

Shear-Induced Modulated Structure in Blend of Polycarbonate/Nylon6-co-12 Random Copolymer

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ABSTRACT: The morphology of the polycarbonate (PC)/Nylon12 blend was compared with that of PC/Nylon6-12 random copolymer (Nylon6-co-12, 6 content: 64 mol%) blend. Specific interaction between PC and Nylon was not detected by FT-IR. DSC and DMA data indicated the presence of double T_g 's, corresponding to each component. For the Nylon6-co-12 blend, particles of a minor phase were smaller than those of the other blend. In PC/Nylon6-co-12(50/50) blend, a modulated structure was obtained when melt mixed at 500 s^{-1} . On the other hand, in PC/Nylon12 (50/50) blend, isolated dispersion particles were observed. The formation of modulated structure was interpreted in terms of shear-induced miscibility. PC and Nylon6-co-12 may be miscible under a high shear field in twin-screw kneader, whereas PC and Nylon12 are immiscible under the same processing conditions.

KEY WORDS Polycarbonate/Nylon6-co-12/Nylon12 / Morphology / Shear-Induced Miscibility / Interfacial Tension / Modulated Structure /

In studies on polymer blends, blends containing polycarbonate (PC) or Nylon have been much investigated.¹⁻⁶ However, there are a few studies⁷⁻¹¹ on PC/Nylon blend. Gattigillia *et al.*^{7,8} reported that in Nylon-rich blends, mechanical properties were improved by PC-Nylon random copolymer *via* an interchange reaction. The poor adhesion is improved by the addition of SEBS-*g*-MAH.⁹ Our previous work^{10,11} reported that poly(allyl-co-maleic anhydride) as a compatibilizer, prevents the interchange reaction in melt-mixing. Up to now, compatibilization for PC/Nylon blend can be achieved by the interchange reaction between components and the use of a premade compatibilizer. In this paper, Nylon6-co-12 random copolymer (6 content: 64 mol%) is used as a pair Nylon for PC. In our previous studies,^{10,11} homogeneity in the blends was found to follow the order: Nylon3Me6T > Nylon12 > Nylon6 ≥ Nylon66. This suggests that blend homogeneity may be related to crystallinity of Nylon. The crystallinity and T_g of Nylon random copolymer show a minimum in middle mole fraction range.^{12,13} Zilberman *et al.*¹⁴ suggest that the shift of T_g results from change of self-association in Nylon random copolymer. The physical properties and morphology is investigated in the blend of PC/Nylon6-co-12, as compared with those of PC/Nylon12. Random copolymers often show quite different behavior in solubility, crystallinity, and thermal properties from their parent polymers.¹⁵ The effects of Nylon random copolymerization on compatibility between PC and Nylon should thus be studied.

EXPERIMENTAL

Materials

Polycarbonate (L-1250, $\bar{M}_v = 2.49 \times 10^4$, Teijin Chemicals Ltd.), Nylon6 (NH8001, $\bar{M}_w = 2.1 \times 10^4$, Teijin Chemicals Ltd.), Nylon12 (Rilsan AMNO, $\bar{M}_w = 2.2 \times 10^4$, Atochem Co.), and Nylon6-co-12 ($\bar{M}_n = 1.4 \times 10^4$, CF-6S, EMS Japan Co.) were used. The 6 unit content in Nylon copolymer was 64 mol%.

Sample Preparation

PC/Nylon blends were prepared with kneader (Kurimoto Ltd., co-rotating twin screw, L/D 3-4). A schematic diagram is shown in Figure 1. Each screw bar consists of six paddles and two segment screws. The screw is designed to move sample not only radially but also backwards and forwards along the axis to improve mixing. Samples *ca.* 20 g were put into cylinder at 230°C , 81 rpm, for 120 s, and then mixed at 250 rpm, 90 s under nitrogen. To avoid the interchange reaction between PC and Nylon, we made the mixing time as shortly as possible. The nominal shear rate can be calculated by assuming drag flow in the minimum and maximum gap between the paddles and the barrel. The maximum shear rate was calculated to 500 s^{-1} and the minimum shear rate, 30 s^{-1} at 250 rpm. Shear rate may be assumed as the maximum shear rate since the effect of mixing is expected to better in high shear rate region. After mixing, the samples in kneader, were immediately quenched into cold water for *ca.* 1 h. The blended samples were left for a few days in a desiccator at room temperature before morphology observation. For other measurements, the samples were dried in vacuum oven at 100°C , for 24 h.

