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Fracture mechanisms in rigid core-shell particle modified high performance epoxies

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Abstract The fracture mechanisms of a high performance epoxy system modified with two types of preformed rigid core-shell particles (RCSP) were investigated. The use of the preformed RCSP enables the control of the dispersion of the toughener phase in the epoxy, which, in turn, allows the mechanical properties of the modified epoxy to be optimized. The toughening effect via the RCSP modification is found to be as good as that via the core-shell rubber modification. The moduli and T_g of these RCSP-modified epoxies are virtually unaltered via the RCSP modification, when compared with the neat epoxy resin equivalent. The toughening mechanisms in these toughened systems appear to be predominantly crack deflection, crack bifurcation, and microcracking. Approaches for effective toughening of high performance polymers via rigid polymers are discussed.

Key words Rigid-rigid polymer toughening concept – high performance epoxy – toughening mechanisms – rigid core-shell particle – microcracking

Introduction

The concept for toughening engineering polymers via non-elastomeric plastic particles, i.e., the multi-phase rigid-rigid polymer toughening concept, has been illustrated and discussed in detail [1–3]. The advantages of the rigid-rigid polymer toughening approach over that of the rubber toughening approach are: 1) improved fracture toughness without any sacrifices in modulus, creep resistance, and yield stress; 2) sustained thermal properties; 3) improved and/or balanced physical and mechanical properties; 4) better overall processability; 5) numerous choices of tougheners. Because there is a wide general recognition of these advantages, significant research effort, both academically and industrially, is now focused on the utilization of the rigid-rigid polymer toughening approach to meet the ever-increased demands for high performance (i.e., high T_g ($>200\,^\circ$C), high modulus (>3 GPa), high thermal stability, and good solvent resistance) toughened polymeric systems, which include both thermoplastics and thermosets in applications such as automotive and aerospace structural composites, adhesives, and coatings [1–24].

In principle, the role(s) the toughener phase will play in the multi-phase rigid-rigid polymer toughening concept is virtually the same as that of the well-known rubber toughening concept [3, 25]. That is, depending on the nature of the polymer matrix and the toughening mechanisms to be promoted, the rigid toughener particles need to perform at least one of the following roles to toughen the matrix: 1) serving to relieve the plane strain constraint via the particle cavitational process; 2) serving as stress concentration sites for initiating massive shear bands, crazes, and microcracks; 3) serving as stress concentration sites for crack pinning, crack deflection, and crack bifurcation to take place; 4) stopping (containing) crazes from turning into cracks; and 5) bridging between the opening crack planes. In addition to the above toughening role(s), the rigid toughener phase needs to have physical properties that will either maintain or enhance the overall physical properties of the toughened system. That is, the toughener phase should exhibit comparable or higher modulus, better environmental and solvent resistance, less moisture absorption, lower viscosity, proper interfacial adhesion, and lower cost than the matrix polymer. The issues involved in choosing an appropriate rigid toughener for toughening brittle matrices has been addressed earlier [1–3, 25]. They will not be repeated here. The present work intends to demonstrate that a commercially viable toughened high performance rigid-rigid polymer alloy can indeed exist.

In this study the toughening mechanisms of a high performance epoxy system modified with two types of preformed rigid core-shell particles (RCSP) are conducted. The RCSP are prepared similarly to the core-shell rubber (CSR) particles [26]. They are produced by a two-stage latex emulsion polymerization technique. Typical RCSP are sub-micron in size and coupled with grafted polymeric surfaces (i.e., the shell) featuring various chemistries of coreactivity and polarity [27]. These preformed particles exist as a discrete identifiable phase before and after curing. Therefore, they are well-suited for gaining a fundamental understanding of the role(s) that the toughener particles play during the fracture process. It is noted that the above approach, as opposed to the commonly practiced solvent-solution or dissolution-precipitation approaches [16–18], provides a better control of phase morphology and causes minimal increases in resin viscosity. These characteristics are among the desirable properties in aerospace applications.

