Crystallization of poly(phenylene sulfide) in blends with high density polyethylene and poly(ethylene terephthalate)

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The crystallization kinetics of poly(phenylene sulfide) (PPS) in blends with high density polyethylene (HDPE) and poly(ethylene terephthalate) (PET) is reported. Although the crystallization of PPS took place in the presence of the molten phase of the second component in both cases, the changes observed in the crystallization behaviour of PPS were different. Isothermal crystallization studies indicated that the crystallization of PPS was accelerated in PPS/PET blends whereas it was retarded in PPS/HDPE blends. The presence of the molten phase of the second component was found to affect the crystallization of PPS through changes in both nucleation and growth processes. The differences observed in the crystallization behaviour of PPS are explained on the basis of the physical state of the melt and the possibility of chemical interactions.

(Keywords: crystallization; blends; poly(phenylene sulfide); high density polyethylene; poly(ethylene terephthalate))

Introduction

The properties of polymer blends are governed by the structure developed during processing. In semicrystalline blends, crystallization of the component polymers influences the structure development. The crystallization of a polymer in the blend takes place under conditions different from those encountered in the case of the pure polymer. Nucleation is controlled by the formation of the critical sized nucleus and the transport of the crystallizable units across the crystal–melt (amorphous) interface, whereas crystal growth is governed by the interaction between the natural growth rate of the crystallizing polymer and the diffusional processes of the crystallizing as well as non-crystallizing components. Therefore the nucleation and/or the crystal growth processes of component polymers become modified in the blend.

There have been a number of reports on the melting and crystallization behaviour of component polymers in blends. In miscible polymer blends, melting point depression and reduction in spherulitic growth rate of the crystallizing component have been reported[1–4], whereas in immiscible blends, the changes observed in the crystallization behaviour and morphology have been attributed to nucleation at the interface[5–7] and to rejection, engulfment and deformation of the second component by the crystallizing polymer[5,8–10]. The analysis of the reported results on miscible and immiscible blends indicates that the critical factors governing the extent and direction of change in the overall crystallization rate include miscibility, relative melt viscosities, chemical compatibility, amounts of the component polymers and their domain phase morphology[11].

Although there are a number of reports on the isothermal and non-isothermal crystallization behaviour of poly(phenylene sulfide) (PPS)[12–16], there are very few reports on PPS crystallization in its blends with other thermoplastics[17–22]. This paper reports the results of crystallization studies of PPS in its blends with high density polyethylene (HDPE) and poly(ethylene terephthalate) (PET). Both the blends are immiscible, the second component (HDPE or PET) being dispersed in the form of small droplets in a continuous phase of PPS. It was observed that the phase morphology changes from PPS constituting the continuous phase for PPS-rich compositions, to PPS forming the dispersed phase in a continuous phase of HDPE or PET for blend compositions with lower PPS content. For PPS-rich compositions, the second component formed spherical domains of about 1–4 μm diameter. The crystallization of PPS in both these blends takes place in the presence of the molten phase of the second component. However, the changes observed in the crystallization behaviour of PPS as a result of blending are quite different in the two blend systems. The differences in the crystallization behaviour of PPS in these blend systems are discussed qualitatively with reference to the molecular mobility of the second component in the melt and the possibility of chemical interactions between component polymers.

Experimental

The materials used for blending were Ryton PPS (grade V-1, Philips Petroleum Co., USA), Hostalene HDPE (grade GA 7260, Polyolefins Industries Ltd, India) and Arnite PET (grade A04 300, Cenka Plastics, India).

Three blend compositions of PPS/HDPE and PPS/PET (90/10, 75/25 and 50/50 w/w) were prepared by melt compounding in a Brabender Plasticorder using a batch mixer at 280°C and 40 rev min^{-1} for 5 min[18,19].

The isothermal crystallization studies were carried out using a Perkin Elmer DSC-2 equipped with thermal analysis data station (TADS). The samples were heated to 300°C and then cooled to a preset crystallization temperature after a dwell time of 2 min. The exothermic

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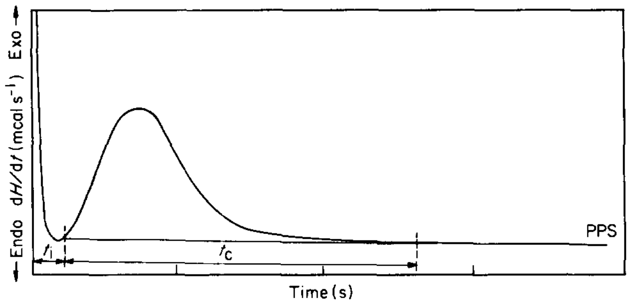

Figure 1 Typical crystallization isotherm showing the induction time, t_i, and total crystallization time, t_c

crystallization peak was recorded and was analysed further.

