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Toughening of polyester resins by rubber modification

Part 1 *Mechanical properties*

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The toughening effect of reactive liquid rubber additions on two polyester resin systems has been investigated. Fracture toughness and crack propagation behaviour have been studied, using the double torsion test. Toughness, as defined by fracture surface energy for crack initiation, increased with rubber content. The magnitude of the increase was dependent upon rubber–resin compatibility. The most successful system, incorporating an experimental butadiene–acrylonitrile rubber, showed an eight-fold increase in toughness, compared with the unmodified resin. Other proprietary systems showed more modest increases. Modulus and heat distortion temperature were also investigated for the different rubber–resin systems. In all cases, some deterioration in these properties was seen. The experimental rubber caused a reduction in resin modulus comparable with that produced by proprietary rubbers; heat distortion temperature in the experimental system was relatively little affected. The experimental rubber also affected the stress–strain behaviour of the resin. Resin modified with the experimental rubber yielded and deformed plastically, in contrast with the unmodified material, which behaved in a brittle manner.

1. Introduction

Rubber additions have been used for many years to improve the fracture toughness and impact strength of otherwise brittle thermoplastics, such as polystyrene [1]. More recently, this technique has been used successfully to toughen epoxy thermosets [2] using liquid butadiene acrylonitrile copolymer rubbers, with reactive terminal groups. These reactive liquid polymers are dissolved in uncured liquid resin, and during resin curing they precipitate out from solution to form a fine dispersion of rubber particles, with diameters of a few microns or less. Improvements in epoxy resin toughness have been attributed to a number of mechanisms, including matrix shear band formation and crazing [3], triaxial dilation of particles in the stress field at the crack tip [4], and particle elongation and tearing behind the crack front [5]. Toughness is greatly affected by particle size, and in epoxy resin a bimodal distribution of particle sizes has been found to optimize the toughening effect [6]. With careful control of rubber–epoxy chemistry and the curing reaction, improvements of up to 50 times in fracture toughness have been attained.

Toughening of polyester resins with commercially available butadiene–acrylonitrile rubbers has proved less successful, and at ambient temperatures it is unusual to obtain greater than four-fold improvements in toughness with these additives [7]. Carboxyl and vinyl terminated butadiene acrylonitrile rubbers are much less chemically compatible with polyester resins than with epoxies [8], and the poor toughening effect of these rubbers on polyester may be due, in part, to separation of the rubber–resin mixture before curing has occurred. These inhomogeneities result in relatively coarse rubber particle distributions in the cured resin [8], which are less efficient tougheners than finer particles.

To produce a successful toughening additive for polyester, it is necessary to use a rubber

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which is compatible with uncured resin, so that the rubber will readily dissolve in the liquid resin, and remain in homogeneous solution until commencement of the curing reaction. At this stage the rubber precipitates out as a fine dispersion of particles. Hydroxyl terminated polyether (polyepichlorohydrin) has been found to be compatible with polyester to levels greater than 10 parts per hundred resin (pph) [8] and such a mixture may produce a fine dispersion of rubber particles, under suitable curing conditions. Improvements in fracture toughness, using this system are, however, still modest; fracture surface energy is approximately doubled with rubber additions of 10 pph [8]. The purpose of this investigation was to assess the toughening effect of a number of candidate additives, both proprietary and experimental, in two common polyester resins.

2. Materials and experimental procedure

Two polyester resins, manufactured by Scott Bader Ltd, were investigated:

1. Crystic 392 – a flexibilized isophthalic–neopentyl glycol polyester resin, which is PVC compatible;
2. Crystic 600PA – an epoxy modified polyester resin, which is preaccelerated.

These resins were modified, using four different reactive liquid polymer rubbers:

1. Hycar 1300X8 – a carboxyl terminated butadiene–acrylonitrile rubber (CTBN) [9];
2. Hycar 1300X23 – a vinyl terminated butadiene–acrylonitrile rubber (VTBN) [9].

These proprietary additives, manufactured by B. F. Goodrich, Chemical Co, have been used to toughen epoxy resins, but previous workers have found them of limited use for toughening polyester resin [8], because of poor rubber–resin compatibility. They are miscible with uncured polyester resin up to around 3 pph rubber, at ambient temperatures.

3. Hycar HTE 2216X1 – a hydroxyl terminated polyether (polyepichlorohydrin) experimental liquid rubber (HTE). This additive which was developed specifically to toughen unsaturated polyester resins, has been shown to be compatible with resin over a wide range of concentrations, and to improve fracture toughness by a factor of two [7];
4. CRC1008 – an experimental reactive liquid rubber, based on butadiene acrylonitrile, developed by Scott Bader Ltd.

Resin plaques 300 mm x 300 mm x 7.5 mm were produced by casting between 12 mm thick glass plates, using steel spacers. The resin was first heated to 60° C and then slowly added to the preweighed rubber, stirring constantly to ensure thorough mixing. The more viscous rubbers were also heated to 60° C, prior to mixing, to improve rubber–resin miscibility. The mixture was then allowed to cool. Catalyst (and accelerator in Crystic 392) was added, and the plaque was cast. Unmodified resin plaques were produced by a similar technique.

