Ternary Blends of Poly(amide-6)/Polycarbonate/Poly(ε-caprolactone)

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SYNOPSIS

Blends of poly(amide-6) (PA) and poly(ε-caprolactone) (PCL) prepared by solution casting and screw extrusion have been investigated by differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). From the measured melting point (T_m) of the solution-cast PA/PCL blends, a T_m depression of the PA was observed for the investigated compositions. No T_m depression was found for the extruded PA/PCL blends, however. In the SEM study of the morphology of the solution-cast PA/PCL blends, phase separation was observed between the PA phase and the PCL phase for all blend compositions. For the extruded PA/PCL blends, however, more pronounced phase separation was observed for all blend compositions. Ternary blends of PA, PCL, and bisphenol-A polycarbonate (PC) have also been prepared by screw extrusion. From the study of morphology and extrudate swell of the PA/PC binary blends and the extruded PA/PC/PCL ternary blends, it appears that PCL could be used as a compatibilizer for the extruded PA/PC/PCL blends. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The blending of polyamides with various polymers has been a subject of recent interest.[1,2] In order to increase the toughness of polyamides, investigators have studied the blends of polyamides with ethylene propylene diene monomer (EPDM) rubber[3-6] or ethylene–propylene copolymer rubber.[7,8] Other polymer blends of polyamides that have been reported have contained poly(ethylene terephthalate) (PET),[9-11] polyethylene,[12-15] polystyrene,[14] amorphous aromatic polyamide,[16] poly(2-vinyl pyridine),[17] poly(acrylic acid),[18] poly(phenylene oxide),[19] poly(ethylene oxide),[20] bisphenol-A polycarbonate (PC),[21,22] poly(styrene-co-acrylonitrile) (SAN),[23] and poly(acrylonitrile–butadiene–styrene).[24]

For the blends of poly(ε-caprolactone) (PCL) with various polymers, many investigators have studied the blends with PC,[25,26] SAN,[27] poly(vinyl chloride),[28-31] chlorinated polyethylene[31,32] or polypropylene,[33] and Saran (a random copolymer of vinylidene chloride with vinyl chloride).[34] Most of these blends with PCL have been found to be miscible. For the blending of PCL with amorphous aromatic polyamide, Ellis has observed two glass-transition temperatures.[16] The blending of PCL and aliphatic poly(amide-6) (PA), however, has not been reported. For the blending of PC with various polymers, several papers have been reported for both miscible blends[25,26,35,36] and immiscible blends.[37-41]

PCL is known to have some unique properties such as a relatively low molecular weight and a carbonyl group in the repeating unit. The carbonyl oxygen in the PCL could be used for the formation of hydrogen bonding with hydrogen in the other polymer.[42] Hydrogen bonding is known to be one of the specific interactions useful in forming miscible polymer blends.[1] In a study of poly(amide-6,6) (PA-66) and PET by Pillon et al,[9] hydrogen bonding was

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found to contribute to the solution blending of the two polymers.

Recently, ternary polymer blends have been studied successfully by many investigators.[43-53] Ternary blends that have contained PCL include blends of PC/PCL/polyhydroxy ether of bisphenol-A and blends of PC/PCL/SAN that have been studied by Christiansen et al.[43] and Shah et al.,[44] respectively. For the above two blend systems,[43,44] PCL was used as a compatibilizing agent or polymeric solvent to form the miscible ternary blends.

In our present study, we examine the miscibility of the PA/PCL binary blends and the PA/PC/PCL ternary blends by determining experimentally the melting point (T_m), the glass-transition temperature (T_g), and the morphology of the blends.

EXPERIMENTAL

Polymers

The polymers used in this study were obtained from commercial sources. The characteristics and sources of the PA, PCL, and PC polymers are shown in Table I. The sample of PA was supplied by Polysciences, Inc., and the sample designated PCL 700 was supplied by Union Carbide Corp. The PC sample designated PC 101 was Lexan polycarbonate, supplied by General Electric Co.

