# Thermal Properties of Epoxy/Thermoplastic Blends

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**Abstract**

Incorporation of thermoplastics into the epoxy resin is a potential route for the development of toughened epoxy thermoset with augmented properties. The ultimate properties of the blend depend on the various transitions and transformations during epoxy polymerization such as the viscoelastic phase separation, secondary phase separation, gelation, and vitrification. In this chapter, it is aimed to give a detailed description on the various approaches for improving the fracture toughness of epoxy by blending with thermoplastics, the toughening mechanisms involved, and their effects on the thermal properties of the

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blends. All the systems have been analyzed with a special attention on their thermal properties. Thus, the thermoplastic-modified epoxy resins with improved fracture toughness along with the inherent properties of epoxy resins fall in the class of engineering materials, which is eligible for many high-end applications.

**Keywords**
Epoxy thermoset • Thermal transitions • Thermoplastics • Thermal mending • Glass transition temperature

## Abbreviations

| | |
|---|---|
| 3D | Three dimensional |
| ABS | Poly(acrylonitrile-*block*-butadiene-*block*-styrene) |
| AFM | Atomic force microscopy |
| AN | Acrylonitrile |
| BCP | Block copolymers |
| °C | Degree Celsius |
| DDM | 4,4′-Diamino diphenyl methane |
| DDS | 4,4′-Diamino diphenyl sulfone |
| DEB | Differential expansive bleeding |
| DGEBA | Diglycidyl ether of bisphenol-A |
| DMA | Dynamic mechanical analysis |
| DMTA | Dynamic mechanical thermal analysis |
| DSC | Differential scanning calorimetry |
| $E''$ | Loss modulus |
| ECN | Epoxy cresol novolac |
| EP | Epoxy |
| EPN | Epoxy phenol novolac |
| ER | Epoxy resin |
| eSBS | Epoxidized styrene butadiene styrene |
| $G'$ | Storage modulus |
| HDT | Heat deflection temperature |
| HTPB | Hydroxyl-terminated polybutadiene |
| LED | Light emitting diode |
| MCDEA | 4,4′-Methylene *bis* (3-chloro-2,6-diethyl aniline) |
| MDA | Methylene dianiline |
| MF | Melamine formaldehyde |
| MMA | Methyl methacrylate |
| MOCA | 4,4′-Methylene *bis* (2-chloraniline) |
| MWCNT | Multiwalled carbon nanotube |
| NBR | Poly(acrylonitrile) rubber |
| NG | Nucleation and growth |
| NMR | Nuclear magnetic resonance spectroscopy |

| | |
|---|---|
| OM | Optical microscopy |
| P(MMA-VAc)-PEGDA | Poly(methyl methacrylate-vinyl acetate)-*co*-poly(ethylene glycol) diacrylate |
| PB | Polybutadiene |
| PCL | Poly(ε-caprolactone) |
| PCL-PPC-PCL | Poly(ε-caprolactone)-*block*-poly(propylene carbonate)-*block*-poly(ε-caprolactone) |
| PDMS | Poly(dimethyl siloxane) |
| PEGDA | Poly(ethylene glycol) diacrylate |
| PEI | Poly(ether imide) |
| PEO | Poly(ethylene oxide) |
| PEP | Poly(ethylene-*alt*-propylene) |
| PF | Phenol formaldehyde |
| PGA | Poly(glycolic acid) |
| phr | Parts per hundred resin |
| PMMA | Poly(methyl methacrylate) |
| POM | Polyoxymethylene |
| PPC | Poly(propylene carbonate) |
| PPE | Poly(2,6-dimethyl-1,4-phenylene ether) |
| PPO | Poly(propylene oxide) |
| PS | Polystyrene |
| P-SBMMA | Poly(styrene-*block*-butadiene-*block*-methyl methacrylate) |
| PS-*b*-PGA | Polystyrene-*block*-poly(glycolic acid) |
| PVAc | Poly(vinyl acetate) |
| RIPS | Reaction-induced phase separation |
| SALLS | Small-angle laser light scattering |
| SAN | Styrene-acrylonitrile |
| SAXS | Small-angle X-ray scattering |
| SBS | Poly(styrene-*block*-butadiene-*block*-styrene) |
| SEM | Scanning electron microscopy |
| SIS | Epoxidized poly(styrene-*block*-isoprene-*block*-styrene) |
| $Sn(Oct)_2$ | Stannous octoate |
| tan $\delta$ | Loss tangent |
| TEM | Transmission electron microscopy |
| $T_g$ | Glass transition temperature |
| $T_{g0}$ | $T_g$ of unreacted epoxy resin |
| TGA | Thermo gravimetric analysis |
| TGAP | Triglycidyl-*p*-amino phenol |
| TGDDM | Tetraglycidyl-4,4″-diamino diphenyl methane |
| $T_{g\alpha}$ | Transition temperature of fully cured epoxy resin |
| Tm | Crystalline melting temperature |
| TMA | Thermomechanical analysis |
| TP | Thermoplastic |
| TS | Thermoset |

| | |
|---|---|
| TTT | Isothermal time versus temperature transformation |
| UCST | Upper critical solution temperature |
| UF | Urea formaldehyde |
| VAc | Vinyl acetate |

## Contents

## Introduction

Polymer blending is a simple and versatile method to develop structurally advanced polymeric materials. The ultimate properties of the polymer blends can be manipulated according to the end use by the proper selection of constituent polymers and processing method. Polymer blending can simply be done by proper mixing of two or more miscible or immiscible constituent polymers to reactive multicomponent systems based on thermosetting resin/thermoplastic (TS/TP) polymers. The latter system has recently gained much fundamental as well as practical interest from the scientific community and industrialist towards the development of new high-performance materials. Thermosetting polymers that include epoxy, unsaturated polyester, phenolics, or melamine formaldehyde are being increasingly used in diverse applications, ranging from aerospace structures to simple dental fillers. By the formation of a covalently cross-linked and thermally stable network through cross-linking reaction, the thermoset materials undergo a permanent change under the influence of heat, even if they possess good processability and excellent chemicomechanical properties. The reactive oligomers grow in molecular weight to form tough and strong three-dimensional structure during cross-linking.

Due to the exceptionally good mechanical properties and chemical and/or degradation resistance, high tensile and impact strength, stiffness, environmental stability, insulating and adhesion properties, ease of processing, low-temperature cure, cost-effectiveness, and easiness in fabrication of complex and very large shapes thermoset-based polymer systems are preferred over thermoplastics for high-performance structural applications. Among the thermosets, for example, phenol formaldehyde (PF), urea formaldehyde (UF), or melamine formaldehyde (MF) and epoxy resin (ER) based on diglycidyl ether of bisphenol-A (DGEBA) are versatile groups which find structural and adhesive applications in various fields such as aerospace, electronics, construction, submarine, etc. (May 1988).

Epoxy is a common term representing both the basic components and the cured products of epoxy resins. This thermosetting resins are a class of reactive pre-polymers which contain epoxide groups capable of reacting (cross-linking) either with themselves through catalytic homopolymerization or with a variety of co-reactants which are generally called as hardeners or cross-linking agents. Cross-linking reaction of polyepoxides with polyfunctional curing agents, for example, polyfunctional amines, acids/acid anhydrides, phenols, or thiols etc., forms a thermosetting polymer, often having high mechanical, thermal, and chemical properties. Epoxy has a wide range of applications, including metal coatings, electronics/electrical components, light-emitting diodes (LED), high tension electrical insulators, fiber-reinforced plastics, flooring and casting, protective coatings, high-performance composite, bonding, and structural adhesives.

Compared to other thermosetting resins, primary advantage of epoxy resins is that it can cross-link with the reactive functional groups of cross-linking agents without the evolution of any volatile products. The cross-linked epoxy possesses excellent thermomechanical and chemical properties. Their unique properties are primarily obtained from the cross-linked 3D-network structures and the presence of highly stable epoxide groups. Eventhough they possess high degree of chemical cross-linking, epoxy resins are highly brittle which is one of their major drawbacks. Low fracture toughness and brittleness also limit their use in many advanced high-performance applications (Kinloch 1986); hence, it has caught the attention of researchers globally to modify the brittle epoxy resins by blending with elastomers (Zhang and Berglund 1993; Hsich 1990), thermoplastics (Bucknall et al. 1994; Riccardi et al. 1996; Yu et al. 2004), block copolymers (Mijovic et al. 2000; Ritzenthaler et al. 2002), etc. Among the above mentioned methods, incorporation of thermoplastics into the epoxy resin is a potential route for the development of toughened epoxy thermosets with augmented properties. Blending the brittle epoxy resins with suitable thermoplastics, having high elastic modulus and high glass transition temperature ($T_g$), with an aim to enhance their fracture toughness and thermal resistance (higher $T_g$) has been a topic of interest for the researchers for the past two decades (Natarajan and Rao 1994; Pena et al. 2003; Das et al. 1994; Schauer et al. 2002; Paul and Bucknall 2000; Tribut et al. 2007; Blanco et al. 2004). These blends are generated by a reaction-induced phase separation process determined by cure conditions, compositions, nature of modifier, molecular weights, and molecular weight distribution of tougheners. The ultimate properties were dependent on the various transitions and transformations during epoxy polymerization such as the viscoelastic phase separation, secondary phase separation, gelation, and vitrification.

Morphological structures thus formed by blending the epoxy with thermoplastics are classified into three: (i) sea-island structure formed with low thermoplastic loadings, (ii) nodular structure formed at high thermoplastic concentrations, and (iii) bicontinuous, salami, or layered structure formed in the middle thermoplastic concentration range (Park and Kim 1996; Francis et al. 2006; Kim et al. 2008; Zhang et al. 2011). Backbone structure, molecular weight, and the end-group chemistry of the thermoplastic are the influencing factors which determine the morphology of the blend. Each of these three aspects influences the thermomechanical properties of the epoxy-thermoplastic blend in a unique way (Williams et al. 1996; Girard-Reydet et al. 1997, 1998; Pearson 1993). As the molecular weight of epoxy increases, phase separation will be induced which gradually slows down and finally stops as the gelation increases. Hence, curing reaction and phase separation play critical roles in the development of structure and morphology of the final blend (Bonnet et al. 1999a, b; Swier and Mele 2003; Swier et al. 2005; Liu et al. 2010). Epoxy-thermoplastic blends thus made have been used as engineering materials for aircraft, electronic, and automobile applications where they have modified epoxy resin with poly(ether sulfone) (PES), poly(ether imide) (PEI), poly(propylene oxide) (PPO), etc. (Paul and Bucknall 2000; Tribut et al. 2007; Blanco et al. 2004). In this chapter, it is intended to give a detailed description on the various approaches for toughening epoxy with thermoplastics and the toughening mechanism with special attention to the thermal properties of the blends.

