

Miscibility in Binary Blends of Aromatic and Alicyclic Polyamides

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Received 22 December 2004; accepted 26 April 2005

DOI 10.1002/app.22912

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Miscibility was studied for four polyamide blends of 6I/6T [copolymer consisting of 1,6-hexamethylene diamine and isophthalic acid (6I) (70 wt %) and terephthalic acid (6T) (30 wt %)] with MXD6 (polyamide of *m*-xylenediamine and adipic acid), BAC6 (polyamide of 1,3-bis(aminomethyl)cyclohexane and adipic acid), TR55 (copolymer consisting of nylon 11 (30 wt %), and polyamide of bis(3-methyl, 4-aminocyclohexyl)methane (30 wt %) and isophthalic acid (70 wt %), and CX7323 (polyamide of bis(4-aminocyclohexyl)methane and dodecanedicarboxylic acid), using differential scanning calorimetry, X-ray diffraction method, and electronmicroscopic observation. In quenched MXD6/(6I/

6T) and BAC6/(6I/6T) blends, MXD6 and BAC6 components were miscible to 6I/6T, but TR55 and CX7323 components were completely phase-separated from 6I/6T. Interestingly on electronmicroscopic observations, TR55 and CX7323 components were seen as droplets in 6I/6T medium when the content is low, but when 50 wt %, a layered structure was constructed with 6I/6T, reminiscent of morphological structure in block copolymer. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 3971–3978, 2006

Key words: polyamides; miscibility; blends; DSC; electron microscopy

INTRODUCTION

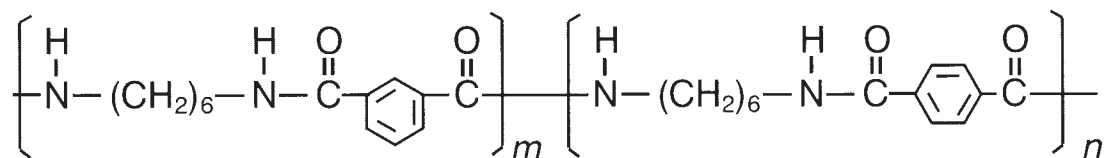
Polyamide blends are important and conventional plastics, and so the miscibility has been extensively studied to expand application as industrial plastic materials.^{1–7} Mean field interaction and solubility parameter models have explained miscibility in polyamides from chemical structure,^{1–4} but more experimental results need to understand miscibility. Transamidation between two polyamides frequently produced uniform polyamides.^{8–11} As well known, odd nylons such as nylon 7 and 17, having odd number carbon atoms between successive amide groups, show ferroelectricity in the crystalline phase,^{12–15} but noticeably it was reported by Murata, Tsunashima, and Koizumi^{16–18} that ferroelectricity generates even in amorphous phase for aromatic or alicyclic polyamides. A kind of Curie temperature (T_p), at which remanent polarization disappeared, coincided with the glass transition (T_g). Very recently, we communicated¹⁹ that amorphous MXD6/(6I/6T) polyamide blends are ferroelectric, where 6I/6T is polyamide copolymer consisting of 1,6-hexamethylene diamine and isophthalic acid

(6I) (70 wt %) and terephthalic acid (6T) (30 wt %) and MXD6 is polyamide of *m*-xylenediamine and adipic acid, whose chemical structures are depicted in Figure 1. The values of T_p for 100% 6I/6T and 100% MXD6 nylon were fairly well consistent with glass transition temperatures (T_g), 125 and 85°C, respectively, consistent with the results by Murata et al. In the MXD6/(6I/6T) blends, the two components are miscible to each other, indicating only one T_g , and change of T_g with MXD6 content obeyed Gordon-Taylor equation with $k = 3.64$, but T_p decreased straightforwardly to MXD6 content, being higher than T_g . These results encouraged us to investigate miscibility of aromatic or alicyclic polyamide blends. In this article, we report miscibility for four binary blends of 6I/6T with aromatic and alicyclic polyamides, MXD6, polyamide of 1,3-bis(aminomethyl)cyclohexane and 1,6-hexamethylene dicarboxylic acid (BAC6), copolymer consisting of nylon 11(30 wt %) and polyamide of bis(3-methyl, 4-aminocyclohexyl)methane and isophthalic acid (70 wt %) (TR55) and polyamide of bis(4-aminocyclohexyl)methane, and dodecanedicarboxylic acid (CX7323). The chemical structures are listed in Figure 1.

