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Effect of the compatibilizer on the morphology of a phenoxy-resin/nylon-12 polymer alloy: A scanning transmission X-ray microscopy study

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Abstract. In this study, we used scanning transmission X-ray microscopy (STXM) to investigate how the addition of a compatibilizer changes the morphology of a polymer alloy composed of phenoxy resin and nylon 12. The morphology was observed to change in a manner that depended on the type and amount of compatibilizer. In addition, compatibilizer segregation is discussed in terms of changes observed in the carbon *K*-edge spectrum in each region of the polymer alloy. Hence, the desired mechanical properties can be achieved by controlling the morphology of the polymer alloy through the use of a compatibilizer, and that STXM is a suitable technique for observing morphological changes in polymer alloys.

INTRODUCTION

In general, the mechanical and thermal properties of a polymer alloy (PA) composed of two or more polymers with different chemical structures are strongly related to its phase-separation structure [1], and a compatibilizer can be used to improve the toughness and glass-transition temperature by controlling the morphology and heterogeneity of the PA. Therefore, investigating compatibilizer localization and the interfaces between various phases is important. Transmission electron microscopy (TEM) has a spatial resolution of less than 1 nm and is a powerful tool for observing phase-separation structures with electron-staining agents. However, TEM is inappropriate for organic compounds because the chemical structures (functional groups, chemical bonds, valence, etc.) of samples cannot be observed by heavy-element staining, and the electron beam can severely damage such materials. The use of atomic force microscopy (AFM) to examine the interfaces of separated phases with different mechanical properties, such as hardness, has been reported.

Scanning transmission X-ray microscopy (STXM) is an X-ray absorption imaging technique that uses synchrotron X-ray radiation to analyze chemical structures. Soft X-ray beams are less damaging than electron beams and are capable of distinguishing each polymer phase based on its chemical structure. X-ray microscopy has advanced over the past few decades owing to improvements in lithographic fabrication techniques, thereby facilitating the use of optical devices, such as Fresnel zone plates (FZP), with spatial resolutions of approximately 50 nm. In this study, we used STXM to investigate how the compatibilizer controls the phase-separation morphology in a PA. In addition, the segregation of each compatibilizer is discussed in terms of the carbon *K*-edge spectrum in each PA region.

SAMPLE PREPARATION

Five samples were prepared, namely PAs of phenoxy resin and nylon 12 (blended with the same mass ratio) with and without 5 or 10 mass% of one of two compatibilizers, as summarized in Table 1. PhenoTohto YP50S (NIPPON STEEL Chemical & Material Co., Ltd.) and UBESTA® 3024U (PA12) (UBE Corporation) were used as the phenoxy resin and nylon 12, respectively, with (I) UMEX® 1010 (1010) (Sanyo Chemical Industries, Ltd.) and (II) XIBOND® 160 (X160) (Polyscope Polymers B.V.) used as compatibilizers. Figures 1(a) and (b) show the chemical structures of the phenoxy resin and nylon 12, respectively, with the chemical structures of the compatibilizers shown in Figs. 1(c) and (d). The weight-average molecular weights (M_ws) of (I) and (II) are 4000 and 115000, respectively, and their degeneration rates are 54 and 250 mg KOH/g, respectively. A Labo Plastomill® (4C150, Toyo Seiki Seisaku-sho, Ltd.) milling machine with a twin-screw extruder was used (2D15W (L/D=17), Toyo Seiki Seisaku-sho, Ltd.), with a screw-rotation rate and cylinder temperature of 60–90 rpm and 503 K, respectively. Resins and/or compatibilizer pellets were placed into the milling machine and kneaded in the twin-screw extruder, and the extruded strand sample was cooled with water at room temperature.

TABLE 1. Composition of each PA sample (mass%)