## Epoxy Resins

Epoxy resin is a commercially important thermosetting resin, which has molecule with multiple epoxy groups capable of being hardened into a usable product. After commercial launching in 1946, epoxy resin industry has undergone a fast development and presently has taken up a substantial share of (nearly 35%) the world's total thermoset market with an yearly consumption of around 90 k tones (Analysis 2004). Figure 1 shows the major market consumption and application of epoxy resins. When cured, the epoxy resins form a highly cross-linked 3D infinite network with unique microstructure which impart the desirable engineering properties. The superior chemical, environmental, and corrosion resistance; good mechanical and thermal properties; outstanding adhesion to various substrates including ceramics and metals; low shrinkage upon cure; durability, toughness, and flexibility in processing; good electrical and electronic properties; and ability to be processed under a variety of conditions make them an attractive candidate for the high-performance engineering applications (Mc Adams and Gannon 1986).

Epoxy resins contain more than one α-epoxy group, which can be converted to a useful thermoset form. Epoxide group is usually a 1,2- or α-epoxide (epoxy group) as shown in Scheme 1, called the glycidyl group. The glycidyl group firmly attached to the rest of the functional molecules by an oxygen, nitrogen, or carboxyl linkage, which is called as glycidyl ether, glycidyl amine, or glycidyl ester, respectively. Epoxy resins are available in various physical forms ranging from low viscosity liquids to tack free solids which greatly depends on the molecular weight of the resin.

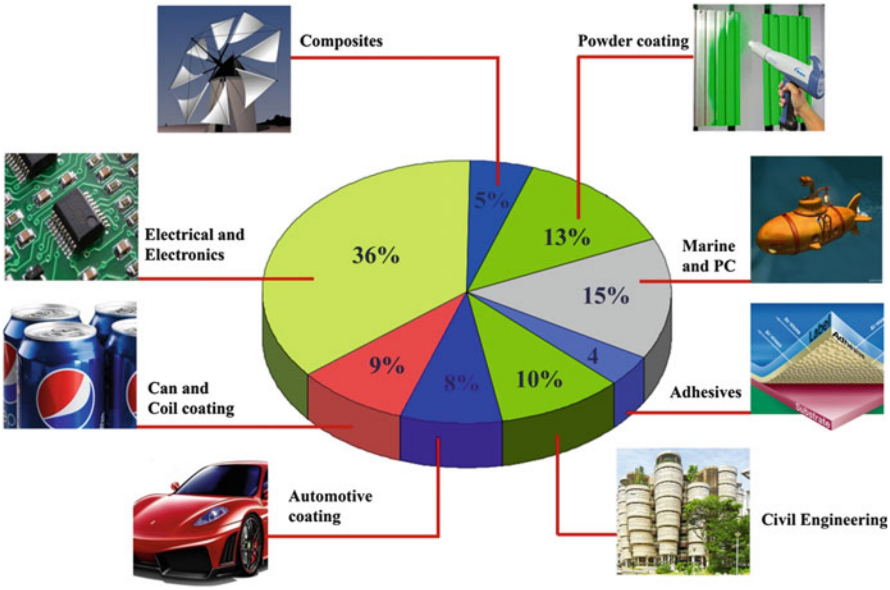
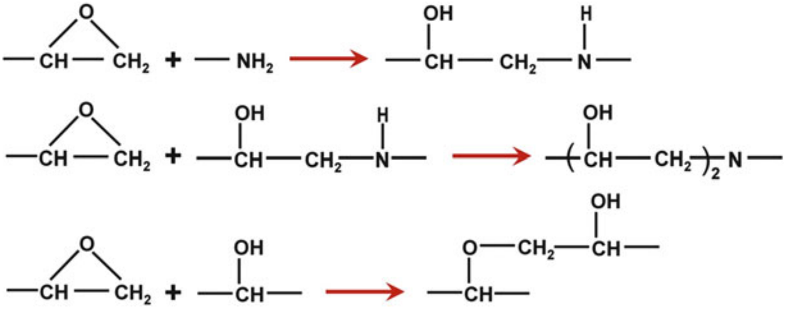


**Fig. 1** The global market share of epoxy consumption in different applications



**Scheme 1** Reaction between amine curing agent and epoxy resin

The most popular commercial grade bifunctional epoxy resin is DGEBA. Specific multifunctional aromatic glycidyl ether resins such as epoxy phenol novolac (EPN) as well as epoxy cresol novolac (ECN) resins impart excellent thermal and chemical resistance owing to the high functionality. Because of the aromatic backbone, multifunctional glycidyl amine resins like triglycidyl-*p*-aminophenol (TGAP) and tetraglycidyl-4,4′-diaminodiphenyl methane (TGDDM) offer excellent elevated temperature properties and are used as binders in graphite reinforced composites. The transformation of epoxy resins from liquid or semisolid monomers into infusible and insoluble thermoset 3D network is taking place through the cross-linking reaction and/or polymerization by thermal, ultraviolet, or microwave radiation.

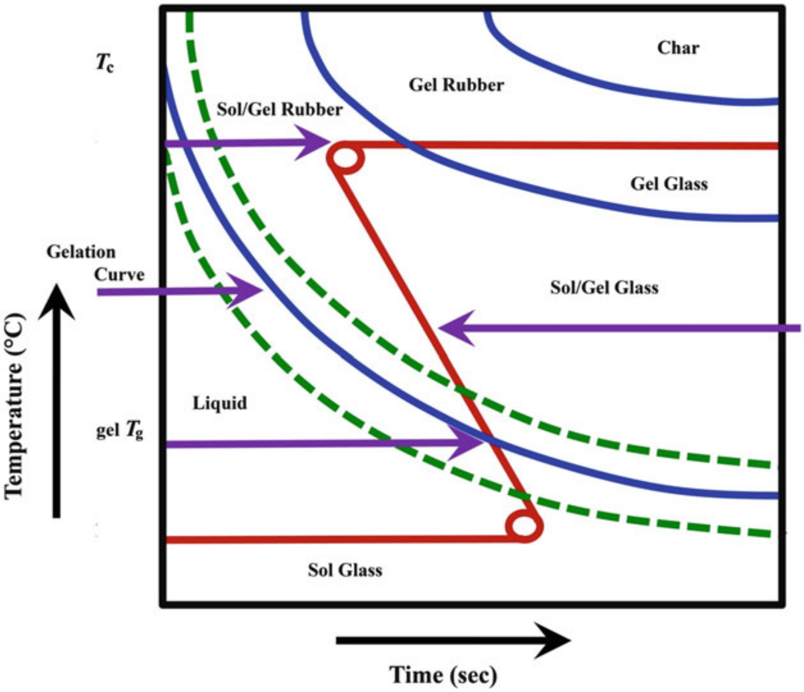


**Fig. 2** Time-temperature-transformation diagram of polymers (Adopted from Gillham 1986)

Cross-linking initially leads to chain extension and branching due to molecular weight buildup, and finally the individual clusters join to form a 3D network of infinite molecular weight. Gel point is defined as the point where irreversible transformation from viscous to elastic gel takes place. Beyond gel point, the uninhibited polymerization reaction proceeds toward the formation of infinite network assuming the shape of the reaction vessel with tremendous hike in cross-link density, glass transition temperature ($T_g$), and ultimate physical properties. The isothermal time versus temperature transformation (TTT) cure diagram is a very useful tool for studying cross-linking processes of epoxy-based polymer systems (Fig. 2) (Gillham 1986). In the TTT cure diagram, the times to gelation and vitrification are plotted as a function of the isothermal cure temperature. The "S"-shaped gelation and vitrification curves of liquid, gelled rubber, sol-glass, and gelled glass (the four intermediate states of epoxy resins curing process) divide TTT diagram into four distinct stages of the thermosetting curing process. At a temperatures below the $T_g$ of unreacted epoxy resin ($T_{g0}$), the cross-linking process occurs in slow reaction rate and kinetics as it is confined to the solid state. The storage temperature for unreacted resins is defined by $T_{g0}$. The resin start to react above $T_{g0}$ which leads to the vitrification. Between $T_{g0}$ and gel $T_g$, the resin will react until $T_g$ becomes equal to the cure temperature; thereafter, the reaction becomes diffusion controlled. At this stage, the vitrification is complete, and the resin is eventually quenched. Between gel $T_g$ and glass transition temperature of fully cured epoxy resin ($T_{g\alpha}$), gelation precedes vitrification and a cross-linked rubbery network forms, which continues until its $T_g$ coincides with the cure temperature and the reaction will be quenched. $T_{g\alpha}$ is defined as the minimum cure temperature required for the complete curing of the resin. Above this temperature ($T_{g\alpha}$), the resin will be in the rubbery state after gelation, if there is no other cure reactions like oxidative cross-linking or chain scission. The handling, processing, and properties of the cured resins are greatly influenced by the rate of gelation and vitrification.

The strained three-membered ring structure of an epoxy group is highly reactive toward many nucleophilic and electrophilic reagents. Because of their effectiveness and availability, compounds with active hydrogen atoms such as amines, phenols, alcohols, thiols, carboxylic acids, and acid anhydrides have been used as curatives. The ultimate cured resin properties are highly influenced by the nature of the cross-linker. Epoxies cured by aromatic amine offer excellent resistance to water absorption (Wu and Xu 2007). Epoxy resins cured with anhydrides have excellent outdoor weathering resistance. Some of them have high heat deflection temperature (HDT) and excellent retention of strength at high temperature. These systems have low viscosity and long pot life. Polyamines are among the most commonly used curing agents for epoxy resins and make up around 22% of the commercial market (Ashcroft 1993). All primary, secondary, and tertiary amines can be employed to initiate cure in epoxy systems. The reaction between epoxy resin and an amine curing agent is given in Scheme 1.

The reaction of primary amine with epoxy leads to the formation of a secondary amine and secondary hydroxyl group. The secondary amine reacts with epoxy group to form a tertiary amine and two secondary hydroxyl groups. Depending on the reaction temperature, the tendency of the etherification reaction takes place (Lunak and Dusek 1975; Riccardi and Williams 1986), and the basicity of the diamine increases with increase of epoxy/amine ratio. For primary and secondary amines, stoichiometric amounts are generally employed, while the tertiary amines are used in catalytic quantities (Riccardi and Williams 1986). The selection of amine is crucial that it influences the formation of polymer networks (cross-link density and hence glass transition temperature) which, in turn, has great effect on the resin performance. For ambient temperature curing, low viscosity aliphatic amine was preferred and, for high-temperature properties, chemical resistance, long pot life, and low moisture absorption aromatic amine are employed as the curing agent.

