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The fracture toughness and fracture morphology of polyester resins

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The change in fracture toughness of an orthophthalate based medium reactivity polyester resin with change in resin flexibility, catalyst content, cure temperature and liquid environment, has been investigated. Various specimen geometries including simple double cantilever beam and tapered double cantilever beam have been used and the results obtained with the different geometries are in good agreement. The critical flaw size for the resin has been determined and an estimate obtained of the radius of the plastic zone under plane strain conditions. The solvent absorption characteristics of the resin were found to be effected by catalyst content, resin flexibility and by residual strains. Observations of the fracture behaviour, using both fracture toughness and tensile specimens have revealed a fracture surface morphology very similar to that of glass but with limited plastic deformation occurring.

1. Introduction

Thermosetting unsaturated polyesters are used extensively as matrix materials in fibre-reinforced composite systems. The polyester resins, before gelation, have sufficiently low viscosities at room temperature to enable them to penetrate between closely packed fibres without significantly damaging them. The matrix material in these systems must be able to transfer stress to the fibre and will have a significant effect on the overall fracture resistance of the composite.

Common commercial resins are supplied as relatively low molecular weight linear polyesters in solution with a monomer such as styrene and are cross-linked by addition polymerization with the monomer. With an optimum amount of monomer, (about 30% styrene for common resins) this results in an average of two styrene units per cross-link between polyester chains [1, 2]. Excess styrene leads to longer styrene linkages [3] and styrene-rich areas which can affect the resultant materials properties and produce problems such as crazing [4] and increased shrinkage on curing [1].

The cured resins can vary from being very flexible to hard brittle materials. The latter are generally stronger and more resistant to chemicals and thus form the basis for most commercial resins for structural applications.

Among thermosetting materials there are likely to be significant differences depending on their chemical constitution and the mechanisms of cross-linking. There is, however, evidence from electron microscope observations that some thermosetting resins form globular structures in the size range of 10 to 90 μm [5–11] and microstructure within such globules has been detected in one case [10]. Also, structures in the size range 20 to 90 μm have been observed in some epoxy resins [12, 13]. It is to be expected that the super molecular structure of these thermosetting resins may be reflected in some of the physical and mechanical properties and in the fracture surface morphology of these materials.

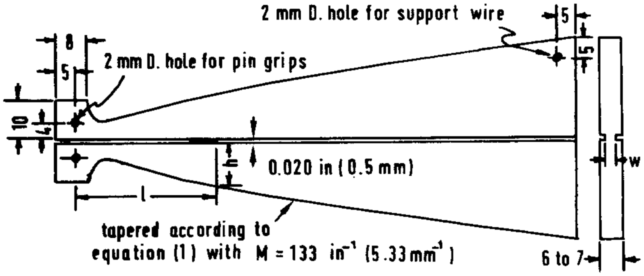
The presence of a small crack in a brittle homogeneous material will considerably reduce its strength from that of the unflawed state and it is well known that flaws of submicroscopic dimensions can seriously affect the strength of glass [14, 15]. In an ideal elastic material the work required to fracture the specimen would equal the surface energy associated with the resultant new surfaces [14, 16]. However, when plastic deformation accompanies fracture the fracture energy can greatly exceed the expected surface energy [17, 18] and this happens even in the case of glass. This has been attributed to miniscule plastic flow at the tip of the crack [19, 20]. Obviously, if a brittle material can be altered slightly to provide more plastic flow without seriously affecting its strength, an improvement in fracture toughness would be expected. Consequently, the objectives of this investigation were to study fracture processes in polyester resins, the effect of the addition of a flexible resin, changes in catalyst concentration and the effect of environments on the fracture toughness and fracture morphology of the resins.

2. Experimental

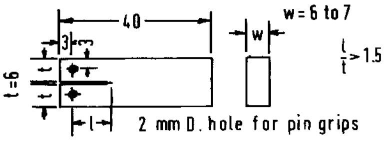
2.1. Materials

The polyester resins used were Filabond 8000, an orthophthalate-based medium reactivity "rigid" resin, and Filamond 8151, a phthalate-based "flexible" resin, which can be blended with the former. These resins were supplied by Synthetic Resins Ltd. Catalyst K (a 30% MEK peroxide solution) and Accelerators C and SC (6 and 1% solutions of cobalt naphanate in styrene respectively) were obtained from the same source. The catalyst was used in concentrations from 0.25 to 2.0% of the total volume and the accelerator concentrations were from 0.125 to 1%.

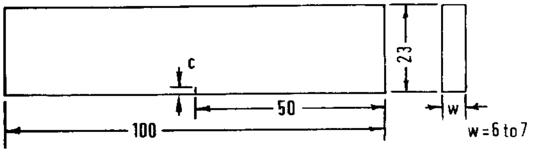
The accelerator, purple in colour, was mixed into the resin using a slow speed electric stirrer until it had dispersed to give a uniform pink colour. The catalyst was then added and stirred in until a uniform straw colour was obtained. Care was taken to avoid the introduction of bubbles during the mixing process. The catalyzed resin was then poured into a mould consisting of two glass plates, 200 mm x 200 mm, with a neoprene rubber gasket between them enclosing three sides; four clamps held the glass plates tight against the rubber gasket. The mould was then placed vertically inside a preheated oven to allow the resin to gel and cure. After curing it was allowed to cool and after a further 24 h the resin was post-cured. Curing was carried out at various temperatures from (343 to 403 K) for 1 h and post-curing at 353 K (343 K when the cure temperature was also 343 K) for 3 h.



tDCB : Tapered Double Cantilever Beam



suDCB : Simple Unslotted Double Cantilever Beam



SEN : Single Edge-Notched Tension Specimen

Dimensions in millimetres unless otherwise noted

Figure 1 Fracture toughness specimens.