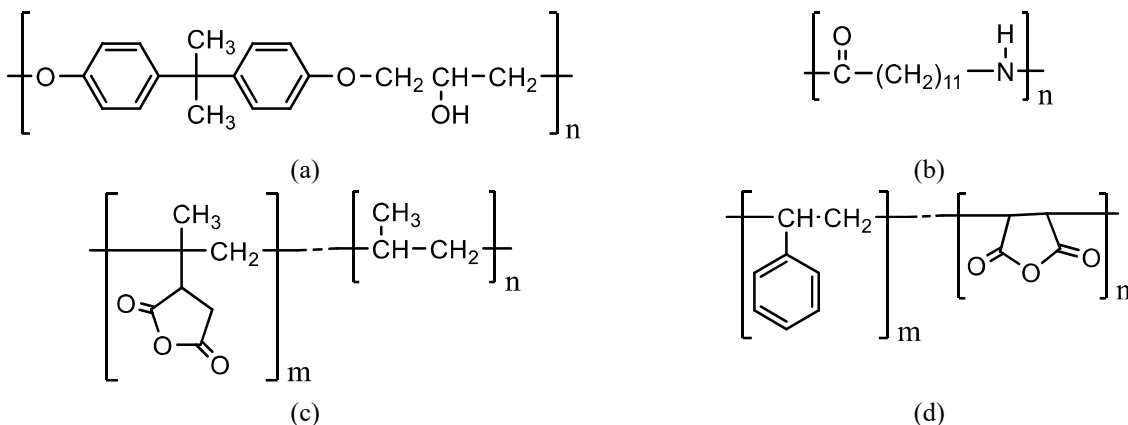|	PhenoTohto YP50S	UBESTA® 3024U (PA12)	(I) UMEX® 1010	(II) XIBOND® 160
No. 1	50	50	-	-
No. 2	47.5	47.5	5	-
No. 3	45	45	10	-
No. 4	47.5	47.5	-	5
No. 5	45	45	-	10

FIGURE 1. Chemical structures of (a) phenoxy resin, (b) nylon 12, and compatibilizers (c) (I) and (d) (II).

EXPERIMENTAL

Each PA sample (Nos.1–5 in Table 1) was sliced into ~100-nm-thick films using an ultramicrotome for STXM. In addition, X-ray absorption near-edge structure (XANES) spectra of single-phase compatibilizers were acquired using ~100-nm-thick films of each compatibilizer. STXM was performed using a compact STXM (cSTXM) instrument [2] at the BL-19A beamline of the Photon Factory of the High-Energy Accelerator Research Organization (KEK) in Japan. STXM enables XANES mapping at a spatial resolution of approximately 50 nm. While the APPLE-II undulator of BL-19 can generate circularly and linearly polarized synchrotron X-rays [3], polarization was fixed in linear-horizontal (LH) mode in this study. Image-stack data, in which a XANES spectrum is acquired around the carbon K-edge at each sample position, were collected, with aXis2000 software used to analyze the STXM data [4].

RESULTS & DISCUSSION

Figures 2(a)–(c) show X-ray absorption images (30 × 30 μm; pixel size: 50 × 50 nm) at E = (a) 285.4, (b) 288.4, and (c) 292.0 eV for the No. 1 sample, with optical density (OD) as contrast. The observed peaks at E = 285.4, 288.4, and 292.0 eV are derived from double bonds involving carbon, amide bonds, and single bonds involving carbon, respectively. Each image exhibits a contrast that reflects the position and amount of each chemical structure. Furthermore, Fig. 2(d) shows average carbon K-edge spectra of the lighter and darker regions in Fig. 2(a), along with standard spectra of compatibilizers (I) and (II). By comparing the chemical structures in Figs. 1(a) and (b), we confirmed that the lighter regions in Fig. 2(a) correspond to the phenoxy resin, while the darker regions in Fig. 2(a) correspond to nylon 12. In Fig. 2(b), each resin is drawn with contrast opposite to that in Fig. 2(a).
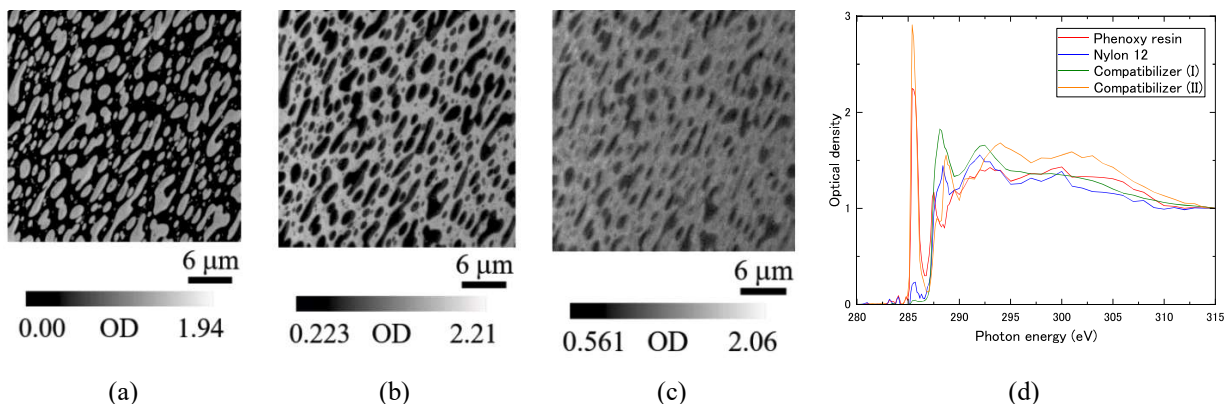

