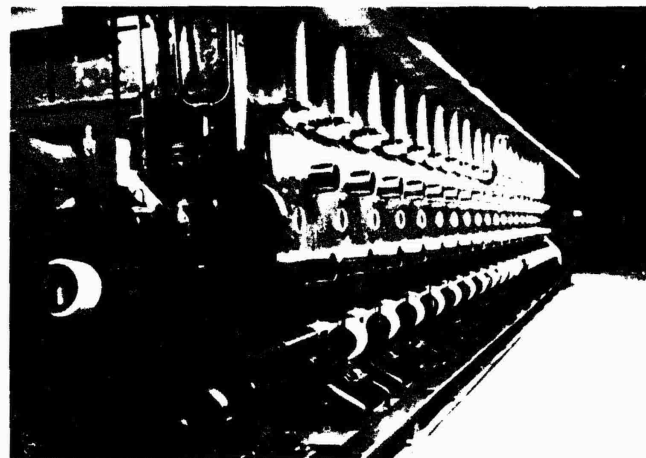


Fig. 15. - Windup floor at Seaford - 1940

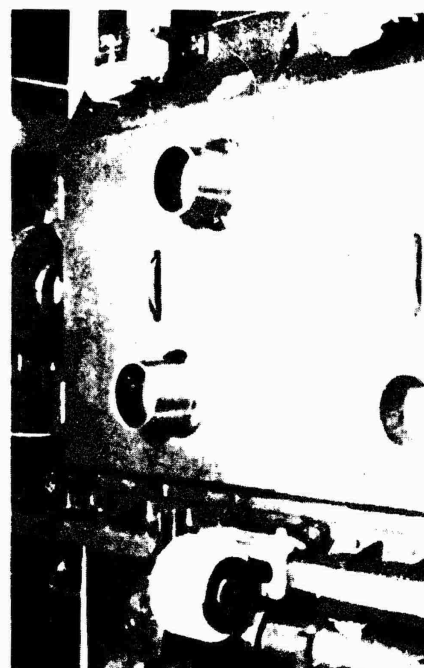


Fig. 16. - Seaford windup, 1940: 1 end per position

The spun bobbins were then taken to drawtwisters where the yarn was drawn or stretched by removing it from the bobbins at a fixed rate, snubbing it on a ceramic pin and passing it over a draw roll rotating at a speed higher than the feed rate by a factor depending on the amount of drawing desired. The drawn yarn was wound up via a standard ring and traveler mechanism to give it twist for coherence and taken up on a pirn for shipment. Actual weight of yarn on a pirn was one pound. Figures 17 and 18 show a Seaford drawtwister.

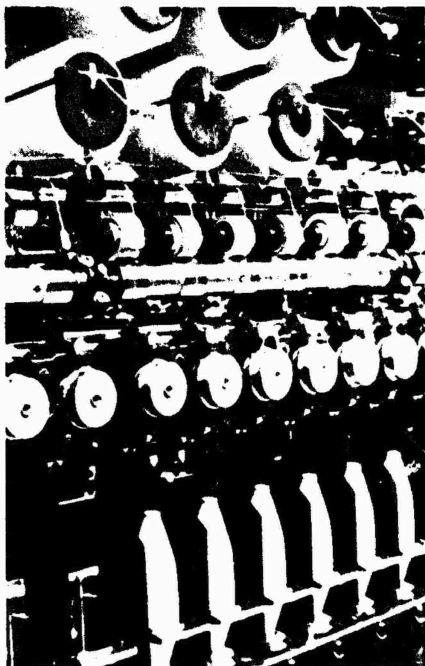


Fig. 17. - Seaford, 1940: Whitin RG-4 drawtwister



Fig. 18. - Doffing a drawtwister: Seaford, 1940

The first two decades after Seaford saw filament yarns being wound up at higher speeds, bigger spin packages, and multiple cakes of yarn on each bobbin. Tandem winding, where each bobbin drive roll drove two spin bobbins, replaced the single bobbin windup of the original Seaford machines; Figure 19 shows this configuration. Spinning windups became available in a variety of designs: some had the packages parallel to the machine face - as in the original Type 8 machine - and others had the windups perpendicular to the machine face. Windup speeds of 2000 yards/min. were attainable and the packages went up to the 20 to 30 lb. range. Figures 20 and 21 show such windups.

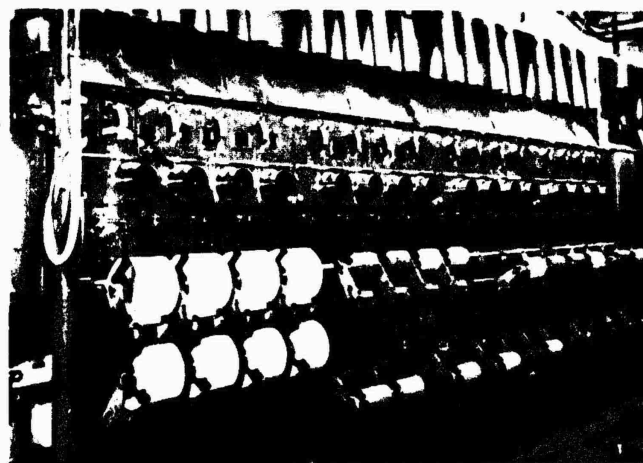


Fig. 19. - Windup floor, 1950's: tandem windups

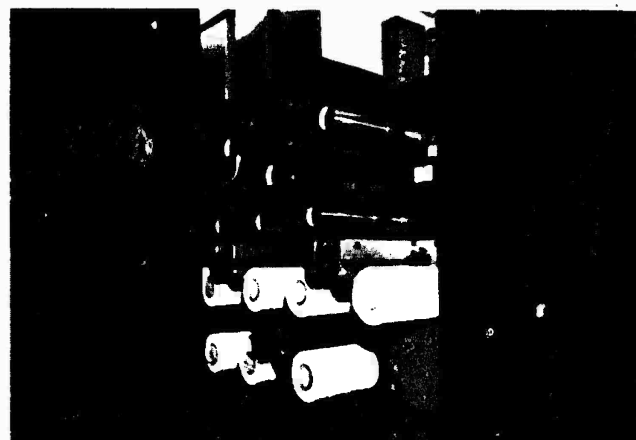


Fig. 20. - Multi-cake, tandem windups: 1960's & 1970's

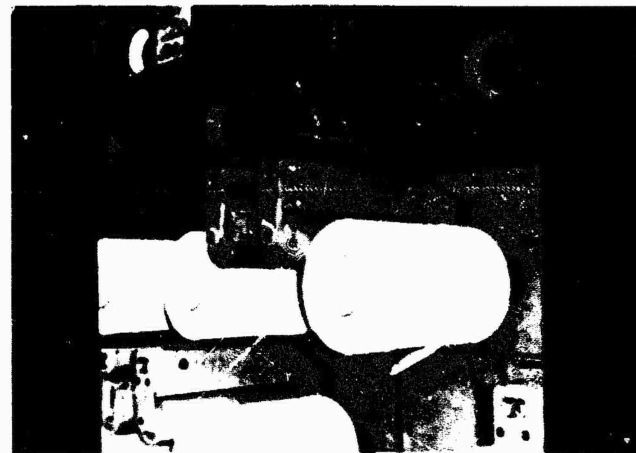


Fig. 21. - Multi-cake, tandem windups: 1960's & 1970's

At the same time the drawtwister was being improved to provide the yarns needed for new applications. Heated draw pins and draw rolls were introduced, speeds were increased, larger pins accommodated and highly refined mechanical designs incorporated into the machine. The principles remained the same but the equipment was much more versatile and reliable. By and large, our Rip would not have been uncomfortable with all that he saw in spinning and drawtwisting.

Spinning on one machine and drawing on another - the "split process" - was not the ultimate in

efficiency regardless of evolutionary improvements so that if spinning and drawing could be "coupled" and done continuously it would be a quantum jump in technology. DuPont accomplished this revolution in 1959 by the simultaneous development of high speed winders necessary for economics and the use of fluid jets to tangle the yarn as a twist substitute. The first application was to polyester textile yarn followed in 1960 by nylon tire and apparel yarns. Split process yarns were at a disadvantage both in economics and performance and the death knell of the drawtwister had been sounded.

The coupled process must rank in the forefront of technical advances made in the 40 years of melt spinning. Combined with continuous polymerization it represents the preferred process for filament yarns of nylon and polyester; for polypropylene the coupled process is used with extruder melting of flake in place of continuous polymerization. Figures 22 and 23 show coupled process installations.

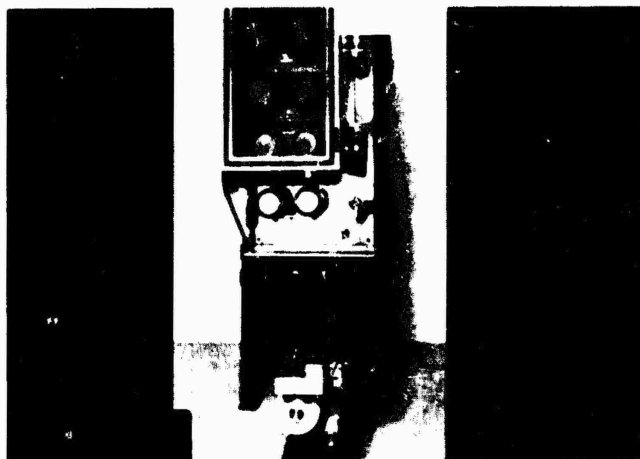


Fig. 22. - Coupled process: equipment arrangement

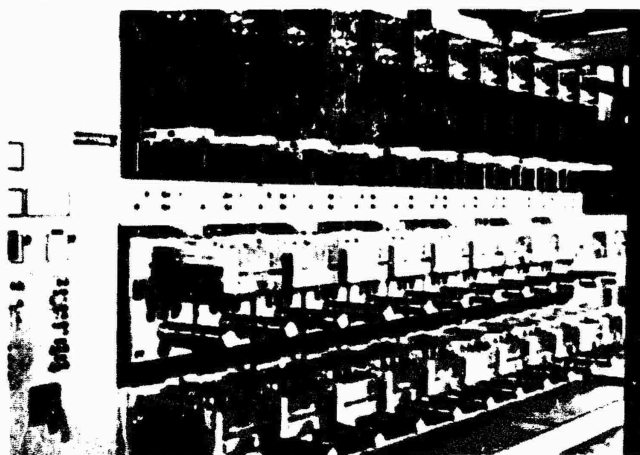


Fig. 23. - Modern coupled process windup floor

From the 2000 m/min. winder speeds of the early 60's we have come to 6000 m/min. in 1980. Package sizes have increased and are still increasing - the 4-5 kg. packages of the first coupled-process yarns have progressed into 25 kg. packages of today - and they are still growing. Another development has been "godet-less" spinning in which the filaments pass directly from the spinneret to the take-up without passing over any godets; the drawing takes place in the chimney as the filaments are subjected to the forces of the winder. Other developments have been multiple-package winders such as shown in Figures 24 and 25 and automated winders which doff full packages and string up empty bobbins automatically, illustrated in Figure 26. Looking at equipment of this type would leave our counterpart Rip speechless.

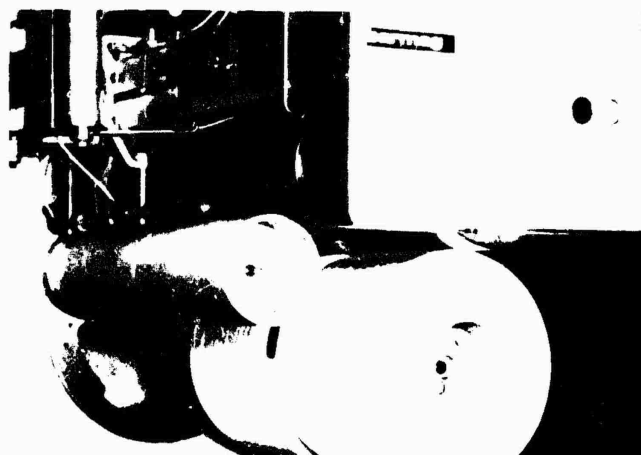


Fig. 24. - High speed, twin cake winder



Fig. 25. - High speed, twin cake winder: full packages

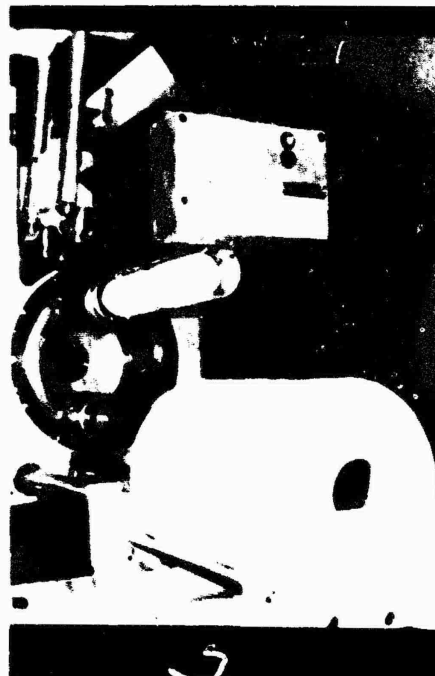


Fig. 26. - High speed, twin cake turret winder

The mid 50's saw the introduction of texture to melt spun yarns, both by mechanical and fluid jet processes. Texturing processes give filaments different kinds of crimp, providing either stretch for hosiery yarns or bulk for apparel and carpet yarns. Initially texturing processes were split processes, taking the fully drawn yarns to a separate machine where they were textured, but it was not too long before in-line texturing was developed using fluid-jet techniques. Mechanical texturing is still largely a split process as most systems cannot operate at the speeds necessary for in-line processing. The carpet yarns of today are textured in-line by fluid jet processes but texturing of textile denier yarns is overwhelmingly by mechanical means on separate machines. In-line texturing of carpet yarns is shown in Figures 27, 28 and 29. Again, our latter day Van Winkle would shake his head in disbelief.

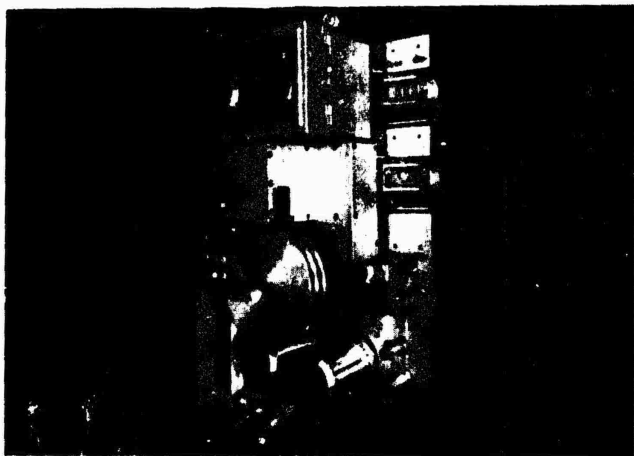


Fig. 27. - Spindrawtexturing carpet yarns: Rieter



Fig. 28. - Spindrawtexturing carpet yarns: Neumag

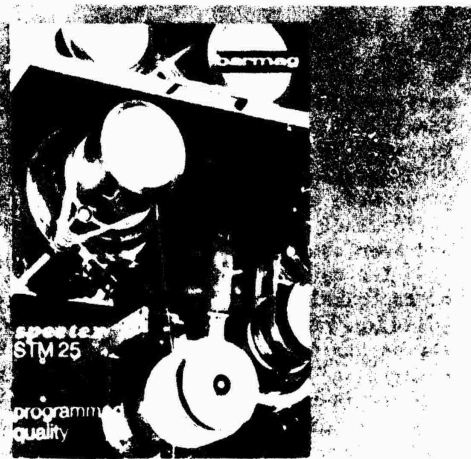


Fig. 29. - Spindrawtexturing carpet yarns: Barmag

Developments in staple have followed the same general theme as for filaments: bigger, faster and cheaper. The first staple line (in 1947) used batch polymerization and Type 8 spinning. Today continuous polymerization plus direct spinning is the norm. In a typical polyester staple process the filaments are combined from the spinning machine and coiled into cans which are then used as the feed for the next stages; it is a split process.

The cans are creeled and the tows combined, hot-wet drawn and dried. Finish is applied after which the tow is crimped, dried, heat-set, cut and baled. Tows of several million total denier are common and processing speeds go up to around 400 m/min. The forces exerted in drawing are rather robust: 10-12 tons. Figure 30 shows a typical draw-stand.

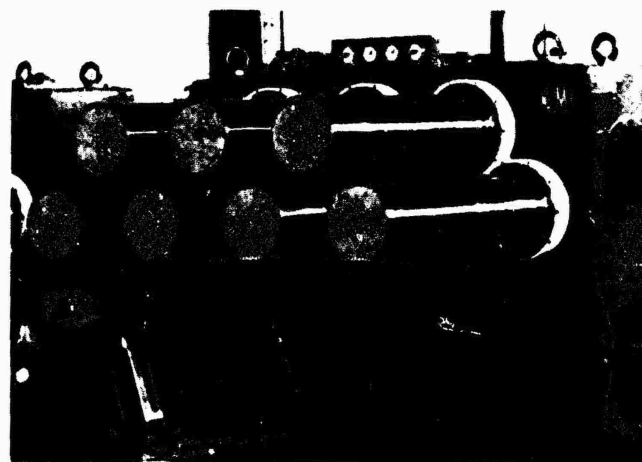


Fig. 30. - Draw-stand for tow drawing (split process)

As Rip had never seen any of these operations following spinning, he would have a hard time believing his eyes.

The most recent development is to use a coupled process for staple production also and Figure 31 shows a schematic of such a process. The threadlines from several metered streams are combined and drawn; the drawn tows from several positions are in turn combined and fed to an in-line crimper, cutter and baler.

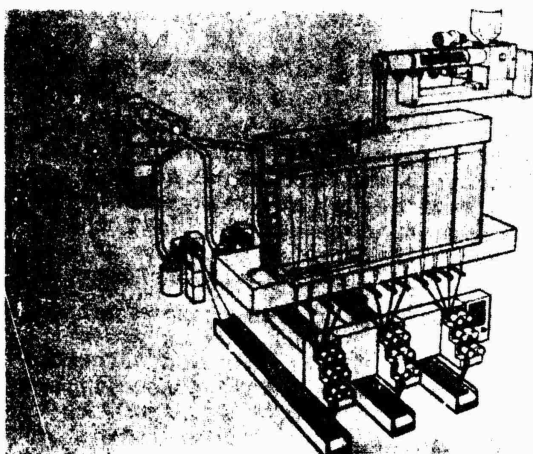


Fig. 31. - Coupled process for staple

DRIVES

Drive systems are designed to insure that all rotating elements are turning at their proper speeds with as little variability as possible.

The Seaford Type 8 machine used a 50 HP, 1200 rpm synchronous motor to provide power to a mechanical system of gears, chain drives and line shafts shown in Figures 32 and 33. Proper choice or change gears gave the range of speeds desired. Vertical shafts were used to provide power to the meter pumps and the bobbin take-ups were run from a coupled line shaft extending the length of the machine. The total assembly of gears, chain belts and line shafts made for a rather imposing mechanical array.



Fig. 32. - Seaford, 1938



Fig. 33. - Seaford, 1939

The system had two major faults: attainable speeds were too low and the variability was too great, running as high as several percent. All subsequent spinning machines have adopted electrical drive systems which can operate at much higher speeds with much less variation. Line shafts and gears have disappeared and individual motor drives are used as much as possible, with timing belts employed for any necessary mechanical power transmission.

The general principle of electrical drive systems is to provide a controlled frequency current to synchronous motors. Various electrical systems were designed and used during the late 40's and the 50's, and speed control to $\pm 1/2\%$ was standard.

With the advent of the inverter in the 60's, electronics took over completely. With individual synchronous motors fed from inverters, speed control of $\pm 0.006\%$ is readily achieved. It is doubtful that closer speed control will serve any useful purpose. Rip would never have seen an inverter and the control achieved in today's plants would be hard for him to conceive.

CONCLUSION

Perhaps an analogy is an appropriate way to summarize:

Our modern Rip Van Winkle went to sleep in the era of the DC-3 and awakened in the time of the Concorde; he found things are now much bigger and go much faster. With bigger and faster airplanes and more of them, the need for control had escalated and instruments undreamed of in 1940 were guiding people safely through the skies. The same principles have applied in melt spinning and our Concordes are the Toray "Zero Person Plant" polyester filament plant in Japan - where there are no line operators in the traditional sense, only maintenance men for the automated system - and the recent DuPont nylon BCF plant "with computer controlled processing and computerized QC" (Quality Progress, Jan. 1980, p. 40).

The analogy with air travel can be carried a step into the future; if these plants are melt spinning's Concorde today, what will be its space shuttle tomorrow?

If we had another Rip Van Winkle who went to sleep in Ishikawa or Waynesboro today, what would he see if he woke up in 2020?

ACKNOWLEDGEMENTS

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We are especially grateful to Dr. Otis L. Shealy of the Textile Fibers Department of E. I. DuPont de Nemours & Co., who, with his associates, went to considerable effort to give us invaluable material concerning operation of the Seaford plant in 1939-40 and to confirm the dates of innovations introduced by DuPont.

RECENT DEVELOPMENTS IN THE OPTIMIZATION OF A MELT SPINNING PROCESS

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In industrial applications, the most important problems of melt spinning and drawing are a) the optimization of the process with respect to a given fiber property, b) the transfer of an optimized process from one type of equipment to some other type and c) the modifications of an optimized process to account for changes in product and equipment modifications. In this study we review analytical techniques which greatly facilitate the optimization of a melt spinning process. The method is based on the finding that (1) the temperature and deformation rate histories of the fiber in the spinning and drawing steps control the quality and properties of the final product and (2) the digital simulation of the process can be used to match filament temperature and deformation histories when process rates, spinnerette and quench stack designs are changed. An example of process optimization is presented with respect to fiber strength and the origin of perturbation is discussed which affect adversely the filament and yarn properties.

INTRODUCTION

Experimental and analytical studies of the melt spinning process have been carried out by many authors. Most of the studies were concerned with the rheological and heat transfer aspects of the melt spinning process (Ref. 1-5, for example). Recently, some authors investigated the change of fiber structure in the spinway by use of x-ray and birefringence devices (Ref. 6-7, for example). The findings from these studies help one understand the dynamics of filament thinning, filament quenching and change of fiber structure in the melt spinning process.

In industrial applications, the most important problems of melt spinning are:

- a) the optimization of the process with respect to a given fiber property, a set of properties, a set of properties coupled with some other factors such as, production rate, quality of the final product, product uniformity, etc.
- b) the transfer of an optimized process from one type of equipment to some other type, and
- c) the modifications of an optimized process to account for changes in product specifications, alterations in the spinway, etc.

The present understanding of melt spinning and drawing processes is, in most cases, insufficient to predict without

extensive experimentation the optimum conditions for a given product. As a rule, these goals are achieved by various types of experimental work.

The transfer of an optimized process from one type of equipment to another, and the modifications in the process to account for changes in production rate, alterations in equipment design, etc., on the other hand, can be greatly facilitated by means of modern computational and simulation techniques.

In this article, we describe a method to optimize the spinning and drawing process in terms of filament temperature and deformation history and describe a method to modify the process or transfer the process from one type of equipment to another. The principle of the method is based on the assumption that the properties of the fiber are uniquely defined by its temperature and deformation rate history. The mathematical problem is, therefore, to establish the changes in operational variables to match the temperature and deformation rate history of the filaments when equipment design or production rates are changed. The study is limited to fibers which can be spun and drawn via an essentially amorphous undrawn yarn.

EXPERIMENTAL

A. Determination of Optimal Spinning

Conditions. Schematics of the experimental spinning system are shown in Fig. 1. It is similar to an ordinary melt spinning system with the spinnerette die at top and the take up roll at the bottom. The special feature of this spinning system is the series of sleeves which are stacked in vertical direction, surrounding the spinway. Individual sleeve had an internal diameter of 10 cm (4 inches) and a length of 15 cm (6 inches) and the sidewall is wrapped with heating band and insulation materials. The sleeve is made of two halves of a cylinder which are combined by the hinge in order to facilitate opening the sleeve when necessary. The sidewall has five circular openings. The observation window at the front center is provided for observation of filament when the probe for filament temperature measurement is inserted through the temperature probe access hole and is brought into contact with the filament. The openings for the air inlet and air outlet are installed on individual sleeve to facilitate the variation of air temperature and air velocity locally. The additional access hole on the left hand side was installed to allow illumination of the filament while photograph of the filament was taken by a camera through the front observation window for the purpose of determining the filament diameter. A thermocouple tip was placed on the inner wall of the sleeve to monitor the sleeve wall temperature. The air temperature inside the sleeve was measured by inserting a thermocouple through the temperature probe access hole and the air velocity was measured by inserting an anemometer through the same access hole.

Using this spinning system, the experimental optimization of the process for maximizing the tensile strength of filament obtained by drawing after spinning was

carried out as follows:

1. After setting up the system, the extrusion was started at a prescribed rate with the melt at the spinning die fixed at a suitable temperature.
2. The sleeve temperatures were set to an initial profile and the air flow was set to an initial pattern.
3. Then, the filament was taken up by the take up roll at an initial take up speed.
4. An experiment for optimization was carried out to establish optimum drawing conditions.
5. The spun yarn was drawn to a fixed high draw ratio at the optimum drawing conditions.
6. The spun yarn was drawn to maximum at the optimum drawing conditions.
7. After the drawing under conditions established in item 6 above, the tensile strength of the filament was measured.
8. Then, sequentially, systematic variations were made of the take up speed, sleeve temperatures, and air flow rate.
9. The run which gave the maximum tensile strength was repeated and, at this time, measurements were made of the filament temperature and filament diameter at each of the sleeves. The filament temperature was measured by the contact null point device (12) and the filament diameter was measured by close up photography.
10. The temperature and diameter data were interpolated by the digital simulation technique.

Thus, by the experimental optimization and digital simulation for interpolating the experimentally measured temperature and diameter profiles, we could establish the complete profiles of temperature and diameter for an optimized spinning process.

Next, the extrusion rate was varied and then the same optimization experiment was repeated to achieve the maximum tensile strength of the filament. Again, from the experimental data, the optimal temperature profile and diameter profile were established by interpolating the data by the digital simulation technique. Then, the optimal profiles thus established were compared to each other to examine the similarity in the real time history of temperature and elongation rate in the spinway.

The examination of plots of the filament temperature vs. time and those of the deformation rate $\frac{dv}{dz}$ vs. time in the spinway showed that the optimal spinning conditions are achieved when:

- a) The deformation rate $\frac{dv}{dz}$ is at a critical high value at which further increases in

$\frac{dv}{dz}$ lead to an abrupt deterioration of filament uniformity.

- b) The filament cooling rate $\frac{dT}{dt}$ is at a critical high value at which further increases in $\frac{dT}{dt}$ lead to an abrupt deterioration of filament uniformity, and
- c) the time at which the maxima in dv/dz and dT/dt are observed is at a critical low value at which further decreases lead to an abrupt deterioration of filament uniformity.

It should also be noted that the conditions (a), (b), and (c) are related and that the optimization of one leads automatically to the optimization of the other two.

B. Characterization of Undrawn Filaments: Minimum Order Hypothesis. All filaments investigated in this study were essentially amorphous by wide angle x-ray analysis but oriented as indicated by birefringence measurements. Plots of birefringence vs. strength revealed an interesting relationship. With fibers spun from the same polymer under a variety of conditions, we observed only a minimal scatter about the line having a well defined maximum at very low values of birefringence. Below this value the strength dropped abruptly while at higher than optimal values the decrease was monotonic but rather slow. Since the existence of the maximum could be easily verified by repeating the experiments, we originally speculated the maximum in strength reflects a fiber morphology which is particularly suitable for producing high strength fibers.

A thorough examination of undrawn fibers by small angle and wide angle x-ray diffraction and optical and electron microscopy failed to reveal a structural characteristic which could explain the maximum. The measurement of tension during spinning, birefringence along the filament and diameter of filament showed, however, that at conditions on the left of the maximum the above quantities show abruptly a much larger fluctuation and scatter than at conditions at the maximum and on the right of the maximum.

From these results we concluded that at the conditions on the left of the maximum we were unable to control the spinning as effectively as at the conditions corresponding to optimum or higher than optimum birefringence. Therefore, the maximum in strength is not related to a specific fiber morphology but must be attributed to the onset of instability in spinning at very low take up tensions.

It should be noted that such maxima in strength are observed only in experiments where special efforts are made to prepare undrawn fibers with no or minimal orientation. Furthermore, when the results from various types of spinning experiment are compared the position of the maximum varies with the quality of equipment.

The comparison of plots of strength vs. birefringence and fluctuations vs.

birefringence are also revealing. For values of birefringence exceeding the optimal value, the fiber average strength decreases in spite of the fact that fluctuations in fiber strength and uniformity also decrease. This suggests that in the spinning process we should make an attempt to minimize the order and orientation. This finding is not surprising if one considers that in the drawing process, the original structure is first completely destroyed and then reorganized and reoriented into an entirely new fiber morphology. This follows from our morphology studies. These showed that within the resolution of our analytical techniques we were unable to detect significant morphological differences in fibers drawn from different precursors provided the drawing conditions were maintained constant. The only change in the process is the drawing tension which increases with increasing birefringence. We, therefore, visualize that drawing tension involves tension to destroy the preexisting order in the undrawn fiber and tension to align the molecules, form microfibrils and shear the microfibrils at high draw ratios.

In order to achieve maximum fiber strengths from a given polymer by melt spinning it is, therefore, necessary to: a) select spinning conditions which minimize the order and orientation in the spun fiber, and b) design equipment with minimal perturbations such as: filament swaying, temperature and pressure fluctuations, etc.

C. Optimal Drawing Conditions. In order to determine the optimal drawing conditions we carried out a series of one step and a series of two step drawing experiments using a two roll set up and a flat heating element. This experimental set up allowed the direct observation of the drawing zone, control and calculation of filament temperature as well as variations in draw ratio and the rate of deformation. The average filament temperature in various sections of the drawing zone was calculated by solving the heat transfer equation which includes viscous heat generation term

$$\rho C_p v_z \frac{d\langle T \rangle}{dz} = k \frac{d^2 \langle T \rangle}{dz^2} + e_v + q$$

here

- ρ = density
- C_p = heat capacity per mass
- v_z = fiber velocity
- z = axial coordinate
- k = thermal conductivity of the fiber
- $\langle T \rangle$ = average temperature across the fiber
- e_v = viscous heat generation per unit volume
- q = rate of energy input per unit volume via heat transfer with the surroundings.

In order to determine the viscous heat generation term we consider a small segment of the fiber of length Δz . The work rate input or viscous heat generation for that

segment is given by

$$E_v = F \Delta v_z$$

where F is the (constant) drawing force and Δv_z is the change in axial velocity across the segment. Since the volume of the segment is given by $A \Delta z$, where A is the (fiber) cross sectional area of the segment, the work rate per unit volume is given by

$$e_v = \frac{F \Delta v_z}{A \Delta z}$$

Taking the limit as Δz goes to zero, we obtain a differential expression for the viscous heat generation term

$$e_v = \sigma \frac{dv_z}{dz}$$

where σ is the local axial stress.

The examination of the shape of the drawing form by means of optical microscopy and photography showed that under drawing conditions which lead to strong fibers the drawing differs from that observed in constant load experiment (Fig. 2). At drawing conditions used in this study the drawing zone consists of a yield zone and a post yield deformation zone as shown schematically in Fig. 3. The examination of drawing zone deformation and temperature profiles showed that the drawing process can be described in the following terms; diameter ratio D_0/D_1 and D_1/D_2 and temperature at the end of drawing zone and at the post yield drawing zone. The important conclusion of this study was that the optimal drawing conditions, regardless of the heating medium involved;

- 1) a ratio D_0/D_1 corresponding to a draw ratio of about 2.2X
- 2) the yield temperature at D_0 of $\sim 125^\circ\text{C}$
- 3) the temperature at the end of post yield drawing did not exceed 160°C .

Very similar results were obtained in a two stage drawing process where it was possible to control independently the extent of the two deformation processes discussed above; yielding (D_0/D_1) and post yield drawing (D_1/D_2) as well as the yield temperature and the temperature of the post yield drawing. The comparison of draw tension data with birefringence and some modulus of fibers drawn to maximum shows that at optimal drawing conditions the temperature in the drawing zone is at a critical high value at which further increases in draw zone temperatures lead to an abrupt decrease in the orientation of fibers drawn to maximum. The drawing tension, on the other hand, is at a critical low value at which further decreases lead to an abrupt decrease in orientation function.

TRANSFER AND MODIFICATIONS OF OPTIMAL SPINNING PROCESS

The transfer of an optimized process from one type of equipment to some other type, and the modification of the process to meet given requirements (such as increase in production rates, changes in fiber properties or polymer molecular weight, etc.), can be carried out in the following way.

Referring to Fig. 4, which depicts the schematics of a melt spinning process, let us consider a small particle of the fiber material leaving the spinneret at $t = 0$ (deroting the real time) and traveling down the spinway toward the take-up roll while being subjected to a certain conditioning history. For simplicity, we assume that at a position z (or time t), condition of the fiber material is uniform across the radius of filament. In other words, we disregard the distributed nature of the system and treat it as a lumped parameter system. Suppose that the state of fiber material can be completely described by n state variables of $x_1, x_2, \dots, x_n$ (or $\underline{x}$ in shorthand notation) which vary with time by the dynamic relation of

$$\frac{dx_i}{dt} = f_i(x_1, x_2, \dots, x_n, u_1, u_2, \dots, u_m) \quad (1)$$

where u_i indicates the process control variables. If the objective function J (the tensile strength, for example) to be optimized can be expressed by

$$J = F(\underline{x}(t_f)) + \int_0^{t_f} L(\underline{x}, \underline{u}) dt \quad (2)$$

then the problem of optimizing the melt spinning process to achieve a desired optimal value of the objective function J is mainly that of a numerical computation based on the mathematical principles of optimization.

The real problem we face in spinning process analysis, like in many other physical processes, is that we do not have complete knowledge of the relations, such as Eq. (1) and (2). Thus, frequently in reality, the only available way of optimizing the melting spinning process is experimentation.

After an optimal process is established by experimental procedure, it is often desirable to scale up the process while achieving the same objective. Again, due to the lack of knowledge of the relations of Eq. (1) and (2), the scale-up work necessitates an experimental optimization. In this case, however, if the real time history of the state variables, $\underline{x}(t)$, is known for the first process, then the second process, i.e., the scaled-up process can be expected to yield a same value of the objective function, J , if the history of $\underline{x}(t)$ is somehow kept same. This is so although we do not know the relation of Eq. (2). In other words, between process 1 and process 2, if

$$\underline{x}_1(t) = \underline{x}_2(t) \quad \text{for } t = 0 - t_f \quad (3a)$$

then we can expect:

$$J_1 = J_2 \quad (3b)$$

Thus, scale up of an optimal process can be achieved by achieving the similarity of the history of state variables.

For the above mentioned simplified lumped parameter system of a melt spinning process, we consider the filament temperature, $T(t)$, and the rate of filament thinning, $dV(t)/dz$, as the two state variables of the system which predominantly affect the changes in properties of the fiber during spinning. Denoting the temperature history and the

thinning rate history of the filament in the first optimized melt spinning process by $T_1(t)$ and $dV_1(t)/dz$, respectively, and those of the second scaled up process by $T_2(t)$ and $dV_2(t)/dz$ for $t = 0 - t_f$, we hypothesize that, if

$$T_1(t) = T_2(t) \quad (4a)$$

$$\text{and } dV_1(t)/dz = dV_2(t)/dz \quad (4b)$$

$$\text{then } J_1 = J_2$$

The idea underlying this hypothesis is that, as long as the temperature history and deformation rate history of a fiber material starting from the same initial state are same, the changes in the material characteristics, such as molecular weight distribution and morphology should also be same.

Now, let us examine whether it is possible to achieve the relations of (4a) and (4b) in a melt spinning process and, if it is, then under what condition. Referring to Fig. 5 in which two spinning processes are compared, let w , H , D and V denote the mass rate of spinning material, height of the spinway, filament diameter and filament velocity, respectively, and let the numeral subscripts 1 and 2 refer to the process 1 and 2. The position variable z is related to the velocity V by

$$dz = V dt \quad (5)$$

Therefore,

$$\frac{dV}{dz} = \frac{1}{V} \frac{dV}{dt} = \frac{d \ln V}{dz} \quad (6a)$$

So, the relation of Eq. (4b) dictates

$$\frac{V_1(t)}{V_1(0)} = \frac{V_2(t)}{V_2(0)} = s(t) \quad (6b)$$

which means that the stretch ratio based on the initial filament velocity, $s(t)$, is same between process 1 and process 2.

If we set the scale up factors for the mass rate and the filament diameter at take up to c and r , respectively,

$$w_2 = c w_1 \quad (7)$$

and

$$D_{2f} = r D_{1f} \quad (8)$$

where the subscript f indicates the final take up point in the spinway. The mass balance at the take up point requires

$$V_{2f} = (c/r^2) V_{1f} \quad (9)$$

and Eq. (6b) extends (9) to

$$V_2(t) = (c/r^2) V_1(t) \quad (10a)$$

$$V_2(0) = (c/r^2) V_1(0) \quad (10b)$$

$$D_2(t) = r D_1(t) \quad (10c)$$

The spinway height, H , is given by

$$H = \int_0^{t_f} V(t) dt = V(0) \int_0^{t_f} s(t) dt$$

$$\frac{H_2}{H_1} = \frac{V_2 \frac{C}{V_1(0)}}{V_1 \frac{C}{V_1(0)}} = \frac{C_2}{C_1} \quad (11)$$

The equality relations of (4a) and (4b) require the equality of the elongational stress, $\sigma(t)$, between process 1 and 2. Under the one dimensional elongation, $\sigma(t)$ is given by

$$\sigma(t) = \eta_T [dV(t)/dz] \quad (12)$$

where η_T is the tensile viscosity. Tensile viscosity has been found to be a function of the temperature only (8) or to be a function of temperature and elongation rate, dV/dz , (9). In either case, Eq. (4a) and (4b) would result in

$$\eta_{T1}(t) = \eta_{T2}(t) \quad (13)$$

and

$$\sigma_1(t) = \sigma_2(t) \quad (14)$$

The "rheological force", F_{rheo} , has been defined conventionally by

$$F_{rheo}(t) = \sigma(t) \cdot 0.785 [D(t)]^2 \quad (15)$$

In view of (10c) and (14), then, we have

$$F_{rheo2}(t) = r^2 F_{rheo1}(t) \quad (16)$$

Equations (6) - (16) are the relations which would result if the requirements of (4a) and (4b) are fulfilled. Now, we have to ask under what conditions these requirements can be realized.

Obviously, the first requirement is the controllability of filament temperature, $T(t)$, for achieving $T_2(t) = T_1(t)$. Eq. (4a) implies

$$\frac{dT_1(t)}{dt} = \frac{dT_2(t)}{dt} \quad (17)$$

For the simplified one dimensional system, dynamics of the filament quenching can be approximated by:

$$\begin{aligned} \rho C_p (0.785 D^2) dz (dT/dt) \\ = -3.14 D dz h_c (T - T_a) \\ - 3.14 D dz h_r (T_k^4 - T_{sk}^4) \end{aligned} \quad (18)$$

where ρ , C_p , h_c , h_r and T_a represent the density of fiber, heat capacity of fiber, convective heat transfer coefficient, radiative heat transfer coefficient and the ambient air temperature. T_k and T_{sk} denote the

filament temperature and spinway wall temperature in Kelvin scale. Eq. (18) simplifies to:

$$\begin{aligned} dT/dt = (-4/\rho C_p D) h_c (T - T_a) - \\ (4/\rho C_p D) h_r (T_k^4 - T_{sk}^4) \end{aligned} \quad (19)$$

Eq. (17) necessitates the relation

$$\begin{aligned} \frac{h_{c1}(t)}{D_1(t)} [T_1(t) - T_{a1}(t)] + \frac{h_{r1}(t)}{D_1(t)} (T_{k1}(t))^4 \\ - (T_{sk1}(t))^4 \\ = \frac{h_{c2}(t)}{D_2(t)} [T_2(t) - T_{a2}(t)] + \frac{h_{r2}(t)}{D_2(t)} (T_{k2}(t))^4 \\ - (T_{sk2}(t))^4 \end{aligned} \quad (20)$$

Thus, there are four variables which can be manipulated in Eq. (20) to achieve the equality of Eq. (17): h_c , h_r , T_a , and T_{sk} .

Consider a case, for example, in which $D_1(t) = D_2(t)$ but the speed of filament is increased by a factor of 2. When the quench air and filament flow in parallel direction, the convective heat transfer coefficient, h_c , is correlated to air flow condition by Muller's correlation (10), i.e.

$$\frac{h_c D}{k_a} = 0.42 \left(\frac{VD \rho_a}{\mu_a} \right)^{0.33}$$

where k_a , ρ_a , μ_a denote the thermal conductivity, density and viscosity of air, respectively. So, increase of V raises the value of h_c and, in order to maintain the equality of Eq. (2), it is necessary to raise $T_{sk}(t)$ and/or $T_{sk2}(t)$ to offset the effect. One means of providing the variation of T_{sk} is the heated sleeves surrounding the spinway.

In this way, the controllability of filament temperature hinges on whether the equality of Eq. (20) can be maintained by the manipulation of the above said four variables within the allowable and attainable ranges. However, it is physically impossible to manipulate these variables from point to point. Practically, the only feasible way of manipulating these variables is to do it by segments of finite lengths. Therefore, in a rigorous sense, the control can be achieved only approximately. Experimental runs which we made have shown, however, that the actual controllability of temperature in the scale up of a moderate ratio is fairly good.

After the temperature controllability, another controllability problem is related to the rheological force, F_{rheo} , given by Eq.

(15). Denoting the take up tension by F_T , F_{rheo} at position z in a spinway of height H can be approximated by:

$$\begin{aligned} F_{rheo}(z) = F_T + \int_z^H \rho g D^2 dz / 4 - \int_z^H \tau D dz \\ = w [V_z - V(z)] \end{aligned} \quad (22)$$

where g is the gravity constant and τ is the skin friction at filament surface due to the air drag. Thus, the second, third and fourth terms on the right hand side are for the filament weight effect, air drag effect and the inertia effect on the filament tension,

respectively.

Eq. (14) and (15) necessitate the relation:

$$\frac{F_{rheo_1}(t)}{[D_1(t)]^2} = \frac{F_{rheo_2}(t)}{[D_2(t)]^2}$$

or

$$r^2 F_{rheo_1}(t) = F_{rheo_2}(t) \quad (23)$$

If, in Eq. (22) $F_{rheo}(z) = F_T$, that is, the total sum of the effects of gravity, air drag and inertia is negligible relative to F_T , then it can be shown that Eq. (23) holds by itself once the temperature is controllable. When this is not the case, (22) and (23) require

$$\begin{aligned} & r^2 \left[\int_{z_1(t)}^H \rho g \frac{\pi D_1^2}{4} dz_1 - \int_{z_1(t)}^H \tau_1 \pi D_1 dz_1 - w_1 [V_{1f} - V_1(z_1)] \right] \\ & = \int_{z_2(t)}^H \rho g \frac{\pi D_2^2}{4} dz_2 - \int_{z_2(t)}^H \tau_2 \pi D_2 dz_2 - w_2 [V_2 - V_2(z_2)] \end{aligned} \quad (24)$$

Equality of Eq. (24) is achieved to a good approximation if

$$c = r^2 \quad (25)$$

which means, due to Eq. (9),

$$V_1(t) = V_2(t) \quad (26)$$

Otherwise, the equality does not hold strictly and the requirement for Eq. (23) can not be held rigorously. However, we have found through experiments that the equality can be maintained approximately when the scale up ratio is moderate.

In order to minimize the deviations between $T_1(t)$, $dV_1(t)/dz$ and $T_2(t)$, $dV_2(t)/dz$, one can use the Pontryagin's minimum principle (11) to minimize the deviation function:

$$\begin{aligned} \Delta = & \int_0^t [(T_1(t) - T_2(t))^2 \\ & + \beta \left(\frac{dV_1(t)}{dz} - \frac{dV_2(t)}{dz} \right)^2] dt \end{aligned} \quad (27)$$

by optimal selection of $T_a(t)$, $T_{sk}(t)$ and $V_a(t)$ where $V_a(t)$ is the quench air velocity which affects the convective heat transfer coefficient, h_c , and the skin friction due to air drag, τ . Details of this numerical procedure will be described elsewhere. Here, it suffices to say that the result of this procedure provides the guidance for varying the values of T_a , T_{sk} and V_a as the function of the position.

MULTIFILAMENT PROCESS AND PERTURBATIONS

In multifilament spinning the strength of yarn is always less than in single filament process even if temperature and deformation histories are equal.

This is caused by filament nonuniformities which cannot be completely eliminated even with greatest care in the process design and operations. A plot of translational efficiency in multifilament yarn strength as function of the coefficient of the variation in single filament strength is shown in Fig. 6.

Furthermore, a multifilament process is always more perturbed than a single filament process and within the limits of practical design of spinning equipment and production rates, it is usually impossible to:

- eliminate differences in temperature and deformation histories between the filaments in the yarn, and
- match the average condition for the filament with the optimal conditions established by a single filament experiment discussed above.

A technologically important task is to establish the modification in the process leading to the largest possible improvement in the quality of the yarn. This requires the analysis of the perturbation which affect the filament uniformity along the filament and across the bundle. The fluctuations in orientation, diameter, polymer molecular weight, etc., can be related to; a) deficiencies in equipment design (temperature and throughput variations), b) inherent perturbations such as turbulent air flow, filament swaying, etc., or c) polymer quality (presence of gel particles, poor judgment dispersion, or other solid particles, etc.).

The identification of major factors contributing to substandard quality of yarn is always very difficult and involves the analysis of property, structure and polymer quality fluctuations.

Most frequently, these analyses are based on the analysis of birefringence, filament denier and strength distribution along the filaments and across the bundle, molecular weight fluctuation in thin and thick filaments, fiber surface characteristics, presence of foreign matter in the polymer, and examination of broken fiber ends.

In Fig. 7 is shown schematically the scatter in filament strength as a function of filament denier for the entire yarn and along a single filament. Domain "B" indicates the scatter observed in the entire bundle while the domain "F" represents the same quantities measured along the same filament in the yarn. Filament denier fluctuations in "W_B" reflect the sum of hole to hole throughput variation and factors contributing to the denier fluctuation in an isolated filament. Fluctuations in "W_F" are related to the sum of filament swaying, pump and throughput fluctuations and possible fluctuations in polymer molecular weight and polymer quality. In addition to these characteristics of the

scatter it is desirable to estimate also the magnitude of angle "a" which reflects whether the filament properties are affected by the filament denier. If such a relationship exist it is very likely that the strength decreases rapidly with the volume of the test specimen which is a strong indication that the polymer may be contaminated with foreign matter.

CONCLUSIONS

With melt spinning and drawing processes of fibers which can be processed via an essentially amorphous undrawn filament, the optimal spinning conditions with regard to strength occur when;

- a) The filament deformation rate $\frac{dv}{dz}$ in the spinway is at a critical high value at which further increases in $\frac{dv}{dz}$ lead to an abrupt decrease in filament quality;
- b) The filament cooling rate $\frac{dT}{dt}$ is at a critical high value at which further increases in $\frac{dv}{dz}$ lead to an abrupt decrease in filament uniformity, and
- c) The time at which the maxima in $\frac{dv}{dz}$ and $\frac{dT}{dt}$ occur is at a critical low value at which further decreases in this time lead to an abrupt decrease in filament quality.

Optimal drawing conditions in a single step drawing process involve a complex deformation process in which yielding is immediately followed by a post yield drawing. The diameter decrease in yielding corresponds to a draw ratio of 2.2. The temperature in the drawing zone is at a critical high value at which further increases in drawing temperature lead to an abrupt decrease in fiber orientation. The draw tension, on the other hand, is at a critical low value at which further decreases lead to an abrupt decrease in fiber orientation.

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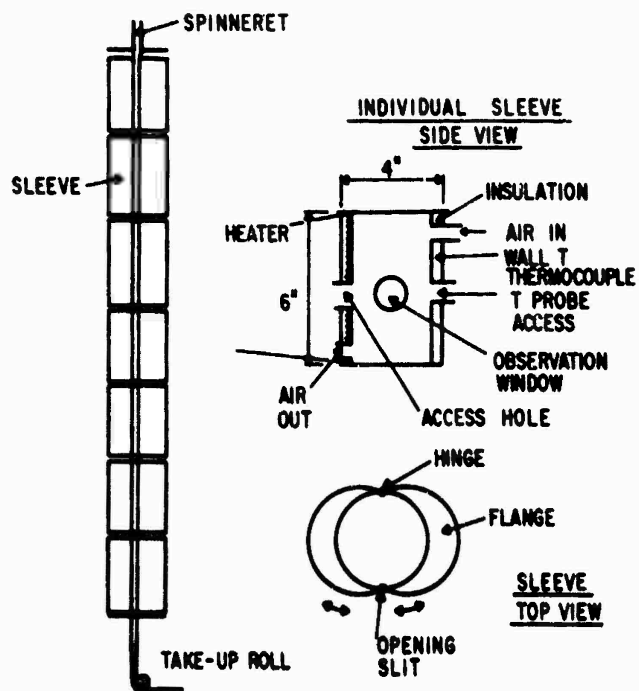


FIGURE 1. SCHEMATICS OF EXPERIMENTAL SPINNING SYSTEM



FIGURE 2. YIELDING OF FIBERS IN CONSTANT LOAD EXPERIMENTS

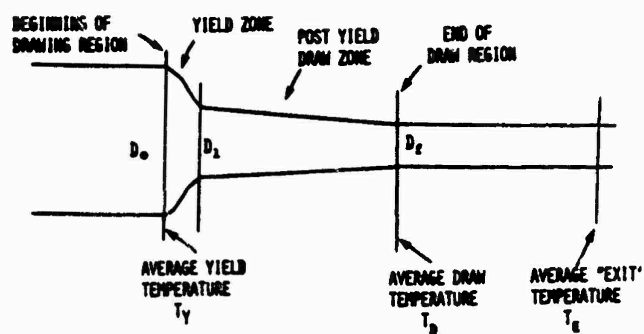


FIGURE 3. SCHEMATICS AND DEFINITION ON DRAWING ZONES AND TEMPERATURE

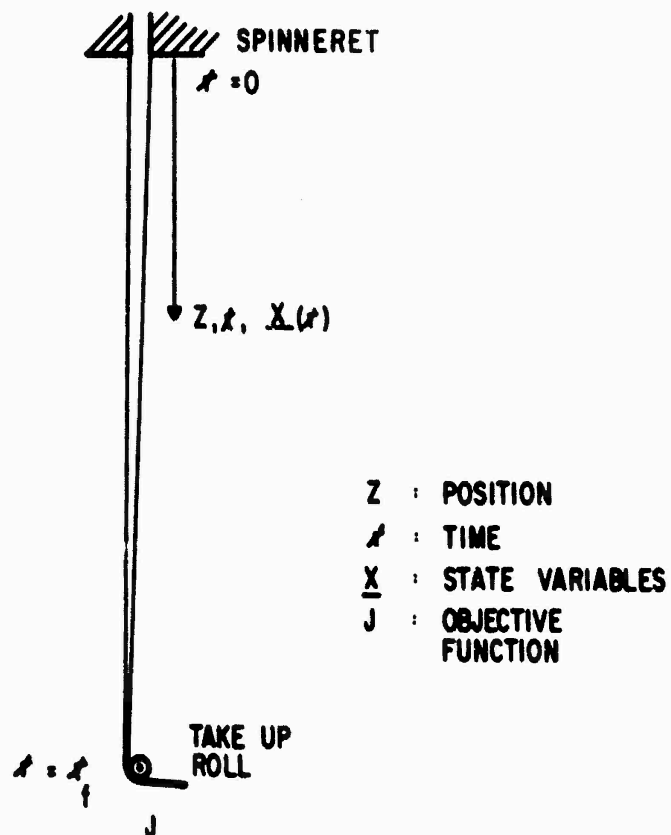


FIGURE 4. SCHEMATICS OF A SPINNING SYSTEM

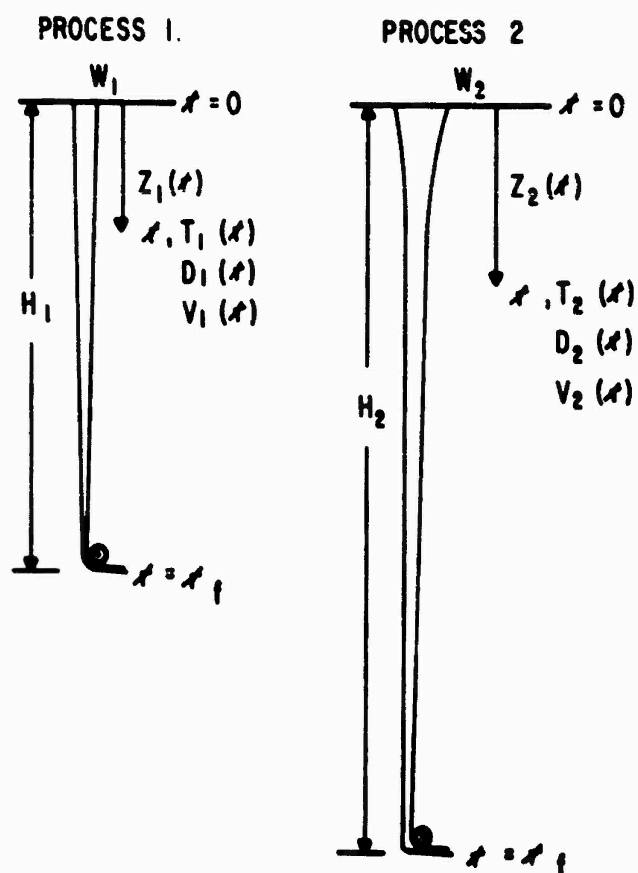


FIGURE 5. TWO SPINNING PROCESSES

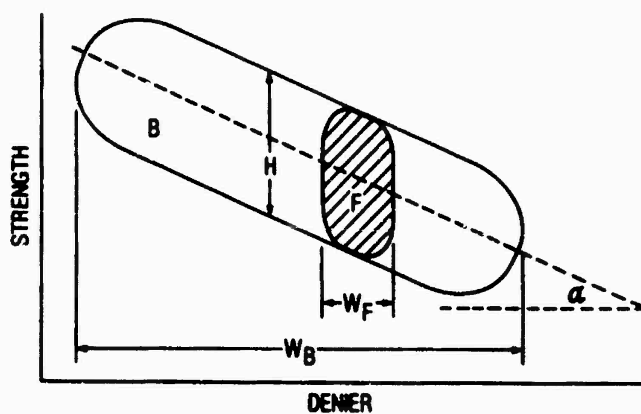


FIGURE 7. SCHEMATIC OF ACROSS THE BUNDLE AND ALONG THE FILAMENT SCATTER IN STRENGTH: B = ACROSS THE BUNDLE SCATTER, F , ALONG THE FILAMENT SCATTER, W_B = SUM OF HOLE TO HOLE THROUGHPUT VARIATION AND FILAMENT SWAYING, W_F = FILAMENT SWAYING AND PUMP THROUGHPUT VARIATIONS, H = QUANTITY PROPORTIONAL TO POLYMER QUALITY, $W_B/W_F = \alpha$ = FACTOR REFLECTING POLYMER QUALITY.

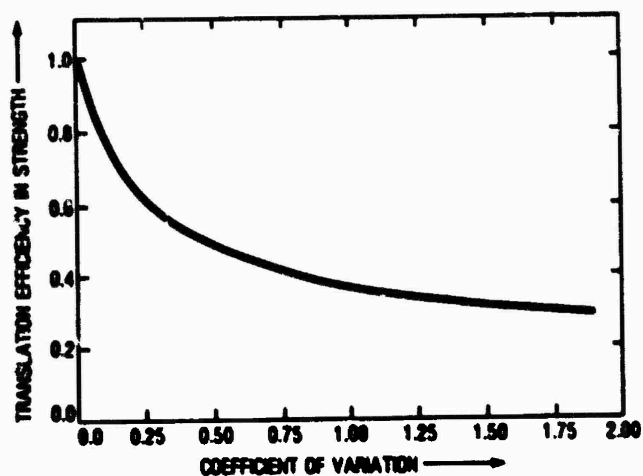


FIGURE 6. EFFECT OF FILAMENT SCATTER IN STRENGTH ON YARN TRANSLATIONAL EFFICIENCY OF STRENGTH.

REMARKS

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Introduction to the Session on "High Performance Fibers"

It is indeed an honor to participate in this symposium honoring our Geheimrat. It was his reputation that attracted me to Brooklyn Poly 30 years ago to begin a career in polymer chemistry - and I've known and admired him ever since.

There has been a lot said about Professor Mark's contributions to polymer science. Before beginning this afternoon's session on "High Performance Fibers", I would like to acknowledge his contributions to the DuPont Company's Textile Fibers Department. Professor Mark began consulting with us in 1940 - the early days of nylon. In those days, our young scientists had little or no training in polymers. They came from the universities as organic and physical chemists - polymer chemistry wasn't taught much in the schools then. He taught them such things as polymerization kinetics, rheology of spinning, molecular weight distribution, light scattering and X-rays. It was Professor Mark who in the early days saw and stressed the important connection between structure and fiber properties. He taught us the basic analytical tools and how to use them in designing new polymers and fibers. He helped us to understand how to get high tenacity into nylon, how to build wool-like resilience into Orlon® acrylic and how to get good work recovery and resilience into Dacron® polyester. This went on for years - it went on for decades!

It was Professor Mark who repeatedly told us that the strength and modulus of our highest performance fibers were nowhere near the theoretical values - that were only on the fringes of fiber potential. He challenged us on this - he encouraged us to work in this area - and we did - and he was right!

This brings us to the subject of this afternoon's session. In researching the history of high performance fibers, it comes as no surprise to any of us that the earliest references bear tribute to the insight and vision of our honored guest. The earliest reference we found was a publication in 1932 that treats the theoretical tenacity of an infinitely long chain molecule. The author writes:

"The force necessary to break a main valence, polymer chain of cellulose, amounts to 2×10^{10} kg per chain. Since a 1 mm^2 cross-section contains $3 \text{ to } 5 \times 10^{12}$ chains, it follows that the tensile strength of a filament consisting of infinitely long chains would be about 800 kg/mm^2 . One sees that this value is extraordinarily high and significantly exceeds the experimentally determined values of tensile strength." Dr. John Schaeffgen in our

Pioneering Research Laboratory at Du Pont has translated the above value of 800 kg/mm^2 into modern terms. This translates into 57 gpd for cellulose, 89 gpd for polyethylene, 74 gpd for 66-nylon and 64 gpd for Kevlar® aramid - figures that we are beginning to approach in today's synthetic fibers.

This quotation was from Pages 61-62 of a book entitled "Physik und Chemie Der Cellulose", Julius Springer Verlag, Berlin, Germany, 1932. The author - Herman Mark!

The earliest reference that we found to super high modulus was in Transactions of the Faraday Society 32 143-145 (1939) describing the Sixty-Third General Discussion held in Cambridge, England, in 1935. The subject under discussion was "The Phenomena of Polymerization and Condensation". Overseas guests included Professor Kurt Meyer from Geneva, Dr. W.H. Carothers from Wilmington, Dr. F. Eirich from Vienna, Professor H. Mark from Vienna, Dr. E. Proskauer from Leipzig, and Professor H. Staudinger from Freiburg. Following a paper by Dr. R. Houwink on elasticity of polymers, the following comments were made by one of the participants: "It seems to me very reasonable to try now to get quantitative results on the theoretical interpretation of the mechanical behavior of synthetic resins and fibers." The participant then proceeded to predict that modulus is due to bond angle deformation involving 1000-1500 cal/mol for 10% elongation or to bond straining involving 5000-6000 cal/mol. Again, Dr. John Schaeffgen has calculated that in structures such as polyethylene or nylon, this translates into 420 gpd and for structures such as Kevlar® aramid into 1900 gpd - figures that we are approaching (and in some cases exceeding) in today's high performance fibers. Who made these predictions back in 1935? - Our Geheimrat!

Hence, Professor Mark's vision and theoretical predictions on ultimate strength and modulus are proving correct as we will see from this afternoon's symposium.

And now, Professor Mark, we dedicate this symposium to you - our teacher, our mentor, our friend --- with affection and respect on your 85th birthday.

For this occasion, we have compiled a series of papers that illustrates the breadth of activity in high performance fibers. The first paper deals with graphite, one of the earliest commercial high performance fibers. The second is on Kevlar®, the most recent commercial high performance fiber. Then we have three papers covering experimental work on new high performance fibers. Finally, we have a paper on FP Alumina Fiber, a new inorganic high performance fiber. Following each talk there will be time for questions.

CARBON FIBERS

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ABSTRACT

The carbon fiber industry has grown, since its infancy twenty years ago, to a substantial worldwide business. Its primary use is in reinforcement of plastics. Property advantages over conventionally reinforced or unreinforced plastics include: high mechanical stiffness, low density, low thermal expansion, good thermal stability, and electrical conductivity. Properties of the composite are strongly affected by the major physical and chemical properties of the fiber which can be varied over wide ranges: in some cases, more than an order of magnitude. These properties are determined by three key fiber parameters: carbon content, crystallinity, and preferred orientation. The important process variables controlling these parameters are described for each of the major carbon fiber processes, using rayon, polyacrylonitrile, and mesophase pitch as precursors. The available carbon fiber properties are used to advantage in many applications, some of which are briefly described.

THE CONSUMPTION OF CARBON FIBERS has increased, since they were developed just over twenty years ago, to more than 400 tons per annum in the free world, and the present annual growth rate is over 25%. Although used primarily as a reinforcement for plastics, carbon fibers are also used to reinforce other matrix materials: metals, ceramics, and carbon itself. In noncomposite applications, they are the major or sole component in valve and pump packings, thermal insulation, and electrodes used for electrochemical applications.

Carbon fibers are manufactured by the thermal treatment (pyrolysis) of organic precursor fibers. Control of the precursor and of the process parameters determines the intrinsic fiber structure which, in turn, determines the fiber properties. These relationships, and the way in which they are manipulated to produce useful composite materials, are discussed in this paper.

The interested reader may consult several extensive review articles or books on carbon fibers and their composites which have been written during the past decade. These cover manufacturing processes based on rayon (1,2,3*), PAN (2,3), and other (2,3) precursors; structure-property relationships (1,4); and compositing methods and applications (5,6,7,8). The newest entry to the family of carbon fibers, those made from mesophase pitch, are described in a relatively few recent articles (9-14).

*Numbers in parentheses designate References at end of paper

PROPERTY ADVANTAGES OF CARBON-FIBER REINFORCED PLASTICS

Since carbon-fiber reinforced plastics are expensive compared with most other plastic composites, their growing utilization is due to the fact that property advantages are being realized. The main advantages are high mechanical stiffness, good fatigue resistance, dimensional stability, and good wear resistance. These advantages are directly traceable to the unique physical properties of the carbon fibers themselves (see Table 1).

STIFFNESS - Where high stiffness is required, carbon fibers possess the highest Young's modulus of any fiber: up to ten times that of E-glass. Carbon-fiber/epoxy laminates possessing stiffnesses equivalent to aluminum plates are in common use.

FATIGUE RESISTANCE - The high modulus of carbon fibers, combined with virtually 100 percent elastic recovery, results in mechanical fatigue resistance in the composite. If stresses are directed along the fiber direction, only small deformations in the matrix can occur, and almost no permanent creep results. Hence, composite integrity is maintained after millions of stress cycles.

DIMENSIONAL STABILITY - When a composite material of low thermal expansion is required, carbon fibers are uniquely suitable, since high Young's modulus fibers also possess a negative coefficient of thermal expansion (below 400°C). Combined with a low modulus plastic, a zero thermal expansion material (in the fiber direction) can result.

ELECTRICAL CONDUCTIVITY - Plastics possessing appreciable electrical conductivity require a conductive filler. Carbon blacks are commonly used, but high loadings are required to achieve particle-to-particle contact. The high aspect ratios of even "short" carbon fibers permit electrical contact at relatively low loadings. Since carbon fibers possess electrical conductivities as high as 5000 (ohm cm)⁻¹, no other filler (except, possibly, aluminum fiber or flakes) is more suitable.

