Introduction to Epoxy/Block-Copolymer Blends

28

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Abstract

Formation of nanostructures inside epoxy thermosets by the inclusion of appropriate block copolymers (BCPs) has been emerged as a promising approach to optimize epoxy thermoset material properties for potential applications. For the last two decades, tremendous efforts have been made by researchers to create ordered or disordered nanostructures in epoxy thermosets by the incorporation of reactive or nonreactive BCPs in an attempt to develop toughened thermosets suitable for specific applications. This chapter briefly reviews the different mechanisms of phase separation in epoxy/BCP systems, such as self-assembly and reaction-induced microphase separation (RIMPS), and outlines some of the important features of nanostructured morphologies and their influence on fracture toughness of fabricated products.

Keywords

Epoxy resins • Block copolymers • Self-assembly • Reaction-induced microphase separation • Nanostructured morphology • Fracture toughness

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Contents

Introduction

Epoxy resins, probably the most versatile family of structural adhesives, are extensively used as matrices for the fabrication of high-performance polymeric materials for engineering applications, especially in automobile and aerospace industries (Pascault and Williams 2010). Their global market size is forecasted to reach ca. US\$ 10.55 billion in 2020 from US\$ 7.1 billion in 2014, registering an increase of ca. 50% in a 6-year period (www.transparencymarketresearch.com/epoxy-resins-market.html). It is widely recognized that the intrinsic brittleness, considered as the main limitation which restricts epoxy thermosets to be used as potential materials for many engineering applications, can be alleviated by the incorporation of appropriate amount of judiciously selected functionalized elastomers and engineering thermoplastics but at the expense of stiffness and/or use temperature. Nowadays, researchers and industrialists are more interested in block copolymer (BCP) modified tough thermosetting systems, which neither compromise with stiffness nor with T_g. In general, amphiphilic BCPs have at least one of their blocks miscible with epoxy thermoset while reactive BCPs contain functional groups in one of the blocks to facilitate specific interactions which enhance chemical compatibility with the matrix.

The pioneering work of Hillmyer et al. (1997) on the self-assembly and polymerization of epoxy resin/BCP system reported that the cross-linking of the epoxy matrix without macrophase separation of BCP yields optically homogenous materials containing nanoscopic core/shell-like morphology. In the following year, Hillmyer and coworkers (Lipic et al. 1998) established that a sequence of morphologies such as lamellar, cylindrical, cubic, and disordered micelles could be achieved by varying the composition of epoxy/BCP system without a curing agent, while cured system retains nanostructure without undergoing macrophase separation. This remarkable discovery instigates enormous interest among researchers and opens a fundamentally new class of nanostructured epoxy/BCP systems, using a novel method of templating ordered structures in thermosetting matrix on a nanometer scale. This fascinating property of BCP to self-assemble into highly ordered nanostructures in thermosetting matrix make them suitable candidates for the fabrication of nanoporous materials having many potential applications including templating, surface patterning, support for catalysts, and size-selective separation. Figure 1 shows the TEM micrographs of various nanostructured morphologies generated in epoxy/BCP blends (Dean et al. 2003).
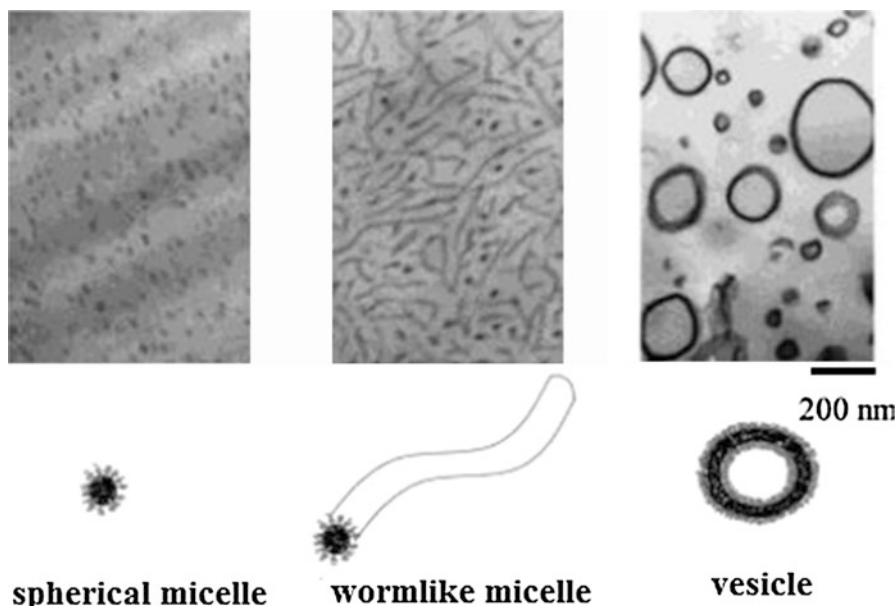
Fig. 1 TEM images showing various nanostructured morphologies generated in epoxy/BCP blends (Reprinted with permission) (Dean et al. 2003)

