

Physical Properties of Polycapraamide/Cationic Dyeable Poly(ethylene terephthalate) Polyblended Fibers

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ABSTRACT: Polycapraamide (PCA) and cationic dyeable poly(ethylene terephthalate) (CDP) polymers were blended mechanically (in ratios of 75/25, 50/50, and 25/75) in a melt twin-screw extruder to prepare three PCA/CDP polyblended materials. The blends of PCA and CDP were spun into fibers. The molar ratio of dimethyl 5-sulfoisophthalate sodium salt for CDP was 2%. This study investigated the physical properties of PCA/CDP polyblended fibers with nuclear magnetic resonance, gel permeation chromatography, gas chromatography, potentiometer, differential scanning calorimetry (DSC), thermogravimetric analysis, scanning electron microscopy (SEM), extension stress-strain

measurements, density gradient analysis, and rheometry. The experimental results of DSC proved that PCA and CDP formed an immiscible system. In an SEM image of a 50/50 PCA/CDP blend, the morphological aggregation of a larger size, from 3 to 5 μm in diameter, was observed. The rheological behavior of the PCA/CDP polyblended materials exhibited negative-deviation blends, and the 50/50 blend of the PCA/CDP polyblended fibers showed a minimum tenacity value. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1710–1715, 2004

Key words: rheology; miscibility; morphology

INTRODUCTION

To extend the possible applications of polymers, more and more polymer blends and composites are being produced. Polymer blends are mixtures of two or more polymers that can either mix completely on a molecular scale or form a two-phase structure. Polymer blends can exhibit new combinations of properties that depend on the properties of their components and strongly on the morphology of the blended materials. The morphology resulting from a blending process depends mainly on the rheological and interfacial properties of the molten components, the blending conditions, and the weight ratio of the blended polymers.^{1–3} Polymer blends can be characterized by their phase behavior as being either miscible or immiscible. The thermal, mechanical, and rheological properties and the degree of phase separation of a polymer blend depend strongly on its miscibility.⁴

The thermodynamic principles of polymer–polymer miscibility and methods for determining polymer–polymer miscibility have been studied.^{5–7} The homogeneity of a polymer–polymer mixture, because of its very high viscosity in the molten state and its very slow rate of diffusion, depends very much on the methods of preparation and the time and temperature

to which the mixture is subjected. In dispersed multiphase polymeric systems, there are many interrelated variables that affect the ultimate physical properties of the finished product. For instance, the method of preparation controls the morphology of a mixture, which, in turn, controls the rheological properties of the mixture. However, the rheological properties strongly dictate the choice of the processing conditions, which, in turn, strongly influence the morphology and, therefore, the ultimate physical properties of the finished product.

There have been some reports on the miscibility of polycapraamide (PCA) with other polymers such as poly(ethylene terephthalate),^{8,9} poly(butylene terephthalate),¹⁰ polyethylene,^{11,12} and polypropylene.^{13,14} Because PCA and cationic dyeable poly(ethylene terephthalate) (CDP) possess amide ($-\text{NHCO}-$) and dimethyl 5-sulfoisophthalate sodium salt (SIPM; $-\text{SO}_3\text{Na}$) functional groups, respectively,^{15–17} the interfacial interactions play a critical role for PCA/CDP polyblended materials. In this study, we have thoroughly investigated the compatibility behavior and physical properties of polyblended fibers of PCA and CDP.

EXPERIMENTAL

Materials and spinning conditions

The PCA chips were kindly donated by LiPeng Enterprise Co., Ltd. (Taiwan, China), and the CDP chips were obtained from Shingkong Synthetic Fibers Corp.

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TABLE I
Characteristics of PCA and CDP Chips

Code	SIPM (mol %)	$[\eta]^a$ (dL/g)	\bar{M}_w (g/mol)	\bar{M}_w/\bar{M}_n	DEG (%)	R—COOH (mequiv/kg)	T_m (°C)	T_d^b (°C)
PCA ^c	0	—	32,221	2.31	—	—	220.6	324
CDP	2.06	0.48	31,453	2.24	1.97	43.1	244.5	381

\bar{M}_w = weight-average molecular weight; \bar{M}_n = number-average molecular weight.

^a Intrinsic viscosity of the CDP polymer was obtained by a mixed solution of 0.5 g/dL in phenol/tetrachloroethane (60/40) at 30°C.

^b Degradation temperature.

