

Enhancing the resistance to fatigue crack propagation of epoxy using triblock copolymers

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Adding triblock copolymers to an epoxy resin significantly increases its resistance to fatigue crack propagation (by more than 130%) without reducing its glass transition temperature or ductility.

Epoxy resins are a special class of high-performance thermosetting polymers that are used in a variety of today's automotive, aerospace, and energy applications (e.g., as adhesives and coatings, or as polymeric matrices for fiber-reinforced composites). Such polymers combine excellent mechanical properties with high adhesive strength, low shrinkage and water absorption, and high thermal and chemical stability.

Although epoxies have a number of superior properties compared with other polymers, they have the drawback of being inherently brittle. This leads to low fracture toughness and poor resistance to fatigue crack propagation (FCP). Various strategies have been investigated to overcome this problem by toughening epoxy resins, e.g., by modifying the resin with phases of a compliant nature, such as rubber. Unfortunately, the introduction of rubber modifiers usually decreases the glass transition temperature (T_g) and reduces the strength and elastic modulus of the thermoset. A fairly new approach to toughening epoxy resins while maintaining their mechanical properties and T_g is to introduce block copolymers (BCPs) as a second phase.^{1,2}

BCPs comprise at least two chemically different constituents (i.e., A, B, C, ...) and generate polymeric macromolecules of various compositions, such as diblock (AB), triblock (ABA, ABC), multiblock (ABCD), or alternating compositions (ABABAB...). In contrast to classical tougheners, such as liquid rubbers, the use of BCPs enables a variety of nanosized structures to be obtained in thermosets (e.g., spherical and cylindrical micelles, vesicles, and other continuous and discontinuous structures). These phases form due to thermodynamic forces between the BCP and the epoxy molecules. The structure can thereby occur prior to curing,³ during the curing process,⁴ or in combinations thereof.⁵ Understanding and subsequently gaining control over the phase-separation mechanisms of BCPs in thermosetting polymers

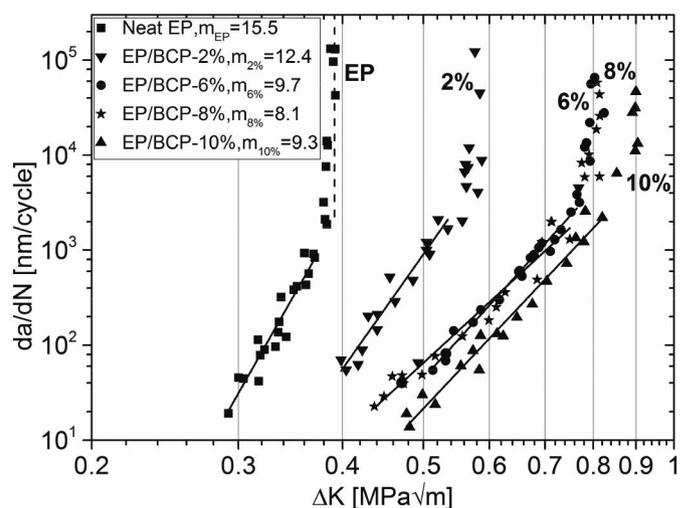


Figure 1. Fatigue crack propagation results (da/dN vs. ΔK) of an epoxy resin (EP)—D.E.R. 331 from Dow Chemical—with different concentrations (0, 2, 6, 8, and 10wt%) of an ABA-type triblock copolymer (Nanostrength M53 from Arkema). da/dN : Fatigue crack growth rate per cycle of loading. ΔK : Stress-intensity-factor range. EP: D.E.R. 331. BCP: Block copolymer.

will therefore enable a BCP phase morphology to be tailored for a required application and the specific properties of the base thermoset to be improved.

In our work, we have evaluated the effect of modifying an epoxy with BCP on the FCP behavior of the epoxy. To this end, we blended a bisphenol-A-based epoxy resin (D.E.R. 331, DGEBA from Dow Chemical) with different concentrations of an ABA-type triblock copolymer (Nanostrength M53 from Arkema) consisting of polymethylmethacrylate-blocks (A-block) surrounding a central polybutylacrylate-block (B-block). We then stoichiometrically cured the system using 3,3'-dimethyl-4,4'-diaminodicyclohexylmethane

