

## ORIGINAL ARTICLE

# Control of nanostructures in epoxy/acrylic block copolymer blends by the *in situ* generation of functional groups

Kazuyoshi Yamada<sup>1,2</sup> and Hajime Kishi<sup>1</sup>

The phase structures obtained from blends consisting of an epoxy resin, an aromatic amine and a PMMA-*b*-PnBA-*b*-PMMA triblock copolymer (BCP) were studied, in terms of the effect of the process used to blend the BCP into the epoxy/amine mixture. The thermal dissolution of the BCP in the amine was found to promote the *in situ* generation of carboxylic acids in the PMMA segments of the BCP. This enhanced the compatibility of the BCP with the cured epoxy/aromatic amine resin, allowing the self-assembly of the BCP to form nanophase structures in the polymeric matrix. This work also determined that modification of the heating conditions was an effective means of controlling the quantity of carboxyl groups generated (that is, the acid value). Such variations led to the formation of different types of micelle structures, such as curved lamellae, coexisting of worm-like micelles and vesicles and spheres, from epoxy/amine/BCP blends having the same composition.

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## INTRODUCTION

Epoxy thermoset resins typically exhibit excellent mechanical and electrical properties, in addition to being resistant to heat and various chemicals. Hence, epoxy resins have been widely used in applications such as adhesives, coatings, electronics and composite matrices. The desirable properties of these materials result from the three-dimensional networks formed by cross-linking reactions. However, highly cross-linked epoxy resins readily undergo brittle failure. For this reason, there is currently a requirement for resins with enhanced toughness for use in cutting-edge technologies such as aviation and semiconductor sealing materials. Reaction-induced phase separation during the curing (or polymerization) of the epoxy resin in which a liquid rubber or thermoplastic has been dissolved has long been considered to represent a means of generating tougher resins.<sup>1–5</sup> The curing of these materials increases the free energy of the mixture, inducing phase separation, while the increased viscosity generated by the cross-linking reaction prevents the development of phase-separated structures. These two processes lead to gelation of the resin prior to thermodynamic equilibrium, producing fixed phase structures.<sup>6,7</sup>

In recent years, a number of studies have been performed with the aim of enhancing the toughness of epoxy resins through forming phase structures with sizes on the order of several tens of nanometers, based on the self-assembly of block copolymers (BCPs).<sup>8–21</sup> Bates and colleagues showed that the incorporation of an amphiphilic BCP into an epoxy resin forms nanophase structures.<sup>8,9</sup> In their work, a mixture of a poly(ethylene oxide)-*b*-poly(ethylene-alt-propylene) (PEO-PEE) diblock copolymer and the diglycidyl ether of bisphenol-A (DGEBA)

was cured with 4,4'-methylenedianiline (MDA). Various phase structures were observed depending on the PEO-PEE concentration.<sup>11</sup> Nanostructured epoxy blends using poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) (PEO-PPO-PEO) triblock copolymers or poly(ethylene oxide)-*b*-poly(1,2-butadiene) diblock copolymers (PEO-PB) were also studied.<sup>12,13</sup> The phase structures of the PEO-PB diblock copolymer/DGEBA/MDA blends were found to transition from vesicles to worm-like micelles and then to spherical micelles with increasing concentrations of PEO in the BCP.

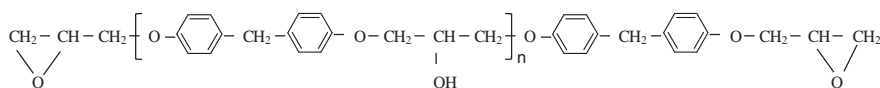
Rebizant *et al.*<sup>15</sup> studied the phase structures of 4,4'-diaminodiphenylsulfone (DDS)-cured DGEBA blends using a polystyrene-*b*-polybutadiene-*b*-poly(methyl methacrylate)-*b*-poly(glycidyl methacrylate) (SBMG) tetrablock copolymer or a polystyrene-*b*-polybutadiene-*b*-poly(methyl methacrylate)-stat-(methacrylic acid) (SBMA) triblock copolymer.<sup>16</sup> Functional groups such as glycidyl methacrylate or methacrylic acid were introduced into the BCPs to make the nanostructured blends, and the phase structures were found to be determined by the proportions of these functional groups. An epoxidized polybutadiene BCP was also introduced into a polystyrene-*b*-polybutadiene (PS-PB) diblock copolymer/DGEBA blend to control the nanostructure.<sup>17</sup> Different nanostructures, including worm-like micelles or hexagonally packed cylindrical micelles, were obtained, depending on the epoxidation degree of the polybutadiene block in the PS-PB BCP and the percentage of the epoxy-modified PS-PB copolymer.

