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Morphology and coarsening behavior in Polycarbonate/Nylon6-co-12 blends with and without compatibilizer

Y.H. Kim[a,1], M. Kikuchi[a], S. Akiyama[a,*], K. Sho[b], S. Izawa[a,2]

[a]*Department of Chemical Science and Technology, Faculty of Technology, Tokyo University of Agriculture and Technology, 2-24-16, Naka-machi, Koganei-Shi, Tokyo 184-0012, Japan*

[b]*Asahi Chemical Industry Co., Ltd., 1-3-1, Yakoh, Kawasaki-shi, Kanagawa-ken, 210 Japan*

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Abstract

The morphology and the coarsening behavior with and without compatibilizer were investigated by using scanning electron microscope. As a new compatibilizer, styrene–acrylonitrile–maleic anhydride terpolymer (S–AN–MAH) was used. For Polycarbonate (PC) /Nylon6-co-12(50/50) blend, modulated structure was observed. And coarsening behavior was similar to that of spinodal decomposition. However, for PC/Nylon6-co-12(50/50) blend with S–AN–MAH, sea–island structure was developed and the size of domain did not increase although the sample was annealed for 90 min, at above T_m. It was confirmed that S–AN–MAH retards coarsening of morphology.

Keywords: Polycarbonate; Nylon 6-co-12; Morphology

1. Introduction

In polymer blends, properties are related with their morphology, directly [1]. Earlier studies [2–3] were reported about morphology in polymer blends. In general, four types of structures are observed for two-phase polymer systems; sea–island structure, co-continuous structure, salami structure and modulated structure. Among them, the modulated structure is formed via spinodal decomposition from a single-phase mixture. The structure can be obtained in only a few polymer blends, because most polymer pairs are immiscible. However, even though immiscible system, in the case that polymer pairs have small differences in the solubility parameter, the same structure is observed in solution-cast films [4]. For polymer blends, which are rapidly precipitated, a similar behavior is expected [5].

Recently, as another method for developing the modulated structure, melt blending was discussed. In our previous work [6–7], modulated structure was observed in melt blended PC/Nylon blends, which indicates that melt blending can be also the method for obtaining this structure. The reason why the structure is developed in melt mixed immiscible system, was interpreted by shear-induced miscibility [8]. The present study aims at two objectives. One is to observe the coarsening of morphology via annealing for investigating the possibility of spinodal decomposition in PC/Nylon6-co-12 blends. The other is to observe the effects of compatibilizer on morphology stabilization. It was reported that added block copolymer retard phase-separation [9]. Therefore, it is expected that the structure obtained by melt-blending can be stabilized by compatibilizer. We investigated the morphology of the blends with scanning electron microscope (SEM).

2. Molecular design of compatibilizer

The compatibilizers for polymer A/B blends can be classified: A–B type, A–C type, and C–D type [10]. If a functional group is C, a reactive compatibilizer is included in A–C type and C–D type. That is, compatibilizer is composed of functional group and same polymer with polymer, A or the group which has a good affinity with A. For a C–D type compatibilizer for PC/Nylon blends, maleic anhydride is suitable as a functional group. However, there are a few polymers, which have good affinity with PC. For example, styrene/maleic anhydride copolymer is not suitable because styrene has poor interaction with PC. Keitz et al. [11]

* Corresponding author.

[1] Present address: Advanced Polymeric Materials Engineering, Toyota Technological Institute, 2-12-1 Hisakata, Tempaku, Nagoya-shi, Aichi-ken 468-8511, Japan.

[2] Present address: 3-10-11, No. 303 Takashima daira, Itabashi-ku, Tokyo 175, Japan.

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Table 1
The molar volumes at room temperature and the solubility parameters calculated by Fedors method[17]

Polymer	V(cm^3/mol)	δ (cal/cm^3)$^{1/2}$
PS	86.5	10.55
PC	174.6	11.24
AN	39.1	14.39
MAH	28.0	17.87

reported that the interaction between PC and SAN depends on the AN contents of SAN copolymer. The calculated interfacial tension between PC and SAN at 270°C, shows minimum value at the range of AN contents; 15–20 wt.% [3,12].

