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Role of particle cavitation in rubber-toughened epoxies: 1. Microvoid toughening

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The significance of particle cavitation in rubber-toughened polymers remains controversial. While some researchers believe void formation promotes shear yielding in the polymer matrix, others consider it as a secondary energy consuming process. The research described here was undertaken to further elucidate the role of particle cavitation in toughening through comparative examination of epoxies modified by conventional rubber modifiers and hollow plastic particles. The results of this study illustrate that rubber particles with different cavitation resistance and pre-existing microvoids toughen the present epoxy matrix in the same manner. Therefore, we conclude that the cavitation resistance of the rubbery phase does not directly contribute to toughness, but instead simply allows the matrix to deform by shear. An additional mechanism of microcracking was observed when 40-μm hollow plastic particles were employed. Despite the similar behaviour in fracture toughness testing, rubber particles and microvoids differ considerably in how they affect the compressive yield strength of the blend. The results of this study suggest the possible importance of inter-particle distance in toughening of epoxies. This concept will be examined in part 2 of this study. Copyright © 1996 Elsevier Science Ltd.

(Keywords: rubber-toughened epoxies; cavitation; hollow plastic particle)

INTRODUCTION

Addition of a rubbery particulate phase to a glassy polymer often enhances fracture toughness without significantly compromising the other desirable engineering properties. Successful application of this technique to overcome the inherent brittleness of epoxy resins was first reported in the early 1970s[1,2]. Since then, many investigations have been performed to elucidate the exact role of rubber particles in toughening of brittle epoxies[3–12]. Early models were based on the rubber particle bridging mechanism and claimed that the work consumed in the tearing of the stretched rubber particles across the crack wake contributes significantly to toughening[5,6]. This proposal could not be accepted as a major toughening mechanism since it did not take the role of matrix into account and could not explain other experimental observations. It has been shown that the fracture toughness of rubber-modified epoxies depends strongly on the structure of the matrix; looser epoxy networks result in higher toughness[10,11].

The most recent mechanism proposed for rubber-toughened epoxies is based on cavitation of rubber particles followed by plastic deformation of the matrix[7–10]. It is generally agreed that the major contribution in toughening is due to the plastic deformation of the matrix[10–13]. However, there is a debate on the role of particle cavitation. It is argued that cavitation itself does not consume a considerable amount of energy[13]. However, its influence on the plastic deformation of the matrix and therefore, on the sequence of events in toughening are under question[13,14]. Two main hypotheses in this regard are as follows.

The first hypothesis is that the consequence of cavitation is a local reduction in the bulk modulus and hydrostatic stress component in the vicinity of the crack tip and a corresponding increase of the deviatoric component of stress[12,15]. According to this hypothesis, cavitation of rubber particles occurs at the crack tip upon the build up of a critical hydrostatic stress. As a result, a process zone forms at the tip of the crack. The onset of cavitation and the size of the process zone depend on the cavitation resistance of the rubbery phase[12]. Massive but localized shear banding of the matrix then occurs within this zone of relieved constraint and contributes to toughening[12,15–17]. Evidence of this hypothesis has been reported by the investigators who observed a plastically deformed region within a larger cavitation zone at the onset of unstable crack growth in rubber modified epoxies[12,16]. According to this hypothesis, cavitation of rubber particles promotes shear banding and, therefore, is a prerequisite for massive shear yielding of the matrix[12,15–17].

Li *et al.*[18] were able to suppress cavitation of rubber particles in the fracture process through imposing an external hydrostatic compression. These researchers observed that in the absence of cavitation, rubber-modified resin was no tougher than the next epoxy. However, both neat and modified epoxies were significantly tough under that testing condition. Li *et al.*[18] attributed this observation to the necessity of cavitation in toughening and claimed that rubber particles do not

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induce massive shear yielding, and thus do not improve fracture toughness if cavitation is suppressed. Pearson and Yee[12] also speculated that higher cavitation resistance of rubber particles may further improve the fracture toughness. Their rationale was that delayed particle cavitation, due to higher cavitation resistance, results in the build up of a larger elastic energy prior to shear yielding of the matrix. Larger elastic energy may then cause a faster growth of shear bands and thus, a larger plastic zone forms and a higher toughness is obtained[12].

Lazzeri and Bucknall[19] have recently offered a more detailed explanation of the toughening mechanism in rubber-modified polymers. Their proposal which is parallel to the aforementioned hypothesis, considers cavitation as a promoter for the shear yielding of the matrix. Lazzeri and Bucknall[19] referred some experimental studies that have found the maximum dilation of particles occurring within the shear bands. These researchers, therefore, modelled the effect of cavitation on shear yielding in the form of dilatational bands. According to this model, cavitation which occurs at a certain volumetric strain, lowers the yield stress of the matrix and focuses shear yielding within dilatational bands[19]. Lazzeri and Bucknall[19] did not comment on the influence of cavitation resistance of the rubbery phase on fracture toughness of the blend.

The second hypothesis on the role of cavitation refutes the idea of stress state change and that particle cavitation promotes shear banding. It is claimed that the role of cavitation is to initiate plastic dilatation within the matrix and that this process is independent of shear banding[20,21]. This hypothesis is based on the results of some finite-element analyses which examined the stress fields in a glassy matrix around a rubber particle and a void, i.e. equivalent to a cavitated rubber particle[14,22]. The results of these analyses showed that the stresses in the glassy matrix adjacent to a rubber particle are of a similar magnitude whether the rubber particle has cavitated or not. Using finite-element technique, Huang and Kinloch[23] were able to show that for a given matrix, depending upon the Poisson's ratio and the modulus of rubber particles, cavitation can occur either before or after shear banding. They claimed that a low Poisson's ratio and a high modulus of rubber particles may postpone cavitation after shear banding of the matrix[23].

