

# Epoxy Toughening with Nano-Sized Amphiphilic Block Copolymer Micelles

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## ABSTRACT

An amphiphilic poly(ethylene-*alt*-propylene)-*b*-poly(ethylene oxide) (PEP-PEO) block copolymer (BCP) was blended with a bisphenol A-based epoxy resin formulation and self-assembled into a worm-like micelle structure. With an incorporation of 5 wt% of the BCP material, the fracture toughness was improved by more than 100% over the neat epoxy. The morphology and mechanical properties of this BCP-modified epoxy were investigated using transmission electron microscopy (TEM) and fracture toughness measurements. Toughening mechanisms from the worm-like micelle modified material were investigated using the double-notch four-point-bending (DN-4PB) technique, and the results are compared to data obtained from the same epoxy thermoset formulation containing a BCP that self-assembled into spherical micelles. Elongated cylindrical micelles produce improved toughness, which is interpreted based on a combination of mechanisms including crack tip blunting, cavitation, particle debonding, limited shear yielding, and crack bridging. The implications of the present study for polymer toughening in general are also discussed.

**Keywords:** epoxy toughening, rubber, block copolymer, micelle, worm-like micelle

## 1 INTRODUCTION

Block copolymers (BCP) have been shown to be highly effective at improving epoxy mechanical properties. At low concentrations in epoxy resins, a BCP may self-assemble into well-defined micro-/nano-structures in the form of three distinct morphologies: spherical micelles, worm-like micelles, and vesicles. The type of structure formed depends on the molecular weight, block length, composition, and block-block and block-matrix interaction parameters. These morphologies mimic those of the BCP when dispersed in selective solvents or homopolymers. When the solvent or the homopolymer is highly selective for one block, symmetric BCP form spherical micelles in the dilute limit, while asymmetric BCP form either worm-like micelles or vesicles. In thermosetting systems, the phase behavior is primarily guided by the same fundamental physics operative in solvents and in homopolymer blends, which involves selective solvation of the miscible block.

Although BCP previously have been studied as toughening agents with epoxy resins, most of the BCP studied are in the form of spherical micelles. Only a limited number of investigations have addressed other self-assembled morphologies, especially the worm-like micelles, attributable to a narrow BCP composition window needed to control and stabilize the worm-like micelle structure. In addition, there have been inconsistent results in the toughening effects from BCP structures with different morphologies. For both fundamental research and commercial applications, it is necessary to fully explore the ability of BCP to produce morphologies other than spherical micelles and to investigate their influences on the mechanical properties of cured epoxy matrices.

In our previous publications<sup>1-4</sup> we have discussed in detail the mechanical properties and toughening mechanisms of a model diglycidyl ether of bisphenol A (DGEBA) epoxy resin thermoset modified with poly(ethylene-*alt*-propylene)-*b*-poly(ethylene oxide) (PEP-PEO) amphiphilic BCP that forms 15 nm diameter spherical micelles. The addition of this BCP toughening agent can improve the epoxy fracture toughness by as much as 180%. The major operative toughening mechanism in the modified epoxies has been found to be BCP micelle particle cavitation-induced matrix shear banding. In the current work, focus is placed on the mechanical properties and fracture behavior of an epoxy resin thermoset composition modified with 5 wt% of a PEP-PEO BCP that yields worm-like micelles. This morphology was achieved by tuning the molecular weight and poly(ethylene oxide) (PEO) fraction of the PEP-PEO copolymer and the crosslink density of the epoxy matrix. Fracture toughness ( $K_{IC}$ , critical stress intensity factor) results are presented and compared with the same epoxy resin that contains spherical micelles. The implications of the present study for polymer toughening in general are also discussed.

## 2 EXPERIMENTAL

### 2.1 Materials

Diglycidyl ether of bisphenol-A (DGEBA) epoxy resin (D.E.R.<sup>®</sup> 332, Dow Chemical), 1,1,1-tris(4-hydroxyphenyl)ethane (THPE, Aldrich), and bisphenol A (BPA, PARABIS, Dow Chemical) were used as the matrix, crosslinker, and difunctional chain extender, respectively. Ethyltriphenylphosphonium acetate (70% in methanol, Alfa Aesar) was added as a catalyst to reduce the cure time.