Eventually, various researchers have attempted several interesting variations to this protocol and revealed that significant improvements in fracture toughness can be achieved without compromising the stiffness, modulus, and T_g by incorporation of a small amount of microphase-separated amphiphilic BCP into epoxy thermoset. In the succeeding years, researchers were successful to develop another promising approach to generate nanostructures in thermosetting matrix through a mechanism called reaction-induced microphase separation (RIMPS). These two approaches, viz., self-assembly and RIMPS, now regarded as convenient and time-proven means to create nanostructures in thermosetting matrix, could be employed to develop epoxy system with remarkably enhanced toughness.

Mechanism of Phase Separation

Self-Assembly

The creation of self-assembly nanostructures discovered by Hillmyer and colleagues is regarded as one of the most outstanding achievements in this field. In this approach, precursors of epoxy form a selective solvent for BCPs, which usually contain "epoxy-philic" and "epoxy-phobic" blocks. Before curing reaction, depending on the blend composition, BCPs self-assemble into micellar structures so that the mixture exhibits distinct morphologies with lamellar, bicontinuous, wormlike,
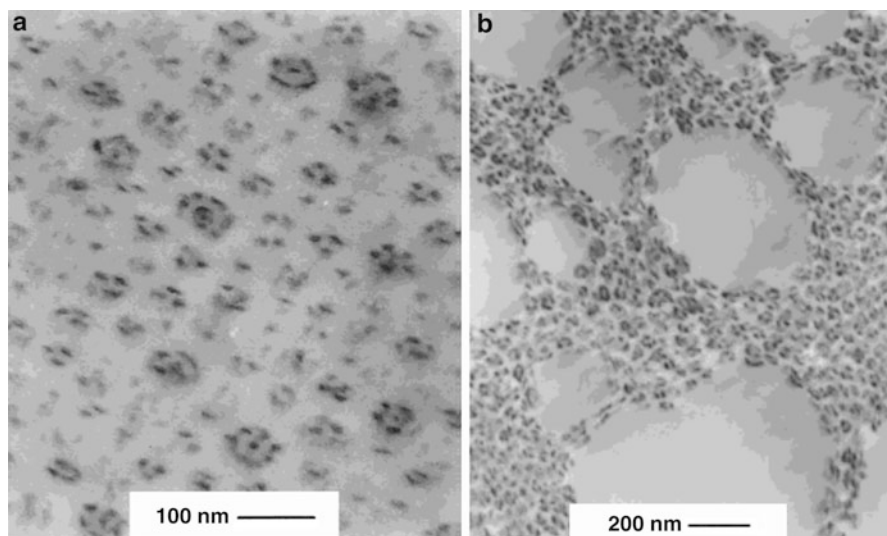
Fig. 2 TEM images (**a**) showing "raspberry-like" morphology for epoxy/SBM cured with MCDEA (**b**) the same system cured with DDS showing macrophase separation (Reprinted with permission) (Ritzenthaler et al. 2002)

spherical, and other interesting structures. Figure 2 shows the morphologies derived from the self-assembly of BCP in epoxy thermosets (Ritzenthaler et al. 2002).

In addition to blend composition, other parameters like molecular weights, block length, and block-block and block-matrix interaction parameters have profound influence on the type of self-organized structures. These preformed structures are fixed through the subsequent cross-linking with the introduction of hardeners, when curing reaction lock in the generated morphology. Note that there may be small changes in the nanostructures before and after curing reaction. Table 1 displays some of the epoxy/BCP systems which form nanostructured morphology via self-assembly.

Reaction-Induced Microphase Separation

In contrast to self-assembly approach, the RIMPS technique does not necessitate the formation of self-organized micellar structures before curing reaction. In this case, BCP will be miscible with the epoxy precursors before curing reaction, and a part of BCP gets microphase separated during curing because the polymerization increases the molecular weight of the epoxy thermoset and thereby reduces the combinatorial entropy contribution towards the free energy of mixing.

