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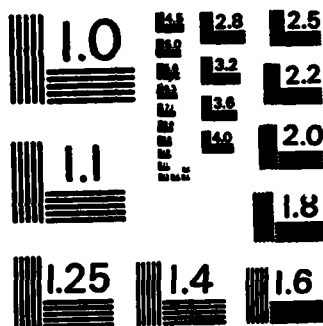
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THE FRACTURE OF THERMOSETTING
RESINS AFTER EXPOSURE TO WATER

by

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

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Chain lengths below $M_n = 1000$ resulted in inferior initial fracture toughness and inferior hydrolytic behavior.

Related studies of the viscoelastic characteristics of the unimmersed resins are outlined. A brittle-ductile transition was observed, and changes in fracture toughness were found, at 28°C.

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THE FRACTURE OF THERMOSETTING
RESINS AFTER EXPOSURE TO WATER

SUMMARY

This report summarizes the conclusions from a study of the effect of molecular weight and molecular weight distribution on the hydrolytic stability and the mechanical properties of polyester resins immersed in water.

Comparison of fractionated resins with unfractionated ones, with and without vacuum stripping, leads to the conclusion that water absorption is extremely dependent on the presence of traces of low molecular weight, water-soluble substances. The extent of change of compressive modulus, and certain other mechanical properties, reflected water absorption behavior, but fracture toughness was not very dependent on water uptake, at least until the stage of irreversible damage was reached.

Chain lengths below $M_n = 1000$ resulted in inferior initial fracture toughness and inferior hydrolytic behavior.

Related studies of the viscoelastic characteristics of the unimmersed resins are outlined. A brittle-ductile transition was observed, and changes in fracture toughness were found, at 28°C.

Keywords: Polyester, epoxide, resin, fracture, toughness, water, fractionation, mechanical, molecular weight, hydrolysis, leaching.

THE FRACTURE OF THERMOSETTING RESINS AFTER EXPOSURE TO WATER

1. INTRODUCTION

Property retention in adverse environments has attracted the attention of many materials specialists concerned with fiber-resin composites. The latest applications of advanced composites require resistance to natural weathering in hot, sunny or tropical climates,¹ to rain erosion,² to chemicals, and to heat and such conditions as lightning strikes.³ The consensus of opinion, however, is that water is the most widespread threat to composite durability overall, and that of all the potential advances in materials formulation, an improvement in resistance to hot water would bring the most useful benefits.

Many studies have been made of the effect of hot water on glass-epoxy⁴, graphite-epoxy⁵, and glass-polyester composites⁶, and there have also been some investigations of the durability (as measured by mechanical property retention) of composites based on aramid and boron fibers and on advanced resins. It can be concluded from these studies that (i) glass fibers are particularly susceptible to moisture, and (ii) the available resins are unsatisfactory in that they fail to protect the fibers against moisture. Almost all the present generation of matrix resins contain a substantial quantity of hydrophilic chemical groups, which facilitate the ready diffusion of water to the fibers and the interface. Moreover, even when the fibers are entirely resistant to water, diffusion of water into the resin almost invariably means that the load transfer mechanism becomes weakened.

This project concentrates on the hygrothermal stability of the matrix. Specifically, the aim was to establish how the chain length (or molecular weight, M_n) and the chain length distribution (or molecular weight distribution, MWD) affect the hygrothermal characteristics of an unsaturated polyester resin. The characteristics of interest were:

- (i) fracture toughness
- (ii) brittle/ductile behavior (studied in compression)
- (iii) water absorption

It was surmised that the conclusions might to some extent be adaptable to other matrix resins besides polyesters, such as epoxides.

It was necessary to make substantial quantities (approximately half a kilogramme) of each of a number of resins, in fractionated form, and since present methods of large scale fractionation are extremely time-consuming, there could not be enough fractionated resin to expose

hygrothermally at several different temperatures. Therefore a single temperature was taken for the majority of the work, with a limited amount of accelerated testing at higher temperatures. The chosen temperature was a few degrees below the heat distortion temperature (HDT) since (a) resins are not used in practical service life above their HDT, (b) accelerated testing above the HDT is widely regarded with suspicion, and with good reason, since it gives pessimistic results.

2. SUMMARY OF WORK REPORTED IN FIRST ANNUAL REPORT (1980)

Before the investigation of the effect of chain length and chain length distribution on hydrolytic stability was carried out, there was already considerable information available about the behavior of one particular polyester resin system in water. This information was of use in designing the experiments carried out as part of the U.S. Army sponsored project, and was therefore reported in the 1980 report. The resin formulation (given as formulation 1 in table 1) differed from that used subsequently, only in one significant respect, namely that it used isophthalic acid instead of phthalic anhydride.

The immersion of the isophthalic resin (formulation 1) in water and in dilute aqueous solutions at 65°C caused the following changes in the material.

Water absorption

The observed (net) weight increase reached a maximum and then fell sharply, eventually becoming negative. Drying of the test samples after immersion invariably resulted in a weight loss, because of leaching of low molecular weight substances, including those originally present, and degradation products. The "true" water uptake was deduced, allowing for losses of organic material by leaching. However, this was derived on the assumption that all the absorbed water could eventually be desorbed by programmed vacuum desiccation. Ideally this could be checked by radiotracers, but dynamic mechanical evidence suggests that polyesters do dry out when treated in a phosphorus pentoxide-filled vacuum desiccator at room temperature.⁷

The peak in net weight increase was found to follow the stage where osmotic disc crack development could be observed. Evidence from the rate of formation of cracks in dilute sodium chloride solution, dilute sulphuric acid, and relatively concentrated sodium chloride, supported the hypothesis that the cracks were generated osmotically, and residual propylene glycol was found to be the main osmotic center. The formation of disc cracks was observed to occur along dendritic pathways at first, as if each crack had been produced by stress fields generated by the previous one. The cracks resulted in greatly accelerated water absorption rates and, judging from the leaching curves, in hydrolysis rates. There were clear signs of free isophthalic

acid in the regions of the disc cracks after long immersion times; this was thought to be a consequence of the cracks rather than a cause. Immersion in dilute salt solutions produced similar effects, delayed by the lower osmotic pressure in glycol-rich pockets. No variation in MWD was made at this stage.

Mechanical property changes

The critical stress intensity factor (K_{IC}), measured by means of the center-notched specimen geometry, was initially about $0.70 \text{ MNm}^{-3/2}$, and this fell slowly as a result of water immersion, to become about $0.45 \text{ MNm}^{-3/2}$ after 16000 hours (approximately two years) at 65°C . Drying the specimens caused almost complete recovery prior to disc crack formation, but afterwards, recovery was less and less successful. This observation supports the view that irreversible hydrolysis dominates the later stages of the immersion period. Changes in K_{IC} at 30°C were very small.

Observations were also made of the changes in conventional compressive yield stress, which was approximately halved by 13000 hours' immersion in water at 65°C , but partly restored by subsequent drying. This enabled the radius of the plastic zone at the crack tip, r_y , to be calculated from the equation

$$r_y = \frac{K_{IC}^2}{6\pi\sigma_y^2}$$

where K_{IC} = stress intensity factor

σ_y = compressive yield stress.

Values of r_y increased from $1.5 \mu\text{m}$ to nearly $3 \mu\text{m}$ after 13000 hours in water at 65°C , but fell to $1.3 \mu\text{m}$ on drying. Larger values of r_y were found in 0.78M and in 2M sodium chloride solutions; for example after 13000 hours in 2M solution r_y was calculated to be in excess of $16 \mu\text{m}$.

A few values of the critical strain energy release rate, G_{IC} , were estimated from the plane strain equation

$$G_{IC} = \frac{K_{IC}^2}{E(1 - \mu^2)}$$

where μ = Poisson's ratio
(measured by strain gauge method)

and E = Young's modulus, which was also
measured specifically for this purpose.

The modulus fell by about half after 10,000 hours in water at 65°C , but was restored to a higher value than the original on drying, suggesting that the leached substances had acted as plasticizers. The tensile

strength, however, was not fully restored, even after quite brief immersion periods, and neither was the inherent flaw size (a_1) when calculated from the equation⁸

$$a_1 = \frac{\pi K_{Ic}^2}{4\sigma^2}$$

Studies of the fracture surfaces after immersion were complicated by the presence of disc cracks, but it was apparent that the region of stable crack growth had increased, and the river markings were more regular.

3. SUBSEQUENT EXPERIMENTAL PROCEDURES

The main project, for which U.S. Army funding was provided, followed on from the work described in the previous section. Briefly, it consisted of the following steps.

- (a) Synthesis of several unsaturated polyester resins by the methods described in the 1981 report. These resins all had the same formulation, i.e. formulation 2 in table 1. The acid value and molecular weight were the only deliberately introduced variables. One resin was subjected to 60 minutes of high vacuum stripping during the last stages of heating.
- (b) Analysis and characterization of a whole family of resins, including the measurement of acid value, molecular weight, molecular weight distribution, maleic:fumaric ratio and, in some cases, hydroxyl value. Procedures are outlined in the 1981 report.
- (c) Fractionation of certain resins to produce high, middle and low fractions. Again, procedures are given in the 1981 report.
- (d) Crosslinking of resins and fractions. The low molecular weight fractions did not crosslink very satisfactorily, and only a little of this material was used. The behaviour of the middle and high fractions was always very similar, and therefore they are not discussed separately.
- (e) Measurement of several mechanical properties of resins and fractions.
- (f) Immersion of crosslinked samples in distilled water, mainly at 50°C, but to a lesser extent at 60°C and 75°C.
- (g) Observation of weight changes, time of initiation of disc cracks, and changes in mechanical properties.

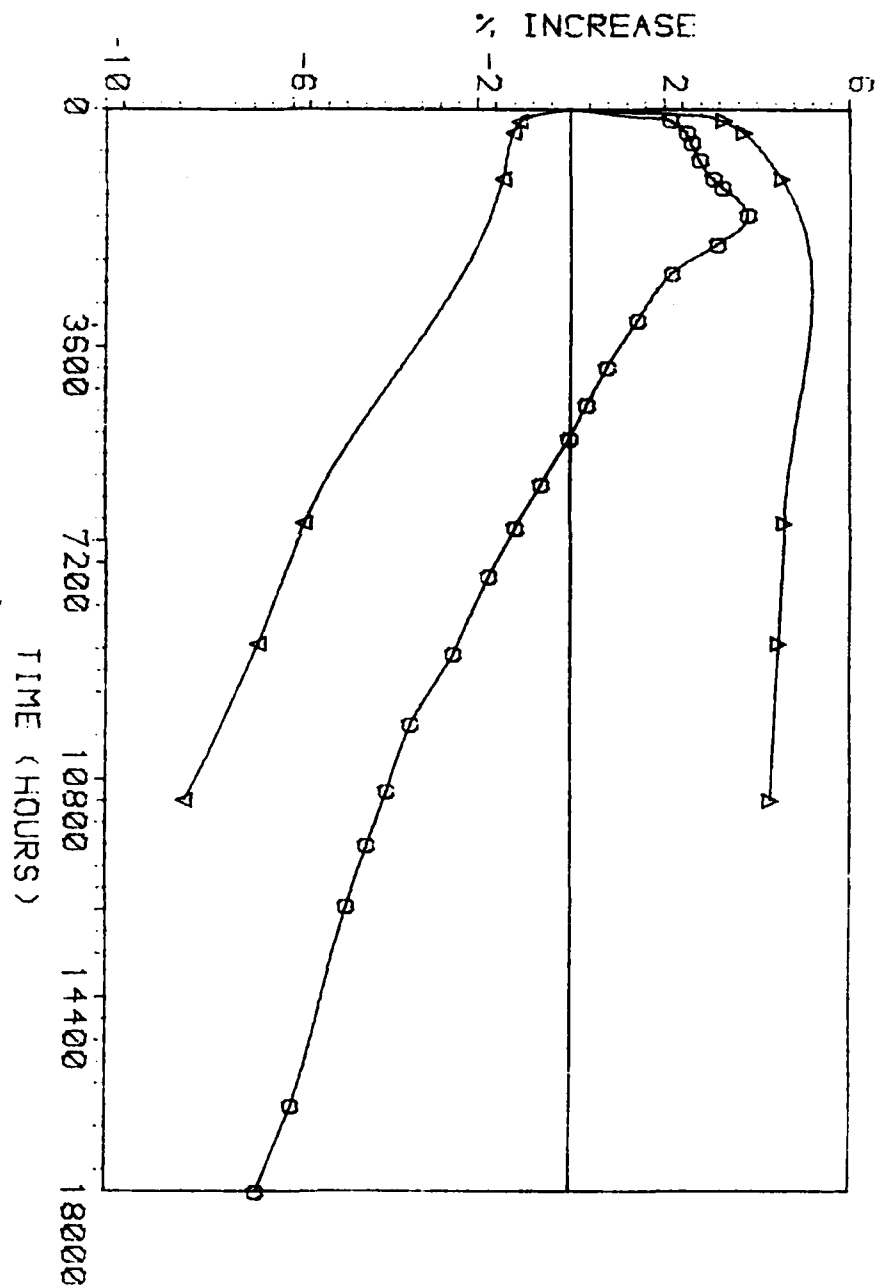
- (h) Careful re-drying (to avoid cracking) and measurement of the extent of recovery of mechanical properties. This drying process required long periods of vacuum desiccation. It is not certain that all the bound water could be removed, although the final weights were always less than those of the virgin specimens.