DENSITY - Lying between 1.3 and 2.1 g/cc, the density of carbon fibers is less than that of any common reinforcement except aramid fibers.

THERMAL STABILITY - Though enhanced by most reinforcements, the thermal stability of plastic composites is ultimately limited by the properties of the matrix. However, in cases requiring short-term stability in a severe thermal environment, carbon fibers are unequalled by other reinforcements. For example, rocket nozzle exit cones made of phenolic resin reinforced with carbon fibers survive the firing period because the resin, as it decomposes to a char, is held intact by the fibers. The extremely high sublimation point of carbon fibers and their high thermal conductivity combine to achieve this result.

WEAR - The well-known friction and wear properties of graphite which make it a unique material for use as brushes for electrical machinery and seal rings for jet engines are found as well in carbon fibers. In addition, their high thermal conductivity permits heat to be dissipated quickly from the rubbing surface, thus preventing melting of the plastic matrix.

STRUCTURE-PROPERTY RELATIONSHIPS

The most important structural parameters in carbon fibers are (a) carbon content, (b) crystallinity, and (c) preferred orientation of crystallites. The chemical and physical properties of the fibers can be varied over wide limits by control of these parameters. The structure is controlled, in turn, by the details of the manufacturing process, which will be covered in a later section.

Table 1 - Representative Carbon Fiber Properties

Fiber Type	Young's Modulus 10 ⁶ psi	Tensile Strength 10 ³ psi	Therm. Exp. Coefficient 10 ⁻⁶ (°F) ⁻¹	Electrical Conductivity (ohm cm) ⁻¹	Density g/cc
Carbon:					
Low modulus ^a	8	100	1	300	1.35
High strength ^b	33	450	-0.3	550	1.75
High modulus ^b	55	350	-0.4	1050	1.85
Very high mod. ^c	75-100	>300	-0.7	2000-5000	2.02
S-Glass	13	500	2.8	~ 0	2.5
Steel wire	30	500	7	~ 20000	7.8

a: Rayon-based.

b: PAN-based.

c: Mesophase pitch-based.

CARBON CONTENT - In most commercial carbon fibers, the carbon content lies between approximately 85 and 100 percent, depending upon both the precursor and the final heat treatment temperature. Residual impurities are, in the main, hydrogen, oxygen, and (sometimes) nitrogen.

CRYSTALLINITY - The basic structural unit of carbon fibers is the two-dimensional graphitic layer plane, analogous to the linear molecular chain in conventional polymers. "Crystallinity" is determined by the size and perfection of the graphitic layers and by the degree of stacking of these layers into three-dimensional "crystallites." The most commonly used crystallinity parameters are those obtained by X-ray diffraction analysis: L_a , the average length or width of the layer, and L_c , the average height of the stack.

The parameter L_c varies from ~1 to over 20 nm. However, high resolution electron microscopy reveals that the layers undulate and, in some cases, continue for hundreds of nm.

The parameter L_c also varies from ~1 to over 20 nm. Since the layers are stacked with a spacing of 0.34 nm, the smallest values of L_c occur when only a few layers comprise the "crystallite."

As the heat treatment temperature increases and impurity atoms are driven out, the layers grow in perfection, size, and flatness, and more and more of them are brought into a parallel stacking arrangement. Only in exceptional cases, however, is the three-dimensional order characteristic of the true graphite crystal achieved.

PREFERRED ORIENTATION - The most important structural feature of a carbon fiber is its axial preferred orientation, i.e., degree of preferential alignment of graphitic layers parallel with the fiber axis. Preferred orientation can be made to vary over wide limits, from none (random alignment) to a "maximum," in which nearly all layers lie within a few degrees of the fiber axis. Axial preferred orientation is measured by analyzing the X-ray diffraction pattern from a parallel bundle of fibers (Fig. 1).

Another type of preferred orientation may sometimes be observed by examination of fiber cross-sections in polarized light. When the graphitic layers are parallel with the fiber axis, they may be randomly oriented in the transverse plane or they may be preferentially oriented parallel with or perpendicular to fiber radii (Fig. 2).

DEPENDENCE OF PROPERTIES ON STRUCTURE - The physical properties of carbon fibers depend on the properties of the graphitic "crystallites" (often highly impure and imperfect) and their degree of preferred orientation. The graphite crystal is highly anisotropic with respect to physical properties. Properties are quite different, depending upon whether the measurements are taken in the direction parallel with the layer planes or perpendicular to them: Young's modulus is 50 times greater in the parallel direction

than it is in the perpendicular direction; thermal expansion decreases to zero and then becomes negative when measured in the parallel direction (compared with only positive values obtained when measured in the perpendicular direction); and electrical conductivity is 1000 times greater in the parallel direction than it is in the perpendicular direction.

The anisotropy of physical properties increases with crystalline perfection and purity. Thus, the "ultimate" properties (e.g., Young's modulus, tensile strength, thermal and electrical conductivities) tend to be achieved when both the crystallinity and the degree of preferred orientation are high. There are exceptions, however: as these structural features improve, the internal shear strength of the fiber decreases, whereas tensile strain-to-failure reaches a maximum and then decreases.

We now consider briefly some of the important "scalar" properties which do not depend directly on the anisotropic fiber structure. Both density and

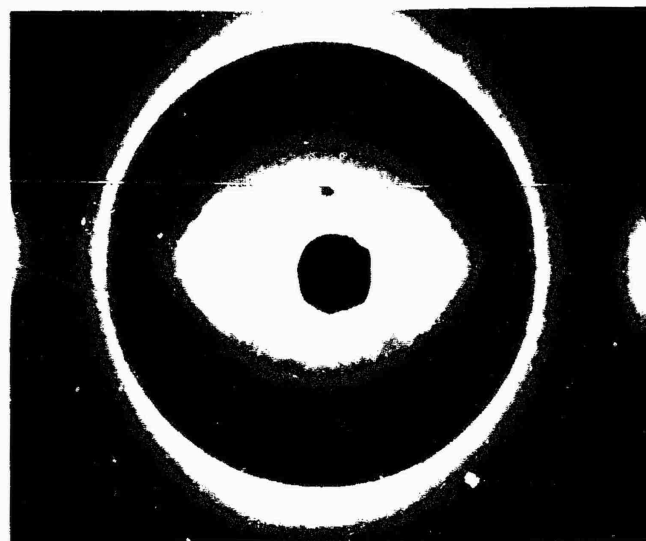


Fig. 1 - X-ray diffraction pattern of high modulus rayon-based carbon fibers showing (002) and (004) arcs and (10) band. Fiber axis vertical

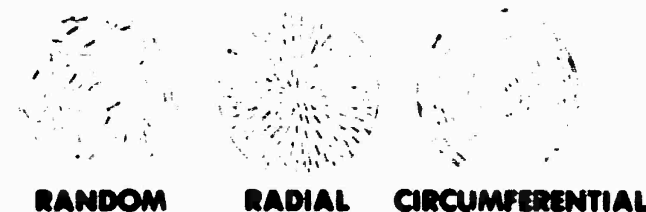


Fig. 2 - Schematics of three simple types of transverse preferred orientation in carbon fibers

oxidation resistance tend to increase as fiber crystallinity and purity improve. Bond strength between the fiber surface and the resin matrix in a composite is degraded, as is mechanical wear resistance; however, coefficient of friction is also reduced. These "interface" properties are enhanced by the presence of functional groups on the fiber surface.

EFFECTS OF MANUFACTURING PROCESS ON FIBER STRUCTURE

To some degree, fiber structure and, hence, fiber properties may be controlled through choice of manufacturing process, as we shall now describe.

PRECURSOR FIBER - All important commercial processes (see Fig. 3) for making carbon fibers are based on thermal processing of an organic precursor fiber, which usually consists of rayon, polyacrylonitrile, or pitch. The highest degrees of purity and crystallinity are achieved by carrying the thermal processing to very high temperatures. However, the ease with which these properties are achieved depends strongly upon the precursor used. In particular, the crystallinity achievable depends upon how easily the starting polymer can be converted to an incipient graphitic structure. Of the three major precursors, rayon is least easily converted to a graphitic structure, PAN is next, and pitch is most easily converted.

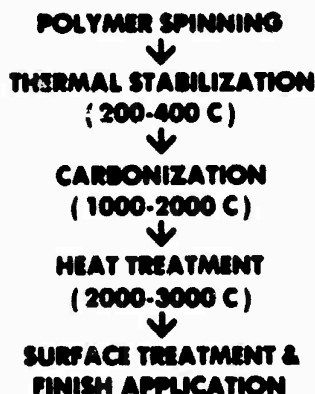


Fig. 3 - General process scheme for production of carbon fibers from organic precursors

Two types of pitch precursors are used: isotropic or "ordinary" pitch and anisotropic or "mesophase" pitch. Mesophase pitch is a liquid crystalline pitch which is spun into a molecularly oriented fiber. Isotropic pitch is spun into an unoriented fiber and is used only for the production of low-modulus carbon fibers; for that reason, it will not be discussed in detail.

Other precursor fibers, such as lignin, polyvinyl alcohol, and phenolic resin, have been used for carbon fiber manufacture, but their use has not achieved much commercial importance.

THERMAL STABILIZATION - The precursor fiber must be thermally stabilized to prevent excessive weight loss, molecular disorientation, or fiber fusing during subsequent processing. Thermal stabilization consists of a relatively slow heating process to approximately 300-400°C, usually in the presence of air or some other oxidizing agent.

CARBONIZATION - The thermally stabilized fiber is next carbonized by heating in a nonoxidizing atmosphere to a temperature usually between 1000°C and 1500°C. Although considerable weight loss takes place, the heating can be carried out in less than one minute in continuous processing. The carbonized fiber consists of 85-99 percent carbon and possesses a very disordered structure which is still relatively reactive

chemically. The carbonized fiber bonds well to resins and, in the case of PAN-based fibers, may be exceedingly strong (e.g., 500,000 psi tensile strength) and moderately stiff (30-35 million psi Young's modulus).

HEAT TREATMENT - Although the majority of present-day applications make use of fibers which have been carbonized only (to take advantage of their high strength), the achievement of many other ultimate properties requires a high-temperature heat treatment. This heat treatment usually takes place at temperatures between 2000°C and 3000°C and renders the fiber virtually 100 percent carbon. Young's modulus may be as high as 100 million psi. Graphitic layer size increases markedly, as does the degree of parallel stacking of layers. In the case of mesophase pitch-based fibers, true three-dimensional graphite crystallinity can be achieved by heat treating to very high temperature (11).

CONTROL OF PREFERRED ORIENTATION - Although the preceding discussion has indicated how processing variations can be used to control carbon content and crystallinity, the third important structural parameter, preferred orientation, requires special discussion. Molecular orientation is the most important factor in controlling modulus, strength, thermal expansion, and thermal and electrical conductivities. A highly oriented carbon fiber is one in which graphitic layers are preferentially oriented parallel with the fiber axis. How this orientation is controlled depends predominantly on which "precursor process" is used.

Historically, the three major precursor processes were commercialized in the following order: rayon, PAN, and mesophase pitch. The three precursors form an interesting series in several respects (see Table 2): in the same order given above, the final carbon fiber weight yield increases, and so do both carbon fiber density and crystallinity. Finally, the achievement of high preferred orientation becomes progressively easier, as we shall now discuss.

Table 2 - Comparison of High Modulus Carbon Fibers from Three Precursors (Young's Modulus 55 million psi)

	Carbon Yield (wt %)	Fiber Density (g/cc)	Crystal Size Parameter (L _c , nm)
Rayon	30	1.70	5
PAN	50	1.85	6
Mesophase pitch	80	2.02	15

Rayon Process - The rayon precursor process was commercialized by Union Carbide in 1958. The rayon fiber, although initially oriented, becomes almost totally disoriented during the early stages of thermal processing. After carbonization, a low modulus carbon fiber results. W. A. Schalamon and the author discovered that a highly-oriented, high-modulus fiber could be produced if the fiber were stretched during heat treatment at temperatures approaching 3000°C (1). Beginning in 1965, fibers with Young's modulus of 25, 50, and, finally, 75 million psi were produced commercially (15). The decreasing availability of rayon fiber along with the high cost of the "hot stretch" process has forced its discontinuance. Only low-modulus fibers are now produced from rayon.

Carbon fibers made from isotropic pitch precursor (16) possess properties somewhat similar to those derived from rayon. They can also be converted to high modulus fibers by a high temperature stretching, but this refinement has never been commercially practiced.

PAN Process - Carbonization of PAN fibers was studied extensively at the Government Industrial Research Institute in Japan and later at the Royal Aircraft

Establishment and at Rolls Royce in England. At the RAE, W. Watt and co-workers discovered that the molecular preferred orientation initially present in the PAN fiber could be preserved if the fiber was held under tension throughout the thermal stabilization step (17). The fiber could then be carbonized without tension to produce an intermediate-modulus (~33 million psi) carbon fiber. This process was commercialized in 1966 under British government license (18). Similar processes are now widely practiced in the U.S. and in Japan.

Higher modulus fibers (~55 million psi) from PAN can be achieved by further heat treatment to temperatures above 2000°C, since the growth and parallel stacking of graphitic layers cause them to become better aligned with the fiber axis. Hot stretching permits achievement of still higher moduli (~75 million psi).

Mesophase Pitch Process - Low modulus carbon fibers have been made from isotropic pitch by Kureha Chemical Co., Japan, since 1969 (19). Singer, at Union Carbide, discovered that highly oriented pitch fibers could be spun from a liquid crystal form of pitch, called "mesophase pitch" (11). This oriented fiber could then be thermally processed to any desired temperature under zero tension without loss of preferred orientation. Depending upon final temperature, carbon fiber moduli as high as 100 million psi can be produced. This process was commercialized in 1974 (9).

APPLICATIONS

Applications for carbon-fiber reinforced plastics are now myriad (5-8). (Table 3 lists some of them.) Fabrication technology, once confined mostly to filament winding or laminating by hand layup methods, now includes pultrusion, warm forming, injection molding, and many other methods (20).

Most applications still use "high-strength" PAN-based carbon fibers in thermosetting (epoxy or polyester) resins for aerospace structures and sporting equipment. However, a growing market is developing for discontinuous or chopped fibers (of all types) and for "high modulus" or "very high modulus" fibers made from either PAN or mesophase pitch. These are often used with thermoplastic resins (e.g., Nylon 6/6, polysulfone, polyphenylene sulfide, polyamide-imide) in lower-cost automotive or industrial applications.

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Carbon fibers are starting to be used in hybrid composites with glass fibers. The carbon fibers provide the desired stiffness, but they fail at relatively low strains; glass fiber additions can protect against catastrophic failure while reducing material costs.

Table 3 - Applications for Carbon-Fiber Reinforced Plastics

Sporting and recreational equipment

Golf club shafts, fishing rods, tennis racquets, skis and poles, arrows, bicycle frames, sailboat spars and masts, oars, gliders, speaker cones, sounding boards.

Aircraft and helicopters

Horizontal and vertical stabilizers, rudders, speed brakes, spoilers, wing structures and skins, landing gear doors, turbine engine parts, brakes (C/C)^a, helicopter rotor blades and shafts.

Missiles and space

Space shuttle cargo doors, space antennas, space platforms, rocket motor nozzles (C/C) and exit cones, heat shields (C/C).

Automotive

Drive shafts, springs, RF shielded panels, chassis reinforcement, door hinges, air conditioner brackets, pump impellers, fan blades, brake linings.

Industrial

X-ray tables and cassettes, textile loom equipment, high-speed printers, ball valves, gears, bushings, oil seals, pump packings.

(s) C/C: Carbon reinforced with carbon fibers

THE FUTURE

Carbon fiber production is expanding rapidly. Producers number at least eight in the U.S., four in Japan, and four in Europe and Great Britain. Fiber prices, once several hundred dollars per pound, are now below \$20/lb for some continuous fibers and below \$8/lb for some discontinuous fibers or heavy tows. Further price decreases are sure to follow as new applications are found. Based on present exponential growth rates, carbon fiber consumption will reach 2000 tons per annum in the free world by 1985.

EXTENDED CHAIN AROMATIC POLYAMIDES

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ABSTRACT

Aromatic polyamides based on p-oriented diamine and dibasic acid intermediates yield liquid crystalline solutions in amide and acid solvents. These liquid crystalline solutions are composed of highly ordered domains containing extended chains. The overall orientation of these domains is random at rest. When shear is applied to these solutions, the domains assume a common orientation along shear direction. On spinning, these solutions give directly highly oriented, high tenacity, high modulus fibers. The level of properties in the as-spun yarn stems from the high degree of alignment of rigid polymer chains. Critical parameters influencing the liquid crystalline state include polymer structure, molecular weight, molecular weight distribution, solvent/polymer interaction, solution concentration and temperature. Kevlar® aramid fibers are based on this type of technology. These fibers have a tenacity of >22 gpd (400,000 psi) and modulus ranging from 500 to >900 (9-16 MN psi). The unique properties of Kevlar® have to-date resulted in commercialization in over 100 end-uses from tires and aerospace applications to sporting goods and safety apparel.

TEXT

The Work Reviewed here summarizes the research of many chemists and engineers working for a period of several years, culminating in commercialization of our newest fiber, Kevlar® aramid yarn in 1971. Kevlar® provides a new level of properties that has aroused a great deal of interest in the scientific and engineering community. The technology behind Kevlar® will be described as an example of how a polymer can be commercialized in a variety of new end-uses in the service of man. The material presented here has been largely drawn from papers presented at the Witco Award Symposium by P. W. Morgan et al (1*) at the 171st National Meeting of the American Chemical Society, New York City, N. Y., 1976, and at the March 25, 1980 meeting of the Polymer Division, American Chemical Society at Houston, Texas (2).

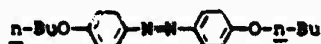
We know that for maximum tensile properties of a fiber, the polymer molecules must exist in extended chain formation and have as perfect crystalline packing as possible. When chain extension is done on a spun fiber by drawing, as in nylon, it is difficult to disentangle the chains in the solid state and align them perfectly.

High properties have been obtained from polymers such as polyethylene which can achieve almost theoretical levels of crystal perfection under special circumstances. Fibers grown as single crystals of PE from

solution, for example, have tensile properties up to $T/M = 39/900$ dN/tex. These high property polyethylene fibers, however, have little commercial value because of low melting point and a strong tendency to creep under load.

In contrast to polyethylene, Nomex® aramid fibers, based on soluble meta-oriented aromatic polyamides, have excellent thermal properties. While these fibers do not form extended chain crystals because of the meta orientation, their properties led to continued effort on the more intractable para-oriented polyamides. The high melting point and glass transition temperatures resulting from the para orientation prevent normal spinning and drawing techniques for other polymers, so a new method was required. A new approach providing almost perfect polymer chain extension was discovered by Kwolek in her studies with poly-p-benzamide (2). She had discovered that this polymer formed liquid crystalline solutions.

Compounds capable of forming liquid crystalline phases have been known for years. In the liquid crystalline state, these compounds have the structure of solids; for example, they exhibit birefringence, they have molecular order, but at the same time, these materials have the flow characteristics of fluids. One of the best known and simplest examples of a material forming a liquid crystalline phase is an azobenzene. In the case of 4,4'-dibutoxyazobenzene, the compound is a crystalline solid to 90°C, where it melts to a



liquid phase but still remains crystalline. This state is maintained to 150°C where it undergoes another transition to an isotropic liquid.

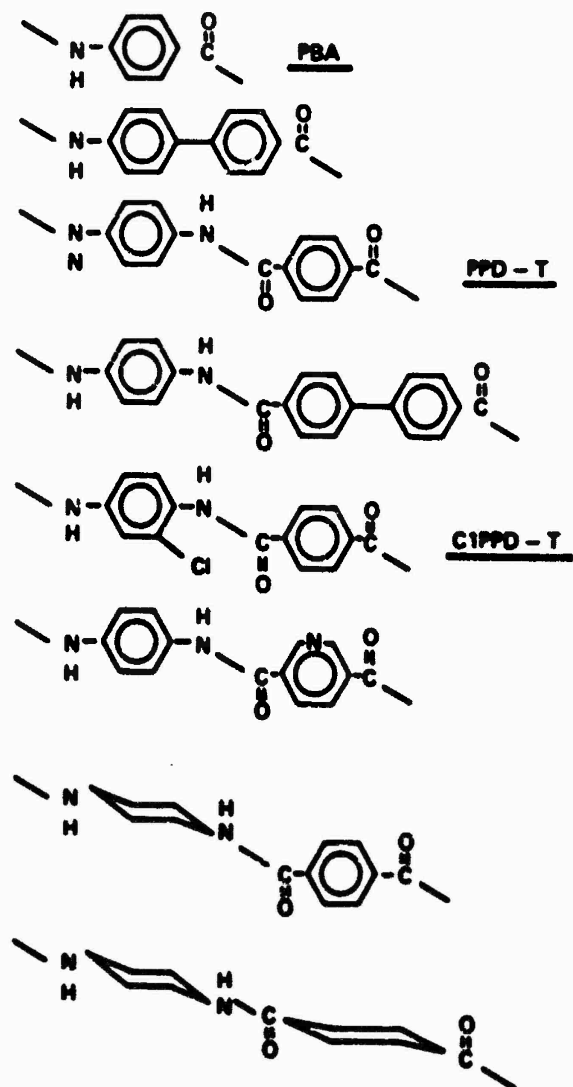
This liquid crystalline behavior has been extended in our laboratories to many polyamides, shown in Table I. Materials discussed in this paper are polybenzamide, poly-p-phenylene terephthalamide (PPD-T) and the chloro-substituted PPD-T polyamide. The common feature of all these polymers is a structure that is inherently rigid, and capable of high crystalline order. The key structural requirement is an all para orientation capable of forming a rod-like molecular structure. Consider what happens as rod-like polymer molecules are dissolved as opposed to more normal flexible chain polymers, as described by Flory in 1956 (3). As the concentration increases, the rods must begin to associate in parallel alignment, much as pencils in a box, and randomly oriented domains of internally highly oriented polymer chains then develop. With flexible chain polymers, on the other hand, a random coil configuration is obtained in solution, and increasing polymer concentration cannot force a higher degree of order.

Polymer concentration is critical, as shown in Figure 1. As the polymer concentration (poly-p-benzamide in DMAc/L:1) increases, the viscosity as a random collection of rods increases, with a critical point of about 5% poly-p-benzamide. As we force more polymer into solution, a second phase, liquid crystalline, begins to form and the viscosity begins to drop. Liquid crystalline domains are almost like particulates which contribute little to solution viscosity. Continued addition of polymer and dissolution forces more polymer into the ordered phase. A minimum is achieved at a totally anisotropic system, and then the viscosity begins to rise again.

The unique aspect of liquid crystalline polymer solutions that can provide a new dimension in fiber processing is their behavior under shear. These solutions exhibit stir-opalescence; with shear, the translucent solutions become opaque and display a pearlescent luster or radiance. This is a consequence of the random domains becoming fully oriented

*Numbers in parentheses designate references at end of paper.

Table I - Polyamides Yielding Liquid Crystalline Solutions



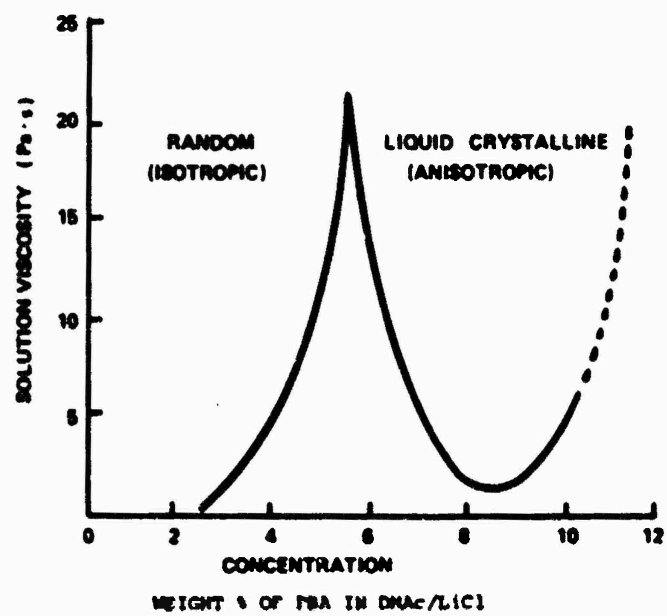


Fig. 1 - Viscosity of liquid crystalline polyamide solutions

in the direction of shear. This happens as these solutions enter a spinneret, and emerge with almost perfect molecular orientation (Figure 2). This supra-molecular structure is almost entirely preserved in the as-spun filament structure due to very slow relaxation of shear-induced orientation. This process is a novel, low energy way of achieving very high orientation of polymer molecules.

This phenomenon can be seen (Figure 3) by microscopic examination of a typical solution with polarized light between crossed polars. The solutions depolarize light as a normal crystalline solid would. The top figure is a solution at rest and clearly shows the domain structure. When sheared by movement of the slide cover slip, interdomain orientation is achieved.

As a result of our early investigation a number of critical variables were defined that had a significant impact on the isotropic/anisotropic phase diagram, in particular, polymer structure, molecular weight, polydispersity, solubility and temperature.

Inherent viscosity has a profound effect on critical concentration for development of anisotropic phase separation. Figure 4 shows the relationship of poly-p-benzamide inherent viscosity (measured at 0.5% in concentrated sulfuric acid) to the critical concentration in DMAc/LiCl. As predicted by the Flory model (3), the longer chain length at higher molecular weight allows anisotropic phase separation at lower concentrations, due to higher axis ratio.

Two-phase systems, such as shown in Figure 5, have been examined. These phases can be separated by centrifugation and homogeneous fractions are obtained. Plotting the amount of ClPPD-T polymer in the separated equilibrium phases as a function of total polymer concentration shows (Figure 6) the amount of polymer in the anisotropic phase is always higher. The anisotropic phase forms by separation of some of the polymer and solvent molecules to form a more dense, ordered arrangement, leaving behind a less concentrated isotropic phase. The polydispersity of ClPPD-T becomes evident on examination of the polymer inherent viscosity of each separated phase (Figure 7). Fractionation occurs with low molecular weight remaining in the isotropic phase. One can then conclude that polymer molecular weight distribution, as well as molecular weight, will have a strong influence on the phase diagrams of these systems.

Through optimization of the critical polymer and solvent parameters, some of which have been described above, almost entirely anisotropic solutions were obtained which in turn led to very strong fibers. Kevlar®, with poly-p-phenylene terephthalamide selected as the substrate, was commercialized in 1971 through this technology. Figures 8 and 9 show the stress-strain curves for Kevlar® and Kevlar® 49 (the high modulus, heat-treated PPD-T fiber) versus incumbent fibers for industrial applications.

Based on the tensile properties of Kevlar® (T/E/M_i = 19.4/44/425 dN/tex) and Kevlar® 49 (T/E/M_i = 19.4/24/800 dN/tex) and other characteristics shown in Table II, these fibers are finding a wide variety of uses in the service of man.

Kevlar® is finding growing use in belts of premium radial tires because of the value-in-use relative to other industrial yarns, and advantages in road hazard resistance and rolling resistance.

Due to high cut resistance and energy absorption characteristics of Kevlar® fabrics, they are widely used for ballistics protection. Bulletproof garments of Kevlar® are particularly effective since the light garment weight encourages extensive use. Protective apparel has been extended to gloves to take advantage of the heat and cut resistance.

Table II - Characteristics of Kevlar® Aramid Fibers

- High Crystallinity
- High Orientation
- Extended Chain Structure
- High Melting Point (ZST 640°C)
- High Glass Transition Temperature (375°C)
- Low Density
(1.45 vs. 2.55 for glass and 1.8 for graphite fibers)
- Low Creep
- High Tensile Fatigue
- High Cut Resistance
- Good Flex Resistance and Textile Processability
- Outstanding Tensile Properties

The low density and high strength are supporting applications for large diameter ropes and cables, particularly for anchor systems of offshore oil rigs. For example, a 1/2 million pound break strength rope of Kevlar® weighs 1.7 lbs/ft, while an equivalent steel cable weighs 7.4 lbs/ft.

The high modulus form of Kevlar®, Kevlar® 49, is finding increased use in the aerospace industry in fiber-reinforced resins to replace metal or fiberglass structures at lower weight. The value of weight saved is very high since it requires approximately 3 lbs of fuel and engine to raise one pound of payload off the ground in a commercial aircraft. This increases to over 20 to 1 in a space vehicle. Uses currently include a substantial number of parts in commercial aircraft, mostly in non-structural applications. Graphite fibers have higher modulus (3200 dN/tex) and higher compressive strength, and continue to be preferred in many primary structural aerospace components. Hybrid composites of Kevlar® 49 and graphite offer an attractive balance of properties and cost, however, and are becoming of increased interest.

The introduction of Kevlar® has resulted in a great deal of commercial interest based on its unique combination of tensile and material properties. To date, over 100 end uses have been identified where Kevlar® fibers have cost/performance advantages over incumbent fibers. We fully expect this number to continue to grow.

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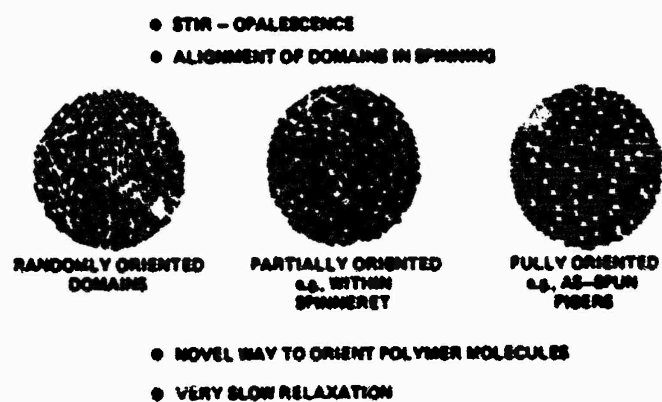
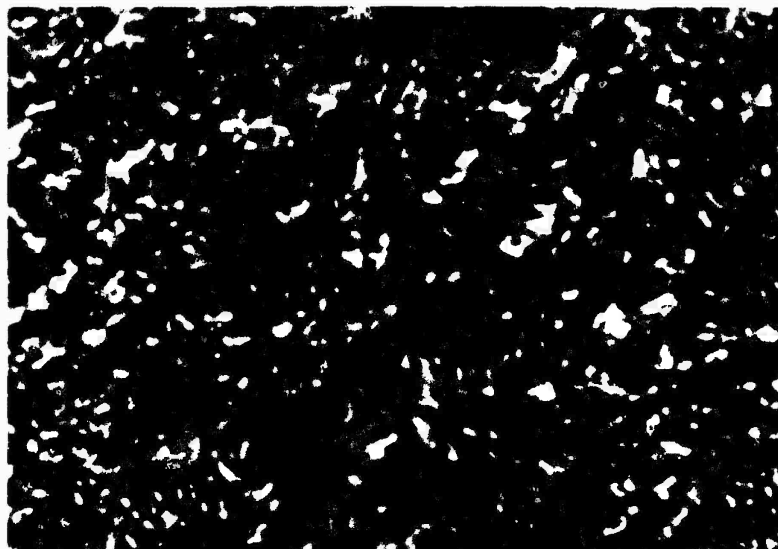


Fig. 2 - Effect of shear on liquid crystal solutions

Solution at Rest



Solution Sheared



DEPOLARIZATION OF PLANE POLARIZED LIGHT
CRYSTAL-LIKE ANISOTROPY

Fig. 3 - Optical properties of PPD-T - H_2SO_4

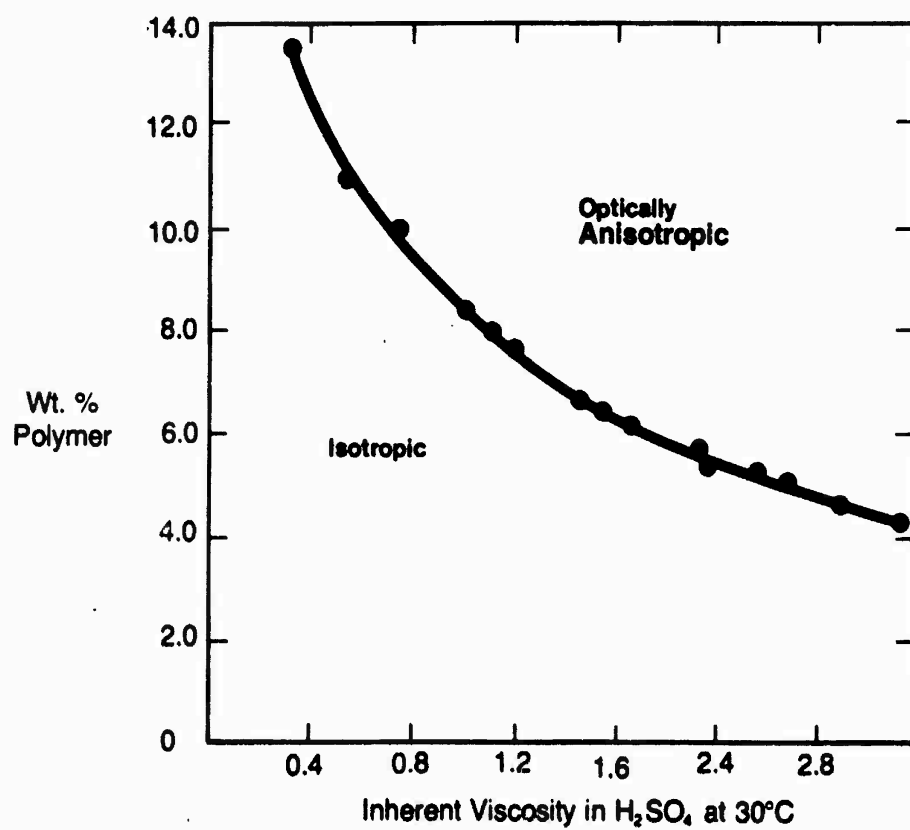


Fig. 4 - Effect of inherent viscosity on critical concentration for poly(1,4-benzamide) in DMAc-4% LiCl

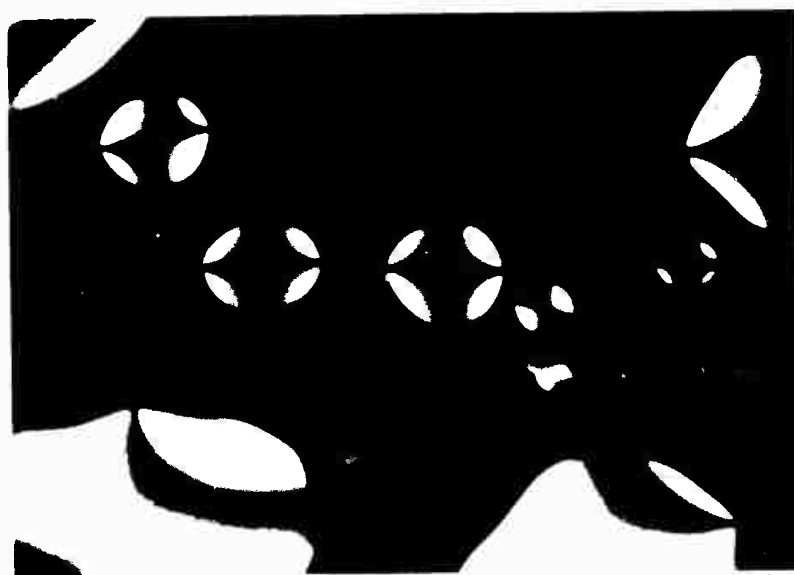
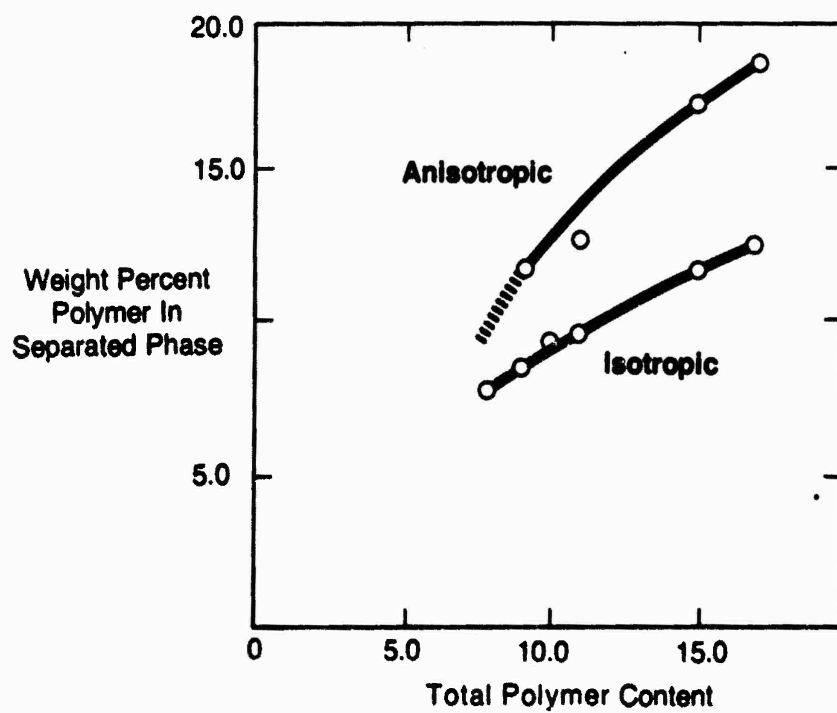
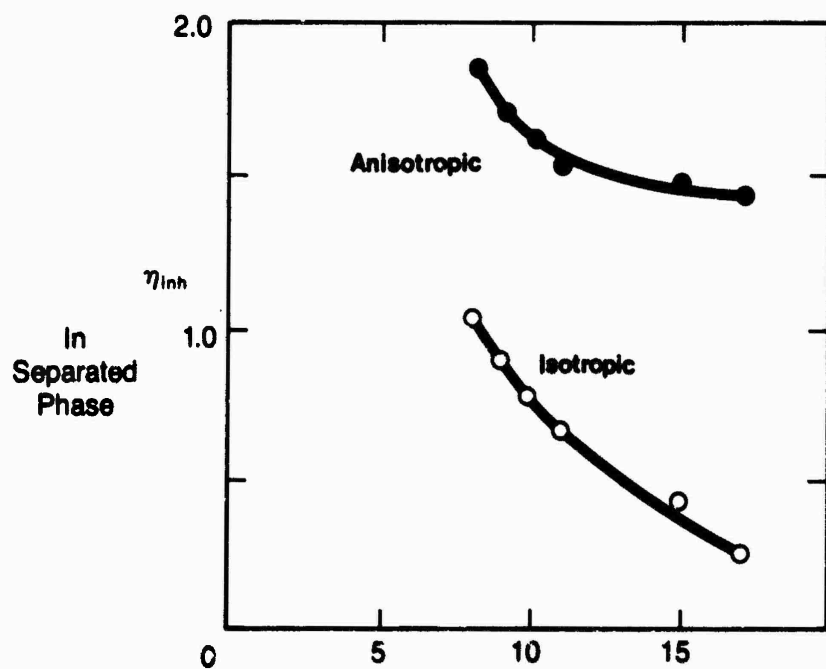


Fig. 5 - Droplets of a liquid-crystalline phase in a dark background of isotropic phase of a solution of poly(chloro-1,4-phenyleneterephthalamide) in dimethylacetamide-LiCl between crossed polarizers.



WEIGHT PERCENT OF ClPPD-T IN DMAc/2.18 LiCl

Fig. 6



WEIGHT PERCENT ClPPD-T POLYMER IN DMAc/2.18 LiCl

STARTING POLYMER $\eta_{inh} = 1.09$

Fig. 7

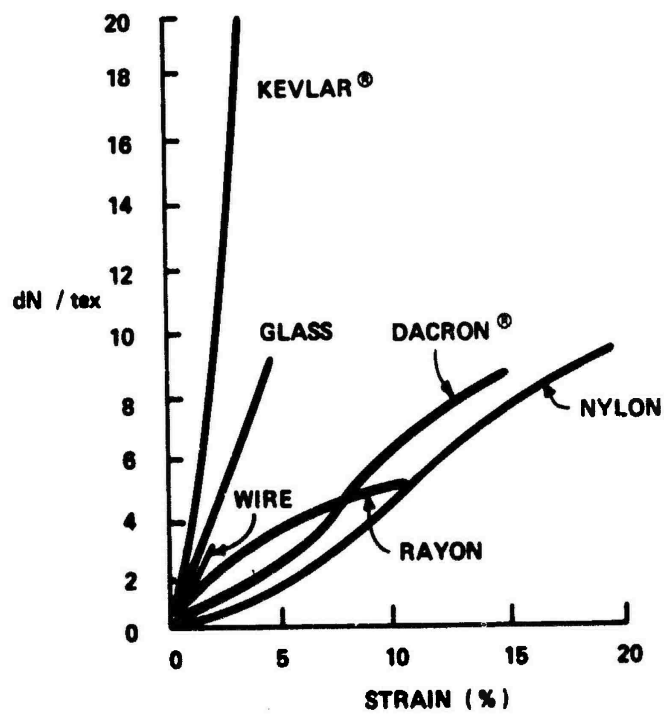


Fig. 8 - Tire yarn stress-strain curves

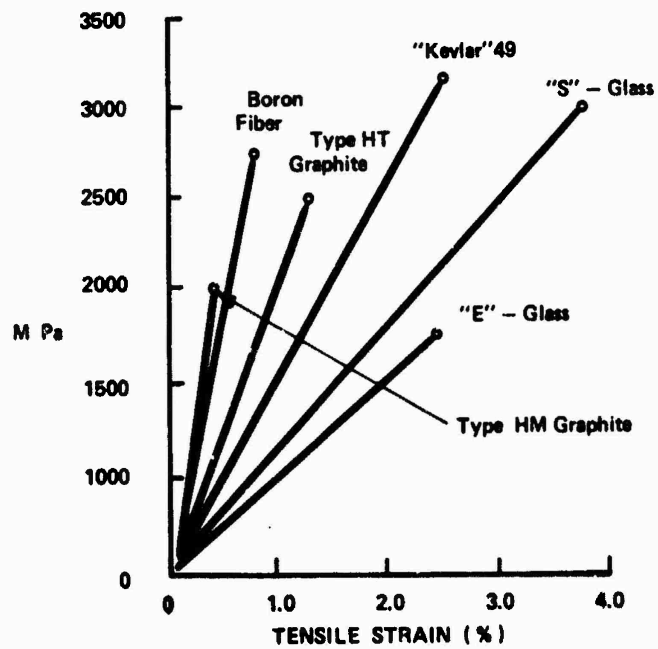


Fig. 9 - Plastics reinforcement fibers

POLYAMIDE-HYDRAZIDE AND COPOLYHYDRAZIDE FIBERS

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ABSTRACT

Polyamide-hydrazides and copolyhydrazides based on para-oriented aromatic ring systems have shown a remarkable propensity for yielding high modulus/high strength fibers useful for application in rigid and flexible composite structures. Interest in para-oriented hydrazide-linked polymers lay largely in the substantial increase in solubility afforded by the hydrazide linkage over that of structurally comparable wholly amide-linked polymers. This increased solubility of hydrazide-linked polymers permits high modulus fibers to be spun directly from solutions of the polymers in the organic solvents in which they are polymerized. Yarn Young's moduli up to 106 GPa (820 gms den⁻¹) have been obtained for fibers spun from a polyamide-hydrazide, and yarn strengths up to 2.7 GPa (21 gms den⁻¹) have been obtained for a copolyhydrazide fiber. The performance of the copolyhydrazide fiber in belts of radial tires was equal to that of steel wire in regard to treadwear.

BACKGROUND

High-modulus fibers of polyamide hydrazide were investigated by Monsanto when over 15 years ago it was seen that quite likely para-oriented aromatic polyamides would have to be spun from strong acid solution owing to their quite poor solubility in organic solvents (1); later high-modulus fibers of copolyhydrazides were also evaluated by Monsanto, Fig. 1. It was realized that substitution of the hydrazide linkage for the amide linkage in a given para-oriented aromatic polymer would make the resultant polymer more soluble in organic solvents. It was felt, however, that the increased thermal and hydrolytic stability of the aromatic amide linkage over that of the more solvable hydrazide linkage argued for replacement of only a portion of the amide linkages by hydrazide bonding. Thus it was that Preston (2) made X-500 polyamide hydrazide, a 50-50 amide-hydrazide copolymer.

We evaluated the X-500 fiber through the early stages of pilot plant spinning and commercial product evaluation in rigid composites and tires. Tires with X-500 belts and nylon carcass plies quickly proved to be the equal of glass-belted nylon tires with respect to treadwear, indicating substantial potential for the high modulus class of fibers provided they could be produced at a

reasonable cost. Concurrently with the tire cord studies, X-500 was evaluated for its potential as a rigid reinforcement fiber to compete with glass and graphite. At the time it was still unknown to any of us outside DuPont that they also had an in-house investigation of high-modulus fibers underway.

We encountered two serious problems with X-500, namely flow instabilities in extrusion of the solution under spinning conditions desired for commercialization, and secondly, poor transverse strength in the fibers (3), a problem now known to be generic to this class of fibers and one that still prevents any aromatic fiber from use in primary structural components of aircraft where compressive forces are important.

It was hoped that both deficiencies could be alleviated adequately without serious loss of either modulus or strength by going to a more flexible para-oriented polymer, the copolyhydrazide, H-202 (4), Fig. 1. The effect this structure change had on the solution behavior and fiber properties is treated later in the course of discussing the two fibers in more detail.

In the case of each X-500 polyamide-hydrazide and H-202 copolyhydrazide, the fibers were spun from isotropic solution, whereas the Kevlar aromatic polyamide fiber is spun from an anisotropic (liquid crystalline) solution. In the DISCUSSION section we will sort out the significant consequences of the two different modes of spinning on the properties of the fibers produced.

DISCUSSION

The stress-strain relations of X-500 and H-202 yarns in comparison with those of Kevlar 49, E- and S-glass as well as with yarns of conventional fibers made of flexible chain polymers are plotted on a specific property basis in Fig. 2, and in Fig. 3 on a cross-section or engineering basis, i.e., where the density of the fiber is not considered. See also Table 1. X-500 has tensile strength and tensile modulus almost as high as those of Kevlar 49 even though X-500 was spun from an isotropic (non-liquid crystalline) solution. Clearly, the high modulus and high strength of the para-aromatic fibers cannot be primarily a function of liquid crystallinity in the polymer solution *per se*. However, it still may be that stress-induced liquid crystallinity is involved in the extrusion process. We considered this possibility but tended to dismiss it as a dominant factor in regard to tensile property results because in the case of the fibers spun from isotropic solutions, the as-spun fibers must be hot drawn several fold in order to achieve either high strength or high modulus. The situation, however, is dramatically different in regard to strength development in the case of Kevlar spun from liquid crystalline solution. In that case, the fully developed strength of up to 21 gpd is obtained with no post

Table 1 Yarn Tensile Properties of Selected High Modulus/High Temperature Aromatic Fibers

Tensile Property	Poly(p-phenylene terephthalamide)			X-500 ^e Polyamide- hydrazide	H-202 ^f Copolyhydrazide
	Kevlar 49 ^a	Fiber B ^b (DP-01) (Kevlar, Kevlar 29)			
Tensile strength, GPa	2.8	2.8 ^c	2.6 ^d	2.4	2.7
Specific strength, g den ⁻¹	22	22 ^c	21 ^f	19	21
Modulus, GPa	124	61 ^c	-	106	57
Specific modulus, g den ⁻¹	980	480 ^c	-	820	440
Elongation-to-break, %	2.5	3.6 ^c	4.0 ^d	2.9	5.7
Denier per filament	1.5	-	1.5	2.7	1.9
Total yarn denier	400	-	1000	-	1600
Filament diameter, mm	0.013	-	0.013	0.023	0.017
Density, g cm ⁻³	1.44	-	-	1.47	1.47

^aDuPont Technical Bulletin K-2, Aramid, Feb. 1979. Kevlar 49 was known as PRD-49 during its precommercialization stage.

^bFiber B (DP-01) was the name of the Kevlar tire yarn during its precommercialization stage.

^cDuPont data.

^dData obtained in Monsanto Laboratories.

^eRef. 18.

^fRef. 9.

spinning hot stretch whatever (5), showing a quite remarkable difference between spinning from isotropic and anisotropic solutions. In the case of X-500, one nevertheless cannot state *a priori* that the results obtained are not dependent to some degree to an inherent propensity of the X-500 polymer to give liquid crystalline solutions because Morgan (6) has shown that X-500 will indeed yield excellent liquid crystalline solutions in sulfuric acid, a solvent which unfortunately tends to degrade the aromatic hydrazide bond.

There are two other results that shed additional light on the matter of liquid crystallinity of X-500. Alfonso (7) has presented evidence that X-500 at relatively high shear rates behaves in a way remarkably analogous at least superficially to the solution behavior of the wholly *para*-oriented aromatic polyamides, Fig. 4. Here we see that at shear rates of 100-300 sec⁻¹, the viscosity dependence of the X-500 polymer solution on concentration shows a maximum at 3-4 wt-%. The decrease in viscosity with increased polymer concentration from 3% to 8% is suggestive of a molecular alignment not unlike that found in flowing anisotropic solutions. Baird et al. (8) have cautioned, however, that flow instabilities have not been completely ruled out as the basis for the lower viscosity observed with increased concentration of X-500 at these high shear rates. In any event, as noted earlier, the as-spun X-500 fiber must be hot stretched in order to obtain the high strength whereas poly-p-phenylene terephthalamide fiber does not, showing that even if there is a stress-induced generation of something akin to

to a liquid crystallinity in the extrusion of X-500 solution, it is not likely the primary factor responsible for the high X-500 strength and modulus levels observed.

Significant additional support for believing that liquid crystallinity is not a necessity for obtaining very high tensile properties is supplied by our work with the H-202 copolyhydrazide. We have spun the somewhat more flexible H-202 polymer to yarns with the same strength as we measured for Fiber B in side-by-side tensile testing, namely 21 gpd on 1600 and 1000-denier yarns, respectively (9). It is apparent that for high strength and high modulus what is essential is that the chain stiffness must be sufficiently great so that the maximum concentration for a liquid solution is on the order of 5 wt-% for nominally high molecular weight polymers.

The very high strength obtained for the as-spun poly-p-phenylene terephthalamide fibers made from liquid crystalline solutions, i.e., fibers not hot drawn after take up, points up an interesting aspect of tensile strength vis à vis tensile modulus in fibers made by solution spinning of *para*-aromatic fibers. For other types of polymers, one normally does not develop the ultimate strength obtainable for a fiber prior to, and certainly no sooner than the point at which the maximum tensile modulus is obtained. Crudely stated, this obtains from the fact that modulus is basically a short range property whereas strength is a long range property. One sees this particularly strongly for fibers generally as it relates to fiber modulus vs. tensile strength as observed in plots of each tensile strength

and modulus as a function of molecular weight. To put it another way, we do not find drawn fibers showing increasingly rubber-like moduli as molecular weight decreases; on the contrary, they tend to be increasingly brittle, i.e., stiff but weaker. It is noteworthy that both high-modulus polyethylene (10,11) and high-modulus aromatic polyesters spun from melts (12-16) show truly extreme tendencies for yielding very high modulus in combination with very low tensile strengths in the as-spun fibers in great contrast to the behavior observed for fibers spun from liquid crystalline solution. In the case of the aromatic polyesters the strength can be increased simply by annealing, and in the case of polyethylene by a combination of proper spinning and careful hot drawing (17). Somewhat analogously to poly-p-phenylene terephthalamide fibers spun from anisotropic solutions, the copolyhydrazide yields very high strength (equal to that of the Kevlar) without giving high modulus, albeit after hot drawing in this instance.

Thus, it appears that solution-spun para-aromatic fibers are unique in regard to their molecular arrangement as spun, whether spun from isotropic or anisotropic solution. Excellent long range order of some sort is obtained before the highly regular short range order needed for high modulus is fully developed.

Rather surprisingly, we found (18) that the crystallite orientation of X-500 was higher than that of even the hot-stretched version of poly-p-phenylene terephthalamide, PRD-49 (precommercial Kevlar 49), as shown by wide angle X-ray scattering. See Fig. 5a and 5b. Clearly, however, the three-dimensional order of PRD-49 is better than that of X-500 as shown by the more evident and sharper h,k,l reflections. We have considered that perhaps one has to draw X-500 and H-202 past the optimum point required for lateral cohesion in order to get maximum tensile strength and tensile modulus, but that is largely speculation.

X-500 and H-202 tend to fibrillate like all high modulus aromatic fibers. The fibrillation is basically a manifestation of quite weak transverse strength. This, of course, is to be expected for any organic fiber in which most of the polymer molecules are stretched out to a very high degree in the direction of the fiber axis. Indeed, high modulus polyethylene fibrillates at least as easily as the high modulus aromatic fibers. In addition to rendering such fibers easily abraded, the low transverse strength of the high-modulus organic fibers very likely is the true basis of the quite poor compressive strength of such fibers. Wu, Holland and the writer (19) found in the case of very highly drawn polyethylene that some kink bands did not traverse the entire cross-section of the specimen. [Kink bands are normally associated with compressive failure (20,21)]. Our finding in the case of the surface kink bands, suggests that the formation of the compressive kink bands in high-modulus polyethylene (and by analogy in

high modulus aromatic fibers as well) can proceed in a stepwise manner across the specimen, providing thereby a low energy pathway for a kink band to traverse the specimen. Accordingly, such highly fibrillating materials would be expected to have quite poor resistance to compressive failure, especially in bending.

A number of physical properties, the stability to various end-use environments, and the end-use utility of the X-500 polyamide-hydrazide and the H-202 copolyhydrazide have been reported extensively in a book edited by the writer and Preston (22) and by Dobinson et al. (9) in the case of H-202. Thus these matters are dealt with only briefly here.

There is little to distinguish the basic physical properties of the para-oriented aromatic polymers such X-500, H-202, poly-p-phenylene terephthalamide, poly-p-benzamide and the like. Their densities are about the same, 1.44-1.47 gm cm⁻³; they are all straw colored; have unusually high crystallinities and birefringence values; have equilibrium moisture contents at a given relative humidity more like those of aliphatic polyamides than polyethylene; and they have very high thermal thermooxidative stabilities, with the polyamides clearly superior in this regard, however.

The relative retentions of tensile properties of the several high modulus fibers upon exposure to heat and also to heat and moisture combined are given in Table 2.

Early in the research on high modulus organic fibers, Zaukelies and Daniels (3) in a study of the utility of X-500 in composites in comparison with S-glass showed that on a specific basis the substantially lower transverse modulus of X-500 (Fig. 6a) is readily compensated for by cross ply laminates, especially by quasi isotropic laminates Fig. 6b, and they showed the very substantial advantage of the higher specific modulus of X-500 over that of S-glass in regard to the flexural stiffness figure of merit for quasi-isotropic laminates, Fig. 6c.

While X-500/epoxy and E-glass/epoxy laminates at a given vol-% reinforcement loading were generally comparable in regard to their electrical properties, the X-500/epoxy laminates were nevertheless superior at radar frequencies (25). Thus the lower weight of the X-500/epoxy laminates gives a clear edge to X-500 over E-glass for use in radomes, especially for radomes to be carried aloft.

The copolyhydrazide, H-202, which was designed specifically for use in tires performed very well for the intended use. In Table 3, the performance of H-202 in the belts of radical tires is compared on a relative basis with that of steel and glass. Clearly H-202 is the equal of steel and glass in treadwear performance.

The writer has reviewed the field of high modulus organic fibers quite extensively in addition to the book based largely on X-500 (18,23,24). The reader is

Table 2 Retention of Tensile Strength and Stiffness After or Upon Various Treatments^a

	Fiber B ^b (Kevlar)	X-500 ^c	H-202 ^d
% Tenacity/Initial Modulus (Ten/Mod) retained after:			
7 days in air at 150°C	84/98	100/-	86/100
7 days in boiling water	82/98		53/90
18 hrs in 18 psig saturated steam	82/-		44/-
% of Rm T Ten/Mod retained:			
at 150°C		68/95	72/71
at 200°C	61/60	48/71	53/60
in water at 90°C	89/83	66/76	64/62

^aSee Fig. 1 for the structural formulas of the polymers.^bData obtained on DuPont produced 1000 filament yarn of 1500 total denier.^cData from ref. 25.^dReference 9.

Table 3 Comparative Automobile Radial Tire Treadwear Ratings for Tires with High Modulus Copolyhydrazide and Steel Belts

Belt Plies	Treadwear Rating ^b	
	Center	Shoulder (av.)
Steel ^a	100	60
Copolyhydrazide H-202 ^a	101	56

^aJR78-15 tires with polyester carcass plies. Belt plies made to equal strength. Tested on Automotive Research Associates track, San Antonio, Texas. Reference 9.^bValues normalized for 100 miles mil⁻¹ for center treadwear for steel control tires.

referred to these sources of additional information regarding the performance of high-modulus/high-strength organic fibers, including high-modulus polyethylene in references 23 and 24.

SUMMARY

It has been shown that one does not have to solution spin a polymer from liquid crystalline solution in order to obtain yarns with modulus and/or strength at the same general level as found in the Kevlar aramid fibers spun from liquid crystalline solution. Tensile strength for H-202 equal to that of Fiber B (Kevlar) tire yarn has been demonstrated in side-by-side tensile testing, and in the case of X-500, both strength and modulus values only about 10% lower than those of Kevlar polyamide fiber were demonstrated. It was speculated that the much

greater hot-stretch required for X-500 versus Kevlar 49 to obtain optimum strength and modulus may result in a somewhat poorer transverse strength for X-500 than for Kevlar 49. X-ray diffraction evidence, while showing that X-500 crystallites were more highly oriented than in Kevlar 49, nevertheless showed that the three-dimensional order in X-500 was significantly poorer.

It was noted in the case of the polyamide-hydrazide, X-500, that an instability of the extrudate flow was encountered under commercially desirable spinning conditions, limiting as a consequence the diameter of the drawn filament to a size substantially larger than that used for the Kevlars and resulting necessarily in greater limitations in flex resistance for X-500.

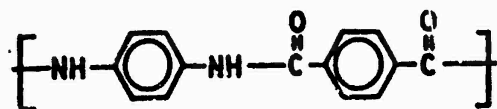
The copolyhydrazide, H-202, designed specifically for use in tires by sacrificing

some molecular stiffness in the polymer backbone for increased tractability, performed as expected in tires.

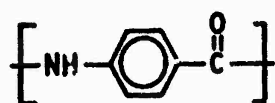
Unquestionably, having to limit oneself to 4-5 wt-% solutions as in the case for isotropic solutions of stiff-chain polymers such as X-500 and H-202 is not an entirely attractive prospect from a commercialization point of view, even though it does permit one to spin the polymer in the same solvent in which the polymer is prepared. But, of course, the only known alternative, that of having to use a strong acid solvent such as sulfuric acid in order to be able to prepare and spin 20% liquid crystalline solutions is rather unattractive also, pointing up the difficulties that senior executives in the synthetic fiber business have had to face in this field of high performance but concomitantly high price fibers.

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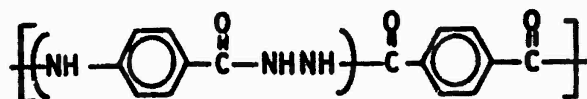
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KEVLAR I



PBA II



X-500 III

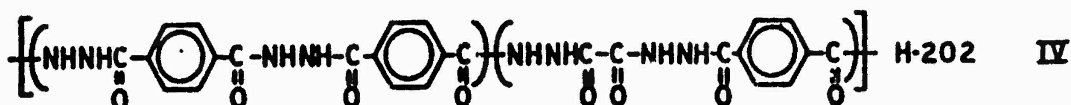


Fig. 1 Chemical structures of poly-p-phenylene terephthalamide (I), poly-p-benzamide (II), polyterephthaloyl derivative of p-aminobenzhydrazide (III), and the copolyterephthaloyl derivative of a 50/50 molar ratio of terephthalhydrazide and oxalylhydrazide (IV).

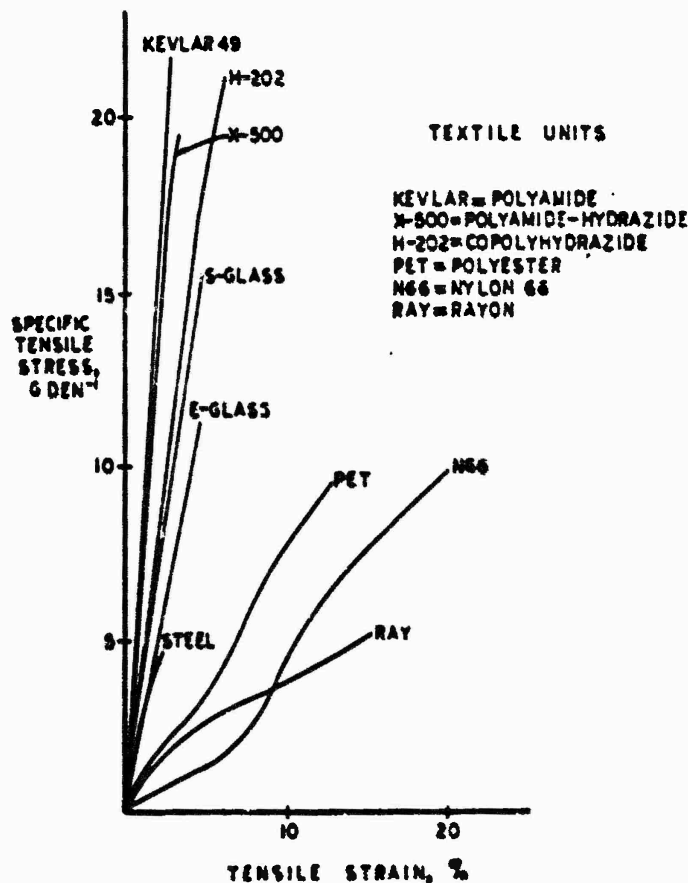


Fig. 2 Comparison on a weight basis of stress-strain curves for high-modulus/high-strength aromatic yarns with those of conventional high strength organic fibers, S-glass, E-glass and steel wire.

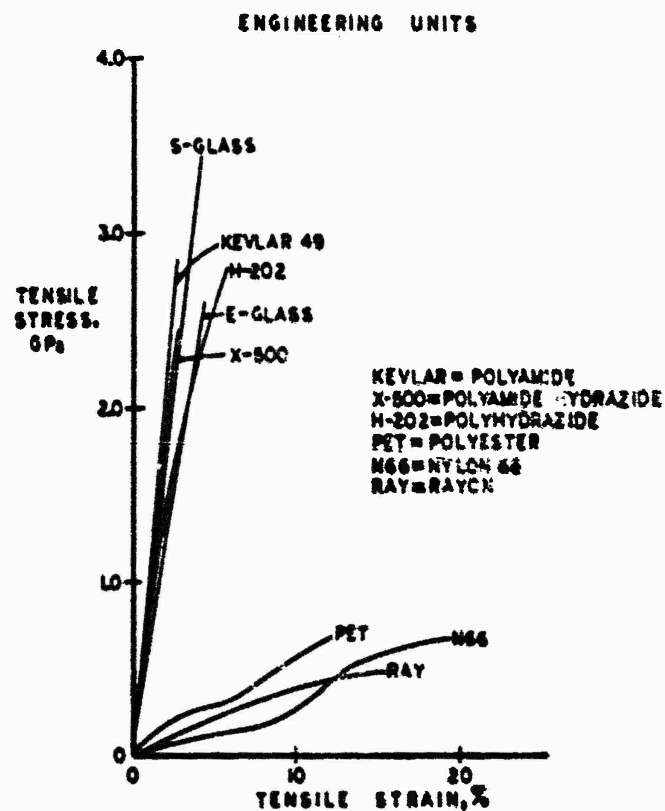


Fig. 3 Cross-sectional or engineering basis comparison of stress-strain curves for high-modulus/high-strength aromatic yarns with those of conventional high-strength organic yarns, S-glass, E-glass and steel wire.