The miscibility of the block segments that constitute the BCPs with the cured epoxy resin, as well as the molecular weights of the block segments, are both important to achieving nanostructures. It is also

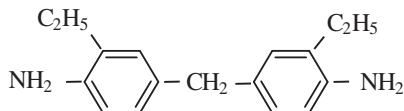
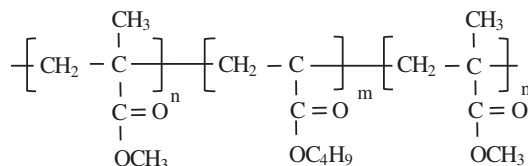
<sup>1</sup>Graduate School of Engineering, University of Hyogo, Himeji, Japan and <sup>2</sup>Technical R&D division, NAMICS Corporation, Niigata, Japan  
Correspondence: K Yamada, Technical R&D division, NAMICS Corporation, 3993 Nigorikawa, Kita-ku, Niigata 950-3131, Japan.  
E-mail: yamadaka@namics.co.jp

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DGEBF



MBOEA

PMMA-*b*-PnBA-*b*-PMMA triblock copolymer**Figure 1** Chemical structures of epoxy resin, aromatic amine and PMMA-*b*-PnBA-*b*-PMMA triblock copolymer.

known that some curing agents will produce nanostructures, while others will form microsize (that is, macroscopic) phase structures, even from the same combination of an epoxy resin and BCP.<sup>18</sup> As an example, a blend of DGEBA, a PMMA-*b*-PnBA-*b*-PMMA triblock copolymer (BCP) and phenol novolac catalyzed with triphenyl phosphine formed a nanostructure.<sup>18,19</sup> In contrast, a blend of DGEBA, BCP and 4,4'-diaminodiphenylsulfone (DDS) resulted in a macrophase structure.<sup>18</sup> It has also been reported that using random copolymers of methyl methacrylate (MMA) and dimethyl acrylamide (DMA) enhances the miscibility between the block segment and the DGEBA, resulting in a nanophase structure in the epoxy/BCP blend.<sup>20</sup> However, this method requires pre-modification of the BCP, such as copolymerization using specific polar monomers or functional monomers, to achieve the optimal miscibility between the BCPs and the epoxy resin.

In the present work, we studied the thermal dissolution of BCPs in resin and determined a new means of achieving nanostructures without prior chemical modification of the BCP. This method also enables control over the sizes and shapes of the nanostructures in the blends.

## EXPERIMENTAL PROCEDURE

### Materials

The epoxy resin used in this study was the diglycidyl ether of bisphenol-F (DGEBF), YDF-8170 (epoxy equivalent weight: 160 g/eq., Nippon Steel & Sumikin Chemical, Tokyo, Japan). The aromatic amine 4,4'-methylene-bis(2-ethylaniline) (MBOEA, active amino-hydrogen equivalent weight: 63.5 g/eq.) was utilized as the curing agent. The acrylic BCP was a poly(methyl methacrylate)-*b*-poly(*n*-butyl acrylate)-*b*-poly(methyl methacrylate) triblock copolymer (Kuraray, Tokyo, Japan), with the weight average molecular mass of 79 000. The poly *n*-butyl acrylate (PnBA) content of the BCP was 77 wt%. The chemical structures of these materials are shown in Figure 1.

### Preparation of cured resins

The BCP was dissolved in the resin using two different processes. In the approach referred to herein as 'Process BE,' the BCP was mixed with the epoxy resin at room temperature, after which the mixture was heated while stirring at 190 °C to dissolve the BCP. The blend was subsequently cooled to room temperature, and the curing agent was added, following by degassing. In 'Process BH,' the BCP was first mixed with the curing agent and then dissolved

using a similar method as in Process BE, with heating at 190 °C. After cooling, the epoxy resin was added to the curing agent/BCP combination and the new mixture was degassed. In both cases, a stoichiometric amount of the amine was added to the epoxy resin, and the BCP constituted 5 wt% of the total resin. Therefore, the resin composition was identical in both cases. The final mixtures were cured at 165 °C for 2 h, then cooled to room temperature.