## Epoxy/Thermoplastic Blends (Homo- and di-block Copolymer)

### Epoxy/Poly(ethylene oxide) (PEO)/Poly(ethylene glycol) (PGA) Blends

Blends of epoxy resin with poly(ε-caprolactone) (PCL) and poly(ethylene oxide) (PEO) have been a topic of high interest for the researchers working on TS/TP blends. Poly(ethylene oxide) has been widely studied as a versatile polymer for preparing polymer blends, due to its good thermomechanical properties and solubility characteristics in water (Prasanth et al. 2014). It has ether linkages, with oxygen atoms present at a suitable interatomic separation to allow segmental motion of the polymeric chain which is beneficial for many electrochemical and electrochromic applications (Prasanth et al. 2014; Shubha et al. 2014). The effect of blending PEO with different polymers to improve the segmental motion, dissociation of ionic salts, and improve the electrochemical performance of the resulting blend has been reported (Prasanth et al. 2014). Meltzer (1979) showed that the presence of ether linkage in the main chain of the polymer is beneficial for preparing compatible blends with different thermoplastic and thermosetting resins. PEO-based polymer blend led to a significant refinement in morphology due to reactive compatibilization with hydroxyl ends of PEO.

Formation of a fine phase-separated morphology by reaction-induced microphase separation mechanism of a novel amphiphilic polystyrene-*block*-poly(glycolic acid) (PS-*b*-PGA)$_3$ three-arm star copolymer upon blending with epoxy precursor has been systematically demonstrated by Francis and Baby (2014). The translucent film formed was characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), and transmission electron microscopy (TEM), and the creation of nanodomains of the PS phase was evident from these analyses. After curing, the miscible PGA block was observed to be well dispersed in the epoxy matrix. The formation of the PS nanodomains in the epoxy−PGA matrix enhanced the toughness and tensile properties of the final epoxy thermoset formed. The AFM micrographs (Fig. 3), SEM, and TEM of the epoxy thermosets containing (PS-*b*-PGA)$_3$ of block copolymer showed ordered nanostructure in the thermoset, which resulted from the star-shaped architecture of the block copolymer as presented in Fig. 4 on the reaction-induced phase separation.

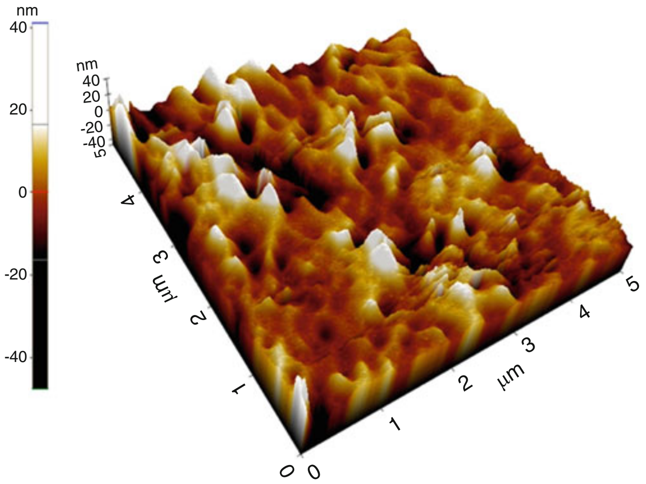


**Fig. 3** AFM image of epoxy thermoset containing 10% of (PS-*b*-PGA)$_3$ block copolymer (topography) (Adopted from Francis and Baby 2014)

He et al. (2014) have blended epoxy with block copolymers containing epoxy resin-miscible PEO or PCL blocks. In their investigation, they have observed an interesting structure and dynamics of the interphase and cross-linked network and the intermolecular interactions between epoxy resin and block copolymers (BCP) with the aid of multiscale solid-state NMR techniques. Interphase thickness of PEO-containing blends was observed to be smaller than that of PCL-containing blends. Furthermore, it is anticipated that the mechanical properties of the blends may be enhanced by the improved rigidity of cross-linked network due to the high

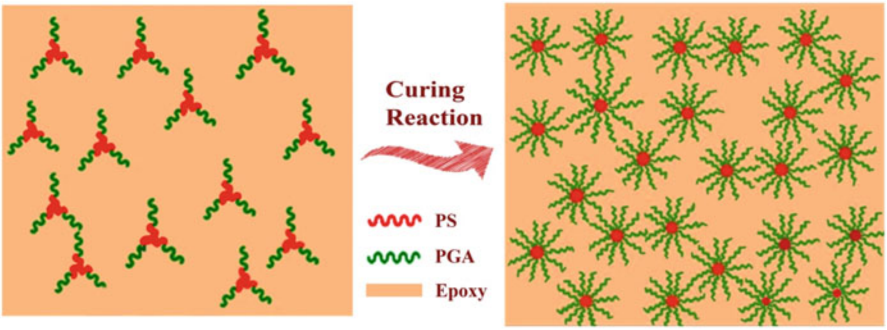


**Fig. 4** Formation of nanostructures in epoxy thermoset by reaction-induced microphase separation (Adopted from Francis and Baby 2014)

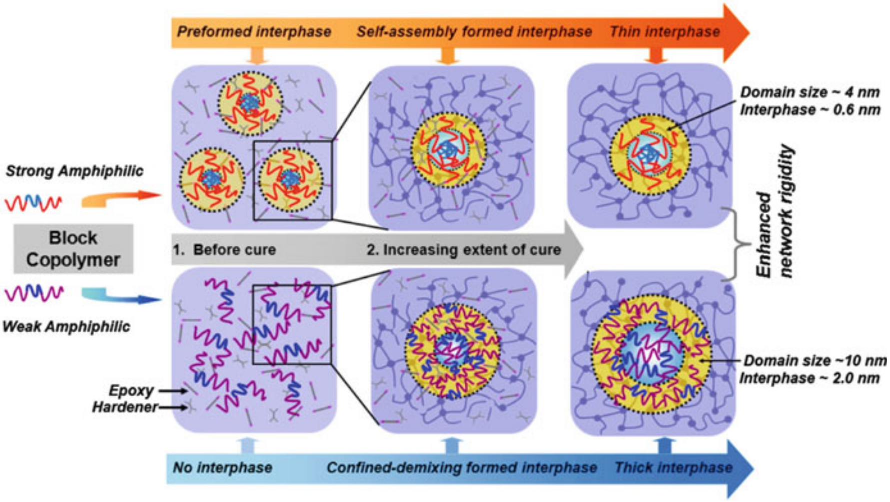
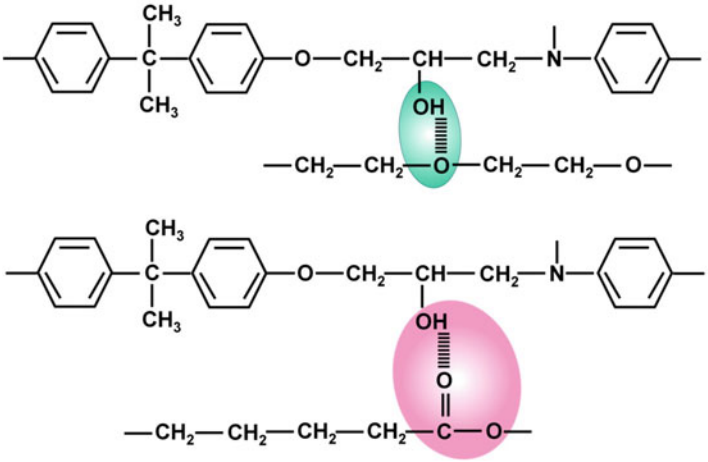


**Fig. 5** Schematic illustration of the model describing two different types of unique structures and dynamics of the interphase and cross-linked network and their underlying formation mechanism in epoxy/BCP blends* (Adopted from He et al. 2014). *The interphase is indicated between two *dotted circles* and filled with *yellow*



**Scheme 2** Intermolecular hydrogen bonding between cross-linked epoxy and **a** PCL and **b** PEO (Adopted from He et al. 2014)

mobility of BCPs. The unique structure and dynamics of the interphase and cross-linked network and their formation mechanism in epoxy/BCP blends have been demonstrated by a proposed scheme as in Fig. 5. In this model, amphiphilic BCPs are mainly divided as strong and weak amphiphilic BCPs. Strong amphiphilic BCPs indicate that there is large difference in thermodynamic interaction parameter $\chi$ between each of the amphiphilic BCP blocks and epoxy before curing, generally shown as large difference in miscibility, and vice versa for weak amphiphilic BCPs. Also it has been suggested that PEO and PCL have intermolecular hydrogen bonding interactions between hydroxyl groups of reacted epoxide-amine, and oxygen of PEO or carbonyl groups of PCL, as shown in Scheme 2, is to be considered as the driving force for the miscibility in thermoset blends.

Hillmyer et al. and Lipic et al. (Hillmyer et al. 1997; Lipic et al. 1998) blended a poly(ethylene oxide)-*block*-poly(ethylene-alt-propylene) (PEO-*b*-PEP) symmetrical di-block copolymer of low molar mass with an epoxy system and methylene dianiline as hardener (MDA). The selected epoxy prepolymer, the classical DGEBA, is initially a selective solvent for the PEO chains. During cross-linking, DGEBA was reacted with MDA to from 3D-network structures. The evolution of the morphology during reaction was recorded by small-angle X-ray scattering (SAXS). No macrophase separation could be observed between the di-block and the epoxy during the whole reaction process. As PEO is expulsed from the epoxy network only at a local scale, the fully cured material presents a well-defined ordered nanostructure. This phenomenon is explained by a synergy between the curing reaction, local phase separation, and energy barriers to nucleation of block copolymer-rich domains. Recently, there are few studies reported on block copolymers having an epoxy-reactive functionality, for example, poly(epoxy isoprene)-*block*-polybutadiene or poly(methyl acrylate-*co*-glycidyl methacrylate)-*block*-polyisoprene as chain modifier for epoxy thermosets (Grubbs et al. 2000). In the same way, nanostructured phenolic networks have been obtained with the use of poly(2-vinylpyridine)-*block*-polyisoprene (Kosonen et al. 2001).