Huang and Kinloch[20,21] raised the importance of plastic dilation of the matrix around the cavitated particles, also called void growth, as an energy consuming process second to shear banding. They claimed that high bulk modulus of the rubber particles prohibits any volumetric deformation until the rubber particles either cavitate internally or debond from the matrix. Cavitation, in this hypothesis, is therefore the onset of plastic dilation which may occur either before or after shear yielding[23,24]. One of the outcomes of this hypothesis, contrary to that of the first one, is that the cavitation resistance of rubber particles should not play a major role in toughening. Haung and Kinloch[25] examined the toughening efficiency of microvoids in a diglycidyl ether of bisphenol A (DGEBA) epoxy using an unreactive liquid rubber. They found that 1-μm voids, with zero cavitation resistance, were able to increase the fracture energy of their neat resin by almost 90% at a concentration of 17 vol%. Observing this considerable improvement, Huang and Kinloch[25] predicted that they would have obtained even higher toughness if they used reactive liquid rubber which provided chemical bonding to the matrix. They attributed the assertion for higher toughness to the bridging effect and not cavitation resistance of rubber particles.

Table 1 Descriptions of the toughening agents used

Modifier[a]	Description of modifier
CTBN	Carboxyl terminated liquid copolymer of butadiene and acrylonitrile from B.F. Goodrich [Hycar CTBN 1300X8]
MBS–COOH	Structured core-shell latex particles comprised of a methacrylated butadiene–styrene copolymer with acid functionality in the PMMA shell from Rohm & Haas [PARALOID EXL-2611]
HLP-0.4	Hollow latex particles with a styrene–acrylic shell from Rohm & Haas [ROPAQUE OP-62]
HLP-1.0	Similar to HLP-0.4 but larger in size [ROPAQUE HP-91]
HLP-15	Hollow micro-spheres with an acrylic shell from Nobel [EXPANCEL 551 DE 20]
HLP-40	Similar to HLP-15 but larger in size [EXPANCEL 091 DE]

[a] Numbers corresponding to the Hollow Latex Particles (HLP) indicate the size of the modifiers in μm. These particles have a typical shell thickness of equal to or less than 10% of their diameter. MBS–COOH particles used have an average particle size of about 0.2 μm. The average particle size, in the case of CTBN rubber varied with the concentration of modifier (*Table 2*)

The ambiguities about the role of cavitation in the literature seems to be a key issue in understanding the exact role of rubber particles in toughening. Consequently, the objective of this work is to further elucidate the role of particle cavitation in rubber-toughened epoxies. The approach selected for this study is based on employing hollow plastic micro-spheres as pre-cavitated toughening agents. In order to investigate the role of cavitation resistance, the influence of microvoids on mechanical properties of a DGEBA epoxy is compared with that of two conventional rubber modifiers with different cavitation resistance[26]. Our previous investigation[27] showed that at 10 vol% of modifier, micron and sub-micron size voids toughen epoxies in the same manner that conventional rubber modifiers do. This study examines the influences of particle size and volume fraction of modifier in a broader range. A following publication[28] will further analyse the results of this study and explore the importance of inter-particle distance in rubber/microvoid toughened epoxies.

EXPERIMENTAL

Material preparation

The model system used in this study is based on a DGEBA epoxy with an epoxy equivalent weight of 187 g/eq (DER 331 from Dow Chemical Co.). The curing agent used is aminoethyl piperazine (AEP) from Air Products and Chemical, Inc. This is a room temperature crosslinker with a short gelation time which allows processing of microvoid-toughened epoxies. The details of curing schedules employed are as follows.

The stoichiometric ratio of the curing agent and resin were mixed and degassed at room temperature for about 20 min. The solution was then cast into a 6-mm-thick aluminium mould. The cast material was allowed to gel for 1 h at room temperature and then post-cured for 2 h

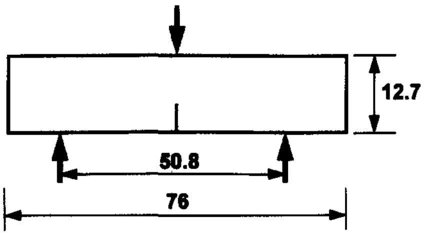

Figure 1 Schematic of the SEN-3PB specimens used for fracture toughness testing. All dimensions are in mm

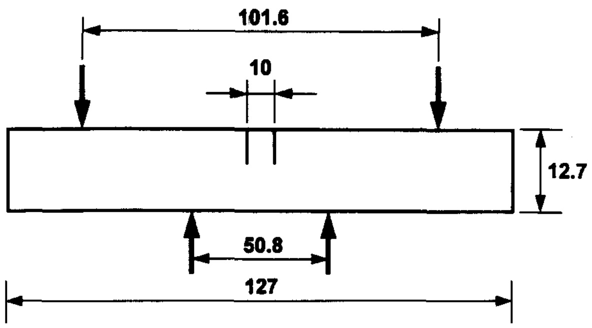

Figure 2 Schematic of the DN-4PB specimens used for observation of the crack tip damage zones. All dimensions are in mm

at 100°C in a circulating air oven. The same curing schedule was employed for all toughened epoxies as well. Modifiers used, including two types of conventional rubber modifiers and four kinds of hollow latex particles (HLP), are listed in *Table 1*.

The modifier content was varied up to 15 phr in the case of CTBN rubber and up to 15 vol% in the case of solid modifiers. CTBN rubber was first pre-reacted with the epoxy resin by mixing at 140°C for 4 h under vacuum. MBS–COOH latex particles were suspended in acetone first and then the acetone was substituted by epoxy under vacuum. Particles were finally pre-reacted with epoxy, similar to that of CTBN rubber. Epoxy/rubber mixtures were cooled down to room temperature before addition of the curing agent.

HLP-0.4 and HLP-1.0 particles were received as emulsions which were then freeze dried to powders. Dried powders were mixed with epoxy at room temperature under vacuum for more than 24 h to obtain a uniform suspension. HLP-15 and HLP-40 particles were received as powders and were simply mixed with epoxy under vacuum for 4 h prior to addition of the curing agent.

Characterization techniques

The cured materials were characterized using a variety of techniques. Glass transition temperatures (T_gs) were determined using a differential scanning calorimetry (d.s.c.) unit at a heating rate of 10°C min^{-1}.