Resin plaques were cured in the mould for 24 h at ambient temperature, after which they were removed, and postcured in an oven, for 2 h at 80° C. Compositions of the plaques produced are summarized in Table I. From each plaque, three testpieces 300 mm x 80 mm x 7.5 mm were machined, for double torsion fracture toughness testing. Crack guide grooves, 1 mm deep x 0.1 mm wide, were cut down the middle of each face of the specimen. The testpieces were then further postcured and stress relieved for 1 h at 80° C.

A sharp precrack was introduced into one end of the specimen, using a razor blade mounted on a Vickers indentation hardness tester. The razor blade was positioned on the back edge of the specimen, in line with the guide grooves, and load was applied until a brittle crack propagated a short distance along the grooves. This precracking technique was found to minimize crack deviation during testing.

Double torsion fracture toughness tests [10] were carried out on a screw driven testing machine, generally using a crosshead speed of 1 mm min^{-1}, although for some formulations crosshead speeds from 0.1 to 100 mm min^{-1} were used. The specimen (Fig. 1) was supported on two parallel stainless steel rollers, 6 mm diameter and 70 mm apart and load was applied across the guide grooves by two small rollers, 20 mm apart. The downward movement of the load point subjected each half of the specimen to an equal torque, which forced

TABLE I Rubber–resin systems tested

Rubber	C392 resin	C600PA resin
CTBN	0, 1, 2, 3,	0, 1, 2, 3,
VTBN	0, 1, 2, 3,	–
HTE	0, 5, 10, 15	0, 5, 10, 15
CRC	0, 2, 4, 6, 9,	0, 3, 6, 9,

Figures are compositions in parts rubber per hundred parts resin (pph).

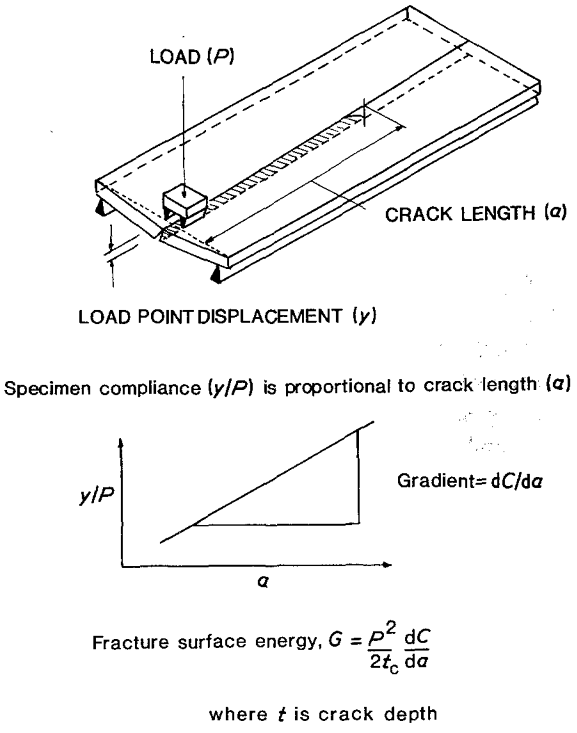

Figure 1 The double torsion test.

the crack to propagate along the specimen, between the guide grooves, in Type 1 fracture mode.

Fracture surface energy (g) was calculated, using the general compliance method, from the equation

$$g = \frac{P^2}{2t_c}\frac{dC}{da}$$

where P is the load required to propagate the crack for a crack front depth t_c. C is the elastic compliance of the specimen, defined by the equation

$$C = y/P$$

where y is the vertical displacement of the load point at load P. In the double torsion test, compliance is directly proportional to crack length, so dC/da is independent of crack length. Compliance calibration curves were plotted directly for specimens which failed in a discontinuous (slip–stick) manner. It was possible to match fracture surface markings, indicating crack arrest, with specific points on the load displacement record, and thus to plot compliance against crack length, to give a value for dC/da. In specimens where continuous crack propagation at approximately constant load occurred, this analysis was not possible and fracture surface energy was calculated using the equation:

$$g = \frac{3P^2}{Et_c}\frac{(1+\nu)\rho^2}{bt^3}$$

where ν is Poisson's ratio, ρ is the moment arm spacing, E is Young's modulus, b is the plate width, and t is the plate thickness [11].

Resistance to impact loading was determined using the Charpy three-point bend configuration, on a Hounsfield pendulum testing machine. The pendulum striking velocity was 2.5 m sec^{-1} and the loading span 40 mm. Specimens 10 mm wide and 50 mm long were cut from cast resin plaques and these were notched to a depth of 1.2 mm with a junior hacksaw blade. The notches were sharpened with a razor blade, prior to testing, so that cracking was initiated from a sharp notch. Ten specimens of each composition were tested. Specimens of similar compositions and dimensions were also impact tested in the unnotched condition; in this case 15 specimens of each composition were tested.

Elastic moduli were determined using a three-point bend configuration for specimens 11 mm high, with a support span of 100 mm. Heat distortion temperature was determined in accordance with BS 2782: Method 351A using a semi-automatic machine, at a bending stress of 0.45 MPa.

The conventional tensile test was found to be unsatisfactory for characterizing the stress–strain behaviour of resins, because tensile specimen suffered brittle failure at stress levels well below the true tensile strength of the material. This was due to brittle crack propagation, from defect sites such as small air bubbles, which had been cast into the material. For this reason, stress–strain data were determined using the plane strain compression test [12], and subsequently converted to tensile data.