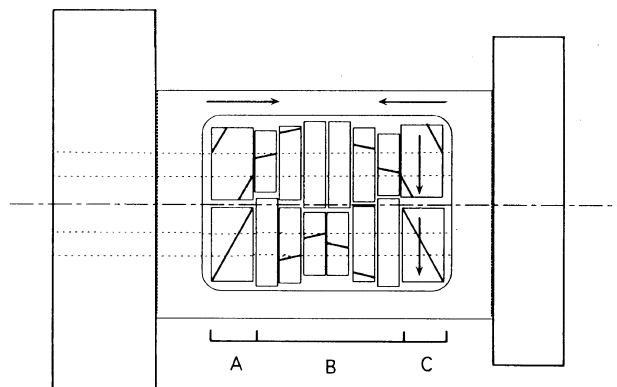


Figure 1. Schematic diagram of mixing part of co-rotating twin screw kneader. A, forward screw; B, helical paddles; C, backward screw. Arrows indicates the direction of flow.

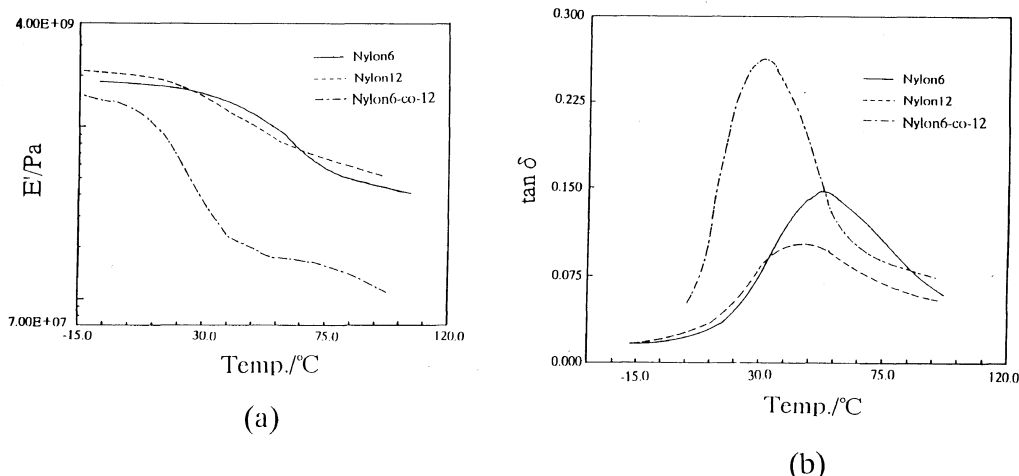


Figure 2. Dynamic mechanical properties for Nylon6, Nylon12, and Nylon6-co-12. (a) E' as a function of temperature; (b) $\tan \delta$ as a function of temperature.

Thermal Properties

Thermodiagrams of samples were obtained with DSC (990, Du Pont Co.). Each sample was heated at $10^{\circ}\text{C min}^{-1}$ from 10 to 215°C for Nylon12 blends or from -20 to 165°C for Nylon6-co-12 blends and cooled at less than $5^{\circ}\text{C min}^{-1}$. Thermal properties were determined after 2nd heating scans. The properties may be different from those of the original mechanical blended samples.

Dynamical Mechanical Analysis

Dynamical mechanical properties were measured by DMS 200 (Seiko Co.) at a frequency of 1 Hz. Heating rate was $2^{\circ}\text{C min}^{-1}$. Samples were prepared in a ram press, annealed above 205°C for 1 h and then quenched into liquid nitrogen.