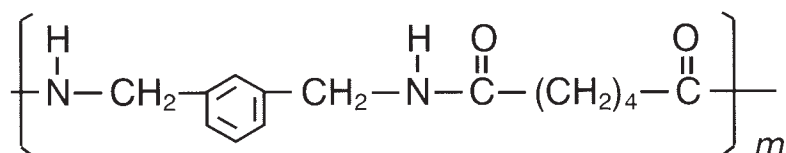
Correspondence to: M. Endo (endo@nirs.go.jp, masahiro@kai-group.com).

EXPERIMENTAL

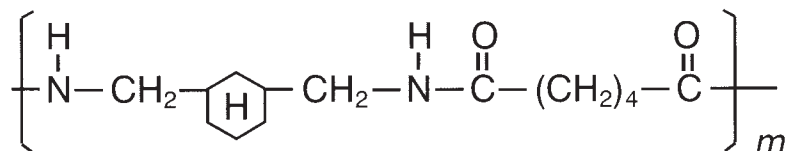
6I/6T(70/30) is Sealer PA3426 of Mitsui Du-Pont Polychemicals (Tokyo) whose melt flow index (MI) is 3.5



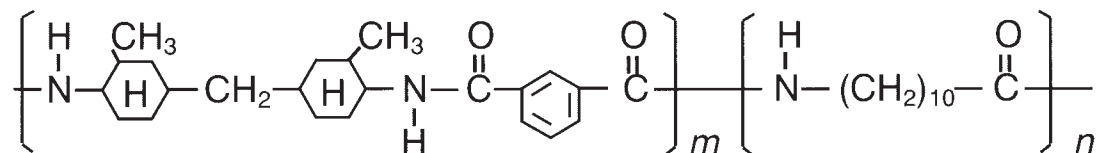
6I/6T (70/30)



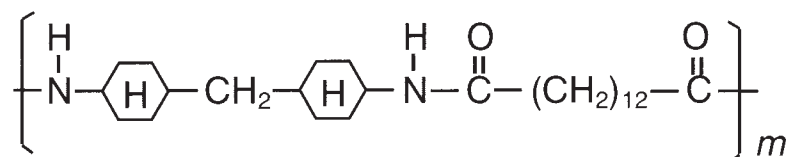
MXD6



BAC6



TR55



CX7323

Figure 1 Chemical structures of polyamides used here. 6I/6T (70/30): polyamide copolymer consist of hexamethylene diamine and isophthalic acid (6I) (70 wt %) and terephthalic acid (6T) (30 wt %). MXD6: polyamide of *m*-xylenediamine and adipic acid. BAC6: polyamide of 1,3-bis(aminomethyl)cyclohexane and adipic acid. TR55: copolymer consisting of nylon11 (30 wt %) and polyamide of bis(3-methyl, 4-amino cyclohexyl)methane and isophthalic acid (70 wt %). CX7323: polyamide of bis(4-aminocyclohexyl)methane and dodecanedicarboxylic acid.

under 2160 g load at 230°C. MXD6 is MX Nylon 6001 from Mitsubishi Gas Chemical (Tokyo). The number average molecular weight (M_n) obtained by an end group method was 15,000–18,000 and the weight-average molecular weight (M_w) obtained by gel permeation chromatography was 50,000–60,000. The MI is 7 at 230°C under 2160 g and the relative viscosity in

0.5% H_2SO_4 was 2.1 at room temperature. BAC6 is a test sample from Mitsubishi Gas Chemical (Tokyo). TR55 is transparent Nylon 12 of EMS Chemie. (Germany) while CX7323 is PACM12 of Daicel Degussa (Japan) whose MI at 270°C under 2160 g and relative viscosity in 0.5% *m*-cresol are 7.6 and 1.85, respectively. Binary blends of 6I/6T with MXD6, BAC6,