## Epoxy/Poly(ϵ-caprolactone) (PCL) Blends

Poly(ε-caprolactone) is a well-known biodegradable polymer having glass transition temperature ($T_g$) of about −60 °C and low melting point of around 60 °C. This polymer is being popularly used as a biopolymer; however, it is also used as an additive for resins to improve the processing characteristics and end-use properties of epoxy system (e.g., impact resistance). As PCL is economically viable, having good processing characteristics and compatible with organic materials, it could be mixed with many polymers such as starch or PEO, which lower its cost and increase biodegradability. It is also reported as a polymeric plasticizer to both thermoplastic and thermosets. Recently, the blend of PCL and epoxy is widely attracted by the scientific community due to its unique thermal and mechanical properties. The differences in miscibility for both anhydride and amine cross-linked epoxy-PCL blends and the effects on mechanical properties have been investigated by Clark et al. (1984) and Hameed and Guo (2008). Chen and Chang studied immiscibility of the blends when an aromatic amine was used as the curing agent (Chen and Chang 1999). This effect is due to the intrachain-specific interaction on the phase behavior. Miscibility and hydrogen bonding interaction between PCL and epoxy resin were frequently reported in the literature (Williams et al. 1996; Meng et al. 2006a). Wu et al. (2012) recently reported the effect of PCL as a modifier on the mechanical properties of epoxy thermosetting resin. They found that with increase in PCL composition, the tensile strength and the elongation at break of the modified epoxy thermoset decreased due to the lack of intermolecular force of attraction in the blend. The primary demerit of PCL is its plasticization effect in the blend. Alternative block copolymers have been developed to modify epoxy resin to overcome this problem

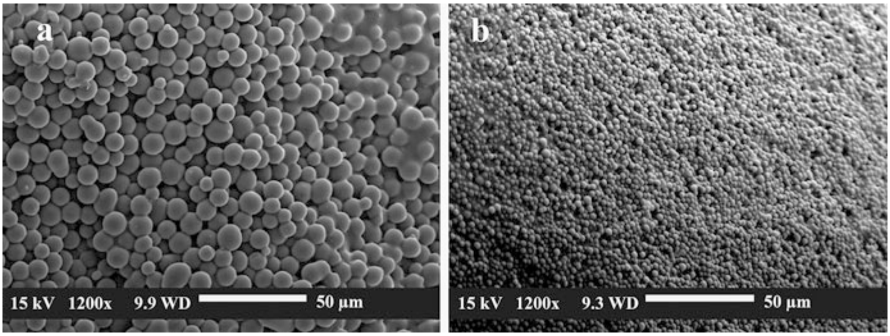


**Fig. 6** SEM images showing the bulk morphologies of fully cured epoxy/PCL blends of different compositions: **a** epoxy/PCL(27.0); **a** epoxy/PCL(34.9) (Adopted from Xiaofan et al. 2009)

(Engelberg and Kohn 1991; Park et al. 2006; Boland et al. 2001; Aghdam et al. 2012). A new broadly applicable strategy to produce thermally mendable polymeric materials, demonstrated with an epoxy/PCL phase-separated blend, has been reported by Xiaofan et al. (2009). A series of morphologies (Fig. 6) produced by varying the weight ratio of DGEBA to PCL. The study reported that PCL is miscible initially in the epoxy matrix; however, PCL undergoes polymerization-induced phase separation during cross-linking reaction, which yields a "bricks and mortar" morphology. As a result, the epoxy phase exists as interconnected spheres (bricks) interpenetrated within the percolating PCL matrix (mortar) (Fig. 7). The cross-linked composite material is tough, strong, and durable. The thermal studies witnessed heating-induced "bleeding" behavior in the form of spontaneous wetting of all free surfaces by the molten PCL phase in the epoxy matrix. Hence, it was observed that thermally induced bleeding is capable of repairing damage by crack wicking and subsequent recrystallization with only minor concomitant softening during the aforementioned process. This bleeding process is attributed to volumetric thermal expansion of PCL in the epoxy brick due to the influence of temperature above the crystalline melting point of PCL, which is termed as differential expansive bleeding (DEB) (Xiaofan et al. 2009). It is reported that, even above the melting temperature of PCL, the blend behaves as a stiff elastic solid, given the relatively low loss modulus ($E''$) and loss tangent ($\tan \delta$) values. Melting the PCL fraction does not fluidize the blend inducing dimensional changes, and this is in line with the microscopic observations of interconnectivity. This is just opposite behavior to that of pure PCL as well as epoxy/PCL blends with high PCL content, which lose mechanical properties or even flow if heated above the melting temperature (Barone et al. 2006). In fact, the material remains stiff until the $T_g$ of the epoxy (203 °C). The composition

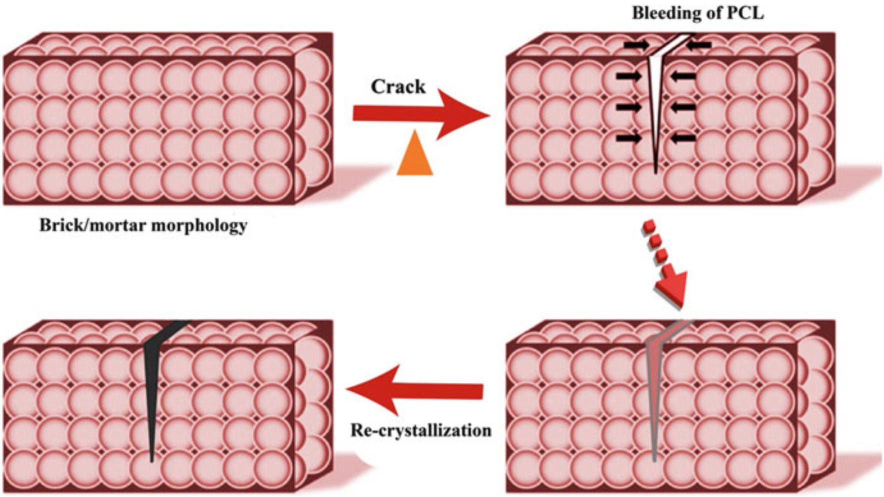


**Fig. 7** Schematic illustration of the overall mechanism of thermal mending (Adopted from Xiaofan et al. 2009)

and morphology of epoxy/PCL blend with 15.5% PCL content display excellent mechanical properties that are caused by the interconnected epoxy "bricks," making the material suitable for various structural applications.

Fractured epoxy when subjected to the same thermal treatment at 190 °C or even higher temperatures of 200–240 °C does not thermally mend. Hence, the thermal-mending ability of epoxy/PCL (15.5) is not due to the curing of epoxy and is due to incorporation of PCL. Finally, it was concluded that the thermal-mending performance is closely related to a "bleeding" phenomenon (Fig. 7).

Heating specimens to a temperature within the range $T_m$ PCL $< T < T_g$ epoxy resulted in spontaneous surface wetting of samples by molten PCL "bleeding" (DEB). Bleeding is initiated with temperature and small liquid droplets formed on the surface, and then the droplets grow and coalesce by contact line motion and impingement of adjacent growing droplets. Eventually (>20 min), a thin layer of fluid PCL covers a large area on the surface. It was reported that the bleeding phenomenon is a consequence of differential thermal expansion between the two interpenetrating phases, with the minor but continuous PCL phase expanding at least 10% more than the epoxy phase because of the melting transition and the large expansivity of the fluid phase (Fig. 8) (Rodgers 1993).

The kinetics of PCL flow to the surface expansion is mainly determined by heat transfer, with visible flow occurring in system with the temperature rise (Fig. 9) (heating-induced "bleeding" behavior). The process of heating-induced "bleeding" behavior was characterized by hot-stage stereomicroscopy coupled with surface temperature monitoring. Images were taken at various time points during heating. As the temperature stabilizes, bleeding completes. PCL displays large bulk modulus (less compressible) and a large liquid expansivity; as a result, a large transient pressure is generated which drives the flow of liquid PCL through the network of epoxy spheres onto the surface within a short period of time. The flow time of PCL is

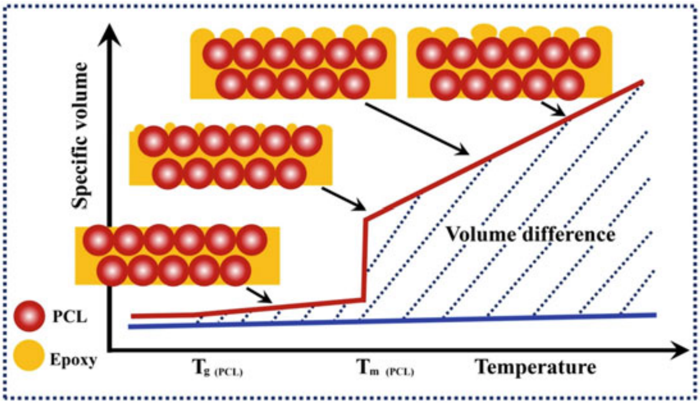


**Fig. 8** Schematic illustration of DEB indicating its origin in differential thermal expansion between PCL and epoxy (Adopted from Xiaofan et al. 2009)

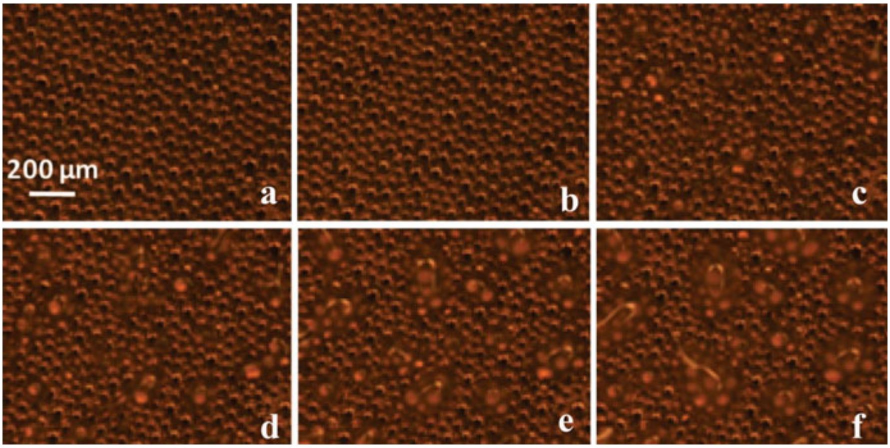


**Fig. 9** Heating-induced “bleeding” behavior of epoxy/PCL blend. Images were taken at various time points during heating, time/temperature (sec.:°C); **a** 0:30, **b** 30:60, **c** 150:120, **d** 200:130, **e** 260:130, **f** 360:130 (Adopted from Xiaofan et al. 2009)

small compared to the time required for heat transfer (Xiaofan et al. 2009). In summary, the “bricks and mortar” morphology of epoxy/PCL blend exhibits unique thermal properties, e.g., differential expansive “bleeding” which enables excellent thermal mending and applicability as a rigid and reversible adhesives. This sort of morphologies can be obtained in many other systems, where a thermoset is blended with an amorphous (Cabanelas et al. 2005; Meynie et al. 2004; Oyanguren et al. 1999; Wang et al. 2004) or semicrystalline (Goossens and Groeninckx 2006; Johnsen et al. 2005) thermoplastic polymer. This in turn leads to broad applicability of this strategy to the design of DEB polymers and polymer composites, based on low raw material cost and ease of manufacturing, for those applications requiring long-lasting material performance and facile repair. Further, the reversible adhesive properties of DEB polymer composites should enable a new paradigm in adhesives as reusable bonding “blocks” that can adhere to or be removed from virtually any surface with a simple heat treatment (Xiaofan et al. 2009).