It turned out that the formation of nanostructured morphologies in particular is affected by the competitive kinetics between polymerization and phase separation and the confinement of miscible polymer chains of BCP on the phase-separated sub-chains. Finally, it is worth noting that the difference in block architecture of BCP

Table 1 Epoxy/BCP systems which form nanostructured morphology via self-assembly

Block copolymer	Hardener	References
Poly(ethylene oxide)-*b*-poly (ethylene-alt-propylene) (PEO-*b*-PEP)	4,4′-methylenedianiline (MDA)	Lipic et al. (1998)
PEO-*b*-PEP, poly(methyl methacrylate-*ran*-glycidyl methacrylate)-poly(2-ethylhexyl methacrylate) (P(MMA-*ran*-GMA)-PEHMA)	Phenol novolac (PN)	Dean et al. (2003)
Polystyrene-*b*-polybutadiene-*b*-poly(methyl methacrylate) (SBM)	4,4′-Methylenebis(3-chloro-2,6-diethylaniline) (MCDEA), 4,4′-diaminodiphenyl sulfone (DDS)	Ritzenthaler et al. (2002)
SBM	MCDEA	Ritzenthaler et al. (2003)
Poly(ethylene glycol-*co*-propylene glycol) (PEO-*b*-PPO), poly (ethylene glycol)-*block*-poly-(propylene glycol)-*block*-poly (ethylene glycol) (PEO-*b*-PPO-*b*-PEO)	MDA	Mijovic et al. (2000)
Poly(methyl acrylate-co-glycidyl methacrylate-*b*-polyisoprene)	MDA	Guo et al. (2003)
Poly(ethylene oxide)-block-poly (dimethylsiloxane) (PEO–PDMS)	MDA	Guo et al. (2006a)
PEO-*b*-PPO	MDA	Guo et al. (2006b)
Poly(hexylene oxide)-b-poly (ethylene oxide) (PHO-PEO)	PN	Thio et al. (2006)
Epoxidised styrene-*b*-butadiene (SepB)	MCDEA	Serrano et al. (2006)
Poly(ε-caprolactone)-b-polydimethylsiloxane-b-poly(ε-caprolactone) (PCL-b-PDMS-b-PCL)	4,4′-Methylene bis(2-chloroaniline) (MOCA)	Xu and Zheng (2007a)
Poly(hydroxyether of bisphenol A)-*b*-polydimethylsiloxane (PH-*alt*-PDMS)	4,4′-Diaminodiphenylmethane (DDM)	Gong et al. (2008)
PEO-*b*-PEP	1,1,1-tris(4-hydroxyphenyl)ethane (THPE)	Thompson et al. (2009) and Liu et al. (2008, 2010)
Poly(2,2,2-trifluoroethyl acrylate)-block-poly(ethylene oxide) (PTFEA-b-PEO)	MOCA	Yi et al. (2009)
Polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA)	DDM	Blanco et al. (2010)
Poly(ε-caprolactone)-block-poly (ethylene-coethylethylene)-block-poly(ε-caprolactone) (PCL-b-PEEE-b-PCL)	MOCA	Hu et al. (2010)

(*continued*)

Table 1 (continued)

Block copolymer	Hardener	References
Poly (methyl methacrylate)-b- poly (n-butyl acrylate) -b- poly (methyl methacrylate) (PMMA-b-PnBA-b-PMMA)	DDS, PN, methyl nadic anhydride (MNA), and 2, 4, 6-tris (dimethylaminomethyl) phenol (DMP)	Kishi et al. (2011)
Poly(2,2,2-trifluoroethyl acrylate)-b-poly(glycidyl methacrylate) (PTFEA-b-PGMA)	MOCA	Yi et al. (2011)
Poly(styrene-b-isoprene-b-styrene) (SIS)	Ancamine 2500	Garate et al. (2011)
Block complex of sulfonated polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (SSEBS) and a tertiary amine-terminated poly(ε-caprolactone), SSEBS-c-PCL	MDA	Wu et al. (2012)
Poly(styrene-b-butadiene-b-styrene) (SBS)	Ancamine 2500	Ramos et al. (2012)
Poly(ε-caprolactone)-block-polyethylene-block-poly (ε-caprolactone) (PCL-b-PE-b-PCL)	MOCA	Zhang et al. (2013)
SBS	MCDEA	Ocando et al. (2013)
Epoxidized poly-(styrene-b-isoprene-b-styrene) (eSIS-AEP)	Ancamine 2500	Garate et al. (2014)
PEO-b-PPO-b-PEO	m-xylylenediamine (MXDA)	Cano et al. (2014)
PEP-b-PEO, polystyrene-b-poly (ethylene oxide) (PS-b-PEO)	Polyether triamine	Redline et al. (2014)
PS-b-PEO	4,4′-methylenebis (2,6-diethylaniline) (MDEA)	Leonardi et al. (2015)
Poly-(heptadecafluorodecyl acrylate)-b-poly(caprolactone) (PaF-b-PCL)	MCDEA	Ocando et al. (2007)

