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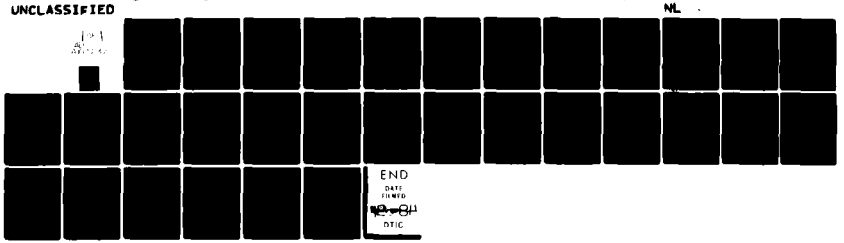

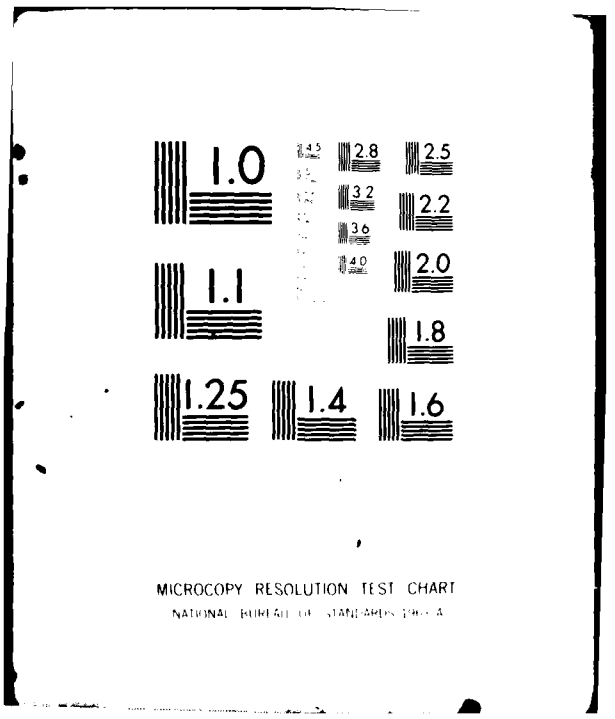
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THE FRACTURE OF THERMOSETTING RESINS AFTER EXPOSURE TO WATER

by

Geoffrey Pritchard,
R.G. Rose, W.E. Douglas, J. Ghotra
and Mrs. D. Ho

September 1981

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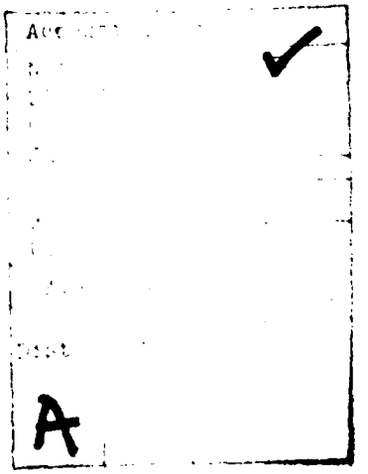
Molecular weight distributions are being measured by gel permeation chromatography and adjusted by combinations of synthetic, blending and fractionating procedures.



THE FRACTURE OF THERMOSETTING RESINS AFTER EXPOSURE TO WATER

SUMMARY

This report considers the importance of molecular weight and molecular weight distribution in determining (a) the hydrolytic stability and (b) the fracture toughness of thermosetting resins.

Experimental work (still incomplete) is described. Several orthophthalic polyester resins have been prepared and characterised, and some of them fractionated by precipitation with solvent : non-solvent mixtures. The fracture parameters, hot water resistance and property retention characteristics of the original resins are being compared with those of the fractions, with a two year period of immersion in distilled water at 50°C. Medium and high molecular weight fractions show improved hot water resistance.

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Keywords: Polyester, resin, fracture, toughness, water, fractionation, GPC, molecular weight, hydrolysis, degradation.

CONTENTS

THE FRACTURE OF THERMOSETTING RESINS AFTER EXPOSURE TO WATER

1. INTRODUCTION

1.1 Project objectives

This project was undertaken because of a belief that the environmental degradation of reinforced plastics is dependent on the fine details of matrix structure. It aims to show that widely different kinds of behaviour can be obtained when batches of resin are immersed in a given fluid at a fixed temperature, even when the batches are always made from the same starting materials in the same proportions, and cured with the same hardeners in the same proportions on each occasion. The kind of structural details believed to have importance are the molecular weight and, more precisely, the molecular weight distribution (MWD) of the resin prior to crosslinking. Most industrial R and D has related to molecular weights rather than MWDs.

The work carried out so far has been entirely concerned with unsaturated polyester resins, but almost certainly the conclusions have some applicability to epoxide resins also. The previous annual report (1) described a preliminary study of the behaviour of a single batch of an isophthalic polyester resin in hot water. The degradation of this resin was monitored by several means, and the mechanical properties, notably fracture toughness, were recorded both for wet and dried-out samples. A mechanism for degradation was proposed (see section 1.2). This work gave some idea of how a polyester resin becomes embrittled in hot water over a period of nearly two years, but it did not involve introducing structural variables.

The next phase of the work, described here, concerns resins made with the same starting materials as before except that phthalic anhydride rather than isophthalic acid was employed. Such resins are termed orthophthalic, and a whole series has now been prepared and characterized. They differ only in molecular weight and molecular weight distribution.

The intention is to establish whether average molecular weight is the important factor distinguishing the rates of embrittlement of these resins by hot water, or whether the dispersity and the shape of the MWD curves obtained by gel permeation chromatography (GPC) is also important. More specifically, it is hoped that the role of low molecular weight components can be ascertained.

1.2 Polyester resin degradation in water

Polyester resins differ from most epoxides in containing hydrolysable groups. However, it does not follow that these groups are entirely responsible for polyester degradation, since the fracture toughness and other mechanical properties of amine-cured epoxides are also severely affected by hot water immersion (2). The previous report proposed the following mode of degradation of polyesters:

(1) Water uptake, leading to reversible plasticization and reduction in modulus.

(2) Slow, slight leaching of non-bound substances originally present.

(3) Attraction of water by osmosis to sites of local concentrations of phase-separated, water-soluble impurities in the resin.

(4) Osmotic cracking at these local sites.

(5) Accelerating hydrolysis caused by, and occurring at or near to the edges of the osmotic cracks.

(6) Further leaching of the hydrolysis breakdown products, with net weight loss.

(7) Proliferation of osmotic cracks.

The novel feature of the report was the specific identification of the chief impurity contributing to the osmotic pressure generation. 1,2 propane diol was shown to have a major effect on crack onset time. This observation is important because commercial resin manufacturers sometimes deliberately add extra diol to their resins, and others do not take steps to minimise trace residual glycol content at the synthesis stage.

Polyester resins made from isophthalic acid are believed to be more water-resistant than orthophthalic ones. (That is, they absorb less moisture, and undergo fewer changes in mechanical and other properties). The only reasons why isophthalic resins should be more resistant are (a) because there may be some inherent superiority in the isophthalic ester group's resistance to hydrolysis and (b) because isophthalic resins are commonly of rather higher molecular weight.

This raises the question: what is the effect of average polycondensation chain length on water resistance? There are four

factors to consider.

(i) The concentration of chain ends, C.

This is inversely proportional to number-average molecular weight, M_n. There are two kinds of ends: carboxylic and hydroxyl. Carboxylic groups probably have a catalytic effect on hydrolysis, and like hydroxyl ends, attract water into the resin. Attempts have been made to determine whether blocking the ends with various blocking agents reduces the rate of hydrolysis and minimises its adverse effect on laminate mechanical properties, but with inconclusive results (3).

(ii) The number-average length of the polycondensation chains, M_n.

The higher M_n is, the greater the average number of styrene bridges by which a given chain is connected to the network and therefore the greater the number of hydrolytic scissions required to sever the polycondensation chain from the network completely.

(iii) The proportion, in the network, of non-bound chains, C_N.