Therefore, styrene/acrylonitrile/maleic anhydride (AN: Ca. 15 wt.%, MAH: 5.2 wt.%) was used as a compatibilizer in this study. There is a possibility that maleic anhydride also reacts with − OH group at the end of PC. However, it is known that reactivity between $-NH_3$ group and maleic anhydride is higher than that between − OH group and maleic anhydride from experimental results [13]. Therefore, the reactivity of the latter is neglected in this study.

Interaction between PC and styrene copolymer may also be changed by copolymerization of MAH. Therefore, interaction parameter between PC and styrene copolymer is calculated.

If there are no excess volume of mixing and no specific interaction, the Flory interaction parameter χ_{12} between polymer 1 and 2 is calculated by [14]

$$\chi_{12} = (V_r/RT)(\delta 1 - \delta 2)^2, \tag{1}$$

where δ i is the solubility parameter. V_r is assumed to be

$$V_r = (V_1 V_2)^{1/2}, \tag{2}$$

where V_1 is molar volume of monomer unit of PC and V_2, molar volume of B/C copolymer is given by

$$V_2 = [(1 - X)V_{B+X}V_C], \tag{3}$$

where X is mole fraction of C in the copolymer. V_B and V_C are molar volume of B and C monomer unit, respectively. Molar volume of B–C–D terpolymer is calculated by

$$V_2 = [(1 - (X_C + X_D))V_B + X_C V_C + X_D V_D], \tag{4}$$

where V_B, V_C and V_D are molar volume for each units [15].

The χ_{12} between homopolymer A(1) and a random copolymer B/C (2) is given by [16]

$$\chi_{12} = (1 - \phi)\chi_{AB} + \phi\chi_{AC} - \phi(1 - \phi)\chi_{BC}, \tag{5}$$

where ϕ is volume fraction of C in the copolymer. Substituting Eq. (1) into Eq. (5),

$$\chi_{12} = (V_r/RT)[(1 - \phi)(\delta_A - \delta_B)^2 + \phi(\delta_A - \delta_C)^2 - \phi(1 - \phi)(\delta_B - \delta_C)^2]. \tag{6}$$

Then, expanding to homopolymer (A) /terpolymer(B/C/D) system,

$$\chi_{12} = [1 - (\phi_C + \phi_D)]\chi_{AB} + \phi_C\chi_{AC} - \phi_D x_{AD} - \phi_C[1 - (\phi_C + \phi_D)]\chi_{BC} - \phi_C\phi_D(1 - \phi_C)\chi_{CD} - \phi_D[1 - (\phi_C + \phi_D)]\chi_{BD}, \tag{7}$$

where ϕ_C and ϕ_D are the volume fractions of C and D in copolymer, respectively. Solubility parameter δ is calculated with group molar attraction constants of Fedors [17], Fi and group molar volume, Vi. If additive rule works in group molar attraction constants and volume, solubility parameter can be calculated by

$$\delta = \Sigma Fi/\Sigma Vi. \tag{8}$$

The results are shown in Table 1. The calculated values of χ_{12} between PC and styrene copolymer are shown in Fig. 1. The χ_{12} is shown to decrease with copolymerization of MAH. The results indicate that S–AN–MAH is expected to have better interaction with PC than S–AN.

