

## Cured Polyesters Based Upon Bisacid A2: Water Absorption, Toluene Resistance, and Resistance to 5% Aqueous HNO<sub>3</sub> and NaOH

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### Synopsis

Earlier papers have described the preparation and purification of bisacid A2,<sup>1,2</sup> the preparation and cure of crosslinkable polyesters,<sup>3</sup> the thermal properties of cast sheet,<sup>4</sup> and the mechanical properties of glass fiber laminates<sup>5</sup> which were made from reactants that included bisacid A2 in two series of cocondensates. The present paper details the water absorption and the long-term effects (up to 12 months) of toluene, 5% aq. HNO<sub>3</sub>, and 5% aq. NaOH. The effects of the last two were found to be negligible, but the water absorption and the toluene resistance appeared to be capable of correlation with the known composition and the inferred structure of the copolyesters.

### WATER ABSORPTION

The water absorption (immersion for 24 hr at 23°C) of maleate/phthalate polyesters of propylene glycol at mole ratios of maleate:phthalate ranging from 40:60 to 60:40 and at styrene contents ranging from 20% to 50% were reported by Slone.<sup>6</sup> It would appear that the styrene content is of little importance and that the water absorption increases with increasing maleate/phthalate ratio. The actual figures were an order of magnitude lower than those obtained in this work: while Slone's figures ranged from 0.17% to 0.28%, the writer's results ranged from 1.0% to 2.6%. It is probable that this is due to the differences in immersion time, the writer's results having been obtained after 72 hr of immersion.

The water absorption figures for a number of commercial resins, obtained according to B.S., 2782, Method 502F are given in the BP Chemicals Data Book No. 6, 1971. (This method uses sheet specimens 50 mm × 50 mm × 3 mm. The weight gain on immersion at 23°C for both 24 hr and one week are reported.) They refer to Cellobond-reinforced plastics materials. Results range from 20–25 mg (24 hr) to 50–60 mg (one week). Since the surface area of the B.S. samples is 56 cm<sup>2</sup> and that of the writer's samples is 10.4 cm<sup>2</sup>, one would expect that the Cellobond figures should be about five times as high as those obtained in the writer's determinations. The weight pickup of the experimental specimens (dimensions 2 × 2 × 0.3 cm) should therefore be between 5 and 12 mg. This assumes that there is no

significant capillary sorption in the glass fiber-filled Cellobond specimens, as far as *short-term* weight pickup on immersion in water is concerned, an assumption which does not seem unreasonable.

In fact, the lowest recorded pickup was 7.2 mg and the highest, 13.2 mg, the majority being between 8 and 10 mg. Thus, assuming that there is no radical difference in water absorption mechanism between the new resins and commercially available polyesters, the results obtained in this work are supported by B.P. literature and suggest that Slone's figures were too low by an order of magnitude.

The following tables (Tables I to V) record the water absorption (% weight gain) for each of five levels of styrene content in turn, together with the known composition of the resins and the number of unsaturations per 1000 molecular weight. (Please note that B.S., 2782, Method 502F, expresses the water absorption in mg for standard-size samples.) The results include series I, series II, and some commercial resins, and these are arranged in ascending order of water absorption. The monomer is styrene unless otherwise indicated.

The interpretation of these results is complex. There are several variables to be considered which tend to blur the picture because of their different directional effects. However, after plotting per cent water absorption versus per cent bisacetate (Figs. 6 to 10), water absorption versus

TABLE I  
Water Absorption of Cast, Cured Polyesters—Monomer Content 30%<sup>a</sup>

Statistical ranking	Series	Phthalate, wt-%	Maleate, wt-%	Bisacetate, wt-%	No. of unsaturations per 1000 MW	Water absorption, %
1	II	0	24.3	59.3	2.17	1.3
4	II	0	27.3	55.6	2.44	1.4
4	II	0	23.2	60.7	2.07	1.4
4	II	0	22.0	62.1	1.97	1.4
4	I	4.0	21.7	58.0	1.94	1.4
4	C <sup>b</sup>	45.5	31.1	0	2.77	1.4
7 <sup>1</sup> / <sub>2</sub>	II	0	25.3	58.1	2.26	1.5
7 <sup>1</sup> / <sub>2</sub>	II	0	20.8	63.7	1.86	1.5
9	C <sup>c</sup>	45.5	31.1	0	2.77	1.6
10	I	30.4	27.7	21.2	2.47	1.7
12	I	21.7	27.0	30.9	2.42	1.8
12	II	0	32.4	49.4	2.85	1.8
12	II	0	30.0	52.3	2.54	1.8
14	I	37.6	29.3	11.2	2.59	1.9
15	I <sup>d</sup>	45.5	31.1	0	2.77	2.1

<sup>a</sup> All acid values about 10, except in the commercial resins, where it was 35.

<sup>b</sup> Standard maleic/phthalic 1:1 resin made by Scott Bader, cast and cured by the makers.

<sup>c</sup> As (a), but cast and cured by the writer.

<sup>d</sup> Comparable to the above, but made to AV10, cast and cured by the writer.

TABLE II  
Water Absorption of Cast, Cured Polyesters—Monomer Content 35%<sup>a</sup>

Statistical ranking	Series	Phthalate, wt-%	Maleate, wt-%	Bisacetate, wt-%	No. of unsaturations per 1000 MW	Water absorption, %
2	II	0	23.2	60.7	2.07	1.5
2	II	0	22.0	62.1	1.97	1.5
2	II	0	20.8	63.7	1.86	1.5
4	II	0	25.3	58.1	2.26	1.6
5 <sup>1/2</sup>	II	0	27.3	55.6	2.44	1.7
5 <sup>1/2</sup>	II	0	24.3	59.3	2.17	1.7
7 <sup>1/2</sup>	I	37.6	37.6	11.2	2.59	2.0
7 <sup>1/2</sup>	II	0	30.0	52.3	2.54	2.0
9	II	0	32.4	49.4	2.85	2.1
10	I	45.5	31.1	0	2.77	2.3
11	I <sup>b</sup>	45.5	31.1	0	2.77	2.4

<sup>a</sup> Acid values all ~10.

<sup>b</sup> Monomer is methyl methacrylate.

number of unsaturations per 1000 MW at each styrene level in turn (Figs. 1 to 5), and water absorption versus log of combined maleate-phthalate contents (Figs. 11 to 15), a number of inferences may be drawn, as follows:

1. When plotting water absorption versus number of unsaturations per 100 molecular weight of series II (maleic/bisacid A2) polyesters, it is seen that there is an increase in water absorption with increasing unsaturation at low monomers contents (30% and 35%, Figs. 1 and 2). At higher monomer contents (45%, 50%, 55%, Figs. 3 to 5), a maximum occurs beyond which the water absorption decreases again as the unsaturation increases further. This can be explained by a tendency for increasing water absorp-

TABLE III  
Water Absorption of Cast, Cured Polyesters—Monomer Content 45%

Statistical ranking	Series	Phthalate, wt-%	Maleate, wt-%	Bisacetate, wt-%	No. of unsaturations per 1000 MW	Water absorption, %
1	II	0	20.8	63.7	1.86	1.0
2 <sup>1/2</sup>	II	0	45.2	33.9	3.97	1.4
2 <sup>1/2</sup>	II	0	20.8	63.7	1.86	1.4
4	II <sup>a</sup>	0	40.2	40.2	3.52	1.5
5	II	0	40.2	40.2	3.52	1.7
7	II	0	32.4	49.4	2.85	1.8
7	II	0	30.0	52.3	2.54	1.8
7	II <sup>b</sup>	0	30.0	52.3	2.54	1.8
9 <sup>1/2</sup>	II	0	32.4	49.4	2.85	2.1
9 <sup>1/2</sup>	I	45.5	31.1	0	2.77	2.1

<sup>a</sup> Acid value 23.5; all other acid values about 10.

<sup>b</sup> Monomer, equimolar mixture of styrene/methyl methacrylate.

TABLE IV  
Water Absorption of Cast, Cured Polyesters—Monomer Content 50%

Statistical ranking	Series	Phthalate, wt-%	Maleate, wt-%	Bisacetate, wt-%	No. of unsaturations per 1000 MW	Water absorption, %
1	C <sup>a</sup>	0	26.9	0	2.36	1.0
3	II	0	20.8	63.7	1.88	1.4
3	II <sup>b</sup>	0	40.2	40.2	3.52	1.4
3	C <sup>c</sup>	0	26.9	0	2.36	1.4
6	C <sup>d</sup>	0	26.9	0	2.36	1.5
6	II	0	40.2	40.2	3.52	1.5
6	II	0	20.8	63.7	1.86	1.5
8	II	0	45.2	33.9	3.97	1.6
9	II	0	30.0	52.3	2.54	2.2
10	II <sup>e</sup>	0	30.0	52.3	2.54	2.2

<sup>a</sup> Bisphenol glycol/maleic polyester from Scott Bader, cast and cured by the writer. Styrene content 48%.