leads to quite different RIMPS behavior. Table 2 shows some of the epoxy/BCP systems, which follow RIMPS for the generation of nanostructured morphology.

Morphology: Formation of Nanostructures

Immense contributions from researchers during the last several years have unequivocally established that a wide range of morphologies can be generated by self-assembly or RIMPS approaches. It is worth emphasizing that the shape, size, and distribution of nanostructures in thermosetting matrix depend on a number of parameters related to the epoxy precursors, curing agents, and BCPs. As mentioned

Table 2 Epoxy/BCP systems which form nanostructured morphology via RIMPS

Block copolymer	Hardener	References
PS-*b*-PEO	MOCA	Meng et al. (2006a)
Poly(ε-caprolactone)-*block*-poly-(*n*-butyl acrylate) (PCL-*b*-PBA)	MOCA	Xu and Zheng (2007b)
PS-b-PCL, PS-b-PCL-b-PS, and PCL-b-PS-b-PCL	MOCA	Yu et al. (2012)
PCL-*b*-PS	MOCA	Meng et al. (2008)
Epoxidized poly(styrene-b-isoprene-b-styrene) (eSIS)	Ancamine 2500	Garate et al. (2013)
PS-*b*-PMMA	Tertiary amine (benzyldimethylamine, BDMA), DDS	Girard-Reydet et al. (2002)
Polydimethylsiloxane-*block*-poly(ε-caprolactone)-*block*-polystyrene (PDMS-*b*-PCL-*b*-PS)	MOCA	Fan et al. (2009)[a]
Polystyrene-block-poly(ε-caprolactone)-block-poly(n-butyl acrylate) (PS-b-PCL-b-PBA)	MOCA	Fan et al. (2010)
Poly(ethylene oxide)-block-poly (ε-caprolactone)-block-polystyrene (PEO-b-PCL-b-PS)	MOCA, DDS	Yu and Zheng (2011)
PS-b-PMMA	MDEA	Romeo et al. (2013)
SBS	DDM	George et al. (2015)
PEO-b-PCL	MOCA, DDS	Meng et al. (2006b)
Polyisoprene-*b*-poly(4-vinyl pyridine) (PI-*b*-P4VP)	MDA	Guo et al. (2008)
PS-*b*-PMMA	MOCA	Fan and Zheng (2008)
Poly(ε-caprolactone)-block-poly(butadiene-co-acrylonitrile)-blockpoly(ε-caprolactone) triblock copolymer (PCL-b-PBN-b-PCL)	MOCA	Yang et al. (2009)
Poly(ethylene glycol)-*b*-carboxyl terminated butadiene-acrylonitrile rubber (PEG-*b*-CTBN)	MOCA	Heng et al. (2015)
Epoxidized poly(styrene-b-butadiene) (SepB)	MCDEA	Serrano et al. (2009)
PS-*alt*-PEO	MOCA	Hu and Zheng (2009)
PEO-b-PPO-b-PEO	DDS	Parameswaranpillai et al. (2017)