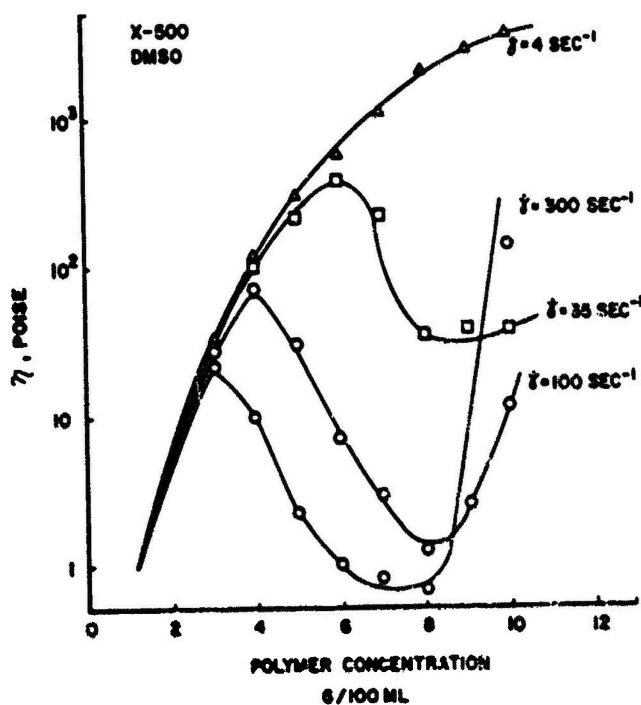


Fig. 4 Viscosity of a dimethylsulfoxide solutions of X-500 as a function of polymer concentration at the indicated shear rates, $\dot{\gamma}$. X-500 intrinsic viscosity = 4.82 dl gm⁻¹; T = 20°C.

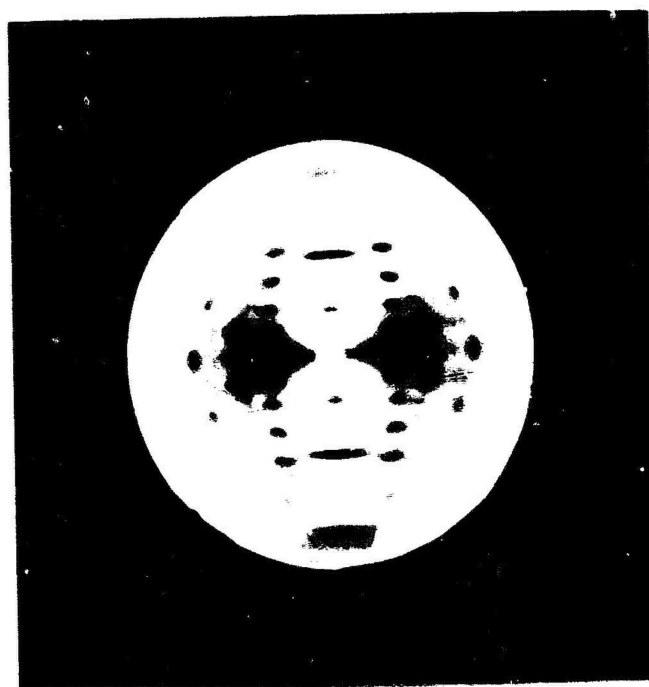


Fig. 5b WAXS pattern of PRD-49, Type III. Courtesy of P. G. Simpson.

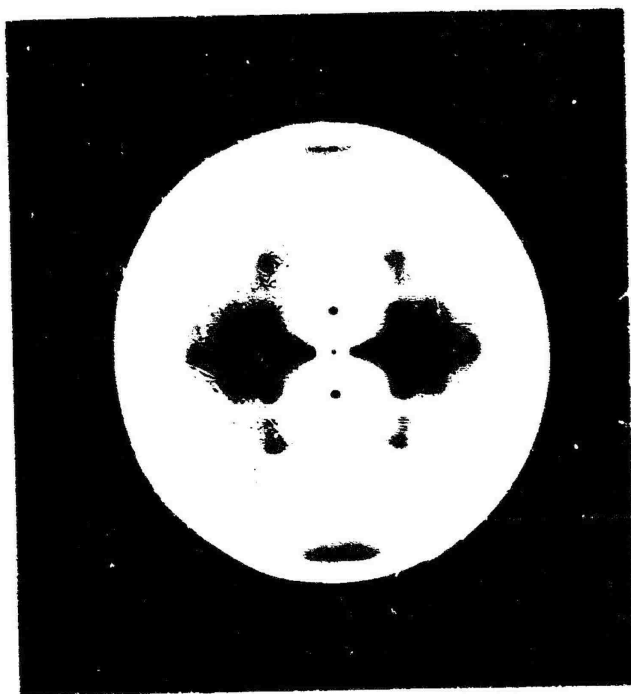


Fig. 5a Wide angle X-ray scattering (WAXS) pattern of X-500. Ten/Elon/Mod of particular yarn used = 18.7 gm den⁻¹/2.92/328 gm den⁻¹. Courtesy of P. G. Simpson.

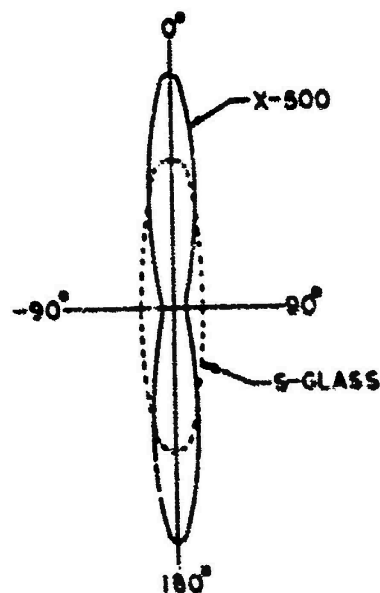


Fig. 6a Specific Young's moduli of X-500 and S-glass unidirectional composites; 60 v/o fiber; arbitrary units; 0°, 0°.

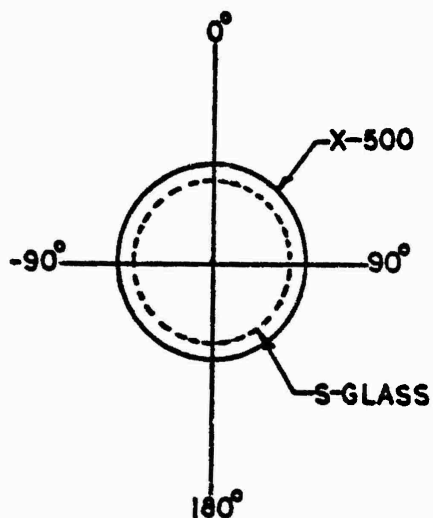


Fig. 6b Specific Young's moduli of X-500 and S-glass quasi-isotropic laminates; arbitrary units; 0°, 60°, -60°, -60°, 60°, 0°; 60 v/o fiber.

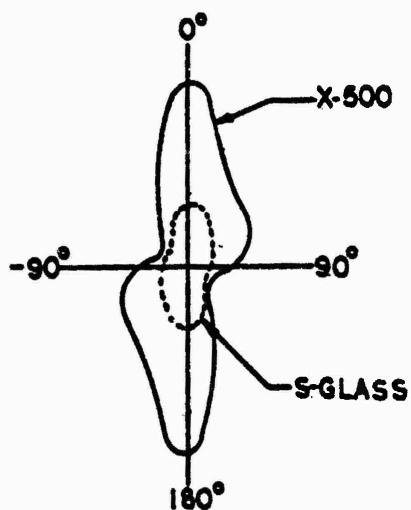


Fig. 6c Flexural stiffness figure of merit for quasi-isotropic X-500 and S-glass laminates; arbitrary units; 0°, 60°, -60°, -60°, 60°, 0°; 60 v/o fiber.

FIBERS FROM ANISOTROPIC MELTS

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ABSTRACT

The formation of high strength fibers by solution spinning of lyotropic polyamides has led to substantial research aimed at identifying thermotropic liquid crystalline polymers which can be melt spun to high strength fibers of comparable properties. A variety of thermotropic polymers have been identified. Those that have been shown to form high strength fibers are mainly polyesters and polyazomethines which contain a significant proportion of linear and planar linkages. Through formation of suitable copolymers, selection of certain aromatic substituents, or copolymerization with some aliphatic components, melt processable thermotropic polymers have been obtained. Fibers from some of these polymers equal or even exceed those of the liquid crystalline polyamides.

INTRODUCTION

Anisotropic melts of polymers having backbone structures comparable to known nematic liquid crystals may be expected to have highly oriented extended chain morphology. Fibers prepared from such melts could be expected to have superior modulus and tenacity, by analogy with other systems of similar morphology. For example, Zwiijnenburg & Pennings(1*) have shown that fibrillar crystals of polyethylene grown from solution possess remarkably high modulus and tenacity which can be attributed to the extended chain backbone of the fibrils. Lyotropic aramids (aromatic polyamides) can be processed to give exceptionally strong fibers with extended chain structures(2). Typical properties for a commercial aramid yarn(3) are 22 gpd tenacity, 3-4% elongation, and 480 gpd modulus for Kevlar® 29 and 28 gpd tenacity, 2-8% elongation, and 1000 gpd modulus for Kevlar® 49. Spinning a lyotropic, and therefore highly oriented, extended chain aramid solution gives superior fibers compared with spinning an isotropic solution of equivalent polymer(4). From a practical point of view, a system is desirable which combines the ease of materials handling associated with melt spinning with the extended chain morphology and high fiber properties that arise from processing a liquid crystalline polymer. In addition, a polymer capable of forming these anisotropic melts should have the structure, T_g and T_m compatible with the requirements of an industrial yarn. It is expected that polymers with relatively rigid and linear backbones would be required in order to produce fibers with extended chain morphology and property retention under use conditions.

*Numbers in parentheses designate Reference at end of paper.

As a consequence, efforts to prepare fibers from anisotropic melts have been almost exclusively devoted to using aromatic rigid rod polymers. As used in this paper, aromatic rigid rod refers to a largely aromatic backbone structure having a limited number of ring substituents (usually zero to one) per repeat unit, which consist of chains of four or fewer atoms. The aromatic rings are linked by rigid (azomethine) or semi-rigid (ester) functional groups, and most connecting bonds are positioned in oppositely directing positions. Some 1,3-phenylene, ether, aliphatic or other non-linear groups may be present. A special case of aromatic rigid rod polymers is the anisotropic pitch precursor to graphite fiber(5). A discussion of its formation, properties, and processing falls outside the scope of this paper and has been mentioned in an earlier paper of this symposium. Other thermotropic polymers include semi-rigid backbone polymers, i.e., certain nylon 1's(6) and polyphosphazenes(7), as well as some block copolymers(8,9), and "comb polymers" with rigid side chains (10,11,12). However, fibers from these polymers which have the exceptional tenacities and moduli desired are not known. The following discussion will be limited to two general classes of rigid rod, thermotropic polymers: aromatic polyesters and polyazomethines. These are the only thermotropic polymers in the literature which have been shown to have a high level of fiber properties.

THERMOTROPIC RIGID ROD POLYMERS

The concept of a thermotropic aromatic rigid rod polymer should seem reasonable and obtainable, since low molecular weight, liquid crystal models of both ester and azomethine functionality are well known(13, 14), and aromatic amides have also been shown to form thermotropic melts(15). Since aramids and many aromatic polyesters are not melt processable, various structural modifications, especially copolymerization and backbone substitution, would offer routes to lowering melting temperatures. An early attempt to modify aramid structures through N-substitution produced melt processable polymers, but no anisotropy was reported and fiber properties were unremarkable(16).

Table 1 - N-Phenyl Substituted Polymers

Polymer	T_m , °C	Spin Method	Fiber Properties		
			T_g/d	E, %	M, g/d
$\left[\text{N} \begin{array}{c} \text{O} \\ \end{array} \text{N} \text{CO} \begin{array}{c} \text{O} \\ \end{array} \text{CO} \right]_n$	390	Dry	2.7	3.6	98 (drawn 5x in steam)
$\left[\text{N} \begin{array}{c} \text{O} \\ \end{array} \text{N} \text{CO}_2 \begin{array}{c} \text{O} \\ \end{array} \text{O}_2\text{C} \right]_n$	290	Melt	3.6	22	42 (as spun)

Cottie, Economy, and Nowak(17,22) showed that certain copolymers of aromatic polyesters can be conventionally melt processed (Table 2).

Although these polymers were not described as forming thermotropic melts, it is apparent that at least some of the compositions would be liquid crystalline. Since 1972, a large body of U.S. and foreign patents have issued specifically describing various thermotropic polyesters and polyazomethines. These patents are listed in References 17 to 48. In addition, numerous Japanese patents describing thermotropic polyesters have appeared.

Another approach to depressing polymer melting temperatures is the use of ring substituents. Ring substituted low molecular weight liquid crystal esters have significantly lowered melting points and isotropic transition temperatures, but the breadth of the nematic range is not appreciably affected(49). This

has also proven effective for polymers (Table 3).

Table 2 - Melt Processable Aromatic Copolyesters

Polymer	Reference	T _m	Fiber Properties*		
			T _g /d	E, %	M _g /d
HBA/TA/HQ 1/1/1	17	510°	-	-	-
HBA/TA/IA/BP 60/15/5/20	22	<350°	12 (heat treated)	1.3	800
HBA: p-hydroxybenzoic acid			HQ: hydroquinone		
TA: terephthalic acid			BP: 4,4'-biphenol		
IA: isophthalic acid					

Table 3 - Effect of Ring Substituents on Melting Temperatures

Liquid Crystal	Reference	T _m , °C	T _i , °C	T _i -T _m , °C
MeO-C ₆ H ₄ -CO ₂ -C ₆ H ₄ -O ₂ C-C ₆ H ₄ -OMe	13	213	297	84
MeO-C ₆ H ₄ -CO ₂ -C ₆ H ₃ (Me)-O ₂ C-C ₆ H ₄ -OMe	49	169-70	250	80
MeO-C ₆ H ₄ -CO ₂ -C ₆ H ₃ (Cl)-O ₂ C-C ₆ H ₄ -OMe	49	165-166.5	254	88
[O-C ₆ H ₄ -O-CO-C ₆ H ₄ -CO] _n	17	650(est.)	-	-
[O-C ₆ H ₃ (φ)-O-CO-C ₆ H ₄ -CO] _n	41	341	-	-

Thus, modifications which disrupt the regularity of the polymer chain can be sufficient to depress the melting point without destroying the spatial configuration and interactions necessary for forming thermotropic melts. Other types of chain disruption that have been appropriate include copolymerization of low levels of flexible units, (sp³ backbone atoms), bent rigid units (1,3-phenylenes), or crankshaft rigid rods (2,6-naphthylene, 1,4-ethenylphenylene). Recent developments show that substantial melting point depressions can be obtained by proper selection of monomers, ring substituents, and monomer ratios in the cases of copolymers.

The thermotropic, conventionally processable polymers formed by the synthetic approaches described above can be classified into several groups according to common structural features (Table 4). These classifications may appear somewhat arbitrary and overlapping, but they help to show those approaches which have proven successful. Frequently, combination of several of these groups in one copolymer system has proven to be the best method of achieving the desired melting temperature range.

POLYMER SYNTHESIS

The polymers of interest have been almost exclusively polyesters and polyazomethines. The polyesters are usually prepared by transesterification or acidolysis of derivatives of diacids, diols and/or hydroxy acids, directly or indirectly, in the melt or a heat transfer medium. Transesterification has usually involved phenyl esters and acidolysis has generally used the acetates. The reactions are run under anhydrous conditions in inert atmospheres and may or may not use catalysts such as antimony trioxide, magnesium, sodium acetate and dibutyl tin oxide. The

* Calculated from cited reference assuming ρ = 1.4 g/cm³.

indirect routes have included the use of phenylacetate, phenylcarbonate and acetic anhydride. Preparation directly from aromatic acids and phenols using catalysts such as n-butylstannic acid and tetrabutyl titanate(33) is also reported. The solubility of both monomers and polymers is generally low which has precluded solution methods.

Polyazomethines are made from the corresponding diamines, dialdehydes, diketones and/or aminoaldehydes or ketones(26,35). The reactions are run under anhydrous conditions and inert atmospheres. By-products are removed with heating or alternately a solvent for the reactants which forms an azeotrope may be used. Low temperature solution polymerization with polar solvents such as dimethylacetamide is also reported.

Table 4 - Structural Classification of Thermotropic Polymers

Description	Characteristic Features
I. Unsubstituted Aromatic Copolymers	
A. Linear Rigid Chains	
B. "Crankshaft" Rigid Chains	
C. Bent Rigid Chains	
D. Flexible Chains	
II. Unsubstituted Aromatic-Aliphatic Copolymers	
A. Aliphatic Monomers	
B. Aliphatic/Aromatic Monomers	
III. Ring Substituted Homo and Copolymers	
	X = Cl, Br, CH ₃ , φ
IV. Combinations of Groups I, II, and III	

On melting, the polymer may further polymerize with a resulting increase in melting point and viscosity. Controlling MW by the addition of chain stoppers has been employed to achieve stability during spinning.

The MW's are generally low for the η_{inh} viscosities reported, which is probably due to a large Mark-Houwink constant as noted for the stiff chain polymers which form lyotropic systems(4). Where measured MW's are generally around 20,000 or more and η_{inh} 's range from 0.5 up but are generally around 2-7. Post polymerizations through solid state reaction either before (e.g., 24,42) or after extrusion are also reported(46).

DETECTION OF ANISOTROPIC MELTS

The detection of both lyotropic and thermotropic liquid crystalline materials is usually easily done by observation with the naked eye when the sample is large, or with an optical microscope when the sample is small. Typically, isotropic solutions or melts are clear, but as they become anisotropic they exhibit shear opalescence, and can become opaque at high shear and when the sample thickness is great enough. Anisotropic materials depolarize plane polarized light, and therefore an anisotropic sample will cause incident plane polarized light to be transmitted through a crossed polarizer(50). The intensity of the light transmitted can be taken as a measure of "degree of optical anisotropy"(4). Apparatus for observing the transmission caused by an anisotropic melt has been described by Kirshenbaum, Isaacson, and Feist(51), and by Schaeffgen(34). Figure 1 shows typical transmission patterns for polymers yielding isotropic and anisotropic melts(34).

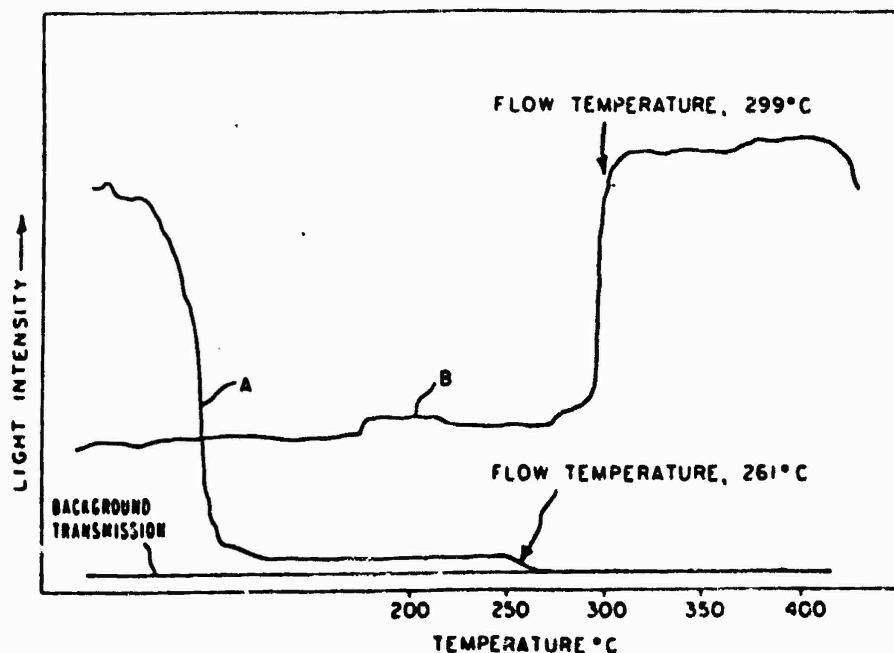


Fig. 1 - Transmission of incident plane polarized light as a function of temperature(34)

- A. Polymer forming an isotropic melt.
- B. Polymer forming an anisotropic melt.

POLYMER PROPERTIES

MELTING TEMPERATURE - The requirements for a melt processable polymer are stability in the melt phase over a temperature range of 20° or more, and a sufficiently low melting temperature so that an economically viable process can be developed. A group of polymers utilizing ethylene glycol as the comonomer to depress melting temperature has been developed by Eastman Kodak(52). Typically, poly(ethylene terephthalate)

(PET) undergoes an acidolysis/polymerization reaction with p-acetoxybenzoic acid to form a random copolymer.

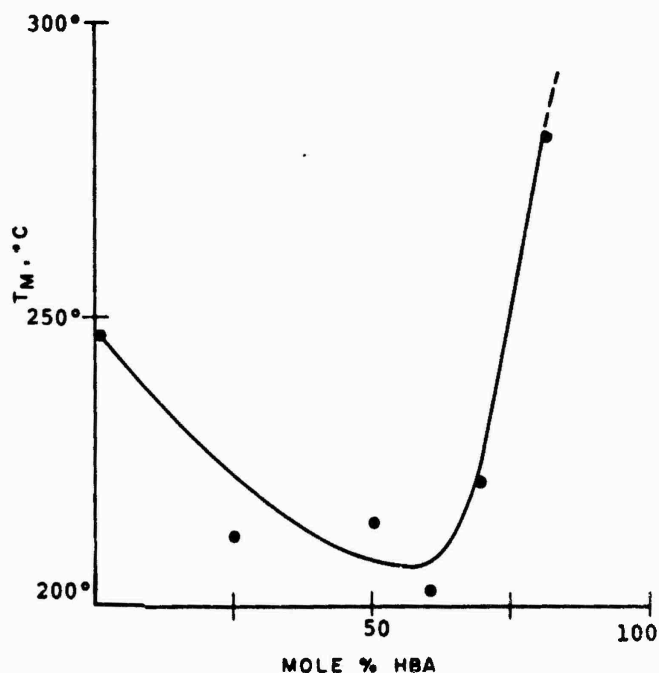


Fig. 2 - Effect of HBA/PET on T_m (53)

Some of these copolymers exhibit extremely low crystalline melting points (Figure 2)(53). Approximately 20 mole % PET is required to produce a polymer which melts before decomposition. In systems formed by copolymerizing monomers which give only intractable homopolymers, equally dramatic melting point depressions have been observed. In addition, the melting temperatures of some of these systems are more sensitive to small changes in composition. Figure 3 shows that changing 2,6-naphthalenedicarboxylic acid con-

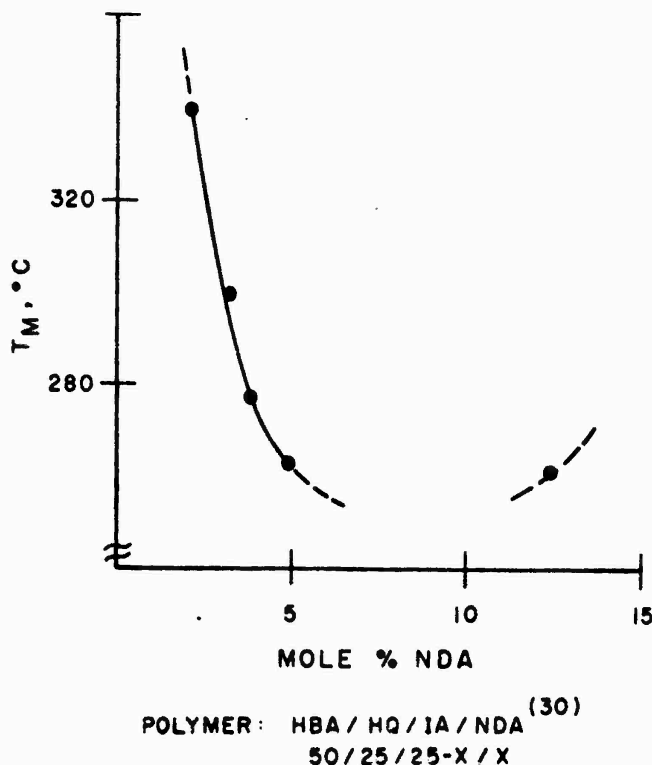


Fig. 3 - Effect of composition on T_m

tent from 2% to 5% of a polyester prepared from 50 mole % p-hydroxybenzoic acid (p-HBA), 25 mole % hydroquinone (HQ) and the balance isophthalic acid (IPA) produces a melting temperature change from 340° to 263°C(30). The melting point depression is not always so dramatic, but U-shaped curves usually result when T_m is plotted against changing composition, as seen in Figure 4(31).

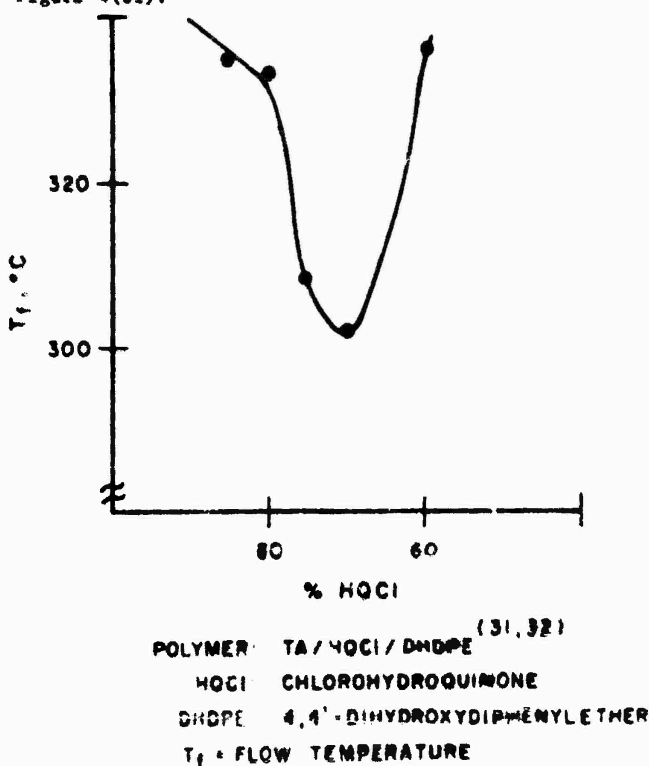


Fig. 4 - Effect of composition on T_f

Many of these thermotropic polyesters have melting points that approach that of PET, and could be expected to be processable using the same temperatures and heating methods employed in PET processing. This, of course, is an incentive towards practical application of these compositions.

RHEOLOGY - Very little has been published regarding the melt rheology of thermotropic polymers. Jackson and Kuhfuss(52) have reported the melt viscosity of PET copolymers, modified with varying amounts of p-oxybenzoyl units. All copolymers were of comparable molecular weights. Melt viscosity is shown to increase with increasing p-oxybenzoyl units to about 30 mole %. With further increase in modification, the melt viscosity significantly decreases to a minimum at about 70 mole % and then starts to rise sharply. The data are reproduced below (Figure 5).

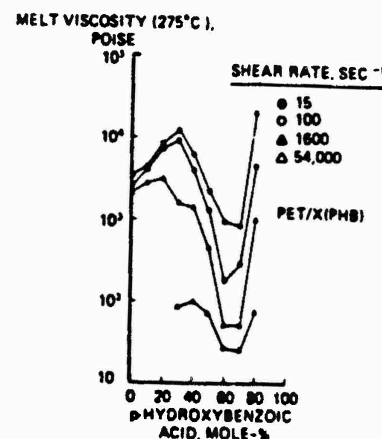


Fig. 5 - Melt viscosity of modified PET
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The initial viscosity increase is expected from known structure-property relations involving the replacement of flexible units with less flexible ones. The unexpected drop in melt viscosity with increasing modification is also accompanied by the onset of order in the melt ascribed to a liquid crystalline state. The lowering of viscosity in going from an isotropic to anisotropic state has been reported for nematic organic compounds(55) and for lyotropic polymer solutions(4). This feature of anisotropic melts and solutions is very important as, otherwise, processing of these stiff chain polymers would be most difficult.

FIBER PREPARATION AND PROPERTIES

Melt spinning of polymers to fibers is done in a conventional manner and spin stretch factors generally range from 15 to 500. As spun fibers are highly oriented. Orientation angles are low and where reported are usually in the range of 20°. This is believed to be a consequence of the molecular order in the anisotropic melt. Drawing is generally omitted, is not required to achieve high levels of properties, and in the usual sense (i.e., >100%) is not even possible (e.g., 23,24).

Special quenching techniques have not been cited and a room temperature air or N₂ quench is frequently used.

Heat treatment of fibers to improve physical properties is generally noted. However, almost all

treatments involve a lengthy static exposure near the melting temperature in a relaxed state. Increases in both polymer melting temperature and polymer MW are noted (e.g., 22,46).

Fiber properties of thermotropic polymers are the highest of any melt spun polymer, and some exceed those of lyotropic polyamides. All fiber properties reported here are restricted to those in patent examples and, consequently, discussion of structure property relationships can only be brief, and indicate very general relationships.

The thermotropic polyesters prepared from PET and p-hydroxybenzoic acid were the first described, and were the first whose fiber properties were reported(20). Only low as-spun properties were reported, but a similar polyester (80/20 ClHQ/PET) structure has shown 11 gpd tenacity and 378 gpd modulus (29) after heat treatment. Polymers containing ethylene glycol as ether residues, as in bis(4-carboxyphenoxy)-1,2-ethane, exhibit similar properties(23)(Table 5).

As with melting temperature, fiber properties vary with changing composition. Increases in physical properties have been attributed to increases in anisotropy for polymer systems in which one structural component is known to form only isotropic melts(54). In many of the wholly aromatic system, more complex effects of changing composition apparently exist, and predictions are difficult to make. In the copolymer of chlorohydroquinone and 4,4'-dihydroxydiphenyl ether with terephthalic acid(31), tenacity of heat treated fibers goes through a maximum value (at minimum polymer melting temperature) as chlorohydroquinone content varies (Figure 6a). Modulus decreases as the backbone becomes more flexible (Figure 6b), and modulus shows a good correlation with orientation angle for both as-spun and heat treated fibers (Figure 6c). For the system in which the ratio of 2,6-naphthalenedicarboxylic acid to isophthalic acid is varied(30) the same tenacity, melting point and composition relations are observed, but modulus does not correlate predictably

Table 5 - Fiber Properties of Thermotropic Polyesters Containing Oxyethylene Units

Polymer	Reference	Spinning Temp., °C	Fiber Properties			
			Ten., g/d	Elong., %	Mod., g/d	
PET/HBA 40/60	20	260	3.3	5	196	(as spun)
PET/ClHQ 20/80	29	346	2.1	0.7	342	(as spun)
			11.1	3.4	378	(heat treated)
ClHQ/ClHQCPE 70/30	23	318	7.7	2.5	433	(as spun)
			13	5.2	306	(heat treated)

ClHQ: chlorohydroquinone
CPE: bis(4-carboxyphenoxy)-1,2-ethane

The wholly aromatic thermotropic polyesters have higher heat treated tenacities and moduli than do the less rigid, partially aliphatic polymers(30,34,41,42). Tenacities exceeding 20 gpd and moduli exceeding 500 gpd are not unusual (Table 6). Elongations are about

with composition changes (Figures 7a and 7b). For a system, when the copolymer contains only rigid linear units and "crankshaft" units, the change of both tenacity and modulus with composition ceased to be regular(42). Apparently as the polymer backbone becomes

Table 6 - Fiber Properties of Wholly Aromatic Thermotropic Polyesters

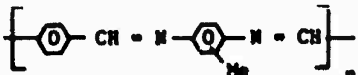
Polymer	Reference	Spinning Temp., °C	Fiber Properties			
			Ten., g/d	Elong., %	Mod., g/d	
TA/NDA/ClHQ 35/15/50	34,41	325	7.0	1.8	533	(as spun)
			34.9	4.7	597	(heat treated)
TA/φHQ/R 50/47.5/2.5	41	335	6.3	1.7	434	(as spun)
			29.7	4.4	559	(heat treated)
HBA/NDA/TA/HQ 60/10/10/20	30	299	10.6	2.4	596	(as spun)
			23.6	5.2	438	(heat treated)

NDA: 2,6-naphthalenedicarboxylic acid
φHQ: phenylhydroquinone
R: resorcinol

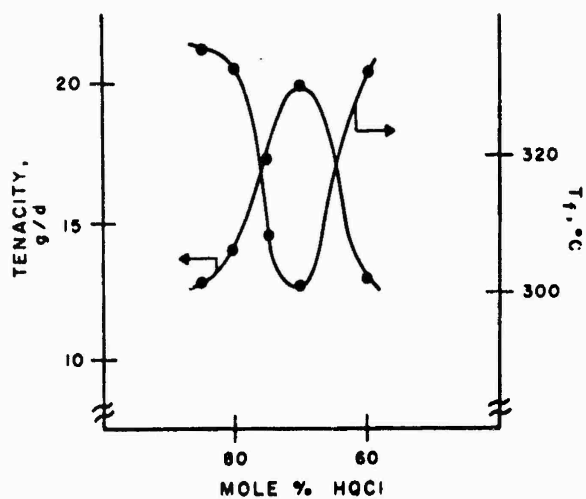
5%, which is generally two to three times the as-spun value. A few examples of polyester fibers with tenacities equal to or exceeding 30 gpd have been reported(34,41), but the best fiber properties known for a thermotropic polymer were from a polyazomethine prepared from terephthalaldehyde and methyl-1,4-diaminobenzene(26) (Table 7).

more and more rigid, the effects of changing composition become more subtle and therefore less easily predictable.

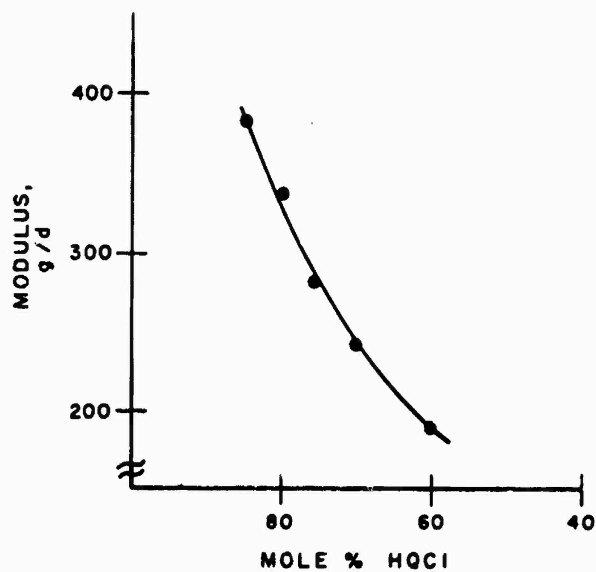
Table 7 - Polyazomethine Fiber

Polymer	Spinning Temp., °C	Fiber Properties*		
		Ten., g/d	Elong., %	Mod., g/d
	260	38	4.4	1012
			(heat treated)	

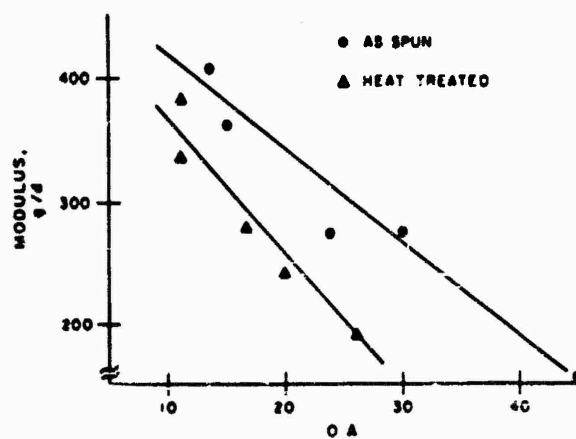
* Best single filament tenacity: 44 gpd.



(Fig. 6a)



(Fig. 6b)



(Fig. 6c)

Fig. 6 - Effect of composition on fiber properties (heat treated)
Polymer system: TA/HQCl/DHDPE(31,32)

The feasibility of preparing polymers which have anisotropic melts and from which fibers with high strengths and high moduli can be prepared has clearly been shown. A review of the available literature demonstrates that numerous approaches and combinations of monomers can be used to produce anisotropic melts which are stable to processing. Some of the fiber properties quoted in the patent examples equal or surpass those of the lyotropic aromatic polyamides. Whether any of these polymers are commercially viable will depend on a number of in use properties not apparent in the available literature as well as the polymer and fiber economics.

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Fig. 7 - Effect of composition on fiber properties (heat treated)
Polymer system: NBA/HQ/IA/NDA(30)
50/25/25-x/x

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PROCESSING OF HIGH STRENGTH, HIGH TEMPERATURE POLYMERS

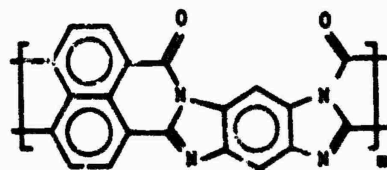
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ABSTRACT

The Materials Laboratory, Air Force Wright Aeronautical Laboratories (AFWAL/ML) and the Air Force Office of Scientific Research (AFOSR) are engaged in a research and development program directed toward the preparation and processing of very high strength, high temperature, environmentally resistant polymers for use as structural materials in aerospace vehicles. The principal objective of the multifaceted program is the attainment of mechanical properties for a structural material comparable with those currently obtained from fiber reinforced composites. However, this goal is being sought with materials possessing significantly higher thermal stability and greater environmental resistance than that exhibited by current structural composites and without the use of fiber reinforcement. The principal efforts of this program have been concerned with the choice of the macromolecular chemical structure, while concurrent studies, theoretical and experimental, have been considering the problems of characterization, evaluation, and processing.

BACKGROUND

The origins of this program are found in the extensive research carried out within and under the sponsorship of the AFWAL/ML during the last decade which sought improvement in the thermal and oxidative stability of polymeric materials. These efforts focused on aromatic heterocyclic structures and included consideration of ladder polymer structures which ultimately led to the observation of a unique film forming phenomena. The first observation of this was for the ladder polymer BBL (1).



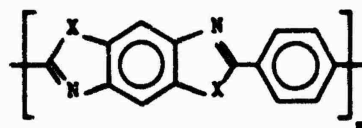
BBL

When BBL was dried from a nonsolvent precipitated slurry, a precipitated film, possessing excellent mechanical properties, was formed by the coalescence of discrete particles of solid matter, without going through a melt phase. Although further research considering the relationship between the macromolecular structure and this film forming phenomena showed that the molecular geometry of the polymer chain was the critical factor, (2) the film forming phenomena was only observed for aromatic heterocyclic ladder polymers. Concurrent work within AFWAL/ML attempting to improve the molecular ordering of aromatic heterocyclic polymers in fiber form subsequently was combined with the ladder polymer film studies. The result of this merger was the observation that certain rigid rod, extended chain aromatic heterocyclic polymers formed precipitated films comparable to those previously observed only for highly extended ladder polymer molecules. Furthermore, it was proposed that the high strength of these unique precipitated

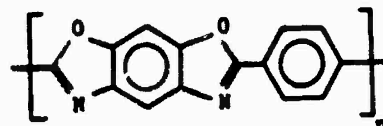
films stemmed from their "composite" character (3a), (3b). They were considered "composites" because the precipitated films were formed by the aggregation and coalescence of individual microscopic sheets of precipitated polymer. The high strength was attributed to the inherent strength of the microscopic sheets due to their high degree of molecular order. These observations and other considerations led to the hypothesis that a non-reinforced composite with useful mechanical properties might be achieved with appropriate polymer chain geometry and suitable processing, the key factor for success being the ability to achieve a high degree of molecular order.

DISCUSSION

Materials - Within the context of the observations made above, the choice of molecular design has centered on that of an extended chain, rigid rod molecule for reasons of molecular ordering and an aromatic heterocyclic structure for thermal and oxidative stability. Three such polymers have been synthesized, PDIAB (4), PBO (3), and PBT (5).

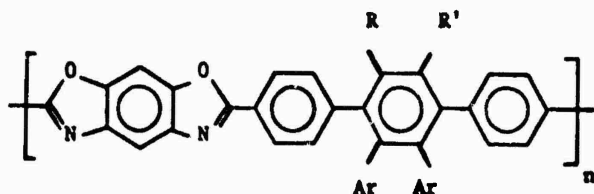


PDIAB (X = NH), PBT (X = S)

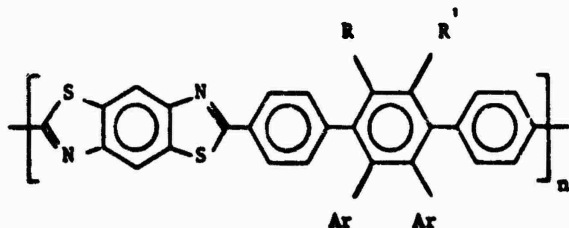


PBO

The PBO polymer system offers improved stability over PDIAB and does not pick-up the moisture that the benzimidazole structure does; whereas PBT provides the best thermal and oxidative stability of the three systems (weight retention of 50% after 200 hours at 371°C in circulating air). In addition, PBO and PBT have been shown to be intrinsically non-combustible in air. (18) Although these three materials have been successfully synthesized, they have presented special processing problems because of the extended chain, rigid rod structural character of the molecules. Present processing requires strong mineral or organic acid solvents. This problem of solubility has manifest itself in several ways; the limited number and type of solvents, relatively low solubility and difficulty in polymerization to high molecular weight due to apparent insolubility. This problem has been addressed with two approaches. The first attack of the problem has been an extensive solubility study to discover noncorrosive organic solvents or to determine organic chemical structures that could be expected to dissolve these polymers (6). The results have not provided a pure organic single solvent nor do the results hold significant promise for a new simple processing solvent (7). Current efforts (8) in search of mixed organic solvents for these materials have not been successful. A second approach to the improvement of solubility consists of polymer chain structural modifications either in the form of pendant additions or the introduction of swivel joints into the main chain forming an articulated molecular structure. The former has been accomplished for PBO (9) and PBT (10).



Modified PBO, where R and R' can be H or Ar



Modified PBT, where R and R' can be H or Ar

In neither case were pendant phenyl groups of sufficient influence to significantly improve the solubility or offer processing solvent alternatives of practical value. The synthesis of articulated molecular structures is being carried out⁽¹¹⁾ and is based on theoretical considerations of the phase equilibria of rodlike polymers⁽¹²⁾ and the swivel molecular geometry⁽²⁶⁾.

Characterization - Extensive characterization has been carried out on PBO⁽¹³⁾, (14) establishing that the polymer exhibits rodlike behavior in solution and can exist in either optically isotropic or anisotropic states, depending on temperature, concentration and molecular weight. PBT has also been extensively characterized in solution⁽¹⁵⁾. These data show that PBT is rodlike, protonated in strong acids used as its solvent and is of a fairly high degree of polymerization (a weight average degree of polymerization of approximately seventy). Phase equilibrium data indicate PBT can form stable solutions in the nematic state as can PBO. However, PBO and POIAB, as measured by intrinsic viscosity, have never been polymerized to as high a molecular weight as PBT, $[\eta] = 30.1 \text{ dl/gm}$ ⁽¹⁶⁾. Concerns regarding the kinetics and mechanism for the polymerization of extended chain rigid rod macromolecules to high molecular weight has prompted a study to address this problem⁽¹⁷⁾. The evidence indicates a normal condensation polymerization with molecular weight increasing monotonically with time, but with a narrower molecular weight distribution, $M_w/M_n = 1.8$ or less.

Processing - In order to minimize the sample quantities required and to take advantage of developed technology, the polymer samples have initially been processed into fiber specimens for evaluation of mechanical properties and morphology. Both PBO and PBT have been processed into fiber specimens exhibiting moduli of 700⁽¹⁸⁾ and 2000⁽²²⁾ gpd, respectively, and PBT has provided fiber with a tenacity of 20 gpd. Preliminary investigations of the fiber morphology of PBO⁽¹⁹⁾ and PBT⁽²³⁾ indicate high degrees of orientation. Although the physical properties have been most encouraging, processing conditions have not been optimized and consequently efforts are continuing to study the processing variables⁽²⁴⁾. Preliminary attempts have been made to process PBO and PBT into continuous thin ribbons.⁽²⁴⁾, (25) The results have encouraged continued exploration of this area: modulus of 88GPa for ribbon 0.05 mm thick and 6mm wide. While the efforts to process neat polymers have been underway, the extended chain, rigid rod molecules have also been used as reinforcement in flexible aromatic heterocyclic

polymer matrices to provide composites at the molecular level that are analogous to chopped fiber composites⁽²⁰⁾. These molecular composites have shown a fivefold increase in tensile modulus and strength with only ten percent rodlike polymer in the matrix⁽²¹⁾. The morphology results show pronounced conglomeration or aggregation with a definite structure and strong evidence for molecular ordering. These studies are continuing. Future efforts are being directed toward an improved understanding of the morphology of the "ordered polymers" PBO and PBT, neat or in "composite" form with flexible matrix polymers. Emphasis will continue to be placed on learning to process the extended chain, rigid rod aromatic heterocyclic polymers into useful forms for structural applications.

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INORGANIC ALUMINA FIBERS FOR REINFORCEMENT OF METAL CASTINGS

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ABSTRACT

Inorganic fiber reinforced metal matrix composites show promise as the next generation of advanced composite materials offering advantages over fiber reinforced plastic composites including higher temperature capability, superior moisture resistance and better transverse properties. The major problems limiting the development of metal matrix composites have been the lack of suitable low cost, high temperature inorganic fibers and a practical process to incorporate these fibers into metallic matrices. Considerable R&D resources have been expended both by the government and industry to develop suitable inorganic fibers based on boron, silicon carbide, and alumina. This paper describes an experimental inorganic alumina fiber designated Fiber FP which is spun in the form of flexible continuous multifilament yarns. Fiber FP, essentially a 100% α - Al_2O_3 fiber, is inherently stable at elevated temperatures and is compatible with a variety of metal matrix systems. A versatile, potentially low cost composite fabrication technique has been developed to incorporate 25 to 60% volume loading of Fiber FP into metallic matrices forming a strong fiber/matrix bond. For example, magnesium or aluminum castings reinforced with Fiber FP (50-60% volume loading) have a modulus greater than steel at a density about one-third of steel combined with excellent transverse, compression and fatigue properties and temperature capability twice that of unreinforced castings. The fiber, composite properties and potential applications are discussed.

HISTORY OF MAN is the history of materials:

"Available materials set a limit to the techniques of any age" (Figure 1). Primitive man used readily available materials such as wood and stone to make tools and provide shelter. With the dawn of civilization man learned how to smelt metals. He used copper and bronze tools to aid in food gathering and preparation. The advent of iron allowed man to increase the span of his structures as well as to decrease their bulk. Cast iron was used extensively in the early stages of the Industrial Revolution. The truss structure made from cast iron members was used by the railroads to span rivers and canyons. Despite the versatility of cast iron, it had several serious drawbacks. First the material was brittle: once a flaw developed, the failure was quick and catastrophic. In addition, the flex strength was poor and structures were designed to apply tensile or compression loading to the cast iron members. Towards the end of the Industrial Revolution, iron alloys (called steel) were developed to increase ductility and improve flex strength. Steel expanded the scope of material design from the truss to the cantilever beam. The use of steel and iron, however, was not acceptable for weight sensitive structural applications as the airplane became a viable form of transportation. Here light metals such as aluminum

and magnesium for which modulus on unit weight basis is similar to steel were developed. This allowed designers to produce practical aircraft. During the 1950's and 1960's the emerging space age required lighter, stronger materials with higher temperature capability than aluminum. Titanium alloys filled this need.

Tremendous progress has been made by metallurgists and materials scientists to increase the mechanical properties of metals via alloying, dispersion strengthening and heat treatments; however, the specific properties (strength/density and modulus/density) of metals are reaching a plateau (Figure 2). Fiber reinforced plastic or metal matrix composite materials offer a new level of properties not obtainable with previous materials creating a revolution in materials design and engineering. Tailor-made composite materials reinforce one material with another so as to combine weight savings with mechanical performance. The concept of fiber reinforced composite materials is not new. For instance, the Egyptians made bricks from mud and straw. In this case the mud was the matrix and the straw was the reinforcement. The natural composite material wood is made of reinforcing cellulose fiber in a matrix so that the strength with the grain is greater than the strength across the grain. Man-made composite materials made from organic and inorganic reinforcing fibers have undergone substantial development in the last 15 years.

High performance graphite and Kevlar® reinforced organic matrix composites offer considerable weight savings when compared to metals and are replacing them in many engineering applications. Despite the weight saving advantage of fiber reinforced organic matrix composites, they have several limitations including high temperature capability and high moisture regain. The reinforcement of metals with high modulus inorganic fibers offers several inherent advantages over organic matrix composites (Figure 3). Metal matrix composites have high temperature capability, good hot oil and environmental resistance, good machinability, and low thermal expansion properties. In addition, metal matrix composites have high off-axis properties leading to good transverse and shear strengths. Metal matrix composites should sustain higher insert and stud pull-out loads than obtainable from organic matrix composites. To realize these potentials it is necessary to have a reinforcing fiber that satisfies a number of technical conditions. First the fiber must be thermally and chemically stable in metals, especially at the high temperatures required for composite fabrication. The fiber and metal must bond to one another to realize good transverse properties. And finally the fiber must have high enough strength and modulus properties to be an effective reinforcing element.

Despite the fact that the bulk of composite development work over the last twenty years has been aimed at organic matrix composites, considerable research has been performed on metal matrix compo-

ites by both private industry and government research laboratories. The major efforts in metal matrix composites have focused on using boron, silicon carbide, graphite, and alumina fibers (Figure 4) as reinforcement in nonferrous metals such as aluminum, magnesium, lead, and higher temperature matrices such as titanium and super alloys.

Some of the earlier efforts to produce a viable metal matrix composite focus on the use of a boron fiber in aluminum. The fiber is produced by the chemical vapor disposition of boron on a substrate filament of tungsten or carbon (Ref. 1). The resulting reinforcing element has a relatively large diameter. These fibers are then arranged in the lay-up desired and combined with the metal matrix via diffusion bonding. Borsic® fibers are a modification of boron fibers in that a coating of silicon carbide has been deposited on the surface which provides for a somewhat higher use temperature. Boron and Borsic® reinforcement of metals has found application mainly in the aerospace industry because of the high cost of the fibers and of the composite fabrication technology.

Silicon carbide reinforcement has been used for metal matrix composites both in the form of whiskers and large diameter monofilaments. The whiskers are single crystals leading to short fiber reinforced composites with approximated isotropic properties. The large diameter monofilament of silicon carbide uses fiber and composite fabrication technology similar to boron and Borsic® fiber. Graphite fiber combines light weight with excellent modulus and strength in the fiber direction. Graphite/aluminum composites have good modulus and strength characteristics in the fiber direction but have relatively poor properties in the direction transverse to the reinforcing fibers. A supposed reason for the inferior transverse performance is due to poor bonding between fiber and matrix. In order to produce a graphite reinforced metal matrix composite such as graphite/aluminum, the precursor graphite yarn with a vapor deposited coating of titanium boride is run through a molten bath of aluminum (Ref. 2). The laminate is then made by placing the aluminum coated yarn between foils of aluminum and then subjecting the sandwich to a hot pressing operation. Graphite/aluminum matrix composites are being developed for aerospace applications.

In recent years, several alumina based ceramic fibers have been developed. Such fibers have inherent advantages over graphite and boron such as chemical stability, electrical nonconductivity, and high temperature capabilities. Tyco Laboratories first demonstrated single crystal continuous alumina monofilaments drawn from the melt. These fibers were found to be very expensive for reinforcement applications and showed loss of strength at high temperatures due to twinning on certain crystallographic planes. Imperial Chemical Industries is producing Saphil® short alumina fibers primarily for insulation applications. Minnesota Mining & Manufacturing Company is producing several continuous alumina based ceramic fibers which are woven and braided for insulation applications. These fibers have relatively low modulus for utility in aluminum reinforcement application. In Japan, Sumitomo Company is developing a continuous alumina fiber for metal reinforcement. This fiber is believed to be based on an alumina-silica system having lower modulus than 100% alumina fiber. The Du Pont Company is developing an experimental 100% α - Al_2O_3 fiber designated Fiber-PP for the reinforcement of nonferrous metal castings. A potentially low cost composite fabrication technology based on casting techniques has been developed to produce Fiber PP reinforced nonferrous metal castings. The key features of Fiber PP making it attractive for reinforcement of nonferrous castings are shown in Figure 5.

It is the purpose of this paper to review Fiber PP and Fiber PP/metal matrix composite properties. In addition, current research on end-use applications will be presented to illustrate the design potential of the fiber.

FIBER PP

Fiber PP is experimentally produced as a continuous, polycrystalline α - Al_2O_3 yarn containing 210 filaments. Each filament is round in cross-section with an average diameter of 20 microns. The fiber purity is greater than 99% alumina and the density is 98% of theoretical. The minimum average filament strength in the yarn bundle is 1380 MPa (200 ksi) at 6.4 mm gauge length. The tensile modulus of 379 GPa (55 Mpsi) is considerably higher than alumina fibers which contain large amounts of silica or other metal oxides. Fiber PP filament properties are summarized in Table I.

MICROSTRUCTURE. A typical 500 gm bobbin of Fiber PP yarn and PP filaments are shown in Figure 6. The filament fracture surface clearly exhibits the polycrystalline nature of the inorganic fiber. The internal microstructure of the fiber revealing the fine grains of the polycrystalline fiber is shown in Figure 7. The average grain size of the fiber is estimated to be about 0.5 μ .

SURFACE FEATURES. Since Fiber PP is a high modulus ceramic, it is inherently brittle. In addition, the fiber surface is rough or "cobblestoned" as can be seen in Figure 8. This surface aids in the composite fabrication process by providing a maximum surface area for the fiber-matrix bond which in combination with the polycrystalline nature of the fiber leads to high transverse composite properties. However, the rough surface can provide possible flaw sites for potential fiber failure leading to a relatively large scatter in tensile strength compared to organic fibers.

The tensile strengths of the fiber at gauge lengths of 6.4 mm (0.25"), 25.4 mm (1"), and 254 mm (10") are shown in Figure 9. The effect of gauge length on fiber strength can be predicted by assuming the fiber to be composed of a number of basic elements arranged in series such that failure of any element causes the catastrophic failure of the fiber. Chou and Croman (Ref. 3) have shown that the in-series arrangement has the same shape parameter of fiber strength distribution as the element strength distribution. Using the shape factor for the strength distribution for fibers having a gauge length of 6.4 mm (0.25") a plot as shown in Figure 9 is made of mean fiber strength vs. fiber gauge length. The experimentally measured strengths at 6.4mm (0.25"), 25.4 mm (1"), and 254 mm (10") gauge lengths are seen to be in good agreement with the theoretical prediction.

HIGH TEMPERATURE PROPERTIES. Metal casting of complex shapes is inherently a low cost route to component fabrication. To effectively reinforce metal castings a fiber must fulfill a combination of conditions (Figure 10) such as high temperature capability, compatibility with molten metal, flexibility for complex shape fabrication, corrosion resistance (especially galvanic type at the fiber/matrix interface) and composite castability among others. The critical requirements are the high temperature strength and modulus retention of the fiber at the molten metal temperature required for composite castings. Figure 11(a) compares the strength retention of Fiber PP in air with several other fibers. As can be seen, Fiber PP being a ceramic Al_2O_3 fiber retains about 95% of its room temperature strength at 1000°C. Other fibers begin to oxidize or recrystallize exhibiting strength degradation with increasing temperatures. The effect of exposure time in air on fiber strength retention is shown in Figure 11(b). The strength of Fiber PP

is virtually unchanged after 300 hours exposure in air at 1000°C. Boron and silicon carbide coated boron show substantial strength loss above 500°C after 1 hour exposure in air. The modulus retention of Fiber FP shows a similar behavior as strength retention at elevated temperatures. The room temperature modulus of 379 GPa (55 Mpsi) is retained to 800°C (above the M.P. of aluminum) dropping to 345 GPa at 950°C.

FABRICATION OF FIBER FP REINFORCED NONFERROUS CASTINGS

There are several requirements on materials and processes that must be met to ensure good Fiber FP/metal matrix composite properties. First the molten metal which becomes the composite matrix must wet the fiber surface. Meeting this first requirement is necessary but not sufficient for good composite shear and transverse strengths. The second requirement is placed on the matrix material. Since Fiber FP is a brittle fiber and will fail by a weakest link mechanism, it is necessary that the matrix be sufficiently ductile to blunt the propagation of cracks initiated by fiber failures. The combination of the two requirements mentioned here will result in a composite making good use of the Fiber FP properties. A versatile, potentially low cost composite fabrication technique has been developed to incorporate 25 to 60% volume loading of Fiber FP into metallic matrices forming a strong fiber/matrix bond. Figure 12 shows an SEM of the fracture surface demonstrating good fiber wetting and infiltration of FP/magnesium unidirectional composites having 55 nominal volume loading of fibers. Figure 13 shows various Fiber FP reinforced castings in aluminum and magnesium containing up to 60 fiber volume loading which have been successfully cast.

TRANSLATION OF FIBER FP PROPERTIES TO COMPOSITE PROPERTIES. To evaluate composite quality and fiber/matrix bonding it is beneficial to compare the measured composite properties to theoretical properties estimated from the constituent fiber and matrix properties. The composite longitudinal modulus of a unidirectional fiber lay-up can be adequately estimated from the component moduli by the rule of mixtures,

$$E_c = E_f x + E_m (1-x).$$

where E_c , E_f , and E_m are the moduli of the composite, fiber, and matrix respectively and x is the fiber volume fraction. Computer programs exist to determine the other moduli such as the transverse modulus, shear modulus, and Poisson's ratio. One such code developed by Materials Science Corporation and based on results of Hashin and Rosen (Ref. 4) has been used to determine the elastic constants of a 50 v/o unidirectional FP/Al laminate. The calculated constants are compared to measured values in Table II and are seen to be good agreement.

The tensile strength of a composite is dependent mainly on the bundle strength of the reinforcing fiber, on the matrix and fiber/matrix shear strengths, and on the stress intensity properties of the composite. For efficient fiber utilization, the composite strength should have a lower bound based on the fiber bundle strength. Daniels (Ref. 5) found that the mean fiber bundle strength can be determined from the strength distribution of the fiber. Croman (Ref. 6) derived the mean bundle strength for fibers that have a two parameter Weibull distribution of strength. The mean strength of a large bundle of fibers comprising a composite is given by

$$\mu_b = \frac{\pi S}{\alpha^{1/2}} \exp \left[-\frac{1}{\alpha} \right]$$

where μ_b is the mean bundle strength adjusted for volume loading and hence the lower bound on composite tensile strength, x the fiber volume fraction of the composite, α and S are the scale and shape parameters of the strength distribution of the fiber. For a unidirectional FP/metal matrix composite having a 55% fiber volume loading, the minimum average tensile strength of coupons having a 3-inch gauge length is estimated to be 487 MPa (70.7 ksi). A set of 96 FP/Al 55 v/o unidirectional specimens was found to have an average tensile strength of 587 MPa (85 ksi) with standard deviation of 45 MPa (6.6 ksi). Thus, it can be seen that the fiber tensile properties are efficiently translated into the composite.

COMPOSITE PROPERTIES

As seen in the previous section, the Fiber FP filament properties translate well into composite properties having good fiber/matrix bonding. This is demonstrated by excellent static and dynamic properties of the FP/Al and FP/Mg composites, especially at high temperatures compared to unreinforced aluminum and magnesium alloys. Figures 14 and 15 compare the properties of unidirectional as-cast FP/Al and FP/Mg composites at room temperature and 600°F with unreinforced high strength heat-treated aluminum and magnesium alloys. (These alloys are not the same as the matrix in the composites.) It is seen that the composite castings exhibit significantly higher compression, stiffness, fatigue and tension, especially at 600°F. The room temperature tensile strength of FP/Al composites is about equal to high strength aluminum alloys. The density of FP/Al and FP/Mg castings is higher than aluminum and magnesium alloys. Figure 16 compares the specific unidirectional properties (property/density) with structural metals including titanium alloy (Ti-6Al-4V) and 403 stainless steel. The specific modulus of FP reinforced magnesium and aluminum castings at room temperature is 3 times the modulus of structural metals. The compressive strength is significantly higher and the tensile strength comparable to metals. The dynamic behavior of the FP/Al composites in fatigue is compared with B/Al, Ti and Al alloys in Figure 17. Fiber FP reinforced aluminum and magnesium castings show a flat fatigue behavior whereas unreinforced magnesium and aluminum alloys show more than 50% loss in static strength after 10 million fatigue cycles.

The fiber/matrix bonding in composites is adequately demonstrated by the transverse properties. In general, metal matrix composites have higher transverse and off-axis properties than resin matrix composites due to higher matrix shear strength. Figure 18 compares transverse properties of as-cast FP/Al composites with other aluminum matrix composites and organic matrix composites. The transverse strength of FP/Al composites is found to be slightly higher than the matrix strength indicating good fiber/matrix bonding.

The mechanical behavior of FP/Al and FP/Mg laminates is discussed in the following section.

FP/Al COMPOSITE BEHAVIOR. Effect of Fiber Volume Loading. Figure 19 shows the axial and transverse tensile behavior of FP/Al unidirectional specimens (dimensions 1.27 x 0.25 x 12.7-15.2 cm) as a function of fiber volume fraction. The tensile strength determinations were made for a sampling of specimens whose fiber volume fractions varied from 30% to 60%. As can be seen, doubling the volume loading essentially doubles the axial tensile strength. For $V_f = 0.3$ the strength is 386 MPa (56 ksi) and for $V_f = 0.6$ the strength is 655 MPa (95 ksi). The transverse strength curve has been extrapolated back to $V_f = 0$ and is seen to pass through the aluminum matrix strength. As stated earlier, the transverse tensile strength of FP/Al is seen to be higher than the unreinforced Al matrix alloy, thus indicating good bond strength be-

tween fiber and matrix. The axial modulus follows the traditional "rule of mixtures". A V_f of 0.6 shows an axial Young's modulus of 262 GPa (38 Mpsi). The transverse modulus is also seen to increase with fiber volume loading and the value at V_f of 0.6 is 165 GPa (24 Mpsi).

Stress/Strain Behavior. The stress/strain behavior of an FP/Al composite (nominal 50% volume loading of Fiber FP) specimen is shown in Figure 20. The 0° tensile stress/strain curve is seen to have two linear portions, the primary having a modulus of 198 GPa (28.7 Mpsi) and the secondary with a slightly lower modulus of 179 GPa (25.9 Mpsi). The ultimate strain to failure is low and has average values of 0.3-0.4%. The 90° stress/strain curve has an initial linear portion followed by plastic yielding. The strains to failure are typically less than 0.5%.

Axial compression strengths were determined for unidirectional FP/Al rods ($V_f = 0.55$) having dimensions of 0.36 cm (0.14 in) diameter and 5.08 cm (2 in) gauge length. The compression strengths ranged in value from 2.95 to 3.4 GPa (428 and 495 ksi) with an average value of 3.27 GPa (474 kpsi). The dominant failure mechanism was microbuckling at the end caps.

Transverse compression behavior was measured on 1.27 x 1.27 x 3.18 cm (0.5 x 0.5 x 1.25 in) specimens. Typical stress/strain behavior (Figure 21) for $V_f = 0.5$ shows an initial modulus of 20.8 Mpsi followed by plastic behavior. Strains to failure are typically less than 0.7% with failure strength slightly less than 345 MPa (50 ksi). The compression failure mechanism of FP/Al composites is discussed in detail in Ref. 7.

At 45° fiber orientation, the composite exhibits excellent plastic deformation (4% fracture strain) due to shear flow of the ductile Al matrix (Figure 22).

Elevated Temperature Behavior. The effect of temperature on tensile and flexural strength of FP/Al composites is shown in Figure 23. The specimens were held at temperature for thirty minutes and then tested. The axial strength response to temperature is nearly flat to 316°C (600°F). The transverse strength starts to decrease at a more rapid rate at temperatures above 149°C (300°F). At 316°C (600°F) the matrix alloy decreases in strength by ~80%. The transverse tensile strength of FP/Al is approximately three times that of the matrix alloy at 316°C (600°F).

