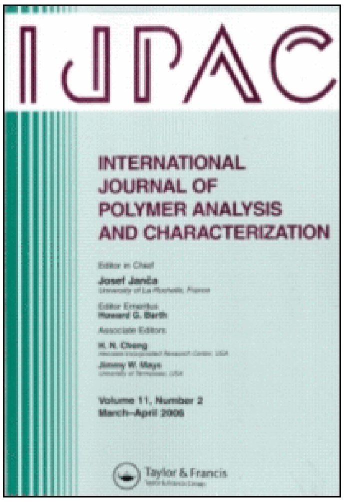

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Shekhar Tankhiwale[a]; M. C. Gupta[a]; S. G. Viswanath[b]
[a] Department of Chemistry, Nagpur University, Nagpur, Maharashtra, India [b] Laxminarayan Institute of Technology, Nagpur, Maharashtra, India

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Nonisothermal Crystallization Behavior of Poly(ethylene terephthalate)-Nylon 6 Blends

SHEKHAR TANKHIWALE[a], M.C. GUPTA[a,*] and S.G. VISWANATH[b]

[a] *Department of Chemistry, Nagpur University, Nagpur 440 010, Maharashtra, India;* [b] *Laxminarayan Institute of Technology, Nagpur 440 010, Maharashtra, India*

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Nonisothermal crystallization behavior of blends of poly(ethylene terephthalate) (PET)-nylon 6 has been investigated. Component polymers in the blends exhibited separate crystallization and melting peaks. Nonisothermal crystallization parameters, like rate of crystallization, has changed for both the component polymers, whereas the degree of crystallinity has increased for PET with increasing amount of nylon 6 in the blends and decreased for nylon 6 with increasing amount of PET in blends. Thus blending seems to have improved crystallization parameters.

Keywords: Polymer blends; PET; Nylon 6; Nonisothermal crystallization; DSC

INTRODUCTION

The study of polymer blends and alloys forms an active area of research in polymer science.[1–3] The properties of molded and extruded products made from thermoplastic blends are governed by morphological features such as domain size, shape, interfacial interactions, degree of crystallinity, crystallite size and the inherent polymer characteristics such as miscibility, melt flow index, and crystallizability of component polymers in blends.[4,5] Therefore understanding of the crystallization

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[*] Corresponding author.

behavior of the component polymers in thermoplastic blends is necessary for optimizing processing conditions and properties.

The heat distortion temperature and toughness of thermoplastic polyesters may be improved by blending with amorphous polymers such as polycarbonate,[6,7] polyarylate[8,9] and phenoxy polymer such as polyhydroxyether of bisphenol A.[10,11] It is reported that blending reduces the degree of crystallinity and lowers the crystallization rate of polyesters.[12] Crystallization in binary polymer blends was discussed by Martuscelli[13] with special reference to the effect of composition and processing conditions on nucleation, growth, overall rate of crystallization, degree of crystallinity and morphology. It was noted that in case of miscible blends, generally a depression in melting point and radial growth rate is observed. Vasile *et al.*[14] have studied the compatibility of polyethylene teraphthalate (PET)-poly(ε-caprolactam) system with an emphasis on effect of heat treatment. The crystallinity and thermal stability of poly(ε-caprolactam) was found to have increased by addition of PET. Recently Runt[15] has reviewed some aspects concerning crystallization in miscible blends with special reference to polymer–polymer interaction using experimental data on melting point depression. The present investigation report nonisothermal crystallization behavior of PET and nylon 6.

EXPERIMENTAL

Materials

The source, melting temperature and the solvent/nonsolvent system used for purification of commercial grade PET (intrinsic viscosity = 0.62 in 60/40 phenol/1,1,2,2-tetrachloroethane at 25°C) and nylon 6 (relative viscosity = 2.4 of 1% solution in 96% H_2SO_4 at 25°C) are given in Table I.

Preparation of Blends

Polymer blends of different composition by mass percent of purified PET and nylon 6 were prepared by dry mixing. Dry mixed powder was homogenized by grinding and meshing through 300 μm for uniform particle size.

TABLE I Source, melting temperature and solvent/nonsolvents used in purification of polymers

Polymer	*Source*	*Melting temperature °C*	*Solvent/nonsolvent*
PET	DCL Polyesters, Nagpur, Maharashtra, India	264	phenol-1,1,2,2-tetrachloro ethane (60 : 40)/acetone
Nylon 6	Garware Nylons, Pune, Maharashtra, India	225	*m*-cresol/ethanol

Phenol, 1,1,2,2-tetrachloro ethane (TCE), m-cresol, acetone and ethanol were procured from Sisco Research Laboratory, Mumbai, Maharashtra, India with a minimum assay of 99%. Phenol was distilled prior to use.

