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Poly(hydroxyether of bisphenol A)-*block*-polydimethylsiloxane alternating block copolymer and its nanostructured blends with epoxy resin

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A B S T R A C T

Mannich condensation was utilized to synthesize poly(hydroxyether of bisphenol A)-*block*-polydimethylsiloxane alternating block copolymer (PH-*alt*-PDMS). The polymerization between the phenolic hydroxyl-terminated oligo(hydroxyether of bisphenol A) and amino-terminated oligodimethylsiloxane with the defined lengths was carried out *via* the formation of benzoxazine ring linkages, which was mediated with paraformaldehyde. The alternating block copolymer was characterized by means of Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR) and gel permeation chromatography (GPC). The block copolymer was incorporated to prepare nanostructured thermosetting blends. The nanostructures of the thermosetting blends were investigated by means of atomic force microscopy (AFM) and small angle X-ray scattering (SAXS). The formation of the nanostructures in the thermosetting composites was judged to follow the self-assembly mechanism in terms of the difference in miscibility of PDMS and PH subchains with epoxy resin after and before curing reaction. The fracture toughness of the nanostructured blends was evaluated in terms of the measurement of stress field intensity factor (K_{IC}). It is noted that the epoxy resin was significantly toughened.

1. Introduction

Thermosets such as epoxy and novolac resins are a class of important polymeric materials; they have widely been used as high performance materials such as adhesives, matrices of composites and electronic encapsulating materials [1,2]. However, these thermosets are inherently of low impact resistance due to their high crosslinking density, which greatly restricts their application. During the past decades considerable efforts have been made to improve the toughness of epoxy thermosets [3–27]. One of the successful routines of toughness improvement is to incorporate polymeric modifiers into thermosetting matrix to form fine morphological structures. The effective polymer modifiers can be elastomers [3–17] or thermoplastics [18–25]. Liquid elastomers such as carboxyl-terminated butadiene–acrylonitrile rubber (CTBN), amine-terminated butadiene–acrylonitrile rubber (ATBN) [3–7] have been exploited for toughness improvement. However, the presence of unsaturated structure in these liquid elastomers is prone to thermal instability and low oxidation resistance. By comparison, organosilicon polymers (*e.g.*, polydimethylsiloxane) possess some superior properties, such as thermal stability, moisture resistance and good electrical properties and thus are more advantageous modifiers [5,8–11,13]. However, polysiloxanes have poor compatibility with the precursors of epoxy due to the big difference in solubility parameter, which is essential for the formation of fine phase-separated structures in thermosets [27].

The control of morphology of thermosets containing elastomers or thermoplastics is generally based on reaction-induced phase separation. In practice, the thermosetting blends are prepared starting from the homogeneous solution composed of precursors of thermosets and the modifiers. With the occurrence of curing reaction, reaction-induced phase separation occurs and fine phase-separated morphologies were obtained [27]. Since the modifiers are some linear homopolymers or random copolymers, the modified thermosets would exhibit the phase-separated morphology on the macroscopic scale. Recently, it is recognized that the formation of ordered (or disordered) nanostructures (microphase separation) in thermosets could further optimize the interactions between thermosetting matrix and modifiers and thus endow materials with improved properties [28–51]. Bates et al. [28,29] have proposed a strategy of creating nanostructures using amphiphilic block copolymers. In their protocol, the precursors of thermosets act as the selective solvents of block copolymers and some self-assembly nanostructures such as lamellar, bicontinuous, cylindrical, and spherical structures are formed in the mixtures depending on the blend composition before curing reaction. These nanostructures can be further fixed *via* subsequent curing with introduction of hardeners. With an appropriate design of block copolymer

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architecture, the block copolymers self-organize to form ordered or disordered nanostructures [28–41,51]. It has more recently shown that the ordered (or disordered) nanostructures in the composite systems of thermosets and amphiphilic block copolymers can alternatively formed *via* so-called reaction-induced microphase separation mechanism [43–50].

Mülhaupt et al. [52,53] reported the modification of epoxy resin with a branched poly(ε-caprolactone)-*block*-polydimethylsiloxane-*block*-poly(ε-caprolactone) block copolymer. It is noted that the inclusion of a small amount of the copolymer (*e.g.*, 5 wt% or more) leads to a significant increase in the toughness of materials whereas the strength of materials (*e.g.*, strength at break and Young's modulus) was not obviously reduced. It was found that in the modified thermosets, the spherical PDMS particles with the size of about 20 nm in diameter are uniformly dispersed in the continuous epoxy matrix. More recently, Xu and Zheng [51] investigated the thermosetting blends of epoxy resin with a linear poly(ε-caprolactone)-*block*-polydimethylsiloxane-*block*-poly(ε-caprolactone) ABA triblock copolymer. It is proposed that the triblock copolymer behaved as a template in the formation of the nanostructured thermosets *via* self-assembly mechanism.

In this work, we will report the synthesis of a novel alternating block copolymer consisting of poly(hydroxyether of bisphenol A) and polydimethylsiloxane blocks (PH-*alt*-PDMS). After that, the alternating block copolymer was incorporated into epoxy to toughen the thermosets *via* the formation of nanostructures in the materials. The utilization of the alternating block copolymer and its modification of epoxy thermosets are based on the following considerations: (i) poly(hydroxyether of bisphenol A) (PH) is miscible with epoxy resin when the blends were cured with 4,4′-diaminodiphenylmethane (DDM) [54] and (ii) polydimethylsiloxane (PDMS) is immiscible with epoxy thermosets. It is expected that the nanostructures will be formed while the alternating block copolymer was incorporated into epoxy thermosets. The morphology of the thermosets was investigated by means of atomic force microscopy (AFM) and small angle X-ray scattering (SAXS). The fracture toughness of the nanostructured epoxy thermosets is evaluated in terms of the measurement of critical stress intensity factors (K_{IC}).

2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol A (DGEBA) with the epoxide equivalent weight of 185–210 was supplied from Shanghai Resin Co., China. 4,4′-Diaminodiphenylmethane (DDM) and bisphenol A were obtained from Shanghai Reagent Co., China. Paraformaldehyde was purchased from Aldrich Co., USA. Diaminopropyl-terminated polydimethylsiloxane (ATPDMS) was kindly supplied by Degussa Co. Germany and it has a quoted number-average molecular weight of $M_n = 2300$. Before use, it was dried *via* azeotropic distillation with anhydrous toluene.

