

Thermal and Mechanical Properties of Poly(trimethylene terephthalate) (PTT)/Cationic Dyeable Poly(trimethylene terephthalate) (CD-PTT) Polyblended Fibers

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ABSTRACT: Poly(trimethylene terephthalate) (PTT) and cationic dyeable poly(trimethylene terephthalate) (CD-PTT) were extruded (in the proportions of 80:20, 60:40, 40:60, and 20:80) from one melt twin-screw extruder to prepare four PTT/CD-PTT polyblended fibers. The molar ratio of 5-sodium sulfonate dimethyl isophthalate (5-SSDMI) for CD-PTT polymer was 2%. This study investigated the thermal and mechanical properties of PTT/CD-PTT polyblended fibers using gel permeation chromatograph, differential scanning calorimetry (DSC), thermogravimetric analysis, potentiometer, a rheometer, the density gradient, wide-angle X-ray diffraction, extension stress-strain measurement, and scanning electron microscope (SEM). Melting behavior of PTT/CD-PTT polyblended polymers exhibited positive-deviation blends, and the blend of PTT/CD-PTT between 60:40 and 40:60 showed a maximum value of the melt viscosity. Experimental results from the DSC indicated that PTT and CD-PTT molecules formed a miscible system. The tenacity of

PTT/CD-PTT polyblended fibers declined as the 5-SSDMI content increased. Crystallinities and densities of PTT/CD-PTT polyblended fibers were also found decrease as the 5-SSDMI content increased. The surface of PTT/CD-PTT polyblended fibers exhibited a uniform morphology, from the SEM observation. It indicated that PTT and CD-PTT polymers were identified to be a miscible system. Though there is a good interfacial adhesion between PTT and CD-PTT polymer, the mechanical properties of PTT/CD-PTT polyblended fibers were largely affected by the 5-SSDMI content. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1008–1013, 2006

Key words: poly(trimethylene terephthalate) (PTT); polyblended fiber; positive-deviation blends (PDBs); morphology; cationic dyeable poly(trimethylene terephthalate) (CD-PTT)

INTRODUCTION

The applications of polyblends are important developments of the plastics and synthetic fiber industries. Polyblends are mixtures of two or more polymers that can either mix completely on a molecular scale or form a two-phase structure. Polyblends can exhibit new combinations of properties that depend on the properties of the components and strongly upon the morphology of the blended materials. The morphology resulting from a blending process depends mainly upon the rheological and interfacial properties of the molten components, the blending conditions, and the weight ratio of the polymers blended.^{1–3} Polyblends can be characterized by their phase behavior as being either miscible or immiscible. The thermal, mechanical, and rheological properties of a polyblend depend strongly on its state of miscibility.⁴

Poly(trimethylene terephthalate) (PTT) is a newly commercialized polyester. With a unique combination

of properties, PTT is a particularly suited for use in textile and carpet fiber application.^{5,6} PTT fibers have the resiliency and softness of nylon fibers and the chemical stability and stain resistance of poly(ethylene terephthalate) (PET) fibers. They will undoubtedly become an important new family of fibers. Fiber-grade PTT resins are being marketed by Shell Chemical Company and DuPont under the trade names of Corterra and Sorona, respectively. Several studies have reported the structure and properties of PTT.^{7–10} There are also some reports on the physical properties of PTT with other polymers such as PET,¹¹ poly(butylene terephthalate),¹² poly(ethylene naphthalate),¹³ and clay.¹⁴ Up to now, there was not any reported in the literature for the polyblended fiber of PTT with cationic dyeable poly(trimethylene terephthalate) (CD-PTT).

PTT polymer does not possess ionic groups. Furthermore, CD-PTT polymer possesses 5-sodium sulfonate dimethyl isophthalate (5-SSDMI; $-\text{SO}_3\text{Na}$ groups). The interfacial adhesion plays a critical role for PTT/CD-PTT polyblended fibers. This study thoroughly investigated the melting behavior, thermal properties, crystallinity, tenacity, density, and morphology of PTT/CD-PTT polyblended fibers.