The flexural strength of FP/Al composites was measured as a function of temperature. Span to depth ratios were 16/1 to 18/1 for all tests. Samples were held at temperature for 30 minutes and then tested for strength in the three point bending mode. As shown in Figure 23, the axial (0°) flexural strength is unchanged to 316°C (600°F). At higher temperatures the strength decreases and at 538°C (1000°F) has a value of 700 MPa (101 ksi). The transverse flex strength is seen to be a monotonically decreasing function of temperature.

Some work has been performed on the isothermal and cyclic thermal exposure effects on FP/Al composites. For instance, Olsen (Ref. 8) found that FP/Al unidirectional specimens exposed at 316°C (600°F) for 2500 hrs showed a 15% increase in axial strength. A specimen cycled between -73 and 316°C (-100 and 600°F), 600 times had a 10% higher strength. Additional thermal fatigue and isothermal exposure results including interface reactions are discussed in Refs. 9 and 10. The data on high temperature dynamic modulus of FP/Al composites is given in Ref. 11.

FP/Mg COMPOSITE BEHAVIOR. Figure 24 shows the stress/strain behavior of Fiber FP/Mg composites (nominal 50% volume loading of Fiber FP) under tensile and compressive loading. The general shape of the stress/strain curves is similar to FP/Al. In 0° tensile loading the primary modulus is 202 GPa

(29.3 Mpsi) and the secondary modulus 180 GPa (26.1 Mpsi). The ultimate tensile strength is 520 MPa (75 ksi). As with FP/Al, the stress/strain curve does not exhibit any plastic behavior and shows a strain to failure of 0.3-0.4%. It should be noted that the axial mechanical behavior of FP/Al and FP/Mg is fiber dominated.

The transverse tensile behavior of a composite is matrix dominated. There is an initial linear portion to the stress/strain curve followed by plastic deformation of the matrix. The transverse strength of the composite increases with the increase in matrix strength. Therefore, if the matrix strength can be increased by heat treatment, a corresponding increase in composite transverse strength should occur.

The axial compressive behavior is seen to be linear to failure (Figure 24). Under transverse compression, the stress/strain curve is nonlinear and initial modulus is found to be 102 GPa (14.8 Mpsi).

Elevated Temperature Behavior. The effect of temperature on the tensile and flexural strength and modulus of FP/Mg composites (commercially pure Mg matrix, Fiber FP normal volume loading of 50%) in the fiber direction is depicted in Figure 25. The unidirectional room temperature properties are essentially unchanged to 316°C (600°F).

POTENTIAL APPLICATIONS

Fiber FP/metal matrix composites offer good stiffness, compression strength and elevated temperature properties. The tensile strength is moderate. In addition, the fiber is an electrical nonconductor and has good corrosion and chemical resistance properties. We are investigating potential end-use applications that would benefit from the Fiber FP composite properties and lead to improved performance and weight savings. Some general end-use areas have been identified and work is progressing in these areas (Figure 26). For example, in automotive engines, the good behavior of FP composites in elevated temperature environments offers potential applications in pistons, connecting rods, wrist pins, and crankshafts utilizing the high temperature, stiffness and compressional properties described in the previous section. The high stiffness of FP/Al and FP/Mg suggest other stiffness critical applications in aircraft engines, missile components, power transmission housings and axles. Other potential end-uses include ordnance and armor, disc brake rotors and calipers.

An active program is underway with Boeing-Vertol Co. to develop FP/Mg helicopter transmission housings. The current housings made from cast magnesium are not stiff enough to resist large deflections and displacements imposed by the power train operating loads. In addition, the current castings allow excessive noise levels which are undesirable for housings close to crew personnel areas. It is felt that an FP/Mg cast helicopter transmission housing will have adequate stiffness to resist the deflections and displacements and also reduce the noise. In addition, the housing will prevent gear misalignment during operation and thus cut down on maintenance costs.

Boeing-Vertol and Du Pont have successfully completed Phase I of this development program which has been partially funded by the U.S. Army Mechanics and Materials Research Center and the Applied Technology Laboratory. The basic component under study is the bevel gear housing located in the forward rotor transmission case of the CH-47C helicopter located directly above the crew operating and pilot control area. As a first step, the housing was broken down into a number of basic sections and cast in commercially pure magnesium with FP reinforcement as shown in Figure 27. These include outer cylindrical rims and outer rim-web-inner rim cross-section. The polished cross-section of the component at the critical flange/web

joint showing complex fiber orientation is shown in Figure 28. These critical sections were instrumented and subjected to test loadings, simulating the operating conditions imposed by the power train. Results of these tests were used to predict the behavior of an FP/Mg transmission housing. The dynamic deflection of the housing at operation speed as a function of gear torque is shown in Figure 29. As can be seen, aluminum and magnesium housings exhibit much higher deflections for a given torque than steel. However, a steel housing is unsuitable for this application due to a substantial weight penalty. The FP/Mg housing should perform almost as well as the steel without the corresponding weight penalty.

CONCLUDING REMARKS

Fiber FP reinforced castings are a new class of engineering materials requiring new manufacturing and design approaches. They have good mechanical and thermal properties and offer weight and fuel savings in higher performance applications. However, technological developments are needed in manufacturing technology and design to realize economic viability (Figure 30).

The use of Fiber FP reinforced nonferrous castings of Al and Mg in high temperature environments should lead to significant weight and fuel savings and better performance in aerospace and automotive applications where steel, titanium or aluminum are now used.

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9. Kim, W. H., Koczak, M. J., and Lawley, A., "Effects of Isothermal and Cyclic Exposures on Interface Structure and Mechanical Properties of FP α -Al₂O₃/Aluminum Composites", AIME Conference, St. Louis, MO (October 1978) to be published by AIME.
10. White, M. K. and Wright, M. A., "Thermal Damage on Alumina Fiber-Reinforced Metals", Preliminary Report, U. of Tennessee Space Institute (September 1978) to be published in the Journal of Materials Science.
11. DiCarlo, J. A., and Maisel, J. E., "High Temperature Dynamic Modulus and Damping of Aluminum and Titanium Matrix Composites", NASA Tech. Memorandum 79080; presented at AIME Symposium on Advanced Fibers and Composites for Elevated Temperatures, New Orleans, LA (February 1979).

FIGURE 1

HISTORY OF MAN IS THE HISTORY OF MATERIALS

"AVAILABLE MATERIALS SET A LIMIT TO THE TECHNIQUES
OF ANY AGE" - J. D. Bernal

- STONE AGE
- COPPER / BRONZE AGE
- IRON AGE
- STEEL AGE - INDUSTRIAL REVOLUTION
- ALUMINUM - SPACE AGE
- TITANIUM - SUPERSONIC TRANSPORT

PLATEAU IN MECHANICAL PROPERTIES HAS BEEN
REACHED WITH STRUCTURAL METALS

FIGURE 2
PROPERTIES OF STRUCTURAL METALS

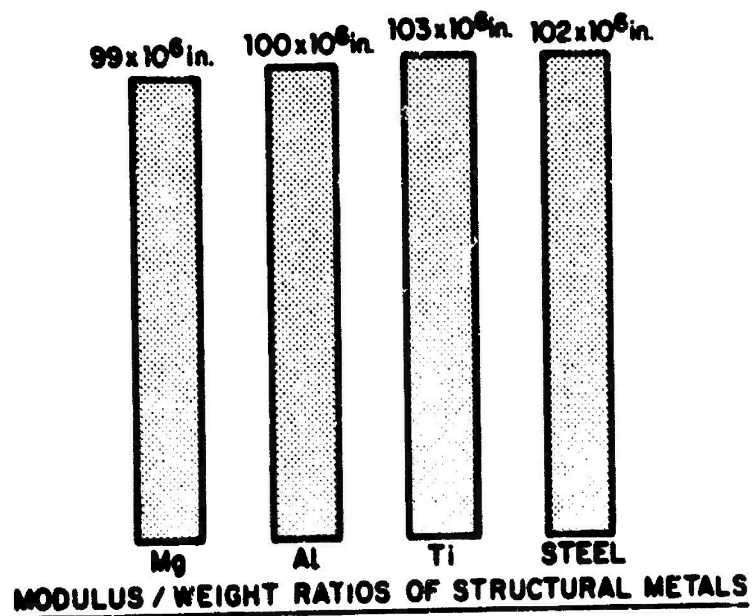
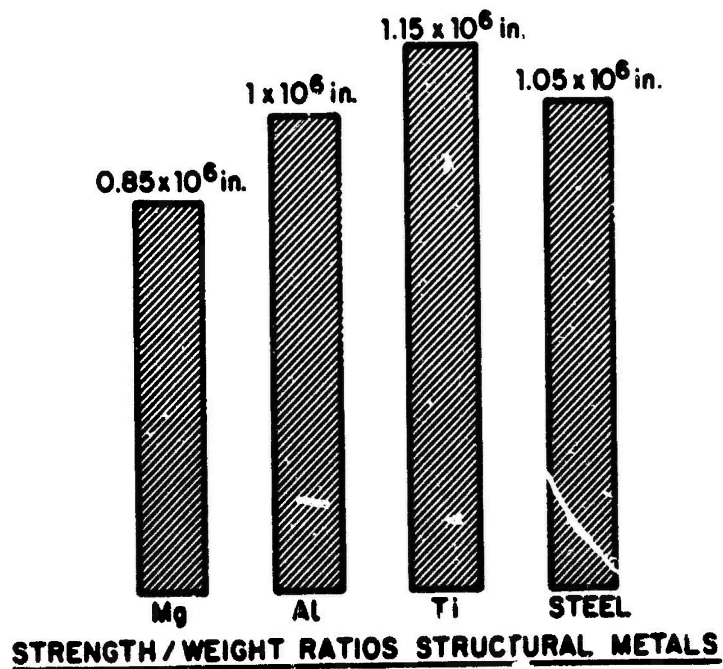


FIGURE 3
ADVANCED COMPOSITE MATERIALS

FIBER REINFORCED RESIN COMPOSITES

- FIBER GLASS
- HIGH PERFORMANCE FIBERS (BORON, GRAPHITE, KEVLAR)
- CREATED A REVOLUTION IN MATERIALS

FIBER REINFORCED METAL COMPOSITES

- NEXT GENERATION MATERIALS

ADVANTAGES OF METAL MATRIX COMPOSITES

- HIGH TEMPERATURE CAPABILITY
- HIGH OFF AXIS (TRANSVERSE AND SHEAR) PROPERTIES
- BETTER HOT OIL AND ENVIRONMENTAL RESISTANCE
- HIGHER INSERT AND STUD PULL OUT LOADS
- LOW THERMAL EXPANSION
- CLOSER MACHINE TOLERANCE

FIGURE 4
FIBERS FOR METALS
REINFORCEMENT

BORON / BORSIC[®]

SILICON CARBIDE

GRAPHITE

ALUMINA / SILICA

- SAPHIL[®]
- 3M CERAMIC FIBERS
- SUMITOMO

ALUMINA

- TYCO (SINGLE CRYSTAL)
- FIBER FP (POLYCRYSTALLINE)
 - >99% α -Al₂O₃
 - TEXTILE SPINNING PROCESS
 - COMPOSITE CASTING

FIGURE 5
FIBER FP
AN EXPERIMENTAL CONTINUOUS FILAMENT α -A₂O₃ YARN

KEY FEATURES

- HIGH MODULUS AND STRENGTH RETENTION AT ELEVATED TEMPERATURES (55 mpsi MODULUS AND 200 ksi STRENGTH RETAINED TO 1000°C)
- OUTSTANDING COMPRESSIVE STRENGTH (1 MILLION psi)
- STABLE IN MOLTEN METALS (COMPOSITE CASTING)
- ELECTRICAL NON-CONDUCTOR (CORROSION RESISTANCE)

FIBER FP REINFORCED CASTINGS

- FP/AL, FP/Mg, FP/Pb
- FIBER VOLUME LOADING > 60%
- COMPLEX SHAPES

TABLE 1

FIBER FP FILAMENT PROPERTIES

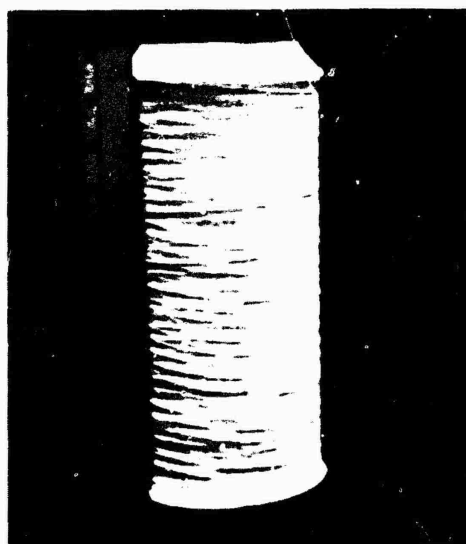
TENSILE STRENGTH	1380 MPa (200 ksi)* 2070 MPa (300 ksi)**
COMPRESSIVE STRENGTH	6.9 GPa (1 Mpsi)***
MODULUS (TENSILE AND COMPRESSIVE)	380 GPa (55 X 10 ⁶ psi)
DENSITY	3.9 G/cm ³ (0.143 lb/in ³)
FILAMENT DIAMETER	20 MICRONS
CROSS SECTION	ROUND
FILAMENTS PER YARN	210
MELTING POINT	2045°C (3713°F)
OXIDATIVE STABILITY	RM. TEMP. STRENGTH AND MODULUS UNCHANGED AFTER 300 hrs AT 1000°C

*MINIMUM TENSILE STRENGTH

**DEMONSTRATED ON SMALL SCALE

***CALCULATED FROM COMPOSITE COMPRESSIVE STRENGTH

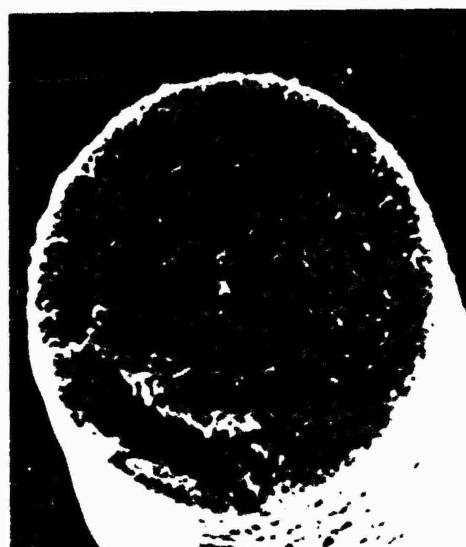
FIGURE 6



TYPICAL 1 lb BOBBIN OF
FIBER FP YARN (200 FILAMENTS)



FP FILAMENTS IN YARN
100X



FIBER FP FRACTURE SURFACE
SHOWING POLYCRYSTALLINE
NATURE OF FIBER - 1000X



FIBER FP SURFACE SHOWING
ROUGHNESS USEFUL FOR FIBER
MATRIX BONDING - 1000X

FIGURE 7

SEM OF THE FIBER FP CROSS SECTION (6000x) SHOWING
POLYCRYSTALLINE FINE GRAINS

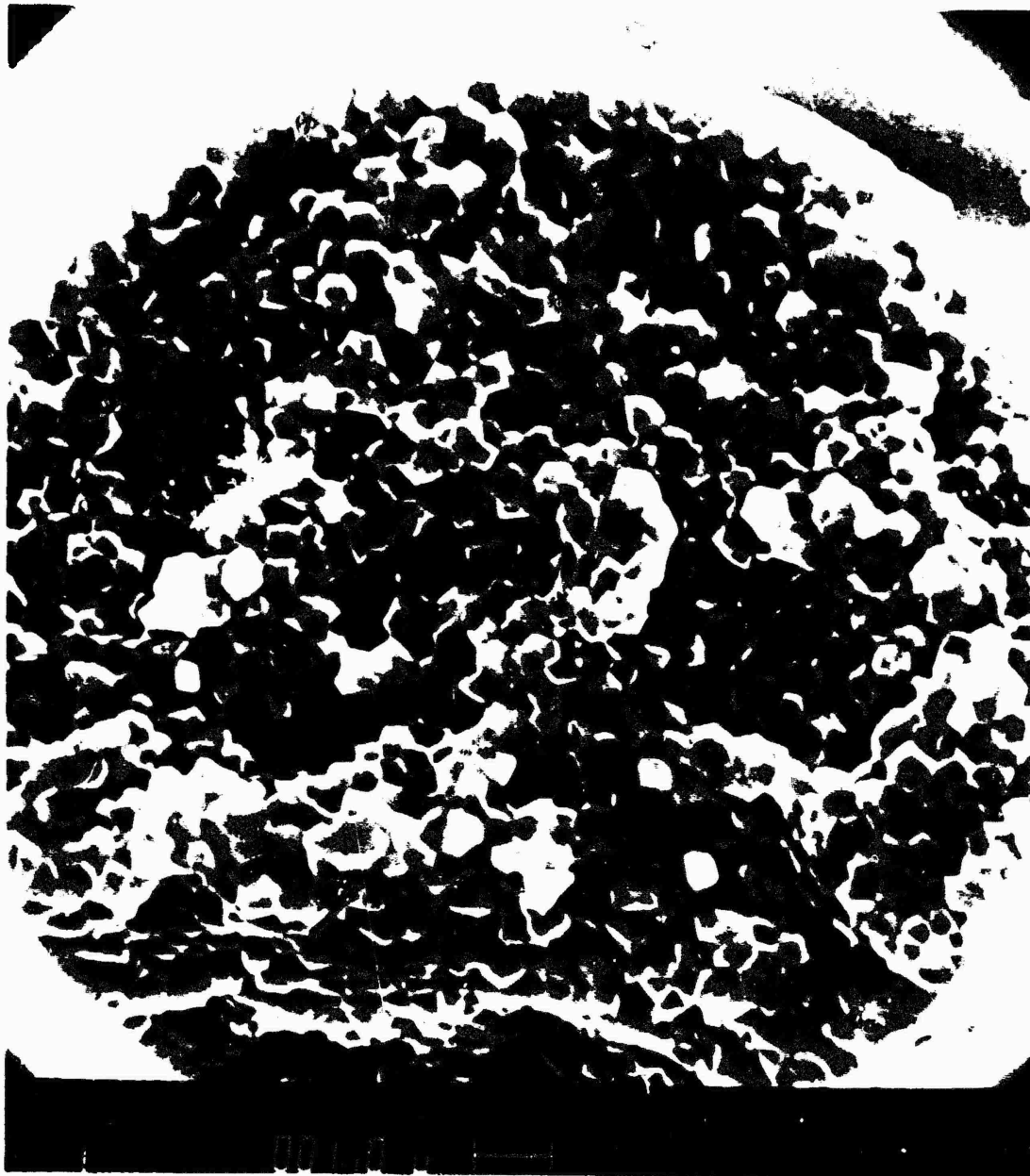


FIGURE 8

SEM OF THE FIBER FP SURFACE (6000x) SHOWING
"COBBLESTONED" MICROSTRUCTURE

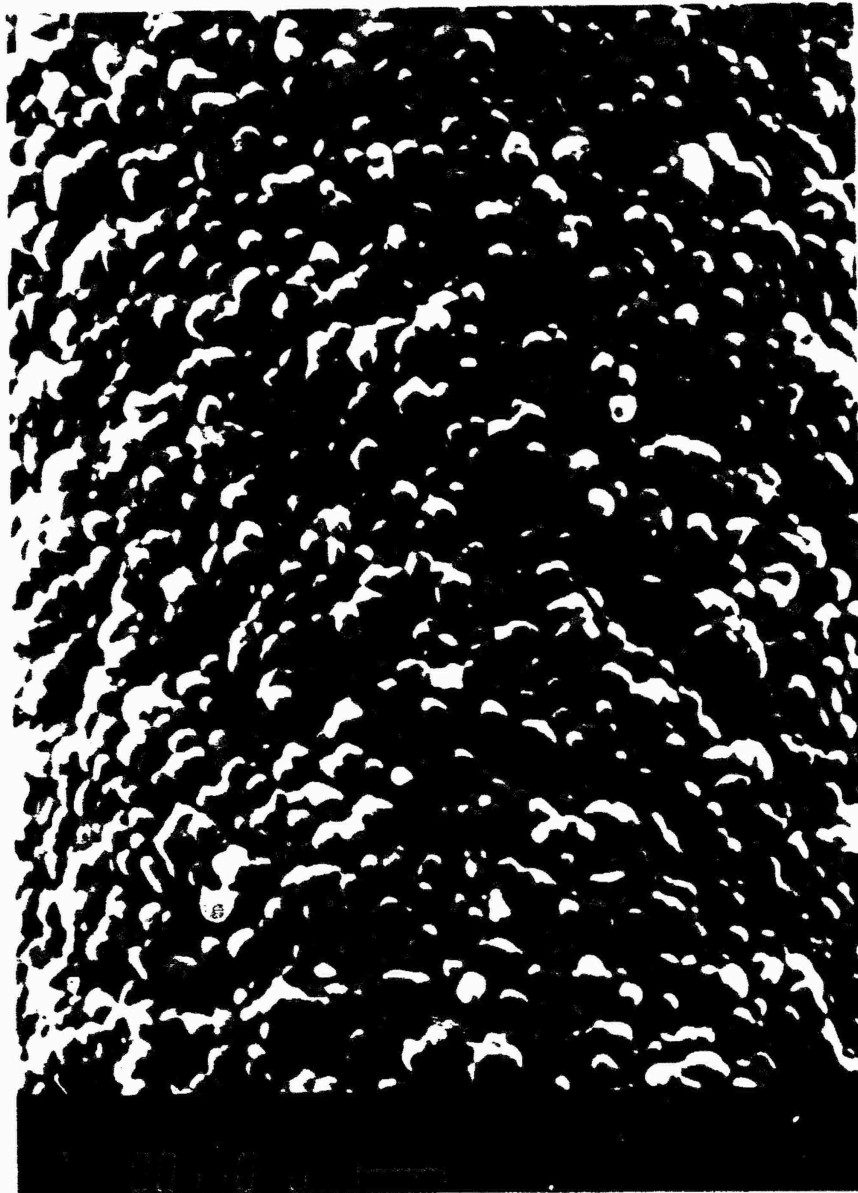


FIGURE 9

FIBER FP TENSILE STRENGTH vs. GAGE LENGTH

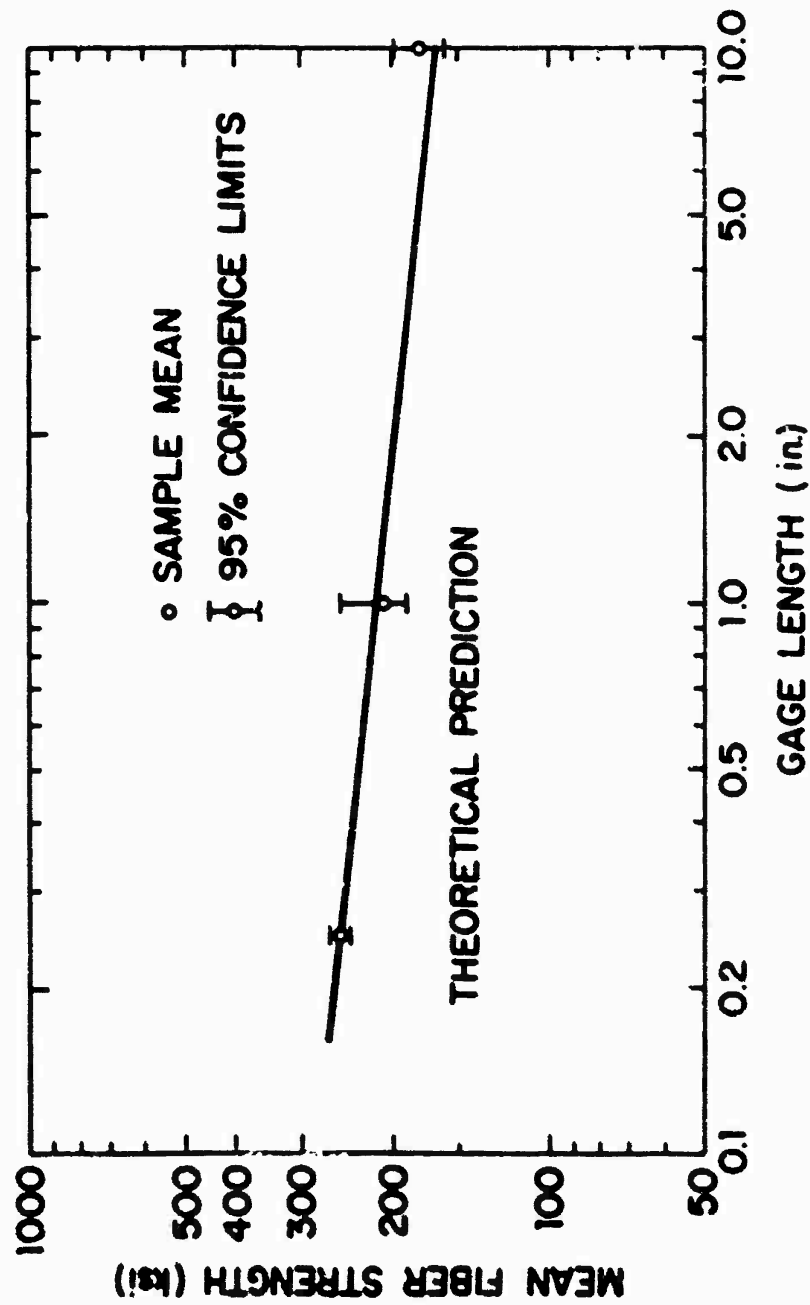


FIGURE 10

FIBER REQUIREMENTS FOR METALS REINFORCEMENTS

MECHANICAL COMPATIBILITY

- HIGH MODULUS AND STRENGTH
- SUPERIOR TRANSVERSE PROPERTIES

THERMAL COMPATIBILITY

- ELEVATED TEMPERATURE BEHAVIOR (700°C)
- RECRYSTALLIZATION TEMPERATURE

CHEMICAL COMPATIBILITY

- STABILITY IN (MOLTEN) METALS
- FIBER / MATRIX BONDING
- INTERFACE REACTIONS AND DUCTILITY
- CORROSION RESISTANCE

COMPOSITE FABRICABILITY

- PRACTICAL MANUFACTURING PROCESS
- LOW COST

FIGURE 11

FIGURE 11a. COMPARISON OF STRENGTH RETENTION IN AIR OF FIBER FP AT ELEVATED TEMPERATURE

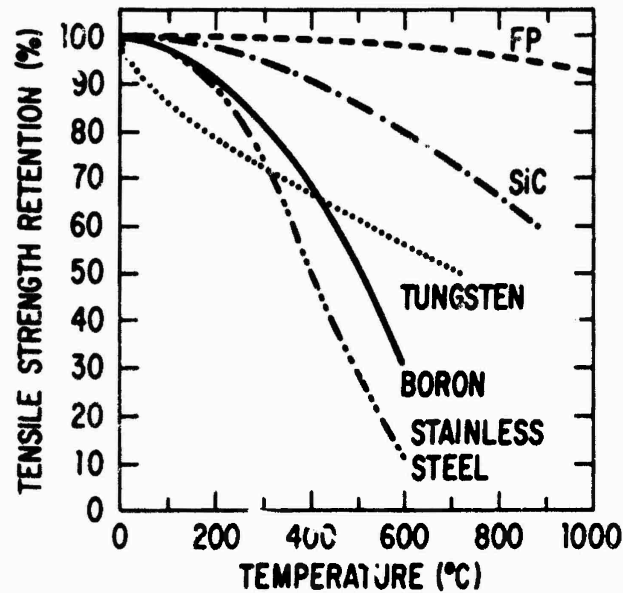


FIGURE 11b. EFFECT OF EXPOSURE TIME IN AIR ON FIBER STRENGTH AT ELEVATED TEMPERATURES

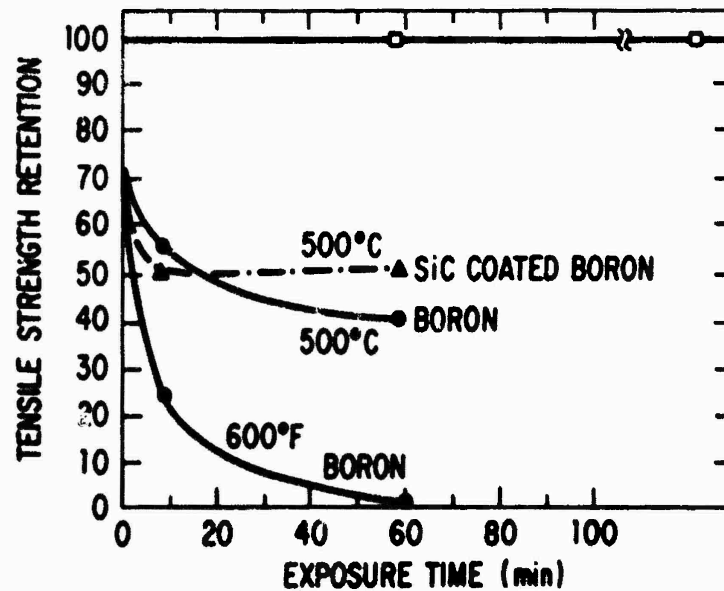


FIGURE 12

SEM OF FRACTURE SURFACE OF FP/MG COMPOSITES
HAVING 55 NOMINAL VOLUME LOADING OF FP FIBERS

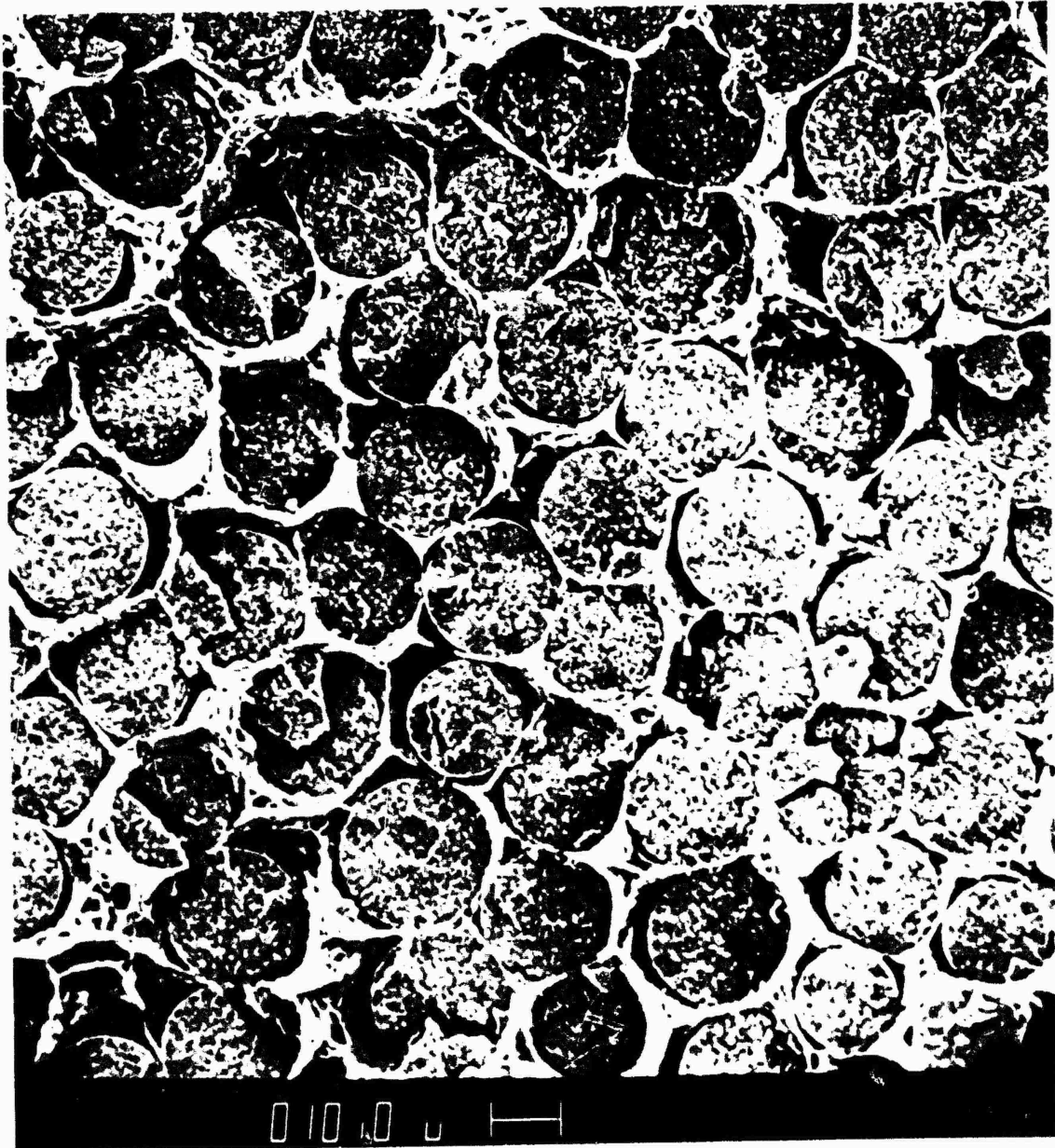


TABLE II
THEORETICAL AND EXPERIMENTAL MODULI AND POISSON'S RATIO OF FP/AL AND FP/Mg CASTINGS

PROPERTY	50% FIBER FP VOLUME LOADING			
	FP/Mg		FP/Al	
	THEORETICAL VALUE GPa ($10^6 \text{ lb}_f/\text{in}^2$)	EXPERIMENTAL VALUE GPa ($10^6 \text{ lb}_f/\text{in}^2$)	THEORETICAL VALUE GPa ($10^6 \text{ lb}_f/\text{in}^2$)	EXPERIMENTAL VALUE GPa ($10^6 \text{ lb}_f/\text{in}^2$)
LONGITUDINAL MODULUS (0° ORIENTATION)	207 (30.0)	207 (30.0)	207 (30.0)	212 (30.8)
TRANSVERSE MODULUS (90° ORIENTATION)	103 (15.0)	102 (14.8)	141 (20.4)	140 (20.3)
TENSILE MODULUS (0°/±60° ORIENTATION)	132 (19.2)	127 (18.3)	—	—
TENSILE MODULUS (±45° ORIENTATION)	110 (15.9)	111 (16.1)	145 (21.0)	126 (18.3)
SHEAR MODULUS (0° ORIENTATION)	39 (5.7)	41 (5.9)	54.5 (7.9)	50 (7.2)
POISSON'S RATIO				
ν_{LT}	0.130	0.110	0.166	0.170
ν_{TL}	0.234	0.243	0.244	0.244
$\nu_{0^\circ/\pm 60^\circ}$	0.26	0.24	—	—
$\nu_{\pm 45^\circ}$	0.39	0.36	0.33	0.31

FIGURE 13

FIBER FP REINFORCED ALUMINUM AND MAGNESIUM COMPOSITES CONTAINING
UP TO 60 FIBER VOLUME LOADING OF FIBER FP

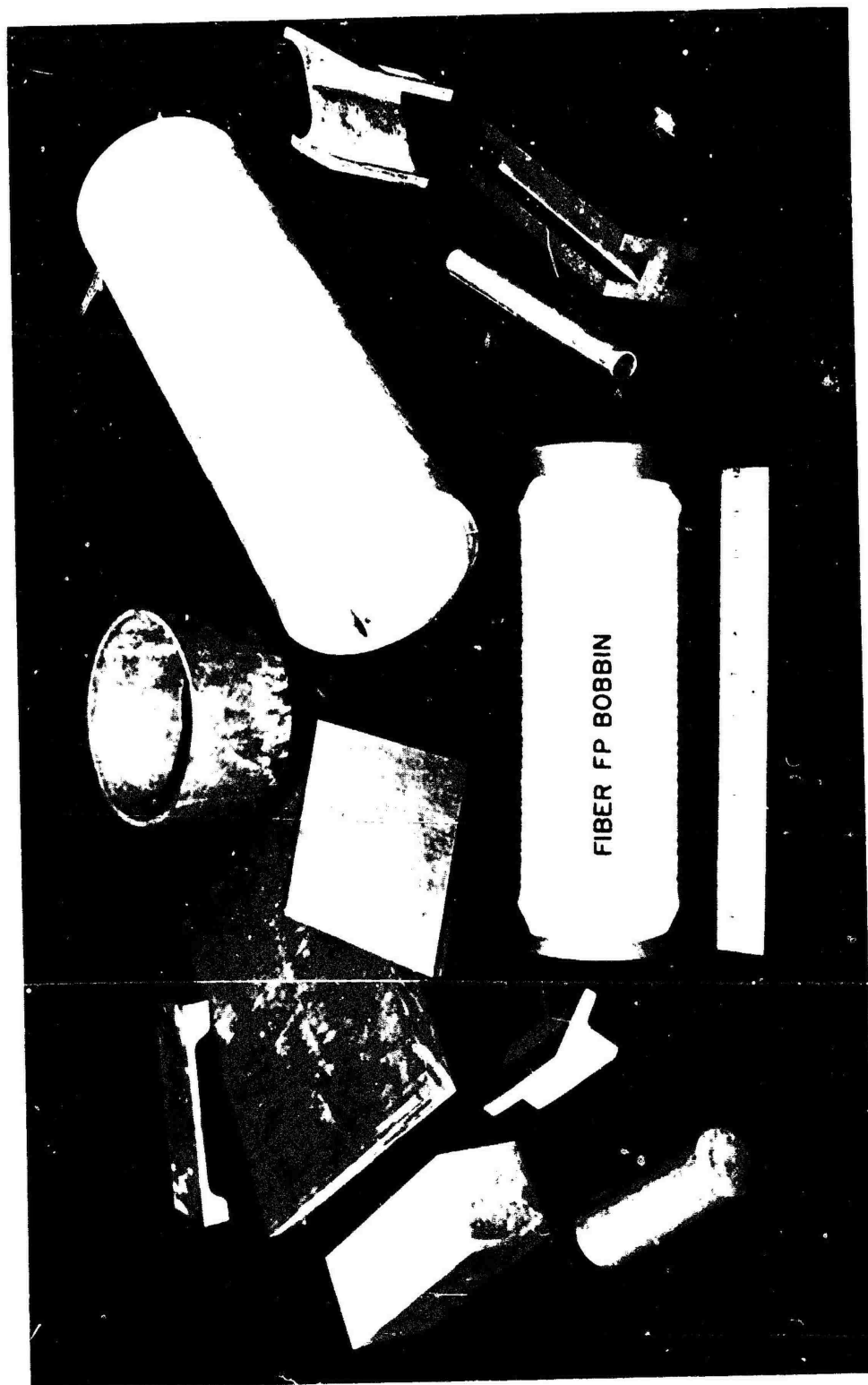


FIGURE 14

**COMPARISON OF UNIDIRECTIONAL FP/Al CASTING
(55 VOLUME LOADING FIBER FP)
WITH ALUMINUM ALLOY (7075-T6)**

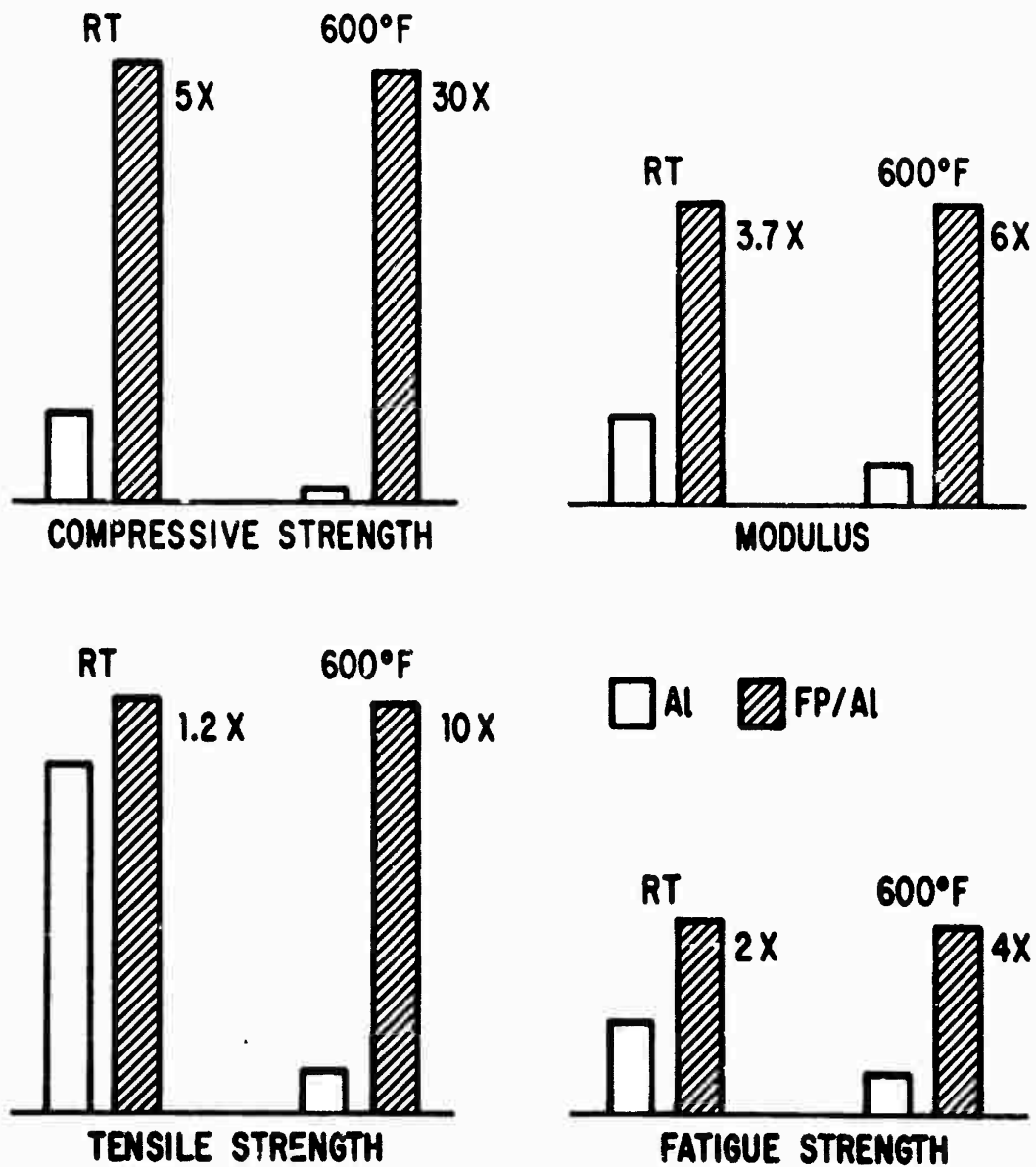


FIGURE 15

COMPARISON OF UNIDIRECTIONAL FP/MAGNESIUM
CASTING (COMMERCIAL PURE Mg MATRIX; 50 v/o
OF FIBER FP) WITH UNREINFORCED MAGNESIUM ALLOY
(QE 22A-T5)

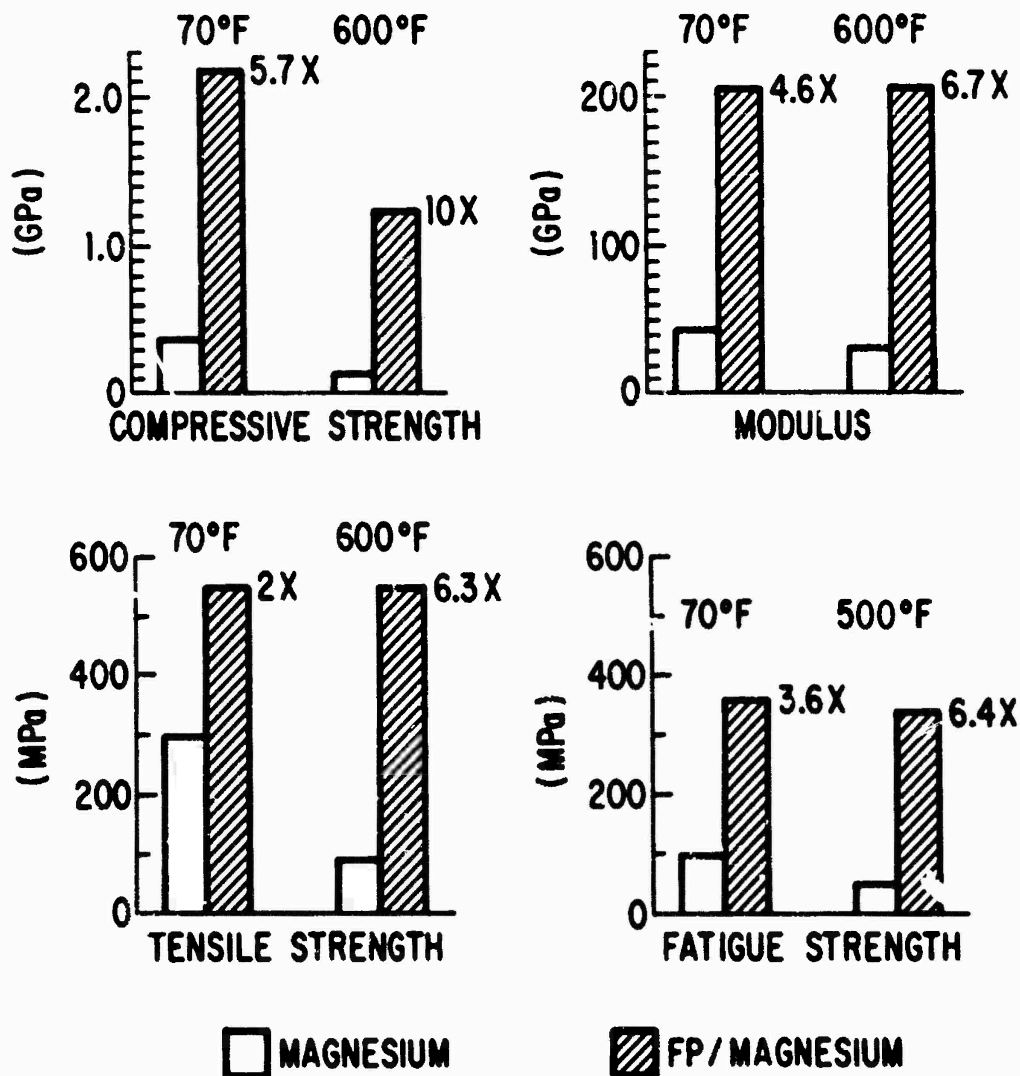


FIGURE 16

COMPARISON OF SPECIFIC PROPERTIES OF
UNIDIRECTIONAL FIBER FP REINFORCED ALUMINUM
AND MAGNESIUM CASTINGS (50 v/o FIBER FP)
WITH STRUCTURAL METALS

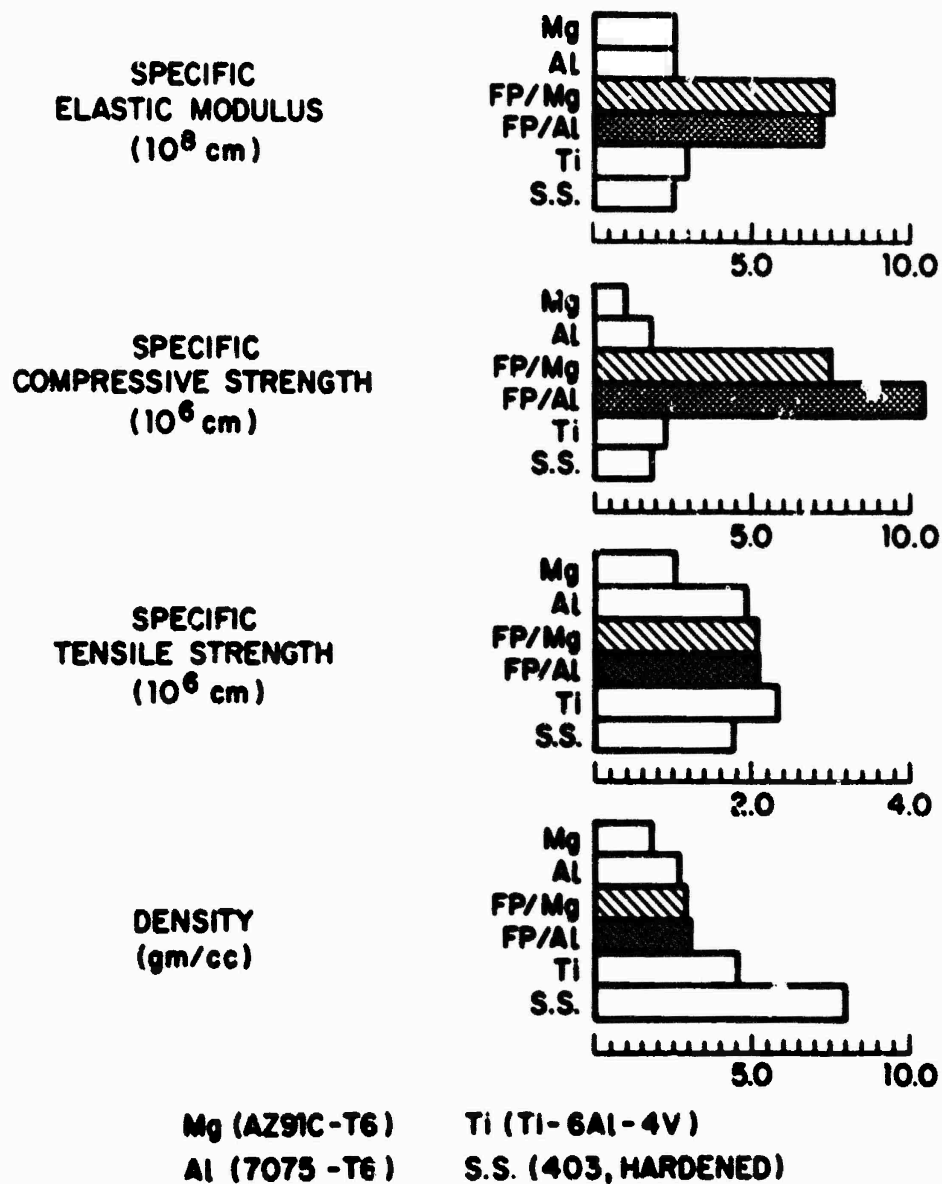


FIGURE 17

FP-ALUMINUM AXIAL STRESS FATIGUE

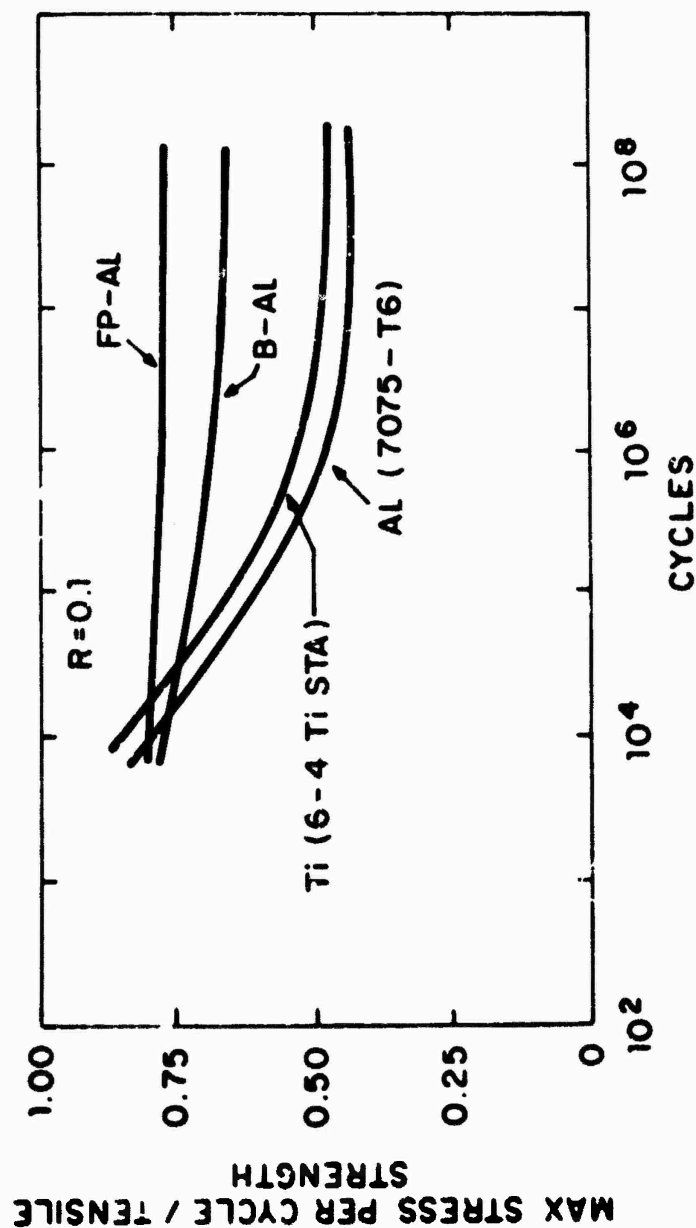


FIGURE 18

**EFFECT OF MATRIX AND FIBER / MATRIX BONDING
ON THE TRANSVERSE STRENGTH OF COMPOSITES**

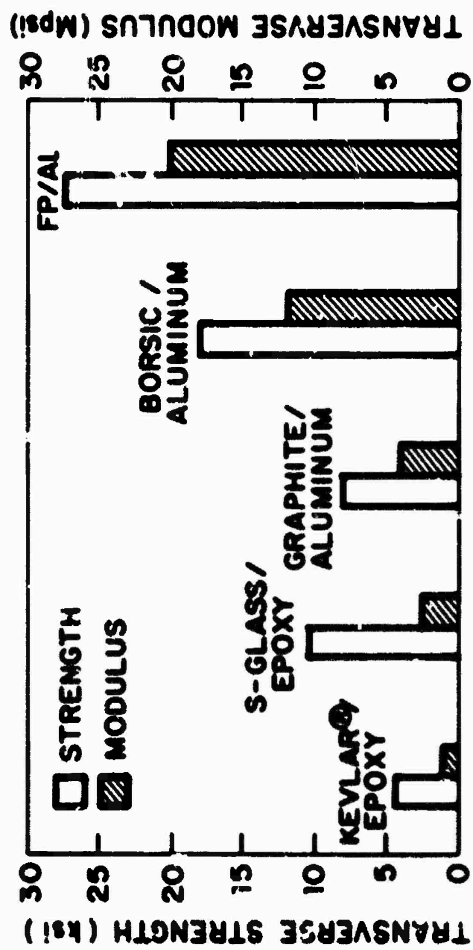


FIGURE 19

EFFECT OF FIBER VOLUME LOADING
ON THE TENSILE STRENGTH AND
MODULUS OF FP/AL CASTINGS

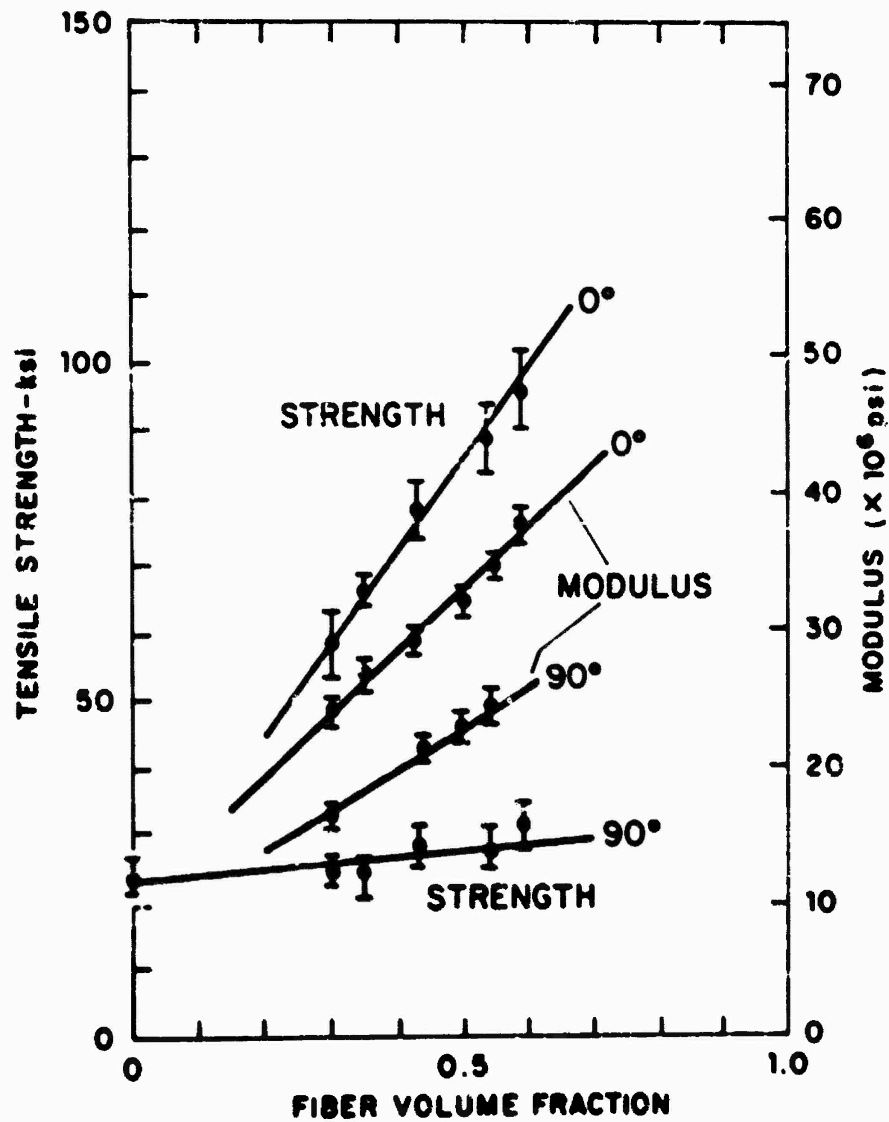


FIGURE 20

STRESS-STRAIN BEHAVIOR OF FP/AL COMPOSITES
(FIBER VOLUME LOADING 50%)

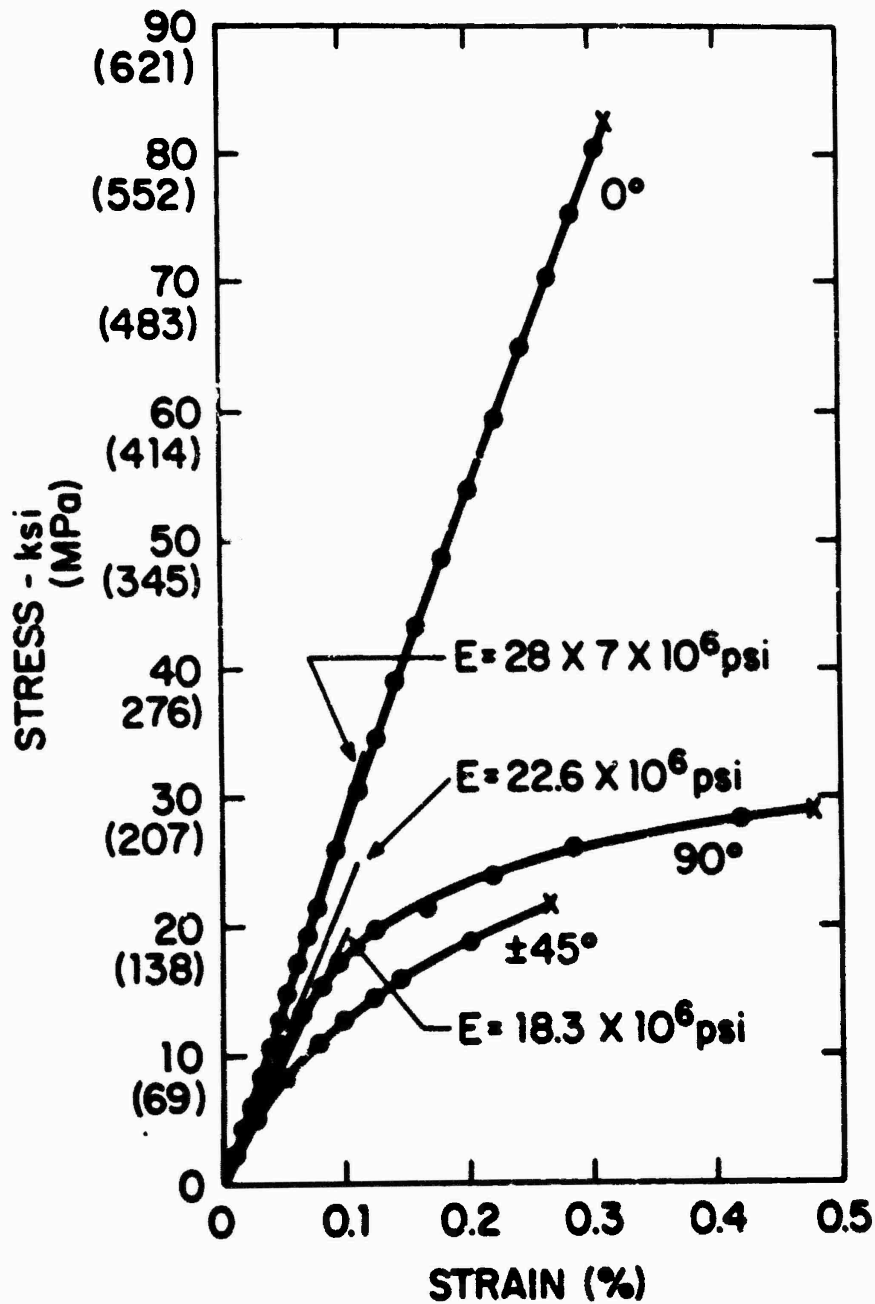


FIGURE 21

TRANSVERSE (90°) COMPRESSIVE STRESS-STRAIN

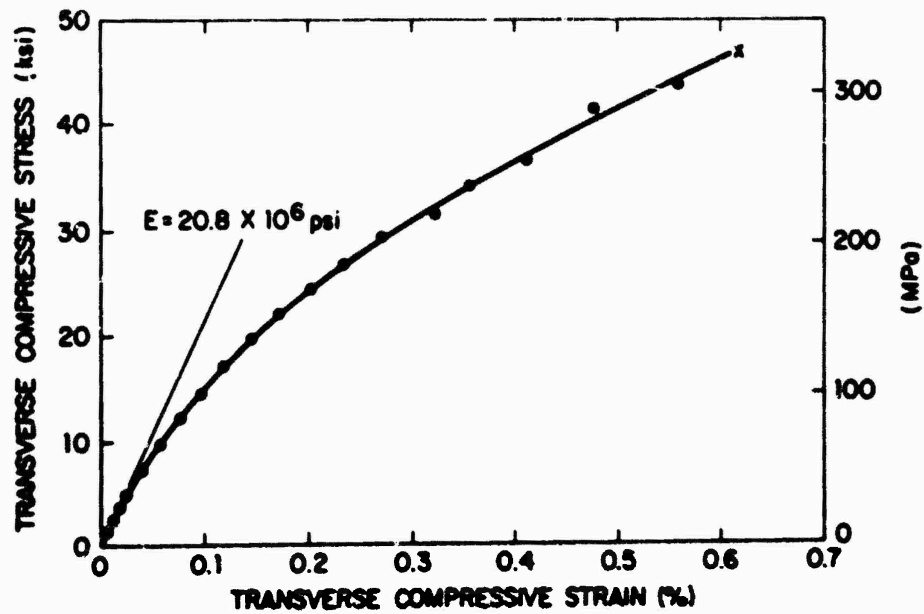


FIGURE 22

STRESS vs STRAIN FOR FP/Al IN THE [0/45°]
FIBER ORIENTATION ($V_f = 0.55$)