The crystallization time, t_c, and the induction time, t_i, were determined from the exothermic crystallization peaks as shown in *Figure 1*. The weight fraction crystallized at time t, X_t, was determined by point-by-point area measurement of the crystallization peak, assuming that the fractional crystallization at a given time is proportional to the ratio of the peak area up to that time, to the total peak area. The data of fractional crystallization–time dependence were analysed by the Avrami[23–25] equation:

$$(1 - X_t) = \exp(-Kt^n) \qquad (1)$$

The crystallization half-times, $t_{0.5}$, were determined from the sigmoidal curves of fractional crystallization *versus* time. The crystallization rate constants, K, were calculated using the equation:

$$K = \ln 2/(t_{0.5})^n \qquad (2)$$

where n is the Avrami exponent.

Optical microscopy studies were carried out using a Leitz microscope equipped with hot stage. The blend samples were sandwiched between a microslide and a cover glass and were melted at 300°C for 2 min. The microslides were then transferred to the hot stage which was maintained at the temperature of crystallization. The samples were isothermally crystallized at two temperatures, 250 and 240°C. The morphology of spherulites of pure PPS and PPS in blends was then studied under crossed polarizers.

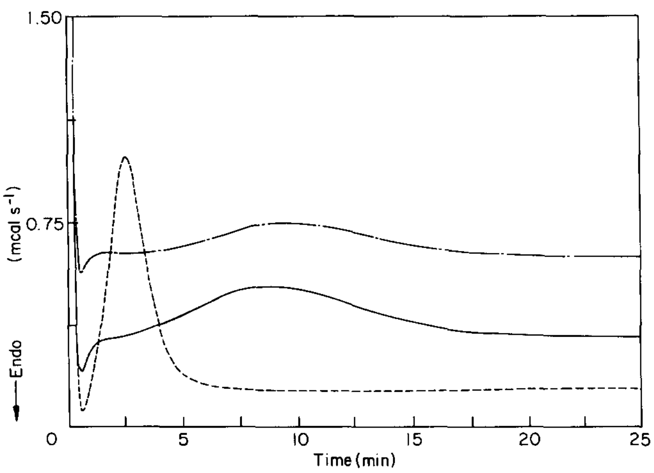

Figure 2 Crystallization isotherms for PPS and PPS/HDPE blends at 255°C: - - -, PPS; ——, PPS/HDPE (90/10); —·—, PPS/HDPE (75/25)

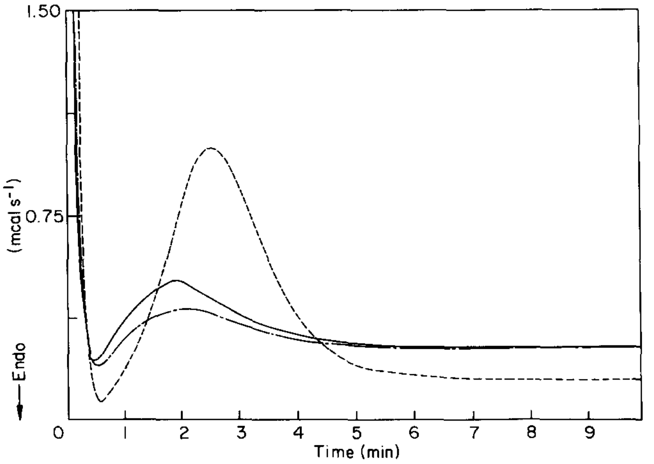

Figure 3 Crystallization isotherms for PPS and PPS/PET blends at 255°C: - - -, PPS; ——, PPS/PET (90/10); —·—, PPS/PET (75/25)