The single-edge-notch three-point-bend (SEN-3PB) specimen geometry is used for measuring the plane strain mode-I fracture toughness (K_{IC}) of the systems. The double-notch four-point-bend (DN-4PB) technique [28, 29], which is known to be effective in probing the toughening mechanisms of rubber-toughened polymers [1–5, 25], is used to generate a sub-critically propagated crack in these experimental RCSP-toughened epoxy systems. Approaches for effective toughening of high performance polymers using the rigid-rigid polymer toughening concept are discussed.

Experimental

A diglycidyl ether of bisphenol A (DGEBA-D.E.R.* 332 epoxy resin), having an epoxy equivalent weight between 172 and 176, was cured at a stoichiometric ratio with 4,4′-diaminodiphenyl sulfone (DDS) for 2 h at 180 °C and 2 h at 220 °C. The experimental RCSPs consist of a lightly crosslinked polyvinyltoluene (VT) core and are grafted with a random copolymer shell, which is about 10 nm thick. Two types of random copolymer shells were utilized: 1) styrene/methylmethacrylate/acrylonitrile/glycidylmethacrylate (S/MMA/AN/GMA = 30:30:25:15 ratio by wt.) and 2) styrene/methylmethacrylate/acrylonitrile (S/MMA/AN = 37.5:37.5:25 ratio by wt.). Owing to the differences in polarity and solubility parameters between the two types of shells, they are expected to disperse differently in epoxy [25]. The RCSPs have a uniform particle size of about 0.12 μm. Approximately, 7.5% by weight of the RCSP was used to modify the DDS-cured epoxy resin matrix.

The RCSPs were mixed with the resin, followed by the addition of DDS and degassed at 130 °C for about 10 min. The curing schedule for the RCSP-toughened DGEBA/DDS systems was as follows: 2 h at 180 °C and 2 h at 220 °C. After the epoxy resin was cured and slowly cooled to room temperature (25 °C) in the oven, the 0.3175 cm (0.125″) thick epoxy plaques were machined into bars with dimensions of 12.7 cm × 1.27 cm × 0.3175 cm (5″ × 0.5″ × 0.125″) for the DN-4PB experiments (see Fig. 1 for the schematic of the DN-4PB geometry) and with dimensions of 6.35 cm × 1.27 cm × 0.3175 cm (2.5″ × 0.5″ × 0.125″) for the SEN-3PB, 3PB-flexural (3PB-F), and dynamic mechanical experiments. The SEN-3PB and DN-4PB bars were then notched with a notch cutter (TMI Model 22-05) having a 250 μm radius, followed by razor blade tapping to wedge open a sharp crack with a parabolic crack front perpendicular to the applied loading direction. The ratio between the final crack length (a) and the specimen width (W) was held in the range between 0.3 and 0.7.

The dynamic mechanical behavior of both the neat resin and the RCSP-modified epoxies was studied using dynamic mechanical spectroscopy (DMS) (Rheometrics RMS-805) under a torsional mode, with 5 °C per step. A constant strain amplitude of 0.05% and a fixed frequency of 1 Hertz were used. The samples were analyzed at temperatures ranging from −150 °C to 250 °C.

The glass transition temperatures (T_g) of the neat and the RCSP-modified epoxy systems were measured using