FT-IR

PC/Nylon blends were analyzed using a FT-IR (JEOL Co., JIR-WINSPEC 50). Samples were prepared as films by melt-quenching between teflon sheets in a ram press. 100 Scans at a resolution of 2 cm^{-1} were signal averaged.

Morphology Observation

Cryogenically fractured surfaces were covered with gold by a sputtering coating unit and observed by scanning a electron microscope (Hitachi Co., H-700H). Image analysis was performed on a Macintosh (model) computer using the public domain NIH Image program (written by Wayne Rasband at the U.S. National Institutes of Health).³⁻⁴ Fields of view and 100–200 diameters are considered for a given sample. The number average diameter, \bar{d}_n and weight average diameter, \bar{d}_w were calculated as follows.

$$\bar{d}_n = \frac{\sum n_i d_i}{\sum n_i} \quad (1)$$

$$\bar{d}_w = \frac{\sum n_i d_i^2}{\sum n_i d_i} \quad (2)$$

where n_i is the number of particles with diameter d_i . The characteristic length of a modulated structure¹⁶ was determined by electron microscope. Further details of this method are given in ref 17.

RESULTS AND DISCUSSION

Storage modulus (E') data for Nylon6, Nylon12, and Nylon6-co-12 are shown in Figure 2(a). A marked decrease of E' value near T_g was observed for Nylon6-co-12, compared with Nylon homopolymers. This indicates that crystallinity of Nylon6-co-12 is much lower. Figure 2(b) shows $\tan \delta$ data for each Nylon. $\tan \delta$ peaks for Nylon6, Nylon12, and Nylon 6-co-12 are observed at 52, 46, and 32°C , respectively. These data show that T_g of Nylon random copolymer is lower than that of each Nylon homopolymer. The above results indicate changes of properties by random copolymerization of Nylon.

The DSC curves of PC/Nylon12 blends are shown in Figure 3. T_g of PC shows almost the same value over a whole range of composition. As T_g of PC and melting region of Nylon12 are overlapped, accurate values can hardly be obtained. T_g of Nylon12 may be also difficult to measure with DSC because of having a small amorphous part.

DSC curves for PC/Nylon6-co-12 blends are shown in Figure 4. For pure Nylon6-co-12, the heating scan shows a broad recrystallization peak at 100°C and broad melting peak at 120°C . Because of the slow crystallization of Nylon6-co-12 at low cooling rate, recrystallization begins to occur at reheating scan, as shown by the DSC curve of polyethylene terephthalate.¹⁸ T_g of Nylon6-co-12 in (50/50) blends shifts to higher temperature slightly, whereas that of PC keeps almost constant. However, in PC/Nylon6-co-12 (30/70) blend, T_g of PC is not observed, as shown in Figure 4. This indicates that T_g of PC shifts to lower temperature and overlaps with the melting peak of Nylon6-co-12 ($T_m = 120^{\circ}\text{C}$). There would be two possibilities for the reason why: one is the partial solubility between PC and Nylon6-co-12, the other is decrease of molecular weight of PC by the ester-amide interchange reaction between PC and Nylon6-co-12. If Nylon-PC copolymer is formed by the interchange reaction, it should prevent the crystallization of Nylon and then T_m and the heat of fusion of Nylon may decrease markedly. Therefore, the observation of crystallinity of Nylon is useful for checking the reaction.¹⁹ Aminolysis is the main reaction between PC and Nylon⁸. Therefore,