<sup>b</sup> Acid value 23.5; all other acid values about 10.

<sup>c</sup> As (a), but using a high-cobalt activator system, cast and cured by the makers.

<sup>d</sup> As (b), but cast and cured by the writer.

<sup>e</sup> Monomer an equimolar mixture of styrene/methyl methacrylate.

tion by the maleic moieties in chains which are inefficiently utilized as crosslink sites. This is likely to be the case when the monomer content is low and the initial viscosity of the liquid resin is high. At higher monomer contents, the viscosity is lower and the crosslink potential of the maleic unsaturation is more efficiently utilized. This will in turn reduce the pore size of the cured system, so that diffusion of water into the structure will become more difficult.

2. In series I (maleic/bisacid A2/phthalic) polyesters, there appears to exist a similar upward trend of water absorption with increasing weight percentages (but constant mole percentages) of maleic (Figs. 1 and 2). The increase in maleic content was accomplished by a higher molar ratio of

TABLE V  
Water Absorption of Cast, Cured Polyesters—Monomer Content 55%<sup>a</sup>

Statistical ranking	Phthalate, wt-%	Maleate, wt-%	Bisacetate, wt-%	No. of unsaturations per 1000 MW	Water absorption, %
1	0	40.2	40.2	3.52	1.1
2	0	20.8	63.7	1.86	1.4
3 <sup>1/2</sup>	0	45.2	33.9	3.97	1.5
3 <sup>1/2</sup>	0	20.8	63.7	1.86	1.5
5 <sup>b</sup>	0	40.2	40.2	3.52	1.6
6	0	32.4	49.4	2.85	1.9

<sup>a</sup> All series II resins.

<sup>b</sup> Acid value 23.5; all other acid values about 10.

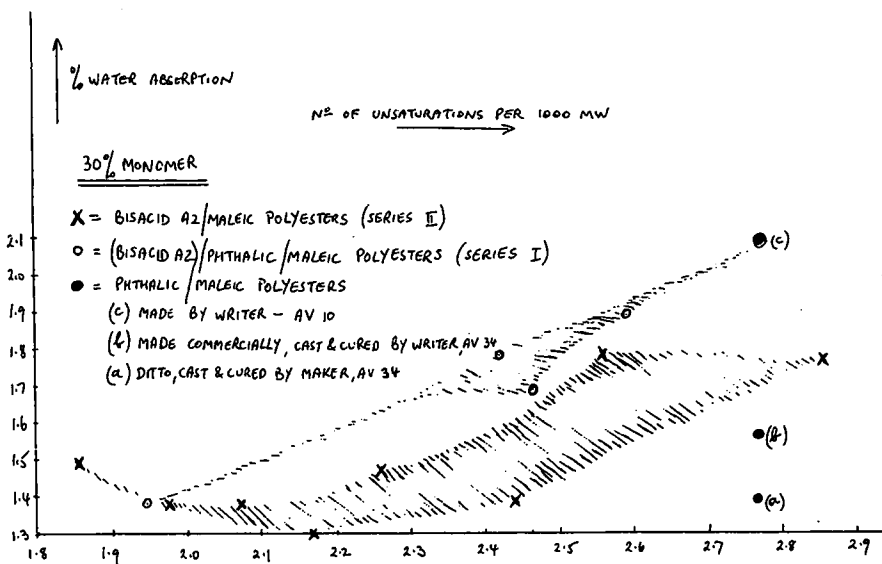


Fig. 1.

phthalic and a corresponding cutback in the bisacid A2 content. The unsaturation, however, was never so high as to show an actual maximum in the plot.

3. A comparison of water absorption in polyesters with different acid values and based upon straight equimolar phthalic/maleic polyesters seems to indicate that a low acid value causes a high water absorption (Fig. 1). This may seem surprising, but it should be borne in mind that efficient crosslinkage would occur more readily in polyesters with low molecular weights, i.e., with high acid values, because in high molecular weight (low acid value) condensates, the curing process will tend to generate increasing

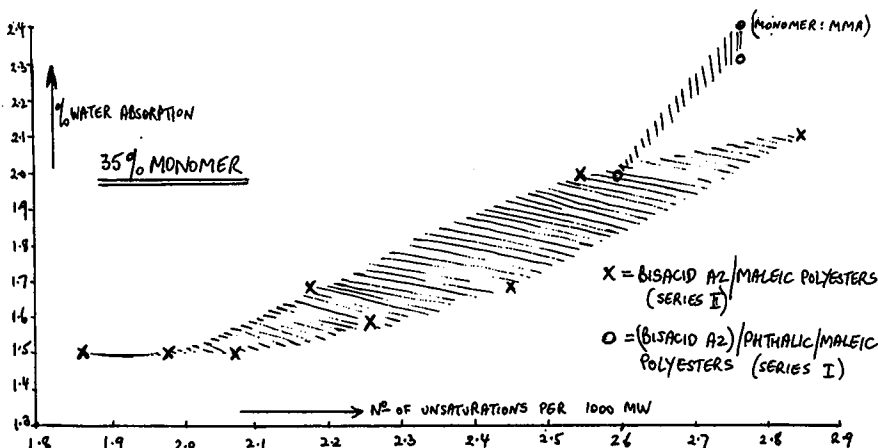


Fig. 2.

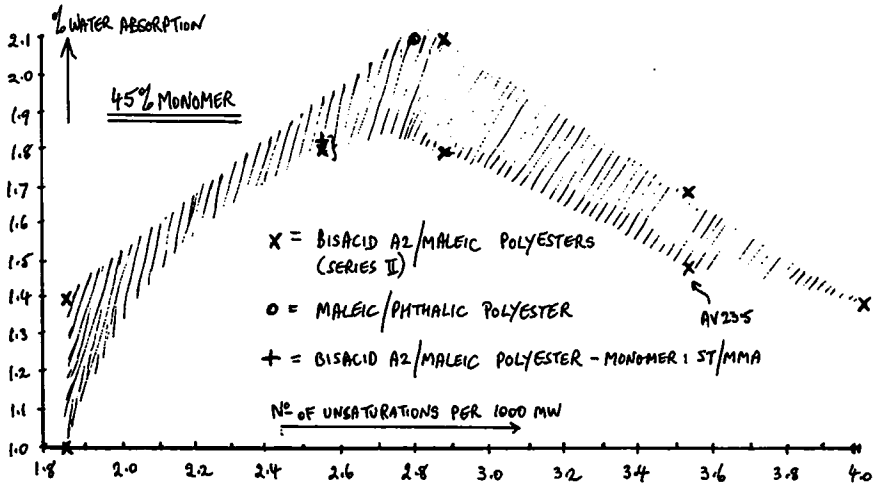


Fig. 3.

strain as it proceeds and so reduce the probability of efficient utilization of potential crosslink sites. This will result in larger pore sizes and make diffusion into the cured structure easier (Figs. 3 and 4). However, when the styrene content is high (Fig. 5), the position is reversed, presumably because the crosslink potential can now be efficiently utilized with little straining, and the pore sizes in the resulting cured structure will be small. In addition, one would expect the water absorption to decrease as the overall composition becomes more polystyrene-like.

4. No significant differences in water absorption were noted between compositions in which the monomer was styrene on its own or a mixture of styrene and methyl methacrylate (Figs. 3 and 4).

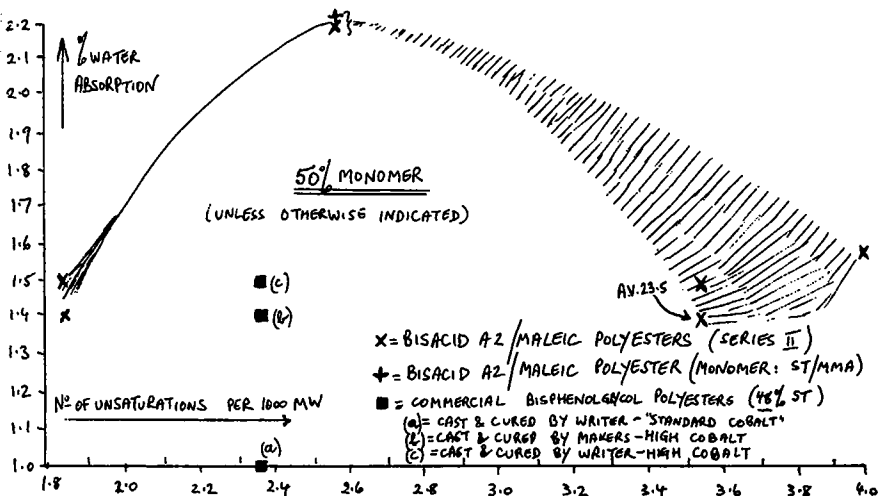


Fig. 4.

