Polymerization-Induced Phase Separation and Resulting Thermomechanical Properties of Thermosetting/Reactive Nonlinear Polymer Blends: A Review

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ABSTRACT: Thermosets, which have a highly crosslinked structure, play a pivotal role in high-performance composite materials because of their excellent mechanical properties, including their high modulus, high strength, and high glass-transition temperature. In general, however, thermosets are brittle materials with a toughness and elongation at break that are unsatisfactory for many applications, especially at high temperatures. The key factor that can greatly influence the toughness of a thermoset material is its cured microstructure or nanostructure. Recently, it has been revealed that the introduction of a reactive modifier into a multicomponent thermosetting prepolymer is a versatile way to finely tune the polymerization-induced phase separation (PIPS) and the microstructure and thermomechanical properties of the resulting thermosets. This review focuses first on the advancement of the methods used to study the PIPS of thermosetting prepolymers. I go on to discuss factors influencing the thermodynamic and the kinetic behavior of PIPS and the resulting morphology and thermomechanical properties of thermosetting blends obtained when nonlinear reactive modifiers are incorporated. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 127: 3279–3292, 2013

INTRODUCTION

Phase separation plays a pivotal role in the microstructural evolution of multicomponent thermosetting prepolymers. With the wide application of thermosets and their polymer composites, tremendous progress has been made in terms of understanding the compatibility, mechanics, and kinetics of the phase separation of thermosetting polymer blends over the past 2 decades. At the molecular level, a polymer blend can produce either a homogeneous mixture or a heterogeneous phase-separated blend over a broad range of temperatures and compositions. This kind of phase separation in polymer blends induced by temperature is an important issue in polymer physics. The other versatile method that can produce a phase-separated microstructure in polymer blends is polymerization-induced phase separation (PIPS). Inoue et al.[1] proposed a spinodal decomposition mechanism of PIPS in a thermoplastic modified thermosets. In an initially homogeneous polymer blend, the molecular weight of the polymer increases with the curing reaction; thus, the entropy of mixing decreases. As a result, the concentration fluctuation gradually increases. Depending on the composition of the quasi-binary blend, the metastable or the unstable region will result in nuclea-

tion and growth (NG) or spinodal decomposition, respectively. This produces various morphological structures, namely, sea-island, bicontinuous, and double phase and nodular structures.[2] An increase in the curing temperature will increase the interdiffusion rate at phase separation. The corresponding higher cure rate also results in a faster molecular weight increase, and this reduces the diffusion rate of the components of the polymer blend and freezes a thermodynamically unstable polymer system. On the other hand, at curing temperatures lower than the glass-transition temperature (T_g) of either of the coexisting phases, vitrification occurs; this fixes the morphology at certain conversion. Crucial in this respect is the ratio of the rate of phase separation to that of polymerization.

The effective use of these highly crosslinked materials is limited by their inherent brittleness. Generally, a high-T_g thermoplastic is often used at the cost of difficult processing. One way to reduce the viscosity of thermoplastics during processing is with solvents. This, however, causes significant disadvantages during and after processing with the potential for disaster during disposal or for the discharge of organic solvents. Moreover, the use of volatile solvents can result in the presence of voids and

irregularities in the material. Therefore, conditions are usually selected that produce appropriate morphologies for the desired application but balance possible deleterious effects on the other mechanical and thermal properties.

The use of a reactive modifier, especially a hyperbranched polymer (HBP), has aroused enormous attention for high-performance thermosets. Triggered by the surge of interest in dendrimers, in recent years, hyperbranched topologies have also experienced broad interest because HBPs are usually synthesized in a one-step reaction. At the same time, they possess specific properties of dendrimers in terms of low solution and melt viscosities, a number of terminal functional groups, and excellent solubility. The terminal functional groups of HBPs endow them with excellent solubility in many common organic solvents and the opportunity to react with thermosetting prepolymers. Recent progress in this field has been documented by some excellent reviews.[3–7] In addition, HBPs have exhibited a remarkable toughening effect on both thermosetting and thermoplastic polymer matrix composites without losses in thermomechanical properties and processability.[8–11] They can be adapted to different thermosetting systems through changes in the end functional groups according to the nature of the thermosets. More interestingly, the solubility and reactivity of HBPs can be adjusted with the terminal tailoring strategy.[12–14] This, in turn, provides a better way to tailor the miscibility and the curing behavior of a thermosetting polymer blend through the incorporation of an HBP. Alternatively, through fixing the phase-separation process at a desirable stage by rationally tuning both the thermodynamic and kinetic factors of phase separation with the reactive polymer, one can dramatically improve both the microstructures and the thermomechanical properties of a thermosetting blend.[15–19]

To date, there have been a number of reviews on the PIPS of thermosetting polymers; this includes significant work by Inoue,[2] Pascault and Williams,[20] Zheng,[21] and Ruiz-Perez et al.[22] The purpose of this article is to expound on the various classes of reactive nonlinear polymeric modifiers, HBPs, and hyperbranched–linear star block copolymers (BCPs). I pay particular attention to the influence of the topological structure of modifiers and to the interaction between the modifier and thermosetting prepolymer on the morphologies and the resulting properties of the thermosets. The bulk of this review is organized into two main parts; the first section deals with the methods used to investigate phase separation. In the next section, attention is focused on the influence of various reactive modifiers on phase separation. Some concluding remarks are then given along with thoughts on the prospects of introducing a reactive nonlinear polymer into thermosetting blends.

OVERVIEW OF METHODS USED TO STUDY THE PIPS OF THERMOSETS

To date, there are many methods available [e.g., differential scanning calorimetry (DSC), Fourier transform infrared (FTIR) spectroscopy, and dynamic mechanical analysis] for investigating the miscibility of a polymer blend. The microstructural evolution of the PIPS process can be successfully monitored and has been studied extensively by scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), optical microscopy (OM), rheological dynamic analysis, small-angle laser light scattering, and the combination of the aforementioned analyses.[23–29] In addition to these methods, cloud-point, dielectric relaxation spectroscopy, and temperature-jump light-scattering and rheometry measurements have also been widely used to investigate PIPS in thermosets.[30–34]

Jyotishkumar et al.[24] traced the dynamics of phase separation and the final morphologies of a poly(acrylonitrile–butadiene–styrene) (ABS) modified diglycidyl ether of bisphenol A (DGEBA) epoxy system *in situ* with OM, DSC, rheometry, and small-angle laser light scattering. AFM investigations of ABS showed that the crosslinked polybutadiene (PB) phase was dispersed in the SAN continuous phase. The dispersed PB domains consisted of small agglomerates of original PB (dark-phase) particles containing some (bright-phase) grafted SAN. The AFM micrographs of the completely crosslinked ABS/epoxy blend exhibited three different phases: two continuous phases forming a cocontinuous structure with substructures (an epoxy continuous phase containing dispersed SAN particles and epoxy particles dispersed in the SAN continuous phase) and the PB dispersed phase with small agglomerates at the blend interface between the cocontinuous structures (Figure 1). Both the DSC and rheology results agreed with the viscoelastic phase separation as revealed by OM.

OM and time-resolved light-scattering (TRLS) methods are also widely used to monitor the microstructural development of polymer blends during the curing process but with some differences. With OM, one can directly observe the change of phase but cannot obtain the *in situ* time resolved of the phase transformation and microstructural evolution. TRLS offers a method for observing the evolution of the scattering intensity and scattering vector (q_m) as a function of time. Rheological analysis is indispensable for determining the relationship between conversion, phase separation, and viscosity evolution for the process simulation. The combination of TRLS with rheology indicated that phase morphology played an important role in poly(ether sulfone) (PES) modified bismaleimide systems. Liu et al.[25] investigated the evolution of the complex viscosity and the evolution of q_m with the curing time. The appearance of the scattering peak, the decreasing of the peak q_m with time, and the maintenance of q_m were indications of the onset of spinodal decomposition phase separation, the development of a regularly phase-separated morphology, and the fixing of the phase morphology, respectively. Combined with the results of TRLS, the jumping-off point of the first rise of complex viscosity was identified; this indicated the occurrence of phase separation.[25]

