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Nanostructure Toughened Epoxy Resins

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Increasing the fracture toughness of brittle epoxies often comes at the expense of modulus and use temperature, creating unacceptable limits on the use of these resins. Our recent efforts have concentrated on using block copolymer self-assembly to toughen epoxies with a minimal impact on the glass transition temperature and modulus and with the advantages of simple processing and low cost.[1−5] Block copolymers self-assembled into vesicles and micelles can significantly increase the fracture resistance of model bisphenol A epoxies (e.g., BPA348) cured with a tetrafunctional aromatic amine curing agent (e.g., MDA).[3,4] Spherical micelles and vesicles share the same basic shape, but the larger dimensions of the vesicles produced up to a 3-fold increase in the fracture resistance. Here, we introduce a new type of modifier morphology—self-assembled wormlike micelles—and demonstrate a remarkable enhancement in fracture resistance with a bisphenol A epoxy cured with phenol novolac, even for epoxy formulations containing brominated epoxies to improve flame retardation. Moreover, this exceptional improvement is accompanied by an increase in the glass transition temperature. This discovery has important implications for the manufacture of printed circuit boards and other applications where use temperature, flame retardation, and toughness are important.

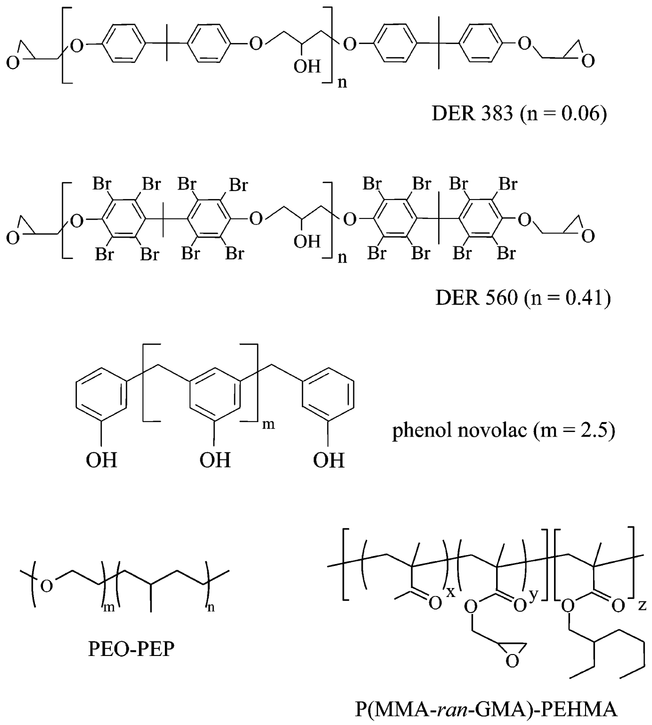

Figure 1. Chemical structures of PEO−PEP and P(MMA-*ran*-GMA)−PEHMA diblock copolymers, phenol novolac curing agent, and bisphenol A type epoxies used in this investigation.

Complete descriptions of the polymerization protocols for the block copolymers used in this study are given elsewhere.[5−7] Two types of amphiphilic block copolymers, poly(ethylene oxide)−poly(ethylene-*alt*-propylene) (PEO−PEP) and poly(methyl methacrylate-*ran*-glycidyl methacrylate)−poly(2-ethylhexyl methacrylate) (P(MMA-*ran*-GMA)−PEHMA), were used, [5,7] as illustrated in Figure 1. Table 1 lists the physical characteristics of the block copolymers including the weight percent and composition of the epoxy miscible blocks (PEO or P(MMA-*ran*-GMA)) and the block copolymer molecular weights and polydispersities.