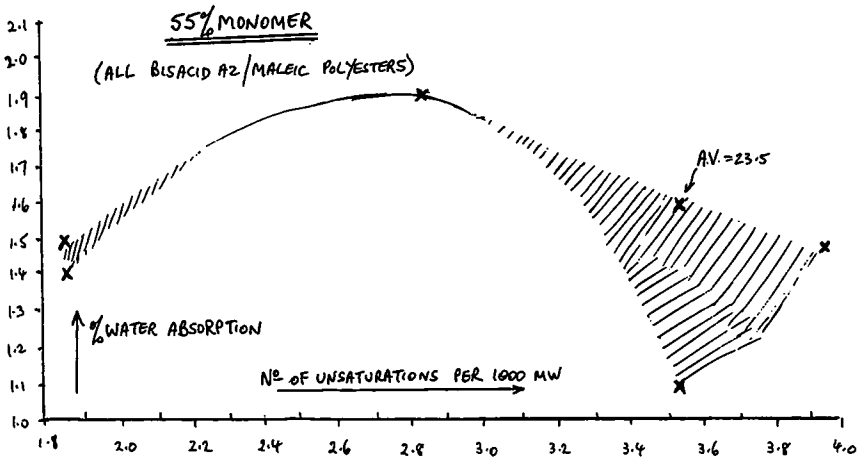


Fig. 5.

5. Bisphenol glycol/maleic polyesters at 50% monomer content showed much the same water absorption as the series II resins, but there seems to be some disadvantage in using the high-cobalt cure advocated in some quarters.

6. Figure 6 to 10 show the same general trends if it is borne in mind that the abscissa is now an increasing weight percentage of bisacetate instead of

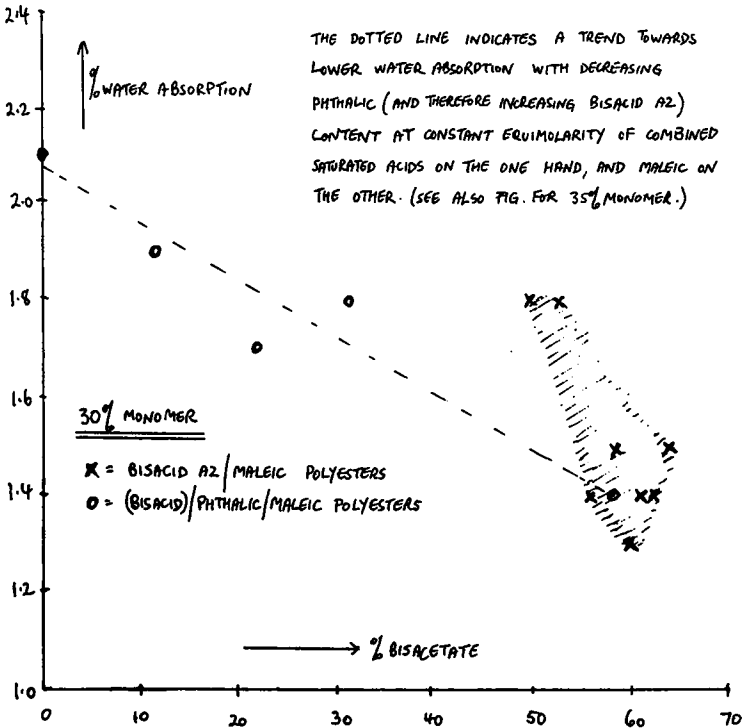


Fig. 6.

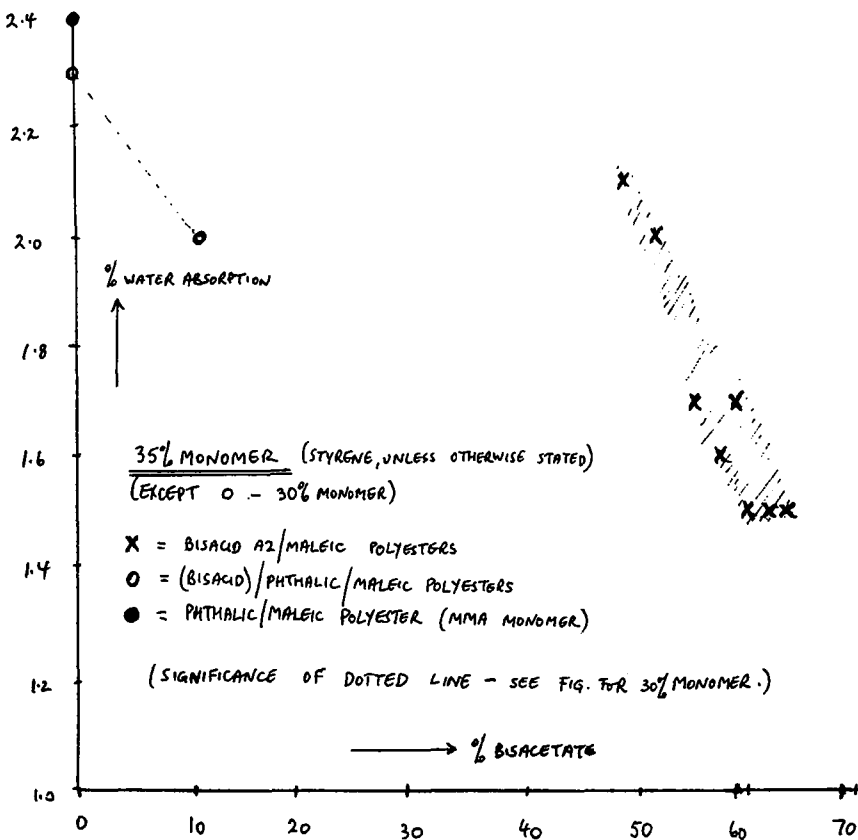


Fig. 7.

an increasing maleic content. At lower monomer contents (30% and 35%, Figs. 6 and 7), increasing amounts of bisacetate tend to produce lower water absorption. At higher monomer contents (45%, 50%, and 55%, Figs. 8 to 10), the plot again appears to go through a maximum at about 50% bisacetate (series II resins). This can again be explained when it is remembered that smaller amounts of bisacetate means more crosslinkable unsaturation and that the higher crosslink potential is readily attainable at high monomer contents because under those conditions the effect of increasing crosslink strains (as curing proceeds) may be discounted. The result is a final structure of smaller pore size, and the rate of diffusion of water into the resin will ipso facto be lower. Series I resins show up unfavorably when compared to series II resins; it is possible that in the former, considerable difficulties to a crosslinking system occur during cure and that these steric problems are associated with the stiffness and dissymmetry of the phthalic units.

7. In yet another method of presentation, the water absorption was plotted versus the log of the combined maleic/phthalic content. The