FIGURE 2. The X-ray absorption images (30 × 30 μm; pixel size: 50 × 50 nm) at E = (a) 285.4, (b) 288.4, and (c) 292.0 eV for sample No.1. (d) Average spectra of the lighter regions (phenoxy resin) and darker regions (nylon 12) in Fig. 2(a), as well as compatibilizers (I) and (II).

Figure 3 shows X-ray absorption images (15 × 15 μm; pixel size: 50 × 50 nm) of each PA at E = 285.4 eV; this absorption corresponds to the $1s$ to π^* excitation of a double bond involving carbon, which distinguishes the phenoxy resin from nylon 12. The PA devoid of compatibilizer (No. 1) exhibits a typical sea–island structure with the phenoxy resin as islands and nylon 12 as the sea, as shown in Fig. 3(a). On the other hand, PAs formed with compatibilizer (I) (Nos. 2 and 3) exhibited co-continuous-like phases with the compatibilizer, rather than a phenoxy resin (sea) and nylon 12 (island) morphology. In contrast, the morphologies of the PAs formed with compatibilizer (II) (Nos. 4 and 5) are structurally inhomogeneous.
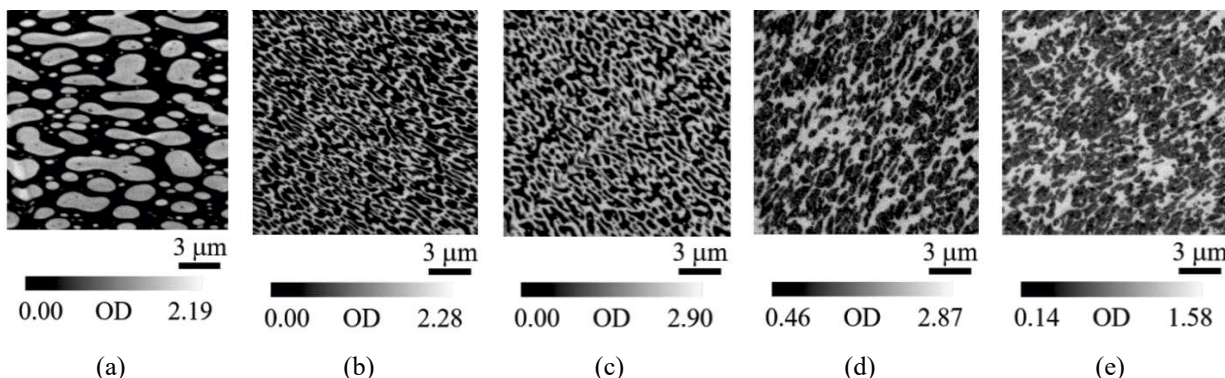

FIGURE 3. X-ray absorption (OD) images of samples Nos. 1–5 at E = 285.4 eV (contrast: OD; image size: 15 × 15 μm; pixel size: 50 × 50 nm).

We subjected each sample to singular-value decomposition (SVD) in aXis2000 to analyze the states of the areas between the regions where phenoxy resin and nylon 12 are the main components, the results of which are shown in

