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## Abstract

The ability of block copolymers to generate nanostructures when mixed with epoxy thermosetting systems is deeply analyzed. Both amphiphilic and chemically modified di- or triblock copolymers have been used with this purpose. In both cases, one of the blocks is miscible with epoxy system (or even can react with it) before and after curing, while the other one is immiscible before or after curing, leading to morphology development by self-assembly (SA) or reaction-induced phase separation (RIPS), respectively. In some cases, nanostructure development can occur by a combination of both mechanisms or even some demixing of the miscible block can also happen, generating different morphologies. Depending on that and on other parameters like employed hardener, cure cycle, copolymer block ratio, and topology among others, different morphologies such as spherical or wormlike micelles, hexagonally packed cylinders, bilayer micelles, or mixtures of them can be obtained. The effect of nanofillers on morphologies of ternary systems based on epoxy systems nanostructured with block copolymers is also analyzed.

## Keywords

Block copolymer • Micelles • Cylinders • Wormlike • Nanostructures

## Contents

Introduction .....	884
Morphologies in Epoxy/Block Copolymer Blends .....	887
Epoxy/Amphiphilic Block Copolymer Blends .....	887
Epoxy/Chemically Modified Block Copolymer Blends .....	901

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Ternary Systems Based on Nanostructured Epoxy and Inorganic Nanoparticles .....	905
Conclusion .....	913
References .....	915

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## Introduction

Block copolymers (BC) are the focus of a great deal of research activity because of their intrinsic ability to self-assemble into different nanoscale structures. This intriguing ability can be used to design new polymeric nanostructures with potentially interesting properties. Self-assembly of block copolymers can be maintained in their blends with different homopolymers. In this way, block copolymers have been widely used and are still being used, as templates for generating nanostructured epoxy matrices with long-range order in both uncured and cured states during last decades (Hillmyer et al. 1997; Ritzenthaler et al. 2002; Rebizant et al. 2004; Yi et al. 2011; Wang et al. 2013; Francis and Baby 2014). The control over morphology of those multicomponent thermosets is important for the improvement of their properties. The formation of nanostructures in thermosets can further optimize the inter-component interactions, improving their properties.

The concept of incorporating amphiphilic block copolymers into thermosets has widely been accepted to prepare materials with ordered or disordered nanostructures. During the last years of 1990 decade, a strategy of creating the nanostructures in thermosets using amphiphilic block copolymers by the mechanism of self-assembly was proposed (Lipic et al. 1998). In the protocol, precursors of thermosets act as selective solvents of block copolymers, and some self-organized structures such as lamellar, bicontinuous, cylindrical, and spherical can be accessed in the mixtures depending on fraction of block copolymers before the curing reaction. In this approach, the role of the curing reaction is to lock in the preformed self-organized nanostructures although it has been identified that the nanostructures could undergo some small changes with the occurrence of the curing reaction.

However, self-organization of amphiphilic block copolymers in the precursors of thermosets does not always occur. In many circumstances all the subchains of block copolymers are actually miscible with the precursors of thermosets. The miscibility (or solubility) is ascribed to the nonnegligible entropic contribution ( $\Delta S_m$ ) to free energy of mixing ( $\Delta G_m$ ) in the mixtures of block copolymers since the precursors (or monomers) of thermosets are generally compounds of low molecular weights. In addition, the presence of the self-organized microphases formed at lower temperatures does not assure the survival of these structures at elevated temperatures that are required for curing of some thermosets, since the mixtures of polymers with precursors of thermosets generally displayed upper critical solution temperature (UCST) behaviors.

Under this circumstance, it has been pointed out that ordered and/or disordered nanostructures can be alternatively formed by reaction-induced microphase separation in thermosets (Larrañaga et al. 2005; Meng et al. 2006a; Ocando et al. 2007;

Sinturel et al. 2007). In this approach, it is not required that the amphiphilic block copolymers are self-organized into nanostructures before curing reaction; all the subchains of block copolymers are miscible with precursors of thermosets, and only a part of subchains of block copolymers are microphase-separated out upon curing.

Formation of nanostructures by self-assembly is based on the equilibrium thermodynamics in the mixtures of precursors of thermosets and amphiphilic block copolymers, which is governed by the nature of precursors of thermosets and block copolymers. On the other hand, the morphological control by reaction-induced microphase separation is quite dependent on the competitive kinetics between polymerization and microphase separation. Compared to reaction-induced phase separation in the blends of thermoset and homopolymers or random copolymers, reaction-induced microphase separation of block copolymers in the thermosets occurs in a confined fashion and on the nanometer scale, owing to the presence of miscible blocks.

Nowadays, with the synthesis of versatile block copolymers, the possibility to control the formation of nanostructures has been clearly favored. Ordered and disordered nanostructures have been obtained by incorporating AB-type amphiphilic diblock copolymers (Yi and Zheng 2009; Blanco et al. 2010; Romeo et al. 2013; Cano et al. 2014) ABA-type triblock copolymers (Yang et al. 2009; Hu et al. 2010; Cong and Zheng 2014) or ABC-type triblock copolymers (Ritzenthaler et al. 2002; Yu and Zheng 2011) into thermosets.

Moreover, a second generation of block copolymers has been developed using the concept of chemical compatibilization. This approach incorporates reactive groups into one block in order to promote covalent bonding with the forming epoxy network without loss of ordering in the resulting blends (Grubbs et al. 2000a, b; Rebizant et al. 2003; Serrano et al. 2006; Hameed et al. 2010; Yi et al. 2011; Garate et al. 2013). This pathway could lead to an improvement in mechanical properties and stability of nanostructured materials.

Many different morphologies such as spherical or wormlike micelles, hexagonally packed cylinders, bilayer micelles, or mixtures of them, among others, have been obtained when nanostructuring epoxy matrices with block copolymers. Many factors affect obtained morphologies, being the nature of the copolymer the most important one. This effect will be deeply analyzed through this chapter. Topology and block sequence (Guo et al. 2006; Fan and Zheng 2008; Meng et al. 2008; Wang et al. 2013), together with block composition (Serrano et al. 2005a), also showed a great effect on obtained morphologies. In that way, for epoxy thermosets containing the linear PCL-*b*-PS diblock copolymer (Meng et al. 2008), spherical PS nanophases were arranged into cubic lattice, whereas the PS nanophases were arranged into lamellar lattice when tetra-armed PCL-*b*-PS block copolymer was added. The difference in nanostructures was interpreted on the basis of the restriction of topological structures of the block copolymers on the formation of nanophases. For PS-*b*-PMMA copolymer (Fan and Zheng 2008), different morphologies were obtained depending on subchain sequence. Both linear (*l*-PS-*b*-PMMA) and star-shaped copolymers with two sequential structures (denoted *s*-PS-*b*-PMMA and *s*-PMMA-*b*-PS) were used. Nanostructures were found in the

thermosets containing *l*-PS-*b*-PMMA and *s*-PS-*b*-PMMA, consisting on spherical and wormlike micelles, being the long-range order of the nanostructures higher for the system containing the linear copolymer. This difference was interpreted on the basis of the effects of topological structure of the miscible subchains (PPMA in this case) on the surface free energy of PS nanodomains. For systems with *s*-PMMA-*b*-PS copolymer, however, the phase separation occurred at the scale of micrometer, due to the insufficient suppression of the PMMA chains of macroscopic phase separation of the tetra-armed PS at shell in the block copolymer. For PEO-*b*-PPO copolymer (Guo et al. 2006), it was found that PEO content and block sequence (different four-arm star-shaped copolymers with different PEO contents) determined final morphology, avoiding macroscopic phase separation by increasing PEO content. Similar conclusions were obtained for PEO-*b*-PPO-*b*-PEO triblock copolymer (Serrano et al. 2005a).

On the other hand, together with the amount of block copolymer in the mixture (Blanco et al. 2010), the hardener employed for curing the epoxy matrix and cure cycle (Ritzenthaler et al. 2002; Serrano et al. 2005a; Meng et al. 2006b; Yu and Zheng 2011; Romeo et al. 2013) also would determine the final morphology of those nanomaterials. The hardener shows a great importance because it can determine the miscibility of blocks with epoxy system before and after cure, affecting nanostructuring mechanism or obtained morphology. In that way, different mechanisms and morphologies have been found depending on the hardener: for PEO-*b*-PCL-*b*-PS (Yu and Zheng 2011), spherical PS domains were formed when cured with 4,4'-methylenebis-(2-chloroaniline) (MOCA), while lamellar morphology was obtained by tandem RIPS of PS and PCL blocks when cured with diaminodiphenylsulfone (DDS). For PEO-*b*-PCL copolymer (Meng et al. 2006b), spherical morphology was obtained when cured with DDS, while homogeneous mixtures were achieved when cured with methylenebis-(3-chloro-2,6-diethylaniline) (MCDEA). For PS-*b*-PB-*b*-PMMA copolymer (Ritzenthaler et al. 2002), "spheres on spheres" morphology was obtained when cured with MCDEA by SA mechanism with partial deswelling of PMMA, and flocculated, elongated nanostructures were obtained by RIPS of PMMA when cured with DDS. Cure temperatures and cycle also can determine obtained morphologies because it affects to the miscibility of blocks in epoxy system. For PS-*b*-PMMA (Romeo et al. 2013), different morphologies (from spherical micelles to a dual morphology consisting on hexagonally packed cylinders and spherical micelles) were obtained depending on cure cycle, due to the change of PMMA miscibility with temperature. For PCL-*b*-PB-*b*-PCL copolymer (Meng et al. 2006c), it was found that PCL was miscible with epoxy monomers before curing and also miscible with MOCA-cured epoxy and that the blend system composed of low molecular weight PB and epoxy precursors displayed an upper critical solution temperature (UCST) behavior. RIPS of PB occurred when blends were cured at elevated temperatures. Therefore, the curing reaction was initiated from a homogeneous solution at a temperature above the UCST of the system to ensure that the curing reactions were carried out without the presence of SA structures, altering morphologies.

Nowadays, in order to reach new requirements in nanotechnology, ternary thermosetting systems modified with inorganic nanoparticles and block copolymers have attracted attention (Tercjak et al. 2009, 2012; Ocando et al. 2010; Gutierrez et al. 2010a; Esposito et al. 2014). Nanostructured thermosetting systems designed using different block copolymers are challenging to obtain multifunctional hybrid inorganic/organic materials, since block copolymers can act as template for the incorporation of inorganic nanoparticles or other components. In the case of these multifunctional thermosetting systems modified with nanoparticles, the main objective has been the control of the distribution and size of nanoparticles due to these parameters limit possible applications of the designed materials. Additionally, the selective confinement of nanoparticles in one of the microphase-separated domains, playing with the capability of block copolymers to nanostructuring epoxy resins, has been investigated by several researchers. In summary, the effect of nanoparticles on the morphologies generated by block copolymers when nanostructuring epoxy matrices and their selective placement on the desired domains are the main challenges for those multifunctional materials.

In the present work the most significant morphologies obtained for epoxy/block copolymer mixtures are presented, as characterized by different microscopical techniques such as atomic force microscopy (AFM), transmission electron microscopy (TEM), or scanning electron microscopy (SEM). The effect of all cited parameters on them are also deeply analyzed, showing the versatility of those systems for giving different nanostructures, offering the possibility to design nanostructured materials with different patterns by controlling the mixture components and cure process.

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## Morphologies in Epoxy/Block Copolymer Blends

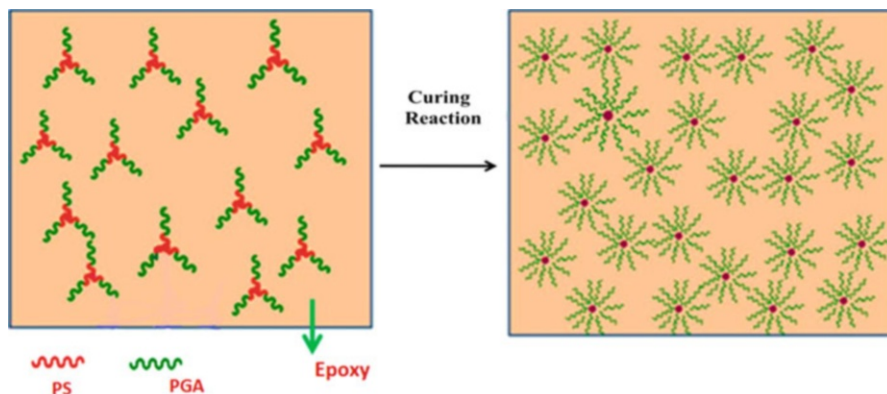
As it was previously pointed out, two main types of copolymers have been used for preparing thermosetting blends with epoxy resins: amphiphilic block copolymers and chemically modified ones.

### Epoxy/Amphiphilic Block Copolymer Blends

Many different morphologies can be obtained with the use of amphiphilic diblock or triblock copolymers (ABA or ABC type) by both self-assembly (SA) or reaction-induced phase separation (RIPS) mechanisms.