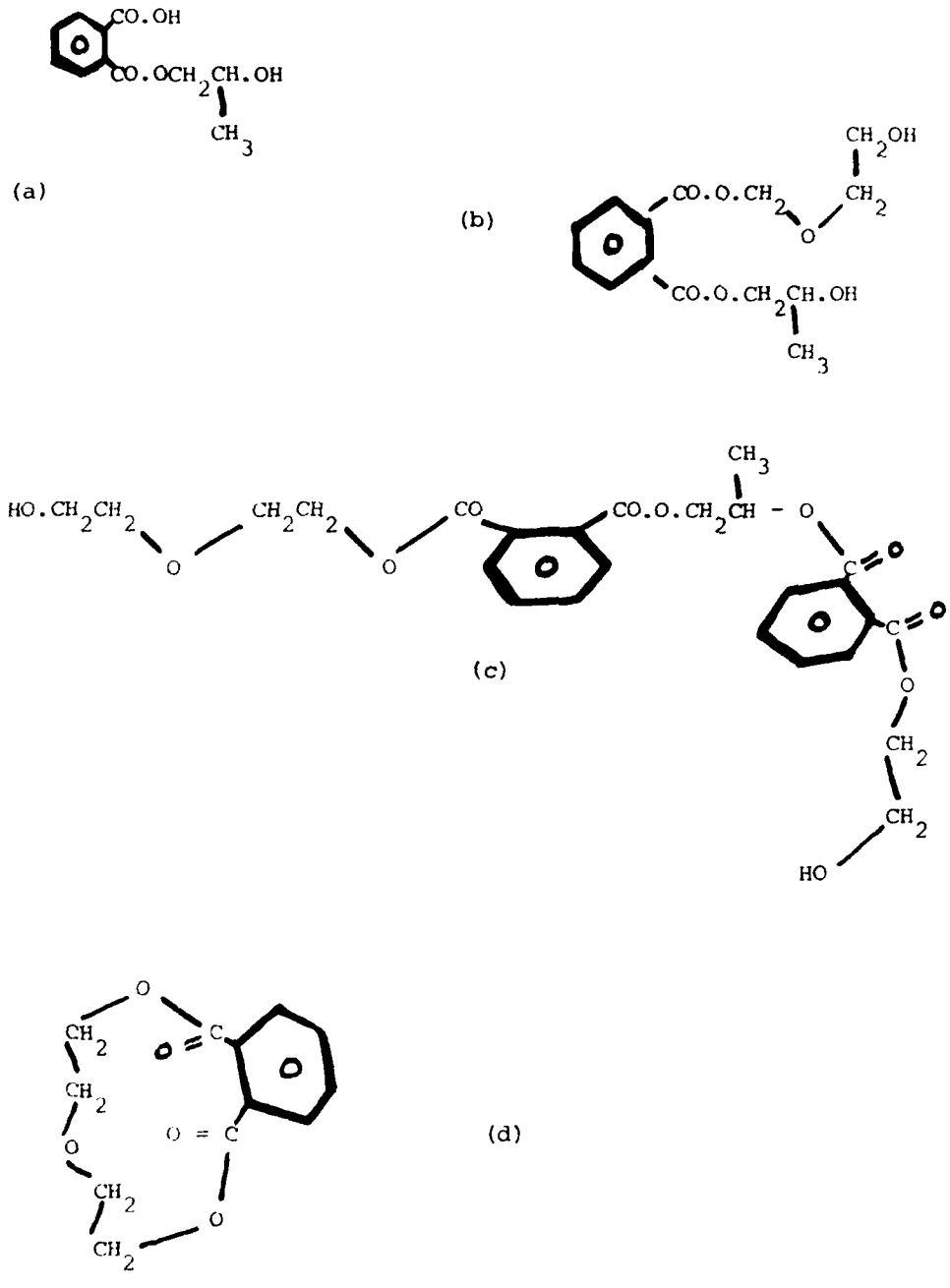
For convenience, it is not necessary to distinguish between unreacted monomer and non-bound oligomers; they can all be regarded as short chains, which have never been linked to the network either because they do not contain the necessary functional groups (i.e., unsaturation) or because cross-linking was incomplete. Some examples are given in fig. 1.

(iv) The solubility of the above-mentioned species in water.

Water solubility favours osmotic crack generation, and accelerated hydrolysis because of the enhanced surface area provided for water contact by internal cracks.

It appears probable that optimum water resistance would be achieved by synthesizing a resin with the highest possible molecular weight, and then removing the low molecular weight "tail", i.e. by maximizing M_n and then minimizing C_N. It remains to be seen whether this would result in optimum mechanical properties, and the question of fracture toughness is considered in the next section.

FIG. 1



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2. THE FRACTURE OF POLYESTERS

2.1 The fracture of crosslinked resins

Fracture mechanics concepts have been applied to many polymers. Early investigations, related to the fracture of uncrosslinked thermoplastic glasses, e.g. polystyrene and polymethylmethacrylate (PMMA) have been reviewed by Rosenfield and Kanninen (4). More recently, the fracture of crosslinked polymers has been reviewed by Pritchard and Rhoades (5) and by Young (6). Many of the studies of the fracture of brittle organic polymers reported values of the fracture surface energy, derived by halving the value of the strain energy release rate, G_c. Recently, there has been increased emphasis on the measurement of K_c, the critical stress intensity factor (7-9) and on the use of specimens for which the stress intensity factor is independent of crack length (10).

Most thermosetting resins are found to fulfil the requirements for application of linear elastic fracture mechanics (LEFM). Some account is taken of plastic flow at the crack tip, but the plane strain plastic zone radius should be less than one fiftieth of the crack length (11). Typical published values for K_c and G_c for various crosslinked polymers are given in table 1. (7-9, 12-19).

TABLE 1.

Literature values of K_c and G_c for crosslinked polymers

Polymer	K_c $MNm^{-3/2}$	G_c Jm^{-2}	Ref.
Unsaturated polyester		20	12
" "	0.72	65	9
" "		80	13
" "		24	14
" "	0.84		15
" "	0.56	90	16
Epoxide (Araldite CT 200)	0.56-0.74		8
" " "		10-200	17
" Epikote 828		330	18
" "	0.9	800	7
" ERLA 4617		80	19

It will be noted that some of the values are given as ranges; these reflect the effect of such variables as the degree of cross-linking and molecular weight.

2.2 Fracture and molecular weight

To our knowledge, no systematic study of the effects of molecular weight on the fracture toughness of unsaturated polyester resins has been reported. Kusy and Turner (20) among others have investigated the effect of molecular weight on the fracture surface energy, $\frac{1}{2}G_c$, of uncrosslinked PMMA and found that increasing the molecular weight increased the toughness. They subsequently found that this result could be correlated with observations of the fracture surfaces (21). This has led to a generalised theory of the total fracture surface energy of glassy organic polymers, based on number-average molecular weight (22). Attempts had previously been made to predict such a relationship (12, 23). There must be great doubt whether such work has any substantial relevance to crosslinked polyesters, but it can be noted that at low M_n, G_c was small and constant, while at high M_n, G_c was large and constant; in between, there was a transition region. The range of M_n values over which failure could be described using LEFM was established. Other workers have found that fracture behaviour is better correlated with the weight-average molecular weight, M_w, than with M_n. This suggests that the longer chains have particular importance.

A detailed investigation of the fracture toughness of vinyl urethane polymers crosslinked with styrene provides an apparent analogy with the present study, since the effect of prepolymer chain length on the fracture toughness of the crosslinked polymer was examined (24). It was found that the fracture toughness increased with increasing chain length, but since there were only two crosslinks per chain, any increase in M_n produced an automatic decrease in crosslink density. The reverse is the case with unsaturated polyesters. The effect of degree of crosslinking on fracture parameters has been studied for methacrylates by Broutman and McGarry (12), for epoxides by Yurechko et al. (25) and for unsaturated polyesters by Pritchard, Rhoades and Rose (16). Kartsovnik and Rosenberg have compared crosslinked epoxides with linear glassy polymers (26).