Generalized two-dimensional (2D) correlation analysis based on 2D TRLS was used to study the phase separation of an epoxy–amine–PES blend.[28] The results of the 2D TRLS correlation spectral analysis provided more detailed information than could be provided from one-dimensional light-scattering spectra. In the diffusion regime of the early stage of phase separation, the coarsening in size of the smaller domain took place earlier than that in the bigger ones. In the hydrodynamic regime of the late stage of phase separation, the smaller domains became larger ones because of the collision and coalescence with each other and hydrodynamic flow.
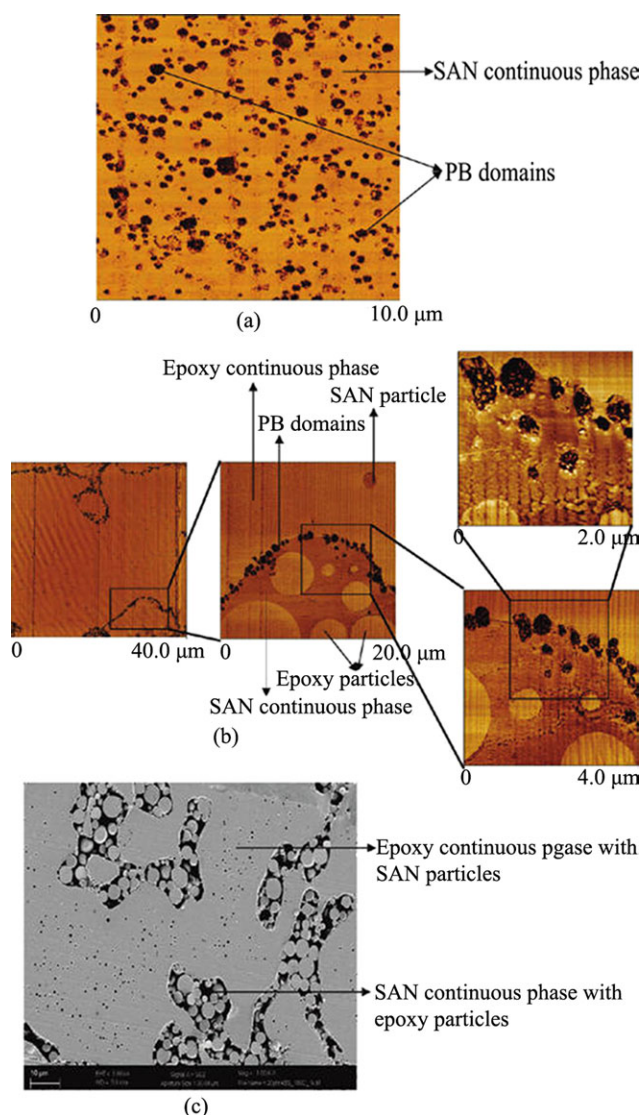
Figure 1. (a) AFM micrograph of neat ABS, (b) AFM micrographs of the ABS-modified epoxy system, and (c) field emission SEM micrograph of the ABS-modified epoxy system. (Reprinted with permission from ref. 24. Copyright 2010 American Chemical Society.) [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Fluorescence characteristics have been widely been used in the past to monitor the curing process of epoxy resin (ER) and its motion equation because the molecular environment can be monitored by a small molecule according to its fluorescence characteristics.[35,36] Such molecules are usually designed so that researchers can examine specific properties of their microenvironment by means of a shift in the maximum wavelength of their emission or changes in their emission intensity. The relationships among the chemical conversion of the curing reaction; the first moment of the fluorescence emission band ($\langle v \rangle$), which arises from a chromophore chemically bonded to the epoxy reactive system; the phase-separation process; and the dynamics of the epoxy thermoset during its curing process were investigated by FTIR spectroscopy in the near range and by fluorescence spectroscopy.[37] $\langle v \rangle$ was very sensitive to physicochemical

changes in the system. On the basis of the DiBenedetto equation, a semiempirical equation that correlated $\langle v \rangle$ with the chemical conversion of α was proposed. In addition, a linear dependence between the inverse of the mean area of the thermoplastic-rich domains and the inverse of the absolute temperature was obtained from image of SEM micrographs.

Solid-state NMR spectroscopy is a powerful technique for probing heterogeneous dynamics and monitoring morphological changes because of its sensitivity to local chemical environments. Through the measurement of the timescale of proton spin diffusion, the length scales in nanoscopic heterogeneities, from a few nanometers up to 100 nm, and the interface between different microdomains can be determined.[38,39] Sun et al.[40] characterized the heterogeneous dynamics, miscibility, and microdomain structure in nanostructured thermoset blends of ER and amphiphilic poly(ethylene oxide) (PEO)-*block*-poly(propylene oxide) (PPO)-*block*-PEO triblock copolymers with solid NMR methods. On the basis of the ¹H spin diffusion and DSC experiments, a possible model for the dynamics and microphase structure in the cured ER/PEO–PPO–PEO blends was proposed (Figure 2).

SEM and TEM are extremely useful tools for obtaining direct representations of morphologies at different levels of the phase-separation process during the curing process.[41] Numerous advances in electron imaging technology have been achieved that have provided many new tools for viewing and characterizing the phase transition and the interfaces between multiple components.
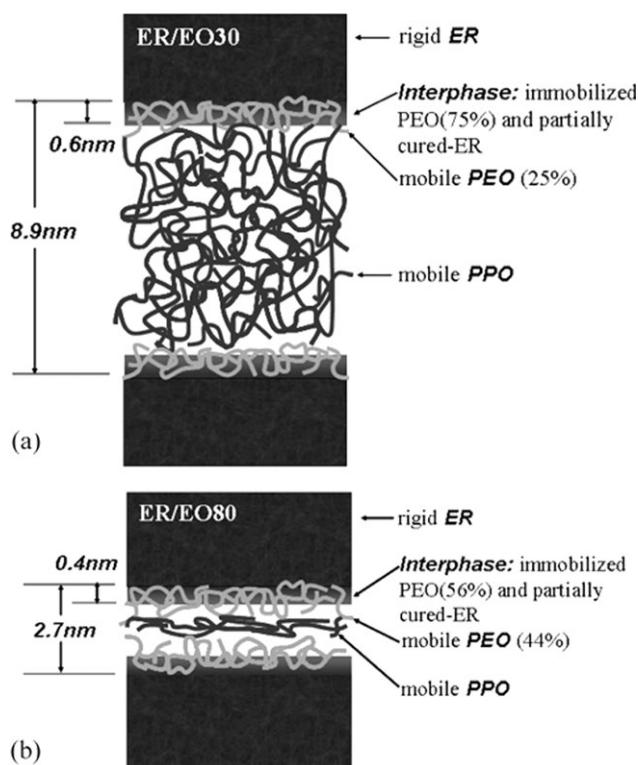

Figure 2. Schematic illustration of the suggested model for the heterogeneous dynamics, miscibility, and microdomain structure in the (a) ER/EO30 (the content of ethylene glycol (EO) in PEO-PPO-PEO is 36%) and (b) ER/EO80 (the content of ethylene glycol (EO) in PEO-PPO-PEO is 79%) blends. (Reprinted with permission from ref. 40. Copyright 2005 American Chemical Society.)
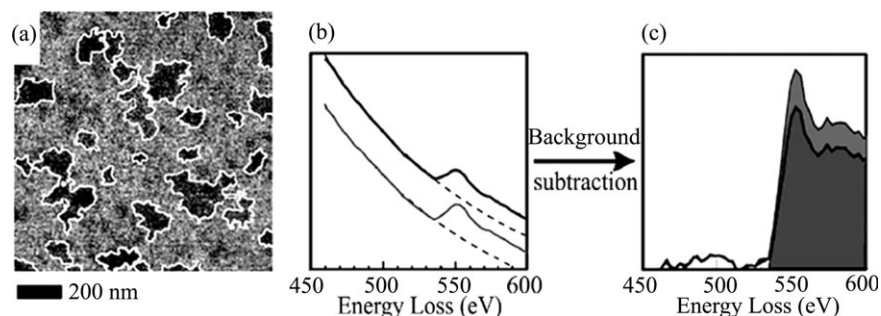
Figure 3. Scheme for the quantitative EELS analysis of the phase-separated morphologies of the PPE/BVPE blends used in this study: (a) an oxygen map separated into oxygen-rich and poor regions, (b) EELS spectra created from the two regions (the gray and black spectra were acquired from the oxygen-rich phase and the oxygen-poor phase, respectively), and (c) the integrated areas under the oxygen core-loss peaks calculated after background subtraction. (Reprinted with permission from ref. [44]. Copyright 2007 Elsevier.)