### Acid values of the acrylic BCP

Each BCP mixture, prepared using either Process BE or Process BH, was dissolved in a solvent consisting of toluene, 2-propanol and water (500/495/5 by volume), followed by titration with a 0.1 M solution of KOH in 2-propanol using a potentiometric titrator. The acid value of the mixture (in mgKOH/g) was determined from the inflection point of the titration curve, and the acid value of the BCP was calculated based on the amount of BCP in the mixture.

### Fourier transform infrared spectroscopy

Infrared spectroscopic measurements were recorded on Fourier transform infrared spectrometer (Perkin Elmer Spectrum 100, Yokohama, Japan) in attenuated transmission reflectance mode at resolution 4 cm<sup>-1</sup> and were averaged from 16 scans. The absorption spectrum of the original BCP and that of the BCP dissolved in the MBOEA were compared.

### Microscopic observations

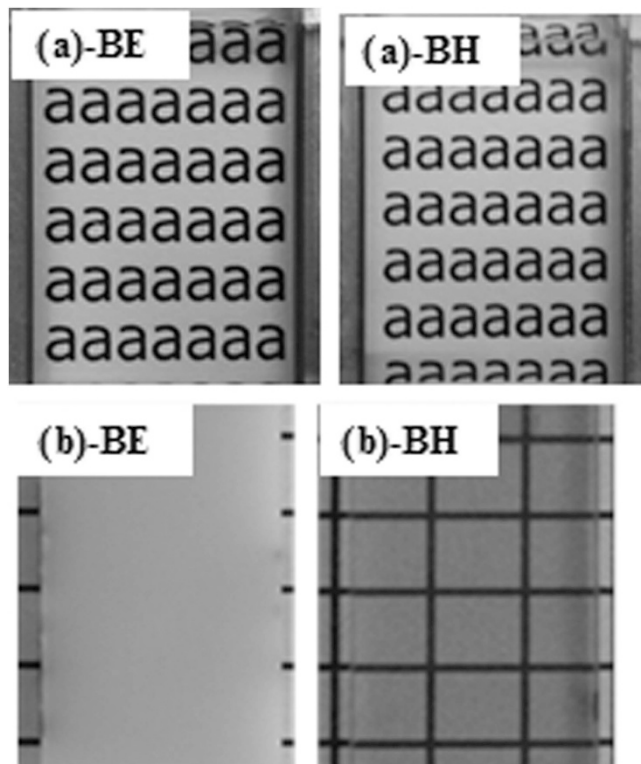
**Field emission scanning electron microscopy.** The surface of the cured resin was smoothed using a microtome at room temperature and was subsequently stained with the vapor from a fresh 0.5 wt% aqueous RuO<sub>4</sub> solution for 10 min at room temperature. The stained surface was then coated with a thin layer of tungsten (ELIONIX ESC-101, Tokyo, Japan) and observed via field emission scanning electron microscopy (JEOL JSM-7500F, Tokyo, Japan). Under these conditions, the PnBA segments were evident as bright phases.

**Transmission electron microscopy.** Thin sections (40–50 nm) of the cured resins were obtained using a cryo-microtome at –80 °C, and then stained with RuO<sub>4</sub> vapor and observed using transmission electron microscopy (HITACHI H-7650, Tokyo, Japan) at an acceleration voltage of 100 kV. In the transmission electron microscopy images, the bright regions were the epoxy matrices and dark regions were the PnBA segments of BCP stained by RuO<sub>4</sub>, as referred in the previous publication.<sup>18,19</sup>

## RESULTS AND DISCUSSION

### Variations in the phase structures of cured epoxy resins with changes in the dissolution process

Figure 2 shows overviews of two different heated mixtures and cured resins, made by dissolving the BCP using the Process BE or the Process BH. As noted, the BCP was dissolved at 190 °C in either the DGEBF or the MBOEA, respectively, at the level of 5 wt% in the cured resin. In the Process BH, both the mixture of amine/BCP/epoxy and the cured resins were transparent. On the other hand, in the Process BE, the mixture before curing was transparent. However, the cured resins were opaque. This suggests that reaction-induced phase separation occurred