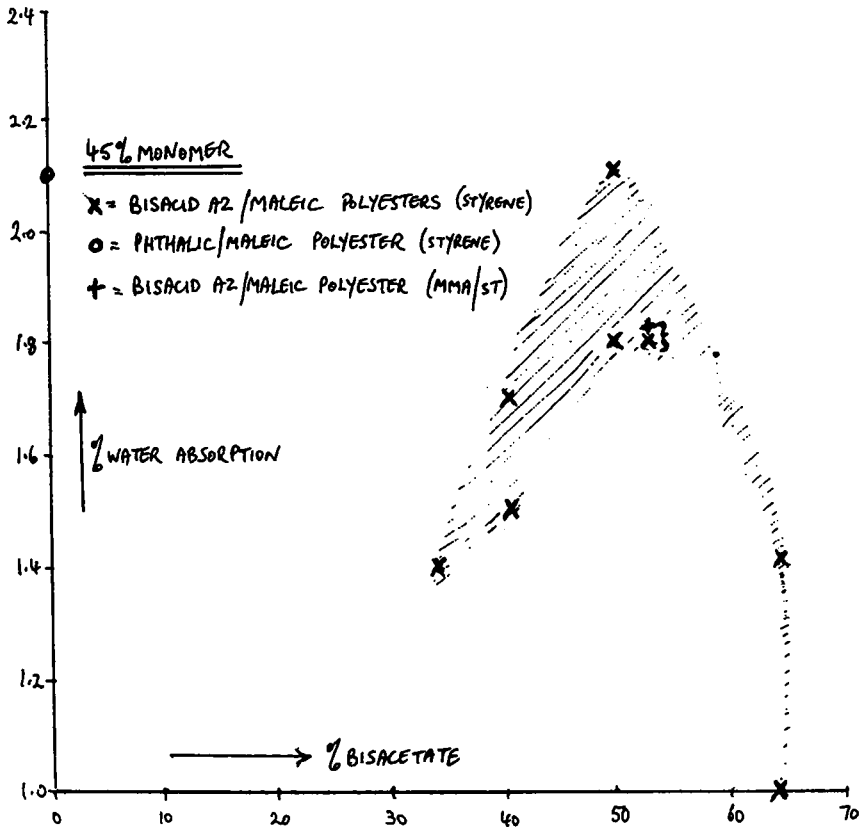
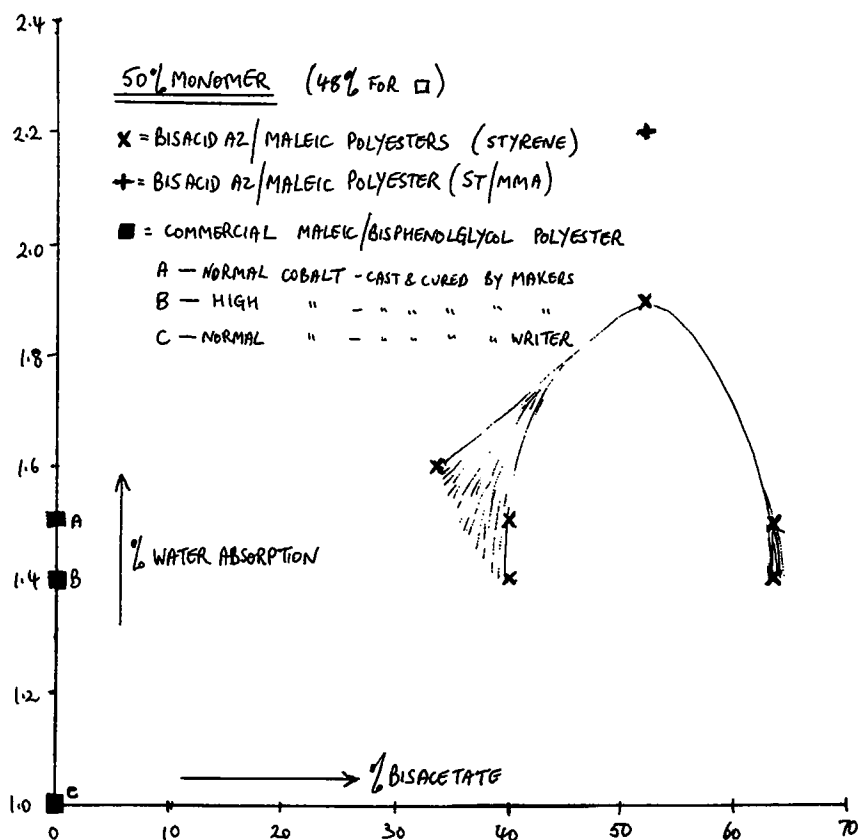


Fig. 8.

semilog plot has the advantage of separating series I and series II resins more neatly while covering a wide range of compositions within a manageable abscissal span (Figs. 11 to 15). In series II resins (zero phthalate), an increase in maleic content means an increase in crosslink potential. At lower monomer content (30% and 35%, Figs. 11 and 12), this potential is not efficiently utilized, and the water absorption increases with increasing maleate, showing that the pore size in the cured resin is still large despite increasing unsaturation, that is to say, increasing crosslink potential. At high maleate contents, the curve again goes through a maximum (Figs. 13 to 15), but more obviously so than in the earlier presentation of Figures 1 to 5, where the abscissa was the number of unsaturations per 1000 molecular weight.

### CHEMICAL RESISTANCE

The chemical resistance of cured unfilled polyester sheet specimens about 3 mm thick and about 2 cm square was determined by immersing the samples (which were cut from cast sheet) in boiling tubes containing toluene, 5%



aqueous NaOH, and 5% aqueous HNO<sub>3</sub>, respectively, at 23°C. The samples under test were inspected at one-monthly intervals up to 12 months.

### Toluene

Exposure to toluene may be expected to result in an attack upon the styrene crosslinks. One would therefore be inclined to think that the mechanism of attack, and the extent of the ensuing visual damage, is governed by a number of factors which derive from a combination of structural parameters and energy balance considerations:

1. The effective crosslink density—and hence the size of the micropores and the magnitude of the cohesive energy which opposes diffusion swelling. These depend on (a) the number of unsaturations per 1000 molecular weight of the polyester main chain before crosslinking, and (b) on the quantity of styrene in the resin, since this in turn governs the degree of effective utilization of the nominally available crosslink sites of the polyester chains, and hence the length of the polystyrene bridges between chains.

2. The molecular weight of the polyester chains, which is inversely related to the acid value.

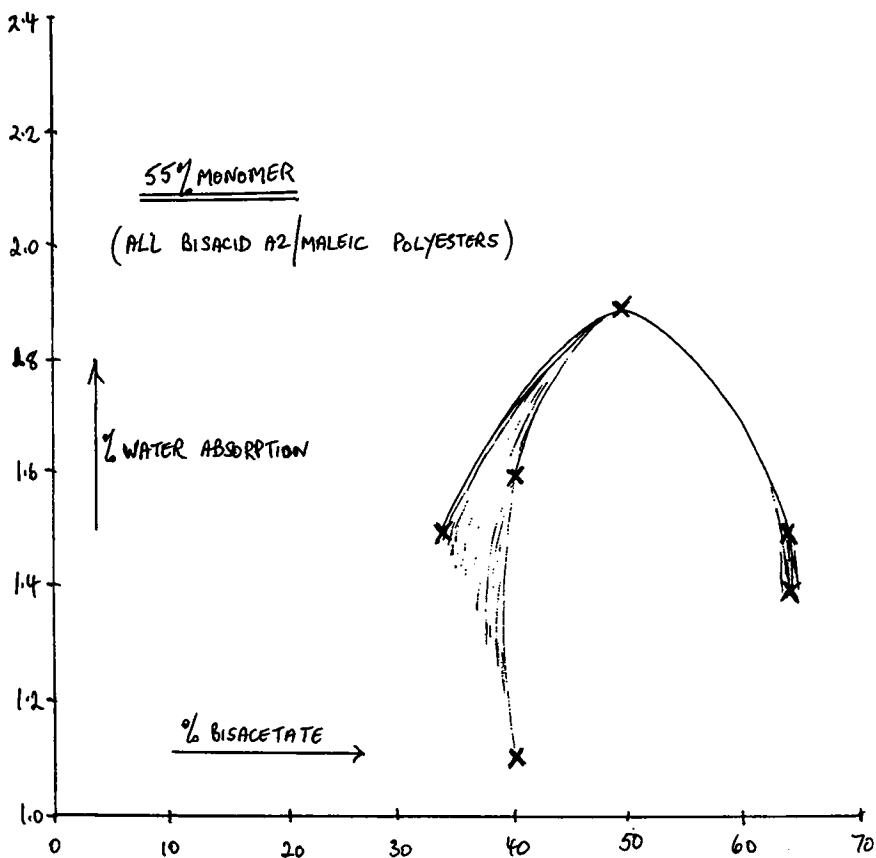


Fig. 10.

3. The actual quantity of styrene in the crosslinked polymer, *after and beyond* the amount necessary for efficient utilization of the available crosslink sites.

4. The stresses which exist between the portion of the specimen in the region where diffusion of the attacking solvent has caused swelling from the cut edges inward and the central portion which has as yet remained unswollen.

5. Swelling is possible only if the crosslink density is low enough for the network to be distorted. If this is not accompanied by cracking, then this may be termed "tough failure by diffusion." If the crosslink density is somewhat higher, then swelling may be accompanied by cracks appearing in the swollen portion, and this may be termed "brittle failure by diffusion." As the crosslink density increases, so swelling will be progressively reduced. At the same time, the stress generated by the diffusion pressure of the solvent will be increasingly opposed by the cohesive force of the primary valence bonds represented by the crosslinks, so that there is little scope left for the dissipation of the constraint by means of a strain response.

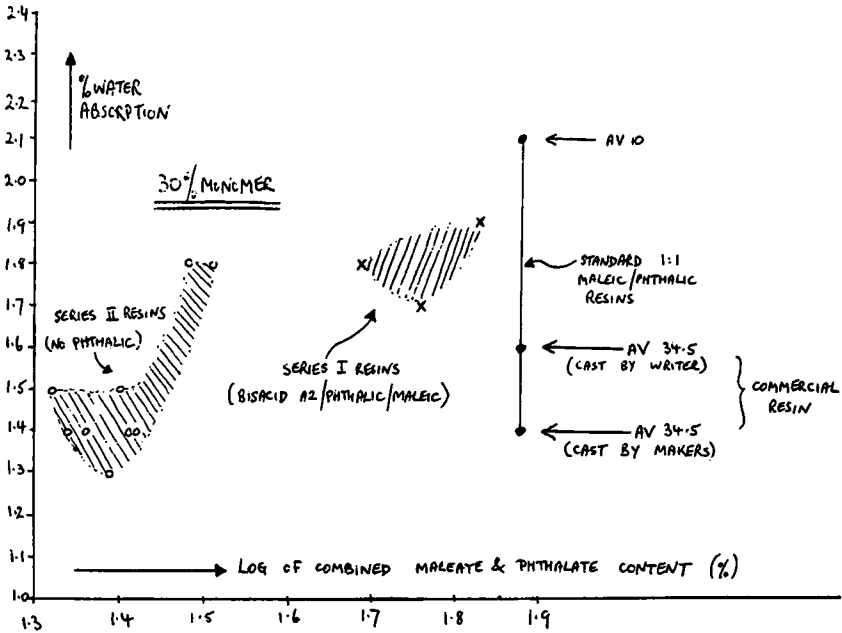


Fig. 11.

