Thermal Properties of Epoxy/ Block-Copolymer Blends

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Abstract

New ways to improve the thermal properties of epoxy systems have been interesting topic for polymer researchers for several years. The block copolymer-modified epoxy matrix has received a great deal of attention and is still being intensely studied. Differential scanning calorimetry (DSC) is the most commonly used technique to investigate the thermal properties of epoxy/block copolymer systems. It can generally provide information such as phase behavior, miscibility, glass transition temperature, melting temperature, etc. between the block copolymer blocks and the epoxy matrix. In this chapter, we have mainly focused on the changes in the glass transition properties of the thermosets modified with block copolymers. The influence of the type of block copolymers and curing agents used and the effects of cure time and temperature on the phase behavior and microphase separation of epoxy thermosets are also discussed.

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Introduction

Epoxy resin composites exhibit numerous advantageous properties which allow them to be used as structural materials since the 1940s. Thermosetting polymers, in general, and epoxy resins, in particular, have been characterized by excellent properties such as mechanical strength, thermal stability, high chemical and corrosion resistance, good adhesion, and brittleness and have poor crack growth resistance. These characteristics, along with a long service life, make epoxies an important material necessary for the future growth of new technologies. Presently, there is high potential for more sophisticated application of high-performance epoxies in both automotive and aerospace industries. However, the high cross-link density of these materials makes them less ductile and poor resistant to crack propagation which constraint many of its applications. Several approaches have been undertaken to improve the feasibility of these materials particularly thermal properties of resins for practical applications. Since the early works of McGarry and the pioneering advances at B. F. Goodrich Company, the technology of rubber toughening has been applied to epoxy resins (McGarry and Willner 1968; McGarry and Sultan 1968). The common approaches for toughening epoxies include the incorporation of rubbers (mainly copolymers of butadiene and acrylonitrile with different acrylonitrile contents ranging from 0% to 26%), thermoplastics (such as poly(phenyleneoxide) (PPO), polysulfone (PSF), polystyrene (PS), polycarbonate, poly(ether ether ketone)), and rigid particle fillers like silica (Young and Beaumount 1977) glass beads, alumina trihydrate, etc. (Lange and Radford 1971). Among these, the most successful methods comprise the toughening of epoxies with rubber such as carboxyl-terminated butadiene acrylonitrile (CTBN) (Bascom et al. 1975), and acrylonitrile–butadiene rubber (NBR) showed impressive toughening effect. During curing reactions, thermoplastics and rubber get phase separated from the epoxy matrix. Normally, these additives act as stress concentrators and prevent the epoxy matrix from catastrophic failure on application of load. However, there was a significant deterioration in the glass transition temperature, modulus, and cross-link
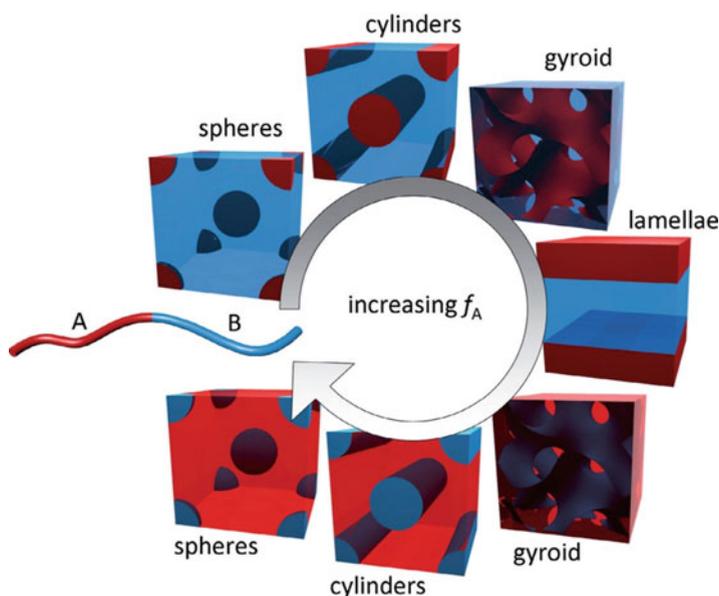
Fig. 1 Schematics of equilibrium morphologies observed for a stable A-b-B block copolymer as an increasing volume fraction of A (Botiz and Darling 2010)

density of cured epoxy resins that makes them not ideal for high-performance structural applications.

The improvement in the fracture toughness of the epoxy blends without affecting the glass transition temperatures is considered as a major challenge in composite industries. To enable this, block copolymers have been emerged as effective candidates for toughening epoxies (Hydro and Pearson 2007; Liu et al. 2010; Guo et al. 2003a, 2006; Mijovic et al. 2000; Wu et al. 2005; Lipic et al. 1998; Sun et al. 2005; Grubbs et al. 2003). The nanoscale self-organization of block copolymers is extensively investigated to create periodic structures in epoxy thermosets. The most common periodic morphologies of block copolymer comprise of spheres, hexagonal cylinders, gyroid, and lamellae with dimensions from 10 to 100 nm, which are detailed in Fig. 1 (Botiz and Darling 2010). Combining these ordered geometries within the thermoset matrix by the addition of small amounts of block copolymers can phase separate on the scale of nanometers, in particular they have capability to improve the mechanical properties and T_gs without sacrificing the optical transparency.

Generally, AB- and ABC-type di- and triblock copolymers with epoxy miscible and immiscible blocks can generate complex nanostructured phases by self-assembly within the uncured epoxy network to form different morphologies (Helfand 1975). Addition of relatively small amount of such block copolymers has been shown to give remarkable improvement in the toughness of epoxies with a minimal impact on the glass transition temperature and modulus. This strategy of creating nanostructures via the mechanism of self-assembly was primarily proposed
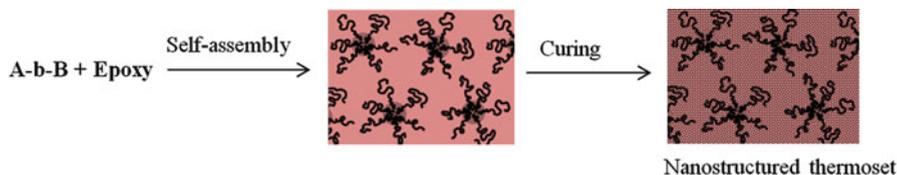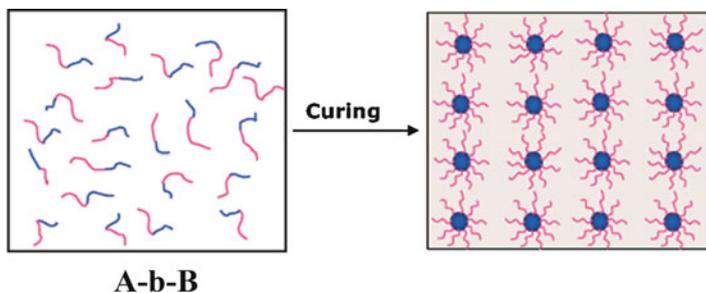
Fig. 2 Formation of nanostructured epoxy thermosets via self-assembly approach

by Hillmayer and co-workers (Lipic et al. 1998) using amphiphilic block copolymers which is shown in Fig. 2. In this mechanism, the preformed self-assembled nanostructures were locked with the introduction of hardeners followed by curing reactions; thus, the nanostructured thermosets can be prepared. The properties and final morphology of a thermoset/block copolymer system are determined by several factors including the cross-linking reaction of the thermoset resin, self-assembly of the block copolymer, and the phase separation of the blend.