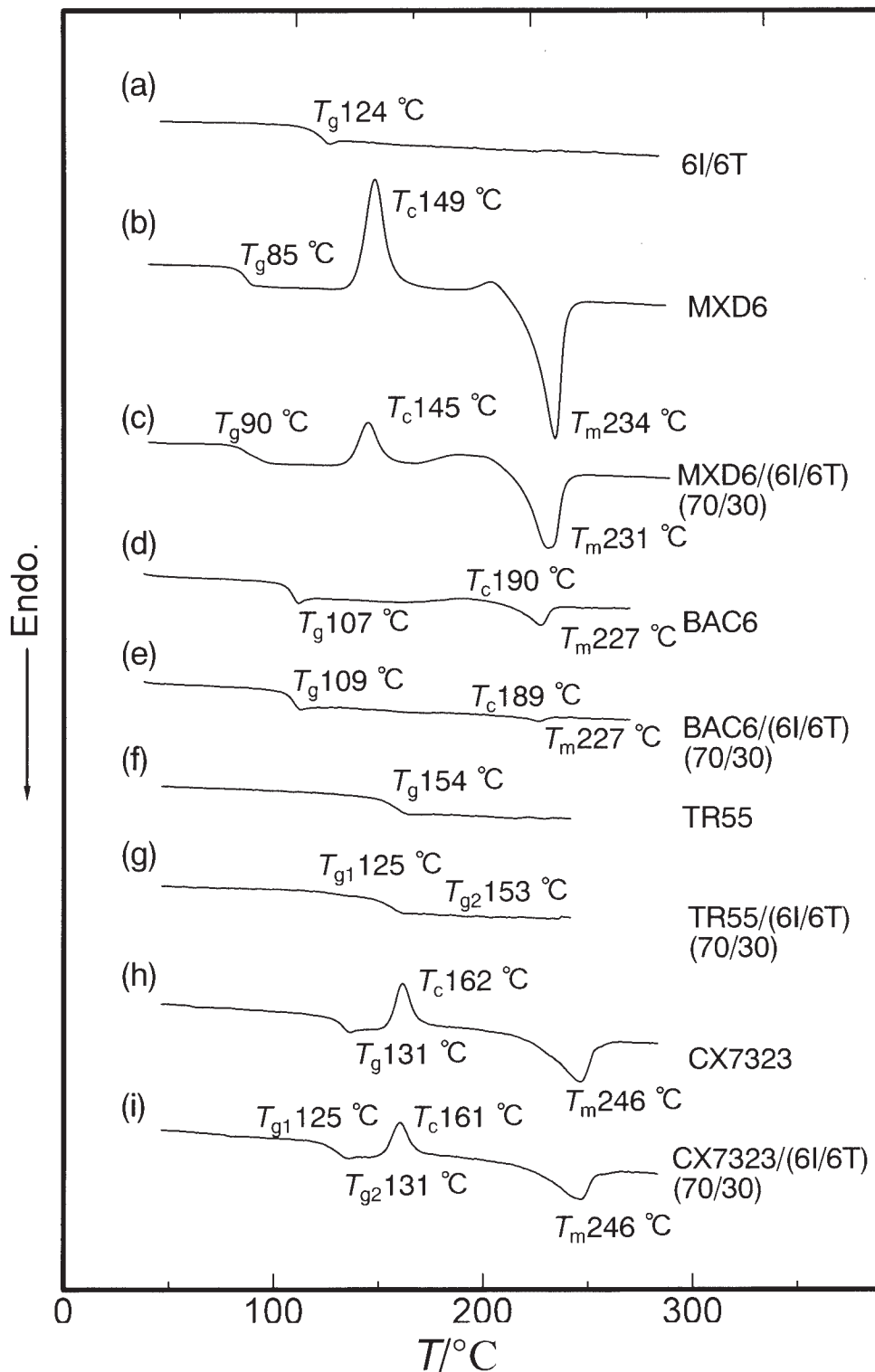


Figure 2 DSC curves for quenched polyamides at the second heating.

TR55, and CX7323 were prepared by using a melt extrusion method: Two components were blended at 280°C in a conventional extruder thoroughly, until the mechanical torque of melt reaches a constant value. Then, the melt was quenched to room temperature on

a chilled drum equipped with the extruder to make the long sheet of about 0.5 mm thick and about 1 m width.

Thermal measurements were performed at a heating/cooling rate of 10°C min⁻¹ by use of a Seiko SSC