2.2. Synthesis of oligo(hydroxyether of biphenol A) with defined length

The synthesis of phenolic hydroxyls-terminated oligo(hydroxyether of biphenol A) (PHOH) with defined length was carried out *via* the polymerization between DGEBA and bisphenol A. Typically, to flask equipped with a mechanical stirrer DGEBA (6.5377 g, 33.34 mmol) and bisphenol A (4.5675 g, 20.00 mmol) were charged and 0.6 wt% tetrabutylammonium bromide (TBAB) was added and used as the catalyst. The reaction was carried out at 150 °C for 10 h with vigorous stirring. Cooled to room temperature, the reacted product was dissolved with 20 ml tetrahydrofuran (THF) and then dropped into petroleum ether to afford the precipitates. After dried at 60 °C in a vacuum oven for 24 h, the resulting product (10.9 g) was obtained with the yield of 98%. FTIR: 3254 (O–H), 2962 (C–H, methylene and methine), 1182 (C–O–C). ^{1}H NMR ($CDCl_3$, ppm): 1.62 (7.34H,–CH_3), 4.10 [4.05H,–CH_2–CH(OH)–CH_2–], 4.34 [1.00H,–CH_2–C*H*(OH)–CH_2–], 6.5–7.2 (9.39H, proton aromatic ring). The molecular weight of the PHOH was estimated to be $M_n = 2500$ in terms of the ratio of integration intensity of methylene (and/or methine) to methyl (and/or aromatic ring) protons.

2.3. Synthesis of PH-alt-PDMS alternating block copolymer

Poly(hydroxyether of bisphenol A)-*block*-polydimethylsiloxane alternating block copolymer (PH-*alt*-PDMS) was synthesized *via* the reaction between the above phenolic hydroxyls-terminated oligo(hydroxyether of biphenol A) (PHOH) and diamino-terminated polydimethylsiloxane (ATPDMS). To a three-necked flask equipped with a mechanical stirrer and a condenser, PHOH (3.5103 g, 1.41 mmol), ATPDMS (3.2295 g, 1.40 mmol) and a suspension of paraformaldehyde (0.1824 g) in 15 ml toluene are charged and 100 ml anhydrous toluene was added. The above reactive system was heated up to 100 °C, at which the polymerization was carried out for 10 h. It is observed that with the polymerization preceding, the initial cloudy and heterogeneous mixture gradually became transparent within 20 min and the viscosity of the system significantly increased. FTIR (KBr window, cm^{-1}): 3428 (ν_s, O–H), 2962 (ν_s, C–H), 1261 ($\nu_{sym\ d}$, C–Si–C), 1092 (ν_s, Si–O-Si). GPC: $M_n = 11{,}000$, $M_w = 27{,}500$.

2.4. Preparation of epoxy thermosets

The desired amount of PH-*alt*-PDMS alternating block copolymer was added to DGEBA with continuous stirring at 100 °C until the mixtures became homogenous and transparent. 4,4′-Diaminodiphenylmethane (DDM) was added with continuous stirring until the full dissolution of the curing agent. The mixtures were poured into Teflon molds and cured at 150 °C for 2 h plus 180 °C for 2 h.

2.5. Measurement and characterization

2.5.1. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra were measured by a Perkin–Elmer Paragon 1000 Fourier transform infrared spectrometer. The block copolymer was dissolved in THF and then the solution was cast onto KBr windows. The solvent was evaporated *in vacuo* at 60 °C to obtain the specimen of films. For the samples of thermosets, the powder was mixed with KBr pellets to press into small flakes. All the specimens were sufficiently thin to be within a range where the Beer–Lambert law is obeyed. In all cases 64 scans at a resolution of 2 cm^{-1} were used to record the spectra.

2.5.2. Nuclear magnetic resonance spectroscopy (NMR)

The block copolymer was dissolved in deuterated chloroform and the ^{1}H NMR measurements were carried out at a Varian Mercury Plus 400 MHz NMR spectrometer with tetramethylsilane (TMS) as an internal reference.

2.5.3. Atomic force microscopy (AFM)

The samples of thermosets were trimmed using a microtome machine and the specimen sections (*ca.* 70 nm in thickness) were used for AFM observations. The AFM experiments were performed with a Nanoscope IIIa scanning probe microscope (Digital Instruments, Santa Barbara, CA). Tapping mode was employed in air using a tip fabricated from silicon (125 μm in length with *ca.* 500 kHz resonant frequency). Typical scan speeds during recording were 0.3–1 line s^{-1} using scan heads with a maximum range of 16×16 μm.

2.5.4. Small angle X-ray scattering (SAXS)

The SAXS measurements were taken on a Bruker Nanostar system. Two dimensional diffraction patterns were recorded using an image intensified CCD detector. The experiments were carried out at room temperature (25 °C) using Cu-Kα radiation ($\lambda = 1.54$ Å, wavelength) operating at 40 kV, 35 mA. The intensity profiles were output as the plot of scattering intensity (I) versus scattering vector, $q = (4/\lambda)\sin(\theta/2)$ (θ = scattering angle).

2.5.5. Differential scanning calorimetry (DSC)

Thermal analysis was performed on a Perkin–Elmer Pyris-1 differential scanning calorimeter in a dry nitrogen atmosphere. The instrument was calibrated with a standard indium. In order to measure glass transition temperatures, all the samples (about 10.0 mg in weight) were first heated up to 200 °C and hold at this temperature for 3 min to eliminate thermal history, followed by quenching to −70 °C. In order to measure glass transition temperatures (T_gs), a heating rate of 20 °C/min was used in all cases. Glass transition temperature (T_g) was taken as the midpoint of the heat capacity change.