The reaction-induced phase separation (RIPS) denotes a method in which the initial homogeneous mixture undergoes a phase separation during the curing reaction. Conventionally, the RIPS occurs at macroscopic scale. Some recent reports identified that the thermosetting polymer blends with an amphiphilic block copolymer with ordered and/or disordered nanostructures can be prepared alternatively through the mechanism of so-called reaction-induced microphase separation (RIMPS) (Xu and Zheng 2007). Here, the nanostructures are accessed by the control of microphase separation of a part of sub-chains of the block copolymer, while the other sub-chains remain miscible with the cross-linked thermosets. In this method, it is not necessary that the amphiphilic block copolymers should phase separate into the nanophases before the curing reaction. The blocks in the block copolymers may be miscible with precursors of thermosets. Generally in any of the abovementioned cases, the self-assembled morphologies in the thermosets are not formed until the curing reaction proceeds with a sufficient conversion of monomers. In comparison to the self-assembly type, the RIPS can apply additional variables to influence the formation of nanophases in thermosets, which are mainly associated with the thermodynamic and kinetic factors such as competitive kinetics between the cure and the microphase separation. A general mechanism of RIPS by block copolymer thermosets is shown in Fig. 3.

RIPS and self-assembly have their own advantages and disadvantages. By knowing the characteristics of these two procedures, one can design the architectures of a block copolymer which may be used to prepare nanostructured thermosets by the combination of these two mechanisms. The incorporation of these materials into epoxies often modifies the thermal properties of the epoxy-based thermosets (Ellis 1993). This chapter discusses the thermal properties of epoxy/block copolymer blends where the knowledge on these properties is very crucial in the processing stage as well as in diverse applications. Differential scanning calorimetry (DSC) is employed to measure the thermal properties of the polymer materials as a direct function of time or temperature. In this technique, the uncured and cured epoxy samples are exposed to heat in a calibrated closed furnace where the heat flow of the epoxy sample is measured in comparison to a blank reference cell. The heat flow data

Fig. 3 Formation of nanostructured epoxy thermosets via RIPS approach

provide a direct method for determining cure kinetics, changes in T_g with respect to cure time, curing temperature, crystallization, and enthalpy of fusion of the samples. Glass transition temperature (T_g) is a unique property of an amorphous polymer which determines the transition from hard glassy to soft rubbery states. The polymer becomes very brittle when the temperature drops below its T_g whereas it attains a rubbery behavior when the temperature rises. Generally, the T_gs of the epoxy matrix can be assessed by means of differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). The chapter provides the detailed information and techniques regarding the DSC analysis of epoxy/block copolymer blends.

Thermal Properties of Epoxy Thermosets Modified with Block Copolymers

The thermal properties of epoxy blends with block copolymers are very different from that of homopolymer or random copolymers. The T_gs of the epoxy/block copolymers are connected with the nanostructures of the epoxy systems as well as the miscibility of the block copolymer blocks with the thermosets before and after curing though it can be affected by the addition of the hardener and the curing processes. Generally, the influence of thermal properties by the incorporation of block copolymer in epoxy matrix can be related with the following factors such as epoxy miscible blocks, epoxy immiscible blocks, and the demixing of partial epoxy miscible blocks. In the following, we will discuss the nanostructured thermosets with block copolymer having commonly used blocks in detail. Generally amphiphilic compounds are selected in such a way that at least one of these blocks promotes sufficient miscibility with thermoset matrix so as to produce toughened thermosets with nanosized inclusions.

Epoxy Thermosets with Poly(ethylene oxide) (PEO)-Based Block Copolymers

Following the pioneer works of Hillmayer et al. (1998), Mijovic et al. (2000), and Guo et al. (2003), different strategies for creating nanostructures using amphiphilic

block copolymers have been proposed. Here, the uncured epoxy resin acts as a solvent to dissolve block copolymers and form nanostructures such as lamellar, cylindrical, and spherical structures, depending on the blend composition. As formed block copolymer morphologies will have effect both on the mechanical and the glass transition temperatures (T_gs) of the block copolymer-modified epoxy systems. Bates and co-workers have pioneered in this field, investigating the effect of block copolymer morphologies on the T_g of modified and unmodified epoxies. Two amphiphilic block copolymers, namely, poly(ethylene oxide)-*block*-poly(ethylene-alt-propylene) (PEO-*b*-PEP) and poly(methyl methacrylate-ran-glycidyl methacrylate)-*block*-poly(2-ethylhexyl methacrylate) ((PMMA-ran-GMA)-*b*-PEHMA), were blended with brominated and non-brominated epoxies cured with phenol novolac (Dean et al. 2003). The system exhibited morphological transitions from spherical micelles to vesicles with the increasing length of the PEP block with regard to PEO blocks. In this study, block copolymers self-assembled into vesicles resulted an increase in T_g of epoxy blends from 89 °C to 109 °C. The self-assembled spherical and wormlike micelles demonstrated a significant increase in T_g along with fracture toughness. The increase in temperature may be due to the high cross-link density of epoxy and hardener when blended with block copolymers. Though diluents normally degrade T_g, the rise in temperature was prominent with wormlike micelles. This indicates that the added block copolymer has an impact on the rate of cross-linking reactions during curing reactions. They concluded that the nanostructures play a critical role in the enhancement of mechanical as well as thermal properties.

In another study, Dean et al. reported (Dean et al. 2001) the changes in the thermal properties of the thermosetting blends by modifying epoxy with symmetric or asymmetric poly(ethylene oxide)-*block*-poly-(ethylene-alt-propylene) (PEO-*b* PEP) block copolymer with PEO volume fractions of 0.5 and 0.26, respectively. These resins exhibited an increased fracture toughness without large reduction in T_g at low block copolymer concentrations (<5 wt%).

In another study, Bates and co-workers have reported that BADGE epoxy resin and poly(hexylene oxide)-*block*-poly(ethylene oxide) (PHO-*b*-PEO) block copolymers curing under phenol novolac resins have shown to be effective in improving T_g and fracture toughness (Thio et al. 2006).

Wu et al. (2005) detailed the experimental methods to establish the morphological features of cured epoxy thermosets with its thermal properties by modifying with bisphenol A-based resin/phenol novolac (PN) curing agent/poly(N-butylene oxide)-*block*-poly(ethylene oxide) (PBO-*b*-PEO) mixtures. The neat epoxy resin exhibits a T_g, at 89 °C, while addition of 5% by weight PBO–PEO-2 (vesicles) results in T_g, of 109 °C. The incorporation of PBO–PEO-6 (spherical micelles) and PBO–PEO-4 (wormlike micelles) leads to even greater glass transition temperatures, such as 122 °C and 127 °C, respectively. More details are displayed in Fig. 4 and Table 1.

Another major system that has been investigated by Hillmayer and co-workers (Liu et al. 2010) is the modification of epoxy resin with poly(ethylene-alt-propylene)-*b*-poly(ethylene oxide) (PEP-*b*-PEO) block copolymer self-assembled into wormlike micelles with improvements in tensile properties without sacrificing its T_g. In these studies, the epoxy resin that selectively dissolves with the PEO block and

Fig. 4 DSC scans obtained from (*a*) the unmodified epoxy resin and modified with (*b*) PBO–PEO-2 (vesicles), (*c*) PBO–PEO-6 (spherical micelles), and (*d*) PBO–PEO-4 (wormlike micelles) at a concentration of 5% by weight (Wu et al. 2005)
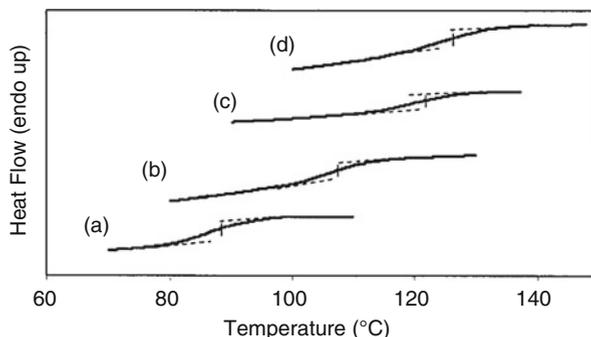
Table 1 Properties of epoxy/PN modified by 5% PBO–PEO block copolymer (Wu et al. 2003, 2005)

Polymer[a]	Morphology in epoxy[b]	T_g[c] (°C)
None		89
PBO–PEO-1	Clustered vesicles	91
PBO–PEO-2	Vesicles	109
PBO–PEO-3	Branched cylinders	122
PBO–PEO-4	Cylinders	127
PBO–PEO-5	Cylinders + spheres	116
PBO–PEO-6	Spheres	122

[a]PBO–PEO block copolymers varying ethylene oxide repeat units and mass fractions of the PEO blocks
[b]Determined from TEM images
[c]Determined from DSC analysis

could swell the PEO domains in the block copolymers without macroscopic phase separation leads to stable nanostructures, thus reducing polymer segment mobility by increasing cross-link density.