The compressive yield stress of materials were evaluated in accordance with the ASTM D695 test method[29]. Specimens were machined down to 5 × 5 × 10 mm from the cured plaques. A screw-driven Instron testing frame at a cross-head speed of 1.5 mm min^{-1} was employed for the compression tests. The results reported are averages of at least four experiments.

Plane strain fracture toughness, K_{IC}, was determined using single-edge-notch (SEN) specimens tested in three-point-bending (3PB) geometry (*Figure 1*). Specimens of thickness 6 mm were used for this test. The ASTM D5045 guideline[29] was followed to measure K_{IC}. Pre-cracks were introduced at the bottom of 2-mm deep notches by hammering a razor blade which was chilled in liquid nitrogen. These tests were performed using a screw-driven Instron testing frame at a cross-head speed of 1 mm min^{-1}. K_{IC} values reported represent averages of a minimum of five tests.

Fracture surfaces of the SEN-3PB specimens were examined using a JEOL 6300F scanning electron microscope (SEM) at an accelerating voltage of 5 kV. Samples were coated with a thin layer of gold–palladium before examination to protect the fracture surfaces from beam damage and also to prevent charge build up.

In order to observe the crack tip damage zone of modified epoxies, double-notched four-point bending (DN-4PB) method in conjunction with transmission optical microscopy (TOM) was employed[30]. Details of this technique are as follows.

First, two edge cracks of equal length are introduced

Table 2 Mechanical characterization of neat and rubber-modified blends

Modifier[a]	Particle size[b] (μm)	Yield stress[c] (MPa)	Fracture toughness[d] (MPa.m$^{0.5}$)
None	None	90.0	0.85
CTBN (1)	0.30	87.0	1.45
CTBN (5)	0.40	81.5	1.95
CTBN (10)	0.55	71.0	2.05
CTBN (15)	0.70	63.5	2.00
MBS–COOH (0.5)	0.20	–[e]	1.05
MBS–COOH (1)	0.20	89.5	1.55
MBS–COOH (5)	0.20	86.0	2.10
MBS–COOH (10)	0.20	82.0	2.20
MBS–COOH (15)	0.20	74.5	2.20

[a] Numbers in parentheses indicate the concentration of the modifiers which are phr for CTBN rubber and vol% for MBS–COOH particles
[b] Average particle size of CTBN-modified materials were measured using SEM micrographs taken from the fast fracture region of 3PB specimens
[c] Yield stress was determined in compression test
[d] Fracture toughness was measured using single edge notched specimens in 3PB geometry
[e] Compression test was not conducted on this material

Table 3 Mechanical characterization of microvoid-toughened blends

Modifier[a]	Particle size (μm)	Yield stress[b] (MPa)	Fracture toughness[c] (MPa.m$^{0.5}$)
HLP-0.4 (1)	0.4	90.0	1.10
HLP-0.4 (5)	0.4	87.0	1.75
HLP-0.4 (10)	0.4	84.5	2.30
HLP-0.4 (15)	0.4	83.0	2.05
HLP-1.0 (1)	1.0	89.5	1.00
HLP-1.0 (10)	1.0	83.0	1.95
HLP-1.0 (15)	1.0	80.0	1.75
HLP-15 (1)	15	88.0	0.90
HLP-15 (5)	15	83.5	1.30
HLP-15 (10)	15	74.0	1.80
HLP-15 (15)	15	67.5	1.65
HLP-40 (5)	40	82.0	1.05
HLP-40 (10)	40	73.0	1.35
HLP-40 (15)	40	64.0	1.70

[a] Numbers in parentheses indicate the volume fraction of the modifiers
[b] Yield stress was determined in compression test
[c] Fracture toughness was measured using single edge notched specimens in 3PB geometry

Figure 3 SEM micrograph of the fracture surface of epoxy toughened by 10 phr CTBN rubber taken from the stress whitened zone

to a bending sample (*Figure 2*). The specimen is then loaded in a four-point bending fixture until damage zones form at the crack tips. Finally, one of the cracks which first reaches the instability point propagates and the sample fractures. The other crack which is unloaded, therefore, contains a well developed damage zone that represents the conditions prior to the failure of the material. This damage zone can be observed using a TOM after thinning via petrographic polishing[30]. (Due to the difficulties in introducing two identical cracks in this technique, in some cases, the subsurface damage of fractured 3PB samples were examined instead.)

Specimens of thickness 6 mm were used for this study. A screw-driven Instron testing frame at a cross-head speed of 1 mm min^{-1} was employed for breaking the samples. Thin specimens (30–50 μm) taken from the mid-plane of samples (plane strain region) were then viewed using an Olympus BH-2 transmission-light microscope. Both bright field and crossed-polarized light conditions were employed.

RESULTS

The d.s.c. analyses revealed a T_g of 105 ± 1°C for all materials made, indicating that no change occurred in the chemical structure of the epoxy matrix by the addition of rubber/microvoids. This observation is particularly important for MBS–COOH toughened epoxies since the absence of a drop in T_g indicates the complete extraction of the solvent used in processing of these materials.

The results of the mechanical testing along with the particle size of the rubber-modified and microvoid-toughened epoxies are found in *Tables 2* and *3*, respectively. Particle size in epoxies modified by CTBN rubber is reported based on the measurements made on SEM pictures taken from the fast fracture region of 3PB samples. The average particle size of the MBS–COOH and hollow plastic particles, reported in *Tables 2* and *3*, respectively, are based on the information provided by the modifier producers.