2.5.6. Fracture toughness measurements

Fracture toughness was measured by the notched three-point bending test with a crosshead speed of 1.3 mm^{-1} according to ASTM E399. The schematic diagram of the three-point bending specimens is shown in Fig. 1. The critical stress intensity factors (K_{IC}s) were calculated using the following equation:

$$K_{IC} = P_C S / B W^{3/2} f\left(\frac{a}{W}\right) \tag{1}$$

where P_C is the load at crack initiation, B is the thickness of the specimens, S is the span width, W is the width of the specimens and a is the crack length. Central Vee-notches were machined. Before measurement, all the specimens were annealed at 80 °C for 24 h and at least five successful measurements were used to obtain the average values of experiments.

3. Results and discussion

3.1. Synthesis and characterization of PH-alt-PDMS alternating block copolymer

The synthesis of alternating rigid-flexible block copolymers is an important strategy to prepare polymers with defined structure and properties. During the past year, this approach has been well established in the synthesis of main-chain liquid crystalline polyesters [55,56], electroluminescent polymers [57] and classic polyurethane-based thermoplastic elastomeric materials [58]. The key to apply this approach to synthesize polymers is to utilize an appropriate polymer reaction and to prepare suitable macromers with defined length. Mannich condensation among phenol, formaldehyde and amine is an important reaction, which can afford benzoxazine ring [59–61]. This reaction possesses some important features such as high selectivity and high conversion of reaction under mild conditions. This reaction has been employed to prepare a variety of benzoxazine monomers to access high performance polybenzoxazine, a modified phenolic thermoset [60–72]. To the best of our knowledge, nonetheless, there has no precedent report on the application of this reaction for polymerization to synthesize alternating block copolymers. In this work, we explored to utilize this reaction to synthesize poly(hydroxyether of bisphenol A)-*block*-polydimethylsiloxane alternating block copolymer (PH-*alt*-PDMS). In the first step, phenolic hydroxyl-terminated oligo(hydroxyether of bisphenol A) (PHOH) with defined molecular weight was prepared *via* the reaction between diglycidyl ether of bisphenol A (DGEBA) and bisphenol A (Scheme 1). This reaction was carried out at 150 °C with tetrabutylammonium bromide (TBAB) as the catalyst [73,74]. By controlling the molar ratio of DGEBA to bisphenol A, the PHOH with the desire molecular weight was obtained and its molecular weight was estimated in terms of the ratio of integration intensity of methylene (and/or methane) protons to that of aromatic ring (or methyl proton) in its proton nuclear magnetic resonance spectrum (see Fig. 1). In this work, the molecular weight of PHOH was controlled to be $M_n = 2500$, which is close to that of the diamino-terminated polydimethylsiloxane (ATPDMS) ($M_n = 2300$). The PHOH was used to react with the stoichiometric amount of ATPDMS and formaldehyde to prepare the alternating block copolymer as depicted in Scheme 2. It is observed that with Mannich condensation reaction proceeding, the initial cloudy and heterogeneous mixture gradually became transparent within 20 min. In the mean time, the viscosity of reactive system significantly increased, indicating the occurrence of polymerization. The polymerization was performed at 100 °C for 10 h with vigorous stirring, to access the complete conversion of the terminal groups for the two macromers. Shown in Fig. 2 is the FTIR spectroscopy of the product. The band at 3428 cm^{-1} is assignable to the stretching vibration of secondary hydroxyl groups in the structural ether structural unit [$-O-CH_2-CH(OH)-CH_2-$] and the stretching vibration of the hydroxyl ether linkage occurs at 1182 cm^{-1}. Besides the above bands' characteristic of oligo(hydroxyether of bisphenol A), the stretching vibration of Si–O–Si bonds is detected at 1092 cm^{-1} in the FTIR spectrum of the product. The FTIR spectroscopy shows that the resulting product combined the structural units from oligo(hydroxyether of bisphenol A) and polydimethylsiloxane (PDMS). This observation can be further evidenced by ^{1}H nuclear magnetic resonance spectroscopy (NMR). Shown in Fig. 3 is the ^{1}H NMR spectrum of the resulting polymer together with the assignment of this spectrum. The resonance of the benzoxazine ring linkage protons can be identified on the expanded ^{1}H NMR spectrum in the range of 3.5–5.5 ppm. The NMR spectroscopy indicates that the polymer possesses the structural features of oligo(hydroxyether of bisphenol A) and polydimethylsiloxane. The curve of gel permeation chromatography (GPC) of the product is shown in Fig. 4. The GPC curve displayed a unimodal peak, suggesting that the polymerization between the two macromers was performed to completion. In another word, there are no detectable unreacted macromers (*i.e.*, PHOH and ATPDMS). The polymer possesses the high molecular weights of $M_n = 11{,}000$ and $M_w = 27{,}500$. The spectral and GPC results indicate that the PH-*alt*-PDMS alternating block copolymer was successfully obtained.