Tests were carried out on rectangular cast resin plaques 50.8 mm x 25.4 mm x 3 mm. These were compressed between two parallel, flat, highly polished dies, 6.35 mm wide, which were lubricated with molybdenum disulphide grease to minimize friction between the plaque and the die. This geometry of testing and specimen size fulfilled the two criteria which ensured that the material deformed in a plane strain mode [12], i.e. (a) the ratio of the platen width to the plaque thickness was between 2 and 4, and (b) the specimen was more than four times as wide as the platens. Under these circumstances, the tensile stress (σ) in the material was calculated from the compressive load (P) using the conversion

$$\sigma = \frac{3^{\frac{1}{2}} P}{2 A}$$

where A is the area of platen–plaque contact. Tests were carried out at a range of testing speed, from 0.5 to 100.0 mm min^{-1} crosshead displacement rate for C392 resin, unmodified and toughened with 9 pph CRC rubber.

3. Results

3.1. Fracture toughness

Three types of load/displacement curves were obtained during double torsion testing, and these corresponded to distinct fracture surface morphologies. In unmodified resins, and in those containing HTE rubber at levels of less than 10 pph, crack propagation was completely stable, once crack initiation had occurred (Fig. 2ai). The crack propagated along the guide grooves, at a constant load P_c, with a velocity of 2 mm sec^{-1}. The corresponding fracture surface was almost featureless (Fig. 2aii). In specimens modified with 10 and 15 pph HTE rubber, mixed mode crack propagation occurred, and the load/deflection curve showed small build ups in load, corresponding to regions of crack arrest, followed by stable crack propagation and then unstable crack jumping (Fig. 2bi). The load levels were higher than those seen in the unmodified resins. The corresponding fracture surface (Fig. 2bii) showed alternating regions of slow stable and rapid unstable crack growth. The regions of rapid growth were featureless; regions of stable growth showed a uniform rough texture.

In CTBN, VTBN and CRC modified resins, crack propagation changed to the unstable "stick-slip" mode (Fig. 2ci). In this mode no propagation occurred until the load built up to a critical value, P_i, which was greater than P_c, and then rapid crack propagation occurred. The crack jumped at a high crack velocity, and load decreased rapidly to a value P_a, when crack arrest occurred. No further gross crack propagation occurred until the load had again built up to P_i; this gave the characteristic "saw tooth" appearance to the load/displacement trace seen in Fig. 2ci. Regions of crack sticking are visible on the fracture surface as well-defined arrest marks (Fig. 2cii) separating the otherwise featureless regions of rapid crack propagation. From these arrest marks, crack lengths were measured, and dC/da were determined.

Resins modified with CRC rubber showed clear evidence of fracture surface stress whitening in regions of crack arrest, which were not seen in other systems. The load/deflection trace for these resins differed from CTBN and VTBN toughened resins in that the increase in load during crack sticking was not completely linear, but was slightly curved, the decreasing gradient indicating that an increase in compliance was occurring.

Fig. 3 shows the effect of rubber additions upon fracture surface energy (G) for C600PA resin modified with CRC1008 rubber. Values of both crack initiation (G_i) and crack arrest (G_a) energies, calculated from mean values of P_i and P_a respectively, are included. In this, and the other systems investigated, G_i increased with rubber additions, whereas G_a showed no major change. Figs. 4 and 5 show the effect of the different rubber additives upon initiation toughness (G_i), in the two resin systems. HTE rubber produced relatively small increases in toughness in both resins. Additions of 15 pph rubber resulted in a factor of 2 improvement in G_i for C392 resin; in C600PA, G_i was improved by a factor of 3. These improvements are of similar magnitude to those found by previous workers for HTE toughened polyester resins [7, 8]. VTBN rubber produced a greater toughening effect in C392 resin; at 3 pph modifier level, G_i was doubled. CTBN rubber produced a comparable, but slightly larger increase in toughness than VTBN at similar levels of modification. Additions of 3 pph CTBN rubber resulted in a 2.5-fold increase in G_i in both resins. These increases, although modest, are greater than those previously reported by Tetlow *et al.* [7] and Rowe [8] for similar systems.

CRC1008 rubber was found to have a toughening effect which was far superior to those of the other additives (Figs. 4 and 5). Testing at 1 mm min^{-1} crosshead speed, 9 pph rubber caused an increase in G_i from 95 to 735 J m^{-2} in C392 resin. In C600PA, G_i increased from 68 to 522 J m^{-2}. In both cases this is an eight-fold improvement in toughness. Previous investigations show that it is unusual to obtain greater than four-fold improvements in fracture surface energy [7] in polyester resin by rubber modification although Sultan and McGarry have reported a nine-fold increase in G, for resin modified with 10 pph CTBN rubber. A seven-fold increase in G has also been reported by