#### Amphiphilic Diblock Copolymers

Different morphologies have been obtained for amphiphilic diblock copolymers by both mechanisms. Starting from those diblock copolymers that separate by RIPS mechanism, as was previously pointed out, both blocks are miscible with epoxy precursor and hardener before curing reaction, and one of the blocks becomes immiscible with cure reaction advance, separating from the continuous epoxy

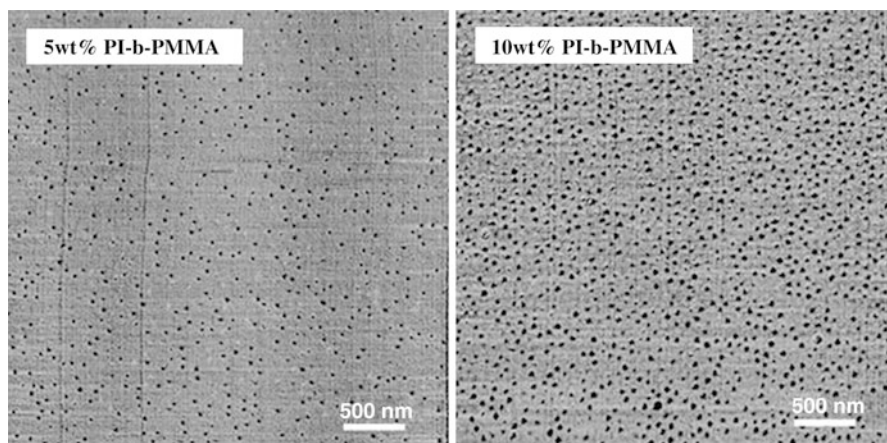


**Scheme 1** Formation of nanostructures in epoxy thermoset by reaction-induced microphase separation (Reproduced with permission of (Francis and Baby), copyright 2014 American Chemical Society)

phase in which the other block remains miscible (or even reacts with the matrix), as it can be seen in Scheme 1, where the poly(glycolic acid) (PGA) block remains miscible during curing, while polystyrene (PS) separates forming its phase at the nanoscale. Both blocks were miscible with epoxy precursors before curing reaction.

Many different diblock copolymers presenting this behavior can be found: poly(styrene-*block*-glycolic acid) (PS-*b*-PGA) with PGA as miscible block (Francis and Baby 2014), poly(isoprene-*block*-methyl methacrylate) (PI-*b*-PMMA) with PMMA as miscible block (Esposito et al. 2013), poly(styrene-*block*-methyl methacrylate) (PS-*b*-PMMA) with PMMA as miscible block (Fan and Zheng 2008), poly(isoprene-*block*-4-vinyl pyridine) (PI-*b*-P4VP) with P4VP as miscible block (Guo et al. 2008), poly( $\epsilon$ -caprolactone-*block*-styrene) (PCL-*b*-PS) with PCL as miscible block (Meng et al. 2006), poly(heptadecafluorodecyl acrylate-*block*-caprolactone) (PaF-*b*-PCL) with PCL as miscible block (Ocando et al. 2007), poly(styrene-*block*-ethylene oxide) (PS-*b*-PEO) with PEO as miscible block (Meng et al. 2006a; Gutierrez et al. 2011), and poly(dimethylsiloxane-*block*-glycidyl methacrylate) (PDMS-*b*-PGMA) with PGMA as miscible block (Hameed et al. 2010). The typical morphology obtained by RIPS mechanism consists on spherical domains of the immiscible block dispersed in a continuous epoxy matrix in which the other block remains miscible, especially for low copolymer contents of around 10 wt.%, as it can be seen in Fig. 1 for PI-*b*-PMMA copolymer as an example.

Increasing block copolymer amount, for many copolymers like PS-*b*-PMMA (Fan and Zheng 2008), PCL-*b*-PS (Meng et al. 2008), and PS-*b*-PEO (Meng et al. 2006a), spherical domains start to coagulate, in which some interconnected domains together with spherical ones appear. Generally the amount of spherical domains increases, maintaining their size almost constant. In some cases, by increasing copolymer content even lamellar morphologies (Gutierrez et al. 2011) can be obtained, as it can be seen in Fig. 2 for PS-*b*-PEO (also called SEO)



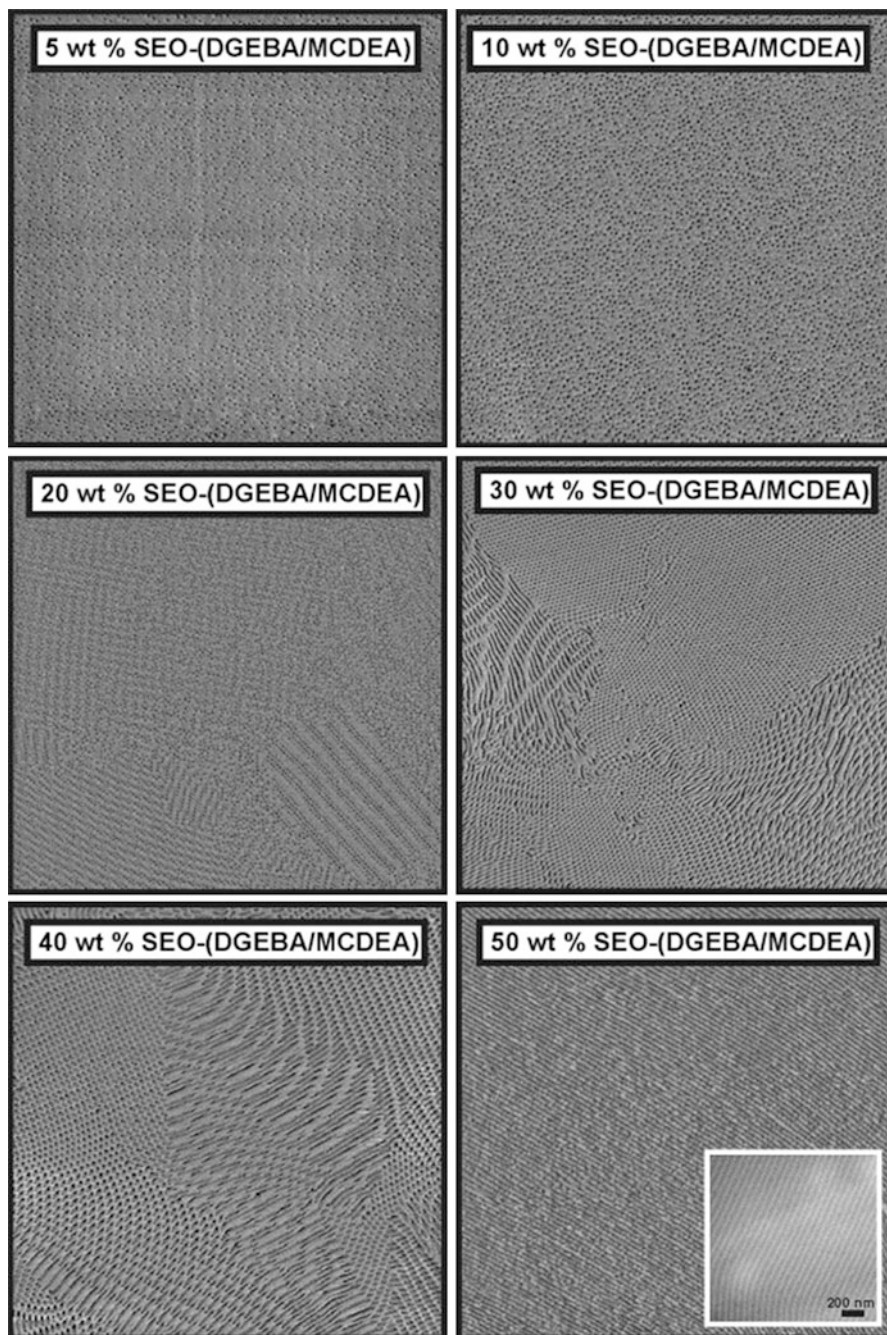
**Fig. 1** AFM-phase images of DGEBA/MCDEA with 5 and 10 wt.% of PI-*b*-PMMA

copolymer. Depending on the copolymer and its amount, other morphologies can also be obtained such as mixtures of spherical and wormlike micelles of the separating block (Ocando et al. 2007) as it can be seen in Fig. 3 or morphologies in which the nanophase can be arranged into the epoxy matrix in cubic lattices (Hameed et al. 2010).

An interesting phenomenon that can occur with some copolymers is that, for high contents, even some miscible subchains can demix from the matrix upon curing, generating corona-like domains with an external layer formed from the partial demixing of the miscible block (Fan and Zheng 2008). This phenomenon has also been found for epoxy/copolymer systems in which nanostructure is generated by self-assembly mechanism (Lipic et al. 1998; Blanco et al. 2010; Yi et al. 2011) and will be analyzed below.

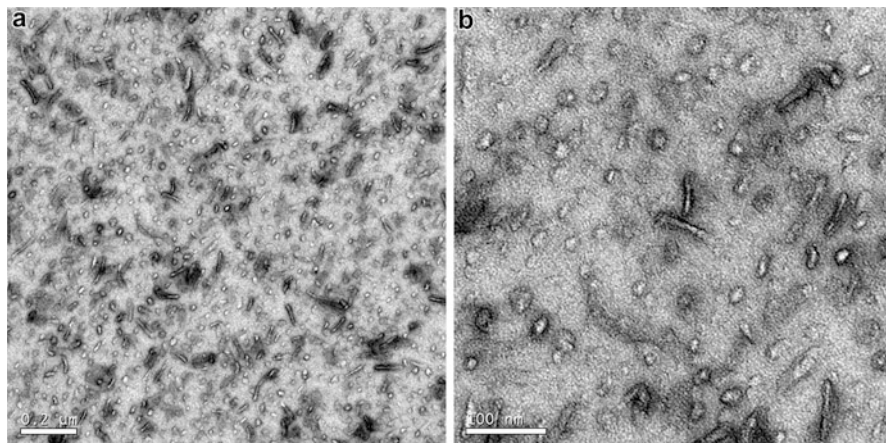
On the other hand, several copolymers have been found to nanostructure epoxy matrix by SA mechanism. As was pointed out previously, precursors of thermosets act as selective solvents of block copolymers accessing self-organized structures, depending on fraction of block copolymers, before the curing reaction. The role of the curing reaction is to lock in those self-organized nanostructures. Many diblock copolymers presenting this behavior can be found: poly(styrene-*block*-2-vinyl pyridine) (PS-*b*-P2VP) with P2VP as miscible block; poly(caprolactone-*block*-2,2,2-trifluoroethyl acrylate) (PCL-*b*-PTFEA) with PCL as miscible block; poly(styrene-*block*-methyl methacrylate) (PS-*b*-PMMA) with PMMA as miscible block (Blanco et al. 2010); poly(ethylene oxide-*block*-dimethylsiloxane) (PEO-*b*-PDMS) with PEO as miscible block; and poly(2,2,2-trifluoroethyl acrylate-*block*-glycidyl methacrylate) (PTFEA-*b*-PGMA) with PGMA as miscible block, among others.

Different self-organized structures such as lamellar, bicontinuous, cylindrical, and spherical can be accessed in the mixtures depending on fraction of block copolymers before the curing reaction. Most common morphology for cured systems with copolymer contents up to 20 wt.% is that composed by spherical micelles



**Fig. 2** AFM-phase images ( $5 \times 5 \mu\text{m}$ ) of binary systems. TEM image of 50 wt.% copolymer inset at the bottom of the corresponding AFM-phase image (Reproduced with permission of (Gutierrez et al.), copyright 2011 Elsevier Ltd)