The PEP-PEO diblock copolymer was synthesized using a multi-step polymerization approach. The weight fraction of EO,  $w_{EO}$ , in the BCP was tuned to 0.32. The number-average molecular weight,  $M_n$ , and the polydispersity index,  $PDI$ , of the BCP were 7300 g/mol and 1.06, respectively. For comparison purposes, the BCP that gave spherical micelles had a  $w_{EO}$  of 0.40 and an  $M_n$  of 9100 g/mol. In epoxy thermostets, PEO is the miscible block and PEP the immiscible block.

## 2.2 Preparation of BCP Worm-Like Micelle-Modified Epoxy

Samples were prepared by solvent casting. A detailed sample preparation procedure is described elsewhere. The BCP was first completely dissolved in acetone and mixed with the epoxy monomer, the crosslinker and the chain extender. The solvent was then removed under dynamic vacuum, first at room temperature, and then gradually heating to 130 °C. Catalyst was then added and the mixture was cured in an oven at 200 °C for 2 h.

Various molecular weights between crosslinks ( $M_c$ ) of the epoxy thermostet compositions were prepared and evaluated, but the long worm-like morphology was only obtained in the system with a theoretical  $M_c$  of 600 g/mol. The total concentration of BCP in the material was 5 wt%. All the specimens were completely dried in a vacuum oven at 80 °C for over 24 h before morphological and mechanical characterizations.

For comparison purpose, a BCP spherical micelle-modified epoxy was also prepared with the same  $M_c$  (600 g/mol). The neat epoxy, BCP worm-like micelle-modified epoxy, and BCP spherical micelle-modified epoxy are designated as CET600, CET600/Worm, and CET/Sphere, respectively.

## 3 RESULTS AND DISCUSSION

### 3.1 Morphology of BCP Worm-like Micelle-Modified Epoxy

The transparency of the epoxy containing worm-like micelles is similar to the one with spherical micelles. TEM micrographs of the RuO<sub>4</sub>-stained sample, shown in Figure 1, reveal well-defined PEP-PEO based worm-like micelles that are homogeneously dispersed in epoxy. Here, epoxy-philic PEO block forms a corona structure surrounding the epoxy-phobic PEP core. The PEO rich region looks slightly darker than the PEP cores in the TEM micrographs and they appear to form a tubular structure with a diameter of ca. 10-15 nm. No macroscopic phase separation or agglomerates were observed.

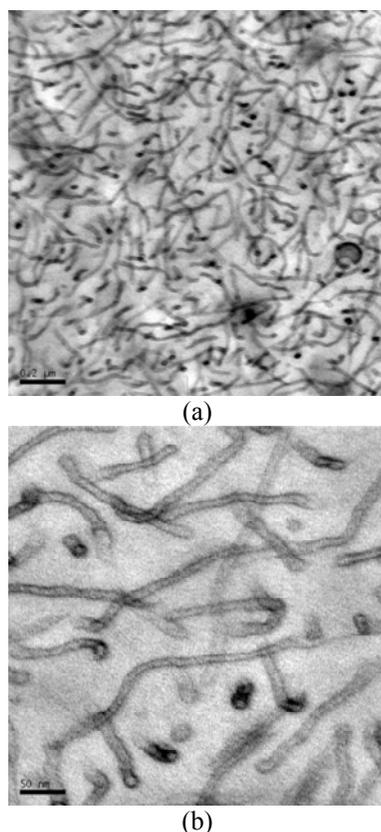


Figure 1: TEM micrographs of BCP worm-like micelle-modified epoxy at (a) low magnification and (b) high magnification.

### 3.2 Fracture Toughness Measurements

The  $K_{IC}$  values of CET600, CET600/Sphere, and CET600/Worm are summarized in Table 1. An improvement in  $K_{IC}$  by 106% over the neat epoxy is observed for the CET600/Worm sample. This improvement is remarkable considering the fact that the total loading of BCP is only 5 wt% and the CET600 has a relatively high crosslink density. In contrast, the spherical micelles are relatively less effective in toughening epoxy networks. To investigate why the worm-like micelles are more effective for epoxy toughening, the fracture mechanisms of CET600/Worm were probed. It is also noted that the fracture toughness value of CET/Worm has a noticeably higher standard deviation than the two control samples. This is probably due to the fact that the natural crack tip radius of epoxy is of the same order as the length of the worm-like structure ( $\approx 0.5 \mu\text{m}$ ). Depending on exactly where the crack tip is located with respect to the worm-like structure, the resistance against crack propagation would vary. In contrast, for epoxies without BCP, or the mixtures containing the 15 nm spherical micelles, the location of the crack tip with respect to the micelle particles becomes irrelevant. This leads to more consistent fracture toughness results.

