JOURNAL OF MATERIALS SCIENCE 15 (1980) 1635–1639

Synthesis procedure and the fracture toughness of highly cross-linked resins

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Experimental values of the plane strain fracture toughness of cross-linked unsaturated polyester resins are presented. It is demonstrated that these values depend not only on nominal resin composition (e.g. nature of diol, or molar ratio, *R*, of unsaturated to saturated acid) but also on the conditions under which polycondensation occurs. It is necessary to define rather precisely the molar ratio of total diol to total acid, and also to assess the efficiency of diol utilization. These considerations become more important as *R* increases. Also, as the value of *R* increases, toughness falls. When samples are immersed in hot water, a reduction in toughness is found. The effect of crack-tip radius on apparent toughness values is more marked with a resin of low than of high cross-link density.

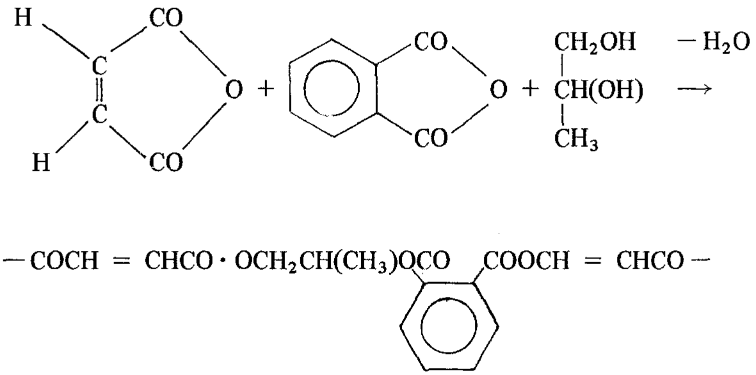
1. Introduction

Attempts have been made to relate the fracture toughness of unsaturated polyester resins, cross-linked with styrene, to gross network structure [1, 2]. The effect of flexibilizing additives has also been considered [3, 4].

The aim of this study was to determine: (a) the importance of the precise diol: acid ratio, and of the methods used to carry the polycondensation reaction almost to completion, in determining the fracture toughness; and (b) the changes in fracture toughness caused by increasing the molar ratio, *R*, of unsaturated to saturated acid, from unity to infinity.

The first part of the aim required that synthesis should be carried out under controlled, reproducible conditions without variation of scale, heating rate, or condenser efficiency. It was also necessary to analyse the resins produced to establish the precise nature of the products.

Synthesis involves heating maleic and phthalic acids or anhydrides with one or more diols, e.g. 1,2 propane diol:



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The added diol is not completely utilised in condensation with acid, because: (a) it is volatile, and a certain amount of evaporation occurs, depending on reaction temperature, heating time, and condenser efficiency, and also on whether a vacuum is applied at the later stages of the reaction; and (b) side-reactions, e.g. addition of diol to unsaturated acid residues, can occur.

As R increases, the evaporation of diol increases. This is because of the higher exotherm caused by the large proportion of unsaturated acid. Also there is more opportunity for addition to the unsaturated acid. This produces an imbalance between acid and diol, affecting chain length.

Analysis of the product is therefore important. It has been assumed [5] that where maleic unsaturation isomerizes to fumaric, as in this case, the overwhelming majority of potential cross-linking sites are utilized by styrene to produce cross-links. (The degree of isomerization can be confirmed by n.m.r. spectroscopy). The hydoxyl group concentration and the acid number are required. Standard methods of determining hydroxyl content by acetylation are rather unsatisfactory, and an improved method was sought [6]. Styrene content had to be determined and kept well within the limits for which Broutman and McGarry [2] found no effect on fracture toughness. It is by no means self-evident that polyester resins can be prepared with adequate control of all variables.

2. Experimental procedure

2.1. Resin preparation

The following resins were prepared: (1) a series of five resins containing maleic anhydride, phthalic anhydride, and 1,2, propane diol, with the following molar ratios (R) of maleic to phthalic anhydride: 1:0, 6:1, 3:1, 2:1, 1:1; (2) one resin for which $R = 1$ but 50 mol% diol was replaced by dihydroxyethyl ether, i.e. diethylene glycol. (This resin is denoted by "D"). Only the resins listed in the first group were used for the main objectives of this study.