Energy-filtering transmission electron microscopy (EFTEM) has a greater potential for providing deep insights into the multiphase structures of polymer materials than conventional TEM. In addition, EFTEM can image polymer nanostructures and perform quantitative chemical characterization of multiphase structures by electron energy loss spectroscopy (EELS) without staining by electron spectroscopic imaging.[42,43] Liao et al.[44] employed EFTEM to investigate the morphological developments of poly(2,6-dimethyl-1,4-phenylene ether) (PPE)/bis(vinyl phenyl) ethane (BVPE) blends. Oxygen mapping identified small differences in the oxygen concentrations of the blends; this indicated that the phase separation was composed of oxygen-rich (PPE-rich) and oxygen-poor (BVPE-rich) regions (Figure 3). Moreover, the morphologies during the phase decomposition processes induced by the crosslinking reactions could be quantitatively characterized by EELS.

Zhang et al.[45] used online tracking of a reaction-induced phase separation for the first time with high-frequency, ultrasonic wave-based Rayleigh scattering of ultrasonic waves on the interface of a multiphase system. Under a high concentration or with an increased reaction temperature, high-connectivity phase structures were produced so that the polymerization surpassed the phase separation. The interface was quickly formed and its area was also improved with the rapid increase in the intensity of ultrasonic wave scattering at the initial stage of phase separation. In the meanwhile, the attenuation coefficient exhibited a jump because of the discretion of the phase structure.

FACTORS AFFECTING PIPS IN THERMOSETTING PREPOLYMERS

The physical properties of a polymer blend strongly depend on its phase-separated morphologies. Phase separation occurs as a result of the increasing size of the growing polymer molecules. The resulting morphology is stabilized by gelation in crosslinking polymerization. Events involved in the PIPS process are determined by thermodynamic and kinetic factors at every point in the material. A thermodynamic analysis enables one to determine the regions, in conversion–composition coordinates, where the system remains stable (no phase separation is produced), metastable (phase separation may take place), or unstable (phase separation does take place). Once the influence of

different variables is rationalized, the types of morphologies produced may be varied by adjustment of the formulation (nature and concentration of a modifier) or the curing cycle (temperature vs time).[46]

Early work[2] indicated that the spinodal decomposition mechanism is mostly convincible in that nucleation growth is recognized to be a very slow process. It can be skipped, and nucleation usually occurs accidentally. Subsequent growth results in an irregular domain structure. It was later found that if there is a large difference in the intrinsic dynamic asymmetry between the two components of blend, phase separation will be affected by the viscoelastic properties.[47] A viscoelastic phase-separation process for the initial phase-inversion morphology near the cloud point of a final bicontinuous phase structure was found by Yu et al.[34] A variety of phase morphologies were obtained and depended on competition between the kinetics of phase separation and the crosslinking chemical reaction, which were governed not only by the curing conditions, compositions, molecular weights, and molecular weight distributions of the modifiers but also by the viscoelastic effects in the thermoset blend. In the following section, I concentrate on the analysis of factors that control the generated morphologies and briefly discuss the properties and structures developed during PIPS.

Curing Schedule

Polymer blends of dissimilar polymers are miscible within limited temperature and composition ranges but are immiscible outside of these ranges; these properties, when induced by chemical reactions and spinodal decomposition, can provide a versatile method for designing novel materials. Through the control of both the reaction and the phase-separation velocity, the morphologies of thermosets can be finely tuned.[48,49] Blanco et al.[9] reported the effect of the curing cycles and end groups of hyperbranched polyesters on the thermomechanical and morphological properties of two epoxy systems. A precuring at medium temperatures (135 and 155°C) and a curing at a higher temperature (180°C) were performed to characterize the viscoelastic and morphological behaviors of bifunctional and trifunctional epoxy systems with hyperbranched polyesters. The postcuring increased the T_g values of the blends and their morphologies such that the combination of devitrification and thermodynamic effects influenced the phase-separation process. Zhang et al.[13] investigated the effect of the heating rate on the

curing behavior and phase separation of PES-modified multi-functional epoxies. With increasing heating rate, a higher epoxy conversion was achieved, and phase-separated macrophases were formed because of the high epoxy conversion.

It was possible to dramatically alter the physical and mechanical properties of the resulting networks through changes in the nature and the content of the curing agent.[50,51] Changing the reactivity of the curing agent resulted in an increased reaction rate and a decreased final domain size because of the earlier formation of the crosslinking network. Nevertheless, this did not affect the scattering profile or the phase-separation mechanism.[52] A subsequent study revealed that the phase-separation mechanism depended on the miscibility of the curing agent with the epoxy.[53] Although miscible BCPs have been explored for generating nanostructures in thermosetting polymers with hardener, the selection of the miscible block is strongly dependent on the hardener selected for curing. Because of the variety of mechanisms of network formation involving different types of hardeners, it is not easy to obtain a desirable miscible block for both the thermosetting polymer and the hardener. Maiez-Tribut et al.[54] generated nanostructured phases in epoxy networks by employing random copolymers of methyl methacrylate (MMA) and N,N-dimethylacrylamide (DMA) as a universal miscible BCP because MMA is soluble with DGEBA and DMA has excellent solubility in both nonpolar and highly polar solvents. Increasing the amount of DMA in the copolymer increased the miscibility because of the strong specific interactions between DMA and the epoxy–amine solvent. This was combined with the repulsion between the DMA and MMA units. In addition, a molar fraction of DMA units in the random copolymer was necessary to prevent phase separation and to stabilize the nanostructure at the end of the reaction. Meng et al.[55] studied the effect of a curing agent on the nanostructure in thermosetting blends of ER and PEO-block-poly(3-caprolactone) (PCL). For a 4,4'-methylene bis(2-chloroaniline) (MOCA) cured thermosetting system, a homogeneous morphology was obtained in the compositions investigated. Nanostructured thermosets were obtained when the blends were cured with 4,4'-diaminodiphenylsulfone. The dependence of the morphological structure on the type of aromatic amines resulted from the difference in hydrogen-bonding interactions due to the structures of the curing agents. Kishi et al.[56] investigated the phase structures and mechanical properties of two types of triblock copolymers with epoxy alloys with several curing agents. They found that an aromatic amine, an acid anhydride, and an anionic polymerization catalyst as curing agents resulted in macrophase separation in the epoxy/triblock copolymer blends during the curing process, whereas nanophase structures in the epoxy blends were created with a phenol novolac (PN) curing agent (Figure 4). The study revealed that the miscibility between the poly(methyl methacrylate) (PMMA) segments of the triblock copolymers and epoxy/curing agents was a key factor in the formation of the nanophase structures in the blends. Mechanical analysis showed that the fracture toughness of the blends was more than 20-fold compared with that of the unmodified ER. The change in the stress state caused by the cavitations of the nanoelastomer phases was responsible for the
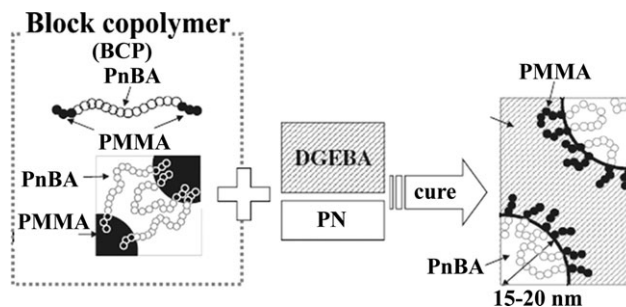

Figure 4. Schematic illustration of the creation of nanophase structures in the epoxy/BCP blends. The PMMA segments of the BCPs were miscible with DGEBA/PN, and the PnBA (n-butyl acrylate) segments were immiscible with DGEBA/PN. (Reprinted with permission from ref. 56. Copyright 2011 Elsevier.)

absorption of the given strain energy. Blanco et al.[57] studied the effect of a curing agent on the phase-separation and rheological behaviors of a reactive thermoplastic (bearing amine reactive end groups) modified epoxy system. Because of the different solubilities of the curing agent in the blend systems, marked differences in both the morphological and viscoelastic behaviors were found.

Content of the Reactive Polymer

Ocando et al.[16] investigated the morphological development mechanisms involved with different contents of epoxidized polybutadiene (PBep) in a mixture of poly(styrene-b-butadiene) (SB) BCPs and uncured ER. The microstructures of the mixtures depended on the compatibilization degree of PBep. For PBep contents near the minimum threshold needed to achieve nanostructuration, microphase separation occurred through the self-assembly of the PBep block and the PIPS of the polystyrene (PS) block. New bilayered structures were developed by the occurrence of the two mechanisms before and during the curing reaction. This led to vesicles or long wormlike micelles, depending on the concentration of BCPs in the overall mixture. In addition, at higher epoxidation degrees, long-range-order microstructures of PS were obtained as a consequence of PIPS because of the initial miscibility of both blocks with ER before curing (Figure 5).

