Nanostructured Thermosets from Self-Assembled Amphiphilic Block Copolymer/Epoxy Resin Mixtures

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Abstract: Thermoset materials containing ordered structures with ∼10-nm dimensions were prepared from a mixture of a low-molecular-weight poly(ethylene oxide)−poly(ethylene-*alt*-propylene) (PEO−PEP) diblock copolymer and a poly(Bisphenol-A-*co*-epichlorohydrin) epoxy resin that selectively mixes with the PEO block. The phase behavior of PEO−PEP/epoxy blends, with compositions spanning 10−93 wt % block copolymer, was investigated in the uncured state (without hardener) using small-angle X-ray scattering (SAXS) and dynamic mechanical spectroscopy. Without hardener, the phase behavior of block copolymer/epoxy blends was similar to model block copolymer/homopolymer blends and varied with changes in the blend composition and temperature. The following morphologies were observed with increasing epoxy concentration: lamellar, cubic bicontinuous, hexagonally packed cylinders, body-centered cubic packed spheres, and disordered micelles. Methylene dianiline, an aromatic amine hardener, was added to the blends, and the real-time evolution of the phase behavior with cure was followed using SAXS measurements. As the epoxy molecular weight increased, the PEO block segregated from the epoxy matrix, as indicated by an increase in the principal spacing of the ordered structures and the occurrence of order−order phase transitions at certain compositions. However, macrophase separation between the epoxy and block copolymer did not occur. These results are interpreted as a transition from an equilibrium morphology to a chemically pinned metastable state as the cross-linking reaction progresses through the gel point.

Introduction

Porous and composite materials with ordered structures on the nanometer scale are interesting because of their potential applications as membranes and catalyst supports. The general route to preparing such materials is a templating scheme where a solution containing an amphiphilic compound and a reactive compound self-assemble to form lamellar, hexagonally packed cylindrical, or cubic structures with dimensions around 1−30 nm. Cross-linking the reactive component fixes the structure and prohibits further change.

Both inorganic and organic matrixes have been prepared, with inorganic materials of good thermal stability receiving a majority of attention. Mesoporous silicates (e.g., MCM-41) are formed by first blending a silicate source, such as tetraethoxysilane, with an organic amphiphile (e.g., an ionic surfactant,[1−5] neutral surfactant,[6−8] or block copolymer[9,10]) under the appropriate polymerization conditions. As the silicate oligomers react, electrostatic interactions between the silicate ions and the head group of the amphiphile affect both the final structure and the reaction kinetics. Therefore the ionic strength, pH, temperature, and composition must be controlled in specifying the resultant structure. After the ceramic has formed, the organic amphiphile can be removed by calcination or extraction, leaving a porous material.

Mesostructured organic materials have been made by polymerizing an organic monomer in either the hydrophobic[11,12] or aqueous[13] phase of a surfactant/water/organic ternary mixture. In these systems, there are no ionic interactions between the monomer and amphiphile, and the polymerization kinetics are unaffected by the presence of other components. Changes in the interactions between the organic reactive component and the amphiphile arise from the increased molecular weight of the polymerizing material, which decreases its miscibility with other compounds. This effect is clearly seen in rubber-modified epoxies (RME's), which are formulated by blending a reactive epoxy system with a miscible rubber.[14−17] As the epoxy cures,

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the associated increase in molecular weight forces macroscopic phase separation of the rubber from the thermoset. This process is often referred to as "polymerization-induced phase separation".[15,16]

Recently we introduced a method of creating nanostructured thermosets using an amphiphilic block copolymer, poly(ethylene oxide)−poly(ethylene-*alt*-propylene) (PEO−PEP), and a reac-
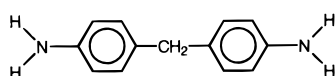
PEO-PEP

BPA348

CH₃

CH₃
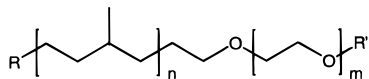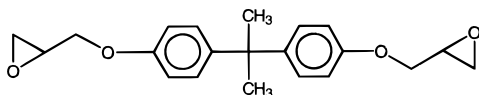
MDA

tive epoxy resin that selectively mixes with the PEO block.[18] This paper explores in more detail the underlying molecular factors controlling the morphology of blends in both the unreacted and reacted states. In the unreacted state, these mixtures form ordered phases with lamellar, bicontinuous, cylindrical, and spherical nanostructures depending on the blend composition. The understanding of this system's equilibrium phase behavior is facilitated by recent theoretical work on block copolymer/homopolymer blends.[19] When hardener is added and the epoxy cures, a highly cross-linked thermoset matrix is formed. Since there are no chemical reactions or ionic interactions between the epoxy and PEO backbone, the well-established epoxy polymerization kinetics[20,21] are largely unaffected by the presence of block copolymer. Unlike with mesoporous silicates, the effects of block copolymer self-assembly and epoxy network formation can be readily decoupled and evaluated. In contrast to RME's, macroscopic phase separation is entirely avoided in the PEO−PEP/epoxy system. However, PEO is expelled locally from the curing resin, thereby inducing minor changes in the microstructure scale and in certain instances driving order−order phase transitions.

The following section details the experimental aspects of the work and is followed by a summary of small-angle X-ray scattering (SAXS) and dynamic mechanical spectroscopy (DMS) results on the systems without hardener. Then in situ SAXS measurements are used to show the evolution of phase behavior when hardener is added to the system and the epoxy matrix cures. Transmission electron microscopy images reveal the real-space nanostructure in the cured materials. Finally, we discuss changes in the structure that accompany curing and speculate on the mechanism responsible for the retention of morphology during network formation.

