

Thermal and Crystallization Behavior of Engineering Polyblends. II. Unfilled Polyphenylene Sulfide with Poly(ethylene terephthalate)*

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SYNOPSIS

The melting and crystallization behavior of blends of poly(phenylene sulfide) (PPS) with poly(ethylene terephthalate) (PET) has been investigated. The component polymers in the blend exhibited separate crystallization peaks and overlapping melting peaks. The nonisothermal DSC scans indicated that the crystallization parameters for PET become modified to a greater extent than do those for PPS in the blends. The PET crystallization peak became narrower with a higher heat of crystallization, suggesting a faster rate of crystallization as a result of blending with PPS. The isothermal crystallization studies revealed that the nucleation of PPS is facilitated by the presence of PET. This contention has been substantiated by polarized light microscopic observations. The spherulites of PPS were found to be smaller in the blends as compared to those in neat PPS. This enhancement in the nucleation of PPS has been attributed to the possibilities of chemical interactions between the component polymers. On the other hand, the increase in the rate of crystallization of PET has been attributed to the heterogeneous nucleation provided by the already-crystallized PPS. The melt crystallized blends exhibited slightly higher heats of fusion compared to the values computed from the rule of proportional additivity. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polymer blends and alloys constitute a major class of engineering plastic materials because of the possibility of achieving specific property combinations in a cost-effective manner. The study of the crystallization behavior of polymers in multicomponent blend systems is of relevance to structure development in polymer processing. The various factors influencing polymer crystallization in blends have been discussed in detail in review articles by Jog and Nadkarni,¹ Paul and Barlow,² and Runt and Martinowitz.³

The published literature on crystalline polymer blends may be categorized in terms of crystalline/amorphous blends⁴⁻¹¹ and crystalline/crystalline

blends.¹²⁻¹⁹ Generally, in the blends of two crystallizable polymers, even if the component polymers are miscible in the molten state, phase segregation would take place as individual components start crystallizing during cooling. However, in some cases, it has been observed that even though the components crystallize separately, they were found to be miscible in the amorphous phase. In such cases, the definition of polymer miscibility was limited only to the amorphous region.¹² In the crystalline/amorphous blends, the crystallization behavior of the crystallizable species has been observed to be affected by the chemical and molecular characteristics of the amorphous component.

The blend system of the present investigation comprises two crystalline polymers exhibiting melting points close to each other, namely, poly(phenylene sulfide) (PPS) and poly(ethylene terephthalate) (PET). Of the two, PPS melts at a higher temperature (280°C) and exhibits a higher rate of

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crystallization, whereas PET with a melting temperature of 255°C is sluggish to crystallize. Thus, PPS would crystallize in the presence of the super-cooled melt of PET in the blend. In our earlier work, the crystallization behavior of blends of glass-reinforced PPS with PET was investigated,²⁰ in which the crystallization of both PET and PPS was found to be accelerated as a result of blending. However, because of the presence of glass fibers, the effect of blending on crystallization of PPS and PET could not be readily discerned. The present paper reports the thermal and crystallization behavior of blends of unfilled PPS with PET.

EXPERIMENTAL

Materials

The unfilled grade of poly(phenylene sulfide) (PES, Ryton V-1) was supplied by Phillips Petroleum Co. (USA). This is a low molecular weight grade ($M_w = 16,500$) of PPS recommended for compression molding. The poly(ethylene terephthalate) (PET) used was a clear injection-molding grade (Arnite A04 300) obtained from Cenka Plastics (India). The physical properties of these two polymers used for blending are summarized in Table I. The polymers were predried at 120°C for 6 h in a vacuum oven before melt compounding.

Preparation of the Blends

The blends were prepared by melt compounding using a Brabender Plasticorder (Model PLE 330) and a roller mixer (Type W 50EH) at a rotor speed of

40 rpm at 285°C. A nitrogen blanket was maintained during blending to prevent degradation of the polymers. Five blend compositions were prepared at PPS/PET weight ratios of 90/10, 75/25, 50/50, 25/75, and 10/90. The component polymers were also subjected to identical processing conditions in order to nullify the effect of their thermal history.

Melting and Nonisothermal Crystallization Studies

The melting and crystallization behavior was investigated using a Perkin-Elmer differential scanning calorimeter (DSC-2C) fitted with a thermal analysis data station (TADS). The temperature and differential energy scales were calibrated using pure indium and tin as the primary standards. To ensure consistency and reproducibility of results, the samples were weighed accurately within 10 (± 0.5) mg and then used for thermal characterization.

The samples were initially heated to 300°C and then cooled at 10°C/min to 50°C. They were reheated to 300°C at a rate of 10°C/min. The melting parameters of the blend samples were determined from the reheating scans, since these would essentially represent morphologies of samples crystallized from the melt under identical conditions. The comparison of reheating scans would also eliminate the effect of different and uncontrolled quench conditions, encountered during the blend preparation on the morphology of the blends. The cooling scans were used to determine the nonisothermal crystallization parameters of the component polymers. The melting and nonisothermal crystallization parameters obtained from these scans are described in greater detail in our earlier publication.²⁰

Table I Physical Properties of the Component Polymers

Physical Property	Polymer	
	PPS	PET
Grade	Ryton (V-1)	Arnite A04 300
Supplier	Phillips Petroleum Co. (USA)	Cenka Plastics (India)
Density (g/cm ³)	1.35	1.34
Melting point (°C)	280	256
Glass transition temperature (°C)	84	69
Melt flow index (g/10 min)	4000-6000 ^a	—
Molecular weight	$M_w = 15,000$ $M_n = 3000$	$M_n = 20,000-25,000$
Melt viscosity at 285° and $\dot{\gamma} = 150 \text{ s}^{-1}$ (Poise)	200	1200

Isothermal Crystallization Studies

The isothermal crystallization studies were performed over a wide temperature range. For PPS, the isothermal crystallization was studied over a range of temperature from 230 to 255°C, whereas for PET, the range of crystallization temperatures was from 190 to 235°C. For these studies, the samples were heated to 300°C and kept at this temperature for 2 min to destroy any residual nuclei that may be present. The samples were then quenched at 160°C/min to a predetermined crystallization temperature (T_c), at which the exothermic peak of isothermal crystallization was recorded on a time base. The induction time (t_i) defined as the time required for the initiation of the crystallization process at a particular temperature of crystallization was determined from the isotherms. The total isothermal crystallization times (t_c) at various temperatures were determined from the base width of the crystallization peak.