Fan et al.[58] synthesized a PS-block-PCL-block-poly(n-butyl acrylate) (PBA) triblock copolymer to access nanostructures in ER. It was found that depending on the concentration of the triblock copolymer, several types of nanophases were formed in the thermosets. At the higher content of the triblcok copolymer, the nanophases were arranged in a lamellar lattice. The formation of nanostructures in the thermosetting blends followed a double-reaction-induced microphase separation mechanism involving PBA and PS blocks. During the curing process, the subchains immiscible with epoxy were separated out to form the PBA nanophases because of the decrease in mixing entropy. The microdomains of the PBA subchains served as the template for the demixing of the PS blocks. The regions of depletion at the vicinity of the interface for the nanophases were restricted because of the formation of networks. Thus, some miscible subchains became unmixed with the matrix (Figure 6).

Topology of the Reactive Polymer

BCPs can induce the formation of nanostructures in thermosets; this provides an important strategy for the toughening of
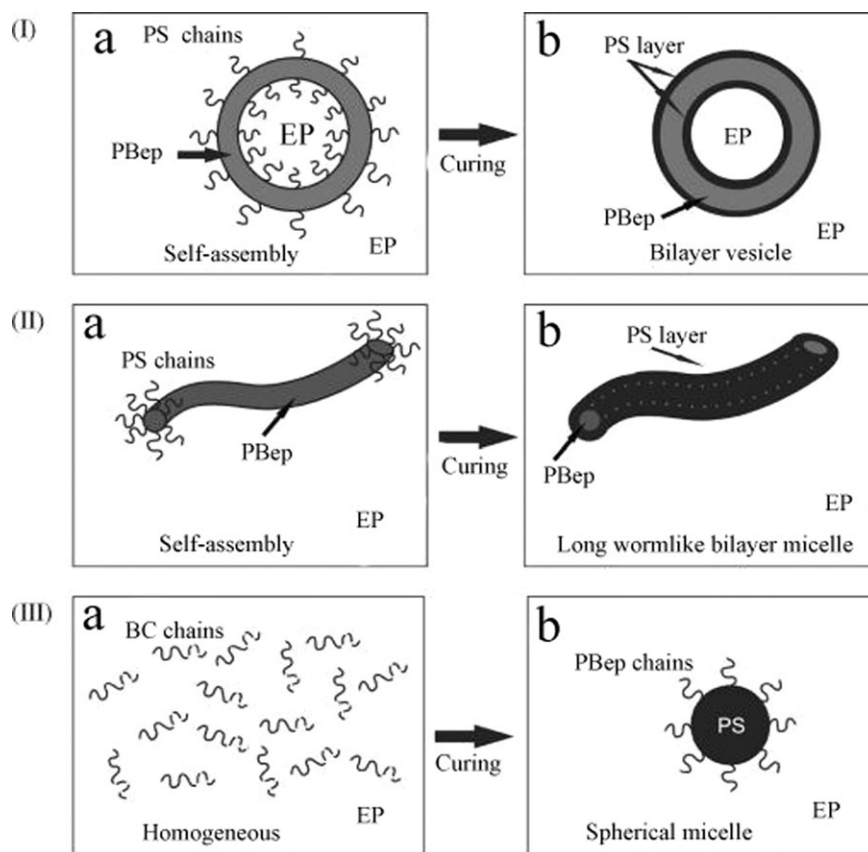
Figure 5. Schematic representations of block organization for the thermosetting epoxy (EP) mixtures containing (I) 10 wt % SB50(2)ep22, (II) 30 wt % SB50(2)ep22, and (III) 10 wt % SB65ep28 BCPs (a) before and (b) after curing. (Reprinted with permission from ref. 16. Copyright 2009 American Chemical Society.)

thermosets. The significant improvement in the fracture toughness of epoxy thermosets has recently been reported for a variety of epoxy thermosets containing BCPs, and it has been realized that the improvement in the mechanical properties is quite dependent on the types of nanophases in the epoxy thermosets.[22] By tuning the content of BCPs, researchers can vary

the morphologies of thermosets from sphere micelles to worm micelles to vesicles.[59–66]

Fan and Zheng[67] synthesized PS-b-PMMA BCPs with linear and tetra-armed, star-shaped topological structures to investigate the influence of topological and sequential structures of BCPs on the formation of nanostructures in epoxy thermosets. Because
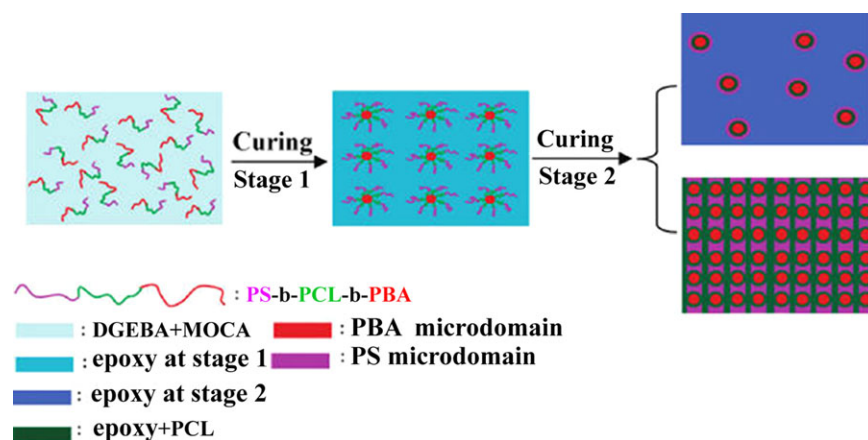

Figure 6. Double-reaction-induced microphase separation in the thermosetting blends of epoxy with the PS-b-PCL-b-PBA triblock copolymer. (Reprinted with permission from ref. 58. Copyright 2010 American Chemical Society.) [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of the increased thermodynamic interactions between the epoxy matrix and PS in the BCPs, nanostructures were formed in the thermosets containing l-PMMA-*b*-PS and s-PS-*b*-PMMA BCPs. However, macroscopic phase separation occurred in the thermosetting blends of ER with s-PMMA-*b*-PS BCP as a consequence of the insufficient suppression of the macroscopic phase separation of the PMMA chains of the tetra-armed PS BCP (Figure 7). Liu et al.[68] investigated the morphology and the toughness of a bisphenol A based ER and an amphiphilic poly(ethylene-*alt*-propylene) (PEP)-*b*-PEO BCP blend by changing the molecular weight and the PEO fraction of the PEP–PEO copolymer. The BCP molecules could self-assemble into well-dispersed wormlike micelles with a diameter of 10–15 nm. The epoxy-miscible PEO block formed a corona surrounding the epoxy-immiscible PEP core. Compared with the neat epoxy counterpart, the materials modified with the elongated cylindrical micelles had an improved toughness (by 106%) and tensile properties (by 8.5%) without any compromise of the T_g and modulus; this was due to the key operative toughening mechanisms, such as crack-tip blunting, cavitation, debonding (voiding), limited shear yielding, and crack bridging, as revealed by the double-notched, four-point-bending technique (Figure 8).

It is well known that the addition of a hyperbranched modifier to a thermosetting polymer gives rise to a phase-separated morphology via a controlled phase-separation inversion. Mezzenga et al.[23] investigated the effects of the chemical structure and shell chemistry of dendritic HBPs on the morphology of different epoxy-functionalized HBPs modified with DGEBA. The miscibility of the modifier with ER increased with increasing number of epoxy groups. At sufficiently high HBP contents, the microstructure consisted of epoxy-rich domains in a continuous HBP-rich matrix. The decrease in the average diameter of the particle, the maximum diameter of the particle, and the total volume fraction with increasing miscibility was thought to be linked both with the thermodynamics of mixing and the kinetics of demixing. Yang et al.[69] investigated a hydroxyl functionalized HBP with a pseudo-generation number of 3 (H30), a modified 4,4′-diaminodiphenylsulfone cured bisphenol A type ER, and interpreted the dependence of the toughening mechanisms on the HBP particle size. The average second-phase diameter increased dramatically when the content of H30 increased further to over 5.0 wt %. For the systems with 2.5 and 5.0 wt % H30 contents, the second H30 phases were nanoscale sized with large specific surface areas, and this contributed to the stress transfer between the H30 particles and the epoxy matrix. This accounted for the improvements in the impact resistance. On the other hand, when the H30 particles were microscale sized, only a particle bridging mechanism worked for toughening the ERs.

