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Epoxy Toughening Using Low Molecular Weight Poly(hexylene oxide)−Poly(ethylene oxide) Diblock Copolymers

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Efforts in the past decades to improve the fracture toughness of brittle epoxies using a secondary phase have focused on the use of rubber[1,2] as well as preformed rigid particles.[2−4] Recent publications from our group and others have reported on epoxy toughening using amphiphilic diblock copolymers that self-assemble into vesicles and micelles within the epoxy matrix,[5−13] analogous to structures formed by surfactants and lipids in water. Earlier[14] we reported the use of a series of poly(butylene oxide)−poly(ethylene oxide) (PBO−PEO) as an example of a commercially viable additive for epoxy toughening. The amphiphilic copolymers, with molecular weights between 15 000 and 20 000 g/mol, produced nanostructures that were dispersed within the epoxy with PBO as the “epoxy-phobic” block and PEO the “epoxy-philic” block. Here we extended the study by using the homologous diblock copolymer poly(hexylene oxide)−poly(ethylene oxide) (PHO−PEO) where the longer alkyl chain in hexylene oxide should cause the segregation between the two blocks (as well as that between PHO and the epoxy) to be stronger than in the PBO−PEO case. The stronger segregation is expected to allow formation of similar morphologies at lower molecular weights. In this study we also employed the method of blending two PHO−PEO copolymers of different compositions to create an intermediate morphology, inspired by previous works from our group and others on the morphological behavior of binary blends of block copolymers in bulk[15−19] as well as in dilute aqueous suspension.[20]

This study used two amphiphilic diblock copolymers poly(hexylene oxide)−poly(ethylene oxide) (PHO−PEO) of different compositions: 9 wt % PEO and 44 wt % PEO. PHO−PEO is illustrated in Figure 1, and the molecular characteristics are listed in Table 1.

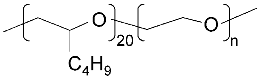

Figure 1. Chemical structures of PHO−PEO used in this study where $n = 5$ (PHO−PEO-1) and 35 (PHO−PEO-2).

Table 1. Molecular Characteristics of Polymer Modifiers

polymer[a]	M_n (g/mol)[b]	M_w/M_n[c]	wt % of PEO
PHO−PEO-1	2220	1.09	9
PHO−PEO-2	3580	1.25	44

[a] PHO = poly(hexylene oxide); PEO = poly(ethylene oxide). [b] M_n determined by NMR: for PHO, ratio of $CH_2{-}O{-}$ in the initiator to the $-CH_3$ of the HO unit; for PHO−PEO, ratio of $-CH_2{-}O{-}$ in the EO unit to $-CH_3$ in the HO unit. [c] Polydispersity determined by size exclusion chromatography.

The block copolymers were prepared by growing the PEO blocks from the same batch of homopolymer PHO. The syntheses of these polymers follow closely the procedure to synthesize PBO−PEO copolymers described earlier.[10] The epoxy resin used was a poly(bisphenol A-*co*-epichlorohydrin) epoxy (DER 383) cured with stoichiometric amounts of a phenol novolac (PN) curing agent without any curing catalyst; the epoxy system is described in greater detailed elsewhere.[10] The resin and curing agent were supplied by the Dow Chemical Co. and were used as received.

We prepared a series of samples of epoxy blends containing 5 wt % of block copolymer. To facilitate homogeneity for each blend, the epoxy resin, curing agent, and the polymer additives were dissolved in acetone and stirred overnight at room temperature. In the case of blending two different block copolymers, they were stirred until homogeneous in acetone (a common solvent for PHO and PEO) prior to mixing with the epoxy resin and curing agent. After a homogeneous mixture was obtained, the acetone was removed under dynamic vacuum. To minimize foam formation during solvent removal, the mixture was stirred under vacuum, heated slowly to 125 °C, typically increasing 25 °C every 30 min, and kept at that temperature until all the solvent had been removed. The mixture was heated to 150 °C and immediately poured into a preheated mold. The mold was then placed in a 150 °C oven (in the presence of air) where curing of the epoxy mixture occurred over 12 h. The epoxy cast was allowed to cool slowly to room temperature and removed from the mold. The plaque, approximately 10 cm by 8 cm by 4 cm, was postcured for 1 h under vacuum at 220 °C to remove voids due to residual solvent or trapped air. We did not observe any evidence for degradation of the material at this elevated temperature. The plaque was finally machined into compact tension and tensile test samples.