RESULTS AND DISCUSSION

The typical DSC reheating and cooling scans for the 50/50 PPS/PET blend composition are shown in Figure 1. The blends exhibited two distinct crystallization peaks corresponding to the crystallization of the component polymers during cooling, whereas the melting peaks of the two polymers overlap because of the proximity of their melting points.

Nonisothermal Crystallization of PPS from the Melt

The nonisothermal crystallization parameters for PPS are summarized in Table II. Based on the DSC cooling scans of the component polymers, the peak appearing at the higher temperature was assigned to PPS, whereas that at the lower temperature was assigned to PET. The blend composition of 10/90 (w/w) PPS/PET did not show any peak corresponding to PPS crystallization even at the maxi-

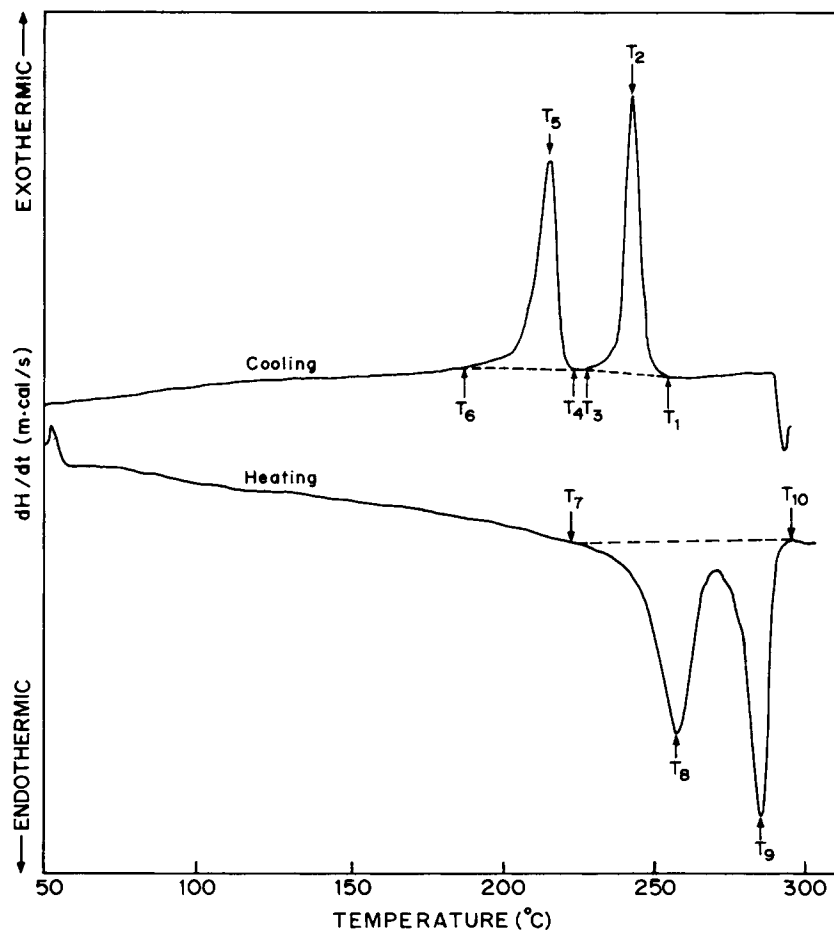


Figure 1 Typical DSC cooling and reheating scans for 50/50 (w/w) PPS/PET blends.

Table II Nonisothermal Crystallization Parameters for PPS in the Blends

No.	Blend Composition PPS/PET	Onset T_1 (°C)	Peak T_2 (°C)	Completion T_3 (°C)	Peak Width $T_1 - T_3$ (°C)	Heat of Crystallization ΔH_c (cal/g)
1	100/0	258	246	226	32	12.3
2	90/10	259	247	230	29	12.0
3	75/25	260	248	231	29	12.0
4	50/50	259	246	232	27	11.0
5	25/75	257	244	234	23	6.2
6	10/90	No peak				

imum instrumental sensitivities. This may be because of the difficulty of detecting a very low amount of heat of crystallization of PPS in the presence of the major PET phase.

It is clear from Table II that the crystallization parameters for PPS become modified only marginally as a result of blending. The onset temperature of crystallization of PPS (T_1) remains unaltered as a result of blending with PET. Thus, in nonisothermal crystallization, which would represent a transient response, the nucleation of PPS appears to be unaffected by the presence of the PET melt. The crystallization peak temperature for PPS in the blends was also found to be comparable to that of neat PPS. The heat of crystallization (ΔH_c) of PPS was found to remain unchanged in all the PPS-rich blend compositions, whereas it dropped by almost 50% in the 25/75 PPS/PET blend composition. This could be attributed to the mobility constraints on PPS due to the major volume filling by the PET phase.

Nonisothermal Crystallization of PET from the Melt

The nonisothermal crystallization parameters for PET are summarized in Table III. It is clear from

the DSC cooling scans (Fig. 1) that the crystallization of PPS takes place prior to that of PET in the blends during cooling at 10°C/min from the melt. The temperature at the onset of crystallization for PET (neat PET subjected to a processing history comparable to the blends) (T_4) increases to higher temperatures in the blends, with a maximum at 25% of PPS by weight. The degree of supercooling ($\Delta T = T_8 - T_4$) required for the PET crystallization in the blends is significantly lower (27–32°C) compared to that required for pure PET (35°C), as shown in Figure 2. The drop in the degree of supercooling implies an accelerated nucleation process for PET in the blends. The degree of supercooling required for PET crystallization also exhibited a minimum at 25/75 PPS/PET composition. With further addition of PPS, the extent of change in the degree of supercooling for PET was found to be reduced.