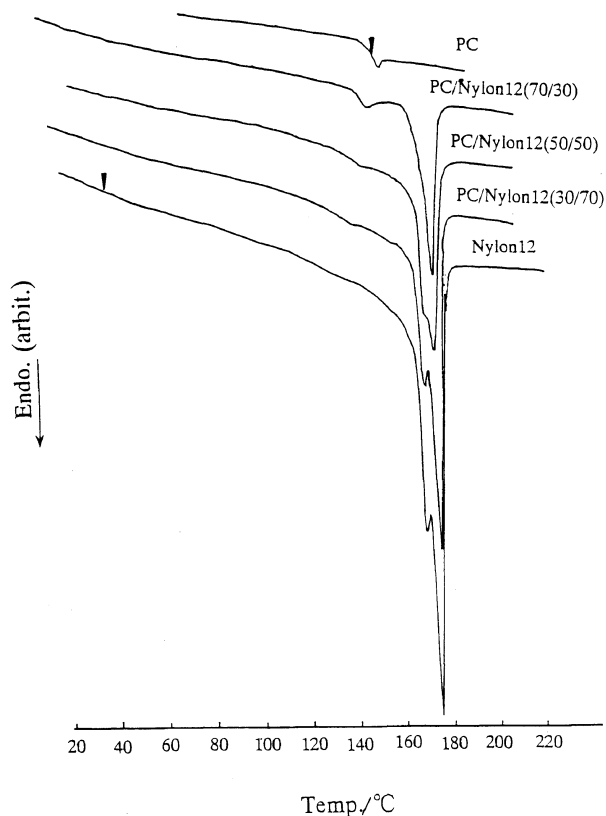


Figure 3. DSC thermograms for PC, Nylon12, and PC/Nylon12 blends.

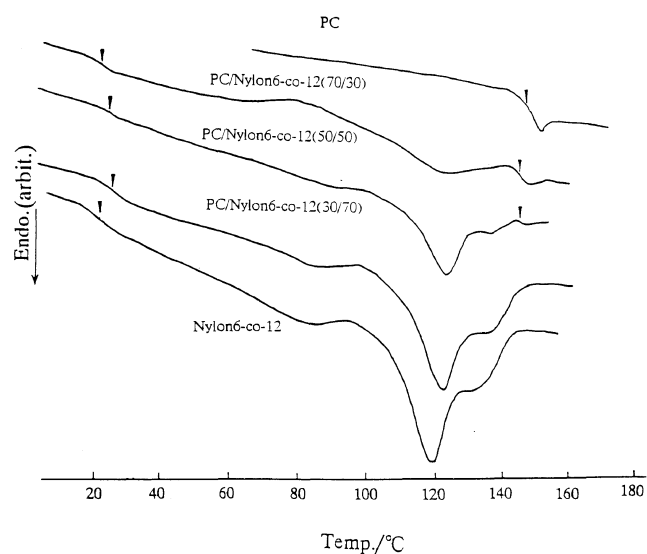


Figure 4. DSC thermograms for PC, Nylon6-co-12, and PC/Nylon6-co-12 blends.

the interchange reaction is expected to occur more easily in Nylon-rich concentration. As shown in Figure 4, T_m 's of Nylon6-co-12 keep almost constant. The crystallinity from heat of fusion of Nylon-rich blend (30/70) is almost the same as that of pure Nylon6-co-12. The above results indicate that the interchange reaction hardly occurs in the blend (30/70), and the T_g shift of PC should come from partial solubility between PC and Nylon 6-co-12. As we can't determine the accurate T_g of blends with DSC, dynamic mechanical testing was also performed.

The loss modulus (E'') behavior for PC/Nylon12 blends are shown in Figure 5. In PC/Nylon12 blend, the

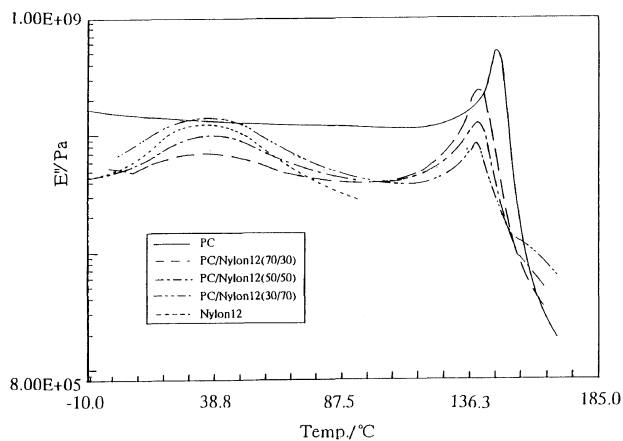


Figure 5. E'' as a function of temperature for PC, Nylon12, and PC/Nylon12 blends.