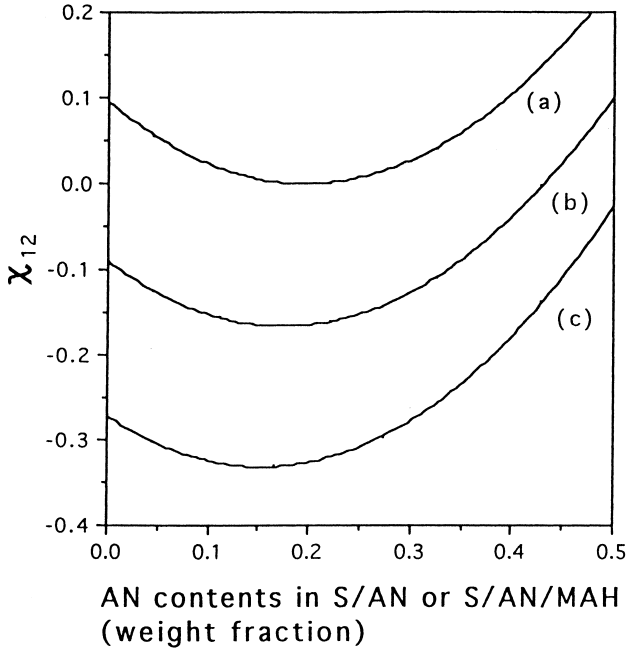

Fig. 1. Variation of χ_{12} with SAN or S–AN–MAH copolymer composition in the blends with PC at room temp. (a) SAN copolymer, (b) S–AN–MAH copolymer (MAH: 2.8 wt.%), (c) S–AN–MAH copolymer (MAH: 5.2 wt.%).

3. Experimental

Polycarbonate ($L - 1250, \overline{Mv} = 2.49 \times 10^4, T_g = 150$°C, Teijin Chemicals) and nylon6-co-12 ($CF - 6S, \overline{Mn} = 1.4 \times 10^4, T_g = 32$°C, EMS Japan) were used. SAN and S–AN–MAH were synthesized. The composition and physical properties for each styrene copolymers are shown in Table

Table 2
The concentration and physical properties of styrene copolymers

Sample	AN%	MAH%	Ml/g/10 min (220°C/10 kg)	Vicat Softening temperature/°C
SAN	15.2	–	44.8	110.0
S-AN-MAH	16.1	5.2	24.0	118.5

2. Another styrene copolymer, styrene–maleic anhydride (SMAH, MAH contents: 24 wt.%, Elf Atochem Japan) was also used.

PC/Nylon6-co-12 blends were prepared with kneader (Kurimoto, co-rotating twin screw, L/D 3-4). Samples ca. 20 g were mixed at; 230°C, 81 rpm for 120 s and then at 250 rpm for 90 s under nitrogen. After blending, samples were quenched with liquid nitrogen. Further details of the kneader are given in Ref. [7].

Blended sample was annealed at 205°C for 30, 60, 90 and 120 min. After that, the samples were quenched with liquid nitrogen.

A scanning electron microscope (SEM, Hitachi, H-700H) was used to take micrographs of quenched samples and annealed samples. Each sample was microtomed to create a plane face. To observe morphology, thin sections (below 1 mm) were prepared. All the samples were etched with chloroform. After that, samples were dried in vacuum oven below T_g, for over 48 h. we focus on the morphology of the skin region of fractured surface, because morphology at the skin was quenched quickly.

4. Results and discussion

The micrographs of PC/styrene copolymer (80/20) blends, are shown in Fig. 2. In PC/SMAH blend, poor dispersity is observed, as shown in Fig. 2(a). Approx.

