

Compatibility of Isotactic Polypropylene/Poly(ϵ -Caprolactone) Blends

NIKOS K. KALFOGLOU, *Laboratory of Chemical Technology,
Department of Chemistry, University of Patra, Patra, Greece*

Synopsis

Blends of poly(ϵ -caprolactone) (PCL)/isotactic polypropylene (iPP), in the solid state and at compositions spanning the complete range, were characterized using the dynamic mechanical, DSC, and optical microscopy techniques. Morphology examination revealed that increasing the PCL content causes a decrease of spherulitic size. The loss modulus spectra at isochronous conditions (110 Hz) reveal an heterophase system with limited phase mixing between the amorphous components of the blend constituents. Melt-mixing and quenching using the DSC causes a considerable melting point depression of the PCL component, attributed to its miscibility with the polypropylene amorphous phase. Addition of PCL caused an increase of iPP crystallinity at intermediate compositions, while at low PCL levels the presence of iPP crystals hinders the growth of PCL crystallites.

INTRODUCTION

It is now recognized that blending of polymers of which one or both are crystalline is associated with principles of applied and theoretical interest.^{1,2} Of practical consequence is, e.g., the observed synergism of these blends at certain compositions,³⁻⁵ the undesirable phase separation due to crystallization of polymeric processing aids,⁶ and the effect of potential miscibility of the amorphous matrices on the overall crystallinity and engineering properties of the blend.^{7,8} Of theoretical significance are questions related with the thermodynamics of miscibility modified by the formation of the crystalline phase,^{2,9} factors associated with its morphology,¹⁰⁻¹² the kinetics of crystallization,¹³ the possibility of cocrystallization,^{4,14} etc. Several cases of blends involving crystalline polymers were cited, and their properties briefly commented on in a recent review.¹⁵

In this work—an extension of a previous investigation¹⁶ on the compatibility of poly(ϵ -caprolactone) (PCL) with low density polyethylene (LDPE)—blends of isotactic polypropylene (iPP) with PCL are examined at various compositions. Earlier investigations of these blends at low PCL contents indicated a crystalline-crystalline association¹⁷ on the basis of their X-ray reflections.^{17,18} Of practical significance is also the fact that combinations of PCL with iPP give fibers of improved tenacity and dyeability.¹⁸

In the present study additional techniques were applied to improve characterization of these blends. These are: optical microscopy to ascertain the influence of changing composition on crystalline gross morphology; the dynamic mechanical, to detect the possibility of amorphous phase mixing (from changes in the mechanical loss spectra), and the effect of bulk crystallinity on blend stiffness (dynamic modulus); and the differential scanning

calorimetry (DSC), to determine the effect of composition and thermal treatment on the crystallinity level of each of the blend components and ultimately relate it to other observed mechanical and morphological properties.

EXPERIMENTAL

Materials and Specimen Preparation

PCL used was donated by Union Carbide (PCL-700). Its \bar{M}_w was reported to be ca. 40,000. Other characterization data are available in the literature.^{18,19} iPP was obtained from EGA-Chemie, Europe. T_g and mp were reported to be 26°C and 189°C, respectively. \bar{M}_v determined in decalin at 135°C was 2.0×10^5 .

Blends were prepared by dissolving at ca. 120°C in *p*-xylene and coprecipitating in chilled methanol. The vacuum-dried blends were compression molded between Teflon sheets into films, at ca. 200°C and 80 kg/cm³, relaxed, and quenched at 0°C. At low PCL contents (10%), the melt and film produced were transparent. Increased amounts of PCL gave opaque white films with a fibrillar texture, especially at the intermediate compositions (50%). At the other extreme of compositions, the films were transparent and brittle.

For the DSC measurements the first heating cycle (1 cy) refers to samples which after preparation were aged for ca. 1 week at room temperature (30°C). Additional heating cycles (2 cy, 3 cy etc.,) were performed by heating to 190°C, quenching within ca. 2 min to 0°C and repeating the scan between these limits. Annealing was performed by keeping the melted blend at 130°C for 2 h in an evacuated oven and subsequently storing it at 30°C. The following compositions were studied, 0P/100, 10P/90, 20P/80, 50P/50, 80P/20, 100P/0, the first numeral denoting the percentage by weight of PCL.