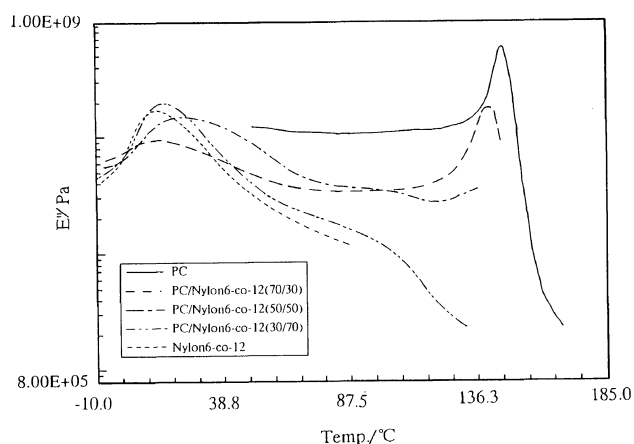


Figure 6. E'' as a function of temperature for PC, Nylon6-co-12, and PC/Nylon6-co-12 blends.

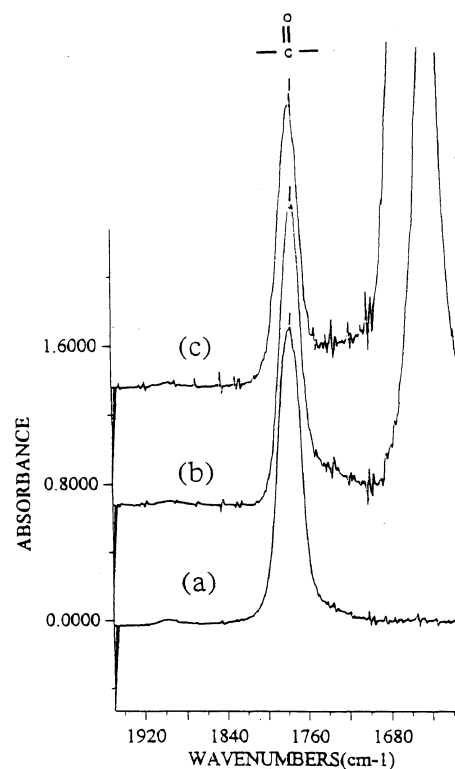


Figure 7. FT-IR spectra for PC/Nylon blends. (a) pure PC; (b) PC/Nylon12 (30/70); (c) PC/Nylon6-co-12 (30/70).

α -transition of Nylon12 is almost constant in all compositions, whereas that of PC decreases slightly. However, a composition dependency is not observed.

The loss modulus (E'') behavior for PC/Nylon6-co-12 blends is shown in Figure 6. For the original Nylon6-co-12, the α -transition occurs at 12.7°C, while for PC, at 145.9°C. The observed E'' peak for Nylon6-co-12 in blends shifts to higher temperature. This is quite similar to the previous DSC results in Figure 4. The E'' peak of PC shifts to lower temperature slightly in PC/Nylon6-co-12 (70/30) blend. The E'' peak of PC for a blend containing 50% or more Nylon cannot be obtained, because of fluidity of the sample. Though measuring conditions for DSC and DMA were different, almost the same behavior was observed. The above results suggest that compatibility in the Nylon6-co-12 blends is better than that of the Nylon12 blends.

For checking interaction between PC and Nylon, FT-IR was used. The FT-IR spectra of PC/Nylon (30/70)

blends are shown in Figure 7. We focused on carbonyl group of PC to study the effects of Nylon on PC, as the carbonyl band is sensitive in specific interaction such as hydrogen bonding.²⁰ For neat PC, the peak of carbonyl group is observed at 1776 cm⁻¹. For each blend sample, the peak shifts slightly within experimental error range. Peaks for amide group show the almost same behavior (though abbreviated here). The specific interaction such as hydrogen bonding is not clearly observed in either blend.