The eventual outcome of this confrontation of forces is either rupture of crosslinks which will produce fracture cracks and may be termed "brittle failure by diffusion" or, provided the crosslink density and the cohesive energy is high enough, the establishment of equilibrium, that is to say, a

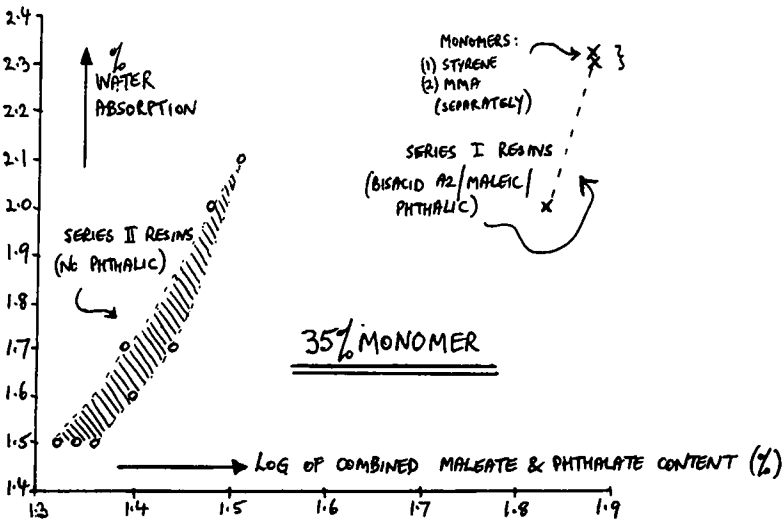


Fig. 12.

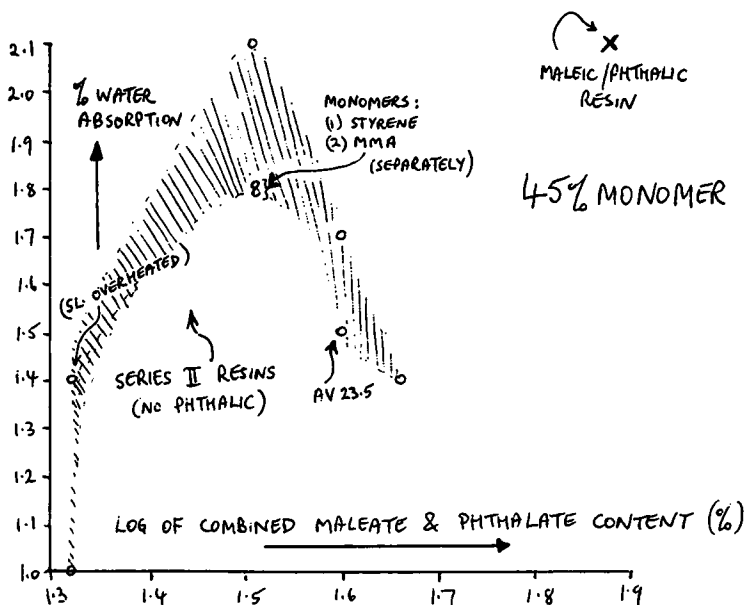


Fig. 13.

situation where the maximum diffusion pressure which can be generated is insufficient to effect mechanochemical breakdown.

6. If a high degree of crosslinkage is coupled with a long initial polyester chain (low acid value), then there are likely to exist appreciable internal stresses which weaken the structure in the face of the diffusion pressure, and this may cause brittle failure. But if the cured resin was based on a shorter initial polyester chain (high acid value), the resulting structure will be sufficiently free to remove the constraint by small but critical strain adjustments; and having thus removed or minimized its inherent structural weakness, it will be better able to resist the stress generated by the diffusion pressure.

Considering the obvious importance of diffusion, a fundamental examination of the observed phenomena is indicated. This could be done by considering diffusion effects in the classical terms of a concentration-dependent diffusion coefficient as embodied in Fick's law. But Alfrey, Gurnee, and Lloyd<sup>7</sup> have pointed out that "anomalous" diffusion effects are commonly encountered when glassy polymers are involved. These cannot be explained on the basis of Fick's law. This situation exists when a slab, a cylinder, or a sphere of the material is immersed in a solvent. Whereas Fickian diffusion occurs initially (showing itself by a proportionality between total weight increase and the square root of time), this proportionality presently gives way to a curvature away from the time axis. In extremely non-Fickian conditions, the solvent penetrates into the glassy polymer through the micropores, assuming that these are large enough or that they can be enlarged by network distortion. A visibly sharp boundary

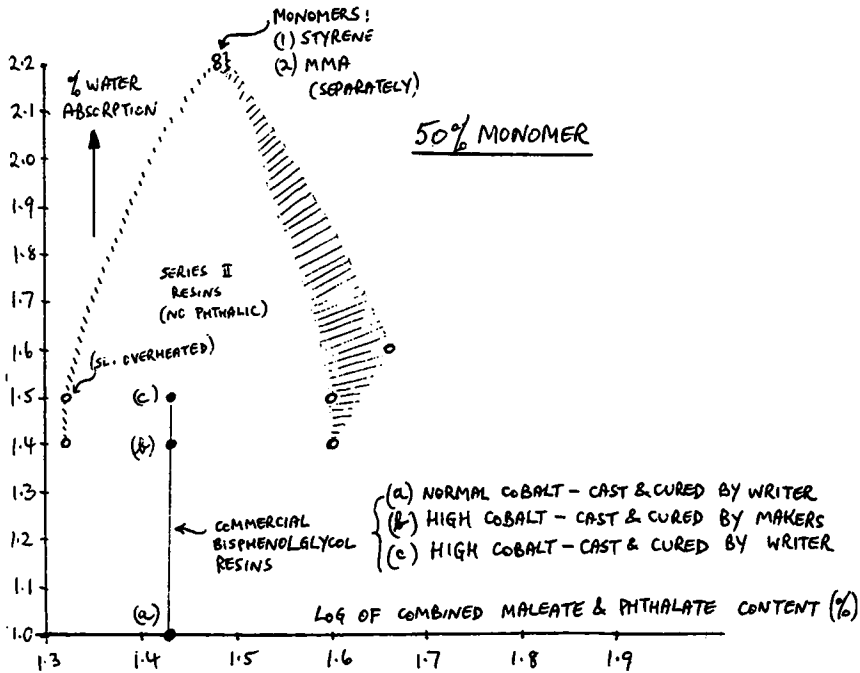


Fig. 14.

between swollen and unswollen material is then produced which advances at a constant rate. The gel itself is essentially in an equilibrium state of swelling, except where the as yet unswollen core exercises a constraint upon the gel and puts it under local stress.

After summarizing the literature (19 references) Alfrey and his colleagues attempt a quantitative theory which will not be recounted here. This is followed by a description of the phenomenology of fracture of thin discs by swelling stresses, based upon observations on a copolymer of 5% divinylbenzene-95% styrene in chloroform at 25°C. Disintegration of the latter by "ping splash" fracture and throwing of solvent occurred in a matter of hours.

However, in the polyester systems reported here, the solvent (toluene) is evidently not so aggressive as chloroform is toward the DVB-styrene copolymer, and the rate of attack is very much less. But the *pattern* of fracture is strikingly similar to that observed by the aforementioned workers for thin discs, the discs first splitting off crescent-shaped segments so as to produce a slightly bulged square. The prints which follow (Figs. 16a through m) show that the same cracking pattern showed itself in those cured polyesters in which brittle failure by diffusion occurred.

