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The effect of crosslink density on the fracture toughness of core–shell modified epoxy resins

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It has long been recognized that many epoxy resins offering a high glass transition temperature are inherently brittle materials absorbing insignificant amounts of energy during the fracture process. In an attempt to trigger energy-dissipating mechanisms in brittle epoxy resins, a number of workers have investigated the potential benefits of incorporating small inclusions such as rubber particles [1–5], thermoplastic spheres [6–8] and, more recently, core–shell particles consisting of a rubbery core surrounded by a thermoplastic shell [9]. Core–shell modified epoxies have recently attracted interest since an unusual craze-like damage has been observed in such systems [9]. At present, however, it is not clear if similar toughening mechanisms operate in highly crosslinked epoxy resins similar to those currently used in the aerospace industry.

A number of workers have shown that the degree of toughness enhancement in a particle-modified epoxy depends upon the crosslink density of the network structure [10–12]. It is generally recognized that epoxy resins which have a high crosslink density, and therefore a high glass transition temperature T_g, are more difficult to toughen than their low crosslink density counterparts. This difficulty in achieving high toughness in certain epoxies appears to be related to the materials' inability to undergo appreciable plastic flow in high stress fields.

The objective of this work was to investigate the influence of crosslink density of the toughness and the failure mechanisms in a series of core–shell modified epoxy resins. The materials examined and the curing procedures employed in this study are summarized in Table I.

Two epoxide phenolic novolac resins, Araldite® EPN1138 and Araldite® EPN1139, and two hardeners, bisphenol A (4,4′-isopropylidenediphenol) and DDS (4,4′-diamino diphenyl sulphone), were used. The bisphenol A cured systems resulted in materials A, B and C and the DDS-cured systems in materials D and E. The average crosslink density within each of the five epoxy systems was determined from rubber elasticity theory following the procedure used by Fischer [13], as well as from stoichiometry. The glass transition temperature of each polymer was measured by differential scanning calorimetry (DSC) at a heating rate of $20\,\mathrm{K\,min^{-1}}$.

The core–shell modifier was supplied in powder form consisting of an acrylic/styrene shell and a butadiene-styrene core. The diameters of the particles lay in the range 0.1–0.2 μm. The modifier was added to the pre-polymer and stirred with a high speed mixer prior to the addition of the hardener. In general, a good distribution of the particles was achieved although large agglomerations were occasionally observed. For simplicity, the core–shell modified systems are prefixed by the letter M.

The mode I critical strain energy release rate G_{Ic} for each material was determined using the compact tension specimen geometry in accordance with the

TABLE I Summary of the compositions, curing schedules and physical properties of the epoxy resins examined in this study

Polymer	Resin		hardener		Curing procedure[b]	M_R[c] (g mol^{-1})	M_C[d] (g mol^{-1})	T_g (°C)
	EPN 1138	EPN 1139	BA[a]	DDS				
A	10	90	64	0	K	1927	1886	81
B	50	50	64	0	K	751	706	90
C	100	0	64	0	K	494	458	100
D	0	100	0	35	L	247	230	198
E	100	0	0	35	L	168	122	235

[a] 0.16 g 2-ethyl-4-methyl-imidazole added.
[b] K, cure for 2 h at 140 °C and 2 h at 180 °C; L, cure for 1 h at 180 °C and 2 h at 210 °C.
[c] Averaged molecular mass between crosslinks as calculated from stoichiometry.
[d] Molecular mass measured experimentally.

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European Structural Integrity Society (ESIS) protocol [14, 15]. The failure mechanisms and energy-dissipating mechanisms occurring within the crack region were investigated by preparing thin polished sections removed from double-notched four-point bend specimens [16].

Table I also shows the predicted and measured values of molecular weight between crosslinks, M_R and M_C, respectively, as well as the glass transition temperatures of the five polymers. From the table, it is clear that the materials examined in this study span a large range of crosslink densities. There was good agreement between the predicted and measured values of molecular weight between crosslinks, with the former tending to be slightly higher. As would be expected, materials D and E, which were based on the DDS hardener, had the highest crosslink densities and offered the highest glass transitions temperatures.

DSC scans of the modified epoxies indicated that their glass transition temperatures were unchanged and it is believed that the crosslink densities of the five materials were unaffected by the incorporation of the core–shell particles.

Fig. 1 and Table II summarize the variation of G_{Ic} with the measured molecular weight between crosslinks, M_C, for the neat and modified resins. The pure resin data exhibited a rapid increase in G_{Ic} with M_C up to 700 g mol^{-1} and then a less rapid increase beyond this value. It is interesting to note that very similar trends are also apparent in the modified-epoxy data. Clearly, the incorporation of the sub-micrometre particles results in an increase in toughness in all five systems. However, the relative improvement in G_{Ic} is dictated by the crosslink density of the host matrix. This effect is shown in Fig. 2, where the relative improvement in G_{Ic} is presented as a function of M_C. The modification of material E, which had the lowest value of M_C, produced a threefold increase in G_{Ic}, while the incorporation of the particles into material B yielded an eightfold increase in G_{Ic}. Increasing the molecular weight between crosslinks beyond 700 g mol^{-1} does not appear to bring any added benefit in terms of toughness enhancement.