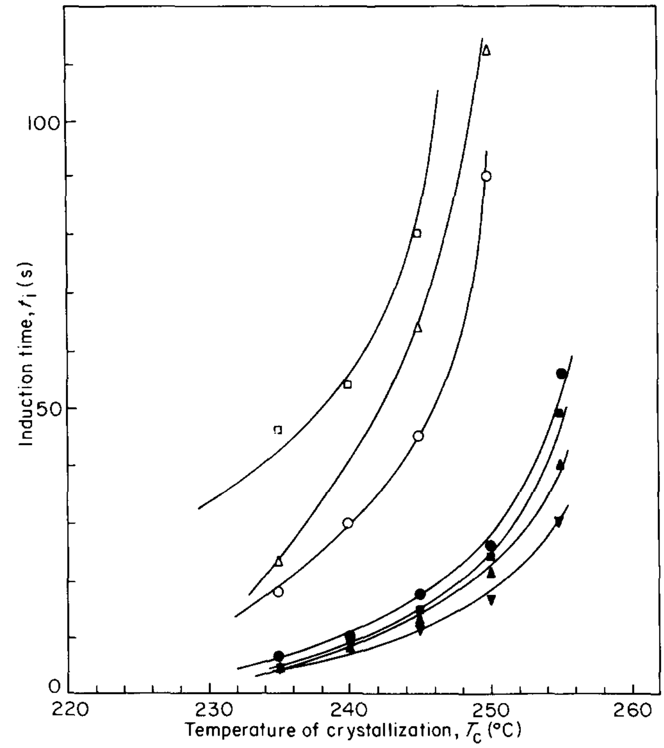

Figure 4 Variation of induction time, t_i, with temperature of crystallization for PPS (●), and PPS/HDPE and PPS/PET blends. PPS/HDPE blend compositions: □, 50/50; △, 75/25; ○, 90/10. PPS/PET blend compositions: ■, 50/50; ▼, 75/25; ▲, 90/10

Results and discussion

The isothermal crystallization of PPS in blends with HDPE and PET was studied over a temperature range of 225–255°C. *Figures 2* and *3* show the crystallization isotherms for PPS in PPS/HDPE and PPS/PET blends, respectively, at low degrees of supercooling at 255°C. It was observed that the crystallization time, t_c, for PPS increased significantly in the PPS/HDPE blends, indicating that the crystallization of PPS is retarded by the presence of molten HDPE in all three blend compositions. On the other hand, in the PPS/PET blend t_c was found to decrease, indicating accelerated crystallization in the presence of molten PET. Similar trends were observed for the induction time, t_i (*Figure 4*), and the crystallization half-time, $t_{0.5}$ (*Figure 5*). Significantly higher induction time was observed for PPS in its blends with HDPE, suggesting suppression of the nucleation process. On the other hand, enhanced nucleation was observed in PPS/PET blends as evidenced by the lower values of induction times. These

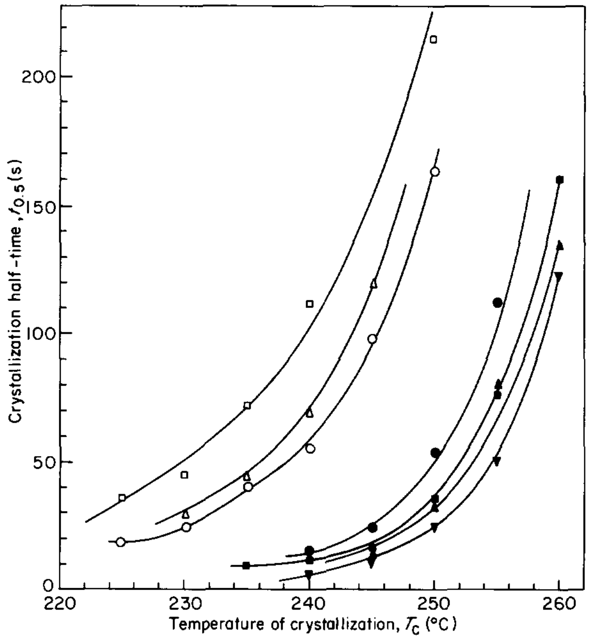

Figure 5 Variation of crystallization half-time, $t_{0.5}$, with temperature of crystallization for PPS (●), and PPS/HDPE and PPS/PET blends. PPS/HDPE blend compositions: □, 50/50; △, 75/25; ○, 90/10. PPS/PET blend compositions: ■, 50/50; ▼, 75/25; ▲, 90/10

Table 1 Avrami constant, *n*, and crystallization rate constant, *K* ($\times 10^4$ s^{-1}), for PPS/HDPE blends

