The role of cavitation and debonding in the toughening of core–shell rubber modified epoxy systems

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Epoxy systems EPN/BA and EPN/DDS having significantly different cross-link densities have been modified using core–shell rubber particles. The toughening mechanisms have been investigated and the results show that cavitation and particle–matrix debonding play different roles in the low and high cross-link density epoxy resins.

1. Introduction

It has been known for more than two decades that the toughening of low cross-link density epoxies via elastomeric modification can be very effective [1]. Understanding the toughening mechanisms through which the elastomeric modifier influences the response of the matrix during the toughening process is important and a great deal of work has been done in this area. Pearson and Yee [2, 3] stated that cavitation of the rubber particles followed by shear deformation within the matrix are the major toughening mechanisms in a CTBN rubber-modified low cross-link density epoxy. Huang and Kinloch [4] reported that cavitation (or debonding) of the rubbery particles allowing plastic void growth to occur in the epoxy matrix is a source of considerable energy dissipation. More recently, Sue [5] used a grafted-rubber concentrate core–shell modifier to toughen a DGEBA epoxy and observed a craze-like damage feature in the crack tip region. Transmission electron micrographs showed highly localized line arrays of cavitated rubber particles linked by deformed matrix material. This feature was referred to as a "croid", which is derived from the words "crack" and "void". To date, little success has been achieved in the toughening of highly cross-linked epoxy resins [6, 7]. In such resins particle bridging is believed to be a primary toughening mechanism [4, 8]. The poor toughenability of those resins can simply be explained by the fact that highly cross-linked systems do not readily undergo plastic deformation. However, the precise mechanisms need to be investigated in greater detail. It appears that cavitation is, in many cases, extremely important and apparently necessary. It has not yet, however, been established to what extent cavitation influences toughening and why its effect is different in low and high cross-link density epoxies.

In the present work, a core–shell rubber modifier was used to toughen both low and high cross-link density epoxy systems. Because the main objective of this study was to investigate the nature of the intrinsic toughening mechanisms as a function of cross-link density, a fixed value of toughener concentration has been used.

2. Experimental procedure

A mixture of prepolymer Epoxide Phenolic Novolac resins ®Araldite EPN1138 and EPN1139 (Ciba-Giegy AG) cured with bisphenol A (BA) yielded the lightly cross-linked system "A" (EPN/BA), see Table I. Prepolymer EPN1139 cured with diamino diphenyl sulphone (DDS) resulted in the highly cross-linked system "D" (EPN/DDS). The toughener used in this study was a core–shell impact modifier with an acrylic/styrene shell and a styrene/butadiene rubber core. A fixed concentration of 10 p.h.r. (parts per hundred parts of resin by weight) of core–shell modifier was added to systems A and D, resulting in the modified systems "RA" and "RD", respectively.

In order to identify and analyse the fundamental mechanisms of deformation and fracture occurring within these materials, mechanical, acoustical, optical and electron microscopical methods have been used. Plane strain compression tests were employed to determine the material's yield stress. The mode I fracture toughness, K_{IC}, of the pure and modified systems, was determined according to the ESIS protocol [9] as a function of temperature, using the compact tension specimen geometry at a loading rate of $2\ \text{mm min}^{-1}$. Thin sections were taken from the mid-section (plane strain region) of the subcritical crack damage zone and observed using transmission optical microscopy. The fracture surfaces of the compact tension

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TABLE I The epoxy systems examined

Polymer	Resin (g)		Hardener (g)			Procedure[a]	Characterization	
	EPN1138	EPN1139	BA	CAT[b]	DDS		M_c(g mol^{-1})	T_g(°C)
A	10	90	64	0.16	0	K	1886	81
D	0	100	0	0	35	L	230	198

[a] Procedure K: cure 2 h at 140 °C and 2 h at 180 °C. Procedure L: cure 1 h at 180 °C and 2 h at 210 °C.
[b] CAT: 2-ethyl-4-methyl-imidazole.

specimens were examined by scanning electron microscopy (SEM). A Weiss Messtechnik acoustic emission device was used to record emissions occurring during the material's failure process by placing an acoustic emission sensor on a number of dog-bone tensile specimens. Here, an acoustic emission threshold level of 50 dB and a loading rate 2 mm min^{-1} was used.