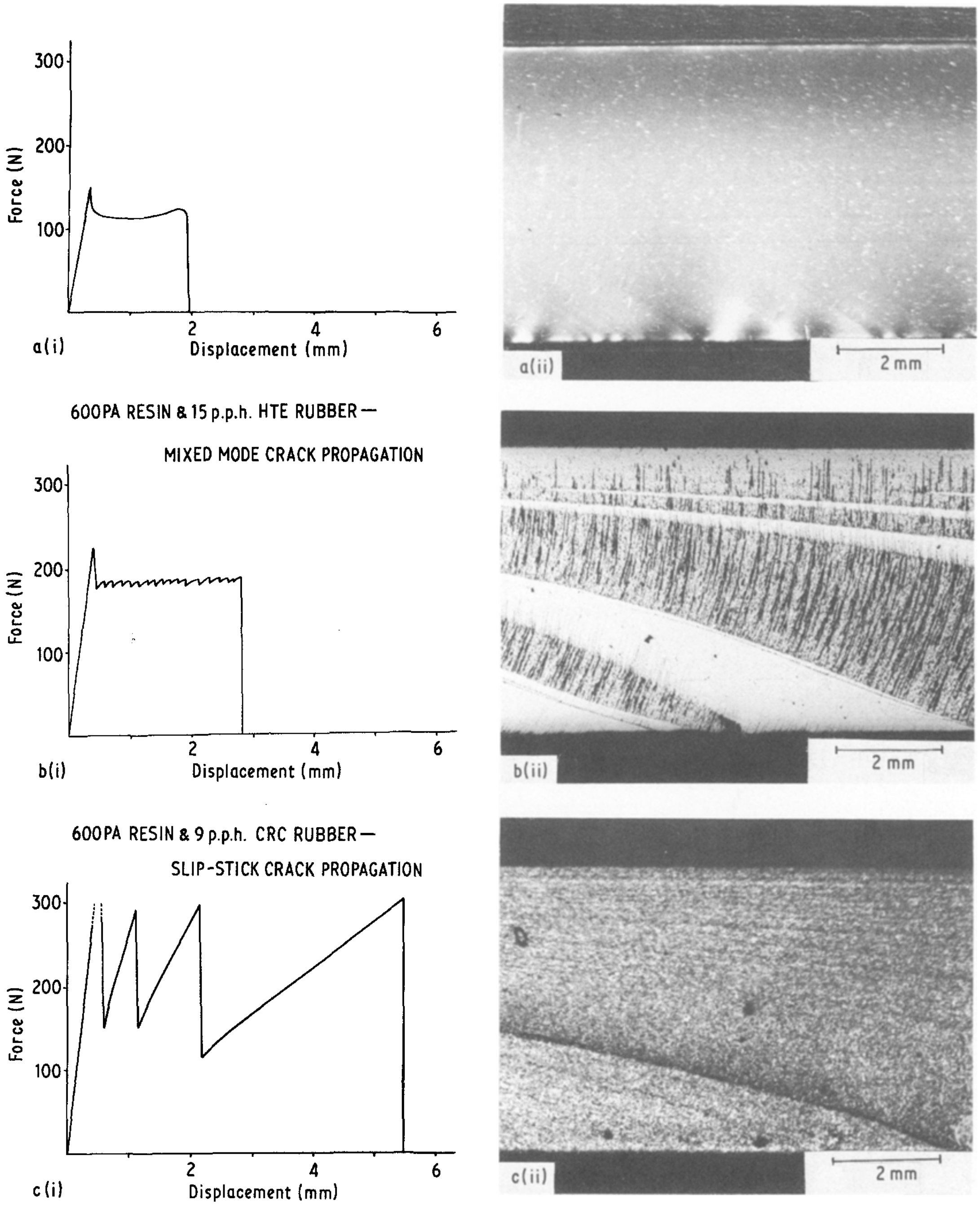

Figure 2 Load/displacement curves and corresponding fracture surface features for double torsion tests: (a) stable crack propagation; (b) mixed mode propagation; (c) slip–stick propagation.

Tetlow *et al.* [7] for VTBN modified polyester, but in this case, fracture toughness testing was carried out at 150° C.

Rate of testing was found to have a very pronounced effect upon the toughness of modified resin. Fig. 6 shows the effect of crosshead speed upon G_i and G_a for C392 resin modified with 9 pph CRC rubber. Over three decades of crosshead speeds, G_a remains constant at $210\,\text{J m}^{-2}$, G_i, however, decreased greatly over the same range, from $1235\,\text{J m}^{-2}$ at $0.1\,\text{mm min}^{-1}$ to $410\,\text{J m}^{-2}$ at $100\,\text{mm min}^{-1}$. Over a more limited range of testing speeds, the toughness of unmodified resin was found to be only slightly altered.

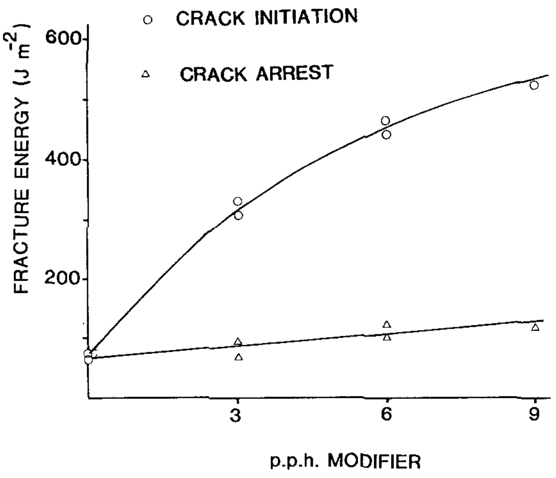

Figure 3 The effect of modification upon crack initiation (G_i) and crack arrest (G_a) fracture surface energy of C600PA resin with additions of CRC1008 rubber.