2.2. Mechanical testing

2.2.1. *Fracture toughness tests*

In this work single edge-notched (SEN) tensile specimens, simple double cantilever beam specimens [21] (s DCB) and larger tapered double cantilever beam specimens [22] (t DCB) were used. The SEN specimens were used primarily for the fracture morphology studies. The shapes and sizes of these specimens are illustrated in Fig. 1. Sharp notches were introduced into the specimens by the propagation and sharpening of an originally duller crack by forcing apart the two sides of the sample with a wedge.

It was found that the crack was usually deflected from the initial plane of propagation and in order to reduce this effect the DCB were tested with (ss DCB) and without (sμ DCB) slots on each side of the sheet parallel to the direction of crack propagation. All the t DCB specimens were slotted. Slotting also helped in controlling the initial crack length. Despite this, slots in the t DCB specimens were only 50% successful in preventing the initial crack from completely leaving the slot but the only values of fracture energy used in this case were those calculated from a crack fully within the slot. The taper in the t DCB specimen was such as to maintain the compliance at a constant ratio to crack length so that a crack would not propagate catastrophically but continuously or in a series of steps. This specimen does not require an additional determination of Young's modulus for the surface energy calculation, as do the other fracture toughness tests.

To prepare the various fracture toughness specimens the cured plates were marked off and cut into sections. Where necessary slots were machined in with a screw-slotting saw to a depth of between 1.5 and 2 m.

The final outline of the t DCB specimen was derived using an equation giving a linear relationship between compliance and crack length [22].

$$l = \{[Mh - (1 + \nu)]^{1/2} - 1.2\}\frac{h}{2} \qquad (1)$$

where l is the length of the crack tip from the loading pin action line, M is a selected constant, h is the height of the cantilever edge above or below the slot and ν is Poisson's ratio. The value of M was selected to be 5.33 mm^{-1} [22].

The fracture energy of the t DCB specimens were calculated using the equation [22].

$$\gamma = \frac{p^2}{4w}\frac{dc}{dl} \qquad (2)$$

where γ is the fracture energy (at initiation, arrest or during propagation) p is the applied force, w is the width of the specimen between the slots, c is the compliance (specimen deflection per unit force) and l is the length of the crack from the action line of the pin grips to the crack tip.

The energies of the DCB specimens (sμ DCB and ss DCB) were calculated using the equation [21]

$$\gamma = \frac{6p^2l^2}{Ew^2t^3}\left[1 + 1.32\left(\frac{t}{l}\right) + 0.542\left(\frac{t}{l}\right)^2\right], \qquad (3)$$

where γ is the fracture energy (for initiation only in this case) E is the Young's modulus and t is the depth of the beam between the crack plane and either parallel surface.

When using different methods to evaluate fracture parameters the data must be related to the failure mode, namely, initiation and propagation [23]. In this work, γ_i is used to define the appearance of a stable crack and is governed mainly by the rate dependence of the fracture process and by the specimen geometry. γ_p defines the point at which the crack becomes unstable when significant crack jumping occurs.

The SEN, ss DCB and sμ DCB specimens were tested at 0.5 mm min^{-1} and the t DCB specimens at 0.2 mm min^{-1}.

2.2.2. *Tensile and compressive tests*

Conventional tension and compression tests were used to provide additional data for the polyesters. The tensile specimens were tapered from both grip regions towards the centre to localize failure away from the grip. The distance between grips was 70 mm and the reduced cross-section was 6 mm square. The specimens were shaped with a Tensilkut machine and polished with a series of successively fine emery papers, alternately at about ± 30° angles to the long axis, rinsing with water after each polish, finally finishing with 4/0 paper and metal polish. The specimens were tested at 0.2 mm min^{-1}.

The compression test is of value as the polyesters will undergo yield in compression, thus providing an upper limit on strength. Also, by comparing the tensile fracture strength with the measured compressive yield strength an estimate can be made of how close the sample is to the plastic condition, this being of some importance if linear elastic fracture mechanics are to be applied without an estimation of plastic zone sizes. The yield stress is defined here as the maximum in the engineering stress–strain curve. Compression tests are generally considered valid for length-to-thickness ratios of two or three to one, which optimizes between the complications of end effects and buckling failures. The specimens used were 2 mm square and 6.3 mm high and were cut to fit polishing jigs in which the sides were polished to a 600 grade finish. The moduli calculated from compression tests were corrected for machine softness.