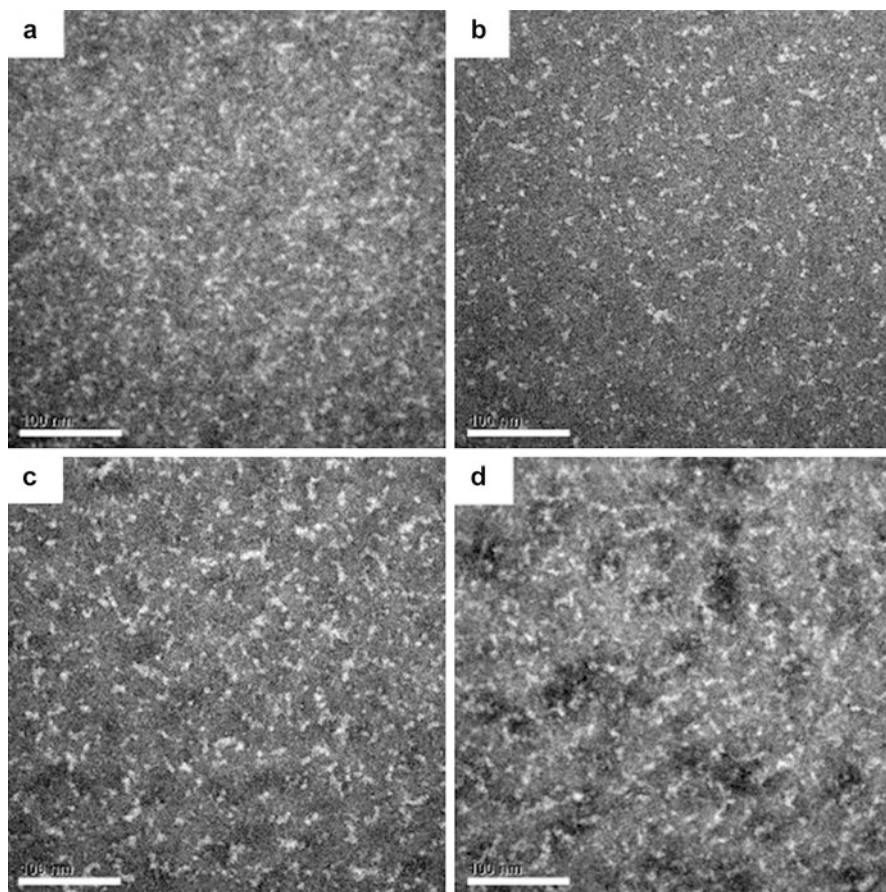


**Fig. 3** TEM images at different magnifications for DGEBA/MCDEA cured blend containing 35 wt.% PaF-*b*-PCL. The samples have been stained with RuO<sub>4</sub> for 4 min. Scale bar: (a) 0.2 μm and (b) 100 nm (Reproduced with permission of (Ocando et al.), copyright 2007 American Chemical Society)

that has been obtained for different copolymers: for PCL-*b*-PTFEA (Wang et al. 2013), PTFEA spherical nanodomains dispersed in a continuous epoxy matrix in which PCL remained miscible; for PEO-*b*-PDMS (Guo et al. 2006), spherical PDMS micelles in a continuous epoxy matrix in which PEO block remained miscible; and for PTFEA-*b*-PGMA (Yi et al. 2011), spherical PTFEA domains in a continuous epoxy matrix in which PGMA remained miscible. Increasing block copolymer content, in many cases spherical domains start to coagulate, increasing their size and generating morphologies composed by spherical and wormlike micelles, as it was found for PEO-*b*-PDMS, PTFEA-*b*-PGMA, or PS-*b*-PMMA copolymers. Examples can be seen in Figs. 4, 5, and 6 for PEO-*b*-PDMS, PCL-*b*-PTFEA, and PTFEA-*b*-PGMA copolymers, respectively. Commonly, for high copolymer contents (from 40 to 60 wt.% depending on the copolymer) macroscopic phase separation is obtained.

However, depending on the copolymer some other morphologies like cylinders can also be obtained. For epoxy mixtures with PS-*b*-P2VP copolymer (Casaban et al. 2013), a morphology consisting on PS cylinders dispersed in a continuous epoxy phase in which P2VP block remained miscible was obtained, for 30 wt.% of copolymer. For epoxy mixtures with PEO-*b*-PEP copolymer (Lipic et al. 1998), a morphology consisting on cylindrical PEP cores surrounded by a PEO shell enclosed by the epoxy matrix was found.

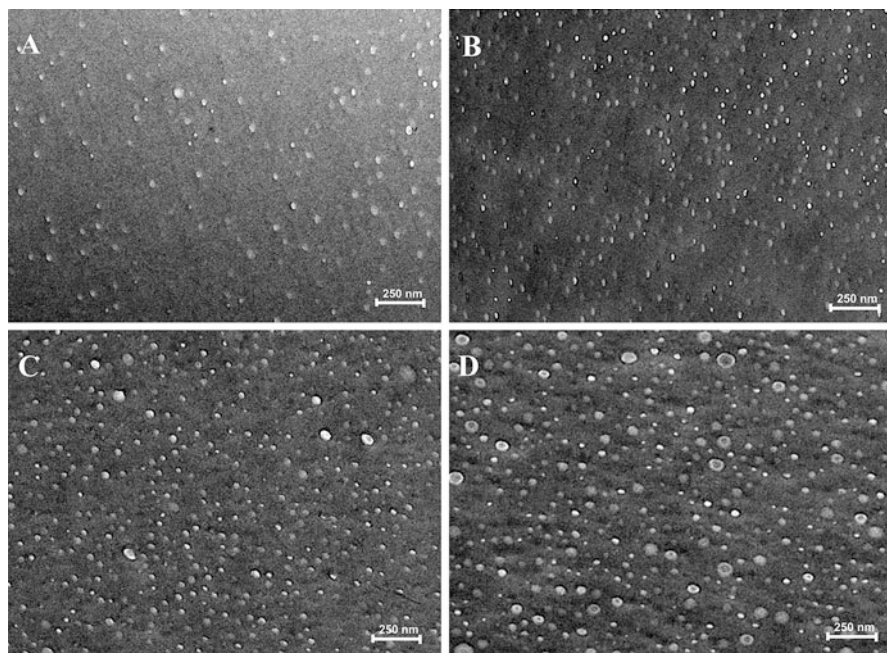
Moreover, as was also described for RIPS mechanism, the partial demixing of the miscible block has also been found to occur, affecting obtained morphologies. In that way, for PS-*b*-PMMA copolymer (Blanco et al. 2010), it was found that micellar self-assembled PS block chains formed the micelle nucleus. This micellar nanostructure was stabilized by the partial demixing of PMMA block close to



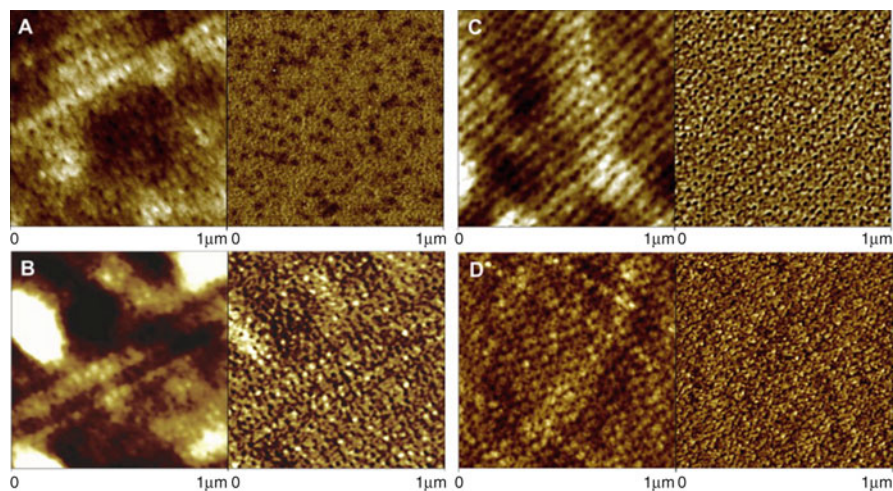
**Fig. 4** TEM micrographs of (a) 80/20, (b) 70/30, (c) 60/40, and (d) 50/50 MDA-cured ER/PEO-PDMS blends. The scale bars represent 100 nm (Reproduced with permission of (Guo et al.), copyright 2006 Wiley Periodicals Inc)

gelation of epoxy matrix. For PTFEA-*b*-PGMA copolymer mixtures with epoxy (Yi et al. 2011), the spherical nanodomains obtained for low copolymer contents started to be interconnected, appearing some wormlike micellar morphology. As their size decreased with copolymer content, it can be concluded that a demixing of PGMA block at the surface of PTFEA nanodomains occurred. The miscible block demixed from epoxy matrix during curing process, as it can be seen in Scheme 2.

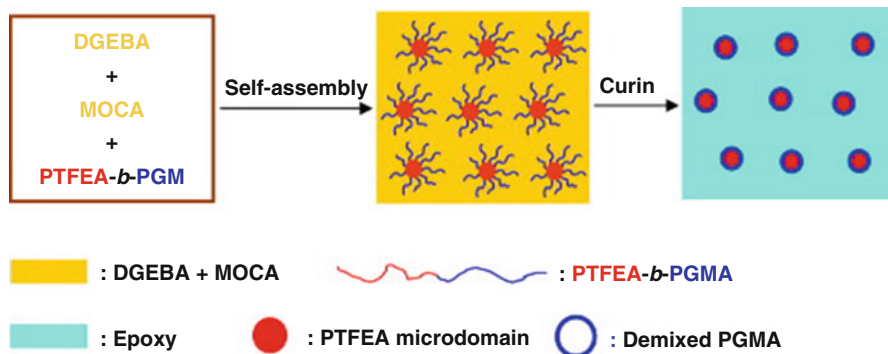
A similar behavior was found for mixtures of epoxy with PEO-*b*-PEP copolymer (Lipic et al. 1998). The epoxy resin has selectively swollen the PEO chains. As the amount of epoxy added to the block copolymer was increased, the microstructure evolved from lamellar to gyroid, to cylinders, and to body-centered cubic-packed spheres and ultimately disordered micelles. When hardener was added and the epoxy cured, the system retained the nanostructure and macrophase separation



**Fig. 5** TEM micrographs of the thermosets containing (a) 10, (b) 20, (c) 30, and (d) 40 wt.% of PCL-*b*-PTFEA diblock copolymer (Reproduced with permission of (Wang et al.), copyright 2013 American Chemical Society)



**Fig. 6** AFM images of epoxy thermosets containing: (a) 10, (b) 20, (c) 30, and (d) 40 wt.% of PTFEA-*b*-PGMA diblock copolymer. *Left*, topography; *right*, phase contrast images (Reproduced with permission of (Yi et al.), copyright 2011 Elsevier Ltd)



**Scheme 2** Formation of nanostructures in epoxy thermosets and demixing of PGMA blocks out of epoxy-amine matrix (Reproduced with permission of (Yi et al.), copyright 2011 Elsevier Ltd)

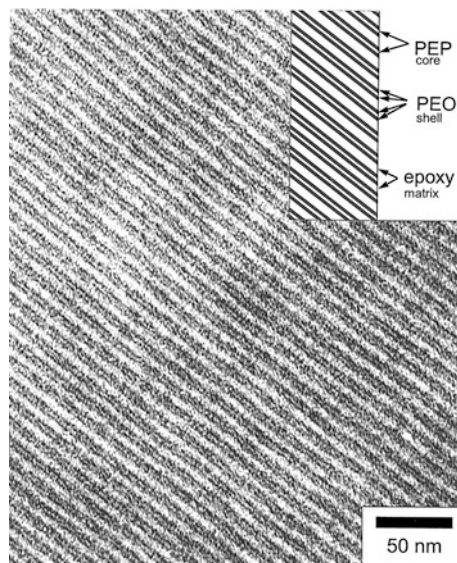
between the block copolymer and epoxy was avoided. However, the PEO block was expelled from the reactive matrix on a local level as the molecular weight of the epoxy increased, leading to cure-induced phase transitions and regions of relatively pure crystalline PEO. There was a transition from an equilibrium morphology to a chemically pinned metastable state as the cross-linking reaction progressed through the gel point.

Expulsion of PEO by the epoxy network was restricted to a local scale, and there was no disruption of long-range order. Chemical curing, and the associated increase in molecular weight, ejected the PEO from the curing epoxy. A “wet” brush to “dry” brush transition with cure was depicted, as it can be seen in Fig. 7.

### Amphiphilic ABA-Type Triblock Copolymers

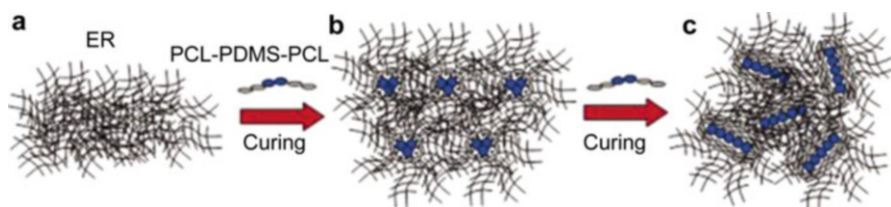
Different morphologies have been obtained for amphiphilic ABA-type triblock copolymers by both mechanisms. Usually A block is miscible with epoxy matrix, while B block separates before (SA mechanism) or during cure (RIPS). Several ABA copolymers have been found to generate nanostructures in their mixtures with epoxy systems by RIPS mechanism: poly( $\epsilon$ -caprolactone-*block*-(styrene-*co*-acrylonitrile)-*block*- $\epsilon$ -caprolactone) (PCL-*b*-PBS-*b*-PCL) with PCL as miscible block (Cong and Zheng 2014), poly( $\epsilon$ -caprolactone-*block*-dimethylsiloxane-*block*- $\epsilon$ -caprolactone) (PCL-*b*-PDMS-*b*-PCL) with PCL as miscible block (Hameed et al. 2010), poly( $\epsilon$ -caprolactone-*block*-polybutadiene-*block*- $\epsilon$ -caprolactone) (PCL-*b*-PB-*b*-PCL) with PCL as miscible block (Meng et al. 2006c), poly( $\epsilon$ -caprolactone-*block*-(butadiene-*co*-acrylonitrile)-*block*- $\epsilon$ -caprolactone) (PCL-*b*-PBN-*b*-PCL) with PCL as miscible block (Yang et al. 2009), poly(methyl methacrylate-*block*-butyl acrylate-*block*-methyl methacrylate) (PMMA-*b*-PbuA-*b*-PMMA) with PMMA as miscible block (Bashar et al. 2014), and poly(ethylene oxide-*block*-propylene oxide-*block*-ethylene oxide) (PEO-*b*-PPO-*b*-PEO) with PEO as miscible block (Guo et al. 2002; Serrano et al. 2005a). As it can be seen in most of cases, PCL has