3.2. Impact

Results for notched impact tests are shown in Figs. 7 and 8. Energies absorbed have been divided by specimen cross-sectional area, to give values of impact energy per unit area of fracture surface created. Mean impact energy and 95% confidence limit is shown for each resin composition. In both modified and unmodified resins, the impact energies are generally greater than those determined during low-speed toughness testing, even for highly modified formulations. It is clear from Figs. 7 and 8 that additions of up to 9 pph CRC

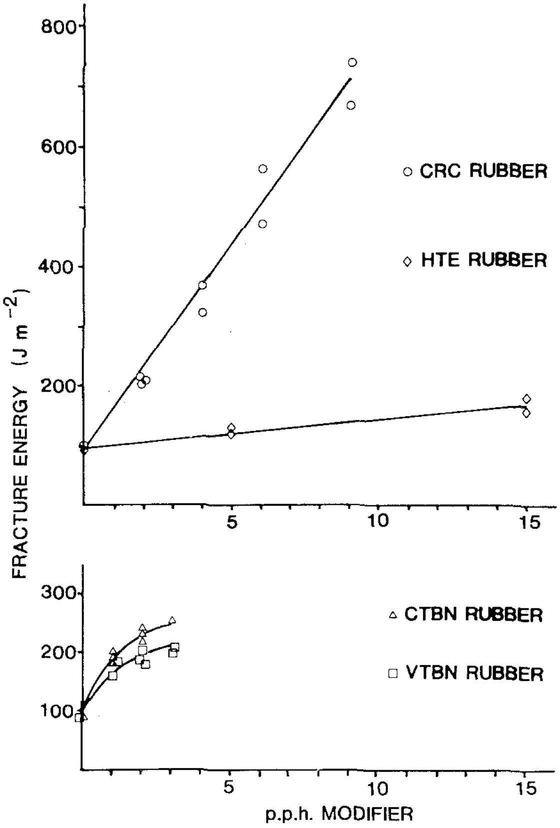

Figure 4 The effect of rubber modifiers upon fracture surface energy (G_i) of C392 resin.

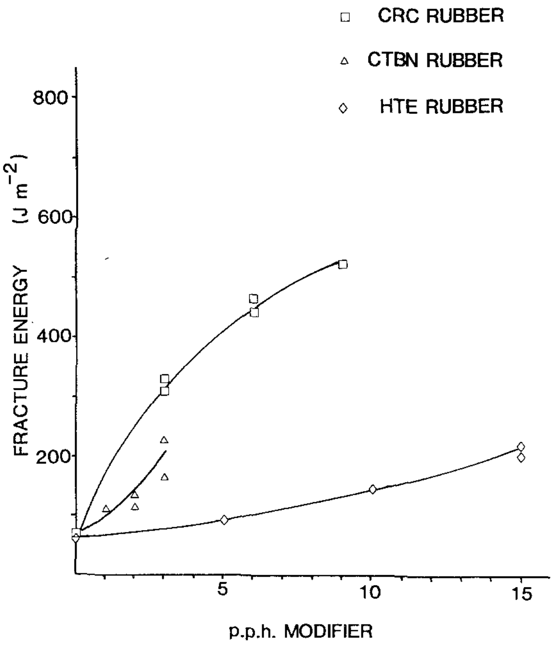

Figure 5 The effect of rubber modifiers upon fracture surface energy (G_i) of C600PA resin.

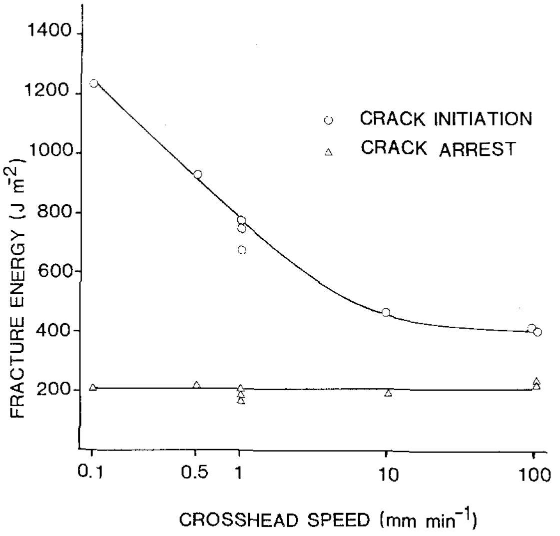

Figure 6 The effect of testing rate upon initiation (G_i) and arrest (G_a) fracture surface energy of C392 resin modified with 9 pph CRC1008 rubber.

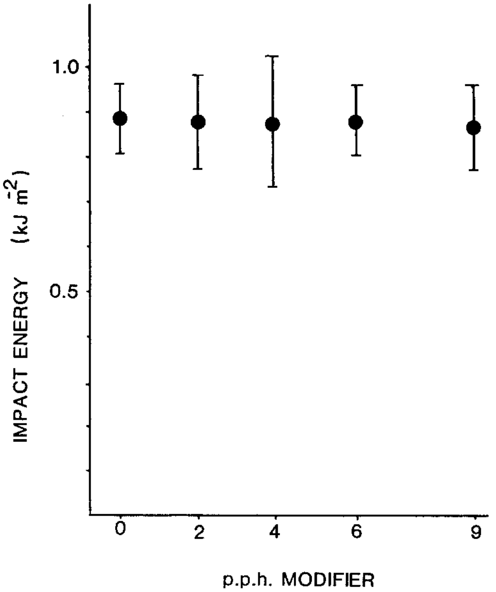

Figure 7 The effect of CRC1008 rubber modifier upon notched Charpy impact energy for C392 resin.

rubber have no significant effect upon notched impact energy.