This present study is concerned with the effect of both M_n and the dispersity, M_w/M_n, of the prepolymer or the initial fracture toughness and on toughness retention in hot water. We expect increases in M_n to increase toughness, but the role of dispersity is more difficult to predict. At constant M_n, an increased dispersity means an increase in the concentration of both the longer and the shorter prepolymer chains. While the longer ones probably contribute to toughness, the shorter ones could either increase it by promoting crack blunting, or reduce it by facilitating intermolecular motion. There are few published studies of the effect of

MWD. Selby and Miller suggest that a small excess of epoxide hardener, over the stoichiometrically required quantity, could blunt the crack tip, raising toughness, while greater excesses would reduce it (7). Owen and Rose (9) found that the addition of a second, plasticizing resin produced a minimum toughness at a certain concentration. Kinloch and Williams observe that local crack blunting by water can increase toughness (27), and Christiansen and Shortall (14) also envisaged that small molecules in cross-linked polyesters would have this effect. Our own work on the isophthalic resin system (1, 28) showed that 5% w/w glycol increased toughness by about 40%, at the expense of water resistance.

2.3 Fracture and degree of cure

One variable requiring control in this study is the degree of cure of the resin. The effect of postcure time on the fracture toughness of the isophthalic resin has already been reported (1). Astbury and Wake (29) found that postcuring epoxy resins caused substantial increases in the aggregate size of supermolecular globular structures or nodules, and this affected the fracture behaviour. An effect of postcure time on fracture and nodular morphology in an epoxy resin was also observed by Mijovic and Koutsky (18), but they attributed the change in fracture energy to additional crosslinking in the internodular matrix. Degree of cure is not being investigated in this project and standardized cure schedules are employed.

2.4 Environmental effects

The effect of absorbed low molecular weight substances on the structure of crosslinked polyesters has been investigated recently by Prokofyeva (30). The molecular and supermolecular structural changes were found to be independent of network density, but dependent on chain mobility and on the flexibility of the polyester chains. There is little published information on the effect of absorbed liquids on the fracture characteristics of polyesters, but exposure to various humidities for up to three years at 66° to 93°C has been investigated (31). A decrease in tensile strength and in elongation at fracture resulted. Investigations of the effect of water immersion on the fracture toughness of polyesters have been made by Diugwa (13) and by Pritchard, Rose and Taneja (15) but both were relatively brief exposure-time projects. The reliability of accelerated test programmes at elevated temperatures is being studied in a separate project in this laboratory, with a view to understanding the necessary conditions for forecasting by extrapolation.

3. EXPERIMENTAL APPROACH

3.1 Introduction

This account is not a definitive summary of procedures; it is designed to outline the reasons for the procedures adopted, and to indicate the state of progress at the time of writing.

3.2 Resin synthesis and characterization

It would be desirable to produce a series of well-characterized polyester resins having widely differing M_n and MWD, and to determine the relationship between the initial mode-1 plane strain critical stress intensity factor, K_{IC}, and these structural parameters, before going on to environmental degradation studies. This was basically the intention, but two difficulties arose.

(a) It is difficult to produce unsaturated polyester resins of very high M_n. Methods have been proposed for producing saturated polyesters with abnormally high molecular weights, but these methods were judged to be impractical for unsaturated polyesters. Consequently the highest M_n achieved by standard procedures was only about 1800. The molecular weights of these "original" resins, synthesized by the method already given (1) were then in some cases enhanced by fractionation, to achieve M_n values of up to 4700, but the fractionation process naturally altered the MWD. It also introduced other problems; traces of solvent could sometimes be retained

(b) It became apparent that although most polyester resins do fulfil the requirements for LEFM, some of the medium and low molecular weight resins prepared to this formulation showed significant departures from linearity in stress-strain tension tests, although without necking. The values obtained for K_{IC} were in many cases dependent on temperature and strain rate to a greater extent than those already reported for the isophthalic resin. Values for K_{IC} must therefore be qualified by noting the non-linearity associated with certain resins; these will be identified in the final report.

The resins synthesized by the standard procedure were condensed for various periods of time to achieve various M_n values. A preliminary estimate of the state of the reaction on completion was obtained by an acid value (or acid number) titration, and 14 resins have so far been produced, with acid numbers ranging from 14

to 54 (see fig. 2). M_n determinations were made in dioxane solution by using a Knauer vapour phase osmometer (VPO), and in most cases the heat distortion temperature (HDT) of the crosslinked resin was measured by the method of B.S. 2782 (102 G) to ensure that this always exceeded the water immersion temperature, i.e. 50°C. Hydroxyl number, Ferranti viscosity, gel time, residual glycol and volatile content determinations were carried out on some of the resins. The cis-trans isomerization ratio was checked by NMR using the two peaks marked C, T on the spectrum shown in fig. 3. Initial tensile and compressive properties are being determined for each resin. (Characterization is incomplete). The resins are listed in table 2.

3.3 Resin identification codes in table 2.

Each resin was assigned a code number for reference purposes. This consisted of two letters followed by a one or two digit number, e.g. DY 6. The code DY 6/11 indicates a blend (approx. 50:50) of resin DY 6 with DY 11, used to achieve a desired M_n. The codes DY 6 HB and DY 6B refer respectively to the high, middle and low molecular weight fractions obtained by fractionating resin DY 6 roughly at their centres. The code DY 6AB refers to a "tail-chopped" version of DY 6.

3.4 Fractionation

For the fractionation it was not possible to adopt idealised procedures [illegible] large quantities of fractionated resin. The main methods considered were gel permeation chromatography, elution chromatography, and fractional precipitation. For fairly large quantities of fractionated resin, fractional precipitation is regarded as the most practical method, although tedious and far from efficient. Ideally, if fractions of narrow molecular weight distribution are to be obtained the experimental conditions must be carefully chosen. Solvent and non-solvent must be [illegible] boiling temperature [illegible] and the precipitant should have a good precipitating power. [illegible] decrease in solubility with [illegible] given polymer series. The [illegible] of the polymer in the [illegible] should be at the temperature of the [illegible]. The solution is stirred slowly during precipitation, [illegible] allowed to settle. The supernatant phase [illegible] polymer and the precipitated phase is recovered either by drying or by precipitation in a large excess of precipitant. The [illegible] precipitant is added to the [illegible] operation, and the operation [illegible]

Each polymer species is partitioned between two phases. All polymer, regardless of chain length, is more soluble in the precipitated phase, but the smaller species will be distributed at more nearly equal concentrations in the two phases. This may be regarded as an entropy effect.

For efficiency, the ratio of the volumes of the supernatant to precipitated phases should be as large as possible, but since the precipitated phase is highly swollen, this objective can be achieved only by using a very dilute polymer solution. Unfortunately, the requirement for obtaining large quantities of fractionated polymer (and subsequently removing all traces of solvent, since this interferes both with mechanical property measurements and with hydrolytic degradation studies) makes the use of very dilute solutions highly inconvenient.

As a result of these difficulties, the method used was much simplified in comparison with the above, and designed to produce just three fractions, each of which was expected to overlap considerably with the next.

Typical Procedure

50 g of polyester resin (without styrene) was dissolved in 150 cm³ of acetone. This solution was stirred in a two-necked, pear-shaped flask fitted with a tap-funnel for addition of non-solvent, and a drain tap. Petroleum ether, 40°/60°, was used as non-solvent, and added dropwise to the solution with constant stirring by a glass propeller. When the ratio of solvent to non-solvent was 3 to 1, the mixture was left to settle overnight, and the lower layer removed. The solvent/non-solvent mixture contained in this layer was distilled off under vacuum at ambient to 50°C, with final vacuum stripping at 10^{-3} mm Hg.

More non-solvent was added, to make a solvent to non-solvent ratio of 1 to 1. The precipitated resin layer was removed, and treated as before. Finally the remaining, upper layer was removed and vacuum-stripped.

GPC

The [illegible] and their fractions were submitted for GPC examination. [illegible] GPC systems were tried, involving three [illegible] laboratories. The values for M_n and M_w obtained must be considered satisfactory for comparison within a given system, since calibration procedures, detectors, columns etc. affect the result. The [illegible] systems are given in table 3, where each system is [illegible] (for the GPC laboratory) and a number [illegible] (for the particular procedure used at a given laboratory). In

the majority of cases, and unless otherwise stated, reference will be to results obtained by system A2. A2 differed from A1 only in that A2 computed average molecular weights after taking into account all of the very low molecular weight oligomers in the resin, whereas A1 ignored these. System A2 gave M_n values nearest to those obtained by VPO.