SEM photographs of PC/Nylon blends are shown in Figure 8. The particles in the Nylon6-co-12 blend are smaller, compared with those of the Nylon12 blend. Average particle diameters (\bar{d}_n , \bar{d}_w) and polydispersity (\bar{d}_w/\bar{d}_n) are indicated in Table I. For PC/Nylon6-co-12 (30/70) blend, \bar{d}_w and polydispersity are 0.37 μm and 1.10, respectively. This means that the particle size was uniformly controlled to less than 0.5 μm . A microdomain structure in polymer blend has been observed in miscible

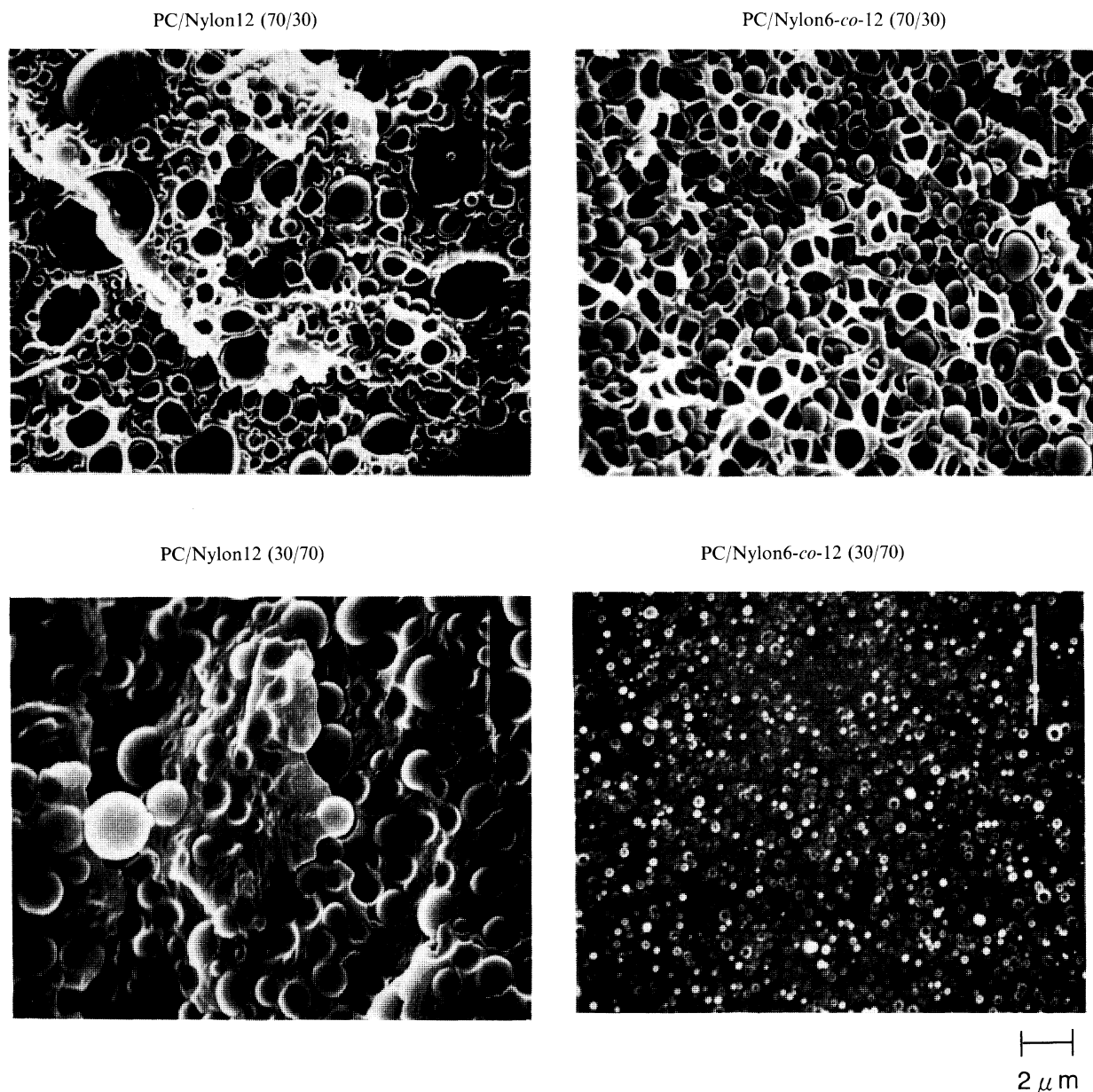


Figure 8. Scanning electron micrographs of PC/Nylon blends (230°C; shear rate, 500 s⁻¹).