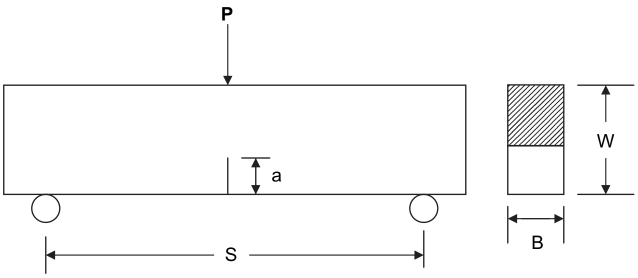
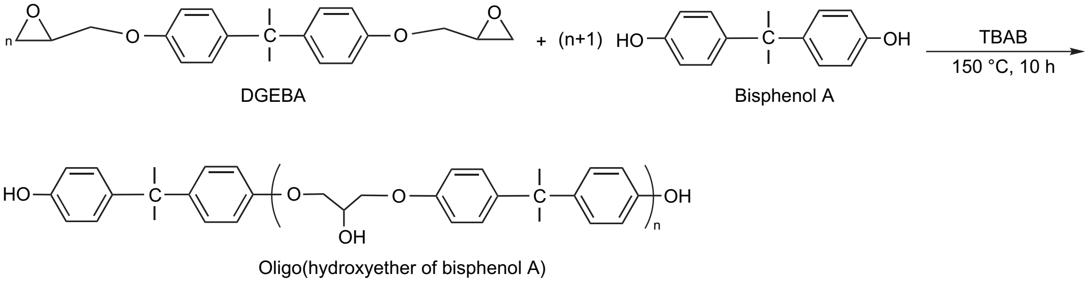
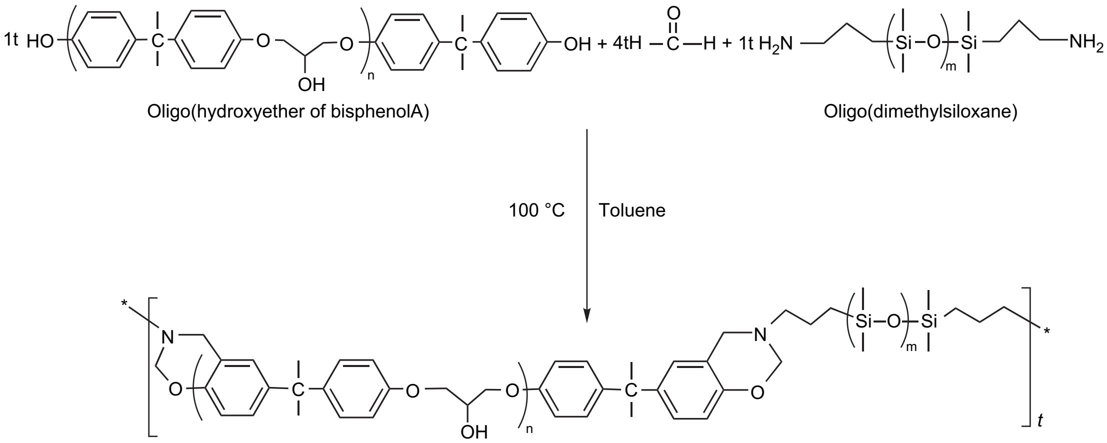


Fig. 1. Schematic diagram of three-point bending specimen for the measurement of critical stress intensity factor (K_{IC}).

It is expected that the alternating block copolymer is microphase-separated since it is composed of two immiscible blocks (*viz.* PH and PDMS). The microphase-separated morphology can be



Scheme 1. Synthesis of oligo(hydroxyether of bisphenol A).



Scheme 2. Poly(hydroxyether of bisphenol A)-*block*-polydimethylsiloxane alternating block copolymer.

investigated by means of differential scanning calorimetry (DSC) and small angle X-ray scattering. The DSC curve of the PH-*alt*-PDMS is shown in Fig. 5. In the range of experimental temperature, the polymer displayed a single glass transition temperature at *ca.* 52 °C, which is ascribed to the PH phase of the block copolymer. It should be pointed out that the very low T_g of PDMS block (*ca.* −123 °C) cannot be measured within this range of experimental temperature (−70 to 200 °C). Nonetheless, it is noted that the value of the observed T_g is quite close to that of oligo(hydroxyether of bisphenol A), suggesting that the block copolymer is microphase-separated.

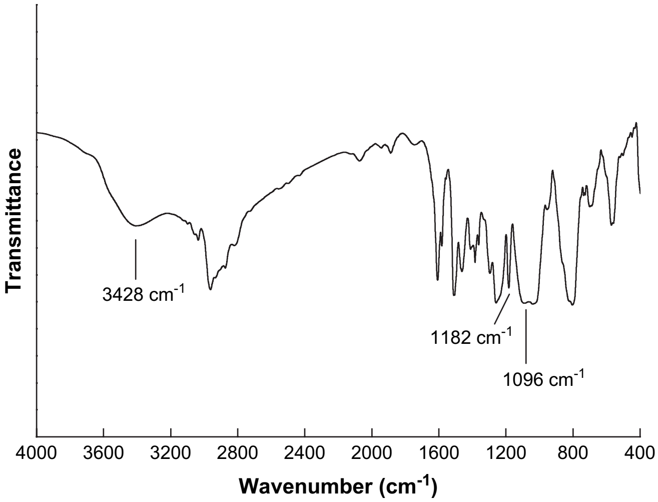


Fig. 2. FTIR spectrum of PH-*alt*-PDMS alternating block copolymer.

This judgment can be further confirmed with small angle X-ray scattering (SAXS). The SAXS profile of the PH-*alt*-PDMS alternating block copolymer is shown in Fig. 6. The polymer exhibited a scattering maximum at $q_m = 0.97\ nm^{-1}$, indicating that the block copolymer possesses the nanostructure, *i.e.*, the polymer is microphase-separated.

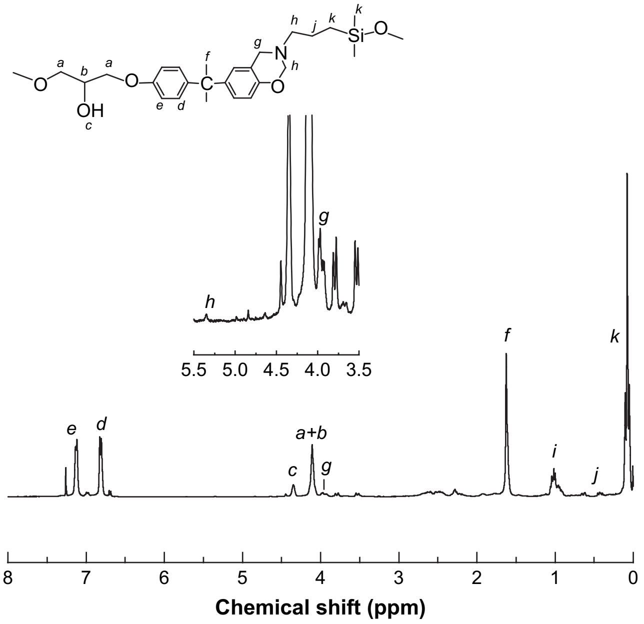


Fig. 3. ^{1}H NMR spectrum of PH-*alt*-PDMS alternating block copolymer.