Attention is drawn to the fact that many of the resins exhibited marked viscoelastic behavior, and were sometimes found to break in a ductile fashion in tension. This was traced to a transition at around 25°-30°C. Below this temperature, the tensile dumbbells (machined from sheet with the aid of a computer-controlled tool) broke in tension in a brittle fashion, and the control fracture toughness values were around 0.50 MNm^{-3/2}. Above this temperature, tensile specimens broke in a ductile mode, and values of K_{IC} were about 1.0 MNm^{-3/2}, with a change in fracture surface from glossy to matt, observable without magnification. Therefore the measurement of K_{IC} was confined to a temperature of 20°C. Large changes in crosshead speed also caused brittle-ductile changes. The temperature range at which the transition was normally observed did not coincide with the T_g, which was determined by means of a free vibration torsional pendulum to be 80°C approx.

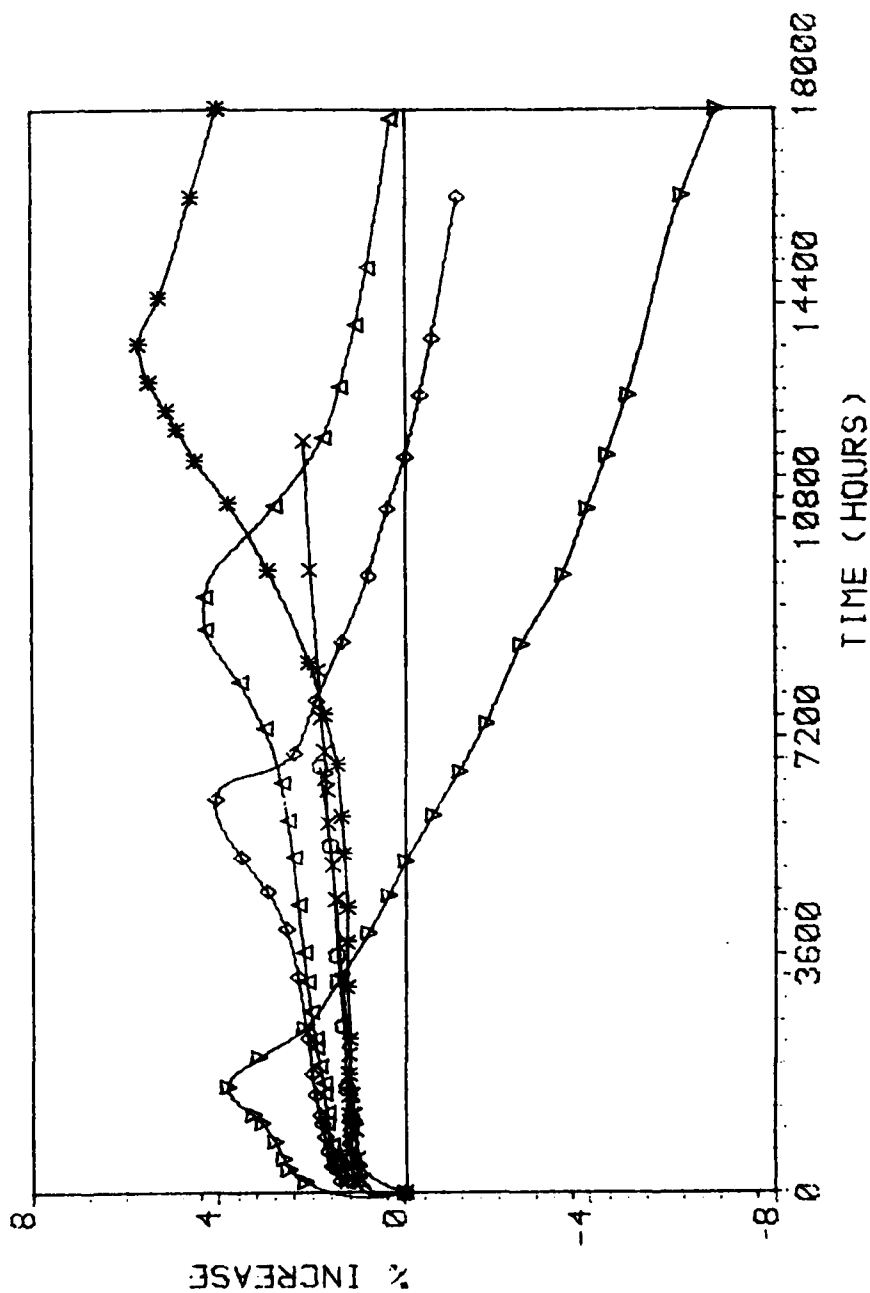
Accordingly, a brief investigation of the viscoelasticity of one of the lower molecular weight resins was made, and is reported in Appendix 1.

Finally, a few measurements of the strain energy release rate (G_{IC}) were made by the tapered cleavage geometry, using both an isophthalic and an orthophthalic specimen. The effect of immersion of the isophthalic resin in water was observed. Measurements of G_{IC} were also made when glass fibers were laid across the crack path at 10 mm intervals. Specimen dimensions are given in Appendix 2.

4. RESULTS: (FIGURES 1 TO 17)



▲ = TRUE WEIGHT OF WATER UPTAKE
 ▼ = TRUE WEIGHT OF LEACHED OUT MATERIALS
 □ = NET WEIGHT CHANGE
 FIG.1 CHANGE IN WEIGHT (%) WITH IMMERSION TIME (HOURS)
 (RESIN:DY4, MN=875)



Δ = DY2 (MN=1592) / * = JG2B (MN=2215; MIDDLE FRACTION)
 $\diamond$ = DY3 (MN=1294) / O = DY14B (MN=3077; MIDDLE FRACTION)
 ∇ = DY4 (MN=875) / X = DY7 (MN=1454; VACUUMED RESIN)
 FIG.2.2 CHANGE IN NET WEIGHT(%) WITH IMMERSION TIME(HOURS)
 AT 50C IN WATER

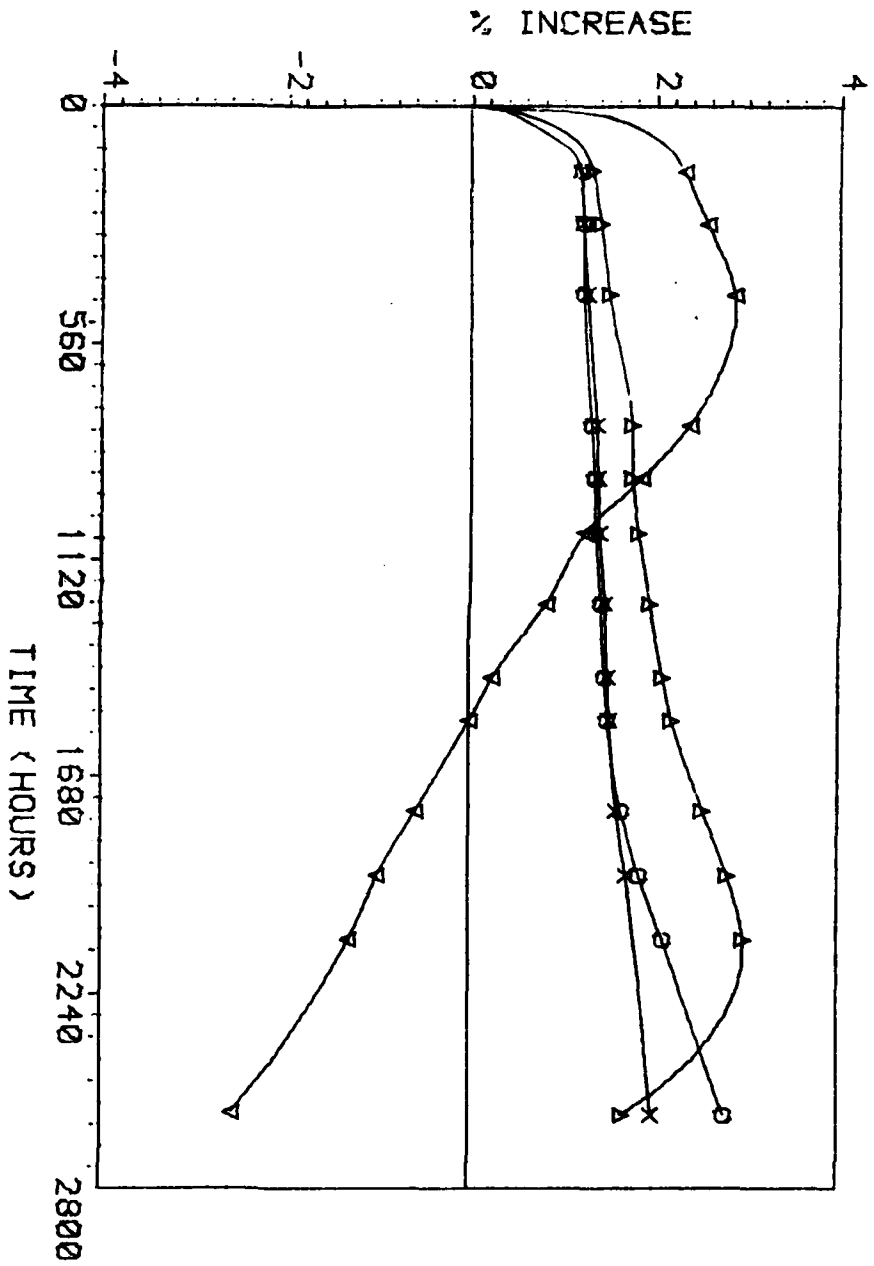
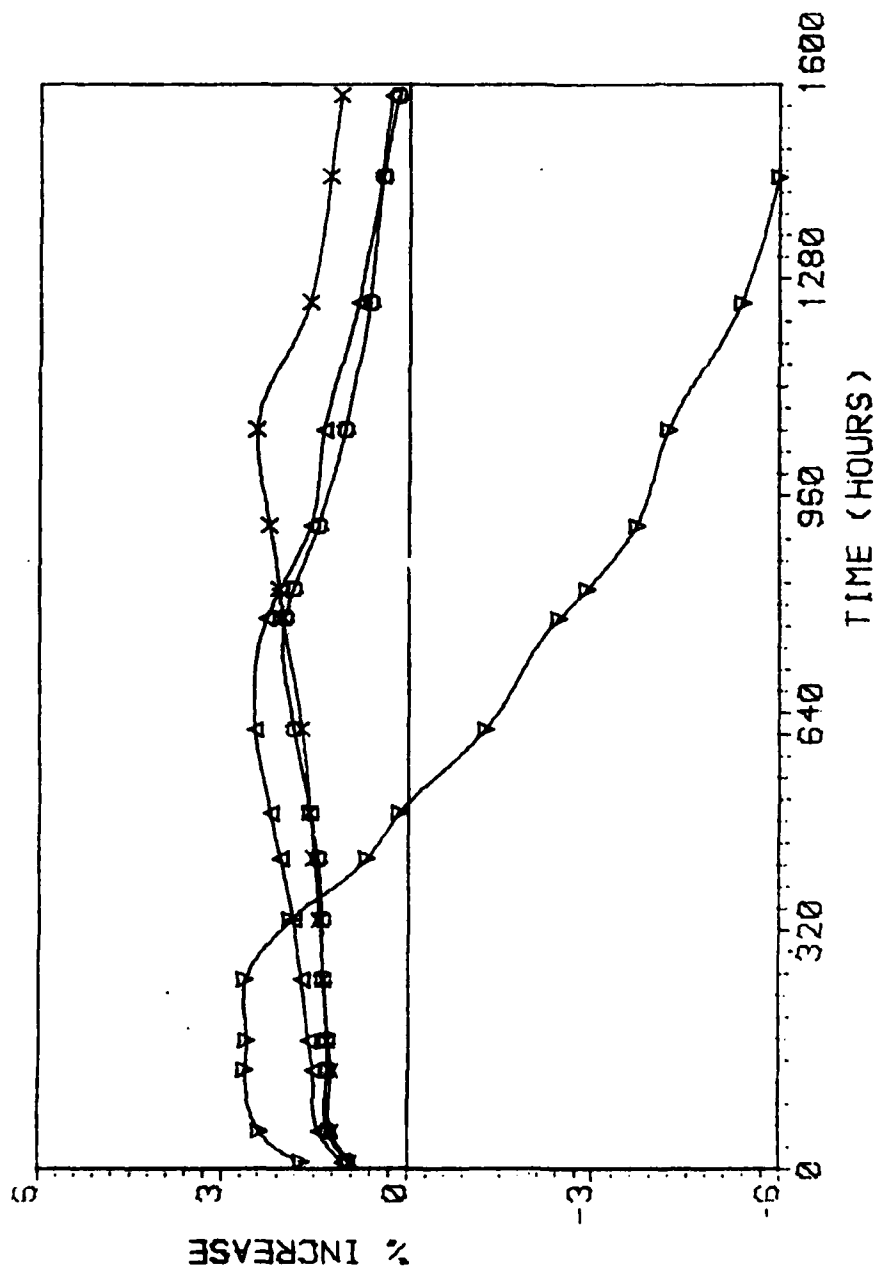