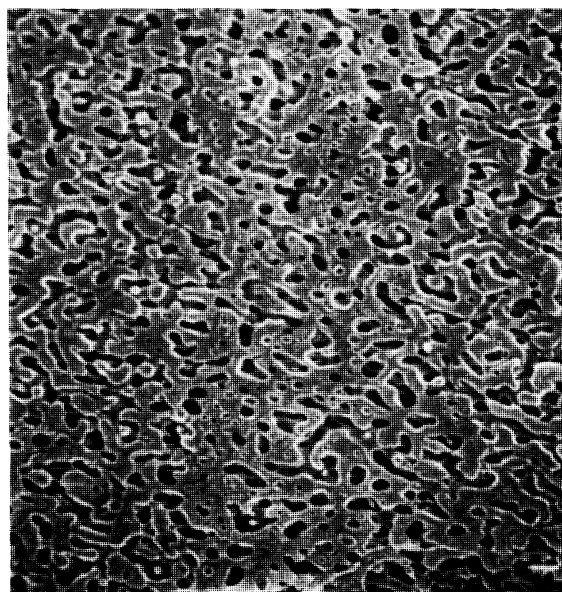
Table I. Average particle diameters and polydispersities in PC/Nylon blends

Sample	\bar{d}_n (μm)	\bar{d}_w (μm)	\bar{d}_w/\bar{d}_n
PC/Nylon6-co-12 (30/70)	0.34	0.37	1.10
PC/Nylon6-co-12 (70/30)	0.78	0.85	1.10
PC/Nylon12 (30/70)	1.28	1.46	1.14
PC/Nylon12 (70/30)	0.82	1.07	1.31

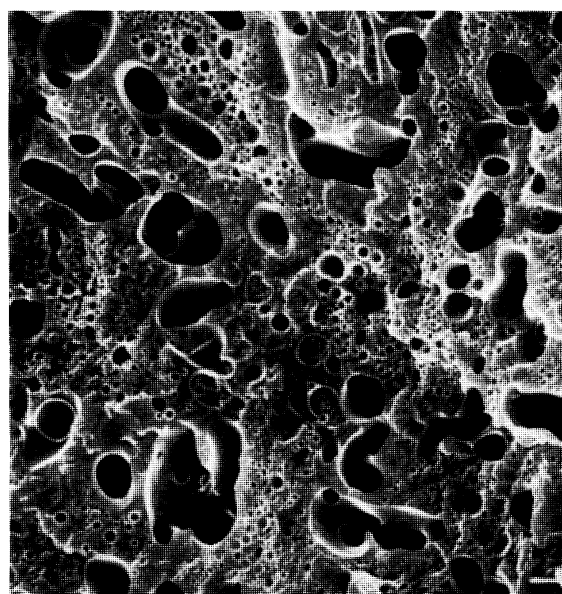
Table II. Calculated density and surface tension for polymers

Polymer	ρ (25°C) ^a	γ_s (25°C) ^b	ρ (240°C)	γ_s (240°C)
PC	1.2	40.0	1.1	28.0
Nylon12	0.99	40.5	0.87	24.2
Nylon6	1.08	51.0	0.96	31.8
Nylon6-co-12 _(64:36 mol%)	—	47.2	—	29.1

^a Density of glassy amorphous polymer (ref 30). ^b Calculated by the Parachor method.