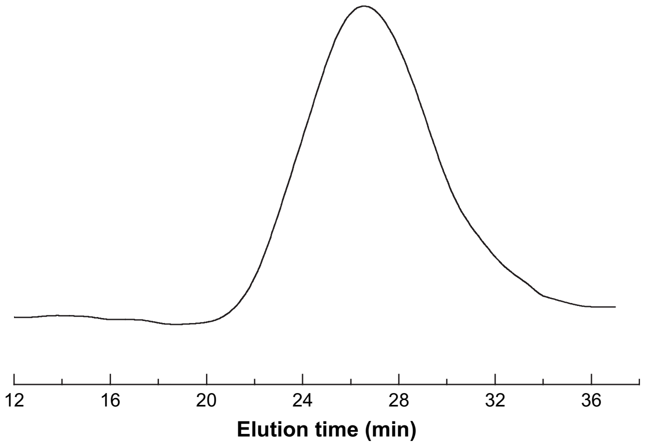


Fig. 4. Gel permeation chromatography (GPC) curve of PH-*alt*-PDMS alternating block copolymer.

3.2. Nanostructured blends of epoxy resin and PH-alt-PDMS

3.2.1. Morphology of thermosets

The PH-*alt*-PDMS alternating block copolymer was incorporated into epoxy resin to prepare the nanostructured thermosets. Before curing, all the mixtures of the epoxy precursors (DGEBA and DDM) with PH-*alt*-PDMS alternating block copolymer were homogenous and transparent at room and elevated temperatures, implying that no macroscopic phase separation occurred. This observation is in marked contrast to the case of the mixtures of the polydimethylsiloxane (*i.e.*, ATPDMS) with the monomers of epoxy resin (*viz.* DGEBA and DDM). The clarity suggests that the presence of miscible PH blocks in the alternating block copolymer improves the dispersion of PDMS chains in the mixtures. It should be pointed out that the clarity of the mixtures composed of PH-*alt*-PDMS, DGEBA and DDM does not exclude the possibility that the mixtures are microphase-separated since the scale of microphase separation could be significantly lower than wavelengths of visible light. The small angle X-ray scattering (SAXS) confirmed the presence of microphase separation before curing reaction as in the mixture of epoxy precursors with poly(ε-caprolactone)-*block*-poly-dimethylsiloxane-*block*-poly(ε-caprolactone). (The SAXS profiles not shown for brevity.) [51] After cured at 150 °C for 2 h plus 180 °C for 2 h, the thermosetting blends of epoxy resin with PH-*alt*-PDMS were obtained with the content of PH-*alt*-PDMS up to 20 wt%. It is seen that all the cured thermosets are homogenous and transparent, indicating that no macroscopic phase separation occurred at least on the scale exceeding the wavelength of visible light. The morphology of the epoxy thermosets was examined by means of atomic force microscopy (AFM) and small angle X-ray scattering (SAXS).

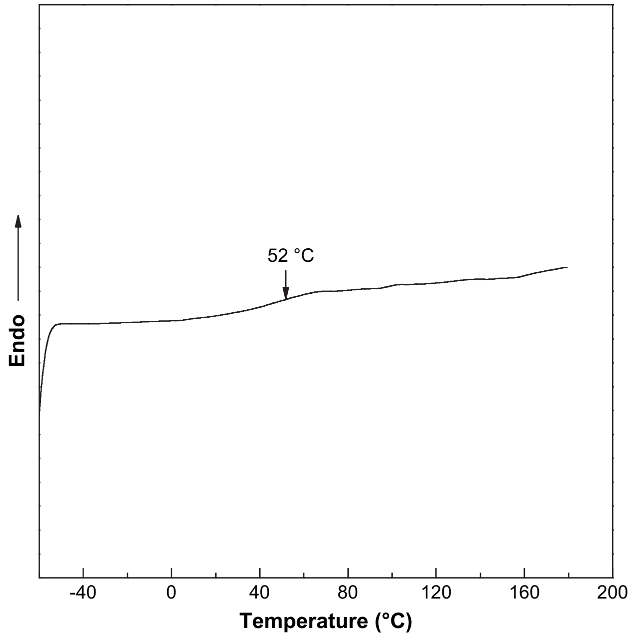


Fig. 5. DSC curve of PH-*alt*-PDMS alternating block copolymer.

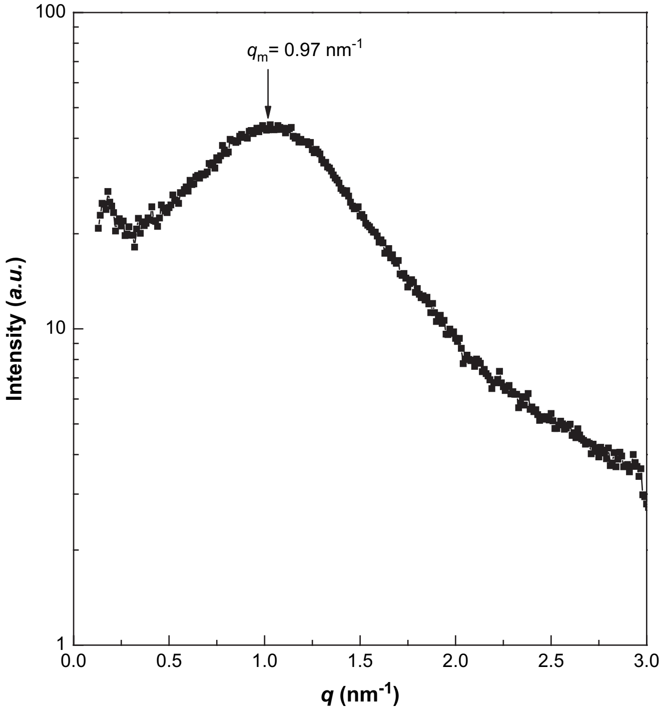


Fig. 6. SAXS profile of PH-*alt*-PDMS alternating block copolymer.

Shown in Fig. 7 are the AFM micrographs of the thermosets containing PH-*alt*-PDMS alternating block copolymer. The left-hand side of each micrograph is topography image and the right is the phase image. The topography images showed that the surfaces of the as-prepared specimens are free of visible defects and are quite smooth, and thus the effect of roughness resulting from the specimen trimming on morphology is negligible. In terms of the difference in viscoelastic properties and volume fraction of the matrix (*viz.* epoxy and PH) and PDMS, the dark regions are attributed to the PDMS domains whereas the light regions to epoxy matrix. It is seen that spherical PDMS particles with the size of 10–20 nm were homogeneously dispersed in the continuous epoxy matrix (Fig. 7A). With increasing the content of PH-*alt*-PDMS alternating block copolymer, the spherical nanoparticles began to coagulate in the continuous epoxy matrix, and some worm-like nanodomains of PDMS appeared; *i.e.*, the epoxy thermosets possessed a combined morphology in which both spherical PDMS domains and some interconnected PDMS domains were present (Fig. 7B–D). The AFM results indicate that the epoxy thermosets possess the microphase-separated morphology.

