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Role of particle cavitation in rubber-toughened epoxies: II. Inter-particle distance

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Abstract

Two types of conventional rubber modifiers and a series of hollow plastic micro-spheres were employed as toughening agents in a diglycidyl ether of bisphenol A (DGEBA) epoxy in Part I (Bagheri R, Pearson RA. Polymer 1996;37:4529) of this study. It was found that the rubber modifiers with different cavitation resistance and hollow plastic micro-spheres which act as pre-existing microvoids toughen epoxies in the same manner. The current study is composed to further examine the previous results in terms of the role inter-particle distance in rubber/microvoid toughened epoxies. It is shown that the fracture toughness in toughened blends goes through a ductile-to-brittle transition with inter-particle distance. The source of this transition is found to be a stress state change provided by voided particles. The ligament between neighboring particles, thus, experiences a transition from plane strain to plane stress state by decreasing the inter-particle distance. Interestingly, it is shown that the transition in toughened blends does not occur at a specific inter-particle distance as frequently proposed in literature, but varies with the size of the modifier. Therefore, there is an influence of particle size on yielding of the toughened epoxies that is responsible for the shift in transition. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Toughened epoxies; Cavitation; Inter-particle distance

1. Introduction

Rubber modification has been found as a very successful approach to overcome the inherent brittleness of many engineering polymers. Cavitation of rubber particles followed by plastic deformation of the matrix is believed to be the major toughening mechanism in many rubber-toughened polymers [1–4]. Researchers agree that cavitation alone is not a considerable source of toughening [4–7]. However, its importance on the plastic deformation of the matrix has been the subject of much debate [2,4,6,8]. Therefore, many investigations have been focused on the role of particle cavitation in rubber-toughened polymers [8–21]. In addition, the discussion on the role of particle cavitation has yielded interests in studying the function of the pre-existing voids in toughening of polymers [4,9,10,22–25] since microvoids may play the same scenario that rubber particles do. Some studies, indeed, have shown that the microvoids are capable of toughening the polymer matrices [10,23,25].

In an earlier study [24], we employed a novel approach by incorporating hollow plastic micro-spheres in an epoxy resin to compare the function of pre-existing voids with that of rubber particles in toughening of the epoxy polymers. The results of that study revealed that the hollow plastic particles toughen the epoxy resin in the same manner that rubber particles do. Recently, in Part I of the current study [25], we investigated the concept of microvoid toughening of epoxies in more detail by incorporating different size and concentration of particles. The results of this study showed that micron and sub-micron size particles, no matter rubber or hollow, toughen epoxy polymers by promoting shear yielding in the matrix. Moreover, it is believed that the cavitation resistance of the rubbery phase does not play any role in the toughening mechanism as long as the particles can cavitate.

The results of Part I [25] of this study also suggested an influence of the inter-particle distance on fracture toughness values obtained since at a given concentration of the modifier, the toughness was found to be highly dependent on the particle size. This part of the study, therefore, is dedicated to the issue of the role of inter-particle distance in rubber-toughened epoxies. The goal of this study is to further understand the process of rubber toughening and hence, provide a more clear picture of the role of particle cavitation

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Table 1
Description of the toughening agents used

Modifier[a]	Description of the 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 coploymer with acid funtionality 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 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 case of CTBN rubber varied with the concentration of the modifier [25].

in rubber-toughened polymers. This part includes a deeper analysis of the data obtained in Part I [25]. Additionally, in order to compare the variation of the inter-particle distance in rubber-modified blends with that of the thickness in the neat epoxy, fracture toughness test has been carried out on the unmodified epoxy sheets with different thickness.

2. Experimental approach

The details of the materials and the techniques used are found in Part I [25]. In brief, the epoxy system used is a diglycidyl ether of bisphenol A (DGEBA) epoxy with an epoxy equivalent weight of 187 g/eq. Aminoethyl piperazine (AEP) is used as the curing agent. Two types of conventional rubber modifiers and four kinds of hollow latex particles (HLP) were incorporated as the toughening agents. These modifiers are listed in Table 1.

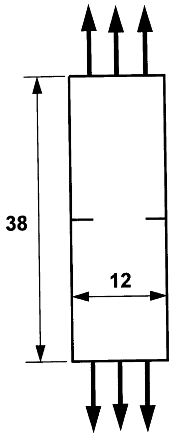

Fig. 1. Schematic diagram of double-edge notched (DEN) specimens used for fracture toughness assessment. All dimensions are in millimeters.