Experimental Section

Block Copolymer Synthesis. The synthesis of PEO−PEP diblock copolymers has been described in detail by Hillmyer and Bates;[22] therefore, only the general scheme is given here. A multistep technique was used that begins with the anionic polymerization of isoprene in cyclohexane at 40 °C with *sec*-butyllithium as the initiator. The poly-(isoprenyl) chains were endcapped with ethylene oxide and liberated with acidic methanol (1:10 HCl:methanol). This produced hydroxy-terminated poly(isoprene) (PI-OH), which was catalytically hydrogenated to form hydroxy-terminated poly(ethylene-*alt*-propylene) (PEP-OH). Dried PEP-OH was dissolved in purified tetrahydrofuran (THF) under an inert atmosphere and titrated with a THF solution of potassium naphthalene to give the corresponding alkoxide. Ethylene oxide was polymerized at 40 °C to produce the second block, and the reaction was terminated with acidic methanol. The PEO−PEP was concentrated, redissolved in chloroform, and washed five times with distilled water to remove the KCl salts. The polymer was then vacuum-dried at elevated temperatures to remove the residual solvent and volatile byproducts (THF, naphthalene, and dihydronaphthalene).

^{1}H NMR spectroscopy was used to confirm the PI-OH degree of polymerization using the methyl hydrogens on the *sec*-butyl initiator group which can be resolved at low molecular weights. Complete saturation of the PEP-OH was also verified by ^{1}H NMR spectroscopy. The mole fraction of the final PEO−PEP was calculated from ^{1}H NMR results and converted into volume fractions using published densities for PEP ($\rho = 0.790$ g/cm³) and PEO ($\rho = 1.064$ g/cm³) at 140 °C.[23] PEO−PEP-5 (OP5), the diblock used for this study, has a PEO volume fraction of, $f_{PEO} = 0.51$, a number-averaged molecular weight of $M_n = 2700$ g/mol, and a polydispersity index $M_w/M_n = 1.10$.

Epoxy System. The epoxy system was a two-part mixture consisting of an epoxy resin and an aromatic amine hardener. Poly(Bisphenol-A-*co*-epichlorohydrin) (Aldrich, as received) with a molecular weight of 348 g/mol (BPA348) was the epoxy resin, and methylene dianiline (MDA) (Aldrich, as received) was the aromatic amine hardener. Hardener and epoxy resins were mixed in stoichiometric amounts (2 mol of epoxy resin:1 mol of hardener).

Blend Protocol. BPA348 and OP5 were blended under vacuum in glass vials while submerged in an oil bath at 150 °C. For cured samples, MDA was added after the block copolymer and epoxy were mixed. Details for making the 52 wt % OP5 cured sample are as follows: 0.69 g of BPA348 was transferred to a tared 20-mL glass vial containing a PTFE-coated stirbar. The glass vial was sealed with a one-hole rubber stopper connected to a vacuum line, immersed in a 150 °C oil bath, and the BPA348 was stirred and degassed at 150 °C for 10 min. The vial was removed from the oil bath and allowed to cool to room temperature, then 0.95 g of OP5 was added. The OP5/BPA348 mixture was stirred and degassed under vacuum in the 150 °C oil bath for 1 h, then cooled to room temperature. MDA (0.20 g) was added, and the OP5/BPA348/MDA mixture was evacuated and immersed in the 150 °C oil bath for 2 min to melt and mix the MDA (melting temperature of MDA is 91 °C). Given the small sample size, the MDA melts in a matter of seconds, allowing a homogeneous sample to be mixed in 2 min. Curing occurs while blending at this temperature; therefore, it is important to keep the sample at elevated temperatures for the shortest time necessary to ensure complete mixing. Throughout this paper, the stated concentration of different blend samples refers to the concentration of diblock in the blend. For example, 52 wt % OP5/BPA348 and 52 wt % OP5/BPA348/MDA both contain 52 wt % OP5. When the mixture contains hardener, the BPA348 and MDA are blended in stoichiometric quantities.

Curing Protocol. Within 2 h after sample preparation (the mixtures were kept at room temperature during this time), OP5/BPA348/MDA blends were cured in situ while performing SAXS measurements. Samples were mounted in an evacuated sample chamber on a resistance-heated/water-cooled sample stage and initially cured for 8 or 10 h at 100 °C, then post-cured at 150 and 180 °C. (Note: a stoichiometric

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mixture of BPA348/MDA reacts to >95% completion within 15 min at 180 °C).[20] The initial cure temperature was chosen to be below the order−disorder transition temperature of the blends (see Results) to ensure the sample was ordered when cured. Temperature changes were made stepwise (not ramped), and the exact cure profile for each sample studied is given in the Results.

Small-Angle X-ray Scattering. SAXS measurements were taken at the University of Minnesota on a custom-built system utilizing Franks mirror optics and a Rigaku RU-200BVH rotating anode generator to produce Cu Kα X-rays. Two-dimensional diffraction patterns were collected on a multiwire detector, corrected for response characteristics, and converted to one-dimensional format (intensity vs q) by azimuthally averaging the data, where q is the scattering wavevector. Blends in ordered phases have a very sharp first-order scattering peak, which was fit with a Gaussian function to determine the peak position, q^*. The principal spacing, d^*, is inversely related to q^*, $d^* = 2\pi/q^*$. In these blends, the PEO and epoxy are essentially contrast matched, and scattering arises between the PEP domain and the PEO/epoxy domain. Data were collected continuously during cure experiments and separated into data sets every 10 or 20 min.

Dynamic Mechanical Spectroscopy. Dynamic elastic and loss shear moduli, G' and G'', of the OP5/BPA348 blends were obtained using a Rheometrics RSAII solids analyzer with a shear sandwich fixture. Order−disorder transition temperatures (T_{ODT}'s) were identified by a large discontinuous decrease in modulus on heating at 1 °C/min with 1% strain and a frequency of 1 rad/s.