Fig. 4 shows the GPC curves obtained by system A2 for the resin coded CW 1 along with its high fraction CW 1A. It should be noted that the areas under the two curves are not comparable, since the detector response scales are different. M_n of the high fraction (by GPC) was approximately doubled.

Systems B1, B2 differed from each other only in the detectors used. They gave lower, but nevertheless plausible, values of M_n. Fig. 5 gives a qualitative description of the efficiency of the first attempt at fractionating a resin. Fig. 6 gives actual molecular weights obtained by the B1 system for the same base resin, computed using Q-factors (32.33) obtained by the method outlined in fig. 7. Systems C1, C2 gave still lower M_n values but similar MWD curves.

3.6 Initial mechanical properties

The determination of K_{IC} is being performed by the method already given (1). Measurement of the compressive properties of the resins after casting is by standard procedures, essentially the same as those described by Kinloch and Williams (27). A more detailed account of this aspect of the project will be given subsequently.

3.7 Exposure in hot water

Fracture toughness specimens are being immersed in distilled water at 50°C and periodically weighed, measured and observed for disc cracks. At various time intervals samples are broken in order to obtain fracture or compressive data. Cracks are sharpened after immersion and samples tested either in the wet state after cooling in cold water, or after prolonged drying at 50°C under vacuum.

4. RESULTS AND COMMENTS

Only an interim report can be provided at this stage, since the specimens are being subjected to ageing.

Fig. 8 shows the water absorption characteristics of three resins of M_n 875, 1592 and 2215 (by VPO). The water absorption rate is clearly lowest for the highest M_n value over the first 2500 hours, and although the lowest M_n resin then shows a lower net weight increase, its behaviour is consistent with advanced leaching (1). The water absorption of the highest M_n resin at 50°C is unusually low, considering

the specimen geometry. It should be noted that this sample was a fraction.

Table 4 gives the time to onset of disc cracking for four resins of various acid values and M_n values. This shows improvements with high molecular weights and also shows the most desirable behaviour to be associated with a fractionated sample.

Table 5 lists resins obtained by fractionation of those given in table 2.

It is already clear that the water resistance of the resins is improved by increasing M_n, and by removal of the low molecular weight fraction. The effect of these operations on initial and retained K_{IC} will be reported later, along with other mechanical property results. The evidence to date suggests that fractions A and B (high and medium) have initially higher K_{IC} values than the original resins. At a temperature of around 30°C, the fracture surfaces of some of the resins change from featureless to rough, with a doubling of toughness. The dependence of K_{IC} on temperature is given for one of the lowest molecular weight resins (DY 6) in fig. 9.

5. CONCLUSIONS

A large number of polyester resins have been prepared and characterized using various analytical techniques. The initial mechanical properties are being measured and correlated with GPC data. Some of these resins have been fractionated, and it is already apparent that medium and high molecular weight fractions show superior water resistance, although their property retention performance has yet to be assessed. Some of the resins do not show linear stress-strain behaviour in unnotched tensile experiments. Work is still proceeding.

6. REFERENCES

1. G. Pritchard and R.G. Rose, Annual report, U.S. Army Research Contract DAJA 37-79-C-0505, Kingston Polytechnic, England (1980).

2. D.H. Kaelble and P.J. Dynes, J. Adhesion, 8, 195 (1977).

3. C. Papaspyrides and A.W. Birley, Polymer, 19, 1474 (1978).

4. A.R. Rosenfield and M.F. Kanninen, J. Macromol. Sci., Phys., 7B, 609 (1973).

5. G. Pritchard and G.V. Rhoades, Mater. Sci. Engng., 26, 1, (1976).

6. R.J. Young, chapter 6 of "Developments in Polymer Fracture - 1" ed. E.H. Andrews, Applied Science, London (1979).

7. K. Selby and L.E. Miller, J. Mater. Sci., 10, 12 (1975).

8. W.T. Evans and B.I.G. Barr, J. Strain Anal., 9, 166 (1974).

9. M.J. Owen and R.G. Rose, J. Phys. D., Appl. Phys., 6, 42 (1973).

10. R.J. Young, chapter 9 of "Developments in Reinforced Plastics - 1" ed. G. Pritchard, Applied Science, London (1980).

11. J.F. Knott, "Fundamentals of fracture mechanics", p. 134, Butterworths, London (1973).

12. L.J. Broutman and F.J. McGarry, J. Appl. Polym. Sci., 9, 609 (1965).

13. A.D.S. Diggwa, Polymer, 15, 101 (1974).

14. A. Christiansen and J.R. Shortall, J. Mater. Sci., 11, 1113 (1976).

15. G. Pritchard, R.G. Rose and N. Taneja, J. Mater. Sci., 11, 718 (1976).

16. G. Pritchard, G.V. Rhoades and R.G. Rose, J. Mater. Sci., 15, 1635 (1980).

17. R. Griffiths and D.G. Holloway, J. Mater. Sci., 5, 302 (1970).

18. J.S. Mijovic and J.A. Koutsky, J. Appl. Polym. Sci., 23, 1037 (1979).

19. R.C. Laible, J.N. Sultan and F.J. McGarry, 32nd Ann. Tech. Conf., SPE (1974).

20. R.P. Kusy and D.T. Turner, Polymer, 17, 161 (1976).

21. R.P. Kusy and D.T. Turner, Polymer, 18, 391 (1977).

22. R.P. Kusy and M.J. Katz, Polymer, 19, 1348 (1978).

23. J.P. Berry, J. Polym. Sci., A, 2, 4069 (1964).

24. I.M. Ward, Stud. Phys. Theor. Chem., 10, (Struct. Prop. Amorphous Polym.) 119-143 (1980).

25. N.A. Yurechko et al., Polym. Sci. U.S.S.R., 22, 1, (1980).

26. V.I. Kartsovnik and B.A. Rosenberg, Polym. Sci. U.S.S.R., 21, 2603 (1979).

27. A.J. Kinloch and J.G. Williams, J. Mater. Sci., 15, 987 (1980).

28. H.P. Abeysinghe, Ph.D. thesis, "The fracture toughness of a polyester resin after immersion in aqueous liquids", Kingston Polytechnic, England (1980).

29. P.J. Astbury and W.C. Wake, Brit. Polym. J., 11, 17 (1979).

30. T.A. Prokofyeva, Polym. Sci. U.S.S.R., 22, 196 (1980).

31. R.J. Gardner and J.R. Martin, J. Appl. Polym. Sci., 25, 2353 (1980).

32. L.E. Maley, J. Polym. Sci., C8, 253 (1965).

33. J. Cazes, J. Chem. Educ., 43, A 567 (1966); and A 625 (1966).

TABLE 2.

LIST OF RESINS SYNTHESIZED

RESIN IDENTIFICATION CODE	DY 2	DY 3	DY 4	DY 7	DY 18	DY 6	DY 13	DY 6/13	JG 2	DY 14	DY 15	DY 16	DY 17	CW 1
INTENDED USE	← Direct Immersion in Water →					✱ Blending		✱	← For fractionation					→
REACTION TIME (h)	24	17	11	30	15	11½	23	N/A		24		10	17	20
ACID VALUE mg	20	26	54	14*	30	42	22	29	23	22	22	48	26	24
HYDROXYL VALUE mg			31	16		27	20							
HEAT DISTORTION TEMP., °C, BS 2782/102 G	62	61	53	67	60	56		60						
M_n (VPO)	1592	1294	875	1454	1290	940	1412		1672	1669	1826	1058	1360	
M_w (GPC) (syst.A2)	-	-								3.94	2.69			1.79
$\frac{M_w}{M_n}$ (syst.B1)		2.03	1.62							-	-			-
STYRENE CONTENT (w/w)		30		31	31	31	28	33						
FERRANTI VISCOSITY (25°C) (poises)	8.71	8.25	4.84	19.5				3.9						
at shear rate (sec^{-1})	13	13	13	8.8				8.8						

* Vacuum applied for 30 minutes during synthesis.
(Blank spaces indicate data still incomplete).