The acceleration in the nucleation of PET crystallization has been attributed to the presence of already-crystallized PPS particles. These PPS crystallites with a finite surface area can act as heterogeneous nuclei during PET crystallization. The diminishing effect of heterogeneous nucleation offered by PPS to the crystallizing PET molecules observed in the PPS-rich blends has been attributed to the

Table III Nonisothermal Crystallization Parameters for PET in the Blends

No.	Blend Composition PPS/PET	Onset T_4 (°C)	Peak T_5 (°C)	Completion T_6 (°C)	Peak Width $T_4 - T_6$ (°C)	Heat of Crystallization ΔH_c (cal/g)
1	0/100	221	203	165	56	10.4
2	10/90	225	215	174	51	12.1
3	25/75	231	219	184	47	13.1
4	50/50	229	219	192	37	11.9
5	75/25	227	220	200	27	11.6
6	90/10	221	215	200	21	9.7

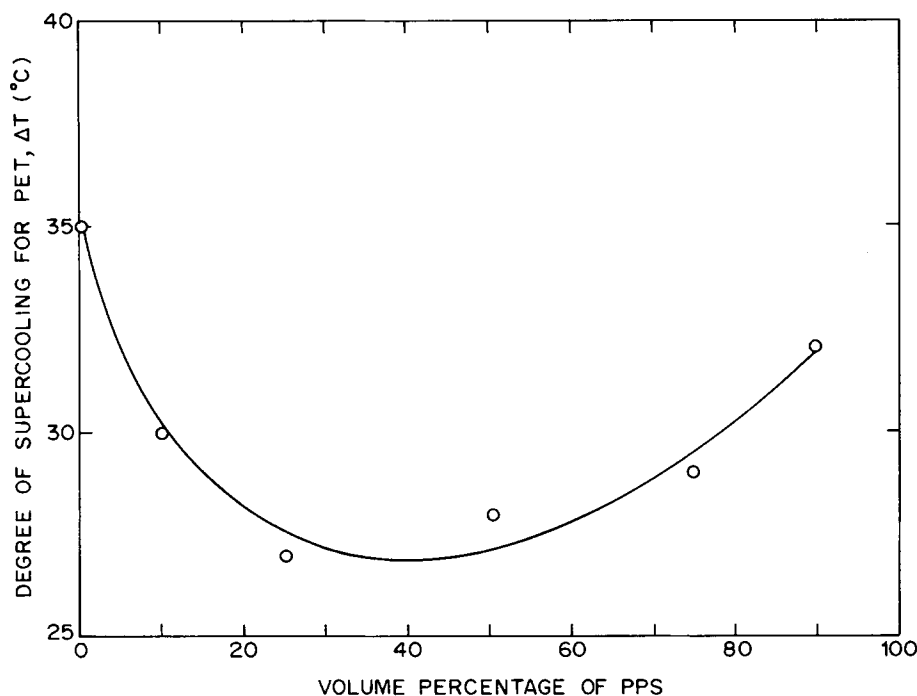


Figure 2 Composition dependence of the degree of supercooling (ΔT) for PPS in the blends.

constraints on crystal growth of PET in the presence of higher amounts of PPS.

The peak (T_5) temperature for PET crystallization also shifted significantly to higher temperatures as a result of blending. This also suggests that the PET crystallization becomes accelerated as a result of blending. The PET crystallization peak width ($T_4 - T_6$) was found to decrease monotonically with increasing amounts of PPS in the blends as shown in Figure 3. This reduction in the crystallization peak width indicates the narrowing down of the temperature range of crystallization for PET as a result of blending.

The heat of PET crystallization (ΔH_c) in the blends was found to increase significantly as a result of blending with PPS. The heat of crystallization of PET increased considerably even at 10% PPS in the blend. The heat of crystallization for PET was maximum in the 25/75 PPS/PET blend composition, and a further increase in the PPS content had an adverse effect on the heat of crystallization of PET in PPS-rich compositions. The increase in the heat of crystallization can be attributed to the nucleating effects of already-crystallized PPS. The drop in the heat of crystallization for PET in PPS-rich blends can be attributed to the mobility restrictions imposed by PPS solid particles for the PET crystal growth.

The incorporation of suitable nucleating agents to accelerate crystallization in PET is well known.²¹ These include graphite, talc, magnesium oxide, titanium dioxide, calcium benzoate, calcium silicate, sodium stearate, zinc stearate, *p*-hydroxybenzoic acid, etc. Because of the heterogeneous nucleating ability, these additives accelerate the otherwise slower nucleation step involved in the PET crystallization and thereby develop a considerable amount of crystallinity in PET. The incorporation of such nucleating agents allows faster molding cycles and the use of lower mold temperatures during the injection-molding process.

An increase in the degree of crystallinity of PET was observed in its blends with nylon 66 by Kamal et al.²² The observed increase in the degree of crystallinity of PET was attributed to the nucleating effects of nylon 66, which crystallizes prior to PET crystallization. Recently, Nadkarni and Jog²³ reported the modification of the crystallization behavior of PET by blending with poly(methyl methacrylate) (PMMA). In this investigation, they observed PET to crystallize faster as a result of blending with about 10–20% by weight of PMMA. The blends could be molded into crystalline specimens even at mold temperatures as low as 19°C. The results of the present investigation also show similar trends in terms of the modifications of the

