

Control of inclusion size and toughness by reactivity of multiblock copolymer in epoxy composites



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ABSTRACT

In this paper, the strategy to achieve high fracture toughness and impact strength of epoxy blends by introducing a new family of reactive block copolymer (RBCP), poly[styrene-*alt*-(maleic anhydride)]-*block*-polystyrene-*block*-poly(n-butyl acrylate)-*block*-polystyrene, with different reactivity is reported. Inclusions size of RBCP in cured blends was controlled from nanometer to micrometer by simply adjusting the fraction of reactive block in RBCP. The systematical study on the structure–property relationship revealed that the thermal and mechanical properties of modified blends strongly depend on inclusion size. The results suggested that blends containing nano inclusions of RBCP were more sensitive to test rates. And blends containing sub-micron inclusions showed substantially increased toughness in SENB measurements and IZOD impact tests without loss in T_g . The findings of this work provide an insight on developing toughened epoxy thermosets utilized for both high and low fracture rates via innovative reactive blending.

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1. Introduction

Epoxy resin is widely used in the fields of electron, machine, architecture, and so on for its outstanding mechanical, adhesive, and insulating properties. Since the brittleness is one of its major drawbacks, toughening of epoxy thermosets has been adequately developed in past few decades [1–6]. One of the most common and successful strategies is to incorporate a second phase such as rubbers, thermoplastic particles, or mineral fillers into epoxy matrices [7–14]. Among these studies, it has been demonstrated that mechanical toughness could be significantly improved by using diblock and triblock copolymers [15–21]. The incorporation of such block copolymers (BCPs) self-assemble and form various nanostructures in epoxy matrix [22–24]. Compared to traditional micro fillers, these nano-sized inclusions confer unique features to epoxy blends [25,26]. One of these features relates to the interfacial area, where the distance between inclusions is comparable to the size of interfacial region [27]. This feature promotes interfacial stress

transfer leading to significantly increased toughness of epoxy blends.

A strategy to obtain nano-sized inclusions is to facilitate interfacial effect by forming covalent links between the matrix and inclusion based on the chemical miscible concept. In this fashion, reactive groups are incorporated into initially miscible or immiscible block copolymers to promote covalent linkages binding two phases in blends [28,29]. Epoxy groups are frequently introduced to BCPs to react with the amine end groups of hardeners [30–32]. And Nanostructured thermosets were obtained by introducing reactive block copolymer containing glycidyl methacrylate into epoxy blends [31]. By epoxidizing the residual double bond in polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS), domain size of epoxidized SBS in epoxy matrix was significantly reduced compare to SBS [33–35]. In general, BCPs containing reactive groups were estimated to be more effective in epoxy modification with better control of morphology compared to nonreactive BCPs [30]. Chemical bonding between BCPs and epoxy matrix can result in better toughening effects [36,37]. However, the influence of reactivity of reactive BCP on the morphologies and mechanical performance of blends was not fully investigated.

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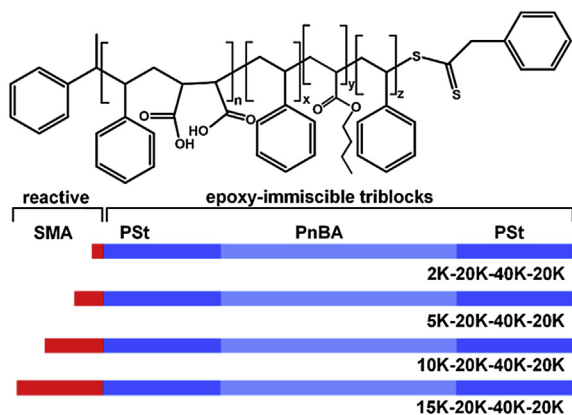
The reactivity between copolymer containing maleic anhydride and epoxy blend was reported [38]. Reactive block copolymer, polystyrene-*block*-polybutadiene-*block*-poly[(methyl methacrylate)-*stat*-(methacrylic acid)] SB(MA), modified epoxy blends were found to have almost no increase in fracture toughness compared to neat epoxy [39]. However, it would be more efficient in toughening if the sparse distributed reactive groups are concentrated in reactive block copolymers. We wonder if tetrablock copolymer, consisting of maleic-anhydride alternating structure which is epoxy-reactive and hard-soft-hard traditional elastomeric copolymer block sequence which is epoxy-immiscible, is efficient for toughness modification for thermosets. In our prior works, poly[styrene-*alt*-(maleic anhydride)]-*block*-polystyrene-*block*-poly(*n*-butyl acrylate)-*block*-polystyrene tetrablock copolymers (SMA-PSt-PnBA-PSt) containing SMA as reactive block were prepared [40]. Taking advantage of recently developed RAFT polymerization, the reactivity of block copolymer can be tailored in a wide composition window.