The morphologies of the thermosetting blends were further investigated by small angle X-ray scattering (SAXS) and the SAXS profiles are shown in Fig. 8. For the pure PH-*alt*-PDMS alternating block copolymer, a scattering maximum was situated at the position of $q_m = 0.97\ nm^{-1}$ (See Fig. 6), indicating that PH-*alt*-PDMS alternating block copolymer is microphase-separated. The

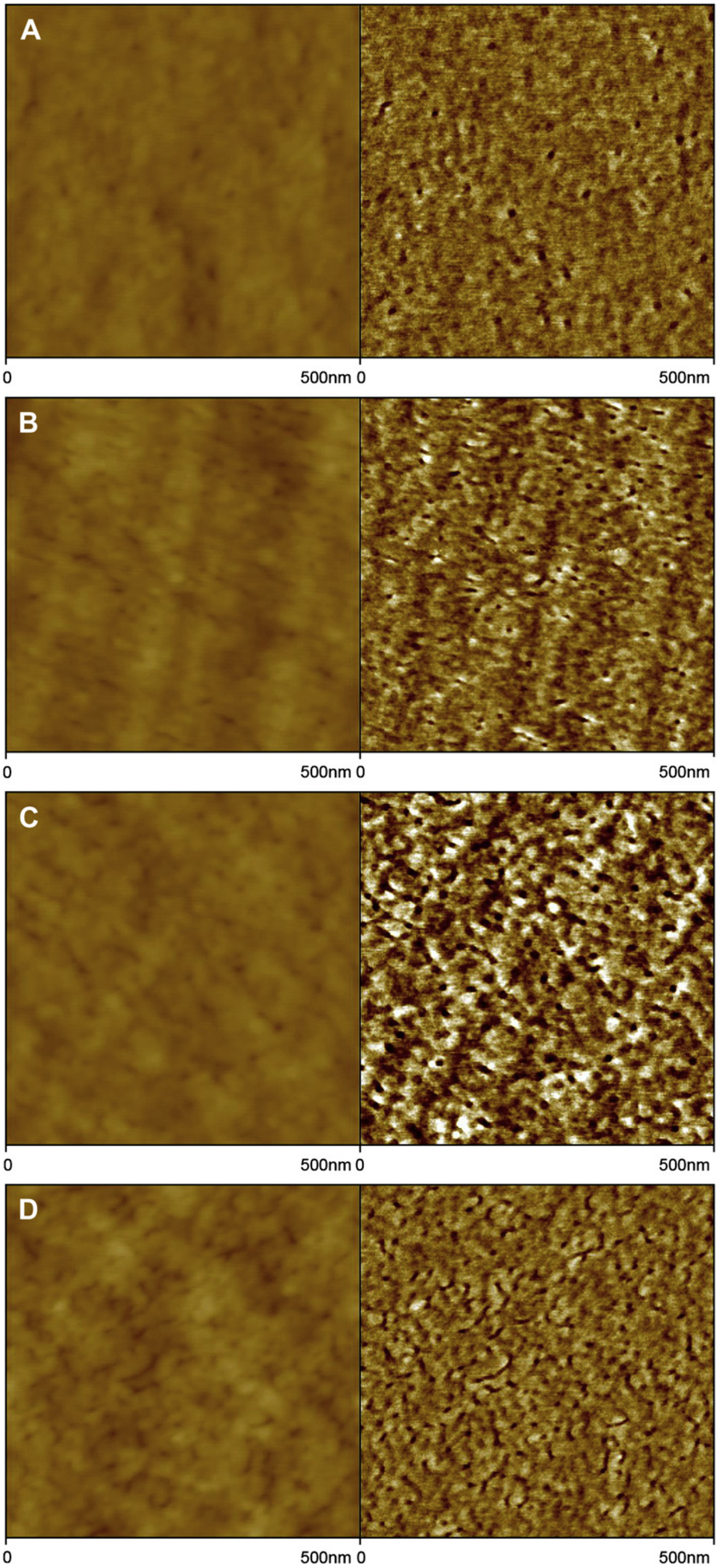


Fig. 7. AFM images of the epoxy thermosets containing (A) 5, (B) 10, (C) 15, and (D) 20 wt% of PH-*alt*-PDMS alternating block copolymer. Left: topography; right: phase contrast images.

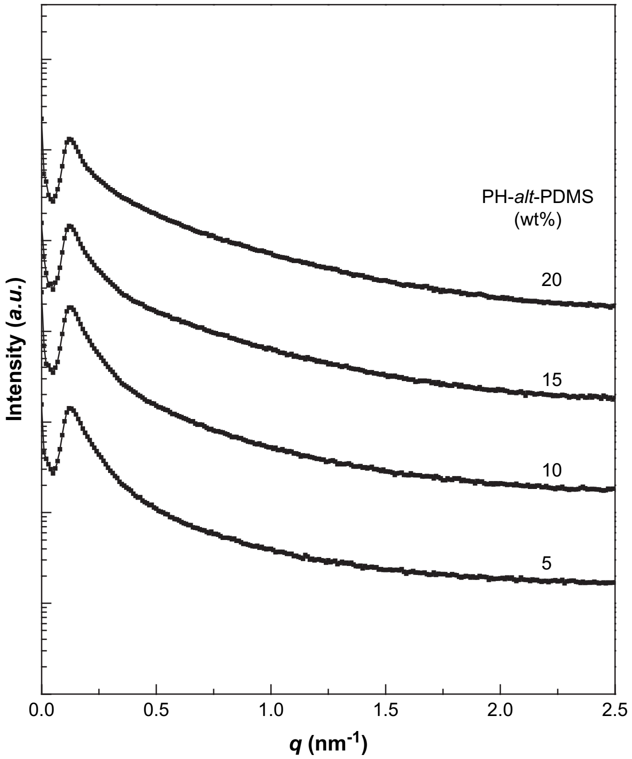


Fig. 8. SAXS profiles of the epoxy thermosets containing PH-*alt*-PDMS alternating block copolymer.