FIG. 3 CHANGE IN NET WEIGHT (%) WITH IMMERSION TIME (HOURS)
AT 60°C IN WATER

Δ = DY2 (MN=1592) O = DY14B (MN=3077; MIDDLE FRACTION)
 ∇ = DY4 (MN=875) X = DY7 (MN=1454; VACUUMED RESIN)



Δ = DY2 (MN=1592) O = DY14B (MN=3077; MIDDLE FRACTION)
 ∇ = DY4 (MN=875) X = DY7 (MN=1454; VACUUMED RESIN)

FIG. 4 CHANGE IN NET WEIGHT (%) WITH IMMERSION TIME (HOURS)
 AT 75°C IN WATER

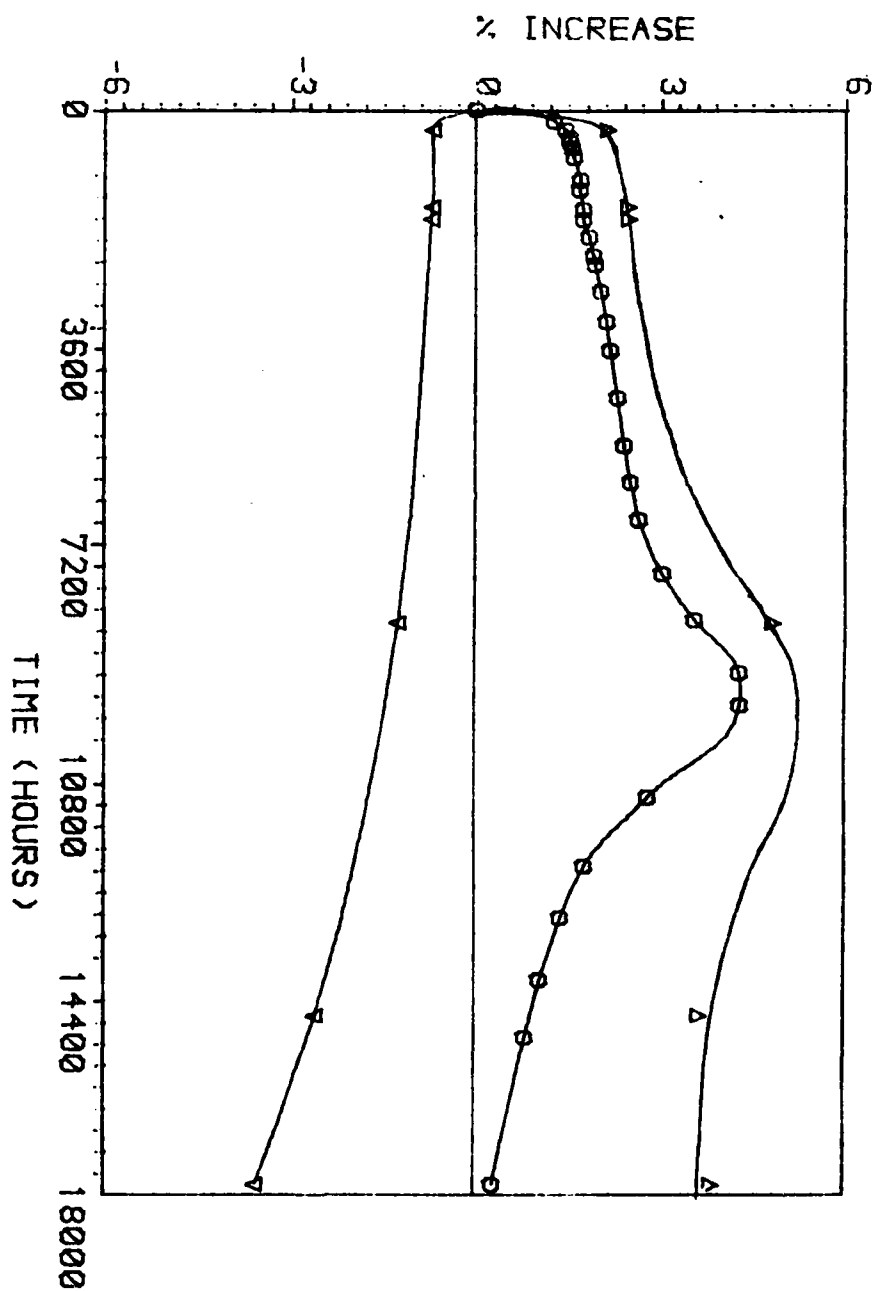
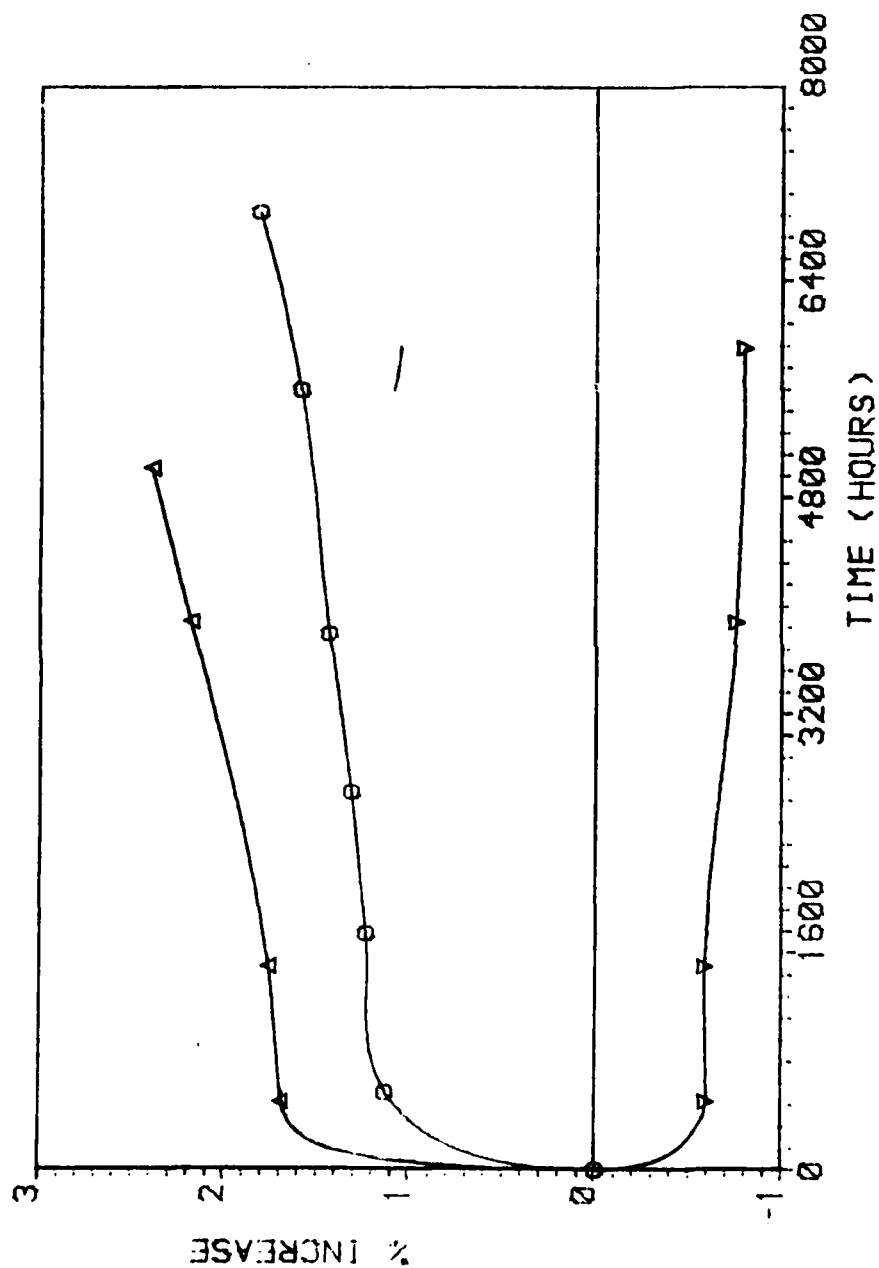


FIG.5 CHANGE IN WEIGHT(%) WITH IMMERSION TIME(HOURS) (50°C)
 (RESIN:DY2, MN=1592)



Δ = TRUE WEIGHT OF WATER UPTAKE
 ∇ = TRUE WEIGHT OF LEACHED OUT MATERIALS
 $\circ$ = NET WEIGHT CHANGE

FIG. 6 CHANGE IN WEIGHT (%) WITH IMMERSION TIME (HOURS) (50°C)
 (RESIN: DY14B, MIDDLE FRACTION, MN=3077)

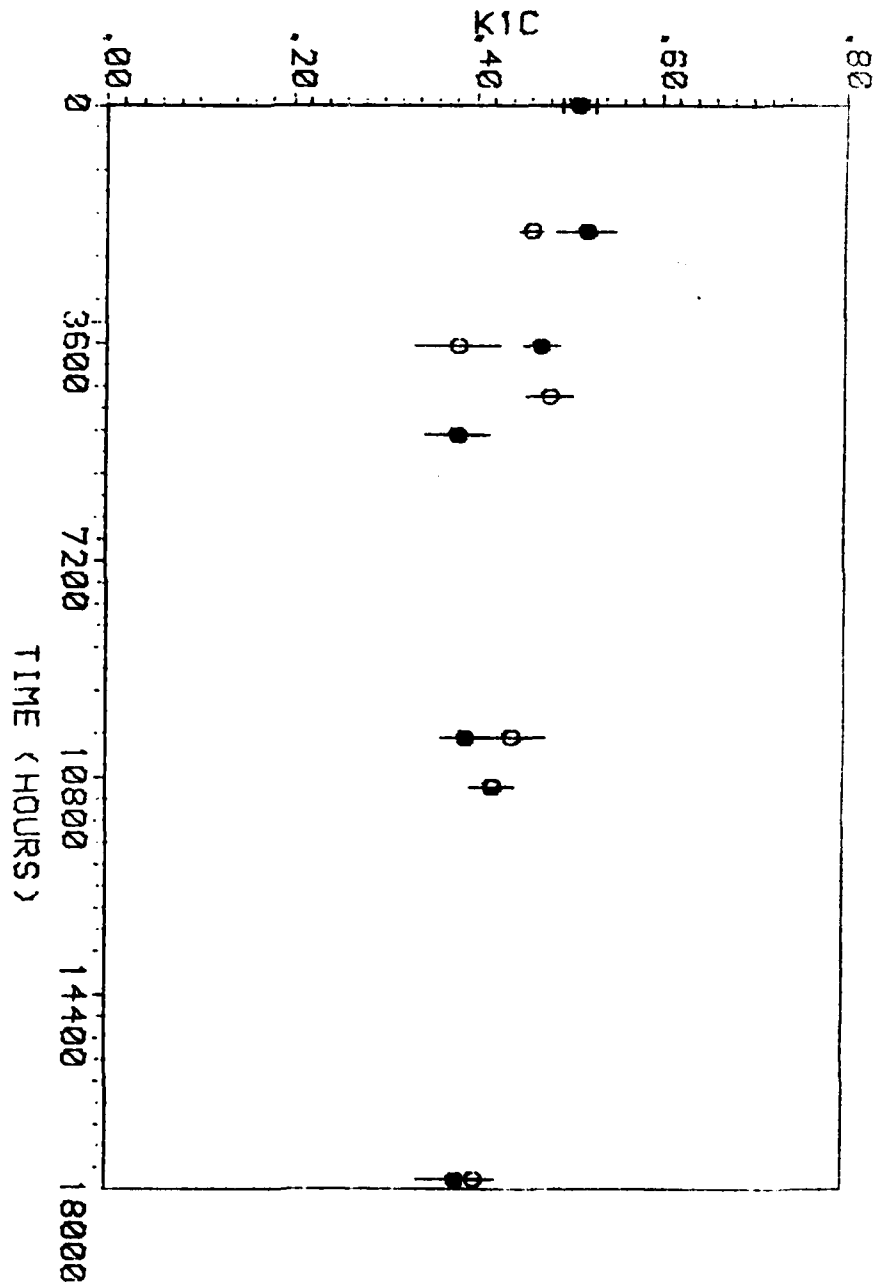


FIG.7 CHANGE IN K1C (MN/M^{-3/2}) WITH IMMERSION/ TIME (HOURS)
AT 50C (RESIN:DY2, MN=1592)