The effect of the polymer topology on the curing and gelation of a well-defined multiarm star copolymer, hyperbranched polyglycidol-*b*-poly(ε-caprolactone), and DGEBA mixture was also studied by Morell et al.[70] The linear topology increased the viscosity of the DGEBA formulations because of the entanglement; this was in contrast to that observed with the addition of starlike polycaprolactone (s-PCL). The impact strength was improved when both s-PCL and linear polycaprolactone (l-PCL)
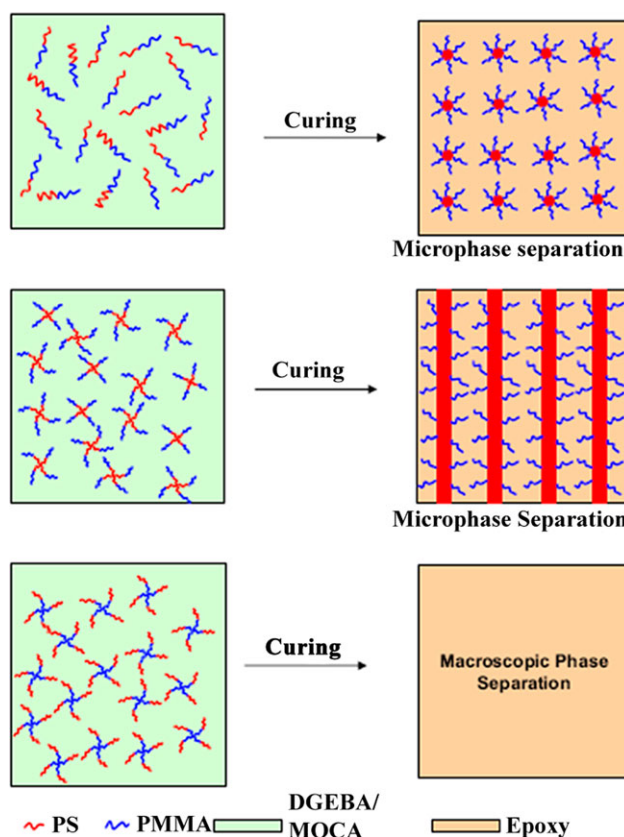

Figure 7. Formation of a phase-separated morphology in the epoxy thermosets containing PMMA-*b*-PS BCP. (Reprinted with permission from ref. 67 Copyright 2008 Elsevier.) [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

were added, but the highest value was obtained when 10 wt % s-PCL was added to the formulation. The covalent incorporation of s-PCL to the matrix changed the fracture surface of the modified material from brittle to ductile. Foix et al.[71] also studied the effect of the degree of branching (DB) of a hyperbranched polyester added as a modifier of DGEBA. It was indicated that the DB of the modifier did not appreciably affect the thermal stability and chemical reworkability, but the shrinkage of DGEBA exhibited a significant reduction when the DB of the hyperbranched polyester was increased. The thermomechanical characteristics were also improved with increasing DB. It was shown that the best combination of effects of the HBP modifier on the overall properties was achieved with the polymers of maximum DB. Cicala and Recca[72] studied the thermomechanical and morphological properties of some epoxy blends modified with HBPs of pseudo-generation numbers from the second to the fourth. It was indicated that the reduction of the pseudo-generation number influenced both the catalytic activity and the miscibility of the HBPs. The difference in the shell chemistry of hyperbranched polyesters resulted in different devitrification and thermodynamic effects, which in turn, profoundly influenced the phase separation.

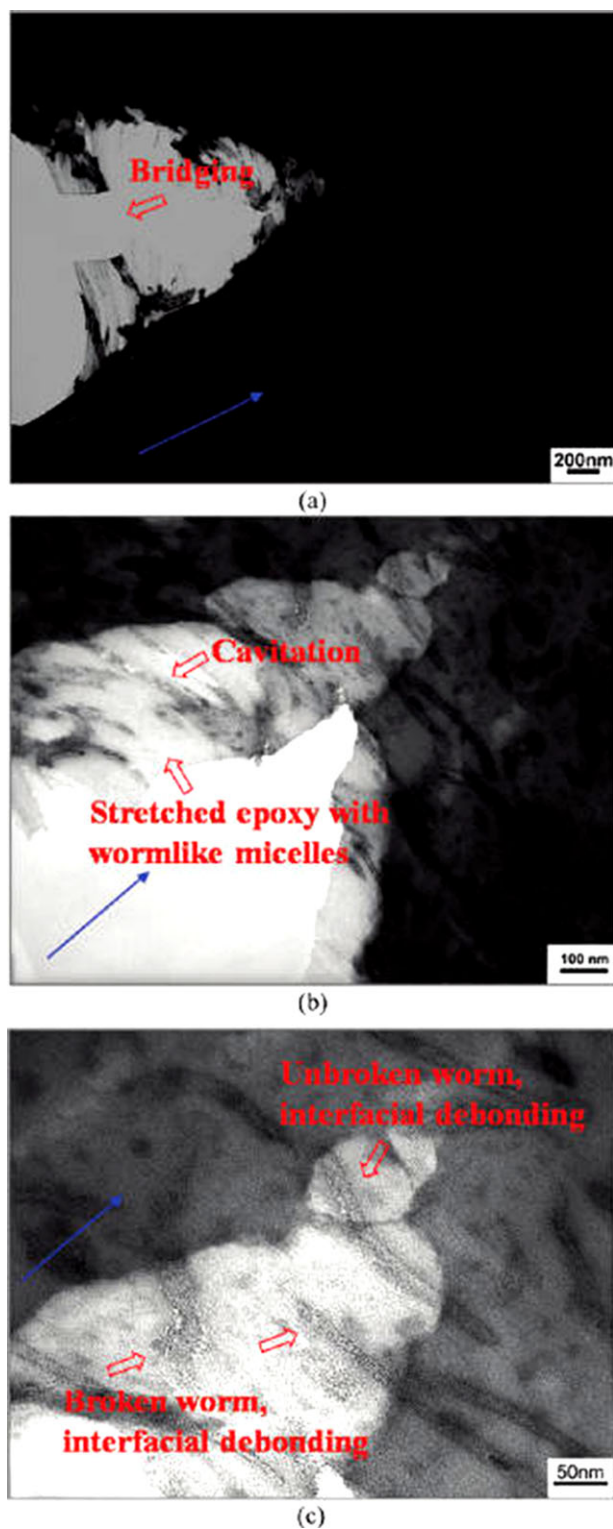A multiarm star copolymer, hyperbranched polyglycidol-*b*-PMMA, was used as a modifier of DGEBA by Morell et al.[73]

Figure 8. TEM micrographs of the crack-tip, double-notch, four-point-bending specimen of BCP-toughened epoxy: (a) overview of the crack tip, (b) evidence of wormlike structure cavitation or fragmentation after severe stretching, and (c) evidence of interfacial debonding or voiding. The thin arrows (blue in the online figure) in the micrographs indicate the direction of crack propagation. (Reprinted with permission from ref. 68. Copyright 2010 American Chemical Society.) [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The addition of the starlike modifier led to an improvement in the mechanical characteristics, including the impact strength and microhardness, over those of the neat material. The presence of a rougher nanostructured surface, especially when hyperbranched polyglycidol-*b*-PMMA was added at a concentration of 10 wt %, could have been responsible for the improvement of the matrix yielding and the subsequent increased toughness without harmfully affecting the curing, processability, and thermomechanical characteristics. When a multiarm star copolymer, hyperbranched polyglycidol-*b*-poly(ε-caprolactone), was used to modify DGEBA formulations, the global shrinkage decreased, and the conversion at gelation increased. The addition of the starlike structure produced a more toughened fracture of the thermoset in comparison to pure DGEBA.[74]

Hydrogen Interaction between the Thermosetting Prepolymer and the Reactive Polymer

HBPs exhibit melt or solution viscosities that are an order of magnitude lower than that of linear analogs of similar molecular weight. On the other hand, the high density of the functional end groups of HBPs offers the potential for tailoring the compatibility with the other polymer via changes in the chemistry of the end groups through the formation of a noncovalent bond with the matrix. The previous two unique characteristics, lower viscosity and the tailoring of the chemistry of the end groups, endow them great potential as high-performance polymer composites.

