

Thermal Behavior and Morphological Characteristics of Cationic Dyeable Poly(ethylene terephthalate) (CD-PET)/Metallocene Isotactic Polypropylene (*m*-iPP) Conjugated Fibers

Yao-Chi Shu,¹ Kai-Jen Hsiao²

¹Department of Polymer Materials, Vanung University, Chungli City, Taiwan 320, Republic of China

²Fiber Technology Division, MCL/ITRI, Hsinchu, Taiwan 300, Republic of China

Received 5 February 2006; accepted 12 June 2006

DOI 10.1002/app.24990

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

ABSTRACT: Cationic dyeable poly(ethylene terephthalate) (CD-PET) and metallocene isotactic polypropylene (*m*-iPP) polymers were extruded (in the proportions of 75/25, 50/50, 25/75) from two melt twin-screw extruders to prepare CD-PET/*m*-iPP (and *m*-iPP/CD-PET)-conjugated fibers of the island-in-sea type. This study investigated the thermal behavior and mechanical and morphological characteristics of the conjugated fibers using DSC, TGA, WAXD, melting viscosity rheometer, density indicator, tenacity measurement, and a polarizing microscope. Melting behavior of CD-PET/*m*-iPP polyblended polymers exhibited negative-deviation blends (NDB) and the 50/50 blend showed a minimum value of the melt viscosity. Experimental results of the DSC indicated CD-PET and *m*-iPP molecules formed a partial miscible system. The tenacity of CD-PET/*m*-iPP-conjugated fibers decreased initially and then increased as the *m*-iPP content increased. Crystallinities and densities of CD-PET/

m-iPP-conjugated fibers presented a linear relation with the blend ratio. On the morphological observation, it was revealed that the blends were in a dispersed phase structure. In this study, the CD-PET microfibers were successfully produced with enhanced diameters (from 2.2 to 2.5 μm). Additionally, *m*-iPP colored fibers (*m*-iPP fibers covered with CD-PET polymer) were also successfully prepared. Meanwhile, the presence of PP-graft-MA compatibilizer improved the tenacity considerably. Blends with 10 wt % compatibilizer exhibited maximum improvement in the tenacity for *m*-iPP colored fibers. The dye exhaustions of various fabrics followed the order: *m*-iPP colored fibers > conventional CD-PET fibers > CD-PET microfibers. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5396–5405, 2006

Key words: conjugated fibers; properties; CD-PET/*m*-iPP blends

INTRODUCTION

Poly(ethylene terephthalate) (PET) is a useful fiber because it is strong, inert, and thermally stable. These properties also favor its use widely in the textile and industrial fields. The polyester has a regular linear structure characterized by repeated units that form the backbone of the molecular chain. In addition, PET microfibers of island-in-sea type are successfully produced commercially. Fabrics produced with PET island-in-sea-type conjugated fibers have a soft touch, ventilation and comfort, and excellent weatherproofing etc and are moisture-permeable and waterproof. Applications of these fabrics included weaving (used as warp to make fabric with suede effect and soft touch) and knitting (fabric surface had suede feel after sanding). Products based on these fabrics included casual wears, jackets, overcoats, raincoats, skirts, suits, etc. Both conventional and microfibers PET fabrics are commonly dyed with disperse dyes in pressurized

vessels at 130°C.¹ To improve the condition of dyeing for PET polymer, cationic dyeable poly(ethylene terephthalate) (CD-PET) polymer was developed. Conventional CD-PET fabrics are commonly dyed with basic dyes in normalized vessels at 100°C. Though CD-PET fabrics present deep and brilliant colors and soft touch characteristics, no literature data was found for CD-PET microfiber fabrics. There are also some reports on the physical properties of CD-PET polymers and fibers.^{2–8} Nevertheless, there was not any report in the literature for the properties of CD-PET microfibers.

Additionally, polypropylene (PP) resins had been produced from Ziegler–Natta catalysts for over 45 years now. These polymers were typically high molecular weight and broad molecular weight distribution (MWD) resins as produced in the polymerization reactor. In recent years, these resins were frequently given a postreactor treatment to a narrow their MWD and lower their molecular weight when they were to be used for fiber spinning. This treatment typically consisted of extrusion in the presence of a peroxide compound, which produced the desired result by thermal oxidative degradation of

Correspondence to: K.-J. Hsiao (KJHsiao@itri.org.tw).

TABLE I
Characteristics of CD-PET and *m*-iPP Chips

Chip	I.V. (dL/g) ^a	MFI ^b	5-SSDMI (mol %)	$\overline{M}w$ (g/mol)	$\overline{M}w/\overline{M}n^c$	R-COOH (meq/kg)	T_m (°C)	T_d (°C) ^d
CD-PET	0.46	–	2.1	30,000	2.05	58	246.3	380
<i>m</i> -iPP	–	24	–	176,000	1.92	0	150.5	374

^a Intrinsic viscosity (I.V.) of CD-PET polymer was obtained by a mixed solution of 0.5 g/100 mL in phenol/tetrachloroethane (60/40) at 30°C. The molar ratio of 5-sodium sulfonate dimethyl isophthalate (5-SSDMI) for CD-PET polymer was 2.1%.

^b Melt flow index (MFI, g/10 min.) of *m*-iPP polymer was measured from ASTM D1238 method (230°C/2.16 kg).

^c Molecular weight distribution (MWD) of polymer. MWDs of CD-PET and *m*-iPP polymers were measured in HFIP (1,1,1,3,3,3 hexafluoro-2-propanol) and TCB (trichlorobenzene) solvent systems, respectively.

^d Degradation temperature of polymer.

the reactor resin. This method is known as the controlled rheology process (commercial PP was called the Ziegler–Natta PP). A major advantage for the use of metallocene catalysts for preparing polypropylene (commercial PP was called the metallocene PP) was that narrow MWD resins could be obtained directly from the reactor without the need for secondary processing.⁹ Nowadays, PP was extensively used in international markets, because of its low cost, low density, and good thermal stability. PP fibers possessed some drawbacks such as hydrophobic property, poor moisture absorption, and static charge formation by fiber friction. In addition, the absence of hydrophilic reactive groups in PP macromolecules prevented its dyeing by basic, reactive dyes.¹⁰

Polyblends were important developments of the plastics and synthetic fiber industries. Polyblends could 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.¹¹ CD-PET polymer possessed ionic groups. Nevertheless, *m*-iPP polymer did not possess any functional group. The interfacial adhesion played a critical role for CD-PET/*m*-iPP-conjugated fibers. In this study, CD-PET and *m*-iPP polymers were selected because of two reasons. The first, no literature data was found for CD-PET microfibers. Moreover, PP is a low cost material compared with the easily soluble PET (ESPET). The second, *m*-iPP colored fibers (*m*-iPP fibers covered with CD-PET polymer) were produced using the conjugated spinning on the island (*m*-iPP)-in-sea (CD-PET) type. Both *m*-iPP and CD-PET did not need be removed from *m*-iPP/CD-PET-conjugated fibers, so it was important in the interface adhesion between *m*-iPP and CD-PET. To increase the mechanical properties of *m*-iPP/CD-PET-conjugated fiber, the compatibilizer of PP-*graft*-MA was added to the fibers. *M*-iPP polymer was elected because its physical properties were better than that of Ziegler–Natta isotactic PP (ZN-iPP).