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TABLE I
Characteristics of PTT and CD-PTT Chips

	Chip	
	PTT	CD-PTT
IV (dL/g) ^a	0.88	0.76
5-SSDMI ^b	—	2
\bar{M}_w (g/mol)	34,000	23,000
\bar{M}_w/\bar{M}_n^c	1.92	1.91
R-COOH (meq/kg)	18	20
T_m (°C)	229.1	225.3
T_d (°C) ^d	358	351

^a IVs of polymer was obtained using a mixed solution of 0.5 g/100 mL in phenol/tetrachloroethane (60:40; w/w) at 30°C.

^b Data was obtained from NMR measurement.

^c MWD of polymer. MWDs of PTT and CD-PTT polymers were measured in HFIP (1,1,1,3,3,3 hexafluoro-2-propanol) solvent system.

^d Degradation temperature of polymer.

EXPERIMENTS

Materials and polyblended spinning

PTT chips were supplied by Shinkong Synthetic Fibers Corp. (Taoyuan, Taiwan). Its intrinsic viscosity (IV) is 0.88 dL/g. CD-PTT chips were obtained from the Union Chemical Laboratories/Industrial Technology Research Institute (UCL/ITRI, Taiwan, Hsinchu). The CD-PTT polymer, a white pellet with an average diameter size of 3–5 mm, is specially designed for the fiber spinning process. Its IV is 0.76 dL/g. Table I lists the synthetic characteristics of PTT and CD-PTT chips. Prior to blending, PTT and CD-PTT were dried for 4 h at 120°C and 8 h at 160°C. PTT and CD-PTT were extruded (in the proportions of 80:20, 60:40, 40:60, and 20:80) from one melt twin-screw extruder to prepare four PTT/CD-PTT polyblended polymers. The extruder conditions were as follows: screw diameter (30 mm), L/D (36.8), blending temperature (265°C), blending time (4.5 min), and screw speed (60 rpm). Melt spinning was carried out using a capillary rheometer. Undrawn yarns (UDYs) were extruded at 265°C, and at a constant wind speed of 500 m/min was used for all samples. Then, UDYs were drawn thrice to produce full drawn yarns (FDYs), by a drawn-winder machine. The draw temperature and take-up speed were 120°C and 300 m/min, respectively. The specification of FDYs is 30D/10F (3 dpf). Table II shows the compositions of the PTT/CD-PTT polyblended fibers. Scanning electron microscope (SEM), Cambridge Stereoscan-600, was used to examine the surface morphology of sample, which was sputter-coated with Au to prevent oxidation.

Measurements

Gel permeation chromatograph data were obtained from a Waters Model 510 Type. MWDs of PTT and

CD-PTT polymers were measured in HFIP (1,1,1,3,3,3 hexafluoro-2-propanol) solvent system. IVs of PTT and CD-PTT polymer were obtained by a mixed solution of 0.5 g/100 mL in phenol/tetrachloroethane (60:40) at 30°C.¹⁵ Wide-angle X-ray diffraction (WAXD) studies of samples were conducted using a MAC Science X-ray unit operated at 35 kV and 30 mA. X-ray diffraction was then performed, with Cu K α radiation and scan from 10° to 40° (2 θ) with a scan speed of 4°/min.^{16–18} Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements of the samples were made using a Perkin-Elmer Pyrix-1. The heating rate for TGA measurement was 10°C/min from 30 to 600°C. Both the heating rate and cooling rate were 10°C/min from 30 to 300°C, and the temperature was held for 3 min at 300°C for DSC measurement. The crystallinity by the DSC method was calculated from the following equation: crystallinity (%) = $\Delta H_m/\Delta H_m^0 \times 100$ (%), where ΔH_m and ΔH_m^0 are the heat of fusion (J/g) of repeating unit for the sample and 100% crystallinity, respectively. ΔH_m^0 of pure PTT is equal to 145.6 J/g.¹⁹ The densities of samples were determined using the density gradient method. A mixture of *n*-heptane and carbon tetrachloride was used for the purpose. Densities of *n*-heptane and carbon tetrachloride solvents were 0.684 and 1.595 g/cm³, respectively. The scale of density gradient method was prepared from 1.200 to 1.500 g/cm³. The melt viscosities of samples were measured by a capillary rheometer, and the length-to-diameter ratio of the capillary is 30. The observations of SEM pictures were performed from a JEOL-200CX Type. All stress–strain data of samples were obtained on a Zwick 1511 type Instron instrument at an extension rate of 200 mm/min.