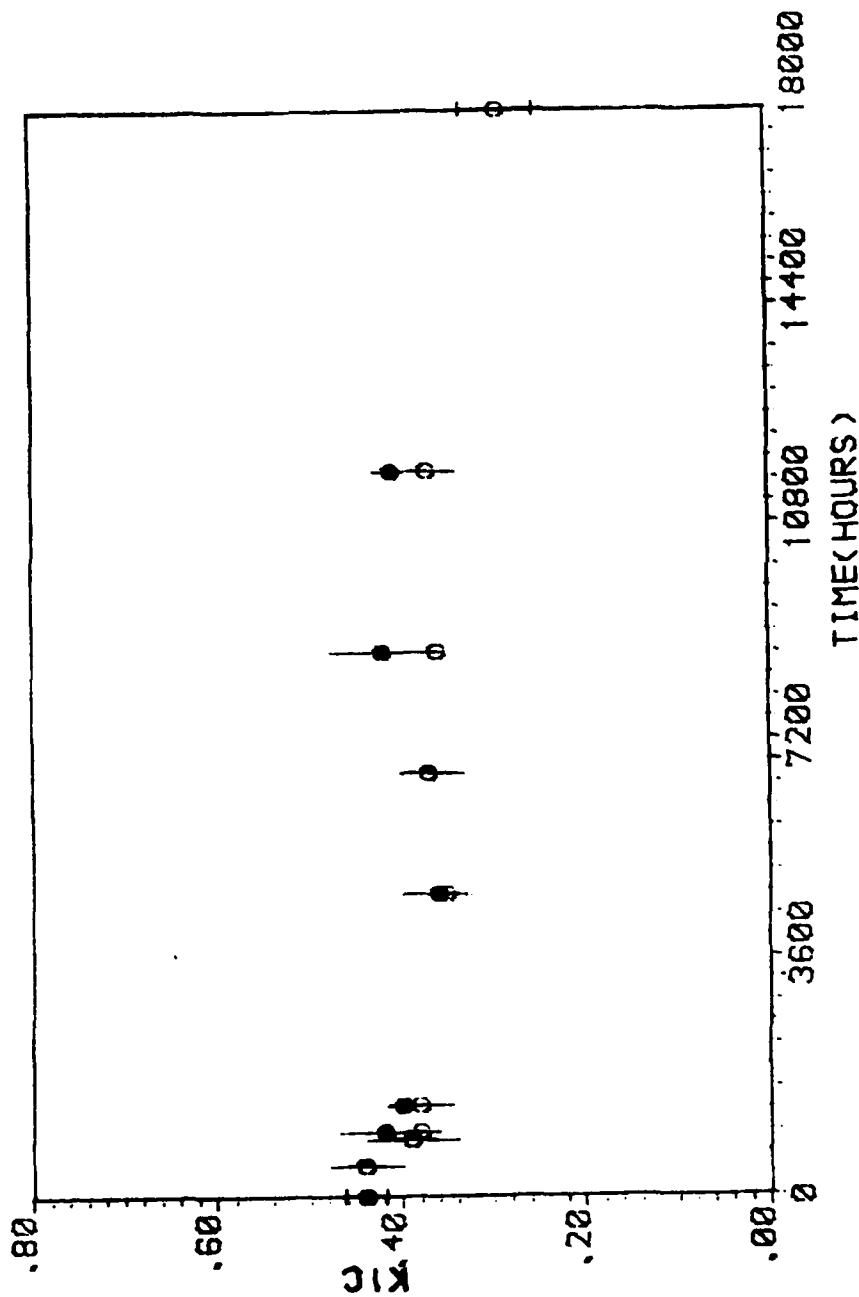
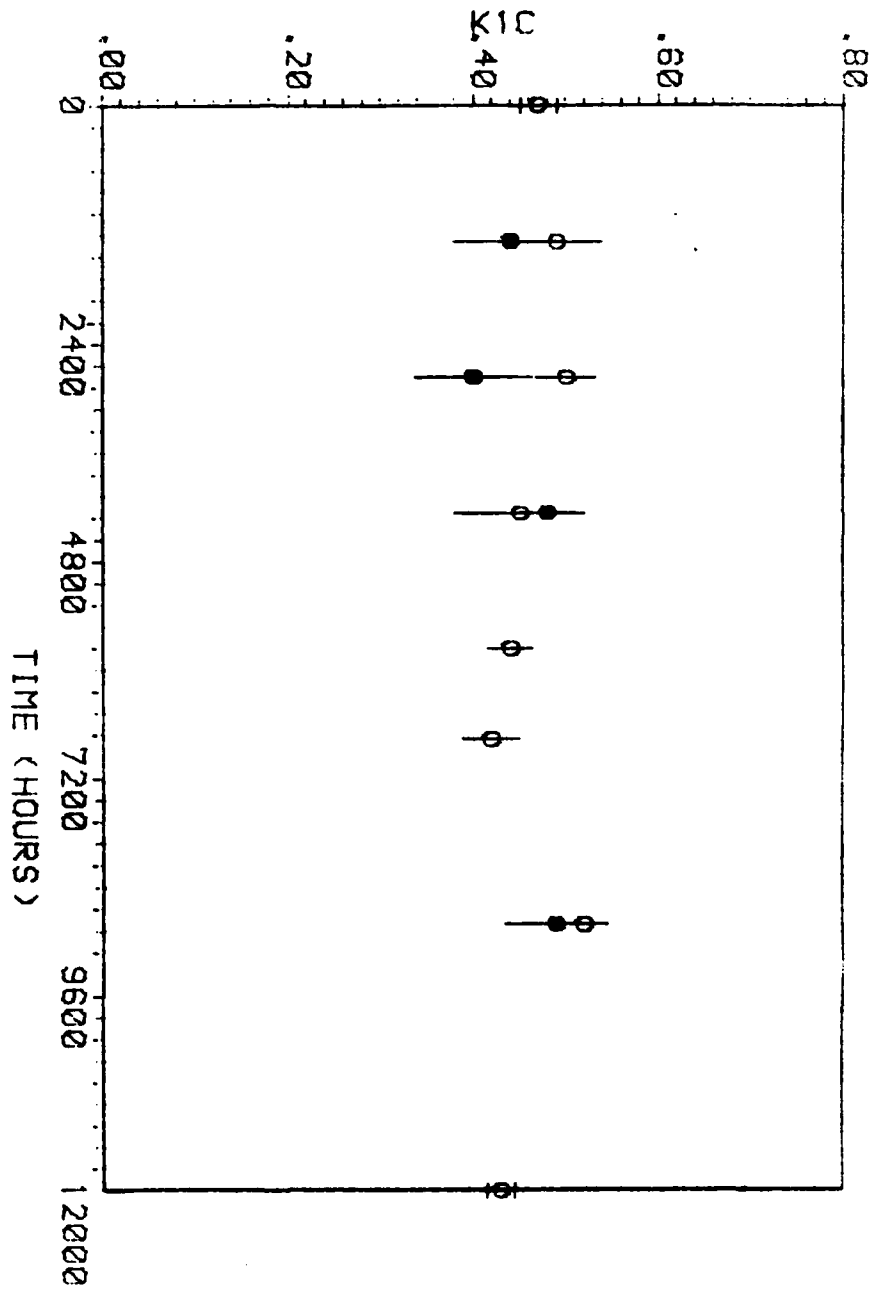
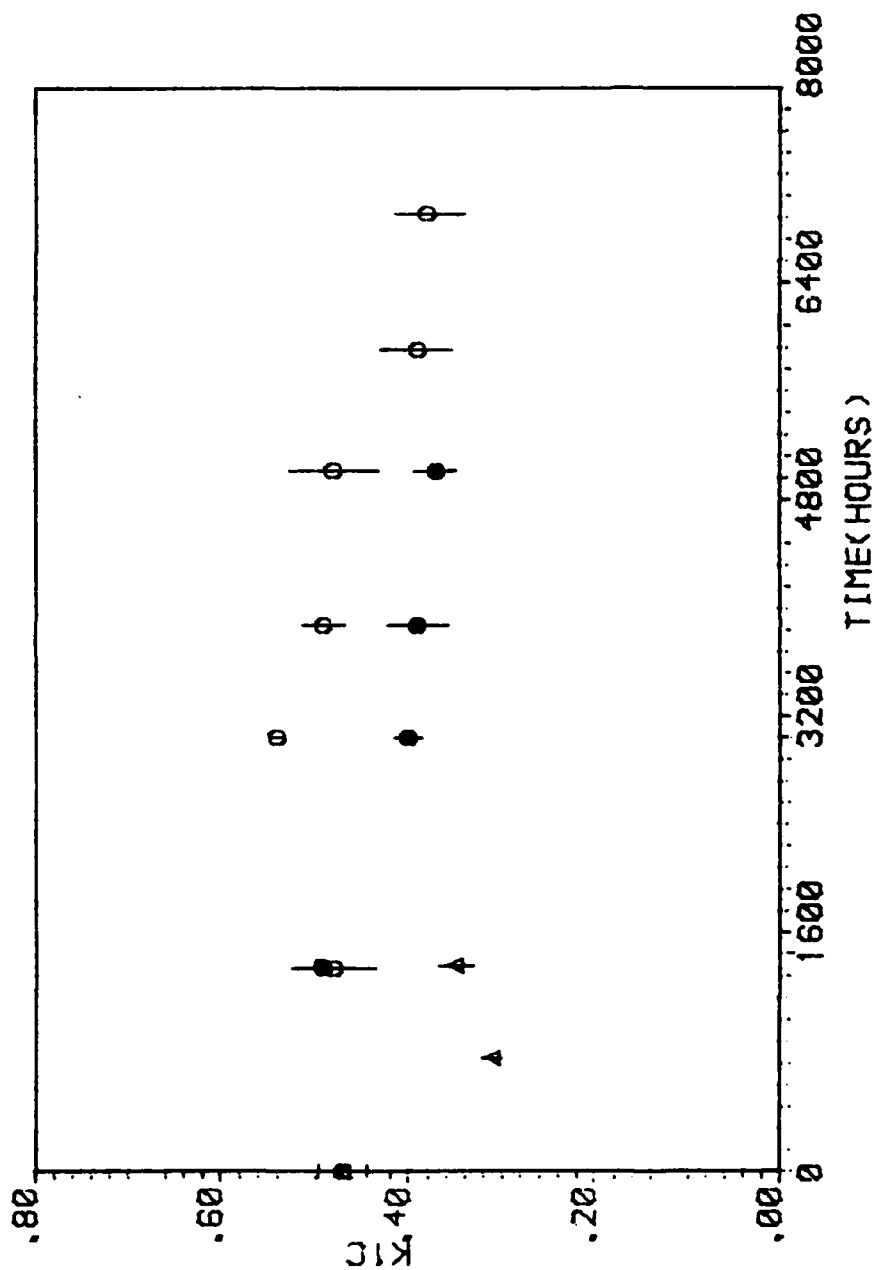


FIG.8 CHANGE IN K1C (MN/M^{3/2}) WITH IMMERSION TIME (HOURS)
 AT 50C
 (RESIN:DY4, MN=875)



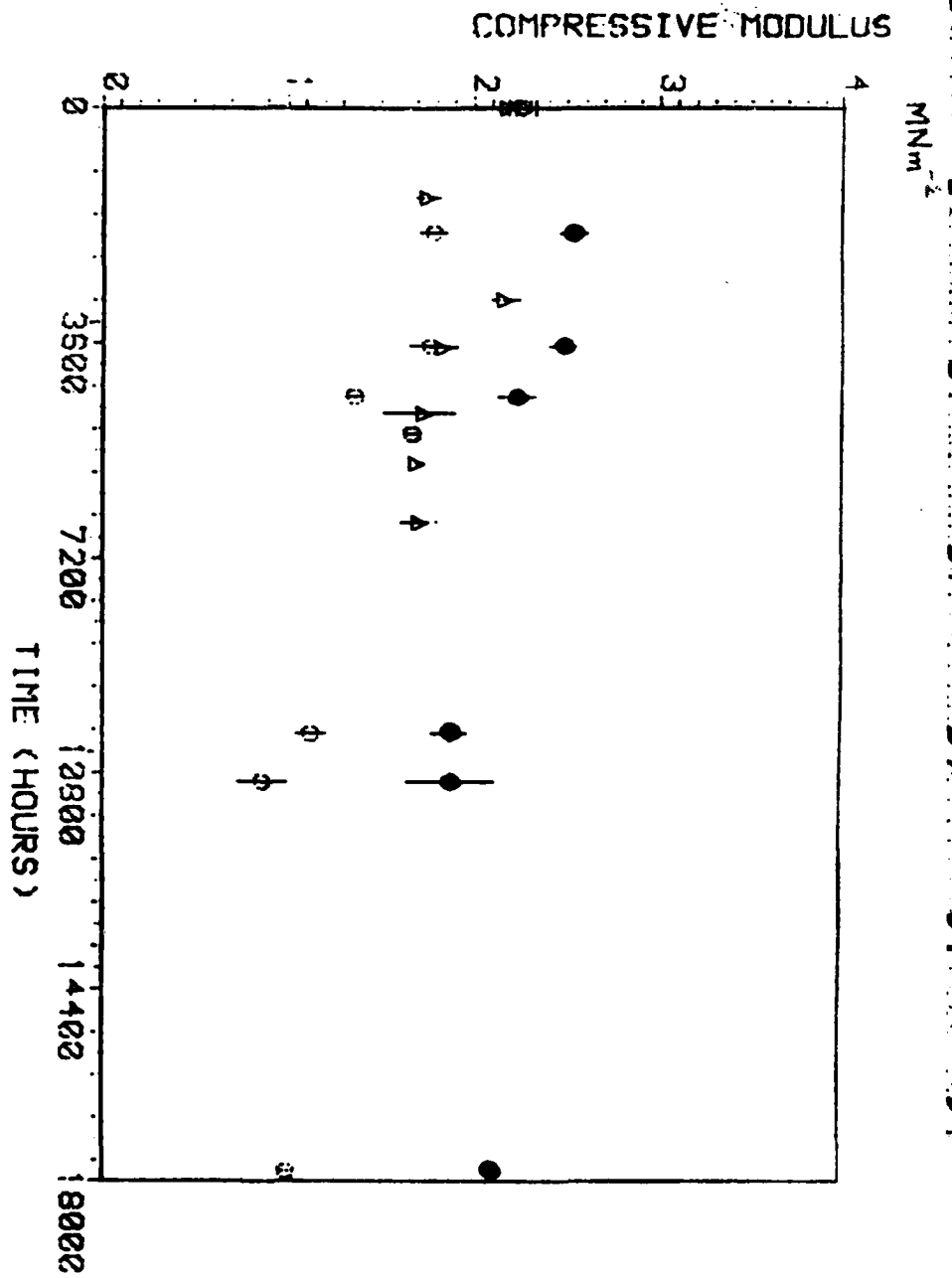
○ = WET ● = DRY

FIG.9 CHANGE IN K1C (MN/M^{-3/2}) WITH IMMERSION TIME (HOURS)
AT 50C (RESIN:DY7, MN=1454 ; VACUUMED)