As seen in *Table 2*, the average particle size in CTBN-modified epoxies varies with the modifier content. This

Figure 4 SEM micrograph of the fracture surface of epoxy toughened by 10 vol% MBS–COOH rubber taken from the stress whitened zone

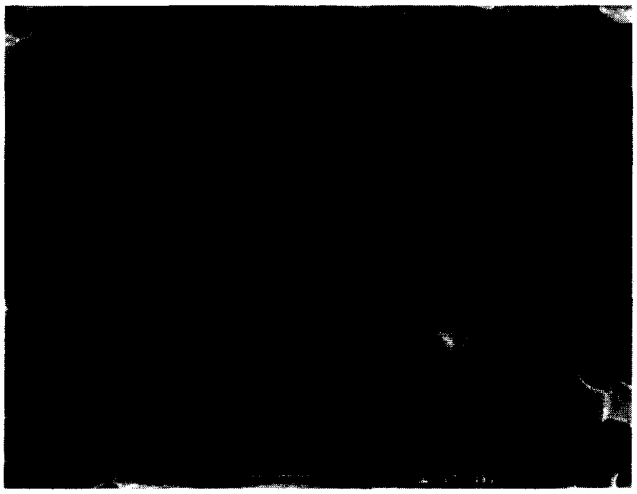

Figure 5 SEM micrograph of the fracture surface of epoxy toughened by 10 vol% HLP-0.4 particles taken from the stress whitened zone

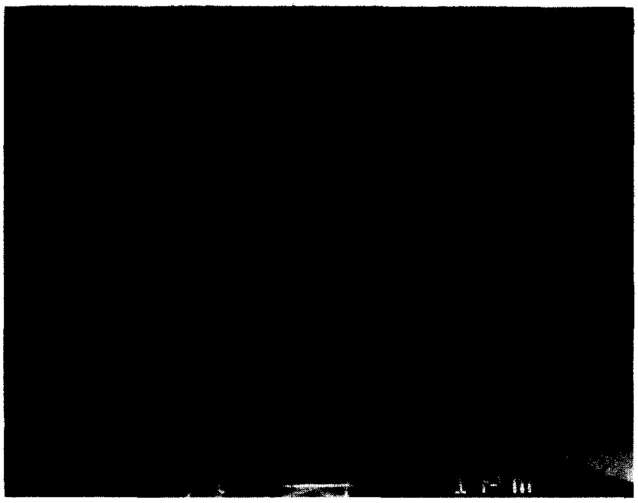

Figure 6 SEM micrograph of the fracture surface of epoxy toughened by 10 vol% HLP-1.0 particles taken from the stress whitened zone

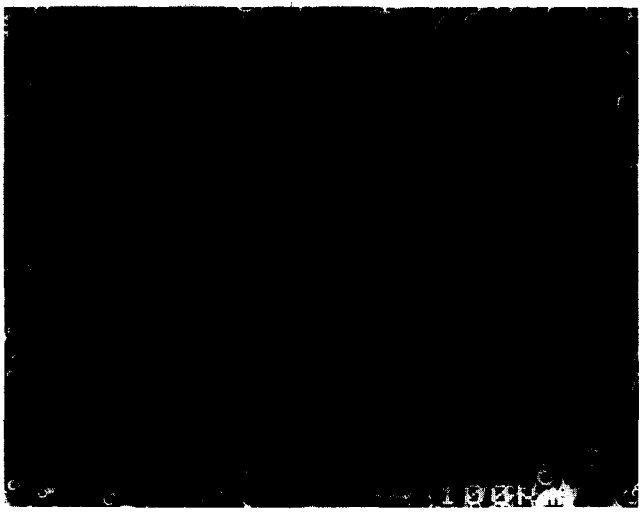

Figure 7 SEM micrograph of the fracture surface of epoxy toughened by 10 vol% HLP-15 particles taken from the stress whitened zone

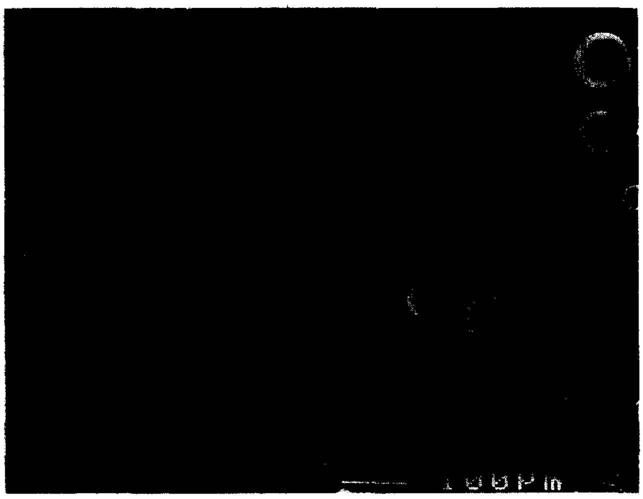

Figure 8 SEM micrograph of the fracture surface of epoxy toughened by 10 vol% HLP-40 particles taken from the stress whitened zone

Figure 9 TOM micrograph of the crack tip damage zone in epoxy toughened by 10 phr CTBN rubber viewed in bright field. Thin sample is taken from the mid-plane of a DN-4PB specimen

Figure 10 TOM micrograph of the crack tip damage zone in epoxy toughened by 10 vol% MBS–COOH rubber viewed in bright field. Thin sample is taken from the mid-plane of a DN-4PB specimen

fact which is one of the disadvantages of using liquid rubbers[8,31], eliminates systematic study of volume fraction of modifier since both concentration and size of the second phase particles are changing simultaneously.

Figures 3–8 illustrate the SEM micrographs taken from the stress whitened zone of the fracture surface of blends toughened by 10% CTBN, MBS–COOH, HLP-0.4, HLP-1.0, HLP-15, and HLP-40 particles, respectively. These figures represent a uniform dispersion of second-phase particles in all modified blends. Additionally, the SEM micrographs of the epoxies toughened by hollow plastic particles, *Figures 5–8*, illustrate perfect bonding between the particles and the matrix.