**Fig. 7** TEM image of the OP5/BPA348/MDA blend (52 wt.% OP5). The inset provides an interpretation of the morphology; cylindrical PEP cores (*thin white lines*) surrounded by a PEO shell (*black*), enclosed by the epoxy matrix (Reproduced with permission of (Lipic et al.), copyright 1998 American Chemical Society)

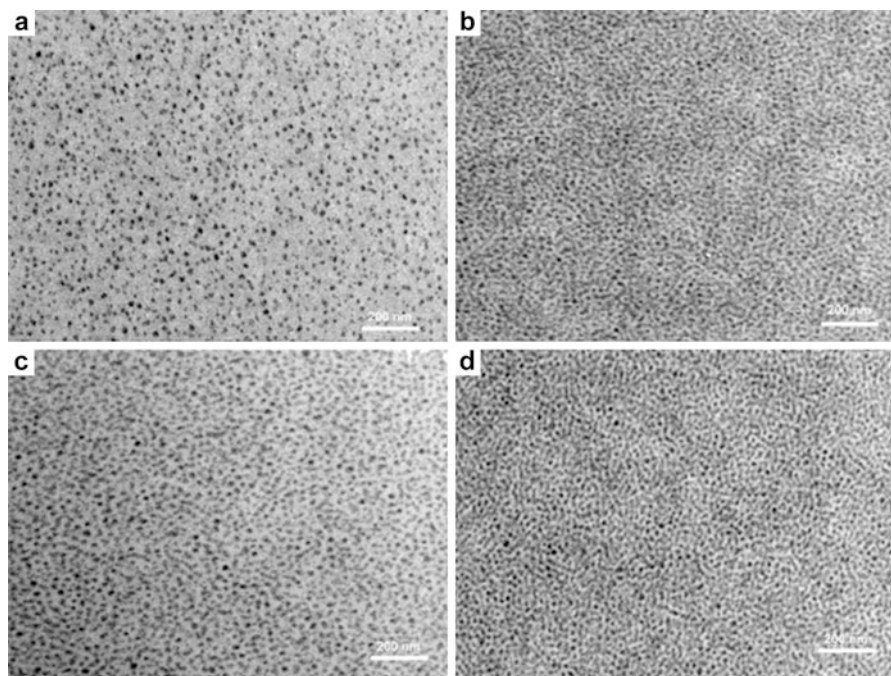


been chosen as the miscible block. The typical morphology obtained by RIPS mechanism with ABA copolymers, especially for those containing PCL blocks, consists on spherical domains of the immiscible block dispersed in a continuous epoxy matrix in which the other block remains miscible, especially for low copolymer contents of around 10 wt.%. By increasing copolymer content, spherical domains (usually increasing in number and/or size) start to coagulate, resulting in interconnected domains, obtaining morphologies composed by a mixture of spherical and interconnected domains (for mixtures with around 20–30 wt.% of copolymer). For higher copolymer contents (around 40 wt.% and higher), wormlike morphologies are usually obtained. This behavior has been found for ABA copolymers in which PCL is the A block, such as PCL-*b*-PDMS-*b*-PCL, PCL-*b*-PBS-*b*-PCL, PCL-*b*-PB-*b*-PCL, and PCL-*b*-PBN-*b*-PCL. As an example, Scheme 3 shows the schematic representation of different morphologies for PCL-*b*-PDMS-*b*-PCL copolymer, while Fig. 8 shows the described evolution of nanostructures with copolymer content for PCL-*b*-PBS-*b*-PCL copolymer.

Some other morphologies like bilayer vesicles or bicontinuous have also been found with other ABA-type triblock copolymers. For PMMA-*b*-PBuA-*b*-PMMA copolymer, a morphology consisting in randomly dispersed bilayer vesicles has been found (Bashar et al. 2014), being PBuA the immiscible block. For PEO-*b*-PPO-*b*-PEO copolymers with different PEO contents (Guo et al. 2002), different morphologies have been found, as it can be seen in Fig. 9 for the copolymer with the lower PEO content of 30 wt.%, EO30. For the copolymer with higher PEO amount (80 wt.% of PEO, called EO80 and not shown in the figure), a behavior quite similar to that described above (spherical domains that coagulate resulting in wormlike

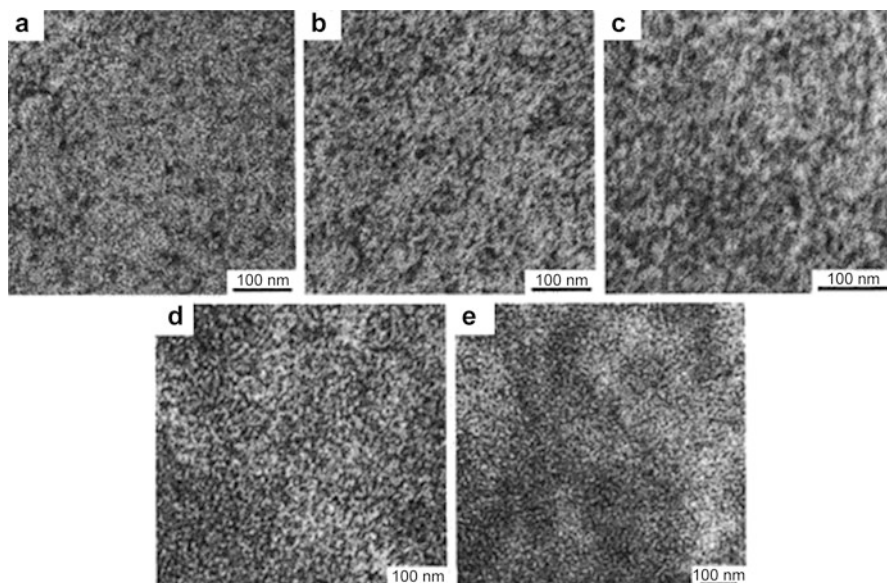


**Scheme 3** Schematic representation of different phase morphologies in ER/PCL-*b*-PDMS-*b*-PCL blends: (a) MDA-cured ER, (b) spherical microdomains at 5–20 wt.% PCL-*b*-PDMS-*b*-PCL concentration, and (c) wormlike microdomains at 30–50 wt.% PCL-*b*-PDMS-*b*-PCL concentration (Reproduced with permission of (Hameed et al.), copyright 2010 Wiley Interscience)



**Fig. 8** TEM images of the thermosets containing: (a) 10, (b) 20, (c) 30, and (d) 40 wt.% of PCL-*b*-PBS-*b*-PCL triblock copolymer (Reproduced with permission of (Cong and Zheng), copyright 2014 Elsevier Ltd)

morphology) was found. For the copolymer with lower PEO amount (EO30), hierarchical nanostructures were found with bicontinuous morphology or mixtures of wormlike and bicontinuous. For 20 wt.% of copolymer, a structural inhomogeneity was found: microphases composed of cross-linked epoxy network swollen with small amount of miscible PEO block, areas of PPO domains shielded by coronae of PEO blocks, and areas with insufficient cross-linked epoxy and more PEO blocks. Because of unfavorable interactions of PPO with the epoxy network as



**Fig. 9** TEM micrographs of (a) 90/10, (b) 80/20, (c) 70/30, (d) 60/40, and (e) 50/50 MDA-cured ER/EO30 blends (Reproduced with permission of (Guo et al.), copyright 2002 American Chemical Society)

well as with the insufficiently cured epoxy, microphase separation took place within both the phases to form the PPO spherical domains. For mixtures with 50 wt.% of copolymer, bicontinuous microphase structure was achieved, with both spherical and wormlike micelles of PPO.

Regarding ABA triblock copolymer that nanostructure epoxy systems via RIPS mechanism, the most important ones have been those copolymers obtained by chemical modification of one of the blocks in previously cited copolymers. In that way, PBS block in PCL-*b*-PBS-*b*-PCL has been converted into poly(ethylene-*co*-ethyl ethylene) (PEEES) (Cong and Zheng 2014), and PB block in PCL-*b*-PB-*b*-PCL has been converted into PEEE by hydrogenation (Hu et al. 2010). In both cases, the nanostructuring mechanism changed from RIPS to SA. The driving force for the RIPS of PBS or PB blocks is the decrease in entropic contribution to free energy of mixing with the occurrence of cross-linking reactions. It is proposed that the following two factors affect the formation of PBS or PB nanophases: (i) the immiscibility of PBS and PB with the cross-linked epoxy and (ii) the competitive kinetics between polymerization and microphase separation. The former is governed by the factors of thermodynamics in the blends of epoxy with PBS or PB, whereas the latter affected the morphologies of the thermosets since the PBS or PB nanophases were formed under the nonequilibrium condition. As the curing reaction proceeds, the mixtures underwent a series of structural changes involving chain extension, branching, and cross-linking in succession, and the viscosity of system was significantly increased and the system was converted into

the three-dimensional networks due to the occurrence of gelation. For the systems containing PCL-*b*-PEEES-*b*-PCL or PCL-*b*-PEEE-*b*-PCL, the curing reaction was started from the self-organized mixtures composed of epoxy system and the copolymer. The formation of PEEES or PEEE nanophases was governed by the equilibrium thermodynamics of the triblock copolymer in the precursors of epoxy, i.e., the size and shape of the micelles were dependent on the establishment of epoxy-phobic and epoxy-philic balances with PEEES or PEEE and PCL blocks, respectively. With identical concentrations of the copolymers, the size of PEEES or PEEE nanophases is larger than that of PBS or PB under the same curing conditions. In both cases, the morphologies obtained and their evolution were very similar than that explained above for RIPS mechanism: spherical micelles for low content, interconnected domains by increasing block copolymer amount, and wormlike micelles for higher contents. Very similar evolution of morphology generated by SA was found for PCL-*b*-PDMS-*b*-PCL (Xu and Zheng 2007) and PCL-*b*-PE-*b*-PCL (Zhang and Zheng 2013) copolymers. In the last case, besides described morphology, the crystallization of PE was found to occur in confined manner.

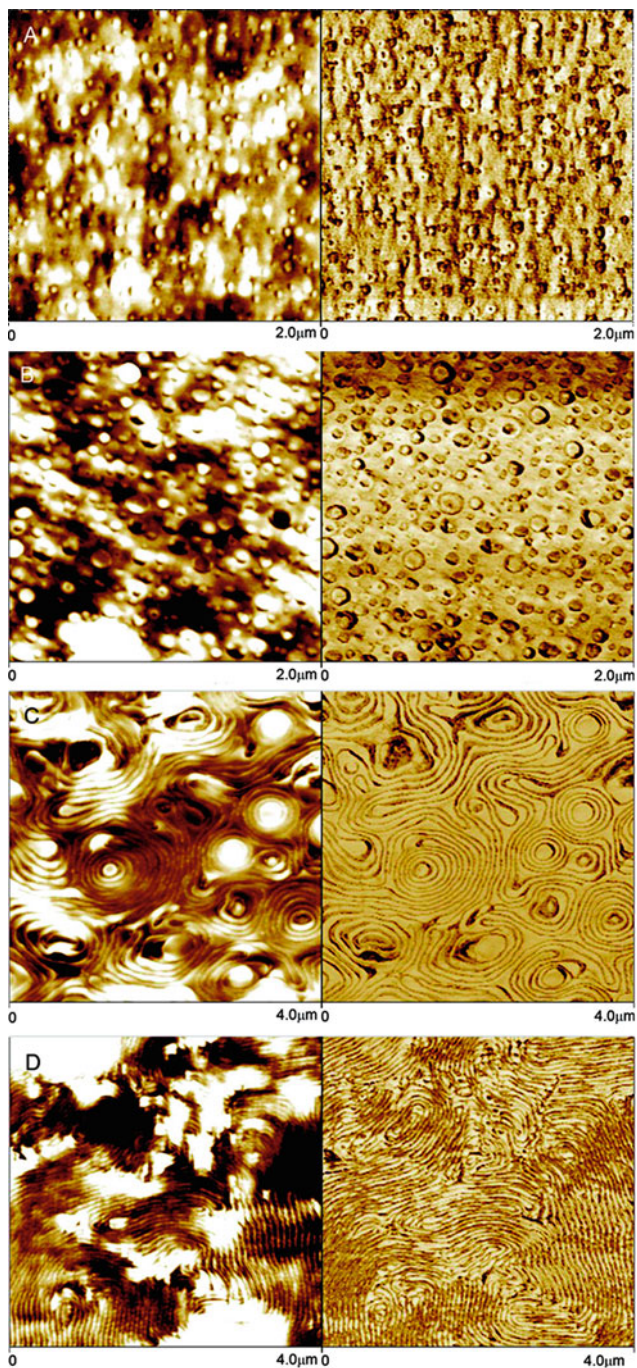
### Amphiphilic ABC-Type Triblock Copolymers

The presence of three different blocks with different solubility in epoxy precursors and cured systems complicates obtained morphologies and mechanisms for their obtention. A combination of RIPS and SA mechanisms (Fan et al. 2009), a tandem RIPS mechanism (Yu and Zheng 2011), and SA with partial deswelling of one of the blocks (Ritzenthaler et al. 2002) during cure have been described. For mixtures of epoxy with PDMS-*b*-PCL-*b*-PS copolymer, a combination of RIPS and SA mechanism has been found. PDMS block is immiscible with epoxy precursors before cure, forming spherical or wormlike micelles before cure. During cure, RIPS of PS subchains occurred in the presence of PDMS nanophases, while PCL remained miscible. Preformed PDMS nanophases acted as template of the RIPS of PS, confining PS subchains around PDMS nanophases. Obtained morphologies can be seen in Fig. 10 for different block copolymer contents. For 10 and 20 wt.% of copolymer, spherical nanodomains were found, assignable to the immiscible components (i.e., PDMS and PS), whereas the continuous matrix to epoxy is miscible with PCL subchain. Dispersed nanodomains were not homogeneous and displayed a “core-shell” structure. The “core” could be ascribed to PDMS subchain, whereas the “shell” could be attributed to PS subchain. For higher copolymer contents different morphologies were found.