Table 1: Fracture Toughness  $K_{IC}$  ( $\text{MPa}\cdot\text{m}^{1/2}$ ) of CET600, CET600/Sphere, and CET600/Worm.

	CET600	CET600/Sphere	CET600/Worm
$K_{IC}$ ( $\text{MPa}\cdot\text{m}^{1/2}$ )	0.87±0.04	1.60±0.04	1.79±0.12
Relative Increase	-	+84%	+106%

### 3.3 Toughening Mechanisms Investigation

In order to gain a fundamental understanding of the toughening mechanisms, the DN-4PB test was employed to probe the detailed micromechanical deformation of BCP-toughened epoxy upon fracture. Complete descriptions and schematics of the DN-4PB technique can be found elsewhere.<sup>1</sup>

The toughening mechanisms of the BCP worm-like micelle-toughened epoxy network were investigated by examining the crack tip damage zone of the DN-4PB specimens using TEM.

TEM micrographs were taken at the subcritical crack tip region of the DN-4PB specimens. As shown in Figure 2a, it is evident that the worm-like micelles bridge between the opening crack planes. Because the micrograph was taken based on the unloaded specimen, it is uncertain if the worm-like domains were stretched during loading. If so, it might help contribute to the observed toughening effect. A higher magnification observation at the crack tip region (Figure 2b) further reveals the morphology of the stretched, thinned epoxy matrix that contained worm-like micelles at the edge of the crack, which is indicative of the high ductility of the CET600/Worm.

Careful investigation of the micrographs reveals cavitation of the soft rubber inside the worm-like micelles in this stretched epoxy region. Interestingly, at the very tip region of the crack where the epoxy has been thinned but not yet broken (see Figure 2c), both “broken worms” and “unbroken worms” are found bridging the crack tip. The “unbroken worms” are likely to be broken if the crack further opens up. It is interesting to note that both ends of the “broken worms” appear to have been stretched when the crack develops. Meanwhile, partial interfacial debonding or voiding is observed around both “broken worms” and “unbroken worms”, which is not seen in the case of spherical micelles-modified epoxies. We speculate that such debonding or voiding occurs mainly because of the relatively short EO block length of the BCP at the interface, causing disentanglement of the BCP upon stretching.

Based on the evidence presented here, we believe the improvement in fracture toughness is likely to derive from a combination of several toughening mechanisms: voiding or debonding at the interface between the phases, limited matrix shear yielding, crack tip blunting, crack bridging, and viscoelastic energy dissipation. However, it is worth mentioning that none of these mechanisms alone dominates the fracture energy dissipation process in this case. As reported earlier,<sup>3</sup> the CET900/Sphere sample with