## Epoxy/Poly(methyl methacrylate) (PMMA) Blends

Poly(methyl methacrylate) (PMMA) is a polar polymer with exceptional transparency, biocompatibility, and weather resistance. The properties of PMMA can be easily designed by changing the polymerization conditions and polymerization technique during its synthesis. PMMA has wide applications in building and construction; optical, automotive, consumer goods; and medical applications. Recently, many epoxy/PMMA blends having unique properties are reported. Natarajan and Rao (1994) modified the epoxy resin based on DGEBA with PMMA and nitrile rubber (NBR). The resulting blend is cured with a stoichiometric quantity of 4,4′-diaminodiphenyl methane (DDM). The effect of adding PMMA and NBR on the morphology, mechanical properties, and thermal properties of the modified epoxy network is investigated. It has been observed that the modified epoxy network showed an enhancement in thermomechanical properties (elongation, tensile strength, ductility, impact strength, toughness, and glass transition temperature). The improvement in mechanical strength is due to the inclusion of NBR, while the shifting of $T_g$ to the higher end ($T_g$) is due to the inclusion of PMMA into the blend. The improvement in tensile strength and thermal properties is due to the incorporation of PMMA into the blend, while the addition of rubbery particles is effective in increasing the fracture toughness of epoxy resin. The phase separation at elevated temperature and the thermal stability of the blend were addressed by using PMMA as the chain modifier in the blend system (Natarajan and Rao 1994; Pena et al. 2003; Das et al. 1994; Schauer et al. 2002). It has been shown that the thermoplastic-modified epoxies exhibit various types of morphology and unique thermal properties which is crucially dependent on the backbone structure, molecular weight, molecular weight distribution, and the end-group chemistry of the thermoplastic chain modifier. Recently, there are many reports on the thermal properties of the epoxy/NBR blend. The dynamic mechanical thermal analysis (DMTA) showed that as temperature increases, damping goes through a maximum in the transition region and then decreases in the rubbery region. The structure and extent to which the polymer is cross-linked is examined by the position and height of the tan δ peaks. They observed that tan δ peak is shifted from higher region to lower region in the unmodified blend (without PMMA). This may be due to lowering of cross-linking density in the unmodified cured sample. During the curing of epoxy resin, phase-separated thermoplastic domains may occupy the space in between the reaction sites, thereby impairing the cross-linking reaction. This, in turn reduces the cross-link density of the cured systems. It is reported that the $T_g$ of modified blend is 164 °C, which is ~16.5% higher than the $T_g$ value of unmodified blend (Padma and Natarajan 2014).

## Epoxy/Poly(ether sulfone) (PES) Blends

Linear, high molecular weight thermoplastics are inherently tough and may be expected to reduce the brittleness of a thermoset without affecting their other properties significantly. Alessi et al. (2009) studied the epoxy resin/thermoplastic blends cured by ionizing radiation. The blend of difunctional epoxy resin and poly (ether sulfone) is cured by electron beam (e-beam) at about 60 °C using strong acid salt as initiator. Selected cured samples have been subjected to post-irradiation thermal curing. Both e-beam cured and thermally post-cured samples are aged hydrothermally before the thermal characterization.

From the DMTA, only irradiated sample exhibits two relaxation peaks, corresponding to the glass transitions of clusters with different network densities.

This is attributed to the vitrification phenomenon occurring during irradiation at low temperature. On contrary, the second peak is due to the relaxation of both high cross-linked portions of materials (resulted by irradiation) and increase in cross-link density due to the transformation from lower to higher cross-linking by the thermal treatment happening in the DMTA itself. From the cross-linking degree point of view, it is reasonable that post-curing treatment (after e-beam curing) at a higher temperature which is sufficiently high to overcome vitrification effects (between the two relaxations) is able to make the system more homogeneous. The tan δ curve for such condition shows only one peak at a temperature almost corresponding to the second peak of the only irradiated system.

The accelerated hydrothermal aging on the irradiated sample causes a significant change in the tan δ curve with a "homogenization" of the cross-linking density due to both plasticization and thermal curing effects, while for the post-irradiation thermally cured sample, a not dramatic decrease of $T_g$ is observed, justified by its lower water absorption.

## Epoxy/Poly(2,6 dimethyl 1,4 phenylene ether) (PPE) Blends

Poly(2,6-dimethyl-1,4-phenylene ether) (PPE) is one of the polymers having wide applications in electronic industry due to its low dielectric constant(2.45), dissipation factor ($7 \times 10^{-4}$), and high $T_g$ (210 °C). Because of the unique properties, PPE gained great interest for modifying epoxy resins to improve its toughness and ductility. The high $T_g$ of PPE makes its processing difficult and limits practical applications. To reduce the viscosity of PPE, solvents have been introduced during processing, which incurs the following disadvantages during and after processing:

(a) Requires the disposal or discharge of organic solvent.
(b) Volatilization of the solvent from the material.
(c) Causes the presence of voids and irregularities in the material.
(d) Considerable amount of time and energy is required for the solvent removal.
(e) Causes environmental issues.
(f) Increases the post-processing cost.

These problems could be addressed by using thermosetting monomers as the solvents. If then instead of solvent removal during and post-processing, thermosets monomers can be polymerized into a constituent of the final material, which gives a uniform blend of thermoplastic and thermosetting polymers. In addition, by choosing an appropriate thermoset monomer as a solvent, reduction in $T_g$ of thermoplastics during processing can be prevented.

Venderbosch et al. (1994a) reported that the DGEBA is an excellent reactive solvent for making epoxy/PPE resin system. Also PPE/DGEBA epoxy system observed an upper critical solution temperature (UCST) phase diagram. During processing, the DGEBA (act as solvent in the system) significantly reduce the processing temperature and viscosity of the polymer. After the molding process, DGEBA is converted into the interpenetrating network by polymerization reaction. It is reported that in 20–50 wt.% of PPE content in the blend system, phase separation is accompanied by phase inversion, leads to a unique morphology of epoxy-rich spheres uniformly dispersed in PPE matrix. The phenomenon of locking the original solvent by the phase inversion (polymerizing to thermosetting resins) inside the thermoplastic matrix material is termed as "reaction-induced or chemically induced phase separation (Williams et al. 1996). In 2000, Yoshiyuki and Ryan (2000) investigated the reaction-induced phase separation of epoxy/PPE blends using a specially constructed time-resolved light scattering camera equipped with DSC and observed the chemical gel point not being a true phase transition; however, the reaction remains homogeneous throughout matrix. Because of this, the thermodynamics of the mixture (monomers inside the homopolymer matrix) is considered to be a pseudo-binary system, in which one phase is the homopolymer and the other is the reactant mixture (Venderbosch et al. 1994b; Cahn and Hilliard 1958).

The thermal analysis of epoxy/PPE system revealed the demixing and vitrification of the blend. It was reported that after quenching, the epoxy/PPE blend behaves as a two-component system which gives two separate $T_g$ which are associated with the $T_g$ of the PPE-rich phase and epoxy-rich phase. For example, the blend having 60 wt.% PPE shows two transition temperatures at $-5$ and 110 °C, which corresponds to the $T_g$ of PPE and epoxy, respectively. When thermal analysis is performed on a 20% solution of PPE, only the lower $T_g$ is observed (Yoshiyuki and Ryan 2000). The thermal studies showed that the vitrification of the PPE-rich phase occurs when the phase reaches the Berghmans point (Callister et al. 1990), which is the intersection between the coexistence curve and $T_g$ composition line defined by the Fox equation (Fox and Loshaek 1955), and no phase separation is possible thereafter. It is also reported that due to the small heat of mixing, there is no thermal transition in association with phase separation (Vandweerdt et al. 1991).

## Epoxy/Terpolymer or Tri-block Copolymer Blends

### Epoxy/Poly(acrylonitrile-*block*-butadiene-*block*-styrene) (ABS) Blends

Terpolymers are a special class of macromolecules from three species of monomers to exploit the advantageous properties of different polymers, which are not easy to make the miscible blends. Terpolymers of poly(methyl methacrylate-acrylonitrile-vinyl acetate) {P(MMA-AN-VAc)} (Liao et al. 2009; Chen et al. 2011; Kim 1998, 2000; Kim and Yang-Kook 1998) and poly(methyl methacrylate-vinyl acetate)-*co*-poly(ethylene glycol) diacrylate {P(MMA-VAc)-PEGDA} (Liao et al. 2011) have been reported for different applications. It is found that the comprehensive performances of terpolymer are much better than that of copolymer or its blends. The tri-block copolymers have been widely used as modifiers to toughen epoxy resins. One of the most important properties of these block copolymers is its ability to self-assemble into different nanoscale structures in the thermosetting matrix via interpenetration or phase separation. The unique nanoscale morphologies of the thermoplastic tri-block polymers are generally formed before or during the curing process. These microphase-separated or interpenetrated network structures result from the competition between chain connectivity and block immiscibility. For such tri-block copolymers, e.g., poly(styrene-*block*-butadiene-*block*-methyl methacrylate) (P-SBMMA) or poly(acrylonitrile-*block*-butadiene-*block*-styrene) tri-block copolymers abbreviated as ABS, the morphology is influenced by the repulsive forces between the polybutadiene (PB) mid-block and both polystyrene (PS) and poly(acrylonitrile) end blocks.