Guo et al. (2002) explored new principles for creating nanostructures in DGEBA-type epoxy resin (ER) with amphiphilic poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) PEO-*b*-PPO-*b*-PEO triblock copolymers by carefully choosing the curing condition. PEO-*b*-PPO-*b*-PEO triblock copolymers with different ethylene oxide contents, such as 30 wt% EO content (EO30) and with 80 wt% EO content (EO80), lead to stable nanostructures in DGEBA-type epoxy using 4,4′-methylenedianiline (MDA) as curing agent.

Figure 5 shows DSC curves of the second scan of the MDA-cured epoxy, EO30, and the MDA-cured epoxy/EO30 thermosetting blends. The block copolymer shows a melting temperature at 33 °C and a T_g at −64 °C. In Fig. 5, it can be seen that the cured epoxy displays T_g at 172 °C, which shifts down to lower temperature with increasing EO30 content. When the EO30 content in the blends increases, T_g of the thermosets decreases which means EO30/epoxy components are miscible or at least partially miscible at these compositions. The reduction in T_g of the cured blends suggests the combination of internal and external plasticization effects. Figure 5 also shows the T_m (EO30) values from the second scans as a function of the blend

Fig. 5 DSC thermograms of
the second scan of the
MDA-cured ER/EO30 blends
(Guo et al. 2002)
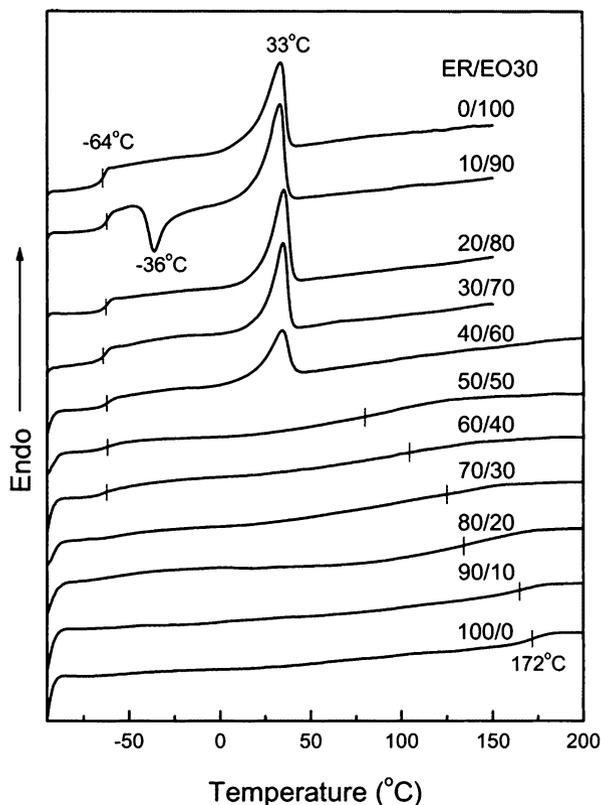
composition. The T_m values remain unchanged up to 50 wt% of EO30 showing immiscible or partially miscible blends with a crystalline component.

Figure 6 displays the DSC cooling scan of epoxy/EO30 blends. From the cooling scan, pure EO30 copolymer displays a crystallization peak at −27 °C that remains unchanged until 60 wt% EO30 which indicates an immiscible blend. There is another crystallization peak observed at −13 °C for 80 wt% of block copolymer and that becomes a shoulder peak for blends with 70 wt% of EO30. This is due to the higher content of epoxy which acts as a nucleation agent in ER/EO30 blends. At 90 wt% of EO30, the crystallization peak shifts down to lower values representing a reduced crystallization rate.

In a study, Guo et al. (2003) investigated the nanoscale confinement on the crystallization kinetics in MDA-cured epoxy resin with a low molecular weight polyethylene-*block*-poly(ethylene oxide) (PE-*b*-PEO) diblock copolymer. DSC measurements show two melting peaks at 23 °C and 106 °C representing crystalline PEO blocks and the crystalline PE blocks.

Figure 7 shows that the thermosets with up to 40 wt% of block copolymer did not display melting peak for the PEO blocks. This indicates the miscibility of PEO blocks with epoxy resins. The T_g of the cured epoxy shifts down from 177 °C to

Fig. 6 DSC thermograms of crystallization curves of the MDA-cured ER/EO30 blends (Guo et al. 2002)
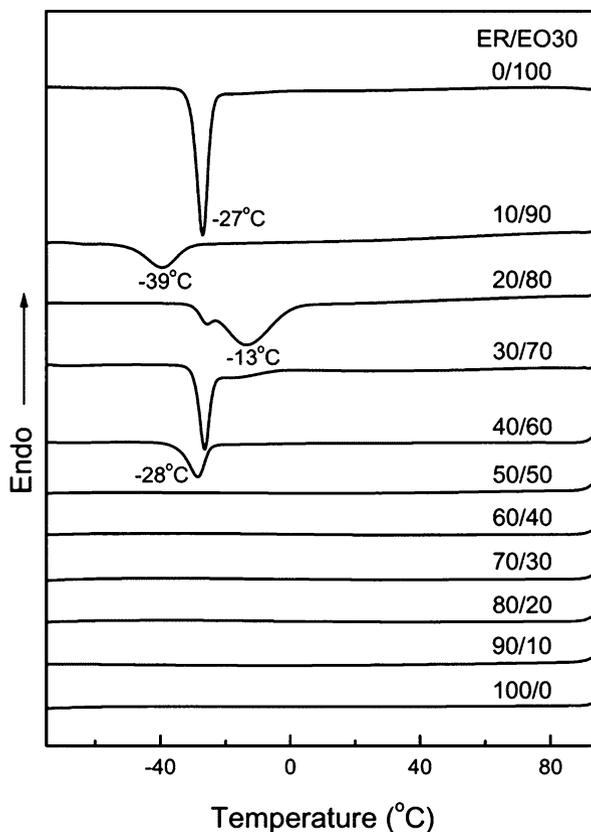
lower temperatures with increase in the PE-*b*-PEO content up to 20 wt% and finally disappears at high content of the block copolymer. This again confirms the miscibility or at least partial miscibility between epoxy resin and PEO blocks in the block copolymer. The reduction in T_g is due to the dilution effect of the PEO component that causes a reduction in cross-linking density of the network.

Figure 8 shows DSC thermograms of the cooling scan for the cured ER/EEO blends. The crystallization peak (T_c), at 3 °C, denotes the crystallization of the PEO blocks which shifts down to lower values with increasing ER content in the cured blends. At 18/82 ER/EEO blend composition, PEO showed a crystallization exotherm at −11 °C beyond the crystallization peak at −5 °C which can be attributed to heterogeneous and homogeneous nucleation, respectively. The homogeneous nucleation of PEO slowly becomes dominant when the epoxy content in the blends increases from 25 to 50 wt%, whereas at 50 wt% the peak becomes small and shifts down to −31 °C, indicating a declined crystallization rate. At very high epoxy content, PEO becomes completely miscible with the matrix; hence, no crystallization exotherm is observed for EEO. The major crystallization peak observed at 93 °C denotes the T_c of PE which does not disappear even with very low content of EEO in the blends.