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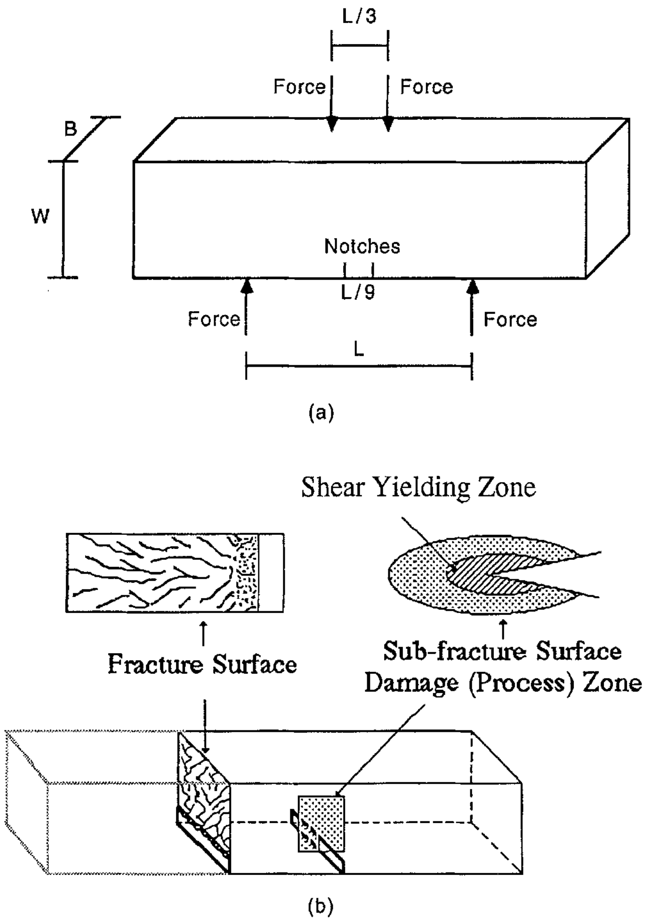

Fig. 1 Schematic of the fracture surface and the sub-fracture surface zone studied in the DN-4PB specimen

a Mettler DC-30 differential scanning calorimeter (DSC), ranging from 25 °C to 250 °C, with a heating rate of 10 °C/min. The T_g from the second-heat was recorded and reported in Table 1.

A Sintech-2 screw-driven mechanical testing machine was used to conduct both the SEN-3PB and the DN-4PB experiments, at a crosshead speed of 0.508 mm/min. (0.02″/min.) at room temperature (25 °C). At least 10 SEN-3PB bars were used to calculate the K_{IC} [30–32] of the VT-RCSPs. When the DN-4PB experiment was performed, care was taken to ensure that the upper contact loading points were touching the specimen simultaneously. For the 3PB-F test, a crosshead speed of 0.125 cm/min. (0.05″/min.) was adopted. The flexural modulus (E_f) was calculated based on the ASTM D790 method.

For the transmission electron microscopy (TEM) experiment, the damage zone around the surviving DN-4PB crack was cut along the thickness direction into two halves using a diamond saw (Fig. 1). The damage zone in the plane strain core region of the specimen was carefully trimmed to an appropriate size, i.e., an area of ≈ 3 mm × 3 mm, and embedded in D.E.R. 331 epoxy resin/diethylene triamine (12:1 ratio by wt.). It was cured at 38 °C for 16 h. The cured block was then further trimmed to a size of ≈ 0.3 mm × 0.3 mm with the crack tip in the damage zone roughly at the center of the trimmed surface. Ultra-thin sections, ranging from 60 to 80 nm, were cut using a Reichert–Jung Ultracut-E microtome with a diamond knife. The thin sections were placed in a vial containing 1 g of 99.9% pure OsO_4 crystals and stained for 65 h. In some cases, the modified epoxy systems were stained with aqueous solution of RuO_4 (0.5 wt%) for 40 min to enhance contrast along the phase boundaries. The thin sections were then placed on 200-mesh formvar-coated copper grids and examined using a JEOL 2000FX ATEM operated at an accelerating voltage of 100 kV for TEM investigation.

Results and discussion

The present work focuses on utilizing the rigid-rigid polymer toughening concept to toughen high performance epoxies.

Table 1 Mechanical Properties of the VT-RCSP-Modified Epoxies

Neat epoxy modified with	T_g^3 (°C)	K_{IC}, @25 °C (MPa·m$^{0.5}$)	G_{IC}^4, @25 °C (J/m^2)	E_f, @25 °C (MPa)	G', @25 °C (MPa)
None	220	0.83 ± 0.02	200	2940	1160
VT-RCSP[1] (Random)	221	1.12 ± 0.04	340	3200	1210
VT-RCSP[2] (Clustered)	223	1.21 ± 0.07	400	3220	1260
CSR[1] (Random)	220	1.20 ± 0.04	500	2500	1030

[1] Shell composition: S/MMA/AN/GMA = 30:30:25:15 ratio by wt.
[2] Shell composition: S/MMA/AN = 37.5:37.5:25 ratio by wt.
[3] DSC second-heat T_g was recorded.
[4] $G_{IC} = K_{IC}^2(1 - \nu^2)/E$; ν is assumed to be 0.36 and E is assumed to be the same as E_f.