	Composition							
	100/0		90/10		75/25		50/50	
T_c (°C)	*n*	*K*	*n*	*K*	*n*	*K*	*n*	*K*
255	2.15	0.26						
250	2.00	2.40	2.34	0.05	2.30	0.03		
245	1.80	23.0	2.12	0.41	2.20	0.19	2.09	0.09
240	1.85	49.0	2.15	1.20	2.05	1.20	2.03	0.48
235	1.86	84.0	2.14	2.50	2.08	2.70	1.93	1.76
230	1.99	130.0	2.21	6.30	2.19	4.00	1.78	7.80

Table 2 Avrami constant, *n*, and crystallization rate constant, *K* ($\times 10^4$ s^{-1}), for PPS/PET blends

	Composition							
	100/0		90/10		75/25		50/50	
T_c (°C)	*n*	*K*	*n*	*K*	*n*	*K*	*n*	*K*
260			2.27	0.10	2.26	0.13	2.03	0.23
255	2.15	0.26	2.19	0.46	2.25	1.00	2.30	0.32
250	2.00	2.40	2.06	5.40	1.95	13.70	2.07	4.30
245	1.80	23.0	1.825	7.00	1.89	80.00	1.99	31.00
240	1.85	49.0	1.92	71.00	1.68	320.00	2.28	43.00
235	1.86	84.0	1.98	200.00	1.89	415.00	2.09	62.00

observations are consistent with the results of the non-isothermal crystallization studies reported earlier[18,19]. The crystallization rate constants determined from the experimental data using the Avrami equation are summarized in *Tables 1* and *2* for PPS/HDPE and PPS/PET blends, respectively.

It is clear from *Figure 5* that the crystallization of PPS in PPS/PET blends is accelerated for compositions 90/10 and 75/25, in which PET is the dispersed phase. For composition 50/50 the crystallization decelerates as the morphology changes from continuous-dispersed to co-continuous. These modifications in the crystallization behaviour of PPS may be attributed to the changes in interfacial area between the component polymers. It is postulated that the PET phase enhances the nucleation process of PPS because of its supercooled state. The nucleation is governed by the interfacial area. When PET is the dispersed phase the interfacial area is greater (compositions 90/10 and 75/25) as compared to the co-continuous phase morphology for blend composition 50/50. Thus it can be concluded that when the second component is present as a dispersed phase, its size and shape do affect the crystallization of the matrix polymer.

The optical microscopy studies indicated that PPS exhibits spherulitic morphology for low concentrations of the second component (up to 25 wt%) in both the blends. However, the spherulite size was smaller in PPS/PET blends than in PPS/HDPE blends. *Figure 6* illustrates the effect of the presence of the second component on the spherulitic morphology of PPS in PPS/HDPE and PPS/PET 90/10 blend compositions crystallized at 240°C. The reduced size of the spherulites in PPS/PET blends confirms the conclusion of d.s.c. experiments, that there is enhanced nucleation in these blends as compared to PPS/HDPE blends.

Thus it can be concluded that both the nucleation and the crystal growth of PPS are retarded in PPS/HDPE blends, whereas they are accelerated in PPS/PET blends. The observed effects of the presence of the second molten phase on the crystallization of PPS in its blends with HDPE and PET may be explained as follows. In the case of PPS/HDPE blends, at the crystallization temperature of PPS, HDPE is about 120°C above its melting point. As a result, no long-range order would be expected in the HDPE melt. Also, there would be a certain degree of interpenetration/entanglement of molecules of the two components; therefore the HDPE chains would disturb the nucleation process. Accordingly the PPS molecules would require a higher degree of supercooling and longer induction times and thus would exhibit retardation in the crystallization rate of PPS in PPS/HDPE blends.

There are two factors that could cause acceleration of the overall crystallization of PPS as a result of blending with PET. The first is the supercooled nature of the PET melt at the crystallization temperature of PPS (260–230°C). The supercooled PET melt could exhibit a higher order than in the molten state (at temperatures above 260°C) and therefore would enhance the nucleation of PPS. The second factor is the similarity between the chemical structure of PET and PPS. In view of the aromatic chain structure and polar linkages in both PPS and PET, greater secondary molecular interaction would be expected in their blends. The low values of the interaction parameter ($X_{12} = 5.4 \times 10^{-4}$), computed from the solubility parameters of the component polymers, suggests the possibility of such interactions in PPS/PET blends. Both these factors would lead to an increase in the local ordering ('nematic' alignment of the polymer chains) in the blends. Such a phenomenon has been reported[26] for PVDF/PMMA blends in which chemical interactions between the component polymers are known to exist. They have made an attempt to quantify the presence of nematic alignment of the polymer chains by defining an 'order parameter'