[a]Both self-assembly and RIMPS

earlier, concentration of BCP, block length, block-block interaction, molecular weights of blocks, the type of matrix, matrix-matrix interactions, the type of curing agent, cure cycle, etc. are the important factors which influence the nature of final nanostructured morphology. AFM images given in Fig. 3 show that as the concentration of BCP changes, morphology of epoxy/BCP blends shifts from spherical nanodomains to interconnected nanoobjects at intermediate concentrations and then
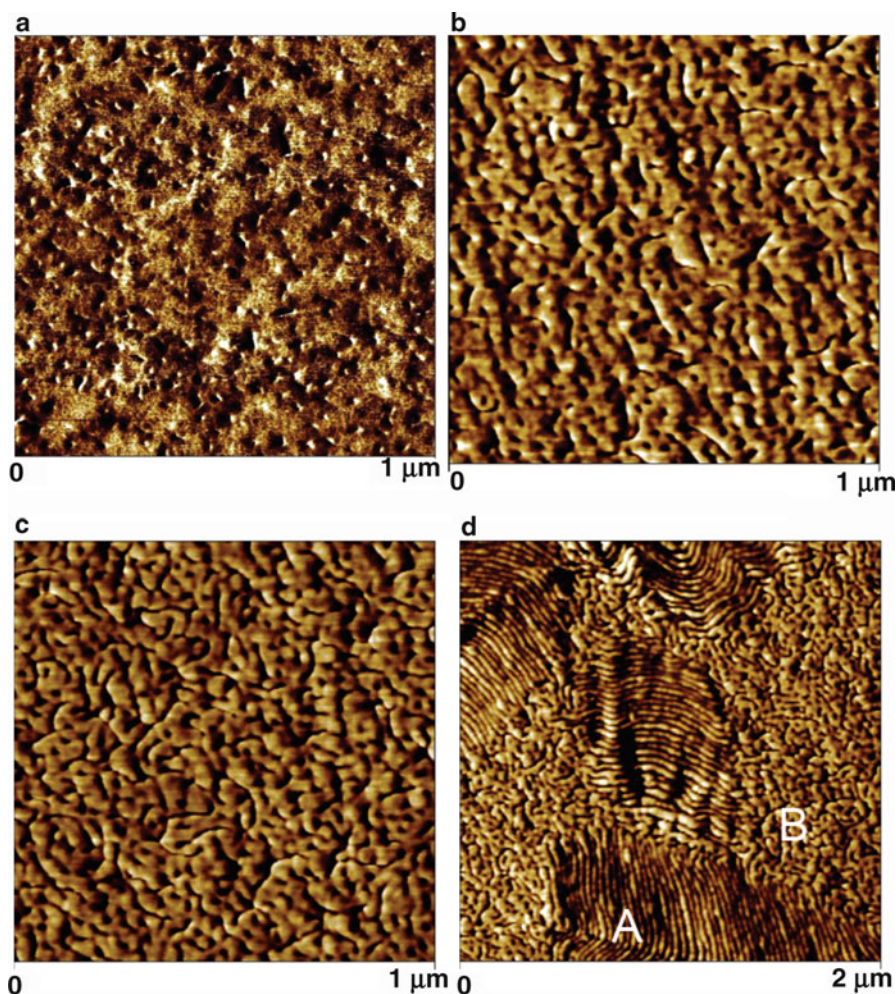
Fig. 3 AFM images of epoxy/BCP/MOCA blends containing (**a**) 10, (**b**) 20, (**c**) 30, and (**d**) 40 wt.% of BCP. Increasing the concentration of the BCP shifted the morphology from spherical domains to lamellar nanostructures besides the interconnected nanoobjects (Reprinted with permission) (Xu and Zheng 2007b)

to lamellar nanostructures besides the interconnected nanoobjects at higher concentrations (Xu and Zheng 2007b).

In addition, the competitive dynamics between the curing reaction, phase separation, and thermodynamic factors including hydrogen bonding interactions are some other important aspects which should be considered to evaluate the development of final micro- or nanostructured morphology. The following schematic model (Fig. 4) illustrates the unique structure and dynamics of thermoset/BCP interphase and the underlying principle of formation of final-phase structure in epoxy resin/
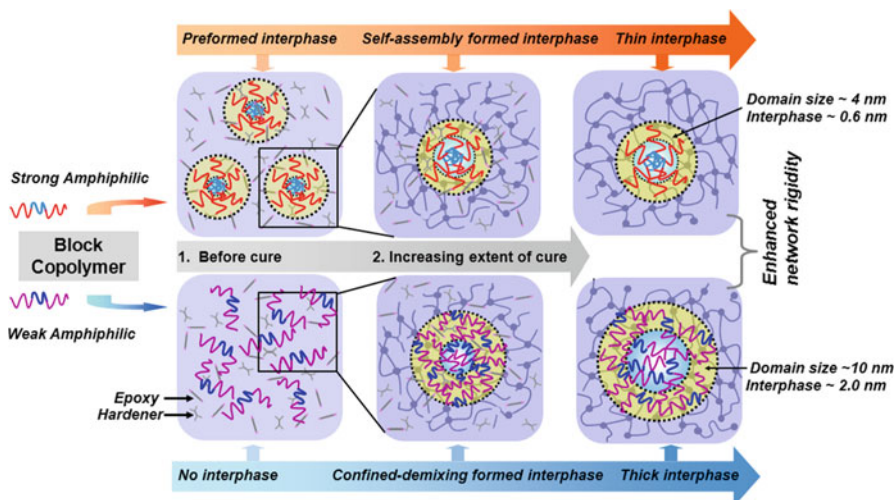
Fig. 4 Schematic representation of the model describing two different types of interphase structures and their underlying formation mechanism in epoxy resin/BCP blends (Reprinted with permission) (He et al. 2014)

BCP blends. This model displays two types of interphase structures generated by self-assembly and RIMPS and provides microlevel information about the morphology (He et al. 2014).