This study thoroughly investigated the preparation and physical properties (including melting behavior, thermal properties, crystallinity, tenacity, density, and

morphology) of the conjugated fibers of the island-in-sea type. Also, the dye exhaustions of the fabrics of a series of CD-PET fibers were compared.

EXPERIMENTAL

Materials and conjugated spinning

Cationic dyeable poly(ethylene terephthalate) (CD-PET) chips were obtained from the Material and Chemical Research Laboratories/Industrial technology research Institute (MCL/ITRI) in Taiwan (Hsinchu). The CD-PET polymer, a white pellet with an average diameter size of 3–5 mm, is specially designed for the fiber spinning process. Its intrinsic viscosity (I.V.) is 0.46 dL/g. The molar ratio of 5-sodium sulfonate dimethyl isophthalate (5-SSDMI) for CD-PET polymer was 2.1%. Before spinning, CD-PET was dried for 4 h/120°C and 12 h/150°C in the vacuum box. Metallocene isotactic polypropylene (*m*-iPP) chips were obtained from the Exxon Mobil Chemical Company (Houston, TX). The *m*-iPP resin (ACHIEVE™ 3854), a white pellet with an average diameter size of 3–5 mm, is specially designed for the fiber spinning process. Its

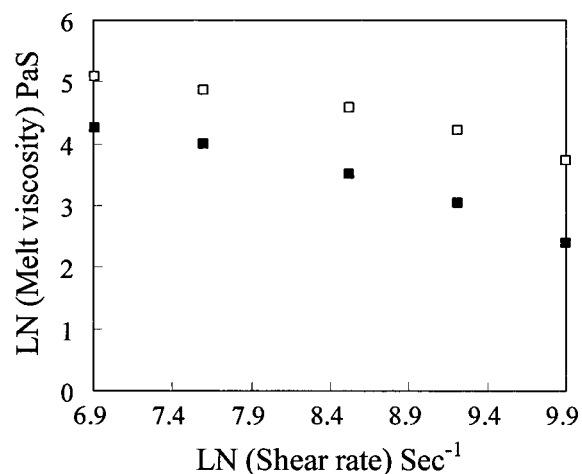


Figure 1 Relation between the melt viscosities and shear rate for CD-PET and *m*-iPP polymers at 260°C. (□): CD-PET, (■): *m*-iPP.

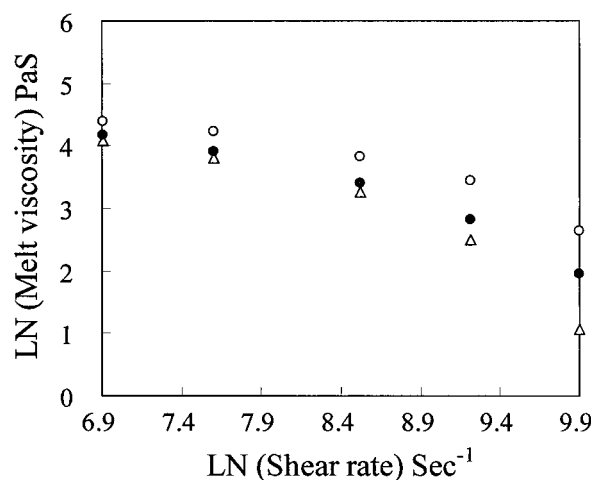


Figure 2 Relation between the melt viscosities and shear rate for CD-PET/*m*-iPP polyblended polymers at 260°C. (○): CD-PET/*m*-iPP (75/25), (△): CD-PET/*m*-iPP (50/50), (●): CD-PET/*m*-iPP (25/75).

MFI (melt flow index) was 24 g/10 min at 230°C. Polypropylene grafted with maleic anhydride (PP-graft-MA; Polybond 3200) was supplied by the courtesy of Crompton Corp. (Middlebury, CT). The grafting degree of MA content was 1 wt % and MFI 110 g/10 min. Table I lists the synthetic characteristics of CD-PET and *m*-iPP polymers. CD-PET and *m*-iPP polymers were extruded in the proportions of 75/25, 50/50, 25/75 from two melt twin-screw extruders to prepare the conjugated fibers.

All conjugated fibers were prepared on AW-909 bi-component precision conjugated fiber winding machine, which consists of two "one inch" extruders, two metering pumps, a bicomponent spin pack purchased from Teijin Seiki company of Japan, a 15-ft stack with a cross air cooling channel, a spin finish applicator, and a speed winder. The two melt twin-screw extruders characteristics and temperature profiles were: screw diameter (30 mm), L/D (36.8), extrusion temperature profiles (CD-PET: 245, 255, 265, 275, 285, and 285°C; *m*-iPP: 180, 185, 190, 195, 200, 200°C), extrusion retention time (5–10 min) and screw speeds (25–100 rpm).

The cross sections of CD-PTT/*m*-iPP (or *m*-iPP/CD-PET) conjugated fiber were prepared to an island-in-sea type and the combine melts were extruded through 24 circular holes of 0.2 mm diameter (37 islands/hole). Three different mass flow rate combinations of CD-PTT/*m*-iPP (or *m*-iPP/CD-PET) were used. The extruded conjugated fibers were quenched and subsequently wound to yield the conjugated POY (partially oriented yarn) filaments. Also, a single component CD-PET POY and *m*-iPP POY were produced. The take-up speed of the winder for all POY fibers was 2500 m/min. Then, POY fibers were drawn 1.8 times to form FDY (fully drawn yarn) filaments by a drawn-winder machine.

The draw temperature and take-up speed were 120°C and 500 m/min, respectively. The specification of FDY filaments was 75 denier/24 filaments \times 37 (islands). It indicated that denier/filament (dpf) was approximately 3.13 and one filament had 37 islands. A polarizing microscope, Leitz Laborlux 12 P01, was used to examine the morphological structure of sample. The 75/25 CD-PET (island)/*m*-iPP (sea) conjugated fibers were treated in paraffin oil at 140°C for 1 h. Finally, *m*-iPP polymers were removed and CD-PET microfibrils were obtained. The dye used for this study was C.I. Basic Blue 1. For the dyeing rate study, the dyestuff used was 1% owf (on the weight of fabric). The liquor-to-goods ratio was 20:1. For the constant temperature dyeing rate study, the dye bath was heated to the dyeing temperature (100°C) before the addition of the fabric.