Molecular weights for the PC were measured by gel permeation chromatography (GPC) at 25°C in tetrahydrofuran (THF). The T_g and specific heat increment (ΔC_p) at T_g were measured by differential scanning calorimetry (DSC), using procedures reported earlier.[38] 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP), used as solvent for the preparation of cast films of the PA/PCL blends, was purchased from Aldrich Chemical Co., Inc.
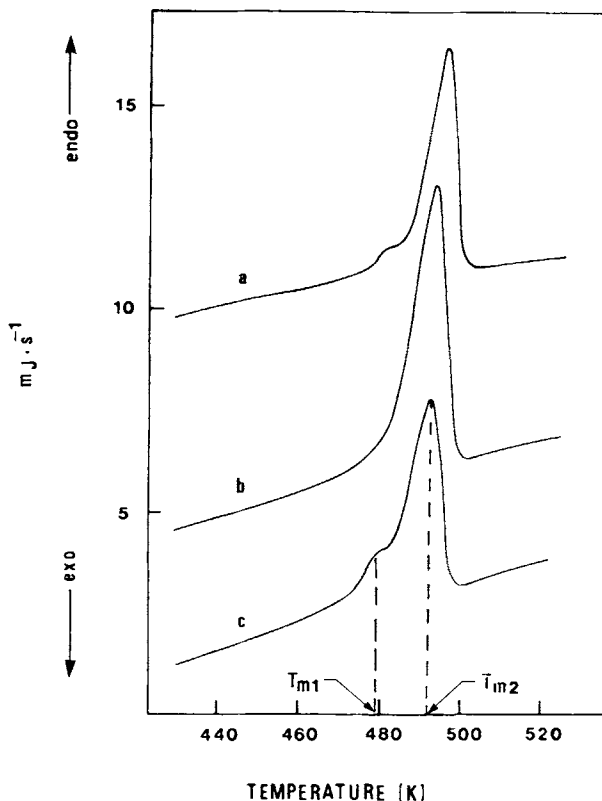

Figure 1 Thermograms showing the melting point (T_m) of PA in the second DSC heating curve for the PA/PCL blends by solution casting. Weight fractions of PA: (a) 1.00; (b) 0.90; (c) 0.80.

Blend Preparations

Blends were prepared by both solution casting and screw extrusion. For solution casting, PA and PCL mixtures with weight fractions of PA from 0.0 to 1.0 in 0.1 increments were dissolved in HFIP to form solutions with an overall concentration of 1.5 g/100

Table I   Characteristics of Polymers Used in This Study

Sample	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	T_m (K)[a]	T_g (K)[a]	ΔC_p (Jg^{-1}K^{-1})[a]
PA[b]	35,000[c]	—	2.0	493.4	322.2	—
PCL 700[d]	40,400[e]	15,500	2.61	333.7	221.1	0.095
PC 101[f]	29,000[g]	12,300	2.36	—	421.5	0.222

[a] Measured in our laboratory by DSC.
[b] Supplied by Polysciences, Inc.
[c] Data from supplier.
[d] Supplied by Union Carbide Corp.
[e] Data from ref. 26.
[f] Supplied by General Electric Co.
[g] Measured in our laboratory by GPC (ref. 38).

Table II   Melting Point (T_m) of PA and PCL in PA/PCL Solution-Cast Blends

	PA				PCL			
	First Heating[b]		Second Heating[c]		First Heating[b]		Second Heating[c]	
Blend[a]	T_{m_2} (K)	ΔT_{m_2}	T_{m_2} (K)	ΔT_{m_2}	T_m (K)	ΔT_m	T_m (K)	ΔT_m
1.00	494.0	0.0	493.4	0.0	—	—	—	—
0.90	492.2	1.8	491.8	1.6	—	—	—	—
0.80	492.9	1.1	491.8	1.6	—	—	—	—
0.70	492.4	1.6	491.3	2.1	—	—	—	—
0.60	491.8	2.2	491.0	2.4	339.6	0.9	332.8	0.9
0.50	491.9	2.1	491.2	2.2	340.2	0.3	333.3	0.4
0.40	491.7	2.3	490.0	2.5	340.3	0.2	333.1	0.6
0.30	—	—	—	—	340.2	0.3	333.0	0.7
0.20	—	—	—	—	339.7	0.8	333.2	0.5
0.10	—	—	—	—	340.2	0.3	333.4	0.3
0.00	—	—	—	—	340.5	0.0	333.7	0.0

[a] Blend composition given as weight fraction of PA in the PA/PCL blend.
[b] 20 K/min heating from 308 K to 523 K.
[c] 20 K/min heating from 308 K to 523 K followed by 320 K/min cooling to 308 K, rescanned at 20 K/min heating from 308 K to 523 K.

mL. Blends were cast on glass plates and all films were dried under vacuum for 7 days at room temperature. Cast film thickness was 20 ± 3 μm.