In an earlier work (Finaz et al. 1967), block copolymers are limited to soluble polymers which are dissolved in reactive solvents like styrene; however, the method is revalorized recently using thermoset precursors like epoxy (Mijovic et al. 2000; Lipic et al. 1998) and phenolic systems (Kosonen et al. 2001). In a classical thermoplastic linear homopolymer-modified thermosetting system, the thermoplastic chain modifier and the thermosets prepolymer are initially miscible. During curing process, the molar mass of the epoxy resin and its increase involves a decrease in the conformational entropy of mixing, which leads to the phase separation between the thermoplastic and the step-growing thermoset network, generally well before gelation (Pascault and Williams 2000). On contrary to the classical linear homopolymer-modified thermosetting system, macroscopic phase separation can be suppressed or avoided with block copolymers due to the fact that amphiphilic di-block or tri-block thermoplastic copolymers, with one block miscible with the thermoset, are not only dispersible in a reactive prepolymer thermosetting system but also able to order themselves on the micrometer to nanometer scale in both the thermoset prepolymer and cross-linked states, which is successfully demonstrated by different research groups (Mijovic et al. 2000; Hillmyer et al. 1997; Kosonen et al. 2001). Inspiration from di-block copolymer system, tri-block thermoplastic polymers such as ABS (Jyotishkumar et al. 2009, 2011), poly(ε-caprolactone)-*block*-PPC-*block*-poly(ε-caprolactone) (PCL-PPC-PCL) (Fanliang et al. 2006), and polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) tri-block copolymers (Ritzenthaler et al. 2002) have been investigated as chain modifier in the epoxy thermosetting systems.

Poly(acrylonitrile butadiene styrene) (chemical formula, $(C_8H_8)_x{\cdot}(C_4H_6)_y{\cdot}(C_3H_3N)_z$) is a common thermoplastic polymer having glass transition temperature of approximately 105 °C. ABS is an amorphous terpolymer prepared from styrene and acrylonitrile monomers polymerized in the presence of polybutadiene and has no true melting point. Recently, the thermal properties of ABS-modified epoxy blends are reported by Jyotishkumar et al. (2009). The study showed complex phase separation in ABS-modified epoxy/4,4′-diaminodiphenyl sulfone (DDS) blends. The amount of ABS in the blends was kept from 5 to 20 parts per hundred parts of epoxy resin (phr). At a lower concentration of ABS ($<10$ phr), the phase separation of the system takes place through nucleation and growth (NG), while at higher concentrations ($>15$ phr), the phase separation occurs due to both NG and spinodal decomposition. It is reported that the epoxy blend is heterogeneous in nature.

In DMA studies, the authors observed a higher relaxation peak around 210 and lower relaxation peak at 110 °C, which corresponds to the $T_g$ of the epoxy-rich and SAN-rich phase of ABS, respectively, in the modified blends. The tan $\delta$ curve of the unmodified epoxy network and the cross-linked epoxy blends however showed a relaxation peak of very low amplitude at around −65 °C which caused by the segmental motions of glycidyl units in the network (Guo et al. 2001). The dynamic mechanical spectrum of pristine ABS (tan δ vs. temperature plot) has two sharp relaxation peaks at −88 °C and 107 °C corresponding to the $T_g$ of the polybutadiene and SAN-rich phase, respectively. For the unmodified epoxy network, there is a well-defined sharp relaxation peak centered at 216 °C and corresponds to the $T_g$ of the amine-cured epoxy resin which is in well agreement with the $T_g$ of the cross-linked epoxy/DDS system in the literature (Grillet et al. 1989). The modification of epoxy with ABS caused a slight shift in $T_g$ of epoxy-rich phase to the lower side. The shifting of $T_g$ to the lower end is explained by the following reasons:

(a) The decrease in the cross-link density of the cured blends, due to the increase in viscosity by the addition of thermoplastic material in to the epoxy system, in turn result in an incomplete cross-linking due to the kinetic factors.
(b) The addition of thermoplastic causes dilution effect, which may also result in an incomplete cross-linking.
(c) The addition of thermoplastics into the epoxy cause the formation of substructures, which results in subinclusions of the ABS-rich phase in the continuous cross-linked epoxy region, leading to increased miscibility between both the epoxy and ABS phases.

The $T_g$ of the SAN phase of ABS remains the same for 5 and 10 phr in epoxy/ABS blends. For 15 and 20 phr ABS-modified epoxy blends, however, the $T_g$ of the SAN phase increases to a higher temperature. The intensity of tan $\delta$ peak for cross-linked epoxy/ABS blends is reported to be higher than for the unmodified amine cross-linked epoxy resin which is associated with changes in the cross-link density. This may also be due to a small amount of ABS molecules dissolved in the epoxy system. Rao et al. (2005) also reported that the addition of the thermoplastic to the epoxy resin increases the viscosity of the material, and hence, the cross-link density decreases upon curing, which results in higher segmental mobility, thereby higher peak intensity. The peak areas and peak widths of the epoxy blends, however, are comparable to those of the unmodified epoxy cross-linked resin. There are two inflection points observed for the ABS-modified cross-linked epoxy blend, one at the $T_g$ of the SAN phase of ABS and the other at the $T_g$ of the cross-linked epoxy resin, while the unmodified cross-linked epoxy resin has only one inflection. The storage modulus of the blends (ABS content $\leq$15%) is higher than unmodified epoxy network for the entire spectrum of temperature. As the ABS content increase from 10 phr, the storage modulus of the cross-linked epoxy blends is higher than the unmodified epoxy network up to 110 °C; thereafter, it goes down to that of the unmodified epoxy network, which may be due to the bicontinuous nature of the blends (Jyotishkumar et al. 2009).

Jyotishkumar et al. (2011) studied the stress relaxation and thermomechanical properties of poly(acrylonitrile butadiene styrene)-modified epoxy-amine systems. Epoxy networks based on DGEBA cured with DDS (both ABS modified and unmodified) were prepared according to two different cure schedules. One set of samples were prepared through a single-step and the other through a two-step curing process. The lower concentration of ABS (≤6.9 wt.%) in the epoxy resin resulted in more than 100% increase in tensile toughness compared to neat cross-linked epoxy. The presence of internal stress affects the dimensional stability of the blends at high temperatures (above the $T_g$ of ABS). The internal stress however can be removed by two-step curing. The impact of the cure schedules and the increasing ABS concentration on properties were carefully analyzed. Irrespective of the cure schedule, the thermal and mechanical properties remain comparable. On the other hand, the mechanical and morphological properties are affected by blending with the thermoplastic (Jyotishkumar et al. 2011).

## Epoxy/Polyoxymethylene (POM) Blends

The mutual influence between isothermal crystallization and reaction-induced phase separation in epoxy/polyoxymethylene (POM) blends is recently reported by Sara and Gabriël (2006). The development of phase morphology in blends of DGEBA/POM/DDS was studied at cure temperatures between 140 and 150 °C, which is lower than the melting temperature of POM. The phase separation behavior of the blends varying from 5 to 30 wt.% POM content was examined with optical microscopy (OM), small-angle laser light scattering (SALLS), and SEM. Different demixing mechanisms were observed depending on the blend composition. At a high curing temperature (150 °C), a reaction-induced phase separation (RIPS) followed by crystallization inside the POM-rich matrix phase was observed. When the sample was cured at 145 °C, all blends showed spherulitic crystallization starting before the RIPS which leads to a gradient of phase-separated structures. This characteristic of the blend is attributed to the inter-spherulitic demixing that may be suppressed by the increase in the nucleation density. In brief, the properties of the blend can be altered by changing the thermal history of the thermoplastic in the blends or by lowering the cure temperature to 140 °C. The increase of the growth rate has been attributed to the increase of the super cooling due to the decrease of the melting point depression caused by the polymerization of the epoxy resin (Sara and Gabriël 2006).

## Epoxy/PCL-PPC/PB-PCL Blends

Recently, it is reported that interactions between thermoset matrix and modifiers can further be optimized by the formation of ordered (disordered) nanostructures in thermosets, which endow the materials with improved properties (Hillmyer et al. 1997; Lipic et al. 1998). Based on the catch, there are few reports on epoxy-based nanostructures formed with thermoplastic modifiers. Epoxy blended with PCL-PPC-PCL or PC-PB-PCL is a tri-block copolymer caught attention recently due to the miscibility of PCL in epoxy. The use of PCL-PPC-PCL or PCL-PB-PCL enables innovative application of PPC as a toughening agent of epoxy thermosets. Fenget et al. (Fanliang et al. 2006) reported the application of sustainable PPC copolymer for toughening epoxy thermosets. PPC is used as a novel initiator for ε-caprolactone polymerization to produce the tri-block copolymer.

PCL-PPC-PCL (Chen et al. 2015) and PCL-PB-PCL (Fanliang et al. 2006) were synthesized via the ring-opening polymerization of ε-caprolactone in the presence of a hydroxyl-terminated polybutadiene (HTPB), and the polymerization reaction is catalyzed by stannous octoate [$Sn(Oct)_2$]. The resulting amphiphilic PCL-PPC-PCL or PCL-PB-PCL tri-block copolymer is used to prepare the nanostructured epoxy thermosets via blending with epoxy resin (Chen et al. 2015) or in situ polymerization (Fanliang et al. 2006). The epoxy monomers are polymerized in the presence of PCL-PB-PCL or PCL-PPC-PCL, which is dissolved in THF at the temperature above the upper critical solution temperature of DGEBA and HTPB blends, and 4,4′-methylene *bis* (2-chloroaniline) (MOCA) is used as the cross-linking agent.