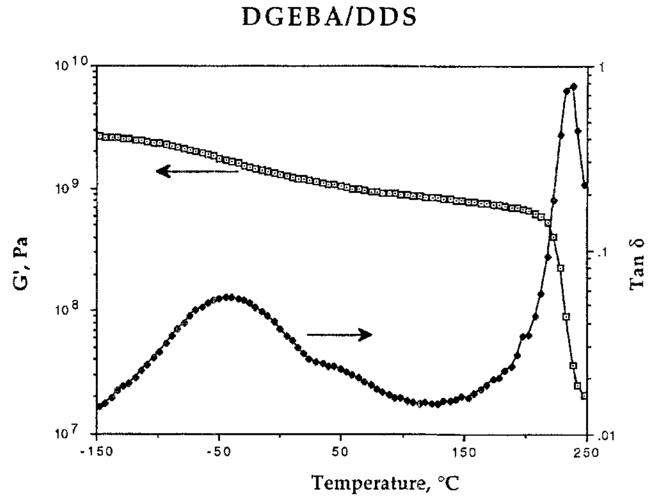

Fig. 2 DMS of the DGEBA/DDS system

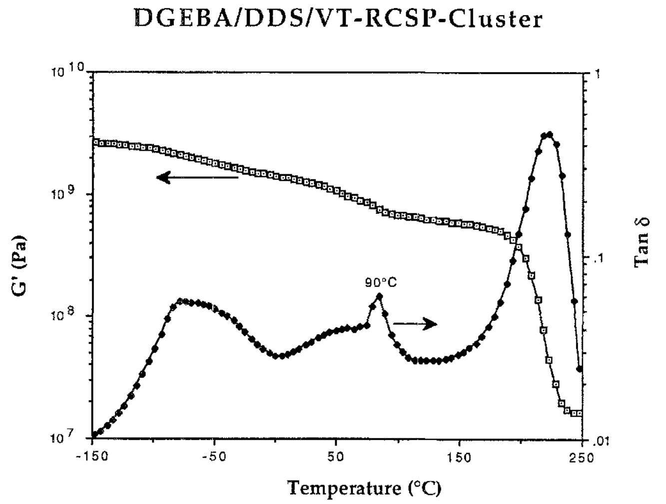

Fig. 3 DMS of the DGEBA/DDS/7.5% VT-RCSP-cluster system. The DMS of the DGEBA/DDS/7.5% VT-RCSP-random is virtually the same as the above

To ascertain that the use of RCSP does not cause any reduction of T_g and modulus of the epoxy resin, the DSC, DMS and 3PB-F experiments are conducted. As shown in Table 1, it is clear that the T_g of the modified epoxies is not affected by the presence of the VT-RCSP modifiers. The 3PB-F moduli (E_f) and the dynamic shear storage moduli (G') @25 °C of the VT-RCSP-modified epoxies, with the VT-RCSP either randomly dispersed or clustered in the matrix, appear to be slightly enhanced. This implies that the higher modulus nature of the VT-RCSP helps stiffen the matrix. This is an added advantage for the utilization of the rigid-rigid polymer toughening approach. For comparison purposes, the T_g and moduli of the neat and CSR-modified epoxies are listed in Table 1.