^c Relative viscosity (RV) of the PCA polymer was obtained by a solution of 1.0 g/dL in 85% formic acid at 20°C. RV of the PCA polymer was 2.4.

(Taiwan). Table I lists the synthetic characteristics of PCA and CDP. PCA and CDP were blended mechanically in ratios of 75/25, 50/50, and 25/75 in a melt twin-screw extruder for the preparation of three PCA/CDP polyblended materials. Before the blending, PCA was dried for 24 h at 90°C, and CDP was dried for the same period but at 130°C. Melt spinning was carried out with a capillary rheometer. Undrawn yarns (UDYs) were extruded at two different temperature: 260°C for PCA and 285°C for PCA/CDP polyblended materials and CDP at a constant winding speed of 600 m/min. UDYs that were extruded through a die with a diameter of 0.6 mm were taken up. Then, UDYs were drawn to 2.5 times their original length to form fully oriented yarns (FOYs) with a drawn-winder machine. The draw temperature and take-up speed were 120°C and 200 m/min, respectively. The specification for FOYs was 30 den/10 filaments.

5890 AII gas chromatograph and a KEM AT-400 potentiometric automatic titrator, respectively. The differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements of the samples were made with a PerkinElmer Pyrix 1 instrument. 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 the DSC measurements. The heating rate of the TGA measurements was 10°C/min from 30 to 600°C. The densities of the samples were measured at 25°C by a density gradient method with toluene/carbon tetrachloride mixtures. The melt viscosities of the samples were measured with a capillary rheometer, and the length-to-diameter ratio of the capillary was 5. Scanning electron microscopy (SEM) images were acquired with a JEOL 200CX instrument. All stress-strain data for the samples were obtained on a Zwick 1511 Instron instrument at an extension rate of 500 mm/min.

Measurements

The relative viscosity of the PCA chips was obtained with a 1.0 g/dL solution in 85% formic acid at 20°C. The intrinsic viscosity of the CDP chips was obtained with a 0.5 g/dL mixed solution in phenol/tetrachloroethane (60/40) at 30°C. The SIPM content of CDP was obtained with a Bruker AM-400 nuclear magnetic resonance spectrometer. Gel permeation chromatography data were measured with a Waters model 510 instrument. The diethylene glycol (DEG) and carboxyl end group (R—COOH) contents of CDP were measured with an HP

RESULTS AND DISCUSSION

Thermal properties

Table II and Figure 1 display the thermal properties of PCA, CDP, and three PCA/CDP polyblended fibers. During the DSC heating process, the endothermic peaks of PCA and CDP fibers occurred at 221.7 and 252.3°C, respectively. The endothermic peak [melting temperature (T_m)] was due to the melting of the samples. The T_m values of PCA and CDP fibers are compared with those of PCA and CDP chips in Tables I

TABLE II
Thermal Properties of Polyblended Fibers of PCA with CDP

PCA/CDP blend ratio	Heating process				Cooling process			
	T_{m1} (°C)	ΔH_{m1} (J/g)	T_{m2} (°C)	ΔH_{m2} (J/g)	T_{cc1} (°C)	ΔH_{cc1} (J/g)	T_{cc2} (°C)	ΔH_{cc2} (J/g)
100/0	221.7	70.1	—	—	184.8	62.7	—	—
75/25	221.2	50.6	251.9	12.1	185.2	49.0	197.4	11.9
50/50	221.5	38.1	252.0	25.3	184.5	29.4	196.9	19.7
25/75	221.9	17.6	251.8	40.4	185.9	15.7	197.3	31.6
0/100	—	—	252.3	52.6	—	—	196.6	39.5

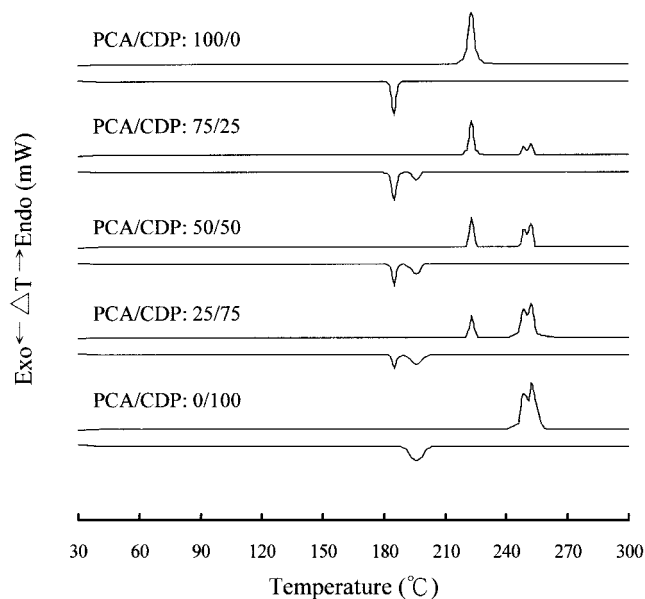


Figure 1 DSC curves of PCA/CDP polyblended fibers.