Nonisothermal Crystallization

Nonisothermal crystallization studies were carried out on a differential scanning calorimeter (Mettler FP-800 with a FP-82 furnace) at a heating/cooling rate of 5 K/min. All samples were heated up to 300 K and held for 3 min at that temperature. It was then cooled at the rate of 5 K/min to 30 K and reheated from 30 to 300 K. The thermal parameters were obtained from cooling and reheating scans for the crystallization and melting behavior.

RESULTS AND DISCUSSIONS

Nonisothermal Crystallization of PET

DSC cooling scans for different blend compositions are shown in Figure 1. Normal temperature range for crystallization of PET from melt is 210–230°C. A shift in the temperature at the onset of crystallization would signify modification in nucleation process. The changes in the crystallization peak width and heat of crystallization is related to the composition of the blend, effect of blending on the rate of crystal growth, and the degree of crystallinity. Thus, in blends first crystallization of PET occurs and then nylon 6 crystallizes out of the melt. The heat of crystallization parameters for PET in blends are recorded in Table II.

It is observed that crystallization peak width decreases up to 30% nylon 6 in the blends and there after increases. This suggests an acceleration of crystallization of PET in blend of 30% content of nylon 6. It is further observed that PET crystallizes at higher temperature over

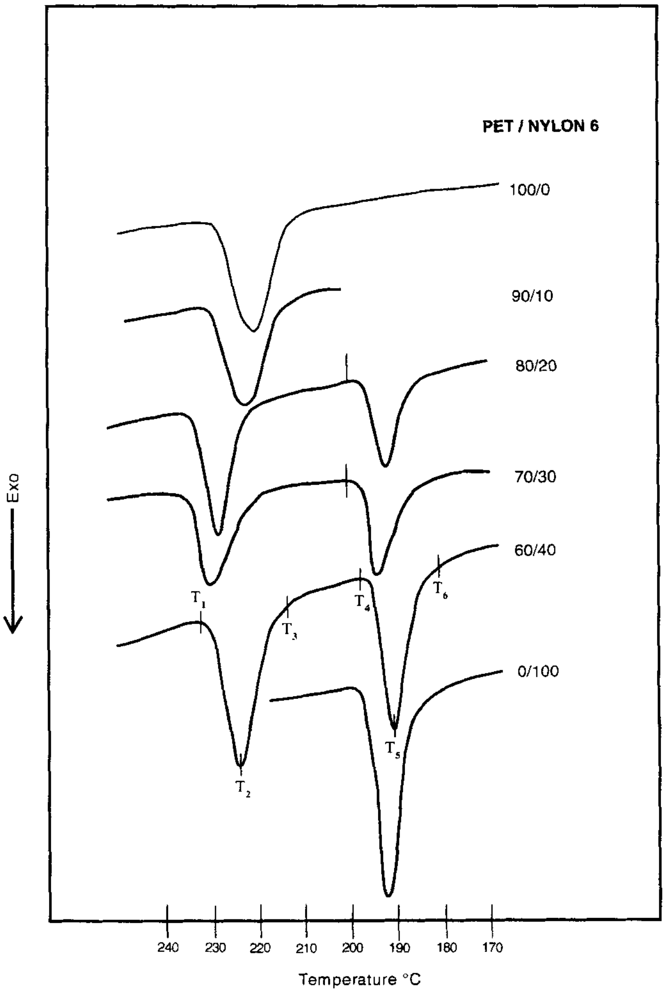

FIGURE 1 Typical DSC cooling scans for PET/nylon 6 blends; T_1 = crystallization onset temperature for PET, T_2 = crystallization peak temperature for PET, T_3 = crystallization end temperature for PET, T_4 = crystallization onset temperature for nylon 6, T_5 = crystallization peak temperature for nylon 6, T_6 = crystallization end temperature for nylon 6.

the entire range of composition which shows that the nucleation of PET is facilitated in blends with nylon 6. However, the increase in temperature at the onset of crystallization is not significant which may be due to the presence of molten nylon 6. This molten nylon 6 offers