microphase-separated morphology results from the immiscibility of the component blocks due to the big difference in solubility parameters between PH and PDMS. With the value of q_m, the long period (L) of the alternating block copolymer was estimated to be about 6.5 nm according to the Bragg scattering equation (*viz.* $L = 2\pi/q_m$). For each thermosetting blends, a single well-defined scattering peak was displayed in the neighbor of $q_m = 0.12\ \text{nm}^{-1}$, indicating that the thermosets containing PH-*alt*-PDMS are microphase-separated. According to the position of the primary scattering peaks the average distance ($L = 2\pi/q_m$) between neighboring PDMS nanodomains can be estimated to be about 50 nm in the thermosets containing the alternating block copolymer. It is noted that the average distance between neighboring domains remains almost invariant. The average distance between the adjacent nanodomains in the thermosetting blends is greatly bigger than that in the PH-*alt*-PDMS alternating block copolymer, which is ascribed to the effect of dilution of miscible epoxy matrix on the PDMS nanodomains. The SAXS results are in a good agreement with those obtained by means of AFM.

3.2.2. *Interpretation of nanostructure formation*

It is recognized that the formation of nanostructures in thermosets containing block copolymers could follow two different mechanisms: (i) self-assembly [28–41,51], (ii) reaction-induced microphase separation [43–50]. In the mechanism of self-assembly, the precursors of thermosets act as selective solvents of block copolymers and self-organized nanostructures (*i.e.*, micelle) are formed prior to curing. The self-organized nanostructures can further be fixed with the subsequent curing reaction. In this approach, the role of curing reaction is to lock in the preformed morphology [28,29]. The prerequisite for the self-assembly approach is that block copolymers should self-organize into nanostructures in their mixtures with precursors of thermosets prior to curing. From the viewpoint of miscibility, it is required that one or more of subchains of block copolymers are immiscible whereas other subchains are miscible with thermosets after and before curing. For the formation of nanostructures *via* reaction-induced microphase separation mechanism, all the subchains of the block copolymer are miscible with thermosets before curing whereas only a part of subchains was microphase-separated out after curing. Therefore, it is crucial to know the miscibility of all the subchains with thermosets after and before curing reaction for the judgment of the formation mechanism of the nanostructures in thermosets containing amphiphilic block copolymers.

In the present case, the design and synthesis of PH-*alt*-PDMS alternating block copolymer are based on the knowledge that the PH blocks are miscible with the epoxy whereas PDMS is immiscible with epoxy after and before curing reaction. It has been reported that poly(hydroxyether of bisphenol A) (*i.e.*, PH) is miscible with epoxy resin (DGEBA and DDM) after and before curing [55]. In the present work, the miscibility of PH with epoxy matrix can be evidenced in views of the glass transition behavior of the thermosetting blends. The above nanostructured epoxy thermosets containing the PH-*alt*-PDMS alternating block copolymer were subjected to thermal analysis. Shown in Fig. 9 are the DSC curves of the thermosetting blends. In the experimental range of temperature (0–200 °C), the alternating block copolymer PH-*alt*-PDMS displayed a glass transition at 52 °C, which is ascribed to the PH block. This value of T_g is much lower than that of control epoxy (174 °C). For the nanostructured thermosets containing PH-*alt*-PDMS, each DSC curve exhibited a single glass transition at about 160 °C, which is assignable to epoxy matrix of the nanostructured blends. It is seen that the T_gs of the thermosetting blends decreased with increasing the content of PH-*alt*-PDMS alternating block copolymer. The decreased T_gs are responsible for the plasticization effect of the PH blocks on the epoxy matrix. It should be pointed out that the glass transition observed in the present temperature range is only ascribed to the epoxy matrix which is interpenetrated with the PH subchains of the block copolymers since the T_g of PDMS domains (approximately −123 °C) is beyond the temperature range of the DSC measurement. As for the binary blends of epoxy resin with PDMS, it is recognized that the system is immiscible after and before curing reaction [52,53]. The immiscibility is responsible for the big difference in solubility parameter between epoxy resin and

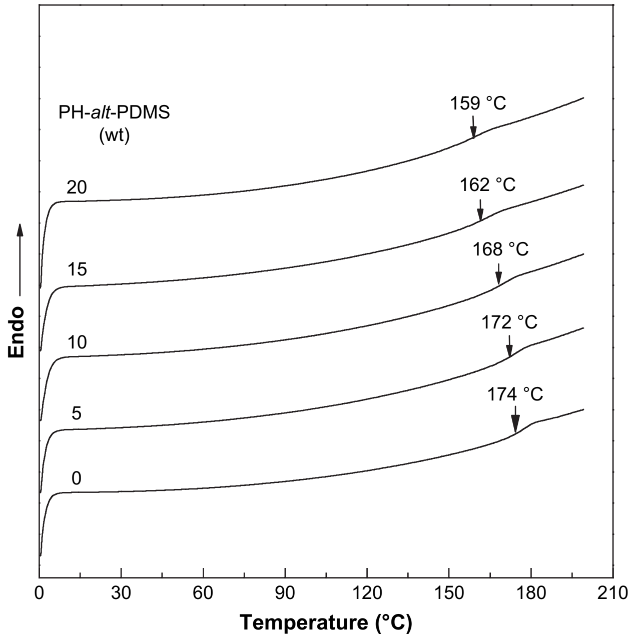


Fig. 9. DSC curves of the epoxy thermosets containing PH-*alt*-PDMS alternating block copolymer.

the inorganic polymer. It should be pointed that the decreased T_gs could be additionally responsible for the reaction of the terminal amino and phenolic hydroxyl groups of the block copolymers with DGEBA. This situation is just like case that the curing agent is excessive with respect to the epoxide groups of DGEBA and thus the crosslinking density of the thermosetting matrix is some extent decreased.