3. Results and discussion

The compressive yield stress of the four systems has been measured as a function of temperature (Fig. 1). As expected, the yield stress decreases in an approximately monotonical fashion with temperature. The temperature dependence of the mode I fracture toughness, K_{IC}, was subsequently determined and is shown in Fig. 2. There is a rather small temperature effect on the toughness of the unmodified epoxy system A in the region between 23 and 60 °C. This observation is ascribed to the fact that in the determination of K_q the increase in specimen compliance and the associated non-linearity effects due to the increased temperature are just offsetting the higher forces attainable due to the appearance of a crack-tip processing zone (apparent crack blunting). On the other hand, the unmodified highly cross-linked system D is rather brittle at room temperature. It is for this reason that the effect of "crack blunting" is more pronounced, leading to a much stronger temperature dependency in system D. Logically, the low cross-link density system A has a distinctly higher value of K_{IC} at room temperature than system D, because its lightly cross-linked molecular network allows for more plastic deformation and therefore more extensive crack blunting prior to fracture.

As a result of the addition of the core–shell rubber modifier, the system RA exhibits an improvement of around 300% in K_{IC} at room temperature. Similar observations have been reported and explained by other workers [6, 7, 10]. The toughening effect in system RD is not as significant as that observed above (around 100%). However, the toughness of RD increases continuously with temperature in the range 80–140 °C (whereas the yield stress decreases) and the toughness is very close to that of the pure resin D. At 160 °C there is a cross-over of the K_{IC} values (Fig. 2). Overall, RD does not show as much improvement with temperature as the pure resin does. The toughening mechanisms in systems RA and RD seem, therefore, to be different.

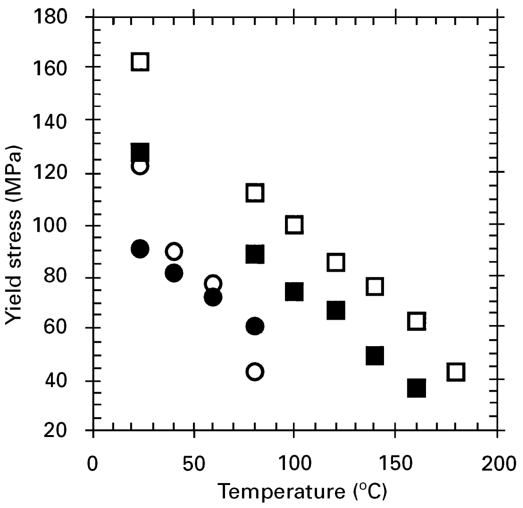

Figure 1 Yield stress versus temperature for the pure and modified resins. (○) polymer A, (□) polymer D, (●) polymer RA, (■) polymer RD.

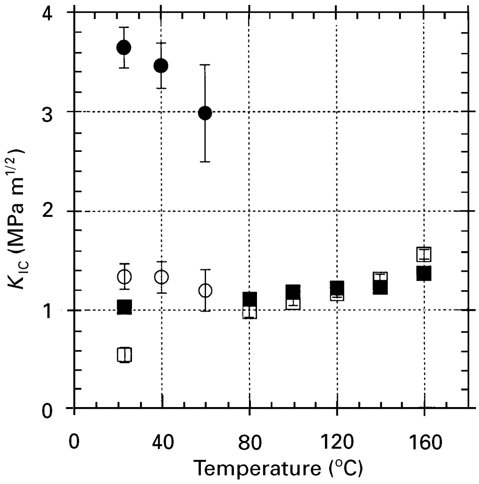

Figure 2 Mode I fracture toughness versus temperature. For key, see Fig. 1.