**Figure 2** Overviews of the mixtures and the cured resins in the different processes at 190 °C: (a) heated mixtures: (a)-BE, Process BE, transparent; (a)-BH, Process BH, transparent; and (b) cured resins: (b)-BE, Process BE, opaque; (b)-BH, Process BH, transparent. A full color version of this figure is available at *Polymer Journal* online.

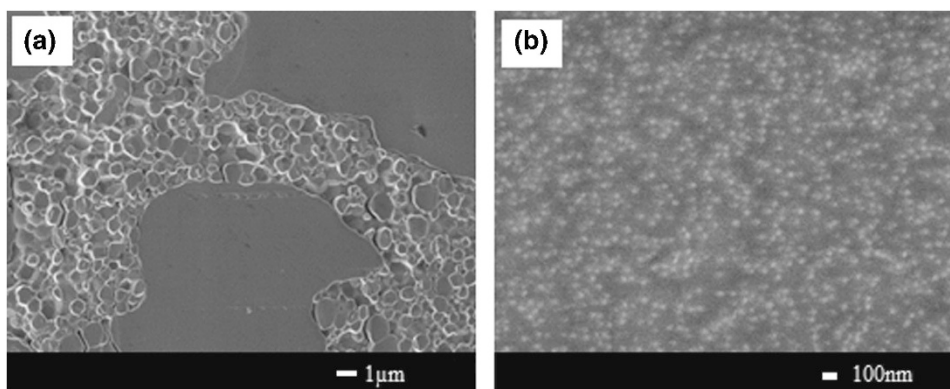
in the Process BE. Field emission scanning electron microscopy observations of the phase structures indicated that the cured Process BE resin exhibited a macrophase structure caused by reaction-induced phase separation, while the Process BH resin showed nanostructures with sizes on the order of several tens of nanometers (Figure 3). Thus, although the resin composition was identical in both cases, the phase structures of the cured resins were different due to the change in the manner of dissolving the BCP. Therefore, utilizing different dissolution processes enables the selective formation of different phase structures: macrophase or nanostructures.

### Variations in the acrylic BCP acid value with the dissolution process

The acid values of the BCP dissolved at 190 °C was evaluated and the results are summarized in Figure 4. In the case of the Process BE specimen, the acid value was not changed upon extending the heating time, while the Process BH sample exhibited an increase in acid value upon prolonged heating. We also evaluated the acid values of the BCP dissolved using the Process BH at different heating temperatures: 170 and 180 °C (Figure 5). Similar to the results obtained at 190 °C, longer heating times correlated with higher acid values. Comparing the acid values at the same points in time, the values are seen to double with each 10 °C increment in temperature. The phase structure of the Process BH resin was also evaluated in terms of the relationship with the acid value of the BCP (Figure 6). A low acid value evidently promoted the formation of curved lamellar structures. In contrast, an acid value of approximately 10 mgKOH/g resulted in coexisting of worm-like micelles and vesicles, and then spherical structures were obtained at 20 mg KOH per g.

An equivalent evaluation was conducted at lower dissolution temperatures of 170 and 180 °C. At the same heating times, different phase structures were formed depending on the processing temperature. However, similar curved lamellar structures were obtained after treating Process BH specimens for 8 h at 170 °C, 4 h at 180 °C or 2 h at 190 °C (Figure 7). These data indicate that the phase structures were determined by the acid value of the BCP. Each 10 °C increase in heating temperature halved the heating time required to obtain a given acid value. The acid value of the BCP that gave a curved lamellar structure was also constant, at approximately 5 mgKOH/g, at all heating temperatures. The apparent correlation between variation in the BCP acid value and the morphology of the phase structure suggests that the chemical structure of the BCP is modified during dissolution.