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Table 1. Molecular Characteristics of Block Copolymer Modifiers[a]

A−B diblock[b,c]	wt % A block	mole fraction GMA in P(MMA-*ran*-GMA)	M_n (g/mol)	M_w/M_n
PEO−PEP-15	32		8 000	1.04
PEO−PEP-9	48		16 800	1.10
P(MMA-*ran*-GMA)−PEHMA-0	20	0	18 500	1.27
P(MMA-*ran*-GMA)−PEHMA-1	18	0.2	21 500	1.22
P(MMA-*ran*-GMA)−PEHMA-2	19	0.4	21 050	1.21
P(MMA-*ran*-GMA)−PEHMA-3	22	0.4	25 500	1.21
P(MMA-*ran*-GMA)−PEHMA-4	14	0.4	38 500	1.24

[a] See refs 3, 4, and 7 for a description of these polymers. [b] A block is epoxy resin miscible. [c] PEO = poly(ethylene oxide); PEP = poly(ethylene-*alt*-propylene); PMMA = poly(methyl methacrylate); P(MMA-*ran*-GMA) = poly(methyl methacrylate-*ran*-glycidyl methyl methacrylate); PEHMA = poly(2-ethylhexyl methacrylate).

Our resins were formulated by mixing two poly(Bisphenol A-*co*-epichlorohydrin) epoxies: one with brominated aromatic rings (DER 560, $M_w = 900$ g/mol) and one without bromination (DER 383, $M_w = 360$ g/mol). Both epoxies were cured with stoichiometric amounts of a phenol novolac hardener (PN, $M_w = 472.5$ g/mol). These chemicals were supplied by The Dow Chemical Co. and used as received. Figure 1 shows the structure of the epoxies and curing agent.

We employed the neutral solvent acetone to facilitate homogeneous mixing of the block copolymer, epoxy, and curing agent at room temperature, typically adding 23 mL of acetone to a 40 g batch of resin containing 1−2 g of block copolymer. Once complete homogeneity was achieved (this required several minutes to several days), the solvent was removed under vacuum at 50 °C (1 h), followed by additional drying at 75 °C (1 h) and at 100 °C (30 min). This procedure minimized condensation of the epoxy and alcohol groups prior to casting. Uniform and bubble-free plaques were obtained by heating the dried mixture to 150 °C and then quickly pouring the liquid into a preheated mold. After curing (in air) overnight at 150 °C, the casts were slowly cooled to room temperature, demolded, and postcured for 1 h at 220 °C under vacuum. This produced a homogeneous, void-free, and fully cured slab approximately 10 cm × 8 cm × 4 mm in size, which was then machined into compact tension, tensile, and three-point bend specimens.

The morphologies of these block copolymer modified epoxy composites were determined by transmission electron microscopy (TEM). A representative piece of the epoxy sheet was microtomed at room temperature using a Reichert Ultra-microtome S equipped with a diamond knife. Thin (ca. 70 nm) sections were floated on water, recovered on copper grids, and stained with the vapors of a 0.5 wt % aqueous solution of RuO_4.[8,9] For the PEP−PEO blends, RuO_4 preferentially stains in the following order: PEO > epoxy > PEP. For the methacrylic-based block copolymers, RuO_4 stains in the following order: P(MMA-*ran*-GMA) > epoxy > EH. While P(MMA-*ran*-GMA) does not absorb the RuO_4 stain,[8,9] the stain apparently penetrates the epoxy around this polymer to a greater degree than the bulk epoxy. In addition, any unreacted glycidyl groups in the epoxy miscible block react with RuO_4, and this combination of effects gives the appearance that the P(MMA-*ran*-GMA) is stained black. The staining time with RuO_4 for either type of block copolymer was 20 min. Stained samples were then imaged with a JEOL 1210 TEM at an accelerating voltage of 120 kV.

Modified and unmodified samples were tested in a three-point bend configuration in a Rheometrics Scientific Mark IV dynamic mechanical testing apparatus (DMTA). The samples were subjected to a sinusoidal deformation to measure the dynamic elastic (E') and loss (E'') flexure moduli at a fixed frequency of 10 rad/s and strain of 0.01% while increasing the temperature at 2 °C/min from 25 to 185 °C. Test specimens were machined to 28 mm long, 6 mm wide, and 2 mm thick. At least two, but typically five, samples of each material were tested. The glass transition in these materials is closely correlated with the temperature T_δ, where $\tan \delta = E''/E'$ peaks; to a close approximation $T_g = T_\delta - 20$ °C.[10]