Unnotched impact energies (Fig. 9) were considerably higher than the notched ones, and showed more scatter. As with the unnotched impact tests no significant changes in energy were seen as rubber content was increased.

3.3. Heat distortion temperature

The effect of rubber modification on heat distortion temperature (HDT) is illustrated in Figs. 10 and 11. In C392 resin, HTE rubber caused a rapid fall in HDT from 90 to 75° C at 5 pph modifier level, but further additions up to 15 pph rubber had no effect. C600PA resin showed a similar fall in HDT, from 94 to 80° C, with additions of 15 pph rubber, but this was more gradual, over the range investigated. The HDT of C392 resin was little affected by additions of up to 3 pph CTBN and VTBN rubbers; C600PA did, however, show some deterioration in HDT with additions of CTBN.

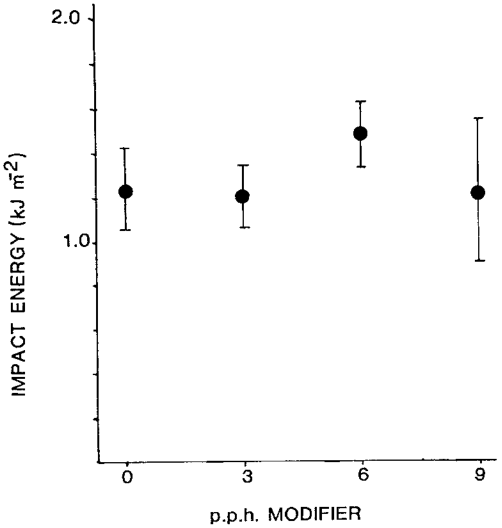

Figure 8 The effect of CRC1008 rubber modifier upon notched Charpy impact energy for C600PA resin.

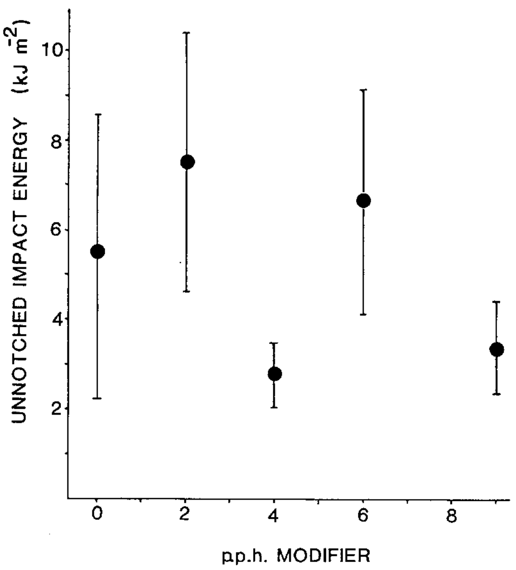

Figure 9 The effect of CRC1008 rubber modifier upon unnotched Charpy impact energy for C392 resin.

Unexpectedly, CRC1008 rubber additions resulted in increased HDT, in both resin systems. In C392 resin, additions of this rubber caused an initial drop in HDT of 8° C at around 2 pph rubber, but further modifications caused the HDT to rise to 3° C below that of the untoughened resin, at 9 pph rubber. In C600PA resin, HDT rose to around 6 pph rubber, and then dropped off with further additions. HDT at 9 pph rubber concentration was the same as that of the untoughened resin.

3.4. Modulus

Fig. 12 shows the effect of rubber modification upon elastic modulus of toughened resins. All rubber additions resulted in decreased stiffness, and the CRC1008 modifier was not notably worse than the others. Nine pph additions of CRC1008 rubber to C392 resin resulted in a

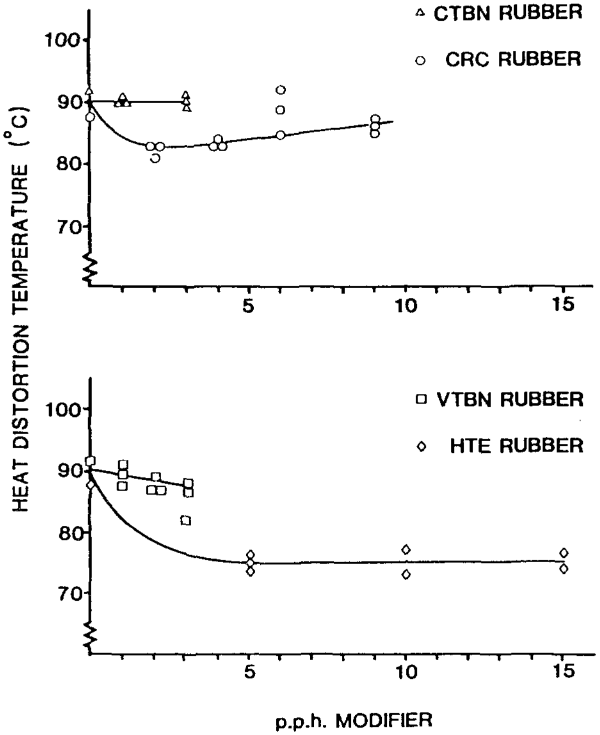

Figure 10 The effect of rubber modifiers upon heat distortion temperature (HDT) for C392 resin (BS 2782: Method 351A, 0.45 MPa).