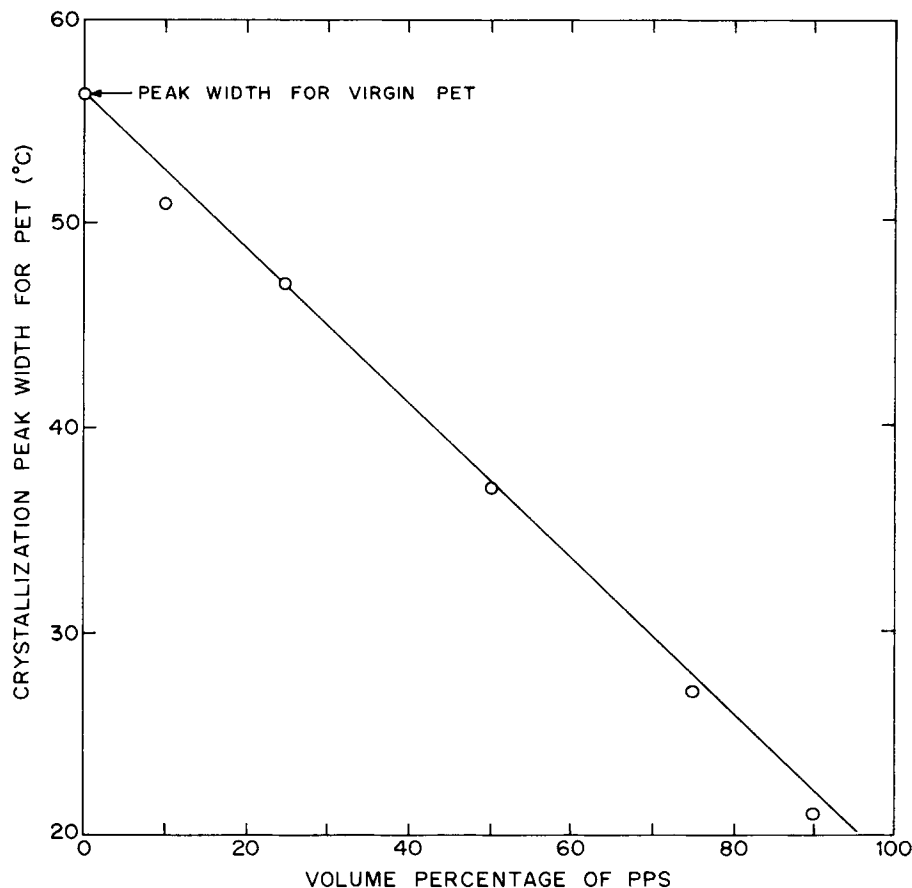


Figure 3 Composition dependence of the crystallization peak width for PET in the blends.

crystallization behavior of PET due to blending with PPS. However, it seems that the accelerating influence of PPS on PET crystallization is reduced at higher (> 25%) amounts of PPS.

Melting Behavior of the Melt-Crystallized Blends

Because of the overlapping nature of the melting peaks, as mentioned earlier, it was not possible to pinpoint the exact temperature at completion of PET melting and the temperature at the onset of PPS melting. It was observed that the melting peak temperatures for both PET (T_8) and PPS (T_9) do not change significantly as a result of blending. However, it is evident from Table IV that the onset temperature of melting of PET in the blends (T_7) shifts considerably to higher temperatures and varies with composition between 218 and 227°C. Among the component polymers, since PET is the lower melting polymer, the increase in the onset temperature of melting in the blends may be attributed to the increased crystallite size of PET in the blends.

Since the PET crystallization takes place at significantly higher temperature as a result of blending, one may expect an increase in the crystallite size of PET in the blends. Also, the temperature at the completion of melting (T_{10}) was found to vary only slightly with the composition.

The variation in the combined heat of fusion (ΔH_f) for the blends with the composition is shown in Figure 4. In all the blend compositions, the observed heat of fusion was higher than the heat of fusion calculated by using proportional additivity rule for mixtures (dotted line). This increase in the heat of fusion indicates a marginal increase in the degree of crystallinity of the component polymers in the blends. It should be noted here that while analyzing the cooling scans of the component polymers a marginal change in the heat of crystallization for PPS was observed, particularly in PPS-rich compositions, whereas there was a significant increase in the heat of crystallization of PET in these compositions (except in 90/10 PPS/PET composition). Therefore, it appears that the major con-

Table IV Melting Parameters for PPS/PET Blends

No.	Blend Composition PPS/PET	Onset T_7 (°C)	Peak		Completion T_{10} (°C)	Peak Width $T_{10} - T_7$ (°C)	Combined Heat of Fusion ΔH_f (cal/g)	
			PET T_8 (°C)	PPS T_9 (°C)			Exptl	Calcd
1	0/100	215	256	—	267	52	9.3	—
2	10/90	218	255	284	290	72	9.9	9.6
3	25/75	218	258	284	295	77	11.1	10.0
4	50/50	219	257	285	296	77	11.5	10.7
5	75/25	222	256	284	293	71	12.6	11.3
6	90/10	227	253	284	295	68	12.5	11.7
7	100/0	233	—	283	291	58	12.0	—

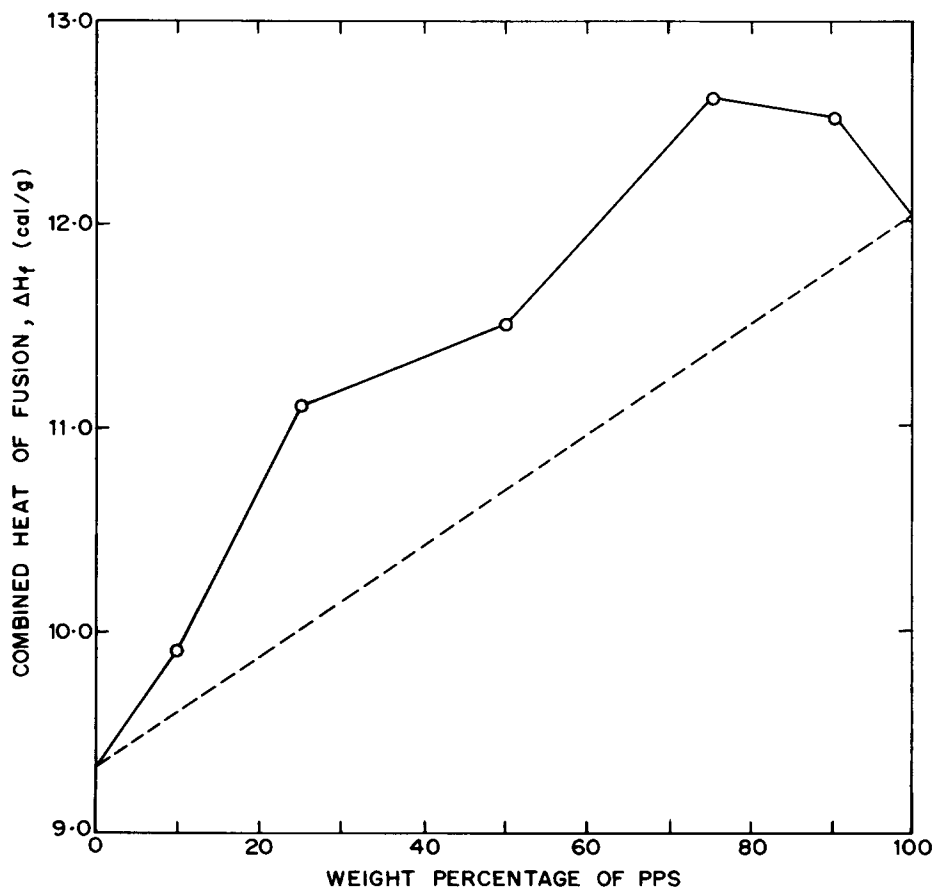
tribution to the increase in the combined heat of fusion in the blends may be from the PET component.