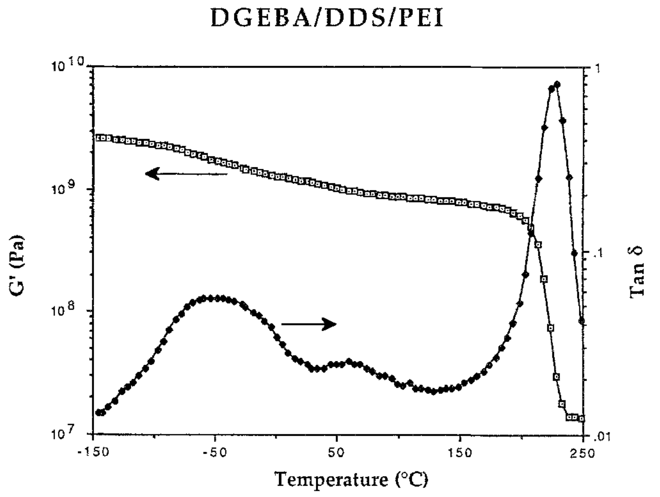

Fig. 4 DMS of the DGEBA/DDS/7.5% PEI system

It is noted that the G' curve for the VT-RCSP system shows a stronger temperature dependency than that of the neat epoxy resin in the range between the T_g of the VT-CSRP (= 90 °C) and the T_g of the epoxy matrix (= 220 °C), as indicated by Figs. 2 and 3. This suggests that so long as the service temperature of the modified epoxy is always below the softening temperature of the toughener phase (i.e., the VT-RCSP), both the T_g and modulus of the epoxy matrix will not be affected by the presence of the rigid toughener particles. However, if the epoxy resin is to be used above 90 °C, it would be advisable to use a higher T_g toughener particles, such as polyetherimide (PEI) and polyphenyleneoxide, to modify the high performance epoxy matrix. For example, when the PEI toughener particles are utilized to toughen the epoxy [11], the G' of the epoxy/PEI system (Fig. 4) is no longer a strong function of temperature up to the T_g of PEI (210 °C). Therefore, it is predicted that if the service temperature of the epoxy resin is going to be high, but below 200 °C, the PEI particles or the like will help sustain the rigidity of the epoxy matrix better than that of the VT-RCSPs [11].

In an effort to study the toughening effect due to the VT-RCSP modification, the SEN-3PB experiment is conducted to measure the fracture toughness of the modified epoxies. The detailed procedures for measuring valid K_{IC} values can be found elsewhere [30–32]. As indicated in Table 1, the VT-RCSPs do improve the K_{IC} of the epoxy matrix. However, only the VT-RCSP-cluster system with a shell composition of S/MMA/AN = 37.5/37.5/25 gives a toughening effect equivalent to that of the CSR-modified epoxy system [33]. In order to understand why and how these RCSPs toughen the epoxy matrix, the fracture mechanisms of these VT-RCSP-modified epoxy systems are studied using the DN-4PB (Fig. 1) and TEM tools.