2.3. Environmental testing

The effect of environments other than air on the fracture toughness of the polyesters is of interest since various liquids are known to lower the strength of many polymers. Water, particularly distilled water, is known to have a deleterious effect on polyester resins, alone [24] or with fibre reinforcement [25, 26]. The absorption of water and several organic solvents into polyester samples was determined by weighing pieces, 7 mm x 12 mm x 28 mm in size, which were immersed in bottles containing the fluid until weighing, when the sample was withdrawn, the surfaces blotted dry and the sample weighed, after which it was replaced in the fluid. Chloroform, acetone, and methanol were useful because of their relatively fast absorption. However, chloroform quickly degraded the structural integrity of the surface layers, and pieces started to crack and fall off within several days. Acetone also attacked the surface of samples exposed for about one week. Samples to be fracture-toughness tested after exposure to these liquids were not left in the liquids long enough for this to occur.

Usually, for tests using an environment the sample was mounted and a trough containing the fluid was brought up to surround the sample before testing. For a few tests a dry sample was tested part way before fluid was gently squirted onto the specimen in the region of the crack tip; this was continued until catastrophic failure occurred.

2.4. Observation of fracture surfaces

The fracture surfaces of the specimens were studied by optical microscopy using either a Zeiss (W.Ger) "Tessovar" Photomacrographic Zoom System, a Carl Zeiss (Jena) stereomicroscope, or a Reichert "Zetopan" polarizing microscope. A number of specimens, after having a thin protective coating of gold–palladium vacuum-deposited on them, were examined by scanning electron microscopy using a Cambridge Mark II "Stereoscan" microscope.

3. Results

3.1. Fracture toughness tests

The effect on fracture energy values, using t DCB and ss DCB specimens, of decreasing the amount of catalyst from the recommended 2% by a factor of four, for samples cured at 363 K, is shown in Fig. 2. The values of γ for initiation, γ_i, and propagation, γ_p stayed within the range 20 to 27 J m^{-2}. The t DCB specimen gave average values for γ_p of 23 J m^{-2} and ss DCB specimens from the same plate of resin gave an average value for γ of 22.6 J m^{-2}.

Changing the cure temperature had little effect on these values as measured by t DCB specimens, although there was a slight tendency for γ_p to decrease as the cure temperature was increased

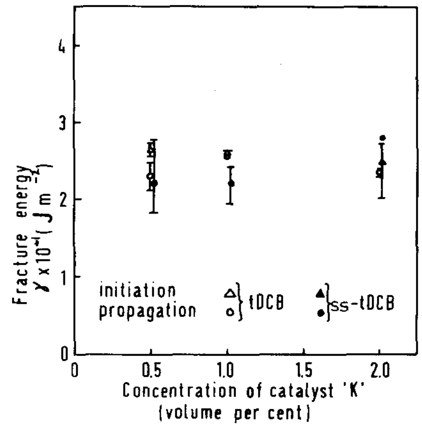


Figure 2 Effect of catalyst concentration on fracture energy (symbols indicate average values, vertical bars indicate the range of results).

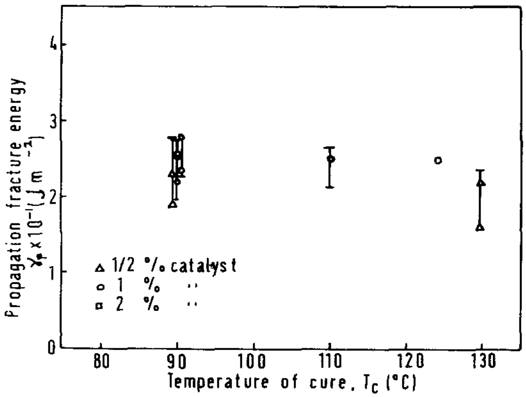


Figure 3 Effect of cure temperature on propagation fracture energy.

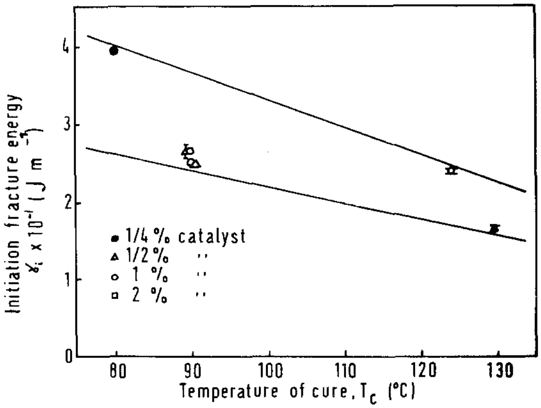


Figure 4 Effect of cure temperature on initiation fracture energy.

(Fig. 3), and the values of γ_i showed the same trend (Fig. 4).

A number of plates of polyester were cast containing various amounts of flexibilizing resin (Filabond 8151) from 10% to 30% in solution with the "rigid" Filabond 8000. Small sμ DCB specimens were obtained from these plates and were tested. The values of γ, modulus, and compressive yield stress for samples containing, 0, 10 and 20% Filabond 8151 are shown in Table I. The flexibilizing resin lowered the modulus and yield strength, and raised the fracture toughness. However, because of the difficulty in controlling crack initiation the results from these specimens are not expected to be as reliable as those from t DCB specimens.