Thus, in summary, it can be stated that the reheating scans of the melt-crystallized blend samples reveal the presence of larger PET crystallites with a comparatively narrower size distribution and a

higher level of crystallinity as evidenced from the higher heat of fusion.

Isothermal Crystallization of PPS in the Blends

The isothermal crystallization studies for PPS in the blends were carried out in the temperature range


Figure 4 Composition dependence of combined heat of fusion for PPS/PET blends.

of 235–260°C. It was observed that for PPS the isothermal crystallization peaks could not be recorded in PET-rich compositions (blends containing less than 50% by weight of PPS). This is due to the low heat of crystallization of PPS in these blend compositions, which cannot be recorded even with the maximum instrumental sensitivity.

The induction time (t_i), isothermal crystallization time (t_c), and the crystallization half-time ($t_{0.5}$) were determined from the crystallization peaks obtained for PPS at different crystallization temperatures (T_c). Figure 5 demonstrates the manner in which the isothermal crystallization of PPS becomes modified as a result of blending with PET at the crystallization temperature of 255°C in 90/10, 75/25, and 50/50 PPS/PET blend compositions. Referring to Figure 5, it is clear that both the induction time and the total crystallization time for PPS decreased as a result of blending with PET. Figure 6 shows the variation of the induction time for PPS crystallization (t_i) with the temperature of crystallization (T_c). It is clear from the figure that at any given temperature the induction time for PPS in the blends is shorter than that for virgin PPS. The accelerating influence of the PET melt on PPS nucleation was found to be more pronounced at higher temperatures ($T_c > 255^\circ\text{C}$) than at lower temperatures of crystallization. This is further illustrated in Figure 7, showing the composition dependence of the induction time for PPS in the blends at 255, 250, and 245°C. It was also found that the induction time

for PPS crystallization is minimum around the 75/25 PPS/PET composition.

The composition dependence of the induction time for PPS is significant at higher temperatures ($T_c > 255^\circ\text{C}$) compared to that at lower temperatures (Fig. 7). Since it is known that at higher crystallization temperatures the overall crystallization process is controlled by nucleation, it is hypothesized that the PET melt accelerates the nucleation of PPS in the blends. It may be relevant to note that no change was observed in the degree of supercooling required to initiate the nonisothermal crystallization of PPS in the blends. On the other hand, the isothermal crystallization results indicate an acceleration in the nucleation of PPS at temperatures close to the melting point of PET. These observations have been attributed to the "time effects" that play a major role in the nucleation process. These effects are not seen in the nonisothermal cooling mode owing to the dynamic mode of operation.

The enhanced nucleation of PPS in the presence of PET was also confirmed by the results obtained by polarized light microscopic studies. Figure 8 shows the polarized light micrographs of PPS and 90/10 PPS/PET blend composition at 240°C. The spherulites seen in the micrographs are of PPS and it appears that at this temperature the number of growing PPS spherulites are considerably higher in the blend than in virgin PPS. This observation fully supports the fact that nucleation of PPS is facilitated in the presence of PET. Further microscopic

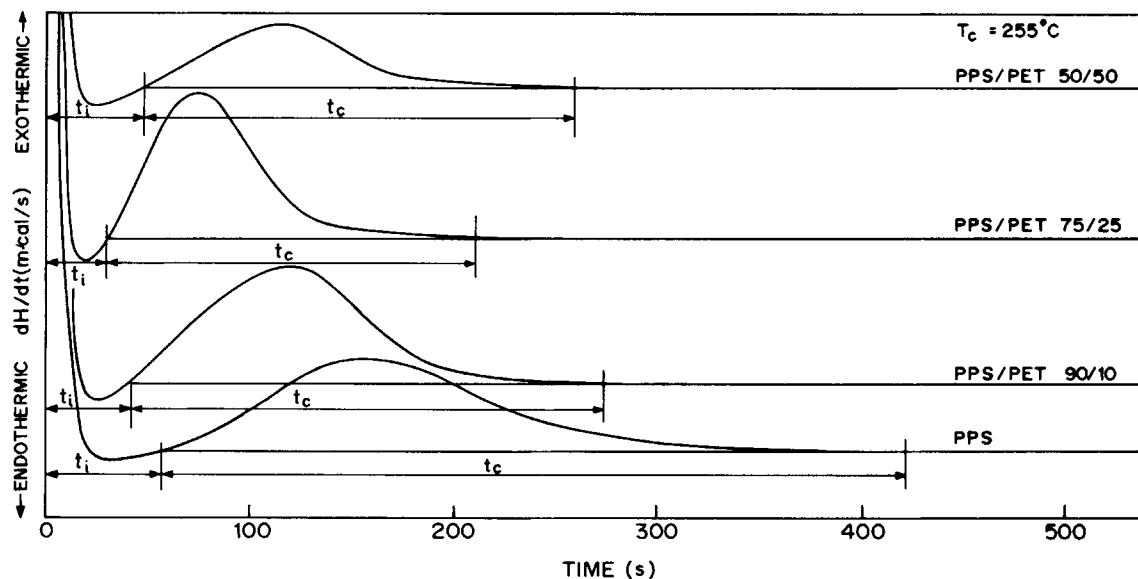


Figure 5 Crystallization isotherms for PPS in the virgin form and in the blends at $T_c = 255^\circ\text{C}$.