Similar differences are observed with respect to the morphological changes ahead of the crack tip in these four systems. Hardly any features are apparent on the fracture surface of system A at room temperature. However, a prominent craze-like feature observed in the crack-tip damage zone in the modified system RA (Fig. 3), which was described by Sue [5] as a craze-like arrangement of voids which he referred to as "croids".

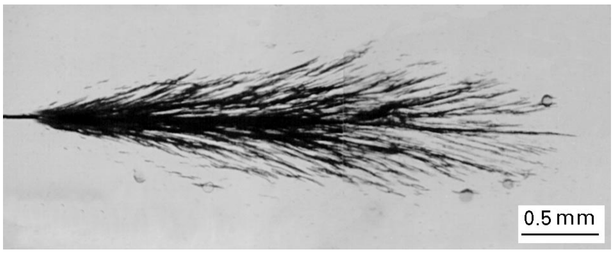

Figure 3 Transmission optical micrograph of plane-strain crack tip damage zone as typically observed in system RA in the temperature range between 23 and 60 °C.

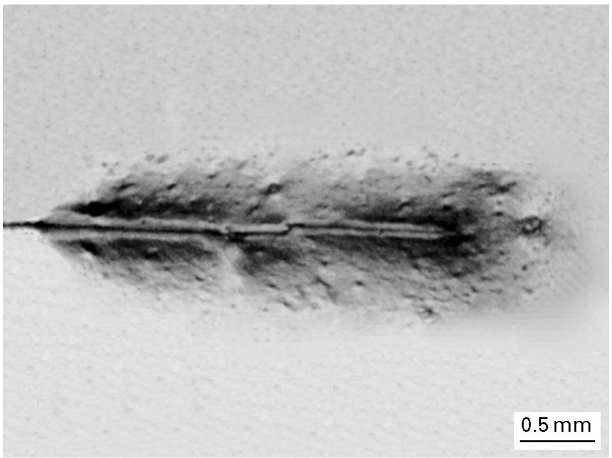

Figure 4 Transmission optical micrograph of plane-strain crack tip damage zone in RD, 160 °C.

Brittle fracture without any process zone in front of the crack tip occurred in system RD at temperatures between 23 and 140 °C, resulting in an almost featureless fracture surface; it was only at 160 °C that a relatively small process zone was observed (Fig. 4).

The fracture surfaces of the modified systems tested at the two extremes of temperature were also examined under a scanning electron microscope (SEM). Two different morphologies were observed on the fracture surface of system RA, a stress-whitened region associated with stable, slow crack growth, and a smoother area related to unstable fast crack growth. Fig. 5a shows the slow to fast crack transition region. The detailed features appearing in this region are presented in Fig. 5b and c, respectively. In the stress-whitened region (Fig. 5b) voids can clearly be observed with diameters of between 0.2 and 0.5 μm which is considerably larger than the original particle size of 0.1–0.2 μm. It must be concluded, therefore, that considerable plastic deformation of the matrix around the particles had occurred. According to general experience, this indicates that the stress necessary for matrix flow had been attained around the particles. Guild and Young [12] have calculated the stress concentration factor at the particle–matrix interface, and have shown that the maximum value at the particle equator is 2.4 for 10% by weight modified systems (approximately 20% volume fraction).