The samples were assessed in categories, as follows: (0) no change; (1) crazing (which may be slight), no swelling or cracking; (2) crazing, with swelling round the edges, but no cracking; (3) crazing, swelling throughout,

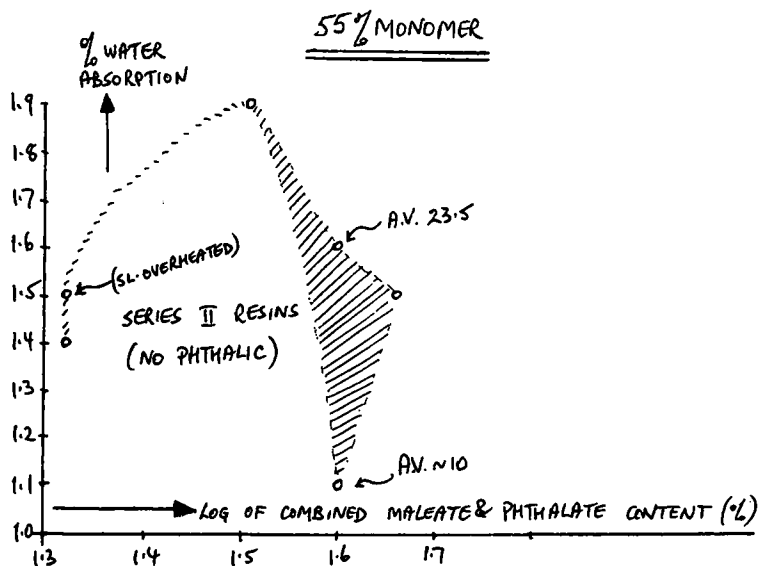


Fig. 15.

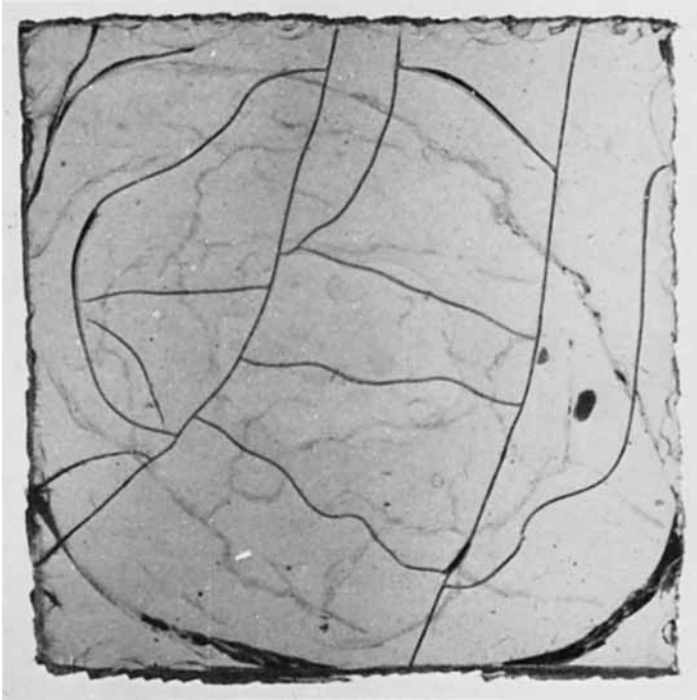
with a resulting warped rubbery appearance, but no cracking; (4) cracking and disintegration round the edges, with or without swelling; (5) extensive cracking from the edges inward, with or without swelling, but still leaving a recognizable coherent (if cracked) central portion; (6) total disintegration into cracked fragments.

The results are tabulated in Tables VI and VII. The first of these shows the coded behavior of series I resins (saturated to unsaturated acids in molar ratio of 1:1, variable ratio of bisacid A2 to phthalic), as well as samples of standard commercial maleic/phthalic and bisphenol glycol polyesters. The batch number and styrene contents are indicated before and after the stroke in the first column, respectively.

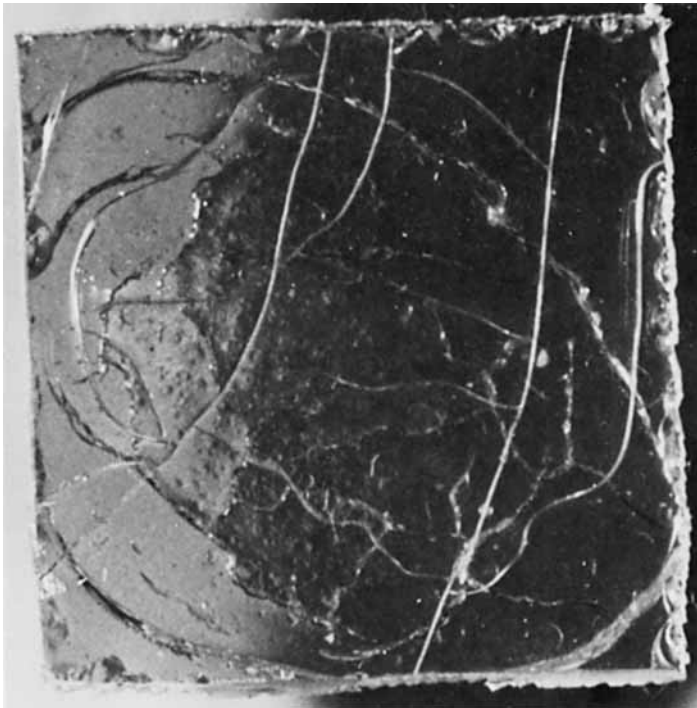
Tables VII shows the toluene resistance of series II resins, which do not contain any phthalic, but in which the ratio of unsaturated to saturated acids (i.e. maleic to Bisacid A2) ranges from 1 to 4 on a molar basis.

The results in Tables VI and VII confirm some of the considerations which were elicited earlier on: The first four resins in Table VI have no bisacid A2. They are maleic/phthalic controls which differ from the commercial resins (at similar styrene content) mainly in that they were reacted to a much lower acid value. The polyester chains, therefore, have a high molecular weight, and consequently some internal stresses are likely to develop during crosslinking. The susceptibility to toluene attack of these resins (compared to the commercial resins of higher acid value) is remarkable.

There was no significant batch-to-batch difference, nor was there any detectable difference in the toluene resistance when comparing liquid resins which were cast and cured in different laboratories.



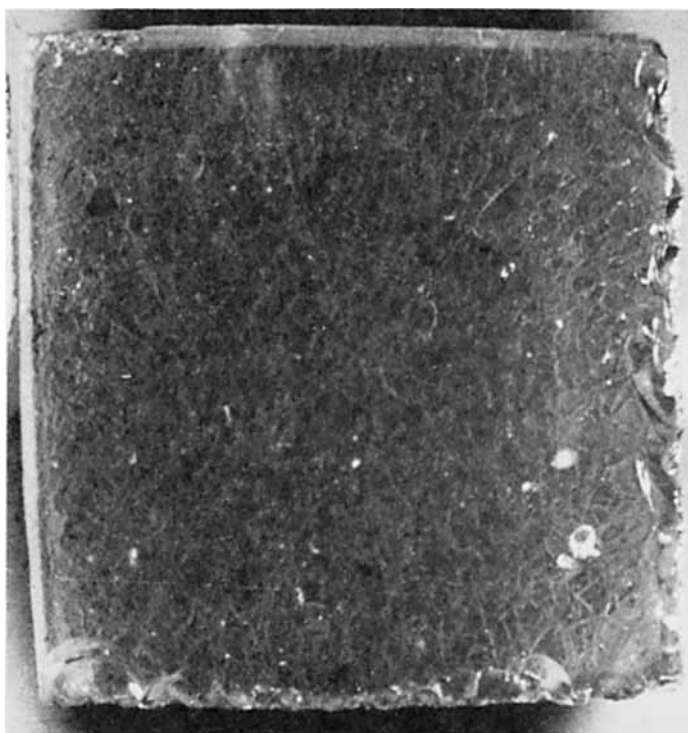
(a)



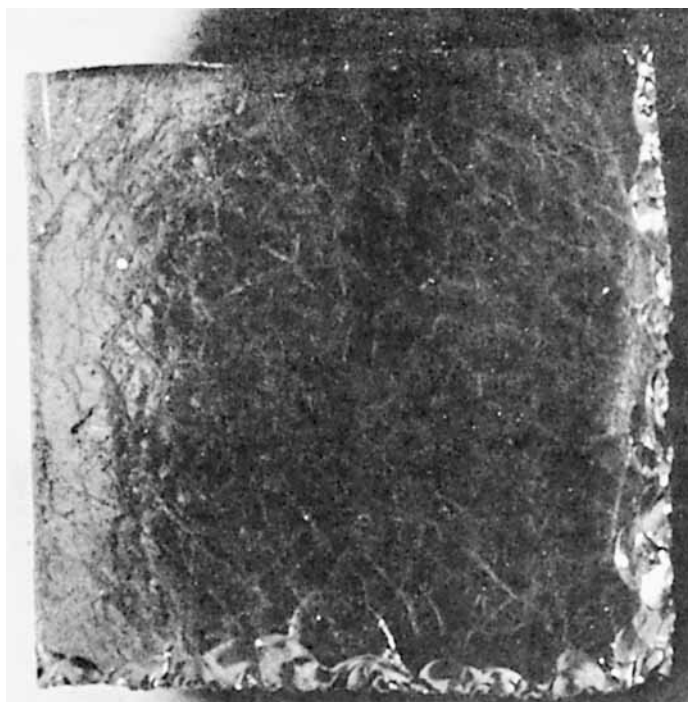
(b)