Maleic anhydride (Monsanto) was reacted with propane 1,2. diol (Shell) and phthalic anhydride (Laporte). The resins were dissolved in styrene monomer (Forth Chemicals). The required molar proportions of diol and anhydride were heated to 185 to 190° C and maintained at that temperature for 3 h, by which time 60% of the theoretical quantity of water had been collected. Xylene was then added, and the vessel temperature was increased to 200° C for a further 2 h. Subsequently, resins were either (A) heated until an acid number of approximately 35 was reached, followed by vacuum stripping of xylene for 5 min without heating, or (B) heated to an acid number of 45 and then the vacuum applied, still heating, to remove water, until an acid number of 35 was reached. Inhibitor was added (10 ml 10% wt/wt hydroquinone in dibutyl phthalate for the 40 mol total charge) and styrene was stirred in as further cooling took place.

In all cases, whatever the nominal value of R, a known small excess of diol (5 to 10 mol %) was used to counteract losses by evaporation or addition. This diol excess was varied systematically to determine its effect on fracture toughness.

2.2. Resin analysis

Resin viscosities were adjusted to 8 P at 20° C (determined by Brookfield LVT, no. 3 spindle), for convenience of sample preparation, by addition of styrene. The styrene content was then checked by standard volatile content procedures. Acid number was determined by titration with methanolic potassium hydroxide solution, and hydroxyl number by a modification of the method of Hase and Hase [6]; i.e. resins were reacted with chlorotrimethyl silane, to give a nine-fold enhancement of the carboxyl and hydroxyl n.m.r. signal. The combined acid and hydroxyl value was then found by comparing the integral with that of *p*-nitroacetophenone standard. The hydroxyl value was obtained by subtraction of the acid value; prior removal of carboxyl functions with diazomethane proved unsatisfactory.

2.3. Measurement of mechanical properties

Parallel-sided and dumb-bell shaped specimens (B.S. 2782, 301 J) were prepared. The resins were cross-linked with one part by weight, per hundred parts of resin, of methyl ethyl ketone peroxide and one part of 0.5% cobalt naphthenate solution. Gelation occurred after 45 min at 20 ± 2° C and the cure time was 18 h at ambient temperature, followed by 3 h at 80° C.

An Instron 1114 machine was used to measure tensile modulus and critical stress intensity factor, K_{IC}. Tensile modulus was measured using a cross-head displacement rate of 10 mm min^{-1}. Critical stress intensity factors were measured using single-edge notched specimens with parallel

TABLE I Typical analyses of resins

R	Synthesis method	Diol excess (mol %)	Acid Value (mg g^{-1})	Styrene proportion (wt/wt%)	Hydroxyl number (mg g^{-1})
6	B	10	37	38	35
3	B	5	38	47	20
3	B	7.5	34	43	25
3	B	10	32	37	30
2	B	7.5	35	36	30
2	A	7.5	37	35	30
1	A	10	32	32	50
1	B	10	39	31	75

sides, 3.2 mm thick. The ratio of crack length to specimen width was 1 : 1. Notch tips were produced by scalpel, by razor sawing and by razor tapping to give crack-tip radii (r) varying from 0.125 mm to 2.25×10^{-4} mm. Values of K_{IC} were plotted as a function of $r^{1/2}$.

Some measurements of fracture toughness were also made after immersion in water and in sulphuric acid.

3. Results and discussion

3.1. Resin constitution (see Table I)

Styrene proportions (determined by the need for convenient viscosities) were within accepted limits [2]. However, difficulties were found in synthezing some resins in the series $R = 1$ to $R = \infty$. As R increased, it became impracticable to synthesize the resins without high diol excesses, for the reasons anticipated and described earlier. Also, although most of the acid numbers were within the range 35 ± 4, diol losses sometimes made this difficult to achieve without prolonged reaction times. Hydroxyl numbers were found to depend both on the percentage diol excess and on whether procedure A (vacuum applied only briefly) or procedure B (vacuum applied for a longer period) was adopted. The latter treatment would be expected to remove low molecular weight substances.

3.2. Mechanical properties

Values of the fracture stress (σ_f), tensile modulus (E), critical stress intensity factor (K_{IC}) and specific surface energy (γ) are listed in Table II as a function of the maleic:phthalic molar ratio (R) of the polyester resins. The listed values are the average values obtained from ten specimens.

Tensile modulus was calculated from the initial slope of the load–extension curve of un-notched dumb-bell specimens loaded to failure. The strain to failure in all cases was less than 2%.

Values of K_{IC} for single-edge notched specimens were obtained [7] and the surface energy per unit area (γ) was derived from the expression

$$\gamma = \frac{K_{IC}^2}{2E(1-\nu^2)}$$

where E is the tensile modulus and ν is Poisson's ratio.