3.2. Tension and compression tests

From each of the plates used for fracture toughness testing a reduced cross-section tensile specimen was prepared and tested and gave the values listed in Table I. These results indicate that under tensile fracture conditions the fracture stress is about half the compressive yield stress.

The compression tests, after accounting for machine softness, showed a linear stress–strain curve up to about two thirds the yield stress, i.e. beyond the stress at which fracture occurs in the unnotched tensile specimens.

3.3. Environmental tests

t DCB specimens were presoaked in water for periods of 24 and 792 h, taken out for final test preparations and mounting in the grips, and then quickly immersed in a trough of water and tested within several minutes. One sample had not been presoaked but was immersed for the few minutes before the test began. The results shown in Fig. 5 indicate that long term soaking increased fracture energy slightly. Unexpectedly, the sample immersed for only a few minutes showed a larger fracture energy than those soaked for much longer times.

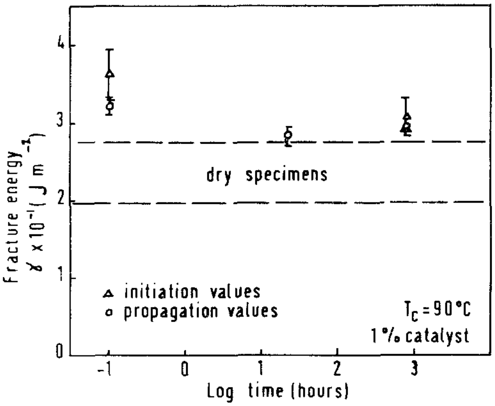


Figure 5 The effect on fracture energy of soaking in water.

In absorption weight–time experiments water was absorbed much more slowly than the three organic liquids used, as can be seen from Fig. 6. Initial tests on specimens presoaked in acetone or chloroform for 24 h, after which the samples were tested in air within minutes, showed an average increase of fracture energy which was within the range obtained for the water-immersed samples. The scatter of results when using the organic liquids

TABLE I Fracture energy, tensile and compressive properties of polyester resins with added flexibilizer*

Flexibilizer content (%)	γ (J m^{-2})	Compression modulus‡ (MN m^{-2})	Compression yield stress‡ (MN m^{-2})	Tensile strength (MN m^{-2})
0	22.8†	4630	134	56
10	28.1†	4050	126	63
20	28.5†	3900	119	63

*Filabond 8000 resin with added Filabond 8151, with 1% catalyst K cured at 397K.
†Values of γ are the average of 3, 2, and 6 specimens, respectively.
‡Modulus and yield stress values are averages from the same three samples.

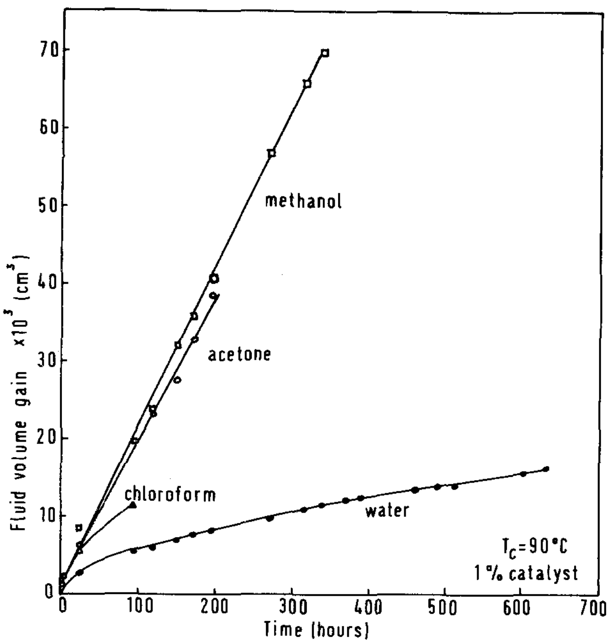


Figure 6 Absorption of four liquids into polyester specimens.

was greater. Attempts to perform tests on long-term pre-soaked specimens immersed in an environment of acetone or methanol did not succeed because the loads rose to such unexpectedly high values without fracturing that the tests were terminated to avoid damaging the pin grips. However, one specimen was tested dry to a crack arrest point still within the slot. When subsequently immersed in methanol the crack did not re-initiate until the calculated fracture energy reached 169 J m^{-2}, about seven times that for the previously dry portion, and then ran catastrophically to the far end of the specimen. The resultant surface showed a rib line at the crack arrest point much more pronounced than for stopping points on dry specimens. The lack of success in testing during immersion prompted a few experiments in which steadily moving cracks were propagated in dry specimens before introducing liquid into the slot region around the crack tip. Using acetone it was found that the initiation fracture energy was increased considerably,to 86 or 91 J m^{-2} from a "dry" value of 26 J m^{-2}, and that prominent ribmarks were left on these specimens. In one case the crack had been slowly propagating at the time the liquid first contacted the specimen and crack