RESULTS AND DISCUSSION

Melting behavior of polyblended polymers

Figures 1 and 2 present capillary flow data at temperatures and shear rates applicable to the spinning process. Figure 1 shows the melt viscosities of PTT and CD-PTT polymers at 260°C versus shear rate. From 1000 to 20,000 s⁻¹, two polymers exhibited pseudo-

TABLE II
Compositions of the PTT/CD-PTT Polyblended Fibers

Polymer code	PTT/CD-PTT blend ratio	5-SSDMI content (mol%)
Sample 1	100:0	0
Sample 2	80:20	0.4
Sample 3	60:40	0.8
Sample 4	40:60	1.2
Sample 5	20:80	1.6
Sample 6	0:100	2.0

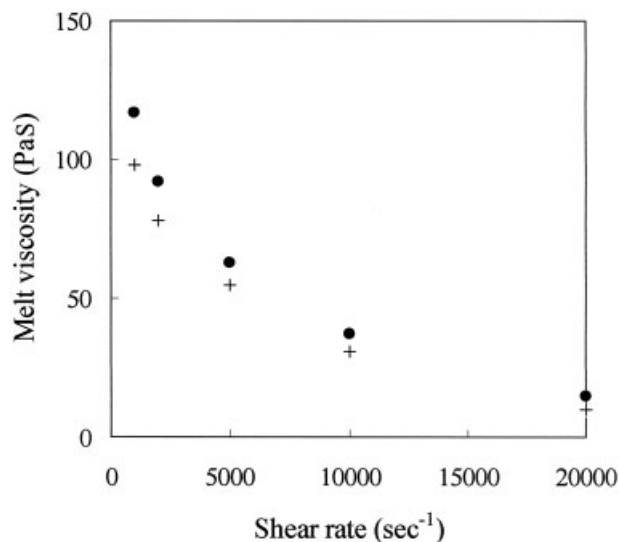


Figure 1 Relation between the melt viscosities and shear rate at 260°C of PTT and CD-PTT polymers: (●) PTT/CD-PTT (100:0), (+) PTT/CD-PTT (0:100).

plastic flow behavior. The rheological curves indicated the melt viscosity of the PTT polymer was higher than that of the CD-PTT polymer over the entire shear rate range. Figure 2 displays the melt viscosities of PTT/CD-PTT polyblended polymers at 260°C versus shear rate. The melt viscosities of PTT/CD-PTT polyblended polymers also exhibited pseudoplastic flow behavior. This trend was independent of the blend ratio. Figure 3 shows the melt viscosities of PTT/CD-PTT polyblended polymers exhibited positive-deviation blends (PDBs).^{20–24} Notably, the 60:40–40:60 blend of PTT/CD-PTT showed a maximum melt viscosity value at

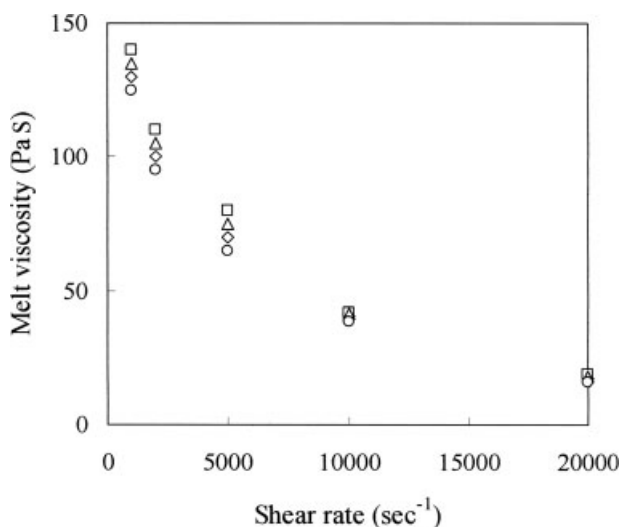


Figure 2 Relation between the melt viscosities and shear rate at 260°C of PTT/CD-PTT polyblended polymers: (◇) PTT/CD-PTT (80:20), (□) PTT/CD-PTT (60:40), (△) PTT/CD-PTT (40:60), (○) PTT/CD-PTT (20:80).