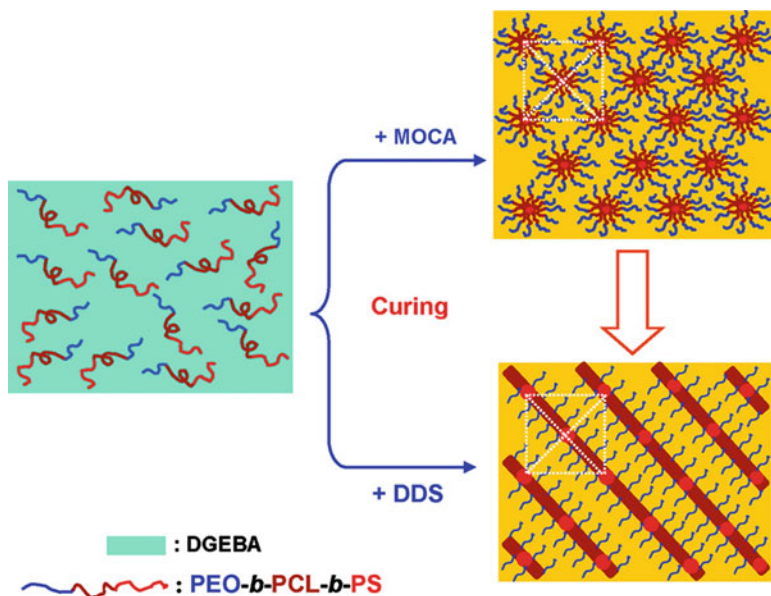
Thermosets containing 30 wt.% PDMS-*b*-PCL-*b*-PS showed large-scaled circled and lamellar structures, and all the features were concentric circled (Fig. 9c). This was the first observation of the formation of concentric-circled nanostructures in epoxy thermosets. With increasing the content of triblock copolymer, the concentric-circled lamellar morphology was transformed into the large-scaled lamellar nanostructures (Fig. 9d).

For PEO-*b*-PCL-*b*-PS copolymer (Yu and Zheng 2011), a tandem RIPS mechanism was found. When cured with MOCA hardener, morphologies consisting on





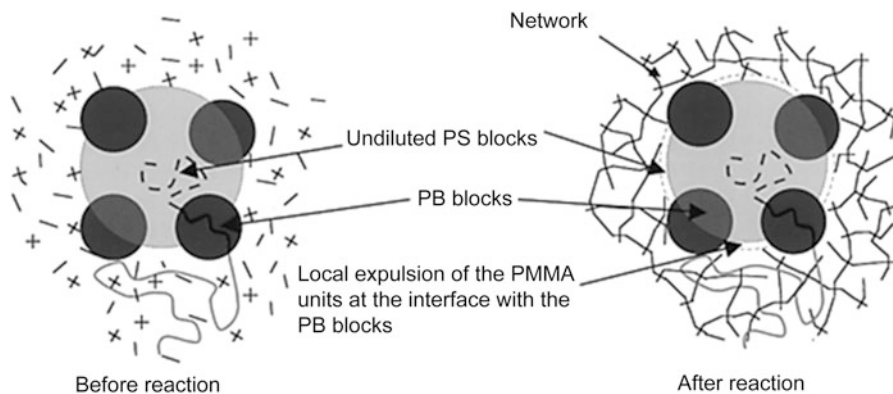
**Fig. 10** AFM images of epoxy thermosets containing PDMS-*b*-PCL-*b*-PS triblock copolymer. *Left*, height image; *right*, phase image. (a) 10, (b) 20, (c) 30, and (d) 40 wt.% of PDMS-*b*-PCL-*b*-PS triblock copolymer (Reproduced with permission of (Fan et al.), copyright 2009 American Chemical Society)



**Scheme 4** Formation of spherical and lamellar nanophases in epoxy thermosets containing PEO-*b*-PCL-*b*-PS triblock copolymer (Reproduced with permission of (Yu and Zheng), copyright 2011 American Chemical Society)

spherical nanophases of PS arranged into body-centered cubic lattice were found, formed by RIPS of PS subchains. Increasing copolymer content, spherical domains began to interconnect, resulting finally in wormlike micellar morphology. When DDS was used as hardener, due to the immiscibility of PCL with cured epoxy/DDS system, a RIPS of PS and PCL occurred, resulting in spherical nanodomains of PS and PCL (for copolymer contents less than 20 wt.%) dispersed in a continuous epoxy phase where PEO was solved. For 30 wt.% of copolymer and higher, lamellar morphology was obtained, being each nanolayer composed by PS and PCL. The scheme of this mechanism can be seen in Scheme 4.

Finally, for PS-*b*-PB-*b*-PMMA copolymer, Ritzenthaler et al. (2002) found that morphologies when mixed with an epoxy system depended on hardener. Before cure, three block self-organized in PS spheres surrounded by PB nodules while PMMA remained soluble forming a swollen corona. So SA mechanism was followed for nanostructuring. When cured with MCDEA, undiluted PS and PB blocks formed a “spheres on spheres” morphology, while most of PMMA was embedded in the matrix, but with a partial deswelling of PMMA resulting in a pure PMMA phase at the interface with PB blocks. Scheme 5 shows the process of nanostructure formation. If cure was carried out with DDS, the RIPS of PMMA occurred at early stages of cure, leading to flocculated, micrometer-size elongated nanostructures.

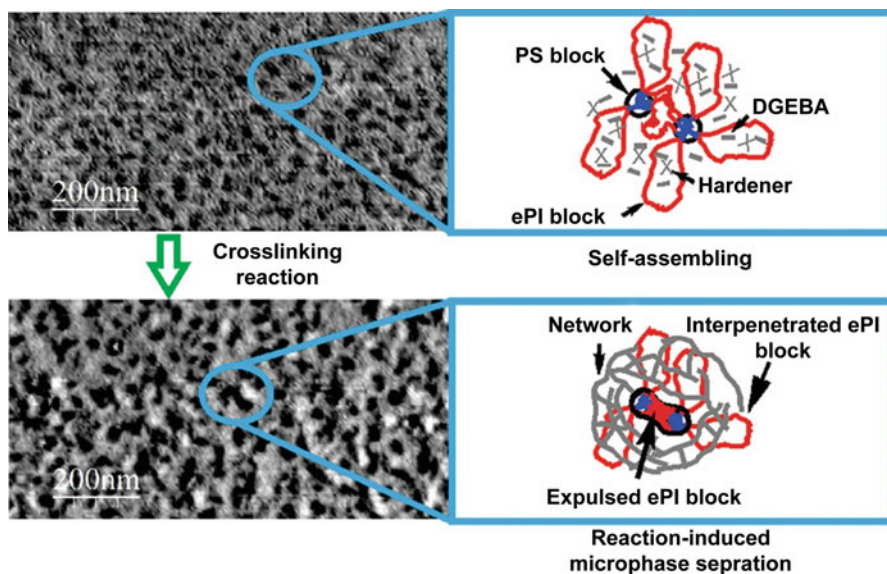


**Scheme 5** Schematic description of the evolution of the triblock organization in the DGEBA–MCDEA thermoset system before and after reaction (Reproduced with permission of (Ritzentaler et al.), copyright 2002 American Chemical Society)

## Epoxy/Chemically Modified Block Copolymer Blends

A second generation of block copolymers has been developed using the concept of chemical compatibilization that consists on chemical modification of one of the blocks in the copolymer in order to compatibilize and react with epoxy matrix. In this way, the epoxidation of the elastomeric block in thermoplastic elastomer (TPE) di- and triblock copolymers has been the main trend: epoxidation of poly(isoprene) block in poly(styrene-*block*-isoprene-*block*-styrene) (PS-*b*-PI-*b*-PS) copolymer (Garate et al. 2011, 2013, 2014) and epoxidation of poly(butadiene) block in poly(styrene-*block*-butadiene-*block*-styrene) (PS-*b*-PB-*b*-PS) or poly(styrene-*block*-butadiene) (PS-*b*-PB) copolymers (Serrano et al. 2005b, 2006, 2007; Ocando et al. 2008a, 2009; George et al. 2012, 2013).

Starting with triblock copolymers, for epoxidized PS-*b*-PI-*b*-PS (Garate et al. 2011, 2013, 2014), epoxidation degree has been found to determine obtained nanostructured pattern. In the uncured state, PS blocks self-assembled in sphere-like nanodomains with a short-range order, while epoxidized polyisoprene (ePI) subchains were initially miscible with the epoxy precursors. As cure proceeded the PS nanodomains became gradually distorted switching to bigger and less organized structures, due to RIPS of ePI subchains which became immiscible with the epoxy system as the curing process occurs. However, this demixing process was partial because of the reaction between ePI subchains and the epoxy matrix, which reduced ePI subchains mobility. The higher the epoxidation degree was, the lower the demixing process was, and therefore less interconnected sphere-like structures were formed. For high epoxidation degrees, nanostructured pattern changed from distorted and interconnected sphere-like nanodomains when the epoxidation degree was 65% to sphere-like nanostructures for 100% of epoxidation. Figure 11 shows obtained morphologies and a schematic representation of their obtention. When an epoxidized PS-*b*-PI-*b*-PS copolymer incorporating amine-reactive functionalities

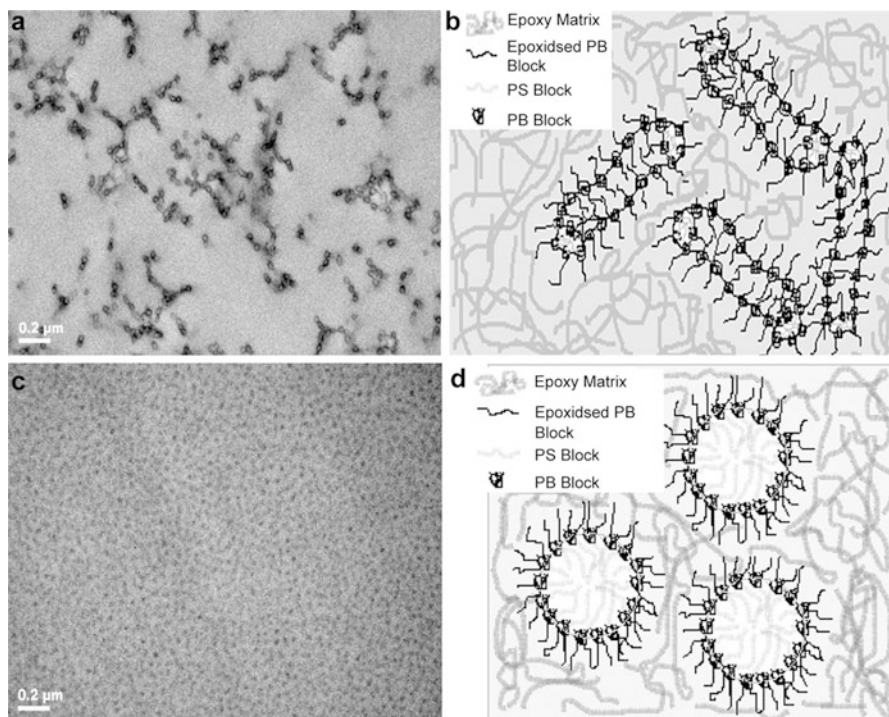


**Fig. 11** AFM images and schematic description of morphologies obtained for epoxy mixtures with 23% of PS-*b*-PI-*b*-PS 100% epoxidized (Reproduced with permission of (Garate et al.), copyright 2013 American Chemical Society)

(eSIS-AEP) in the epoxidized block was used, nanostructured materials with sphere-like nanodomains were formed before curing by SA of PS blocks. Conversely to the typical ePI demixing process previously cited, for the case of eSIS-AEP, the nanodomain morphology was preserved, which indicated that no ePI-AEP demixing process occurred as a consequence of the enhanced reactivity of eSIS-AEP with epoxy matrix.

Regarding epoxidized PS-*b*-PB-*b*-PS copolymer (George et al. 2012, 2013), it was found that nanostructures were generated for epoxidation degrees of 39% and higher. Without epoxidation and with lower epoxidation degrees (25%), macroseparation or generation of microstructures was obtained. So epoxidized copolymers at high degree of epoxidation (39% and 47%) could be able to create nanostructured templates in epoxy resins, as it can be seen in Fig. 12.