TABLE 3.

OUTLINE OF GPC SYSTEM CONDITIONS

System Code	Calibration	Column: Packing	Size Range (A^O)	Solvent	Conc.^{n} (%)	Detector
A1, A2	as for polystyrene	Styragel	100 to 500	T.H.F.	0.2	Refractive index
B1	Q=21.4	Micro-styragel	100 to 10^4	T.H.F.	0.2	Refractive index
B2	Q=17.4	Micro-styragel	100 to 10^4	T.H.F.	0.2	ultra-violet
C1	Q=21.3	Styragel	60 to $3x10^5$	T.H.F.	5.0	Refractive index
C2	Q=21.3	Styragel	500 to $1x10^5$	dichloro-methane	5.0	Refractive index

TABLE 4.

TIME TO ONSET OF DISC CRACKING

Resin acid value	Time to onset of internal disc cracking at 50°C in distilled water (hours)
54	850
26	3600
20	4760
17*	5170

* This was a middle fraction

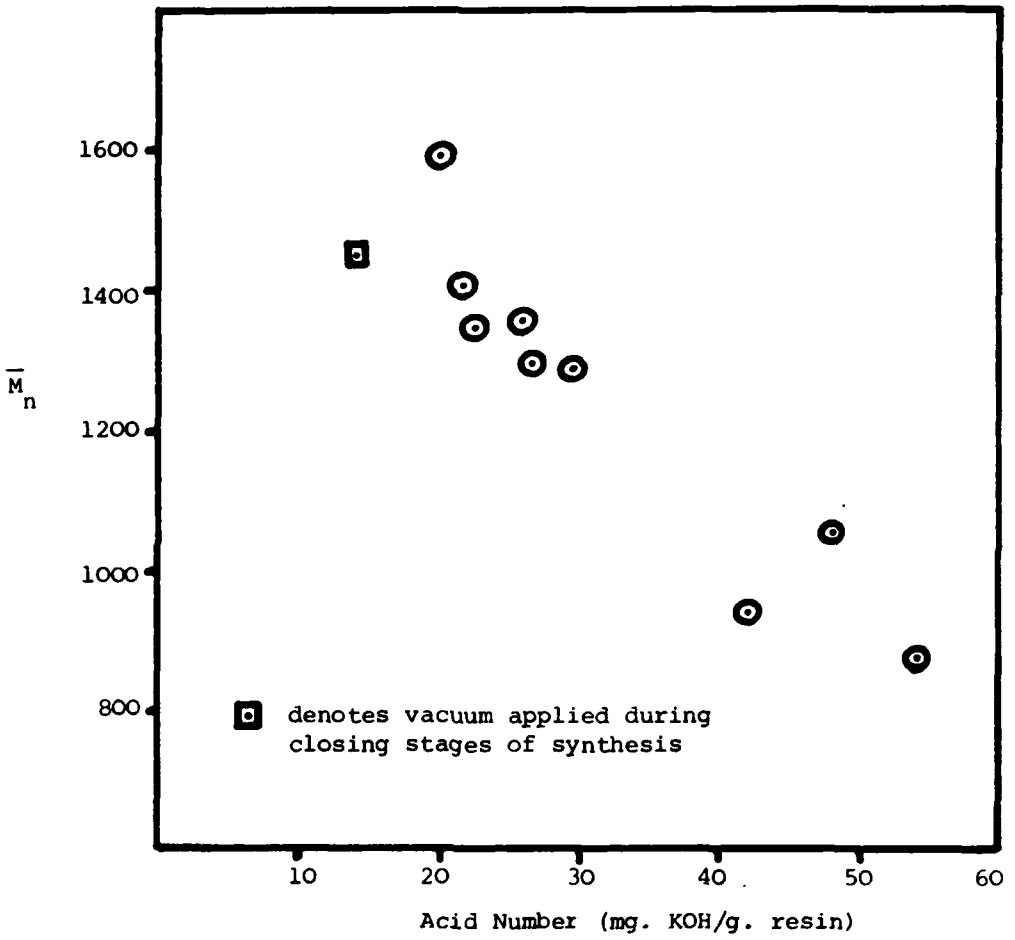
TABLE 5.

LIST OF FRACTIONATED RESINS

RESIN IDENTIFICATION CODE	JG 2A	JG 2B	JG 2C	DY 14A	DY 14B	DY 14C	DY 15AB	CW 1A	CW 1B
ACID VALUE (mg)	15	17	83	17	17	72	17	14	15
HEAT DISTORTION TEMP., $O^{O}C$, BS 2782/1026		62		67	62		62		
STYRENE CONTENT (w/w)				35	34		32		
M_n (V.P.O.)	3278	2215	517	4707	3077	592	3077		
$\frac{M_w}{M_n}$ (system A2)	-	-	-	4.04	2.33	3.06	2.74	2.38	1.79
(system B1)	2.71	1.82	2.13	-	-	-	-	-	-

Blank spaces indicate data still incomplete.

Fig. 2.



Number-average Molecular Weight (determined by Vapour Pressure Osmometry) versus Acid Number.