In this work, DGEBA/DDM epoxy thermosets was modified by 10 wt% of RBCP SMA-PSt-PnBA-PSt in different reactivity (molecular structure shown in Scheme 1). This paper would like to fully reveal the effect of maleic anhydride as reactive groups in copolymers on the nanostructure and mechanical performance of thermosets. The morphologies of blends were verified by TEM and FESEM observations. Thermal properties were investigated using dynamical mechanical thermal analysis. Toughness were evaluated by fracture toughness measurements and notched IZOD impact tests. The main emphasis of this research lies in reactivity of block copolymer on the improvement of miscibility, structural, and mechanical performance in modifying epoxy thermosets.

2. Experimental

2.1. Materials

A series of RBCP poly[styrene-*alt*-(maleic anhydride)]-*block*-polystyrene-*block*-poly(*n*-butyl acrylate)-*block*-polystyrene (CABA type) were synthesized via RAFT miniemulsion polymerization mediated by amphiphilic macroRAFT agent. The synthesis method and process was described in literature [40]. The chemical structures of the tetrablock copolymers are presented in Table 1. The tetrablock copolymer had SMA weight fractions (w_{SMA}) ranging from 2.15 wt% to 15.93 wt%. The maleic anhydride was partially hydrolyzed during emulsion polymerization. The epoxy resin used in this study was diglycidyl ether of bisphenol A (DGEBA) (E51, Shanghai Resin Production, epoxy value 0.51 mol/100 g). 4, 4'-



Scheme 1. Molecular structures of SMA-PSt-PnBA-PSt RBCP used in this study.

diamino diphenyl methane (DDM, Aldrich) was used as hardener. Amino hydrogen to epoxy stoichiometric ratio of one was selected for all the systems. Tetrahydrofuran (THF, 99.9%, Aldrich) was used as cosolvent to obtain homogeneous mixtures of high molecular weight BCP and DGEBA.

2.2. Blending and curing of reactive block copolymer modified thermosets

Due to the high molecular weight of RBCPs, THF was employed as cosolvent to facilitate homogeneous mixing of epoxy and RBCP at room temperature. Once homogeneity was achieved, the mixture was heated to 90 °C for complete removal of the solvent. Then a stoichiometric amount of hardener DDM was added to the mixture, magnetic stirred, until the hardener was completely dissolved. Uniform and bubble-free plaques were obtained by pouring the mixture into a preheated mold and kept in a vacuum oven for 3 h. The blends were cured at 50 °C for 2 h, 100 °C for 3 h and 150 °C for 3 h in the oven and then slowly cooled down to room temperature. The absence of bubbles in the cured parallelepiped bars indicated that the solvent was removed.

2.3. Measurements and characterization

UV-vis measurements were carried out to study the optical transparency of cured RBCP modified epoxy blends. The spectra of cured blends (4 mm thickness) were obtained with a SpectraMax M2 in the range between 200 and 800 nm at 50 nm per step.

FESEM images were obtained using ULTRA 55 FESEM based on the renowned GEMINI®FESEM column with beam booster (Nano Technology Systems Division, Carl Zeiss NTS GmbH, Germany) with a tungsten gun and applying 5 kV as the accelerating voltage. The fracture samples for morphology observation were prepared after cooling in liquid N₂ then coated with gold by vapor deposition before observation. To obtain better resolution, fracture surface of RBCP modified epoxy blends were etched in tetrahydrofuran for 30 min, wash with water. The etched surface was observed by FESEM (shown in Fig. S1 of the Supporting information).

TEM images of RBCP modified epoxy blends was obtained by JEOL JEM-1230L microscope by applying an acceleration voltage of 120 kV. The ultrathin sections were prepared using LEICA Ultracut ultramicrotome cooled in liquid N₂ and collected on a copper grid.

The temperature dependences of the viscoelastic properties (storage modulus: G' and loss tangent: $\tan \delta$) of the cured epoxy or cured blends were examined by TA Q800 (TA Instruments). Dimensions of specimens were 35.5 × 12 × 1.5 mm³. The analysis were evaluated in torsion mode, a fixed frequency 1 Hz, amplitude 15 μm, and run from -100 °C to 200 °C with temperature increases of 5 °C per minute. The peak in $\tan \delta$ was considered to be the glass-transition temperature (T_g).

Fracture toughness measurements were performed following the linear elastic fracture mechanics (LEFM) approach by single edge notched three-point bending (SEN-3PB) method according to ASTM D5045-99. The dimensions of parallelepiped specimens are 60 × 10 × 5 mm³. Zwick/Roell Z020 universal material tester was used to perform the tests at a test speed of 10 mm/min (23 °C). The cracks were carefully generated first cutting a notch of approximately 4.5 mm using diamond saw blade then tapping a liquid N₂ chilled fresh razor blade. Critical stress intensity factor was calculated by average at least 3 specimens.

The impact strength of cured blends was tested using CEAST Resil Impactor apparatus at room temperature (23 °C) according to standard GB/T1843. Notched Izod bars with dimensions 80 × 10 × 4 mm³ were impacted by 1 J hammer. 5 specimens were tested and results averaged. The notches were 2 mm depth, 45°

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