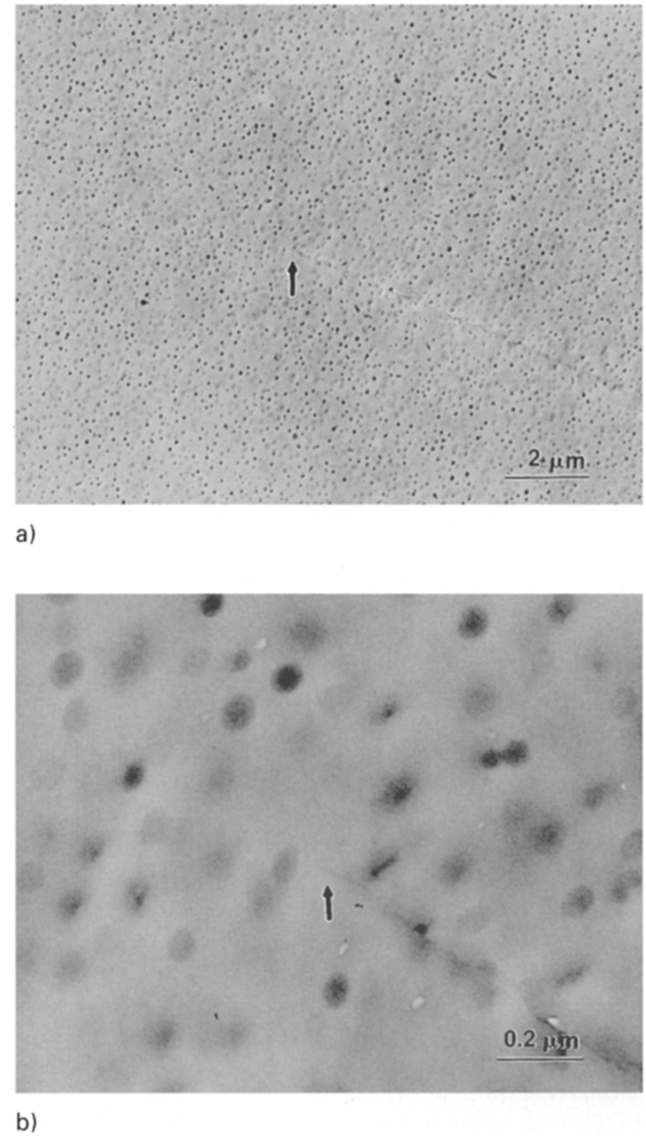

Fig. 5 Transmission electron micrographs of a damaged DN-4PB sample of the VT-RCSP-random modified epoxy system taken around the crack tip region (The arrow indicates the crack tip). Limited crack tip yielding, as manifested by the elongated VT-RCSP, is observed. a) low magnification and b) high magnification

Since the size of the RCSP is too small for optical microscopy observations, only TEM is employed for fracture mechanism investigations. In general, the major fracture mechanisms in these VT-RCSP modified epoxies (Figs. 5–9) are crack deflection, crack bifurcation, and microcracking, which are different from those of the CSR-modified epoxy where extensive rubber particle cavitation and matrix shear yielding are present [33]. No signs of extensive toughener particle cavitation and/or matrix shear yielding are observed in the VT-RCSP-modified epoxies.

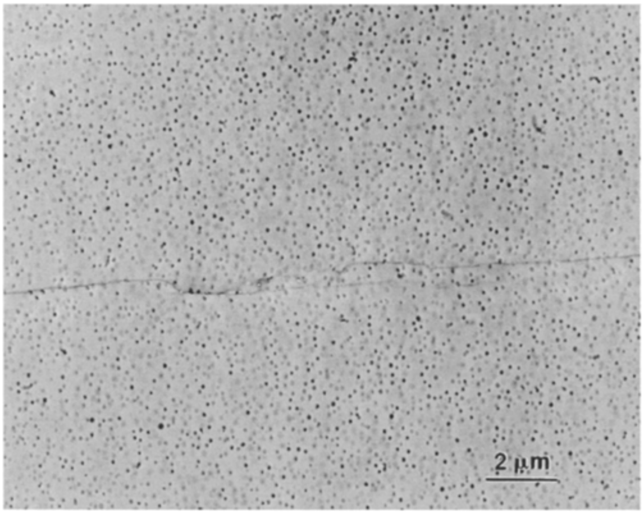

Fig. 6 Transmission electron micrograph of a damaged DN-4PB sample of the VT-RCSP-random modified epoxy system taken at the crack wake. Crack bifurcation is readily observed

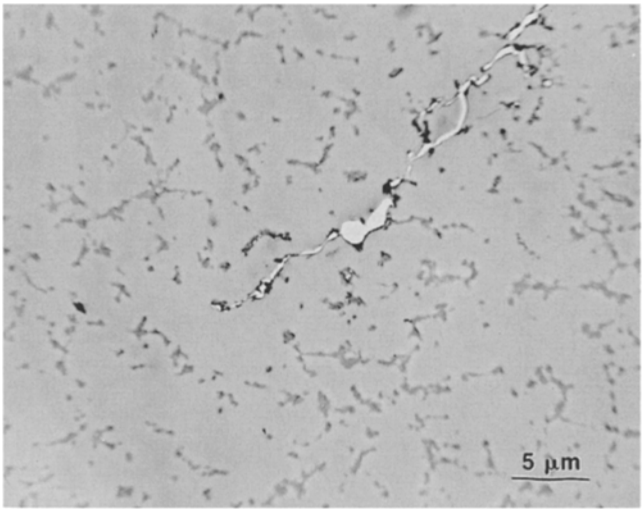

Fig. 7 Transmission electron micrograph of a damaged DN-4PB sample of the VT-RCSP-cluster modified epoxy system taken around the crack tip region. Crack deflection, crack bifurcation, and microcracking (see arrows) are observed