Transmission Electron Microscopy. Electron microscopy was used to obtain real-space images of the cured blends. Samples were microtomed at room temperature with a Reichert Ultramicrotome S equipped with a diamond knife, and the resulting ultrathin sections (∼80 nm thick) were floated on water. The floating samples were picked up on Cu grids and stained in the vapors of a 0.5 wt % aqueous solution of RuO₄ for 15−30 min. RuO₄ selectively stains the components in the following order (most stained to least stained) PEO > epoxy > PEP.[24,25] In the images presented here, PEO appears black, epoxy gray, and PEP white. Stained samples were imaged in a JEOL 1210 transmission electron microscope with an accelerating voltage of 120 kV.

Differential Scanning Calorimetry. PEO crystallinity in cured samples from the SAXS experiments was analyzed using a Perkin-Elmer DSC7, calibrated with an indium standard. Before taking measurements, samples were heated to 80 °C, then cooled to 20 °C and annealed for 1 h. Measurements were then taken on heating from 20 to 80 °C. Temperature ramps at 5 °C/min were used for all heating and cooling steps.

Gel-Point Determination. Gelation of the curing epoxy matrix was determined using dissolution measurements. Samples at the same composition as samples cured in the X-ray beam were made and cured under vacuum using an oil bath. At specified time intervals samples were dissolved in THF to give a dilute solution (<0.5% w/v). The gel point was identified when the sample no longer dissolved.

Results and Analysis

Blends of Block Copolymer and Epoxy (OP5/BPA348 Blends). Before forming the cross-linked thermoset material, it is important to understand the initial uncured equilibrium phase behavior of block copolymer/epoxy mixtures without hardener. Figure 1 and Table 1 summarize the phase behavior of the OP5/BPA348 system with compositions ranging from pure block copolymer to 10 wt % block copolymer. Order−disorder transition temperatures (T_{ODT}'s, black squares in Figure 1) were determined rheologically with isochronal heating ramps (1 °C/min, 1 rad/s, 1% strain).[26,27] No phase transitions were detected below T_{ODT}; therefore, the phase boundaries are plotted vertically.

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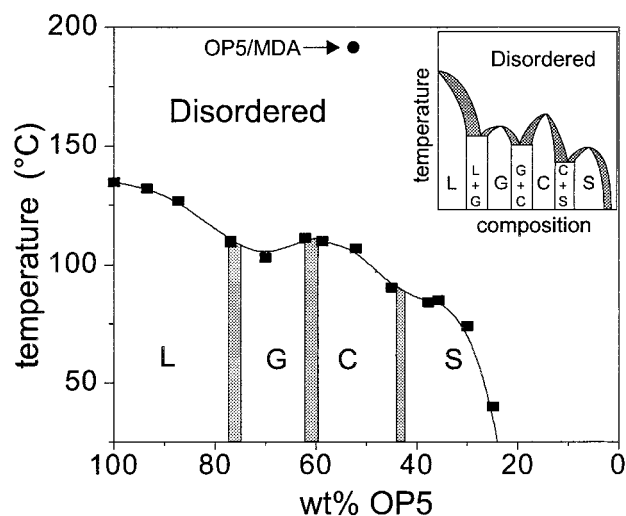

Figure 1. Phase diagram for OP5/BPA348 blends without hardener. Filled squares represent T_{ODT}'s measured by dynamic mechanical spectroscopy during isochronal heating. Ordered phase morphologies (lamellar (L), gyroid (G), cylindrical (C), and spheres (S)) were identified with SAXS. The shaded regions denote two-phase coexistence. A thermodynamically proper phase diagram (i.e., one that conforms to the Gibb's phase rule) with expected coexistence windows between the ordered phases and the disordered phase is given in the inset. T_{ODT} for an OP5/MDA blend containing 52 wt % OP5 is identified with the filled circle.

Table 1. Phase Behavior of OP5/BPA348 Blends

wt% OP5	T_{ODT} (°C)	morphology[a]	wt% OP5	T_{ODT} (°C)	morphology[a]
100	135	L	45	90	(C + S)[b]
93	132	L	38	84	S
87	127	L	36	85	S
77	110	(L + G)[b]	30	74	S
70	103	G	25	40	S
62	111	(G + C)[b]	20	<25	DIS
59	110	C	10	<25	DIS
52	107	C			

[a] Phase morphology identified with SAXS measurements. L = lamellar, G = gyroid, C = hexagonally packed cylinders, S = body-centered cubic packed spheres, DIS = disordered spherical micelles. [b] Tentative assignment of two-phase window.

The morphologies of the ordered states were determined with SAXS data. Results from the OP5/BPA348 mixtures were consistent with the Bragg scattering expected for the lamellar (L), bicontinuous cubic gyroid (G), hexagonally packed cylindrical (C), and body-centered cubic packed spherical (S) morphologies. The resulting phase behavior shows the familiar[28] sequence of phases, L−G−C−S−disorder, at low temperatures. Results also suggested the existence of two-phase windows between the ordered phases (consistent with the Gibb's phase rule), and these are shown as shaded regions in Figure 1. A proper phase diagram for a two-component system also has two-phase windows between the ordered and disordered phases. One possible diagram that includes these details is given in the inset of Figure 2. However, within our experimental resolution (±1 °C), we could not establish the precise nature of the region around the ODT.