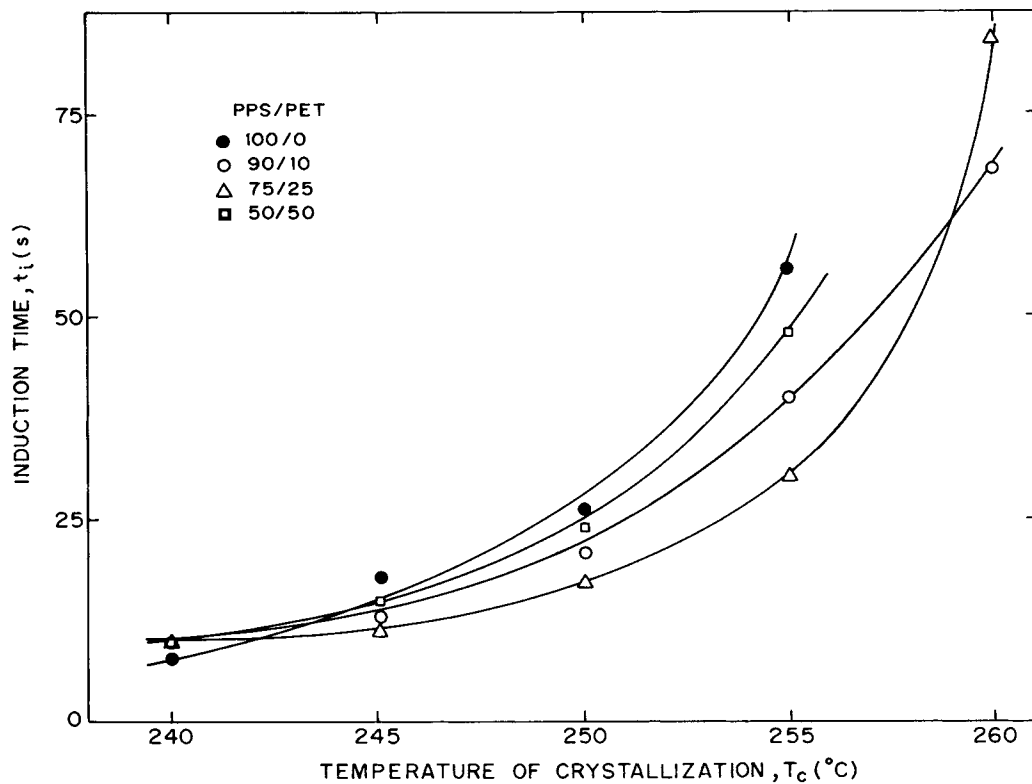


Figure 6 Variation of induction time (t_i) with the temperature of crystallization (T_c) for PPS in the blends.

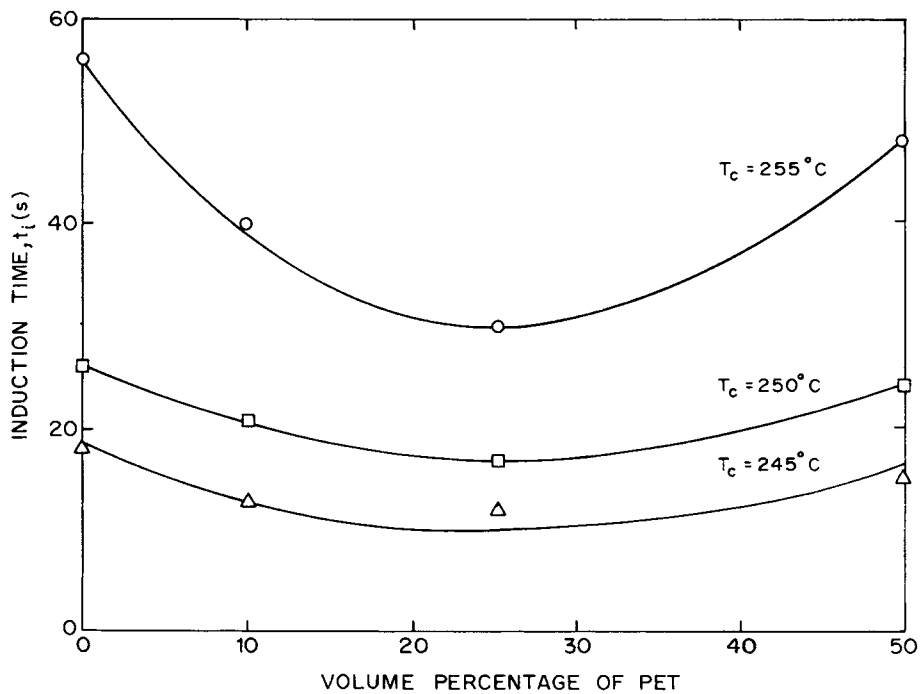
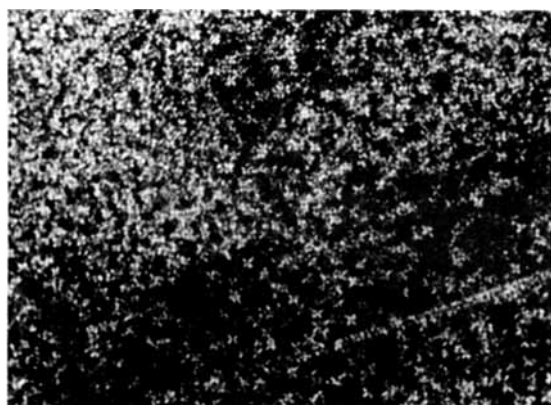


Figure 7 Composition dependence of the induction time (t_i) for PPS in the blends.