Void-free samples for compact tension fracture tests were machined from the epoxy sheets. The stress-intensity factor, K_{Ic}, for the block copolymer modified epoxy material was determined using the compact tension geometry method described in ASTM D5045. Cracks were initiated by lightly tapping a new, liquid nitrogen chilled razor blade in the machined notch. Tests were conducted on an MTS testing frame in tensile mode with a crosshead speed of 10 mm/min. Six to ten samples were tested for each material, and the fracture resistance was calculated from

$$K_{Ic} = \frac{P_{max}}{BW^{1/2}} f(a/W) \tag{1}$$

where P_{max} is the maximum load at failure, B is the sample thickness, W is the overall length, a is the crack length and $f(a/W)$ is an expression accounting for the geometry of the sample identified in ASTM D5045. Each test was verified to ensure that the requirements for small scale yielding were met. The fracture resistance, G_c, was obtained from

$$G_c = \frac{{K_{Ic}}^2}{E}(1 - \nu^2) \quad \text{(plane strain)} \tag{2}$$

where ν is Poisson's ratio, taken to be 0.34, and E is Young's modulus which was measured on the same MTS frame at the same crosshead speed used for the compact tension experiments.

In the dilute limit, block copolymers self-assemble into disordered spherical micelles, wormlike micelles, or vesicles.[11] Each morphology can be generated in brominated and nonbrominated epoxy resins, and representative images obtained from cured specimens are shown in Figure 2. Spherical micelles contain a hydrocarbon core surrounded by an epoxy compatible corona. Vesicles are formed by block copolymer bilayers that encapsulate an epoxy core. In contrast, cylindrical ("wormlike") micelles are composed of long, thin tubes of epoxy immiscible polymer stabilized by a corona of the epoxy miscible block. All three morphologies are formed in the unreacted block copolymer−resin mixture

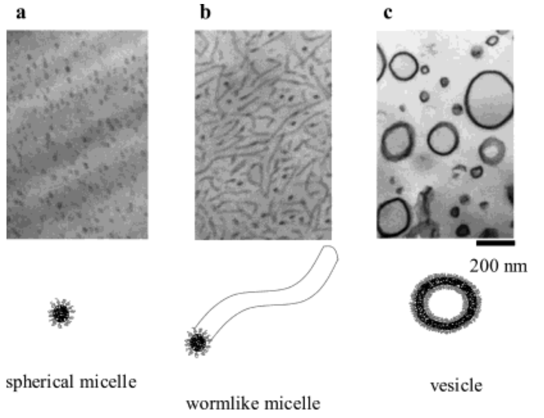

Figure 2. Transmission electron microscopy images of (a) spherical micelles (PEO−PEP-9), (b) wormlike micelles (PEO−PEP-15), and (c) vesicles (P(MMA-*ran*-GMA)−PEHMA-4), each in epoxy formulations containing 25 wt % DER 560 and cured with phenol novolac. These images are representative of the block copolymer modified epoxy morphologies investigated in this study.

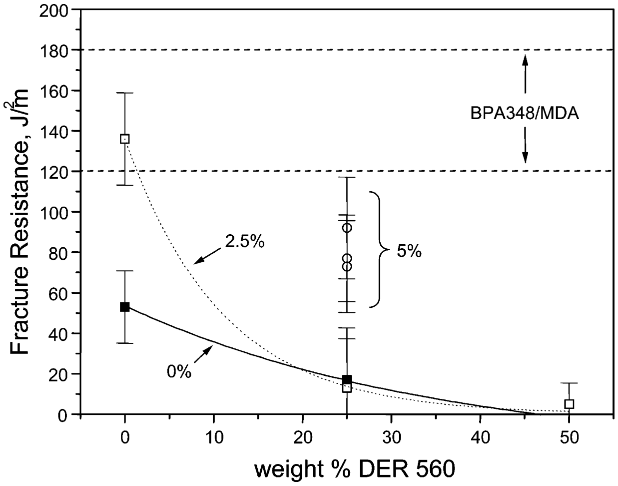

Figure 3. Fracture resistance of diblock copolymer modified DER383/DER560 cured with phenol novolac. Increasing the amount of brominated epoxy without block copolymer (solid symbols and 0% curve) reduces the fracture toughness. Addition of 2.5% P(MMA-*ran*-GMA)-PEHMA-4 (open squares and dashed curve) or 5 wt % P(MMA-*ran*-GMA)−PEHMA-*x* (open circles, $x = 0-3$ in Table 1), all in the form of vesicles, results in modest improvements in fracture resistance.