Fig. 7 DSC thermograms of
the second scan of the
MDA-cured ER/EEO blends
after the cooling scan. The
heating rate is 20 °C/min (Guo
et al. 2003)
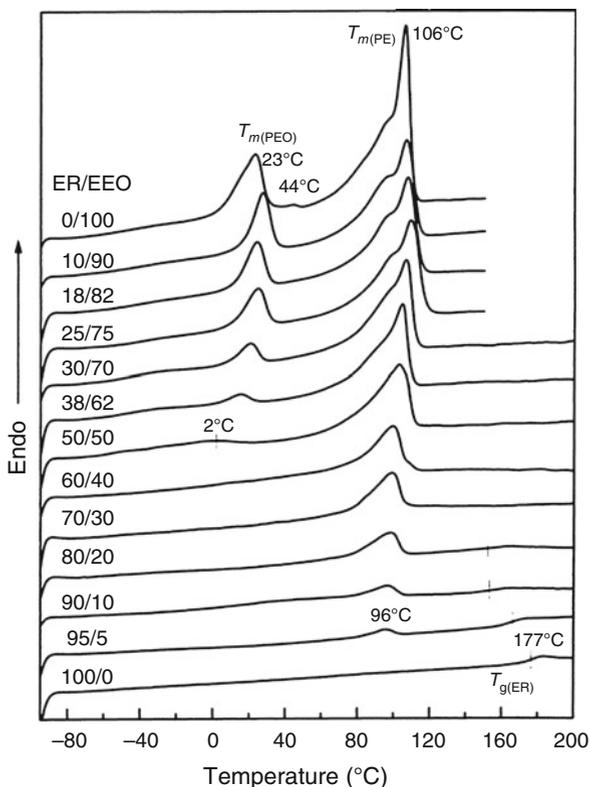
There are a number of studies reported with various morphologies from PEO-based block copolymers with nanostructures controllably produced in diglycidyl ether of bisphenol A (DGEBA)-type epoxy resin. Mijovic et al. (2000) reported preliminary investigation on DGEBA with PEO-b-PPO diblock copolymer and PEO-*b*-PPO-*b*-PEO triblock copolymer. The DSC curves of the epoxy resins with both PEO triblock copolymer and diblock copolymer are detailed in Figs. 9 and 10. It can be seen in Fig. 9 that the T_g of the thermosets broadens and shifts to higher temperature whereas the triblock copolymers showed a phase separation with two distinct T_gs. PEO, being a crystalline polymer, its addition to DGEBA suppress the crystallization and increase its T_g (Mijovic et al. 2000). They observed macrophase separation for epoxy blends with PEO-*b*-PPO-*b*-PEO triblock copolymer in contrast to the microphase separation.

The DSC thermograms of 50/50 DGEBA−MDA/PEO−PPO−PEO blend measured at various times during cure at 120 °C are shown in Fig. 9. Originally the mixture has a single T_g at −41 °C. It is observed that the phase separation occurred between 45 and 60 min giving rise to two glass transitions. The low temperature one belongs to the block copolymer and the higher one related primarily with the DGEBA−MDA phase. Phase separation starts between 45 and 60 min and is

Fig. 8 Crystallization curves of the MDA-cured ER/EEO blends during the cooling at −20 °C/min (Guo et al. 2003)
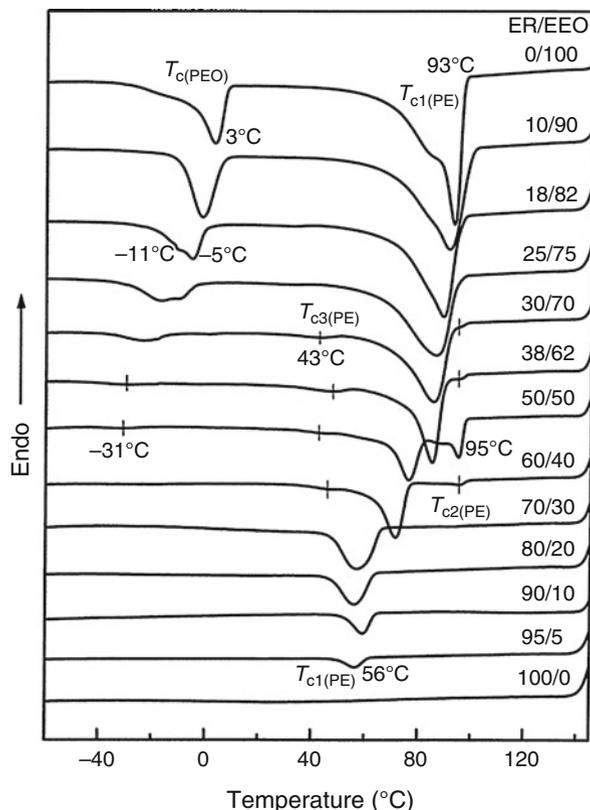

accompanied by the emergence of two transitions: the lower one related mostly to the block copolymer and the higher one associated primarily with the DGEBA−MDA network. As the network continues to grow, the higher T_g increases. Figure 9 shows the thermograms of 50/50 DGEBA−MDA/PEO−PPO blend where it was observed that the T_g broadens, shifts slightly to higher temperature, and flattens out considerably as the curing progresses.

Epoxy Thermosets with PMMA-Based Block Copolymers

Pascault and co-workers (Ritzenthaler 2000) studied the blends of polystyrene-block-polybutadiene-block-poly(methylmethacrylate) (SBM) copolymer with DGEBA by using 4,4′-diaminodiphenyl sulfone (DDS) and 4,4′-methylenebis(3-chloro-2,6-diethylaniline) (MCDEA) as hardeners. Transparent nanostructured thermosets were obtained with MCDEA as hardener, and PMMA remained soluble during curing. They concluded that the solubility of SBM blocks with epoxy is crucial for the formation of nanostructures in the thermosets. The studies have shown that the formation of nanostructured morphologies in PMMA-modified epoxy thermosets depends on the
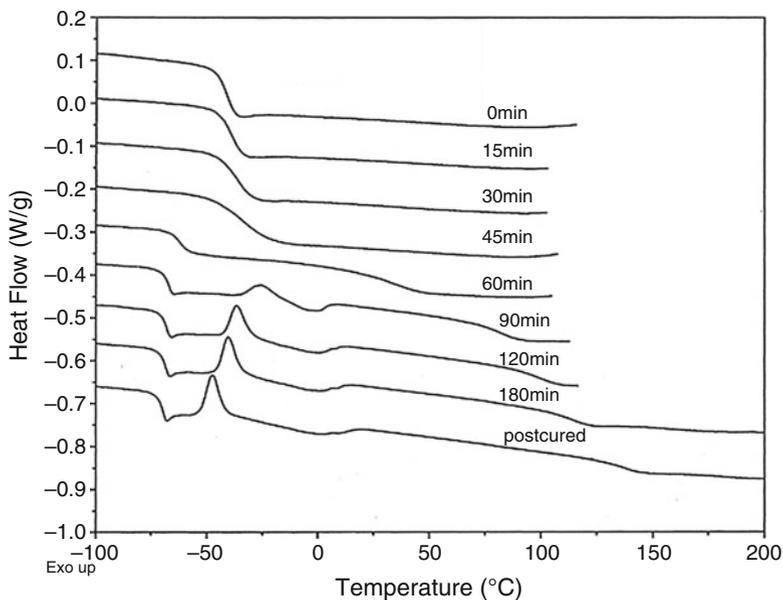
Fig. 9 DSC thermograms of 50/50 DGEBA−MDA/PEO−PPO−PEO blend at various times during reaction at 120 °C (Mijovic et al. 2000)
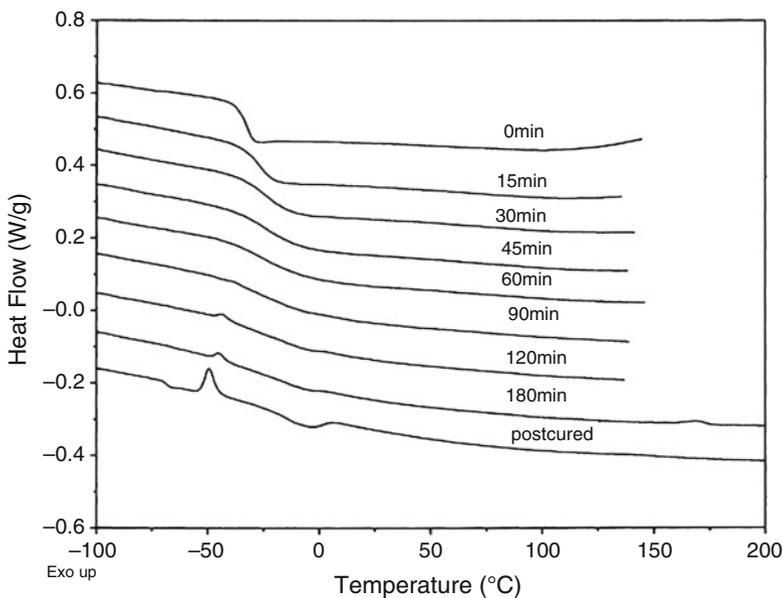
Fig. 10 DSC thermograms of 50/50 DGEBA−MDA/PEO−PPO blend at various times during reaction at 150 °C (Mijovic et al. 2000)