Apparatus and Procedure

Optical micrographs of quenched films were obtained using a Leitz Wetlar polarizing microscope. Samples 0P/100 and 10P/90 were sufficiently transparent to be directly examined. Other compositions were examined by melting the blend on the microscope slide and slightly pressing the molten film with a cover glass, to obtain a sufficiently thin layer. These were subsequently quenched on a metal plate maintained at 0°C.

Dynamic mechanical data were obtained between -120°C and 160°C at 110 Hz using the Rheovibron and the procedure described before.¹⁶

DSC measurements using the 990 DuPont Calorimeter were carried out with a heating rate of 10°C/min and a cooling rate of 20°C/min to obtain the crystallization temperature T_c . Nominal sample weight was 6-8 mg.

RESULTS AND DISCUSSION

Morphology

The micrographs in Figure 1 obtained with crossed polarizers indicate limited amorphous content at the 10P/90 composition. The differences of free (on slide) and constrained (in films) crystallization is demonstrated in

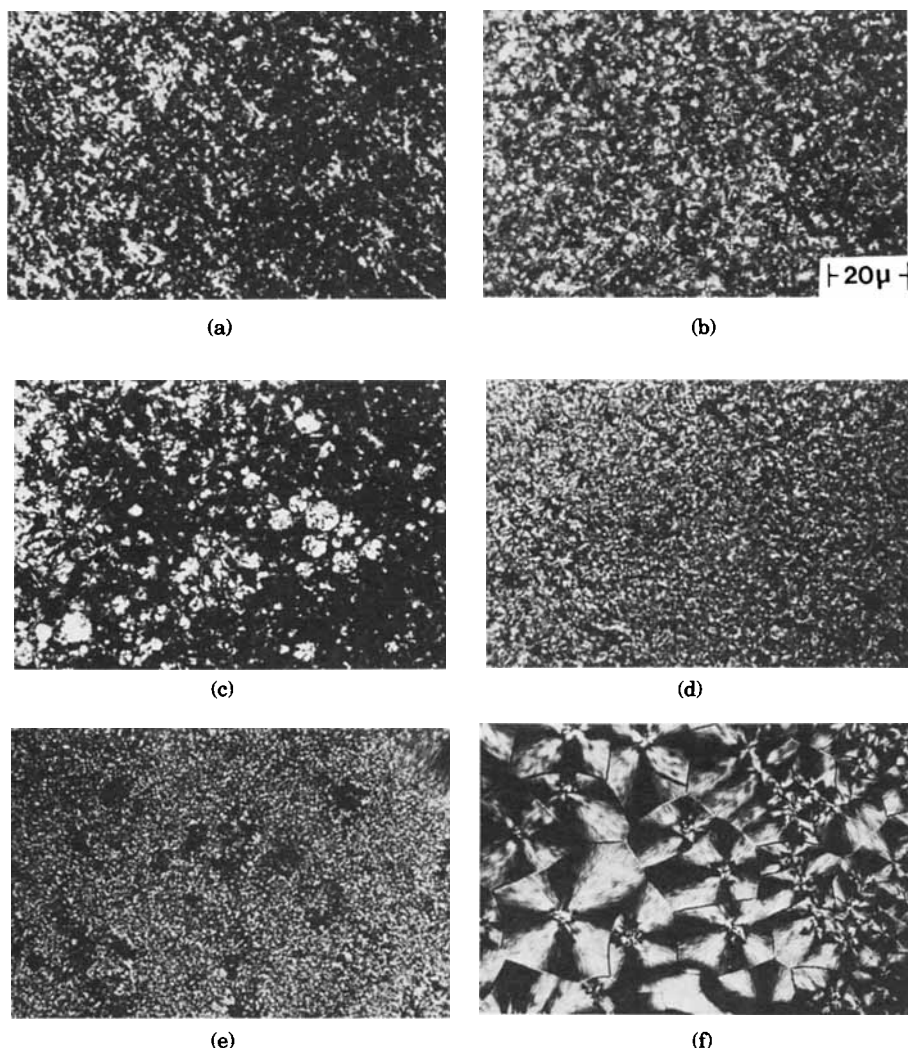


Fig. 1. Optical micrographs of quenched blends with crossed polarizers: (a) 10P/90; (b,c) 20P/80; (d) 50P/50; (e) 80P/20; (f) 100P/0. (c) and (f) freely crystallized on microscope slide.