It is plausible to propose that self-organized microstructures are formed owing to the difference in miscibility of epoxy resin with the blocks of the block copolymer (*viz.* PH and PDMS) while the amphiphilic alternating block copolymer was mixed with the precursors of epoxy resin (*viz.* DGEBA and DDM). After cured at elevated temperatures, the self-organized nanostructures were fixed and reserved until the curing reaction was performed to completion. Therefore, it is concluded that the formation of nanostructures in the present thermosetting system could follow the self-assembly mechanism other than the reaction-induced microphase separation mechanism.

3.3. *Fracture toughness of nanostructured thermosets*

The fracture toughness of the nanostructured thermosets containing PH-*alt*-PDMS alternating block copolymer were evaluated in terms of three-point bending tests to measure the critical stress intensity factors (K_{IC}). The plot of K_{IC} as a function of PH-*alt*-PDMS content for the nanostructured thermosets is shown in Fig. 10. It is seen that the K_{IC} values of all the nanostructured blends are higher than that of the control epoxy thermoset, indicating that the epoxy thermoset was significantly toughened with the inclusion of PH-*alt*-PDMS alternating block copolymer. The K_{IC} values increased with increasing the content of PH-*alt*-PDMS. For the epoxy thermoset containing 20 wt% PH-*alt*-PDMS, the K_{IC} value is enhanced up to 3.0 MN/m$^{3/2}$, which is almost twice as that of the control epoxy thermoset. It is noted that when the content of PH-*alt*-PDMS is more than 10 wt%, the rate of increase in critical stress intensity factor (K_{IC}) is slow down with increasing the content of the block copolymer. It has been well known that the formation of the fine phase-separated morphologies is critical for the modification of thermosets by thermoplastics or elastomers [24]. For thermoplastic-modified epoxy resin, the homogenous morphologies often contribute less increase in fracture toughness of materials as rehearsed in the blends of epoxy resin with polysulfone [75] and in the blends of epoxy resin with phenolphthalein poly(ether ether sulfone) [76]. In the present case, the PH block is miscible with epoxy thermosets cured with DDM. It is plausible to propose that the increase in fracture toughness for the thermosetting blends mainly results from the formation of the microphase-separated morphology for the thermosetting blends due to the fine dispersion of PDMS nanodomains. Compared to the epoxy thermosets containing the liquid rubbers such as CTBN, ATBN and PDMS with the phase-separated morphology at the micrometer scale [2–4], the toughness improvement for the present nanostructured epoxy thermosets could display the following features: (i) the elastomeric component (*viz.* PDMS) was homogenously dispersed in the thermosetting matrix at the nanometer scale, which will greatly optimize the interactions between the thermosetting matrix and the modifier; (ii) the interface interactions between thermosetting matrix and the PDMS nanophases were significantly increased due to the miscibility of PH blocks with the epoxy thermosets. Therefore, the toughness of the blends was significantly enhanced at the small loading of PDMS (*i.e.*, <10 wt%). The results reported in this work are in a good agreement with those obtained in other nanostructured epoxy thermosets by Bates et al. [39,41]. Bates et al. proposed that the toughening mechanisms are quite dependent on type and shape of dispersed nanophases and can be either the debonding of vesicles (or micelles) from epoxy matrix or crack deflection and frictional interlocking for the thermosets possessing the terraced morphology [42]. It is proposed that the energy-dissipation mechanisms could be greatly related to the specific nanostructures of block copolymers-modified epoxy thermosets. Nonetheless, the correlations between toughening mechanisms and nanostructures of thermosets containing block copolymers remain largely unexplored vis-à-vis those for elastomers (and/or thermoplastic)-modified thermosets.

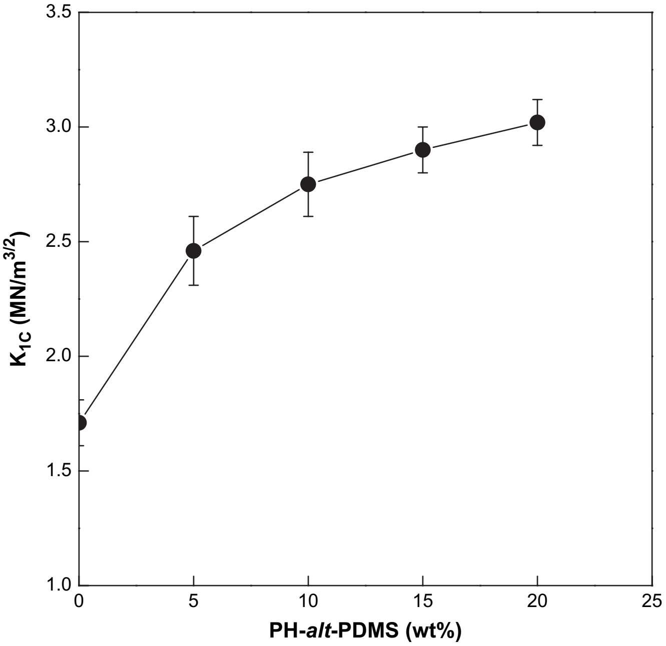


Fig. 10. Plot of K_{IC} as a function of the content of PH-*alt*-PDMS alternating block copolymer in the nanostructured epoxy thermosets.

4. Conclusions

Poly(hydroxyether of bisphenol A)-*block*-polydimethylsiloxane alternating block copolymer (PH-*alt*-PDMS) was synthesized *via* the polymerization between phenolic hydroxyl-terminated oligo-(hydroxyether of bisphenol A) and diamino-terminated oligodimethylsiloxane with the defined length. The polymerization was carried out *via* the formation of benzoxazine ring linkages, which was mediated with paraformaldehyde. The alternating block copolymer was characterized by means of Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR) and gel permeation chromatography (GPC). The block copolymer was incorporated to access the nanostructured thermosetting blends. The nanostructures were investigated by means of atomic force microscopy (AFM) and small angle X-ray scattering (SAXS). The formation of the nanostructures in the thermosetting composites was judged to follow the self-assembly mechanism in terms of the difference in miscibility of PDMS and PH blocks with epoxy resin after and before curing reaction. The fracture toughness of the nanostructured blends was evaluated in terms of the measurement of stress field strength factor (K_{IC}). It is noted that the epoxy resin was significantly toughened.

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