(a)



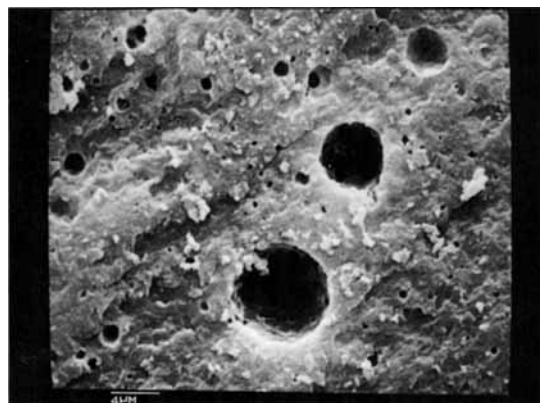
(b)

Figure 8 Polarized light micrographs of (a) PPS and (b) the PPS/PET 90/10 blend at $T_c = 240^\circ\text{C}$ ($320\times$).

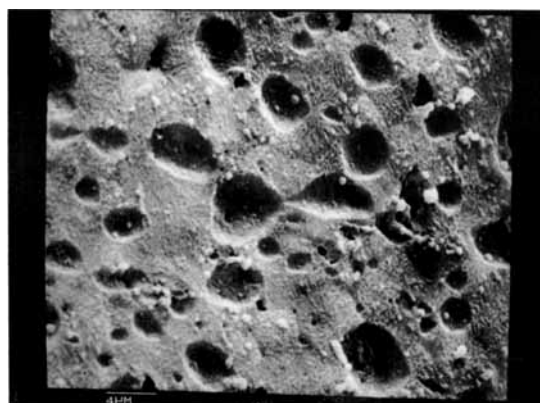
studies involving the development of spherulitic morphology of PPS in these blends are in progress and will be reported separately.

To resolve the composition dependence of the induction time for PPS crystallization, phase morphological characterization was undertaken. PET was selectively extracted from the blends by subjecting the blend samples to solvent extraction using a phenol : tetrachloroethane 60 : 40 (v/v) mixture. The extracted samples were characterized for their phase morphology using a scanning electron microscope. The typical micrographs for the 90/10, 75/25, and 50/50 PPS/PET (PPS-rich) compositions are shown in Figure 9. The 90/10 and 75/25 PPS/PET compositions showed a continuous/dispersed phase morphology, whereas the 50/50 PPS/PET blend composition exhibited a co-continuous phase

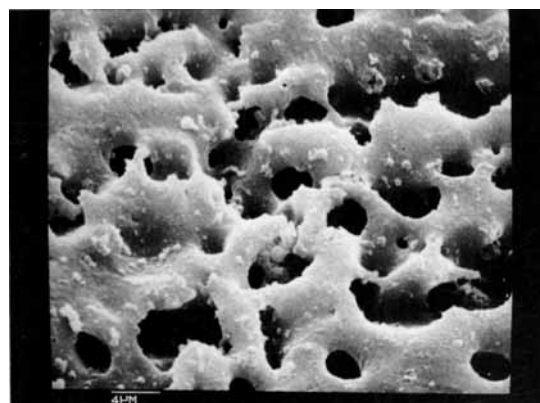
morphology. It was also observed that in the case of the 75/25 PPS/PET composition the PET domains were more volume filling and the interfacial area



(a)



(b)



(c)

Figure 9 Scanning electron micrographs of extracted blend samples: (a) PPS/PET 90/10; (b) PPS/PET 75/25; (c) PPS/PET 50/50.

between the continuous PPS phase and the dispersed PET domains was the highest compared to that in other compositions (90/10 and 50/50 PPS/PET) under investigation. Thus, the highest rate of PPS crystallization observed in 75/25 PPS/PET composition has been attributed to the highest interfacial area between the component polymers in this composition.

The fractional crystallinity was determined from the DSC isotherms by partial area integration, as reported in an earlier publication by the authors.²⁴ The crystallization half-time ($t_{0.5}$) for PPS were de-

termined from the sigmoidal curves obtained by plotting the fractional crystallinity vs. the corresponding time. The variation of half-time ($t_{0.5}$) for PPS crystallization with crystallization temperature is shown in Figure 10. The $t_{0.5}$ vs. T_c curves were shifted to lower crystallization times and higher crystallization temperatures. This indicates that the crystallization of PPS proceeds at a faster rate in its blends with PET. The composition dependence of the crystallization half-times for PPS at three different temperatures, namely, 255, 250, and 245°C, is illustrated in Figure 11. The crystallization half-