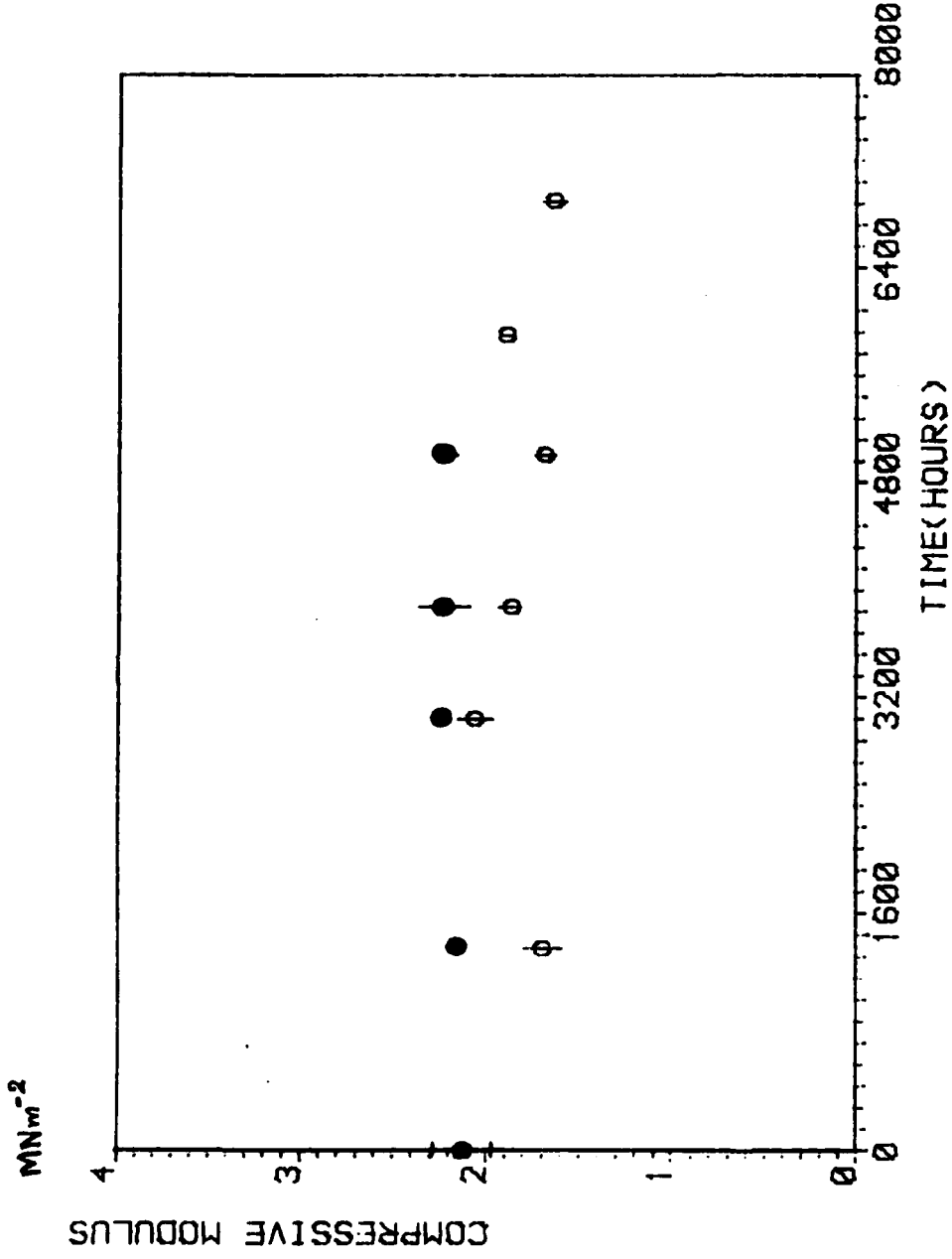


○ = WET (DY14B) ● = DRY (DY14B) Δ = WET (DY14C)
 (DY14B: MN=3077 ; MIDDLE FRACTION)
 (DY14C: MN=592 ; LOW FRACTION)

FIG.10 CHANGE IN KIC (MN-M^{-1/2}) WITH IMMERSION TIME (HOURS)
 AT 50C

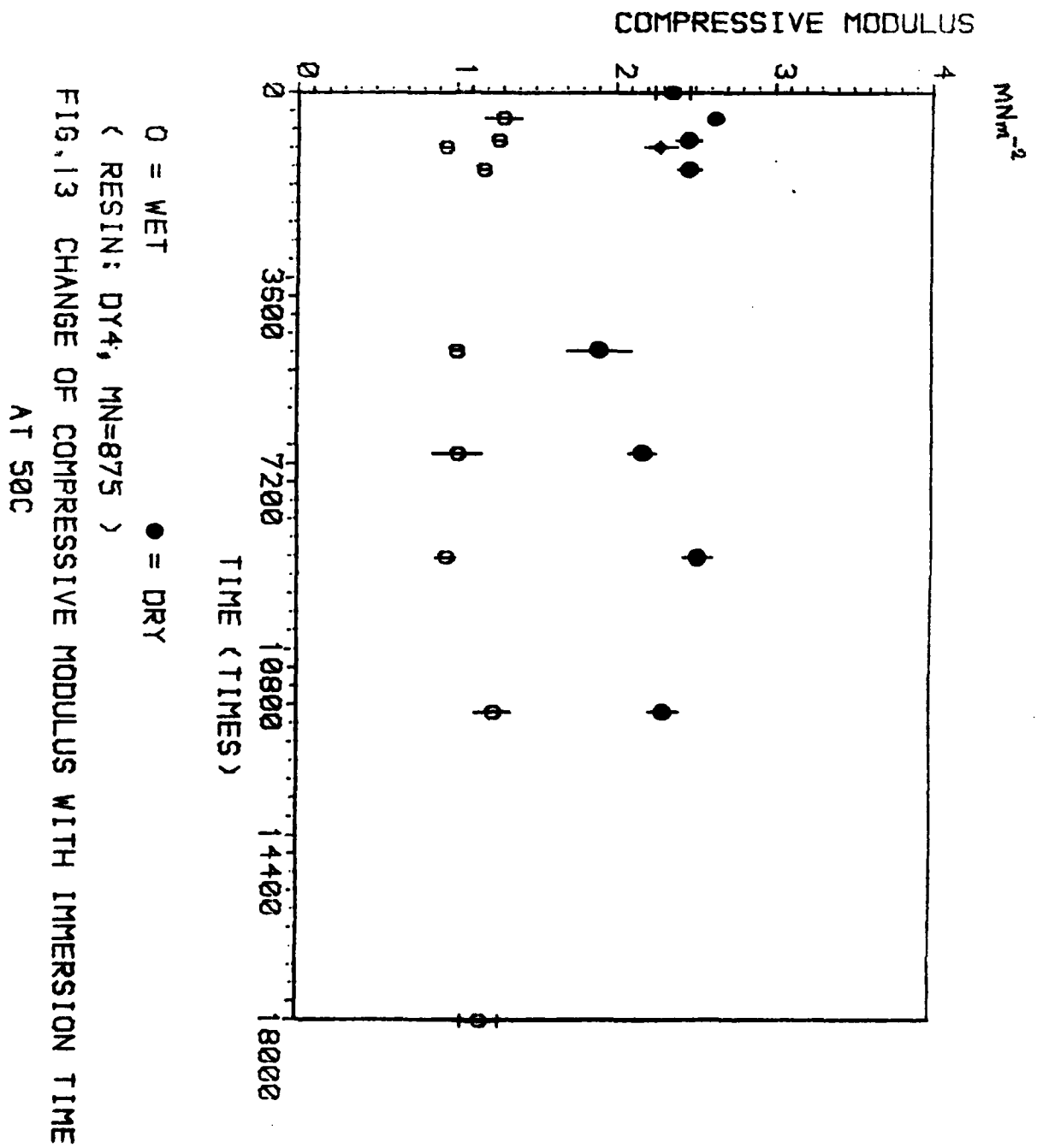


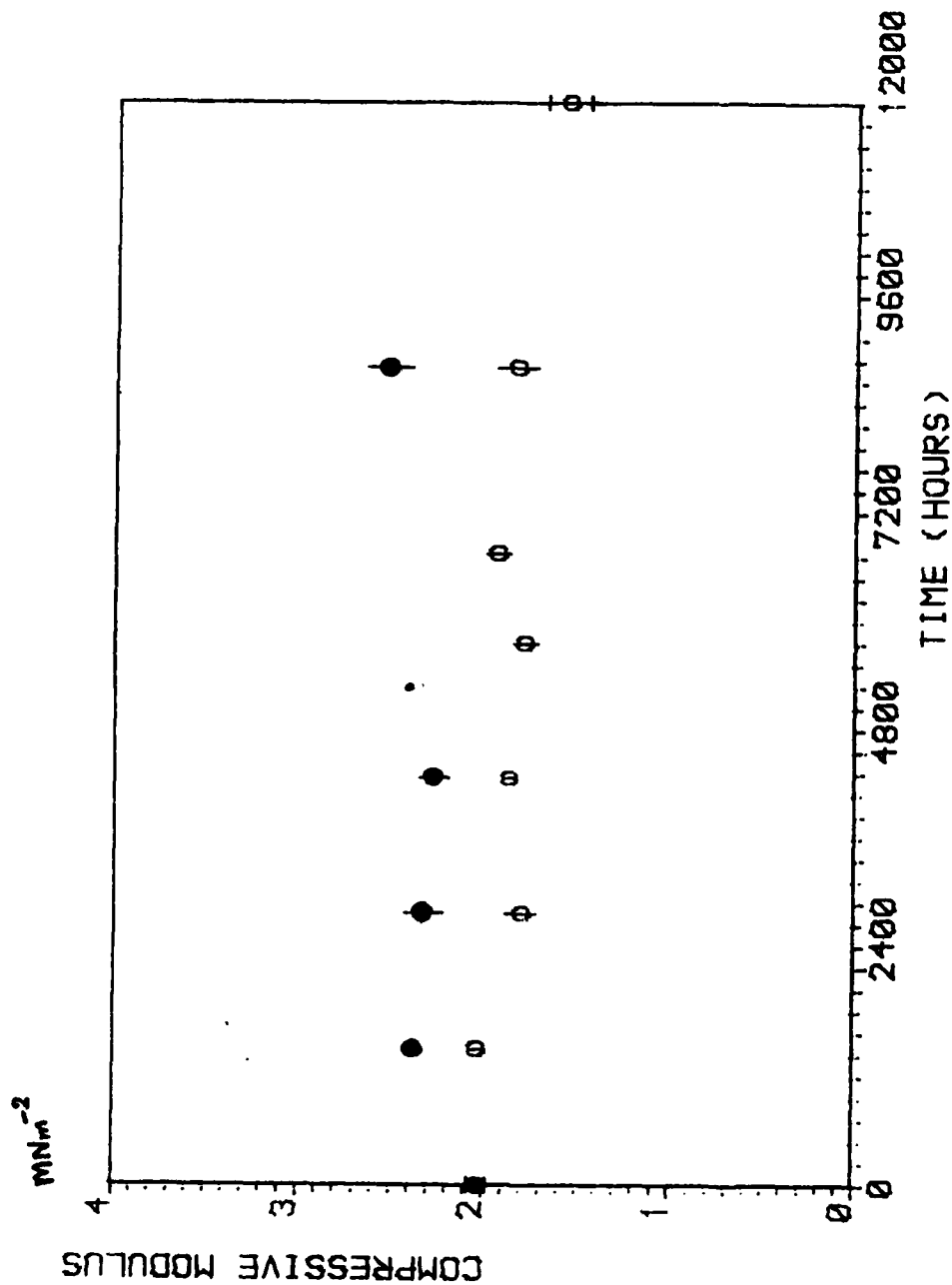
O = WET (DY2) ● = DRY (DY2) Δ = WET (DY15AB)
 (DY2 : BASE RESIN, MN=1592)
 (DY15AB: HIGH/MIDDLE FRACTION, MN=3321)
 FIG.11 CHANGE OF COMPRESSIVE MODULUS WITH IMMERSION TIME
 AT 50C