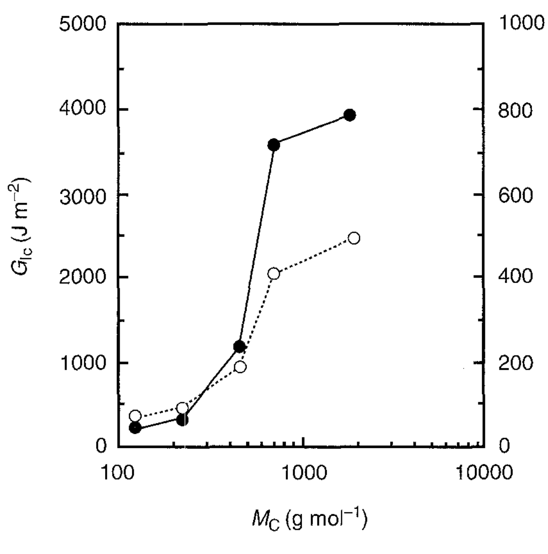

Figure 1 Variation of the mode I strain energy release rate, G_{Ic}, with molecular weight between crosslinks for the (○) pure and (●) modified epoxy resins. Note the difference between the two scales: the left-hand scale applies to the modified resin; the right-hand scale to the pure resin.

TABLE II Summary of the mode I strain energy release data for the neat and modified systems

Polymer	M_C (g mol^{-1})	G_{Ic} neat resin (J m^{-2})	G_{Ic} modified resin (J m^{-2})
A	1886	498	3961
B	706	410	3631
C	458	192	1205
D	230	88	335
E	122	70	218

The failure mechanisms at the tip of the crack were investigated by polishing thin sections removed from the unbroken notch of double-notched four-point bend specimens [16]. Fig. 3a shows the crack tip region in material MA when viewed between crossed-polars, where a large process zone is clearly evident. A closer examination of the edge of the process zone suggested that this region consisted of an agglomeration of small diffuse bands. Sue [9] observed finger-like features in a core–shell modified epoxy and likened their appearance to that of a craze. Using transmission electron microscopy (TEM) techniques, Sue [9] showed that the fine fingers within the process zone consisted of rows of cavitated particles, and suggested that the formation of these fingers serves to relieve the local triaxial stress field and shear yielding. A TEM analysis of the MA system in our laboratory showed that rubber cavitation had occurred along a series of trajectories within the process zone [17, 18]. In this study, it also became apparent that considerable shear deformation and void growth had also occurred once the particles had cavitated [19]. Huang and Kinloch [20] suggested that at higher temperatures, i.e. when the yield stress of the material is low, shear deformation

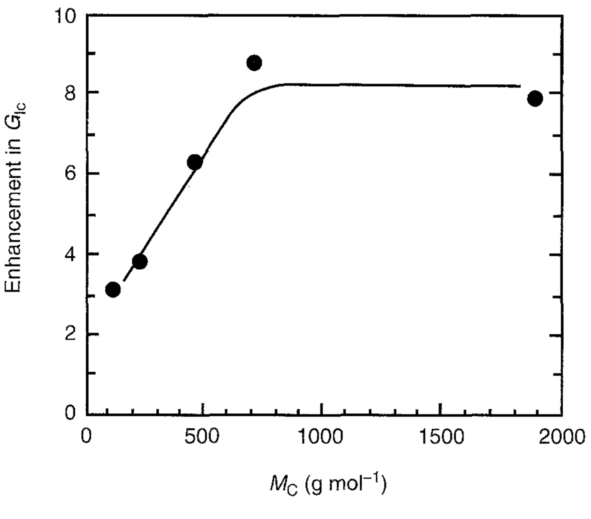

Figure 2 The relative improvement in toughness associated with the incorporation of core–shell particles.