Figures 1(c) and 1(b). Increased amounts of PCL reduce crystallite size and enhance crystallinity. Some amorphous-crystalline phase segregation is observed at the 80P/20 blend. The crystallite size reduction at the higher levels of PCL bears analogy to results on PCL/LDPE blends¹⁶ and to the HDPE/iPP system,⁵ where the presence of PE drastically reduces the size of iPP spherulites. (Neat iPP spherulitic diameters are of the order of 100 μm .)

Dynamic Mechanical Properties

The mechanical spectra are presented in Figure 2, and Table I reports on the temperatures of the main relaxation (β) observed. For iPP there is general agreement²⁰ that the dominant β peak is due to the amorphous

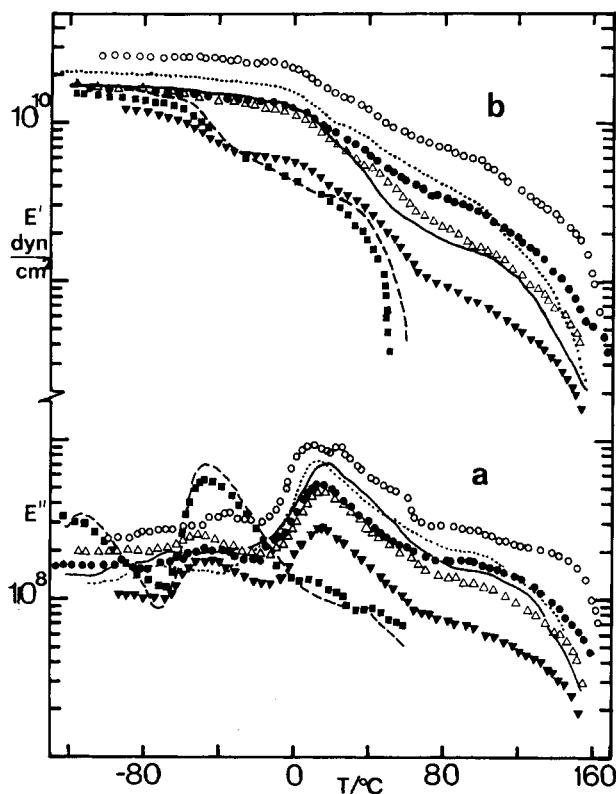


Fig. 2. Composition dependence of dynamic mechanical spectra of blends: (a) loss modulus; (b) storage modulus. Quenched: (—) OP/100; (●) 10P/90; (△) 20P/80; (▼) 50P/50; (■) 80P/20; (- -) 100P/0 Annealed; (· · ·) OP/100; (○) 10P/90.

component of the solid. At 110 Hz this main glass relaxation is located at ca. 20°C for quenched specimens. Annealing causes a shift to lower temperatures, and this has been attributed^{13,20} to increased phase separation of the amorphous material, when the iPP spherulite radii increase. For the main PCL relaxation at ca. -47°C, annealing causes a shift to higher temperatures caused²¹ by the interaction of the crystalline and amorphous phase, increased crystallinity raising the T_g of the sample. The loss modulus spectra [see Fig. 2(a)] reveal a heterophase system with the iPP main peak shifting to lower temperatures with the addition of PCL. This is attributed to amorphous phase mixing between the two constituents and has also been observed¹⁶ in the LDPE/PCL system. No significant change of the β PCL peak temperature was observed except for the 10P/90 annealed sample. This could well be due to increased crystallinity since annealing does not favor mixing. The additional peaks at ca. 26°C for the annealed 10P/90 blend [see Fig. 2(a)] is attributed to premelting phenomena associated with the PCL phase. The spectrum regains its symmetry after the T_m of PCL, at about 60°C. These phenomena were also detected as small endotherms between 20°C and 30°C (see Fig. 3).