Tensile tests were performed on these blends using an Instron 1101 machine with crosshead displacement control and a 5 kN load cell. The tensile samples were machined as bars with 40 mm gage length and 3.2 mm × 3.2 mm cross section. Tests were performed at room temperature and at a constant elongation rate of 1 mm/min. At least four samples were run for each blend. The fracture toughness of the blends was characterized using the energy release rate (G_{Ic}) method, computed from the critical stress concentration factor (K_{Ic}) measured using the compact tension geometry, following ASTM D5045. The equations used are

$$G_{Ic} = \frac{{K_{Ic}}^2}{E}(1 - \nu^2) \qquad (1)$$

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

In eq 1, which applies to plane strain condition, ν is the Poisson’s ratio (taken to be 0.34)[10] and E is the Young’s modulus, measured in the tensile test described above. P_{max} is the maximum load at failure as measured in the compact tension test, B is the sample thickness, W is the overall length of the sample, and $f(a/W)$ is an expression accounting for the ratio of the initial crack length a to W, defined in detail by ASTM D5045. The glass transition temperature T_g of the neat epoxy and the blends were determined by differential scanning calorimetry (DSC).

Transmission electron microscopy (TEM) was used to characterize the resulting morphology of inclusions in the cured epoxy samples. The samples were microtomed into 50−100 nm thick sections using a diamond knife on a Reichert Ultramicrotome S and collected on copper grids. The samples were

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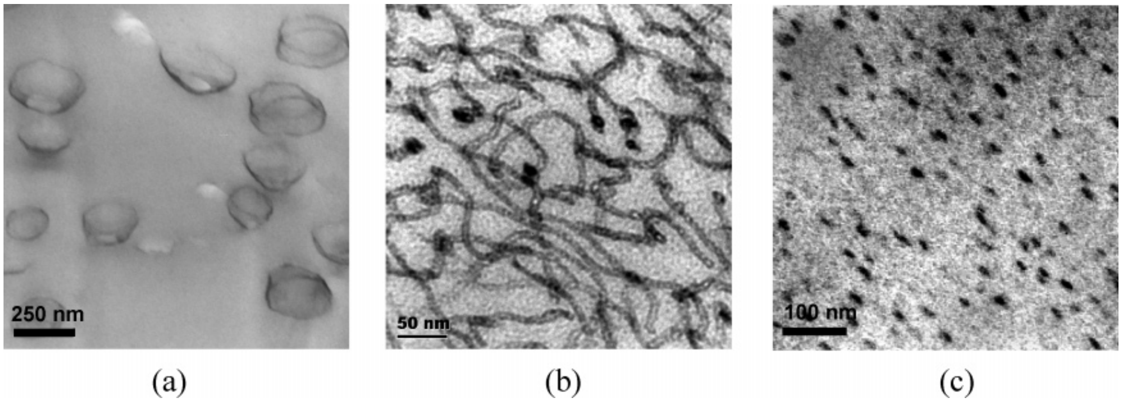

Figure 2. TEM micrographs of blends of DER 383/PN epoxy and 5 wt % block copolymer: (a) PHO−PEO-1, vesicles, (b) mixture of 20 wt % PHO−PEO-1 and 80 wt % PHO−PEO-2, wormlike micelles, and (c) PHO−PEO-2, spherical micelles.

Table 2. Properties of Epoxy Blend Containing 5% of Polymer Additive

polymer	morphology in epoxy	wt % PEO	E (MPa)	K_{Ic} (MPa m$^{1/2}$)	G_c (J/m^2)	T_g (°C)
DER 383/PN			2525 ± 98	0.35 ± 0.05	41.8 ± 12.2	117
PHO−PEO-1	vesicles	9	1530 ± 85	1.26 ± 0.05	920 ± 88	132
20 wt % PHO−PEO-1 80 wt % PHO−PEO-2	cylinders	35	2260 ± 140	2.16 ± 0.27	1830 ± 470	133
PHO−PEO-2	spheres	44	2080 ± 132	0.61 ± 0.11	160 ± 58	126

stained for 30 min using the vapors of a 0.5 wt % aqueous solution of RuO_4, which stains the block copolymers in preference to the epoxy. TEM was performed on a JEOL 1210 microscope at an accelerating voltage of 120 kV. The fracture surfaces resulting from the compact tension test on these blends were examined using a scanning electron microscope (SEM). The samples were given a 50 Å coating of platinum and examined on a JEOL 6500 FEG-SEM at 5 kV accelerating voltage, typically at 6−10 mm working distance.

Figure 2 shows three different morphologies formed by the set of PHO−PEO copolymers in a cured DER 383/PN system. The micrographs show that even at relatively low molecular weights (20−40 repeat units) amphiphilic polyether diblock copolymers can self-assemble within epoxy resin into structures ranging from 20 to 30 nm spheres to 250 nm vesicular bilayers.