Poisson's ratio was assumed to be 0.35 [4] and by neglecting the probably small changes in ν as $R \rightarrow \infty$, γ was calculated; it increased significantly as R decreased (Table II). This can be attributed to greater opportunity for segmental motion and viscous flow. It is known that γ is very much larger than expected when cross-linking restrictions on flow are entirely removed [8]. But there is uncertainty about the nature of flow in cross-linked resins. Movement of "islands" of highly cross-linked material within a lightly cross-linked matrix has been suggested [9]. Little evidence has been found for crazing in thermosetting resins.

Load–extension curves were found to be sensibly linear up to the fracture load, for all the resins with various R values. Although the dumb-bell specimens were not especially polished, values

TABLE II Dependence of mechanical properties on maleic: phthalic ratio (resin series A; diol excess 10 mol %)

Ratio R	E (GPa)	K_{IC} (MN $m^{-3/2}$)	γ (J m^{-2})
∞	2.7	0.32	16.6
6	2.7	0.45	32.9
3	3.1	0.56	44.4
2	3.5	0.61	46.7
1	3.7	0.71	58.2

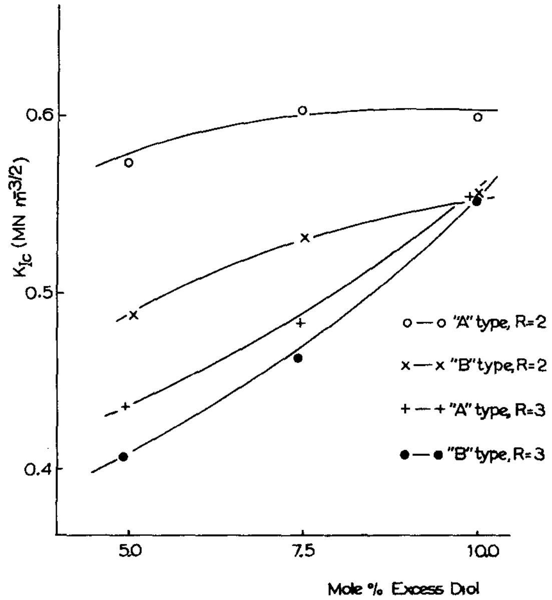

Figure 1 Critical stress intensity factor, K_{IC}, as a function of diol excess. R = molar ratio of maleic:phthalic components. A and B refer to alternative vacuum stripping procedures.

of the critical flaw size ($2c$) were obtained from the expression

$$c = \frac{K_{IC}^2}{\pi\sigma_f^2} \quad (\sigma_f = \text{nominal fracture stress}).$$

Qualitatively, the results indicated a substantial fall in the critical flow size as $R \to \infty$.

The hydroxyl number itself did not affect toughness, but, within a given R series, an increase in the diol excess increased K_{IC} (see Fig. 1). This is explained by the achievement of a given acid value with a lower molecular weight with high diol excess resins. A low molecular weight product probably contains a significant proportion of polyester chains with only one, or even no, fumarate cross-linking site, and this facilitates molecular movement in the network.

3.3. Immersion in water

Total immersion of previously notched samples in distilled water at 50° C invariably produced a marked reduction in the fracture toughness of wiped (but undried) samples (see Table III). This is in accordance with the previous findings of Pritchard *et al.* [10], who used an isophthalic resin for which $R = 3$, and the experimental details were similar in that case. There is some indication that as R increases, the embrittlement becomes more severe, and determinations of K_{IC} for the case $R = \infty$ were abandoned because of specimen fragility.

TABLE III Effect of immersion in aqueous liquids on fracture toughness

Synthesis procedure	R	Time of immersion (h)		K_{IC} (MN $m^{-3/2}$)
		H_2O	4 M H_2SO_4	
A	∞	0	0	0.32 ± 0.04
A	∞	500	–	0.13 ± 0.03
A	∞	1000	–	*
A	∞	–	500	0.34 ± 0.07
B	6	0	0	0.45 ± 0.10
B	6	500	–	0.34 ± 0.04
B	6	1000	–	0.27 ± 0.04
B	6	–	500	0.49 ± 0.10
B	3	0	0	0.41 ± 0.16
B	3	500	–	0.28 ± 0.04
B	3	1000	–	0.18 ± 0.01
B	3	–	500	0.48 ± 0.06
B	1	0	0	0.72 ± 0.12
B	1	500	–	0.53 ± 0.06
B	1	1000	–	0.37 ± 0.08
B	1	–	500	0.55 ± 0.05

*Measurements abandoned.