For the copolymer 39% epoxidized, wormlike micellar morphology was obtained. The reduced compatibility of epoxidized PB blocks in epoxy matrix was due to the presence of unepoxidized PB block that produced a tendency toward aggregation of vesicles and hence a wormlike micelle morphology. For the copolymer 47% epoxidized, these interconnected wormlike micelle morphologies changed to long-range ordered nanostructured spherical micelles. Regarding the mechanism that led to described morphologies, since PB subchains remained immiscible in the epoxy resin, the formation of PB core by SA before curing followed by RIPS of PS phase over the PB phase could be expected. However, there was a small unepoxidized PB phase present in the mixture. During cure, a part



**Fig. 12** TEM images of epoxy/eSBS/DDM blends containing 10 wt.% eSBS epoxidized at (a) 39 and (c) 47 mol%, schematic representation of epoxy/eSBS/DDM blends containing 10 wt.% eSBS epoxidized at (b) 39 and (d) 47 mol% (Reproduced with permission of (George et al.), copyright 2013 American Chemical Society)

of the PS subchain phase is separated to form nanosized PS core, followed by reaction-induced self-assembly of most of the unepoxidized PB phase to form a shell of PB chains over the PS core.

The minimum degree of epoxidation needed for nanostructuring epoxy system with PS-*b*-PB-*b*-PS copolymer has also been investigated, together with the effect of PS block content (Ocando et al. 2008b). A minimum of 27 mol% of epoxidation, which corresponds to 4.8 wt.% of epoxidized PB units in the overall mixture, was needed to ensure nanostructuring of final mixtures. Generated morphologies were found to be very dependent on PS content. PS contents between 16 and 20 wt.% in the overall mixture were needed to obtain hexagonally ordered nanostructures. Additionally, as the amount of block copolymer added to the epoxy matrix increased, the morphologies in the mixtures develop from micelles to vesicles, to wormlike and finally to hexagonally ordered nanostructures. Morphologies were generated by RIPS of PS block, together with some local demixing of PB block. An increase of epoxidation produced a decrease in domains size, probably due to a smaller amount of phase-separated non-epoxidized PB units around PS domains.

PS-*b*-PB diblock copolymer (both linear and star shape) has also been epoxidized in order to obtain nanostructured mixtures with epoxy systems (Serrano et al. 2005, 2006, 2007; Ocando et al. 2009). For linear PS-*b*-PB (Serrano et al. 2007), depending on the block copolymer content and its epoxidation degree, the PS domains can display micellar, wormlike, or hexagonally packed cylinder structures. Independent of the copolymer percentage and epoxidation degree used (37% and 46%), cured blends containing epoxidized copolymers were nanostructured. With 30 wt.% of copolymer, morphology consisting on wormlike or cylindrical irregular domains of PS was obtained for lower epoxidation degree, while hexagonally ordered structure was obtained for the copolymer 46% epoxidized. With 10 wt.% of copolymer, micellar structures were obtained for both epoxidation degrees. Morphology development was by RIPS of PS block, while reactive epoxidized PB block remained mostly miscible with the growing thermosetting epoxy system during the polymerization reaction (among some local expulsion). Nanostructuring occurred through an epoxy-miscible block.

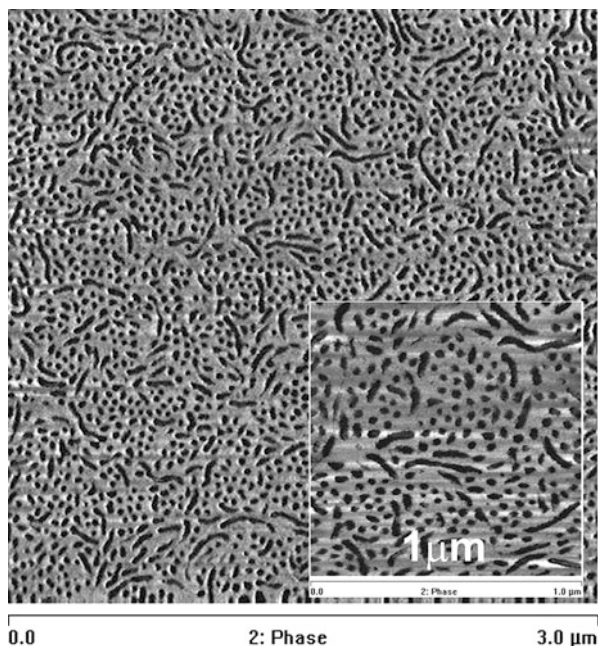
The critical epoxidation threshold to achieve nanostructuring of epoxy systems with PS-*b*-PB copolymer has also been investigated (Ocando et al. 2009). Different mechanisms are involved through morphology development, depending on the content of epoxidized PB (PBep) in the initial mixture.

A minimum threshold of around 27% was found. Near this threshold, microphase separation was obtained through SA mechanism of PBep and RIPS of PS block. New bilayered structures developed by the occurrence of these two mechanisms, leading to vesicles or long wormlike micelles depending on the concentration of block copolymer in the overall mixture. When the epoxidation degree was considerable lower than the minimum threshold, macrophase separation occurred as expected. Nevertheless, at higher epoxidation degree, long-range order microstructures of PS were obtained as a consequence of RIPS because the initial miscibility of both blocks with the epoxy resin before curing, as it can be seen in Fig. 13.

In the AFM image, a morphology consisting in hexagonally packed PS cylinders oriented parallelly and perpendicularly to the cutting surface can be seen. The schematic representation of morphology development for different epoxidation degrees can be seen in Scheme 6.

Epoxidation of PS-*b*-PB star block copolymer has also been developed (Serrano et al. 2007) in order to analyze the effect of epoxidation degree on the ability of these copolymers to produce nanostructures inside the epoxy matrix. The epoxidation threshold was found to be around 40%, higher than that of linear copolymer. As epoxidation of PB block enhanced the miscibility of copolymers and the epoxy resin, nearly nanoordered structures were obtained for uncured blends, even for high epoxy resin content. So SA mechanism is followed for morphology development. For epoxidation degrees lower than 40%, copolymer macrophase separated, forming an inverted morphology, with epoxy particles dispersed in a continuous copolymer matrix. For epoxidation degrees higher than the threshold, a morphology consisting on PS cylinders arranged in the epoxy-rich phase was obtained, with the presence of PB units in both the epoxy-rich phase and near to the PS cylinders. For

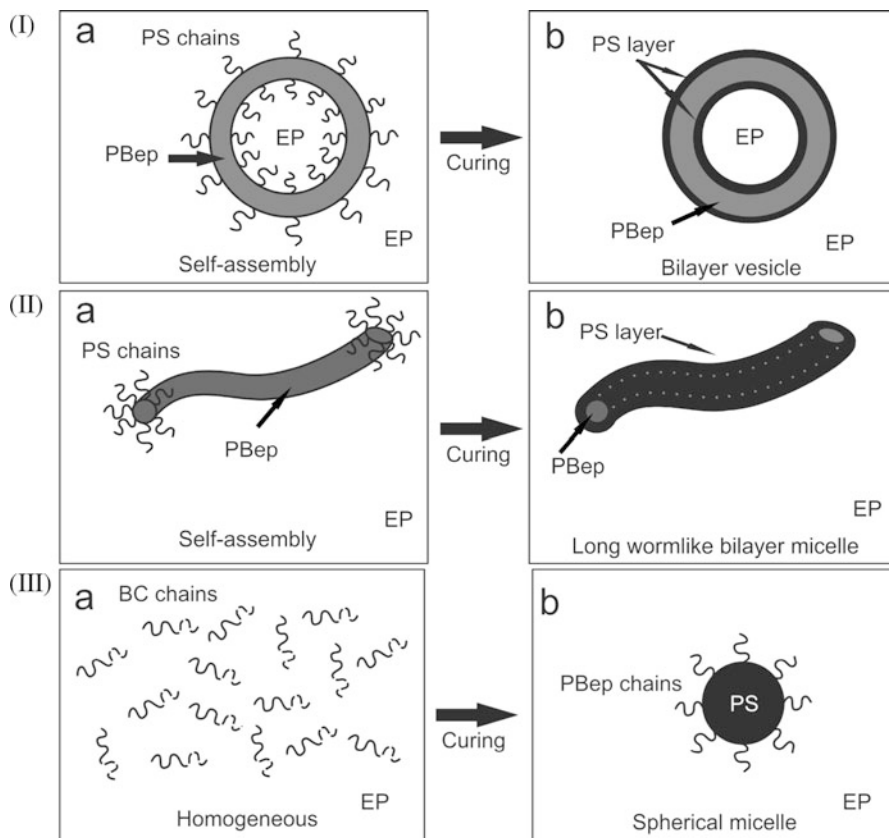
**Fig. 13** TM–AFM-phase image for epoxy mixture containing 30 wt.% SB50(1) ep35. PS block appears *dark* in AFM images (Reproduced with permission of (Ocando et al.), copyright 2009 American Chemical Society)



an epoxidation degree of 61%, a morphology consisting in PS cylinders arranged in an epoxy-rich phase containing both epoxidized and non-epoxidized PB segments was obtained, which indicate at least some partial miscibility of the epoxidized PB block with the cured epoxy matrix as a consequence of the non-epoxidized segments of PB block. For the highest epoxidation degree achieved (76%), a long-order hexagonal structure was obtained. Obtained morphologies can be seen in Fig. 14.

### **Ternary Systems Based on Nanostructured Epoxy and Inorganic Nanoparticles**

The development of new materials based on ternary systems composed by epoxy matrices nanostructured with block copolymers in which inorganic nanoparticles can be placed has received the attention of several authors during the last years. Nanoparticles can be synthesized in situ during nanocomposite preparation (Gutierrez et al. 2010a; Tercjak et al. 2012) by techniques like sol–gel or previously synthesized nanoparticles can be added during nanocomposite preparation (Ocando et al. 2010; Esposito et al. 2014). Several reasons can be found for this strategy. From one side, the poor fracture toughness of thermosetting polymers has represented an important drawback for many potential engineering applications. In order to overcome this problem, the preparation of nanostructured materials via SA or RIPS of block copolymers modified epoxy matrices has been one of the most important approaches. This



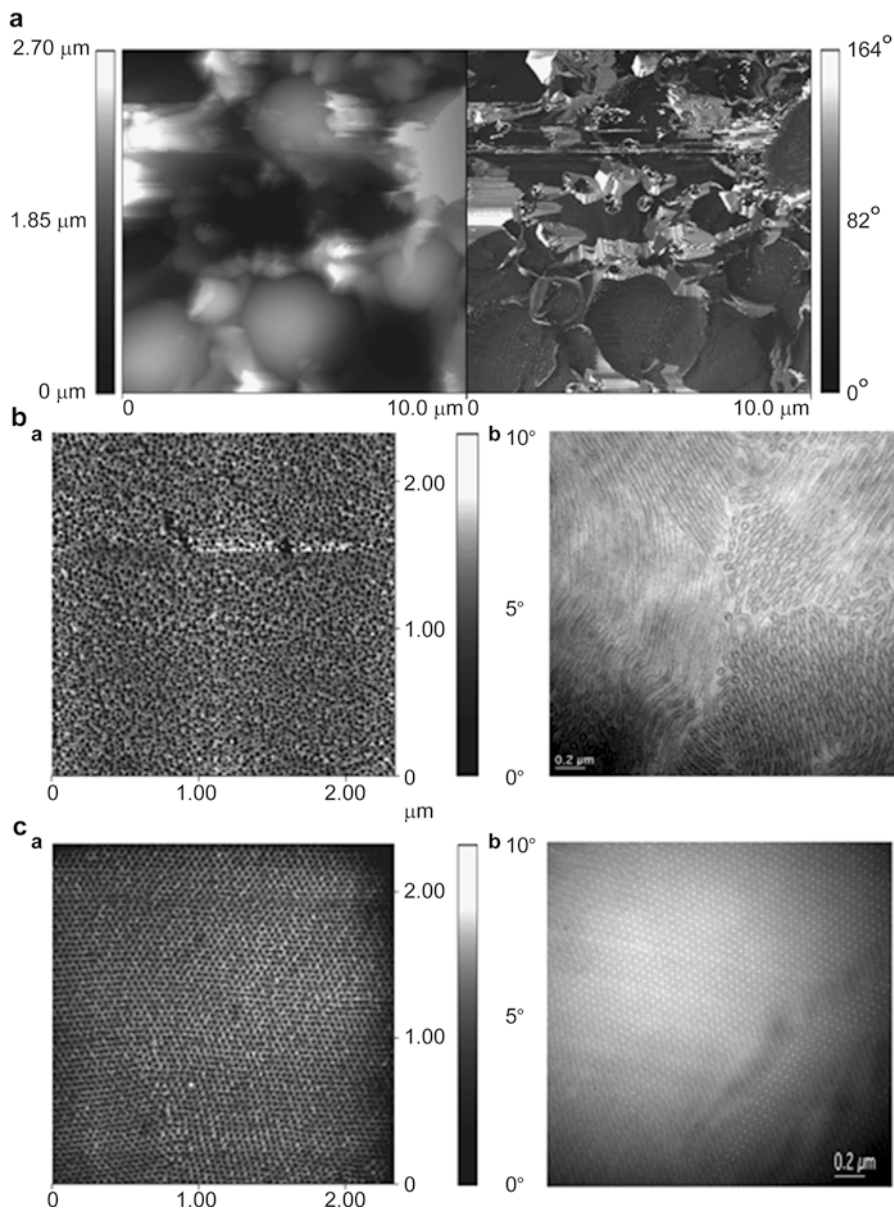
**Scheme 6** Schematic representations of blocks organization for the thermosetting mixtures containing: (I) 10 wt.% SBep22, (II) 30 wt.% SBep22, and (III) 10 wt.% SBep28 block copolymers before (a) and after curing (b) (Reproduced with permission of (Ocando et al.), copyright 2009 American Chemical Society)

strategy can further optimize the fracture toughness of brittle epoxy matrices and in the same time can retain their transparency because phase separation in these systems generally occurs at nanometer scale (Thio et al. 2006; Larrañaga et al. 2007; Liu et al. 2008). Block copolymers with one block chemically modified in order to make it compatible with the epoxy matrix, such as epoxidized SBS, have been used for this purpose (Serrano et al. 2005a, 2007; Ocando et al. 2009). Nevertheless, one disadvantage of block copolymers is the risk of sacrificing the stiffness of the epoxy matrix (Ocando et al. 2008b). An approach to avoid this behavior can be the addition of inorganic nanoparticles into the epoxy matrix to enhance its mechanical behavior by lowering the plasticization effect obtained by inorganic additives and also preserving an optical transparency (Johnsen et al. 2007; Ocando et al. 2010).