Ratna and Simon[8] investigated the curing and phase-separation behaviors of a hydroxyl-functionalized HBP and epoxy blend. SEM analysis revealed the transformation of the morphology from discrete to bicontinuous as the concentration of the HBP increased. The hydrogen bonding between the HBP and epoxy matrix was responsible for the improved curing rate and the toughness of the cured epoxy. Fröhlich et al.[75] synthesized novel reactive core/shell type hyperbranched block copolyethers as flexibilizers and toughening agents of anhydride-cured ERs. It was indicated that a matching polarity and compatibility between the HBPs and ER was vital for the achievement of rubber phase separation and interfacial adhesion during curing. The hyperbranched block copolyether carrying epoxy, phenol, and stearate end groups afforded the phase separation of the rubber microparticles with an average diameter around 12 mm, whereas epoxy-terminated polyesters containing epoxidized fatty ester end groups produced polyester phases with an average size of 200 nm and exhibited more effective performances as stress concentrators. Lipic et al.[60] prepared thermoset materials with a low-molecular-weight PEO–PEP diblock copolymer and a poly(bisphenol A-*co*-epichlorohydrin) (BPA348) ER. The ER could selectively swell the PEO chains and create a spontaneous interfacial curvature between the PEP and PEO/epoxy domains. As the amount of epoxy was increased, a swollen wet PEO brush was produced; this led to an increased volume per PEO chain. This asymmetry in volume per chain induced curvature at the PEO/PEP interface. The lamellar morphology could not support interfacial curvature; therefore, the blend microstructure evolved from lamellar to gyroid, cylinders, body-centered cubic packed spheres, and ultimately disordered micelles as the amount of BPA348 was increased (Figure 9). Larrañaga et al.[76] analyzed the
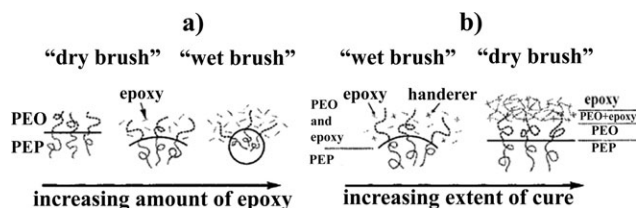
Figure 9. (a) Illustration of the swelling-induced changes in the interfacial curvature in the OP5/BPA348 blends. The PEO blocks extended from the neat PEO/PEP interface as a dry brush. Epoxy selectively swelled the PEO brush, creating a wet brush, and the PEO/PEP interface curved to accommodate this change within the constraint of constant density while minimizing PEP and PEO chain distortions. The swelling of the PEO block drove changes from a lamellar morphology to G (gyroid), C (hexagonally packed cylinders), and S (body-centered cubic packed spheres). (b) Illustration of the PEO block expulsion as the epoxy matrix crosslinked and its molecular weight diverged. The system initially had a curved interface because of the selective swelling of the PEO blocks by the epoxy. As the epoxy cured, the PEO blocks were expelled; this transformed the wet brush to a dry brush and thereby reduced the interfacial curvature. (Reprinted with permission from ref. 60. Copyright 1998 American Chemical Society.)

microstructural features of DGEBA/DDM epoxy matrices modified with three PEO–PPO–PEO BCPs having different block ratios and molecular weights. Because of the physical interactions between the thermosets and PEO block during the curing process, PEO phase separation was prevented, whereas the PPO block tended to separate from the thermoset. A rational design of thermosetting epoxy matrices structured at the nanoscale could be obtained through the control of the molar ratio and the molecular weight of the PEO–PPO–PEO BCPs. Zhang et al.[77] investigated the phase behavior and the morphology of blends of a tetrafunctional ER, tetraglycidyl-4,4′-diaminodiphenylmethane, and a hydroxyl-functionalized hyperbranched polyester, Boltorn H40. As for the blend with a low H40 content (5 phr), no phase separation occurred. However, other cured epoxy/H40 blends exhibited a particulate morphology with discrete H40-rich particles dispersed in a continuous epoxy-rich matrix. FTIR spectroscopy revealed the formation of both bimodal and monomodal particle size distributions, and this gave rise to improved fracture toughness, whereas the monomodal particle size distribution showed a stronger toughening effect. The difference in toughness resulted from the distinction of hydrogen-bonding interactions between the epoxy network and the HBP modifier. Liu and Jing[78] synthesized hyperbranched polyborates (HBs) terminated with phenol hydroxyl and boric acid hydroxyl functional groups, respectively. The HB-modified thermosets exhibited both versatile phase morphologies and improved thermal properties because of the formation of hydrogen bonds between hydroxyl groups of HB and phenolic resin (PR). The method of introducing reactive thermal HBs into a thermosetting prepolymer provided a versatile route for improving the toughness, thermal properties, and modulus of thermosets simultaneously without compromising the other properties.

Block ionomer complexes based on BCPs containing ionic and nonionic chain blocks have attracted great attention recently. Wu et al.[79] reported a novel approach for preparing nanostructured thermosets with block ionomer complexes of sulfonated

polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene (SSEBS) with a tertiary amine-terminated PCL (SSEBS-*c*-PCL). The SSEBS-*c*-PCL contained epoxy-miscible PCL side chains that could be dissolved in the cured epoxy matrix, and the epoxy-immiscible SSEBS main chain could form nanostructures. Macroscopic phase separation could be avoided because the epoxy was miscible with PCL side chains in SSEBS-*c*-PCL because of the ionic interaction or hydrogen bonding between the sulfonate groups and the 4,4′-methylenedianiline (MDA) or DGEBA precursor.

Covalent Interaction between the Thermosetting Prepolymer and the Reactive Polymer

The phase-separation behavior of thermoset precursors modified with a thermoplastic polymer bearing reactive end groups is more complicated compared to that with a modifier that has no reactive groups. The discovery that amphiphilic BCPs of PEP and PEO are not only dispersible in a model epoxy system but are also capable of ordering epoxy networks on the nanometer scale in both the uncured and cured states indicated important applications for the homogeneous modification of epoxy-based materials.[59,80,81]

To obtain optimum adhesion between the matrix and the BCP, Wu et al.[64] incorporated reactive sites into the epoxy-miscible block to further fix these ordered morphologies in rigid thermoset matrices. It was shown that ordered microstructures were formed in blends of reactive poly(epoxy isoprene)-*b*-polybutadiene copolymers or poly(methyl acrylate-*co*-glycidyl methacrylate)-*b*-polyisoprene copolymers with epoxy precursors. The formation of vesicles and covalent linkages between the copolymer and the epoxy matrix were beneficial for the fracture toughness of the modified epoxy. Rebizant et al.[63] indicated that any functional groups on the nanostructured block capable of reacting with either the epoxy or amine groups could cure with the epoxy without macrophase separation. The existence of a certain amount of grafts in the early stage of curing was sufficient to stabilize the interfaces and preserve the nanostructure until the gel point. Soares et al.[80] prepared a series of isocyanate-functionalized liquid polybutadiene-block-epoxy prepolymer (DGEBA-*b*-PBNCO) copolymers with multibranched topologies and used them to develop nanostructured rubber-modified epoxy thermosets. The hydroxyl-terminated liquid polybutadiene (HTPB) used for the synthesis of PBNCO presented a hydroxyl functionality of around 2.35; about 25% of them have functionality greater than 3. During the curing process, the incompatible PB subchains tended to separate out from the epoxy system, but the multigrafted ER segments attached well to the PB chains and confined the rubber inside the epoxy matrix. The macroscopic phase separation of the PB chains was suppressed, and only nanoscopic domains were formed (Figure 10). A unique combination of outstanding toughness, increased modulus, and T_g was achieved in these modified systems; this was attributed to the peculiar morphology associated with the strong interfacial adhesion imparted by the reaction between the isocyanate and hydroxyl groups present in the PBNCO and ER.