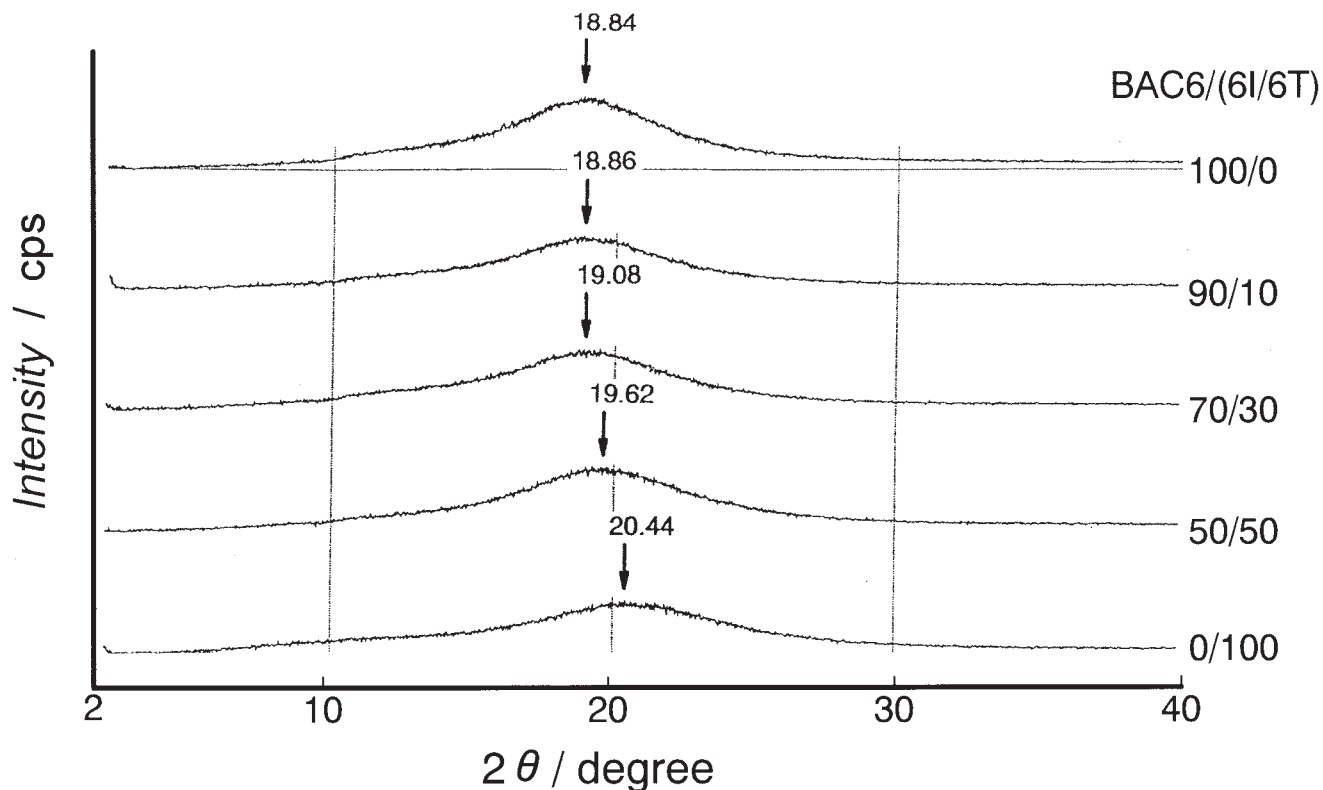


Figure 3 Wide angle X-ray diffraction patterns at room temperature for the quenched BAC6/(6I/6T) blends as a typical example.

5000 differential scanning calorimeter (DSC). Phase transition temperature and enthalpy change were calibrated using In and Sn standards. Electron micrographs were taken at room temperature using an electron microscope (Nihon Denshi, type JSM-6300).

Sheets were cracked after immersing in liquid nitrogen and the cracked section was coated with Pt by use of a sputtering method, and then micrographs were taken for Pt-coated surface at room temperature. X-ray diffraction patterns were recorded with a reflection

TABLE I
Phase Transition Parameters at the Second Heating of Polyamide Blends

Blends	Blend ratio	T_{g1} (°C)	T_{g2} (°C)	T_c (°C)/ ΔH_c^a (J g ⁻¹)	T_m (°C)/ ΔH_m^a (J g ⁻¹)
MXD6/(6I/6T)	100/0	85		149/-41	234/59
	70/30	90		145/-15	231/41
	50/50	94		148/-2	231/2
	30/70	101		147/-1	230/1
	0/100	124		-	-
BCA6/(6I/6T)	100/0	107		190/-6	227/6
	90/10	108		198/-2	227/2
	70/30	109		189/-1	227/1
	50/50	112		197/-0.2	228/0.5
TR55/(6I/6T)	100/0	-	154		
	90/10	124	154		
	70/30	125	153		
	50/50	124	153		
CX7323/(6I/6T)	100/0	-	131	162/-17	246/26
	90/10	126	131	160/-16	246/27
	70/30	125	131	161/-13	246/22
	50/50	125	133	163/-8	246/13

^a Enthalpy change of crystallization.

^b Melting enthalpy change.