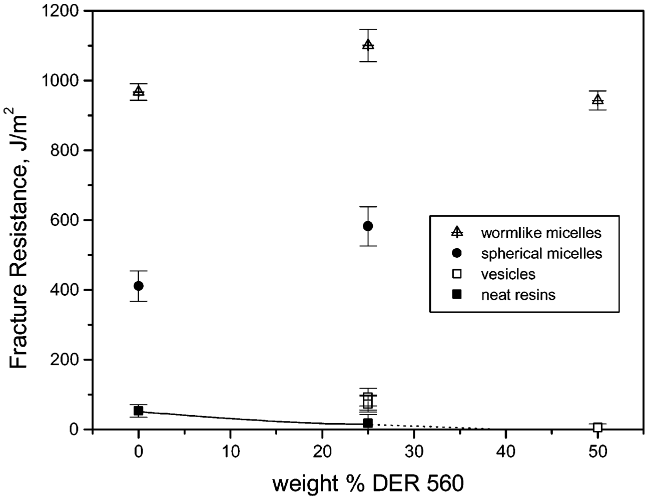

Figure 4. Fracture resistance for DER383/DER560/PN containing 5 wt % diblock copolymer; the result denoted vesicles at 50% DER560 contains 2.5% block copolymer. Spherical and wormlike micelles were obtained from PEO−PEP-9 and PEO−PEP-15 diblock copolymers, respectively, while vesicles were generated with the P(MMA-*ran*-GMA)−PEHMA compounds.

with the equilibrium phase determined by the block copolymer composition (i.e., the relative length of the epoxy miscible block). Previous research has demonstrated that the morphology becomes permanently fixed during the curing stage.[1,2] The balance of molecular scale factors responsible for this type of self-assembly mirrors that found in aqueous systems.[12,13]

The principal objective of this Communication is to report preliminary findings that reveal remarkable toughening associated with the creation of nanostructure in the DER/PN system, especially for the flame-retardant brominated resins. Addition of brominated monomer (DER 560) to the DER 383 epoxy resin reduces the fracture resistance of the cured materials. Even without bromination these epoxies are relatively brittle. DER 383/PN exhibits a fracture resistance of $G_c = 55 \pm 15$ J/m^2 (see Figure 3); for comparison, BPA348/ MDA, a well-studied less fragile thermoset material,[1−4] has $G_c = 150 \pm 30$ J/m^2. Adding the brominated monomer DER 560 to DER 383 compromises the fracture resistance of the PN-cured plastic as illustrated in Figure 3. Just 25 wt % of this flame-retardant monomer decreased G_c by 75%, while cured mixtures containing 50% DER 560 were extremely brittle, which complicated machining of test specimens; we did not implement more sophisticated machining methods We have obtained some improvement in fracture resistance by incorporating 2.5 wt % vesicle forming block copolymers (P(MMA-*ran*-GMA)−PEHMA, Table 1) into the 0%, 25%, and 50% DER 560 blended epoxy resins as shown in Figure 3. However, the results were somewhat erratic. For undiluted DER 383/PN we obtained a 250% increase in G_c, consistent with improvements realized with BPA348/ MDA using low concentrations of vesicles.[4] However, with 25% DER 560 there was no significant improvement while the 50% material was barely tough enough ($G_c \approx 5$ J/m^2) to machine compact tension specimens with our simple methods. Increasing the concentration of block copolymer to 5% in the system containing 25% DER 560 raised G_c to about 80 J/m^2, roughly 4 times the value of the neat plastic; this improvement did not depend on the detailed composition of the P(MMA-*ran*-GMA)−PEHMA blocks. These results are consistent with previously reported trends[3,4] in BPA348/MDA, i.e., 2−4-fold increases in G_c with 2 to 5 wt % vesicles. Significantly, our previous studies indicated that vesicles generally outperformed nanoscale micelles as toughening additives.