The effect due to the variation of the shell copolymer composition in CSR-modified epoxies has been studied in detail previously [27]. In brief, the closer the solubility parameter of the shell to the epoxy matrix, the easier the core-shell particles can randomly disperse in the epoxy matrix. With the acrylonitrile copolymer ratio in the shell kept constant, the presence of the GMA in the shell can greatly help disperse the core-shell particles. Consequently, it is anticipated that a copolymer composition of S/MMA/AN/GMA = 30/30/25/15 in the shell will result

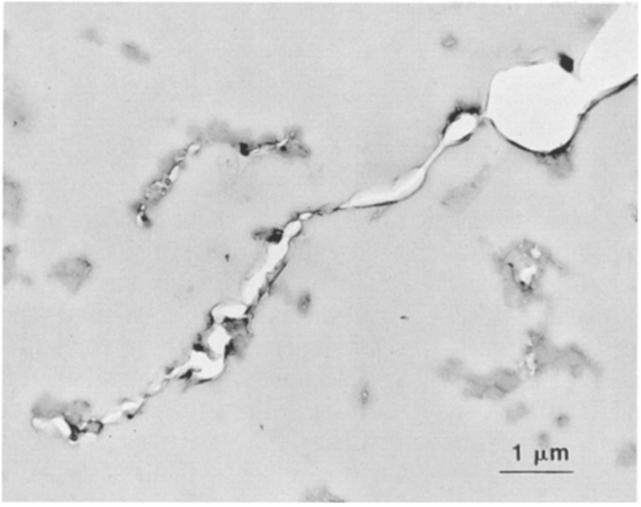

Fig. 8 Transmission electron micrograph taken at the location the same as Fig. 7, except at a higher magnification

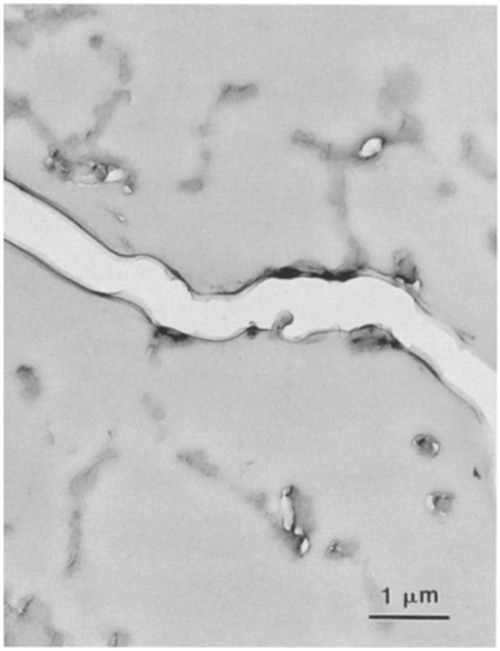

Fig. 9 Transmission electron micrograph of a damaged DN-4PB sample of the VT-RCSP-cluster modified epoxy system taken at crack wake. Microcracking (see arrows) is readily observed

in a random dispersion of VT-RCSP in the epoxy matrix. Indeed, as shown in Figs. 5 and 6, the VT-RCSP are found to be randomly dispersed in the epoxy matrix. The fracture mechanisms in this system are highly localized yielding of the matrix near the crack tip (Fig. 5) and occasional crack bifurcation (Fig. 6). A few scattered cavities along the crack wake and around the crack tip are also observed (see arrows in Fig. 5). However, it is uncertain whether or not these cavities are formed due to the fracture process. Even if the presence of the cavities around the crack is real, i.e., the cavities are not formed due to the sample preparation procedure, the amount and extent of cavitation around the propagating crack is probably not sufficient to relieve the plane strain constraint induced by the presence of the sharp crack. As a result, only about 35% improvement in K_{IC} is obtained (0.83 vs. 1.12 $MPa \cdot m^{0.5}$).