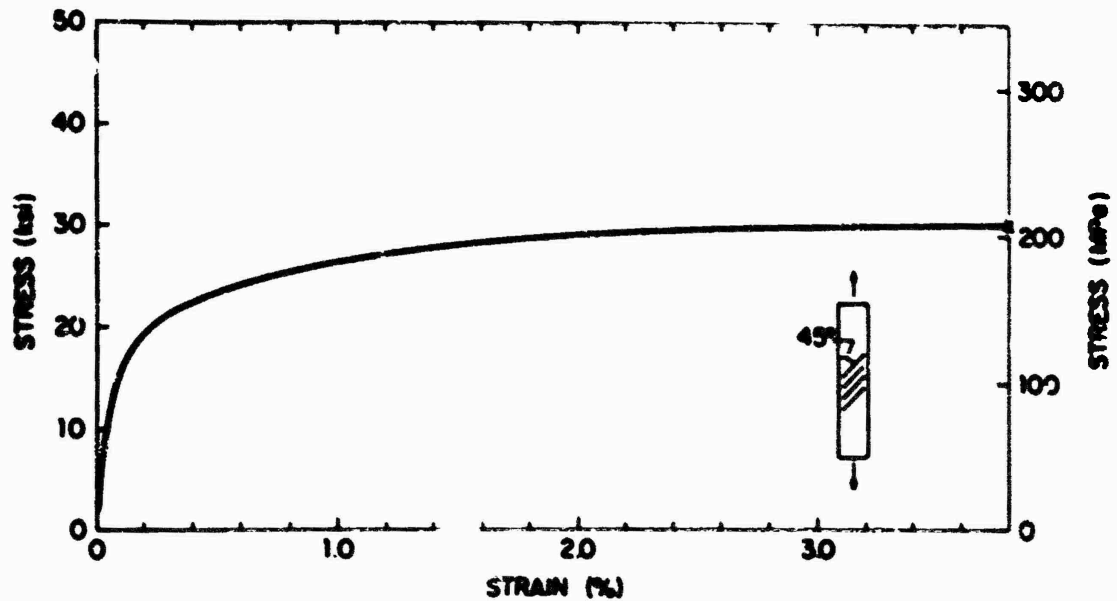


FIGURE 23

**EFFECT OF TEMPERATURE ON THE TENSILE AND
FLEXURAL STRENGTH OF FP/Al COMPOSITES
(FIBER VOLUME LOADING 55%)**

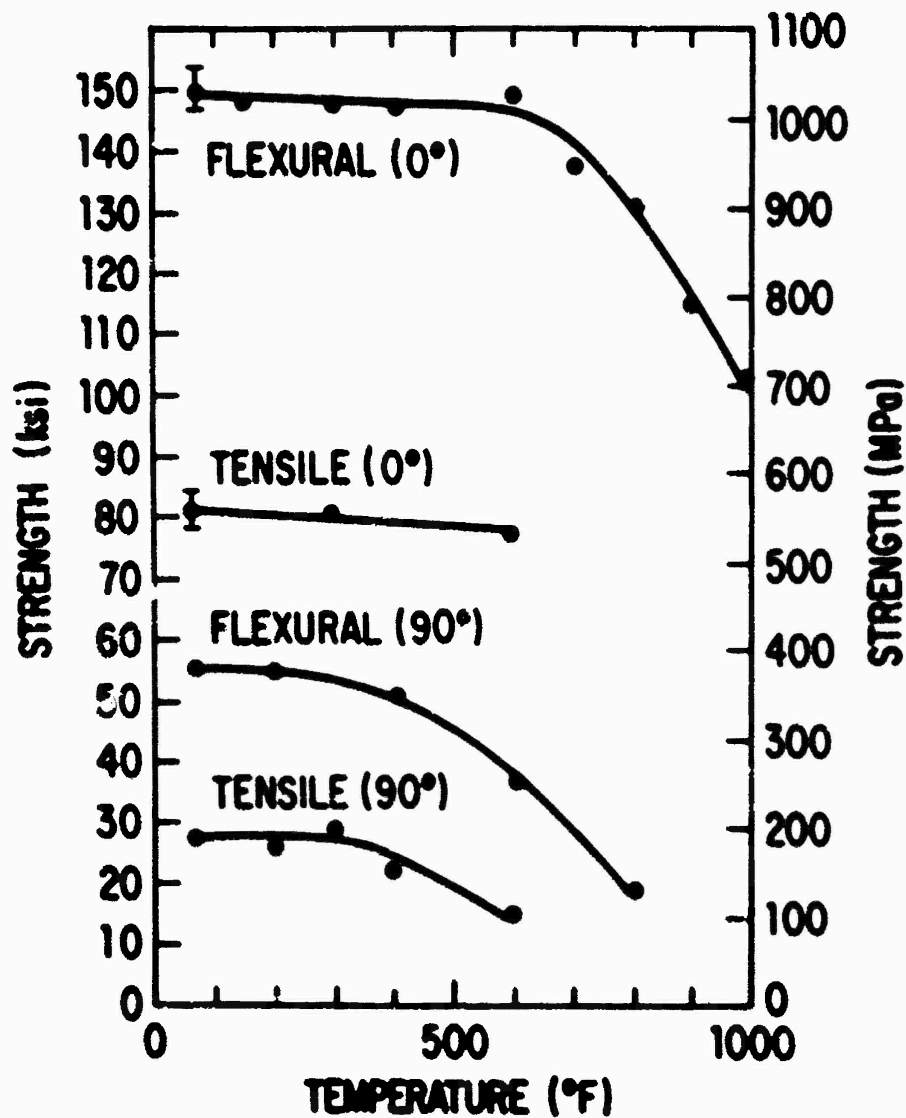


FIGURE 24

STRESS STRAIN BEHAVIOR OF FP-Mg COMPOSITES

(FIBER VOLUME LOADING 50%)

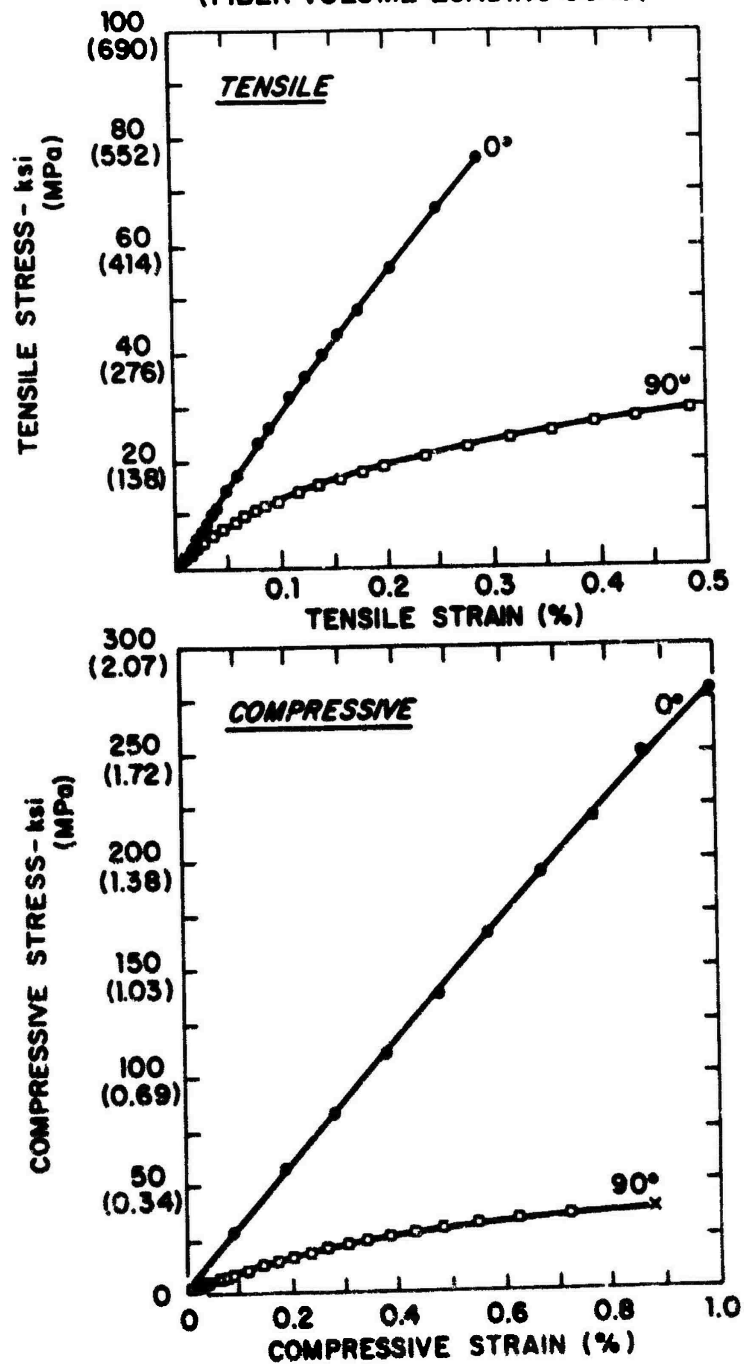


FIGURE 25

**EFFECT OF TEMPERATURE
ON TENSILE AND FLEXURAL PROPERTIES
FP/MAGNESIUM CASTINGS (50 % FIBER FP)**

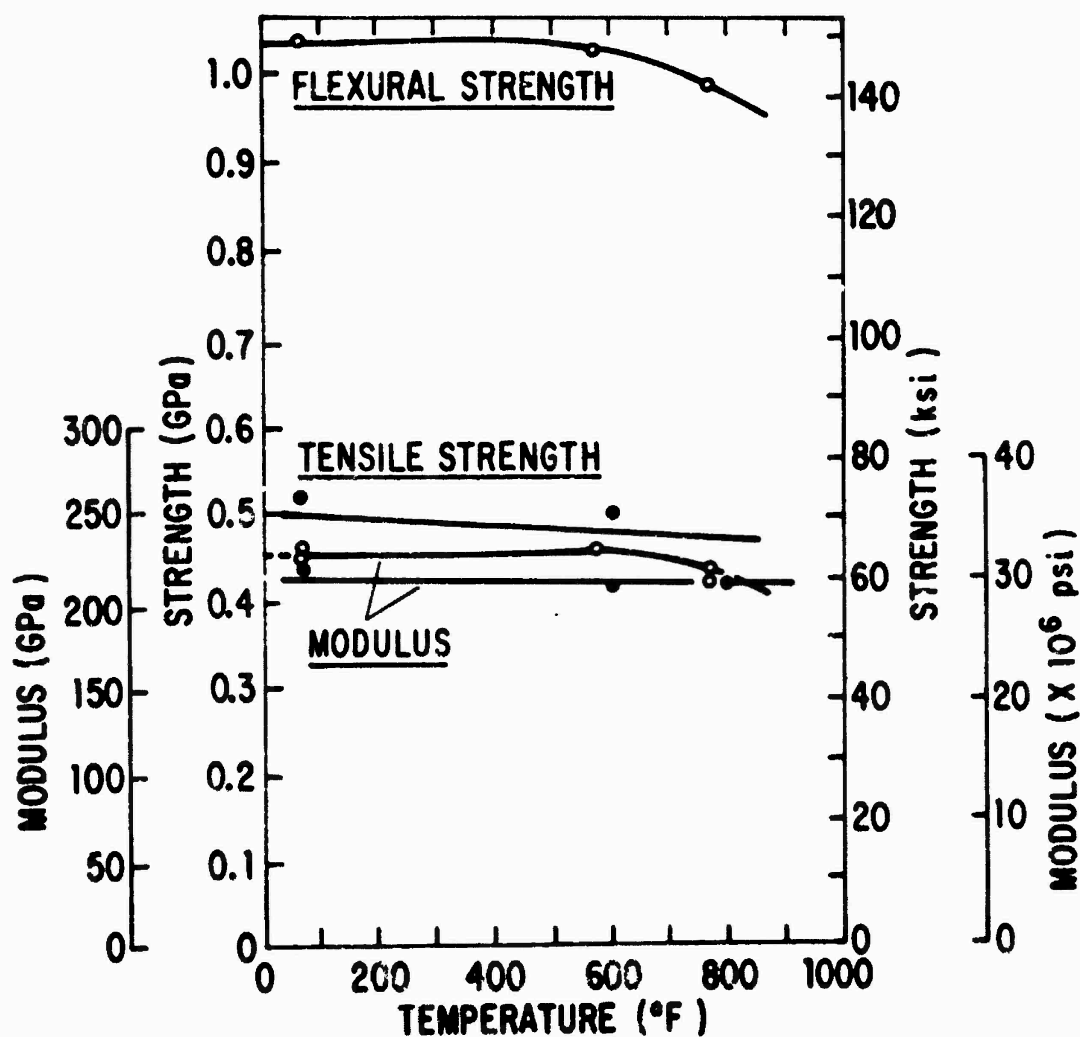


FIGURE 26

APPLICATION DEVELOPMENT PROGRAMS

<u>APPLICATION</u>	<u>MOTIVATION</u>
HELICOPTER HOUSING	REDUCED NOISE, VIBRATION AND MAINTENANCE
AUTOMOTIVE ENGINES	REDUCE FUEL, LONGER FATIGUE LIFE
JET ENGINES	WEIGHT REDUCTION, HIGHER OPERATING TEMPERATURES
AEROSPACE STRUCTURES	WEIGHT SAVING
ARMOR	HYBRID CERAMIC ARMOR

FIGURE 27

FIBER FR/MAGNESIUM COMPONENT TEST SPECIMENS AND CASE ASSEMBLY

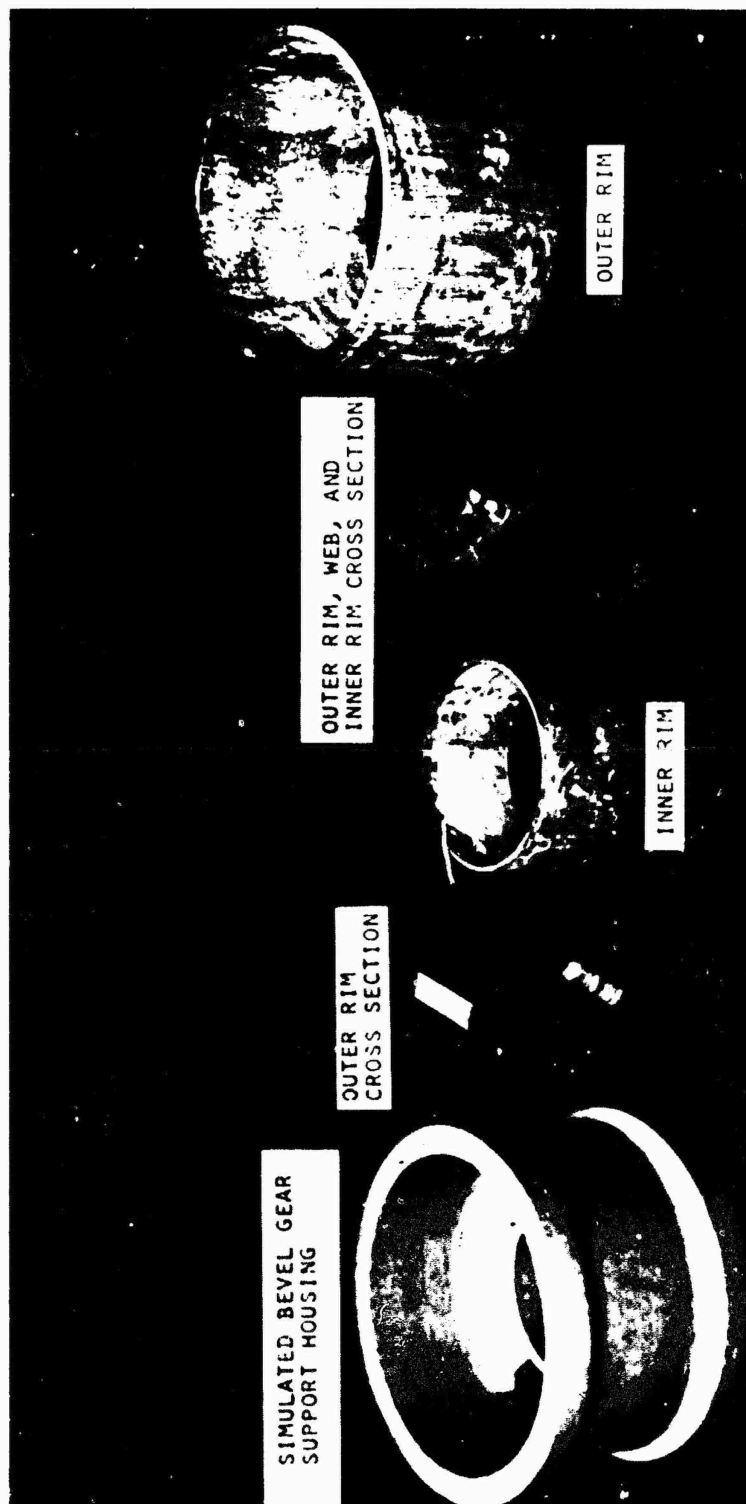
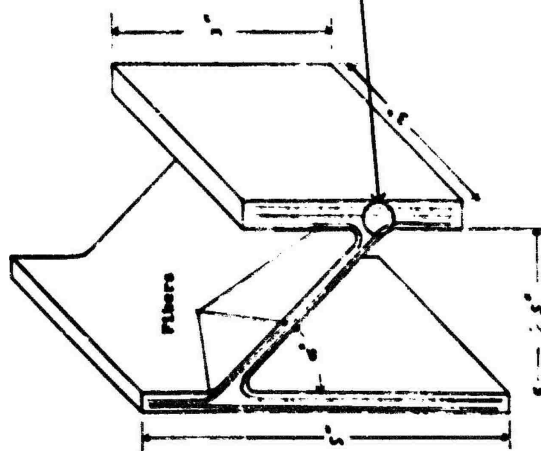


FIGURE 28

STEEL SECTION CONNECT



FIBER FR. PLATE LAY UP

Flanges: Eighteen Plies $\pm 60^\circ(6)/0^\circ(6)/\pm 60^\circ(6)$
 Web: Nine Plies $0^\circ/\pm 60^\circ(2)/0^\circ(3)/\pm 60^\circ(2)/0^\circ$

MAGNIFICATION
20X

FIGURE 29

CH-47C FORWARD TRANSMISSION HOUSING DYNAMIC DEFLECTION AT OPERATING SPEED

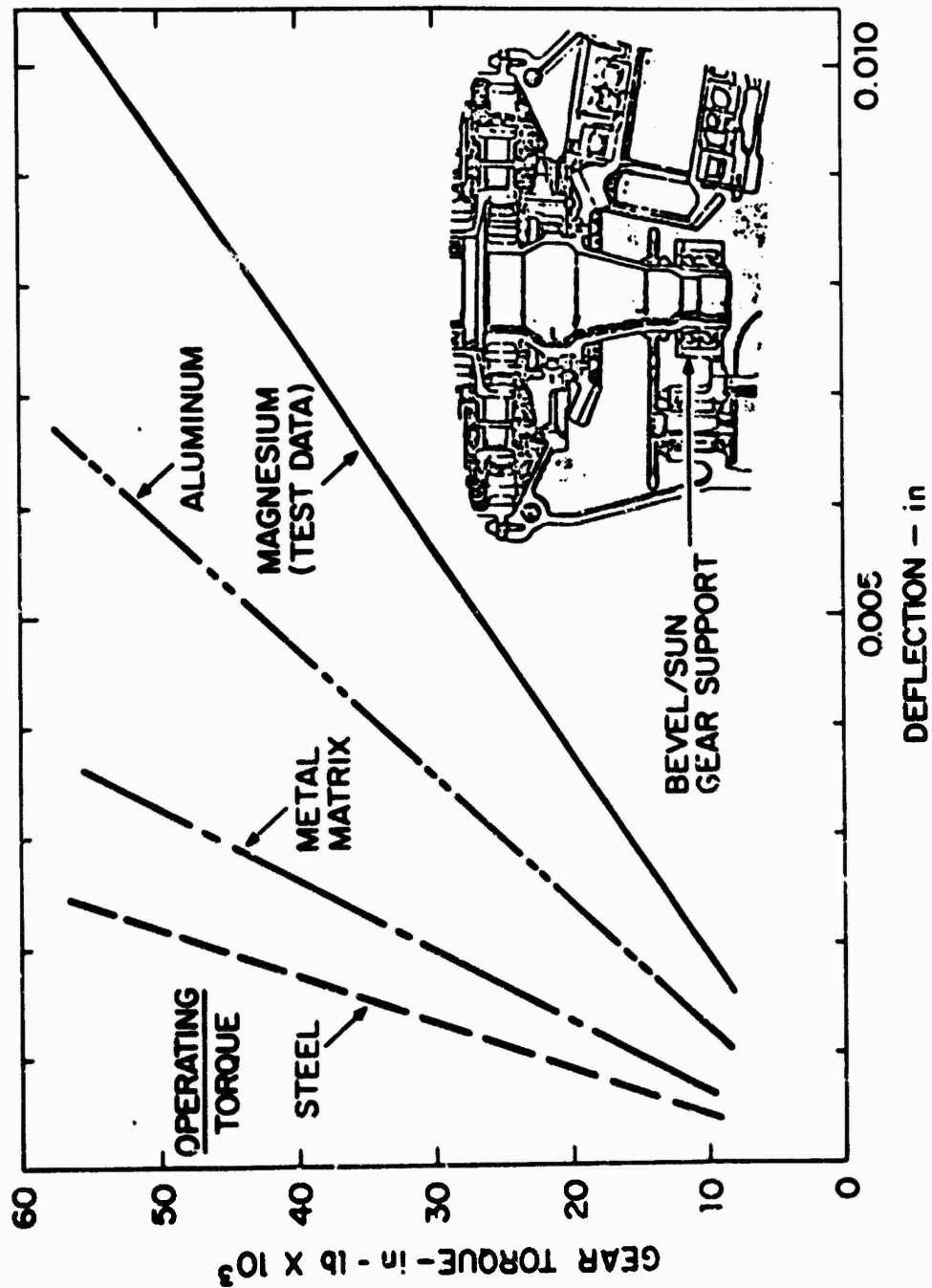


FIGURE 30

DEVELOPMENT NEEDS

APPLICATIONS AND VALUE-IN-USE

COMPOSITE DESIGN DATA

COMPOSITE CASTING PROCESS

- SELECTIVE REINFORCEMENT
- INVESTMENT CASTING
- PRESSURE CASTING

TECHNOLOGY FOR USE

- MACHINING
- NDT
- JOINING

PLASTIC AIRPLANES

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ABSTRACT

The aircraft industry is moving at an accelerating pace in the use of fiber reinforced plastic structures. The major motivation is to reduce weight and fuel consumption and to improve performance; however, reduced cost and improved durability are increasingly important factors. In the 1960's, only a few experimental parts were flown. 1970 initiated a decade of substantial growth with the first production part, the F-14 horizontal stabilizer. By the end of the decade, the F-18 with 10% composite and the AV88 with 20% composite were flying and airlines had a few parts in commercial service. The next decade will see substantial increases with military aircraft tending toward 50% composites and the development of composite wings and fuselage for commercial transport.

(Text was not provided for publication.)

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ABSTRACT

The state of the art of PAN-based carbon-fiber manufacture and the science of fiber behavior is briefly surveyed. A review is given of the stabilization by oxidation and the subsequent carbonization of fibers; of the apparent structure of fibers deduced from scanning electron microscopy, from x-ray scattering, and from similarities with soft carbons; and of the known relations between fiber properties and heat treatment temperature. A somewhat simplified model is invoked to explain the electrical properties of fibers, and recent quantum chemical calculations on atomic clusters are used to elucidate some aspects of fiber conductivity. Finally, some effects of intercalation and oxidative modification of finished fibers are summarized.

BACKGROUND

Polymers are catenated arrays of carbon and other atoms, sometimes branched and cross-linked, which resemble and act like a mass of spot-welded angleworms; that is, with limited freedom of movement between cross-links at higher temperatures, but frozen in rather rigid, tangled structures below the glass transition temperature. Carbon fibers are the glassy polymers that remain when most other elements are driven off at elevated temperature, leaving twisted, edge-linked carbon ring sheets somewhat resembling turbostratic graphite (graphite with irregular spacing and stacking). The fibers are very stiff and quite strong in tension. Best of all, they are relatively inexpensive to manufacture. Blended with normal polymers, they provide composite materials with a wide range of useful properties that, within limits, can be tailored to many needs (1*). For example, such composites have exceptionally good specific stiffness and tensile strength; in fact, the high stiffness-to-weight ratio of these composites is their chief asset as structural materials. Thus, carbon fibers are of interest to polymer chemists, not only because they are polymer-like in nature, but also because they extend the useful applications of the many classes of normal organic polymers.

Until recently, most commercial fibers were made from polyacrylonitrile (PAN), and the present paper will be concerned primarily with PAN-based fibers with which we have had the most research experience. However, recent advances in fiber manufacture from mesophase pitch suggest that such fibers, with excellent mechanical properties, may also be made inexpensively (2, 3).

CARBONIZATION OF PAN

The homopolymer PAN has the formula $(-\text{CH}_2\text{CH}(\text{CN})-)_n$ (Fig. 1). Typically, the degree of polymerization n

*Numbers in parentheses designate References at end of paper.

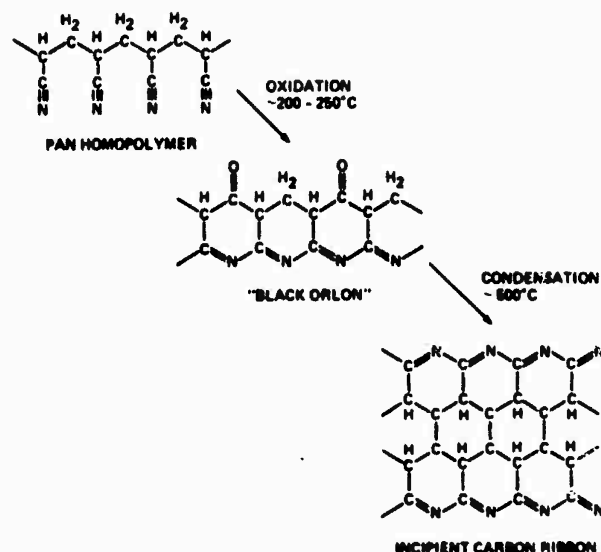


Fig. 1. - Carbonization of PAN

is greater than 2,000. Most commercial PAN fibers also contain copolymers (e.g., vinyl acetate, vinyl chloride, or styrene) which improve certain properties, such as the ability to stretch or the affinity for dyes (4). These copolymers can influence the properties of the fully carbonized fiber.

The PAN fiber is first oxidized under tension at temperatures near 200°-250°C; CO_2 , CO, and HCN are given off (5). The tension keeps the polymer chains aligned along the fiber axis, a condition necessary for high modulus fibers; without tension, the molecular chains curl at the elevated temperature and the resulting fiber has low strength and stiffness. Watt (6) postulates that ketone groups are formed while the polymer cyclizes to give the ladder structure known as "black orlon." In the next step, carbonization occurs in an inert atmosphere at heat treatment temperatures (HTT's) that may range from 800°C to more than 2500°C. The rate, amount, and kinds of gas given off at various HTT depends on the rate of heating (or soaking time), but in general NH_3 , H_2 , and CH_4 are given off at HTT's of about 600°-800°C; HCN peaks near 900°C, and N_2 continues to be driven off at HTT well above 1200°C. The ladder polymers coalesce into ribbons and warped sheets of carbon ring structure. Some nitrogen is retained even at HTT's above 1500°C; all the nitrogen is shown at edge sites in the incipient ribbon structure of Fig. 1, but the amount of N retained suggests that it may also occupy interior sites in the carbon rings.

Figure 2a shows the small furnaces used at the Chemical Research Projects Office of Ames Research Center to make and modify carbon fibers (7). Threads of PAN fibers, called tows, consisting of about 94 separate 10- μ diameter filaments of PAN, are oxidized from 8 to 40 hr at 200°C in the low-temperature furnace at the right, weights hung from the tows keep them under tension during the oxidation. The tows are subsequently placed in the high-temperature furnace and surrounded with an inert gas (N_2) while subjected to high temperature (600°-2000°C) for about 20 min. The fibers shrink in diameter to about 8 μ ; they also shrink in length as they become carbonized.

Figure 2b shows the HTT furnace used to carbonize pilot scale batches of fiber at the Calanese Research Laboratories. The PAN fiber has previously been oxidized in a large two-story furnace and wound on drums like the one shown in the foreground. The black orlon is unwound from the drum and feeds continuously through the furnace in the presence of a nitrogen atmosphere supplied from the 220-ft³ storage cylinder shown alongside the furnace. The 3-in. tapes of black orlon

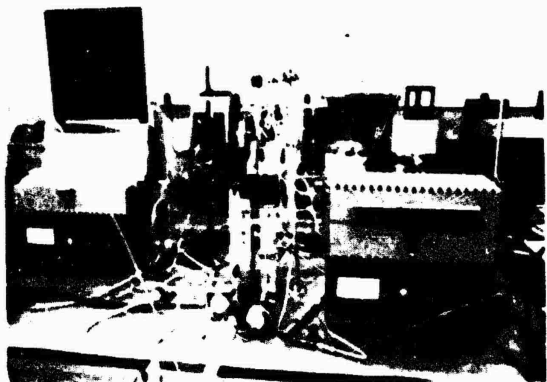


Fig. 2a. - Furnaces for carbon fiber manufacture at the Ames Research Center

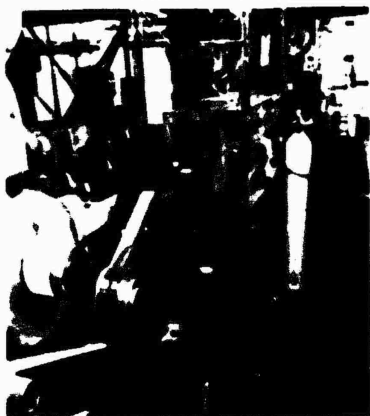


Fig. 2b. - High temperature carbonizing furnace at Celanese Research Laboratories, Summit, N.J.

consist of 300 yarns laid side by side, in contrast to the two- or three-yarn batches processed statically in the small furnaces used at Ames. Very large-scale commercial production, centered primarily in Japan, makes use of considerably larger facilities, of course.

Figures 3a-3c show cross-section scanning electron microscope (SEM) photos of the original PAN fibers, the oxidized fibers, and the carbonized fibers. The cross section shrinks from about 3×10^{-6} to 1.3×10^{-6} cm² in the process. The dogbone cross section is typical of many fibers (such as GY70 SE), but others are circular (such as Celion 6000, Thornel 300, and Hercules HMS). A circular fiber is shown in the SEM photograph in Fig. 3d, taken at the Stanford University Material Sciences Laboratory (8).



Fig. 3a. - Pan precursor fibers (embedded in epoxy)
 $\bar{A} = 3.3 \times 10^{-6}$ cm²



Fig. 3b. - Pan fibers oxidized at 250°C, 32 hrs
 $\bar{A} = 3.1 \times 10^{-6}$ cm²



Fig. 3c. - Oxidized fibers carbonized at 800°C, 20 min
 $\bar{A} = 1.3 \times 10^{-6}$ cm²



Fig. 3d. - SEM of circular cross section carbon fibers

STRUCTURE OF CARBON FIBERS

The structure of carbon fibers is deduced partly from noting correlations between properties of the fiber and of graphite, and from SEM photographs such as those shown in Fig. 3; however, the best evidence for the structure is probably that obtained from x-ray scattering measurements (4). The structure is deduced to be somewhat as shown in Fig. 4. A three-dimensional network of warped carbon ring sheets exists which is locally like turbostratic graphite. The sheets have random stacking and variable spacing between them that

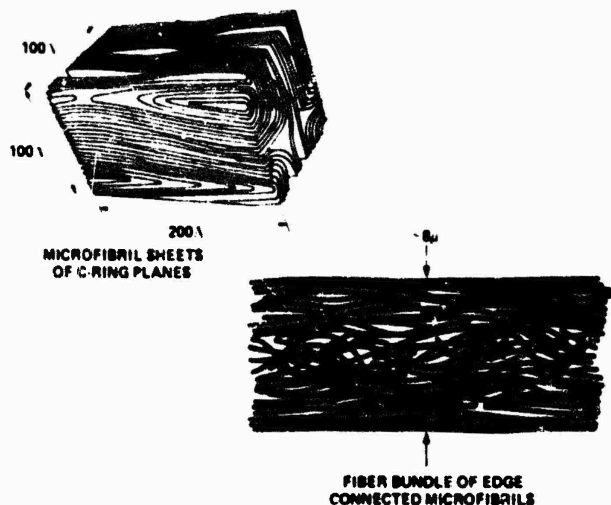


Fig. 4. - Carbon fiber structure

decreases on the average from about $3.7 \text{ \AA}$ at low HTT to $3.4 \text{ \AA}$ at high HTT, approaching the exact $3.354 \text{ \AA}$ spacing of ordered graphite. This warped three-dimensional structure gives the fiber good shear resistance in any plane parallel to the axis. The size of more or less uniform domains is deduced from peaks in x-ray diffraction; the variability in size relates to the broadening of these peaks.

The total fiber can be viewed as a bundle of smaller microfibrils with many strained edge connections between microfibril domains. These give the fiber great stiffness. Typically a microfibril can be many thousands of angstroms in length, but dislocations or warping in the structure occurs every $100\text{--}200 \text{ \AA}$ or so along the fiber and every $30\text{--}50 \text{ \AA}$ perpendicular to the fiber axis. Many needle-shaped voids also appear, with typical lengths from $10\text{--}50 \text{ \AA}$; these seem to be inaccessible to helium and can account for 5% to 30% of the total fiber volume. Fibers made at low to moderate HTT's seem to be reasonably homogeneous, but fibers produced at HTT's of 2500°C or more may have a thin skin ($\sim 100 \text{ \AA}$) of oriented microfibrils with basal planes largely parallel to the surface.

Figure 5 shows typical x-ray diffraction patterns obtained by carbonization of polymers at different temperatures. The patterns shown are for phenolic resin (4) rather than for P/M, but similar patterns are obtained in any case. The sharp, well-defined lines are the pattern given by highly ordered graphite. The 002 line corresponds to the grating spacing of $3.354 \text{ \AA}$ between basal planes and is the strongest; next strongest

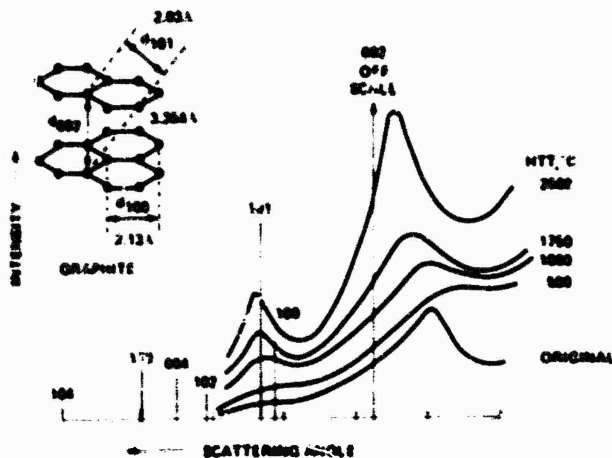


Fig. 5. - X-ray diffraction patterns for phenolic resin char

is the 101 line corresponding to the $2.03 \text{ \AA}$ spacing between planes cutting through identical C-atoms in ABA stacking. The third strongest line is 100, corresponding to the $2.13 \text{ \AA}$ spacing of identical atoms in the basal planes. The pattern of still weaker lines correspond to larger scattering angles from more closely spaced planes of atoms having smaller atom density. In contrast to the ordered graphite pattern, the carbonized polymers give very broad lines that indicate both a variable spacing between basal planes and a somewhat larger average spacing than in ordered graphite. The pattern is similar to that obtained from turbostratic graphite where the spacing between planes is variable and stacking deviates from ABA. As the carbonization temperature increases, the spacing approaches that of graphite, and the peaks become more pronounced, showing that the structure becomes more orderly.

PROPERTIES OF CARBON FIBERS

Representative properties of carbon fibers are shown in Fig. 6 as a function of HTT. Actual properties can vary by factors of 2 or more for different

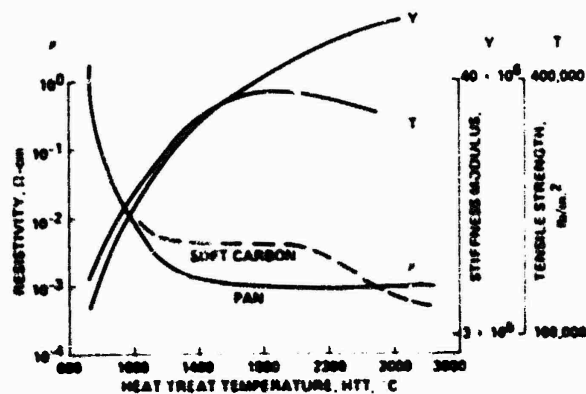


Fig. 6. - Properties of C-fibers as a function of HTT

fibers. The high modulus and strength of carbon fibers derives from the covalent sp^2 bonds in the hexagonally arrayed rings of carbon atoms. These bonds are actually stronger than the sp^3 bonds of diamond; they give graphite a basal plane stiffness modulus of $150 \times 10^6 \text{ psi}$ (9). To approach this stiffness the carbon ring sheets must be aligned with the fiber axis and the fibers carbonized at high temperature to permit domain growth of these ring sheets; commercial fibers can approach 30% to 50% of the theoretical graphite stiffness limit, with tensile strengths of $300,000\text{--}450,000 \text{ psi}$, about 10% to 15% of the measured single crystal limit (9). These are quite remarkable stiffness and strength characteristics considering the impurities remaining in the fiber structure. Typically, the tensile strength peaks at HTT's of about 1500°C ; as a result, many commercial fibers are finished near this temperature. The stiffness increases monotonically with HTT, but the extra energy cost of stiffer fibers is warranted only for very special applications. Also, the stiffer fibers have less impact toughness, a characteristic proportional to the area under the stress-strain curve.

The thermal and electrical conductivities of fibers are related properties which have similarities to those properties in soft carbons and graphite and also distinct differences. Polymeric PAN is a good insulator with resistivity of the order of 10^{15} ohm-cm . As the polymer is oxidized, the resistivity drops to about 10^6 ohm-cm , and as it pyrolyzes it drops to 10^{-3} ohm-cm at an HTT of about 1000°C . At this HTT the

resistivities of soft-carbon precursors reach a plateau, while the PAN-based fibers continue to drop to about 10^{-3} ohm-cm before reaching their plateau. No increase in HTT will change the PAN-based fiber appreciably. At an HTT of about 2000°C, however, the soft carbons graphitize more completely and the C-plane resistivity drops to about 10^{-4} ohm-cm and becomes semi-metal in character (the resistivity in graphite normal to the C-plane is more than 100 times greater).

Electrical conductivity of an irregular structure like carbon fiber cannot be fully explained in terms of a simple band-gap model. The gaps between valence and conduction bands are highly variable and localized characteristics; both p- and n-type carriers arise from different mechanisms in the structure, and their mobilities are affected by localized strain and structural warping. At present, the "average" values of band gap, n- and p-type carrier density, effective mass, and mobility can be only partly disentangled by simultaneous measurements of several parameters. Those parameters may include the following: resistivity; Hall coefficient (magnitude of transverse electric field produced by current flow in the presence of a transverse magnetic field); thermoelectric power (voltage produced by temperature gradient); magnetoresistance (change in resistance when a magnetic field is present); cyclotron resonance; and electron spin resonance signals. In spite of these uncertainties, somewhat tentative models of the conductivity of carbonizing matter have been elucidated by Mrozowski (10, 11) and by Spain (12) that permit us to understand, qualitatively at least, some of the mechanisms that occur in both soft carbons and fibers.

At very low HTT's (600°-800°C) hydrogen atoms are removed from edge ring sites, leaving unpaired σ -state electrons. These can give rise to impurity states in the band gap. Also some π electrons may be pulled out of the structure to form stable spin pairs at these edge sites, leaving holes in the valence band. (To a first approximation, carrier charge is indicated by the sign of the Hall coefficient or of thermoelectric power (TEP), and unpaired π -electron density is indicated by the strength of electron spin resonance signals.) As HTT increases, the number of structural defects and holes increases; at the same time carrier scattering decreases as the sizes of regular domains build and the "effective" band gap decreases due to the increase in long-range order. For the very low HTT fibers, Lerner (13) measured characteristics similar to an impurity-dominated semiconductor with constant band gap; at higher HTT there is little doubt that decreasing band gap is a major factor in the increased conductivity. The gap decreases from about 0.6 eV at an HTT of 600°C to 0.01 eV at an HTT of 1200°C. All these effects contribute to the dramatic decrease in resistivity with increasing HTT. Near an HTT of 900°C the number of holes becomes large and the π -band becomes depleted of electrons so that n-type conduction in the unfilled π -valence band begins to dominate; experimentally the TEP changes sign to negative. At still higher HTT, the edge-site spin pairs are gradually eliminated, the number of carriers decreases, and the Fermi level rises to refill the π -valence band. At an HTT of about 1600°C p-type conduction again dominates and the sign of the TEP changes back to positive. At the same time, the carrier mobilities continue to increase as a result of longer mean free paths in the more orderly structure; this effects the decrease in carrier density and results in a resistivity plateau in both soft carbons and PAN-based fibers. Because the fibers remain frozen in a more highly strained, defect-ridden condition, the carrier density never drops to the low value that occurs in soft carbons; as a result, the conductivity of the fibers is about one order of magnitude larger than that of soft carbon in the plateau region. In addition, nitrogen scattering centers continue to be driven from

the PAN-based fibers up to an HTT of about 1600°C, and somewhat higher HTT's are required to bring the fibers fully to their plateau region.

The carbon fibers refuse to graphitize upon further heat treatment; they remain frozen in a strained condition and p-type conduction remains essentially constant even to an HTT of 3000°C. The soft carbons, on the other hand, begin to rearrange to a more perfect ABA-stacked graphite structure at HTT's above 2000°C. The valence and conduction bands then develop a small overlap, scattering is further reduced as the perfected domains grow, and the Hall coefficient goes through a positive maximum and then becomes slightly negative when the n and p carriers become about equal in density (the n-carriers then dominate because of their greater mobility).

The conductivity of carbon fibers is often considered to be uniquely related to stiffness. However, Cagliostro (7) has found that low-HTT fibers with relatively high resistivity can be made considerably stronger, without affecting resistivity appreciably, by pretreating the PAN fiber with an agent such as benzoic acid, which catalyzes cross-linking, and by carbonizing the fibers in hydrocarbon atmospheres, such as methane or acetylene. Some weight uptake is noted in the latter treatment and the resulting fibers probably have fewer surface defects than normally produced fibers (14).

QUANTUM CHEMISTRY MODELS OF C FIBERS

Buthus and Yang of Surface Analytic Research Inc. have performed some quantum chemical calculations of atomic cluster models of carbon rings with N retained in the structure (15) using a combination of semi-empirical MINDO/3 and HAH/3 programs. They have also looked at highly strained cluster structures. These are based on empirically adjusted Slater-type orbitals, so the results cannot be expected to have high quantitative accuracy. We believe, however, that they suggest some valid qualitative facets of electron distribution geometry that may actually exist in carbon fibers.

At present, the location of nitrogen in the fiber structure is unknown. All we really know is that N atoms are quite numerous in the structure and are rather stably bound (N/C ratios on the order of 0.1 are observed to HTT in excess of 1000°C). The large amount of N retained leads to a consideration of both edge and interior sites for bound N atoms. There is considerable uncertainty whether a mechanism could exist for forming interior nitrogen bridges during the carbonization process (cycl(1,3,3)azine is known to be rather unstable) but a number of stable heterocyclic compounds with bridgehead nitrogen atoms have been synthesized, so the possibility of interior cyclazine-like structures has been left open.

Referring to Fig. 7, the edge sites are calculated to be more energetically favorable than interior sites

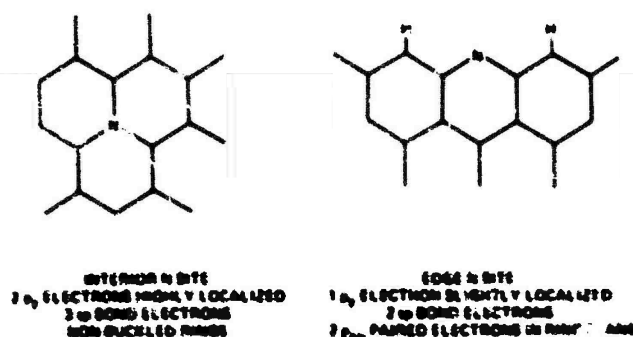


Fig. 7. - Atomic cluster models of carbon fiber electron structure

for N atoms. If this approximate result holds, one would then expect that interior N atoms would most readily leave the structure as HTT increases, or perhaps migrate to edge sites. The rings are not buckled by substitution of N for C, consistent with experimental knowledge of pyridine structures.

The electron distribution of the orbitals indicates that three of the interior nitrogen valence electrons occupy sp hybrid bonding orbitals with neighboring carbons that are quite similar in shape and size to the normal C-C bond orbitals. However, the remaining two valence electrons of nitrogen occupy rather localized and paired p_z states that have very little overlap with the carbon p_z states. Thus, if the interior N are distributed in a random manner, they will provide a random perturbation on the normally periodic potential field that will scatter the conducting electrons and reduce the conductivity. Also, the more localized bonding will tend to locally flatten the π band. The first consequence of band flattening is that the effective carrier mass increases (effective mass is inversely proportional to the curvature of carrier energy versus momentum) and the mobility is thus lowered. A second consequence is that a flatter band opens up the band gap, the effective band gap increases, and at any given temperature the electron density in the conduction band is decreased. All these effects tend to reduce conductivity.

At an edge-located nitrogen on the other hand, two valence electrons occupy rather normal s-p hybrid bond orbitals with neighboring carbons, two more occupy spin-paired p_{xy} orbitals lying in the plane of the ring with a geometry and size rather similar to the paired electrons in a normal C-H bond, and the final valence electron of N occupies a single p_z orbital (out of the ring plane) that is only slightly localized. Thus, an edge-located nitrogen is expected to behave electronically almost the same as an edge C-H group; the principal effect on conductivity is that fewer unpaired states will exist at the edge sites leading to fewer holes in the valence band and therefore lower conductivity. In either case, the removal of nitrogen by high HTT should increase conductivity, a result consistent with experiment.

The original PAN starts with a C-to-N ratio of 3:1. During carbonization, nitrogen is driven off in quantity, but a sizable fraction of N remains even at HTT's exceeding 1500°C, consistent with the known stability of nitrogen in C-ring structures. Typical C-to-N ratios in the fibers finished at low to moderate HTT may range (approximately) from 2:1 to 12:1. From knowledge of domain size, we conclude that there are not enough edge sites to accommodate all these N atoms, so at least some of them may be located at interior sites. However, at the highest HTT the nitrogen will be progressively driven out and replaced by carbon or by free radical sites, in either case leading to an increase in conductivity. These calculations of nitrogen in the structure are merely precursors of the kind of information that will increasingly flow from the rapidly developing science of quantum chemistry applied to polymer molecules.

INTERCALATION OF CARBON FIBERS

Graphite is known to intercalate compounds such as metal halides and HNO_3 . If one edge of the graphite is sealed, the intercalation is greatly reduced. In this respect, some pitch-based fibers behave like unsealed graphite and can take up large amounts of intercalant (of the order of 100% or more) and like graphite these fibers tend to exfoliate in the process. High-stiffness PAN-based fibers, on the other hand, accept smaller amounts of intercalant (5% to 20%), similar to the amount taken up by edge-sealed graphite. In both graphite and carbon fibers these intercalants increase

the conductivity, presumably due to the perturbation broadening of the bands and by providing band-gap energy states (or increased band overlap in the case of graphite). Thompson (16) found that modest decreases in conductivity (~2%) can be obtained in PAN fibers intercalated with FeCl_3 , or AlCl_3 , and subsequently oxidized at 320°C for 16 hr. He obtained a somewhat larger decrease in conductivity (20%) by treating PAN fibers in HNO_3 /fuming H_2SO_4 mixtures up to 1 hr, after which no fiber decomposition occurred. Vogel (17) reports similar results. These oxidation treatments probably localize a fraction of the π electrons in the structure, but enough normal π electrons remain to keep conductivity relatively high. The oxidized pitch fibers show much greater decreases in conductivity (~50%) but at the expense of fiber deterioration.

CONCLUDING REMARKS

As an empirical science, carbon-fiber technology is well advanced. Inexpensive fibers can be made with a wide range in the values of elastic modulus, tensile strength, and thermal and electrical conductivity. When the fibers are blended with chemically inert matrix polymers, the composite materials are very stiff, strong, and inert — at least at normal temperatures. Some problems in matrix-fiber interface bonding remain as well as problems in polymer stability at elevated temperatures, at high photon or particle radiation fluxes, or in a periodically moist-dry environment. However, the current composites perform very well in environments that are moderate in temperature, radiation and weathering conditions.

From a basic physics and chemistry viewpoint, carbon-fiber science is still immature; much remains to be learned about fibers before we will know how to optimize their characteristics. Numerical quantum chemistry is just now developing to the point where it can help provide some of this basic knowledge.

Many important applications for carbon-fiber polymer matrix composites exist. Among the more spectacular are (1) in materials for aircraft construction that could reduce aircraft weight by as much as half, thus greatly improving performance; (2) in materials for battery plates that might reduce battery weight per unit energy by a factor of 3 or more and perhaps open an era of useful electric vehicles and more economical electric energy storage; (3) in noncorrosive materials for desalination plants or other chemical plants where the processing of corrosive materials imposes high maintenance costs and short lifetimes for metal parts; and (4) consumer products, such as tennis rackets, skis, and, perhaps, futuristic strong, lightweight automotive vehicles with improved fuel mileage.

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ABSTRACT

The value of resin/carbon-fiber composites as lightweight structures for aircraft and other vehicle applications is dependent on many properties: environmental stability, strength, toughness, resistance to burning, smoke produced when burning, raw material costs, and complexity of processing. In the work reported here, a number of woven-carbon-fiber and epoxy-resin composites were made. The epoxy resin was commercially available tetraglycidylmethylene dianiline. In addition, composites were made using epoxy resin modified with amine and carboxyl-terminated butadiene-acrylonitrile copolymer. Strength and toughness in flexure as well as Oxygen Index Flammability and NBS smoke chamber tests of the composites are also reported.

SUBSTANTIAL WEIGHT AND FUEL SAVINGS can be achieved by using lightweight resin-fiber composite materials in place of metal components in transport aircraft (1).^{*} Design requirements for the composites include high strength, toughness, environmental stability, and resistance to burning. A number of investigators have studied the effect on the toughness of resins of adding liquid rubber (2-11). The use of butadiene acrylonitrile rubbers with terminal reactive groups will toughen epoxy resins by bonding the rubber and the glassy polymer. The two-phase system of brittle epoxy resin and rubber microgels increases the impact strength by means of a crack-terminating mechanism. These studies include the effect of the modification of diglycidyl ether of bisphenol A (DGEBA). It has also been reported that highly cross-linked epoxy resins such as tetraglycidylmethylene dianiline (TGMDA) have very high modulus, but it is attained at the expense of toughness (12).

In this investigation we studied the properties of TGMDA modified with liquid rubber. The TGMDA was modified with amine-terminated (ATBN) and carboxyl-terminated (CTBN) copolymer of butadiene and acrylonitrile. ATBN is a reactive liquid copolymer having terminal secondary amine groups, tertiary amine groups, and amide groups in the chemical structure; ATBN will react with epoxy resins. CTBN is a reactive liquid copolymer with terminal carboxyl groups. The reactions of CTBN with epoxy resin is well documented (11). The room temperature flexural strength and toughness of the modified TGMDA were determined; thermal stability, flammability, and smoke tests were also conducted.

EXPERIMENTAL

Composites were prepared using commercially available epoxy resin (TGMDA) and woven graphite cloth. The woven graphite cloth was an 8-harness satin weave cloth prepared from Celion[†] 3000 fiber (yarn count - 24 x 24).

^{*}Numbers in parentheses designate references at end of paper.

[†]The use of trade names or names of manufacturers in this report does not constitute an official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration.

The standard epoxy resin varnish was modified with 2, 5, and 10 parts per hundred ATBN (B. F. Goodrich, Hycar ATBN, 1300 x 16) and CTBN (B. F. Goodrich, Hycar CTBN, 1300 x 8). The epoxy-resin/ATBN was cured with diaminodiphenyl sulfone (DDS) and the epoxy-CTBN was cured with trimethylaminomethyl phenol (DMP-30). The chemical structures of the resin and the liquid-rubber copolymers are shown in Fig. 1, and the composite fabrication procedure is given in Table 1. In all cases the composites were prepared by coating the woven graphite cloth with the resin-solvent varnish, staging the cloth or "pre-preg," and curing the composites, using heat and pressure.

The evaluation of the epoxy-graphite composites consisted of (1) glass transition temperature of the resin (Dynamic Mechanical Analysis), (2) oxygen index flammability (ASTM D 2863), (3) NBS smoke test, (4) boiling water stability (ASTM D2344), and (5) flexural strength (ASTM D 790-70).

Because composite materials exhibit large deflections during testing, at least in some cases, a four-point loading system - utilizing two load points equally spaced from their adjacent support points, with a distance between load points of one third of the support span - was used. An Instron testing machine with the constant rate of crosshead movement was used. Span distance was 3 in.; the total length of the specimen was about 4 in., and the width was about 0.5 in.

The Instron instrument is capable of automatically recording crosshead motion as a function of the load; however, the true deflection is also recorded on the chart by the operator, using an electrically operated pen marker.

Flexural strength is equal to the maximum stress in the outer fibers at the moment of break. It is calculated using the following equation:

$$\text{Flexural strength} = PL/bd^2 \text{ (lb/in.}^2\text{)}$$

where

P = the load at the moment of break, lb
L = support span, in.
b = width of beam, in.
d = depth of beam, in.

Tangent modulus of elasticity is calculated using the following equation:

$$E_B = \frac{0.21 L^3 m}{b d^3}$$

where

E_B = modulus of elasticity in bending, psi
m = slope of the tangent to the initial straight-line portion of the load-deflection curve, lb/in.

and L, b, and d are defined above.

The maximum strain in the outer fibers occurs mid-span and is calculated as follows:

$$r = \frac{4.70 Dd}{L^2}$$

where

r = maximum strain in the outer fibers, in./in.
 D = maximum deflection of the center of the beam, in.
 L = support span, in.
 d = depth, in.

Fracture toughness is calculated using the following equation where σ = stress and ϵ = strain:

$$\begin{aligned} \text{Fracture toughness} &= \int_{\epsilon=0}^{\epsilon \text{ at break}} \sigma \, d\epsilon \\ &= \int_{\Delta L=0}^{\Delta L \text{ at break}} \frac{P}{A_0} d\left(\frac{\Delta L}{L_0}\right) \\ &= \frac{1}{A_0 L_0} \int_{\Delta L=0}^{\Delta L \text{ at break}} P \cdot d(\Delta L) \end{aligned}$$

$$\frac{\text{toughness or breaking energy}}{\text{volume of sample between span}} = \frac{\text{integrated area under the load versus elongation curve}}{\text{(area of cross section) (span)}}$$

Where P is in pounds, ΔL is in feet, and fracture toughness is in foot-pounds per cubic inch.

Modulus of elasticity values inform the designer how much dimensional stability is attainable if a particular composite material is used in a structure; that is, how much the structure would deflect under the application of flexural load. A very low E value would lead to sagging of the whole structure under load, and sagging leads to failure of the structure, even under the application of a small fraction of the allowable load. Normally, the highest E values attainable are preferred because they lead to stiff and dimensionally stable structures.

The maximum strength values are important in determining the factor of safety and allowable load levels. Fracture toughness, or the total energy expended per unit volume before fracture, gives an approximate but important clue to the behavior of the material under different strain-rate conditions, such as creep or impact. For example, if two composite materials have different values of fracture toughness, the material with the higher toughness value will withstand impact more effectively and will withstand creep loading at the same temperature for a longer time. Normally, the composite material with higher modulus of elasticity, maximum strength, and fracture toughness is preferred.

TEST RESULTS

Flammability, thermochemical, and mechanical tests were performed on both the neat resin used to make the composites and on the resin-graphite fabric composites. Results of the flammability, thermal stability, and smoke tests are given in Table 2.

Thermal stability of the neat resin was determined by thermogravimetric analysis in nitrogen at a heating rate of 10°C/min; it is reported as char yield (ash residue at 1073 K). The char yield ranged from 17.6% for the TGMDA modified with 10% ATBN to 24% for the TGMDA modified with 10% CTBN. The char yield of the control epoxy resin was 20%.

The glass transition-temperature (T_g) was determined with composite specimens, using dynamic mechanical analysis (DMA). DMA, which measures modulus and

damping, provides a means for quickly determining transition temperature (13). The glass transition-temperatures ranged between 416 K for the control and 491 K for the 5% ATBN-modified system.

The flammability tests (oxygen index) were performed according to ASTM D 2863. Of the neat-resin samples, the control had the highest value (oxygen index 28) of all the samples. This was also true when the resins were tested as composites. The oxygen index tests indicated that addition of the rubber modifiers will lower the flammability properties slightly.

The smoke tests were performed using composite specimens in the NBS-Aminco smoke density chamber. This smoke chamber and the testing procedures are well defined in the literature (1, 14, and 15). All samples tested were evaluated as very good, with specific optical density (D_s) less than 10 after a 4-min exposure to a heat flux of 2.5 W/cm². The addition of the rubber to the epoxy had no measurable effect on the amount of smoke generated by burning the composites.

Moisture absorption was determined by placing test specimens in boiling demineralized water and by periodically removing them, wiping off surface moisture, and weighing them. The test results are shown in Fig. 2. The amount of moisture absorption in boiling water for the rubber-modified epoxy resin was similar to that of the control. After 24 hr, the moisture absorption was about 1%; it increased slightly after the third and fourth days and remained constant in the range of 1 to 1.8%.

Table 3 lists the flexural strength, modulus, and maximum strain of the ATBN-modified epoxy-resin composites. An increase in ATBN results in a corresponding increase in flexural strength. The higher value of the control compared with the 2% ATBN is attributed to different production methods: the control was commercially produced and the modified samples were prepared in the laboratory. The addition of the rubber slightly increased the modulus of elasticity, and the maximum strain was essentially unchanged.

Toughness in flexure of the ATBN-modified epoxy composites is given in Fig. 3. An increase in toughness is observed as the amount of ATBN is increased. Toughness is determined by dividing the integrated area under the load-versus-elongation curve by the volume of the span.

CONCLUSIONS

These preliminary results indicate that the use of the amine-terminated reactive liquid rubber polymers increases the flexural strength and toughness of epoxy-resin/carbon-fiber composites. There was a slight loss in flammability properties, but the values for smoke, boiling water stability, and thermal stability characteristics were as good as or better than those of the control.

Future work will include evaluation of the properties of carboxyl-terminated rubber polymers as an epoxy modifier; and flexural and tensile tests, at elevated temperatures, of the amine-terminated copolymer.

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Table 1 - Composite Processing

Sample	Formulation, in parts	Staging time	Cure Cycle
Control	100 TGMDA 30 DDS 87 MEK	5 min at 353 K+ 10 min at 393 K	345 kPa (50 psi) 2 hr at 450 K
2% ATBN	100 TGMDA 30 DDS 2.6 ATBN 88 MEK	Same	Heat to 450 K at contact pressure, hold 5 min, 345 kPa (50 psi)
5% ATBN	100 TGMDA 30 DDS 7 ATBN 91 MEK	Same	Same
10% ATBN	100 TGMDA 30 DDS 14 ATBN 96 MEK	Same	Same
2% CTBN	100 TGMDA 5 DMP-30 2 CTBN 107 MEK	10 min at 353 K	345 kPa (50 psi) 2 hr at 450 K
5% CTBN	100 TGMDA 5 DMP-30 5 CTBN 110 MEK	Same	Same
10% CTBN	100 TGMDA 5 DMP-30 11 CTBN 116 MEK	Same	Same

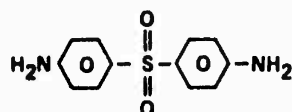
Table 2 - Thermal Properties

Sample	Char yield, % 1073 K, N ₂	T _g °K (°F)	Heat	Oxygen index, composite (resin content)	Smoke, D _s 2 min 4 min		Smoke, max D _s (time, min)
Control (TGMDA)	20	416 (289)	28	40 (32)	0	3.2	168 (17)
2% TBN	23	452 (354)	27	37 (29)	0	2.1	151 (20)
5% ATBN	22	491 (424)	26	37 (29)	0	6.5	188 (20)
10% ATBN	17	461 (370)	27	36 (33)	0	5.2	229 (18)
2% CTBN	23	454 (357)	25	34 (34)		---	
5% CTBN	18	468 (383)	24	35 (34)	0.3	1.5	146 (20)
10% CTBN	24	459 (367)	26	34 (34)		---	

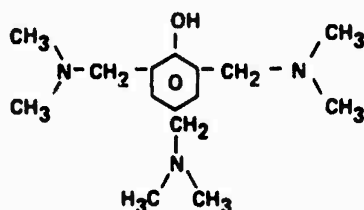
Table 3 - Flexural Properties

Material	Flexural strength, MPa (10^3 psi)	Modulus of elasticity, GPa (10^6 psi)	Max. strain, cm/cm, $\times 10^{-2}$
TGMDA/DDS/satin weave carbon cloth	600.0 $\pm$ 43.4 (87.04 $\pm$ 6.3)	62.5 $\pm$ 2.2 (9.07 $\pm$ 0.32)	1.143 $\pm$ 0.141
TGMDA/DDS/2% ATBN/satin weave carbon cloth	541.7 $\pm$ 37.2 (78.56 $\pm$ 5.4)	66.6 $\pm$ 1.6 (9.66 $\pm$ 0.23)	1.049 $\pm$ 0.076
TGMDA/DDS/5% ATBN/satin weave carbon cloth	624.0 $\pm$ 22.1 (90.49 $\pm$ 3.2)	70.6 $\pm$ 3.9 (10.24 $\pm$ 0.56)	1.114 $\pm$ 0.049
TGMDA/DDS/10% ATBN/satin weave carbon cloth	677.7 $\pm$ 12.4 (98.28 $\pm$ 1.8)	69.9 $\pm$ 2.7 (10.14 $\pm$ 0.39)	1.108 $\pm$ 0.037

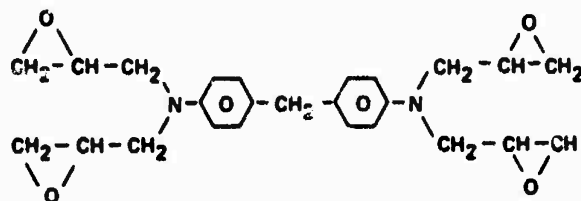
① DIAMINO DIPHENYL SULFONE (DDS)



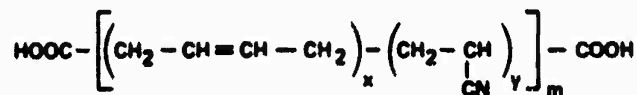
② TRIDIMETHYL AMINO METHYL PHENOL (DMP-30)



③ TETRAGLYCIDYMETHYLENE DIANILINE (TGMDA)



④ CARBOXYL-TERMINATED, LIQUID COPOLYMER OF BUTADIENE AND ACRYLONITRILE (CTBN)



⑤ AMINE-TERMINATED BUTADIENE/ACRYLONITRILE (ATBN)

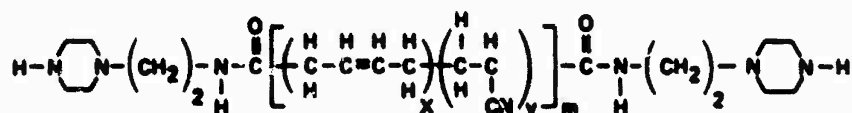


Fig. 1 - Chemical structures

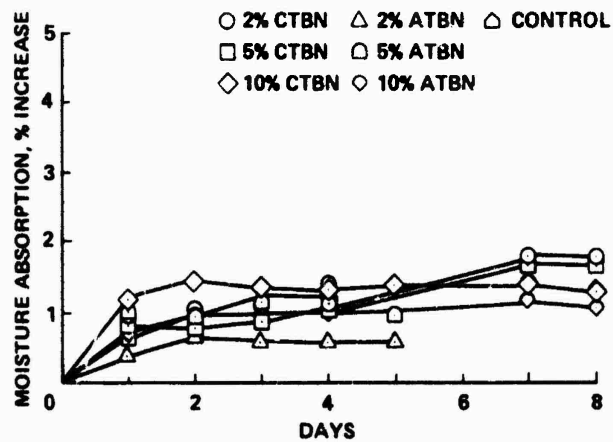


Fig. 2 - Boiling water moisture absorption

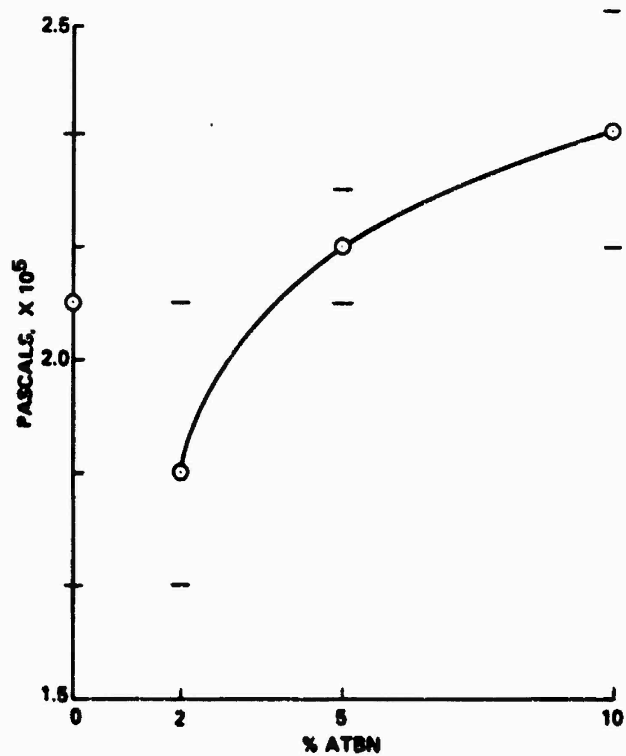


Fig. 3 - Toughness in flexure ATBN modified epoxy

IMPROVING THE FRACTURE RESISTANCE OF COMPOSITE LAMINATES

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ABSTRACT

The fracture process in composite laminates generally involves the initiation, growth, and accumulation of cracks by several competing fracture mechanisms. Although final tensile failure must involve cracking of reinforcing fibers, much composite damage in the form of transverse ply cracks and delamination between plies is associated with a matrix (or fiber-matrix interface) controlled fracture process. The initiation and growth of these matrix dominated cracks are a cause of great concern because, under more complex structural loads, they may lead to catastrophic failure; while in other cases, they may cause degradation of the mechanical properties of the laminate.