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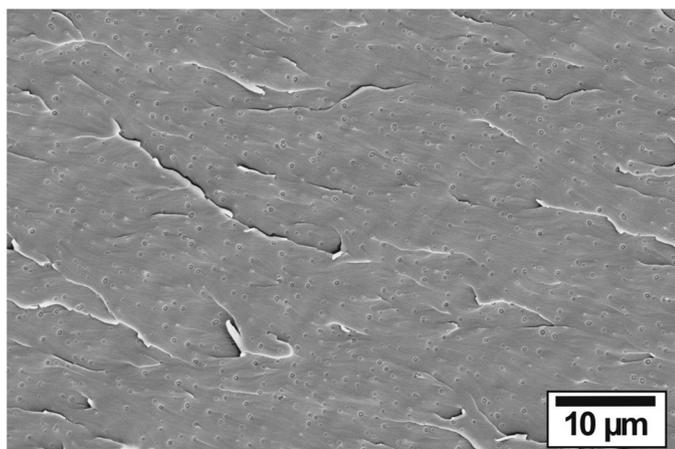


Figure 2. Fatigue fracture surface of EP with 2wt% BCP.

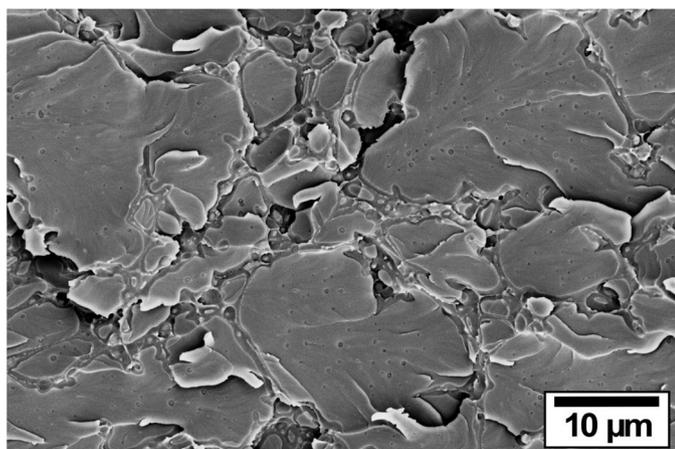


Figure 3. Fatigue fracture surface of EP with 6wt% BCP.

(HY 2954 from Hunstman), a cycloaliphatic amine curing agent. After preparing compact tension specimens, we examined the materials' resistance to the propagation of an artificially introduced crack during fatigue loading.

We found that the resistance of the epoxy to FCP was significantly enhanced by the addition of the BCP.⁶ The fatigue crack growth rate per cycle of loading was gradually reduced with increasing BCP concentration, and at the same time the material was able to withstand much higher stresses at the crack tip (see Figure 1). The BCP-modified epoxy reached critical stress-intensity-factor ranges (ΔK_{Ic}) of more than double the reference epoxy system. Furthermore, T_g slightly increased, from 175°C (neat) to 183°C (with 2wt% BCP).

We analyzed scanning electron micrographs of the composites to determine the mechanisms behind this toughening effect. In the case of epoxy with BCP concentrations of below 6wt%, we were able to

ascribe the toughening effect to the composite's microstructure, which comprised microphase-separated and well-dispersed spherical BCP-rich inclusions (see Figure 2). In the epoxy composites with BCP concentrations of 6wt% and higher, on the other hand, we observed the formation of interconnected, isle-like epoxy-rich domain structures that also contained spherical BCP-rich inclusions (see Figure 3). We did not, however, detect any phase inversion.⁶ The spherical BCP-rich particles induced a variety of toughening mechanisms, such as crack pinning, cavitation, debonding, as well as fibrillation and bridging. These mechanisms resulted in a reduction of the crack driving force. However, we found that the BCP-rich domains plastically deform and debond from the epoxy-rich matrix, followed by a total rupture of the phases.

In summary, we have demonstrated that adding a commercially available triblock copolymer to an epoxy resin enhances its toughness and significantly increases its resistance to FCP. We have thus obtained a comprehensive and expanded understanding of the toughening effects of a block-copolymer-modified epoxy and were able to show that it is possible to significantly toughen a highly brittle thermosetting matrix against FCP without reducing the T_g . For example, we developed a low-cost epoxy system containing 6wt% BCP that provides a reduction of the fatigue crack growth rate of 37% and an increase in ΔK_{Ic} of more than 100% compared with the neat epoxy system.⁶ In our future work, we aim to focus on obtaining a deeper understanding of the effect of different BCP compositions on epoxy resins. Specifically, we hope to make use of the self-assembling character of these materials for fiber-reinforced structures.

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