Measurements

Gel permeation chromatograph (GPC) data were measured from a Waters Model 510 Type. Two solvent systems were used in GPC measurement. MWDs of CD-PET and *m*-iPP polymers were measured in 1,1,1,3,3,3 hexafluoro-2-propanol (HFIP) and trichlorobenzene (TCB) solvent systems, respectively. Intrinsic viscosity (I.V.) of CD-PET polymer was obtained by a mixed solution of 0.5 g/100 mL in phenol/tetrachloroethane (60/40) at 30°C. Wide-angle X-ray diffraction (WAXD) studies of samples were conducted using a MAC Science X-ray unit operated at 35 kV and 20 mA. X-ray diffraction was then used with Cu K α radiation and scanned from 5 to 40° (2 θ) with a scan speed of 4°/min.¹² Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements of samples were

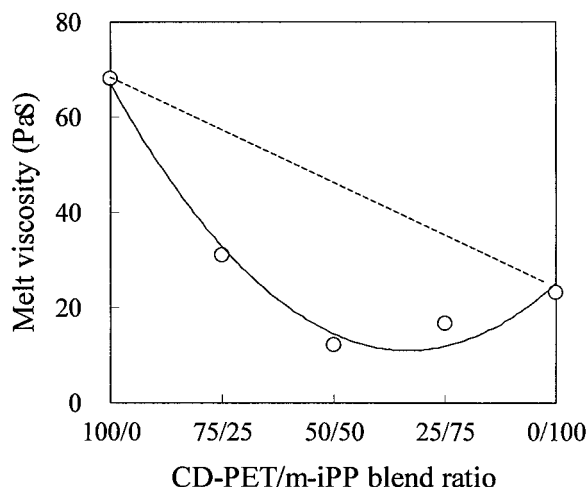


Figure 3 Relation between the melt viscosities and blend ratio for CD-PET/*m*-iPP polyblended polymers at 260°C/10⁴ s⁻¹. (-----): Calculated theoretical value, (○): Experimental value.

TABLE II
Thermal Properties of CD-PET-, *m*-iPP-, and CD-PET/*m*-iPP-Conjugated Fibers

CD-PET/ <i>m</i> -iPP blend ratio	Heating process				Cooling process					
	CD-PET		<i>m</i> -iPP		CD-PET			<i>m</i> -iPP		
	T_{m1} (°C)	ΔH_{m1} (J/g)	T_{m2} (°C)	ΔH_{m2} (J/g)	T_{cc1} (°C)	ΔH_{cc1} (J/g)	Half-time (s)	T_{cc2} (°C)	ΔH_{cc2} (J/g)	Half-time (s)
100/0	252.4	53.6	–	–	204.8	42.3	92.8	–	–	–
75/25	250.7	40.2	154.2	24.2	202.9	31.7	–	105.7	24.7	–
50/50	248.6	26.8	153.6	48.5	200.5	21.2	–	104.6	49.4	–
25/75	247.3	13.4	153.1	72.7	197.8	10.6	–	103.1	74.0	–
0/100	–	–	151.8	96.9	–	–	–	102.5	98.7	46.8

made using a Perkin–Elmer Pyrix-1. The heating rate of TGA measurement in N₂ atmosphere 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 of the DSC method was calculated from the following equation: crystallinity (%) = $\Delta H_m / \Delta H_m^\circ \times 100$ (%), where ΔH_m and ΔH_m° are the heat of fusion in J/g of repeating unit for the sample and 100% crystallinity, respectively. ΔH_m° of pure PET (and pure PP) is equal to 140.1 (and 209.0) J/g.^{13,14} The densities of samples were determined using the density gradient method. A mixture of *n*-heptane and carbontetrachloride was used for the purpose. Densities of *n*-heptane and carbontetrachloride solvents were 0.684 g/cm³ and 1.595 g/cm³, respectively. The scale of density gradient method was prepared from 0.800 g/cm³ 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 polarizing microscope pictures observed using a Leitz Laborlux 12 P01. All tenacities of samples were obtained on a Zwick 1511 type Instron instrument at an extension rate of 200 mm/min (ASTM C1557-03).

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 CD-PET and *m*-iPP polymers at 260°C versus shear rate. From 10³ to 2 × 10⁴ s⁻¹, the two polymers exhibited pseudoplastic flow behavior. The rheological curves indicated that the melt viscosity of the CD-PET polymer was higher than that of the *m*-iPP polymer over the entire shear rate range. Figure 2 displays the melt viscosities of CD-PET/*m*-iPP polyblended polymers at 260°C versus shear rate. The melt viscosities of CD-PET/*m*-iPP polyblended polymers also exhibited pseudoplastic flow behavior. This tendency was independent of the blend ratio. Figure 3 shows that the melt viscosities of CD-PET/*m*-iPP polyblended poly-

mers exhibited negative-deviation blends (NDB).^{15–18} Notably, the 50/50 blend of CD-PET/*m*-iPP showed a minimum value of the melt viscosity than that predicted by the rule of mixtures at 260°C and 10⁴ s⁻¹. The rheological results indicated a poor interfacial adhesion between the CD-PET and *m*-iPP polymers. The melt viscosities of CD-PET, *m*-iPP, and their blends followed the order CD-PET > CD-PET/*m*-iPP (75/25) > *m*-iPP > CD-PET/*m*-iPP (25/75) > CD-PET/*m*-iPP (50/50).

Previous to this work, CD-PET/*m*-iPP polyblended fibers were produced by a traditional melting spin-

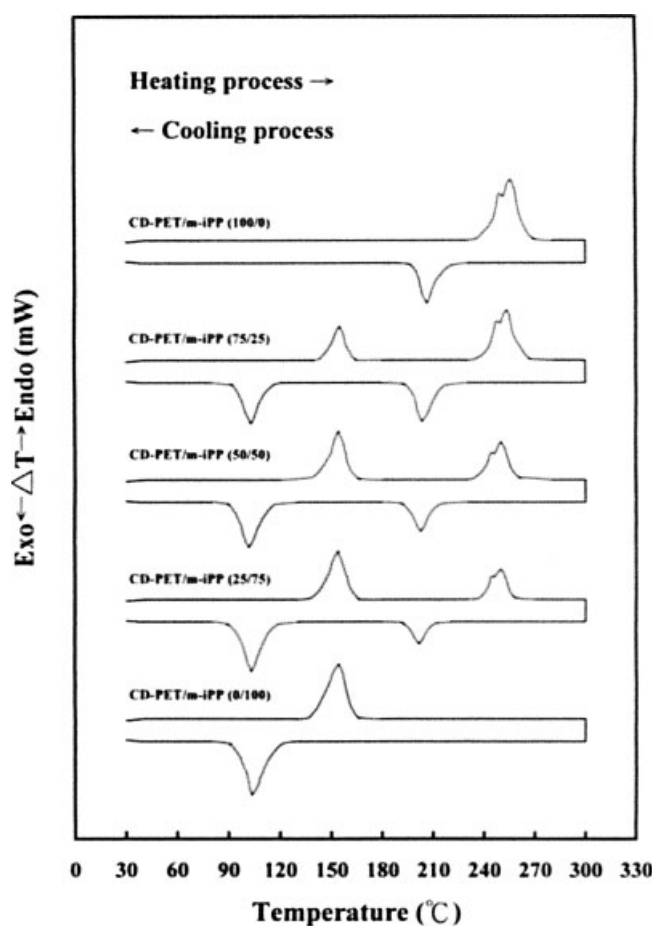


Figure 4 DSC curves of CD-PET, *m*-iPP, and CD-PET/*m*-iPP polyblended fibers.