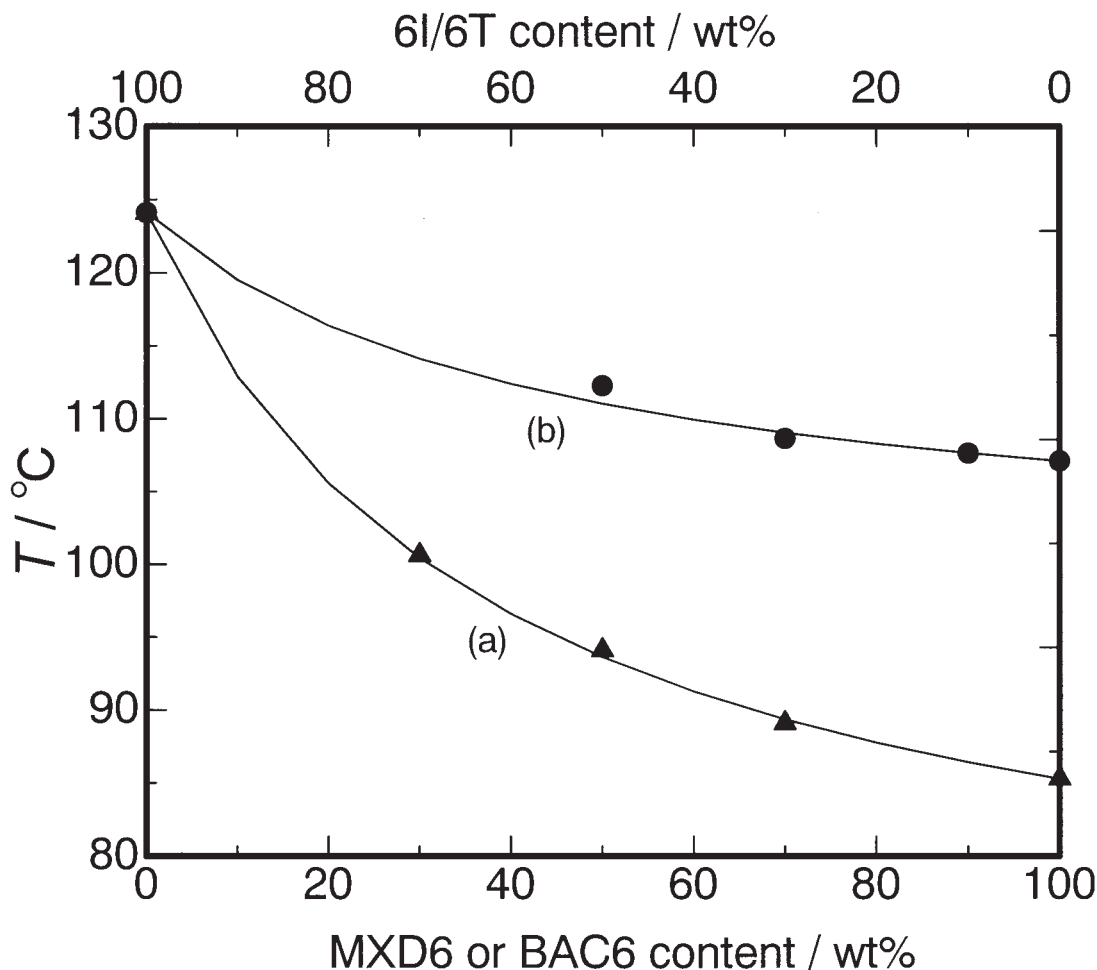


Figure 4 Plots of glass transition temperature, T_g , versus MXD6 content for MXD6/(6I/6T) blends (▲) and BAC6 content for BAC6/(6I/6T) blends (●). Solid line: Gordon-Taylor equation of $k = 3.64$ for (a) and 3.32 for (b).

method, using X-ray diffractometer (Rigaku Denki RINTO 2100-Ultima⁺) with monochromatic Cu-K α radiation (40 kV, 30 mA). Scattering intensities were measured by a scintillation counter as a function of scattering angle (2θ), where divergence and scattering slits of 1° and receiving slit of 15 mm were used. The densities at 25°C for polyamides were measured with a buoyancy method using *n*-hexane as a solvent.

RESULTS AND DISCUSSION

Figure 2 shows DSC curves at second heating for quenched binary polyamide blends (The quenched blends already undergo first heating and cooling processes, when they were prepared by a melt extruder method as mentioned in Experimental section.). In quenched 100% 6I/6T (a) and 100% TR55 (f) polyamides, there is only one abrupt change near 124 and 154°C , respectively, which is related to a glass transition. DSC curves for quenched 100% MXD6 (b), BAC6 (d), and CX7323 (h) show T_g changes near 85 , 107 , and 131°C , respectively, exothermic peaks near 149 , 190 ,