For the VT-RCSP that possesses a copolymer of S/MMA/AN = 37.5/37.5/25 in the shell, it is expected that the particle dispersion will be globally well-dispersed but locally clustered [27]. As predicted, this is indeed the case (Figs. 7–9). As a result of this morphological feature, the microcracking mechanism, which is induced from inside the clustered VT particles, is found to be operative. The microcracking mechanism, if optimized, can be very effective in toughening brittle epoxies [34, 35]. This is because the microcracking process can induce a local dilatational field around the crack wake, which will help shield the crack from further opening. This toughens the matrix. Furthermore, the crack deflection and crack bifurcation mechanisms are found to be operative during the fracture process (Figs. 7–9). No signs of extensive matrix shear yielding are noticed. The additive contributions from microcracking, crack deflection, and crack bifurcation help improve the K_{IC} from 0.83 for the neat resin to 1.21 $MPa \cdot m^{0.5}$ for the modified system (a 47% improvement), which is equivalent to the toughening effect due to the CSR modification (Table 1) [33].

Unlike the CSR particles where the particles still exhibit individual identity as separate particles, the morphology of the VT-RCSP-cluster appears to indicate fusion among the VT-RCSP (Figs. 7–9). This implies that the crosslink density of the VT-RCSP is probably less than that of the CSR particles. As a result, irregularly shaped particles are formed in the epoxy matrix. Also, the clustered VT-RCSP appears to be more brittle (or possessing lower cohesive strength) than the epoxy matrix. In other words, the crack has a stronger tendency to initiate and grow from inside the clustered VT-RCSP domain than from the epoxy matrix. This may explain the occurrence of microcracking, crack deflection, and crack bifurcation in this VT-RCSP-modified epoxy matrix. The reason the randomly dispersed VT-RCSP does not form microcracks is probably due to its small size and/or fewer defects in the VT-RCSP domain [36–38].

As mentioned earlier, the use of the core-shell particles is an excellent method to gain better control of the toughener particle size and dispersion in the epoxy matrix. The alteration of the shell copolymer composition can strongly influence the dispersion of the toughener particles in the epoxy matrix [27]. If other routes, such as dissolving the toughener particles in the epoxy monomer or mixing the toughener particles with the epoxy using co-solvent, are used, then the resultant morphology of the toughener phase in the epoxy matrix can become very complex [39, 40]. Even with extreme care, depending on the phase formation mechanism(s) and kinetics, the exact composition and size of the toughener phase can vary dramatically with the resin cure schedule. This may, in turn, lead to poor reproducibility of the resin physical and mechanical properties.

The present study has clearly demonstrated that the rigid-rigid polymer toughening concept is a feasible approach for toughening high performance polymers for structural applications. Depending on the specific needs, whether it is physical, chemical, processing, mechanical, or combinations of the above, the rigid-rigid polymer toughening approach has the versatility to meet the demands. At this stage, however, it is still uncertain how effectively the rigid-rigid polymer toughening approach can promote crazing and/or shear yielding of the matrix. Preliminary results have indicated that it is possible for the rigid toughener particles to promote crazing and shear yielding of some engineering polymers, if the type and size of the toughener particles utilized are appropriate [41–43]. Additional effort is currently underway to quantify the effectiveness of each fracture mechanism in rigid-rigid polymer alloy systems.

Conclusion

The mechanical behavior and toughening mechanisms of two VT-RCSP-toughened epoxy/DDS systems were investigated using the DN-4PB and TEM techniques. The toughening effect in the clustered VT-RCSP-modified epoxy is found to be as effective as that of the CSR-modified epoxy. Crack deflection, crack bifurcation, and microcracking are found to give this toughness improvement. For the randomly dispersed VT-RCSP/epoxy system, however, only limited crack bifurcation and crack tip shear yielding are observed. The usefulness of the rigid-rigid polymer toughening concept is demonstrated by the model VT-RCSP-modified epoxies investigated here. That is, without any apparent loss of stiffness and T_g, a significant toughening effect can be obtained via the rigid toughener particles.

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