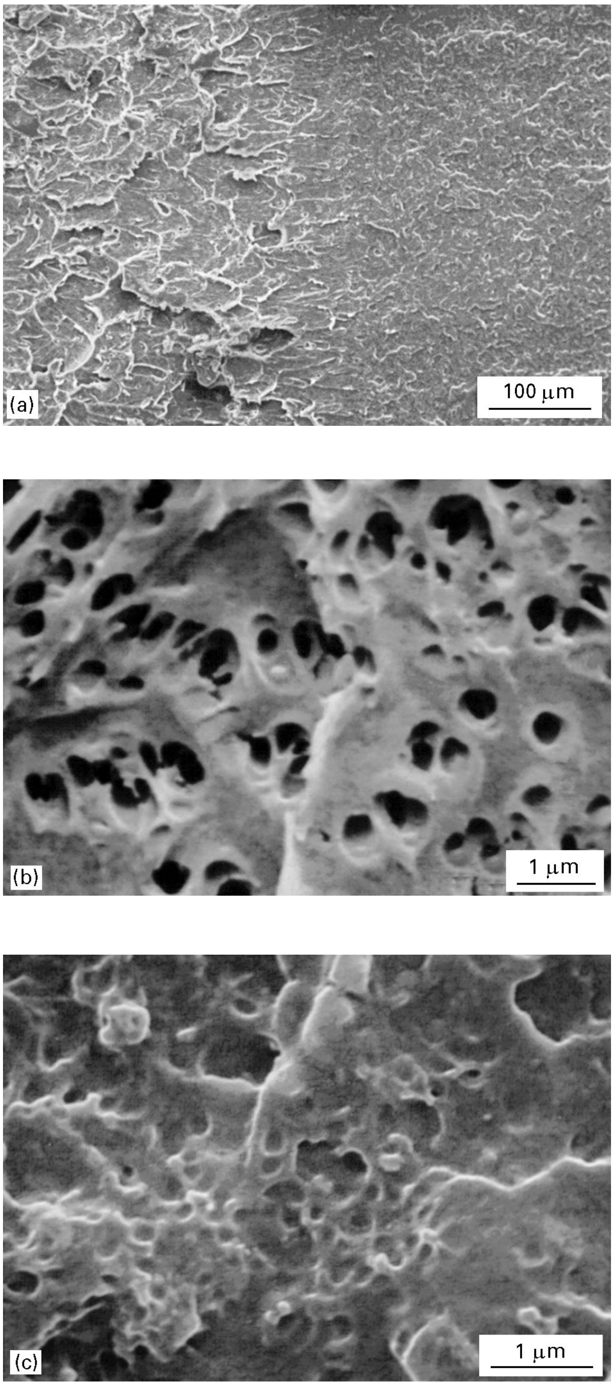

Figure 5 Scanning electron micrographs of fracture surfaces of system RA, tested at 23 °C, (a) showing the slow crack growth to fast fracture transition area, crack propagating from left to right; (b) stress-whitened area; (c) fast fracture area.

Apart from voids having diameters of around 0.1–0.2 μm (Fig. 6), the fracture surface of system RD tested at room temperature was essentially featureless up to a magnification of × 10 000. The voids were roughly the same size as that of the modifiers. This means that no detectable void growth or shear deformation have occurred during the failure process. Because the modifier particles cannot be seen in the SEM it is very difficult to say whether or not cavitation has occurred. However, recent calculations by Fond *et al.* [14] of the total elastic energy of a system comprised of core–shell modifier particles in a polymer matrix have shown that particle cavitation can already occur

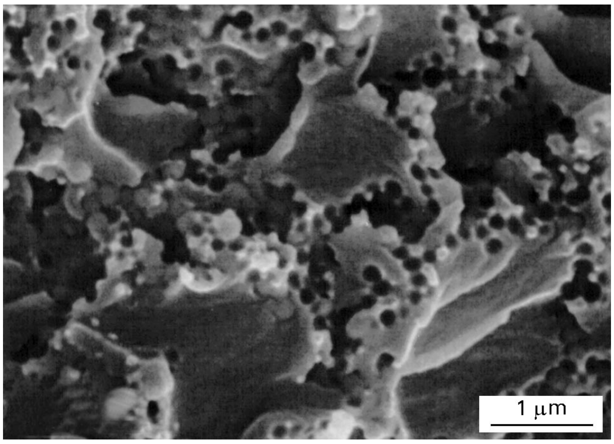

Figure 6 Scanning electron micrograph of a fracture surface of system RD, tested at 23 °C.