and 162°C due to crystallization, respectively, and endothermic peaks near 234 , 227 , and 246°C due to melting of crystallites, respectively. In second cooling after the second heating, an exothermic peak was seen near 174°C for 100% MXD6 and 185°C for 100% CX7323, but not for 100% BAC6 because of too small peak. Glass transition change was observed for all polyamides as well as that in the second heating. In third heating after the second cooling, both glass transition changes and melting peaks were seen, but no crystallization peaks appeared so far. These data show that 100% 6I/6T and 100% TR55 are amorphous, and that 100% MXD6, BAC6, and CX7323 are amorphous by quenching, but substantially semicrystalline. In the second heating DSC curve for four binary blends of 6I/6T (30 wt %) with polyamide (70 wt %), one glass transition is seen at 90°C for MXD6/(6I/6T) (c) and at 109°C for BAC6/(6I/6T) (e), but two glass transitions take place at 125 and 153°C for TR55/(6I/6T) (g) and at 125 and 131°C for CX7323/(6I/6T) (i). These data indicates that MXD6 and BAC6 are miscible to 6I/6T, but TR55 and CX7323 are immiscible.

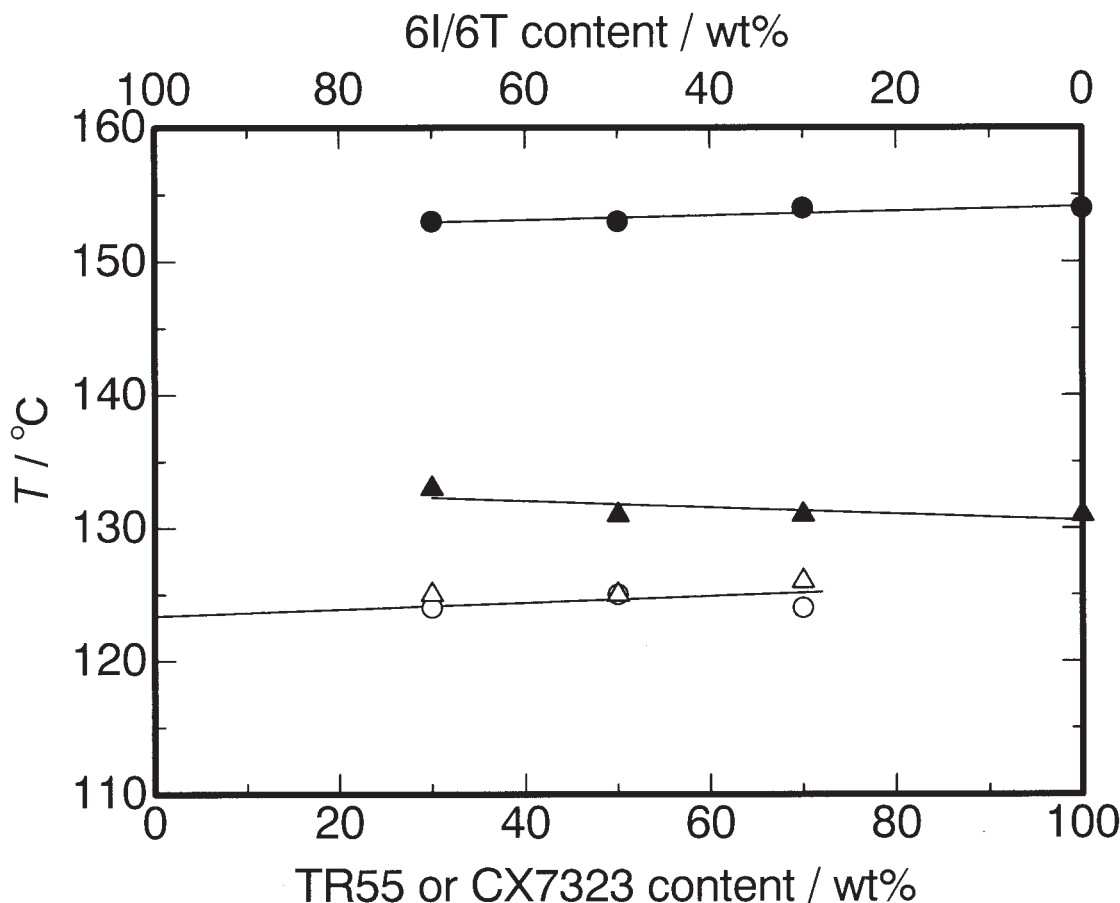


Figure 5 Plots of glass transition temperatures, T_{g1} and T_{g2} , versus TR55 content for TR55/(6I/6T) blends (T_{g1} : \circ , T_{g2} : \bullet) and CX7323 content for CX7323/(6I/6T) blends (T_{g1} : \triangle , T_{g2} : \blacktriangle).