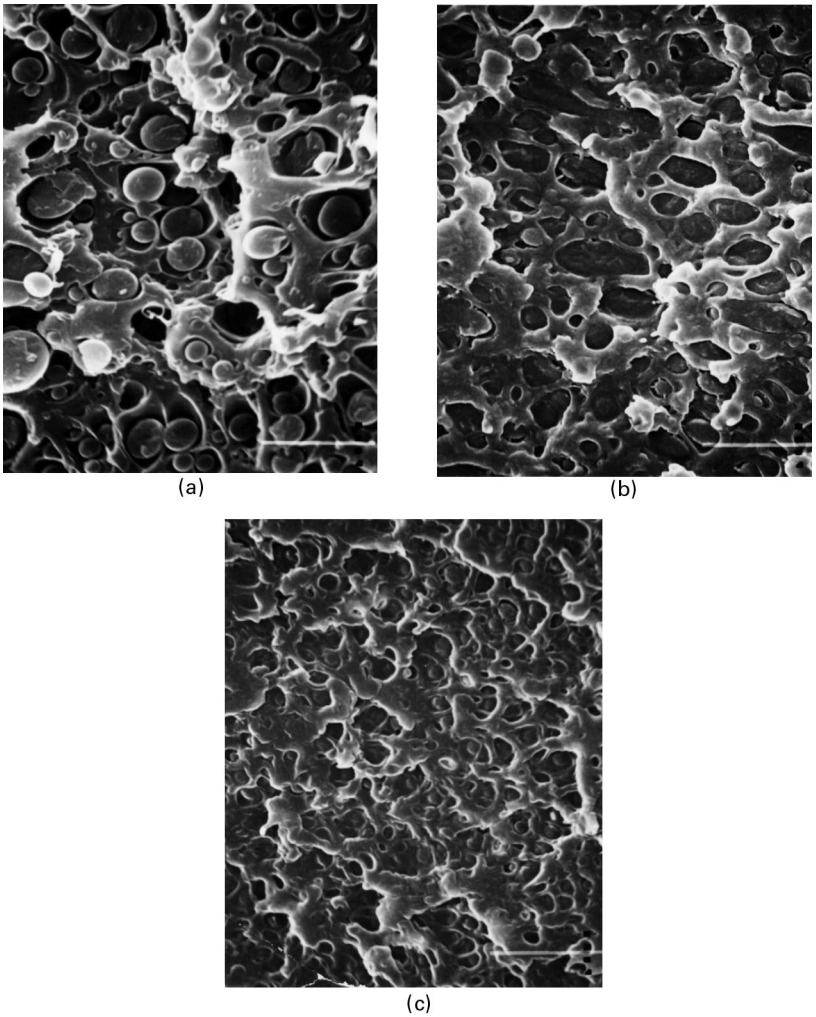

Fig. 2. Scanning electron micrographs of PC/styrene copolymer(80/20) blends. (a) PC/SMAH (MAH: 24wt.%), (b) PC/SAN (AN: 15.2 wt.%), (c) PC/S–AN–MAH (AN: 16.1 wt.%, MAH: 5.2 wt.%).

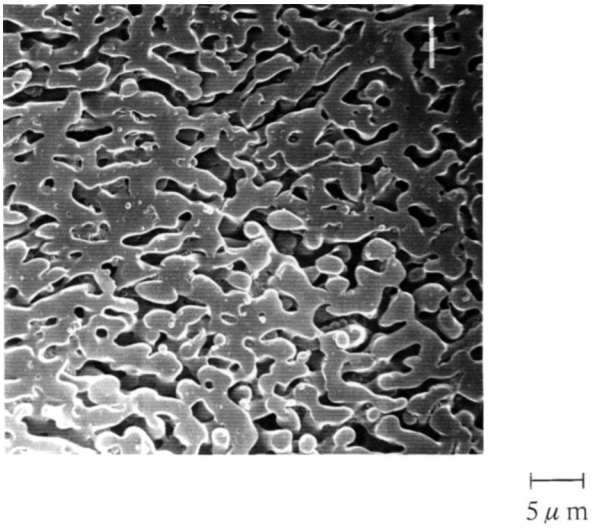

Fig. 3. Scanning electron micrograph of PC/Nylon 6-co-12(50/50) blend.

2 μm particles are dispersed and the interface between PC and SMAH is separated. This result shows that SMAH is not suitable as a compatibilizer in PC/nylon blends. The content of MAH in SMAH is 24 wt.%, and then the possibility of the chemical reaction is higher than the other system. If chemical reaction occurs in PC/SMAH blend, good dispersity has to be observed. However we cannot detect this. So the effect of chemical reaction between terminal hydroxyl group of PC and MAH on the morphology can be neglected. For PC/SAN blend, the domain size is almost the same as that of PC/SMAH blend. However, the interface doesn't come apart. As shown in Fig. 2(c), better dispersity is observed in PC/S–AN–MAH blend, as compared to the other system. This is the expected result from the calculation of χ_{12} (Fig. 1). The decrease of particle diameter in PC/S–AN–MAH blend may come from the improvement of interaction. In this study, by using S–AN–MAH, the effects of compatibilizer will be discussed.

The micrographs of PC/nylon6-co-12(50/50) blend are shown in Fig. 3. As reported in previous article [7], modulated structure is observed. Two phases are interconnected and uniform spacing is observed. The morphology can be obtained by rapid quenching after processing.