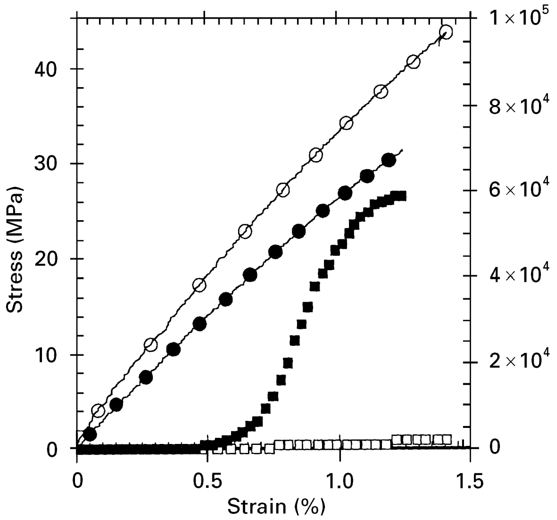

Figure 7 Acoustic emission results. (○, ●) Stress, (□, ■) AE events for (○, □) System D, (●, ■) system RD.

at dilatational strains of the order of a few per cent. In fact, an acoustic emission analysis (Fig. 7) has shown that emissions occurred in system RD at strains between 0.5% and 1%, whilst very few were detected in system D at this level of deformation. It can be concluded, therefore, that the presence of the secondary phase at a strain level of less than 1% gives rise to local, noise-emitting events. Not yet knowing the exact mechanism, it is at present assumed that matrix cracking occurs in the proximity of cavitated or debounded particles [15].

In the case of the RD specimen tested at 160 °C, a slightly stress-whitened region was observed, this corresponds to the left-hand side of Fig. 8a. In the same figure, the transition from slow to fast crack growth can be identified. The rather limited amount of local plastic deformation in the slow crack growth area becomes apparent from Fig. 8b. The size of many of the voids may just be sufficient to account for particle cavitation. The rapid crack-growth region (Fig. 8c) shows very shallow cavities without any significant evidence of plastic deformation. It is believed that these shallow cavities were caused by the failure of particle–matrix interface during the rapid tearing of the particles away from the matrix. This would also explain why the toughness of material RD at 160 °C is lower than that of resin D. It is interesting to note that similar cavities were also observed in the slow crack growth area of RD, suggesting that failure of the particle–matrix interface (in other words "debonding") may also occur during this phase of the fracture process.