To prepare the melt-extruded blends, the PA and the PC were first dried in a vacuum oven at 80°C for 2 days. The PCL was dried similarly at 40°C. Blends of PA/PCL, PA/PC, PC/PCL, and PA/PC/PCL were prepared using a ½ in. (12.7 mm) diameter laboratory scale screw extruder, with a 27 : 1 length : diameter ratio.[40] The length : diameter ratio of the circular die was 19.0 with a diameter of 0.32 mm. Temperatures of the extruder were set at 230–250°C, in each zone (die, die head, and barrel zones) depending on blend composition.

DSC Measurements

The thermal properties of all samples were measured calorimetrically using a Perkin–Elmer DSC, Model DSC-7, with a Perkin–Elmer thermal analysis data station. The sample size was 3–10 mg depending on blend ratio. The sample was surrounded by a nitrogen atmosphere, and ice water was used for cooling. Blend samples were heated from 308 K to 523 K at a heating rate of 20 K min⁻¹ and a cooling rate of 320 K min⁻¹ a certain number of times under the same thermal regime. A temperature range of 173 K–373 K using liquid nitrogen cooling was used to

measure the T_g of PCL-rich compositions. In our experiments, the uncertainty in T_m was found to be about ±0.5 K for the blended polymers.

Scanning Electron Microscopy (SEM)

The morphology of the cross-section surface of the solution-cast films and the extrudates for all the blends was examined by scanning electron microscopy in a Cambridge Model 250-MK3 microscope and a JEOL Model JSM-840 microscope at 15 kV
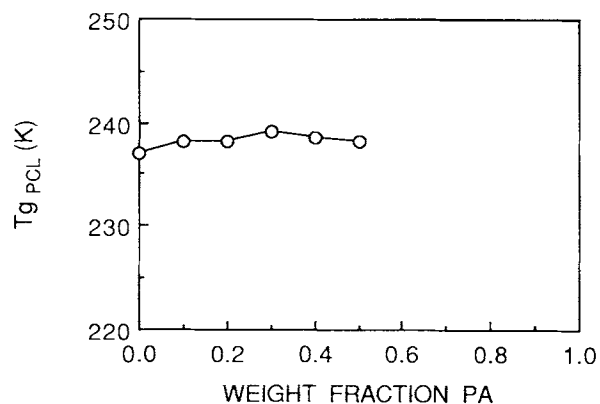