It is well known that heating an ester in the presence of a base can hydrolyze the ester. Therefore, it can be predicted that carboxylic acids



**Figure 3** FE-SEM images of the cured resins, heated at 190 °C for 8 h: (a) Process BE: macrophase structures, (b) Process BH: nanophase structures. FE-SEM, field emission scanning electron microscopy.

would be generated as a result of the hydrolysis of the ester groups in the BCP during Process BH. Acrylic BCP has two types of ester groups: methyl methacrylate and *n*-butyl acrylate. Thus, as model experiments, the acid values of two homopolymers treated by Process

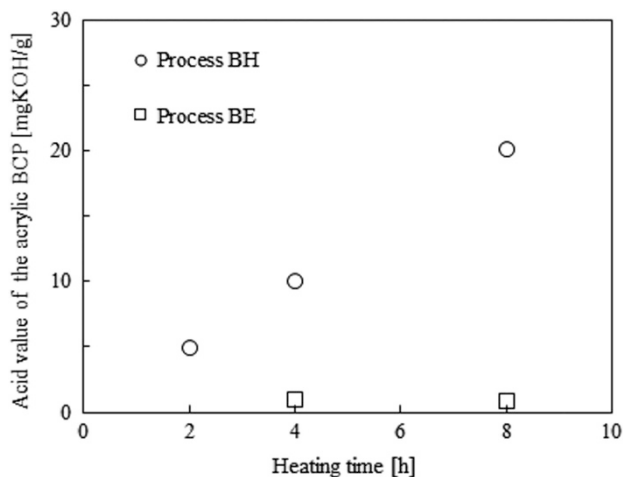


Figure 4 Acid values of the BCP of two different processes.

BH at 190 °C were investigated, as a means of understanding the details of BCP hydrolysis. In these trials, either poly(methyl methacrylate) (PMMA) or poly(*n*-butyl acrylate) (PnBA) were

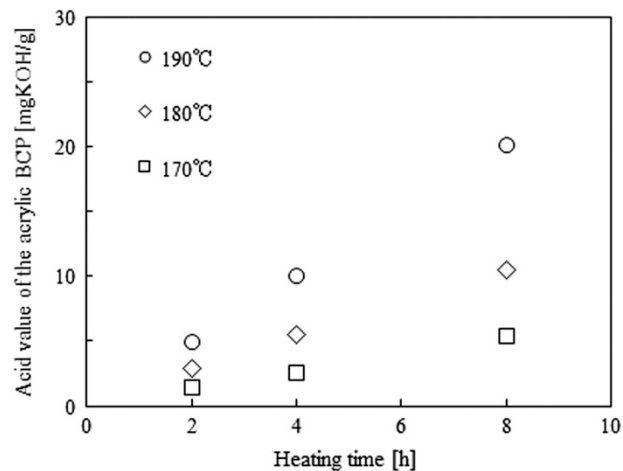


Figure 5 Relationship between acid value of the BCP and heating temperatures in the Process BH.