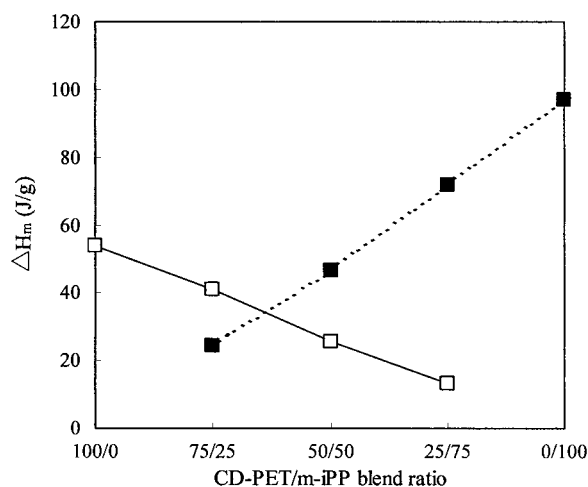


Figure 5 Relation between ΔH_m and blend ratio of CD-PET/*m*-iPP conjugated fibers. (□): CD-PET, (■): *m*-iPP.

ning process (one melt twin-screw extruder). However, not only the spinnability and processibility were bad but also the polyblended fibers presented poor physical properties. So, for this reason, in this work the conjugated spinning process was used (two melt twin-screw extruders). From experimental results, CD-PET/*m*-iPP-conjugated fibers were easily produced from the conjugated spinning process on the island-in-sea type. Not only the CD-PET (island)/*m*-iPP (sea) but also the *m*-iPP (island)/CD-PET (sea) conjugated fibers. CD-PET microfibers were prepared from CD-PET (island)/*m*-iPP (sea) conjugated fibers. Additionally, *m*-iPP colored fibers were produced from *m*-iPP (island)/CD-PET (sea) conjugated fibers. Of course, *m*-iPP colored fibers also were obtained using the conjugated spinning on the sheath (CD-PET) and core (*m*-iPP) type. We considered the contact surfaces between CD-PET polymers and *m*-iPP molecules. The contact surface of the island/sea type was higher than that of the sheath/core type. Therefore, the island/sea type of conjugated spinning was adopted in this study.

Thermal properties and crystallinity of conjugated fibers

Table II displays the thermal properties of CD-PET, *m*-iPP, and three CD-PET/*m*-iPP-conjugated fibers. In the DSC heating process, the endothermic peaks of CD-PET and *m*-iPP fibers occurred at 252.4 and 151.8°C, respectively. The endothermic peak (T_m) is due to the melting of the sample. The T_m of CD-PET/or *m*-iPP fiber compared with that of CD-PET/or *m*-iPP chip as seen in Table I and Table II. Because of the influences of the orientation and crystallization, the T_m of CD-PET/or *m*-iPP fiber was slightly higher than that of CD-PET/or *m*-iPP chip. The T_m of CD-PET fiber was higher than that of *m*-iPP, approximately 100.6°C. This DSC data displayed a clearly

melting endothermic peak, indicating that CD-PET and *m*-iPP fibers were originally crystalline. Figure 4 shows that a double melting endothermic peak was obtained from the CD-PET fiber, and only a single melting peak was observed for *m*-iPP fiber. Interestingly, large-SO₃Na side groups in CD-PET polymers prevented the chain molecules from tightly coagulating and obstructed the formation of larger crystals.¹⁹ Owing to the effect of a -SO₃Na side group on polymer, thermal behavior of the CD-PET/*m*-iPP-conjugated fibers resembled that of the CD-PET fiber. The experimental phenomenon resembled the observation of Pal et al. for cationic dyeable polymer.²⁰

In the DSC cooling process, the exothermic peaks (the T_{cc} points) of CD-PET and *m*-iPP fibers occurred at 204.8 and 102.5°C, respectively. The exothermic peak was due to the recrystallization behavior of the melting polymer. Obviously, the half-time of the recrystallization for *m*-iPP fiber was shorter than that of CD-PET fiber, implying that the recrystallization rate of *m*-iPP fiber was faster than that of CD-PET fiber. For all CD-PET/*m*-iPP-conjugated fibers, T_m of CD-PET segments (T_{m1}) nearly did not shift and appeared around 247–251°C. Additionally, T_m of *m*-iPP molecules (T_{m2}) also did not clearly change and appeared at 153–155°C. In other words, the T_m change was independent of the blend ratio.

Figure 5 displays the linear variations of the heat fusion (ΔH_m) with the blend ratio of CD-PET/*m*-iPP-conjugated fibers. ΔH_m of CD-PET molecules (ΔH_{m1}) proportionally declined with an increasing *m*-iPP content. Meanwhile, ΔH_m of *m*-iPP molecules (ΔH_{m2}) proportionally increased with increasing *m*-iPP content. For all CD-PET/*m*-iPP-conjugated fibers, the T_{cc} point of CD-PET molecules (T_{cc1}) also nearly did not change and appeared around 197–203°C. The T_{cc} point of *m*-iPP molecules (T_{cc2}) was observed around

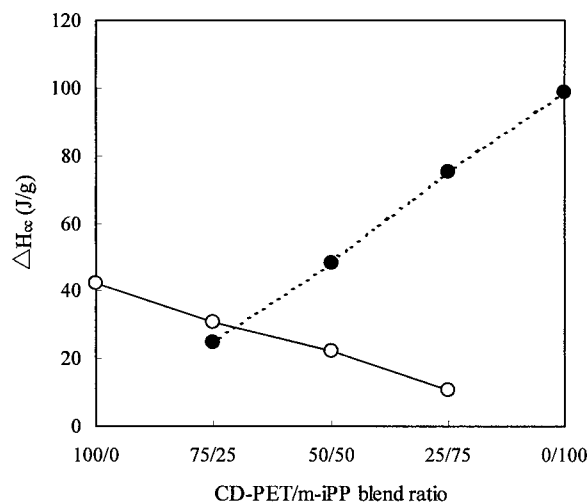


Figure 6 Relation between ΔH_{cc} and blend ratio of CD-PET/*m*-iPP conjugated fibers. (○): CD-PET, (●): *m*-iPP.

TABLE III
Crystallinities of CD-PET, *m*-iPP, and CD-PET/*m*-iPP-Conjugated Fibers

CD-PET/ <i>m</i> -iPP blend ratio	DSC method				Total X_c (%) of fiber	WAXD method Total X_c (%) of fiber
	CD-PET part		<i>m</i> -iPP part			
	ΔH_{m1} (J/g)	X_c (%) of CD-PET	ΔH_{m2} (J/g)	X_c (%) of <i>m</i> -iPP		
100/0	53.6	38.3	–	–	38.3	35.1
75/25	40.2	28.7	24.2	11.6	40.3	36.3
50/50	26.8	19.1	48.5	23.2	42.3	38.8
25/75	13.4	9.6	72.7	34.8	44.3	41.5
0/100	–	–	96.9	46.4	46.4	43.4

103–106°C. Figure 6 also shows the linear variations of the recrystallization heat of the exothermic peak (ΔH_{cc}) with the blend ratios of CD-PET/*m*-iPP-conjugated fibers. ΔH_{cc} of CD-PET molecules (ΔH_{cc1}) proportionally decreased with increasing *m*-iPP content. Meanwhile, ΔH_{cc} of *m*-iPP molecules (ΔH_{cc2}) proportionally increased with increasing *m*-iPP content. The DSC experimental results indicated that CD-PET and *m*-iPP macromolecules were partially miscible.