Blends of Block Copolymer, Epoxy, and Hardener (OP5/BPA348/MDA Blends). Adding MDA to the OP5/BPA348

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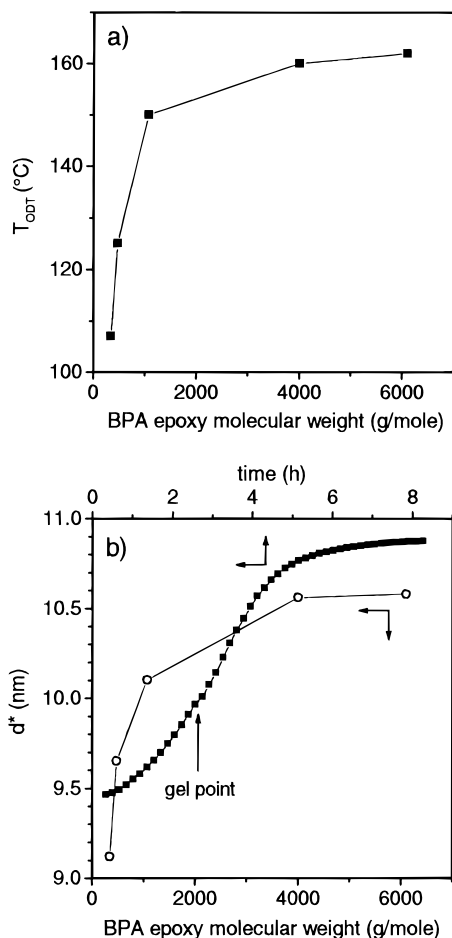
Figure 2. Effect of blending 52 wt % OP5 with BPA epoxy resins of varying molecular weight: (a) increase in T_{ODT} with increasing epoxy molecular weight; (b) increase in principal spacing, d^*, with increasing epoxy molecular weight (open circles) or with cure for the 52 wt % OP5/BPA348/MDA blend (filled squares) at 100 °C.

Table 2. Phase Behavior of Uncured Blends with Hardener

wt% OP5	morphology[a]	wt% OP5	morphology[a]
OP5/BPA348/MDA blends			
85	L	52	C
80	L	35	S
69	G	12	DIS
OP5/MDA only			
52	C		

[a] Phase morphology identified with SAXS measurements.

mixtures complicates the determination of phase behavior since the blend is now a three-component mixture and since condensation of amine and epoxy groups leads to an increase in molecular weight as discussed below. Fortunately BPA348 and MDA are both selective solvents for PEO, and nonsolvents for PEP, and the addition of MDA does not have a large effect on the uncured phase behavior. We have determined that the room-temperature morphologies shown in Figure 1 are not affected when MDA is mixed with, or substituted for, BPA348 (Table 2). Moreover, at comparable compositions (52 wt % OP5), OP5/BPA348 and OP5/BPA348/MDA blends have similar microdomain spacings (d^* = 9.1 and 9.5 nm, respectively, at 100 °C). However, MDA mixtures do exhibit significantly higher ODT temperatures than the corresponding BPA348 blends. For example, an ODT was recorded at 192 °C for a mixture containing 52 wt % OP5 in MDA, which is about 80 °C higher than that obtained for OP5/BPA348 (see Figure 1,

filled circle). This result suggests MDA is an even poorer solvent than BPA348 for PEP and/or a better one for PEO. Additionally, the increased molecular weight of the matrix from the epoxy and hardener polymerization may also increase T_{ODT}. Blends of 52 wt % OP5 with BPA epoxy resin of larger molecular weight (480, 1075, 4000, and 6100 g/mol; SAXS measurements confirmed that all blends had the hexagonally packed cylindrical morphology) all had increased T_{ODT}'s (Figure 2a). We assume that T_{ODT}'s for OP5/BPA348/MDA mixtures, which we treat as a pseudo-two-component system, lie at values intermediate to the T_{ODT}'s measured from OP5/BPA348 and OP5/MDA blends. Our assessment of the curing behavior of these blends is not significantly affected by this assumption.

Representative samples taken from each ordered region of the phase diagram were cured in the X-ray beam, and the evolution of morphology was tracked during cross-linking. Qualitatively, diblock and epoxy macrophase separation during cure is easily determined by visual characterization of the sample. A macrophase-separated sample is opaque, whereas a uniformly ordered sample with ~10-nm scale structure is transparent. All of the cured samples were transparent, indicating no macroscopic phase separation of epoxy and block copolymer in the final cured states.

Changes in principal spacing, d^*, with cure for the 52 wt % OP5/BPA348/MDA blend obtained from SAXS data collected for 8 h at 100 °C ($T_{ODT} > 107$ °C) are plotted in Figure 2b (filled squares). Gelation of the epoxy (3 h) did not have a noticeable effect on the rate of d^* change. An increase in principal spacing of almost 15% (from 9.5 to 10.9 nm) is measured as the epoxy cures, with a leveling off of d^* at high degrees of epoxy conversion. SAXS measurements confirmed that this sample retained the cylindrical morphology during cure.

Also plotted in Figure 2b are principal spacing data (at 100 °C) for blends containing 52 wt % OP5 with epoxy resins of different molecular weights (the same blends found in Figure 2a). A 16% increase in spacing (from 9.1 to 10.6 nm) is recorded when the epoxy resin molecular weight increases from 348 to 6100 g/mol, with a limiting value of d^* at the higher epoxy resin molecular weights. Thus, either increasing the molecular weight of the epoxy resin or cross-linking the low-molecular-weight epoxy resin produces roughly the same change in principal spacing when the sample contains 52 wt % OP5.

Figure 3 is a high-magnification TEM image of the cured 52 wt % OP5/BPA348/MDA sample from the SAXS experiment. The nanoscale structure is evident in this side view of the cylinders.

The SAXS data obtained during the isothermal (100 °C, $T_{ODT} > 103$ °C) cure of the 69 wt % OP5/BPA348/MDA specimen are plotted as a function of time in Figure 4a. Initially two reflections are observed at relative q spacings of $\sqrt{6}:\sqrt{8}$, which we have attributed to the (211) and (220) spacings of the gyroid morphology. (This sequence of principal reflections with an intensity ratio of 10 to 1 is a rather unambiguous signature of the G phase as discussed elsewhere.[29]) At around 5 h (at 100 °C) the (220) reflection disappeared and was slowly replaced by a peak at $2q^*$. After 10 h at 100 °C this transformation was complete. These SAXS results indicate that the sample went through a cure-induced phase transition from G to L. Principal spacing data from this cure (Figure 4b) show an increase in the rate of change of d^* when the sample transforms from G to L, but like the 52 wt % OP5 cure sample, there is no apparent discontinuity in d^* at the gel point (6 h).