When the PC/nylon6-co-12(50/50) blend was annealed at 205°C, the structure coarsening was observed as shown in Fig. 4. Negative films were used for observing morphology because it is easier to observe the coarsening of structure. For quenched sample, morphology with irregular shaped domains is obtained, as shown in Fig. 4(a). After annealing for 30 min, morphology is coarsened, which is similar with co-continuous structure. This behavior indicates that the morphology of Fig. 4(a) is the previous stage of that which shown in Fig. 3. The difference of morphology between Figs. 3 and 4(a) may come from the error of quenching time, because coarsening occurs rapidly, when shear rate becomes zero at processing temperature (above 230°C).

After further annealing, coarsening progresses, as shown in Fig. 4(c) and (d). The above results indicate the reason why a modulated structure is formed in this system. The

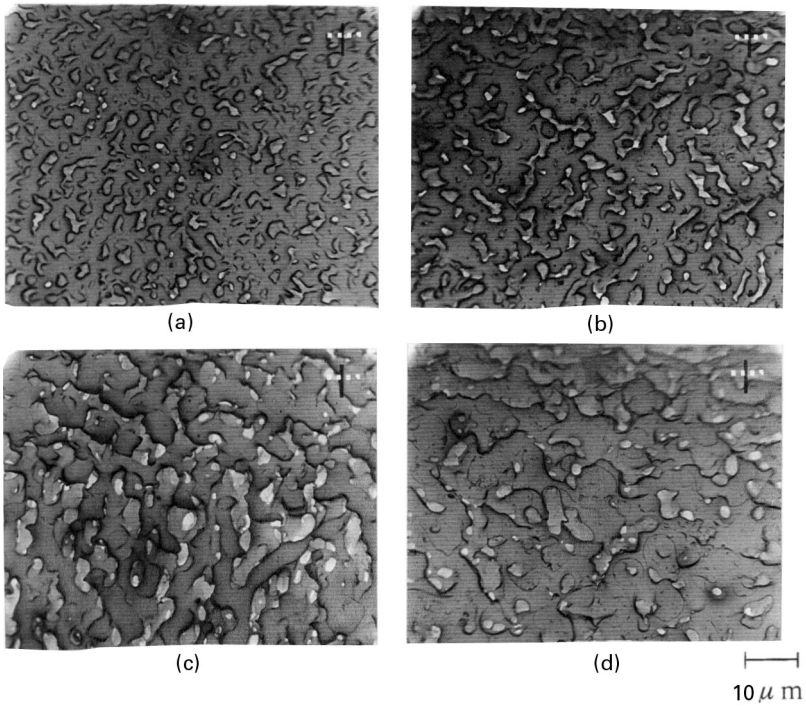

Fig. 4. Scanning electron micrographs of PC/Nylon 6-co-12(50/50) blend quenched with liguid nitrogen from the melt after various annealing times at 205°C. 0 min (b) 30 min (c) 90 min (d) 150 min.

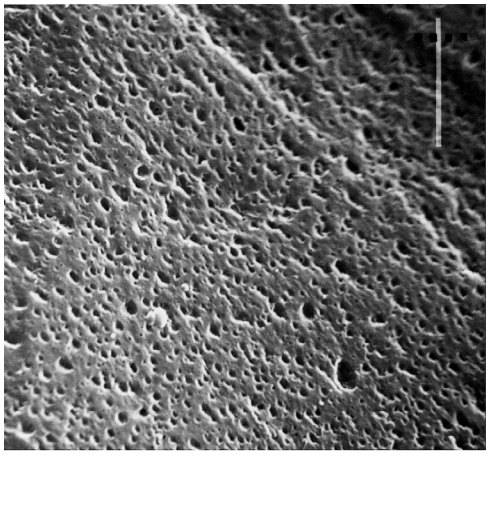

Fig. 5. Scanning electron micrograph of PC/Nylon6-co-12(50/50) blend with S–AN–MAH (5 wt.%).

coarsening behavior and the morphologies are very different with that of other immiscible system. In the case of an immiscible system, a co-continuous structure is developed under shear field in phase inversion region, for example Ref. [18]. However, for this system, after processing, irregular shaped domains becomes co-continuous structure and then coarsening occurs until vitrification. Observations of Fig. 4(a)–(d) are similar with that reported for late stage of phase separation of copolyester/PET blends [19].