The heat of fusion was used to indicate the crystalline fraction of the material. A higher value of heat of fusion was expected to be found with a higher crystallinity. Table III reveals the crystallinities of CD-PET, *m*-iPP, and CD-PET/*m*-iPP-conjugated fibers. The heat of fusion of melting was used to calculate crystallinity. The crystallinities of CD-PET and *m*-iPP fibers were 38.3 and 46.4%, respectively. The crystallinity of *m*-iPP fiber was 8.1% higher than that of CD-PET fiber. After blending, the total crystallinity of CD-PET/*m*-iPP-conjugated fibers increased with the proportion of *m*-iPP increased. Crystallinities of WAXD method were slightly lower than those of DSC method. Figure 7 displays the relation between the crystallinities and the blend ratios of CD-PET/*m*-iPP-conjugated fibers. For all CD-PET/*m*-iPP-conjugated fibers, the experimental crystallinities agree fairly well with the calculated theoretical values.

Tenacity and density measurements of conjugated fibers

Figure 8 shows the relation between the tenacities and the blend ratios of CD-PET/*m*-iPP-conjugated fibers. The tenacities of CD-PET/*m*-iPP-conjugated fibers declined initially and then increased when the proportion of *m*-iPP increased. Obviously, the 50/50 CD-PET/*m*-iPP blend displayed a minimum tenacity value. The poor interfacial interactions between CD-PET and *m*-iPP indicated poor mechanical properties. The tendency agreed with the flow behavior, and the 50/50 CD-PET/*m*-iPP blend displayed a minimum tenacity value. Figure 9 displays the relation between the densities and the blend ratios of CD-PET/*m*-iPP-conjugated fibers. For all CD-PET/*m*-iPP-conjugated fibers, the experimental densities agree

fairly well with the calculated theoretical values. This indicated that CD-PET and *m*-iPP formed basically an immiscible system. The experimental results for the densities were consistent with the thermal behavior, flow behavior, crystallinity, and tenacity of CD-PET/*m*-iPP-conjugated fibers.

Morphologies of CD-PET microfibers

In this stage of our work we tried to produce CD-PET microfibers using the conjugated spinning on the island (CD-PET)-in-sea (*m*-iPP) type. Because CD-PET polymer must be removed from CD-PET/*m*-iPP-conjugated fibers, interfacial adhesion of CD-PET and *m*-iPP polymers was not important. Moreover, PP is a low cost polymer compared to the ESPET polymer. Therefore, it was tried to substitute ESPET for PP in the conjugated fibers using the ratio 75/25 CD-PET/*m*-iPP blend. On the morphological observation, it was revealed that the blends were in a dispersed phase structure. As shown in Figure 10(a, b), both the CD-PET and the *m*-iPP fiber had uniform surface structure on the cross section of fiber. Figure 10(c) reveals the 37 islands/filament of CD-PET/*m*-iPP (75/25) conjugated fibers on the cross section before paraffin oil treatment which were not evident

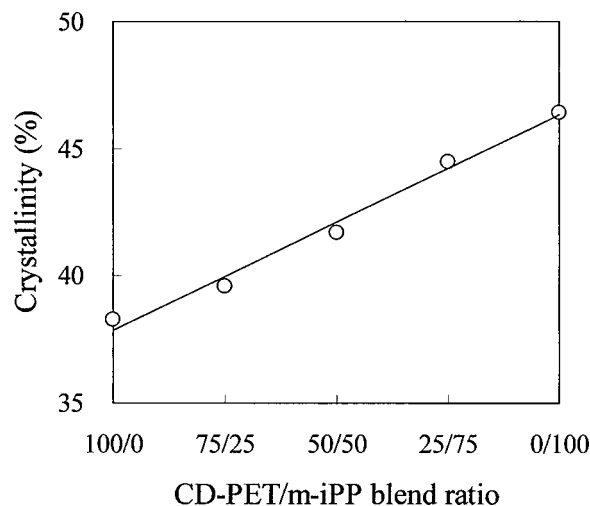


Figure 7 Relation between the crystallinities and blend ratio of CD-PET/*m*-iPP-conjugated fibers.

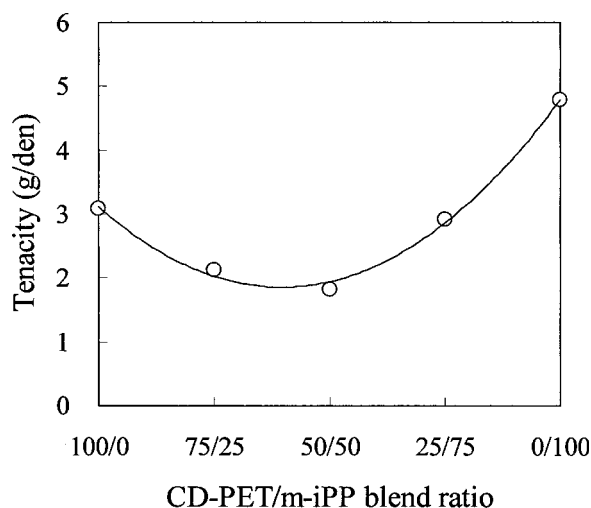


Figure 8 Relation between the tenacities and blend ratio of CD-PET/*m*-iPP-conjugated fibers.

from the observations from the polarizing microscope photographs. Figure 10(d) displays the morphology of CD-PET microfibers (37 islands/filament), which possess a larger size that varies from 2.2 to 2.5 μm (0.05–0.06 dpf) in diameter and was clearly observed after paraffin oil treatment (*m*-iPP was removed) on the cross section of CD-PET/*m*-iPP (75/25)-conjugated fibers. The morphological result could infer that CD-PET and *m*-iPP could be divided into two parts. Figure 10(e) shows the model of the 75/25 CD-PET (island)/*m*-iPP (sea) blend conjugated fibers. The white and black parts were the CD-PET (island) and *m*-iPP (sea), respectively.

Morphologies and tenacities of *m*-iPP colored fibers

Above mentioned CD-PET microfibers were successfully produced from 75/25 CD-PET (island)/*m*-iPP (sea) conjugated fibers (after *m*-iPP was removed). In this stage of our work we tried to produce *m*-iPP colored fibers using the conjugated spinning on the island (*m*-iPP)-in-sea (CD-PET) type. Similarly, both the mechanical properties of fibers and the size design of conjugated spinning spinneret were judiciously considered. The 75/25 *m*-iPP (island)/CD-PET (sea) blend conjugated fibers were elected to prepare. In this case, both *m*-iPP and CD-PET polymers did not need be removed from *m*-iPP (island)/CD-PET (sea) conjugated fibers, so it was important for the interface adhesion between *m*-iPP and CD-PET polymers.