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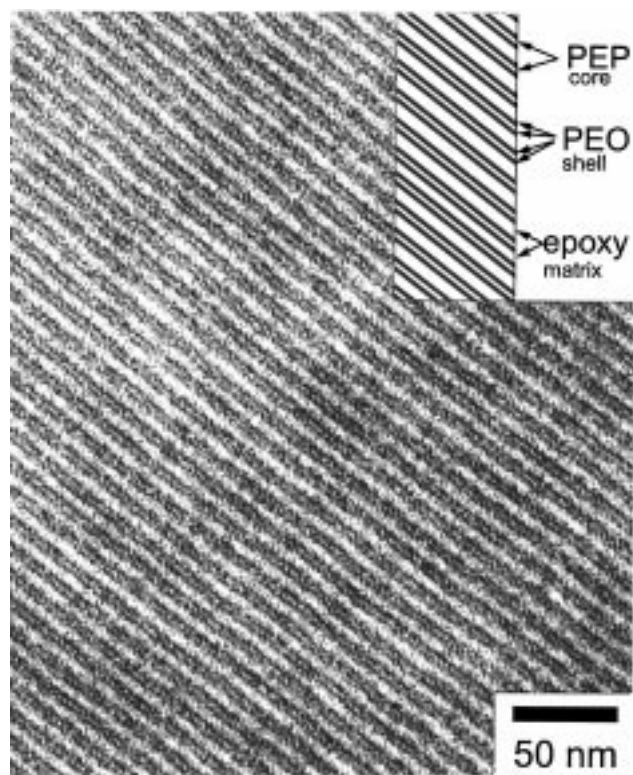
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Figure 3. TEM image of the OP5/BPA348/MDA blend (52 wt % OP5) cured during the SAXS experiment shown in Figure 2. The inset provides an interpretation of the morphology; cylindrical PEP cores (thin white lines) surrounded by a PEO shell (black), enclosed by the epoxy matrix.

A sample containing 35 wt % OP5 was also cured while collecting SAXS data. This sample displayed a cubic packed spherical morphology before reaction and during the first 10 h of cure at 60 °C (gelation occurred at 8 h). After heating this sample to 100 °C, a transition to the cylinder morphology occurred, despite the fact that the epoxy resin had passed the gel point. When cured at room temperature, which required an extended length of time (months), this mixture retained the spherical morphology. Thus, at certain compositions, both temperature and extent of cure may influence the morphology of these nanostructured composites.

Discussion

The sequence of morphologies identified in the OP5/BPA348 blends as a function of block copolymer concentration (see Figure 1) mimics prior experimental results obtained with block copolymer/homopolymer blends,[30-33] as anticipated by mean-field theoretical calculations.[19] This progression of morphologies can be rationalized by considering the PEO chains as brushes extending from the PEO/PEP interface (Figure 5a). The PEO exists as a "dry" brush in the neat block copolymer, leading to an interfacial curvature that is controlled by the block symmetry. Selective incorporation of the epoxy monomer in the PEO domains produces a swollen "wet" PEO brush, leading to an increased volume per PEO chain, while the volume per

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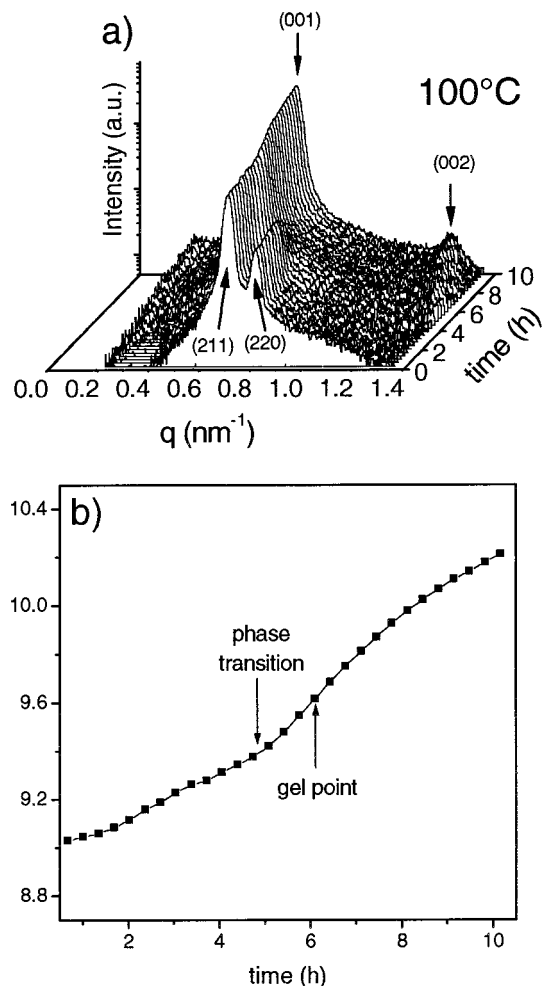

Figure 4. In situ SAXS data obtained during cure from an OP5/ BPA348/MDA mixture containing 69 wt % OP5. (a) SAXS patterns collected while the sample was held at 100 °C for 10 h. Extinction of the (220) reflection and growth of the (002) reflection indicates a transition from the G to the L phase at about 5 h of cure. (b) Change in principal spacing, d^*, as a function of cure time.

PEP chain remains essentially constant. This asymmetry in volume per chain induces curvature at the PEO/PEP interface, arising from the connectivity of the PEO and PEP chains and the constraint of constant density and minimization of chain stretching. The lamellar morphology cannot support interfacial curvature; therefore, the system transforms to the G, C, and S morphologies as the amount of BPA348 is increased. We note these morphological changes arise from the swelling of the PEO chains versus simply increasing the volume of the PEO domain. If the epoxy selectively went to the PEO domain, but did not swell the PEO chains, there would be no change in interfacial curvature (only dilation of the PEO layer) and no change in morphology. On the basis of experiments with OP5/ BPA348/MDA mixtures, we can conclude that this "dry"-to-"wet" brush scenario also applies to the uncured three-component system.