Figure 2   Effect of blend composition on the T_g(PCL) of the PA/PCL blends by solution casting.
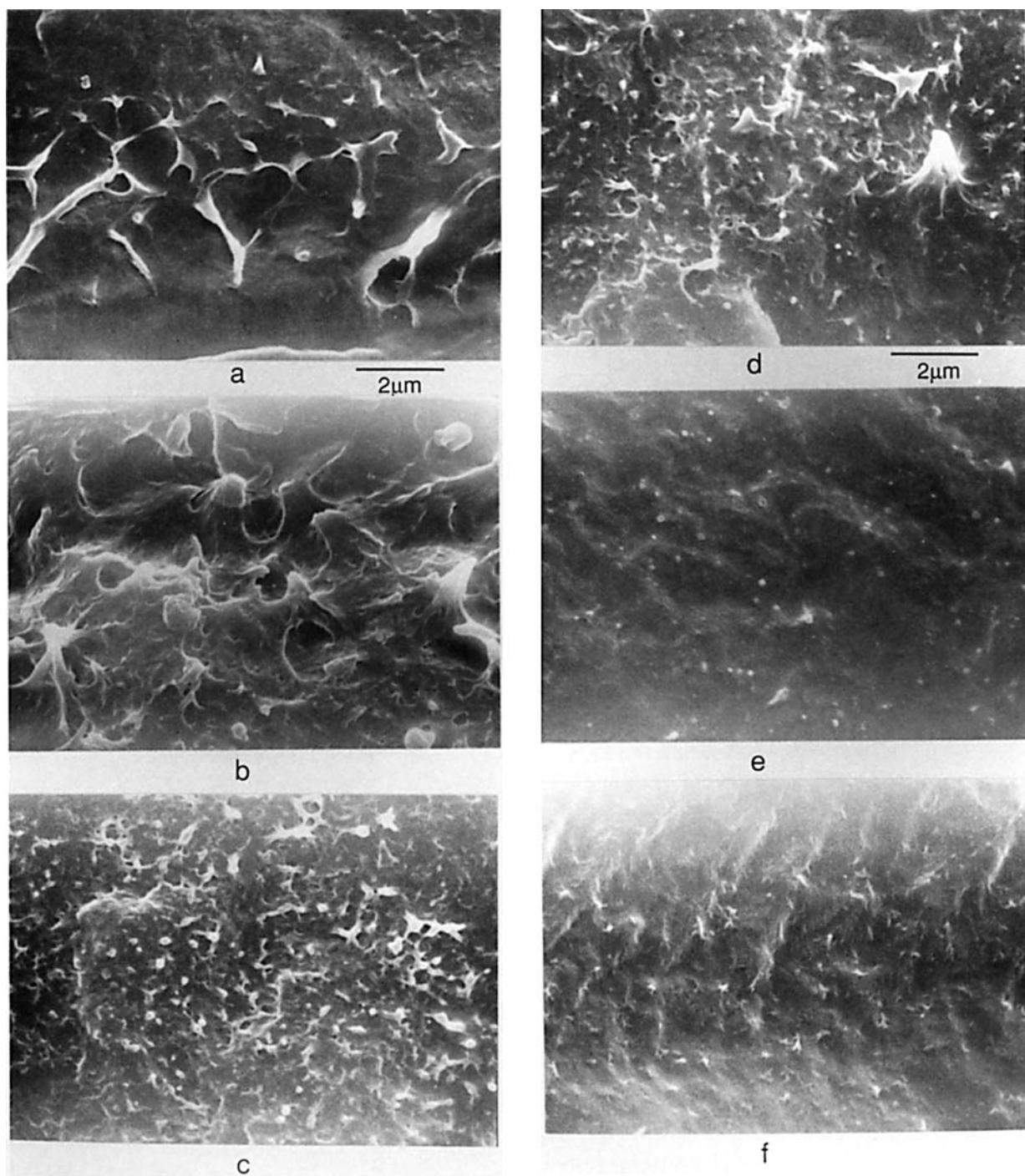
Figure 3   Scanning electron micrographs obtained from cryogenically fractured cross-section surfaces of solution-cast films of the PA/PCL blends. Weight fractions of PA: (a) 0.90; (b) 0.80; (c) 0.70; (d) 0.60; (e) 0.50; (f) 0.40; (g) 0.30; (h) 0.20; (i) 0.10.

accelerating voltage after gold sputter coating (50 nm). The fractured surfaces of both the cast films and the extrudates were prepared by cryogenic fracturing.