In the following, the effect of the compatibilizer on morphology will be discussed. As shown in Fig. 5, it is noticed that modulated structure is changed to sea–island structure by adding S–AN–MAH. Particle diameter is below 1 μm and uniform. In this study, the compatibilizer was used for stabilizing morphology. However, the type of morphology is changed greatly by adding S–AN–MAH. The difference could be caused by the in situ formed nylon-(S–AN–MAH) graft copolymer, as the asymmetric copolymer prefers an interface with large curvature, i.e., more spherical particles.

Sundararaj et al. reported that the one of the important effects of compatibilizer is stabilization of morphology [20]. For checking the effect, coarsening of morphology was observed.

The morphology of the annealed PC/Nylon 6-co-12 with compatibilizer is shown in Fig. 6. Even after annealing for 120 min, a significant coarsening is not observed. In early stage, irregular shaped dispersed phase (PC) are observed. After annealing for 120 min, a sea–island structure is observed. The size of domain is still less than 5 μm. This behavior is very different from that of the neat blend, as shown in Fig. 4. The results indicate that compatibilizer locates at the interface between PC and Nylon6-co-12 and then coarsening is prevented.

5. Conclusion

For PC/Nylon6-co-12(50/50) blend, it was observed that coarsening behavior by annealing is similar to that of

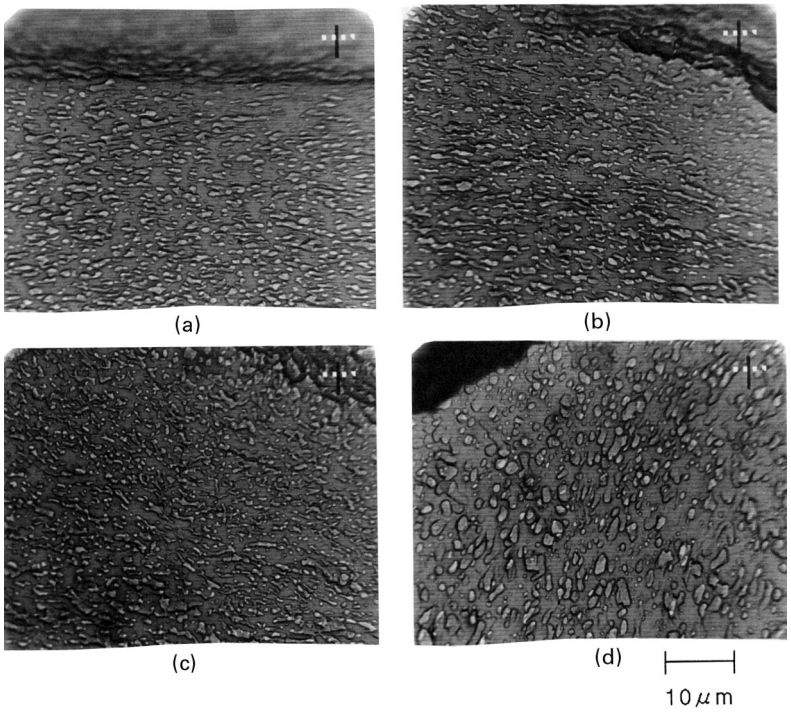

Fig. 6. Scanning electron micrographs of PC/Nylon6-co-12(50/50) blend with S–AN–MAH (5 wt.%) quenched with liquid nitrogen from the melt after various annealing times at 205°C. (a) 0 min, (b) 30 min, (c) 90 min, (d) 120 min.

spinodal decomposition from single-phase mixture. It indicates that shear-induced miscibility may occur in PC/Nylone6-co-12 blends. When S–AN–MAH was added, instead of the modulated structure the sea–island structure was formed. The sea–island structure hardly coarsened with annealing.

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