TABLE II Crystallization and melting parameters for PET in the blends

Sample no.	*Nylon 6/ PET*	*Crystallization*			*Peak width* $T_1 - T_3$ (°C)	*Heat of crystallization* (J/g)	*Melting*			*Peak width* $T_{12} - T_{10}$ (°C)	*Heat of fusion* (J/g)
		Onset T_1 (°C)	*Peak* T_2 (°C)	*Completion* T_3 (°C)			*Onset* T_{10} (°C)	*Peak* T_{11} (°C)	*Completion* T_{12} (°C)		
1	0/100	228.7	221.2	214.4	14.3	39.0	250.3	264.3	270.3	20.0	28.4
2	10/90	228.7	223.0	214.6	14.1	41.8	250.0	262.2	270.0	20.0	31.6
3	20/80	230.2	226.0	218.7	11.5	42.9	253.0	261.4	270.7	17.7	32.8
4	30/70	230.8	227.1	221.3	9.5	32.0	252.0	260.2	269.0	17.0	25.0
5	40/60	229.9	225.1	217.8	12.1	42.3	253.0	260.8	270.8	17.8	29.0

caging of PET chains and may disturb the amorphous phase by reducing the sedimental mobility. The blends exhibit higher heat of crystallization (Table II) than pure PET indicating that crystallization of the component polymer is enhanced as a result of blending and the degree of crystallinity is increased.

Nonisothermal Crystallization of Nylon 6

The crystallization parameters for nylon 6 in blends are summarized in Table III which shows substantial changes in the parameters. The onset of crystallization decreases with an increase in PET content. This means that nucleation is retarded in PET-rich blends. The crystallization peak temperature also shifts to lower temperature. The peak width changes slightly which may be due to a change in the rate of crystallization. The heat of crystallization of nylon 6 decreases with an increasing amount of PET in the blends suggesting a reduced degree of crystallinity for nylon 6 in the blends.

Increasing amount of nylon 6 in PET decreases the degree of supercooling (degree of supercooling = peak melting − onset of crystallization) for PET crystallization suggesting an enhanced crystallization. Degree of supercooling for nylon 6 crystallization remains almost same and increases slightly for nylon 6 homopolymer as shown in Table IV.

Melting Behavior of Blends

DSC melting scans show the occurence of dual melting peaks in some blends. This may be due to either low heating rate (5 K/min) or tendency of the polymer to melt, recrystallize and melt at a lower heating rate.[16–18] In all such cases first peak is considered as true melting peak.[19]

It is observed from Tables II and III that the onset of melting temperature of PET increases (250–253°C) with the increase in nylon 6 in the blends, whereas there is no significant change in the onset of nylon 6 with composition. Similarly, heat of fusion of PET increases with an increase in nylon 6 in the blends and that of nylon 6 decreases with an increasing amount of PET in the blends. This may be due to the morphological changes with the composition such as the crystallite size.

TABLE III Crystallization and melting parameters for nylon 6 in the blends

Sample no.	*Nylon 6/ PET*	*Crystallization*			*Peak width* $T_4 - T_6$ (°C)	*Heat of crystallization* (J/g)	*Melting*			*Peak width* $T_9 - T_7$ (°C)	*Heat of fusion* (J/g)
		Onset T_4 (°C)	*Peak* T_5 (°C)	*Completion* T_6 (°C)			*Onset* T_7 (°C)	*Peak* T_8 (°C)	*Completion* T_9 (°C)		
1	100/0	197.9	194.0	187.5	10.4	65.5	214.4	225.3	233.5	19.1	58.5
2	40/60	197.0	193.5	187.4	9.6	51.3	216.0	221.5	231.8	15.8	42.2
3	30/70	196.5	193.2	187.4	9.1	39.7	214.3	221.0	231.8	17.5	34.3
4	20/80	196.0	192.7	186.5	9.5	52.0	214.3	220.6	230.8	16.5	37.5
5	10/90	184.1	181.4	174.0	10.1	6.0			No peak		

TABLE IV Degree of supercooling (DOS) of blends

Sample no.	*Blend composition (nylon 6/PET)*	*DOS for PET crystallization* (°C)	*DOS for nylon 6 crystallization* (°C)
1	0/100	35.6	—
2	10/90	33.5	No melting peak
3	20/80	31.2	24.6
4	30/70	29.4	24.5
5	40/60	30.9	24.5
6	100/0	—	27.4

The crystallites do not melt at the constant temperature depending on their size and also on the nature of interfacial structure between crystallites and amorphous phases.[20]

CONCLUSIONS

(i) The crystallization rate of PET component increases slightly and the degree of crystallization also increases with increasing amount of nylon 6 in the blends.

(ii) The crystallization rate of nylon 6 decreases slightly and the degree of crystallinity also decreases with increasing amount of PET in the blends.

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