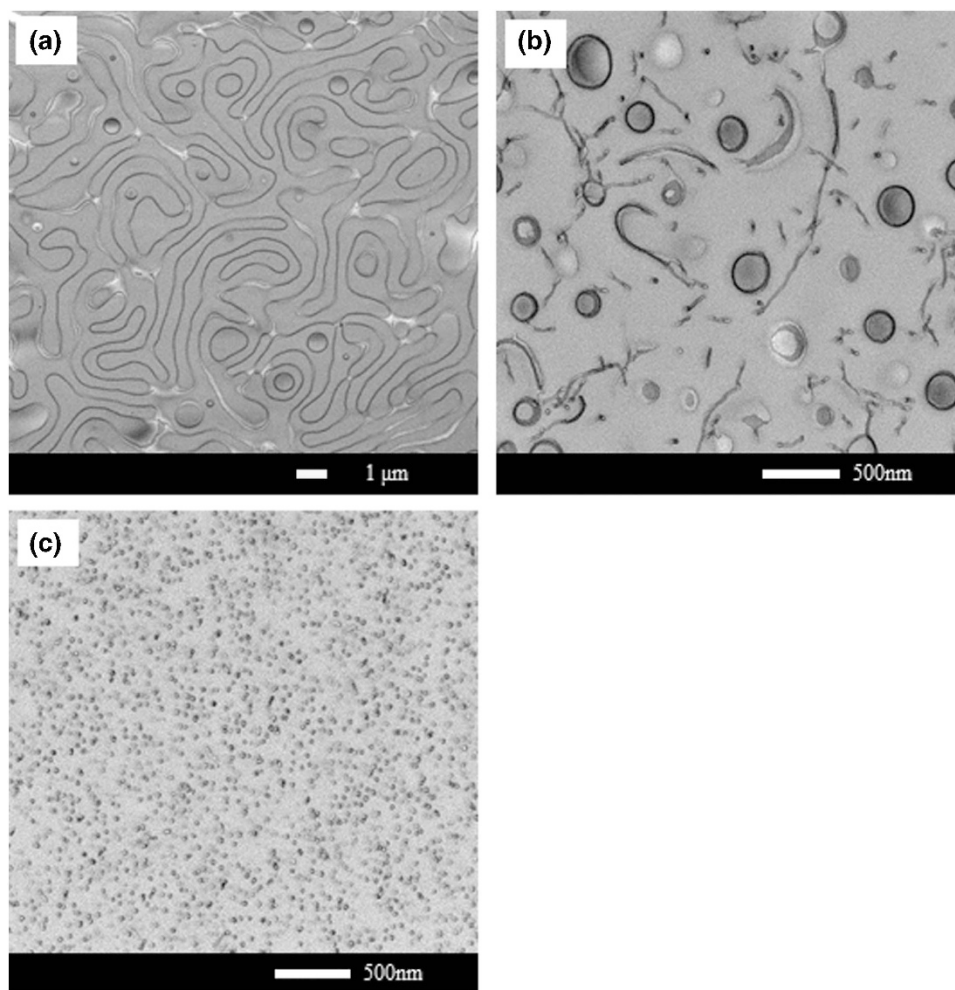
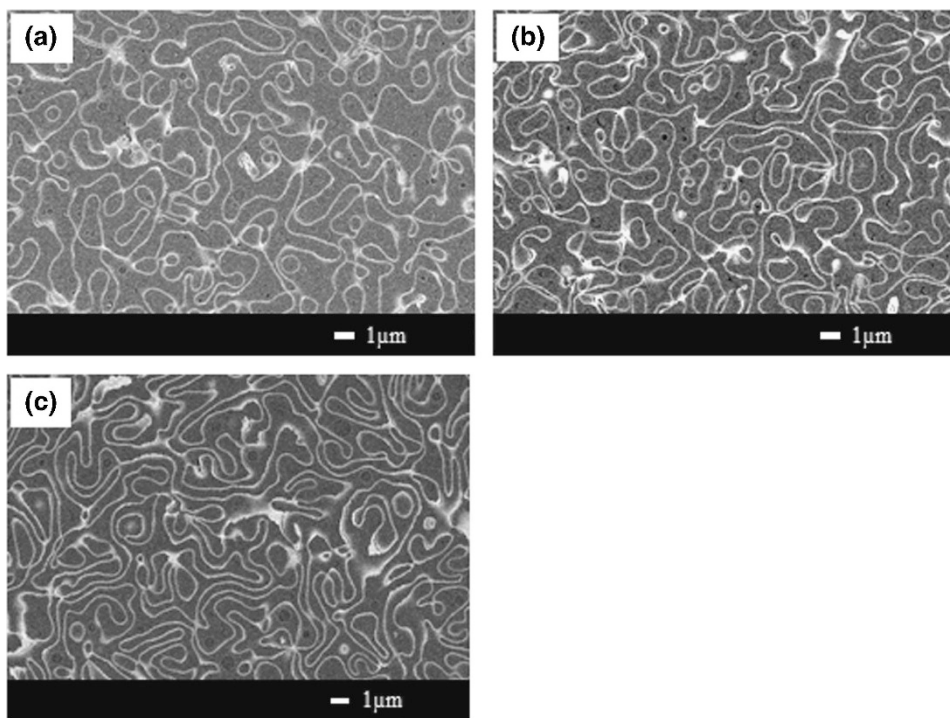
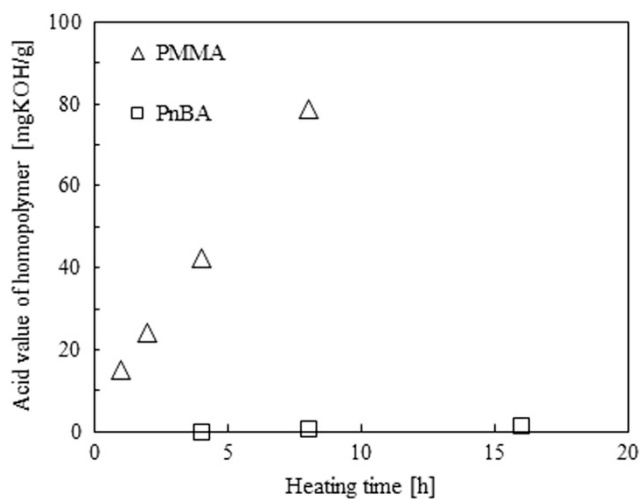