O = WET ● = DRY
 (RESIN: DY14B, MN=3077 ; MIDDLE FRACTION)

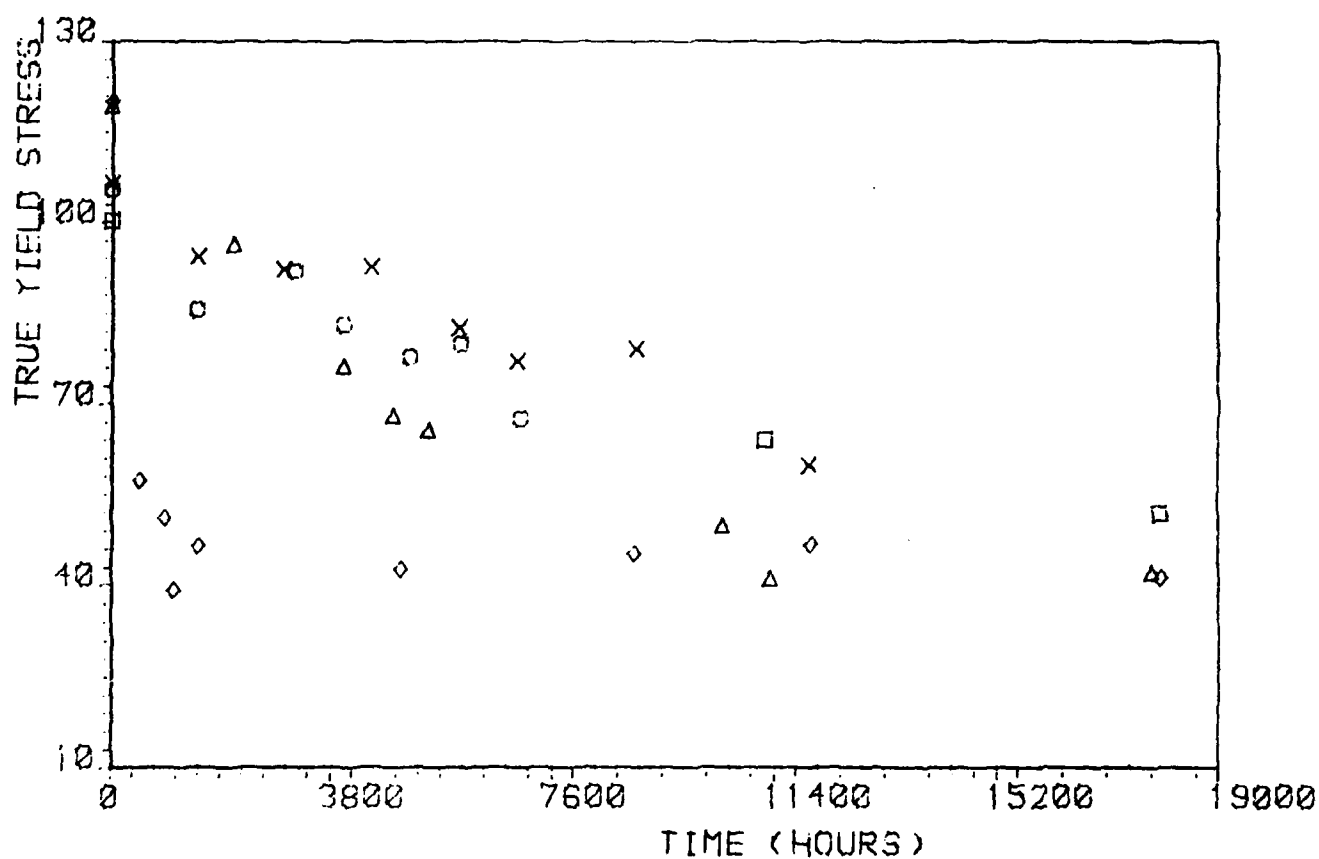
FIG.12 CHANGE OF COMPRESSIVE MODULUS WITH IMMERSION TIME
AT 50C





○ = WET
 ● = DRY
 (RESIN: DY7, MN=1454 ; VACUUMED)

FIG.14 CHANGE OF COMPRESSIVE MODULUS WITH IMMERSION TIME
 AT 50C



- ▲ = DY2 (MN=1592) ● = DY14B (MN=3077, MIDDLE FRACTION)
 ◆ = DY4 (MN=875) ◻ = J62B (MN=2215; MIDDLE FRACTION)
 × = DY7 (MN=1454; VACUUMED RESIN)

FIG.15 CHANGE IN TRUE COMPRESSIVE YIELD STRESS (MN/M²)
WITH IMMERSION TIME (HOURS) AT 50C IN WATER ; WET

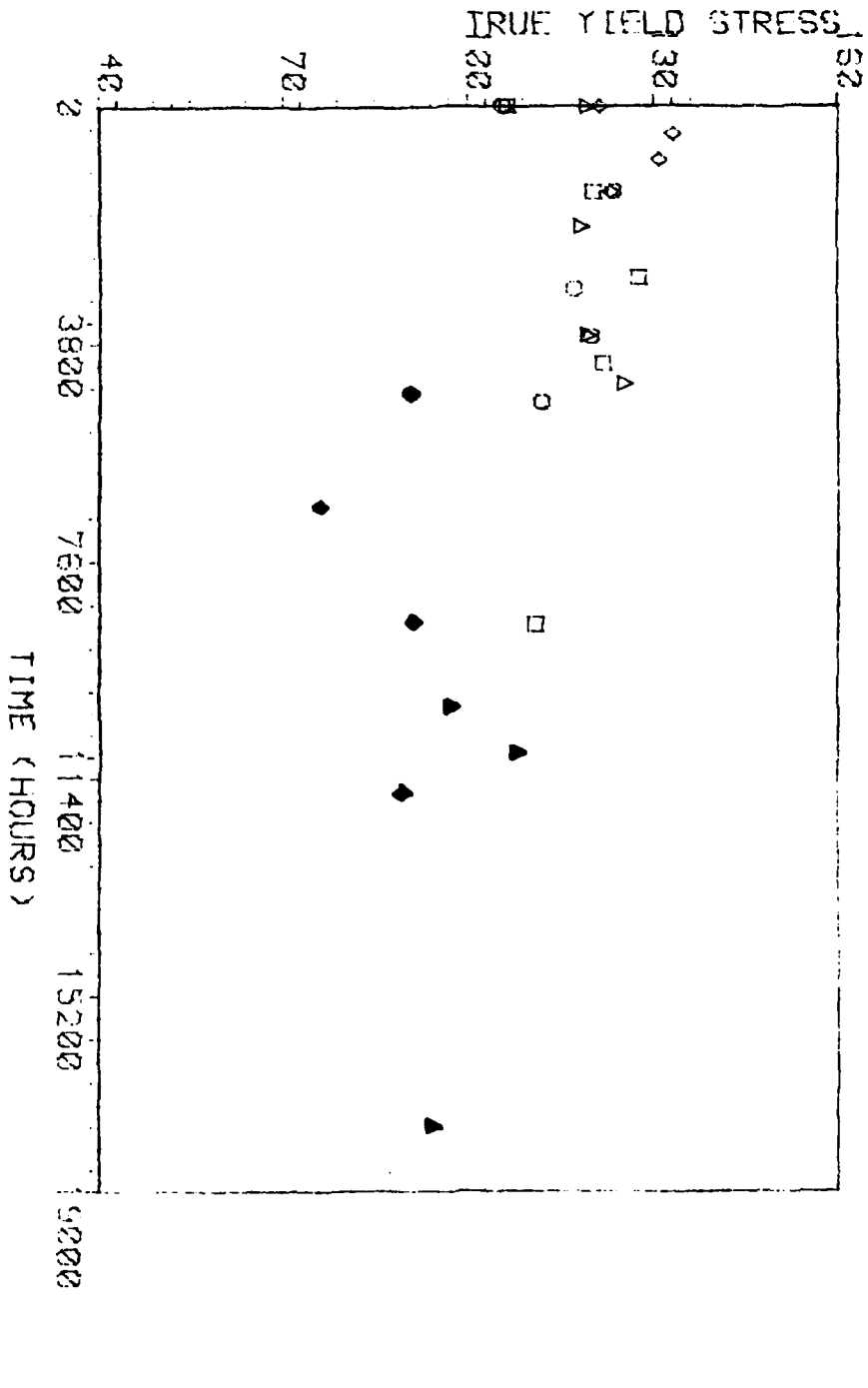
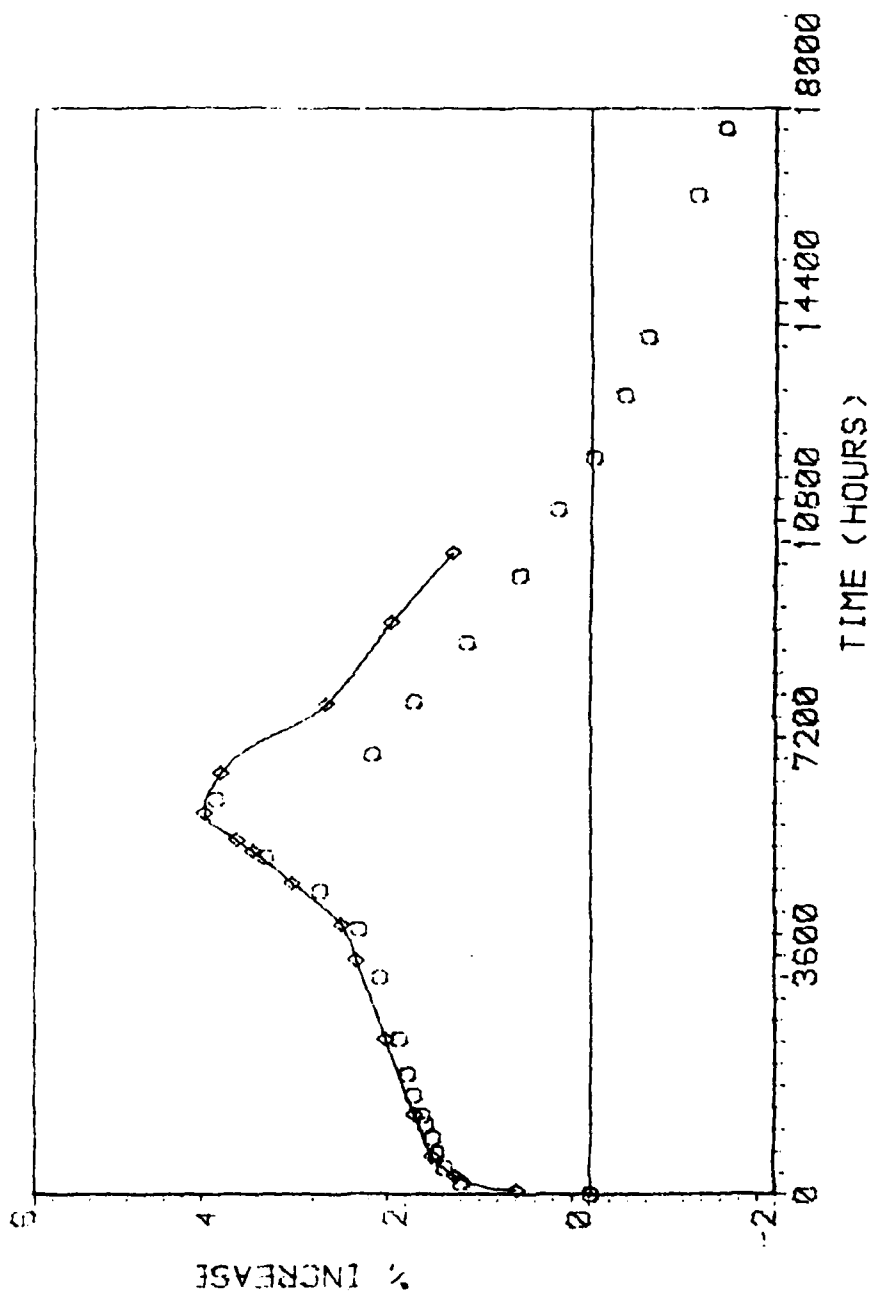


FIG.16 CHANGE IN TRUE COMPRESSIVE YIELD STRESS (MN/M²) WITH IMMERSION TIME (HOURS) AT 50C IN WATER ; DRY



O = DY3 (MN=1294)

◇ = BR = DY6/13/50:50 = BLENDED RESIN (MN:1294)

FIG.17 CHANGE IN NET WEIGHT (%) WITH IMMERSION TIME (HOURS)
AT 50C IN WATER

5. DISCUSSION

5.1 Synthesis and fractionation

The characteristics of the resins synthesized were given in table 2 of the 1981 report, and this table is reproduced here for convenience, again as table 2. The references to GPC systems A2, B1 etc. are explained in table 3 of the previous report. One more table, giving details of the fractionated resins, is also reproduced here, this time as table 3.

