



Microstructure and performance of block copolymer modified epoxy coatings



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ABSTRACT

The effects of two diblock copolymers, poly(ethylene-*alt*-propylene)-*b*-poly(ethylene oxide) (PEP-PEO) and poly(1,2-butadiene)-*b*-poly(2-vinyl pyridine) (PB-P2VP) on the mechanical properties of epoxy coatings were studied. Both modifiers self-assembled into spherical micelles of 10–20 nm diameter in cured bulk epoxy. This morphology was preserved in 15 μm thick coatings; however, micelle segregation to the coating/substrate interface was also observed. The critical strain energy release rate, G_{1c} , of bulk thermosets was enhanced by up to fivefold with the addition of block copolymers. Likewise, the abrasive wear resistance of thin coatings increased with modifier inclusion. The results showed that at 5 wt.% of loading, block copolymers were able to impart a 40% increase in abrasive wear resistance to modified coatings over neat ones. Block copolymer modifiers did not sacrifice the modulus and glass transition temperature of bulk thermosets and coatings, or the hardness and transparency of coatings.

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1. Introduction

Epoxy coatings are widely used as protective barriers for marine, construction, aerospace and automotive components. These applications require that the coatings possess a high modulus, chemical and thermal stability, resistance to wear, and good adhesion to various substrates [1–5]. The highly cross-linked structure of epoxies imparts many of these properties, but it also leads to low fracture resistance [6,7]. To make epoxy thermosets more effective for coating applications, a means for improving the fracture toughness is needed.

Amphiphilic block copolymers, containing an epoxy-philic and an epoxy-phobic block, are effective second-phase modifiers for enhancing the toughness of bulk epoxy thermosets [8–12]. At relatively low loadings (<5 wt.%), the presence of such block copolymers raises the critical strain energy release rate (G_{1c}) of epoxies by up to 20 times that of the neat material [8,13–15]. This is a significant improvement over other traditional toughening

agents, particularly rubber modifiers, which require loadings of 10–20 wt.% and typically yield a less than 10-fold increase in G_{1c} [6,7]. The low required loading for block copolymers also offers the advantage that the reductions in modulus and glass transition temperature typically observed with the incorporation of rubber modifiers are mitigated [9,16–22].

The effectiveness of block copolymer modifiers is linked to their microphase separation in epoxy resins. Appropriately designed amphiphilic block copolymers self-assemble into various nanostructures, such as bi-layer vesicles, wormlike micelles, and spherical micelles, in the uncured epoxy precursor, and these nanostructures are preserved in the cured thermosets [23]. It has been shown that block copolymer nanostructure affects the resultant toughening. For instance, several authors have demonstrated that wormlike micelles are more desirable for toughening than spherical micelles [9,15,20,21] with a difference of up to 250% in critical stress intensity factor (K_{1c}) in favor of the former. Although advances in the understanding of the performance of block copolymer toughening agents have been made during the last decade, little attention has been given to the toughening capabilities of block copolymers in epoxy coatings, with a majority of the work focused on bulk materials. In fact, the mechanical performance of rubber-toughened epoxy coatings has also been the subject of few studies [24].

Incorporation of block copolymer toughening agents into epoxy coatings presents new challenges. For instance, Ramos et al. [25]

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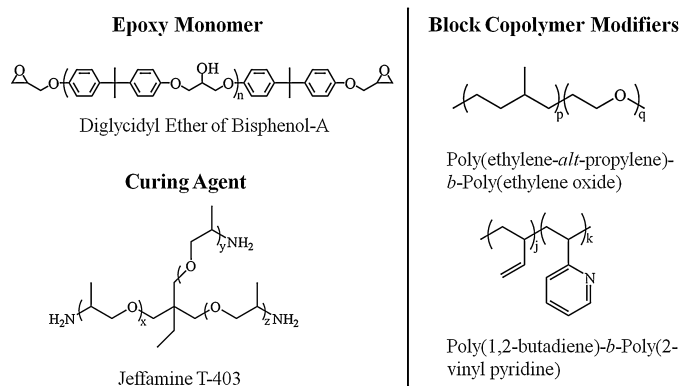


Fig. 1. Chemical structure of epoxy precursors and block copolymer modifiers.

recently showed that in the case of low block copolymer loading (<10 wt.%), fast curing and relatively slow evaporation of casting solvents causes differential segregation of block copolymers through the thickness of epoxy films, resulting in a gradient of morphologies; however, a small thickness and faster solvent evaporation led to a homogeneous film. Garate et al. [26] also investigated the block copolymer self-assembly in nanostructured epoxy thin films. They observed the block copolymer morphology transition from a short-range ordered spherical structure to some larger and less organized nanodomains as the curing reaction proceeded. While these authors did not explore the resultant influences on coating mechanical properties, their findings suggest that the block copolymer performance as a toughening agent may be affected by transitioning from bulk to coatings. As such, block copolymer modified epoxy coatings warrant study to better understand how observed property enhancement of bulk materials translates to coating applications.