and II. Because of the influence of the orientation and crystallization, the T_m values of PCA and CDP fibers were obviously higher than those of PCA and CDP chips. However, a double endothermic peak was observed for the CDP fibers, and only a single melting peak was obtained for the PCA fibers. The reason for the double endothermic peak for the CDP fibers was that the large $-\text{SO}_3\text{Na}$ side group in CDP prevented the chain molecules from crystallizing close to one another and forming two crystalline particles. The experimental phenomenon resembled the observation of Pal and coworkers^{18,19} for polyester fibers. Usually, T_m of PCA fibers is noted to be 215–222°C.^{20–22} This DSC curve showed only a melting endothermic peak, indicating that the PCA fibers were originally crystalline. The endothermic peak of 221.7°C corresponded to the α phase of the PCA fibers.^{23,24} In the DSC cooling process, the exothermic peaks of the PCA and CDP fibers occurred at 184.8 and 196.6°C, respectively. The exothermic peak (the T_{cc} point) was due to the recrystallization behavior of the melting polymer. Because of the effect of a $-\text{SO}_3\text{Na}$ side group on the polymer, the thermal behavior of PCA/CDP polyblended fibers resembled that of the CDP fibers.

For all PCA/CDP polyblended fibers, T_m of PCA molecules (T_{m1}) nearly did not change and appeared around 221.7°C. Additionally, T_m of CDP molecules (T_{m2}) also did not noticeably shift and appeared at 252.3°C. In other words, the T_m change was independent of the blend ratio. Figure 2 displays the linear variations of the heat of fusion (ΔH_m) with the blend ratio of PCA/CDP polyblended fibers. ΔH_m of PCA molecules (ΔH_{m1}) proportionally decreased with an increasing CDP content. Meanwhile, ΔH_m of CDP mol-

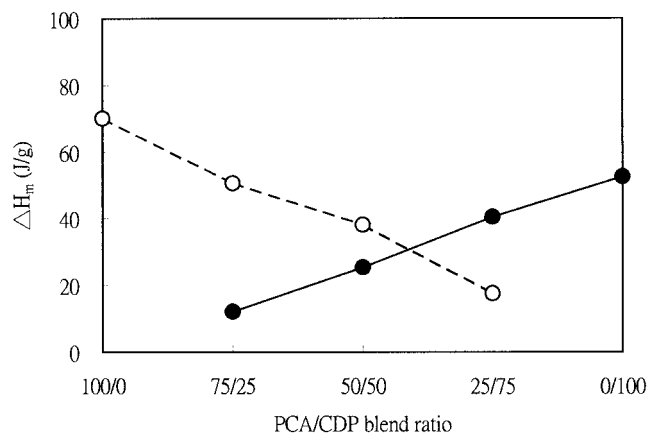


Figure 2 Relationship between ΔH_m and the blend ratio of PCA/CDP polyblended fibers: (○) PCA and (●) CDP.

ecules (ΔH_{m2}) proportionally increased with an increasing CDP content. For all PCA/CDP polyblended fibers, the T_{cc} point of PCA molecules (T_{cc1}) also nearly did not change and appeared around 184.8°C. The T_{cc} point of CDP molecules (T_{cc2}) was observed around 196.1°C. Figure 3 displays the linear variations of the recrystallization heat of the exothermic peak (ΔH_{cc}) with the blend ratios of PCA/CDP polyblended fibers. ΔH_{cc} of PCA molecules (ΔH_{cc1}) proportionally decreased with an increasing CDP content. Meanwhile, ΔH_{cc} of CDP molecules (ΔH_{cc2}) proportionally increased with an increasing CDP content. The DSC experimental results indicated that PCA and CDP molecules easily formed individual domains.