Measurement of Extrudate Swell

In order to measure the extrudate swell, the extruded round filament was air-quenched and collected in
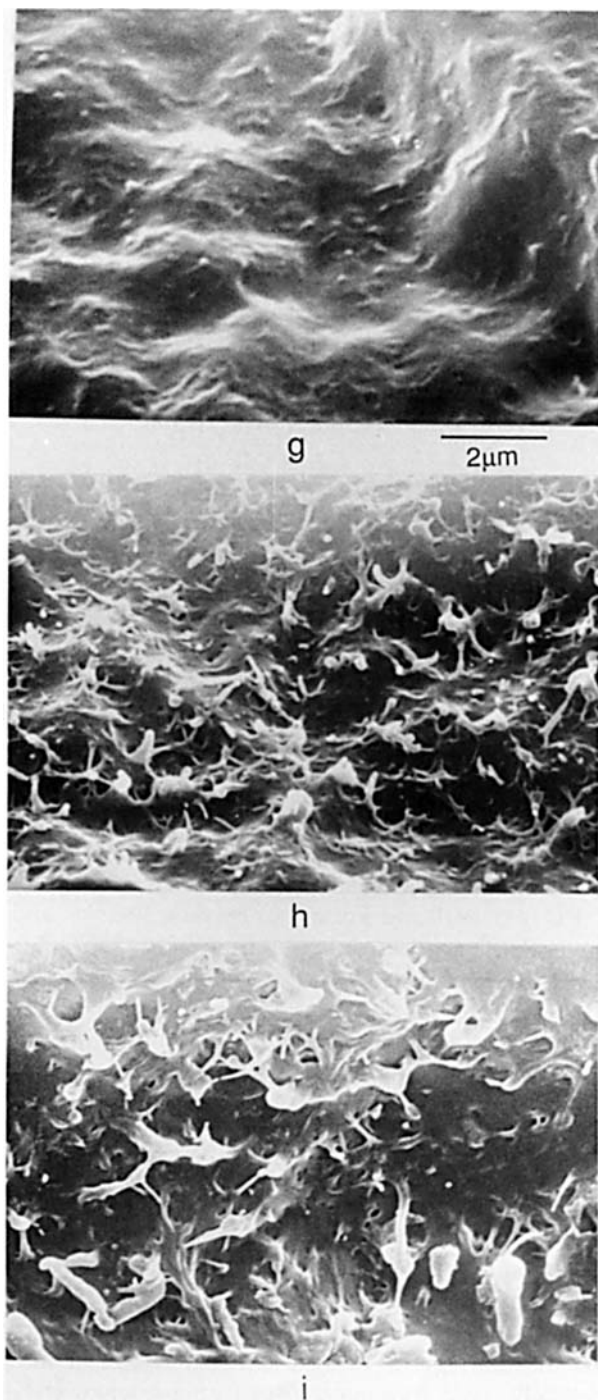
Figure 3   (*Continued from the previous page*)

lengths of about 10 cm. After standing at room temperature for more than 1 day, the extrudate diameter was measured with a micrometer at points around the circumference about 1 cm from the leading end of the sample. Extrudate swell was calculated as the ratio of the diameters of the extrudate and the capillary die.[40,54]

RESULTS AND DISCUSSION

Thermal Analysis of PA/PCL Blends

In Figure 1 the DSC curves of solution-cast blends of PA/PCL containing 1.0, 0.9, and 0.8 weight fractions of PA are presented. The second heating curve of the PA/PCL blends from 308 K to 523 K is shown. Two melting peaks at about 475 K and 490 K can be seen. The first melting peak (T_{m_1}) is slightly smaller than T_{m_2}. In the study of melting behavior using thermal analysis by Liberti and Wunderlich,[55] they also observed multiple melting peaks from PA crystallites grown from the melt or from solution. They interpret these multiple melting peaks to be caused by the reorganization or recrystallization of originally ill-crystallized polymer during heating. In our earlier study of blends of isotactic polystyrene and polybutadiene,[56] we also observed multiple melting peaks of isotactic polystyrene by DSC, and explained them in the same manner.

The T_m depressions of the PA and the PCL in the solution-cast PA/PCL blends from the first and second heating curves are presented in Table II. The T_m depression of the PA for the second heating is seen to be about 1.6–2.5 K over the composition range investigated. The T_m depressions of PA (ΔT_{m_2}) in the solution-cast PA/PCL blends are seen to have almost the same values after the first and second heatings. From Table II, we can see that the T_m depression of PCL is found to be from 0.3 K to 0.9 K, which is within the DSC measurement error range. We also measured T_m of the PA and the PCL in the extruded PA/PCL blends, but found no significant T_m depression for either component.

We could interpret the above results as the effect of the PCL component on the crystallization of the PA. The observed T_m depression could be accounted for on a kinetic basis as a thinning of the lamellae or a decreasing of the lateral crystal size of PA.[57]