Recent studies in the United States and Great Britain have demonstrated that successful prediction of the onset and growth of matrix dominated transverse cracks and delamination must account for size effects which cannot be determined from stress analysis alone. Linear elastic fracture mechanics concepts have been applied to the analysis of crack initiation and growth and have proven useful in predicting the load levels at which individual fracture mechanisms become operative and the sequence of these events.

These concepts are applied here to assess several alternate means of toughening composite laminates to matrix controlled fracture. These methods can be applied at three levels: (1) at the laminate level, by varying ply stacking sequence; (2) at the ply level, by decreasing ply thickness and by use of rubber modified polymer matrices reinforced by woven fibers; and (3) at the microstructural level, where toughness can be improved by increased fiber-matrix bond strength, increased compressive interface residual stress, and matrix toughening agents which act on a scale comparable to the interfiber spacing.

(Text was not provided for publication.)

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For the purpose of this discussion, advanced composites are defined as a combination of resins and continuous fiber reinforcement all or part of which is graphite fiber.

In attempting to make the transition from the use of these composites in aerospace applications to the automotive (and truck) industry, the vast differences in regard to both the number of units produced and the premium the manufacturer is willing to pay for weight saved must be recognized. Over the next decade, it is probable that no more than 50 Space Shuttle vehicles will be built. Because weight is a paramount factor, a premium of \$1,000 to \$2,000 is a reasonable estimate of what the producer would pay for a pound of weight saved. For commercial aircraft, it is difficult to predict the number to be built in the 1980's. However, let us assume that it will not exceed the entire jet fleet built since 1958 (about 5,000 planes). For this application, plane builders appear willing to pay between \$100 and \$200 per pound of weight saved. By contrast to these, the total production of cars and trucks in an average year is about 10 million units. Automotive manufacturers would prefer to pay a premium for weight savings of only fifty cents per pound but might consider a one dollar premium.

With this background, the weight saving obtained when various materials are used in place of steel is presented in Table I. This comparison is based on a fixed volume part and it is clear that a very substantial weight saving can be attained with any of the substitutes. However, when economic factors are applied (Fig. 1), things are quite different. Data for these curves are based on fiber suppliers' estimates, data from American Institute for the Steel Industry, aluminum manufacturers, etc. for the period 1978 to 1988. The plot for "composite" is based on an 80:20 by weight mixture of fiberglass and graphite fiber reinforcement. An all graphite part is impractical as indicated by the two asterisks on the curve. For 1978, the raw material cost of the resin-graphite combination was \$18/lb. and drops to \$6/lb. by 1988.

From Fig. 1, it can be seen that only fiberglass composites can replace steel in a part where the only criteria are weight savings and low cost. Therefore, it is apparent that advanced composites will be used only where their unique properties such as strength or stiffness are required. Therefore, in Fig. 2, potential costs are examined for a strength specific

part. It is immediately evident that, for this part, aluminum will not be cost effective as a steel replacement any time during the decade considered. However, a part of matching strength can be obtained with the "hybrid" advanced composite which will be cost effective late in the decade. If the \$1/lb. premium is accepted by automotive manufacturers, cost effectiveness for such a part can occur as early as 1981. For a part where stiffness is the major criterion, (Fig. 3) none of the replacements can be used if the economics discussed above are considered. This implies that if advanced composites are to be used in a cost effective manner, the particular part must be designed to take advantage of the attributes of these materials.

Let us examine this aspect in developing a drive shaft for lightweight trucks. The major criteria are (1) stability at a critical speed (5,000-5,700 rpm), (2) strength retention at 250°F after exposure to salt spray, and (3) resistance to torque fatigue both at -40°F and +250°F. In Table II, a steel shaft is compared with a hybrid design. Because the latter provides a greater length of shaft before critical stability is exceeded, a weight saving of 17 pounds (>50%) is achieved as the result of elimination of hanger fixtures and a union between the individual pieces of the steel drive shaft. This design is also cost competitive. However, it should be noted that this analysis assumes that no projections or protuberances occur on the truck bottom which will prevent use of a one-piece shaft. If they are present, the advantage of the composite is considerably diminished as a result of the weight penalty for the union.

In the Rockwell study of such shafts, it became apparent that the state-of-the-art low cost styrene-unsaturated polyesters could not be used because they do not meet the 250°F performance requirement. Aerospace epoxies which meet this criterion are unsuitable not only because of cost but, more so, due to the very slow processing (long cure times, post cures, etc.) that these systems require. There are a very limited number of epoxy resins which do meet both the temperature requirement and can be processed in a reasonably rapid fashion. The high cost of graphite fiber is a fact of life which will diminish with increasing use. However, the surface treatment of the fiber can play a major role in drive shaft performance and care should be given to selection of the proper treatment. Finally, both ends of a drive shaft must be joined to something. This involves U-joints and bonding to the shaft. It was Rockwell's opinion that this could best be achieved by applying adhesive to the joints and then overwrapping with the combination of resin and fiber while the drive shaft was being produced. This approach requires that the adhesive and resin be compatible i.e. cure over the same temperature range, do not inhibit the curing of either or both, and produce a strong bond when tested under the prescribed conditions. That we at Rockwell were able to achieve this is noteworthy and augurs well for the use of advanced composites in automotive applications.

However, there are many problem areas associated with the introduction of these materials and they include cost, the definition of design allowables, adaptation to high volume manufacturing, joining techniques, fatigue/creep behavior, and environmental resistance. Cost has been discussed above. In regard to design allowables, it must be recognized that many steel parts are overdesigned and that a redesign may make it difficult to replace them with composites. As indicated above, automotive production is so large that, without the ability to produce composites in high volume (an as yet unattained goal), there will be no place for these materials in the

automotive market. Prior experience in aerospace has indicated that joining techniques can be difficult with composites. If adhesive bonding is the method of choice, the reliability of such bonds in the environment and over the lifetime of a car (or truck) must be established. Finally, little is known at present about the long term creep and fatigue behavior of advanced composites.

With these problems facing the introduction of advanced composites in the automotive area, it is not surprising that the projection for the period up to 1988 is for relatively slow growth in the use of these materials and for a very careful selection of applications where they will be employed. Broadening the area and increasing the use of advanced composites will occur more rapidly if faster processing resins become available, a better understanding of fatigue/creep behavior is obtained, and if lower cost processing procedures are developed.

Table I

WEIGHT SAVINGS FOR SUBSTITUTE MATERIALS

	<u>PART WEIGHT (FIXED VOLUME), LBS.</u>
STEEL	1
ALUMINUM	0.34
FIBERGLASS/RESIN	0.26
GRAPHITE/RESIN	0.21
GRAPHITE/FIBERGLASS/RESIN	0.237
20 : 80	

Table II

STEEL vs. COMPOSITE- For TRUCK DRIVE SHAFT*

	MAXIMUM LENGTH FOR CRITICAL SPEED, IN.	PART WEIGHT, LBS.
STEEL	67	33 (2 PIECE)
GRAPHITE/GLASS COMPOSITE	81	16 (1 PIECE)

* TUBE, 4" O.D.

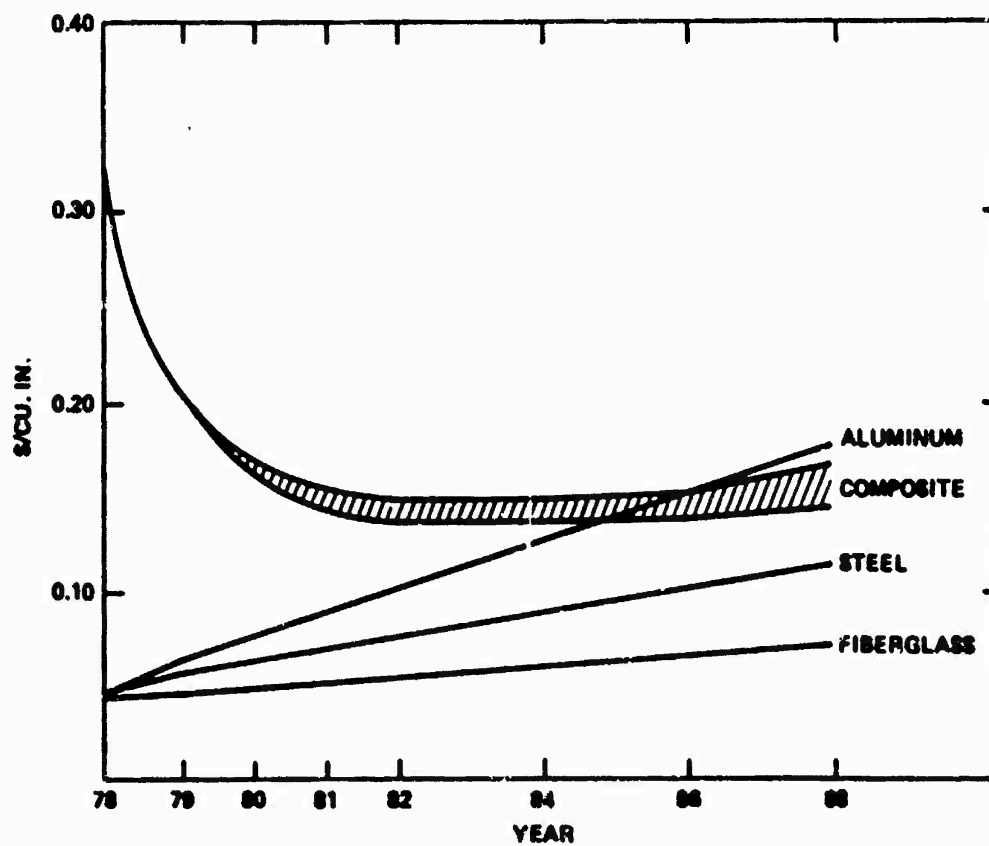


Figure 1

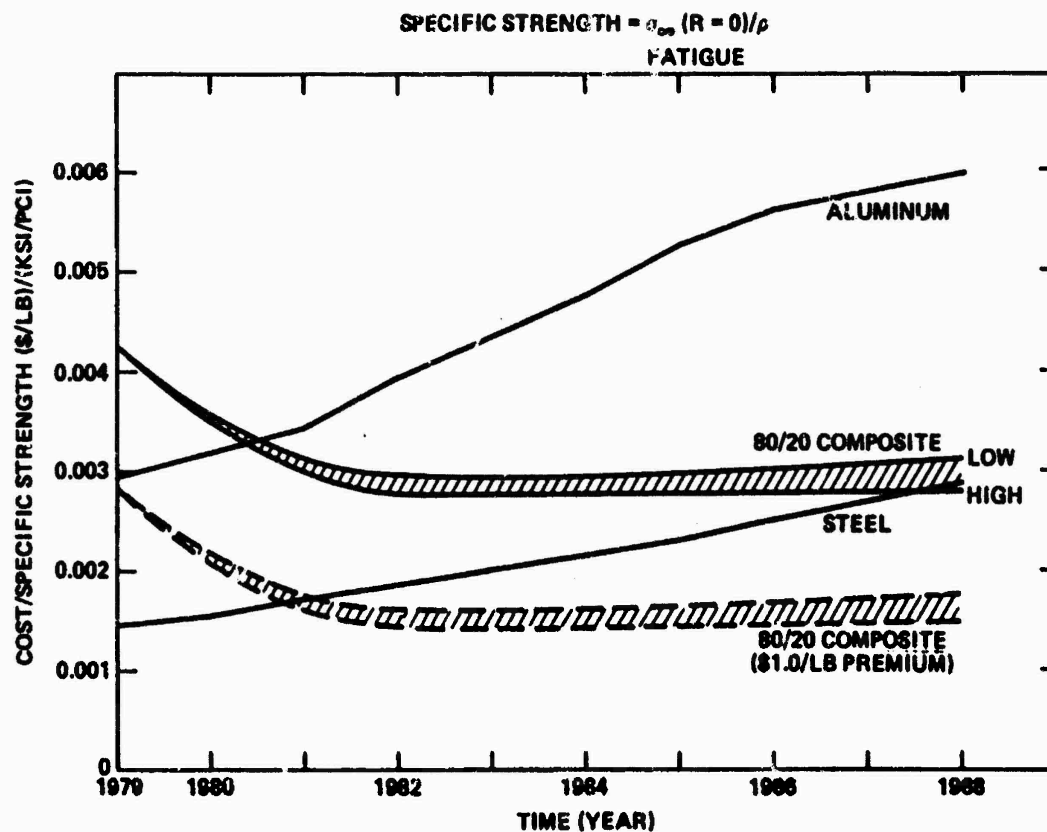


Figure 2

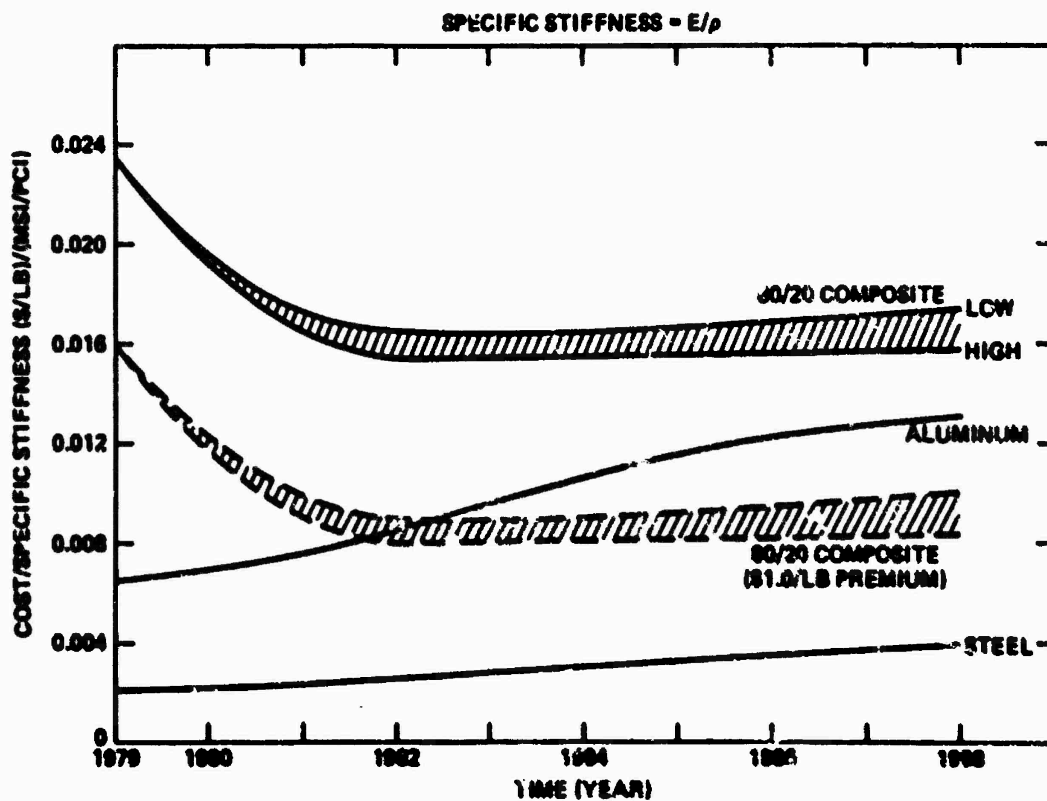


Figure 3

SPATIAL DISTRIBUTION OF VOLATILE COMPOUNDS IN GRAPHITE COMPOSITES*

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ABSTRACT

The distribution of water and other volatile compounds, such as acetone and phenol, was measured as a function of depth in four graphite resin matrix composites. Precision abrasion mass spectrometry was used to qualitatively and quantitatively characterize the indigenous volatile compounds in the as-received condition and after drying in an environmentally controlled oven. The total amount of water in the composites varied from 0.12 wt% (in a phenolicxylok[®] resin) to 1.1 wt% (in a bismaleimide resin) and the times required to dry the samples ranged from less than 96 h (in the bismaleimide resin) to much greater than 555 h (in an epoxy resin).

A NEW ANALYTICAL TECHNIQUE, called precision abrasion mass spectroscopy (PAMS) (1-4), has been used to qualitatively and quantitatively characterize the distribution of indigenous volatile compounds trapped within solid graphite resin matrix composites. Solid samples are precisely abraded within the ion-source housing of a time-of-flight mass spectrometer (TOFMS). The volatile compounds released during abrasion expand into the ion source and are ionized, mass analyzed, detected, and recorded. The H₂O distribution was measured in four composites in the as-received condition (i.e., saturated by exposure to constant humidity for extended periods of time) and after drying in a controlled-environment oven. In addition to water, one test composite contained appreciable quantities of acetone, while another contained phenol and other higher molecular weight aromatic compounds.

*This research was conducted under NASA Ames Research Center Contract NAS A67827B.

EXPERIMENTAL

SPECIMEN DESCRIPTION - The specimens tested were graphite composites which were prepared utilizing the following resin matrices and processing parameters.

Sample 1008-1: The resin used was an amine-cured polyfunctional glycidyl amine-type epoxy resin. This resin is extensively used in the preparation of aerospace graphite composites.

Sample 1004-F: The resin used was a phenolic-xylok[®] resin which is essentially the product of the condensation of dihydroxymethyl-xylene and a phenol (5). These phenolic novolac-type resins are usually cured with hexamethylenediamine to yield thermally stable, cross-linked polymers possessing good long-term performance to 230°C.

Samples 1013-B and 1013-E: The resin used was a bismaleimide resin designated as bismaleimide B. The chemistry of this resin has been described in detail previously (6). Bismaleimide B is a hot-melt maleimide-type resin which forms a low-viscosity fluid when molten. This resin is processed by hot-melt coating techniques into graphite prepreg with excellent tack and drape. Bismaleimide B is a eutectic ternary mixture of bismaleimides. Cure is accomplished by both chain extension and poly-addition. The chemical structures for the resin matrices utilized are shown in Table 1.

PREPREG PREPARATION - All composites were fabricated utilizing 18 layers of plain Thornel graphite designated as style W 134 fabric weighing 180 g/cm². Prepregs were prepared utilizing this graphite cloth as a standard reinforcement in order to assess the effect of resin matrix on the moisture absorption and retention properties of the composites.

Table 1 - Chemical Structures of the Resins Used to Prepare the Graphite Composites

Resin/Curing Agent	Typical Chemical Structure
Epoxy Sample 1008-1	Amine
Phenolic xylok [®] Sample 1004-F	Phenolic
Bismaleimide B Sample 1013-BE	Bismaleimide

The 1008-1 epoxy/graphite was prepared by passing the graphite cloth through a solution of the epoxy resin. The coated fabric was then passed through a vertical drying tower which provided a programmed drying procedure for the prepreg. Drying was accomplished at 120°C for 10 min. The 1004-F phenolic-xyloc®/graphite prepreg was prepared essentially the same as the epoxy/graphite prepreg. The 1013-B and 1013-E bismaleimide B/graphite were prepared by heating a resin solution consisting of 17.4 parts by weight (pbw) of resin, 5.2 pbw diethylene glycol monoethylether, and 12.2 pbw of dioxane at 100°C for 2 h. The impregnation bath is heated to 40°C to prevent the resin from crystallizing.

The prepreps containing the resins described above were laminated using the pressures, curing, and postcuring conditions outlined in Table 2. All laminates fabricated consisted of 18 plies of graphite cloth.

APPARATUS - The sample to be analyzed is precisely abraded inside the ion-source housing of a time-of-flight mass spectrometer while selected ions are continuously monitored. A schematic view of the PAMS system is shown in Figure 1. The sample is mounted on a carefully controlled three-axis stage which can be stepped stepped (3.175×10^{-4} cm) at rates varying from 1 step/min to 4000

steps/s into an end-mill whose rotary speed can be varied from 1 to 3000 rpm. The complete mass spectrum (from 12 to 250 daltons) of the evolved products can be measured, or as many as eight individual ions can be monitored continuously during the abrasion process. Thus, a complete depth profile of the compounds of interest is generated (3). In addition to monitoring the ions of interest, the pressure in the ion source, the stage position, and the stepping rate are monitored by appropriate transducers. The data are processed by a microprocessor (MINC, Digital Equipment Co.), stored in the processor memory, and displayed as text or graphs on a terminal (Digital VT105) and copied on a video unit (Tektronix 4632).

PROCEDURE - Prior to PAMS analysis in the TOFMS, the temperature rise in the samples resulting from the abrasion process is measured. A small hole is drilled into the back side of the composite, and a microthermocouple is imbedded in the hole. The sample temperature is monitored during abrasion while the PAMS system is mounted on a bench jig. The maximum temperature rise, just before the thermocouple is destroyed by the drill, is only 5°C above ambient. Therefore, we conclude that the material observed during abrasion is evolved indigenous compounds and not thermal decomposition products.

Table 2 - Conditions Used to Prepare the Graphite Resin Matrix Composites

Resin matrix	Cure		Postcure
Epoxy (Sample 1008-1)	30 min @ 23°C, 15 min @ 116°C, 45 min @ 116-124°C, 160-200 min @ 177-182°C, cool.	Vacuum Vacuum 6.9 kPa 6.9 kPa Vacuum	None
Phenolic-xyloc® (Sample 1004-F)	1 h @ 82°C, 1 h @ 121°C, 4 h @ 232°C, 4 h @ 246°C, in autoclave	13.8 kPa 13.8 kPa 13.8 kPa 13.8 kPa	6 h @ 175°C 4 h from 175-200°C 13 h from 200-250°C Slow cool down to ambient in air oven
Bismaleimide B (Sample 1013E)	15 min @ 9°C, 80 min @ 150°C, 315 min @ 23°C, in autoclave	Vacuum Vacuum 40 kPa	15 h @ 250°C in air oven

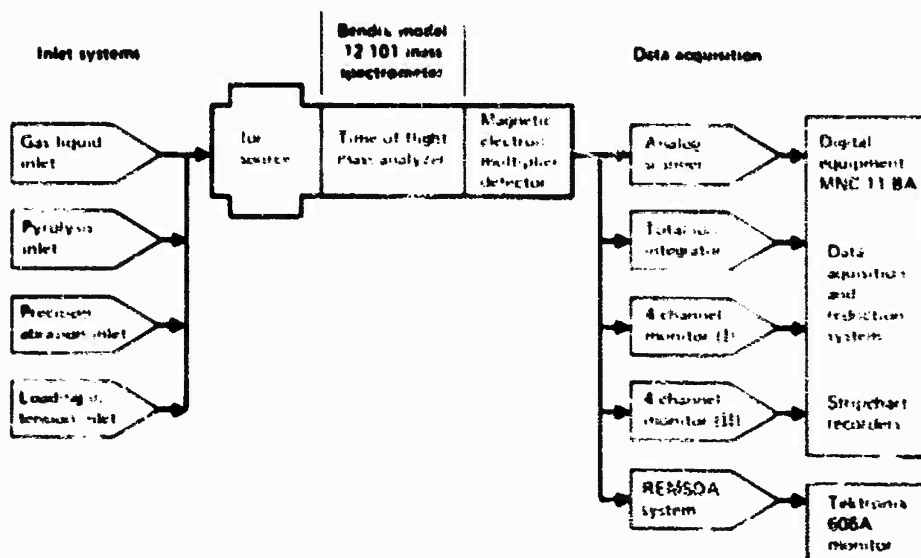


Fig. 1 - Schematic diagram of the Precision Abrasion Mass Spectrometer (PAMS) System

To ensure that volatile compounds are not lost when the sample is exposed to the vacuum in the ion-source chamber [approximately 15-30 min are required to evacuate the system to 1×10^{-4} Pa (10^{-6} Torr) after loading], the sample is covered with a thin cover plate (1-2 mm thick). A sandwich consisting of a cover plate (1 mm), mylar (8×10^{-2} mm), aluminum foil, sample, mylar (8×10^{-2} mm), aluminum foil, and a second cover plate is used. The aluminum foil is electrically connected to a capacitive charging circuit to define the boundaries of the sample, the mylar insulates the aluminum from the sample, and the cover plates minimize the loss of volatile compounds to the source vacuum. During a typical experiment, the material released from both the cover plate and the sample is monitored.

TEST SAMPLES - The distribution of H₂O from a typical sample of a 1013-B graphite epoxy composite is shown in Figure 3 where the weight percent is plotted as a function of depth (mm). The data shown in the legend of this figure are explained in Table 3.

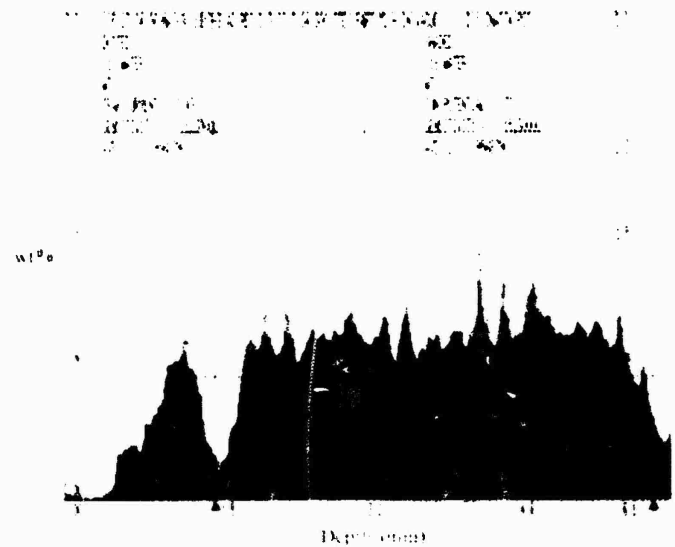


Fig. 3 - Distribution of water in a 1013-B composite

[illegible]

The marks on the abscissa by the dashed lines correspond to the position of the aluminum foil and indicate the surface of the composite. The weight percent water averaged throughout this particular analysis of the 1013-B composite corresponds to 0.97%; however, the average value for eight separate analyses is 1.1 ± 0.1 wt%.

The water distribution was remeasured after the sample was dried at approximately $80 (\pm 10)^\circ\text{C}$ for 96 h; the data are shown in Figure 4. For comparison, the data are shown on the same scale as that used in Figure 3 (the weight percent shown in Figure 4, 2.4×10^{-2} wt%, is more than three orders of magnitude larger than the minimum quantity detectable by PAMS).

The water distribution of a similar composite, 1013-E, in the as-received state is shown in Figure 5; the average water concentration from this particular hole is 0.79 wt%, and the average value of eight separate analyses is 1.1 ± 0.1 wt%, the same as found in the 1013-B series. However, water is apparently more difficult to remove from the B-series than the E-series. The amount of water remaining after a 1013-B composite is heated for 313 h at 80°C is 0.069 ± 0.012 wt% (average of four analyses); the distribution for one such analysis is shown in Figure 6. The large water peaks observed at positions less than 1.5 mm and greater than 6.0 mm are produced by H_2O released from the protective scrap covers.

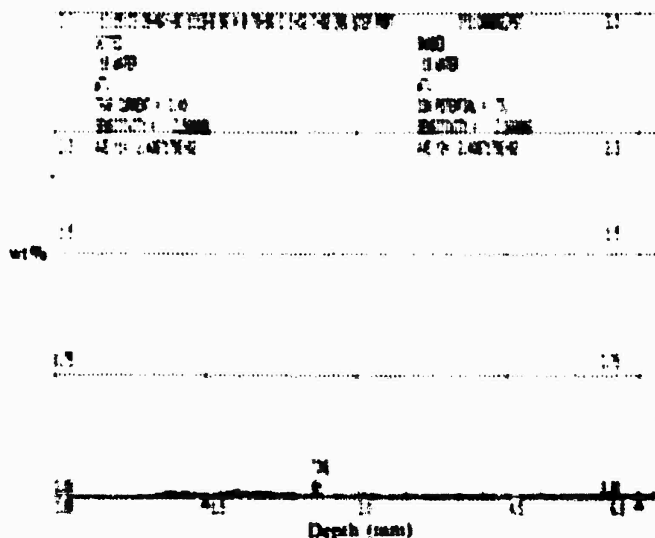


Fig. 4 - Distribution of water in a 1013-B composite after heating 96 h at -80°C

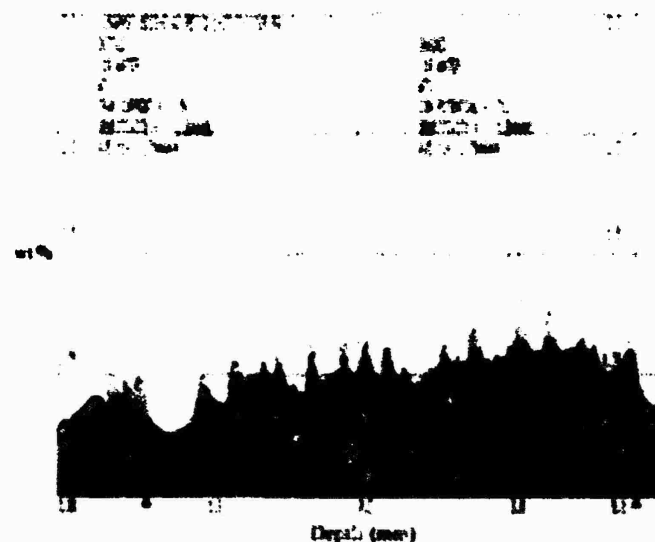


Fig. 5 - Distribution of water in a 1013-E composite

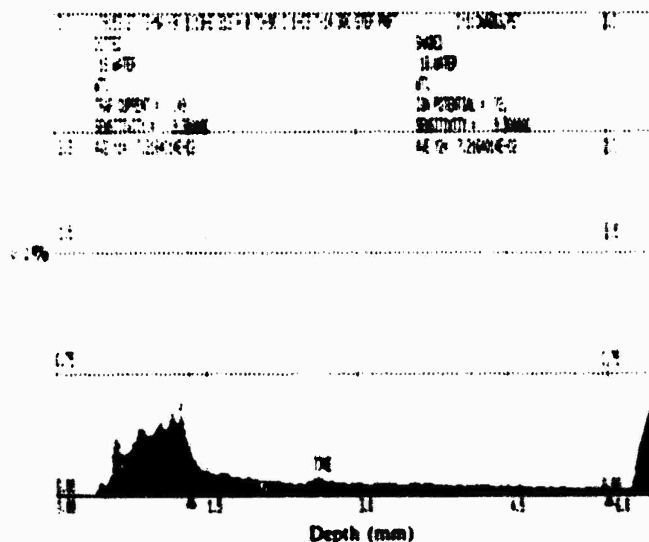


Fig. 6 - Distribution of water in a 1013-E composite after heating 313 h at -80°C

The water distribution from typical as-received and heated 1008-1 composites is shown in Figures 7 and 8 respectively. The bimodal distribution exhibited in the as-received sample suggests that it was not saturated at the beginning of the experiment but the concentration from this particular hole corresponded to 0.29 wt%. The water is tightly held by this material; only one-half is released when it is heated for 555 h at 80°C . The large peak between 0 and 1.3 mm in Figure 8 is due to water in the scrap cover, and the actual water in this sample (between 1.5 and 5.2 mm) corresponds to 0.10 wt%. This particular composite, 1008-1, also exhibited appreciable quantities of acetone, noted by its characteristic ions at $m/z = 58$ and 43. Since the 43 peak is considerably larger than the 58 peak ($43/58 = 3/1$), the acetone concentration is monitored by the ion current at $m/z = 43$. The distribution of acetone in a typical 1008-1 composite is shown in Figure 9. The average acetone concentration corresponds to 0.016 ± 0.003 (average of 15 analyses). No acetone could be detected after the sample was heated at 80°C for 555 h; thus its concentration is less than the minimum detectable quantity, 10^{-5} wt%.

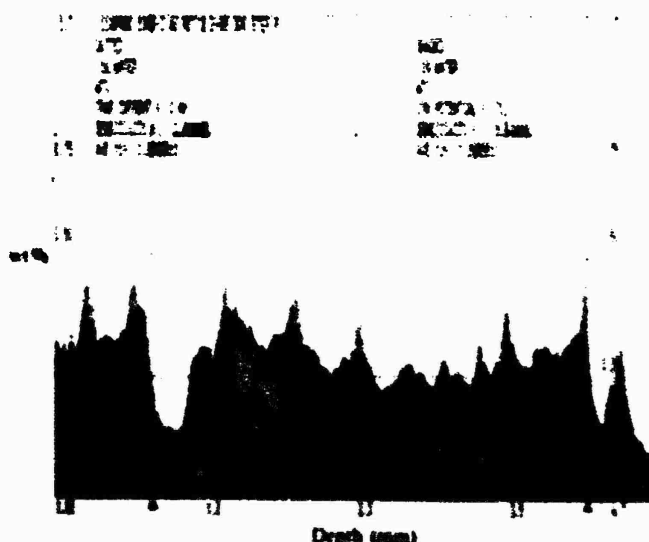


Fig. 7 - Distribution of water in a 1008-1 composite

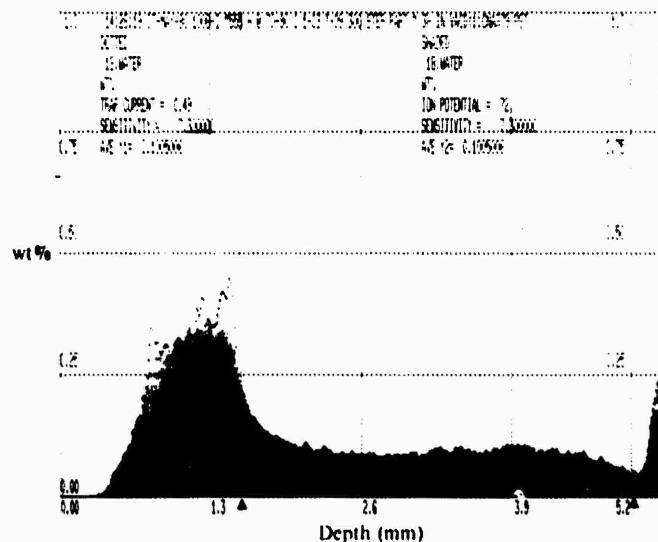


Fig. 8 - Distribution of water in a 1008-1 composite after heating 555 h at -80°C

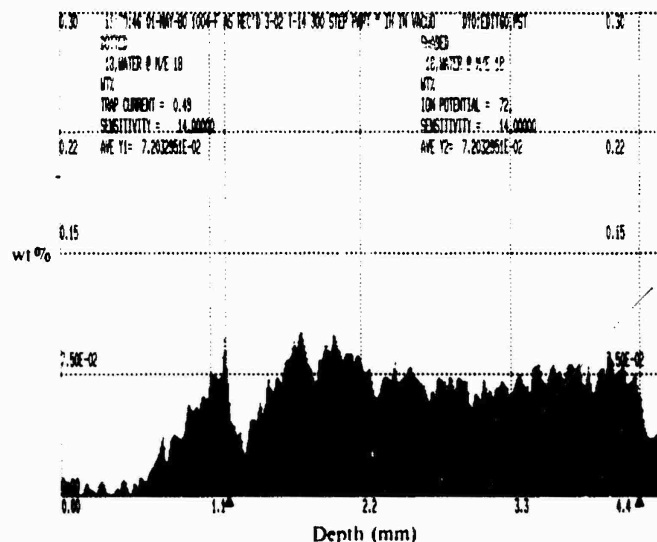


Fig. 10 - Distribution of water in a 1004-F composite

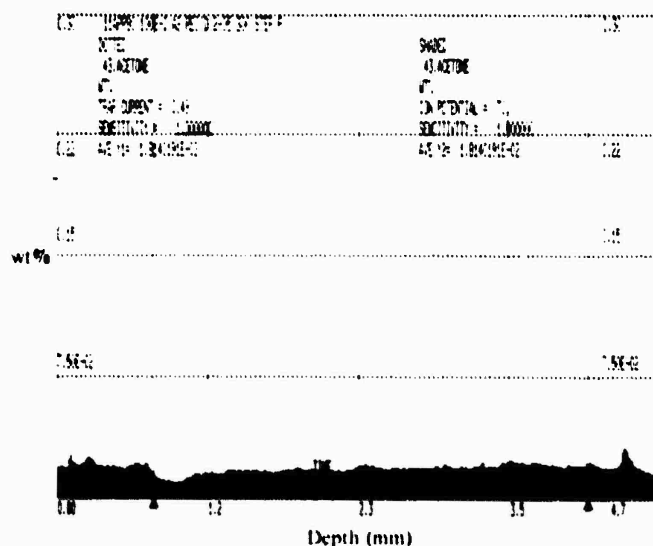


Fig. 9 - Distribution of acetone in a 1008-1 composite

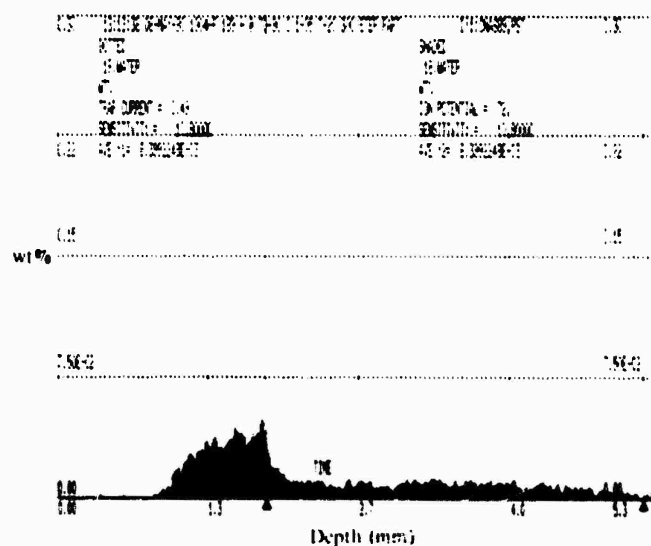


Fig. 11 - Distribution of water in a 1004-F composite after heating 189 h at -80°C

The water distribution in a typical as-received 1004-F composite is shown in Figure 10; the average water concentration corresponds to 0.12 ± 0.02 wt% (average of six analyses). After the sample was heated for 189 h at 80°C , the average water concentration decreased to 0.017 ± 0.003 wt% (average of six analyses); a typical H_2O distribution curve, measured after the 1004-F was heated is shown in Figure 11. No acetone is observed in this composite; however, phenol, toluene, and an unknown ion ($m/z = 132$) are observed.

The distribution of phenol (measured at $m/z = 94$) from a typical as-received 1004-F composite is shown in Figure 12; the average concentration corresponds to 0.0012 ± 0.0004 wt% (average of six analyses). Phenol, a solid at room temperature with a relatively low vapor pressure [less than 150 Pa (1 Torr)], does not evolve from the abraded surface as rapidly as a volatile compound such as water or CO_2 ; however, it is readily detected. The average phenol concentration was reduced to $5.4 \times 10^{-4} \pm 2.3 \times 10^{-4}$ wt% when the 1004-F composite was heated at 80°C for 189 h; a typical phenol distribution is shown in Figure 13.

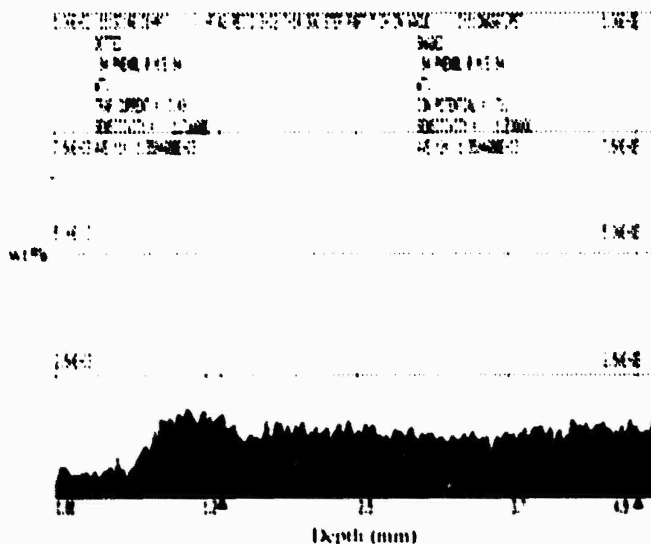


Fig. 12 - Distribution of phenol in a 1004-F composite

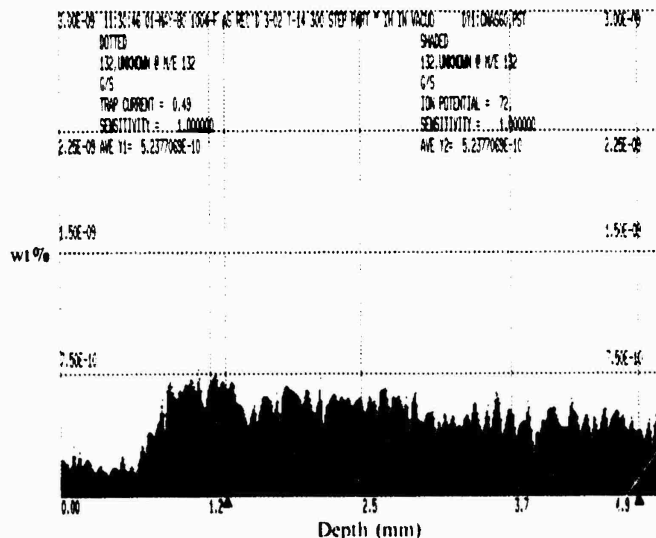


Fig. 14 - Distribution of compound (ion at $m/s = 132$) in a 1004-F composite

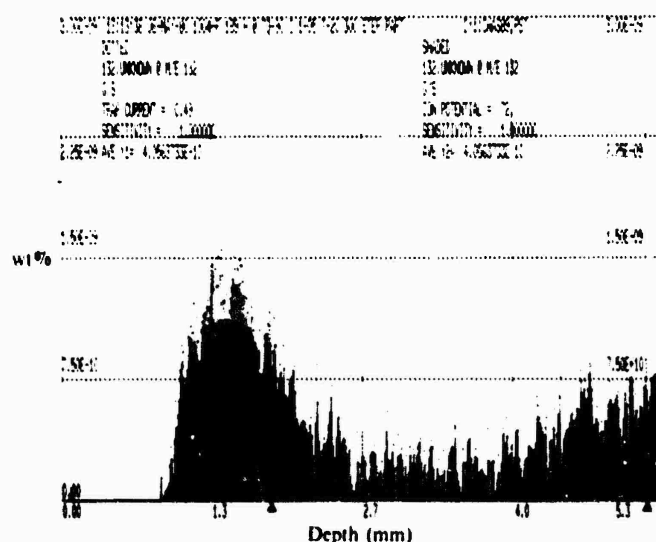


Fig. 15 - Distribution of compound (ion at $m/z = 132$) after heating 189 h at -80°C

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TSCA AND THE PAINT AND COATINGS INDUSTRY

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Government RegulationsAffecting the Paint and Coatings Industry

Federal Hazardous Substances Act	(1960)
Hazardous Materials Control Act	(1970)
Occupational Safety & Health Act	(1970)
Federal Insecticide, Fungicide, and Rodenticide Act	(1947)
Air Quality Act	(1967)
Clean Air Act	(1970, 1977)
Federal Water Pollution Control Act	(1948)
Clean Water Act	(1977)
Resource Conservation and Recovery Act	(1976)
Toxic Substances Control Act	(1976)

ABSTRACT

The Toxic Substances Control Act (TSCA) of 1976 is designed to prevent unreasonable risk to health or the environment stemming from the manufacturing, processing, use or disposal of chemical substances. An inventory of close to 50,000 chemicals currently in commerce in the U.S. has been published by EPA and an analytical search is now underway to identify those considered hazardous to health or the environment. Chemicals found to pose an unreasonable risk will be banned or controlled in some way. To date control action has been taken on polychlorinated biphenyls and chlorofluorocarbons and there are near-term plans for asbestos. Through its pre-manufacture notification provisions, TSCA gives EPA the authority to screen new chemicals before commercial manufacture or importation begins. Of 150 notices received to date, polymers are the largest single class of new substances planned by industry for introduction into commerce.

TSCA AND THE PAINT AND COATINGS INDUSTRY

The paint and coatings industry, like the rest of the chemical industry, is coming under increasing control and regulation by Federal, State and local governments. Personal safety and health and protection of the environment are the goals established by Congress in enacting the various laws which impact on industry. And there are a number of laws some of which I have indicated on this first table. (Table 1)

The Federal Hazardous Substances Act of 1969 now administered by the Consumer Product Safety Commission defines as hazardous all products which would cause substantial personal injury or illness through handling or use. Transportation of flammable chemicals and other dangerous materials is regulated by the Hazardous Materials Control Act of 1970. The Occupational Safety and Health Act of 1970 sets workplace standards to protect workers in the production and use of various materials and products. The Federal Insecticide, Fungicide and Rodenticide Act of 1947 administered by EPA requires the registration of chemicals used for these purposes and exercises strict control over their use. The Air Quality Act of 1967 with amendments added by the Clean Air Act of 1970 and 1977 establishes national standards for air quality to protect public health. Similarly, the Federal Water Pollution Control Act of 1948 with several amendments including the Clean Water Act of

1977 was enacted by Congress to achieve high water effluent guidelines. The Resource Conservation and Recovery Act of 1976 provides technical and financial assistance for the development of management plans and facilities for recovery of energy from discarded materials for recovery of energy from discarded materials and to regulate management of hazardous waste.

Perhaps the most important recent legislation affecting the chemical industry is the Toxic Substances Control Act of 1976, TSCA as it is called, which is designed to prevent unreasonable risk of injury to health or the environment stemming from the manufacturing, processing, use or disposal of chemical substances. This is the law I shall cover today to discuss its potential impact on the paint and coatings industry. I say potential impact because EPA is just in the early stages of implementing this complex act.

However, before I discuss TSCA, let me orient you with respect to the paint and coatings industry. (Table 2) It is one of the older and smaller segments of the broad chemical industry characterized by relatively slow, stable growth geared directly to overall economic conditions. The value of shipments in 1978 is estimated to have been about 5.3 billion dollars representing about 5% of the business volume of the chemical industry.

The paint and coatings industry is also one of the least concentrated sectors of the chemical industry. There are roughly 1,300 companies in the paint and coatings business. In 1978, the top four companies accounted for 30% of the total value of industry shipments and the top 20 firms did 62% of the total. This is in sharp contrast to most sectors of the industry in which the value of shipments is concentrated - more than 75% - in the top 10 firms.

The U.S. Paint and Coatings Industry

(1978)

Sales

Architectural paints	\$2.2 MM
Product finishes	2.1 MM
Special purpose coatings	1.0 MM
Total	\$5.3 MM

Top 4 companies	\$1.6 MM (30%)
Next 5 companies	0.9 MM (17%)
Next 10 companies	0.8 MM (15%)
Remaining 1,280 companies	2.0 MM (38%)
Total	\$5.3 MM (100%)

Companies 1,300

Employees 60,400

This meant that about one-third of the paint and coatings business in 1978 was handled by over 1,200 companies averaging about 1.5 million dollars in sales. So it is not surprising that most of the manufacturing plants have fewer than 50 employees.

I should point out that high transportation cost is one of the reasons for the existence of these many small companies and their wide geographical distribution. Another important reason is that most of these companies are formulators of paint and coating compositions designed to meet specific end use requirements and they are not manufacturers of the basic polymers and other ingredients. Under TSCA, therefore, most of these companies are classed as processors of chemicals and not manufacturers.

An important feature of this industry is that it is one of the more innovative as manufacturers and processors have developed new products and new technology to meet the demands of government safety and pollution regulations and spiraling energy and labor costs. Complicating the picture is the wide diversity of end use and application requirements as well as the ever present market demand for improved coating performance.

The general trends in the industry however, are clear as solvent-based systems with their inherent safety and pollution problems are being replaced with aqueous-based systems, high-solid content liquid coatings, and powder coatings. By 1995, industry sources predict the use of solvents in paints and coatings is expected to be less than one-third of the total U.S. industry production with water-based systems accounting for one-third, and the remaining one-third comprised of high-solids and powder coatings.

Keeping these characteristics of the paint and coatings industry in mind, let me discuss the implementation of TSCA as it is being carried out by the Environmental

An initial inventory has been compiled of all chemicals manufactured, imported or processed for commercial purposes in the U.S. We expect to publish within the next several months a final revised inventory. Thirty days after this is published it will be unlawful to manufacture, import, process or use any chemical not on the list.

So for the first time, all of us in the U.S. know exactly what chemicals and roughly how much of these chemicals are in our marketplace. However, the extent to which we are exposed to these chemicals or how much is lost to the environment each year is unknown.

For the most part we know the general hazards associated with these chemicals such as their flammability, corrosiveness, instability and so forth and even the more common acute health effects such as skin and eye sensitivity, inhalation and ingestion effects. But we are largely ignorant of both chronic health effects, including carcinogenicity, and effects of these chemicals on our environment.

It is exactly this situation we find ourselves in that prompted Congress after five years of debate to enact the Toxic Substances Control Act in 1976. The policy is clearly stated in Section 2 of this Act. (Table 3)

Table III

Toxic Substances Control Act (TSCA)October 11, 1976Congress Adopted the Policy -

- that adequate data should be developed by industry on the health and environmental effects of chemical substances.
- to provide adequate authority to control chemicals that pose an imminent hazard or an unreasonable risk to health or the environment.
- to exercise this authority in a way that does not unduly impede or create unnecessary economic barriers to technological innovation.

Those of you who are familiar with this Act will recognize the critical importance of the term "unreasonable risk" and the honest debate going on today to translate this into a broadly acceptable and measurable parameter. And, the third policy statement reflects the concern Congress has with the evergrowing regulatory burden being placed on U.S. industry.

This concern was made clear in the statement of intent for this law in charging the Administrator "to implement TSCA in a reasonable and prudent manner...taking into

consideration the environmental, economic, and social impact of any action."

There is general agreement that smaller business firms are harder hit by government regulations and Congress recognized this by including provisions within TSCA designed to minimize the regulatory burden on small business. This is especially true of EPA's efforts to simplify record-keeping and reporting requirements for those manufacturers and processors who qualify as small business concerns.

The Agency has proposed several rules to implement various sections of TSCA. Our procedure is to hold informal discussions between the EPA people assigned to rule proposals and knowledgeable members of industry and public interest groups prior to formal proposals in the Federal Register. In these give-and-take sessions, many viewpoints are expressed as all parties search for a fair and workable common ground of final regulations. I don't mean to give you the impression that this is a love feast - far from it - for many of these discussions on proposed rules bring into sharp focus the conflict between on the one hand the Agency's need for data in order to assess human health and environmental risks, and on the other hand, the burden and costs to industry to provide these data as well as the possibility that valuable trade secrets will be divulged.

And, of course, as with any inexact science such as human health and environmental behavior, in which new technical advances and knowledge are gained each year, there will always be a debate on the relevance of certain data and therefore, the need for some tests. But we are making progress even though the Agency has been sued for slow action or inaction on some aspects of TSCA.

Let me point out just a few of the more important rules affecting the chemical industry broadly and specifically the paint and coatings industry. One of these in the early proposal stages is to require manufacturers, importers and processors of hazardous substances or mixtures to provide appropriate warning labels for containers of these materials. These labels need to be consistent with those required by other government agencies - transportation for example - and with international rules. Current practices of industry also need to be taken into consideration so there is a lot of patient and painstaking effort underway to propose and ultimately promulgate a final rule which meets the objective of TSCA.

Another proposed rule is to require reporting of production and use data on some 2,300 chemicals selected on the basis of either high volume of production or some evidence of toxicity. This would be an initial screening step to be followed by requests for more detailed information on a fewer number of most concern with respect to risk to health and environment.

A third proposed rule would require reporting and record-keeping of health and safety data on a priority list of chemicals

suspected of posing some potentially serious risks to health and the environment. It is the goal of EPA to issue final rules for all of these sections of TSCA before year end.

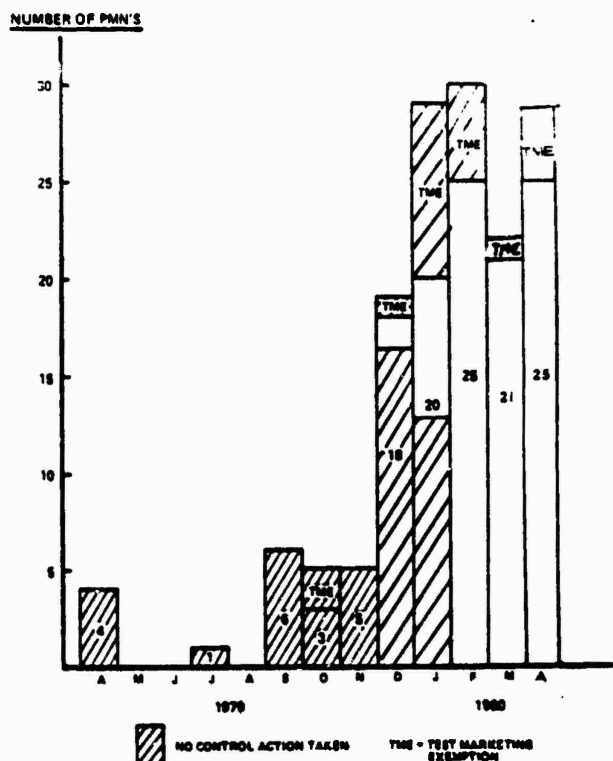
Let me close this talk on TSCA with a discussion of the pre-manufacture notification requirement which went into effect on July 1, 1979 and is the most distinctive feature of the Act. Section 5 of TSCA gives EPA the authority to act before harmful substances threaten human health or the environment. Other laws largely enable the government to take action only after widespread and possibly serious harm has occurred. As new chemicals, which are defined as those not listed on the Inventory, proceed from the R&D stage to commercial scale, companies must notify EPA at least 90 days in advance of their intent to manufacture or import such a chemical.

Since July of last year, EPA had received over 150 pre-manufacture notices (PMN for short) with the rate of receipt shown on this table (Table 4). It would appear that we can expect to receive from 300 to 400 notices this year. I have indicated with a cross-hatch the number which we have decided to take no regulatory action. Our procedure is to assign a team of experts - toxicologists, chemists, engineers, economists - to work on each PMN and, with the best available knowledge, assess the potential hazards associated with the commercialization of each new chemical and decide if the risk to health and environment is reasonable. If unreasonable, some type of control action would be taken before the new chemical would be permitted to enter the market.

On April 28 of this year EPA took its first control action on new chemicals in prohibiting the introduction into commerce of six new phthalate esters designed for use as plasticizers. EPA's order was triggered by data obtained in studies of structurally-similar commercial phthalate esters which strongly indicated carcinogenic and mutagenic activity in laboratory animals and fish. Although no toxicity data on the new chemicals were submitted, the production ban is in effect until such time as ample evidence can be developed to show that they can be produced, processed and used in ways that will avoid serious harm to people or the environment. Meanwhile, the Agency plans to require more complete testing of the existing phthalate plasticizers for health and environmental effects.

EPA is not surprised at the general lack of data supplied by submitters of PMNs on chronic health effects, such as, carcinogenicity, since tests for these effects are lengthy and expensive and not generally run before a firm determination is made of the marketability of the product. But the Agency is concerned about the dearth of data being submitted by some companies on acute health effects. So in full cooperation with leading trade associations, we are trying to encourage industry to provide us with more meaningful health and safety data on new chemicals so we can do a better job in implementing this very important aspect of TSCA and to do it efficiently with the resources at hand.

PRE-MANUFACTURE NOTICES



Of special interest to this audience is the fact that of the approximately 150 PMNs submitted up through the end of April, 59 or 40% were for new polymeric materials. Just how many of these were intended for use in paints and coatings cannot be disclosed since a substantial portion of the end use information was claimed confidential.

If PMNs are to be considered a measure of the innovativeness of the chemical industry, it appears that polymer chemists are playing a major role. Furthermore, since these new polymers were undoubtedly developed to improve the performance or reduce the costs of existing consumer and industrial products and in some cases to replace them with safer and less toxic ones, then the polymer chemist has well served his fellow man. For its part, the Environmental Protection Agency is doing its best through administration of the Toxic Substances Control Act to protect public health and the environment from unreasonable risk from hazardous chemicals.

COATINGS FROM ACRYLIC POLYMERS

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ABSTRACT

Since World War II acrylic polymers have become one of the most important raw materials for the coating industry because of their superior properties, and the versatility that they offer.

The polymers form brilliantly clear, durable films, which can be varied in hardness and flexibility within wide limits. When acrylic coatings were first introduced they provided an almost unbelievable improvement over most existing film formers; today they provide the standard against which any new material will be measured.

The stability and durability of the acrylic binders has greatly increased the range of colors and pigments that can be used. Bright, transparent colors previously impractical, have become the norm. Coated objects retain their attractive appearance and need recoating less often. Our surroundings are cleaner and brighter and can be kept that way with less effort.

The discovery of acrylic polymers, coincided with the beginning of this century. To a large extent it also coincides with the life of Herman Marks, whom we are honoring here.

Otto Röhm synthesized acrylic esters during his thesis studies for his doctorate. He became intrigued with the properties of the rubbery substances that he could make from these esters and eventually developed a reasonable synthesis and studied variations in structure and their effects on properties in detail.

The potential for using acrylic polymers as substitutes for various materials used in coating was actually recognized fairly early but their lack of commercial availability and high cost prevented this potential from being exploited. It should be recognized also that the coatings industry in the first quarter of the 20th century was hardly the aggressively innovative industry that it is today. The mainstay of the industry were drying oils and varnishes, some natural gums, shellacs and phenolic resins. Oxidation was just about the only crosslinking mechanism known, and such developments as sprayable nitrocellulose lacquers, alkyds, and thermal crosslinking by aminoplasts were still in the laboratory stage or were developed much later.

The early work of Herman Mark and other pioneers first proved the intrinsic nature of polymers and established the fundamentals of polymer science. Mark was also responsible for the introduction of polymer science into American University curricula. Thus, a group of young scientists, taught or influenced by him, carried this new science into the industrial laboratories, including those involved in the development of new coatings.

The interest in acrylic esters as coating raw material began in the 1930's as evidenced by the number of references in Chemical Abstracts. Starting with the 3rd decennial index the following number of references were listed:

REFERENCES TO ACRYLIC POLYMERS IN COATINGS - TABLE I

1927-36	none
1937-46	about 2-3 per year
1947-56	about 7 per year
1957-61	about 13 per year
1962-66	about 17 per year
1967-71	about 147 per year

These numbers were extracted from the Coatings section only and are probably not exhaustive, but the rate of growth is probably representative of the interest in the field. These numbers reflect commercial rather than research interest, since by 1965 acrylic coatings had captured over one fifth of the total market.

What are these materials, and why have they been so successful? What service or value-in-use do they provide that allowed them to displace competing coatings, often at no initial reduction in cost, and sometimes at an increase in initial cost?

Acrylic esters are propenoic acid or 2-methyl propenoic acid ester that polymerize readily through the double bond. Variation of the alcohol changes physical and chemical properties. It has also been found possible to utilize the alkoxy group of the ester to attach functional groups to the molecule, which make it possible to carry out other reactions after polymerization, or after formation of a coating. One can prepare monomers which contain hydroxyl, amine, epoxy or isocyanate groups, as well as literally any length alkyl group containing from one to greater than 18 carbon atoms. Various unsaturated as well as cyclic esters have also been prepared and used commercially.

The advantages that are offered by the use of acrylic polymers as binders in coatings are:

- (1) Excellent resistance to chemical attack, which leads to outstanding durability;
- (2) Variability in physical and chemical properties achievable by choice of monomers;
- (3) Wide range of monomers (acrylic or non-acrylic) suitable for copolymerization;
- (4) Versatility in form of polymers - bulk, solution, dispersion, emulsion - lacquers, enamels.

This combination of properties has been so successful that acrylic binders probably represent almost half the total binders used today in coatings.

Alkyl acrylates or alkyl methacrylates form water white, colorless polymers that give clear, durable films. By varying the length of the alkyl group and by using either acrylic or methacrylic acid derivatives one can vary the glass transition temperature of the polymers from 380°K to 195°K.

(TABLE II)

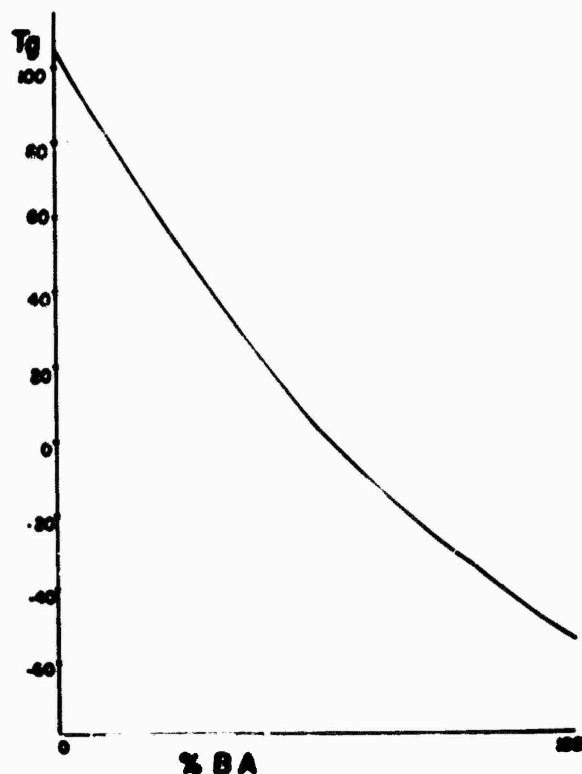
However, it is not necessary to produce all of these esters to prepare a polymer with any desired T_g, since the various monomers copolymerize readily and the copolymers will usually have a balance of properties that is an average of the homopolymers of monomers used. Thus a copolymer of methyl methacrylate

TABLE II

GLASS TRANSITION TEMPERATURE (T_g) OF ACRYLIC ESTERS
AS A FUNCTION OF ACID AND ALCOHOL

ALCOHOL	ACRYLATE T _g °C	METHACRYLATE T _g
METHYL	8	105
ETHYL	-22	65
1-PROPYL	-48	35
2-PROPYL	-8	78
1-BUTYL	-54	20
2-BUTYL	-20	45
2-METHYL-1-PROPYL	-17	48
2-METHYL-2-PROPYL	-22	107
1-HEXYL	-60	-5
2-ETHYL-1-HEXYL	-65	-15
CYCLOHEXYL	16	66

and butyl acrylate will be softer and more soluble than poly (methyl methacrylate) but harder than poly (butyl acrylate). The exact balance achieved will depend on the ratios used.