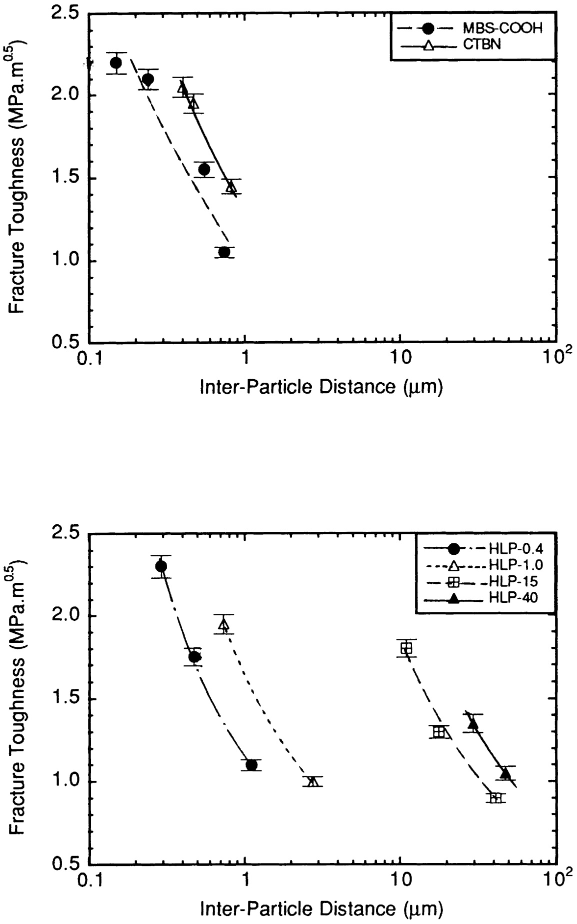

Fig. 2. Fracture toughness versus inter-particle distance in rubber-modified (top) and microvoid-toughened (bottom) epoxies. The inter-particle distance is calculated using Eq. (1). As mentioned in Part I [25], the average particle size for MBS and CTBN rubber is 0.2 and 0.5 μm, respectively. In case of hollow latex particles (HLP), the corresponding numbers represent the average particle size in microns.

Fracture toughness of the modified epoxies, as mentioned earlier [25], was measured in three-point bending (3PB) geometry. Selected fracture surfaces were subjected to scanning electron microscopy (SEM) for investigation of the crack tip/particle interactions.

In order to investigate the influence of the plate thickness on the fracture toughness of the neat resin, epoxy sheets with thickness of 3 mm or less were made and subjected to toughness testing. The details of processing the epoxy sheets are similar to that mentioned in Part I [25]. A different approach, however, was used to measure the fracture toughness since the 3PB technique employed before was not applicable to the thin sheets. The technique employed here consists of double-edge notched (DEN) samples subjected to uniform tensile stress (Fig. 1). Cracks were introduced at the bottom of 2 mm deep side notches by scrolling a chilled razor blade. The critical stress intensity factor, K_C, values were determined by the help of the information provided in Ref. [26]. K_C numbers reported are averages of at least four tests for each thickness.

3. Brittle-to-tough transition in modified epoxies

The results of fracture toughness evaluations of rubber-modified and microvoid-toughened epoxies presented in Part I [25] revealed that not only the concentration, but the size of the second phase particles play a role in determining the toughness of the blend. It was found that for a given volume fraction, use of larger modifiers resulted in lower toughness values [25].

An approach to examine the effects of volume fraction and size of the second phase particles, simultaneously, is to employ the concept of inter-particle distance. Assuming a cubic array of particles, the surface-to-surface distance between particles is found through the following equation:

$$\mathrm{ID} = D_\mathrm{P}\left[\left(\frac{\pi}{6V_\mathrm{f}}\right)^{1/3} - 1\right] \tag{1}$$

where, ID is surface-to-surface inter-particle distance, D_P is the diameter of the second phase particles and V_f is the volume fraction of the second phase.

Fig. 2 illustrates fracture toughness data versus inter-particle distance for both rubber-modified and microvoid-toughened epoxies. It should be mentioned that the data presented in Fig. 2 belong to the blends containing 10 vol% or less of the modifier. As shown in Part I [25], up to 10 vol% modifier, fracture toughness increased steadily in all cases. Beyond this level, however, different blends behaved differently due to the changes in the toughening mechanism [25]. Therefore, we focus our attention to the modifier range of up to 10 vol%.