Figures 9–14 illustrate the TOM micrographs taken from epoxies toughened by 10% of CTBN, MBS–COOH, HLP-0.4, HLP-1.0, HLP-15, and HLP-40 particles, respectively. As seen in these figures, shear yielding which is usually seen dark in reflective light and bright in cross-polarized light[12], is evidenced in all cases. However, shear bands are much finer in case of epoxies toughened by smaller size modifiers (*Figures 9–12*). Massive shear banding at the tip of the crack, seen in *Figures 9–12*, is similar to that observed

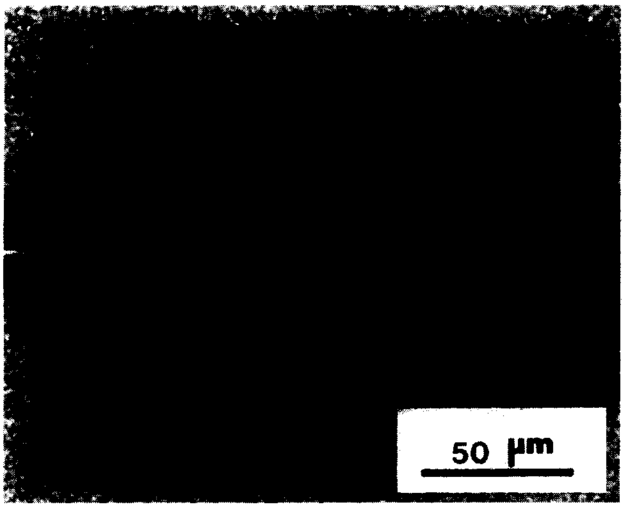

Figure 11 TOM micrograph of the crack tip damage zone in epoxy toughened by 10vol% HLP-0.4 particles viewed under bright field. Thin sample is taken from the mid-plane of a DN-4PB specimen

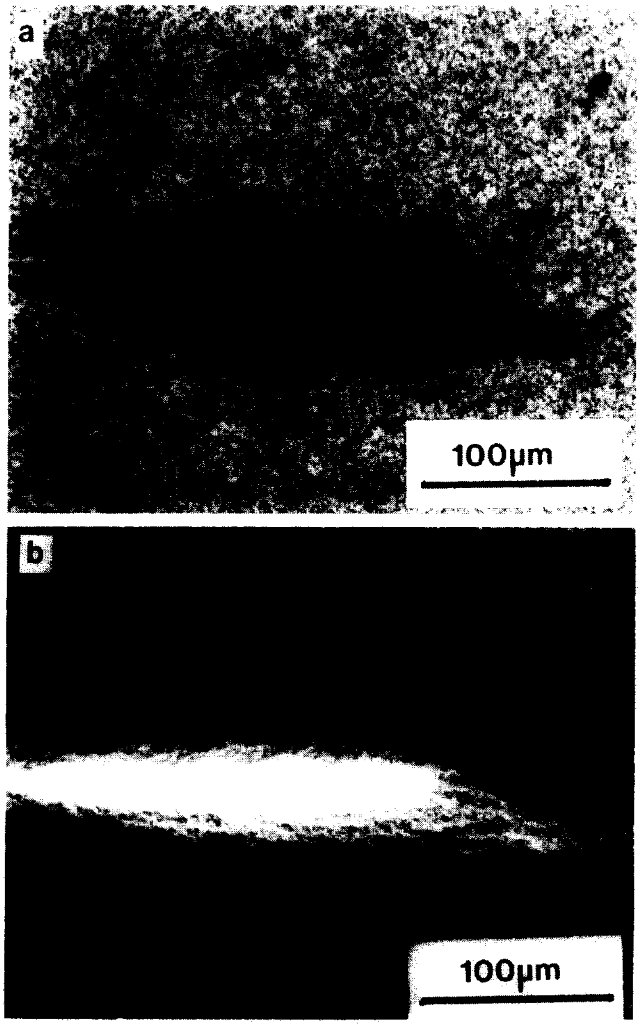

Figure 12 TOM micrograph of the crack tip damage zone in epoxy toughened by 10vol% HLP-1.0 particles viewed under (a) bright field and (b) cross-polars. Thin sample is taken from the mid-plane of a DN-4PB specimen

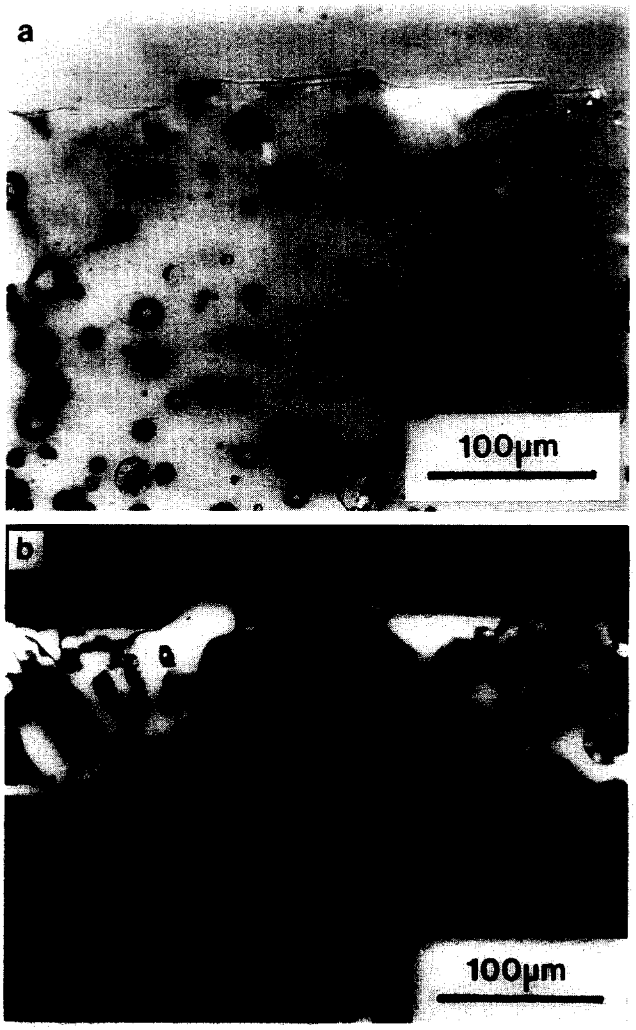

Figure 13 TOM micrograph of the sub-surface damage zone in epoxy toughened by 10vol% HLP-15 particles viewed under (a) bright field and (b) cross-polars. Thin sample is taken from the mid-plane of a 3PB specimen. Crack growth direction is from left to right

by other investigators[12,16] in rubber-toughened epoxies and indicates that micron- or sub-micron size hollow particles toughen epoxies in the same manner that conventional rubber modifiers do. In the case of epoxy toughened by HLP-40 particles, micro-cracks are also seen at the equator of particles in the vicinity of the crack tip (*Figure 14*). This observation indicates that two mechanisms of shear yielding and microcracking are operating in this material simultaneously.