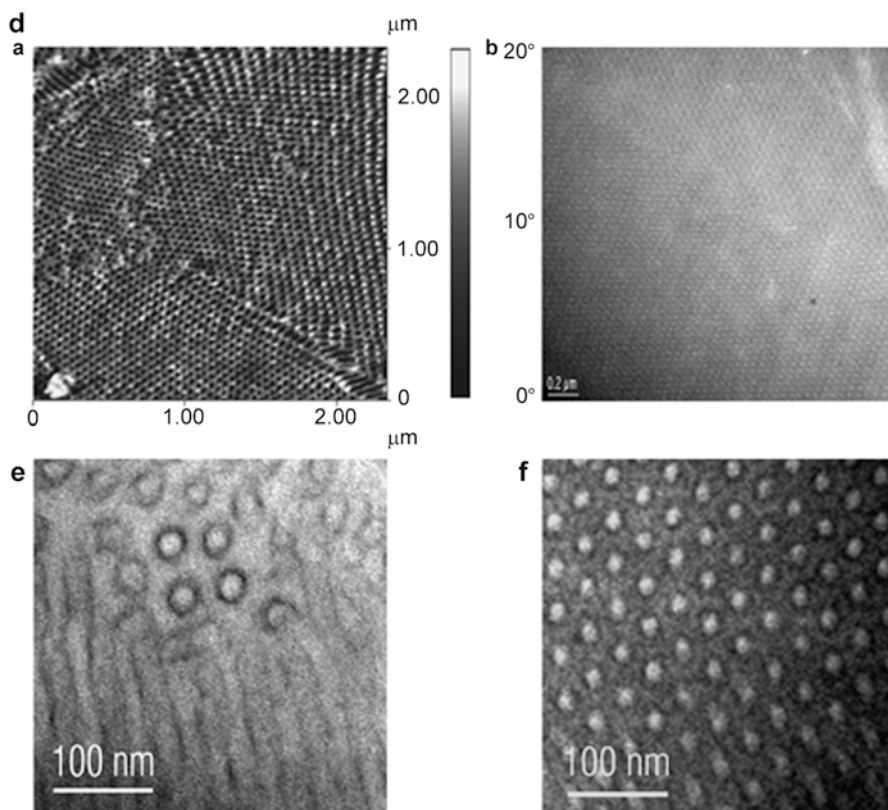
On the other hand, the fabrication of inorganic/organic epoxy-based materials modified with nanoparticles is an active research field due to optic, magnetic,



conductive, photonic, and other properties of the inorganic filler (Tercjak et al. 2009; Tercjak and Mondragon 2010; Pethrick et al. 2010; Gutierrez et al. 2010a). Nanostructured epoxy-based materials can act as templates for nanoparticles and allow the control of their distribution and size playing with



**Fig. 14** (continued)



**Fig. 14** TM–AFM-phase (I) and TEM (II) images for DGEBA/MCDEA blends containing 30 wt.% of: (a) SepB15, (b) SepB40, (c) SepB61, and (d) SepB76 copolymers. (e, f) Figures show higher magnification of TEM images for SepB40- and SepB61-modified systems, respectively (Reproduced with permission of (Serrano et al.), copyright 2006 American Chemical Society)

preparation conditions, concentration of nanoparticles, type of matrix used as a template, and others (Tercjak et al. 2009; Tercjak and Mondragon 2010; Pethrick et al. 2010; Gutierrez et al. 2010b).

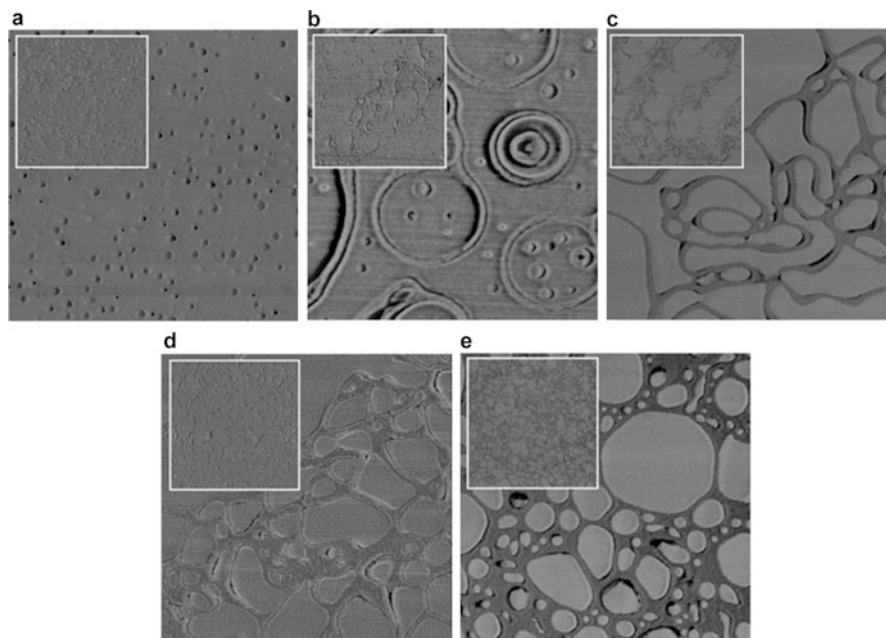
Besides mechanical, electric, or magnetic properties incorporated by inorganic nanoparticles, the morphology or nanostructures obtained for epoxy/block copolymer blends may be altered or not by the presence of nanoparticles. Regarding the main interest of this chapter, how different nanoparticles such as  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ , or carbon nanotubes (CNT) affect morphologies obtained for epoxy/block copolymer mixtures will be analyzed below, also pointing out the positioning of inorganic nanofillers in the generated nanodomains.

Starting with ternary systems based on epoxy matrices nanostructured with block copolymers and inorganic nanofillers in situ synthesized, nanocomposites with  $\text{TiO}_2$  nanoparticles obtained by sol–gel must be underlined. Multifunctional hybrid nanostructured thermosetting materials obtained by using poly(styrene-*b*-

ethylene oxide) (SEO) as a template for selective location of TiO<sub>2</sub> nanoparticles (Gutierrez et al. 2010a; Tercjak et al. 2012) have shown some morphological changes when compared with the corresponding binary systems, especially for high inorganic contents. Binary epoxy/SEO systems with 40 wt.% of copolymer resulted in a hexagonally ordered structure with PS block cylinders mainly perpendicularly oriented, since PEO block is miscible with the epoxy matrix and segregation of PS block-rich phase took place during network formation (Gutierrez et al. 2010a). For ternary systems, similar morphologies were obtained but with PS cylinders arranged parallel and perpendicular. Nanoparticles appeared in the interface between PEO-modified epoxy matrix and microphase-separated PS block domains. By increasing inorganic content, morphology changed to spherical PS domains uniformly dispersed in the continuous epoxy matrix where PEO block remained miscible. Moreover, a higher amount of uniformly distributed nanoparticles was detected in the epoxy-rich matrix, due to their interaction.

As it is interesting to check the effect of block content in the copolymer, let us have a look at ternary systems that were prepared with a SEO copolymer with low PEO content and TiO<sub>2</sub> nanoparticles (Tercjak et al. 2012). No many morphological changes have been detected with the addition of nanoparticles. However, nanoparticles appeared placed mainly in the PEO-/epoxy-rich phase. Starting with epoxy/SEO binary systems, it has to be pointed out that by using a SEO copolymer with low PEO content, unusual morphologies can be obtained, for systems containing less than 30 wt.% SEO. This is explained by the UCST behavior of PS in the epoxy system (at around 100 °C, while cure is carried out at 190 °C) and also by the short PEO block, which results in difficulties to stabilize PS domains by PEO block. For 40 wt.%, phase inversion takes place. Morphologies obtained for those systems can be seen in Fig. 15.

For systems with 5 wt.% of SEO (Fig. 15a), a morphology consisting of spherical PS block domains dispersed in epoxy/PEO matrix is formed. PEO remains miscible due to the intermolecular hydrogen bonding interactions between the hydroxyl groups of amine-cured epoxy and ether oxygen atom of PEO. Increasing SEO content, morphology changes to long wormlike micelles passing through-out vesicle-like morphology. For 10 wt.% SEO (Fig. 15b), vesicles of PS with different size can be seen dispersed in the continuous epoxy/PEO phase. This vesicles present layered structure, with two separated phases in each vesicle domain: outer layers of PS block phase confining between them an inner layer of PEO/epoxy phase forming the vesicle shell with the core being related to the epoxy-rich phase. Some vesicles can appear interconnected forming wormlike micelles. With 20 wt.% PEO (Fig. 15c), a morphology change is detected, with long interconnected wormlike micelles (with bilayered structure) well dispersed in the epoxy/PEO continuous phase. The system with 30 wt.% SEO shows a very similar morphology (Fig. 15d). Addition of 40 wt.% SEO provokes phase inversion, in which PEO/epoxy phase is macrophase separated into continuous PS-rich phase (Fig. 15e). The effect of sol-gel solution adding (and thus TiO<sub>2</sub> nanoparticles) on morphologies is analyzed next. Independently on the generated morphology, nanoparticles are confined into PEO-/epoxy-rich phase near the microphase-



**Fig. 15** TM-AFM-phase image ( $5 \times 5 \mu\text{m}$ ) of different SEO-(DGEBA/MCDEA) systems containing: (a) 5 wt.%, (b) 10 wt.%, (c) 20 wt.%, (d) 30 wt.%, (e) 40 wt.% SEO block copolymer. *Left, top inset* in each figure corresponds to  $15 \times 15 \mu\text{m}$  (Reproduced with permission of (Tercjak et al. 2012), copyright 2012 Elsevier Ltd)

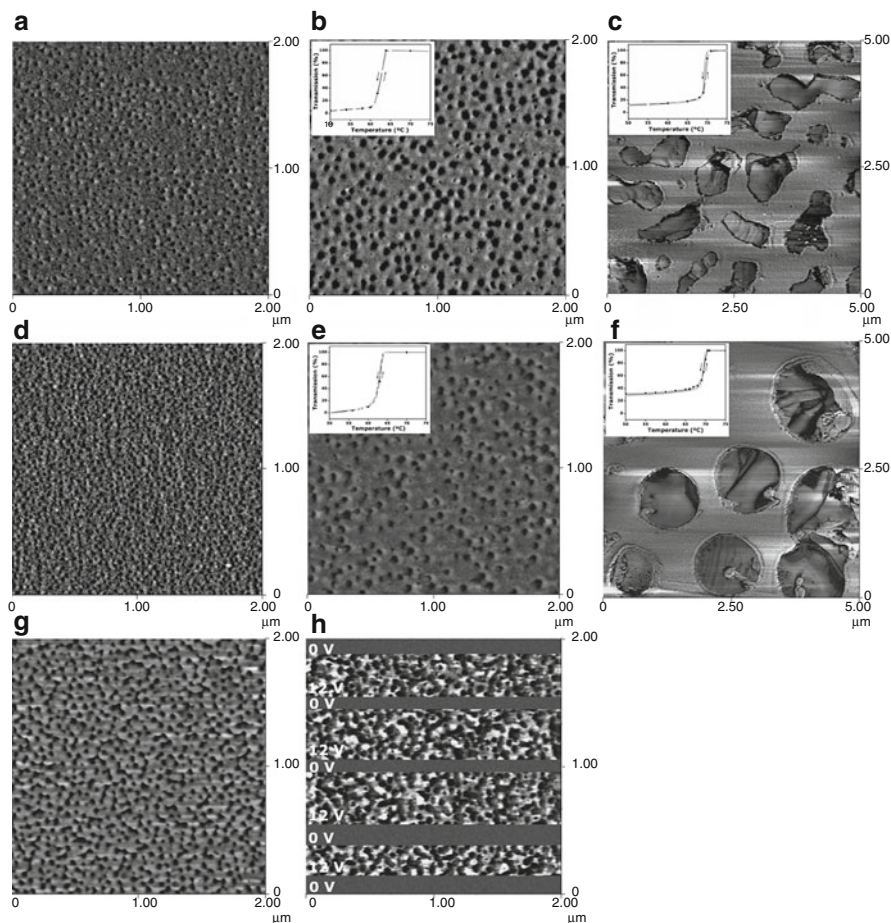
separated PS block. For the nanocomposite based on the system with 5 wt.% of SEO, separated domains have been found to be much bigger than those of the binary system, due to the nanoparticles confinement in the interphase between PS block-rich phase and epoxy/PEO phase. Similar behavior can be found for the nanocomposite with 10 wt.% SEO with nanoparticles located into the epoxy-rich phase confined between the bilayered PS-rich phases formed vesicle structure. For the nanocomposite with 20 wt.% of SEO, when compared with the binary system, nanoparticles were located in some of the separated PEO/epoxy-rich domains and confined between microphase-separated long PS block wormlike micelles.