Fig. 11 DSC curves of the DGEBA–MCDEA-cured PS-b-PMMA systems prepared by the non-solvent method (**a**) and by the solvent method (**b**). The dotted line in each graph indicates the theoretical T_g values calculated by the Fox equation (Cano et al. 2015)
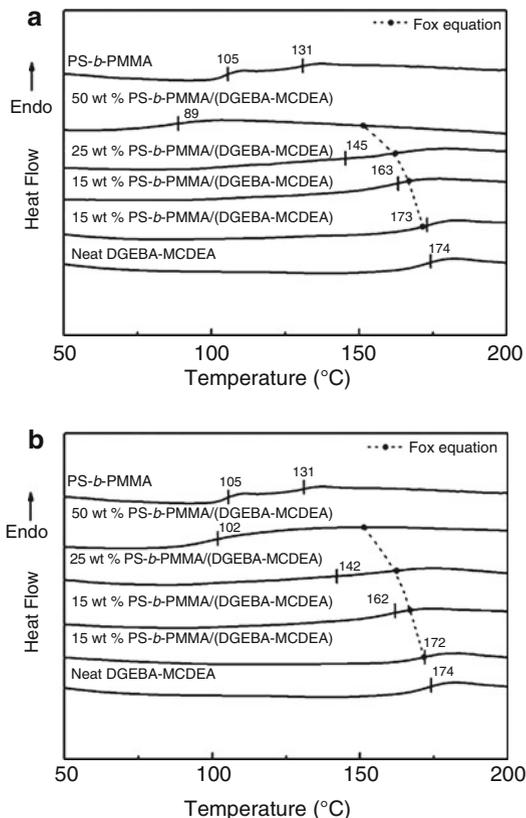
nature of curing agents used. Macrophase separation could take place when hardeners such as 4,4′-diaminodiphenyl sulfone (DDS) or 4,4′-methylenedianiline (MDA) are used. Going from homo-PMMA to triblock SBM, similar trends have been observed (Court et al. 2001; Ritzenthaler et al. 2000, 2002, 2003; Girard-Reydet et al. 2003).

Tercjak (Cano et al. 2015) investigated the nanostructure morphologies in a DGEBA epoxy monomer-based thermosetting system modified with polystyrene-block-polymethyl methacrylate (PS-b-PMMA) block copolymer and MCEDA as the curing agent. The thermosets were prepared by two different preparation methods such as solvent and non-solvent methods.

Figure 11 summarizes the thermal properties of the PS-b-PMMA modified with MCDEA-cured epoxy resins. The T_gs of the neat epoxy, the block copolymers, are 174 °C, 105 °C, and 131 °C, respectively. As the composition of block copolymer in the epoxy increases, the T_g of the epoxy decreases indicating the miscibility between the block copolymer and epoxy (Blanco et al. 2010; Cano et al. 2014). It has been proven that the PMMA is miscible with epoxy up to the end of curing whereas PS block phase separates before the gel point. Figure 11b represents the theoretical

values of the glass transitions of the thermosets, calculated using Fox equation which is represented as (Larrañaga et al. 2007)

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \tag{1}$$

where w_1 and w_2 are weight fractions of components 1 and 2, respectively. By analyzing the T_g values under with or without solvent conditions, systems prepared by the solvent method showed slightly lower T_g values than that of without solvent up to a 25 wt% PS-b-PMMA block copolymer content. This denotes that a better miscibility was obtained under solvent method. It was interesting to note that at 50 wt% block copolymer content, the blends prepared under two different conditions showed a lower T_g. This low T_g of the thermosets pointed out that the high amount of the block copolymer content creates the dilution effect in the matrix which significantly delays the curing reaction (Cano et al. 2014; George et al. 2012).

Guo et al. (2001) reported an existence of three different glass transition temperatures when blending DDM-cured epoxy with an immiscible polystyrene-*block*-polybutadiene (PS-b-PB) block copolymer. DSC thermograms of the blends, cured epoxy, and pure block copolymer are shown in Fig. 12. The blends show a T_g around

Fig. 12 DSC thermograms of the second scan of ER/SB blends (Guo et al. 2001)
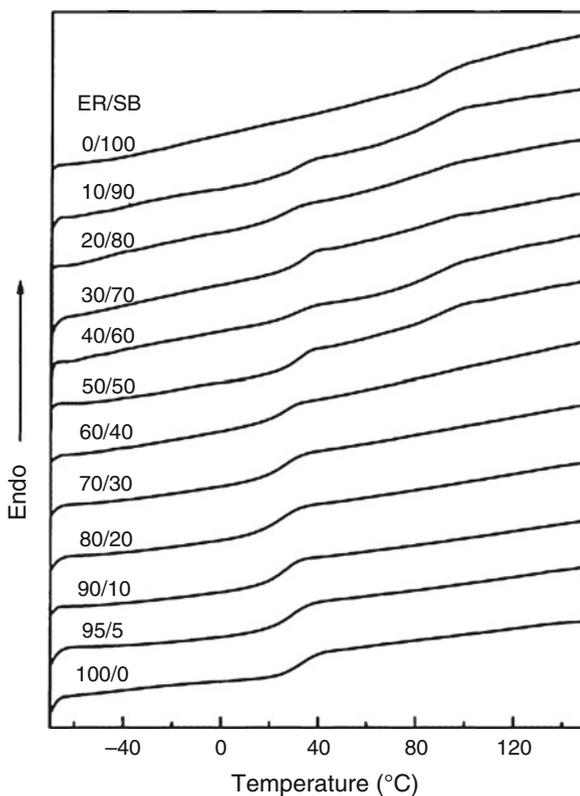
Table 2 T_gs of epoxidized PB-rich phase in the SBSep46 and their mixtures with 10, 20, and 30 wt% epoxy before and after curing determined by DSC

| System	T_g ePB (°C)		ΔT_g epoxy matrix (°C)
	Before curing	After curing	
SBSep46	−31		
90SBSep46/10epoxy	−23	−12	11
80SBSep46/20epoxy	−18	4	22
70SBSep46/30epoxy	−14	33	47

30 °C represents the cured epoxy. At high content of block copolymer, there is a T_g observed at 90 °C that corresponds to the PS blocks in the blends. But the T_g of the PB block was not detectable under the used experimental conditions.