Recently, it was found that thermoplastic–thermosetting crossover materials can also be considered to be potentially useful
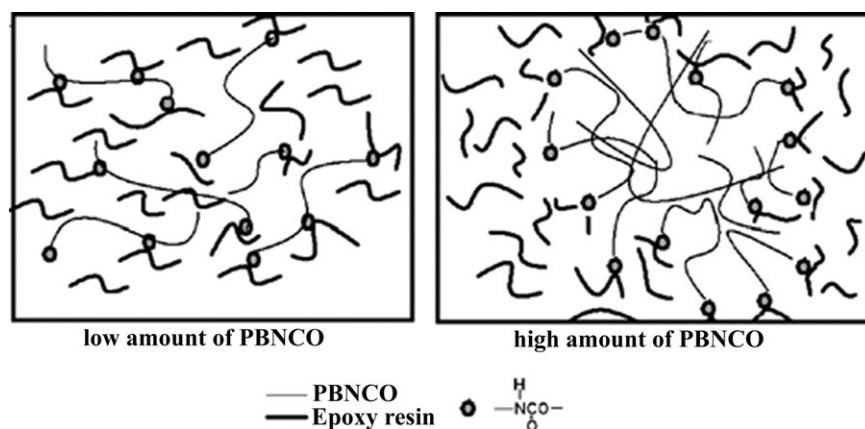
Figure 10. Scheme of the multibranched PBNCO surrounded by ER. (Reprinted with permission from ref. [80]. Copyright 2011 Elsevier.)

tougheners. Sawaryn et al.[82] achieved toughened polybenzoxazine systems by combining a strong covalent attachment of the main phases with a series of multifunctional thermoplastic main-chain benzoxazine prepolymers based on bisphenol A and amino-functionalized poly(tetramethylene oxide) (PTMO) and PPO. During the curing process, the toughener separated out in a controlled manner by covalently bonding to the surrounding matrix because of the benzoxazine units in the main-chain benzoxazine prepolymers (Figure 11). In addition, the variation of the PTMO/PPO ratio allowed control of the morphology of TBox-toughened polybenzoxazines, which allowed control of such important mechanical parameters as Young's modulus and the fracture toughness and led to thermosets with improved overall properties.

Hyperbranched polymers have a high concentration of surface reactive groups, which can be covalently linked to or modified to enhance the miscibility with the thermosetting polymer. Ratna and Simon[83] examined the phase separation of an epoxy-functionalized HBP in a blend with a conventional ER. HBP was miscible in ER solvent at 120°C and underwent phase separation during the curing reaction. This led to a two-phase microstructure that maintained a dispersed morphology up to 20 wt % HBP. The free volume fraction increased with the incorporation of HBP with a strong negative deviation. This was related to good (reacted) interfaces and some miscibility of a proportion of the HBP in the

epoxy matrix. Foix et al.[84–88] revealed that the morphology and thermomechanical properties of DGEBA thermosets were strongly dependent on the nature of the HBP employed. Hydroxyl-functionalized hyperbranched polyesters (HBPs) were prepared, and the HBPs were modified further by the blocking of part of the hydroxyl groups with trimethylsilyl or benzoyl groups.[86] The curing behaviors of DGEBA with various proportions of two modified HBPs were investigated. The relative proportion and type of terminal groups played a pivotal role in the evolution of curing and the resulting properties of the thermosets. Hydroxyl groups promoted the covalent incorporation of the HBP into the network via hydroxyl-induced chain-transfer reactions, whereas benzoyl groups promoted phase separation because of the different hydrophilic characteristics and the molecular interactions of the HBP core and the benzoyl groups. Formulations containing HBP blocked with benzoyl groups showed two phases connected through covalent linkages between the HBP-rich phase and the epoxy matrix. Fernández-Francos et al.[12] investigated the cationic polymerization of DGEBA with two H30s functionalized with epoxy (H30epo) or vinyl (H30vin) end groups, respectively. Both H30epo and H30vin slowed down the curing of DGEBA because of a mobility decrease in the system, the dilution of epoxy groups, and topological restrictions. The epoxy groups of H30epo were more reactive than the DGEBA groups, and therefore, they were able to covalently incorporate into the network structure. As a
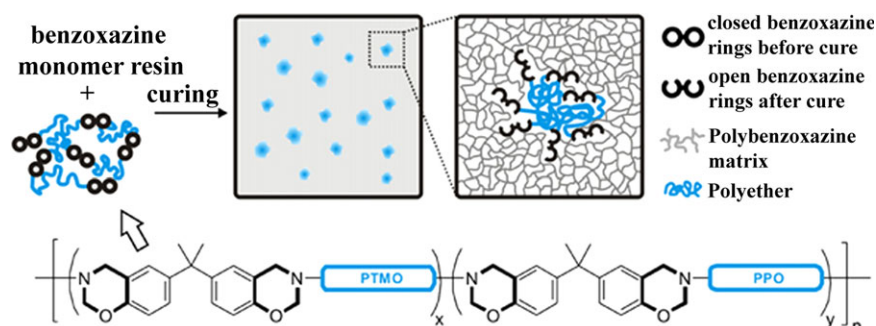

Figure 11. Schematic illustration of the morphology of the cured polybenzoxazine toughened with a thermoplastic main-chain benzoxazine prepolymer (TBox)/resin mixture due to microphase separation. (Reprinted with permission from ref. [82]. Copyright 2011 Elsevier.) [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

result, the morphology and thermomechanical properties of the DGEBA system were strongly dependent on the chemistry of the end groups of the employed HBPs. Maji and Bhowmick[89] explored the curing kinetics of a polyurethane prepolymer with hyperbranched polyols containing different numbers of functional groups. The thermal, mechanical, and thermomechanical properties were enhanced when the number of functional groups in the hyperbranched polyols was increased. The phase morphology of the cured polyurethane, investigated by AFM analysis, revealed that the nanophase domain size decreased with increasing functionality of the HBP. As the number of functional groups increased, DMTA suggested an increase in the storage modulus and a decrease in the peak tan δ due to the more efficient urethane linkage between the molecules.

HBPs have been reportedly used in the crosslinking of different thermoset polymers. Santiago et al.[90] investigated the curing behavior of hyperbranched polyethyleneimines (Hbpei's) as curing agents as compared with diethylenetriamine for thermosets. The curing mechanisms using both amines were very similar and followed a general epoxy–amine polycondensation mechanism. Gelation took place earlier with Hbpei because the higher functionality of the hyperbranched amine decreased the conversion at the gel point. The tertiary amines were preexisting branching points in Hbpei, which improved the crosslinking density of diethylenetriamine for thermosets and the resulting relaxed modulus. Lin et al.[91] investigated a series of hyperbranched polyester-amides (S1, S2, and S3) with trimethylolpropane as crosslinkers for polyurethane curing systems. The numerous amide and ester groups in HBP created hydrogen bonds between the adjacent molecular chains. The excess HBPs could not participate in the crosslinking reaction, and this caused the plasticization of polyurethane. The study demonstrated the excellent potential of these hydroxyl-terminated hyperbranched polyester-amides as crosslinkers for polyurethane curing systems.

Viscoelastic, Diffusion, and Relaxation Effects

When a thermoset precursor reacts, a decrease in the reaction rate is exhibited by the onset of gelation and vitrification in that the curing reactions become diffusion-controlled. In the latter stages, the thermoset/thermoplastic blend separates into two phases because the average molecular weight is increased and reaches a point where a homogeneous mixture is no longer favored; this is accompanied by a difference in the T_g values between the two components during the entire phase separation. The changes in the values of the storage shear modulus and loss shear modulus are attributed to the onset of phase separation and gelation. Obviously, this blend should be a dynamic asymmetry system in the relaxation and diffusion of segments, and phase separation should be influenced by the viscoelastic behavior. In addition, at the onset of phase separation, the rheological behavior is influenced by the amount of thermoplastics in the epoxy/thermoplastic blends.[92]

Gan et al.[93] discussed the viscoelastic effect on the phase separation of a methyltetrahydrophthalic anhydride/poly(ether imide) (PEI)/epoxy system. The phase separation in thermoplastic-modified ER took place according to the spinodal decomposition mechanism. Because of the kinetic factor and the viscoelastic effect associated with the dynamic asymmetry arising from the T_g difference between the components in polymer blends, the phase separation was extensively influenced, and the final morphologies exhibited various morphologies. The viscoelastic behavior of the methyltetrahydrophthalic anhydride/PE)/epoxy system followed the viscoelastic spinodal decomposition model of Tanaka. Thomas et al.[94] investigated DGEBA and various contents of hydroxyl-terminated PB blends using an anhydride as a hardener to observe the effect of rubber modification. It was evident that the gel time increased with increasing rubber concentration. The delay in gel time with the inclusion of rubber was attributed to the lower reactivity of the modified epoxy produced as a result of chain extension and the increase in the viscosity of the medium. Maximum impact properties were observed for the 10-phr rubber–epoxy blend with uniformly distributed rubber particles. The flexural properties were found to decrease with the phase-separated rubber domains because of the decreased crosslinking density of the network. New microsubstructures and nanosubstructures in crosslinked epoxy/ABS blends were also investigated as a function of the concentration of ABS in epoxy systems for the first time.[95] At concentrations lower than 10 phr, the system phase-separated through NG. However, at higher concentrations, 15 and 20 phr, the blends phase-separated through both the NG and spinodal decomposition mechanisms, and a bicontinuous phase morphology with substructures of the ABS phase dispersed in the epoxy phase and substructures of the epoxy phase dispersed in the continuous ABS phase were formed. The phenomena of microsubstructures and nanosubstructures resulted from the combined effect of hydrodynamics and viscoelastic effects acting on the system followed by phase inversion. TEM micrographs of the 20-phr ABS-modified ER showed nanosubstructures of bicontinuous morphology with ABS dispersed in the microsubstructure of the epoxy phase and the epoxy phase also dispersed in the continuous ABS phase (Figure 12).