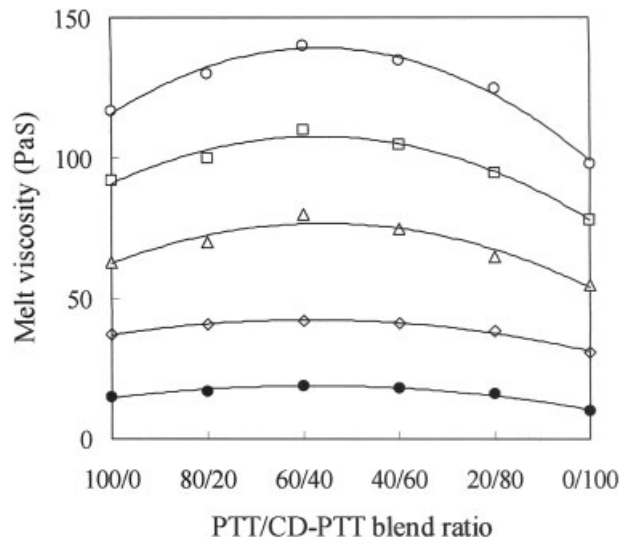


Figure 3 Relation between the melt viscosities and blend ratio at 260°C of PTT/CD-PTT polyblended polymers: (○) 1000 s⁻¹, (□) 2000 s⁻¹, (△) 5000 s⁻¹, (◇) 10,000 s⁻¹, (●) 20,000 s⁻¹.

260°C than that predicted by the additivity rule. The rheological results indicated a good interfacial adhesion between the PTT and CD-PTT polymers. The melt viscosities of PTT, CD-PTT, and their blends followed the order PTT/CD-PTT (60:40) > PTT/CD-PTT (40:60) > PTT/CD-PTT (80:20) > PTT/CD-PTT (20:80) > PTT > CD-PTT.

Thermal behavior of polyblended fibers

Table III displays the thermal properties of PTT, CD-PTT, and four PTT/CD-PTT polyblended fibers. In the DSC heating process, the endothermic peaks of the PTT and CD-PTT fibers occurred at 232.5 and 227.3°C, respectively. The endothermic peak (T_m) is due to the melting of the sample. The T_m of the PTT or CD-PTT fiber was compared with that of the PTT or CD-PTT chip (see Tables I and III). Because of the influences of the orientation and crystallization, the T_m of the PTT or CD-PTT fiber was clearly higher than that of the PTT or CD-PTT chip. The T_m of the PTT fiber was slightly higher (5.2°C) than that of the CD-PTT. DSC data displayed a clear melting endothermic peak, indicating that the PTT and CD-PTT fibers were originally crystalline. For all PTT/CD-PTT polyblended fibers, the DSC data also displayed obviously melting endothermic peaks, indicating that PTT/CD-PTT polyblended fibers were also crystalline materials and the T_m of all the samples was between 228 and 232°C. Meanwhile, the T_m of the PTT/CD-PTT polyblended fibers decreased as the 5-SSDMI content increased. In addition, the glass transition temperature (T_g) is related to the initiation of the micro-Brownian motion of the amorphous chains and it is, for all samples, be-

TABLE III
Thermal Properties of PTT, CD-PTT, and PTT/CD-PTT Polyblended Fibers

Polymer code	Heating process			Cooling process		
	T_g (°C)	T_m (°C)	ΔH_m (J/g)	T_{cc} (°C)	ΔH_{cc} (J/g)	Half-time (s)
Sample 1	53.6	232.5	56.1	184.7	53.6	83.8
Sample 2	53.2	231.5	53.7	181.1	52.0	84.9
Sample 3	52.7	230.4	52.6	177.4	50.3	86.1
Sample 4	52.3	229.4	50.2	173.8	48.7	87.2
Sample 5	51.8	228.3	48.9	170.1	47.0	88.4
Sample 6	51.4	227.3	47.5	166.5	45.4	89.5

tween 51 and 54°C. Clearly, the T_g of the PTT/CD-PTT polyblended fibers also declined as the 5-SSDMI content increased.