Toughening by Nanostructures: Structure-Property Correlation

Since the intrinsic brittleness of epoxy thermosets makes them susceptible to fracture failure, the extent of improvement in toughness and the related mechanisms in BCP-modified epoxy systems are of greatest importance in terms of scientific and technological perspective. The final nanostructured morphology governed by self-assembly and RIMPS differ in terms of size, shape, and distribution of nanodomains, and therefore the correlation between nanostructure parameters and fracture toughness will provide an intuitive insight on the structure property correlation in other toughened thermosets as well.

Researchers have shown that improvement in toughness without compromising stiffness and modulus of thermoset can be explained in terms of various mechanisms including crack-tip blunting, debonding, crack bridging, shear yielding, cavitation, etc. Attention should be paid to the fact that the enhancement of toughness in epoxy thermosets modified with BCP depends on nanodomain morphology, which in turn depends on the nature and thickness of epoxy/BCP interphase. Despite the fact that there are still unsettled issues and unresolved problems in this regard, different nanostructures lead to different levels of toughening improvement (Fig. 5). For example, irrespective of the same basic shape of
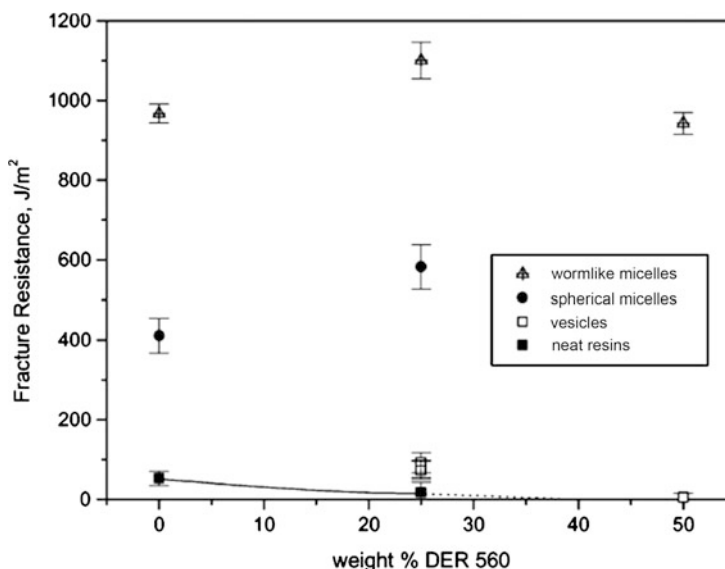
Fig. 5 Fracture resistance for DER383/DER560/PN containing 5 wt.% BCP; spherical and wormlike micelles were obtained from PEO-*b*-PEP-9 and PEO-*b*-PEP-15 BCPs, respectively, while vesicles were generated with the P(MMA-ran-GMA)-PEHMA compounds (Reprinted with permission) (Dean et al. 2003)

the spherical micelles and vesicles, larger size of vesicles results in greater fracture toughness. Similarly, wormlike micelles can produce greater improvement in fracture toughness compared to spherical micelles, mainly because of the crack-tip blunting and crack-bridging mechanisms whereas spheres are more effective in deflecting the progressive crack away from the original crack plane.

Conclusions

Block copolymers (BCPs) are extensively used for enhancing fracture toughness of brittle epoxies, without compromising modulus, stiffness, and use temperature. BCPs form wide variety of structures at nanometer scale in thermosetting matrix via self-assembly and reaction-induced microphase separation mechanisms. The formation of nanostructured morphology depends on several factors including blend composition, type of BCP, molecular weights of blocks, block architecture, matrix-block and block-block interactions, type of curing agent, and curing cycle. Since the end-use structural applications of epoxy thermosets are assessed in terms of the toughness of the product by judicial selection BCPs and optimization of curing conditions, nanostructured morphology could be tuned in such a way that tough polymeric materials with attractive thermomechanical properties suitable for demanding applications can be developed.

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