DISCUSSION

Yield stress measurements

The results of yield stress measurements presented in *Tables 2* and *3* are graphically shown in *Figures 15a* and *15b*, respectively, which illustrate the yield stress as a function of volume fraction for different modifiers. The nearly linear dependence of the yield stress to the volume fraction, seen in *Figure 15*, agrees well with the other published results in the literature[8,13,14,32,33]. Guild and Young[14] explained the linear relationship by means of stress concentration effect since their finite element analysis showed a linear increase in concentration of the von Mises stress up to 20vol% of rubber. Therefore,

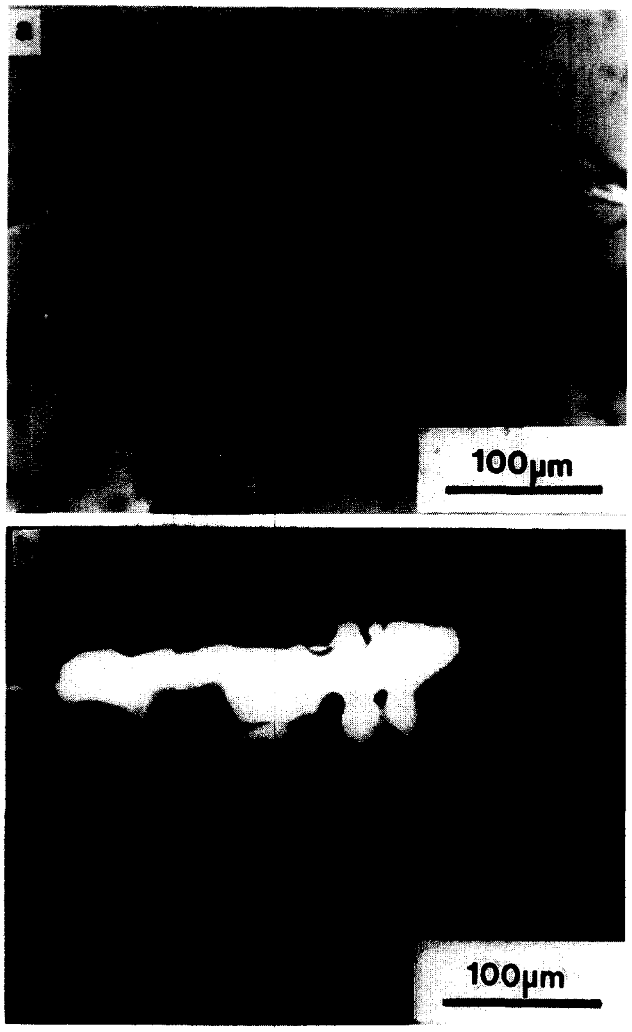

Figure 14 TOM micrograph of the sub-surface damage zone in epoxy toughened by 10 vol% HLP-40 particles viewed under (a) bright field and (b) cross-polars. Thin sample is taken from the mid-plane of a 3PB specimen. Crack growth direction is from left to right

we may borrow the same analogy and claim that the pre-cavitated, hollow, plastic particles and the non-cavitated, rubber, particles have a similar influence on the yield stress of the blend due to their stress concentration effect. Within the concentration range examined, the correlation between the yield stress of the blends and the volume fraction of the modifiers can be written as follows:

$$\sigma_{\mathrm{y,mod}} = \sigma_{\mathrm{y,neat}} - m(V_f) \qquad (1)$$

where $\sigma_{\mathrm{y,mod}}$ and $\sigma_{\mathrm{y,neat}}$ are the yield stresses of the modified and the neat epoxies, respectively. The volume fraction of the modifier is shown by V_f and m represents the slope of the '$\sigma_{\mathrm{y,mod}} - V_f$' lines.

While *Figure 15* illustrates a linear relationship between the yield stress and the vol% of modifier, it shows that the slope of the fitted lines, *m*, are different for different modifiers. In other words, the modifiers used in this investigation have similar, but not identical influences on the yield stress of the blend. Since the particle size is a major difference among the modifiers used in this study, the slope of the fitted lines in *Figure 15* (*m* in equation (1)) is plotted *versus* the particle size in *Figure 16*. As seen in this figure, *m* increases linearly with the particle size. Therefore, the larger the size of the particle, the steeper would be the '$\sigma_{\mathrm{y,mod}} - V_f$' line, or the larger the drop in yield stress per increase in volume fraction of the toughening agent.

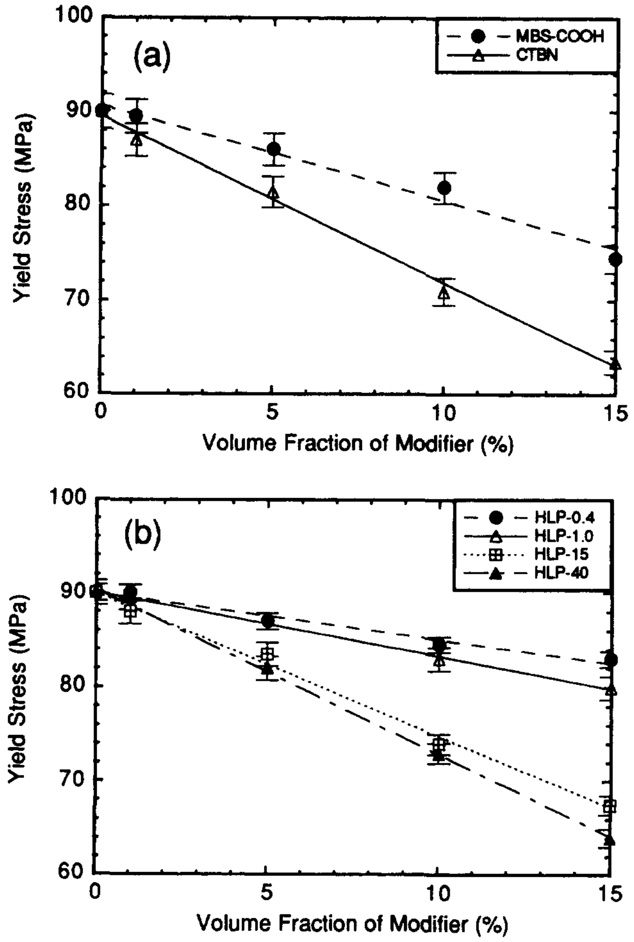

Figure 15 Yield stress as a function of modifier content in (a) rubber-modified and (b) microvoid-toughened epoxies