When hardener is added to the block copolymer/epoxy system, condensation of the epoxy and amine groups leads to an increase in molecular weight of the additive. At the gel point (on the basis of classical mean-field theory,[34] gelation occurs at 58% conversion in stoichiometric BPA348/MDA blends, which compares favorably with our experimental value of 56

(34) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; pp 348−354.
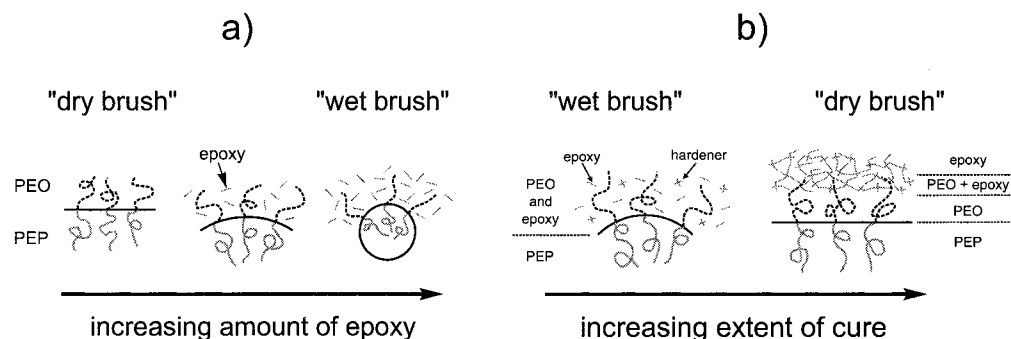
Figure 5. (a) Illustration of swelling-induced change in the interfacial curvature for OP5/BPA348 blends. PEO blocks extend from the neat PEO/PEP interface as a "dry brush". Epoxy selectively swells the PEO brush, creating a "wet brush" and the PEO/PEP interface curves to accommodate this change within the constraint of constant density while minimizing PEP and PEO chain distortions. Swelling of the PEO block drives changes from a lamellar morphology to G, C, and S. (b) Illustration of PEO block expulsion as the epoxy matrix cross-links and its molecular weight diverges. The system initially has a curved interface due to selective swelling of the PEO blocks by the epoxy. As the epoxy cures, the PEO blocks are expelled, transforming the "wet brush" to a "dry brush", thereby reducing the interfacial curvature.

± 3%[35]), an infinite network is formed corresponding to a divergence in the weight-average molecular weight, M_w.[36] Because M_w is the moment in the molecular weight distribution that controls polymer−polymer miscibility, macroscopic phase separation usually precedes gelation in polymer-modified epoxy composites.[14−17] This does not seem to apply to any of the block copolymer modified BPA348/MDA blends.

Although we do not understand the detailed nature of the events that lead to the well-defined ordered nanocomposites described in the previous section, the evidence presented here suggests a synergy between the cross-linking reaction, local phase separation, and free energy barriers to nucleation of block copolymer rich domains. Careful inspection of Figure 3 provides evidence of block copolymer segregation in the cured state. The inset in Figure 3 shows our interpretation of the image as cylindrical PEP cores surrounded by a PEO shell, all enclosed in an epoxy matrix.[37] However, expulsion of PEO by the epoxy network is restricted to a local scale, and there is no disruption of long-range order. Apparently, chemical curing, and the associated increase in molecular weight, ejects the PEO from the curing epoxy. This "wet" brush to "dry" brush transition with cure is depicted in Figure 5b.

Supportive evidence for this mechanism is provided by the order−order phase transitions that accompanied two of the reactions. The 69 wt % OP5/BPA348/MDA mixture transformed from G to L just prior to gelation as captured by SAXS measurements (Figure 4a). This transition is consistent with brush "drying", which should reduce the local interfacial curvature as shown in Figure 5b. The same line of reasoning can explain why the 35 wt % specimen went from spheres to cylinders upon curing. Surprisingly this phase change occurred after gelation, following an increase in temperature from 60 to 100 °C. Of course gelation corresponds to the point of macroscopic, not microscopic, network formation (i.e., when $M_w \rightarrow \infty$). Restriction of local mobility and sample hardening sets in at considerably greater degrees of conversion.

Our conclusion regarding PEO expulsion is further supported by DSC results for the 52 wt % OP5/BPA348/MDA sample discussed in Figure 2b and Figure 3. A small, but well-resolved fraction (∼7%) of PEO crystallinity present in the neat diblock

copolymer is evident in this cured specimen, and both samples exhibit the same peak melting temperature. If some amount of PEO was not expelled from the epoxy, it could not crystallize. Since the PEO melting temperature for the cured material is nearly the same as the PEO melting temperature for pure OP5, we assume that the PEO crystallites are about the same size in both samples. However, we have not yet attempted to characterize the distribution and orientation of PEO crystallites within the ordered structure.