Rheology

Figure 4 shows the melt viscosity of PCA and CDP at 260°C with the shear rate. From 1000 to 20,000 s^{-1} , all the polymers exhibited the pseudoplastic flow behav-

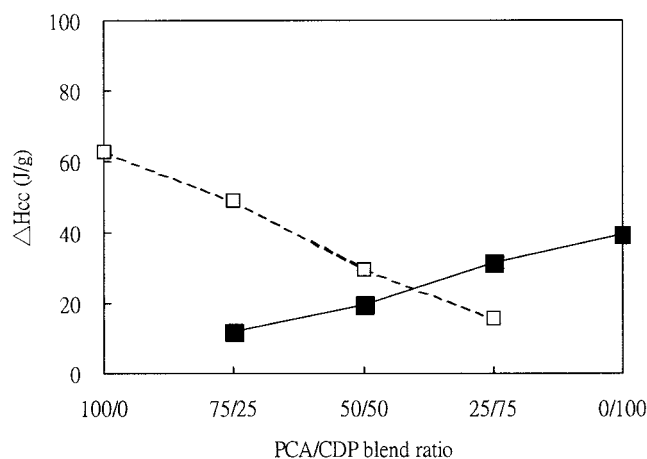


Figure 3 Relationship between ΔH_{cc} and the blend ratio of PCA/CDP polyblended fibers: (□) PCA and (■) CDP.

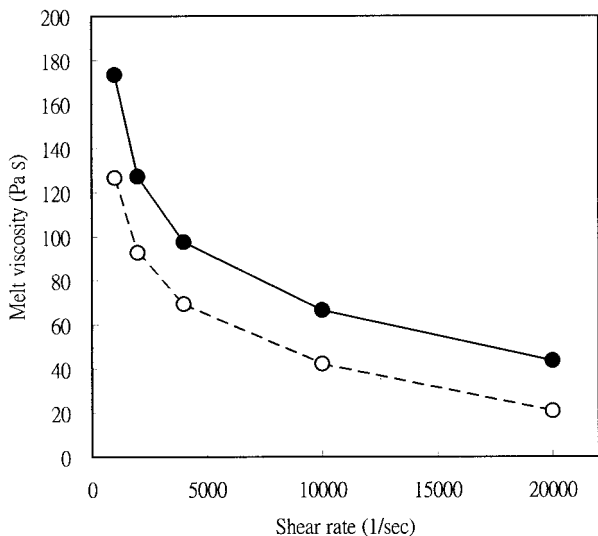


Figure 4 Relationship between the melt viscosity and the shear rate for PCA and CDP polymers at 260°C: (○) PCA and (●) CDP.

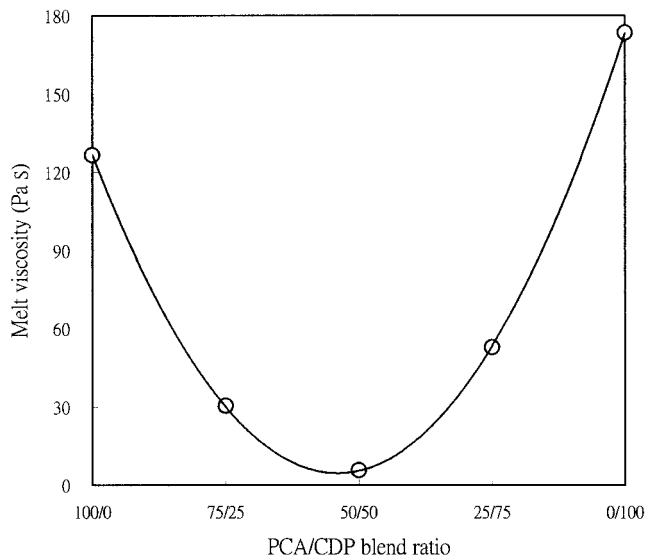


Figure 6 Relationship between the melt viscosity and the blend ratio of PCA/CDP polyblended materials at 260°C and the 1000-s⁻¹ condition.

ior of a non-Newtonian viscoelastic liquid. The rheological curves indicated that the melt viscosity of PCA was lower than that of CDP over the entire shear rate range. Figure 5 displays the melt viscosities of three PCA/CDP polyblended materials at 260°C with the shear rate. The melt viscosities of the PCA/CDP polyblended materials also exhibited the pseudoplastic flow behavior of a non-Newtonian viscoelastic liquid. This tendency was independent of the blend ratio. Under the same rheological conditions, the melt viscosities of the PCA/CDP polyblended materials were in the following order: 25/75 PCA/CDP > 75/25 PCA/CDP > 50/50 PCA/CDP. Figure 6 shows that the melt vis-

cosities of the PCA/CDP polyblended materials exhibited negative-deviation blends (NDBs).²⁵⁻²⁹ Notably, the 50/50 PCA/CDP blend showed a lower value of the melt viscosity than that predicted by the additivity rule at 260°C and the 1000-s⁻¹ condition. The experimental rheological results indicated poor interfacial interactions between PCA and CDP.