Figure 2(b) shows the effect of composition on modulus. Pure PCL has a lower modulus than iPP at all temperatures. However, the 10P/90 annealed

TABLE I
Viscoelastic and Melting Transitions of Blends

Blend ^a	a. Temperature of β -relaxation (°C)		b. Melting and crystallization temperature (°C)									
	iPP		PCL				iPP					
	iPP	PCL	T_m		T_c		T_m		T_c			
	1 cy	2 cy	3 cy	4 cy	1 cy	2 cy	3 cy	4 cy	1 cy	2 cy	3 cy	4 cy
100P/0	—	-47	56.5	55	—	—	—	—	—	—	—	—
80P/20	10 ^c	-47	58.5	55	36	160	161	—	160	161	162	122
50P/50	13	-46 ^b	57	55	35	161	161	—	161	161	162	119.5
20P/80	15	-52	59	53	36	160	162	—	160	162	162	119
10P/90	16	-46	60	53	—	160.5	162	53	160.5	162	162	119
0P/100	20	—	—	—	—	162	162	—	162	162	162	116.5
10P/90 ^c	10	-38	54.5	—	—	161	—	—	161	—	—	—
0P/100 ^c	12	—	—	—	—	—	—	—	—	—	—	—

^a Quenched.

^b Broad.

^c Annealed.

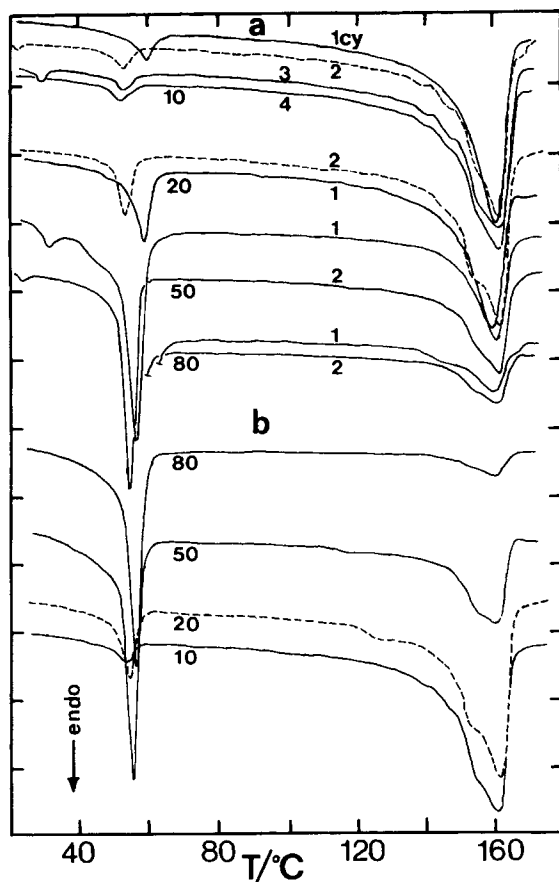


Fig. 3. DSC thermograms of blends: (a) quenched; (b) annealed. Numbers next to curves indicate wt % of PCL. Heating cycle also indicated. [80P/20 in 3(b) run at half-sensitivity.]

and the quenched 10P/90 and 20P/80 samples exhibit higher moduli than either of the pure components. This synergism can be attributed⁵ to increased crystallinity and/or decreased spherulitic size; see the micrographs in Figure 1 and the DSC results below. Of these factors the latter seems to be more decisive since enhanced crystallinity was found at other compositions as well. At intermediate compositions, where the specimens had a strongly fibrillar texture, stiffness is considerably reduced. At the 50P/50 composition, mechanical strength is also low either because of reduced amount of intercrystalline links and/or because of component phase separation. This is usual in blends^{8,16,22} since at this composition it is common for matrix inversion to take place. It is to be noted that at the 80P/20 composition PCL is clearly the matrix; see drop in modulus near the T_m of PCL at ca. 60°C.