25% decrease in modulus; for C600PA resin the decrease was 20%.

3.5. Plane strain compression testing

Additions of CRC rubber had considerable effect upon the stress–strain behaviour of C392 resin. The unmodified resin showed no evidence of yielding or plastic deformation. Load increased in a linear elastic manner, and the specimen failed with little deviation of the load/deflection curve

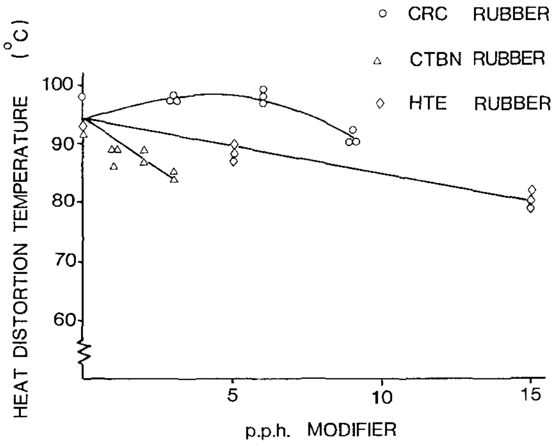

Figure 11 The effect of rubber modifiers upon heat distortion temperature (HDT) for C600PA resin (BS2782: Method 351A, 0.45 MPa).

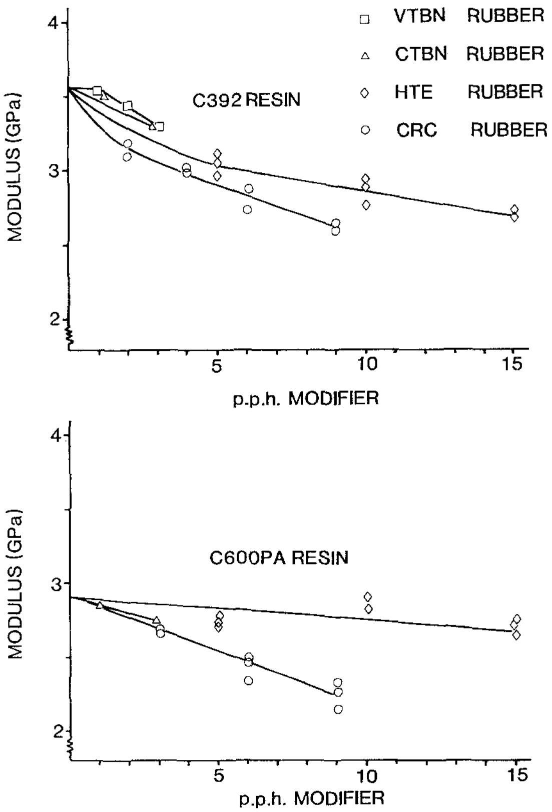

Figure 12 The effect of rubber modifiers upon stiffness of C600PA and C392 resins.

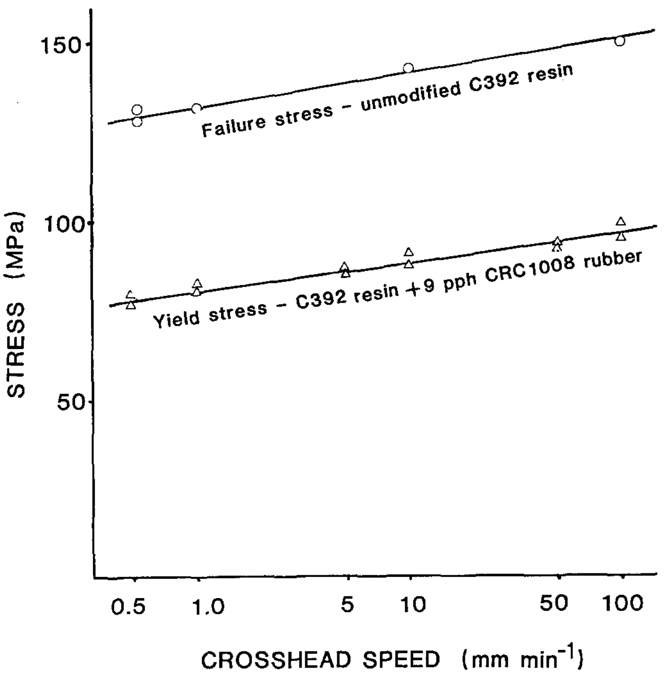

Figure 13 The effect of testing speed upon (a) failure stress in unmodified C392 resin, and (b) yield stress in C392 resin modified with 9 pph CRC1008 rubber.

from a straight line. Fig. 13 shows the variation of failure stress with speed of testing, for unmodified C392 resins. As expected, there was some increase in tensile strength with testing rate, but this was small, about 9 MPa per decade increase in crosshead speed.

In the resin toughened with 9 pph CRC rubber, the stress–strain behaviour was modified, and plastic yielding occurred at considerably lower tensile stresses. Load increased in a linear elastic manner, up to the yield point, but subsequently maintained a plateau value, until near failure, when some load increase occurred, due to friction effects between the plaque and the plates. Fig. 13 shows the variation of yield stress with speed of testing, for modified C392 resin. At the lowest crosshead speed, the yield stress was 78 MPa, compared with a failure stress of 129 MPa in unmodified resin. Yield stress increased with rate of testing, but this increase was again small, about 8 MPa per decade increase in crosshead speed.