Fig. 2 shows a transition from brittle-to-tough behavior by decreasing the inter-particle distance in all cases. Observation of this transition, regardless of the type of the modifier, demands an in-depth examination of the concept.

The importance of the inter-particle distance in brittle-to-tough transition has been reported by several investigators [27–33]. These researchers, however, considered this issue from two different perspectives. One group explains the influence of inter-particle distance based on the stress field around the rubber particles [27,28]. According to these investigators, the perturbations in the stress field between the neighboring particles are additive [28]. The maximum toughness or deformation in the ligament, therefore, is obtained at a critical inter-particle distance where the stress fields of the neighboring particles overlap [27,28]. According to this hypothesis, larger size and higher volume fraction of the rubber particles are preferred for toughening since they facilitate the stress field overlap [28].

The second group of researchers consider variation of inter-particle distance as a transition from plane strain to plane stress state [29,30]. Consequently, they claim that the maximum toughness is obtained at a small enough ID where the ligament between the neighboring particles is in fully plane stress condition. The outcome of this hypothesis is that at a given volume fraction, smaller particles are desired since they provide a smaller inter-particle distance. This hypothesis does not differentiate between the toughening efficiency of different size/type modifiers when they yield the same inter-particle distance [30].

In addition to these two groups, some other researchers have raised the importance of inter-particle distance in rubber-toughened polymers through correlating the critical inter-particle distance to the chemical structure of the polymer matrix [31–33]. According to this proposal, below a critical thickness, polymers show their intrinsic toughness or ductility [31–33]. This critical thickness is believed to be a function of the chemical structure of the polymer [31–33]. These researchers further claim that the intrinsic toughness can be seen in thin ligaments no matter the thin ligament is located between adjacent particles in a rubber-modified polymer or is simply a thin sheet [31–33]. Despite some differences, this idea falls into the second category mentioned above since the critical thickness for plane strain/plane stress transition is related to the plastic zone size [34] and therefore, is a material property.

Looking at Fig. 2, one can easily find that the transition in fracture toughness occurs at different inter-particle distances for different modifiers. In other words, as opposed to the already mentioned hypothesis, there is no specific inter-particle distance in which the brittle-to-tough transition occurs. Sanden [33] claimed that the critical thickness for different epoxies are in the range of 0.2–0.3 μm. Therefore, one may toughen brittle epoxies by generating inter-particle distances equal or less than 0.2–0.3 μm. Fig. 2, however, shows that the transition shifts to two orders of magnitude larger inter-particle distances when 15 and 40 μm particles are used.

The results of this study, shown in Fig. 2, also contradicts the finding by Wu [30] who observed a transition in impact strength of a rubber-toughened nylon at a given inter-particle distance regardless of the size of the rubber particles. It is noteworthy that the rubber particles used by Wu [30] had a particle size range between 0.4 and 3 μm, while the particles used in this study are in the range of 0.2–40 μm. Therefore, a better judgement on the influence of the particle size on brittle-to-tough transition can be made in this study. Additionally, there is no reason to expect the exact reproducibility of the impact data in fracture toughness testing.

Before further examination of the shift in brittle-to-tough transition, it is worth to explore the origin of the transition itself. The curve fittings shown in Fig. 2 revealed that within the transition region, the fracture toughness (K_IC) and the inter-particle distance (ID) are correlated via a power law equation:

$$K_\mathrm{IC} = a \times (\mathrm{ID})^b \tag{2}$$

Table 2
The coefficient and the exponent of power-law equation (Eq. (2)) along with the particle size of the modifiers used

Modifier	Average particle size[a] (μm)	*a*	*b*
MBS-COOH	0.2	1.05	−0.43
HLP-0.4	0.4	1.16	−0.55
CTBN	0.5	1.32	−0.49
HLP-1.0	1.0	1.66	−0.50
HLP-15	15	6.02	−0.52
HLP-40	40	8.00	−0.53

[a] The average particle size in CTBN-modified resins, as mentioned in part I [25], varied with the modifier content from 0.3 μm in 1 vol% blend to 0.7 μm in 15 vol% material. An average of 0.5 μm is selected here for ease of mathematical manipulations.

where *a* and *b* are constant parameters. The magnitude of *a* and *b* for different modifiers used in this study are shown in Table 2. The corresponding particle sizes are also included for comparison purposes. As seen in this table, *b* for all modifiers has a value very close to −0.5. The magnitude of *a*, however, varies from one modifier to the other.