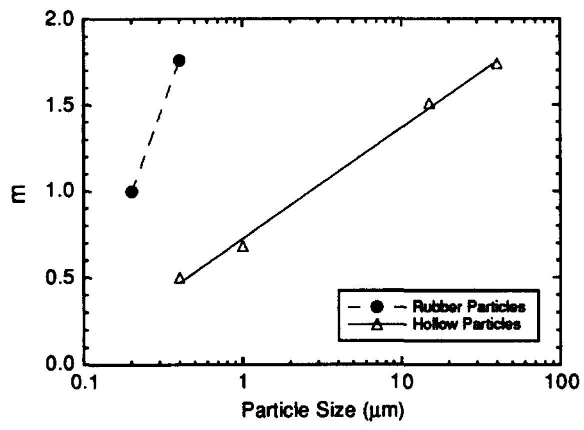

Figure 16 Variation of '*m*' in equation (1) as a function of particle size

It is noteworthy that the dependence of the yield stress to the particle size in rubber-toughened epoxies is not reported in literature. Observation of different yield stress in blends containing different size particles, might be attributed to the influence of the amount of interface between the modifier and the matrix on the yielding of the surrounding matrix. Please note that at a given concentration of modifier, the use of larger particles results in smaller area of the interface. On the other hand, it has been shown that the structure of the matrix in filled polymers is more ordered around the second phase particles compared to the bulk of material[34,35]. A possible reason for the particle size effect may be local ordering of polymer chains at the interface as well as loss of configurational entropy of the polymer segments near the solid surface[35]. Therefore, one may expect a drop in the yield of a modified epoxy when the overall size of the interface decreases by enlarging the particle size.

Another point of interest is that the rubber modifiers used in this study do not follow the order of the hollow plastic particles in affecting the yield stress of the blend. As seen in this figure, for a given particle size, *m*, and thus, the yield stress is larger in microvoid-toughened epoxies than in rubber-modified resins. This observation does not support the analysis by Lazzeri and Bucknall[36] who assumed an identical influence of the volume fraction of the modifier on the yield stress of the blend when they substituted rubber particles by microvoids. It is not clear that why our rubber-modified epoxies have lower values of compressive yield strengths compared to those of similar blends containing same vol% and size of microvoids. The possibility of a difference in stress fields associated with two types of modifiers is subjected to controversy since several FEM (finite element method) analyses have revealed an almost identical stress field around rubber particles and voids[22,24]. However, considering the pressure sensitivity of polymers[37], any difference in the mean stress of blends may result in different yield stresses. The difference in mean stresses, in turn, can be caused by the difference in Poisson's ratio of blends.

An alternative approach to explain the difference between the rubber particles and the microvoids in affecting the yield stress of the epoxy is to again employ the possible influence of the interface. Local ordering of the polymer chains adjacent to a solid surface may increase the strength of the blend. The literature contains no investigation on the ordering of the polymer chains in rubber-toughened blends. However, it seems reasonable that introduction of compliant, rubbery, surfaces results in less ordering of the polymer chains, and therefore causes further reduction of the yield stress. Especially, application of liquid rubbers such as CTBN may result in very limited ordering of epoxy chains at the interface since the precipitation of the rubbery phase and polymerization of the matrix occur simultaneously. Introduction of small, glassy surfaces in microvoid-toughened epoxies, on the other hand, may result in formation of an interface with highly oriented epoxy chains. Formation of such a rigid interface, then, restricts shear yielding of the matrix and shifts the yield stress of the blend to a higher level.

Note that hollow particles used in this study are comprised of nearly the same material (*Table 1*). Therefore, it seems reasonable to explain differences in yield strength by means of a particle size effect. But the two types of rubber modifier used have different surface characteristics. Therefore, one may argue that drawing a line between the rubber-modified data points in *Figure 16* is not correct. In other words, CTBN and MBS–COOH data points should locate on separate lines in *Figure 16*. While we do not disagree with this argument, we believe that the influence of the surface of second phase particles on the yield stress of the blend is not well understood and further investigations are needed to elucidate this subject.

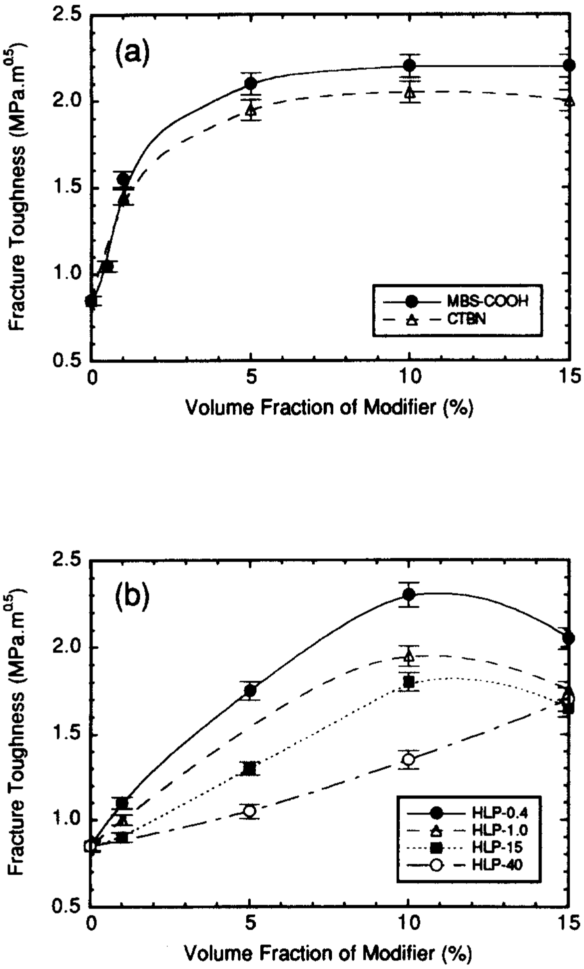

Figure 17 Fracture toughness as a function of modifier content in (a) rubber-modified and (b) microvoid-toughened epoxies