Nanostructured Epoxy Thermosets with Chemically Modified/Reactive Block Copolymers

The formation of nanostructures in epoxy thermosets by the chemical modification of block copolymers is a viable method for inducing the compatibility of at least one block with the epoxy resin. Ocando et al. (2013) reported the design of such a nanostructured system with poly(styrene-*block*-butadiene-*block*-styrene) (SBS) and epoxy by epoxidation of PB blocks. The microphase separation of epoxidized SBS with epoxy was confirmed by DSC and the results are detailed in Table 2. DSC results show that before curing, all the blends show the presence of two glass transition temperatures due to the microphase separation between the components of the mixtures. The T_g of the PS blocks remains constant around 80 °C for all mixtures, whereas the T_g of epoxidized PB blocks shows at lower temperatures. After the addition of 10, 20, and 30 wt% of epoxy content, the T_g of epoxidized PB phase shifts from around −31 °C to higher temperatures. This shows the miscibility of the SBSep46 with epoxy matrix before curing. After curing reaction, the T_g of epoxidized PB shifts to even high temperatures suggesting the cross-linking formation of DGEBA/MCDEA which gets interact with oxirane groups present in epoxidized PB block and that can enhance the T_g.

Hameed et al. (2010) reported the modification of epoxy with a highly ordered poly(dimethyl siloxane)-*block*-poly(glycidyl methacrylate) (PDMS-*b*-PGMA) block copolymer where PGMA reactive block can involve in with epoxy in the network formation.

The DSC scans of the MDA-cured epoxy/PDMS-*block*-PGMA blends are shown in Fig. 13. Pure PDMS-*b*-PGMA block copolymer shows a T_g at 64 °C and after curing with MDA, the T_g shifted to 107 °C. By blending the block copolymer with epoxy, the T_g of the cured blends is shifted to higher temperatures. It can be seen that the T_g of the cured blends increased approximately 28 °C by adding 10 wt% of the reactive diblock copolymer. But, the T_gs of the blends decrease above the 10 wt% of the reactive diblock copolymer composition. This can be attributed to the presence of
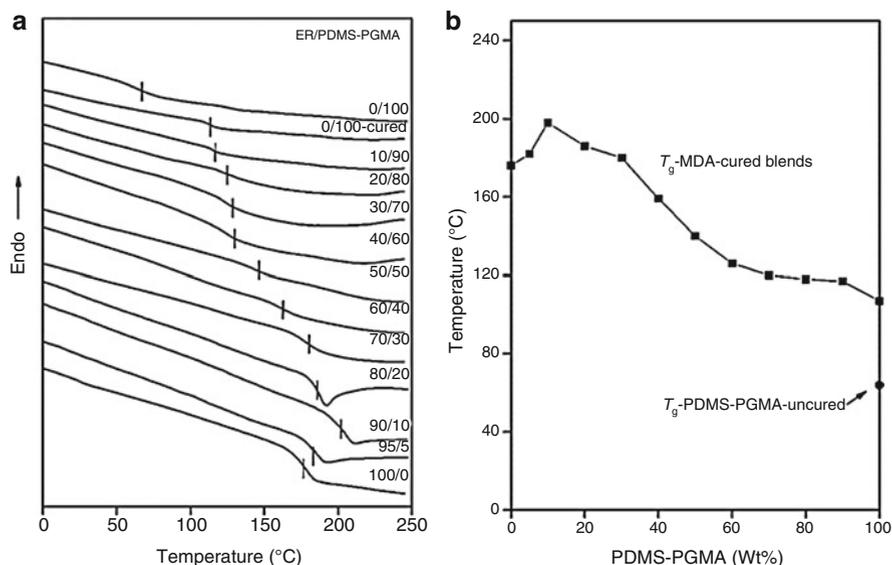
Fig. 13 (**a**) DSC curves of the second scan of ER/PDMS-*b*-PGMA blends and (**b**) glass transition temperature (T_g) versus blend composition from the second scans of ER/PDMS-PGMA blends (Hameed et al. 2010)

microphase-separated rubbery PDMS blocks. There is a reduction in the T_g of nanostructured epoxy with the modification of additives due to the external or internal plasticization of the soft polymer chains, which can take part in the network formation with epoxy by hydrogen-bonding interactions.

Xu et al. (2010) reported an increase in the glass transition temperature of the thermosets by blending epoxy with reactive polystyrene-*block*-poly(glycidyl methacrylate) diblock copolymer (PS-*b*-PGMA). The DSC curves of cross-linked epoxy and nanostructured epoxy/PS-*b*-PGMA thermosets are shown in Fig. 14. It can be seen from the graph that the neat epoxy displays a T_g at 174 °C and the PS-*b*-PGMA diblock copolymer shows that at 100 °C, which indicates PS blocks of the diblock copolymer. The T_gs of the blends are significantly increasing with the addition of block copolymer content in the epoxy. The introduction of the glycidyl methacrylate blocks in the block copolymers can react spontaneously with MDA and form covalent linkages between the reactive copolymers and the cross-linked epoxy matrix. As a result, microphase separation of the other blocks will be restricted because of strong chemical covalent interaction; thereby, the cross-link density of the matrix increases and the T_g of the blends moves to high values.

Mai and co-workers (Wu et al. 2012) reported a novel method for preparing nanostructured thermosets by introducing block ionomer polystyrene-*block*-poly (ethylene-ran-butylene)-*block*-polystyrene (SEBS) with a tertiary amine terminated PCL, which is represented as SSEBS-c-PCL in the block copolymers for modifying epoxies. The thermal studies of cured epoxy/SSEBS-c-PCL thermosets are given in

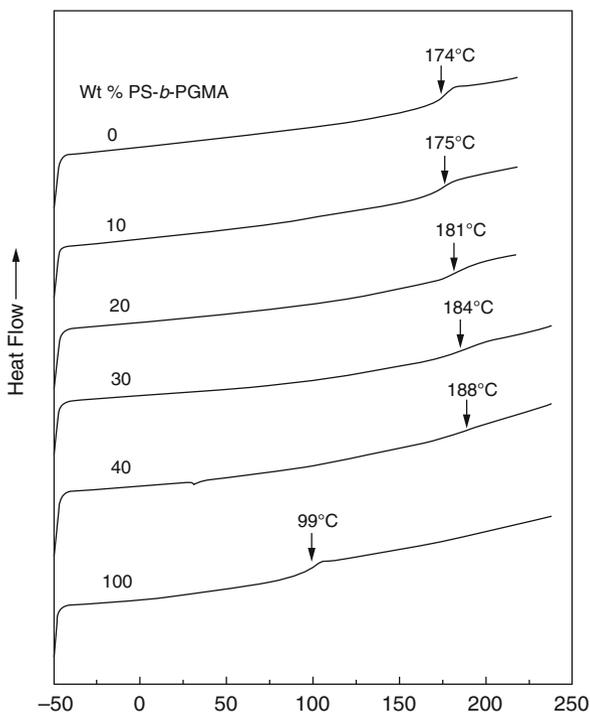**Fig. 14** The DSC thermograms of epoxy resin and epoxy/PS-*b*-PGMA-blended thermosets (Xu et al. 2010)

Fig. 15. The DSC data shows a sharp peak at 49 °C denotes the melting temperature of the PCL blocks in ionomer SSEBS. Melting point depression is the characteristic of a miscible polymer blend involving hydrogen-bonding interactions. It can be seen that the T_m of the PCL side chains in the PCL side chains in the block ionomer SSEBS-c-PCL disappears with increasing epoxy compositions. This depression in T_g of the epoxy-rich phase indicates the miscibility between the PCL side chains and the epoxy matrix. It has already been reported that the epoxy/PCL blends cured with aromatic amine are miscible with aromatic amine-cured epoxy matrix and interpenetrated into the cross-linked epoxy networks (Guo and Groeninckx 2001; Wang et al. 2001). The cured epoxy shows a T_g at 176 °C and is substantially shifted down to lower temperatures with increasing content of the SSEBS-c-PCL which is due to the plasticization effect of the PCL side chains on the epoxy matrix (Guo et al. 2001).