(a)



(b)

—
10 μm

Figure 9. Scanning electron micrographs of PC/Nylon blends (230°C; shear rate, 500 s⁻¹, etched with chloroform). (a) PC/Nylon6-co-12 (50/50); (b) PC/Nylon12 (50/50)

blends in which phase separation occurs.²¹⁻²³

The morphologies for both PC/Nylon (50/50) blends are shown in Figure 9. Samples were etched with chloroform. The modulated structure was clearly found in Nylon6-co-12 blend, as shown in Figure 9(a). Both phases are interconnected with each other and uniform spacing is observed. The characteristics seem to be morphological features of spinodal decomposition, though it should be necessary to check with light scattering method. The characteristic length of modulated structure is *ca.* 3 μm . Recently, we reported that modulated structure is formed in PC/amorphous Nylon3Me6T blend.^{11,24} The formation of a modulated structure can be explained in terms of shear-induced miscibility. A region of homogeneous phase in phase diagram, expands under shear rate.²⁵⁻²⁹ The modulated structure with high interconnectivity, can be obtained, if a single phase is formed under high shear rate.^{25,28,29} In Nylon12 blend, isolated dispersion particles are observed, as shown in Figure 9(b). This indicates that PC and Nylon6-co-12 may become a homogeneous phase and then modulated structure is developed *via* spinodal decomposition when the shearing is stopped. However, PC and Nylon12 are incompatible at the same mixing conditions. The difference of compatibility of two Nylons with PC is confirmed by morphology observation.

Interfacial tension between PC and Nylons was calculated by the following equation:

$$\gamma(T) = \gamma(298)(\rho(T)/\rho(298))^4 \quad (3)$$

where $\gamma(T)$ and $\rho(T)$ are surface tension and density, respectively, at processing temperature, T . $\gamma(298)$ is calculated by the Parachor method. In general, real temperature in kneader during mixing become higher than setting temperature. Processing temperature is assumed as 240°C.

In eq 3, density at T is calculated by the following equation,

$$V_L(T) = V_g(298) + E_g(T_g - 298) + E_L(T - T_g) \quad (4)$$

where V_L and V_g are the molar volume at liquid state and glass states, respectively. E_g and E_L are molar thermal expansivity at glass state and at liquid state. Surface tension of Nylon6-co-12 is calculated by the following equation.

$$\gamma_{\text{Nylon6-co-12}} = x\gamma_{\text{Nylon6}} + (1-x)\gamma_{\text{Nylon12}} \quad (5)$$

where x is the mole fraction of Nylon6. The calculated densities and surface tensions for each polymer are indicated in Table II. If there is no specific interaction such as hydrogen bonding, the interfacial tension can be

calculated approximately with these equations.

$$\gamma_{12} \approx (\gamma_1^{1/2} - \gamma_2^{1/2})^2 \quad (6)$$

Using eq 6, $\gamma_{\text{PC/Nylon12}}$ and $\gamma_{\text{PC/Nylon6-co-12}}$ are calculated in 0.13 and 0.011 mJm⁻², respectively at 240°C. From the above calculation, it is predicted that the fine morphology in PC/Nylon6-co-12 blend may result from lower interfacial tension. As interfacial tension is a function of χ , low interfacial tension indicates small value of $\chi - \chi_c$. Therefore, PC and Nylon6-co-12 may be miscible under the high shear field and the modulated structure appears as phase separation when the shearing is stopped.

CONCLUSIONS

We investigated the morphology of PC/Nylon6-co-12 and PC/Nylon12 blends. In the Nylon6-co-12 blend, particles were smaller than those of the Nylon12 blend. Modulated structure was obtained in the middle concentration of PC/Nylon6-co-12 blend, while a particle/matrix type morphology was observed in the Nylon12 blend. The morphological behavior was explained with the approximate calculation of interfacial tension and the shear-induced miscibility. The above results suggest that the critical shear rate for a phase transition to a single phase for the Nylon6-co-12 blend may be lower than that of the Nylon12 blend. From DSC and DMA, the shift of T_g of Nylon was observed in the Nylon6-co-12 blends, whereas in the Nylon12 blend, no shift was observed. Specific interaction was not observed in FT-IR spectra in both blends.

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