Mechanical properties

Figure 7 shows the relationship between the tenacity and blend ratio of PCA/CDP polyblended fibers. The

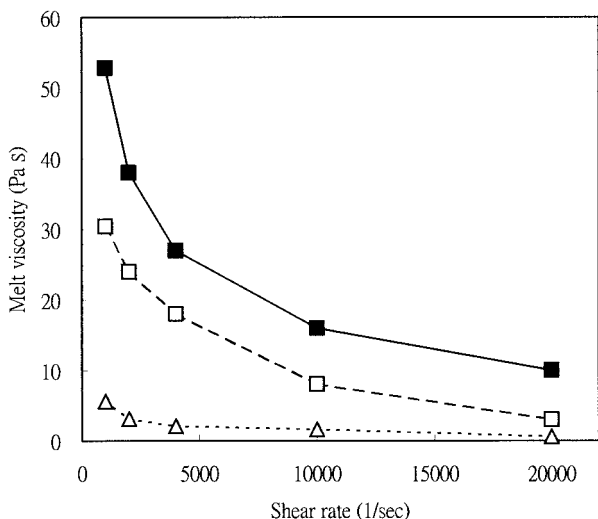


Figure 5 Relationship between the melt viscosity and the shear rate for PCA/CDP polyblended fibers at 260°C: (□) 75/25, (△) 50/50, and (■) 25/75 PCA/CDP.

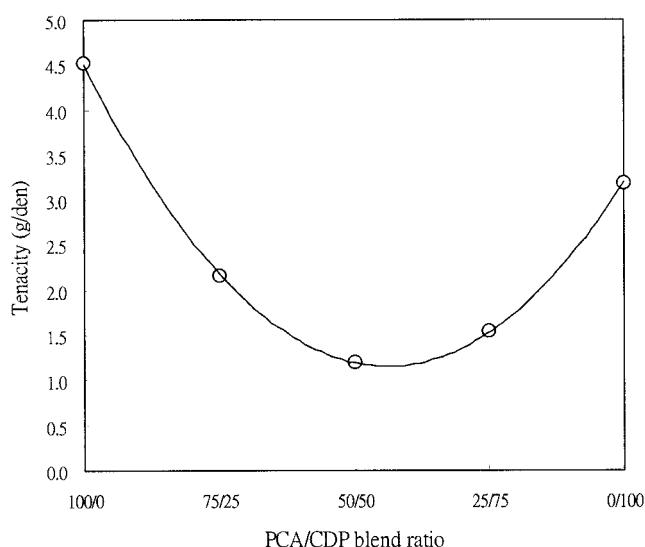


Figure 7 Relationship between the tenacity and the blend ratio of PCA/CDP polyblended fibers.