Interestingly, Broek [35] reported a very similar relation to Eq. (2) in plane strain/plane stress transition of metallic alloys where fracture toughness varies by plate thickness. Borrowing the same concept, one may claim that the transitions seen in Fig. 2 are actually plane strain/plane stress transitions. In other words, a ligament between two neighboring particles may experience a transition from plane strain to plane stress state by decreasing the inter-particle distance. This conclusion which is parallel to the second hypothesis mentioned before [29,30], can be further examined by studying the interaction between crack tip and particles in modified blends.

Investigation of the crack tip/particles interaction was carried out by scanning electron microscopy of fracture surfaces of blends containing the lowest concentration of MBS-COOH, HLP-1.0, HLP-15, and HLP-40 particles. These materials were selected for this study since their relatively large inter-particle distance allows this examination.

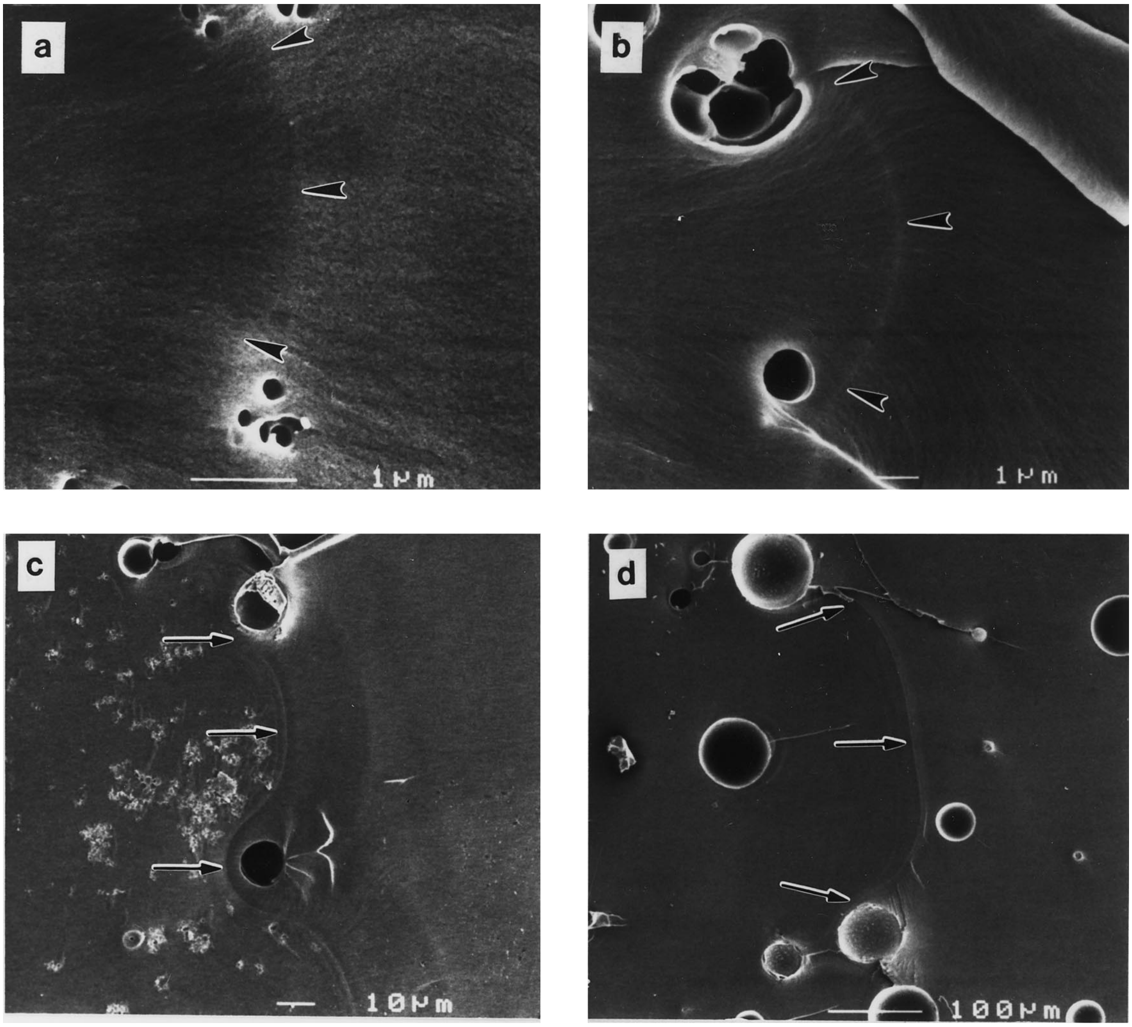

Fig. 3. SEM micrographs taken from the fracture surface of epoxies toughened by (a) 0.5 vol% MBS-COOH, (b) 1 vol% HLP-1.0, (c) 1 vol% HLP-15, and (d) 5 vol% HLP-40 particles. Crack tip bowing between neighboring particles is observed in all cases.

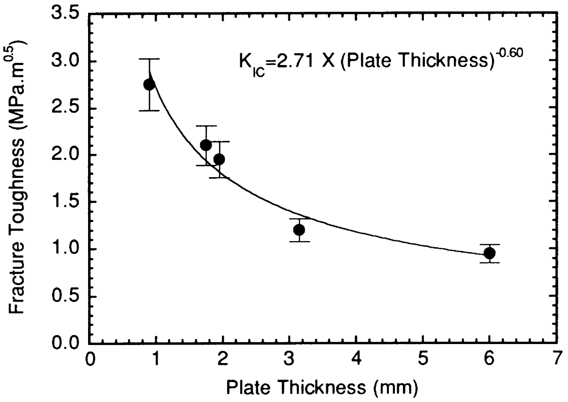

Fig. 4. Fracture toughness versus plate thickness in the neat epoxy. The fracture toughness data are obtained using double-edge notched (DEN) samples loaded in tension.

The resulting micrographs are shown in Fig. 3. This figure shows a common feature among all blends, i.e. crack bowing between particles. This observation illustrates that the crack driving force is lower in the vicinity of the particles compared to the rest of material, thus, causing crack arrest by the particles.

One way to explain this observation is to assume that the rubber/hollow particles pin the crack tip in the same way that solid organic [36] or inorganic [37] particles do. This assumption is easily refuted since neither rubber particles nor hollow micro-spheres are stiff enough to unload the surrounding matrix; a need for effective pinning elements [38].

