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Block Copolymer Toughened Epoxy: Role of Cross-Link Density

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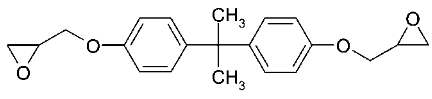
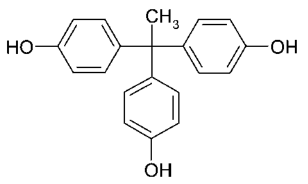
The brittle nature of glassy thermosetting epoxies often necessitates the use of inhomogeneous particles (e.g., core−shell rubber) to provide increased fracture resistance. Recent work has demonstrated that block copolymers may segregate into nanoscale micellar structures in an epoxy matrix at low loadings.[1−9] These block copolymers consist of “epoxy-philic” and “epoxy-phobic” blocks and will form vesicles, wormlike micelles, and spherical micelles within the epoxy matrix that persist after cure. Additionally, the block copolymer modifiers have minimal impact on the glass transition temperature and the Young’s modulus and may provide a dramatic increase in the fracture resistance.[2−4] Previous studies have demonstrated the role of network architecture (i.e., molecular weight between cross-links) on neat and rubber-modified epoxies.[10−14] Here, we extend the investigation of network architecture to an epoxy system modified with a model poly(ethylene oxide)-*b*-poly(ethylene-*alt*-propylene) (OP) block copolymer. We demonstrate an increase in block copolymer toughening upon a decrease in the cross-link density of the epoxy matrix. The maximum fracture toughness obtained with these materials is nearly 3 times the highest value reported previously for an epoxy modified with 5 wt % OP or related diblock copolymers. This phenomenon occurs for both high and low molecular weight diblock additives and to a first approximation is independent of the size of the micelles.

A full description of the protocols used in preparing the OP diblock copolymers may be found elsewhere.[15] Poly(ethylene oxide) (PEO) is the “epoxy-philic” block, and poly(ethylene-*alt*-propylene) (PEP) is the “epoxy-phobic” block. The two block copolymers used in this study are OP3-5 (M_n = 7.8 kg/mol, w_{EO} = 0.35) and OP28-36 (M_n = 63.9 kg/mol, w_{EO} = 0.44).

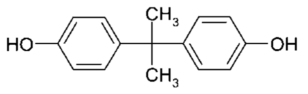
The epoxy resin used for this study was a diglycydyl ether of bisphenol A based epoxy (D.E.R. 332) provided by the Dow Chemical Company. The trifunctional cross-linker 1,1,1-tris(4-hydroxyphenyl)ethane (THPE, Aldrich) and difunctional extender bisphenol A (Parabis, Dow Chemical) were used to systematically alter the network cross-link density. Ethyltriphenylphosphonium acetate (70 wt % in methanol) was purchased from Alfa Aesar and used as a catalyst to decrease cure time. All chemicals were used as received.



D.E.R. 332



THPE



Parabis

Each epoxy plaque was prepared by solvent casting. The block copolymer was placed in a round-bottom flask and completely dissolved in acetone, followed by addition of THPE, Parabis, and D.E.R. 332. Solvent was then removed under dynamic vacuum, first at room temperature and then while gradually heating to 130 °C to ensure full removal of the solvent. Catalyst was added to this mixture (10 μL of the catalyst solution per 40 g of batch solvent free monomer) at 130 °C, followed by stirring for 2 min after which the mixture was poured into a mold that had been preheated to 130 °C. The epoxy-filled mold was placed into an oven and heated to 200 °C for 2 h and

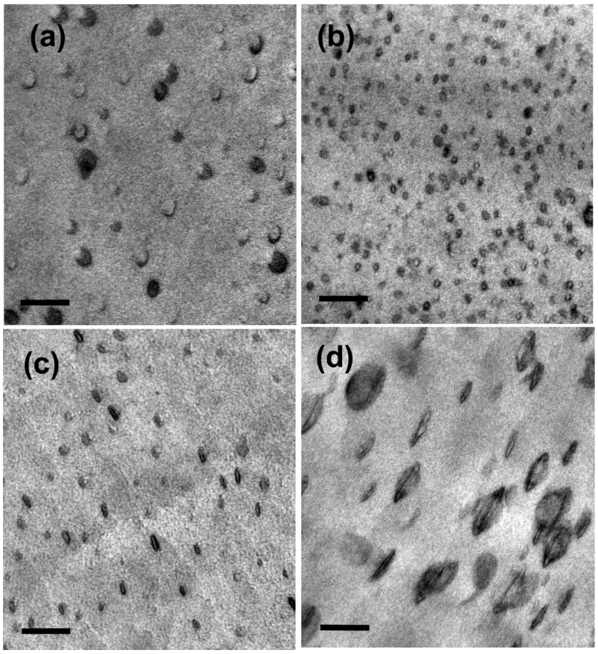


Figure 1. Transmission electron microscopy images of (a, c) OP28-36 and (b, d) OP3-5 modified epoxies. Micrographs were taken from epoxies with molecular weight between cross-links of (a, b) 600 g/mol and (c, d) 3700 g/mol. The block copolymer loading is 5 wt %. Scale bars represent 100 nm.