The T_g of the PCL in solution-cast blends of PA and PCL which are rich in PCL are shown in Figure 2. The magnitude of the T_g(PCL) for compositions rich in PA was so small that the T_g(PCL) was hard to detect by DSC. From Figure 2, we can see that the T_g(PCL) has almost the same value over the investigated composition range. The T_g of PA was not detectable by DSC because of overlapping by the T_m of PCL. Thermal analysis of polymer blends has shown that a miscible polymer blend will exhibit a single T_g between the two T_g of the pure components. For partially miscible systems, the two T_g approach each other but do not become identical, as we demonstrated recently for polycarbonate and polystyrene blends.[38] From these results for PA/
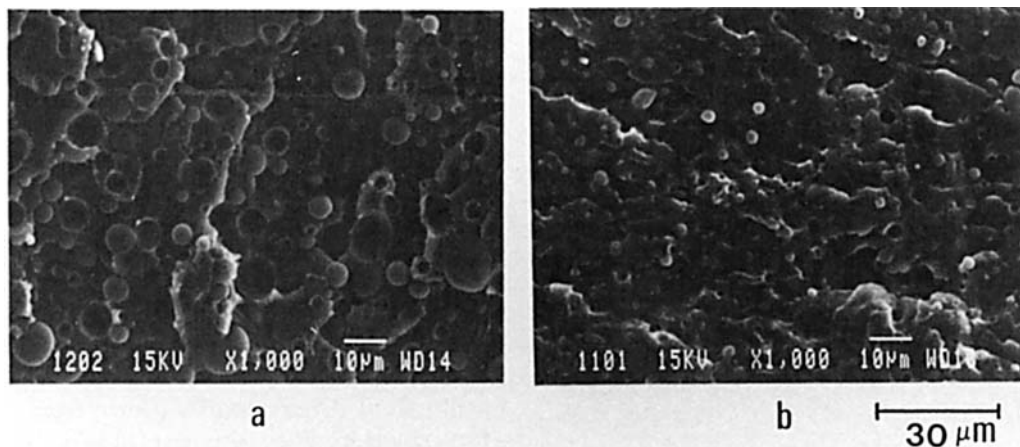
Figure 4   Scanning electron micrographs obtained from cryogenically fractured cross-section surfaces of the extrudates of the PA/PCL blends. Weight fractions of PA: (a) 0.20; (b) 0.10.

PCL blends it appears that the PA and PCL are immiscible.

SEM of PA/PCL Blends

The morphology of the PA/PCL blends prepared by solution casting and by extrusion was studied by SEM. Photomicrographs of cryogenically fractured cross-sectional surfaces of solution-cast blends of PA and PCL containing weight fractions of PA from 0.9 to 0.1 in 0.1 increments are shown in Figure 3. We can see a continuous phase and a dispersed phase of PCL crystallites for all blend compositions. From the micrograph study and the thermal analysis, it appears that PA/PCL is immiscible in the solution-cast blends. However, from the micrograph study, it appears that there is some increased compatibility in the 0.5, 0.4, and 0.3 weight fractions of PA in the PA/PCL blends.

Figure 4 shows photomicrographs of screw-extruded PA/PCL blends containing 0.2 and 0.1 weight fractions of PA. We can see phase separation between the PA phase and the PCL phase, indicating incompatibility for the extruded PA/PCL blends. In the other PA/PCL extruded blends, we also found phase separation between the PA and the PCL.

From Figures 3 and 4, we can see that the phase separation is more pronounced in the extruded blends than in the solution-cast blends. This may suggest that there is a slight increase in compatibility in the solution-cast blends.

SEM of PA/PC Blends and PA/PC/PCL Blends

The morphology of the extruded PA/PC blends and PA/PC/PCL blends was also studied by SEM. Fig-

ure 5 contains photomicrographs of the cryogenically fractured cross-sectional surfaces of the extrudates. Figures 5(a), (c), and (e) contain the micrographs of PA/PC blends containing 0.9, 0.3, and 0.1 weight fractions of PA, respectively. In Figures 5(b), (d), and (f) the micrographs of PA/PC/PCL blends are presented in which PA and PC are in the same ratio, and 10 parts of PCL are added per hundred parts of the PA/PC blends.

PC and PCL are known to be miscible,[25,26] and PA and PC are known to be immiscible.[21] In this experiment, we introduced the PCL to the PA/PC blends in order to investigate the morphology of the ternary PA/PC/PCL blends, and to observe whether the PCL has any compatibilitizing effect on the PA/PC blends.

Although PA and PC are incompatible in the extruded blends, we can see some improvement of compatibility between the PA phase and the PC phase after adding PCL to the PA/PC extruded blends in Figure 5. This phenomenon of increasing the compatibility is also observed in the extrudate swell of the PA/PC/PCL blends. In the study of the morphology of PA/PC blends, Heggs et al.[58] have observed a domain size decrease when PCL was added into the PA/PC blends, which suggest that PCL could act as a "processing aid" in the PA/PC blends.