On their own, PHO−PEO-1 and PHO−PEO-2 form vesicles and spherical micelles, respectively (Figure 2a,c). We demonstrate here for the first time the formation of intermediate structures by blending two block copolymers of different compositions within a curable matrix. A blend of 20% PHO−PEO-1 and 80% PHO−PEO-2—with an overall fraction of 35% PEO—produced cylindrical/wormlike micelles, as displayed in Figure 2b. Indeed, in a similar diblock copolymer and epoxy system, cylindrical micelles are produced by copolymers of intermediate composition between the vesicle-forming and the sphere-forming copolymers.[7] An earlier work on aqueous suspensions of binary blends of amphiphilic block copolymers[20] showed that the equilibrium state may never be achieved if the two block copolymer suspensions are mixed after they already form their individual nanostructures. In the present study, we avoided this kinetic limitation by premixing the two block copolymers in acetone prior to blending with the epoxy resin. Upon removal of acetone, the blend of block copolymers assemble into a morphology intermediate to the unblended forms. A striking feature in Figure 2b is the high aspect ratio of the cylindrical micelles, which are much longer than any reported previously in block copolymer modified epoxy. This trend of longer and less branched cylinders at lower molecular weight mimics the self-assembly behavior of amphiphilic diblock copolymers in water.[16]

Consistent with the size of inclusions in the blends relative to the wavelength of visible light, the blend containing spherical micelles was transparent (like the unmodified epoxy) and the one with wormlike micelles less transparent, whereas the one with vesicles was white and opaque.

The mechanical properties of the blends containing the different morphologies are summarized in Table 2.

The Young's modulus dropped upon addition of block copolymers while the fracture toughness increased in general. Although all the blends contained 5% block copolymer, the one containing the vesicle morphology exhibited the largest decrease in Young's modulus of about 40% from the unmodified DER383/PN. This significant decrease can be attributed to the large effective volume fraction of vesicles, which encapsulate epoxy as can be seen in Figure 1c. Furthermore, the vesicle particles were not strongly bonded to the matrix, and the low molecular weight PHO core of the bilayer had very low load bearing capacity. In effect, a significant fraction of the cured epoxy resided inside the vesicles and did not contribute fully to the bulk Young's modulus of the blend.

The block copolymers in general improved the fracture toughness of the pure epoxy. On the other hand, the absolute effectiveness depends on the PEO fraction with a maximum at intermediate PEO content, which produced wormlike micelles. Previous studies on toughening epoxy using a similar block copolymer[7] also reported that the largest toughening was achieved using wormlike micelles. The high G_{Ic} value measured in this study for the wormlike micelles (1830 ± 470 J/m^2) is comparable within experimental error to the value reported by Wu et al. for blends containing branched wormlike micelles derived from PBO−PEO (1560 ± 110 J/m^2). In this study, the vesicles also increased the toughness significantly whereas the spherical micelles only produced a relatively modest increase. The fracture surfaces of each blend, shown in Figure 3, exhibited distinct traits related to the mechanisms of crack propagation. The blend containing small spherical micelles (Figure 3a) appeared flat with no significant deformation of the matrix prior to fracture. In contrast, the presence of the larger wormlike micelles and bilayer vesicles increased the surface roughness although with different characteristics. The blend with wormlike

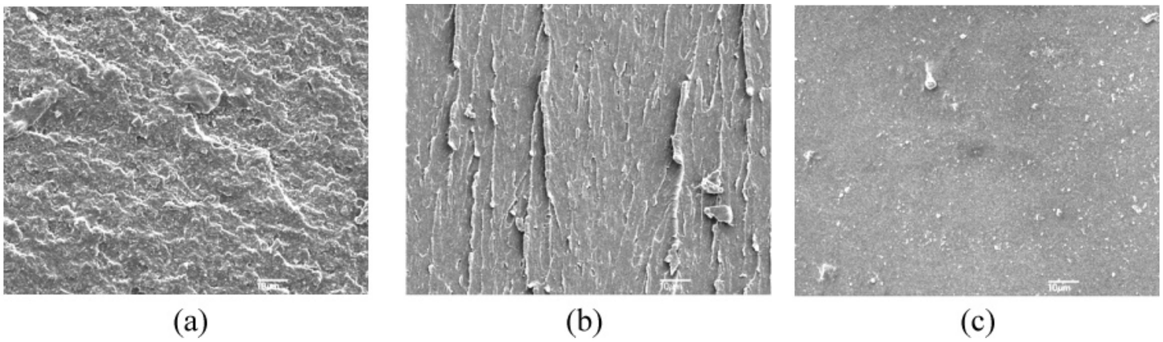

Figure 3. SEM micrographs of fracture surfaces of blends of DER 383/PN epoxy and 5 wt % block copolymer: (a) PHO−PEO-1, (b) mixture of 20% PHO−PEO-1 and 80% PHO−PEO-2, and (c) PHO−PEO-2.

micelles (Figure 3b) showed a surface with steps and “leaflike” structures indicating some small-scale plastic deformation of the matrix. Figure 3c shows even higher surface roughness that appears to be correlated to the size of the vesicles and the large effective volume fraction of particles (because some epoxy resided inside the vesicles).