Nanostructured Epoxy Thermosets via RIPS Approach

Zheng (Xu and Zheng 2007) reported ordered nanostructures via RIPS method by blending epoxy and poly(ε-caprolactone)-*block*-poly(N-butyl acrylate) (PCL-*b*-PBA) in 4,4′-methylenebis(2-chloroaniline) (MOCA). DSC has used to reveal the miscibility and phase behavior of these systems. Here, PCL blocks were miscible

**Fig. 15** DSC curves of second scan of epoxy/SSEBS-c-PCL blends
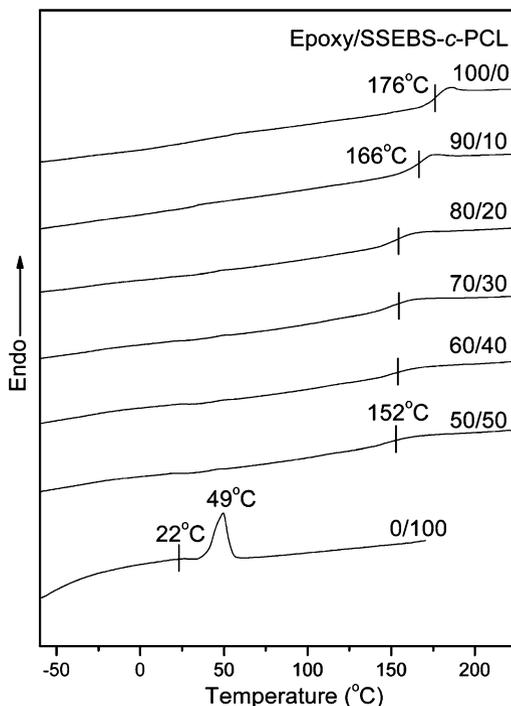
with epoxy before and after curing reaction whereas the mixtures of PBA and epoxy precursors displayed an upper critical solution temperature (UCST) behavior. In Fig. 16, it has been confirmed that the cured blends showed a single, composition-dependant T_g indicating a miscible blend. Pure epoxy shows a T_g at 153 °C and the block copolymer shows a melting peak at 56 °C and T_g at around −51 °C. As the block copolymer composition in the blend increases, lower T_g range is observed due to the miscibility of PCL blocks with epoxy resin.

In another study, Zheng detailed (Yi et al. 2009) nanostructured epoxy by blending poly(2,2,2-trifluoroethyl acrylate)-block-poly(ethylene oxide) amphiphilic diblock copolymer with epoxy resin where PEO is miscible whereas PTFEA is immiscible with epoxy after and before curing. DSC studies in Fig. 17 confirm the miscibility of these blocks with epoxy resins. At higher compositions of epoxy, a depression in T_g was observed which also confirms the miscibility of PEO blocks in the matrix. Though pure block copolymer exhibited an endotherm peak at 54 °C, the blends did not show the melting peak. This is due to the miscible PEO blocks which get trapped into the epoxy network. The broadening of the glass transition range could be attributed to the enrichment of soft PEO chains in the epoxy matrix.

Recently, Gong et al. (2008) have studied the effect of miscibility of block copolymer block with epoxy matrix by analyzing the glass transition behavior of all blend compositions. In their study, they used PH-alt-PDMS alternating block copolymer with epoxy miscible PH blocks and immiscible PDMS blocks with epoxy
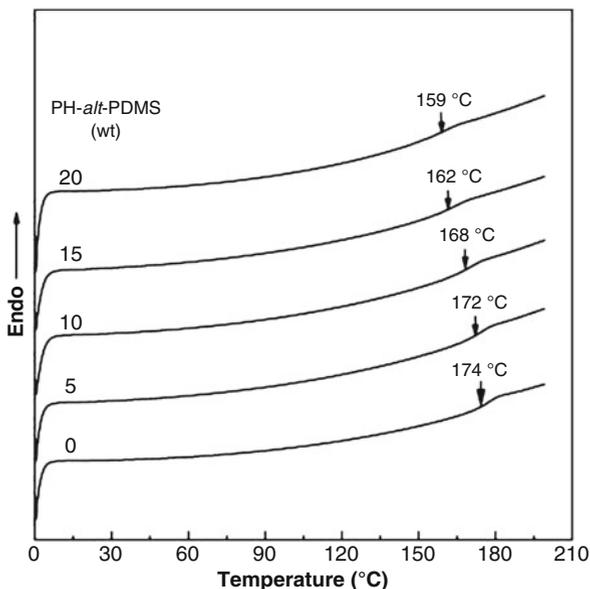
Fig. 16 DSC curves of the control epoxy, PCL-*b*-PBA, and their nanostructured blends
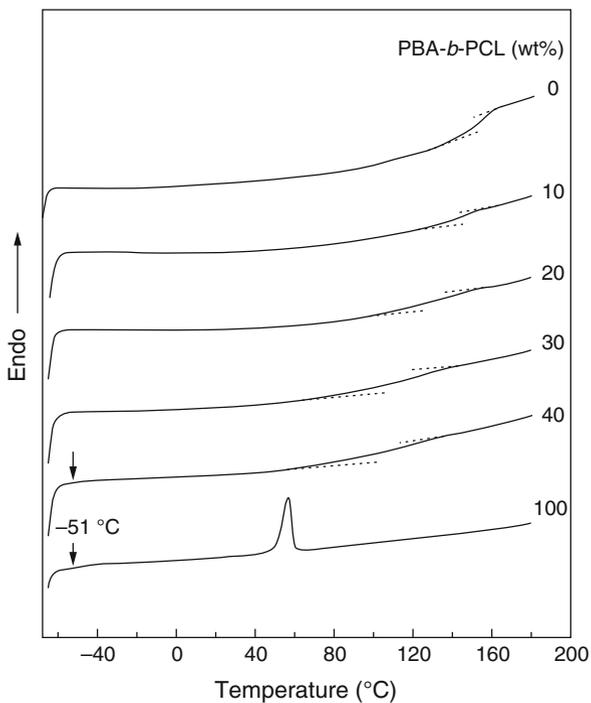
Fig. 17 DSC curves of the nanostructured thermosets containing PTFEA-*b*-PEO diblock copolymer
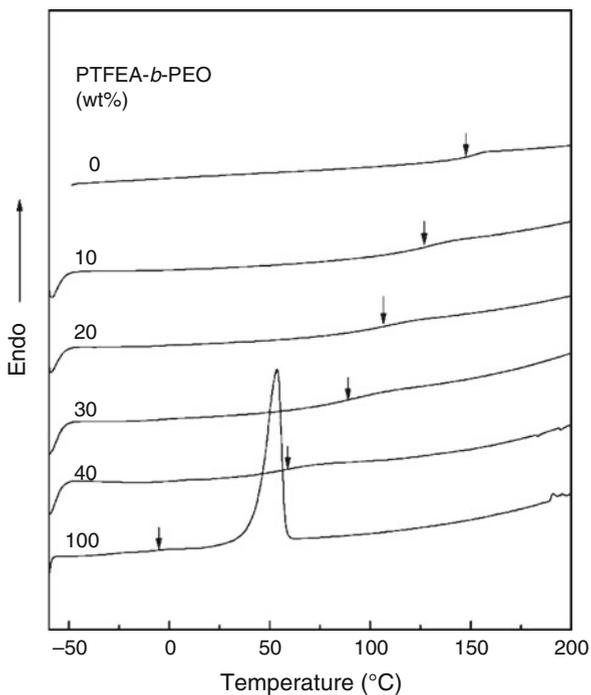
Fig. 18 DSC curves of the epoxy thermosets containing PH-alt-PDMS alternating block copolymer