Extrudate Swell of PA/PC Blends and PA/PC/PCL Blends

Figure 6 presents the variation of extrudate swell ratio with composition for PA/PC blends. The maximum extrudate swell ratio is reached at 0.5 weight fraction of PA. It should be kept in mind
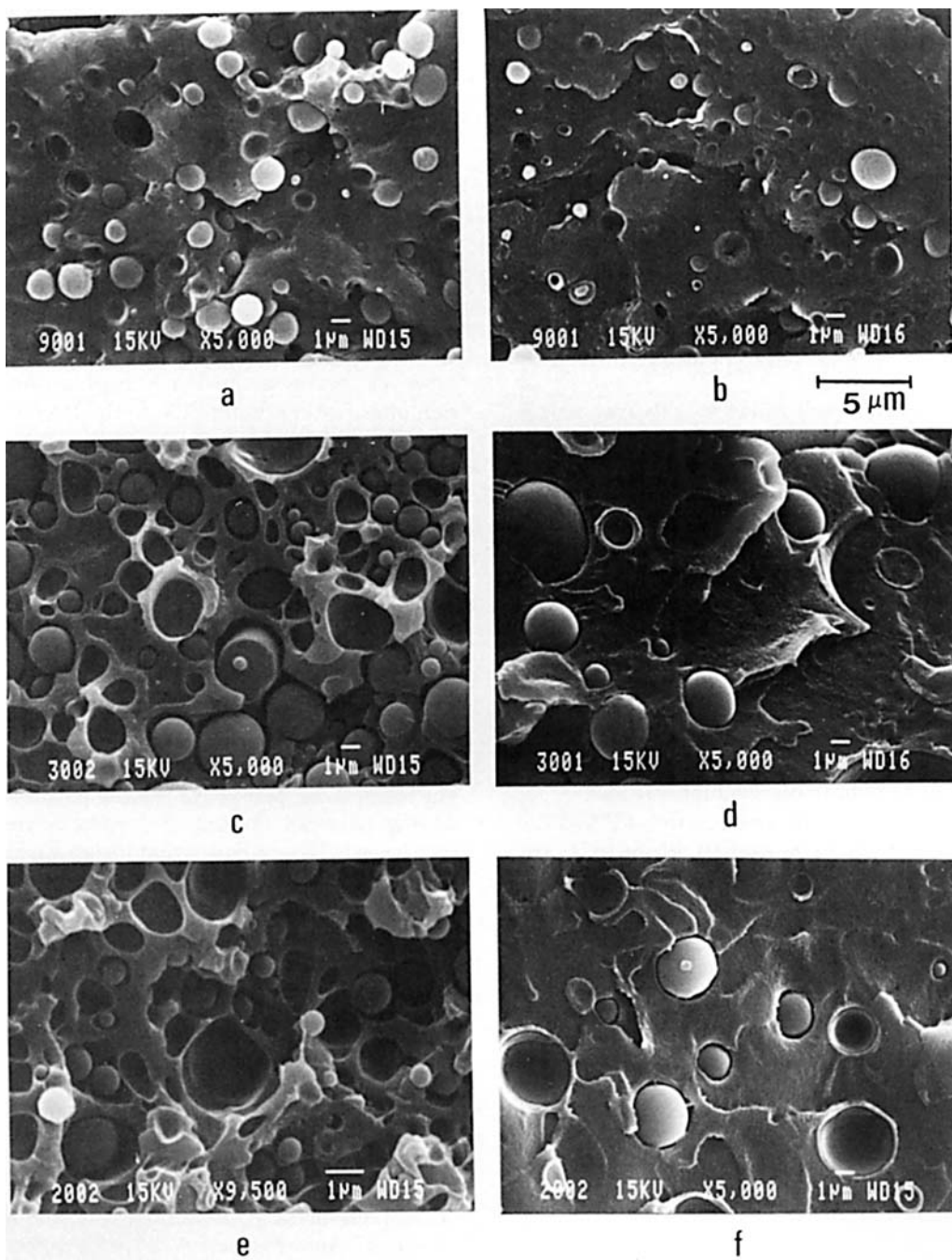
Figure 5 Scanning electron micrographs obtained from cryogenically fractured cross-section surfaces of the extrudates. Binary PA/PC blends (a), (c), and (e). Weight fraction PA: (a) 0.90; (b) 0.30; (c) 0.20. Ternary PA/PC/PCL blends (b), (d), and (f) each containing 10 phr PCL added to PA/PCL blends containing (b) 0.90, (d) 0.30, and (f) 0.20 weight fraction PA.