Figure 6 TEM images: effect of acid value of the BCP on the phase structure, heating temperature at 190 °C in the Process BH: (a) acid value of the BCP: 5 mg KOH per g, (b) acid value of the BCP: 10 mg KOH per g, (c) acid value of the BCP: 20 mg KOH per g. TEM, transmission electron microscopy.



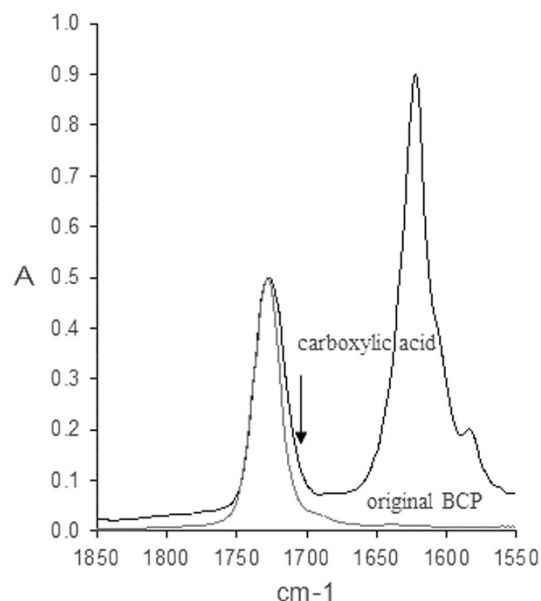
**Figure 7** SEM images: similar curved lamellar structures: (a) heating time 8 h at 170 °C (acid value of the BCP: 5.4 mg KOH per g), (b) heating time 4 h at 180 °C (acid value of the BCP: 5.5 mg KOH per g), (c) heating time 2 h at 190 °C (acid value of the BCP: 5 mg KOH per g). SEM, scanning electron microscopy.



**Figure 8** Relationship between acid value of two homopolymers and heating time in the Process BH.

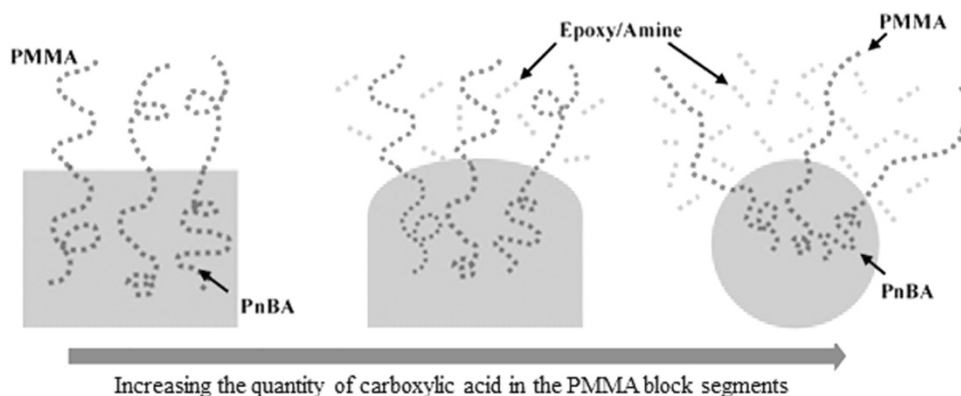
dissolved in MBOEA. Figure 8 shows that the acid value of the dissolved PMMA in the MBOEA increased as the heating time was extended. However, the PnBA did not exhibit any changes in acid value. Figure 9 shows the Fourier transform infrared spectrum of the original BCP and that of the BCP dissolved in the MBOEA at 190 °C. Carboxylic acid was observed as a shoulder at  $1710\text{ cm}^{-1}$  ( $\text{C}=\text{O}$  stretch) in the dissolved BCP. These results suggest that the dissolution of the BCP in the MBOEA generated carboxyl groups via the selective hydrolysis of the PMMA block segments.