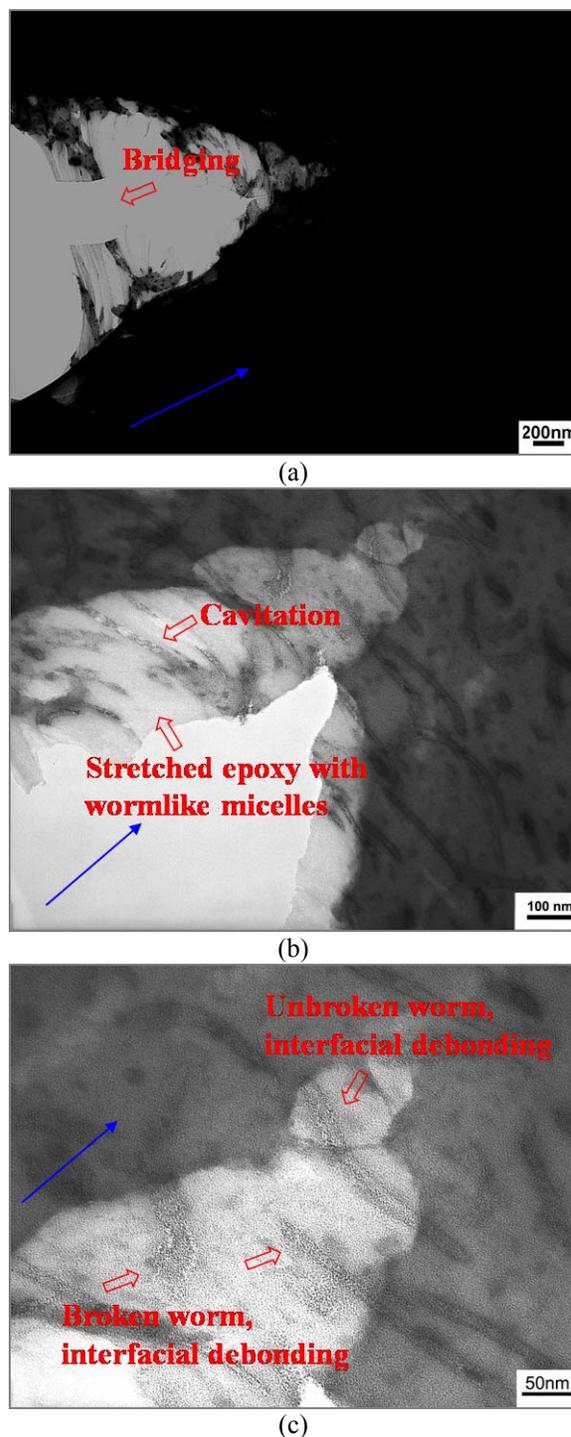


Figure 2: TEM micrographs of the crack tip DN-4PB specimen of BCP-toughened epoxy: (a) overview of the crack tip, (b) evidence of worm-like structure cavitation or fragmentation after severe stretching, and (c) evidence of interfacial debonding or voiding. The blue arrows in the micrographs indicate the direction of crack propagation.

a theoretical  $M_c$  of 900 g/mol exhibited very limited cavitation and matrix shear yielding at the crack tip region upon fracture. Thus, for CET600/Sphere that possesses an

even higher matrix crosslink density, the effectiveness of the cavitation-induced shear yielding mechanism on toughening is expected to be minimal. Meanwhile, interfacial debonding or crack bridging is likely to be negligible because of the small size of the spherical micelle particles with respect to the crack tip radius. Consequently, the CET600/Sphere material exhibits a lower fracture toughness value than the CET600/Worm sample.

## 4 CONCLUSIONS

A PEP-PEO ( $M_n = 7500$  g/mol,  $w_{EO} = 0.32$ ) amphiphilic BCP was used to modify a DGEBA-type of epoxy resin. The BCP molecules self-assemble into well-dispersed worm-like micelles with a diameter of 10-15 nm. The epoxy-miscible PEO block forms a corona surrounding the epoxy-immiscible PEP core. Incorporation of 5 wt% BCP worm-like micelles gives a 100% improvement in  $K_{IC}$ , which is more effective than that of the spherical micelle-modified epoxy. Key operative toughening mechanisms have been identified to be crack tip blunting, cavitation, debonding (voiding), limited shear yielding, and crack bridging.

## REFERENCES

- [1] Liu, J.; Sue, H.-J.; Thompson, Z. J.; Bates, F. S.; Dettloff, M.; Jacob, G.; Verghese, N.; Pham, H. *Macromolecules* **2008**, 41, 7616.
- [2] Liu, J.; Sue, H.-J.; Thompson, Z. J.; Bates, F. S.; Dettloff, M.; Jacob, G.; Verghese, N.; Pham, H. *Acta Mater.* **2009**, 57, 2691.
- [3] Liu, J.; Sue, H.-J.; Thompson, Z. J.; Bates, F. S.; Dettloff, M.; Jacob, G.; Verghese, N.; Pham, H. *Polymer* **2009**, 50, 4683.
- [4] Thompson, Z. J.; Hillmyer, M. A.; Liu, J.; Sue, H.-J.; Dettloff, M.; Bates, F. S. *Macromolecules* **2009**, 42, 2333.