that the extrudate swell ratio is not an absolute value. The ratio also depends on extrusion conditions such as screw speed, extrusion temperature, shear rate, etc. The existence of maximum viscous and elastic properties of two-phase systems at in-

termediate composition ratios has been explained by Han.[59]

In Figure 6, we also see the extrudate swell ratios of PC/PCL blends, which are reported to be miscible.[25,26] No maximum peak occurs in the PC/PCL
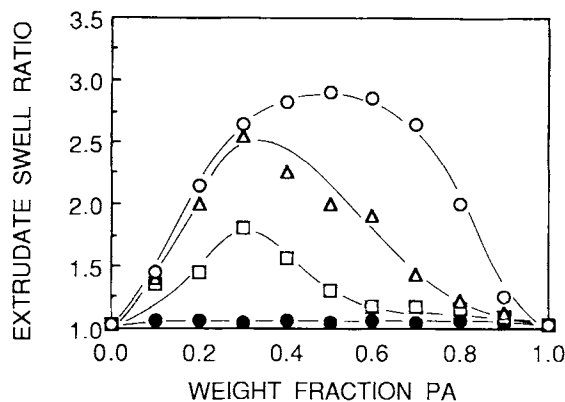
Figure 6 Extrudate swell ratios for different weight compositions: (O) PA/PC blends; (△) PA/PC/PCL (5 phr); (□) PA/PC/PCL (10 phr); (●) PC/PCL blends.

blends and the extrudate swell is almost the same as that of the homopolymers. The maximum in the extrudate swell ratio at a certain composition is behavior typical of incompatible blends. In our previous studies of blends of polycarbonate with PET[60] and with poly(butylene terephthalate),[61] the extrudate swell ratio was shown to decrease when the compatibility was increased or partial miscibility occurred at intermediate blend compositions.

In Figure 6 are extrudate swell ratios of PA/PC/PCL blends in which 5 phr and 10 phr of PCL are added to the PA/PC blends. We can see that the extrudate swell ratio is decreased in the ternary blends compared to the binary PA/PC blends, and a maximum level of extrudate swell is reached at 0.3 weight fraction of PA in the ternary blends. The decrease of the extrudate swell ratio is greater in the PA-rich compositions than in the PC-rich compositions. When the three components are mixed in the ternary blends, it is believed that the PCL would associate preferably with the PC making it more miscible with the PA and diminishing the effect of the PC phase at higher PA concentrations.

CONCLUSIONS

In the study of PA/PCL solution-cast blends, the T_m depression of the PA was found to be 1.6 K to 2.5 K over the investigated composition range. The T_m depression of the PCL in the PA/PCL solution-cast blends was found to be 0.2 K to 0.9 K, which is within the range of experimental error. For the PA/PCL extruded blends, no T_m depression was observed for either of the components.

In the SEM study of the morphology of PA/PCL

solution-cast blends, phase separation was observed between the PA phase and the PCL phase for all the blend compositions. For the extruded PA/PCL blends, more pronounced phase separation was observed. From the study of the T_m depression and the morphology of the PA/PCL blends, it is concluded that PA and PCL are more compatible in the solution-cast blends than in the extruded blends.

In the SEM study of the morphology of PA/PC blends and ternary PA/PC/PCL blends by extrusion, phase separation was observed for both blend systems. An increase of compatibility is observed, however, between the PA-rich phase and the PC-rich phase after adding PCL to the PA/PC extruded blends.

In the study of the extrudate swell of PA/PC blends and ternary PA/PC/PCL blends, a reduction of the extrudate swell ratio was observed in the ternary PA/PC/PCL blends, particularly at higher PA concentrations. This result is consistent with the observed morphology of the extruded PA/PC and PA/PC/PCL blends. From the morphology and extrudate swell ratio, it can be concluded that PCL could be used as a compatibilizer for PA/PC extruded blends.

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