When a low-molar-mass molecule is involved in a reactive process with molten polymers, the miscibility of the low-viscosity reactant and its rates of mixing, diffusion, and reaction can play determining roles in obtaining the desired macromolecular structure, especially when the chemical reaction involved is sensitive to the stoichiometry or to heterogeneities of concentration.[96] Boyard et al.[97] investigated phase-separation-induced crosslinking in thermoset blends based on an unsaturated polyester, styrene, and a low-molar-weight saturated polyester as a low-profile additive. Through application of the Cahn–Hilliard–Cook theory, the early stage of spinodal decomposition and the growth rate of fluctuation concentrations of the occurring phase separation were investigated extensively. The reaction rate and, consequently, the growth of unsaturated polymer chain length and the apparent diffusion coefficient increased with temperature, whereas the higher the content of the low-profile additive was, the lower the apparent diffusion coefficient value was. The final morphology did not present a sharp interface, and this suggested that the spinodal decomposition was frozen in the early stage because of the strong hindrance of gelation. Bella et al.[98] investigated the complex relations between diffusion and reaction in PS/DGEBA–4,4′-methylene bis(2,6-diethylaniline) blends. SEM results of the 60/40 PS/DGEBA–4,4′-methylene
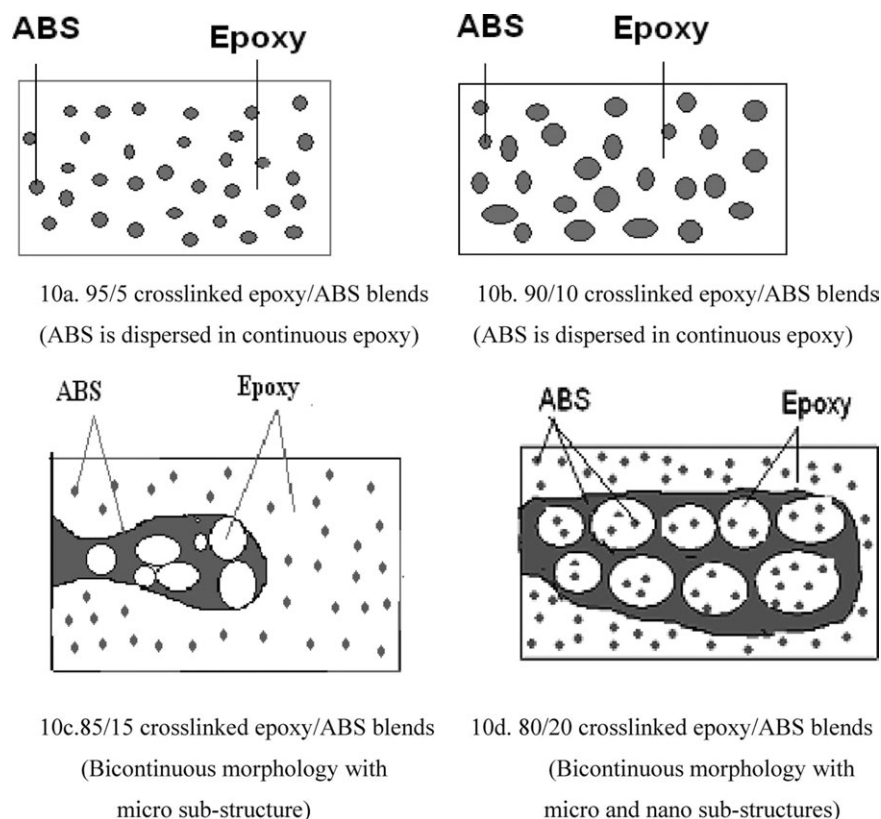
Figure 12. Schematic representation of the crosslinked epoxy–amine/ABS system according to the TEM and SEM micrographs: (a) 95/5 crosslinked epoxy/ABS blends (ABS was dispersed in continuous epoxy), (b) 90/10 crosslinked epoxy/ABS blends (ABS was dispersed in continuous epoxy), (c) 85/15 crosslinked epoxy/ABS blends (bicontinuous morphology with microsubstructures), and (d) 80/20 crosslinked epoxy/ABS blends (bicontinuous morphology with microsubstructures and nanosubstructures). (Reprinted with permission from ref. [95]. Copyright 2009 American Chemical Society.)

bis(2,6-diethylaniline) blend revealed that the monomers and oligomers did not have sufficient time to diffuse, and this resulted in the existence of a gradient of morphology starting at the interface and going to the external sides of the sample. Serrano et al.[32] analyzed the molecular dynamics of a DGEBA/4,4′-methylene bis(3-chloro-2,6-diethyl aniline) epoxy system modified with an epoxidized SB linear BCP during the curing and microphase separation processes. With the Havriliak–Negami, Vogel–Fulcher–Tammann, and Arrhenius equations and fitting parameters, the relaxation behavior of the mixture was modeled. The analysis of the reactive mixtures at zero time revealed the presence of both α and β relaxations of ER (or those of the epoxy-rich phase in the mixture); this could have been related to the normal mode of the epoxidized polybutadiene block (PepB) or to an interfacial polarization process because of the bimodal molar mass distribution of the copolymer. In addition, the interfacial polarization process contributed to the increase of the fitting parameter relaxation strength with temperature. The evolution of molecular dynamics during the polymerization process of ER in the ternary system indicated an increase in the trend of the main relaxation at times. The PIPS of the PS block led to the self-assembly of PS cylinders around 40 nm in diameter in an epoxy-rich phase; this indicated that PS may have hindered the mobility of the epoxy-rich phase and increased the activation energy of the process before gelation.

Despite several attempts, there is still much to study and model of the diffusion, viscoelastic, and relaxation effects on the PIPS kinetics of thermosets, especially when one takes into account the contribution of reactive nonlinear modifiers due to their chemistry and topology.

CONCLUSION AND OUTLOOK

The final morphology and the comprehensive properties of thermosets are strongly dependent on the competitive kinetics, which involve the curing reaction, phase separation, and connectivity of the phases. Reactive polymers, especially HBPs with a lower solution and melt viscosity and a number of functional end groups, have aroused enormous attention in the tailoring of phase separation and morphology and the resulting thermal and mechanical properties of thermosets. These characteristics are modified via changes in the topological structure, the chemistry, and the number of the functional groups of the reactive modifier. However, model reactive polymers are limited, especially those with versatile functionalized groups; the design of building blocks and reaction conditions are prerequisites for highly complex and functional architectures. Furthermore, linear hyperbranched BCPs, which have important differences compared to linear BCPs, can provide a broad range of molecular weights and degrees of branching by deliberate copolymerization with linear units. The difference in the topologies and

molecular weights of reactive modifiers can undoubtedly dramatically influence both the miscibility and the curing behavior of a thermosetting polymer blend; this, however, has not yet been explored in depth. There has been tremendous research on the relationship between the microstructural evolution and the mechanical properties of PIPS thermosets. At the same time, it remains a challenge to describe the mechanism and kinetics of PIPS accurately, especially in those precursor systems incorporating a reactive modifier. The complex architecture of reactive modifiers will motivate theoretical studies correlating the molecular dynamics with the morphology through consideration of the various topological effects during the cure process. This research should, in turn, enrich the strategies used to obtain high-performance thermosets with comprehensive excellent properties.

ACKNOWLEDGMENTS

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