Three facts have to be considered in explaining why water caused K_{IC} to be reduced, and reduced more severely at high maleic : phthalic ratio:

(1) water is more readily attracted to the unsaturated ester groups than to phthalate–diol linkages, and is believed to form bridge structures involving fumarate groups [11];

(2) immersion at 50° C in dilute (4 M) sulphuric acid did not have a very deleterious effect on K_{IC};

(3) no significant alteration in the crack tip geometry could be observed by optical microscopy after immersion.

The evidence suggests that crack propagation is facilitated by ester hydrolysis. The extent of hydrolysis is smaller in dilute acid, and more

TABLE IV Effect of vacuum stripping on critical stress intensity factor

R	diol excess (mol %)	Procedure A or B (B = vacuum stripped)	K_{IC} (MN $m^{-3/2}$)
6	10	A	0.45
6	10	B	0.41
2	7.5	A	0.61
2	7.5	B	0.55
1	10	A	0.71
1	10	B	0.72

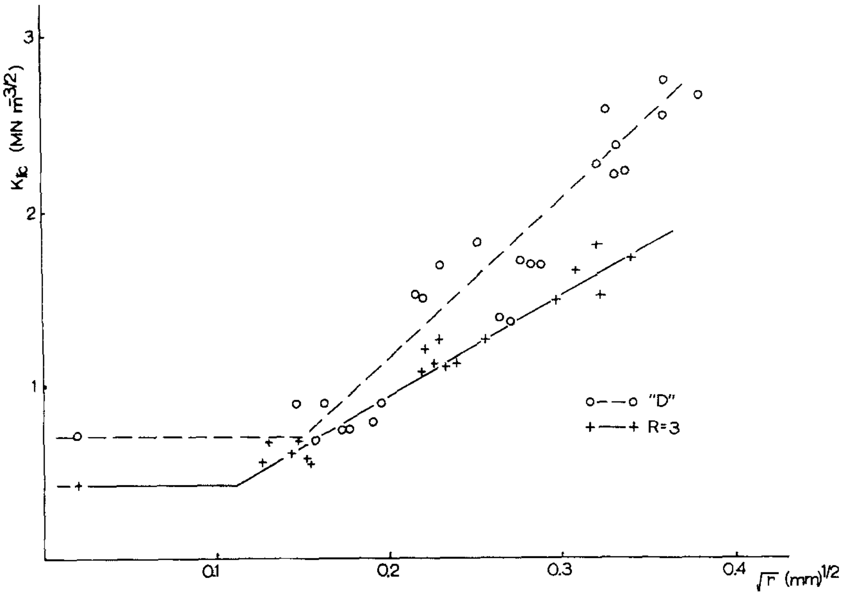

Figure 2 The effect of crack tip radius on apparent fracture toughness for (a) resin "D" and (b) the resin for which $R = 3$.

marked as pH increases; the quantity of water penetrating into the resin increases with R because maleic and fumaric groups are less hydrophobic than phthalic ones.

Table IV shows that the effect of vacuum stripping procedure on K_{IC} is rather slight, but there is a tendency for the prolonged vacuum treatment (B) to remove volatile extra-network material, including some very low molecular weight substances which could plasticize the resins and increase K_{IC}.

3.4. Notch-tip radius

Fig. 2 shows the effect of notch tip radius (r) on the recorded value of K_{IC} for the $R = 3$ resin and for resin D. The more highly cross-linked resin was the less sensitive to notch tip radius. Resin D had a less highly cross-linked structure than any in the series $1 < R < \infty$, because of the diol used.

The K_{IC} values recorded here were those for which $r^{1/2} \leqslant 0.17$ mm. This suggests that any departure from the true minimum values was small.

4. Conclusions

K_{IC} falls as R rises from unity to infinity, but it also depends on the conditions under which polycondensation occurs. It is therefore insufficient to describe a cross-linked polyester resin simply in terms of the reagents used.

Variations in the diol:diacid molar ratio, and in the efficiency of diol retention, also produce considerable changes in fracture toughness.

Acknowledgements

One of us (G.V.R.) acknowledges the receipt of a studentship from International Pinchin Johnson Co Ltd, and this company provided facilities for resin preparation on a suitable scale.

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Received 8 July 1979 and accepted 11 January 1980.