Figure 11(a) shows the 37 islands/filament of the *m*-iPP/CD-PET (75/25)-conjugated fibers on the cross section before HFIP solvent treatment, which were also not obvious from the observation of the polarizing microscope photographs. Figure 11(b) reveals the morphology of the *m*-iPP microfibers (37 islands/filament) possesses a larger size from 2.5 to 2.8 μm

(0.04–0.05 dpf) in diameter was clearly observed after HFIP treatment (CD-PET was removed) on the cross section of *m*-iPP/CD-PET (75/25) conjugated fibers. But *m*-iPP microfibers were not our target in this study. Figure 11(c) displays the model of the 75/25 *m*-iPP (island)/CD-PET (sea) blend conjugated fibers. The white and black parts were *m*-iPP (island) and CD-PET (sea), respectively. The morphological result could also infer that *m*-iPP and CD-PET could be divided into two parts and the islands were *m*-iPP fibers. When the *m*-iPP/CD-PET (75/25) conjugated fibers were not treated with solvent, *m*-iPP colored fibers were produced successfully.

Experimental results indicated that *m*-iPP and CD-PET were partially miscible. To increase the mechanical properties of *m*-iPP (island)/CD-PET (sea)-conjugated fiber, the compatibilizer of PP-*graft*-MA was added to the fibers. Figure 12 displays the variation of the tenacities of 75/25 *m*-iPP (island)/CD-PET (sea) as a function PP-*graft*-MA (0, 1, 3, 5, and 10 wt %). It is noteworthy that the compatibilizer acts as interfacial emulsifying agent. Regarding the tenacities, addition of PP-*graft*-MA increased the tenacities considerably, and the maximum value for the tenacity was found for the blend containing 10 wt % compatibilizer. Here, a 62% increase of the tenacity was noticed. The increase in the tenacity by the addition of compatibilizer is obvious. The compatibilization effect between CD-PET and PP-*graft*-MA was based on the reaction between $-\text{OH}$ groups of CD-PET and MA groups in PP-*graft*-MA.^{21,22}

Dye exhaustions of the fabrics of CD-PET series fibers

Plain weave fabrics (200 g/m²) were produced using the CD-PET series fibers which included conventional CD-PET fibers, CD-PET microfibers and *m*-iPP

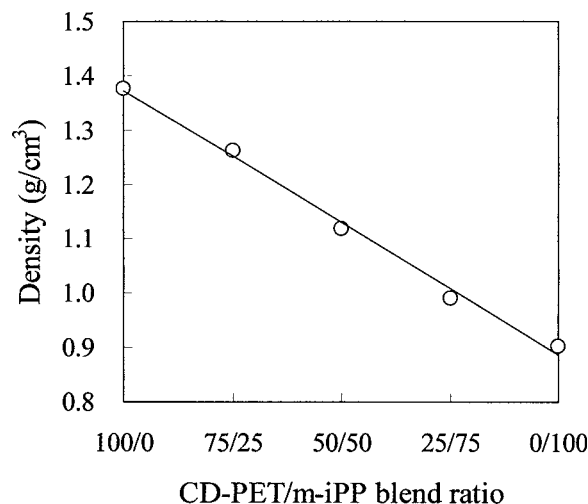


Figure 9 Relation between the densities and blend ratio of CD-PET/*m*-iPP-conjugated fibers.

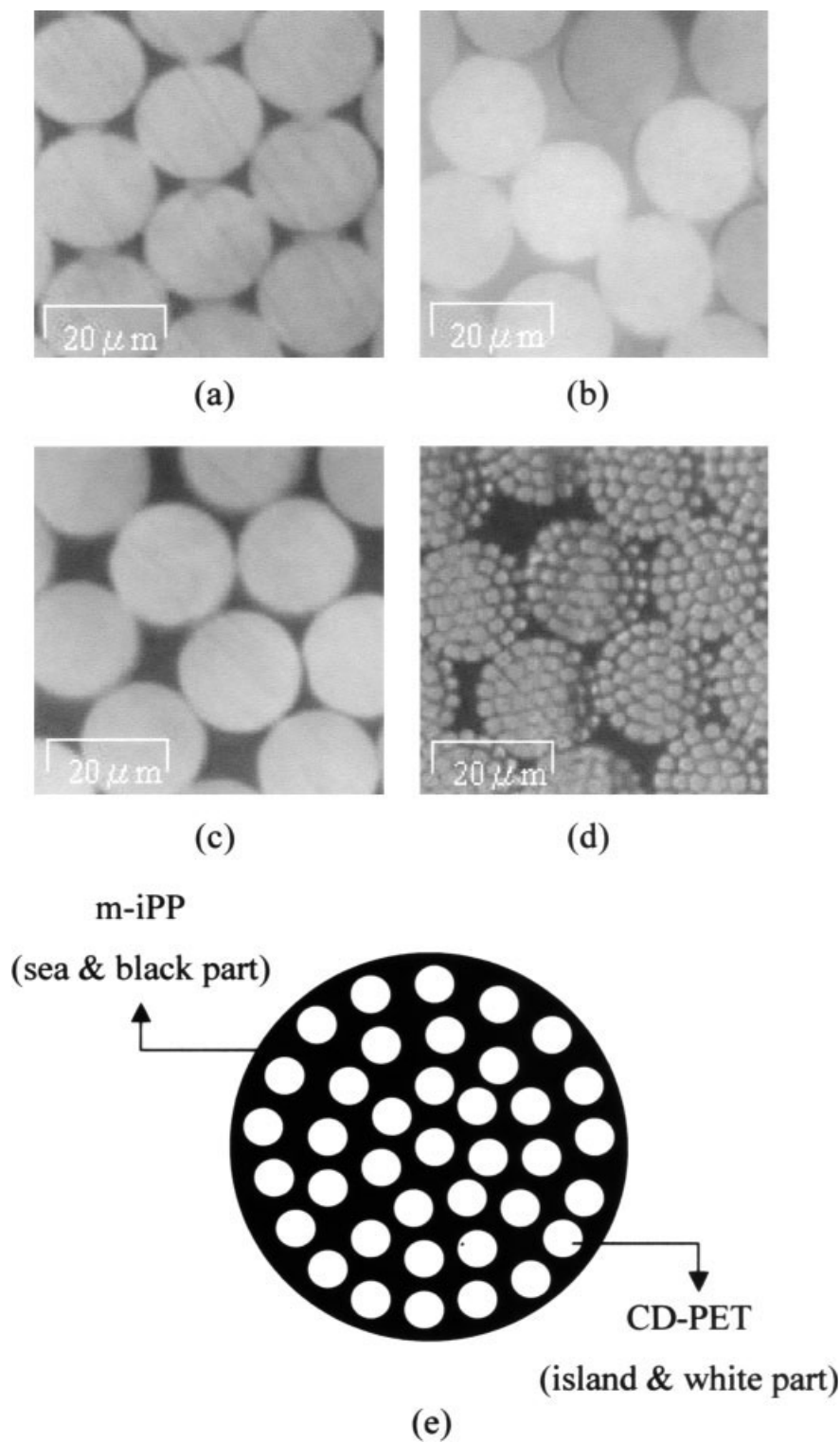


Figure 10 Morphologies of CD-PET, *m*-iPP, and CD-PET/*m*-iPP-conjugated fibers. (a) Pure CD-PET, (b) Pure *m*-iPP, (c) 75/25 CD-PET (island)/*m*-iPP (sea)—before paraffin oil solvent treatment, (d) 75/25 CD-PET (island)/*m*-iPP (sea)—after paraffin oil solvent treatment, (e) Model of 75/25 CD-PET (island)/*m*-iPP (sea)-conjugated fibers.