When amphiphilic tri-block copolymer PCL-PPC-PCL or PCL-PB-PCL tri-block thermoplastic polymer is used to prepare the nanostructured epoxy thermosets, the PCL blocks in the terpolymer are miscible with the cross-linked epoxy networks, i.e., the PCL subchains in the tri-block copolymer are easily interpenetrated into the cross-linked epoxy network at the segmental level; hence, the interfacial interaction between PPC modifiers and epoxy was enhanced significantly. Due to the miscibility of PCL blocks with epoxy matrix, the size of phase-separated PPC modifiers decreased dramatically as the amphiphilic block copolymer formed nanophases in epoxy host. The miscibility of PCL in epoxy facilitates the easy incorporation of 30 wt.% PCL-PPC-PCL modifier in the epoxy thermoset without the formation of any microdomains. For the lower concentration of PCL-PPC-PCL, it is observed that epoxy-rich components are composed of the cross-linked epoxy networks which are interpenetrated by the PCL blocks of the copolymer, whereas the PB domains form the nano-islands due to its incompatibility with epoxy resin. Depending on the content of the block copolymer in the thermosets, the PB domains exhibit spherical and interconnected nano-objects having the particle size varying from 10 to 20 nm. For the TS/TP blend containing 10 wt.% of PCL-PB-PCL tri-block, the nanosized phase-separated PB particles were imbedded in the continuous epoxy matrix at the average size of ca. 10 nm in diameter. When the thermoplastic content increases beyond 10 wt.%, the nanosized phase-separated PB particles began to coagulate in the continuous epoxy matrix resulted in the formation of some PB domains (wormlike objects in the epoxy matrix), and while the concentration of PCL-PB-PCL increased to $\geq 30$ wt.%, the epoxy component began to form some separated nanosized particles or wormlike objects. The number of the spherical objects increased, whereas the average distance between adjacent domains decreased with increasing the content of PCL-PB-PCL in the thermosets; however, the size of the nanoparticles almost remains invariant. When the content of PCL-PB-PCL is 20 wt.%, the spherical particles began to interconnect to some extent; hence, the thermoset at this composition possesses a combined morphology, in which both spherical PB domains and few interconnected PB domains were simultaneously present. When the content of PCL-PB-PCL was increased up to 30 wt.%, the domains of PB were highly interconnected, forming interconnected objects at the nanometer scales. This morphology is a typical structure of bicontinuous microphase separation. The formation of nanostructures takes place on the basis of the mechanism of polymerization-induced microphase separation. The morphology of nanostructures is controlled by the microphase separation of PB blocks, which is induced during the polymerization of epoxy other than by fixing the preformed self-assembly microphases in the mixtures of the block copolymer and the epoxy precursors. The reaction-induced microphase separation of PB blocks in the thermosets predominated due to the its lower entropic contribution to free energy of mixing for the mixing of PB blocks with cross-linked epoxy networks (Fanliang et al. 2006).

The thermal properties of cross-linked epoxy networks with PCL and PPC blocks studied by DMA (Chen et al. 2015) showed that the pristine epoxy exhibited a well-defined $T_g$ (α-transition) at 146 °C. It is also reported that, apart from α-transition, it exhibits a secondary relaxation peak (β- transition) from about −50 to −60 °C, which is predominantly attributed to the motion of hydroxyl ether structural units and diphenyl groups in epoxy (Xu et al. 2007a). Since the $T_g$ of PPC is about −53 °C, the α-transition of PPC nanodomains is overlapped with the β- transition of epoxy in epoxy/PCL-PPC-PCL thermosets, which leads to make difficulties to distinguish $T_g$ of PPC in the DMA analysis of thermosets containing the PCL-PPC-PCL tri-block copolymer. Upon incorporating the thermoplastics PCL-PPC-PCL tri-block copolymer into the thermosets, the $T_g$ of the matrix shifts to a lower temperature, which indicates the miscibility of the PCL subchains and epoxy matrix. The effect is more predominant with increasing PLCL-PPC-PCL tri-block content. As a result of interpenetrating morphology of PCL and the formation of nanodomain of PB in the thermoset, the PCL-PPC-PCL modifier possesses an excellent toughening effect for epoxy thermosets in spite of sacrificing part of the strength and thermal property of the matrix (Chen et al. 2015).

Before curing, all the epoxy precursors, curing agents, and PCL-PPC-PCL (or PPC) were transparent at room and elevated temperatures. After curing at a setting temperature, the thermosetting blend containing PPC and PCL homopolymers becomes cloudy (losing its transparency), implying the occurrence of macroscopic phase separation. All the thermosets containing the PCL-PPC-PCL tri-block copolymer are homogeneous and transparent, which suggests that there is no macroscopic phase separation at least on the scale exceeding the wavelength of visible light (Fig. 10) (Chen et al. 2015). Li et al. also reported that PPC is miscible with EP precursors; however, reaction-induced phase separation occurs during the curing (Li et al. 2010).

## Epoxy/Poly(ether imide) (PEI) Blends

Bonnet and coworkers (1999a) reported the similar thermal behavior in epoxy/Poly (ether imide) (PEI) blends discussed in earlier section “Epoxy/PCL-PPC/PB-PCL Blend” for epoxy/tri-block thermoset thermoplastic blends. In 1999, Bonnet et al. (1999b) studied the rates of epoxy-amine reactions in TS/TP blends with different thermoplastic concentrations. The thermoset system selected for the study was

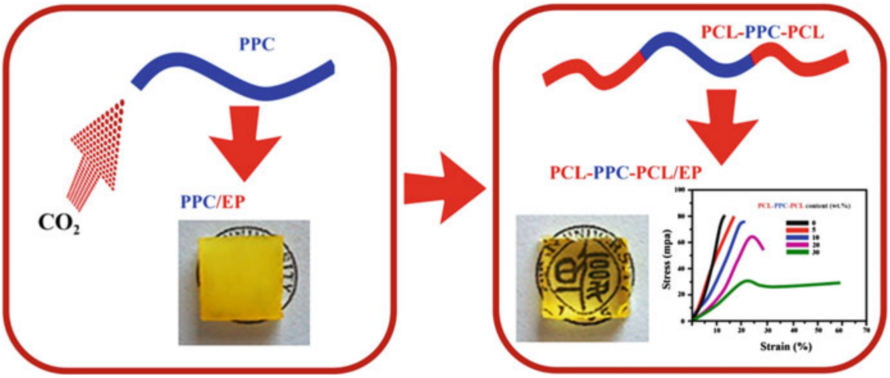


**Fig. 10** The effect of PCL in the transparency of epoxy blend system (Adopted from Chen et al. 2015)

DGEBA-based epoxy cured with 4,4′-methylene *bis*(3-chloro-2,6-diethylaniline) in the presence of varying PEI concentrations (10-64 wt.%). The studies reported the rates of reaction in amorphous thermoplastic-modified epoxy systems depending on the initial concentrations of thermoplastic, and the authors highlighted two specific behaviors of the system as follows:

(i) For thermoplastic concentration ≤10 wt.%, no sudden change in the kinetic rates was detected when phase separation occurred, due to the low quantity of dispersed phase.
(ii) For thermoplastic concentrations higher than 30%, an increase of the reaction rate is observed when phase separation occurred, due to the appearance of a less dilute epoxy-amine phase.

It is well known that block copolymers have the ability to form micelles in the selected nonreactive organic solvents. For instance, poly(styrene acrylonitrile) di-block copolymer in a selective solvent (e.g., acetone) is a good solvent for styrene block but poor for acrylonitrile; hence, the block copolymer molecules tend to associate into acrylonitrile core/styrene shell spherical micelles (Chu et al. 1997).

Buchholz et al. and Könczöl et al. (Buchholz and Mülhaupt 1992; Könczöl et al. 1994) incorporated low molar weight poly(ε-caprolactone)-*block*-poly(dimethyl siloxane), $(PCL)_2$-*b*-PDMS-*b*-$(PCL)_2$, and branched tri-block copolymers in epoxy matrix. The aim was to improve mechanical properties of epoxy network with the immiscible elastomeric PDMS blocks compatibilized by the PCL segments, initially miscible in epoxy precursors. Even if the structure obtained before reaction is not detailed, elastomeric particles of 20 nm in diameter, uniformly dispersed in the epoxy matrix, are generated at the end of the curing process. Addition of tri-block copolymer (>5 wt.%) leads to an increase in the toughness by a factor of more than two, without reduction of the strength at break and Young's modulus when compared to the neat epoxy system.

## Epoxy/Poly(styrene-*block*-butadiene-*block*-methyl methacrylate) (P-SBMMA) Blends

Ritzenthaler et al. (2002) studied the tri-block copolymers/epoxy-diamine blends. The tri-block polymer used is P-SBMMA tri-block copolymers. The tri-block copolymer (P-SBMMA) has been selected in the study due to the following reasons.

(a) When looking in to the literature which are devoted to tri-block copolymers, the most important theoretical (Zheng and Wang 1995) and experimental studies (Auschra and Stadler 1993; Abetz and Goldacker 2000) have been carried out on (P-SBMMA).
(b) More recently, the morphological behavior of a polystyrene-*block*-polybutadiene-*block*-poly(ethylene oxide) tri-block copolymer also has been studied (Bailey et al. 2001).
(c) Polybutadiene (PB) is immiscible with the epoxy precursor, which leads to an initial macrophase separation between PB and epoxy monomers (Chen et al. 1994).
(d) In the initial stage, the homo-polystyrene is partially miscible with the epoxy precursors (a homogeneous solution can obtained at a temperature higher than 90 °C, whereas decreasing temperature involves phase separation between homo-polystyrene and the epoxy monomers).
(e) The homo-poly(methyl methacrylate) was previously shown to be completely miscible with epoxy prepolymer (Ritzenthaler et al. 2000).

Epoxy thermoset blended with P-SBMMA tri-block copolymers (10–50 wt.%) is synthesized anionically and has been investigated for its morphological and thermo-mechanical properties before and after the epoxy-amine reaction. Before the cross-linking reaction, the three blocks self-organize on a nanometer scale, in such a way that PS spheres surrounded by PB nodules, while the PMMA blocks are solubilized with the epoxy precursors, forming a swollen corona. When the PB blocks aggregate into spherical domains at the interface between the epoxy-rich matrix and PS block nano-spheres, the epoxy components swells the MMA blocks, thereby inducing a morphological transition from PB helices around PS cylinders (the morphology of the neat tri-block) to PB spheres on PS spheres. This indicates that the PS blocks are microphase separated from the epoxy system even before reaction. Also even after using MCDEA as hardener, the domain sizes of the thermoplastic chain modifiers remain unaffected throughout the network frames, and the final structure of the blend system has “spheres on spheres” morphology of undiluted PS block sphere formed on PB blocks spheres, while most of the PMMA chain remaining embedded in the epoxy network frames. The thermal behavior of PMMA blocks in the blend system is investigated on the fully reacted sample in different temperature from room temperature to 250 °C using DMA and found that there are three different relaxations that correspond to the $T_g$ of epoxy-rich phase, relaxation of pristine PMMA blocks, and pristine PS microdomains in the blend. The relaxation observed for the epoxy/tri-block blend at 163 °C is associated with the glass transition temperature of the epoxy-rich phase. The shift of relaxation temperature from 163 °C to lower temperature compared to the one of the neat DGEBA-MCDEA network (187 °C) is ascribed to the plastification effect induced by the incorporation of PMMA blocks in the epoxy network. Ritzenthaler et al. (2000) also has reported same phenomena for miscible DGEBA-MCDEA/PMMA homopolymer blends. The high-temperature relaxation at 130 °C ($T_g$ of PMMA homopolymer) and the low-temperature relaxation at 97 °C ($T_g$ of PS homopolymer) ascribed to the chain relaxation of microphase-separated pristine PMMA units from the epoxy-rich matrix and pristine PS domains in the epoxy matrix, respectively.