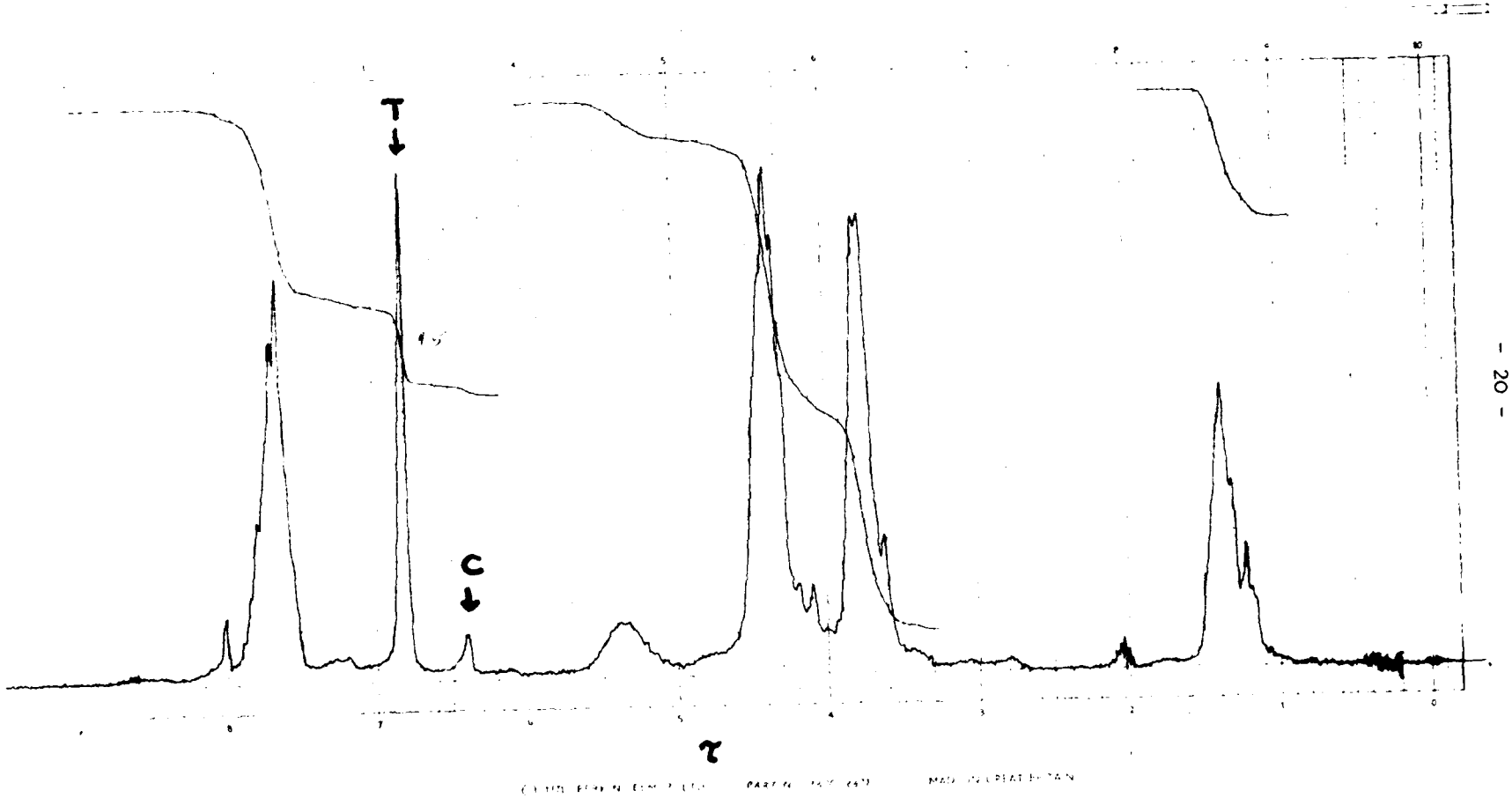
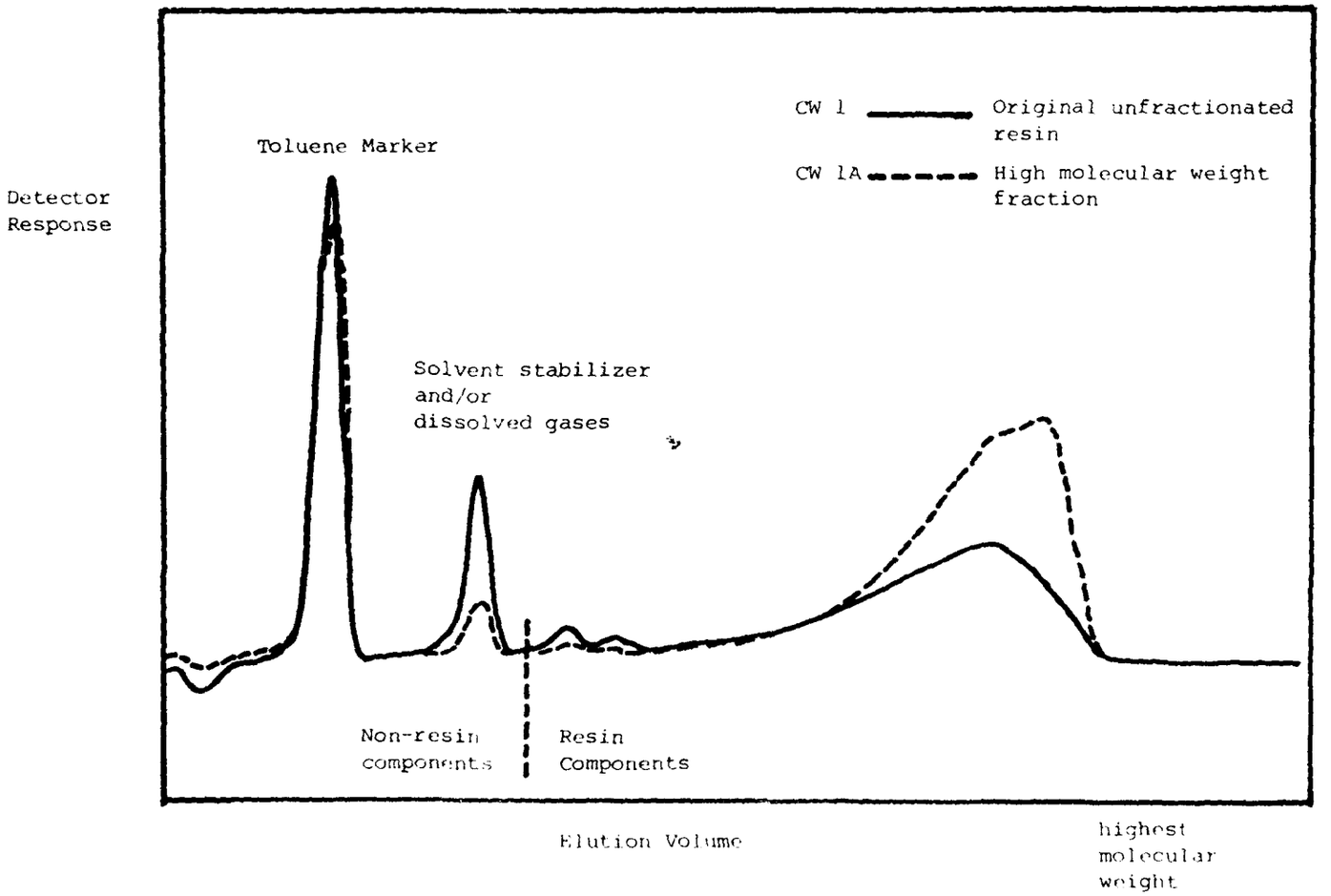


Fig. 3. NMR spectrum of resin DY 4.
C, T refer to cis-(maleic) and trans (fumaric) unsaturation.

Fig. 4. GPC Chromatograms of a resin and its high fraction (GPC System A2)



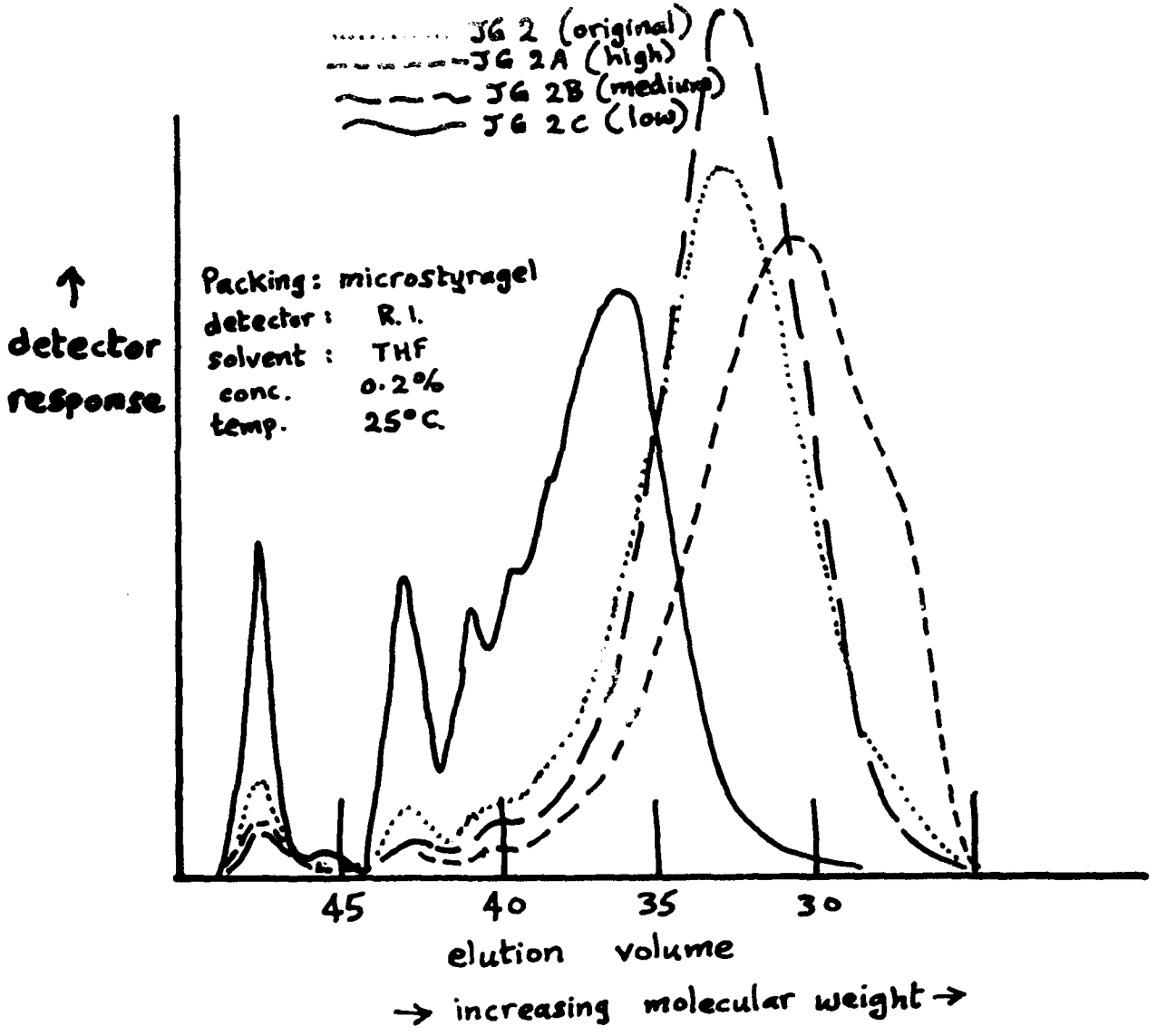


Fig. 5. Qualitative GPC (system B1) of resin JG 2 and its three fractions.