Fig. 16 (continued)



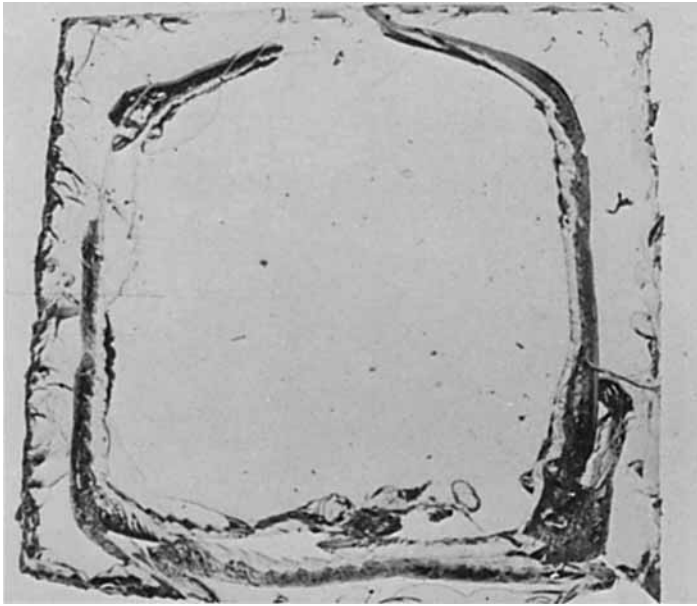


(c)

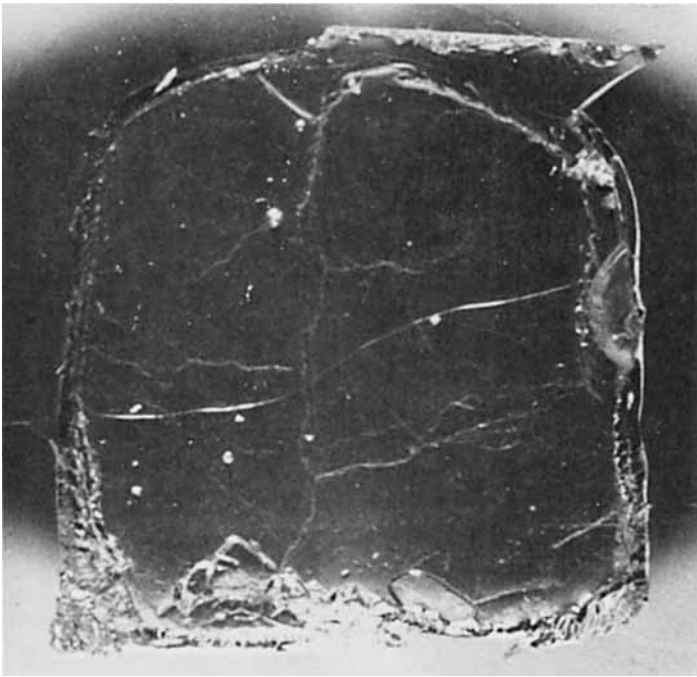


(d)

Fig. 16 (continued)



(e)



(f)

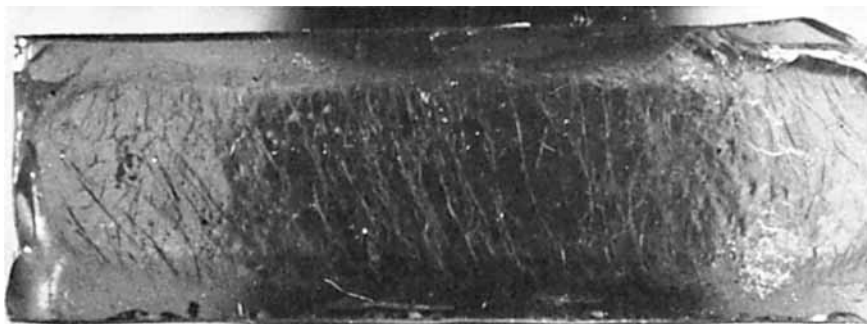
Fig. 16 (continued)

The results on the mixed phthalic/bisacid A2/maleic polyesters were inconclusive, mainly because a shortage of resin material prevented the preparation of a wider range of styrene contents in the liquid resins and observations were confined to a few resins containing 30% or 35% styrene which were very viscous to handle before cure.

The bisphenol glycol resins were virtually unaffected by toluene. No differences is apparent which could be ascribed to the casting and curing in different laboratories. Nor did the results achieved by using a large amount of cobalt catalyst differ from those obtained when the usual amounts of cobalt catalyst were employed. The high-cobalt system is claimed to afford improved chemical resistance (according to the makers of this resin), but this was not borne out with respect to toluene resistance, both formulations giving equally excellent results.

Table VII permits one to draw a number of conclusions which all agree with the *a priori* considerations set out earlier on:

Other parameters being constant, an increase in styrene content will open up the structure to increasingly severe solvent attack. Resin 17 at 30% styrene was totally unaffected for one year, while at 35% styrene some slight



(g)



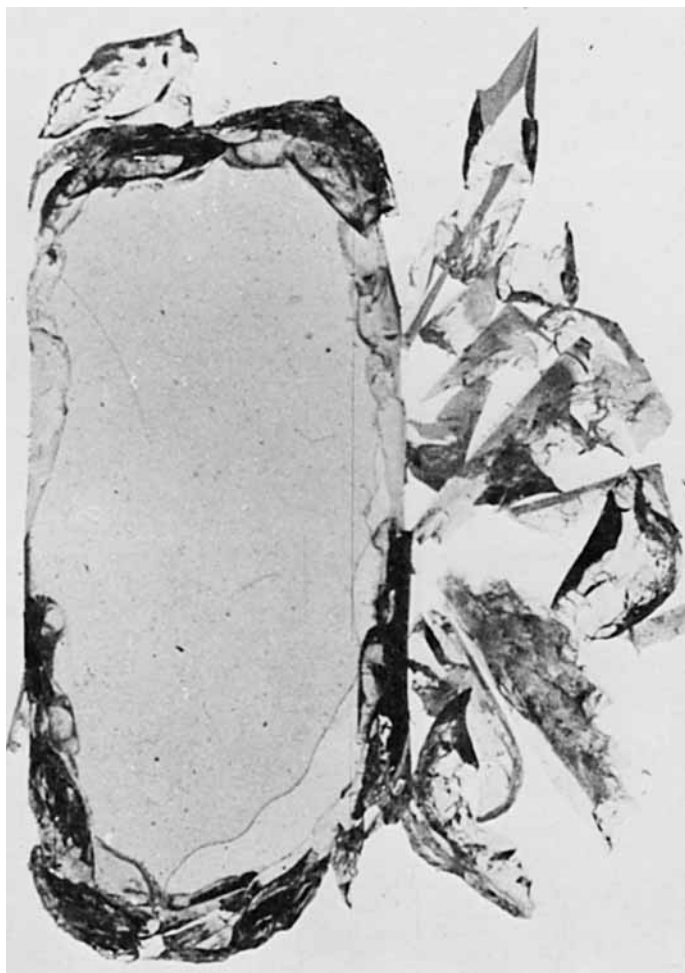
(h)

Fig. 16 (continued)

attack was apparent after four months, and after seven months this became more pronounced. At 45% or more, the structure was found to disintegrated within two months.

With increasing crosslink density (increasing molar ratio of maleic/-bisacid A2), the susceptibility to toluene attack with increasing styrene content diminishes. Thus, resin 11 was still quite unaffected at 45% styrene over one year, but at 50% styrene content it began to deteriorate badly after four months and cracked up progressively until even the central portion had disintegrated after ten months.