Changes in d^* provide another indication of structural changes in the system as the epoxy cures. The principal spacing increased during all three curing reactions, and the most decipherable results were obtained with the 52 wt % OP5 mixture which reacted to near complete conversion under isothermal conditions (Figure 2b). During this reaction the morphology remains as hexagonally packed cylinders, yet well-ordered unit cells dilate about 15% perpendicular to the cylinder axis (i.e., along the [$hk0$] directions). This increase in d^* occurs despite the fact that the nanocomposite density increases with curing, which should reduce d^* roughly 2−6% (the unmodified BPA348/MDA mixture density increases 2−7% during complete reaction).[38]

Figure 6a summarizes the qualitative morphological changes that accompany this increase in d^*. Expulsion of PEO and formation of a core−shell nanostructure cannot account for the shift in the overall unit cell dimensions. Nor can the change in d^* be explained by macroscopic separation of epoxy from the unit cell, as this would bring the PEP cores closer together contrary to the SAXS results. We believe the increase in d^* is another manifestation of the tendency to reduce interfacial curvature when the PEO brush "dries" during cross-linking (see Figure 5b). An increase in the PEP core diameter would alleviate some of the conformational strain produced when the brush "dries", and this would result in an increase in d^*. However, this change must be accompanied by a net reduction in cylinder length since PEP is essentially incompressible. The only way this can be accomplished in a sample of finite material, without varying the number of cylinders, is to adjust the grain aspect ratio as illustrated in Figure 6b. Clearly this must occur before the material hardens.

This change in principal spacing (15%) at 100 °C for the 52 wt % OP5/BPA348/MDA sample during cure (Figure 2b) is very similar to the change in principal spacing (16%) when the higher molecular weight BPA epoxy resins are added to 52 wt % OP5. From theoretical predictions of model block copolymer/

(35) Conversion was determined using gel permeation chromatography; see: Verchère, D.; Sautereau, H.; Pascault, J. P.; Riccardi, C. C.; Moschiar, S. M.; Williams, R. J. J. *Macromolecules* **1990**, *23*, 725−731.

(36) Macosko, C. W.; Miller, D. R. *Macromolecules* **1976**, *9*, 199−206.

(37) See ref 18, Figure 3 for another TEM image and similar analysis of the core/shell morphology in a cylinder sample viewed down the cylinder axis.

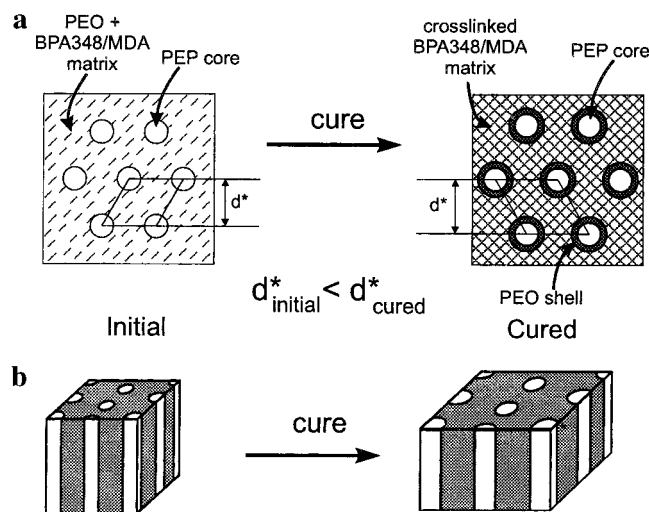(38) Parry, H. L.; Mackay, H. A. *SPE J.* **1958**, 22−24.

Figure 6. Structural changes that accompany curing of an OP5/BPA348/MDA mixture with a hexagonally packed cylindrical microstructure. (a) Cross-linking the epoxy resin leads to a core and shell structure and an increase in the principal spacing d^*. (b) Conservation of PEP volume necessitates macroscopic changes in the ordered grain aspect ratio to accommodate this unit cell dilation.

homopolymer blends,[19] d^* increases with increased homopolymer (i.e., epoxy) molecular weight due to decreased mixing between the homopolymer and block copolymer. On the molecular level, this decreased mixing is manifested as a "dry" PEO brush, creating a core/shell structure. We caution that correlation between the OP5/BPA blends of varying epoxy molecular weight and the curing OP5/BPA348/MDA blend cannot be made directly because the blends with the linear epoxy chains can reach equilibrium, whereas the curing epoxy is highly branched and gelation prevents equilibrium from being attained. However, the presence of a core/shell structure as indicated by the same increase in d^* is present in both cases. The decreased mixing that occurs in blends with the higher molecular weight epoxy resin also sharpens the PEO/PEP interface, which increases the degree of segregation between the PEO and PEP and causes the measured increase in T_{ODT} (Figure 2a).[19]

Alternatively, the system can adjust the constraints on block copolymer conformation by changing phase as described in previous paragraphs. Note however that the mechanism proposed for the cylindrical (and implicitly the lamellar) morphologies (Figure 6b) cannot be operative with the three-dimensionally symmetric S or G cubic phases. This may explain why d^* increases at nearly twice the rate when the 69 wt % specimen switches from G to L (see Figure 4b).

The hypothesis presented in Figure 6b could be tested with shear aligned monodomain specimens. Using oscillatory shear techniques common in the alignment of block copolymers,[39] an aligned 52 wt % OP5/BPA348/MDA blend (cylinders) was produced. The sample was sheared at room temperature and, after cessation of shear, was cured at 90 °C for 16 h and post-cured at 180 °C. A TEM image viewed down the shear axis (Figure 7) shows the long-range order of hexagonally packed cylinders. The core/shell morphology is also evident in some of the cylinders. Two-dimensional SAXS data (inset), with the incident X-ray beam perpendicular to the cylinder axis, confirms macroscopic alignment throughout the bulk specimen which results in two strong equatorial spots (an unaligned sample has an isotropic ring in the two-dimensional scattering pattern).
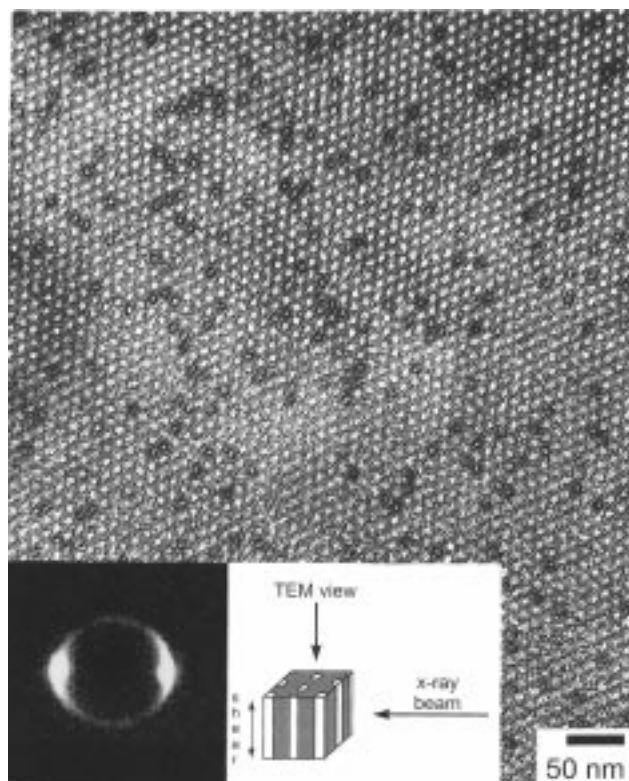