An alternative approach to interpret the crack tip bowing seen in Fig. 3 is to borrow the same concept used in macroscopic fracture of ordinary single phase materials. Crack tip bowing in fracture samples is very well documented as a sign of change in stress state from the surface to the center of the test specimens. Allen [39], for example, observed a parabolic-shaped crack front on the fracture surface of aluminum alloys and attributed that to the development of plane stress which reduces the crack driving force at the free surfaces of the test samples. Similarly, crack tip bowing between neighboring particles seen in Fig. 3 may be attributed to a change in stress state from plane stress, in the vicinity of the particles, to plane strain, at distances from the particles. Decrease in hydrostatic stress at areas close to the particles, i.e. voids, reduces local crack driving force and thus, suppresses crack propagation. One can therefore, claim that the origin of variation of fracture toughness versus inter-particle distance, seen in Fig. 2, is a plane strain/plane stress transition. This concept would be further justified if one can detect a similar transition in fracture toughness of the neat epoxy when the plate thickness is varied.

4. Brittle-to-tough transition in unmodified epoxy

The effect of plate thickness on the fracture toughness is shown in Fig. 4. As seen, fracture toughness goes through a transition with the plate thickness. Interestingly, this transition follows a power-law relation while the exponent of the best fit to the data is about -0.60. Occurrence of this transition and its similarity to the transitions observed in toughened blends (Fig. 2), reinforces the idea of stress state change being responsible for brittle-to-tough behavior in rubber-modified epoxies. Therefore, it can be claimed that the role of particle cavitation is to generate free surfaces that relieve the plane strain constraint from the matrix. The ligament between cavitated particles is then free to undergo plastic deformation, if the matrix is capable of doing so, and improve the fracture resistance of the material.

The importance of rubber particle cavitation in relief of plane strain constraint is in agreement with the hypotheses of Bucknall et al. [3], Sue [5], Pearson and Yee [6], Yee et al. [11], Li et al. [12], and Collias et al. [23]. These researchers believed that particle cavitation is a key function in toughening of rubber-modified polymers since it relieves the plane strain constraint and promotes shear yielding in the matrix. The results of this study, in addition, provide a semi-quantitative approach to take into account the influence of constraint relief on the fracture toughness of the blend through correlating the K_{IC} and the inter-particle distance (Eq. 2).