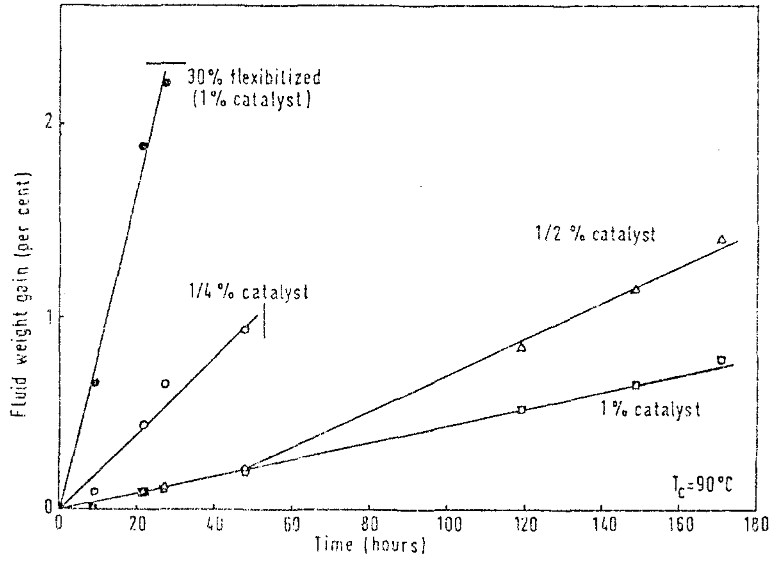


Figure 7 Effects of catalyst concentration and flexibilization of the polyester resin on its absorption of acetone, bars across the absorption curves indicate visible degradation before the next measurement.

growth stopped to produce a pronounced rib mark.

Only one set of composition and curing conditions were used for polyester samples for the environmental tests. It seemed likely, however, that changes in composition and structure could change the characteristics of liquid absorption. This is shown in Fig. 7 where it is seen that a more flexible resin, produced either by addition of flexibilizing resin or a reduction of catalyst concentration, absorbed acetone more quickly than the normal rigid material.

Another factor which affected the results was residual strain, and this is illustrated in Fig. 8. Two pieces were taken from a fairly homogeneous plate cured at 363 K and one was then heated to 413 K for 3 h to produce residual strains along the sides and particularly in the corners. These were noticeable through crossed polars. For a number of specimens observed after 21 h into the soaking period in acetone, the residual-strain specimen showed an increase of birefringence; the more flexible specimens each showed small changes, the others little change. 4 days after being left to dry the 30% flexibilized sample showed a penetration layer discontinuity in from the edges of the specimen and birefringent colour bands further in.

Generally, plates were cut to obtain t DCB specimens in such a way that large birefringence gradients were avoided, especially in the portion where crack growth was measured for calculations. Machining of the side slots did not usually create much more birefringence in the parts on either side of the slot that remained transparent, but the bottom, machined surface of the slot was opaque, and the birefringence could not be evaluated. It was noted that the more flexible the resin (by addition of flexibilizing resin or reduced catalyst content) the more birefringence was observed running parallel to the sides of the slot, with presumably the greatest strain at the slot side. Areas around the holes drilled for specimen grips or support also showed considerable residual strain patterns. The effects of these, especially around the holes, could be lessened considerably by annealing after the machining, but this often redistributed strain so as to increase strain slightly in other parts of the specimen.

3.4. Fracture morphology

The fracture morphology of the thermoset polyesters was very similar to that of glass and other brittle materials. When simple tensile specimens were used the breaking stress was high (about 60 MN m^{-2}) and the resulting fracture surfaces showed small mirror and mist regions quickly giving way to hackle and crack branching. Most often these samples fractured at the minimum of the reduced cross-section and the fracture was usually initiated at the surface of the specimen.

Long narrow features, "river lines", were usually seen running from the initiation point through the mirror and merging into the structure of the mist region (Fig. 9). The lines resulted from the crack propagating at slightly different levels and in the SEN sample long individual gracks could be seen in the mirror region. Extended

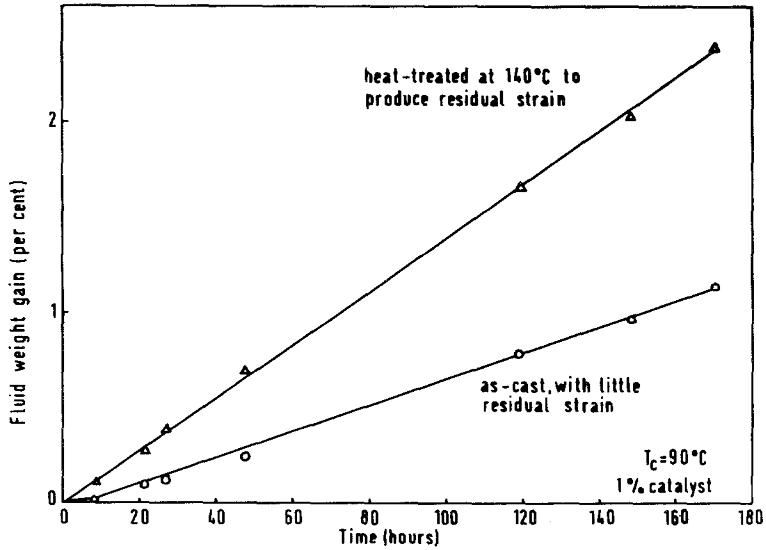


Figure 8 Effects of residual strains in polyester resin on its absorption of acetone.