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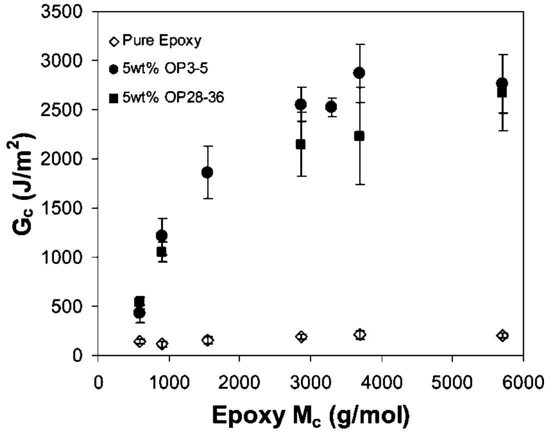

Figure 2. Strain energy release rate (G_c) as a function of epoxy molecular weight between cross-links (M_c). Block copolymer loading is 5 wt %.

then slowly cooled to room temperature in the oven. Differential scanning calorimetry confirmed the plaques were fully cured.

Block copolymer loading in all the epoxy specimens discussed here was 5 wt %. The epoxy formulas were designed based on the theoretical molecular weight between cross-links (M_c), calculated from the stoichiometry of the reactants assuming full conversion. The equation for predicting M_c is

$$\bar{M}_c = \frac{2\left(M_e + \sum_{f=2}^{\infty} \frac{M_f}{f}\Phi_f\right)}{\sum_{f=3}^{\infty} \Phi_f} \qquad (1)$$

where M_e is the epoxide equivalent weight of the resin, f is the functionality of the cross-linker/chain extender, M_f is the molecular weight of the fth functional cross-linker/chain extender, and Φ_f is the mole fraction of hydrogens provided by the fth functional cross-linker/chain extender.

The morphologies of the block copolymer-modified epoxy plaques were established using transmission electron microscopy (TEM). A representative portion of the plaque was microtomed at room temperature using a Reichart Ultra Microtome fitted with a diamond knife. Thin sections (ca. 70 nm) were floated on water and blotted onto a copper grid and then stained with vapor from a 0.5 wt % aqueous solution of RuO_4 for 8−10 min.[16] RuO_4 preferentially stains PEO, then the epoxy, and then PEP for the system examined. Stained samples were imaged with a JEOL 1210 TEM using an accelerating voltage of 120 kV.

Compact tension samples were machined to the geometric specifications outlined in ASTM standard D5045 for fracture under plane-strain conditions. Typical compact tension samples had a thickness (B) of 3.76 mm, a width (W) of 11.86 mm, and a precrack length (a) of ca. 6 mm. The critical stress intensity factor (K_{IC}) for the block copolymer-modified epoxy was calculated from

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

where P_{max} is the peak load at failure and $f(a/W)$ is a geometrical factor found in the ASTM standard. Compact tension samples were run on an Instron Testing System (model 1011) with a crosshead speed of 10 mm/min. At least six specimens were fractured for each calculation. The strain energy release rate was then computed from

$$G_C = \frac{(1 - \nu^2){K_{IC}}^2}{E} \qquad (3)$$

where E is the Young's modulus measured via dynamic mechanical analysis and ν is Poisson's ratio, taken to be 0.34.

Direct visualization of the fracture surface was performed using scanning electron microscopy (SEM). The fracture surfaces were coated with 50 Å of platinum to prevent charging. The surfaces were imaged using a JEOL 6500 FEG-SEM using a 5 kV accelerating voltage and a working distance of 10 mm.

Representative TEM micrographs of the block copolymer-modified epoxy with M_c values of 600 and 3700 g/mol are shown in Figure 1. The micrographs illustrate that the block copolymer has self-assembled to form micelles of various sizes and shape. These micelles were formed before the gel point of the epoxy and persist upon full cure.[17,18] The two block copolymers used in this study formed micelles with diameters between 15 and 100 nm. Interestingly, the micellar structure of the block copolymer can be altered by changing the epoxy network architecture. A spherical micelle forming block copolymer in a highly cross-linked system (Figure 1a,b) may become an ellipsoid or disklike structure in an epoxy with a lower cross-link density (Figure 1d). This topic will be discussed further in a future publication.