Figure 7. TEM image from an OP5/BPA348/MDA mixture containing 52 wt % OP5 that was shear aligned prior to cure. Inset: two-dimensional SAXS pattern obtained with the incident radiation directed perpendicular to the shear direction. The two strong equatorial spots indicate macroscopic alignment of the cylinders in this sample.

What emerges from this discussion is a plausible description of the factors that influence the evolution of structure when a block copolymer modified epoxy formulation is cured. Figure 8 summarizes our findings and deductions. In the unreacted state, the block copolymer/epoxy/hardener mixture is described by established equilibrium theory[19] and conforms to well-understood experimental practice. As the monomers condense, the polymerizing material expels the PEO brush, creating conformational strain which may induce order−order phase transitions. Theory suggests that the "dry" brush mixture should macroscopically phase separate as the epoxy molecular weight increases above that of PEO.[19] (Because the condensation reaction produces a highly branched polydisperse product, quantitative comparison with the theory is unwarranted). This is never observed. Instead, a nonequilibrium, metastable, free-energy trajectory is followed as the condensation reaction progresses. Without knowledge of the epoxy chain mobilities we cannot establish whether the mesostructure becomes kinetically trapped due to diffusion limitations or because the thermodynamic barrier to nucleation of a macroscopic block copolymer phase is prohibitively high. Based on our experience with very slow curing reactions ($\sim$1 month) that did not show macroscopic phase separation, we suspect that the latter is the governing factor. Regardless of the exact mechanism, subsequent complete conversion renders a highly ordered homogeneous nanocomposite.

As a final observation, we note that the criteria for macroscopic phase separation in polymer blends and nanoscale ordering in block copolymers depend on different moments in the molecular weight distributions, M_w and M_n, respectively.[40,41]

(39) Mortensen, K.; Almdal, K.; Bates, F. S.; Koppi, K.; Tirrell, M.; Nordén, B. *Physica B* **1995**, *213 & 214*, 682−684.

(40) Bates, F. S.; Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525−557.
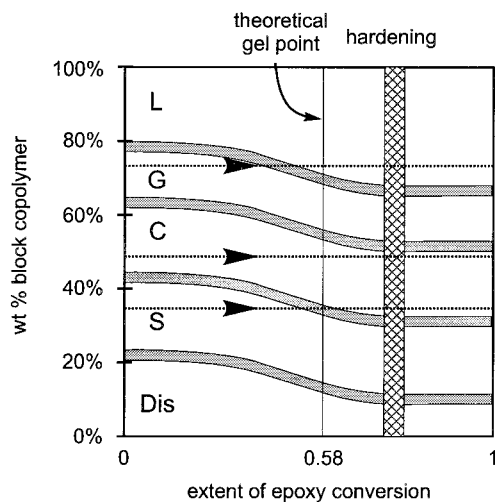
Figure 8. Proposed composition−conversion diagram showing changes in morphology with cure. As the epoxy cures and expels the PEO, morphologies with flatter interfaces become more stable at a given composition. To account for this, the phase boundaries shift to lower block copolymer composition with increasing epoxy conversion. The two-phase coexistence windows are shaded and the dotted lines indicate the path taken by selected samples reported in this study. At high degrees of epoxy conversion, the tightly cross-linked matrix prevents further changes in the morphology and the phase boundaries no longer shift. The location of this hardening transition has not been determined precisely.

Whereas M_w diverges at the gel point, M_n does so at complete conversion. The absolute stability of a (metastable) homogeneous ordered phase relative to an (equilibrium) two-phase state composed of epoxy and block copolymer rich domains will depend on M_w and M_n in different ways. We suspect that the results reported here reflect, as yet ill-defined but general, phenomena which govern the thermodynamics of mixed systems involving elements of ordering and macroscopic phase separation. A more complete understanding of this category of materials awaits a statistical mechanical treatment of structural evolution during network formation in such nanostructured states.

Summary

We have shown a novel method of templating an ordered structure, on the nanometer scale, in a thermoset matrix. This is achieved by blending an amphiphilic diblock copolymer, PEO−PEP, with a polymerizable epoxy resin. The epoxy resin selectively swells the PEO chains, creating a spontaneous interfacial curvature between the PEP and PEO/epoxy domains which controls the morphology. As the amount of epoxy added to the block copolymer is increased, the blend microstructure evolves from lamellar, to gyroid, to cylinders, to body-centered cubic packed spheres and ultimately disordered micelles. When hardener is added and the epoxy cures, the system retains the nanostructure and macrophase separation between the block copolymer and epoxy is avoided. However, we believe the PEO block is expelled from the reactive matrix on a local level as the molecular weight of the epoxy increases, leading to cure-induced phase transitions and regions of relatively pure crystalline PEO.

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(41) Elliniadis, S.; Higgins, J. S.; Clarke, N.; McLeish, T. C. B.; Choudhery, R. A.; Jenkins, S. D. *Polymer* **1997**, *38*, 4855−4862.