The main points to note are as follows.

- (a) The number-average molecular weights (M_n) of the unfractionated resins ranged from 875 to 1826 according to vapour-phase osmometry measurements (VPO). As expected, these values were not the same as the values given by gel permeation chromatography (GPC). The subject of correlating VPO with GPC data for polyesters has recently been discussed by Lyttle⁹, who found that GPC results averaged about 80% of VPO ones. The residual glycol content of unfractionated, unstripped resins was about 0.068% by GLC.
- (b) The MWDs of the unfractionated resins were all qualitatively similar. Small quantities of low molecular weight constituents could be detected, as shown in fig. 6a of the 1981 report.
- (c) Fractionation altered the molecular weight distributions, but did not remove all of the low molecular weight constituents from the higher fractions. This was because they were soluble to some extent in both fractionating solvents.
- (d) Traces of acetone solvent (up to 0.35% w/w) remained tenaciously in the fractions even after prolonged vacuum stripping, together with about 0.03 to 0.04% glycol. These substances were detected by GLC. The acetone may have remained trapped because of its size, especially if association through H-bonding occurred.
- (e) No significant change in the molar ratio phthalate: (maleate + fumarate) could be detected after fractionation although this might have been expected as a result of differences in solubility between phthalate-rich and fumarate-rich chains. The molar ratio was about 1.1 : 1, and the maleic:fumaric ratio was about 1 : 10. These observations were made from

the NMR spectra, and agree with those of Kastanek et al.¹⁰

5.2 Initial mechanical properties

Table 4 indicates some of the main trends observed. These are:

- (1) There was little difference between the K_{IC} values as a result of M_n alone, except that two resins of particularly low M_n also had low K_{IC} . Above a certain threshold of about $M_n = 1000$, K_{IC} therefore seems independent of M_n . Previous studies by Pritchard, Rhoades and Rose¹¹ did, however, find a dependence of K_{IC} on the molecular weight between crosslinks, M_c , and at very high styrene levels indeed, Broutman and McGarry¹² found a dependence on styrene bridge length.
- (2) When the low molecular weight fraction was removed, the M_n of the remainder was much higher, but K_{IC} was not altered at all.

5.3 Water absorption

The term "net weight increase" will be used to refer to the observed increase in weight of specimens during immersion. It is the resultant of (i) actual water uptake, which was always larger, and (ii) loss of weight by leaching. The extent of leaching was deduced by drying out the samples. These parameters are given for a low molecular weight, unfractionated resin in fig. 1.

The net water absorption rates (for castings 76 mm x 20 mm x 3.5 mm) were much lower for the fractionated resins than for the original resins. They were also much lower for high molecular weight, unfractionated resins than for low molecular weight resins in the same series. This can be seen most easily in figure 2 which applies to immersion at 50°C, but also in fig. 3 (immersion at 60°C) and in fig. 4 (immersion at 75°C). The resin codes ending in a number refer to unfractionated resins, those ending in A, B or C refer to high, medium or low molecular weight fractions respectively, and those ending in AB refer to combined high and medium fractions. The prefix BR denotes a blend.

The resin DY 7 was subjected to 60 minutes' high vacuum stripping during the original synthesis, but it was not fractionated. Figs. 2-4 show the water uptake of this resin to be as low as that of the fractionated resins. This suggests that the removal of low molecular weight, volatile constituents is a major step to the improvement of water absorption characteristics. The constituents are probably unreacted glycols and acids. Their removal also raised the average molecular weight.

On this theory, the resins subjected to fractionation should have performed as well or better, because they were vacuum-stripped for much longer. Their water absorption behavior was actually slightly worse than that of DY 7, and this can only be attributed to an unexpectedly strong hydrophilic influence from small traces of strongly held residual acetone. An experiment was designed to confirm that addition of water-soluble substances to the resins increased water absorption substantially. The results are given in table 4, and they show that 5% w/w acetone reduced the time required to reach peak weight increase sixfold, from about 635 hours to little more than 100 at 50°C. The magnitude of the peak was not increased. Similar results applied to the addition of n-propanol and of benzaldehyde. Glycols, however, enormously increased the magnitude of the peak, and reduced the disc crack initiation time, without reducing the time to reach peak water uptake. Considering additive-free resins, those which reached their peak weight increase soonest, also reached the point of negative weight change soonest, and in general, reached the largest overall weight loss in a given time. These were the low molecular weight resins. For example, the resin with $M_n = 875$ peaked at about 1800 hours at 50°C (fig. 2) and underwent a net loss after 5600 hours. It experienced 2% net loss after 8000 hours. The corresponding figures for the resin with $M_n = 1592$ were 9200 (peak), and 18000 (net loss). The 2% net loss stage had not been reached when the experiment was concluded (see fig. 5).

The middle fraction resin JG2B ($M_n = 2215$) reached its peak even later at 14000 and has yet to approach the zero line. Results for another middle fraction resin, DY14B ($M_n = 3077$) are incomplete, and so are those for the vacuum-stripped resin.

In each case, the peak position seemed to be determined by the onset of disc cracking. The peak time was nearly always roughly twice the time required for disc crack initiation (table 5). It has already been explained in previous reports that these cracks are believed to be formed by osmotic pressure in glycol-rich zones, and that they facilitate increased water uptake, faster hydrolysis, increased leaching, and irreversible decline of mechanical properties. Therefore experiments were carried out to determine whether other chemicals besides glycol could also cause disc cracks, either in this polyester resin series or in epoxide resins. There was a practical problem in that some additives did not mix at all with the epoxy resin MY 75C (ex Ciba Geigy) which was used. The epoxy curing agent was 10% triethylene tetramine.

The results (table 5) suggest that disc cracking does occur in epoxides but much more slowly. Normally, in epoxides, suitable chemicals are not available to act as osmotic centers, but when they are, cracking is slower because the resins have much lower diffusivities as well as slightly higher K_{IC} values.

The magnitudes of the peak values were generally around 4%, although the above-mentioned fractionated resin JG2B actually peaked at nearly 6%. Part of this difference can be explained, as there was probably less loss by leaching, to offset the true water uptake. The leaching from the low molecular weight resin ($M_n = 875$) at the peak in net weight change was 1.2%, and although the corresponding data for middle fractions is not yet available, it is expected that leaching will be less than this (fig. 6).

The true water uptake curves, after correction for leaching losses, approach a plateau (figs. 1, 5) as would be expected if no leaching occurred.

5.4 Effects of immersion on mechanical properties

The values of K_{IC} (obtained by using the center-notched geometry) were measured after immersion, and again after re-drying very carefully and slowly to avoid further damage. The results are summarized in figs. 7 to 10.

There was nearly always a small fall in K_{IC} on prolonged immersion, typically 15 to 20%. Comparison with the time of onset of disc cracking suggests that these cracks did not affect K_{IC} appreciably, at least until they were at an advanced stage of development. This is in agreement with previous results from the isophthalic project described earlier. However, a different finding was observed here. Drying out did not always bring about a recovery in K_{IC} , and often reduced it further. This suggests that hydrolysis was more advanced in the orthophthalic series despite generally more moderate immersion temperatures.

Again the lowest molecular weight resins performed least satisfactorily (fig. 8) and the high vacuum stripped resin was exceptional in experiencing no fall in fracture toughness at all during immersion for 12000 hours (fig. 9). The middle fraction in fig. 10 performed well at first but later, the usual fall in K_{IC} began and the toughness was noticeably reduced further by drying.

Some changes in the radius of the plastic yield zone, r_y , are given in table 7. Invariably, these zones were of the order of one to six microns, with increases occurring on immersion. Drying out more than reversed these changes. The largest changes were seen in the low molecular weight resins, and the smallest in the vacuum-stripped resin, with the high and medium fractions only slightly more affected. An anomaly was provided by the low molecular weight resin DY4, for which the r_y values first rose and then after 9000 hours began to fall again. This is explained by the decidedly low K_{IC} values of this resin after prolonged immersions.

The plastic zone radii were calculated from values of the

compressive yield stress, measured by compressing small rectangular blocks of resin. Compressive failure modes were initially ductile, and always so for wet samples, but when drying out took place after long immersion times there were often brittle failures. These brittle failures were confined to dried-out resins containing substantial disc fractures.

Considering the compressive behavior in more detail, figs. 11 to 14 show changes in compressive modulus. Initial values were between 2.0 and 3.2 GNm^{-2} , although the figures in this report show only the lower values in this range. (It is quite difficult to make large numbers of small compressive specimens to close tolerances from sections of immersed castings without drying them out, and the possibility of experimental error has to be considered.) The initial Young's modulus in tension, for comparison, was typically 3.5 GNm^{-2} .

It is apparent that the compressive modulus of the high molecular weight resin was slowly but substantially lowered by water immersion, to approximately half its original value, and restored by drying (fig. 11). The fall in modulus of the low molecular weight resin was extremely rapid (fig. 13) but recovery was nevertheless still complete on drying. The decline in modulus of the middle fraction (shown in fig. 12) was only slightly greater than that of the vacuumed resin (fig. 14). Figs. 11 and 14 suggest an actual increase on drying out, which could be explained if the virgin samples had been plasticized by material later leached away.

The yield stresses of all the above kinds of resin are indicated in fig. 15 (before drying out). They all fell in similar fashion from around 100-120 MNm^{-2} before immersion to rather less than half this value after 18000 hours, although the low molecular weight resin weakened very much more quickly. There was no advantage through vacuum-stripping in this case. Recovery on drying was more or less complete for short immersions, but less so thereafter, and brittle failures usually occurred (see fig. 16). The vacuum-stripped resin did not show brittle failure after drying.

5.5 Blended resin

A comparison was made between the behavior of a medium molecular weight resin, DY3, ($M_n = 1294$) and that of a blend of two other resins, BR6/13, made from DY6 and DY13, to give a wider overall molecular weight distribution but approximately the same M_n . The water absorption characteristics, which have been shown to control many mechanical property changes, are compared in figure 17. There was very close similarity up to the peak stage, with only slightly faster leaching from DY3 thereafter.

5.6 Comparison with fracture toughness values obtained by double cantilever beam experiments

A resin similar to the other orthophthalic resins already described was produced, with an acid value of 23. It was cast, and machined into cantilever specimens, as described in Appendix 2. Strain energy release rates (G_{IC}) were calculated from the critical stress intensity factors, which were in turn obtained using the equation¹²:

$$K_{IC} = \sqrt{\frac{4P^2}{WT} \left(\frac{3a^2}{H^3} + \frac{1}{H} \right)}$$

where p = load
 a = crack length
 W = sheet thickness
 T = sheet thickness at the crack
 H = distance of specimen edge from fracture plane

The results are given in table 8. Stick-slip^{14,15} behavior was observed at the lower of the two temperatures used, and also at the higher of two crosshead speeds. In both these cases, K_{IC} for initiation (K_{ICi}) and for arrest (K_{ICa}) were rather similar to each other, and to the values of K_{IC} obtained by the center-notched geometry at temperatures below 22°C. The other value obtained, without stick-slip, was similar to that obtained by the center-notched geometry above the transition, i.e. at 30°C. The strain energy release rates were very different in the two cases, i.e. with and without stick-slip.

Glass reinforced resins

Values of G_{IC} were also found for an isophthalic resin of formulation 1, using the same type of specimen. The controls displayed stick-slip behavior, which disappeared after soaking in water at 50°C for 2000 hours, but with little or no change in G_{IC} from its initial value of about 110 Jm⁻². Laying glass filament bundles across the crack path every 10 mm increased the virgin G_{IC} to about 200-400 Jm⁻², with crack arrest at each filament. After immersion in water for 2000 hours at 50°C, however, crack propagation was continuous, and it appeared that the partially debonded fibres could not resist the crack progression. However, G_{IC} did not change much.