The dependency of toughness to the inter-particle distance in rubber-toughened polymers, as mentioned earlier, has also been raised by other investigators [29–33]. These researchers, however, believed that the transition from brittle-to-tough behavior occurs at a certain inter-particle distance. While our data, shown in Fig. 2, reveals that there is no specific inter-particle distance in which the brittle-to-tough transition occurs. Therefore, the simple function of constraint relief by cavitation is not all that the rubber particles do and further studies are required to understand the reason for lack of a unique “critical inter-particle distance” in Fig. 2.

5. Role of size and type of modifier in transition

As shown in Table 2, the magnitude of *a* in Eq. (2) increases with particle size. In other words, increasing the particle size shifts the brittle-to-tough transition to the right side in Fig. 2. In the same way, one may assume that the use of extremely large particles shifts the transition all the way right where the plane strain/plane stress transition occurs in the unmodified epoxy (Fig. 4). However, it is noteworthy that application of huge spherical particles may promote other mechanisms such as microcracking that can interfere with the shear yielding mechanism and thus, affect the final results.

The *a* values and the corresponding particle sizes in Table 2 are graphically shown in Fig. 5. As seen in this figure, a single curve can be fitted through the whole data. This observation illustrates that the particle size accounts for

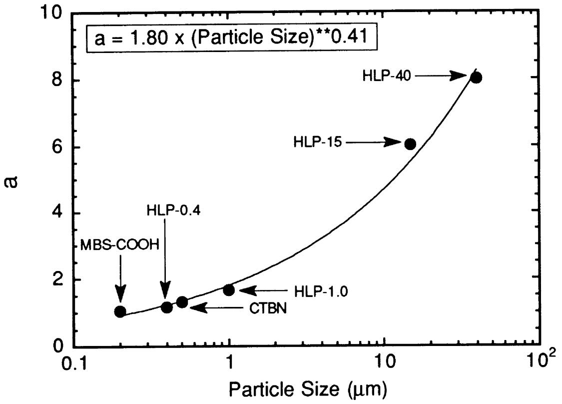

Fig. 5. Variation of *a* in Eq. (2) as a function of particle size.

the shifts in transition seen in Fig. 2. A possible reason for this observation can be found by considering the effect of the particle size on yielding of the blend. Our yield stress data, presented in Part I [25], showed that for a given modifier content, incorporation of larger particles lowers the yield stress of the blend. This is while the volume fraction of modifier needed to maintain a particular inter-particle distance also increases by the particle size (Eq. (1)). Therefore, it is expected to have much more plasticity in the matrix if the same inter-particle distance is obtained by larger particles. In other words, larger particles induce same amount of deformation in the matrix at larger inter-particle distances, i.e. shift of the transition curve to the right when larger size particles are employed.

The results of this study, therefore, indicate that the fracture toughness in rubber- or microvoid-toughened epoxies is explained by means of inter-particle distance and particle size. The influence of inter-particle distance is attributed to the transition in stress state and the size of the particles seems to affect the yielding in the surrounding matrix. The results of this study, however, does not show any influence of the type of modifier on toughening. This finding contradicts previous investigations which raised the importance of cavitation resistance of the rubbery phase in determining the fracture toughness of the blend [6,29,40]. Pearson and Yee [6] believed that higher cavitation resistance may further improve the fracture toughness in a rubber-toughened epoxy. They argued that later 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 then causes a faster growth of shear bands and thus, a larger plastic zone is formed and a higher toughness is obtained [6]. Borggreve et al. [29,40], on the other hand, claimed that lower cavitation resistance of the rubbery phase results in higher impact resistance in a rubber-modified nylon. These researchers speculated that early cavitation and relief of hydrostatic stress allows more plastic deformation which results in more energy absorption prior to fracture.

Another point which was not touched in this study and worth noting is the influence of dispersion of particles. In a different work [41], we showed that inter-connection of preformed core/shell rubber particles can dramatically influence the shear yielding in the matrix and thus, affect the fracture toughness of the blend. Therefore, the concept of inter-particle distance may not be very easily applied to the systems that possess a non-uniform dispersion of particles. Additionally, one should note that accuracy of Eq. (1) for calculation of the inter-particle distance is also limited by dispersion of particles as well as by particle size distribution and volume fraction of the modifier. Although used by many investigators, Eq. (1) is constructed based on the assumption of cubic arrangement of (identical) particles and is not very versatile.