This paper presents an investigation of the performance of diblock copolymers as toughening agents in solvent-cast epoxy coatings. To the authors' knowledge, this is the first such report that explores both block copolymer morphology and the mechanical properties of modified epoxy coatings. Two distinct block copolymer modifiers, poly(ethylene-*alt*-propylene)-*b*-poly(ethylene oxide) and poly(1,2-butadiene)-*b*-poly(2-vinyl pyridine), were investigated. The performance of each block copolymer in bulk epoxy thermosets was explored to confirm the effectiveness of these copolymers as toughening agents. Block copolymer-modified epoxy coatings, prepared using a neutral solvent, were explored in terms of block copolymer morphology, distribution, and coating mechanical properties.

2. Experimental

2.1. Materials

The chemical structures of the epoxy system and block copolymers used in this study are presented in Fig. 1. The epoxy monomer is a diglycidyl ether of bisphenol-A (DGEBA) based epoxy monomer (Epon 828, PolySciences, Inc.). The starting material is a mixture of monomers and short oligomers with $n=0$ (88%), $n=1$ (10%), $n=2$ (2%). A polyether triamine (Jeffamine T-403 with $x+y+z \sim 5.3$, Huntsman Chemical) is used as the curing agent.

Two diblock copolymers, were synthesized and evaluated as the epoxy modifiers. The first copolymer is composed of poly(ethylene oxide) (PEO) as the "epoxy-philic" block and poly(ethylene-*alt*-propylene) as the "epoxy-phobic" block. The polymerization protocol followed in preparing PEP-PEO diblock copolymer can be found elsewhere [27]. The second block copolymer, poly(1,2-butadiene)-*b*-poly(2-vinyl pyridine) is being reported on here for

Table 1
Molecular characteristics of block copolymers.

Diblock ^{a,b}	M_n (kg/mol)	$f_{\text{epoxy-philic}}^c$	M_w/M_n
PEP-PEO	26.5	0.57	1.09
PB-P2VP	10.3	0.50	1.05

^a PEP = poly(ethylene-*alt*-propylene); PEO = poly(ethylene oxide); PB = poly(1,2-butadiene); P2VP = poly(2-vinyl pyridine).

^b PEO and P2VP are the "epoxy-philic" block.

^c Volume fraction of epoxy-philic block calculated using density information [28] and [29].

the first time. Poly(2-vinyl pyridine) (P2VP) is the epoxy-philic block, while the epoxy-phobic block is poly(1,2-butadiene) (PB). The diblock copolymer was synthesized via sequential anionic polymerization using tetrahydrofuran (THF) as the solvent. 1,3-butadiene monomer was first initiated using *sec*-butyl lithium and reacted at -60°C for 1 h, followed by the addition of purified 2-vinyl pyridine monomer. The second block grew for another 30 min, before the termination with methanol. The product was precipitated in distilled water, a poor solvent, at room temperature, and freeze-dried under vacuum for 48 h.

Table 1 summarizes the molecular characteristics of the block copolymers employed in this study. The block copolymer composition was determined using ^1H NMR and end-group analysis. The dispersity was determined by room temperature GPC with polystyrene standards and THF as the solvent. Both copolymers are nearly monodisperse. PEP-PEO is rich in the epoxy-philic PEO block. The molecular weight of PB-P2VP is less than half the molecular weight of PEP-PEO and is symmetric with regards to the volume fractions of the epoxy-philic and epoxy-phobic blocks. Along with differences in composition, the chemistries of the epoxy-philic blocks impart fundamental differences between the two copolymers. P2VP can easily form hydrogen bonds with the epoxy network, which affords exothermic mixing, making it a good alternative for PEO. At room temperature, PEO is semi-crystalline with a melting point near 50°C , while P2VP is a rigid chain with a higher T_g (100°C) than PEO (-60°C). Both epoxy-phobic blocks produce rubbery, compliant cores in the epoxy resin being used.

2.2. Sample preparation

PEP-PEO modified epoxy samples were prepared by first blending the block copolymer with the epoxy monomer at $70\text{--}75^\circ\text{C}$ for 24 h until full dissolution. The blend was then cooled down to 60°C and 46 phr (parts per hundred resin) of the curing agent were added to make the mole ratio of epoxide group to reactive hydrogen on amine group 1:1.6. The blend was stirred at 60°C for 30 min before being degassed under dynamic vacuum for 5–10 min. A portion of this blend was poured into a preheated mold (60°C) to make bulk samples. The remaining material was used to prepare the coating solution, ensuring that bulk samples and coating samples always came from the same batch. The blend designated for the coating solution was left to pre-cure at 60°C for an additional 40 min in order to build up the viscosity of the system, a step which is necessary to prevent dewetting of the coating [30]. Bulk samples also underwent the same pre-curing for consistency, but after being added to the mold due to transfer issues of the thermoset blend after the pre-cure was complete. After the pre-curing, the blend to be used for the coating solution was cooled down to room temperature and dissolved in the casting solvent, toluene, to create solutions of 30 wt.% epoxy resin. The solution was stirred at room temperature overnight until a clear coating solution was obtained.

Coatings were prepared by casting the solution onto an $80\ \mu\text{m}$ polyethylene terephthalate (PET) (3M) substrate using a wire-wound rod (rod number 64) (R.D. Specialties, Inc.). The PET

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