Kishi *et al.*<sup>18</sup> reported that the miscibility between the PMMA block segments of BCP and the cured epoxy is a key factor in forming



**Figure 9** FTIR spectra: comparison of the original BCP and the BCP dissolved in the MBOEA. FTIR, Fourier transform infrared. A full color version of this figure is available at *Polymer Journal* online.

nanostructures.<sup>19</sup> When the balance between the miscibility of each block segment in the BCP and the epoxy/curing agent blend is adequate, nanostructures composed of the cured epoxy resin/BCP are formed due to the self-assembly of the BCP. In the present study, prior to reacting the epoxy and amino groups, the BCP was dissolved in the epoxy/amine mixture. This was possible due to the high degree of miscibility between the PMMA block segments of the BCP and the



**Figure 10** Illustration of the interfacial curvature change. A full color version of this figure is available at *Polymer Journal* online.

mixture. The polarity of epoxy/amine mixture subsequently increased as hydroxyl groups were generated through the reaction of the epoxy and amine, thus reducing the miscibility of the resin with the PMMA block segments. For this reason, homo-PMMA has been found to undergo phase separation in an amine-cured epoxy matrix.<sup>18</sup> This process explains the macrophase separation of the cured epoxy/amine/BCP blends made using Process BE. However, using the new method (Process BH), the methyl ester groups in the PMMA block segments were partially hydrolyzed while being dissolved in the amine, generating carboxylic acids. This *in situ* formation of carboxylic acids (that is, methacrylic acid units) in the PMMA block segments enhanced the compatibility between these block segments and the polar epoxy/amine mixture. As a result, the PMMA methacrylic acid blocks remained miscible with the amine-cured epoxy. Conversely, the PnBA blocks were immiscible with the amine-cured epoxy. Thus, nanophase structures were formed in the cured blends by the self-assembly of the *in situ* functionalized BCP.

The compatibility of the BCP with the cured epoxy/amine mixture was dependent on the acid value, equivalent to the quantity of carboxyl groups in the PMMA blocks. Figure 10 summarizes the variations in the phase structures of the cured epoxy/amine/BCP blends during Process BH. A higher acid value enhances the miscibility (or extension) of the PMMA chain segments in the epoxy/amine matrix. This in turn increases the volume fraction of PMMA segments in the epoxy/amine matrix, increasing the interfacial curvature of the immiscible PnBA phase. The phase structure changes from curved lamellar to coexisting of worm-like micelles and vesicles, then to spherical micelles as the interfacial curvature increases (Figure 10). In this manner, we successfully formed various nanostructures without changing the block composition or the mass percentage of the BCP. As noted, the thermal dissolution of the BCP in the amine promoted the *in situ* formation of carboxylic acids via the hydrolysis of methyl esters in the PMMA blocks. Tuning the amount of carboxyl groups changed the compatibility between the BCP and the cured epoxy/amine matrix, thus varying the self-assembly of the BCP. This enabled the selective formation of various types of nanostructures from the same epoxy/amine/BCP blends.

## CONCLUSIONS

The phase structures of DGEBA/BCP blends made using MBOEA as the curing agent were investigated. Both macrophase separation and nanostructures were obtained, depending on the process used to dissolve the BCP. Nanostructures were formed when employing Process BH, which involved heating the BCP in the MBOEA, as a result of the *in situ* generation of carboxylic acids in the PMMA block

segments of the BCP. These acid groups increased the compatibility between the PMMA block segments of the BCP and the DGEBA/MBOEA matrix. In addition, the nanostructures could be formed into lamellae, coexisting of worm-like micelles and vesicles, and spheres by increasing the quantity of acid in the PMMA block segments, without changing the blend composition.

## CONFLICT OF INTEREST

The authors declare no conflict of interest.

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