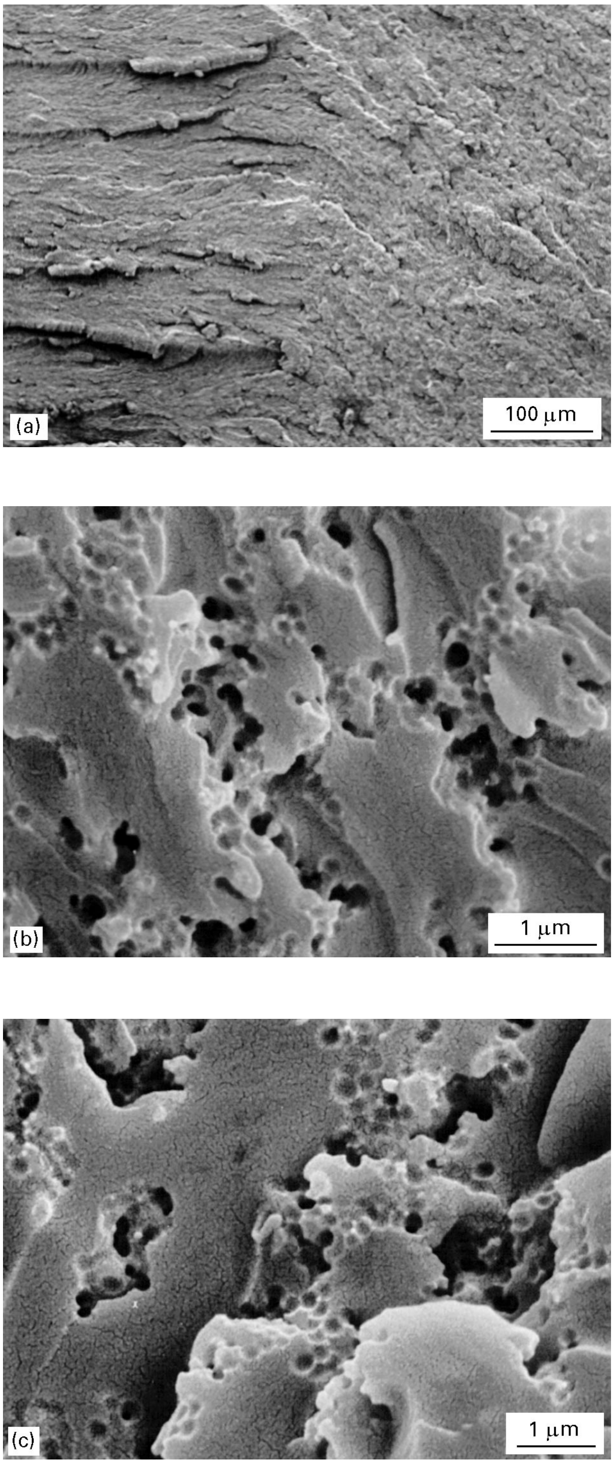

Figure 8 Scanning electron micrographs of fracture surfaces of system RD, tested at 160 °C. (a) Slow crack growth to fast fracture transition area, crack propagating from left to right; (b) stress-whitened area, (c) fast fracture area.

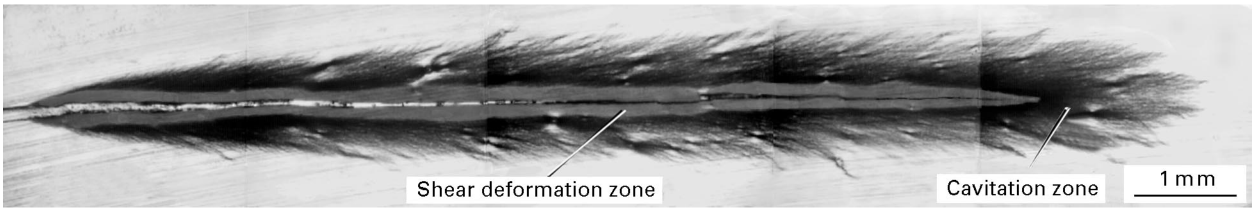

Figure 9 Transmission micrograph of a sub-critical crack in system RA, tested at 60 °C.

4. Conclusion

The mechanical and morphological observations concerning the four different systems can well be explained by considering the differences between the yield stress of a system at a given temperature and the stress level for plastic void expansion, cavitation or debonding, and shear yielding. It is assumed that in the modified resin RA, some particle cavitation occurs as a result of elastic strains in front of the crack tip. The stress concentration around the cavitated particles causes other particles in the same plane to cavitate as well. This triggers plastic deformation of the matrix material between and around the particles giving rise to the feather-like features of "croids" [5]. Further plastic deformation results to such an extent that shear yielding occurs extensively in the centre of the process zone (see Fig. 9). Resin RA seems to fracture according to this same yield-after-cavitation mechanism in the whole temperature range studied. It is therefore appropriate that the toughness of RA depends on the matrix yield stress.

The situation in systems D and RD is different. The yield stress in D is significantly higher and the strain to rupture smaller than in A. The addition of the modifier particles reduces the stiffness of the material and permits some crack blunting. In fact, the addition of 10 p.h.r. modifier to resin D or the increase in temperature to 80 °C lead to comparable values of yield stress and to roughly identical values of K_{IC}. At all temperatures up to 140 °C fracture of resins D and RD occurs without any visible process zone. The acoustic emission results have confirmed that there is *action* on the rubber particles, the absence of croids and of a plastic deformation zone, however, shows that this action does not trigger any interaction between the particles subsequently giving rise to noticeable matrix deformation. The condition for rapid crack propagation is attained in this temperature range before stresses can effectively be relieved by local or general yielding. It is only at the highest of the investigated temperatures that a processing zone with croids and a plastic deformed region is observed. However, the limited deformability of resin D limits the size of this zone.

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