4. Discussion

4.1. Effect of Testing Speed upon Resin Toughness

Fracture toughness results obtained in this investigation showed that resin toughness is strongly dependent upon speed of testing. In CRC toughened polyesters, resins showed large improvements in G_i at slow testing speeds, whereas under high rate and impact conditions, little or no improvement in toughness or impact energy was seen, G_a was, however, independent of testing speed. It may be concluded from these observations that the factors which affect crack initiation are dependent upon testing speed, whereas those affecting crack arrest are independent of it.

Similar observations to those reported here have been made in other thermoset systems by Phillips *et al.* [13]. They showed that, in double torsion tests upon untoughened epoxy resin, G_i decreased linearly as $\log_{10}$ crosshead speed increased, whereas G_a was independent of test speed. This type of behaviour may be explained by considering the rate dependence of deformation at the crack tip. During slip–stick deformation, cracks are initiated from within the region of crack arrest, formed after the previous crack jump, when the crack front is stationary, or moving at very low velocities (see Part 2 of this paper). In this situation, plastic deformation adjacent to the crack tip, and associated crack blunting, can occur, and the degree of crack tip deformation will be dependent upon the material yield stress, which is itself dependent upon deformation rate (Fig. 13). Thus, resins which are fracture toughness tested at slow testing rates will develop zones of plastic deformation around the crack tip, which allow larger specimen loads to be applied before the crack tip stress intensity is sufficient to cause rapid crack propagation. As crosshead speed is increased, the material yield stress increases (Fig. 13), so less plastic deformation can occur at the crack tip, and rapid crack propagation is initiated at lower load levels, giving lower values of G_i.

A different fracture régime is, however, operative during crack arrest. Once crack initiation has occurred and the crack front has passed into regions of material away from the influence of the arrest zone, then the new sharp crack front will be subjected to a stress intensity which is far greater than that needed to propagate the crack through undeformed material. The crack is, therefore, highly unstable and will accelerate to very high crack velocities. At these high crack velocities, there is no time for significant plastic deformation to occur at the crack tip, so the crack runs unhindered until the stored energy in the system is dissipated, and the fracture surface energy falls below the critical energy for crack arrest, G_a. Since the plastic deformation, occurring during the load increase between crack jumps, always causes excess energy to be stored in the material, high crack velocities will always be attained during crack jumping. The attainment of these uniformly high crack velocities over a wide range of testing speeds, make G_a independent of test rate, thus explaining the horizontal line for arrest energy shown in Fig. 6. G_a may, therefore, be considered to be a more fundamental characteristic of a given resin formulation than G_i, since it is dependent only upon resin composition, whereas G_i is dependent upon both composition and test rate. In practical terms, however, G_a is of little interest, since the critical criterion in fracture testing is to determine what loads or stress intensities a material can be subjected to before significant crack propagation occurs, and these are best characterized from values of initiation toughness.

The dependence of toughness upon testing speed also explains why impact energy was found to be unaffected by rubber modification. The rate of loading in impact was very high compared with even the highest loading rate used in double torsion testing. Fig. 6 shows that fracture toughness for crack initiation in rubber toughened polyester is highly sensitive to testing rate, and decreases rapidly as rate of testing increases. At impact rates, it might, therefore, be expected that G_i would be less sensitive to rubber additions than during slow testing. The fact that the overall energy levels in impact are higher than those recorded in the double torsion test may be attributed to two factors. Firstly, the notches in the prenotched Charpy specimens were not as sharp as the cracks formed by crack propagation during the double torsion test, so much higher energies were required to initiate cracking during impact testing. Secondly, the cracks did not always propagate straight across the specimens, so unrealistically large values of fracture energy were obtained. In unnotched impact, even larger energies were required to initiate fracture, and multiple cracking was sometimes seen in failed specimens. This explains why energies recorded in unnotched impact were even higher than those seen in notched, and why there is a large degree of scatter in the unnotched impact results.

5. Conclusions

Additions of reactive liquid rubber modifiers to polyester resins improved resin toughness. The magnitude of the toughening effect was dependent upon the compatibility of the rubber with the resin.

Additions of carboxyl and vinyl terminated butadiene acrylonitrile, which have relatively poor compatibility with polyester resin, produced only modest improvements in resin fracture toughness. Hydroxyl terminated polyether rubber, which has good compatibility with polyester resin, also gave small improvements in toughness even though levels of modification were much higher. CRC1008, the modified butadiene–acrylonitrile rubber produced much larger increases in toughness; additions of 9 pph of this rubber gave eight-fold improvements in fracture surface energy, in both of the resin systems investigated. The toughening effect was highly dependent upon rate of testing; fracture surface energy decreased markedly as testing rate increased. Rubber modification did not increase impact energy.

Rubber additions caused some deterioration in the stiffness and thermal stability of polyester resin. The effect of CRC1008 rubber upon modulus was not significantly worse than that of the other modifiers. Heat distortion temperature was less severely effected by CRC1008 rubber than by the other systems. Additions of this rubber caused increases in HDT at some levels of modification.

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