6. CONCLUSIONS

1. The resins produced were very different in their resistance to water uptake. The results could be summarized as follows:

High-vacuum stripped	best
Middle and high fractions	↓
High molecular weight resins	
Low molecular weight resins	worst

2. The same order of performance was found for the time to onset of disc cracking.
3. The initial critical stress intensity factor (K_{IC}) was broadly independent of M_n , except below 1000, and K_{IC} was not very sensitive to water absorption behavior, although the plastic zone radius changed more rapidly in resins with high water absorption rates.
4. Recovery of K_{IC} on drying was not so noticeable as previously reported for the isophthalic analogue (formulation 1).
5. Compressive moduli fell in water, and the extent of the decline followed the same order as that given in point (1) above. Recovery occurred on drying.
6. Compressive failure modes often changed from ductile to brittle on drying out after prolonged immersion.
7. There was a transition at about 28°C in the tensile behavior of virgin resins. Above this temperature, failures were ductile. Also, K_{IC} values doubled and fracture surfaces changed abruptly.
8. The reason for the improved behavior of the vacuum-stripped resins must be the removal of water-attracting substances, since (a) this is all that the vacuum treatment alone could do and (b) the water absorption rate was drastically reduced. These important substances must have been of low molecular weight to be removed so quickly. The low acid value implies that free acid was removed, and presumably glycol was also volatilized.
9. The reason why the middle and high fractions were slightly inferior to the unfractionated, vacuum-stripped resin is that contamination with fractionation solvents occurred.
10. Fracture toughness values obtained by the center-notched geometry were compared with those obtained by a double cantilever beam. Water immersion affected the stick-slip behavior.
11. Model fiber-resin composite cantilever beams were used to demonstrate changes in the effect of the interface on crack propagation, after water immersion.

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TABLE 1. RESIN FORMULATIONS

Formulation No.	<u>Nominal molar proportions</u>				
	1,2 propylene glycol	diethylene glycol	maleic anhydride	phthalic anhydride	isophthalic acid
1	1	1	1	0	1
2	1	1	1	1	0

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	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																							
M _n (syst.B1)	2.03	1.62	-																							
STYRENE CONTENT (w/w)	30	31	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.
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., °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.

TABLE 4.

% INCREASE IN NET WEIGHT OF DYL4B: EFFECT OF 5% w/w ADDITIVES

No. of hours at 50°C	42	116	260	450	635	745	978	1143	1307	2250	5100
control	0.66	1.00	1.16	1.20	1.24	1.22	1.27	1.29	1.31	1.33	- (*)
propylene glycol	2.26	3.46	4.42	4.85	4.70	4.64	3.93	3.23	2.62	1.53	
diethylene glycol	2.39	3.63	4.48	5.02	5.03	4.87	4.28	3.64	3.11	2.04	
acetone	1.05	1.27	1.14	1.01 (*)	0.92	0.87	0.87	0.93	0.96	1.05	
n-propanol	1.09	1.41	1.42	1.32 (*)	1.22	1.17	1.12	1.13	1.15	1.20	
benzaldehyde	0.89	1.14	1.16	1.11	1.11	1.05	1.04	1.06	1.04	0.97 (*)	

(*) Indicates that disc cracks were observed at this stage.

TABLE 5. TIMES REQUIRED FOR INITIATION OF
DISC CRACKS AT VARIOUS TEMPERATURES

M_n (VPO)	Resin Code	Time of Onset of disc cracks (hours)		
		50°C	60°C*	75°C*
1592	DY2	4763	820	150
1294	DY3	3593	820	150
875	DY4	853	180	70
1454	DY7	7500	1290	280
1294	BR	3400	820	150
2215	JG2B	5170	820	150
4707	DY14A	5100	1000	190
3077	DY14B	5100	1000	190
592	DY14C	100	1100	200
3077	DY15AB1	5100	1100	200
592	DY15AB2	5100	70	10

* Note: these specimens were half the size of
the specimens immersed at 50°C.

TABLE 6. EFFECT OF 5% w/w ADDITIVES ON TIME TO INITIATION OF DISC CRACKS IN POLYESTER AND EPOXIDE RESINS.

Polyester = DY17B (middle fraction)

Epoxide = MY750/triethylene tetramine

	TIME OF ONSET (HOURS)			
	50°C	POLYESTER 60°C	75°C	EPOXIDE 75°C
control	5000	2200	635	>>1350
dimethyl-sulphoxide	18	10	3	>>1350
NN-dimethyl-formamide	20	15	4	400
propan-1,2-diol	45	20	5	-
diethylene glycol	45	20	5	-
diethyl ketone	700	200	65	270
acetone	450	250	110	-
benzaldehyde	2250	450	250	-
n-propanol	450	250	110	-
low molecular wt. polyester	3500	1500	450	-
glycerol	-	-	25	>>1350

Note: (1) No epoxide disc cracks were observed at 50°C within the timescale of the epoxide experiment (1350 hours).

(2) (-) implies no test performed.

TABLE 7. PLASTIC YIELD ZONE RADIUS AT FRACTURE (μm) AFTER IMMERSION
FOR T HOURS AT 50°C.

RESIN CODE	VPO M_n	T	dry	T	wet	dry	T	wet	dry	T	wet	dry
DY2	1592	0	1.0	2100	1.5	0.8	4000	2.0	0.5	11320	5.5	-
DY3	1294	0	1.0	1500	2.4	0.4	3000	1.6	0.6	9485	3.7	-
DY4	875	0	0.7	500	3.4	0.6	933	3.1	0.5	5000	3.4	-
DY7	1454	0	1.0	1500	1.4	0.7	3000	1.6	0.5	4500	1.3	0.8
BR6/13	1294	0	0.8	1500	1.9	0.7	4600	2.8	0.3	10615	2.9	-
DY14A	4707	0	1.3	-	-	-	7080	3.0	-	-	-	-
DY14C	592	0	2.6	840	2.7	-	1520	3.5	-	-	-	-
15AB1	3077	0	1.2	1500	1.9	0.6	3150	1.5	0.7	7050	2.0	-

TABLE 8. DOUBLE CANTILEVER BEAM RESULTS FOR
 ORTHOPHTHALIC RESIN (acid value 33)

Strain Rate mm/min	Temp. °C	No. of Crack Jumps	K_{Ici} $MNm^{-3/2}$	K_{Ica} $MNm^{-3/2}$	G_{Ic} Jm^{-2}
0.1	19	1	1.02	-	269
0.1	9-10	3	0.59	0.46	90
1.0	19	6	0.48	0.42	59

APPENDIX 1

VISCOELASTICITY

An assessment of the viscoelastic behavior of the polyesters used in this work was made. An orthophthalic resin of formulation 2 was synthesized, to produce an acid value of 33, which is towards the lower end of the molecular weight range studied. The resin was cast into sheets of two thicknesses, 1.5 mm and 5 mm. Tensile dumbbells were machined from the sheet, and stress relaxation experiments were performed at temperatures in the range 21°C to 60°C. This provided a range of moduli, at a reference temperature, over twelve decades of log time. The Williams-Landel-Ferry master curve was linear on a semi-log plot. Based on a Wiechert model, the variation was analyzed in terms of a Dirichlet, or Prony, series expansion:

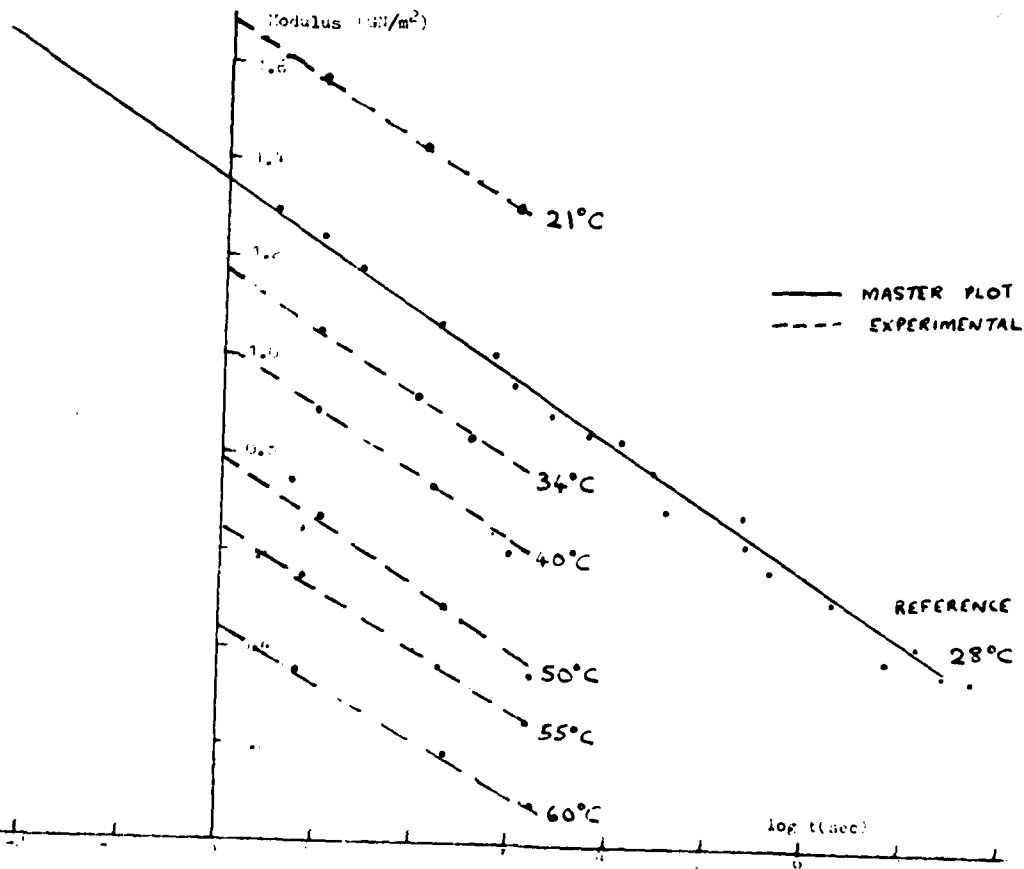
$$E(t) = E_{\infty} + \sum_{i=1}^N E_i \exp(-t/\tau_i)$$

where $E(t)$ = modulus at time t ,

τ_i = relaxation time.

T_g was determined by a torsional pendulum technique, and found to be 80°C. However, for the present purpose, it was decided to use the brittle-ductile transition temperature, 28°C, as the reference temperature. The master curve at 28°C for the 5 mm thick specimens is shown in fig. A.1. Specimens immersed in water at 50°C for about 2000 hours prior to testing showed a drop in relaxation moduli, when tested at ambient temperature over four decades of log time. This gives rise to a shift factor of just over 40°C, when referred to a reference temperature of 28°C.

Fig. A.1



APPENDIX 2

DOUBLE CANTILEVER BEAM SPECIMENS

Isophthalic resins were prepared as tapered cleavage fracture toughness specimens as follows.

- (1) Resin was catalysed with 2% of 50% MEKP and sufficient cobalt accelerator for a one-hour gel time.
- (2) Resin was cast between 300 mm x 300 mm glass plates with a 5 mm rubber spacer. Sheet was postcured at 80°C for 3 hours, and slowly cooled for 24 hours.
- (3) Specimens were machined to the shape shown in fig. A.2.
- (4) An initial fine saw cut was made, to extend 30 mm from the point of load application, along the central groove. (Otherwise the crack deviated from the groove).

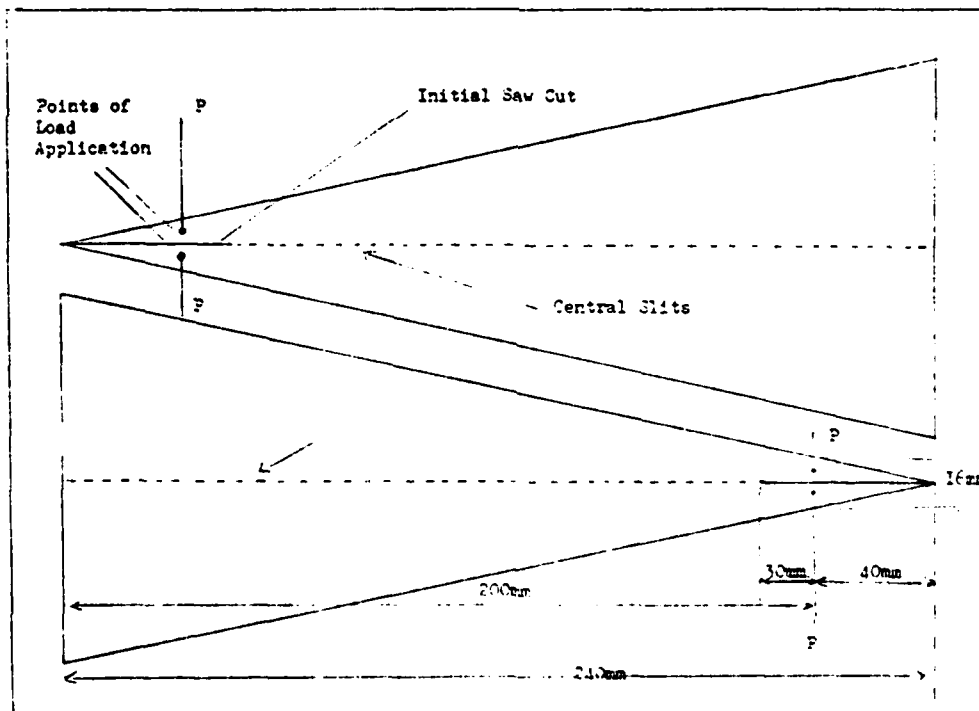


Fig. A.2

END

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DTIC