Figure 3 shows wide angle X-ray diffraction patterns at room temperature for the quenched BAC6/(6I/6T) blends as a typical example. The patterns show only amorphous halo about 19° of scattering (2θ), regardless of the blending ratio, and this was also seen for all the blends used here. Therefore, all quenched blends used here are amorphous at room temperature.

The phase transition parameters for all the blends are listed in Table I. In the MXD6 and CX7323/(6I/6T) blends, enthalpy change of crystallization (ΔH_c) is smaller than melting enthalpy change (ΔH_m), and this may result from an endothermic peak between T_c and T_m (see Fig. 2); when enthalpy change for the peak is added to ΔH_c , the data was almost equal to ΔH_m . ΔH_c and ΔH_m are smaller as 6I/6T content increases; when MXD6, BAC6, and CX7323 components crystallize from the amorphous 6I/6T solvent, the crystallizations are understood to be disturbed by 6I/6T.

Figure 4 shows plots of T_g versus MXD6 content for MXD6/(6I/6T) blend and BAC6 content for BAC6/(6I/6T) blend. Both plots obey the Gordon-Taylor equation, $T_g = (w_a T_{ga} + k w_b T_{gb}) / (w_a + k w_b)$, with $k = 3.64$ for MXD6/(6I/6T) blends and $k = 3.32$ for BAC6/(6I/6T)

blends, where w_a and w_b are weight fractions of MXD6 or BAC6 and 6I/6T, respectively, and T_{ga} and T_{gb} are glass transition temperatures of MXD6 or BAC6 and 6I/6T, respectively. Both blends show one T_g , regardless of blending ratio, and T_g decreases as MXD6 or BAC6 content increases, obeying the Gordon-Taylor equation. This indicates that the two components [MXD6 and 6I/6T in MXD6/(6I/6T) blend, and BAC6 and 6I/6T in BAC6/(6I/6T) blend] are miscible to each other over all blending ratio.

Two glass transitions (T_{g1} and T_{g2}) were seen for TR55 and CX7323/(6I/6T) blends as already described. In Figure 5, T_{g1} and T_{g2} are plotted for TR55 and CX7323 contents. Clearly, both blends show two distinct T_g s, T_{g1} and T_{g2} , corresponding to T_g for 100% 6I/6T and that for 100% TR55 or 100% CX7323, respectively. The values of T_{g1} and T_{g2} scarcely change with the blending ratio, and this suggests that TR55 or CX7323 component is distinctly phase-separated from 6I/6T region. Solubility parameter (δ) by the Hoy method²⁰ are listed in Table II. The δ -values lay about $11 \text{ (J cm}^{-3}\text{)}^{1/2}$ at 25°C for 6I/6T, MXD6, and BAC6, and 8.5 for TR55 and CX7323, which qualitatively explain the miscibilities for present blends.

TABLE II
Lists of Solubility Parameters (δ) for Polyamides used Here

Polyamide	Density (g mL^{-1}) at 25°C	δ (J cm^{-3}) ^{1/2} at 25°C
6I/6T	1.1848	11.3
MXD6	1.1959	11.4
BAC6	1.1189	10.7
TR55	0.9213	8.51
CX7323	0.9170	8.52

Figure 6 shows electron micrographs at room temperature for TR55/(6I/6T) and CX7323/(6I/6T) blends. In CX7323/(6I/6T) blends, Figure 6(a) for 90% CX7323 shows the presence of 6I/6T droplets in

CX7323 medium and the droplets increased in number and size, as CX7323 content increases. When CX7323 content is 50% (Fig. 6(b)), the texture shows layered structure in which two CX7323 and 6I/6T layers are stacked. Images for TR55/(6I/6T) blends resemble with those of CX7323. The 6I/6T droplets are separated from TR55 medium when TR55 content is 90 wt % (Fig. 6(c)). When TR55 content is 50%, both droplets and layered stacking are observed (Fig. 6(d)). These images evidently show that the two components for each blend are completely phase separated in both blends. The morphological change of separated textures with blending ratio is interesting, reminiscent of a morphological change by blending ratio in the phase separation of block copolymers.^{21–23}