colored fibers (*m*-iPP fiber covered with CD-PET polymer). The specifications of CD-PET series fibers were 75 denier/24 filament. Conventional CD-PET fibers and *m*-iPP colored fibers could be directly

used in the weaving process. Nevertheless, the process of the fabric of CD-PET microfibers was first weaving and then the *m*-iPP polymer was removed using paraffin oil solvent. The dpf of conventional

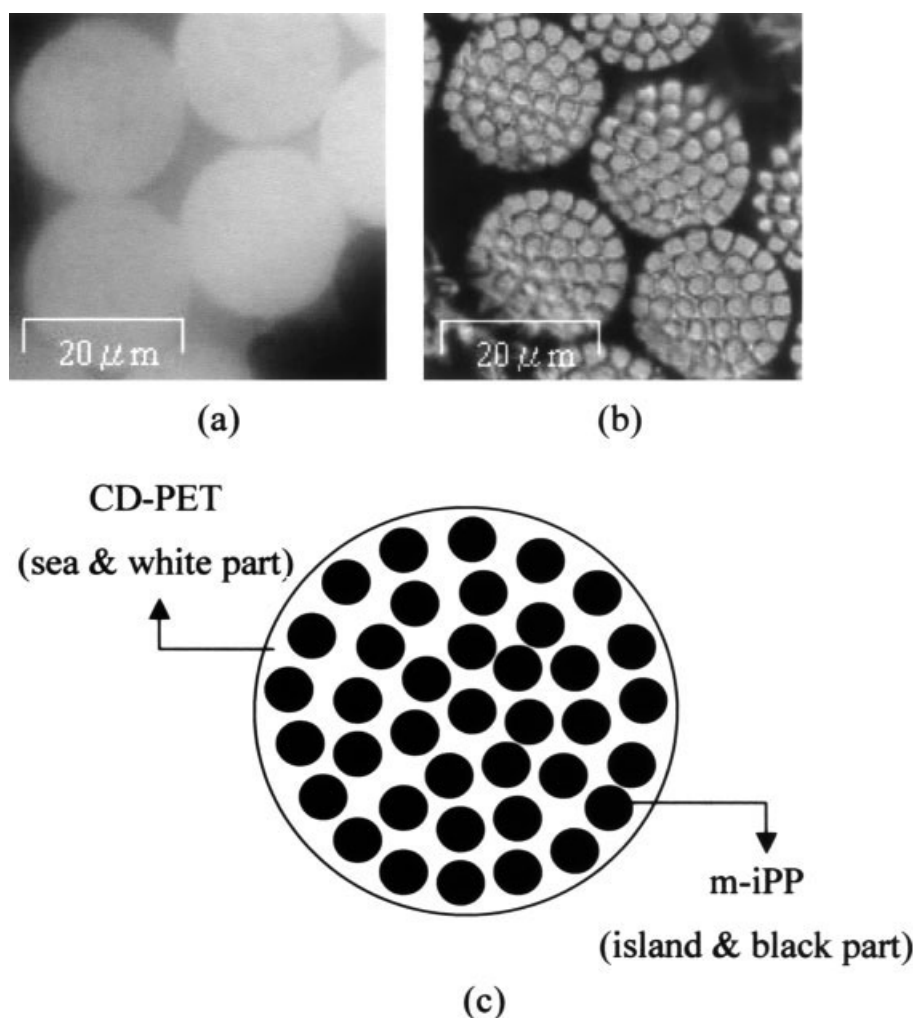


Figure 11 Morphologies of *m*-iPP/CD-PET conjugated fibers. (a) 75/25 *m*-iPP (island)/CD-PET (sea)—before HFIP solvent treatment, (b) 75/25 *m*-iPP (island)/CD-PET (sea)—after HFIP solvent treatment, (c) Model of 75/25 *m*-iPP (island)/CD-PET (sea)-conjugated fibers.

CD-PET fibers/or *m*-iPP colored fibers was approximate 3.13. However, the dpf of CD-PET microfibers was approximate 0.05–0.06 after paraffin oil treatment. Notably, the dpf of CD-PET microfibers was clearly lower than that of conventional CD-PET fibers/or *m*-iPP colored fibers. Additionally, CD-PET polymer content was 25% in *m*-iPP colored fibers. From the above discussion, the dye exhaustion with dyeing time of various CD-PET fabrics was studied next. The discussion about crystallinities of CD-PET- and *m*-iPP-conjugated fibers could be improved by the skin effect concept that related the ease of the dye to enter the fiber when the wall is less crystalline with the more intense color of dyed fiber.

Figure 13(a) displays the relation between the dye exhaustion with dyeing time of various CD-PET fabrics at the same dyeing condition (1% owf basic dyes at 100°C). The dye exhaustions of various fabrics followed the order: *m*-iPP colored fibers > conventional

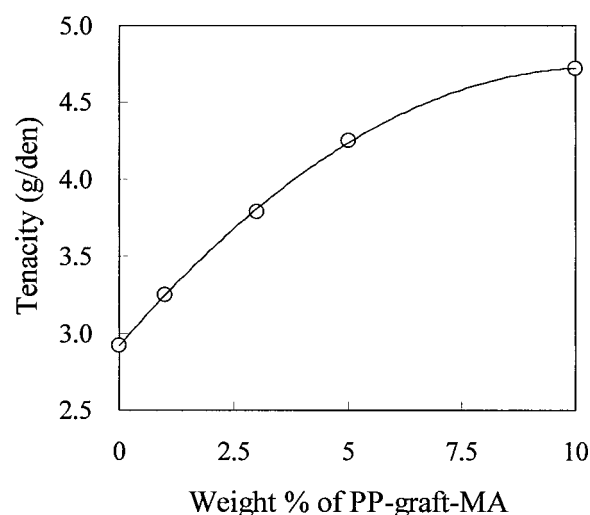


Figure 12 Effect of concentration (0, 1, 3, 5, and 10 wt %) of PP-graft-MA on the tenacities of 75/25 *m*-iPP (island)/CD-PET (sea)-conjugated fibers.