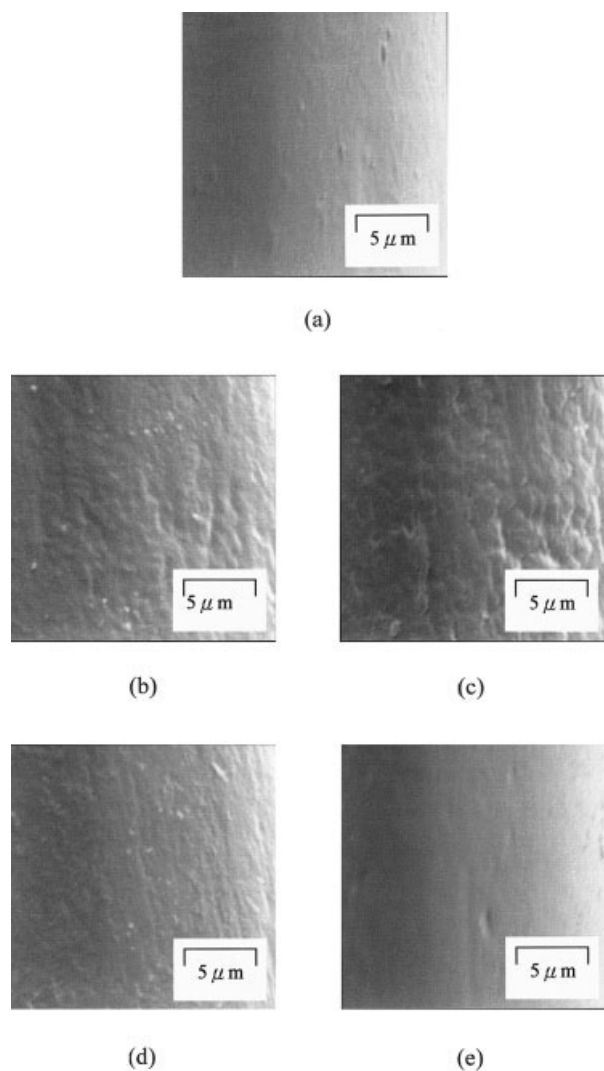


Figure 8 SEM observations of PCA/CDP polyblended fibers with various blend ratios: (a) 100/0, (b) 75/25, (c) 50/50, (d) 25/75, and (e) 0/100 PCA/CDP.

mechanical properties of the PCA/CDP polyblended fibers decreased initially and then increased with the proportion of CDP. Obviously, the 50/50 PCA/CDP blend showed a minimum value. The combination of amide and SIPM functional groups was originally expected to produce good interfacial interactions between the PCA and CDP molecular chains. The poor interfacial interactions between PCA and CDP indicated poor mechanical properties. The tendency agreed with the rheological behavior, and the 50/50 PCA/CDP blend showed a minimum tenacity value. As shown in Figure 8, PCA had a uniform surface structure, but the blends exhibited a granular structure as the amount of CDP increased. The granular structure increased initially and then decreased as the content of CDP increased. When the blend ratio of PCA to CDP was 50/50, the morphological aggregation of a larger size, from 3 to 5 μm in diameter, was

found. The observations of SEM pictures agreed with the results for the mechanical properties.

Density measurements

Figure 9 shows the relationship between the densities and blend ratios of the PCA/CDP polyblended fibers. For all the PCA/CDP polyblended fibers, the experimental densities agreed fairly well with the calculated values. This implied that PCA and CDP formed an immiscible system. The experimental results for the densities were consistent with the thermal, rheological, and mechanical properties and the observations from SEM pictures of the PCA/CDP polyblended fibers.

CONCLUSIONS

The combination of amide functional groups in PCA with SIPM functional groups of CDP was originally expected to produce good interfacial interactions between the PCA polymer and CDP molecular chains. DSC experimental results indicated that the PCA polymer and CDP molecules easily formed individual domains. The rheological behavior of the PCA/CDP polyblended materials exhibited NDBs. In an SEM picture of a 50/50 PCA/CDP blend, the morphological aggregation of a larger size, from 3 to 5 μm in diameter, was observed. The poor interfacial interactions between PCA and CDP indicated poor mechanical properties. Additionally, the measured densities showed a linear variation with the blend ratios of the PCA/CDP polyblended fibers. This study proved that PCA and CDP formed an immiscible system and that

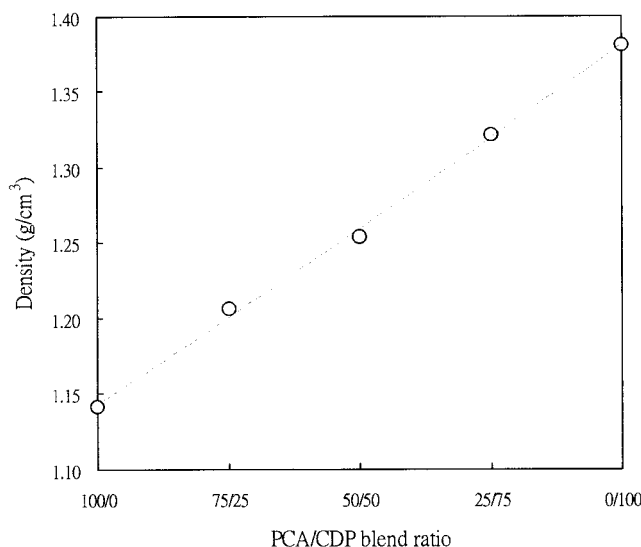


Figure 9 Relationship between the density and the blend ratio of PCA/CDP polyblended fibers: (—) calculated values and (○) experimental values.

50/50 PCA/CDP polyblended fibers showed a minimum tenacity value.

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