In the DSC cooling process, the exothermic peaks (the T_{cc} points) of the PTT and CD-PTT fibers occurred at 184.7 and 166.5°C, respectively. The exothermic peak was due to the recrystallization behavior of the melting polymer. Obviously, the half-time of the recrystallization for PTT fiber was shorter than that of the CD-PTT fiber, implying that the recrystallization rate of the PTT fiber was faster than that of the CD-PTT fiber. The T_{cc} of PTT/CD-PTT polyblended fibers was between 170 and 182°C. Both the heat fusion (ΔH_m) and the recrystallization heat of the exothermic peak (ΔH_{cc}) decreased as the 5-SSDMI content increased. The DSC results indicated that PTT segments and CD-PTT molecules were a miscible system.

Crystallinities of polyblended fibers

The crystallinities of PTT, CD-PTT, and PTT/CDPTT polyblended fibers were determined using DSC, the density gradient, and WAXD methods. In the DSC method, the heat of fusion was used to indicate the crystalline fraction of the material. A higher value of heat of fusion was expected to resort in a higher crystallinity. Table IV reveals the crystallinities of PTT, CD-PTT, and their blends. Notably, increasing the 5-SSDMI content in the PTT/CD-PTT polyblended fibers reduced the heat of fusion, and thus, decreased the crystallinity. The data obtained by the DSC

TABLE IV
Crystallinities of PTT, CD-PTT, and PTT/CD-PTT Polyblended Fibers

Polymer code	DSC		Density		WAXD
	ΔH_m (J/g)	X_c (%)	d (g/cm ³)	X_c (%)	X_c (%)
Sample 1	56.1	38.5	1.3379	40.3	37.4
Sample 2	53.7	36.9	1.3361	38.5	36.3
Sample 3	52.6	36.1	1.3354	37.8	35.2
Sample 4	50.2	34.5	1.3338	36.2	33.8
Sample 5	48.9	33.6	1.3329	35.3	31.9
Sample 6	47.5	32.6	1.3319	34.2	31.2

method was consistent with that obtained by the density gradient method and the WAXD method.

The degree of crystallinity from DSC, the density gradient, and the WAXD methods for all samples was compared. By comparison, it was found that quantifying the crystallinity by the DSC methods and the density gradient method was difficult. In the DSC analysis, the heat of fusion of repeating unit was theoretically computed for 100% crystallinity of the PTT polymer. Regarding the density gradient method, the density of crystalline and amorphous PTT polymer could not be measured accurately, and the literature values for crystalline and amorphous density were assumed theoretically as well. Therefore, the crystallinity by WAXD method was often used in the quantitative analysis of the polymer's crystallinity.

The crystalline peak of the PTT fiber was sharper than that of the CD-PTT fiber, as shown in Figure 4. Meanwhile, seven characteristic peaks of diffracting angles (2θ) at 15.3°, 16.8°, 19.4°, 21.8°, 23.6°, 24.6°, and 27.3°, corresponding to the reflection planes of (010), (01 $\bar{2}$), (012), (10 $\bar{2}$), (102), (11 $\bar{3}$), and (104), did not obviously shift expect for the diffraction intensities.¹⁰ This indicated that the 5-SSDMI did not pack into the original PTT unit cell but concentrated at the PTT crystalline surface and the amorphous regions. Figure 5 displays the relation between the crystallinities and the blend ratios of PTT/CD-PTT polyblended fibers. For all PTT/CD-PTT polyblended fibers, the crystallinities decreased with increase in the proportion of CD-PTT. In this study, crystallinities by WAXD method were slightly lower than those by DSC and density methods.