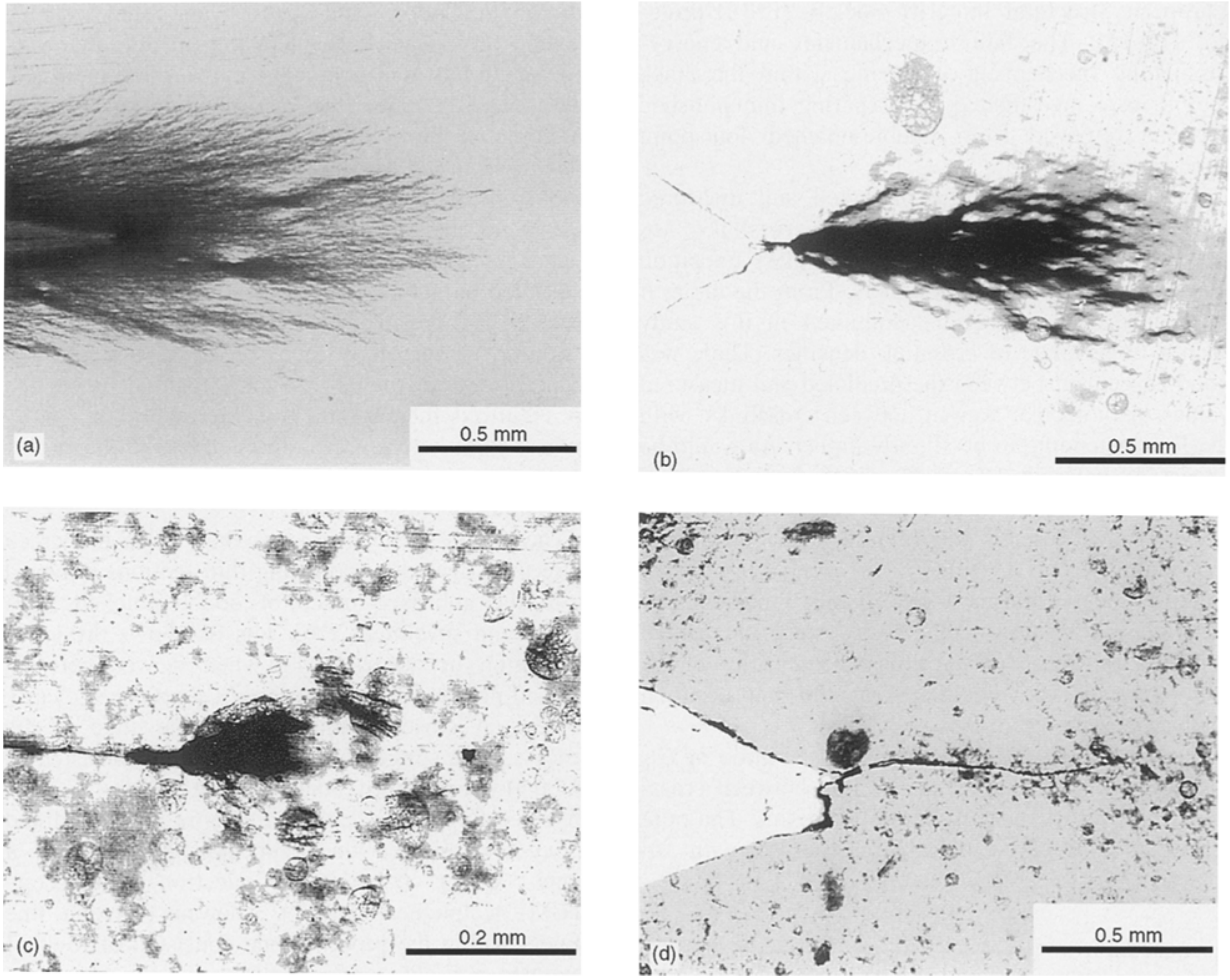

Figure 3 Polished thin sections examined between crossed-polars: (a) MA system, (b) MB system, (c) MC system and (d) MD system.

and void growth were responsible for significant energy dissipation, and hence appreciable toughening, in a carboxyl-terminated butadiene acrylonitrile (CTBN) modified DGEBA epoxy resin. Here, the TEM observations of the lightly crosslinked MA system appear to support this view.

Fig. 3b shows the crack tip region from material MB. Again, a large process zone developed during loading. However, the bands were large and coarser than those observed in the MA system. A more detailed TEM study indicated that the predominant failure modes were again cavitation, void growth and shear yielding. Damage in the crack tip region in material MC (Fig. 3c) was found to be more localized than in the MA and MB systems. Rubber cavitation within the particles was observed in regions very close to the crack tip. A more detailed examination of the crack tip region indicated that the amount of void growth occurring in this system was less than in MA and MB. It is interesting to note that the value of G_{Ic} for this material was only half of that measured in MA and MB. It is believed that much of this difference is related to the limited amount of void growth, as well as the reduced amount of shear yielding.

Finally, no process zone or damage accumulation was observed in either of the relatively brittle MD or ME systems (Fig. 3d). It is quite possible that some rubber cavitation did occur. However, it is believed that the network structure is too rigid to facilitate either void growth or appreciable shear yielding. Nevertheless, the addition of the core–shell modifier did result in a threefold increase in G_{Ic} in the most brittle system, ME, suggesting that a toughening mechanism had been activated. It is believed that particle bridging and crack pinning are the predominant mechanisms in these systems at room temperature. The former has been recognized as a potential toughening mechanism in thermoplastic-modified epoxies [21] and rubber-modified epoxies at low temperatures [20]. Crack pinning, where the presence of adjacent particles is assumed to pin the crack, has been proposed as a toughening mechanism in hard-particle epoxies [22].

The results have shown that core–shell particles can improve the toughness of a wide range of epoxy resins. The degree of toughness enhancement has been shown to depend upon the degree of crosslinking in the epoxy matrix. Energy absorption in the toughest systems appears to be a result of cavitation, void growth and shear yielding, whereas particle bridging and perhaps crack-pinning represent the most significant mechanisms in the highly crosslinked systems.

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