Fig. 1. - T_g of MMA/BA Copolymers

Coatings made from acrylic polymers have excellent weathering resistance. They have no unsaturated groups that undergo rapid oxidation, and do not absorb light in the wavelength regions above 3000 Angstrom Units. The methacrylates also are exceptionally resistant to hydrolysis. Thus the inherent weathering characteristics are excellent.

The kinetics of polymerization of acrylic monomers has been studied in considerable detail. Methyl methacrylate when polymerized by a free radical initiator in bulk, in concentrated solution, or in emulsion is subject to the Trommsdorff effect, which represents an anomaly from the expected kinetic behavior. The rate of polymerization during free radical polymerization is generally given by the equation:

$$R_p = k_p \left(F \frac{K_d [I]}{k_t} \right)^{1/2} [M]$$

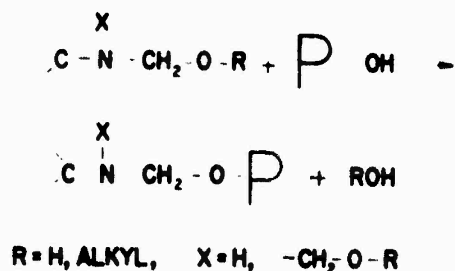
It is generally expected that rate constants remain constant during a reaction. During free radical polymerization, however, k_t can change drastically as the viscosity of the system increases, since this step is the reaction of two chain ends, and is diffusion dependent. Formation of new chains continues, and thus the number of growing polymer chains increases, as does their molecular weight, and bulk rate of conversion. Eventually the monomer concentration becomes sufficiently low to reduce the rate.

Other methacrylate esters, such as butyl methacrylate show a similar effect, although greatly diminished, so that only very sophisticated studies will show it.

Acrylic automotive lacquers represented the first large scale use for acrylic coatings. These were introduced in 1957; by 1959 they had captured that market. Because of their excellent gloss retention, their clarity and resistance to yellowing they allowed the development of a totally different range of colors. Instead of the dark colors and a limited range available previously, a wide range of bright and attractive colors using many new pigments became possible, especially the bright, attractive metallic colors with the "two tone" characteristics.

One major problem that had to be solved was finding a way of balancing molecular weight dependent film properties with application properties. As one improved the other became poorer. The film properties improved as weight average molecular weight increased from 2500 to 125000 while application solids decreased from 30% non-volatiles to 5% non-volatiles over the same range. The solution to the problem was not just finding a compromise molecular weight, but a method of narrowing molecular weight distribution to reduce the high molecular weight tail, which interfered with application. Other problems that needed solving included finding a proper plasticizer, controlling the rheology of metal flakes to maximize the desired color effect and obtaining good adhesion to the primer.

Acrylic enamels were also introduced at that time. Urea formaldehyde and melamine formaldehyde resins had been used many years as crosslinking agents for alkyds with excess hydroxyl groups. By copolymerizing alkyl acrylates and methacrylates with 2-hydroxyethyl acrylate or methacrylate cross-linkable acrylic resins could be made, which were at least as good as alkyds.



MELAMINE RESINS

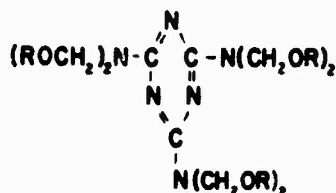


Fig. 2. - Aminoplast crosslinkers - reaction

The hydroxy esters were prepared readily by reacting ethylene oxide or propylene oxide with the appropriate acids.

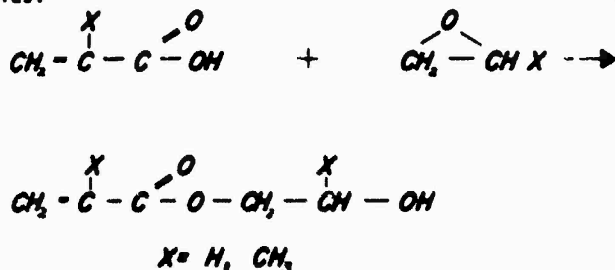


Fig. 3. - Synthesis of hydroxy alkyl acrylate

Coatings based on such resins had excellent properties; they did require higher curing temperature, but the benefits, such as light stability, chemical resistance or exterior durability and the low cost of energy made that disadvantage of minor importance.

Copolymers containing hydroxy alkyl esters could also be cross-linked with di- or polyisocyanates. These blends gave very durable two package coating systems that cured at room temperature, as did drying oil alkyds, but had none of deficiencies normally associated with room temperature curing systems that cured by oxidative polymerization.

A few years later another ingenious approach was introduced. A self crosslinking vehicle was prepared by copolymerizing acrylamide with acrylic or methacrylic esters and then reacting the amide with formaldehyde and an alcohol to form alkoxy methyl acrylamide containing polymers, which would split off formaldehyde and alcohol to form methylene-bis-amide cross links. These polymers had excellent mechanical properties and chemical resistance.

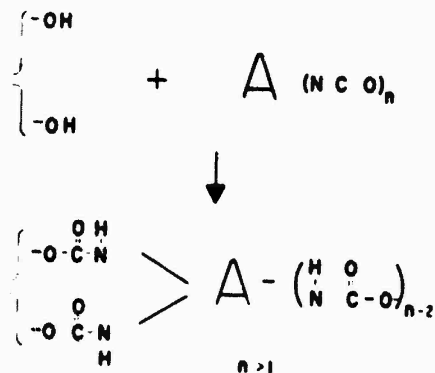


Fig. 4. - Cross-linking with poly(iso cyanates)

Other copolymers, containing glycidyl ester side chains could be crosslinked with poly functional acids, or acid containing copolymers could be crosslinked with difunctional epoxides.

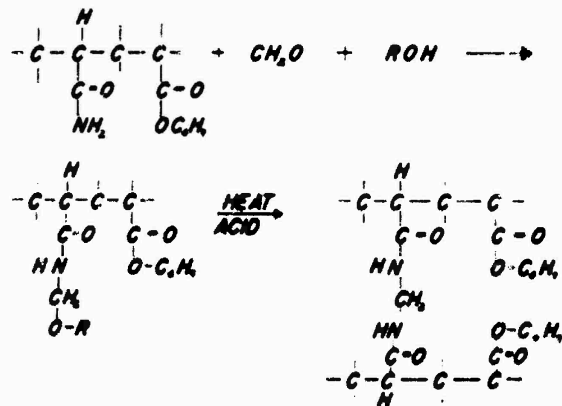


Fig. 5. - Self cross-linking of acrylic enamel

All the systems described above were based on polymers which were formed by polymerizing the unsaturated groups of the acrylic monomer, and if further reaction was desired, carrying out such reactions on sites along the preformed polymer chains.

Another approach, which is also useful, is to polymerize the monomer on the object to be coated, through the double bond, analogous to the styrene/polyester technology. This approach is feasible and the polymerization can be carried out by heat, light or high energy radiation.

The free radical polymerization is at least partially inhibited by atmospheric oxygen, but certain acrylic systems are less affected by O_2 than styrene polyesters. Such monomeric systems reduce or eliminate the need for volatile solvents, and where useable, fit into today's requirement for low pollution causing coatings.

After World War II, the rubber industry had excess capacity for the production of styrene/butadiene copolymers. One outlet for such polymers was latex paint for the interior wall paint market. Between 1950 and 1960 a rapid expansion of such water based coatings took place. The consumer recognized the ease of use of such paints, but also recognized their deficiencies. These were: unsuitability for exterior use and yellowing and embrittlement on interior use. In the early 1960's latex paints, based on emulsion polymerized acrylic esters were introduced, both for the interior and the exterior market. Their advantages were as clearly perceivable in this market as in the industrial and automotive market. After all, the ultimate user was the same, whether the object

painted was a house, a car or an appliance. Soon the consumer became accustomed to the equation:

acrylic equals quality

Today, twenty years later, that has not changed.

What has changed are the constraints placed on coatings by the development of our collective awareness of environmental effects. Materials that had been important ingredients of many coatings have been shown to be toxic or potential threats to the environment. Solvents, so important to the coatings industry must be reduced; lead and chromate based pigments, asbestos, isocyanates, oxiranes, are all suspect and their use is greatly circumscribed. The list grows constantly.

One of the features of polymeric acrylic vehicles is their great versatility. Solutions with their high solvent contents are undesirable? Make dispersions; either aqueous or non-aqueous dispersions are possible and can be used to reduce solvent emissions from coating applications. Latices can also be used in some limited applications. If no solvent is permissible, try powder. Acrylic based powder coatings can be used to coat cars, refrigerators, shelves and furniture. Obviously, not all objects can be coated with powder; they must be able to fit into ovens and tolerate the curing temperature.

Low molecular weight oligomers can be used to make coatings that can be applied at 60-80% weight solids; as mentioned, syrups that can be cured by radiation need no solvent.

All in all, acrylic coatings can be prepared with a wide range of physical properties and physical forms, can be cross-linked by many chemical reactions and can be designed to be applied by every method commercially useful. They offer a balance of cost, utility and chemical resistance that represents an order of magnitude improvement over anything that had been known prior to their introduction. As a result they have improved our ability to surround ourselves with colorful, bright and durable objects, to protect these from sun, rain, light and air and to enjoy these benefits at a reasonable cost.

ADVANCES IN LATEX TECHNOLOGY

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ABSTRACT

Most commercial latexes are produced by a semi-continuous batch process. In this process the particles are initiated from a batch charge of monomer, catalyst, surfactant, and the remaining monomer added to the reaction vessel during the polymerization. Other ingredients, e.g., additional catalyst, surfactant, stabilizer, buffer, etc., may also be added during the polymerization. The order of the additions are varied depending upon the effect desired. Under these operating conditions, a large excess of monomer does not exist in the reaction zone and it is the authors' contention that the classical kinetic control of the polymerization rate is not valid. Rather the polymerization is controlled by mass and heat transfer considerations.

Several novel methods of controlling the emulsion polymer structure to produce the desired performance properties are discussed. In addition a method for the synthesis of gradient polymers and their respective properties as possible coatings polymers are reported.

FOREWORD

It is fitting that the Division of Organic Coatings and Plastics share in the sponsorship of this Symposium on Polymers in the Service of Man. Certainly the scientists and technologists of the Division have been working for over 40 years to this end. It is even more fitting that Professor Mark be awarded the National Medal of Science. It is because of pioneering work such as his and his contemporaries that makes possible the rapid progress of organic coatings and plastics technology we know today. We have progressed from the kitchen table oil cloth to the modern durable vinyl fabric; from the solid rubber tire of the early 1900's to the complex composite radial; from the assembly line bottle-neck of the black finish of the Model-T to the sleek styled auto finish of the 80s (it is said that an auto finish is one pound of polymer that protects 3000 pounds of steel); from the white lead and linseed oil of the late 19th Century to the modern latex house paint which makes each of us a skilled paint craftsman.

Today there is a new challenge, partly caused by our concern for the environment but mostly by the severe political-economic constraints placed on the available petrochemical-feedstocks and petro-energy resources. There is little logic in the continued use of solvent based industrial finishes, and to further compound the dilemma by using more energy to incinerate the low level solvent emissions to protect the environment.

For many years the underlying theme of emulsion polymer research and development has been to duplicate and out-perform the solvent based trade finish. This effort has been, indeed, fruitful for the latex paint has all but replaced the solvent based trade finish of just a few years ago. The obvious extension of the latex finish to the industrial application was the thrust of the early 70s, but from the start the effort was doomed to failure. In the eagerness to exploit the obvious, a direct translation of the products designed for the do-it-yourself craftsman was attempted to the complex requirements and needs of the high speed industrial finishing line. The results were predictable. Because of poor polymer design, formulator inexperience and use of existing coatings equipment, early latex industrial finishes did not apply or perform acceptably.

It is unfortunate that many industrial users now have, because of this costly lesson, a tendency to dismiss the emulsion polymers of today as just another good idea that didn't pass the test of time. Can it be that this judgment is premature and that in reality emulsion polymers do have an important role to play in the protective and decorative industrial finishes of the future? The present paper will discuss a few of the advances in Latex Technology which can be used to custom design emulsion polymers to many industrial applications.

THE SEMICONTINUOUS BATCH PROCESS

Monomer Tanks

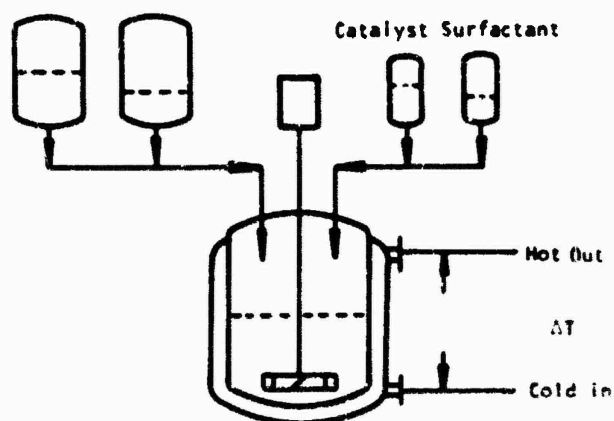


Fig. 1 - Semicontinuous Batch Reactor

Many latexes offered commercially are produced by a semicontinuous batch process (figure 1). In this process the particles are initiated from a small batch charge of monomer, initiator, surfactant, etc., and the remaining monomer is continuously added to the reaction vessel during the course of the polymerization. Other ingredients, such as additional initiator, surfactant, stabilizer, buffer, etc., may also be added during the polymerization. The exact order of the additions is varied depending upon the effects desired by the latex chemist. The usual operating characteristics of the process are:

- (1) The reaction is carried out as warm (hot) as possible because the higher temperatures allow better utilization of heat transfer capacity of the reaction system thus minimizing investment, and optimizing productivity.

- (2) The monomer is fed to just maintain the temperature of reaction, thus utilizing the heat of polymerization to heat the reactor. Under this constraint monomer is added at or very near the rate of polymerization.

Under these operating conditions, a large monomer inventory does not exist in the reaction zone; in this "starved feed process" the solubility of the monomer in the aqueous phase is seldom if ever exceeded. Thus the reaction conditions of the semicontinuous batch process avoid the classical kinetic control and its implied equilibrium for the monomeric species, figure 2.

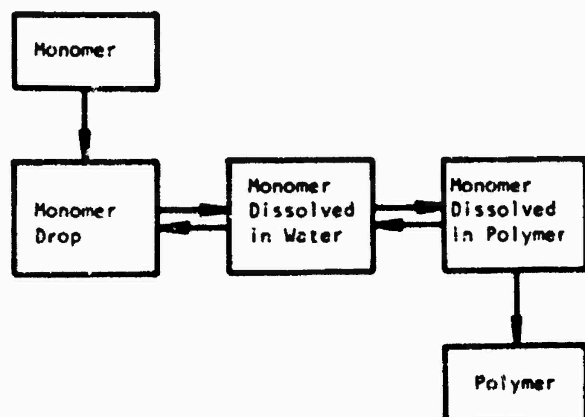


Fig. 2 - Monomer Equilibrium in Kinetic Control

Instead, there is a growing body of evidence which supports the idea that the semicontinuous batch process can provide diffusion control of the polymerization, i.e., mass transfer limited (figure 3). The unique property conferred on the latex particle by mass transfer control is that the surface of the latex particle can and often does have the characteristics of the polymer derived from the composition of the monomer added last.

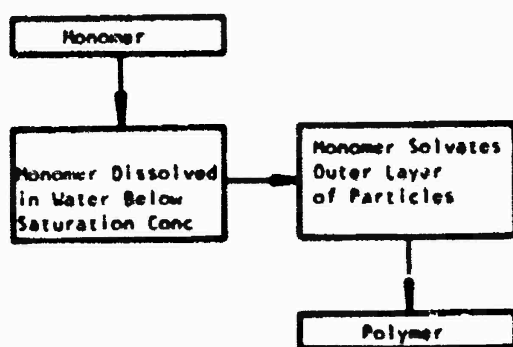


Fig. 3 - Mass Transfer Control of Polymerization

Most of these effects can be explained if it is assumed that the active zone of polymerization is at or near the surface (water-polymer interface) of the particle. In this model the uniform accumulation of polymer at the surface of the initial particles accounts for the growth of the particles and since the conversion at any given time is 98% the infra-structure of the particle follows the chronology of the monomer composition during the course of the

polymerization. Thus, the semicontinuous batch polymerization under monomer starved conditions produces latex particles in which the epigenous polymer formed generally reflects the composition of the entering monomer stream during the course of the polymerization. This is in contrast to polymerization processes either batch or semicontinuous, which are carried out monomer rich; i.e., there is an excess of monomer present during the major portion of the polymerization and only at the very end of the polymerization is the monomer inventory reduced below the saturation level in the aqueous phase. Thus the monomer rich process produces latex particles which are more nearly homogenous polymer alloys (1); the composition is dependent upon the copolymerization kinetics of the monomer species present as a function of time. This type of polymerization follows more closely the classical kinetics described in the literature (2,3)

DIFFUSION CONTROLLED EMULSION POLYMERIZATION

Conceptually diffusion control provides an interesting design concept that enables the latex chemist to create epigenous latex polymers with unusual end-use properties by altering the composition of the monomer feed during the course of the polymerization. There are several mitigating chemical factors which must be accounted for.

In many modern latex polymers, one or more reactive functional groups are incorporated into the polymer structure. The locality of these moieties within the latex particle has important implications on the performance properties of the latex system. The work reported by Bassett and Moy (4) relate the rheological response to pH of certain carboxyl containing latex polymers (figure 4) to the accumulation of carboxyl rich polymer segments on the particle surface. The increase in the viscosity is

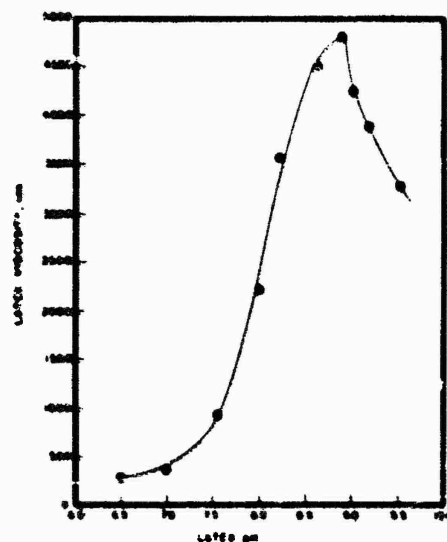


Fig. 4 - Viscosity of an acid containing acrylic latex as a function of pH 60 RPM Brookfield, 46% total solids

related to the ionization, solvation and subsequent expansion of the acid rich layer. The particle response is quantitatively measured via viscometric and sedimentation studies. Figure 5 illustrates

the change of particle morphology as the pH is made alkaline; figure 6 records the particle expansion factor by sedimentation (linear, S_0/S) and viscometry (cubic, α) as a function of pH. When no acid is incorporated in the latex composition, the response is absent, figure 7.

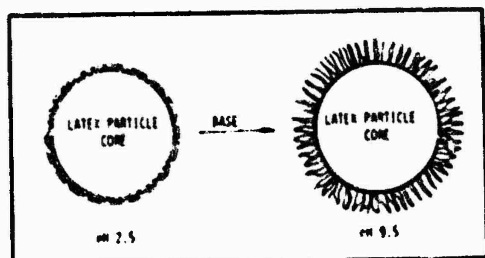


Fig. 5 - Model of acid containing latex particle at pH 2.5, acid un-ionized and collapsed on surface; at pH 9.5, acid ionized and expanded (solvated)

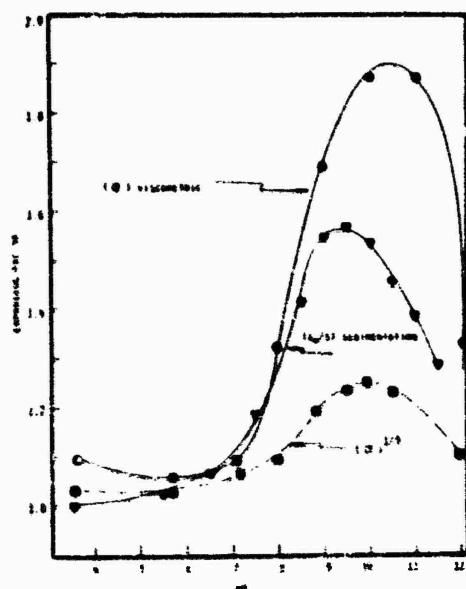


Fig. 6 - Variation of expansion factor with pH

The conclusions reached from these studies are:

- (1) Monomers containing carboxylic functions and other polar groups are incorporated in such a manner that the polar groups are at or very near the polymer-water interface.
- (2) The incorporation of acidic monomer occurs more readily at low pH and therefore it is likely that un-ionized acid rather than carboxylate anion is the active polymerizing species.

- (3) Variation in the order, time and mode of addition of acidic monomers has little effect on the location of the carboxyl group in the final polymer particle; however, these variables do have profound effects on the nature and solvation characteristics of these carboxyl-rich copolymer segments.

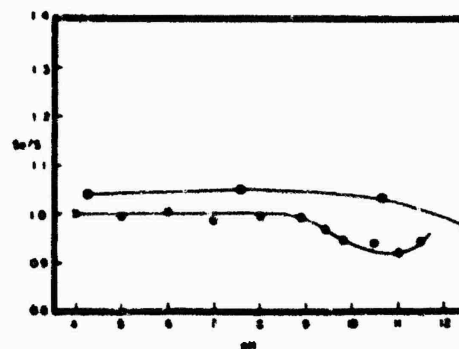


Fig. 7 - Variation of expansion factor of a non-acid bearing latex as a function of pH. (O) sedimentation; (S) viscometric

These results suggest that the strongly polar monomers (acids) do not strictly follow the rule of epigenous polymer formation; but rather, the strongly polar monomers which are incorporated in the particle are by chemical potential oriented towards the surface of the particle where they form a polymer layer which is subject to solvation and expansion as the aqueous environment is altered, e.g., ionic strength, pH, etc. The degree of solvation and expansion is altered by both process variables and chemical structure of the polymer being formed. The process effects they have identified are:

- (1) The expansion is maximized by high instantaneous acid monomer concentrations (feed over a short period of the process) and when fed towards the final stages of polymerization (figure 8).
- (2) Expansion is minimized when the instantaneous acid monomer concentration is kept as low as possible (fed throughout the process).
- (3) The use of an aqueous side stream for the acid monomers tends to equalize expansion but lowers incorporation of acid.
- (4) The trend for maximum effect in acid choice is acrylic > methacrylic >>> itaconic.

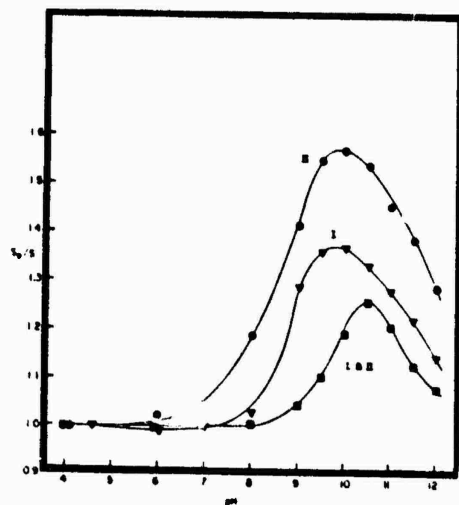


Fig. 8 - Effect of stage of addition of acrylic acid in polymerization on expansion factor (S_0/S vs pH); (●) Stage II; (▲) Stage I; (■) uniform feed

Base polymer structure is the last consideration which can influence the expansion layer. There are two major factors which are important.

- (1) Rigidity of Polymer Segment - If the acid rich polymer segment has a high T_g the expansion is constrained by the rigid glassy character of the polymer backbone; conversely, a low T_g facilitates the expansion process because of the elastomeric low modulus of the polymer (figure 9).

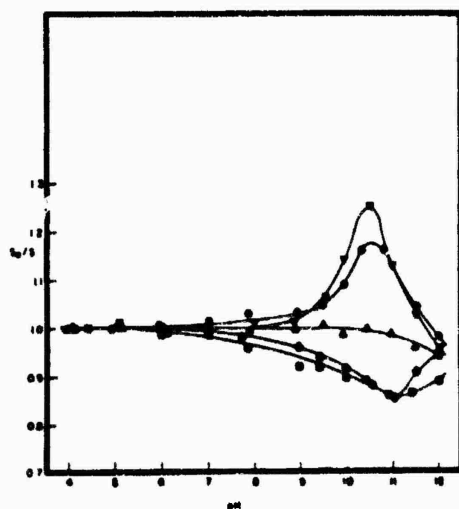


Fig. 9 - Expansion of butyl acrylate/methyl acrylate copolymer acid bearing 2% latexes. (▼) 50/50, T_g 15°C; (●) 37.5/62.5 T_g 33°C; (▲) 31/69 T_g 44°C; (■) 25/75, T_g 54°C; (●) 0/100 T_g 105°C

- (2) Polar/Non-Polar Character of the Polymer Segment - If the base polymer in which the acidic moieties

are contained is nonpolar in character, e.g., hydrocarbon, then expansion is constrained. More polar based polymer segments are readily plasticized by the adsorption of water and can be expanded at alkaline H, (figure 10).

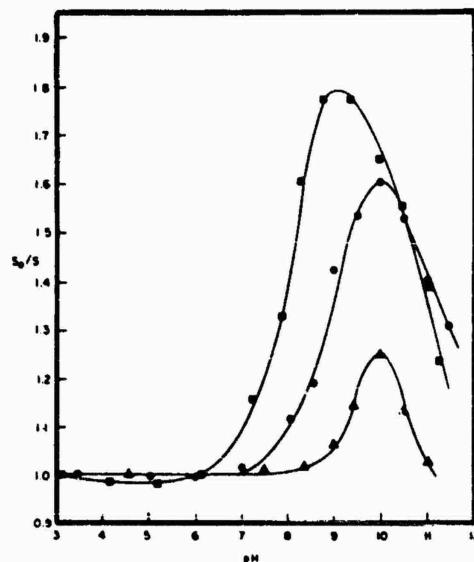


Fig. 10 - Expansion of acrylic copolymer latexes bearing 2% acid, 11. (■) MMA/EA/BA 40/52/6 T_g 15°C; (●) MMA/EA/BA 40/58/0 T_g 18°C; (▲) MMA/EA/BA 49/0/49 T_g 15°C

The relationship between polarity and rigidity is illustrated by figure 11. In figure 11, rigidity is represented by T_g while polarity is the polar solubility parameter. The non-expanding compositions are

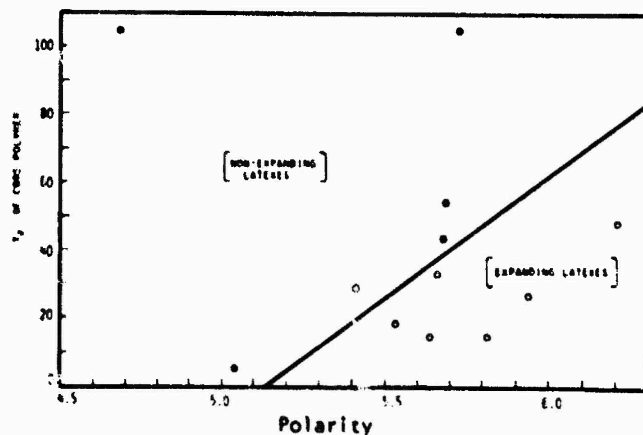


Fig. 11 - Effect of glass transition and polarity on expansion of 2% acid bearing latexes

to the left and above the line on the figure while the expanding latex compositions are to the right and below the line. Once the key elements of the variations of particle structures are well understood as a function of the process employed, it is possible

to apply these to the design of polymers for specific applications.

One of the more unique utilizations of these principles is the development of the gradient emulsion polymer. A gradient emulsion polymer is the epigenous polymer formed as the composition of the entering monomer is altered by a predetermined program. Consider three different epigenous latex polymers which have the same overall composition (MMA/BA/AA, 34/64/2) but have radically different feed pathways. Figure 12 illustrates the three pathways and the

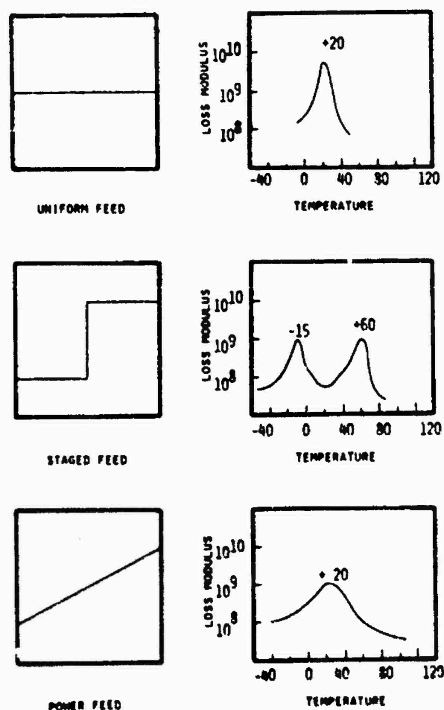


Fig. 12 - Dynamic mechanical properties of uniform feed latex; stage fed latex, and power feed latex

corresponding mechanical loss properties of each polymer. The uniform feed (composition not varied) polymer exhibits a single loss peak at 20°C and forms clear but somewhat tacky films; the stage feed polymer displays two loss peaks in its mechanical spectra which corresponds to the expected T_{gs} of the polymers formed from the stage compositions (-15°C, 60°C). Films from this polymer are not clear, are weak and of little value as a coating material.

The last polymer, see figure 13, was prepared

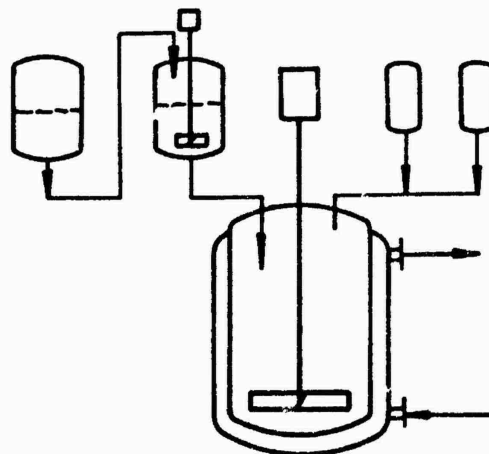


Fig. 13 - Reactor Configuration for Gradient Polymer Syntheses

using a linear power feed profile (5) and has only a single broad peak in the loss spectra at 20°C; it does, however, form clear, dry to touch, tough films and has much more value as a coatings binder than either of the previous polymers.

A second application of the principle of epigenous polymer formation is one in which the particle size distribution of the latex is desired to be extremely broad within certain limits. In this instance, there is a continuous withdrawal of latex particles from the reactor for the first half of the monomer feed and the process is reversed during the last half, i.e., the particles are continuously returned to the reactor for continued growth; figure 14 illustrates the reaction scheme.

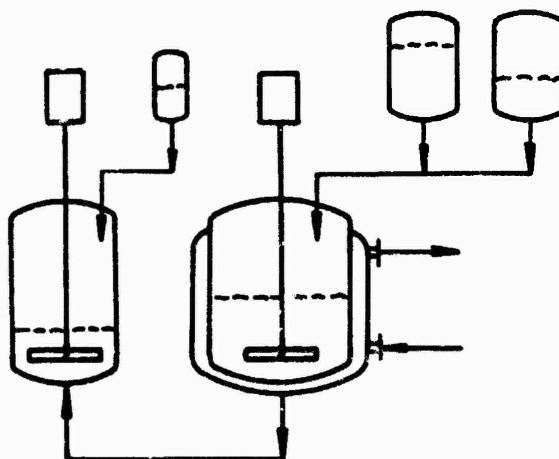


Fig. 14 - Reactor configuration for unique broad polymer size distribution

in this manner latexes of 70-75% solids can be prepared which have viscosities of only 200-500 cps. Other examples of the use of diffusion controlled emulsion polymerization could be cited, but it is not the intent of the authors to complete a compendium of emulsion polymerization procedures, but rather to indicate those techniques which can be effective tools for the further improvement of coatings performance properties especially those which serve the growing needs of our changing society.

ACKNOWLEDGMENT

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BODY

Existing application equipment used in industrial coatings requires a viscosity of the paint system in the range of about 60-200 mPa's. Although, advances are being made in the application of more viscous systems this approach is limited as to the increase in solid content which can be obtained with presently used coating polymers. Therefore, significant increase in application solids can only be achieved by changing the polymer backbone. A typical acrylic thermoplastic polymer used in automotive coatings has a molecular weight of several hundred thousand and an application solids of about 15%. Decreasing the molecular weight to 25,000 and incorporating some functional sites into the polymer backbone for cross-linking permits an increase in application solids to about 25%. (Fig. 1) Further decrease

ABSTRACT

Considerable amounts of organic solvents are emitted into the atmosphere during the application of organic coatings. To reduce this solvent emission and the resulting pollution water borne and high solids coatings are being developed. Water borne and high solids polymers have to be cross-linked to achieve film properties required for a durable coating system. From the many cross-linking mechanisms available to the coating chemist monomeric alkoxymethyl-melamine cross-linkers have shown the broadest utility in high solids and water borne coating systems. The cross-linking reaction is a condensation reaction catalyzed by an acid catalyst. Either pH control or alcohol can be used to adjust stability and reactivity in a water-borne or high solids coating. Alkoxymethyl-melamine cross-linkers are used as cross-linkers in such diversified applications as automotive topcoats, appliance, house siding, mobile homes, can coating, paper and wood coating. In these applications cure temperatures as low as 80°C and as high as 300°C and time cycles from a few seconds to 30 minutes are used. These coatings range from extremely hard to flexible, and significant properties include resistance against U/V, detergent, salt, alkali, acids, water and organic solvents. The ever increasing use of water borne and high solids coatings will significantly reduce pollution from coating operations and also reduce the waste of expensive organic solvents.

BACKGROUND

Significant levels of organic solvent are emitted into the atmosphere during the application and curing process of organic coatings. The solvent emission can in many instances be significantly reduced by converting the presently used low solid coating systems to higher application solids or by the use of a water soluble or dispersible polymer system. Because every application method requires a certain viscosity and rheology of the paint system, a simple increase in non volatile content of the paint formulation without a redesign in the backbone polymer is not possible. To achieve this higher application solids a reduction in molecular weight of the polymer used is required. Water solubility or dispersibility of coating polymers can be accomplished by introduction of hydrophilic or charged groups in the hydrophobic polymer. Neither low molecular weight polymers nor water soluble polymers will give adequate film properties without cross-linking. An ideal cross-linking agent will permit the formulation of a one component stable system and will cross-link functional sites on the polymer after being activated by an external event, such as heat, radiation, moisture or air.

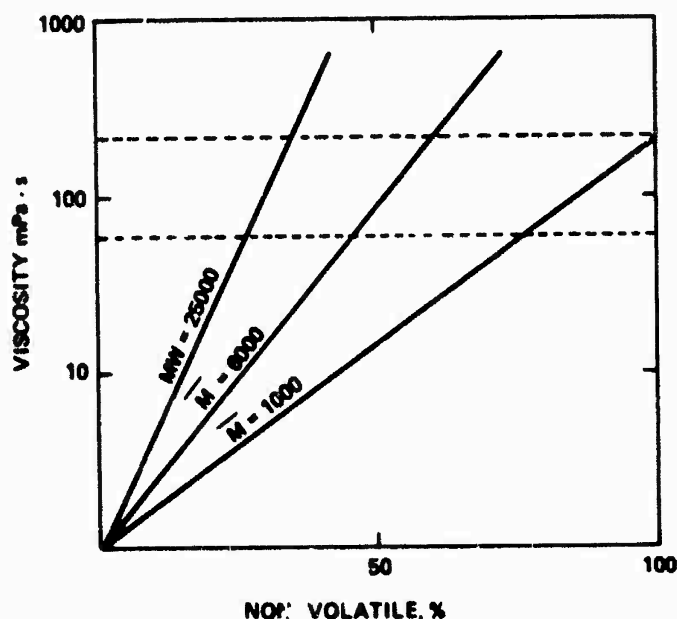


Fig. 1 - Viscosity-molecular weight

in molecular weight to about 1000 can theoretically at least increase the application solids to 100%. A further reduction in molecular weight does not result in lower viscosity because of increased hydrogen bonding between functional sites. This desirable 100% application solids is elusive because such low molecular weight polymer systems have unacceptable pigment wetting characteristics, unsuitable rheology and a tendency to crater and not to wet the substrate.

Therefore, formulated systems even under optimum conditions can rarely be applied at a solid content higher than 70% weight percent.

The decrease in molecular weight of a polymer reduces such physical properties as hardness, tensile strength and elongation. (See Fig. 2) Polymers or oligomers used in high solids coatings with a molecular weight between 1000 to 5000 are soft, sticky or brittle and without useful properties. It is necessary to use some mechanism to increase the molecular weight after the application process. A convenient approach

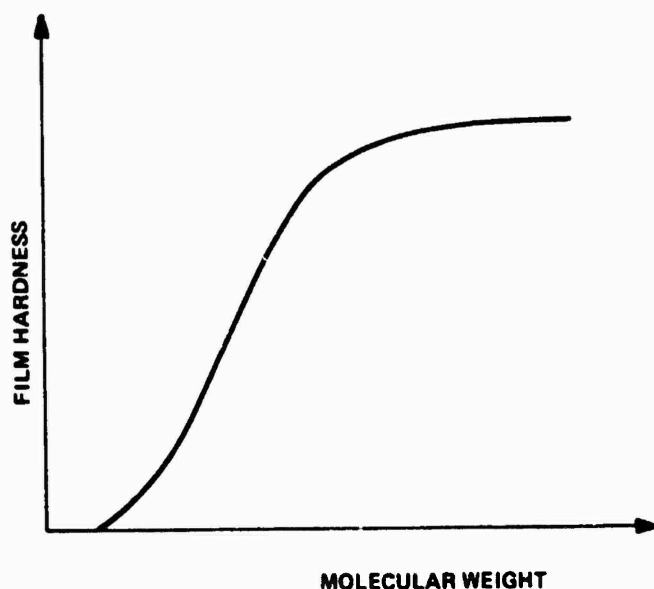


Fig. 2 - Film hardness as function of molecular weight

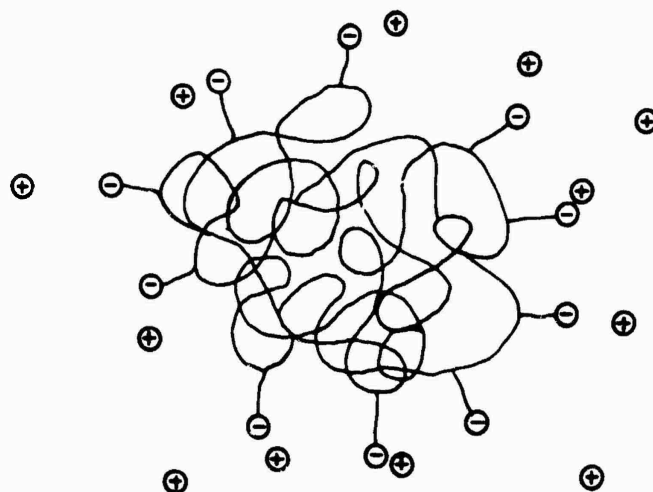


Fig. 4 - Water borne coatings

to this problem is to design the low molecular weight polymers or oligomers with functional sites which can be reacted with an external cross-linking agent. Fig. 3 shows the cross-linking reaction of a functional end group containing polymer with a polyfunctional cross-linker. The cross-linked film represents an infinite network which is not solvent or water soluble and can be hard and flexible based on the design of the polymer backbone.

Water borne polymers such as water soluble or dispersible resins used in industrial coatings are resins with a hydrophobic backbone similar to that used in solvent borne coatings with the exception that water soluble or charged sites such as carboxyl, hydroxyl and amino have been incorporated into the polymer chain. (Fig. 4) These resins can be designed to have high molecular weight at acceptable application solids, therefore cross-linking is not required to achieve physical properties, but cross-linking can be used to destroy functional water sensitive sites on the polymer.

From the many cross-linking agents available to the coating chemist hexakis(methoxymethyl)melamine (H6M)

Fig. 5 has a unique position. It is extremely versa-

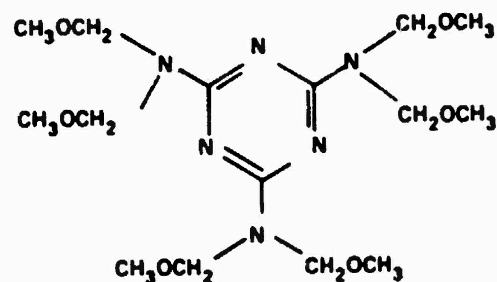


Fig. 5 - Hexa(methoxymethyl)melamine

tile, it can be used in high solids solvent borne and water borne coatings. It is reactive under acid cata-

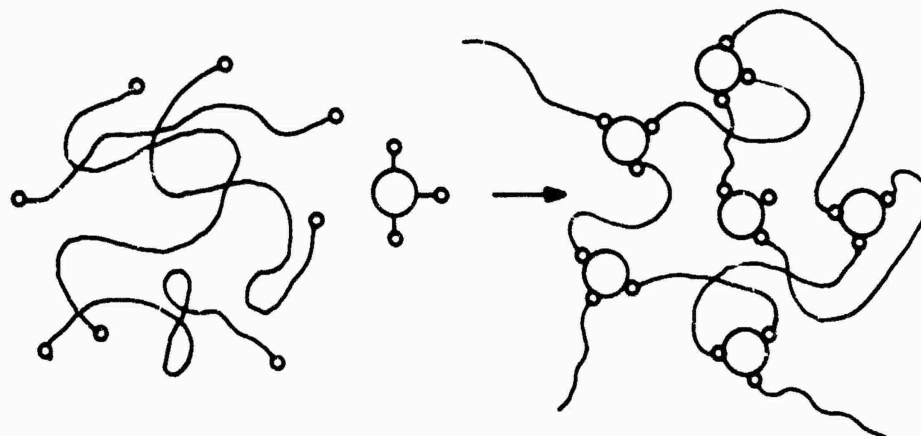


Fig. 3 - High solids coatings

lyzed conditions with hydroxyl, carboxyl, amide functional sites. (Fig. 6) H₂NH is very stable at a pH of

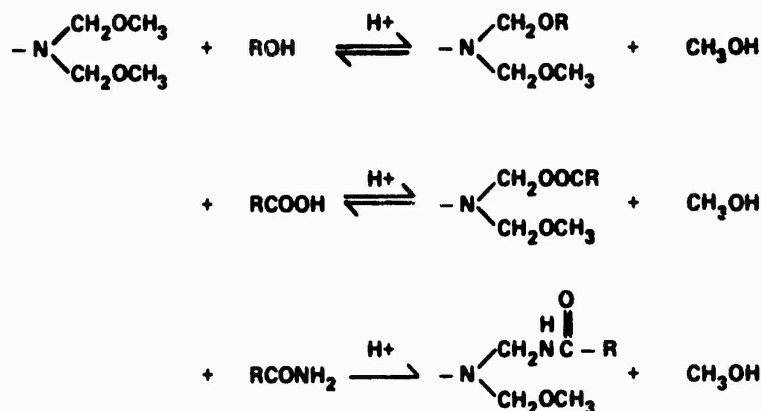


Fig. 6 - Cross-linking reaction

> 7. Amine neutralized, carboxyl functional, water dispersible polymers which are stable and cure after application of heat and evaporation of the amine, can therefore be formulated with H₂NH. (1*) The rate of reaction of H₂NH with hydroxyl and carboxyl functional compounds has been studied extensively. (2) Fig. 7

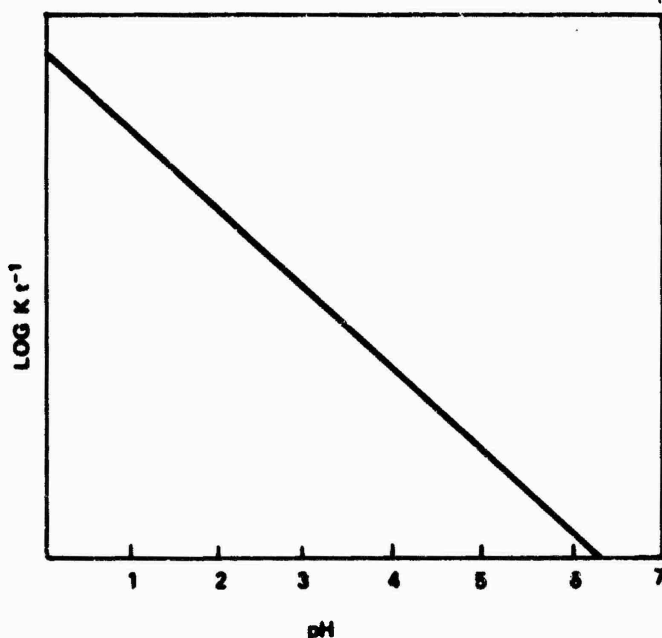


Fig. 7 - Reaction rate

shows the rate dependency of the hydrolysis reaction of H₂NH at different pH. This response clearly shows that specific acid catalysis is the operating mechanism in the catalysis of H₂NH. (3)

Although there is some controversy whether the reaction follows an S_N1 or S_N2 mechanism, the evidence seems to favor an S_N1 mechanism. (3) H₂NH has six functional sites but because of the steric hindrance

and limitations in chain mobility, after gelation of the polymer system, only 2 to 3 functional sites are actually reactive. (Fig. 8; see next page) Exceptions are high solids linear polymers with functional end groups. Here H₂NH shows functionality as high as 4 to 5. One of the effects of cross-linking on the polymer system is an increase in glass transition temperature (T_g) of the polymer. The relationship between starting T_g(l) and cross-linked T_g(c) can be expressed by the following equation. (4)

T_g CROSS-LINKING

$$T_g(c) - T_g(l) = \frac{3.9 \times 10^4}{M_c}$$

(1)

Wherein M_c represents the average molecular weight between cross-links.

This increase in T_g of a polymer during the cross-linking process poses some restraint on the reaction rate of the cross-linking reaction at low temperatures. The overall benefits derived from cross-linking of a polymer are shown in Table 1.

Table 1 - Cross-linking Benefits

HARDNESS - FLEXIBILITY

ADHESION

CHEMICAL RESISTANCE

SOLVENT

SALT

DETERGENT

HUMIDITY

UV

* Numbers in parentheses designate References at end of paper.

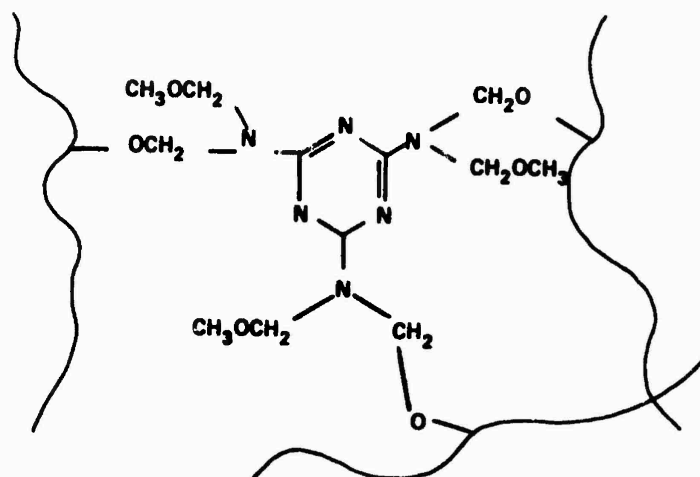


Fig. 8

The improvement in flexibility of a polymer film with cross-linking is possible because low Tg backbone resins can be used and hardness of the film is achieved by the cross-linking process. The resulting network of coiled, entangled and cross-linked chains still can be significantly deformed before breaking. Improvement in adhesion is also related to the lower Tg polymers used in cross-linked systems which permit better wetting of the substrate. The infinite cross-linked molecule formed during cross-linking reduced permeation of solvents, water and other chemicals. Chain scission due to UV attack also leads in a cross-linked network to a lesser decrease in film integrity compared to an uncrosslinked system. The broad utility of HMM in coatings depends to a large extent on the ability to catalyze the system and to obtain the cure response required for many different applications. Fig. 9 shows cure times and temperatures employed in typical application areas for HMM.

Cure schedules from several seconds, at 120-175°C in paper and wood coatings, to 20 minutes at 200°C. in appliance finishes are commercially used. This represents a change in reactivity of more than 10^4 . The increased reaction rate can be accomplished with the use of acid catalysts of different pK_a value and concentration. Of course not all applications and end uses can tolerate the catalyst level required for optimum cure response.

The most severe performance requirements for typical HMM containing high solids and water borne coatings are shown in Table 2. (See next page).

It is appropriate to show the potential impact of high solids water borne coating technology on the emission of organic coatings. If we use the published figure of 390M gallon organic solvents consumed in the coating industry with about 230M gal. of it in industrial coatings and the remainder in trade sales paint, we can calculate that if a complete conversion of all

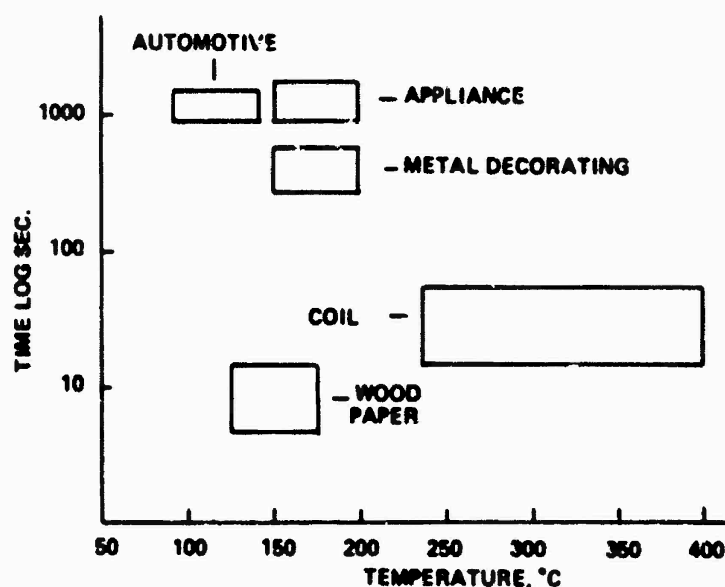


Fig. 9 - Curing time, temperature

	CAR	COIL	APPLIANCE	CAN
EXTERIOR DUR.	X	X		
FLEXIBILITY		X		X
HARDNESS	X	X	X	
ADHESION	X	X	X	X
SOLVENT	X		X	
DETERGENT			X	
SALTSPRAY	X		X	
HUMIDITY	X	X	X	X

Table 2 - Performance Requirement

coatings to high solids or water borne technology can be accomplished a reduction in solvent emission to about 40M gallon could be achieved. Although this is probably an elusive goal it is one worth working for. (Fig. 10).

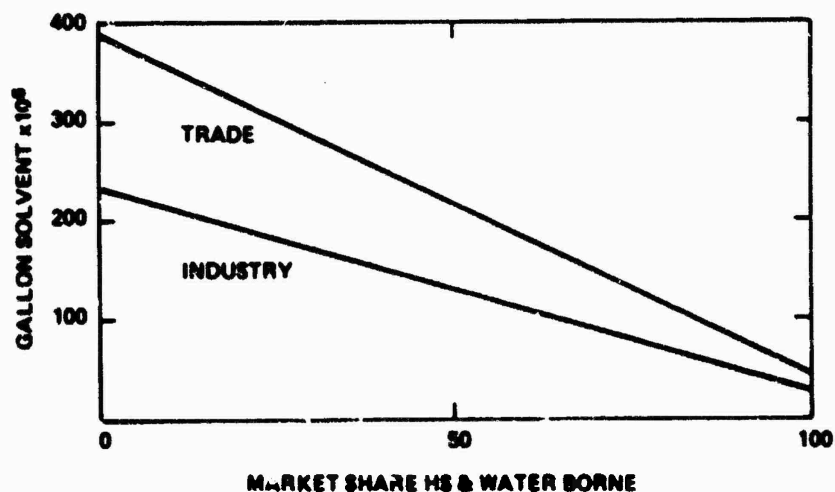


Fig. 10 - Emission of Solvents

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ABSTRACT

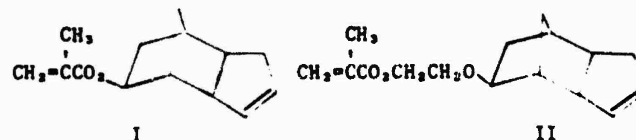
The utilization of oxidative polymerization is an attractive route for designing high solids low temperature curing coatings. A key element in this technology is a solvent-monomer which is stable under anaerobic conditions but which on exposure to oxygen of the air polymerizes with or cures the other components of the coatings formulation. A suitable monomer for demonstration of this concept is dicyclopentenylmethoxyethyl methacrylate. This material is based on readily available raw materials and has the necessary viscosity, volatility, polarity, and toxicity balance for use in this application. Three systems are described which illustrate the use of this reactive diluent. These include formulation of high solids architectural alkyd enamels, high build chlorinated rubber marine and maintenance coatings, and finally a high solids oil-free polyester suitable for a variety of industrial primer applications. All three of these systems offer performance features in solids, cure temperature, and coatings properties which exceed state-of-the-art technology.

In recent years enormous pressure has been placed on the coatings industry to reduce both solvent emissions and the thermal energy required for cure of organic coatings. An attractive tool to achieve this objective is the development of a reactive solvent-diluent which can function as a solvent in the formulation of the coating but which during the cure process (preferably at ambient or force dry temperatures) is converted to an integral part of the film. Such a material must be characterized by low volatility, low toxicity, low odor, and a solubility parameter such that it is a solvent for and compatible with a wide variety of resinous film formers. It should be reasonable in cost and should enhance film build, resistance properties, and mechanical properties of high solids coatings of which it is a key component. A number of approaches to identification of a suitable reactive-diluent have been described in the literature (1),* the most interesting of which is the vinyl dioxolane system developed by the duPont company (2). None of these systems have had, at least to date, the necessary balance of cost/performance for commercialization. A notable exception is Nature's reactive diluent, linseed oil, which is used in a variety of ways even though it has major viscosity, compatibility, and durability limitations.

Our approach to this objective was to design an autoxidizable methacrylate which can be cured at ambient temperature by oxidative polymerization and does in fact meet most of the requirements cited above.

* Numbers in parentheses designate References at end of paper.

Some thirty years ago Bruson synthesized dicyclopentyl methacrylate (I) from the addition of methacrylic acid to dicyclopentadiene (3). He also noted that this ester in the presence of cobalt and oxygen was converted to a hard insoluble film at ambient temperature. Recent examination of dicyclopentyl methacrylate as a reactive diluent has shown that it is of some interest in this context; however, it is too volatile for use in many systems and, even worse, it has a penetrating, persistent, and atrocious odor. Accordingly our attention was focused on dicyclopentenylmethoxyethyl methacrylate (II) which we have designated as DCPEMA throughout this paper. DCPEMA is indeed an interesting reactive diluent polymerizable by oxidative polymerization and its use in several different coating systems will be described here.



PHYSICAL PROPERTIES AND TOXICITY PROFILE OF DCPEMA

Typical physical properties of DCPEMA are summarized in Table I. The monomer does have an odor but it is mild and has generally been considered inoffensive. The significant elements of Table I include the low viscosity, high boiling point, and a solubility parameter of 8.6. Accordingly DCPEMA is a good solvent for and compatible with most common organic film formers. In practical terms DCPEMA is not volatile under air drying cure cycles or at 180°F/30' bakes. At higher temperatures evaporation of monomer competes with cure but with appropriate reactive resins it may be cured at temperatures exceeding 250°F without noticeable monomer loss.

TABLE I

Typical Physical Properties of DCPEMA

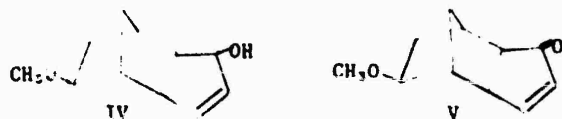
Appearance	clear liquid
Color	100-300 APHA
Viscosity	15-19 cps (25°C)
Density	1.064 g/cm ³ (25°C)
Refractive Index	1.496 (22°C)
Boiling Point	350°C at 760 mm
Solubility Parameter	8.6 (cal/cm ³) ^{1/2}
Flash Point (Pensky-Martens CC)	> 200°F
Cured Film Hardness (KHN)	15
Cure Shrinkage	8.7%
Glass Temperature (homopolymer)	16-18°C
Inhibitor	50 ppm Hydroquinone

A very important consideration in the use of any reactive diluent is its toxicity. The acute toxicity profile is summarized in Table II and suggests that the acute toxicity of this monomer is in fact lower than many commonly used organic solvents.

TABLE II

DCPEMA Toxicity Summary

Acute Oral (rats)	LD ₅₀ 5 g/kg non-toxic
Acute Dermal	LD ₅₀ 5 g/kg non-toxic
Eye Irritation (rabbits)	Non-irritating
Skin Irritation (rabbits)	Draize 0-1-2
Acute Inhalation (rats)	Non-toxic
Ames Mutagenic Test	Non-mutagenic
Skin Sensitization (guinea pig)	Not a sensitizer



The radical flux generated by this autoxidation results in polymerization of the methacrylate functionality of the monomer. The growing methacrylate radical chain is, however, intercepted by oxygen to form a terminal peroxy radical before it can attain high molecular weight. Indeed if sufficient oxygen is present a methacrylate oxygen alternating copolymer is the major product formed. This polymeric peroxide is remarkably stable but is obviously undesirable in terms of achieving maximum coating properties. Analytical studies have shown that in thin films at ambient temperature oxygen copolymer is the primary product. However, in thick films, at elevated temperature (60°C or higher), or in the presence of an effective oxygen scavenger such as drying oil or alkyd, methacrylate homopolymerization is the dominant process. Crosslinking also occurs during the polymerization since addition of the various radicals to the allylic unsaturation is possible.

Unlike the cure of a drying oil the polymerization of DCPDMA is catalytic in oxygen rather than stoichiometric. Indeed monomer cured in bulk shows an interesting difference in the infrared spectra of surface polymer versus interior polymer. The surface material has developed absorption characteristics of hydroxyl and carbonyl groups generated by the autoxidation. Interior polymer shows the typical spectrum of DCPDMA homopolymer prepared in the absence of oxygen. In practical terms this also means that DCPDMA does not have the through-dry problem characteristic of so many alkyds. Finally it should be noted that even though the DCPDMA polymerization is initiated by oxygen in the presence of cobalt there are indications of oxygen inhibition of cure. A film, particularly during the early stages of dry, may exhibit surface tack; however, this disappears since the autoxidation-polymerization mechanism ultimately overcomes this problem.

APPLICATION PERSPECTIVES

DCPDMA is an excellent solvent for many coating resins and it can therefore be used broadly to raise application solids. There are however some systems whose chemistry is incompatible with the DCPDMA oxidative cure mechanism. Non-volatile amines in general complex cobalt and retard cure. Thus, DCPDMA is not useful in amine cured epoxy coatings. Our research has focused on a limited number of coating systems that illustrate different application concepts for DCPDMA. These are:

- High solids drying oil alkyd paints
- High solids low energy cure industrial polyester coatings
- High build chlorinated rubber maintenance paints

HIGH SOLIDS DRYING OIL ALKYD PAINTS - The chemistry of DCPDMA obviously suggests its use as a partial solvent replacement in drying oil alkyds for air pollution compliance. In a brushing formulation (Table III) DCPDMA replaces mineral thinner to yield an overall binder composition of 60 parts of long linseed oil alkyd to 40 parts of DCPDMA. The resulting paint approaches 80 volume solids at brushing viscosity with a CARB emission of only 155 g. per liter. Without

DCPDMA, the paint would formulate at only 55 volume solids and have a CARB value of 350 g/liter.

TABLE III

Low Emission Architectural Alkyd Paint with DCPDMA

Alkyd*/DCPDMA Ratio	100/0	60/40
TiO ₂ /Binder	45/55	45/55
Volume Solids (at 85-90 KU)	55	79
CARB, g/l	350	155
Set Time (hrs)	1	3
Dry-to-Touch (hrs)	4-5	6-7
Zapon Tack Free (hrs)	30	7-8
Properties at Two Weeks		
Tukon Hardness	0.6	1.0
Pencil Hardness	2B	HB
Direct Impact (in-lb)	> 56	40
Gloss	80/90	80/90
Gasoline Softening	5B	B

Drying characteristics of the experimental paint versus the unmodified control reveal interesting and characteristic elements of DCPDMA cure chemistry. Early dry or set time is extended by monomer plasticization of the resin prior to its cure. With the onset of polymerization dry-to-touch time becomes only slightly extended, and dry-hard time (Zapon) is actually greatly reduced.

The cured paint properties typify our experience with a number of medium to long oil alkyds: DCPDMA confers improved thru-hardness and solvent resistance. Accelerated weathering data generally parallel performance of the alkyd being modified.

Very limited work was done using DCPDMA in low temperature (180°F) baking finishes with drying oil alkyds in deference to the fumarate polyester system described in the next section. Best cure response in clear film screening experiments was obtained with a medium-short linseed oil phthalic alkyd.** Tall oil fatty acid and soya alkyds examined thus far have had unacceptable cure response.

HIGH SOLIDS LOW ENERGY CURE POLYESTER COATINGS

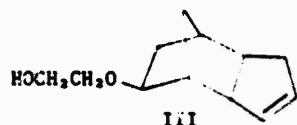
Polyesters with maleate fumarate unsaturation and diluted with styrene or styrene/methyl methacrylate monomer are well known in the coatings industry. High volatility of the monomers, susceptibility to oxygen inhibition, and requirement of highly reactive two-pack catalysis limits extensive use in conventional coating applications. We have found that the DCPDMA chemistry obviates these difficulties and is the basis for a new class of relatively low temperature, heat reactive coatings having good one-pack stability and very high solids.

The methacrylate unsaturation of DCPDMA permits copolymerization with maleate/fumarate while the allylic moiety provides a controlled free radical source for polymerization upon heating the coating in the presence of drier metal. Package stability is achieved with volatile oxime such as methyl ethyl ketone oxime.

Commercially available polyesters are not suitable for this application, however. Most of these resins are based on various ethylene and propylene glycols and all we have examined have poor hydrolytic weathering resistance. There is a class of hydrolysis resistant types made but these are derived from bisphenol A which when present even in minor quantities inhibits oxidative cure.

* 30% phthalic, 60% linseed oil
 ** Spencer-Kollogg Alkyd E515-SOV

SYNTHESIS - Dicyclopentenylmethoxyethyl methacrylate is prepared by a two-step process. The addition of ethylene glycol to dicyclopentadiene catalyzed by strong acid may be selectively carried out in high yield (4). Distillation of the alcohol followed by base catalyzed transesterification with methyl methacrylate provides DCPEMA in excellent yield. The monomer was in most cases used in undistilled form; however, it is a high quality product (> 95% pure) contaminated by small amounts of methyl methacrylate and the alcohol III. The most satisfactory polymerization inhibitor was 50-100 ppm of hydroquinone and monomer so stabilized has excellent shelf life in the dark.



CURE CHEMISTRY OF DCPEMA - Chemically, DCPEMA contains both a polymerizable methacrylate double bond and an allylic group which can serve as a free radical source in the presence of oxygen and conventional metallic driers. It is, therefore, capable not only of homopolymerization to a solid state within coating vehicles but also of interpolymerization with unsaturated resins that may comprise all or part of the vehicle, e.g., drying oil alkyds, fumarate polyesters, polyfunctional acrylates, etc.

The monomer is highly stable in the absence of metallic drier and active free radical sources but it may polymerize in bulk in as little as two days in the presence of driers such as cobalt salts and adventitious oxygen. Excellent formulation stability of systems containing both DCPEMA and cobalt may be achieved however by addition of low levels of volatile oxime, e.g., methyl ethyl ketone oxime. In thin films the oxime evaporates and normal cure is obtained. The use of oximes as anti-skinning agents in alkyd paints is well known. In DCPEMA systems containing cobalt, however, the function of oxime is that of a volatile stabilizer and without it these systems have limited stability. Presumably the oxime complexes the cobalt drier and renders it inactive prior to film formation (5).