Mechanical properties of polyblended fibers

Figure 6 shows the relation between the tenacities and crystallinities with the blend ratios of PTT/CD-PTT polyblended fibers. The tenacities of PTT/CD-PTT polyblended fibers declined as the 5-SSDMI content increased. Figure 7 displays the relation between the densities and crystallinities with different blend ratios of PTT/CD-PTT polyblended fibers. The densities of PTT/CD-PTT polyblended fibers also decreased as the

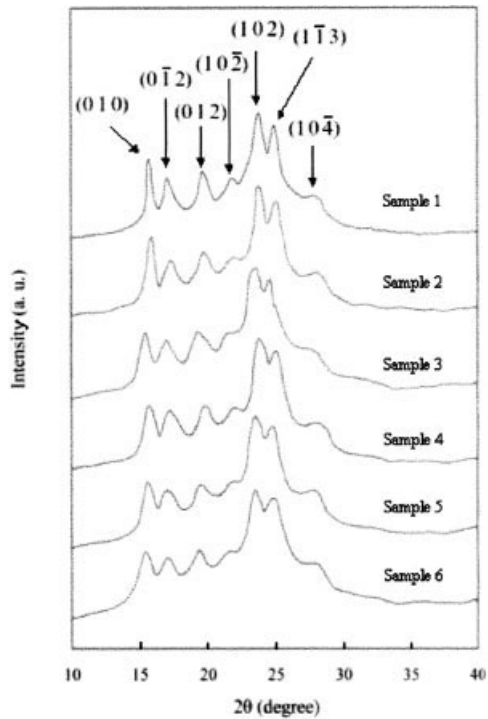


Figure 4 WAXD curves of PTT, CD-PTT, and PTT/CD-PTT polyblended fibers.

5-SSDMI content increased. The experimental result for the tenacity and density methods were consistent with the crystallinity of the PTT/CD-PTT polyblended fibers.

On morphological observation, it was found that the blends were in a miscible structure. As shown in Figures 8(a) and 8(f), both the PTT and the CD-PTT fibers

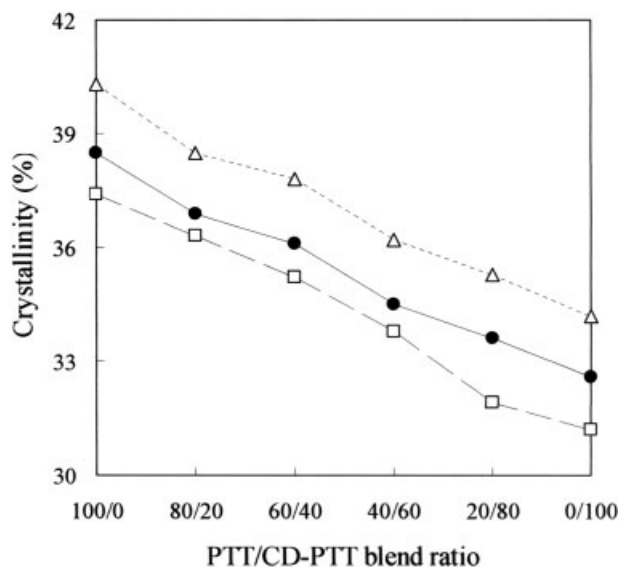


Figure 5 Relation between the crystallinities and the blend ratio of PTT/CD-PTT polyblended fibers: (●) DSC method, (△) density method, (□) WAXD method.

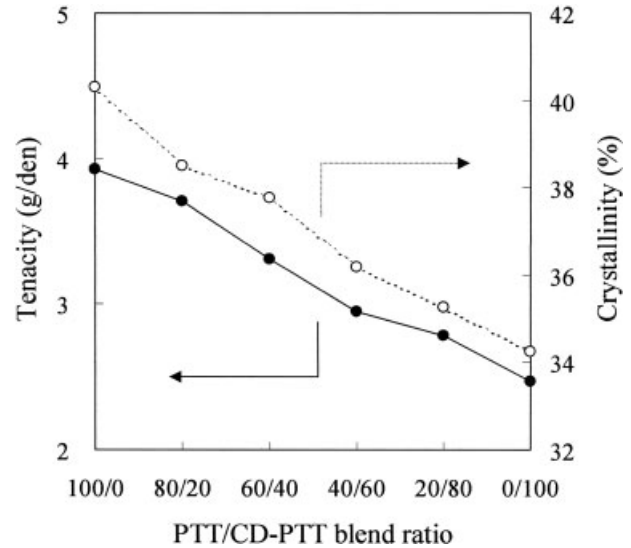


Figure 6 Relation between the tenacities and crystallinities (density method) with the blend ratio of PTT/CD-PTT polyblended fibers: (●) tenacity, (○) crystallinity.

had uniform structure on the surface of fibers. As shown in Figures 8(b)–8(e), PTT/CD-PTT polyblended fibers also had uniform structure on the surface of fibers. PTT and CD-PTT polymers were found to be a miscible system, as inferred from the morphological studies.