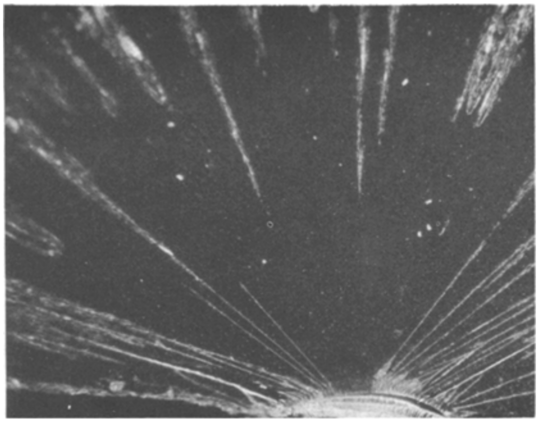


Figure 9 Dark-field optical micrograph showing elongated features running from the initiation region over the flat area in front of the hackle.

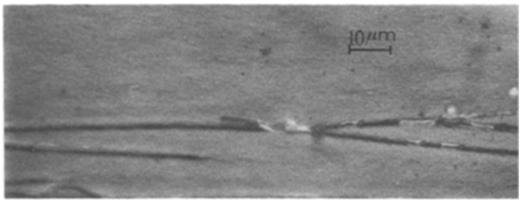


Figure 10 Steep oblique bright-field optical micrograph of tracks (dark) with pieces of filaments (bright) still partially attached.

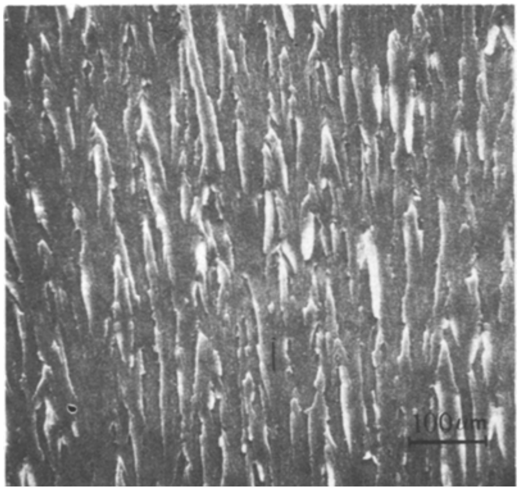


Figure 11 Scanning electron micrograph of microhackle in mist region.

filaments can be seen along the tracks (Fig. 10). Similar observations have recently been made on a brittle phenol-formaldehyde thermoset resin [27, 28]. Further into the mist region the multiple levels of fracture became more pronounced and there is some evidence of a small amount of plastic deformation (Fig. 11). In the hackle region the fracture surface was very uneven, indicating that multiple crack formation and bifircation has occurred, and mounds and depressions left on the surface indicate that some parts of the material maintained structural integrity more than other parts.

In the t DCB specimens where crack propagation was controlled the stress intensity did not become high enough to form coarse hackle. Although at times propagation appeared to be continuous it was not possible to say whether or not the propagation was stepwise with very small steps. After testing, such a specimen would show many small hesitation rib marks associated with a slight change of direction of the crack plane (Fig. 12).

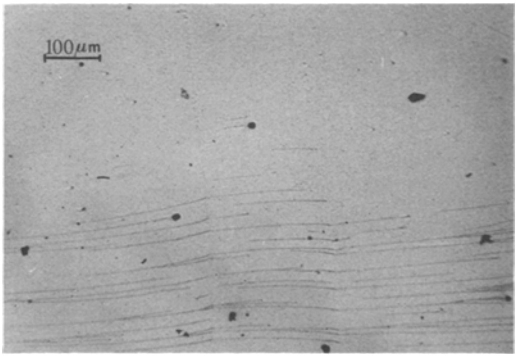


Figure 12 Opitcal micrograph of tracks intersecting hesitation rib marks on a t DCB fracture surface.

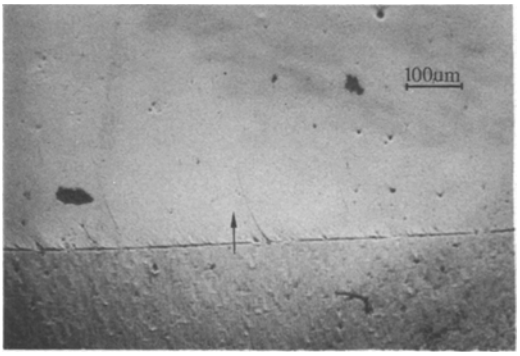


Figure 13 Optical micrograph showing transition from slow growth to fast crack regions.

When samples were soaked for 792 h and tested in water it was noted that after a hesitation point slow growth seemed to be occurring; the surface of the slow growth region was granular but with features elongated slightly in the growth direction (Fig. 13). The area forward of the fast growth line can be seen to be comparatively smooth.

This change between granular and smooth surfaces is parallelled by observations of other specimens: where crack propagation seemed continuous over most of the length the resulting surface was primarily granular with many shorter lengths of smooth regions; conversely, when a specimen cracked discontinuously in a few long jumps the surface was not granular but was smooth, except for the tracks.