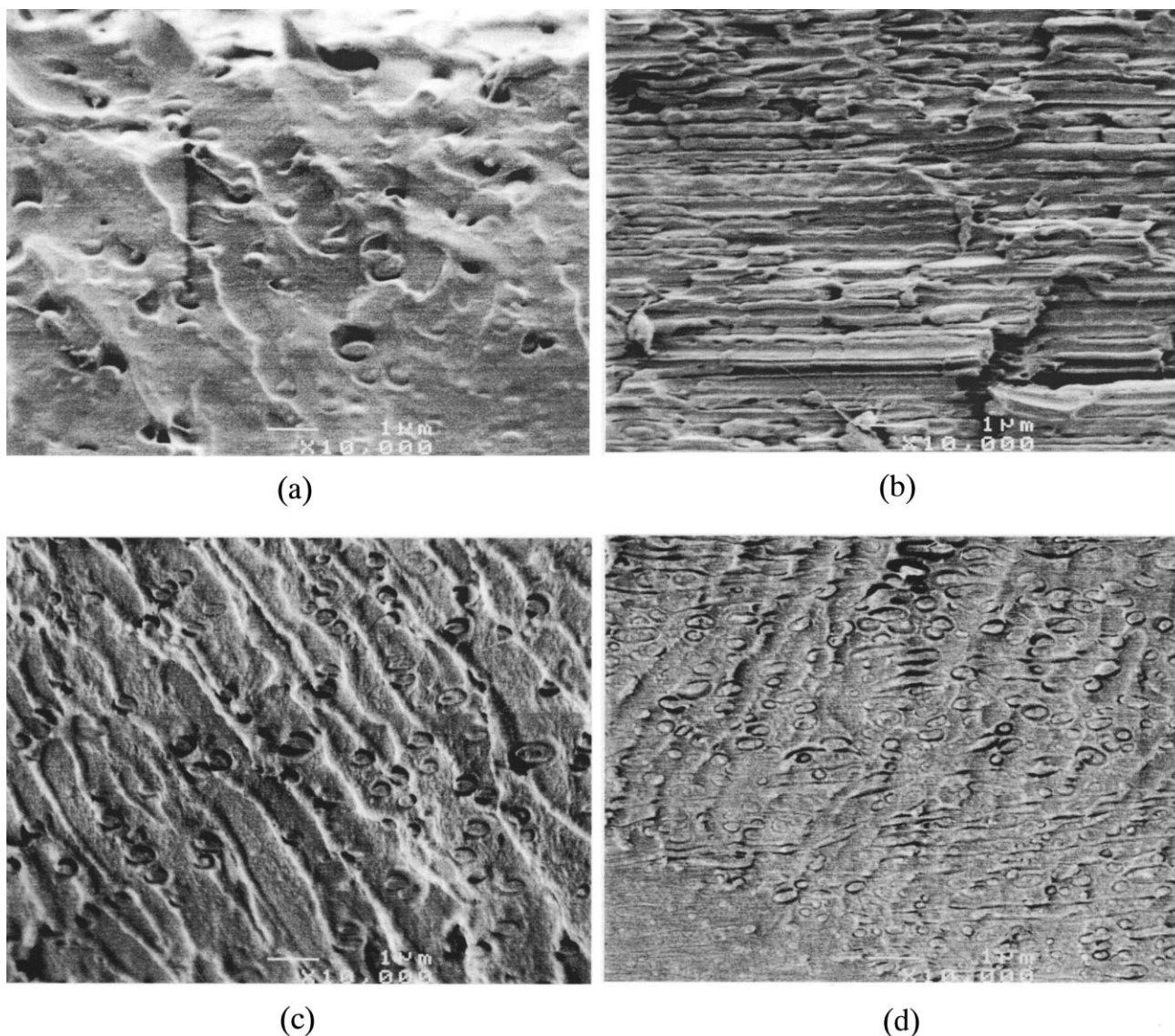


Figure 6 Electron micrographs for (a) CX7323/(6I/6T) (90/10), (b) CX7323/(6I/6T) (50/50), (c) TR55/(6I/6T) (90/10), and (d) TR55/(6I/6T) (50/50) blends.

CONCLUSIONS

Miscibility for four binary blends of 6I/6T polyamide with MXD6, BAC6, TR55, and CX7323 polyamides was studied using DSC and electron microscopy. In MXD6/(6I/6T) and BAC6/(6I/6T) blends, MXD6 and BAC6 were miscible to 6I/6T over all blending ratios, but in TR55/(6I/6T) and CX7323/(6I/6T) blends, TR55 and CX7323 were immiscible to 6I/6T. On electron micrographs, microdomain structures in phase separation were observed for immiscible TR55 and CX7323/(6I/6T) blends. When 6I/6T content is low, 6I/6T component is phase-separated from TR55 or CX7323 medium to make droplets, but when 50%, a layered structure was observed, reminiscent of microdomain structure in block copolymer.

Now it is an opened problem to study how the ferroelectricity in various amorphous polyamides, which are mentioned in Introduction section, changes in polyamide blends. Ferroelectric studies for polyamide blends are progressing in our laboratories and the results will be published elsewhere.

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