Fracture toughness measurements

Figures 17a and *17b* illustrate the results of fracture toughness measurements presented in *Tables 2* and *3*, respectively. These figures present the dependency of the fracture toughness to the modifier content for different blends. Looking at *Figure 17*, one may notice the following points:

1) All modified blends exhibit increased fracture toughness with increasing volume fraction of modifier up to 10%. Beyond this limit, however, the blends behave differently.
2) Fracture toughness of rubber-modified epoxies levels off beyond 10%. In the case of epoxies toughened by HLP-0.4, HLP-1.0, and HLP-15 modifiers, fracture toughness declines beyond 10 vol% and in the case of HLP-40 particles, increased toughness is observed up to 15 vol% of modifier.
3) Generally speaking, at a given modifier content, use of smaller particles leads to higher fracture toughness values.

Observation of an upper limit of the modifier content beyond which the toughness of the blend does not increase and may even decline, has been reported in rubber-toughened polymers[3,8,13,38]. Providing that the shear deformation of the matrix is the major toughening mechanism in rubber-toughened polymers, one may expect to see such a limit. Please observe that although the rubber particles promote shear deformation in the matrix, their presence displaces the matrix and, hence, reduces the concentration of the material that should absorb the energy. Therefore, an optimum modifier content should exist in which the maximum toughness is obtained.

Based on this discussion, one may expect a decline in fracture toughness of rubber-toughened epoxies by further increases of modifier content beyond 15 vol%. The question, however, remains as to why the drop in fracture toughness beyond 10 vol% is so sharp in microvoid-toughened epoxies which differentiates them from the rubber-modified resins possessing close size particles. The answer to this question may be found in the proposal of Fukui *et al.*[39]. These researchers conducted an elastic–plastic FEM analysis using a two dimension model with particle concentration of 20 vol%. This analysis revealed that the rubber particles provide a more favourable situation for toughening than voids, since the latter cause cracking in the matrix at lower strain levels. Lazzeri and Bucknall[36] proposed an analogous hypothesis. These researchers claimed that rubber particles are distinguished from microvoids at later stages of deformation, when they contribute to strain hardening of the ligament and postpone the ligament failure[36]. In other words, when the epoxy ligaments are very thin, rubber particles are more effective toughening agents than pre-existing voids since they can suppress the failure of the ligaments. Such a condition is obtained at either high concentrations of modifier or at later stages of deformation, when the epoxy ligament is smaller than the neighbouring particles.

The difference observed between the influence of HLP-40 particles and that of the other hollow plastic particles beyond 10 vol% modifier (*Figure 17b*), could be attributed to the additional toughening mechanism of microcracking found in this material (*Figure 14*). Notice that the contribution of microcracking increases by increasing the density of microcracks[40], and thus, by increasing the vol% of modifier.

The other point observed in *Figure 17* is that at a given modifier content, application of smaller size particles results in a tougher blend. The influence of particle size on the fracture toughness of rubber-toughened epoxies has been considered by some investigators[2,8,12,13]. Pearson and Yee[12] showed that substitution of 1–2-μm rubber particles with particles as big as 100–200 μm results in a dramatic drop in the fracture toughness of the blend. These researchers[12] were able to show that this change in fracture toughness is associated with a change in toughening mechanism from massive shear yielding in the case of small particles to rubber bridging in the case of large particles. Pearson and Yee[12], therefore, attributed the poor toughness of the blend modified by 100–200-μm particles to the inefficiency of rubber bridging in these systems.

Observation of the particle size effect in this study cannot be explained by means of a change in the toughening mechanism since the TOM micrographs indicate identical toughening mechanisms in most blends (*Figures 9–13*). An alternative approach to elucidate the source of particle size effect is to employ the concept of inter-particle distance, i.e. the surface-to-surface distance between particles. Notice that at a given concentration of modifier, the blend containing smaller particles possesses smaller inter-particle distances. This subject will be examined in detail in a subsequent publication[28].

CONCLUSIONS

In summary, two types of conventional rubber modifiers and four different size hollow plastic particles were employed as toughening agents in a DGEBA epoxy system. Concentration of the second phase was varied up to 15 vol%. Mechanical performance of the neat and toughened blends were examined via compression and fracture toughness test methods. Toughening mechanisms were elucidated via SEM and TOM techniques. The following conclusions are made:

1. Conventional rubber modifiers and small hollow plastic particles ($\leq 15\,\mu$m) toughen epoxies in the same manner; inducing shear yielding at the crack tip. This observation illustrates that the cavitation resistance of the rubbery phase does not play any role in the toughening mechanism of the epoxy matrix studied.
2. In the case of epoxy toughened by 40-μm hollow particles, evidences of both shear yielding and microcracking were observed. The additional mechanism of microcracking, in this case, slightly varies the trend of fracture toughness *versus* modifier content compared to the other blends.
3. In almost all concentrations examined, smaller particles proved to be more effective toughening agents.
4. While rubber particles and microvoids affect fracture toughness very similarly, their influence on the yield stress of the blend measured in uniaxial compression test are quite different. It is shown that providing a given size and concentration of modifier, the blend containing hollow plastic particles has a higher yield stress than the blend modified by rubber particles.
5. Yield stress in toughened epoxies decreases linearly by increasing the vol% of modifier. The slope of this linear relation, however, increases with the particle size.

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