The latter likely contributed to a less optimum toughness due to the smaller volume of epoxy matrix that participated in absorbing energy during fracture. Whether addition of a smaller amount of vesicle-forming block copolymer to the epoxy will generate a higher toughness is a subject of further investigation.

We believe that length scales play a significant role in determining what toughening mechanisms are active. Whereas the small spherical micelles did not seem to contribute as effectively to significant plastic deformation of the epoxy matrix, the large vesicles (or clusters of vesicles) could serve as defects that promoted earlier fracture. The wormlike micelles with a high aspect ratio might present an optimum length scale, resulting in a higher toughness than the other morphologies. The effect of inclusion size on the fracture toughness of these blends will be treated in more detail in a future publication.

We have shown in this study two main results as proof of concept: (1) that low molecular weight block copolymers with strong segregation can self-assemble to form structures in the epoxy matrix comparable to those found in aqueous dispersions, particularly long defect-free wormlike micelles, and (2) that binary blending of block copolymers of different compositions prior to mixing with the epoxy resin is a viable method to form this intermediate structure. The blending method takes considerably less time and effort than the sequential syntheses of copolymers of the corresponding compositions. Furthermore, the resulting structures produced remarkable toughness in the epoxy blends, similar to the highest values measured in other systems of epoxy and block copolymers. These results, if generalized to other epoxy systems toughened by block copolymers, should prove valuable in facilitating the process of exploring, targeting, and evaluating the morphological behavior as well as the mechanical properties of these systems.

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References and Notes

(1) Kinloch, A. J. *MRS Bull.* **2003**, *28*, 445−448.
(2) Hayes, B. S.; Seferis, J. C. *Polym. Compos.* **2001**, *22*, 451−467.
(3) Lee, J.; Yee, A. F. *Polymer* **2001**, *42*, 577−588.
(4) Lee, J.; Yee, A. F. *Polymer* **2001**, *42*, 589−597.
(5) Hillmyer, M. A.; Lipic, P. M.; Hajduk, D. A.; Almdal, K.; Bates, F. S. *J. Am. Chem. Soc.* **1997**, *119*, 2749−2750.
(6) Lipic, P. M.; Bates, F. S.; Hillmyer, M. A. *J. Am. Chem. Soc.* **1998**, *120*, 8963−8970.
(7) Dean, J. M.; Verghese, N. E.; Pham, H. Q.; Bates, F. S. *Macromolecules* **2003**, *36*, 9267−9270.
(8) Dean, J. M.; Grubbs, R. B.; Saad, W.; Cook, R. F.; Bates, F. S. *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *41*, 2444−2456.
(9) Mijovic, J.; Han, Y. F.; Sun, M. Y.; Pejanovic, S. *Macromolecules* **2003**, *36*, 4589−4602.
(10) Ritzenthaler, S.; Court, F.; Girard-Reydet, E.; Leibler, L.; Pascault, J. P. *Macromolecules* **2003**, *36*, 118−126.
(11) Rebizant, V.; Venet, A. S.; Tournilhac, F.; Girard-Reydet, E.; Navarro, C.; Pascault, J. P.; Leibler, L. *Macromolecules* **2004**, *37*, 8017−8027.
(12) Serrano, E.; Tercjak, A.; Kortaberria, G.; Pomposo, J. A.; Mecerreyes, D.; Zafeiropoulos, N. E.; Stamm, M.; Mondragon, I. *Macromolecules* **2006**, *39*, 2254−2261.
(13) Meng, F. L.; Zheng, S. X.; Zhang, W.; Li, H. Q.; Liang, Q. *Macromolecules* **2006**, *39*, 711−719.
(14) Wu, J.; Thio, Y. S.; Bates, F. S. *J. Polym. Sci., Part B: Polym. Phys.* **2005**, *43*, 1950−1965.
(15) Koizumi, S.; Hasegawa, H.; Hashimoto, T. *Macromolecules* **1994**, *27*, 4371−4381.
(16) Shi, A. C.; Noolandi, J. *Macromolecules* **1995**, *28*, 3103−3109.
(17) Koneripalli, N.; Levicky, R.; Bates, F. S.; Matsen, M. W.; Satija, S. K.; Ankner, J.; Kaiser, H. *Macromolecules* **1998**, *31*, 3498−3508.
(18) Lipic, P. M.; Bates, F. S.; Matsen, M. W. *J. Polym. Sci., Part B: Polym. Phys.* **1999**, *37*, 2229−2238.
(19) Yamaguchi, D.; Hashimoto, T. *Macromolecules* **2001**, *34*, 6495−6505.
(20) Jain, S.; Bates, F. S. *Macromolecules* **2004**, *37*, 1511−1523.

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