Figure 4. The spectrum corresponding to each pixel in the image-stack data was linearly fitted to the standard spectra of the phenoxy resin and nylon 12, with coefficients corresponding to the linear combinations of phenoxy resin and nylon 12 shown in red and blue, respectively. We performed two-phase fitting (phenoxy resin and nylon 12) in this study. The spectra of the sea and island areas in Fig. 4(a) (No. 1) were used as the standards for the phenoxy resin and nylon 12, respectively. The images of samples 2–5 (Fig. 4(b)–(e)) show boundaries between adjacent regions that are clearly observed without compatibilizer. In principle, three-phase fitting that also considers the spectrum of the compatibilizer should be performed; however, the carbon K-edge spectrum of (I) is similar to that of nylon 12, while that of (II) is similar to that of the phenoxy resin. Therefore, spectral changes associated with the addition of 5 or 10% of a compatibilizer cannot accurately be observed even when changes in the main spectral structure (285.4 or 288.4 eV) are considered in SVD analysis. We suggest that while the compatibilizer does not obscure the boundaries between areas where the phenoxy resin and nylon 12 are the main components, it changes the viscosities and the interfacial energies of the adjacent regions, which modulates the morphology of the PA.
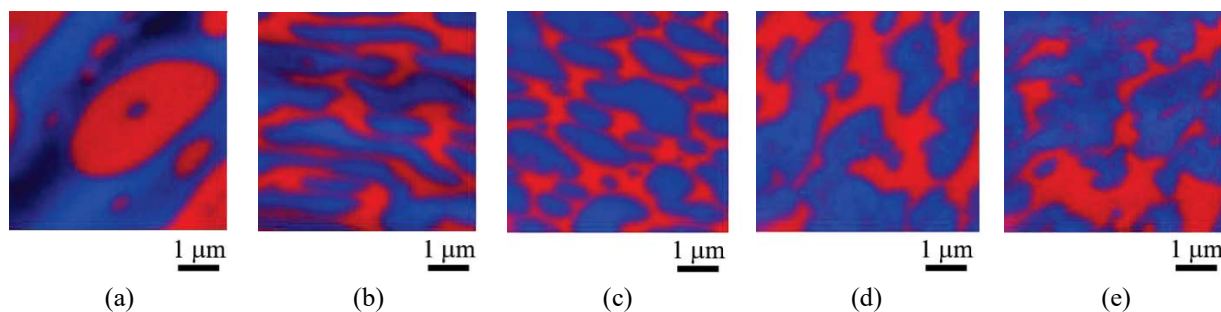

1 μm	1 μm	1 μm	1 μm	1 μm
(a)	(b)	(c)	(d)	(e)

FIGURE 4. SVD analysis image for each PA (Nos.1–5 in Table 1). Image size: 3 × 3 μm; pixel size: 30 × 30 nm. Red and blue regions correspond to areas where the phenoxy resin and nylon 12 are the main components.

To determine where the compatibilizer invades the PA, we compared the average spectra of the red and blue regions in Figs. 4(a)–(e), the results of which are shown in Figs. 5(a) and (b), respectively. In the case of compatibilizer (I), the intensity at $E = 285.4$ eV was observed to decrease with increasing mass fractions of compatibilizer in areas where the phenoxy resin is the main component (red regions in Figs. 4(b) and (c)), as shown in Fig. 5(a), while the intensity at $E = 288.4$ eV was concurrently observed to increase monotonically. On the other hand, the intensity of the peak at $E = 288.4$ eV in areas where nylon 12 is the main component (blue regions in Figs. 4(b) and (c)), which corresponds to amide bonds, increased as the amount of compatibilizer was increased from 5% to 10% (Fig. 5(b)), which suggests that the compatibilizer first invades the red regions at low (5%) fraction, and then invades both the red and blue regions as the amount of compatibilizer is increased.

In the case of compatibilizer (II), the intensity of the peak at $E = 285.4$ eV in the red regions increased as the amount of compatibilizer was increased from 5% to 10% (Fig. 5(a)). On the other hand, the intensity at $E = 285.4$ eV in the blue regions did not change as the amount of compatibilizer was increased (Fig. 5(b)), which suggests that the compatibilizer first mainly invades the blue regions at low (5%) mass fractions, after which both the red and blue regions become invaded as the amount of compatibilizer is increased to 10%.

Compatibilizer (I) first invades the red region due to its high aliphatic property, after which it invades the red and blue regions with increasing mass fraction. On the other hand, the aromatic compatibilizer (compatibilizer (II)) first invades the blue regions and then the red regions with increasing mass fraction. Aliphatic compatibilizers are generally known to invade aliphatic resins, whereas highly aromatic compatibilizers tend to invade highly aromatic resins. However, the intrusion tendency of the compatibilizers revealed in this study cannot be explained by the findings presented above. The degree of compatibility is not only related to the chemical structures of the resin and the compatibilizer, but also to the modification rate and molecular weight. The reaction frequency between each polymer and compatibilizer is high at a high compatibilizer modification rate. Furthermore, we presume that the amide groups of nylon 12 react with anhydride in the compatibilizer when the molecular weight of the compatibilizer is low; hence, it is taken up by the aliphatic chain of nylon 12 and barely interacts with the phenoxy resin. The compatibilizer is also a polymer that is not completely compatible with other polymers. Although the chemical structure of nylon 12 has many reaction points, the blue regions form through cohesive forces derived by the cross-linking of nylon-12 molecules; hence, we speculate that the compatibilizer is excluded from the blue regions. Moreover, even if the compatibilizer itself does not dissolve in each main-component resin, it may reduce the surface energy at the phenoxy-

resin/nylon-12 interface. While the compatibilizer should be present at the boundaries rather than in the red and/or blue regions in this scenario, the spatial resolution and signal-to-noise ratio (S/N) of the present STXM technique is unable to capture this.