before and after curing. Figure 18 shows the DSC thermograms of the PH-alt-PDMS with epoxy cured with 4,4′-diaminodiphenylmethane(DDM). The PH of the PH-alt-PDMS exhibited a glass transition at 52 °C, and epoxy thermoset shows a T_g at 174 °C and is much higher than the T_g corresponding to PH blocks as displayed in Fig. 18. The T_gs of the blends shift to lower temperatures with increasing block copolymer content which is due to the plasticization effect of the PH blocks on the epoxy matrix. In addition to this, the hydrogen-bonding interactions of the phenolic hydroxyl groups of the block copolymers with DGEBA are responsible for the miscibility of PH in the epoxy matrix that causes a decrease in T_g.

Hu et al. (2010) investigated the self-assembly behavior of poly(ε-caprolactone)-*block*-poly(ethylene-coethylethylene)-*block*-poly(ε-caprolactone) (PCL-*b*-PEEE-*b*-PCL) triblock copolymer in epoxy thermosets. Figure 19 shows the blends of epoxy with PCL-*b*-PEEE-*b*-PCL triblock copolymer. The blends displayed T_gs in the range of 60–160 °C, which shows increasing with the content of PCL-*b*-PEEE-*b*-PCL triblock copolymer. The peak at 73 °C corresponds to the melting peak of the nanostructured thermoset which indicates the fusion of PEEE blocks. It is not assigned to the melting transition of PCL since the PCL blocks were not crystalline in the nanostructured thermosets. When the block copolymer content increases in the blends, the intensity of this peak increases.

For understanding the demixing behavior of PCL sub-chains, the glass transition values of PCL/epoxy are considered. Couchman equation (Couchman 1978) is used out of many theoretical equations (Fox 1956; Gordon and Taylor 1952) in this study to understand the dependence of T_g on composition in miscible polymer blends. The

Fig. 19 DSC curves of the nanostructured thermosets containing PCL-b-PEEE-b-PCL triblock copolymer
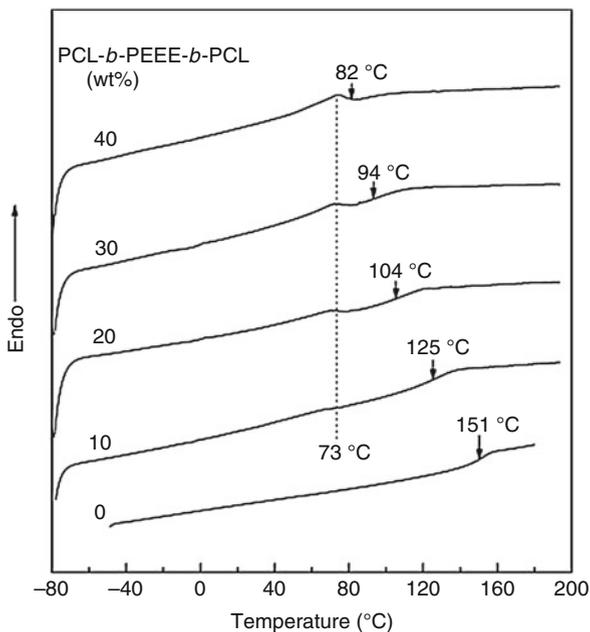
Fig. 20 Plots of T_gs as functions of concentration of PCL for epoxy thermosets containing the block copolymers
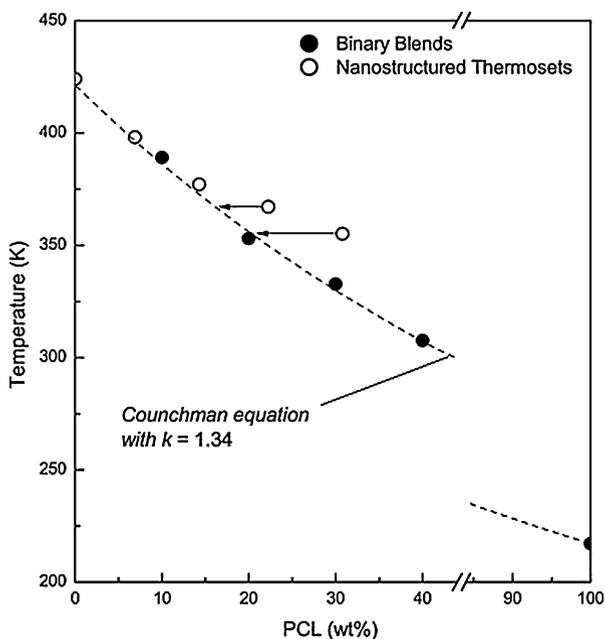
plots of T_gs as functions of the concentration of PCL for the nanostructured thermosets are shown in Fig. 20:

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \qquad (2)$$

where **W1** is the weight fraction of component 1 and T_g is the glass transition temperature of blend; the parameter k is Couchman coefficient defined by

$$k = \frac{\Delta C_{p1}}{\Delta C_{p2}} \qquad (3)$$

where ΔC_p represents the increase in the heat capacity of the material. Figure 20 shows the T_gs of epoxy with PCL-b-PEEE-b-PCL triblock copolymer as well as binary blends of epoxy/PCL where PCL blocks are having the same molecular weight with length of the PCL block in the triblock copolymer. The results pointed out that the thermosets containing 30 and 40 wt% of the block copolymer exhibited higher T_gs than the epoxy/PCL blends with the same compositions of PCL blocks. In the binary blends, homogenous dispersion of PCL blocks takes place via intermolecular hydrogen-bonding interactions with epoxy networks. But in triblock copolymer, due to the steric hindrance, the PCL blocks remain at the surface of PEEE domains. Hence, the miscibility of PCL blocks with epoxy diminishes which weakens the effect of plasticization of PCL blocks with epoxy and increases the T_g of the thermosets.

Moreover, improving the thermal stability and thermal conductivity of epoxy thermosets while maintaining other important physical properties has attracted significant research interest. In general, most of the additives (polymers/fibers/nanoparticles) tend to slightly reduce the thermal stability of epoxy. However, the thermal conductivity of thermosets tends to increase with nanoparticle additives such as carbon nanotubes, graphene, etc.

Conclusions

The modification of epoxy thermosets by block copolymer nanostructures has a tremendous impact on epoxy toughening with some enhancement in thermal and mechanical properties. The nanostructure formation in the thermosets by block copolymers can take place in two approaches, namely, self-assembly and reaction-induced microphase separation (RIMPS). DSC is the primary technique to measure the heat flow of the epoxy/block copolymer materials to investigate the thermal properties such as T_g, T_m, T_c, cure kinetics, phase separation, etc. Most of the works performed to date on nanostructured thermosets with an epoxy miscible chains show a depression in T_g which is due to the plasticization effects of the miscible chains. However, there are several interesting reports addressing the unusual increase in glass transition temperature which is an important finding. These changes in T_g

whether increase or decrease in the epoxy matrix depend mainly on the miscibility, reactivity, and the T_gs of the blocks in the block copolymers with epoxy thermosets.

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