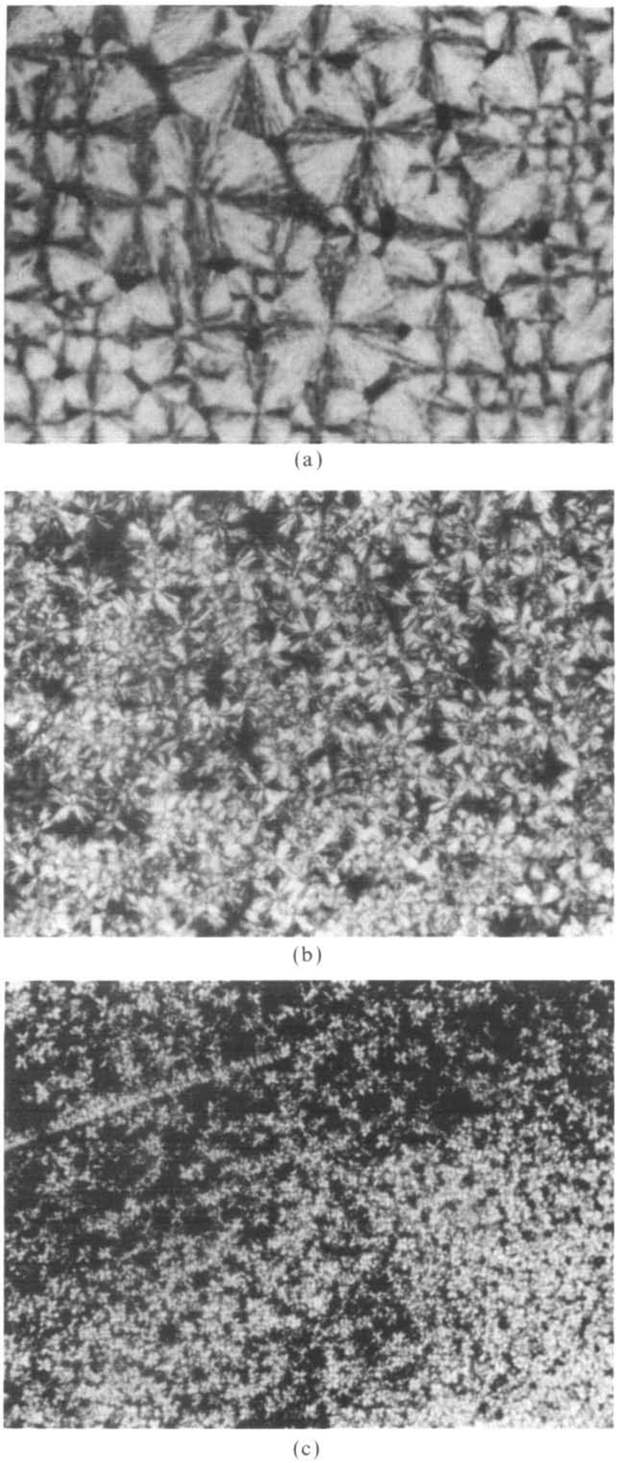

Figure 6 Optical micrographs at 240°C for (a) PPS; (b) PPS/HDPE (90/10); (c) PPS/PET (90/10)

as the number of monomer units arranged parallel to each other. This parameter was found to increase dramatically in these blends. This implies that the local ordering can be induced by intermolecular interactions in polymer melts. The presence of such local ordering in PPS/PET blends may be hypothesized because of the similarity in the chemical structure, which would facilitate the nucleation process. The observed decrease in the induction time for PPS crystallization in PPS/PET blends may thus be attributed to the presence of such local ordering.

Conclusions

The contrasting effects of the presence of the second component on the crystallization behaviour of PPS in its blends with HDPE and PET suggest that in addition to the composition, the mobility and the possibility of chemical interactions between components are important factors governing the direction and extent of modification of the crystallization behaviour of the base polymer. The observed retardation in the crystallization behaviour of PPS in its blends with HDPE is attributed to the HDPE hindering the nucleation and growth processes of PPS. The acceleration of the crystallization of PPS in the PPS/PET blends may be attributed to the presence of local ordering leading to enhanced nucleation.

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