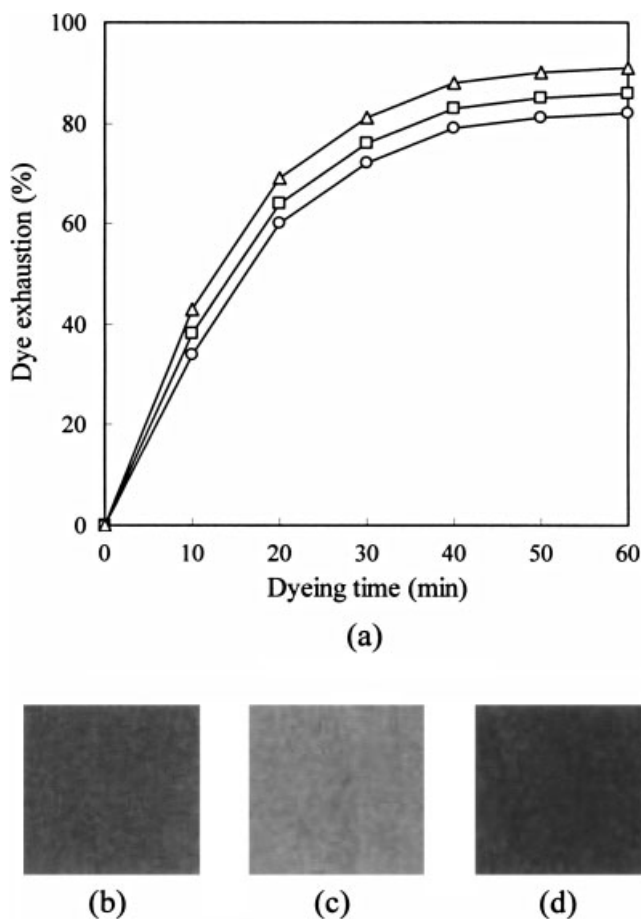


Figure 13 Relation between the dye exhaustion with dyeing time of various CD-PET fabrics at the same dyeing condition. (a) Dye exhaustion of various CD-PET fabrics with 1% owf disperse dyes at 100°C (C.I. Basic Blue 1) (□): conventional CD-PET fibers, (○): CD-PET microfibers, (△): *m*-iPP colored fibers, (b) Color and luster of the fabric for CD-PET microfibers, (c) Color and luster of the fabric for *m*-iPP colored fibers

CD-PET fibers > CD-PET microfibers. Though conventional CD-PET fibers and *m*-iPP colored fibers possessed the same dpf (~ 3.13), CD-PET content of *m*-iPP colored fibers was only 25%. At the same dyeing condition, the dye exhaustion of *m*-iPP colored fibers was higher than that of conventional CD-PET fibers. In addition, the dpf of CD-PET microfibers was obviously lower than that of conventional CD-PET fibers. Consequently, the dye exhaustion of CD-PET microfibers was lower than that of conventional CD-PET fibers. Figure 13(b-d) reveals the dyeing color of various CD-PET fabrics at the same dyeing condition. Luster depth of various fabrics followed the order: *m*-iPP colored fibers > conventional CD-PET fibers > CD-PET microfibers. The experimental results for the colored depth of various CD-PET fabrics were consistent with the dye exhaustion with dyeing time of various CD-PET fabrics.

CONCLUSIONS

The experimental results of the DSC indicated CD-PET and *m*-iPP molecules easily formed individual domains in CD-PET/*m*-iPP-conjugated fibers. The tenacities of CD-PET/*m*-iPP-conjugated fibers declined initially and then increased with the proportion of *m*-iPP. Notably, the 50/50 CD-PET/*m*-iPP blend displayed a minimum tenacity. The experimental crystallinities and densities of CD-PET/*m*-iPP-conjugated fibers agree fairly well with the calculated theoretical values. The morphological result could infer that CD-PET and *m*-iPP could be divided into two parts. From thermal behavior, crystallinity, mechanical property, density measurement, and the morphological observation of CD-PET/*m*-iPP-conjugated fiber, CD-PET/*m*-iPP polymers were identified to be partially miscible. CD-PET microfibers were successfully produced with enhanced diameters (from 2.2 to 2.5 μm) was clearly observed. *M*-iPP colored fibers were also successfully prepared in this study. Meanwhile, the presence of PP-*graft*-MA compatibilizer improved the tenacity considerably. Blends with 10 wt % compatibilizer exhibited maximum improvement in the tenacity. The dye exhaustions of various fabrics followed the order: *m*-iPP colored fibers > conventional CD-PET fibers > CD-PET microfibers.

References

- Clerck, K. D.; Rahier, H.; Mele, B. V.; Kiekens, P. *J Appl Polym Sci* 2003, 89, 3840.
- Hsiao, K. J.; Jen, Z. H.; Lu, C. L. *J Appl Polym Sci* 2002, 86, 3601.
- Hsiao, K. J.; Jen, Z. H.; Yang, J. C.; Chen, L. T. *J Polym Res* 2002, 9, 53.
- Hsiao, K.; Shu, Y. C.; Tsen, W. C. *J Polym Res* 2003, 10, 161.
- Hsiao, K.; Tsen, W. C.; Shu, Y. C. *J Appl Polym Sci* 2004, 91, 1710.
- Tsen, W. C.; Shu, Y. C.; Hsiao, K.; Jen, Z. H. *J Polym Res* 2004, 11, 189.
- Hsiao, K. J.; Kuo, J. L.; Tang, J. W.; Chen, L. T. *J Appl Polym Sci* 2005, 98, 550.
- Tsen, W. C.; Shu, Y. C.; Hsiao, K. *Polym Compos* 2006, 14, 107.
- Steinkamp, R. A.; Grail, T. J. U.S. Pat. 3,862,265 (1975).
- Mosleh, S.; Gawish, S. M.; Khalil, F. H.; Bieniek, R. F. *J Appl Polym Sci* 2005, 98, 2373.
- Barlow, J. W.; Paul, D. R. *Polym Eng Sci* 1981, 21, 985.
- Kunugi, T.; Suzuki, A.; Hashimoto, M. *J Appl Polym Sci* 1981, 26, 1951.
- Wunderlich, B. *J Therm Anal* 1990, 424.
- Godshall, D.; White, C.; Wilks, G. L. *J Appl Polym Sci* 2001, 80, 130.
- Utracki, L. A. *Polym Eng Sci* 1983, 23, 602.
- Han, C. D.; Kim, Y. W. *J Appl Polym Sci* 1975, 19, 2831.
- Shin, C. K. *Polym Eng Sci* 1976, 16, 742.
- Patterson, D. D. *Polym Eng Sci* 1982, 22, 64.
- Chui, Z.; Wang, Y.; Qian, G.; Wu, Z. *J Chin Text Univ* 1988, 14, 16.
- Pal, S. K.; Gandhi, R. S.; Kothari, V. K. *J Appl Polym Sci* 1996, 61, 401.
- Oromiehie, A.; Mamizadeh, A. *Polym Int* 2004, 53, 728.
- Tanrattanakul, V.; Hiltner, A.; Baer, E.; Perkins, W. G.; Massey, F. L.; Moet, A. *Polymer* 1997, 38, 4117.