Regarding the ternary systems based on epoxy matrices nanostructured with block copolymers and previously synthesized inorganic nanofillers, it is worth to note that morphologies obtained for binary systems have not been very affected by the presence of nanofillers such as metal oxide nanoparticles (Ocando et al. 2010) or carbon nanotubes (Esposito et al. 2014). However, the dispersion of the nanofiller has been clearly improved when compared with epoxy/nanofiller binary systems, acting the copolymer as nanostructuring agent and surfactant. In this way, the nanostructuring of epoxy matrix with epoxidized SBS block copolymer has been found to improve the dispersion of  $\text{Al}_2\text{O}_3$  nanoparticles (Ocando et al. 2010). Nanostructured thermosets have been obtained through RIPS microphase

separation of PS block from the epoxy-/PB-rich phase, showing spherical micelles of PS nanodomains dispersed in the epoxy-rich phase for 30 wt.% of copolymer. With the addition of Al<sub>2</sub>O<sub>3</sub> nanoparticles, morphologies have maintained unaffected, with the same spherical micelles than in the binary system but with the presence of well-dispersed individual nanoparticles embedded in the epoxy matrix containing PS microphase-separated nanodomains. In this case, the microphase separation of PS block prevents the agglomeration of nanoparticles. In the same way, the nanostructuring of an epoxy matrix with epoxidized SBS copolymer has been found to be unaltered after the addition of carboxylic acid-modified multiwalled carbon nanotubes (a-MWCNT) (Esposito et al. 2014). With 5, 10, and 20 wt.% of epoxidized SBS, different morphologies can be obtained: spherical micelles of PS in epoxy matrix for 5 wt.% and wormlike ones for 10 and 20 wt.%, respectively. Obtained morphologies have not been affected by the addition of a-MWCNT, but their dispersion has been clearly improved when compared with binary epoxy/a-MWCNT systems: copolymer acted as dispersing agent, due to the  $\pi$ - $\pi$  stacking interactions between MWCNT walls and aromatic rings into microphase-separated PS nanodomains, as well as the interactions between the carboxylic acid groups and epoxy matrix. Those interactions seemed to act synergistically to improve a-MWCNT dispersion.

Going further in the preparation and characterization of hybrid inorganic/organic thermosetting materials, quaternary systems based on nanostructured epoxy with nanoparticles and low molecular weight liquid crystals also have been developed (Tercjak et al. 2009), analyzing the effect of both liquid crystal and nanoparticles on generated morphologies. Firstly the effect of liquid crystal on nanostructured epoxy/block copolymer systems has been analyzed (Tercjak and Mondragon 2008). Different morphologies can be obtained depending on the amount of block copolymer and liquid crystal. Preparing ternary systems based on epoxy modified with SEO copolymer and a liquid crystal such as 4'-(hexyloxy)-4-biphenylcarbonitrile (HOBC) different morphologies has been found (Tercjak and Mondragon 2008), as it can be seen in Fig. 16.

Depending on SEO and HOBC amounts, different morphologies have been obtained: for epoxy system modified with 5, 10, and 15 wt.% SEO, PS block microseparated forming spherical or wormlike micelles as was previously pointed out. For ternary systems with 30 wt.% of liquid crystal, HOBC was within these micelles (increase of microphase-separated domains in the ternary systems when compared with binary ones). When 30 wt.% of HOBC was added, neither systems containing 5 wt.% SEO nor those containing 10 or 15 wt.% SEO presented macrophase-separated domains of the liquid crystal phase. If a SEO copolymer with lower PEO content was used, macrophase-separated domains appeared, thus indicating that the higher PEO content, partially miscible with epoxy resin, led to more stable HOBC/PS block microphase-separated thermoset systems. In the case of the addition of 50 wt.% HOBC to the system with 5 wt.% SEO (Fig. 16c), an almost continuous microstructure was obtained, the liquid crystal clearly altering the morphology of epoxy/SEO system. The effect of adding 50 wt.% of HOBC to the system with 10 or 15 wt.% SEO is the macrophase separation, which included



**Fig. 16** TM–AFM-phase images of DGEBA/MXDA systems modified with different SEO or/and HOBC contents: (a) 5 wt.% SEO, (b) 5 wt.% SEO–30 wt.% HOBC, (c) 5 wt.% SEO–50 wt.% HOBC, (d) 10 wt.% SEO, (e) 10 wt.% SEO–30 wt.% HOBC, (f) 10 wt.% SEO–50 wt.% HOBC, and (g) 15 wt.% SEO–30 wt.% HOBC. (h) AFM-phase images of 15 wt.% SEO–30 wt.% HOBC. The insets show thermo-optical curves during the heating/cooling cycle (Reproduced with permission of (Tercjak and Mondragon 2008), copyright 2008 American Chemical Society)

PS blocks within. This behavior is very similar to that showed by the SEO copolymer with lower amount of PEO block. As morphologies generated in those ternary systems influenced the thermoresponsive behavior of the HOBC provoked by applying an external field such as temperature gradient and electrical field, it can be concluded that those properties can be tuned by controlling obtained morphologies.

After analyzing the effect of liquid crystal, quaternary systems were prepared by adding commercial  $\text{TiO}_2$  nanoparticles (Tercjak et al. 2009), obtaining multiphase

novel materials with interesting properties. 15 wt.% SEO, 40 wt.% HOBC, and 1 wt.% nanoparticles were used for preparing nanocomposites, whose morphologies can be seen in Fig. 17. Ternary system without nanoparticles resulted in a morphology consisting on HOBC/PS nanodomains microseparated from the PEO-/epoxy-rich phase. In quaternary systems, nanoparticles were confined within HOBC/PS nanodomains, increasing their size in an amount very similar to their size (around 20 nm). HOBC acted as surfactant for nanoparticle dispersion. The presence of nanoparticles in HOBC/PS nanodomains was confirmed by electrostatic force microscopy (EFM) measurements and by removing HOBC/PS organic phase by UV irradiation.

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## Conclusion

Block copolymers have been widely used and are still being used, as templates for generating nanostructured epoxy matrices. The control over morphology of those multicomponent thermosets is important for the improvement of their properties.

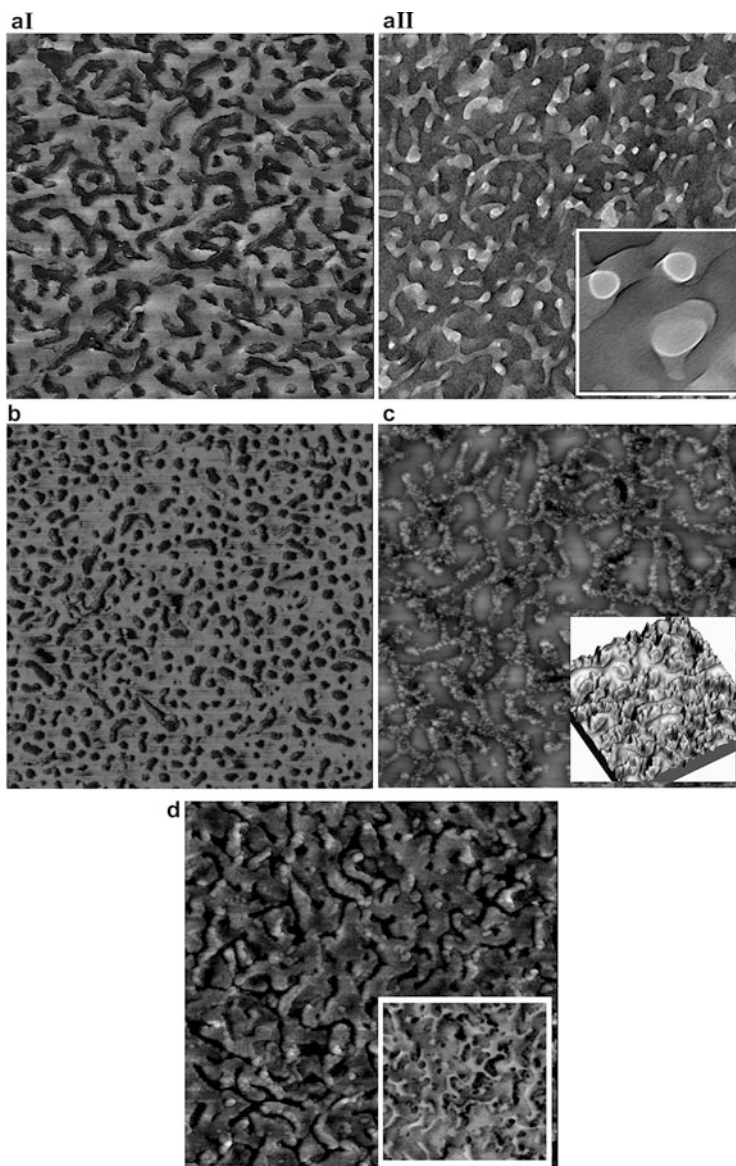
The concept of incorporating amphiphilic di- or triblock copolymers into thermosets has widely been accepted to prepare the materials with ordered nanostructures, achieved by both self-assembly or reaction-induced phase separation mechanisms, in which one of the blocks is miscible with the epoxy system, while the other one separates before or after curing process.

A second generation of di- or triblock copolymers has been developed using the concept of chemical compatibilization. This approach incorporates reactive groups (usually epoxy groups obtained by epoxidation) into one block in order to promote covalent bonding with the forming epoxy network without loss of ordering in the resulting blends.

Many different morphologies, such as spherical or wormlike micelles, hexagonally packed cylinders, bilayer micelles, or mixtures of them, among others, have been obtained when nanostructuring epoxy matrices with block copolymers.

Obtained nanostructures or morphologies depend on many factors apart from the copolymer type, such as cure temperature and hardener employed (affecting the miscibility of blocks in epoxy systems before and/or after cure), copolymer amount in the mixture, and topography or block sequence and composition, which also will determine the affinity with epoxy precursors and cured systems, determining the nanostructure and the mechanism for their formation.

Moreover, ternary or even quaternary systems can be prepared by adding nanoparticles and/or low molecular weight molecules such as liquid crystals in order to prepare novel materials with interesting specific properties. New components can affect somehow the morphology, but in most of cases morphologies of nanostructured epoxy matrices are almost unaltered or can be controlled by component amount or preparation conditions. New components usually give new electrical, magnetic, or optical properties depending on the morphologies, so controlling the former implies to control generated nanostructures.



**Fig. 17** (aI) TM-AFM-phase image ( $2 \times 2 \mu\text{m}^2$ ) of 1 wt.%  $\text{TiO}_2$ , 15 wt.% PSEO, 40 wt.% HBC-(DGEBA/MXDA) epoxy system. (aII) TEM image ( $2 \times 2 \mu\text{m}^2$ ) of 1 wt.%  $\text{TiO}_2$ , 15 wt.% PSEO, 40 wt.% HBC-(DGEBA/MXDA) epoxy system; *inset*: a higher magnification detail. TM-AFM-phase images ( $2 \times 2 \mu\text{m}^2$ ) of (b) 15 wt.% PSEO, 40 wt.% HBC-(DGEBA/MXDA) epoxy system; (c) 1 wt.%  $\text{TiO}_2$ , 15 wt.% PSEO, 40 wt.% HBC-(DGEBA/MXDA) epoxy system after 3 h of UV light exposure; *inset*, 3D image; (d) 1 wt.%  $\text{TiO}_2$ , 15 wt.% PSEO, 40 wt.% HBC-(DGEBA/MXDA) epoxy system after 3 h of applying 12 V by using EFM tip; *inset*, negative image



The versatility of those systems for giving different nanostructures, offering the possibility to design nanostructured materials with different patterns by controlling the mixture components and cure process, has been demonstrated.

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