4. Discussion

The applicability of linear elastic fracture mechanics to the polyester resins used in this work can be justified with a few comments. The tensile fracture stress was about half the compressive yield stress and was still within the linear portion of the stress–strain curve. There is a criterion [29] to determine the width of specimen necessary for plane strain conditions at the crack tip:

$$\omega \geqslant 2.5 \left(\frac{K_C}{\sigma_y}\right)^2 \tag{4}$$

where K_C is the critical stress intensity factor and σ_y is the yield stress. For plane strain:

$$K_c^2 = \frac{EG_c}{(1-\nu)^2}, \tag{5}$$

and G_c = energy release rate = 2γ. Using a Poisson ratio value of 0.35 and values of E, σ_y, and γ from Table I for the 0% flexibilized sample, the specimen width need only be greater than 3×10^{-2} mm, whereas in fact the widths were 3 mm or greater. An estimate of the radius of the assumed plastic zone r_y under plane strain conditions from [29]

$$r_y = \frac{1}{6\pi}\left(\frac{K_c}{\sigma_y}\right)^2 \tag{6}$$

results in a value of 0.8 μm. This value, however, together with those presented in Table I. is not unique and in the viscoelastic materials tested here will vary with the speed of testing and with the crack velocity. It has been shown that tests over a range of cross-head speeds in excess of that used here reveal a decrease in surface energy and fracture toughness and an increase in Young's modulus as the testing speed increases [30, 31].

There is also considerable evidence that the deformation processes at the tip of a crack in thermoplastic viscoelastic materials can be modelled successfully by the Dugdale line plastic zone and the zone length obtained using the expression [30, 31]

$$\Delta = \frac{\pi}{8}\left(\frac{K_c}{\sigma_y}\right)^2. \tag{7}$$

Applying this analysis to the thermosetting material used in this investigation and with values from Table I a figure of 5.26 mm is obtained for the length of such a zone.

The critical flaw size c_0 inherent for the polished tensile specimens can be obtained from the Griffith equation

$$\sigma_f = \frac{2E\gamma}{\pi c(1-\nu^2)} \tag{8}$$

using values of E and γ from Table I. For the same sample the value of c_0 is 22 μm, i.e. about 30 times the estimated size of the plastic zone. The small size of the critical inherent flaw size indicates why surface preparation is so important for these thermoset polyesters even in comparison to such brittle thermoplastics as polystyrene for which $c = 1.1 \times 10^3$ to 1.3×10^3 μm [32, 33] and polymethyl methacrylate, $c_0 = 50$ μm [33, 34]. The inherent flaw size for a cross-linked co-polymer of PMMA has been reported as 18 μm in one case [34] and 12 μm in another [35], and for a thermoset polyester a value of 10 μm has been reported [35].

The value of fracture energy for the Filabond 8000 polyester at recommended catalyst and curing conditions was about 24 J m^{-2}. This compares with values for other polyester resins of about 12 J m^{-2} for Paraplex 43 [35], 65 J m^{-2} for a BIP resin [36], 90 J m^{-2} for Co-Rezyn 1808-2 [37], and 200 J m^{-2} for Bakelite SR 17449 [38].

The strengths and failure strains of thermosetting materials vary with the amount of cross-linking [11]. A decrease from the number of cross-links which give maximum strength properties will usually produce a material with less resistance to deformation. This may be accomplished for thermosetting polyesters in a number of ways, including substituting saturated for unsaturated bonds, using less monomer, decreasing the reaction (cure) temperature, or using a less reactive isomer for the unsaturated species [39]. Lowering the cure temperature for one type of polyester by 353 K is known to double the fracture energy [35]. It has been shown that adding cross-links to normally thermoplastic polymers decreases the fracture energy considerably; for example by irradiating polystyrene [22] or by chemically cross-linking polymethylmethacrylate [34, 35]. With increasing cross-link density the fracture energy of a polyester is reported to increase to a maximum and then decrease [40] and another study [41] reports that change in the post-cure temperature from 293 to 423 K has little effect on the fracture energy of a polyester. An increase of fracture energy with a decrease of cross-linking for the common thermosetting polyesters will eventually be negated by the low strength inherent in the low-molecular weight prepolymer.

The results of varying the catalyst concentration between $\frac{1}{4}$ and 2% showed no significant effect for the system studied here. Also the temperature of cure does not seem to have a marked effect, although any effect could be masked by the scatter of results.

For the t DCB specimens there was generally little difference between initiation and propagation values of fracture energy.

Crack extension in many cases seemed to consist of short quick movements between pauses, rather than a continuous propagation at fairly constant speed. Fracture surface features show the discontinuous nature of crack movement. The values for γ_p do not show a clear effect of cure temperature, and the trend appearing for γ_i is weighted by the result for the sample with both low cure temperature and low catalyst concentration.