The primary objective of this Communication is to report the dramatic effect epoxy network architecture has on the toughening ability of a block copolymer modifier. Compact tension samples were machined from neat and block copolymer-modified epoxies with M_c values ranging from 600 to 5700 g/mol. The strain energy release rate values as a function of M_c are plotted in Figure 2. The fracture resistance of the neat epoxy gradually increases as network cross-link density was reduced

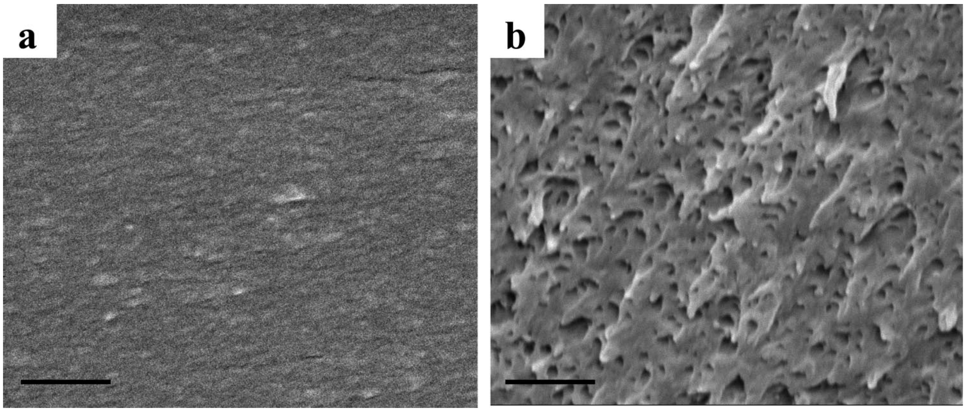

Figure 3. Scanning electron microscopy images of (a) neat and (b) OPMB3-5 modified epoxies. Each epoxy formulation has a molecular weight between cross-links of 2900 g/mol, and the block copolymer loading is 5 wt %. The scale bars represent 500 nm.

from $G_c \cong 120$ J/m^2 to 200 J/m^2 as M_c increases from 600 to 5700 g/mol, consistent with previous reports.[13] Modulus values ranged from 3.0 to 3.9 GPa. Addition of just 5 wt % of the OP additive provides moderate toughening (ca. a 3-fold increase in G_c) at a high cross-link density. The fracture resistance increases dramatically as the cross-link density decreases in the block copolymer-modified materials. At an epoxy M_c value of 2900 g/mol the strain energy release rate reaches 2700 J/m^2 with little additional improvement as M_c rises to 5700 g/mol. This value is significantly higher than maximum G_c values reported previously and is comparable to commercially available rubber toughened epoxies that contain up to 20 wt % of additive.[2−4] Modulus values of the OP-modified epoxies ranged from 3.0 to 3.3 GPa, comparable to modulus values for previously studied block copolymer-modified epoxy systems. This toughening trend was first observed with the addition of the low molecular weight OP3-5 compound. Substitution of the high molecular weight OP28-36 diblock does not significantly alter the toughening profile, including the maximum attainable value of 2700 J/m^2. Previous reports have demonstrated worm-like micelles formed by block copolymers provide the largest increase in toughening in phenolic-cured epoxy thermosets.[2−4] In this study, the outstanding toughness values were achieved using spherical or oval-shaped micelles.

Studies of liquid rubber modified epoxies have demonstrated a substantial increase in fracture resistance upon decreasing the epoxy network cross-link density. Pearson and Yee have shown a linear dependence between epoxy fracture resistance and the molecular weight between cross-links for a carboxyl-terminated copolymer of butadiene and acrylonitrile (CBTN) toughened epoxy.[13] Energy is dissipated around the crack tip through the formation of shear bands in the epoxy matrix, facilitated by cavitation of the rubber particles.[19−21] An increase in the ductility of the matrix through a decrease in the cross-link density further promotes the formation of shear bands. Recent work by Liu et al. provides evidence of nanometer scale cavitation of block copolymer spherical micelles in an epoxy matrix.[22]

Representative SEM micrographs obtained from the fracture surface of neat and OPMB3-5 modified epoxy are shown in Figure 3. The neat epoxy surfaces appear smooth to the naked eye and shows very little surface roughness at high magnification. Dramatically enhanced surface texturing was generated upon the addition of block copolymer. Particle voiding and extensive shear deformation are clearly evident at an M_c value of 2900 g/mol. Macroscopic plastic deformation is visible near the crack tip for highly cross-linked systems, and the deformation zone expands as the cross-link density is decreased. These results indicate that the block copolymer particles toughen using mechanisms similar to those established for liquid rubber toughened epoxy systems. The plateau in the toughening profile may be the result of an ultimate size limit in the process zone ahead of the crack tip. Increasing the ductility of the matrix will have little impact on fracture toughness beyond the regime where the rubber particles have cavitated to relieve triaxial stress.

In this study we have demonstrated how varying the cross-link density of an epoxy network influences the efficacy of block copolymer particles in promoting fracture toughness. Within our experimental precision this toughening effect is independent of the block copolymer molecular weight. At a block copolymer loading of 5 wt % the strain energy release rate ranges from 3 to 13 times the toughness of the neat thermoset counterpart, as the molecular weight between cross-links increases from 600 to 5700 g/mol, respectively. These findings may find practical application with commercial epoxy systems, offering another variable to improve fracture resistance in formulations where control of block copolymer micellar structure is difficult.

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