As mentioned above, the tendency of the compatibilizer to penetrate into each resin is related to the M_ws of the resin and the compatibilizer, the modification rate of the compatibilizer, the reactivities of the resin and the compatibilizer (for example, nylon 12 and the anhydride in the compatibilizer), and the change in interfacial energy between resins resulting from addition of the compatibilizer; unfortunately, separating these effects using only STXM when examining the infiltration tendency of the compatibilizer is difficult. In this study, we used STXM to capture changes in PA morphology resulting from the addition of a compatibilizer and discussed the tendency of the compatibilizer to infiltrate in qualitative terms.
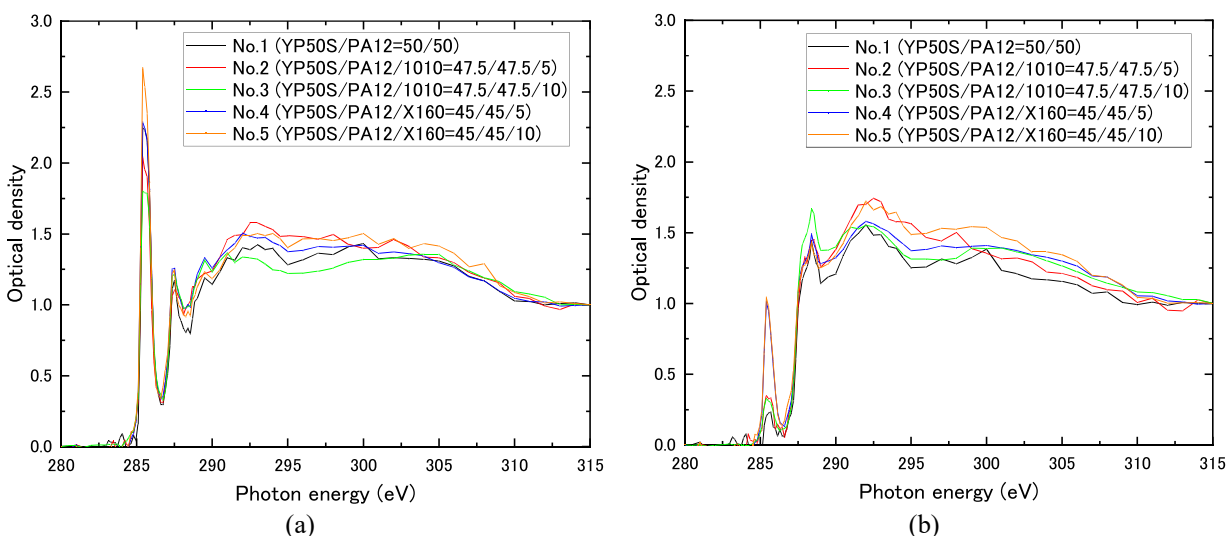

FIGURE 5. Carbon K-edge spectra in regions where the phenoxy resin and nylon 12 are the main components (the red and blue regions in Figs. 4(a)–(e)), respectively. All spectra were normalized against the optical density at $E = 315.0$ eV.

CONCLUSION

In this study, we used STXM to investigate the morphological changes caused by the addition of compatibilizers to a PA composed of phenoxy resin and nylon 12. Morphology was observed to change in a manner that depended on the type and amount of compatibilizer. Changes in the carbon K-edge spectrum of each region revealed that the region in the PA invaded by the compatibilizer depends on the amount added.

Compatibilizer (I) first invaded the phenoxy-resin regions at low mass fraction (5%), however, it was observed to also invade the nylon-12 regions when the amount of compatibilizer was increased. On the other hand, compatibilizer (II) first invaded the nylon-12 regions at low mass fraction (5%), after which it was observed to invade both regions as the amount of compatibilizer was increased from 5% to 10%.

The extent to which the sea-structure resin penetrates into the island structure can be controlled by changing the chemical structure of the compatibilizer. Furthermore, the compatibilities of different materials and the stabilities of the sea and island regions can be controlled by adjusting the amount of compatibilizer added.

ACKNOWLEDGMENTS

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