When comparing different monomers, it was seen that resin 11 at 50% monomer content will show almost complete immunity from toluene attack,

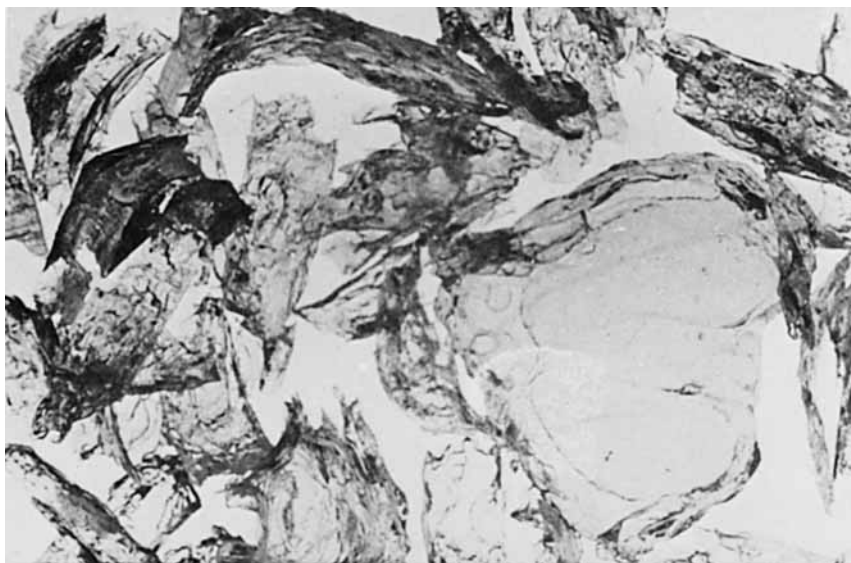


(j)

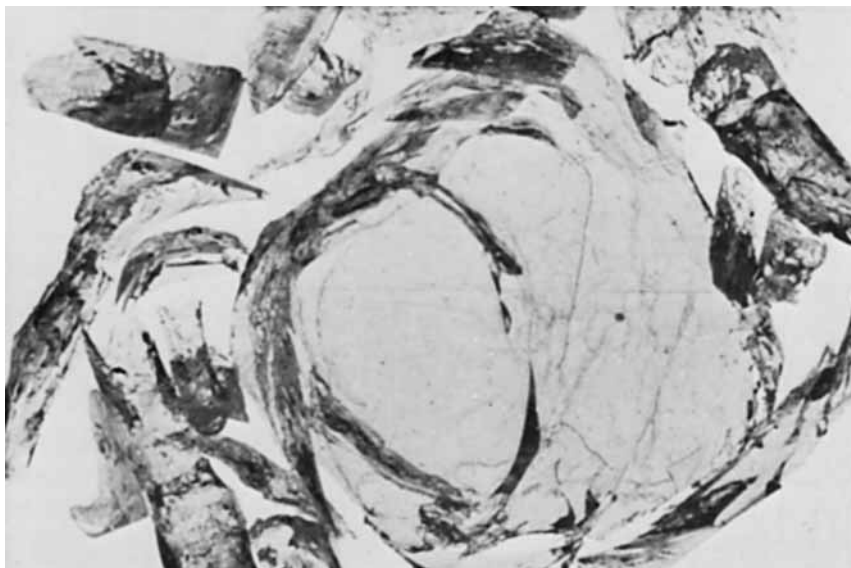
Fig. 16 (continued)

provided the monomer is not styrene by itself, but an equimolar mixture of styrene and methyl methacrylate.

As the molar ratio of maleic/bisacid A2 reaches and exceeds 2:1 (corresponding to about 2.8 unsaturations per 1000 molecular weight in the original polymer chain), so the limit of toluene susceptibility in terms of styrene

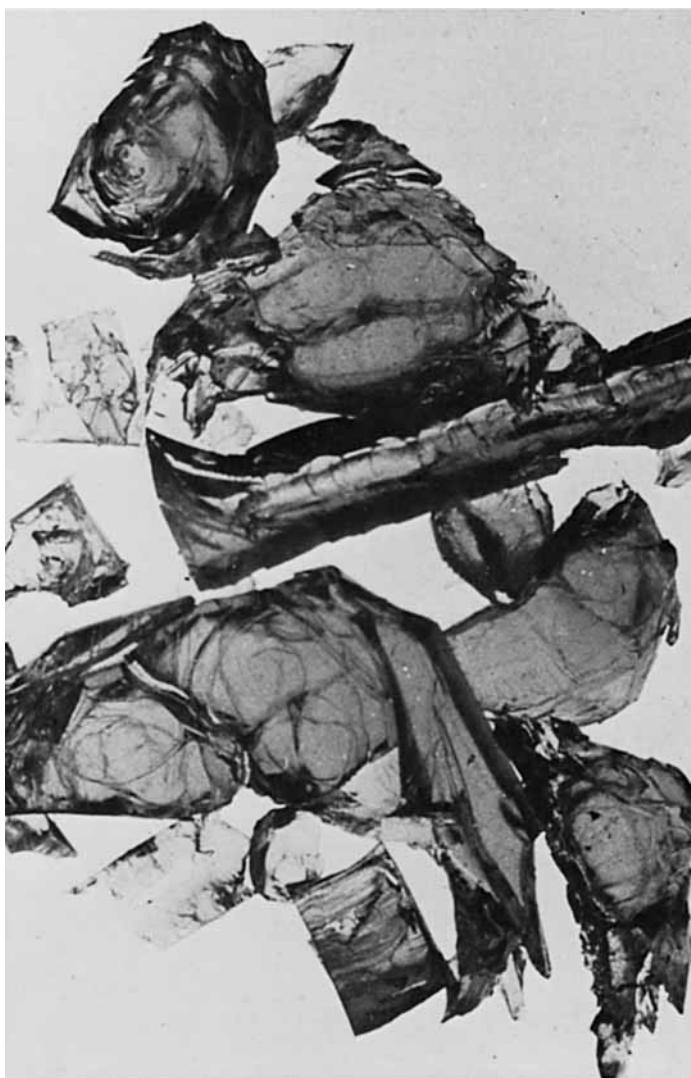


(k)



(l)

Fig. 16 (continued)



(m)

Fig. 16.

content is pushed to 50% and eventually even beyond 55% (resins 10, 20, 21, and 19).

Under these circumstances, the acid value also ceases to be important (resins 20 and 21), presumably because the fairly long crosslinks provide the right balance of elasticity in combination with the high rigidity and small microscope size due to a high crosslink density.

Considerable further work would be necessary if the exact maximum styrene content at which the crosslinked resin is still immune from toluene attack at any given maleic/bisacid A2 ratio were to be established.









In the Figure 16, photographs of various resins are shown after exposure to toluene at 23°C for 11 months which were found to show moderate to severe signs of attack as a result of "diffusion pressure." Unattacked samples are not shown. All samples were photographed under transmitted light from a tungsten lamp (3200°K). Two of the samples (marked a and e) were additionally photographed under transmitted light from a daylight lamp (5400°K) and should be compared with the respective tungsten lamp photographs which are marked b and f, respectively.

The samples are described by Table VIII, which is intended to serve as a legend for the photographs (all acid values about 10; monomer:styrene).

TABLE VIII  
Description of Photographs (Fig. 16)

Plate letter	Batch no.	Styrene content of liquid resin, %	Resin series	No. of unsaturations per 1000 MW	Failure rating (see before)
a	17	35	II	1.86	2 to 3
b					
c	15	35	II	2.07	3
d	16	35	II	1.97	1
e	6.1	35	I	2.77	5
f					
g	4.2	30	I	1.94	4
h	8	30	I	2.47	4
j	6.2	30	I	2.77	5
k	10.2	55	II	2.85	5
l	11	50	II	2.54	6
m	17.2	55	II	1.86	6

#### 5% Aqueous NaOH

Compared to the effect of toluene on styrene-crosslinked polyesters, the effect of 5% aqueous NaOH at 23°C is apparently quite negligible in its visible effects. Indeed, the only observed phenomenon was the appearance of "Schüppchen," or microflakes, in the surrounding liquid. These must have come from the cut edges of the sample. They were first noticed in all samples without exception after about 5 months of immersion. Other than this, there may be some slight tendency toward surface mattness developing after eight to ten months, but there did not appear to be a general pattern of behavior linking it to the known composition of the polyesters.

#### 5% Aqueous HNO<sub>3</sub>

The effect of dilute nitric acid on the cured polyester resins was found to be even less than that of the caustic alkali. Out of 55 samples under test, which represent the whole range of compositions under investigation, together with monomer contents ranging from 30% to 55%, and including

commercial check samples, there were only seven where the slightest (and rather doubtful) sign of mattness might be reported. Otherwise—no change.

### SUMMARY

The water absorption of polyester resins after one week's immersion and the behavior of these resins on exposure to toluene, 5% aqueous NaOH, and 5% aqueous HNO<sub>3</sub> was observed for a period of 12 months. It is suggested that the water absorption results and the observed changes on long-term immersion in toluene can be attributed to the micropore size of the resin structure which, together with the specific affinity of the material toward the environment, controls the diffusion pressure which is generated.

There may not appear to be any visually observable changes in the resin. On the other hand, drastic changes may occur involving swelling, crazing, and cracking from the edges inward, which may result in the progressive cracking off of crescent-shaped fragments until the specimen has disintegrated completely, as shown in some of the photographs. It is suggested that the failure and the manner in which it occurs is determined by a number of interdependent factors which include the residual curing stresses, the micropore size of the crosslinked structure, the effective cross-link density, the stiffness of the molecular network, and the molecular weight (acid value) of the polyester before cure. The effects of the action of diffusion pressure on the network geometry is discussed and a concept of tough, ductile, and brittle failure is put forward. The visual long-term effects of dilute acid and alkali were found to be slight.

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