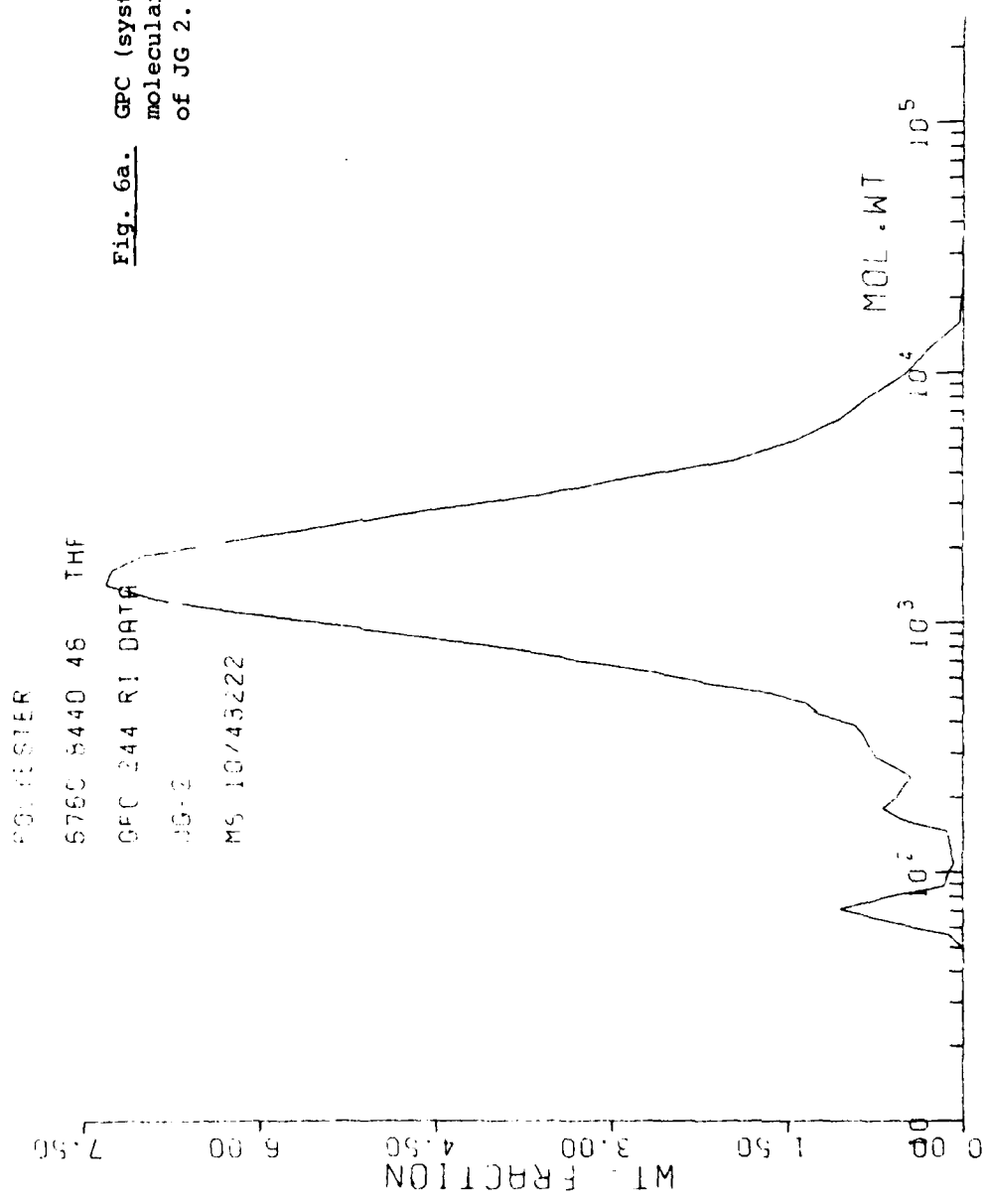


Fig. 6a. GPC (system B1) showing actual molecular weight distributions of JG 2.

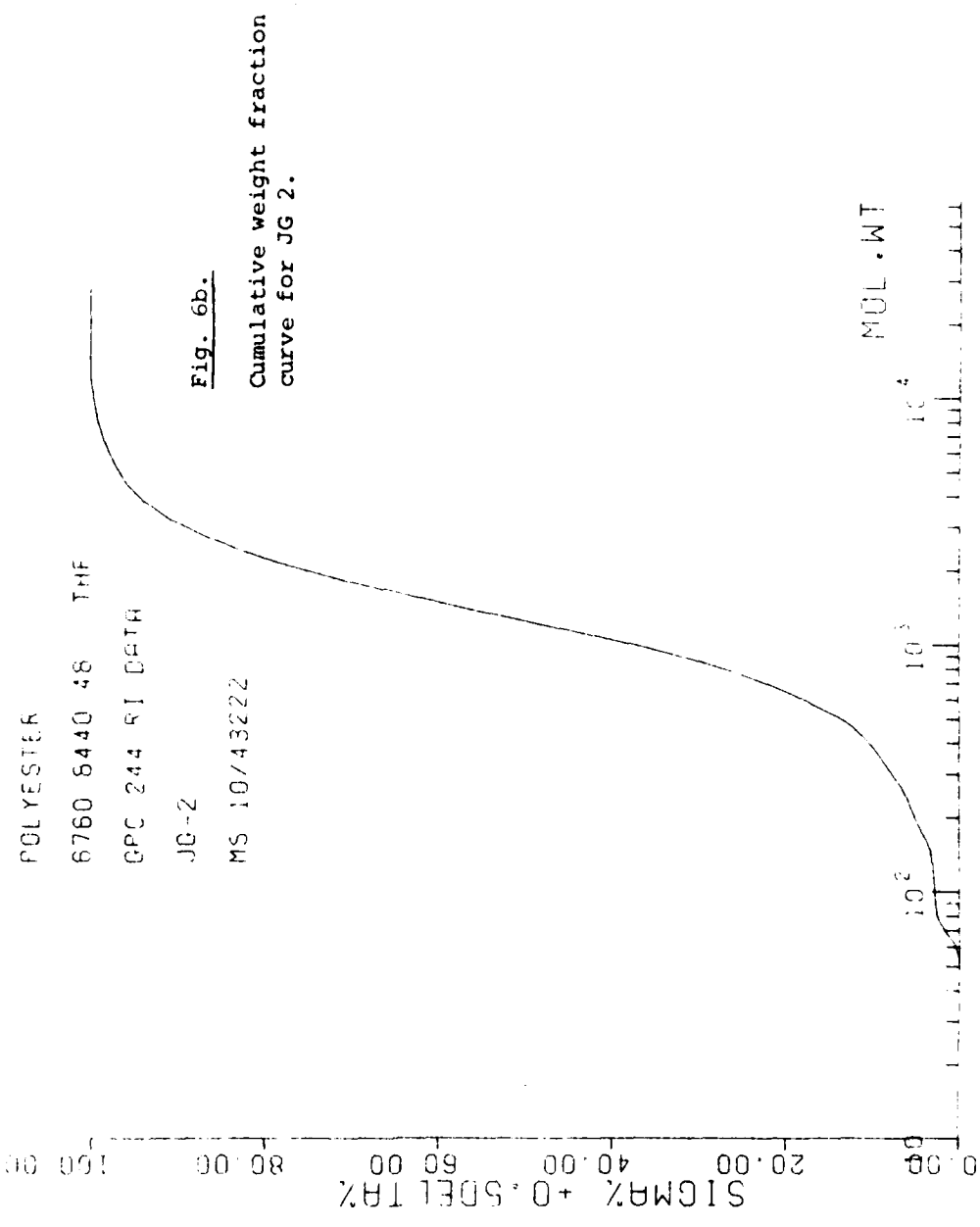
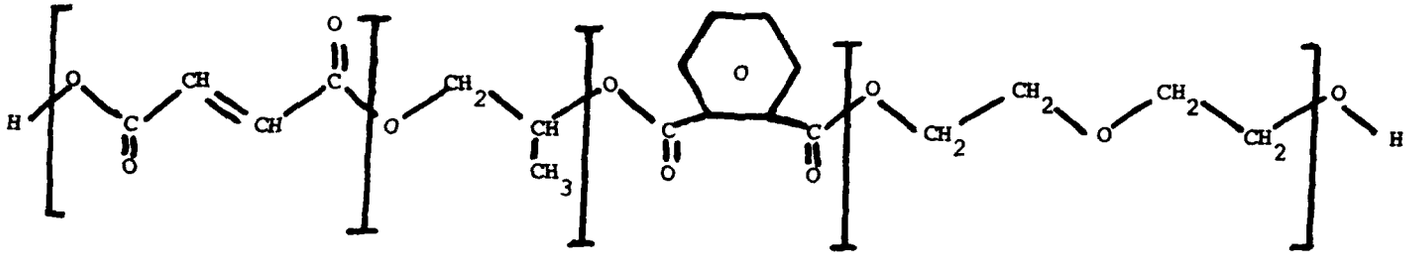