## Epoxy/Poly(styrene-*block*-butadiene-*block*-styrene) (SBS) Blends

Sajeev et al. (2014) recently (in 2014) reported the blend of epoxidized poly(styrene-*block*-butadiene-*block*-styrene) (SBS) tri-block copolymer and epoxy based on DGEBA with 4,4′-diaminodiphenylmethane (DDM) curing agent. Before blending with epoxy, SBS tri-block copolymer is epoxidized to a 47 mol% (denoted as eSBS47, having degree of epoxidation 47%) by hydrogen peroxide in a water/dichloroethane biphasic system, and the thermal properties of the modified system are analyzed using differential scanning calorimetry (DSC), DMA, thermomechanical analysis (TMA), and thermogravimetric analysis (TGA). The epoxy/tri-block copolymer blends with 10–20 wt.% eSBS were prepared by simple solvent casting technique. The onset temperature of molecular chain relaxation, i.e., $T_g$, and heat flow (ΔH) is studied by DSC in a temperature range of −30 to 300 °C on the samples cured for different cure times varying from 0 to 360 min at 90 °C to understand the thermal behavior of epoxy/eSBS tri-block blend system under dynamic conditions. DSC studies revealed that in the case of neat epoxy or blends cured in the shortest times, an exothermic peak was observed in the DSC thermograms which indicates that the curing reaction was not completed during cross-linking reaction, which in turn leave some cross-linking sites in the epoxy/eSBS tri-block blend system. A broad exothermic peak is observed on the DSC thermograms of uncured epoxy blend system (cure time $t = 0$) which is the direct measure for the enthalpy of cross-linking reaction. There is no exothermic peak observed for the completely cured epoxy/eSBS tri-block blend system (cure time $\geq$90 min) and enthalpy of the reaction found to be decreasing with increasing cure time from 0 to 90 min. This does not indicate that all of the entire epoxide groups and amino hydrogen atoms were involved in the formation of 3D-network structures during the cross-linking reactions; however, the mobility of some of the reactive sites might have been frozen, which stops the polymerization reaction. Recently, other than epoxy/amine hardener system, similar exothermic peaks in the DSC thermograms are observed by Garate et al. (2013) for the epoxidized poly(styrene-*block*-isoprene-*block*-styrene) (SIS)/hardener reaction. This behavior, however, is not observed in George et al. (2012) studies for the same epoxy resin and epoxidized styrene-*block*-butadiene-*block*-styrene tri-block copolymer blend systems.

In Sajeev et al. (2014) studies on the blend of eSBS tri-block copolymer and epoxy polymer blend system, upon addition of eSBS to the epoxy matrix, the fracture toughness of the nanostructured thermosets is improved, while the thermal stability was retained; however, the dimensional stability was slightly decreased. The storage modulus (G′) versus temperature curves of the pristine amine-cured epoxy resin showed a higher G′ value compared to the nanostructured epoxy thermosets blends with 10 and 20 wt.% eSBS tri-block copolymer. The lower G′ value of nanostructured epoxy/eSBS tri-block copolymer blends ascribed to the plasticizing effect of less stiff eSBS tri-block copolymer, basically resulted from its miscibility with the epoxy-rich phase, which in turn resulted in reduction in modulus of the TS/TP blends (Xu et al. 2007b). It is also reported that the cross-linked epoxy phase exhibited a well-defined α-transition centered at 130 °C and a weak relaxation at around 40 °C, which is called the ω-relaxation peak due to the lower cross-link density in the epoxy network. On the other hand, in addition to the α and ω transitions, the eSBS nanostructured tri-block thermoplastic blends exhibited an additional minor transition at around 90 °C ($T_g$ of PS) that corresponds to the molecular relaxation of phase-separated PS nanodomains. Also for all the epoxy/eSBS tri-block blend system, the tan δ profile showing a sharp relaxation peak centered at around 150 °C corresponds to the $T_g$ of the amine-cured epoxy resin. A broadening of the tan δ peak is observed for the nanostructured blends and is slightly overlapped with the $T_g$ of the PS domains in the tri-block blend system. The $T_g$ value of the pristine epoxy system was found to be 10 to 20 °C higher than epoxy/tri-block thermoplastic blend with 10 and 20 wt.% eSBS chain modifier. The decrease in $T_g$ in the blend system is due to the:

(a) Plasticizing effect of the nanodispersed eSBS copolymer in epoxy system
(b) Miscibility of eSBS tri-block copolymer with epoxy resin
(c) Uniform dispersion/distribution of eSBS nanodomains in the epoxy
(d) Reduction in crystallinity or enthalpy due to the plasticizing effect of eSBS

The lower $T_g$ of the epoxy/tri-block polymer system indicates that the eSBS tri-block subchains were effectively interpenetrated into the cross-linked epoxy matrix at the segmental level (Meng et al. 2006b). In addition to the main relaxation peak, there were two other minor relaxation peaks of very low amplitude also reported, the one at around −65 and other at 65 °C, called β-relaxation corresponds to the motion of glycidyl units in the epoxy network (Guo et al. 2001) and ω-relaxation peak, which is due to the lower cross-link density in the epoxy network, respectively (Francis et al. 2006).

The thermal stability study of the epoxy/tri-block copolymer blend system showed there is no weight loss or release of any small molecular weight molecules from the host upon heating, and the whole spectrum of the TS/TP blends was thermally stable up to 350 °C. Above 350 °C, considerable weight loss is observed due to the chain scission of polymer molecules. The temperature of the maximum rate of decomposition ($T_{peak}$) was found to be 377–383 with eSBS tri-block copolymer content of 0–20 wt.%. The $T_{max}$ shows an increasing trend with nanodispersed eSBS tri-block nanodomains, and no drastic change in thermal stability is observed for the TS/TP blend system which in turn indicates that the thermal stability of crosslinked epoxy system is not adversely affected by the incorporated eSBS tri-block copolymer chain modifiers.

The influence of temperature on dimensional stability (studied by TMA) is studied and reported that the dimensional changes with temperature for the epoxy/eSBS tri-block copolymer blend system are greater than pristine epoxy system over the complete range of temperature due to the higher molecular vibration at higher temperatures. The increase in molecular vibration in eSBS tri-block copolymer may be due the availability of increased intermolecular distance resulted from the plasticizing effect of tri-block eSBS soft polymer chains, which leads to the increased thermal expansion for the blends. In the case of the pristine epoxy system, a drop in the dimensional change near $T_g$ is observed due to relaxation of nonequilibrium states of the cured samples that are frozen below $T_g$. Similar phenomenon is also recently reported for epoxy/multiwalled carbon nanotube (MWCNT) composites cured with DDS (Jyotishkumar et al. 2013a, b). At a temperature close to the $T_g$, the motion capacity of the chain segment is high enough to unfreeze the frozen chains, so that the vacant spaces will be lost which results in a drop in dimensional change. The schematic (Fig. 11) represents the mechanism behind the freezing of such local sites in the nanostructured thermosets due to the insertion of tri-block

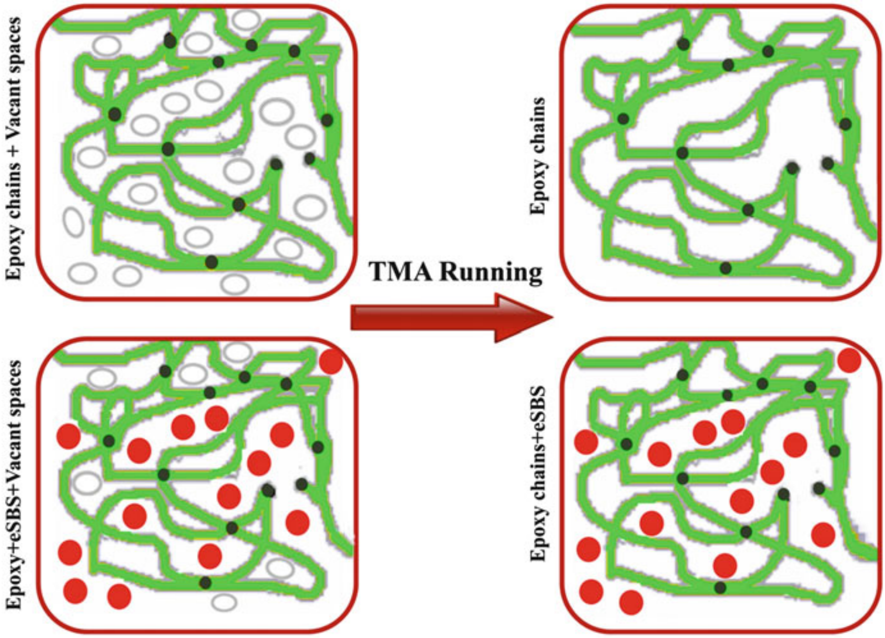


**Fig. 11** Schematic of the mechanism for the drop in dimension change near $T_g$. (Adopted from Sajeev et al. 2014)

thermoplastics or associated mixing in pristine and blend epoxy system (Sajeev et al. 2014).

Recently, it was reported that epoxidized butadiene block of a di-block copolymer poly(styrene−butadiene) and a tri-block copolymer SBS and SIS and isoprene block of SIS for developing the nanostructured thermosets/tri-block copolymer thermoplastic blends (Garate et al. 2013; Serrano et al. 2006, 2007; Ramos et al. 2012; Ocando et al. 2013). The effects of the eSBS tri-block copolymers, however, on the rheological, viscoelastic, thermal, dimensional, and fracture toughness properties in the epoxy/eSBS tri-block copolymer blend system cured with DDM have never been reported.

## Conclusions

Blending of brittle epoxy resins with suitable thermoplastics, having high elastic modulus and high glass transition temperature ($T_g$), with an aim to enhance their fracture toughness and thermal resistance, has been a relevant topic in the current research scenario. Various studies which were carried out using different thermoplastic systems such as ABS, P(MMA-VAc)-PEGDA, PB, PCL-PPC-PCL, PEI, PEO, PGA, PPO, and P-SBMMA for toughening the epoxy resin have been thoroughly analyzed. In this chapter, the authors have tried to give a detailed overview on the various approaches and methods adopted for toughening epoxy resin with thermoplastics and the mechanisms of toughening of epoxy with special attention to the thermal properties of the blends. The important factors which control the thermomechanical behavior and morphology of the epoxy/thermoplastic blend are the backbone structure, molecular weight, and the end-group chemistry of the thermoplastics. Epoxy/thermoplastic blends thus produced find many applications such as engineering materials for aircraft, electronic, construction, and automobile industries.

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