CONCLUSIONS

PTT polymer does not possess ionic groups. Furthermore, CD-PTT polymer possesses 5-sodium sulfonate dimethyl isophthalate (5-SSDMI; $-\text{SO}_3\text{Na}$)

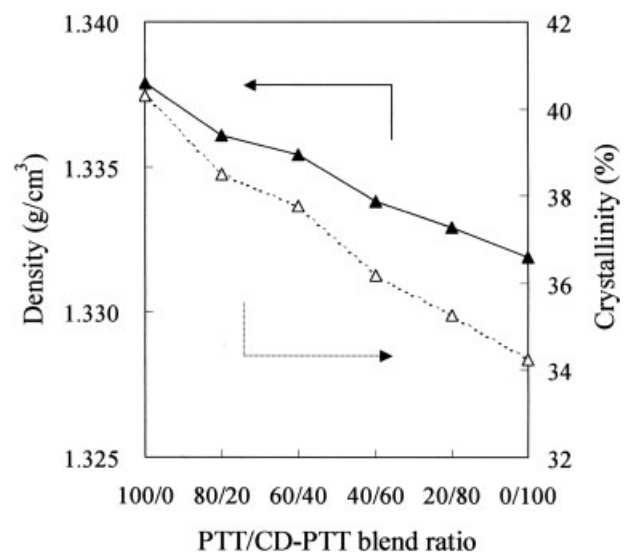


Figure 7 Relation between the densities and crystallinities (density method) with the blend ratio of PTT/CD-PTT polyblended fibers: (▲) density, (△) crystallinity.

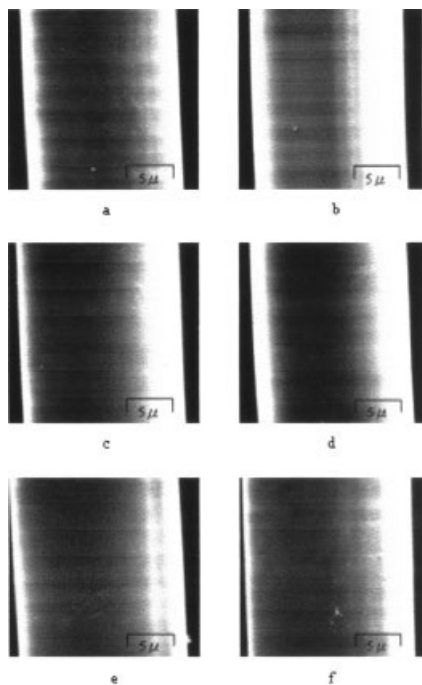


Figure 8 Morphologies of PTT, CD-PTT, and PTT/CD-PTT polyblended fibers on the surface. (a) 100:0, (b) 80:20, (c) 60:40, (d) 40:60, (e) 20:80, (f) 0:100.

groups). The interfacial adhesion plays a critical role for PTT/CD-PTT polyblended fibers. Melting behavior of PTT/CD-PTT polyblended polymers exhibited PDBs. The 60:40–40:60 blend of PTT/CD-PTT showed a maximum melt viscosity value than that predicted by the additivity rule. Flow behavior results indicated a good interfacial adhesion between PTT and CD-PTT polymers. The experimental results of the DSC indicated PTT and CD-PTT molecules easily formed miscible domains. The tenacity of PTT/CD-PTT polyblended fibers declined as the 5-SSDMI content increased. Crystallinities and densities of PTT/CD-PTT polyblended fibers were also found decrease as the 5-SSDMI content increased. From the melting behavior, thermal properties, mechanical properties, and the

morphological observation of polyblended fiber on the surface. PTT/CD-PTT polymers were identified to be a miscible system. Though there is a good interfacial adhesion between PTT and CD-PTT polymer, the mechanical properties of PTT/CD-PTT polyblended fibers were largely affected by 5-SSDMI content.

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