Fig. 6b.

Cumulative weight fraction curve for JG 2.



	fumaric residue	propylene glycol	phthalic acid	diethylene glycol	
Å	1.25	6.04	3.68	5.6	7.2	1.25
M.Wt.	1	98	58	148	88	17

total length = 22.52 Å

molecular weight = 392

Q-factor = 17.41

Fig. 7. Derivation of Q-factor as carried out by GPC Laboratory "B" for the resins used in this program.

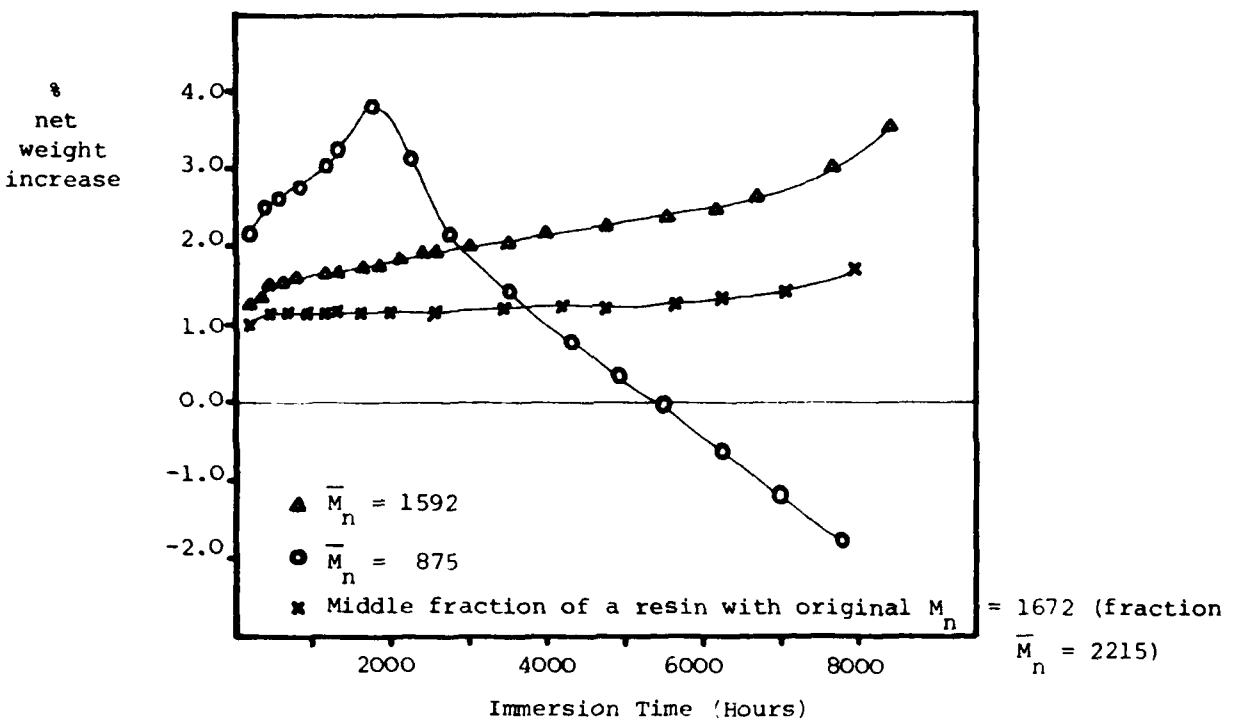


Fig. 8. Net increases in weight observed over the first 8000 hours on total immersion in distilled water at 50°C. The weight increases are the resultant of water uptake and resin leaching.

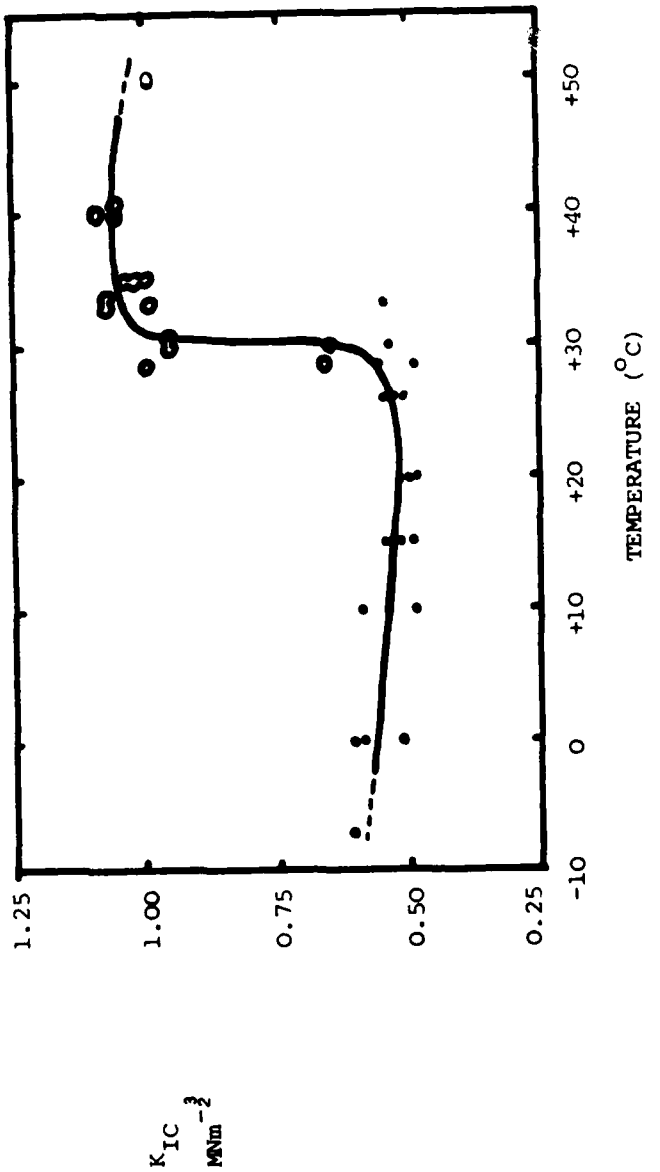


Fig. 9. K_{IC} as a function of temperature, for the low molecular weight resin DY 6 (strain rate, 1 mm min^{-1}). Open circles indicate significant fracture surface roughness.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81