Thermal Properties

Figures 3(a) and 3(b) give thermograms taken after blend preparation and aging at 30°C (1 cy), thermal recycling, and annealing, respectively. During the first heating the T_m of PCL is only slightly increased as the iPP

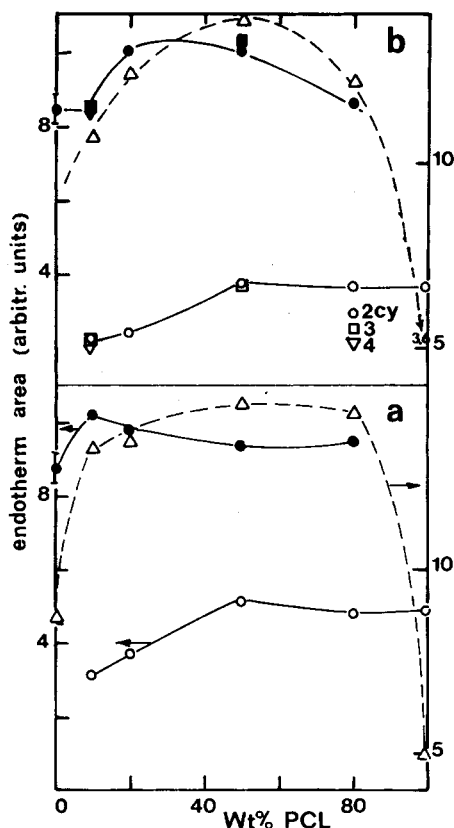


Fig. 4. Composition dependence of the bulk crystallinity of blends and its components: (a) at 1st heating cycle; (b) at subsequent heats. (●) iPP; (○) PCL; (△) total blend crystallinity.

content increases (see also Table I). This reflects increased crystallite size; compare Figure 1(a) with 1(d). Thermal recycling causes a noticeable T_m depression while the T_m of the iPP phase varies less. Some premelting phenomena were observed in the 140–155°C region, possibly associated with the β - to α -iPP crystal transformation.²² This is more evident in the case of the annealed specimens [Fig. 3(b)]. The observed reduction of T_m of PCL is attributed to better mixing of the components after thermal recycling and quenching, yielding smaller crystallites at increased iPP levels. This differentiates recycled blends from those tested after storage (see above, first heat-scan testing). In the latter case PCL crystals may phase-separate during storage.¹⁸ Crystallization temperatures for the iPP increase slightly at high levels of PCL, while at small percentages (~ 10) no T_c for PCL could be detected at the cooling rate employed. It is proposed that at high PCL contents lower molecular weight fractions, or PP molecules of increased disorder, are extracted by dissolution in PCL, in analogy to other blends.²³ Indeed thermal recycling which promotes mixing tends to raise the T_m of iPP (more perfect crystals) (see Table I). On the other extreme, at low PCL compositions because of its alloying with the iPP matrix, crystallite formation is significantly depressed (see below) and eventually hindered because of the T_m - T_g gap reduction² of the surrounding amorphous matrix. In

Figure 4, the endotherm area of each constituent per unit weight, per molar heat of fusion (to obtain a measure of crystallinity) is plotted vs. blend composition. ΔH_f used was 15.88 and 9.41 kJ · mol⁻¹ for PCL¹⁹ and iPP,²⁴ respectively. Crystallinity of iPP is enhanced by the presence of PCL especially at the intermediate compositions in melt mixed, quenched specimens. During aging (1 cy), crystallinity is higher at the lower PCL contents ($\leq 20\%$). This increased iPP crystallinity is attributed to the removal of imperfect PP molecules facilitating its crystallization. Crystallinity of PCL is not hindered or enhanced at low iPP contents (up to 50%). At higher contents, PCL crystallinity is progressively reduced partly because of the hindrance of the iPP crystals already formed, partly because of the miscibility with the diluent. A different behavior was reported¹⁶ in blends of LDPE/PCL where the presence of PE crystals facilitated crystallization of PCL. In the case of HDPE/iPP²⁵ and polybutene/iPP⁸ mutual interference to crystal growth was reported. Regarding total sample crystallinity, both aged and recycled specimens showed increased values at the intermediate compositions. In general, thermal behavior does not indicate the formation of eutectic mixtures or cocrystallization phenomena. The latter should be excluded because of the widely different b and c unit cell parameters of the two components. No epitaxial growth of PCL on iPP was reported,²⁶ though some of the properties observed, e.g., T_m (PCL) depression, iPP crystallinity increase, and the fibrillar texture, bear similarity to corresponding properties observed in the PE/PCL blend where epitaxy was established.²⁷

CONCLUSIONS

The morphological, mechanical and thermal properties of PCL/iPP blends are composition-dependent and chiefly determined by the miscibility of molten PCL with iPP at the extremes of composition.