6. The limit of transition

Maximum toughness in ordinary single phase materials is obtained at fully plane stress condition when the plate thickness is equal to the (plane stress) plastic zone size [34]. Fracture toughness does not increase and may even decline by further thinning of the specimen due to the lack of material for plastic energy absorption [34]. Therefore, the brittle-to-tough transition in ordinary materials terminates at a thickness equal to the (plane stress) plastic zone size, i.e. a material property.

The results of Part I of this study [25], however, showed that the transition from brittle to tough behavior terminates at an inter-particle distance equivalent to roughly about 10 vol% of modifier. Other investigators have also reported an optimum rubber content of about 10 vol% in rubber-toughened epoxies [1,7,42]. Therefore, it seems that the limit of brittle-to-tough transition in toughened epoxies is a function of modifier content and is not a material property.

This observation might be explained by considering the stress concentration effect of particles. Using Eq. (1), one finds that at a given modifier content, the ratio of the inter-particle distance to the particle size is always a constant value. On the other hand, the size of the stress field around a particle is also a function of the particle size. Therefore, for a given modifier content, one can expect a certain degree of stress field over lap within the ligament regardless of the size of the particles. Then, assuming that beyond 10 vol% of modifier there is so much interaction between particles that prohibits extra plastic deformation in the ligament, one may justify the observation of an optimum toughness around this modifier content.

7. Role of matrix ductility in transition

It was hypothesized that extra deformation in the ligament when larger size particles are employed shifts the brittle-to-tough transition to the right side in Fig. 2. Yielding behavior of epoxy polymers can also be altered by their network density [43]. Thus, a shift in brittle-to-tough

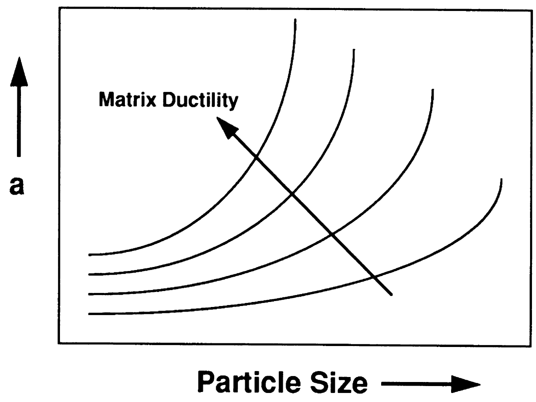

Fig. 6. Schematic showing the influence of ductility of the matrix and the particle size on the *a* value in Eq. (2).

transition is expected in rubber-modified epoxies if the cross-link density of the matrix is varied. Despite the fact that no experiment was designed to address this issue, conclusions can be still made based on the study by Pearson and Yee [44]. These researchers studied the influence of cross-link density on the fracture toughness in rubber-modified DGEBA epoxies. The result of their study revealed a significant increase in the toughenability of epoxy resins by decreasing their network density [44]. Comparing this finding with that of the present study, one may expect a significant increase in the value of *a* in Eq. (2) by decreasing the cross-link density of the resin. The possible influence of matrix ductility on the *a* value is shown schematically in Fig. 6.

The role of ductility of the matrix is therefore, explained by the value of *a* in Eq. (2). However, this value represents the influence of the particle size as well. The reason for this dual dependence is that both matrix ductility and particle size affect the yielding behavior of the blend which causes the shift in brittle-to-tough transition.

8. Conclusions

Fracture toughness data obtained in our earlier work [25] is plotted against the average inter-particle distance in six rubber/microvoid toughened epoxies. It is shown that the blend goes through a brittle-to-tough transition by decreasing the inter-particle distance. The source of this transition is found to be a change from plane strain to plane stress state within the ligament. The role of the particle cavitation, therefore, is to relieve the plane strain constraint from the surrounding matrix and allow plastic deformation in the ligament, if the epoxy resin is capable of doing so. This is in agreement with the notion that highly cross-linked epoxies are not toughened by rubber addition. The reason is that if the epoxy has a very rigid structure, relief of constraint by cavitation does not improve toughness since no deformation can take place in the matrix.

The results of this study also illustrate that the transition in toughened epoxies does not occur at a certain inter-particle distance. It is shown that increase in particle size shifts the transition towards the larger inter-particle distances. This effect is attributed to the influence of particle size on the yielding of epoxy matrix.

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