Substituting PEO−PEP micelles for the vesicle forming diblock copolymers resulted in a remarkable improvement in fracture resistance as illustrated in Figure 4. The most quantitative comparison between morphologies at a constant (5%) block copolymer loading was made with the intermediate 25 wt % DER 560 mixtures. Spherical micelles led to $G_c = 590 \pm 50$ J/m^2 while wormlike micelles yielded $G_c = 1100 \pm 50$ J/m^2, improvements of nearly 40 times and more than 70 times, respectively, over the unmodified thermoset plastic.

These trends were duplicated at other selected concentrations. Although the relative improvement in G_c is smaller in the DER 383 mixture, the absolute values for the spherical and wormlike micelle specimens do not vary significantly with the amount of DER 560.The most spectacular relative improvement came with the 50%

DER 560 blend where $G_c = 950 \pm 25$ J/m^2. Addition of just 5% block copolymer transforms the virtually useless fragile glassy material into a tough resistant plastic suitable for practical applications.

Dynamic mechanical spectroscopy (DMS) measurements revealed that these dramatic improvements were achieved with modest loss in material stiffness. Both the 0% and 25% DER 560 specimens containing 5 wt % block copolymer registered at most 20% reductions in elastic modulus E' from a base value of 3 GPa. For the 50% DER 560 material containing wormlike micelles $E' = 2.8$ GPa; DMS specimens could not be fashioned from the brittle neat resin.

Finally, DMS measurements have revealed that modification of DER 383/DER 560/PN with block copolymer actually enhances the use temperature, which we associate with T_δ ($\cong T_g + 20$ °C). After thermal curing, the unmodified DER 383/PN and the mixed epoxy containing 25% DER 560 are both characterized by $T_\delta = 105$ °C. Surprisingly, modifying these resins with block copolymers boosts T_δ, in some cases as much as 55 °C. Moreover, the increase in T_δ appears to be correlated with the enhancement in fracture resistance. For example, the wormlike micelle modified thermoset materials (PEO−PEP-15) consistently registered $T_\delta \cong 160$ °C, while spherical micelles increased T_δ by no more than 25 °C and vesicles less than 15 °C.

We are puzzled by this effect, since diluents normally degrade T_g. We can only speculate as to the origins of this intriguing behavior. Most likely the added block copolymer has an impact on the rate of cross-linking reactions during curing; i.e., an elevated T_δ and T_g implies more cross-linking. Perhaps the PEO blocks, which make contact with the resin, play a role. In fact, addition of 1.5 wt % PEO homopolymer ($M_n = 8000$ g/mol) to a 50% DER 560 mixture produced $T_\delta \cong 140$ °C, and this sample also was tougher, $G_c = 150 \pm 30$ J/m^2. This amount of PEO homopolymer roughly equals the total amount of PEO added in block form to the mixtures reported in Figure 4. Hence, PEO plays some part in the process, but this explanation fails to account for most of the toughening effect. Furthermore, increasing the cross-link density (and T_g) would be expected to *reduce* fracture resistance. On the basis of this inconsistency, and the systematic differences between the specimens containing wormlike micelles, spherical micelles, and vesicles, we believe that the nanoscale morphology plays a pivotal role. (Here we note that the different epoxy miscible polymer blocks employed with the vesicles (P(MMA-*ran*-GMA)) and micelles (PEO) may introduce additional complications.)

We have demonstrated how to increase the fracture resistance of a class of commercially important epoxy resins. Apparently, these materials do not follow the patterns described in the epoxy toughening literature.[14−16] This discovery has important implications for the microelectronic and aircraft industries where regulations mandate the use of flame-retardant epoxy resins. Typically, increasing the flame retardance of an epoxy resin reduces its fracture resistance, making it difficult to process these materials into finished products. For example, a major problem in the microelectronics industry is the inability to drill small holes in epoxy composites used in printed circuit board fabrication. This deficiency was evident in the neat 1:1 DER 383/DER 560 formulation. We also note that these materials are easy to process since self-assembly occurs spontaneously upon blending, and the resulting viscosity is marginally affected at the low block copolymer loadings described here.

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