In the solid state, the dynamic mechanical data indicate limited miscibility of the amorphous phases when blends are quenched. This affects crystallization behavior in that the PP amorphous portion is extracted; hence crystallinity of iPP is enhanced while that of PCL is depressed at low to intermediate PCL compositions. In this composition range decreased crystallite size causes modulus synergism.

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References

1. T. Nishi, *J. Macromol. Sci. Phys.*, **B17**, 517 (1980).
2. D. R. Paul and J. W. Barlow, *Polym. Sci. Technol.* **11**, 239 (1980).
3. K. L. Smith, A. E. Winslow, and D. E. Petersen, *Ind. Eng. Chem.*, **51**, 1361 (1959).
4. G. A. Lindsay, C. T. Singleton, C. J. Carman, and R. W. Smith, in *Multiphase Polymers*, S. L. Cooper and G. M. Estes, Eds., Adv. Chem. Ser. 176, Am. Chem. Soc., Washington, D.C., 1979, p. 367.
5. A. J. Lovinger and M. L. Williams, *J. Appl. Polym. Sci.*, **25**, 1703 (1980).
6. C. F. Hammer, in *Polymer Blends*, D. R. Paul and S. Newman, Eds., Academic, New York, 1978, Vol. 2, Chap. 7.
7. A. W. Birley, *J. Polym. Sci., Polym. Symp.*, **62**, 343 (1978).
8. A. Siegman, *J. Appl. Polym. Sci.*, **24**, 2333 (1979).

9. T. K. Kwei and T. T. Wang, in *Polymer Blends*, D. R. Paul and S. Newman, Eds., Academic, New York, 1978, Vol. 1, Chap. 4.
10. F. B. Khambatta, F. Warner, T. Russell, and R. S. Stein, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 1391 (1976).
11. R. S. Stein, F. B. Khambatta, F. B. Warner, T. Russell, A. Escala, and E. Balizer, *J. Polym. Sci., Polym. Symp.*, **63**, 313 (1978).
12. J. D. Hoffman and J. J. Weeks, *J. Res. Natl. Bur. Stand.*, **A60**, 13 (1962).
13. H. D. Keith and F. J. Padden, *J. Appl. Phys.*, **35**, 1270, 1286 (1964).
14. H. W. Starkweather, Jr., *J. Appl. Polym. Sci.*, **25**, 139 (1980).
15. D. Olabisi, L. M. Robeson, and M. T. Shaw, *Polymer-Polymer Miscibility*, Academic, New York, 1979, Chap. 5.
16. N. K. Kalfoglou, *J. Appl. Polym. Sci.*, **28**, 2541 (1983).
17. B. C. Edwards and P. J. Phillips, *J. Mater. Sci.*, **9**, 1382 (1974).
18. J. V. Koleske, in *"Polymer Blends"*, D. R. Paul and S. Newman, Eds., Academic, New York, 1978, Vol. 2, Chap. 22.
19. V. Crescenzi, G. Manzini, G. Calzolari, and C. Borri, *Eur. Polym. J.*, **8**, 449 (1972).
20. N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids*, Wiley, New York, 1967, Chap. 10.
21. J. V. Koleske and R. D. Lundberg, *J. Polym. Sci.*, **A2**, **7**, 795 (1969).
22. A. J. Lovinger, J. D. Chua, and C. C. Cryte, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 641 (1977).
23. E. Martuscelli, C. Silvestre, and G. Abate, *Polymer*, **23**, 229 (1982).
24. J. Boor, Jr., and J. C. Mitchell, *J. Polym. Sci.*, **62**, 570 (1962).
25. R. Greco, G. Mucciariello, G. Ragosta, and E. Martuscelli, *J. Mater. Sci.*, **15**, 845 (1980).
26. T. Takahashi, M. Inamura, and I. Tsujimoto, *J. Polym. Sci.*, **B8**, 65 (1970).
27. T. Takahashi, N. Odani, and S. Nagasse, *Chem. Abstr.*, **83**, 193867 (1975).

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