Substitution of flexibilizing resin for part of the normal brittle resin should allow increased deformation both through the introduction of more flexible segments, such as aliphatic species, and through a reduction in the fraction of possible cross-linking sites. The compression modulus and yield strength values of Table I show that the flexibilizing resin changed the mechanical properties significantly, and γ increased slightly with added flexibilizer. This is in agreement with recent results [36] on another polyester resin-flexibilizer system in which the fracture toughness increased by 60% with 30% flexibilizer, and at 50% flexibilizer the net section stress was greater than the 0.1% offset yield stress. However, these gains in toughness at the expense of modulus and strength are not as marked as in rubber-modified thermosets [42, 43]. In the present work the fracture surface morphology of a non-flexibilized resin could not be differentiated from that of a specimen containing 20 vol % flexibilizing resin.

Interpretations of a number of the features which are seen on polymer fracture surfaces have been made [44–46], and correspondences have been shown with similar features in metals; also, a number of the features on the thermoset polyesters are quite similar to those seen on fracture surfaces of glass [47]. Although the gross fracture morphology of these resins indicated that they were quite brittle, more detailed observations revealed a number of features with the rounded and drawn-out appearance associated with plastic deformation and also tracks with somewhat flexible filaments still partially attached. In a recent study of the various stages in the fracture surface morphology of a phenol-formaldehyde thermoset resin [28] filaments were often found attached to tracks in fracture surfaces. The filaments appeared to consist of narrow thin film which had curled tightly. The tracks are sometimes noticeable in work on other thermoset [35, 36, 48, 49] and thermoplastic [50] polymers.

The effects of fluid environments on the fracture toughness of polyesters consists of several effects. The fluid can reduce the strength and modulus properties of the resin by interfering with bonding between chains or even by breaking covalent bonds, especially ester linkages, within the chains. Alternatively, the initial swelling of the surface regions and the high concentration gradients might produce several contradictory effects: either high tensile stresses could be caused in regions near the surface, thus aiding crack initiation and propagation (perhaps best illustrated by the flaking of samples immersed in chloroform for four days or acetone for seven days), or the diffusing fluid might platicize the surface region, blunting sharp cracks to delay initiation while the bulk of the resin retains its dry strength. In thermoplastics the complexity of environmental factors affecting crazing range from solubility and hydrogen bonding parameters [51] to the possible effects of absorbed gases either lowering surface energy [52] or acting as plasticizers [53].

The specimens of polyester soaked in water for 24 h prior to testing showed a small increase of fracture energy, and those soaked for 792 h showed a slightly higher increase. A sample immersed for only a few minutes before testing gave the highest fracture energy of the group. Whereas the long-term soaking results could be indicative of successive plasticization, thus lowering resistance to deformation, the short-term increase might be indicative of selective crack blunting. It has been found for one epoxy resin [54] that when the crack tip was exposed to water the initiation fracture energy increased.

Crack blunting in the organic liquids was indicated by the experiments in which a specimen was partially tested dry without having been previously soaked, and then was either immersed in methanol before stressing again, or was treated with acetone during testing. In all these cases the energy for reinitiating crack extension was greatly increased, and in one case a propagating crack stopped as soon as acetone reached it. Corresponding to the fluid-induced hesitation points on these specimens were ribmarks which were much more prominent than those on dry samples. The organic fluids encouraged crack blunting, presumably by plasticization of the exposed crack tips, which could considerably raise initiation fracture energies. The cracks would then extend in a more catastrophic manner than when dry because of the greater stored energy being released.

The importance of sample preparation and characterization for interpreting and correlating data on environmental and solvent cracking and crazing of thermoplastics [55] should also be considered when thermoset polymers are tested in different environments. The results shown in Figs. 6 and 7 demonstrate that polymer flexibility, cross-linking density (via catalyst concentration), and residual strain can seriously affect the rate at which fluid is absorbed into specimens.

5. Conclusions

The fracture energy of the medium reactivity "rigid" polyester resin studied, containing 1% catalyst concentration and cured at 363 K, averaged about 24 J m^{-2}. This value is only slightly affected by variation in catalyst content over a four-fold range below the optimum and lower cure temperatures resulted in slightly higher fracture energies.

Partial substitution with a flexibilizing resin, up to 20 vol% results in a higher fracture energy as the compression modulus and yield stress both decrease.

Presoaking and testing specimens in water results in slightly higher fracture energies which increase with time of immersion. After crack arrest water penetrates slowly at the crack joint to produce a slow growth region. Short term presoaking for only a few minutes results in higher fracture energies than for specimens soaked for the longer times.

Water is absorbed into the polyester at a much slower rate than methanol, acetone or chloroform. The latter two start to degrade the surface layers within 1 and 4 days respectively.

Lowering the catalyst concentration or partially substituting a flexibilizing resin will increase the rate at which acetone is absorbed into the polyester. This also occurs when there are much higher residual strains in the sample.

The fracture surface morphology of the polyester resin is very similar to that of glass but there are signs of limited plastic deformation. This includes curved filaments of material, often seen attached to tracks on the surface.

The various geometries of fracture toughness specimen used give results in close agreement. The critical flaw size for the polyester is found to be 22 μm and the radius of the plastic zone under plane strain conditions is estimated to be 0.8 μm. An estimate of the Dugdale line plastic zone gives a value of 5.26 mm.

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