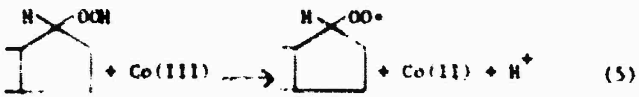
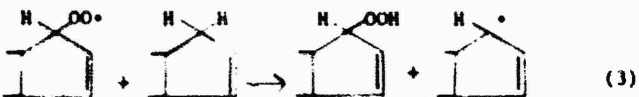
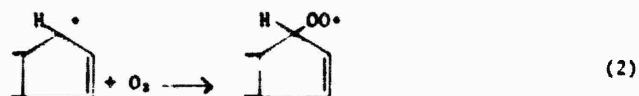
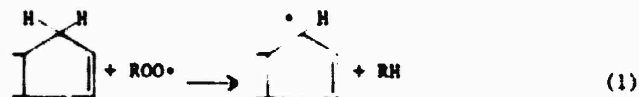
Dicyclopentenylmethoxyethyl methacrylate in the presence of cobalt drier absorbs oxygen and in a 24-36 hour period at room temperature is converted to a hard, brittle insoluble solid (KHN hardness of 15). A typical oxygen absorption curve in the presence of .06% cobalt as naphthenate is observed and may be divided into three distinct phases. First, the system exhibits an induction period whose length depends on the nature and amount of free radical inhibitors present in the monomer and on the amount of cobalt catalyst. The optimum cobalt level is between .05-0.2% metal on monomer and both larger or smaller quantities increase the induction period. The second stage is a period of rapid oxygen absorption where the reaction is probably autocatalytic and is followed by the terminal stage of decreasing oxygen absorption. The amount of oxygen absorbed per mole of DCPEMA varies considerably with the geometry of the sample. In experiments with larger surface area/volume ratios more oxygen is absorbed. In a typical thick film experiment ca. 6 moles of oxygen are absorbed by 100 moles of monomer.

Homopolymers of DCPEMA prepared by metal-catalyzed autoxidation are hard and too brittle for determination of glass transition temperature by torsional modulus. In contrast, DCPEMA homopolymer formed by ultraviolet radiation in the presence of a photoinitiator though also hard, is significantly softer than polymer produced from autoxidation. Both

polymers are crosslinked but the product of irradiation has a broad molecular weight distribution (10,000 to over 1,000,000) while the autoxidation product has a molecular weight of only 1,000 to 2,000.* Apparently, the high radical density produced by radiation causes the monomer to undergo addition polymerization much faster than chain transfer while in the low density radical flux characteristic of autoxidation, chain transfer effectively competes with polymerization to yield low molecular weight products.

At this time, we can only estimate the Tg of DCPEMA homopolymer. In copolymers with other methacrylates, replacement of methyl methacrylate with an equal weight of DCPEMA does not appreciably change the polymer hardness so that the Tg of DCPEMA is ca. 100°C. Determinations of the Tg of DCPEMA homopolymer by DSC thermal techniques provide values of 16-38°C depending on the sample preparation.

The detailed structural chemistry of the DCPEMA cure is a complex question. Almost certainly, however, the process is initiated by an adventitious radical acting on the allylic function of the monomer and this generates the chain reaction described by equations (1)-(3). Equations (4) and (5) are the typical one electron transfer reactions observed from cobalt and organic hydroperoxide. This picture of the chemistry is consistent with the autoxidation of cyclopentene which has been studied in detail (6). It is also supported by our examination of the autoxidation of the model compound dicyclopentenyl methyl ether where the unsaturated alcohol IV and ketone V (the expected decomposition products of the corresponding hydroperoxide) were identified as the only volatile products of the cobalt catalyzed oxidation.



* Cross molecular weight data was determined on DCPEMA polymerized via the two methods in a thermoplastic film matrix of an acrylic copolymer. This technique was used to obtain soluble polymers for gel permeation chromatography.

Accordingly, we have designed a number of hydrolysis resistant polyesters as companion resins for DCPDMA in high solids coatings. Compositions and the function of each of the components in these experimental resins are shown in Table IV; the fundamental components are maleic anhydride and neopentyl glycol to provide cure functionality and hydrolysis resistance respectively. Trimethylpentanediol (TMPD) retards the crystallization tendency of the neopentyl structure while the aliphatic dibasic acids provide softness/flexibility control. The dibasic acids also reduce crystallization tendency and in this regard azelaic acid is somewhat superior to adipic acid. Azelaic acid yields films of hardness comparable to adipic acid at equimolar levels, but which are tougher in critical tests such as gravelometer abrasion.

The volatile loss of DCPDMA in these catalyzed polyester coatings, even at the relatively high baking temperatures of 275°F and greater, is remarkably small, indicating excellent reactivity. In the absence of cobalt, losses of DCPDMA of 50% or greater are found under these conditions. The importance of reactive unsaturation is demonstrated with polyester E of Table IV in which maleic anhydride was replaced by succinic anhydride. The baked films are soft and hazy indicating the lack of cure of the reactive diluent with the resin and moreover a substantial percentage of the DCPDMA is lost by volatilization.

The hardest of the resins of Table IV (polyesters A and B) can be used to formulate high solids coatings for general product finishing which cures to a tack-free state at temperatures as low as 180°F. Complete cure, to achieve maximum hardness and resistance properties, does require baking temperature on the order of 200-250°F. As shown in Table V these polyester coatings compare very favorably with several well known generic types of industrial coatings. In particular, the polyester/DCPDMA system offers very high application solids, less yellowing tendency than alkyds, lack of the formaldehyde emission problem of melamine cures, and in contrast to the premium acrylic/urethane is one-package. Exterior durability of the reactive diluent coating has not been adequately established but accelerated studies show performance at least as good as that of premium short oil alkyds.

The softer polyester resins, especially Resin D of Table IV, are showing excellent promise in very high volume solids automotive spray body primers. Corrosion resistance, adhesion, and gravelometer abrasion resistance equal or exceed the performance of conventional low solids epoxy ester primers. Moreover, they require low temperature for cure.

HIGH BUILD CHLORINATED RUBBER COATINGS - Chlorinated rubber paints have gained wide acceptance for heavy duty industrial and marine maintenance applications. They apply easily, dry relatively quickly, and are forgiving of less than ideal surface preparation. The excellent protective properties of chlorinated rubber paints presumably result from the high moisture barrier properties of the highly chlorinated resin. Maximum protection nevertheless requires a dry film thickness on the order of 7-8 mils to cover high profile steel surfaces resulting from weathering or blast cleaning. Even with "high build" formulations developed in recent years, application solids by airless spray are only 35-40% by volume and as many as 4-5 labor intensive applications are required. Accordingly the twin pressures of cost and pollution control dictate a need for increasing spray solids in these systems.

Our efforts to achieve maximum application solids without sacrifice of important performance properties, especially corrosion resistance, have proceeded in two stages. In the first stage DCPDMA alone was used as reactive diluent; our second stage efforts involve a still proprietary modification of DCPDMA diluent to increase its speed of cure and are not yet complete.

Conventional high build chlorinated rubber coatings comprise chlorinated rubber itself (a very hard resin), a somewhat softer, lower molecular chlorinated resin, and liquid chlorinated paraffin plasticizer. The first formulation listed in Table VI is typical state-of-the-art. In the second formulation, "DCPDMA Hi-Build," chlorinated resin and plasticizer have been replaced in part with 20% DCPDMA, the maximum we considered feasible to avoid embrittlement in the cured film and without objectionable lengthening of drying time. Until cured, DCPDMA acts to plasticize the film. The cure of DCPDMA in typical chlorinated rubber coatings was chromatographically monitored and

TABLE IV

Polyester Resins for DCPDMA

Components (mole ratios)	Function	A	B	C	D	E
maleic anhydride	cure unsaturation	90	90	75	50	--
succinic anhydride	(control)					90
adipic acid	hardness/flexibility	10		25	50	10
azelaic acid	"		10	25	50	10
neopentyl glycol (NPG)	hydrolytic stability	75	75	75	75	75
2,2,4-trimethyl-1,3 pentane diol (TMPD)	crystallization control	25	25	25	25	25
Resin and Coating Properties						
viscosity at 70% solids in n-butyl acetate		2-21	2	V-W	V-	--
Acid number		25	25	22	24	29
Percent DCPDMA volatilized at 275°F/30'		2.7	0.0	0.1	3.1	10.9
Film Hardness (KHN)		15.6	15.7	9.6	2.5	< 0.15 (hazy)

TABLE V

High Solids Polyester/DCPEMA Coating Properties

1.5-2.0 mils on Bonderite 40, TiO₂/Binder = 40/60

	Polyester A/DCPEMA = 60/40		Tall Oil Alkyd ¹		Acrylic/Melamine ²	Acrylic/Urethane ³
Cure Schedule (30')	180°F	250°F	180°F	250°F	250°F	180°F
Spray Solids - volume %	60	60	38	38	50	37
- weight %	73	73	51	51	65	36
Gloss (20°/60°)	73/86	60/75	87/92	--	78/90	76/88
K Color	9.0	13.6	13.2	29.5	6.4	6.2
Tukon Hardness (KHN)	4.5	17.3	1.4	9.1	13.0	18.2
Pencil Hardness	H	5H	2B	F	4H	5H
Mandrel, in. (Pass)	1/8	3/8	3/8	1	3/16	3/16
Direct Impact (in-lb)	45	35	15	15	42	24
Gasoline Softening (15')	3B	4H	6B	2B	H	3H
Mar Resistance	Fair	Exc.	Poor	--	Good	Good
Print Resistance (140°F, 10 worst)	7	3	10+	--	4	7

¹ Freeman 11-8345² Acryloid[®] AT-400/Cymel[®] 325 = 75/25³ Acryloid[®] AU-608/Dasmodur[®] N = 76/24

TABLE VI

High Build Chlorinated Rubber Marine/Maintenance Coatings

Based on Reactive Diluent DCPDMA

(Adjusted to Airless Spray Viscosity of ca. 2 poise ICI)

	Conventional Hi Build	DCPDMA Hi Build	Modified DCPDMA Hi Build
Chlorinated Rubber (5 cps grade)	40.0 (10 cps)	25.0	20.0
Chlorinated Hard Resin	35.0	35.0	17.5
Chlorinated Plasticizer	25.0	20.0	12.5
DCPDMA	--	20.0	50.0 (modified)
Volume % Solids	40	55	69
Weight % Solids	62	75	84
PVC (TiO ₂ /Barytes/Carbon Black)	27.5	27.5	27.5
Volatile Organic Content gram/liter	535	367	265
lb/gallon	4.5	3.2	2.2
Corrosion Resistance (Salt Spray/High Humidity)	Control	Better	Best
Drying Speed	Control	Slightly slower	Equal to slightly slower

show that conversion is quite rapid initially and is nearly complete within one day. Quite remarkably the salt spray corrosion resistance of the DCPDMA coating over steel has been found to be consistently better than that of the conventional coating. We attribute this improved performance to the intrinsic hydrophobicity of DCPDMA and to the low level of crosslinking it appears to impart to these otherwise thermoplastic coatings. In this first stage effort it was possible to elevate application solids from 40 to 55 percent by volume with concomitantly major reduction of solvent pollution.

With a presently proprietary modification of DCPDMA we have not only been able to increase cure speed but also to confer improved flexibility such

that much higher levels of reactive diluent can be used. In the third formulation of Table VI we have used 50 percent of the modified diluent to achieve nearly 70 percent solids by volume, and the most stringent CARR VOC of 250 g of solvent/liter. Moreover, salt spray corrosion resistance of this coating exceeds even that of the initial DCPDMA system.

At this stage of our development the DCPDMA high build paints are not truly one-package. Although oxime stabilization of formulations with cobalt is effective, release of available oximes from the very thick coatings unacceptably retards cure. Our approach is to make a complete paint with the exception of the small amount of cobalt which is then mixed in when the paint is stirred for viscosity adjustment at

the time of application. The catalyzed coatings have several days of working pot life, in marked contrast to two-package epoxy coatings.

In summary the oxidative polymerization of the methacrylate diluent DCPMA provides a rather general route to high solids high film build coatings with interesting properties. A great deal of work remains to be done to fully exploit the potential of this technology but the pressures of solvent cost, pollution, and energy costs suggest that it will have an important place in the future of the coatings industry.

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One means of saving energy is the construction of durable goods from materials with lasting qualities. The fluorinated polymers have intrinsic properties which make them prime candidates for coatings, composites, castings, elastomers, etc., of long service capability. It is essential that life cycle costs be used as a basis of selection since such quality materials would be rarely selected for applications in which only the initial cost were considered. Also, fluoropolymers have been hampered in selection for general purpose use because of the inconvenient means necessary for processing. With the advent of highly fluorinated epoxy, polyurethane and acrylic polymers this inconvenience is no longer necessary. These materials are highly resistant to degradation by the weather, by biological organisms, by physical abuse, and by most conditions encountered by polymeric substances. In addition, they possess a variety of properties such as low friction surfaces, ice release properties and extremely low fluid absorptions not found in the common substances.

BACKGROUND

When Nikita Khrushchev visited the United States in 1959, he was reported to have observed that American houses were not constructed to last long. In those days of cheap energy in seemingly endless supply, it was easy to dismiss Mr. Khrushchev's observation with the smug certainty that he did not understand the dynamic and changing nature of this society. Today, however, with energy costs soaring without bounds, carrying the prices of materials and services in the wake, the concept of life cycle cost as opposed to initial cost is acquiring respectability. In the area of polymeric materials, this should allow an opportunity for high quality polymers, such as the fluoropolymers, to compete more effectively with less expensive materials than has been possible in the past. The inherent strength of the carbon-fluorine bond is such that very long service life is possible with this class of polymers and for many useful applications the fluoropolymers have novel characteristics which are unique.

WHAT'S SPECIAL ABOUT FLUOROPOLYMERS?

The element fluorine occupies one of the extreme positions in the periodic chart of elements, normally being placed in the upper right-hand corner. This is consistent with its being the most electronegative, or "electron loving", of all material substances -- in other words, it is the most nonmetallic of the non-metals. When fluorine reacts with carbon to form fluorocarbons, the resulting chemical bonds are

exceptionally durable, particularly if the carbon atoms are completely fluorinated; or "perfluorinated". A great deal of energy must be supplied to such a molecule to break these bonds whether it be light energy, chemical energy, biological degrading effects, heat, or whatever. The consequence of this is that the fluorocarbon polymers are extremely stable to the disrupting forces of a normal environment and are, therefore, of greater longevity than most polymers under most conditions that do not involve large mechanical stresses. The perfluorinated polymers are often not exceptionally strong in a mechanical sense, but this weakness can be substantially offset by the employment of strong polymers which are partially fluorinated to act as carrier media for the perfluorinated varieties. By the use of this technique, recently synthesized fluoroepoxies, fluoropolyurethanes and fluoroacrylics have been utilized to produce conveniently a wide range of fluoropolymer coatings, plastics, adhesives, composite matrix binders, etc., not previously available.

WHY ARE FLUOROPOLYMERS EXPENSIVE?

Nature has provided man with vast quantities of materials composed principally of carbon and hydrogen, but nowhere is there found an oil well or a coal mine which supplies the fluorocarbon analogues. Each individual fluorocarbon material must be synthesized from hydrocarbon compounds and fluorine, the elemental form of which is expensive to produce and handle because of its extreme reactivity. This probably does not adequately explain the relatively high cost of fluoropolymers, however, because the big volume fluorocarbon compounds of a nonpolymeric nature are not prohibitively expensive. In fact, so much fluorocarbon was blown away into the atmosphere in the rather mundane use as a propellant for spray cans that it allegedly threatened the earth's ozone layer! It is probable that the major factors in the prices of fluoropolymers have been: (1) the fluoropolymer image in the public mind as high priced, specialty materials, (2) the lack of effective competition and marketing with the end objective of price reduction, (3) the lack of necessity for life-cycle cost considerations, and (4) the failure of potential users to appreciate the benefits that fluoropolymers can offer.

HOW CAN FLUOROPOLYMERS SERVE MAN BETTER?

In addition to longevity in the environment, there are a number of special applications of fluoropolymers which could be of great benefit to man. One of these is suggested by the present use of poly(tetrafluoroethylene) as an anti-stick coating on cooking utensils, namely, anti-adhesive coatings. Certain fluorinated polyurethanes containing suspended poly(tetrafluoroethylene) and silicone additives form tough, durable coatings to the surface of which ice can adhere with minimal tenacity. Unlike most ice-release coatings, these materials retain the release property through many cycles. Successful experiments have been performed during the last two winters to evaluate the effectiveness on electrical power systems to prevent switch malfunction and power line collapse due to ice overload and wind action. This application could help make electrical outages far less likely in cold, severe weather.

This release property has also been evaluated for similar fluorinated polyurethane coatings on the underwater external hull of ships to prevent the tenacious adhesion of marine fouling organisms. The economic benefits of a smooth, clean hull to shipping efficiency are well known, and in contrast to the conventional anti-fouling paints which function by

the slow release of a toxic inclusion, these fouling release coatings of a fluoropolymer nature are not toxic and are non-polluting.

Fluoropolymers are the least affected by water and high humidities of synthetic organic materials, and this property suggests a wide range of potential applications. Electronics equipment which is water sensitive can be encapsulated in fluoroepoxy resins to give a high order of protection (1)*. Since certain fluoroepoxies and fluoroacrylics are clear, colorless plastics of good optical quality, fast draining windows to improve the visibility from aircraft during rain storms can be produced from them (2). Coatings which are not readily wetted by water and oils have many potential uses in the marine industry (3), for example, as bilge coatings, galley coatings and as protective topside paints. A particularly attractive feature of the coatings for these applications is the ease of cleanability. The well known soil release properties of heavily fluorinated materials can be used to good advantage to save labor during periodic cleaning. By the expedient of either putting poly(tetrafluoroethylene) into a coating or leaving it out, a quality of low or high frictional coefficients can be imparted since the fluoroepoxies or fluoropolyurethanes are high friction. This property of high friction can be used to advantage on floor coatings. In addition to the low water absorption, fluoropolymers are not nutritious for microorganisms, and fungi, molds, bacteria, etc., not only find such materials inhospitable but also the unattractive growths are often easily removed from fluoropolymer surfaces.

Poly(tetrafluoroethylene) has been extensively investigated as a dry film lubricant, and the use of this material in combination with fluoroepoxies allows the convenient molding of plastic parts which have permanent lubricity and excellent strength. These materials are obvious candidates for use as bearings and gears, but the most interesting potential use which could be of great value to man is in the area of medical prostheses. Replacements for the ball joint of the hip, for example, could be readily molded from strong, inert fluoroepoxy which would possess a permanent lubricity at the mating surface. Also, the fluoroacrylics have substantial promise as dental materials (4). The common acrylic resins have been used extensively in dentistry with a high degree of acceptance, and the inclusion of fluorocarbon into these established materials should result in a substantial increase in resistance to the harsh environment of the human mouth.

These are but a few of the applications of fluoropolymers which could be of great future service to man. As of the present, the technological problems involved in the use of these substances, which were formidable, have been largely solved, and the crux of the present problem is economic. For the fluoroepoxies, fluoropolyurethanes and fluoroacrylics the need for volume production and the resulting economics are obvious, but a fundamental change in image which would bring the fluoropolymers from the prima donna era to a workhorse reality could be of inestimable future benefit.

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RADIATION CURABLE COATINGS offer several advantages over conventional thermally converted solvent based coatings systems. In conventional thermal coatings technology a polymer and reactive crosslinking oligomer is dissolved in a non-reactive diluent solvent. The ratio of solvent to polymer-crosslinking oligomer is usually 50 to 60% of the total coating system. This low viscosity liquid composition is then applied to a substrate and baked in a gas fired oven which removes the solvent and sets the polymer-crosslinking oligomer into a solid three dimensional crosslinked network or finished coating. This process is energy intensive since most of the thermal input energy goes to heat the substrate and remove the nonreactive diluent solvent. Additional thermal energy is also required to activate the crosslinking reaction of the polymer with the crosslinking oligomer in order to effect cure. In many cases the substrate is heat or moisture sensitive and a thermally cured coating operation causes shrinkage-warpage or dehumidification of the substrate which requires an additional manufacturing step to produce a useable finished product. The non-reactive diluent solvent used in conventional coatings technology is usually vented into the atmosphere which causes pollution, burned or is recycled in order to make up part of the thermal energy of the oven used to cure the coating system (Figure 1).

ABSTRACT

Traditional solvent-based coatings technology utilizes thermal energy (gas ovens) for conversion of liquid paint systems into a solid finished product. Some of the disadvantages associated with conventional thermally cured coating systems are energy consumption, volatile solvents which contribute to pollution and additional manufacturing processes for heat removal from the coated substrate product.

Radiation curable coatings utilize electrical energy (wavelengths of light or high energy electrons) for conversion of liquid paint systems into solid finishes but these coatings are 100% convertible so that there are no volatile emissions or pollution associated with this coating-curing process. Radiation curable coatings systems are not energy intensive in that only the energy required for curing is transferred directly to the coating and not lost in unnecessary heating of the substrate. Since heat is not involved in radiation curing of coatings, additional manufacturing processes for substrate heat removal is not required as in conventional thermally cured coatings and this leads to efficient product-production.

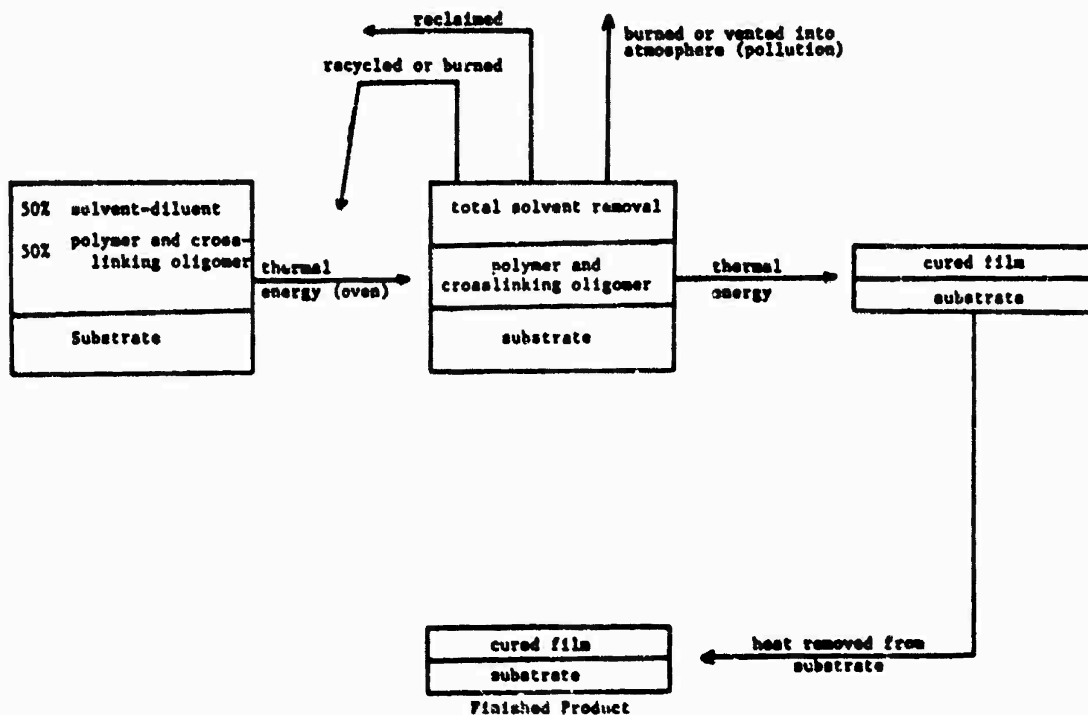


Fig. 1. - Conventional Thermally Cured Coating System

In radiation curable coatings a reactive polymer and coreactive crosslinking oligomer are dissolved in a completely coreactive diluent solvent. This mixture is applied in a similar manner as a conventional thermally cured coating but is cured via electrical or light energy processes and does not require direct thermal expenditure of energy. Since the radiation curable coatings are 100% reactive there are no volatile solvent losses and the liquid coating supplied to the substrate is totally converted into a solid cross-linked film. Since there are essentially no volatile emissions associated with the conversion process, radiation curable coatings are pollution free and are not energy intensive processes. Another advantage to radiation curable coatings is that in the curing process electrical or light energy is absorbed only by the coating and is not wasted in heating the substrate as in the case with conventional thermally cured coating systems. This efficient use of energy allows radiation curable coatings to be applied and processed on heat sensitive substrates resulting in finished products requiring relatively simple manufacturing operations (1*) (Figure 2).

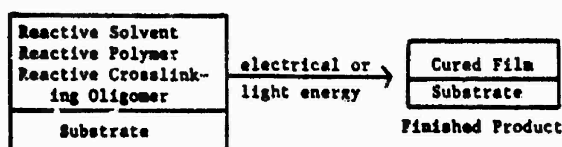


Fig. 2. - Radiation Curable Coating Systems

ENERGY SOURCES USED IN RADIATION CURABLE COATINGS TECHNOLOGIES

Radiation-curable coatings technology utilizes electrical input energy and converts it either into light energy or an accelerated electron beam (Table 1).

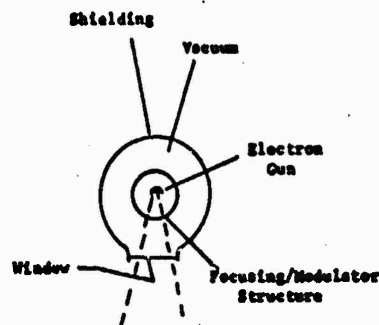
Table 1 - Energy Sources Used in Radiation Curable Coatings Technologies

- (1) ULTRAVIOLET RADIATION
 - (a) MEDIUM PRESSURE MERCURY LAMPS (WITH OR WITHOUT ELECTRODES): MAJOR OUTPUT AT 365 nm
 - (b) LOW PRESSURE MERCURY LAMPS: MAJOR OUTPUT AT 254 nm
 - (c) FLASH LAMPS (UV AND VISIBLE WAVELENGTHS OF LIGHT)
- (2) VISIBLE LIGHT SOURCES
- (3) HIGH ENERGY ELECTRON PROCESSORS
 - (a) ELECTRON BEAM
 - (b) ELECTRON CURTAIN

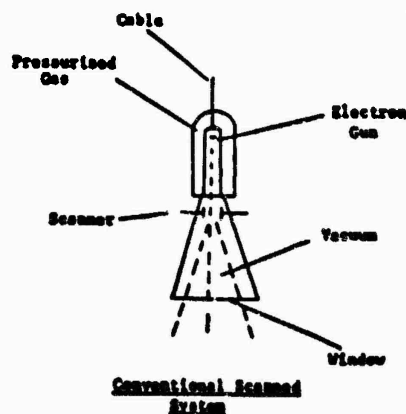
The 100 percent reactive liquid coating systems associated with this technology absorb converted electrical energy from the processor unit (Light Source or Electron Accelerator) and undergo conversion to a solid matrix or cured finish. In the case of light energy convertible coatings a photoactive catalyst is required in order to initiate the curing mechanism, while in electron beam the energy output is sufficient to cause direct ionization-radical formation and subsequent initiation curing reactions of the coating system.

* Numbers in parentheses designate References at end of paper.

ELECTRON BEAM - Electron beam processing units mainly consist of a power supply and electron beam acceleration tube. The power supply steps up and rectifies line current while the accelerator tube generates and focuses the beam as well as control the electron scanning operation. The beam is produced when high voltage energizes a tungsten filament causing electrons to be produced at very high rates of speed. These fast electrons are concentrated to form a high energy beam and are accelerated to full velocity inside the electron gun. Electromagnets placed on the sides of the accelerator tube allow deflection (scanning) of the beam similar to the operation of a television tube. Scanning widths and depths vary from 24 to 72 inches to 4 to 6 inches, respectively. The scanner opening is covered with a thin metal foil (usually titanium) that allows passage of electrons but maintains the high vacuum required for large acceleration voltages (Figure 3)(2).



Curtain Processor
"Electrocurtain"



Conventional Scanned System

Fig. 3. - Electron Beam and Electrocurtain Radiation Curing Processors

Accelerators can vary in power from 200 to 500 kilovolts, have currents in the range of 25 to 200 milliamperes, and are capable of applying dose rates of 1 to 10 megarads per second.

Electron processors (scanned electron beam) suffers from several major disadvantages. The most severe of these is the large area which must be shielded when this technique is used since any surface enclosing the electron accelerator scanner acts as a source of X-rays generated by electrons which are scattered to the wall and these emissions are along the entire length of the system. Another disadvantage is the large space requirement for housing this type of scanner electron beam radiation source.

Advantages of the electron beam processor are its ability to penetrate thick coatings or composites (over 7 mils) and is currently being used to efficiently crosslink insulation and wire cable coverings (3 and 4).

ELECTROCURTAIN - The electrocurtain processor is a high-voltage (150 kilovolt) electron tube which provides a continuous strip of energetic electrons from a linear filament or cathode located on the axis of symmetry of the system. The cylindrical electron gun shapes and processes the electron system in a grid controlled structure; the stream is then accelerated across a vacuum gap to a metal window where it emerges directly into air and travels on to the product. (Figure 3)

The energetic electrons from the processor are absorbed directly in the coating itself where they create the initiating free radicals uniformly in depth. Since electron energies of only 100 eV or less are required to break chemical bonds and to ionize or excite components of the coating system, the shower of scattered electrons produced in the coating leads to a uniform population of free radicals (excited atoms or ions) throughout the coating, which then initiate the polymerization reaction (Figure 4). In the liquid phase

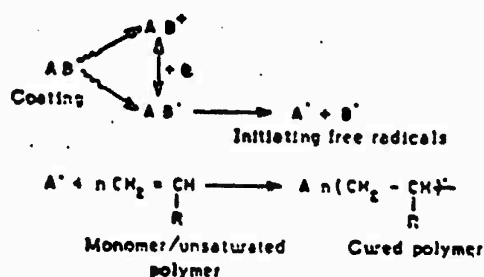


Fig. 4. - Polymerization Initiation and Propagation by Radiation Generated Free Radicals

systems of interest here for coatings work, the polymerization process will propagate until the activity of the growing chain is terminated. These energetic electrons are capable of penetrating many different types of pigmented coatings and are capable of producing through-cure down to the substrate-polymer coating interface. Both the electron beam and the electrocurtain cure pigmented films, but the power of the electrocurtain is substantially less; hence, its maximum curing film thickness range is in the order of 1 to 4 mils.

In the electrocurtain processor, the shielding is clad directly to the tube housing, so that a self-shielded processor results. The size savings is a real advantage since the shielded tube 25 cm in diameter replaces the 3-meter high structure required by the scanned electron beam apparatus. The electrocurtain has a more flexible geometry and can adapt readily to many different types of curing applications (5).

ULTRAVIOLET RADIATION CURING

The concept of ultraviolet irradiation or photocuring of coatings can be divided into five basic segments:

1. a stable light source is needed—one capable of producing ultraviolet wavelengths of light or ultraviolet radiation (near and far UV, 200-400 nm) with sufficient power or intensity to be commercially feasible.

2. a photoinitiator capable of absorbing ultraviolet radiation, at appropriate wavelengths of energy emitted from the light source, is needed.
3. active free radicals must be produced through the action of light absorption by the photochemically active photoinitiator. These free radicals initiate polymerization of unsaturated monomers, oligomers, and polymers. Catalysts are not required in high-energy electron curing processes.
4. unsaturated (high boiling acrylic, methacrylic) monomers, oligomers, crosslinkers and low molecular weight polymers make up the fluid, low viscosity, UV-curable coating system similar to the coatings materials used in high-energy electron curing processes.
5. after free radical initiation of the reactive liquid UV-coating the monomers propagate into a fully cured, crosslinked solid coating or film (6).

LIGHT SOURCE - The light source normally used in commercial photocuring reactions is the medium pressure mercury arc lamp with a quartz or Vicor envelope. These lamps can contain electrodes for electrical to light energy conversion or may be electrodeless in which case a radio frequency wave causes mercury atom excitation and subsequent light emission. The normal power input levels vary from 100 to 400 watts per inch of arc length resulting in sharp peak outputs with approximately 10 nm bandwidths. The major peaks are at 365, 404, 436, 546, and 578 nm with relative outputs (200 watt/inch Kanovia Lamp) of between 6 to 15 watts/inch.

Many other types of light sources can also be used for photopolymerization reactions; for example, low-pressure mercury arcs, flash lamps, fluorescent lamps, and even lasers. A complete review of light sources used in photopolymerization reactions can be found in References 7, 8, and 9.

Light wavelength output energies from the various UV-sources are very small compared to electron beam or electrocurtain processors (2-5 eV to thousandths of eV). Energy associated with 365 nm wavelengths of light is equivalent to 3.4 eV or 82 kcal/mole which is sufficient to cause very selective rearrangements and cleavage of aromatic carbonyl-alkyl carbon bonds (aromatic - C - alkyl) (10, 11).

Light energy alone is not sufficient to cause direct efficient monomer initiation reactions as is the case with high-energy electron curing techniques. Commercial light-induced curing reactions require the use of a special photosensitive catalyst in the coatings formulation. These photosensitive catalysts or photoinitiators are an integral part of the formulation and cost of an ultraviolet radiation-curable coating total system. The type and amount of photoinitiator also influences the relative rate of cure speed and the final properties of the cured film or coating (12).

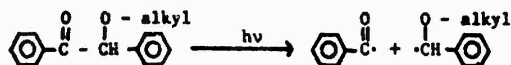
PHOTOINITIATORS - Many theories of photoinitiated polymerization reactions with different light-sensitive catalysts have been reviewed in References 13, 14, and 15. There are, however, two general classes of photoinitiators:

1. Those that undergo direct homolysis upon exposure to UV irradiation and produce active free radical intermediates.

- Those that undergo electron transfer reaction followed by rearrangement into a free radical species.

It is also important to select photosensitizers and photoinitiators with absorption bands that overlap the emission spectra of the various commercial UV-curing light sources (only the light absorbed by a molecule evokes photochemical reactions) (16).

The most common photoinitiation systems in use today are the alkyl ethers of benzoin which undergo direct photofragmentation upon absorption of UV energy at about 360 nm wavelengths to produce two free radical intermediates (17).

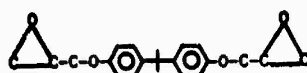


Other photoinitiator structures having similar photofragmentation-rearrangement decomposition processes have been reviewed in References 18 and 19.

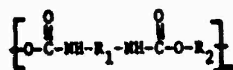
COATING COMPOSITIONS

Conventional thermally cured coating systems are generally based on the following polymer backbone chemical structures:

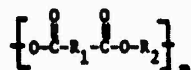
- Epoxy



- Urethane



- Polyester



- Acrylic



Present day thermal curing coatings systems utilize these types of polymer structures as well as fillers, and pigments dissolved or dispersed in an organic solvent for coatable application viscosities. These solvents are then thermally removed and the coating is crosslinked into a three-dimensional network by an energy-rich chemistry requiring a high degree of thermal energy to convert the polymers into useful commercial acceptable properties.

Radiation curable polymer systems are based on the same chemical structural design as the conventional polymer systems but certain modifications are made in order to accommodate reactive unsaturation sites necessary for a radiation induced free radical curing mechanism. Examples of these modifications of conventional polymer structures to form radiation curable polymers are as follows:

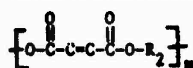
- Unsaturated (Acrylic/Methacrylic) Epoxy



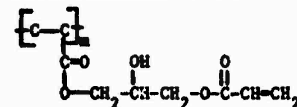
- Unsaturated Urethane



- Unsaturated Polyester



- Unsaturated Acrylic



The monomer in radiation-curable coatings is the analog of the solvent in a conventional paint. Although it performs like a solvent by being a medium for all of the other ingredients and by providing the necessary liquid physical properties and rheology, it differs in that it enters into the copolymerization and is not lost on cure.

Most radiation-curable monomers contain single unsaturation sites and are high-boiling acrylic esters, although in the wood area some coatings use styrene as the monomer. Usually, where styrene is used, most or all of the polymer-polyester unsaturation is fumarate, rather than acrylic.

Crosslinking oligomers in conventional thermosetting coatings formulations are usually melamine resins (acid, hydroxyl-transetherification crosslinking reactions), amine/amide hardeners (oxirane ring opening reactions), and blocked isocyanate prepolymers. Oligomers and crosslinking materials in radiation curing systems are similar to single vinyl-functional monomers except they contain di-, tri-, or multifunctional unsaturation sites. These multifunctional components cause polymer propagation reactions to proceed into three-dimensional network structures of a cured film (Figure 5).

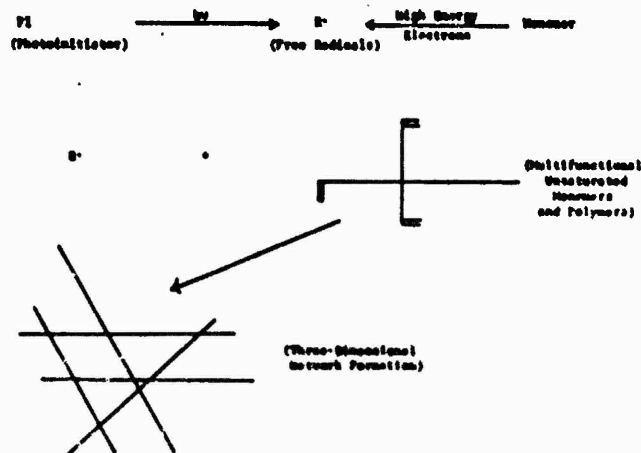


Fig. 5. - Radiation-Induced Crosslinking Reactions

FORMULATION OF RADIATION CURABLE COATINGS

Formulation of radiation curable coatings require a balance in composition among three variables; single unsaturated functional monomers, crosslinking agents (multiunsaturated oligomers), and unsaturated polymers. For example, as the composition of a coating changes from monomer to polymer rich mixtures at a constant crosslinking oligomer concentration the coating viscosity increases, the rate of cure for the coating may decrease and the final film properties would be expected to have good adhesion and better extensibility. If the coating composition changes from a monomer to crosslinking oligomer rich mixture at constant polymer concentration then the rate of cure for the coating will be increased but the final cured film may be brittle and have very little adhesion to certain substrates (20).

The physical properties of the cured film depend upon the initial liquid formulation ingredients with regard to chemical structure, unsaturated reactivity and individual component concentrations.

APPLICATIONS OF RADIATION CURABLE COATINGS

WOOD COATINGS - The wood finishing industry is a major user of radiation curable coatings. These coatings are mainly cured through ultraviolet radiation polymerization techniques which offers a high production efficiency, low cost and excellent finished coating performance characteristics. The UV-curable coating system has instant start-up operation, can be used on heat sensitive substrates and has extended pot-life stability. The temperature of the finished work piece is almost 100-120 F and the cured coating is tough enough to allow sampling or stacking immediately after processing. These coatings cure rapidly preventing adverse penetration into porous surfaces while sealing and producing a smooth finish in one application. Since no volatile solvent is retained in the film (UV-curable coatings are almost 100% reactive) there are no pinholes or crazing problems associated with the system (21, 22).

Although most of the U.S. commercial wood finishing operations are associated with ultraviolet radiation curable technology, there are several European companies utilizing electron beam or high energy electron processors to produce high quality cabinets and doors. These products have 100% reactive filler formulations (similar to UV curable filler systems but without a photosensitizer) and heavily pigmented radiation curable topcoats. These coatings are electron cured, usually under nitrogen atmosphere, to produce a finish that is extremely durable and approaches low pressure laminate quality performance characteristics (23).

In general there are three coatings areas of interest to the wood finishing operation:

1. Filler-sealers (Figure 6)
2. Ground coat or base coat
3. Topcoat

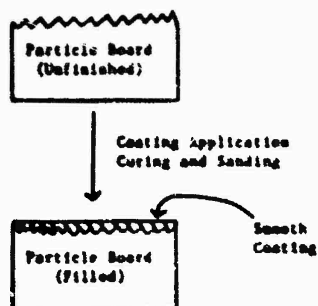


Figure 6. - Unfinished and Finished Particle Board

METAL SUBSTRATES - Radiation curable coatings for metal substrates include a wide range of applications such as beverage can finishes (metal decoration), coil coatings, and coatings for general metals. In each of these products adhesion of the coating to the substrate or adhesion between coatings (primer-topcoat) is of primary importance. The trade-offs in cure speed, flexibility-hardness, ability to take postforming operations, and adhesion to a wide variety of surface-treated substrates have demanded large technical efforts in order to solve these problems (24).

PLASTIC SUBSTRATES - Radiation curable coatings have found wide application on plastic substrates such as vinyl floor tile and polyolefin packaging substrates. The major advantage of using radiation curable coatings for a vinyl floor tile material is the ability to greatly improve abrasion and stain resistance without distortion of the heat sensitive substrate. The radiation curable coating system used in floor tile applications is based on a aliphatic, unsaturated, polyurethane backbone structure which cures into a no-wax-high gloss-floor finish. A similar radiation curable polyurethane coating or adhesive is used in foil/polyolefin film lamination products for the packaging industry (25, 26).

Other possible applications for radiation curable coatings can be found in Table 2.

Table 2 - Future Business Areas for Radiation Curable Coatings

- RADIATION CURABLE COMPOSITES
- RADIATION CURABLE ENCAPSULANTS
- SOLAR CELLS
- ELECTRICAL COMPONENTS
- RADIATION CURABLE LAMINATES
- FILM/FOIL PACKAGING
- RADIATION CURABLE LATEX
- FABRICS
- HEAT SENSITIVE SUBSTRATES
- VINYL FILMS
- WALLPAPER
- RADIATION CURABLE ELECTRO COATING
- METAL COIL AND STRAP
- COIL COATINGS/PRIMER AND TOPCOAT
- OPTICAL FIBERS
- PRESSURE SENSITIVE ADHESIVES
- BARRIER COATINGS
- GRAVURE PRINTING INKS
- FDA APPROVED SYSTEMS

CONCLUSIONS

Radiation-curable coatings technologies [ultraviolet (UV) or electron beam and curtain (EB-EC)] have found acceptance and commercialization with a wide variety of industries concerned with inks, coatings or adhesives for wood, paper, metal, textile, vinyl and other plastic substrates.

Interest in radiation-curable technologies was originally brought about by natural gas shortages and air pollution regulations on the coatings industries. The impetus towards actual commercialization, however, was not necessarily due to energy or pollution requirements, but due to high profitability resulting from faster production speeds, simpler manufacturing processes, higher raw material efficiency (100% solids coverage), superior quality inks and coatings and value added products (cheap substrates having relatively thin but high-quality protective topcoats).

Development and formulation of radiation-curable coatings require knowledge of many complex variables, their interactions, and several interdisciplinary skills. A radiation-curable coatings chemist should be aware of photochemistry, physics of high-energy electrons, polymerization kinetics and network analysis, as

well as solvent-polymer-pigment interactions associated with conventional or traditional ink-coatings formulations.

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OUR DEBT TO THE POLYMER PIONEERS

Edward G. Jefferson, President
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Wilmington, Delaware 19898

In the attached speech, Du Pont President Edward G. Jefferson pays tribute to the polymer scientists whose discoveries have done much to shape the way modern man lives, dresses, travels and communicates.

It is a pleasure to participate in this symposium and to celebrate Dr. Herman Mark, who has done so much for polymer science and the polymer-based industries. I am honored to be asked to talk about our debt to the polymer pioneers in the presence of a man who is indeed a charter member of such a group. As you all know, Herman Mark has written about and explained the history and substance of polymer development with great insight and clarity. And he has probably imparted that understanding to more people in more parts of the world than anyone else.

The accomplishments of the leaders of polymer science laid a firm foundation for the chemical industry as it exists today. The profusion of materials spawned by polymer chemistry has done much to shape how people live, dress, travel and communicate in contemporary society.

In the next few minutes, I will discuss some of those leaders and their landmark discoveries. I'll try to give you a brief glimpse of where polymers have brought us and where they may be taking us in the future.

In thinking about my subject -- our debts to the pioneers -- several general observations seem relevant:

FIRST, we owe much to many people. A large corps of brilliant men and women have built the edifice of polymer science. There are those who advanced the science in a major way -- and I have selected seven whom I will discuss in greater depth in a few minutes. But, in addition to them, there are scientists going back to the early 19th Century who laid the groundwork ... who were compelled by curiosity to seek knowledge about the basic structure of materials. And there are many others in this century who have made invaluable contributions.

SECONDLY, recognition cannot go solely to any one institution or any one segment of society or any one country. The development of polymers was the product of both academic theoreticians and industrial pragmatists. Praise is due not only to those who developed concepts but also to those who saw the usefulness of polymers and who took risks in developing and marketing them. We should also acknowledge the international nature of polymer developments. The great flow of information across borders, fostered by Dr. Mark and others, has moved the science ahead through both the sharing of knowledge and the force of competition.

THIRD, polymer science has progressed very far very quickly.

This is shown graphically in the printed piece that each of you found at your place when you sat down to lunch. It charts on a logarithmic curve the pounds of synthetic polymers produced in the U.S. each year from the 1920's, when polymer science first began to blossom. The number at the bottom of the curve is 15 million pounds for the year 1923. At the top, it's about 49 billion pounds, which is the production figure for 1979.

The chart also shows the time frames for the seven individuals who are preeminent pioneers in the field. The timelines for each of them begin with the year when they first published a paper or were granted a patent relating to polymers.

On the reverse side of this card, you'll find a chronology of material and conceptual milestones in polymer science. This doesn't pretend to be a definitive list. I'll bet Dr. Mark might choose a few different or additional landmarks. But the purpose is to give you a quick glimpse at the "lifeline" of polymer chemistry, particularly in its early stages. In the last 25 years -- beyond the period shown on the "lifeline" list -- many important polymers have been developed, such as aromatic polyamides and polyimides, polyurethanes, ionomers, thermoplastic elastomers, fluorocarbon copolymers and the epoxies, to name a few. Also, new macromolecular concepts have become accepted. But for the purpose of the "lifeline" shown here, the emphasis is on pioneering ideas and discoveries.

Let me review some history. The roots of polymer science are almost as old as organic chemistry. The Swedish chemist, Berzelius, first mentioned polymerization as a word in 1833. Throughout the 19th Century experimentation was continuous, and major discoveries appeared from time to time. But for the most part, scientists didn't fully realize the significance of their findings. The substances which appeared in their retorts and test tubes were intellectually interesting, but of little practical use. Most of the reactions were recorded and their products and processes then set aside.

Near the turn of the century, a few perceptive chemists were getting closer to structural answers. Through some elegant and painstaking work, Emil Fischer recognized that cellulose and polypeptides were, in fact, chain structures. He actually synthesized a chain of peptide units step-by-step. The work went on and, by the end of World War I, many of the broad classes of synthetic polymers had been discovered. Industry had already introduced several synthetic polymers, such as Leo Baekeland's revolutionary phenol formaldehyde plastics, alkyd resins for paints and coatings and some rubbery polybutadienes. But scientists could not agree on the nature and structure of these materials.

The popular theory of the day was that they consisted of small building units held together by strong but mysterious forces. The structures were defined as "associated" or "colloided" or "micellar."

Soon these theories were to be disproved. In retrospect, however, we owe a considerable debt to these very early ideas and the scientists who advanced them. Armed with only the crudest instruments and with a new method for measuring molecular weights just emerging, they blazed the trail and opened up new territory in the understanding of materials. They may have willed their successors a variety of conflicting theories to explain the behavior of these materials, but they also provided a strong base for future understanding.

The pioneer who really changed the course of polymer history was Hermann Staudinger. He pulled together almost eight decades of experiments and theories and gave that work clear meaning.

Staudinger was a scientific skeptic who refused to accept the idea that polymers were loosely bound aggregates of small molecules. In his concept, they were very large molecules in long chains held together by covalent bonds. This idea met the resistance of many scientific colleagues, but he had the determination to stand by his theory. Together with his students, he devised techniques for preparing and characterizing many common and commercially important polymers. His early papers, among the more than 850 he published during his career, also established the important relationship between solution viscosity and polymer molecular weight.

What Staudinger succeeded in doing in a fundamental way was to show that polymers are macromolecules. This perceptive insight laid the groundwork for polymer science as we know it today and, somewhat belatedly, won him a Nobel Prize in 1953.

At about this same time, a university instructor and research chemist 14 years younger than Dr. Staudinger entered the picture. I refer, of course, to Herman Mark. He was among the first to support Staudinger's revolutionary concepts, and he brought a more physical approach to polymer study. An early student of crystallography, he used the techniques of that field to show that the "repeat units" in a polymeric structure could behave like small molecules in forming crystalline domains, thereby altering the polymer's physical characteristics. The finding was an important advance in the science because it greatly aided the synthesis and design of polymers with needed properties.

No matter where Herman Mark worked in this period -- whether in the university or the industrial laboratory -- he made significant contributions. At I.G. Farben, he developed commercial routes to polystyrene, the vinyls and acrylics and made essential improvements in rayon to make it useful as tire cord. At the University of Vienna, his studies of high polymer formation were critical to the advance of polymer science in the 1930's.

Altogether, his work importantly influenced the evolution of polymer science. But his later career as a teacher, mentor and consultant after coming to America in 1940 is just as important. I will have more to say about it after considering some other pioneers.

Another scientist who has special meaning, particularly to us at Du Pont, is, of course, Wallace Carothers. He proved experimentally what Staudinger had proposed theoretically -- that polymers were large molecules whose properties depended on their constitution. It was a powerful breakthrough.

We owe Carothers and his small band of research scientists a great debt. They started us on the road to neoprene and the development of such fiber families as the polyesters and the polyamides. The stimulated major experimental effort around the world that led to a tide of practical fibers, plastics, elastomers and other synthetics.

Let me pause here to make a few observations about the development of polymers up to this stage. If you want to call the early explorations of Fischer, Baekeland and others Stage One in polymer history, then you can call the Staudinger-Mark-Carothers era Stage Two. It was the "Golden Age of Polymers" when theories were being advanced and consolidated and when new structures and products were virtually "exploding" on the commercial scene.

My first observation is that much interplay went on between industry and the universities in cultivating polymer chemistry as a science. It was one of those exemplary cases in science where pragmatist and theoretician collaborated well. The separation often

found between academic and industrial science was absent in the work that centered on polymers.

Today, there is still much interest in polymers on the academic level; but, in the U.S., it is mainly concentrated in engineering and materials sciences departments at about 30 universities. To meet the challenges of the future, more attention in physics and chemistry departments at major universities is needed. This is important if we are going to continue to train exceptional scientists and maintain growth in the polymer industry.

Comment number two is a statement of the obvious. As in the case of any developing field of science or technology, polymer scientist built on the ideas of others. Dr. Mark, in one of his many articles on the history of polymers, stated the principle well. He wrote: "Evidence must be amended and modified as soon as new concepts and techniques become known which bring with them a higher level of preparative perfection and of structural understanding." That approach has permanent validity for all disciplines and for industry.

Successively, higher levels of understanding in polymers continued to be reached well after the breakthroughs of the 20's and 30's. Four other pioneers moved the science forward in a major way. Like Staudinger, Mark and Carothers, all four had the unique ability to think on both practical and theoretical levels.

The names of Ziegler and Natta are frequently linked because of their separate but complementary efforts for which they shared the Nobel Prize in 1963. Ziegler's discovery of catalysts which cause low pressure polymerization of ethylene and other olefins and Natta's published elucidation of the steric structures of crystalline polypropylene by X-ray analysis contributed significantly to the rapid development of these polymers.

Ziegler began a new era in polymer chemistry and the plastics industry by uncovering his now famous "growth reaction" of aluminum alkyls and refining it. When he discovered, late in 1953, that certain transition metal-aluminum alkyl catalysts led to rapid polymerization, he uncovered a very important route to high density polyethylene.

Natta, Ziegler and others quickly extended Professor Ziegler's ethylene polymerization reaction to the synthesis and characterization of stereoregular high polymers from propylene and other olefins. Crystalline polypropylene, prepared by various modifications of Ziegler's catalysts, is a major commercial polymer today, selling in the billions of pounds.

Paul Flory, another Nobel laureate, applied the techniques of the physical chemist to the definition of polymer properties. He introduced and then clarified the concepts of chain transfer and cross-linking, two phenomena that have had profound influence on polymer properties. While in industry and at Cornell and Stanford, he quantified the behavior of polymers. At first, these concepts were applied only to dilute polymer solutions. Subsequently, they've been applied to polymers in bulk form. It can be said that Paul Flory's work led to an understanding of why polymers behave the way they do.

In any discussion of Flory's work, his classic reference books deserve special mention. To most of us in this room, they are like the Old and New Testaments of polymer science. They have probably explained polymer behavior more clearly to more people than any other books ever published.

The final pioneer on my list is Carl "Speed" Marvel. In 1917, his first of over 500 papers should have told us something about his ability to recognize

important areas of study. It was on turbidity in beer. After analyzing that problem, he shifted to polymer chemistry and has spent a lifetime doing deliberate, craftsmanlike synthesis of polymeric molecules. A friend of mine recently put "Speed's" contributions in perspective. "Wallace Carothers," he said, "got the practical side of polymer synthesis underway, but 'Speed' Marvel defined the continental limits." It is hard to believe how many reactions Dr. Marvel has run. And out of this prolific work has come a host of new and unusual polymers, including some with extraordinary heat stability.

"Speed" Marvel has also had tremendous impact as a teacher on the study and development of macromolecules. During his tenure at the University of Illinois from 1920 to 1961, more than 10 percent of all Ph.D.'s in organic chemistry in the U.S. received degrees from that institution. And because Dr. Marvel was interested in polymers, many students followed his example. Many of his over 300 Ph.D.'s and postdoctorates are in key roles in industry and the universities today.

Like all outstanding people in any field, these pioneers were leaders, visionaries, stimulators and exemplars. Some conveyed the important explorative nature of their work simply by doing. Others thrived on the open, vigorous exchange of opinion and advocated the vast potential of their unfolding young discipline. Whether they worked in industry, universities or straddled both worlds, the pioneers stamped colleagues who worked with them and students who trained under them with a thirst for knowledge, a solid grounding in the art of inquiry and an eagerness to "stretch" the horizons of polymer science. For these qualities alone, we owe them much.

While all the pioneers did brilliant, original work, none perhaps has filled so complete a role in the advance of polymer science as Herman Mark. Dr. Mark uniquely spans the whole range of polymer development. He has made important scientific contributions in his own right...he set up the leading academic research institute on polymers in the United States...he has consulted and lectured in industry for decades, providing ideas and inspiration wherever he has gone...and he still serves as a global conduit of information on polymer advances through his journals, travels and meetings. As the *New Yorker* magazine said of him 20 years ago, Dr. Mark is the "most peripatetic polymer chemist anywhere around." And, remarkably, that still holds today in his 85th year.

Equally important as his many broad-ranging contributions is Herman Mark, the person. His informality, personal warmth and enthusiasm have attracted students and scientists to the Institute of Polymer Research for more than 30 years. To a great degree, Herman Mark has left his "mark" on just about everybody who has ever worked in the field of polymers. His influence on polymer scientists reaffirms the fundamental nature of scientific progress, in that one generation learns from another and continues this cycle of knowledge growth.

Dr. Mark has gained a wide reputation for his dedication to polymer advancement. This, combined with his desire to know and the force and magnetism of his personality, helped him establish a special camaraderie among polymer scientists throughout the world. In a real sense, the spirit of fellowship found in polymer meetings from New York and Washington to Rome and Tokyo represents the spirit of Herman Mark.

All of the other pioneers I have mentioned were "giants" in science and education. But none quite fits the mold of Herman Mark. We at Du Pont remember him traveling all night, arriving at a plant in a rural community at six in the morning, and then lecturing chemists new to polymers and consulting with research managers for an entire day without once losing his zest

for the subject. As promoter, promulgator and "energizer" of polymer chemistry, Herman Mark is proof that the exceptional individual still matters in the world of science and technology. In the special issue of the *Journal of Polymer Science* celebrating Dr. Mark's sixtieth birthday, Sir Eric Rideal summed it up well. He said, "There are no workers in the world in polymer chemistry who at some point in their investigations are not indebted to his pioneering work."

It is unlikely that the polymer pioneers ever envisioned the total impact of their work. But it's no exaggeration to say that the fruits of their labor have, in some way or another, touched most of the world. In the industrialized world, new living styles and standards, new uses of resources, new concepts of materials have evolved due, in part, to highly functional, low-cost polymers.

In recent years, it has become fashionable to disparage the so-called "plastic" society. This is nonsense. Synthetic products based on polymer chemistry are central to a society that must face up to the tough reality of rapid change. We are moving to a conservation ethic and will need to turn increasingly to polymers to gain efficiency, to save energy and to survive in a competitive world of scarce resources.

I need only to cite a few facts to clarify my point:

A RECENT PAPER by the Worldwatch Institute, an organization that studies emerging global issues, concludes that the use of man-made fibers, plastics and elastomers requires less energy, in many cases, than natural materials. The report states: "In an oil-short world, we may actually end up using more rather than fewer petrochemically based materials."

LIGHT-WEIGHT PLASTIC in the average automobile today provides total annual energy savings in fuel consumption equivalent to an estimated 14 million barrels of crude oil. The use of engineering plastics in automobiles is expected to double by 1985, with further significant increases in fuel savings.

AND WHEN COMPARING THE TOTAL ENERGY requirements of a polyester/cotton blend shirt with an all-cotton shirt, a National Science Foundation study found that the blends outperformed cotton fabrics. It takes 25 percent more energy to make a polyester/cotton blend shirt than to make one entirely of cotton. However, blend fabrics last longer and require less maintenance than all-cotton fabrics do. So the life-cycle energy requirements of all-cotton clothing in the United States were estimated to be as much as 90 percent higher than the blends.

Another debt we owe the pioneers is the lesson of technological evolution inherent in their work.

In most polymer-based products -- from fibers to plastics to elastomers -- industry has developed two, three, four and more generations of polymer systems with others yet to come. In each step along the way, the properties have become more refined and their uses more sophisticated.

Look at what has happened in man-made fibers, for example. The initial generation of polymeric fibers met basic needs in clothing, home furnishings and industry. With the next wave of improvement, fibers became easier to dye, easier-to-care-for, more stain- and fade-resistant, and more durable. The next generation filled specific needs. In clothing, fibers were given more stretch to conform to body movement, in carpeting, they were designed to be soil resistant and to reduce static electricity; and in industrial uses, they were made flame-retardant and abrasion resistant to meet all sorts of different demands. Now, fibers are being engineered even more precisely. They are being spun to match natural aesthetics.

blended and combined to increase strength and reduce weight in automobiles and aircraft, and engineered for use in difficult industrial environments.

The same kind of evolutionary progress has taken place in plastics. Early brittle polystyrenes have been supplanted by more impact resistant, toughened versions or ABS. New engineering plastics have been developed such as polycarbonate and super-tough nylon. Sophisticated specialty plastics have replaced metals in demanding precision moldings, temperature- and corrosion-resistant parts and lightweight electroplated structures. And the development of plastic materials for even more demanding uses continues.

Similar generations of polymer development can be traced in elastomers, films, finishes and coatings.

What lies on the horizon for polymers? You've heard much about the prospects over the last three days. If there is any one, ongoing legacy that the pioneers left us, it is both the tradition and the determination to forge ahead, to see where else polymer chemistry -- and physics, and biology -- may lead us.

As I've shown in my fibers and plastics examples, polymer systems are adaptable and capable of impressive growth. Some might argue that man-made fibers and plastics and elastomers are mature industries. I am skeptical of such judgments. The opportunity for change is only as far away as the nearest research laboratory.

For instance, polymers have historically filled structural roles, whether it be as a piece of clothing or a plastic part. Today, they are more and more being designed to perform active or dynamic roles. Polymeric membranes are already helping to purify water and produce large-volume chemicals in an environmentally safe way. Photopolymers have high promise for image-making innovations. Optical fibers are making inroads in light and data transmission. Possibly in the future, variants of these active polymers and systems based on them can perform electromechanical, signal amplification, data storage and data manipulation functions.

Major advances are also being made in analytical processes. Polymer chemistry was first put on a scientific footing by characterization methods that identified them as macromolecular chains. Now, through new approaches in instrumentation, spectroscopy and the use of computers, the way is being paved for new resins, raw materials and applications. One benefit is already being reaped and it's in keeping with our interest in conservation. Instrument hookups to computers are being used to monitor chemical reactions and send data back to operators within seconds. With more such instant feedback in the future, rapid process adjustments will become commonplace and will reduce waste, save energy, and improve product quality.

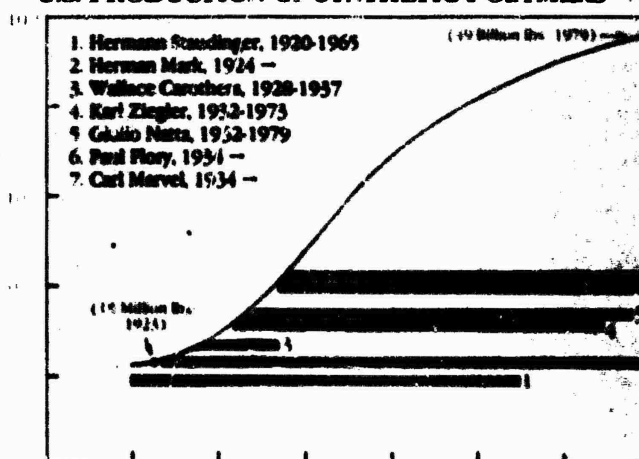
Then, there are areas of polymer science where we have just begun to scratch the surface. One such area is the study of biological macromolecules. Polymers form the basis for life. Proteins, nucleic acids and oligosaccharides are complex polymers which control biological processes. But we are only beginning to understand them, and we have much to learn when it comes to duplicating what nature does in stitching together monomers into macromolecules.

However, through the study of life sciences and biological polymers, we may be able to expand our level of understanding enough to develop highly specific drugs and agricultural chemicals or to catalyze reactions to mass produce chemicals. The field is full of intellectual challenge. It is also capable of yielding quantum leap discoveries. It might not be too far-fetched to say that in another 50 years somebody might be making a speech on our debts to the pioneers of biological polymers. One can already

visualize the early "lifeline," starting with the contributions of Linus Pauling and including the elegant body of experimentation by scientists such as Maurice Wilkins and co-workers, which culminated in James Watson's and Francis Crick's remarkable insight into DNA structure.

What this all amounts to is that those first insights by the pioneers have brought us a long way. A man such as Herman Mark, who was there at the beginning, can surely attest to the long road travelled. But I'd venture to guess that Dr. Mark would be the first to suggest that he and other polymer pioneers really only laid a grand foundation upon which we and succeeding generations must continue to build. That's the greatest legacy the pioneers could possibly leave us: The success of yesterday and the promise of tomorrow. It is our good fortune that Der Geheimrat continues to add much to that promise.

U.S. PRODUCTION OF SYNTHETIC POLYMERS ^{10⁶ lbs/yr}



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 June 1980

A "LIFELINE" OF POLYMER SCIENCE UP TO 1955

Polymeric Materials Discoveries	Macromolecular Concepts
1859 Polymerization of styrene	1855 Cellulose as a chain
1865 Polystyrene succinate	1900 Polypeptide chain structure
1872 Polymerization of vinyl chloride	1910 Chain structures of polystyrene, polyacetylene & rubber
1879 Polymerization of isoprene	1920 Crosslinked network structure for rubber
1900 Polyethylene from diacetylene	1920 Condensation polymers
1901 Alkyd resins	1930 Statistical methods for polymers
1901 Acrylic ester polymers	1930 Molecular weight by viscosity
1907 Fractionation of "Bakelite" phenol formaldehyde resins	1930 Chain conformation
1910 Polymerization of isocyanate	1930 Rubber elasticity
1914 Polymerization of vinyl acetate	1930 Monodisperse synthetic polymers
1930 Polyisoprene	1930 Copolymerization-radical reactivities
1930 Polyester and polyamide fibers	1930 Quantitative theory of emulsion polymerization
1930 Production of polystyrene	1930 Protein alpha-helix
1933 Styrene-butadiene rubber	1953 Structure of DNA
1935 High pressure polyethylene	
1941 Polymethacrylate-dye	
1953 High density polyethylene	
1954 Isotactic polypropylene	