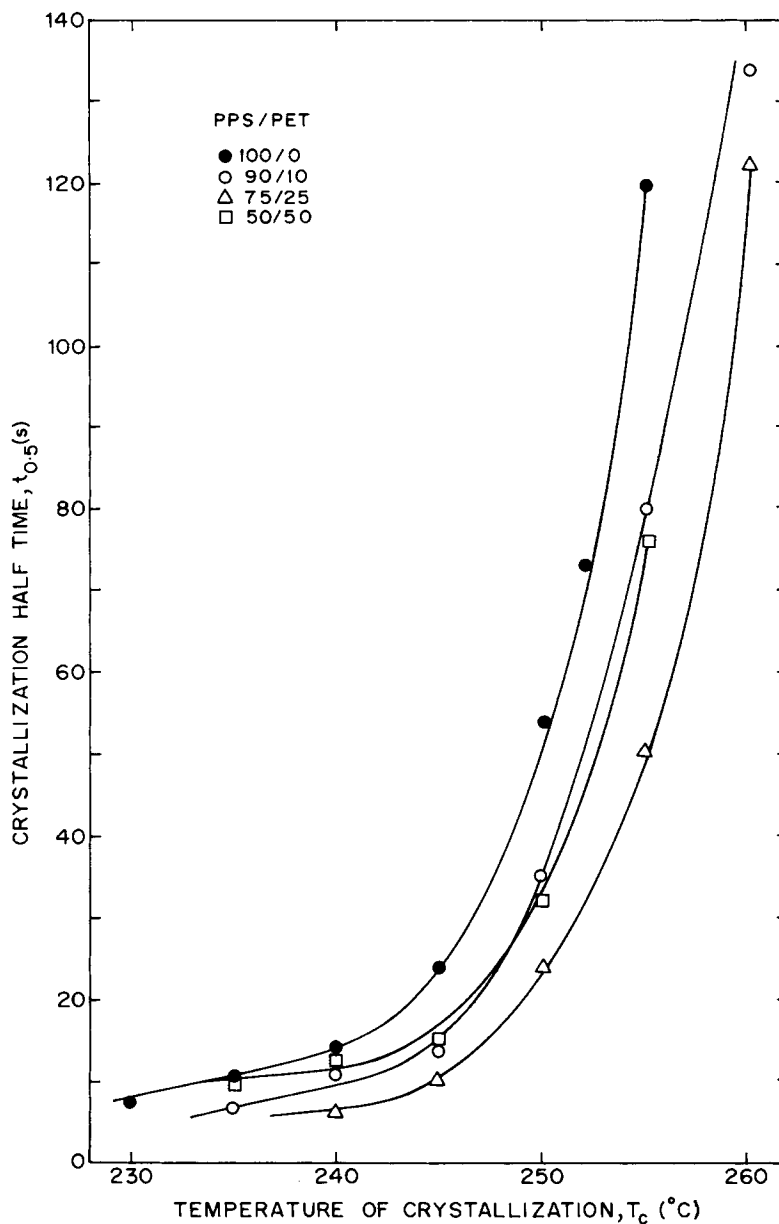


Figure 10 Variation of crystallization half-time ($t_{0.5}$) with the temperature of crystallization (T_c) for PPS in the blends.

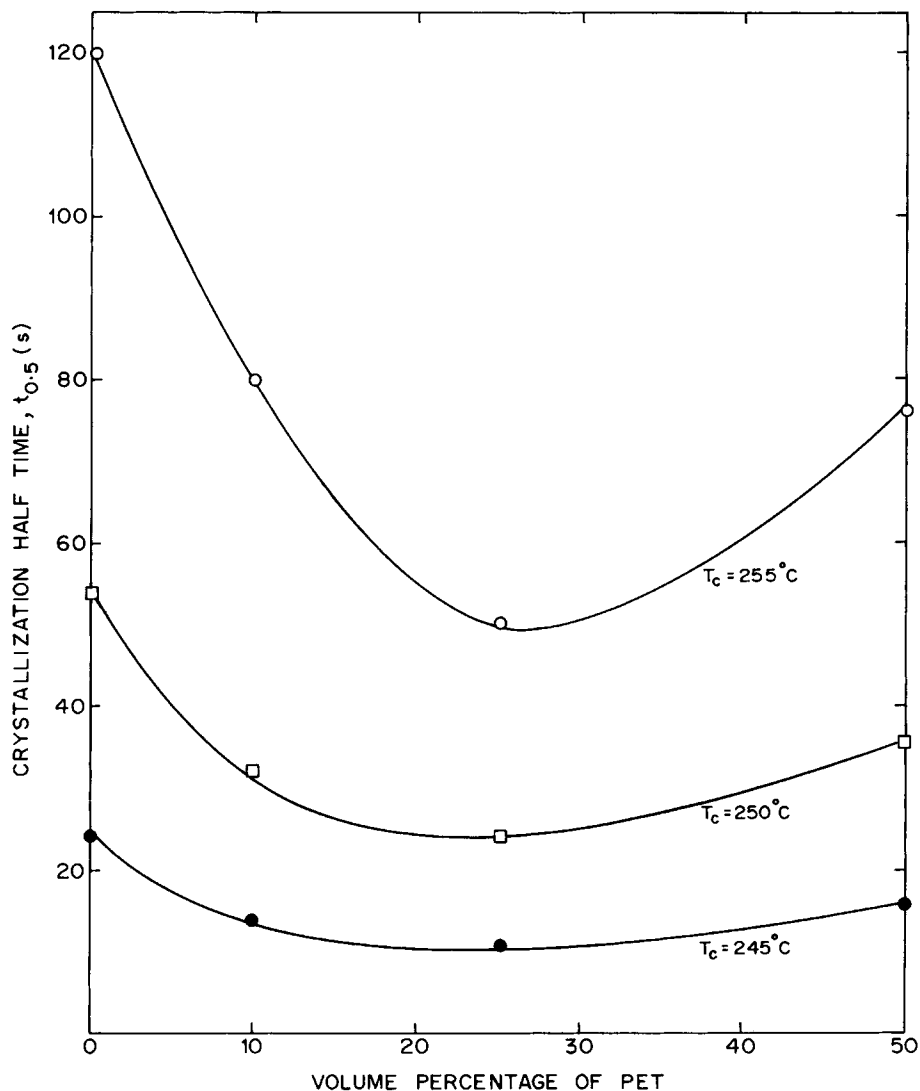


Figure 11 Composition dependence of the crystallization half-time ($t_{0.5}$) for PPS in the blends.

time vs. volume percentage curves passed through a minimum around 25% of PET, suggesting the highest rate of PPS crystallization in 75/25 PPS/PET composition. This has been attributed to the interfacial area effect as described earlier.

The crystallization rate constants (k) for PPS determined from the "S"-shaped curves by Avrami analysis are summarized in Table V. It is clear that at all crystallization temperatures the rate constants for PPS crystallization are higher in the blends than for virgin PPS, suggesting a faster rate of crystallization of PPS in the blends.

The Avrami exponent for PPS in the virgin form as well as in blends was observed to be around 2. The Avrami exponent, having a value of 2, indicates

two possibilities: either instantaneous nucleation followed by two-dimensional growth or the time-dependent nucleation followed by one-dimensional growth. The mode of nucleation and the growth geometry for PPS does not appear to change in the blends since the Avrami exponent values for PPS in the blends are comparable to those for PPS in its virgin form.

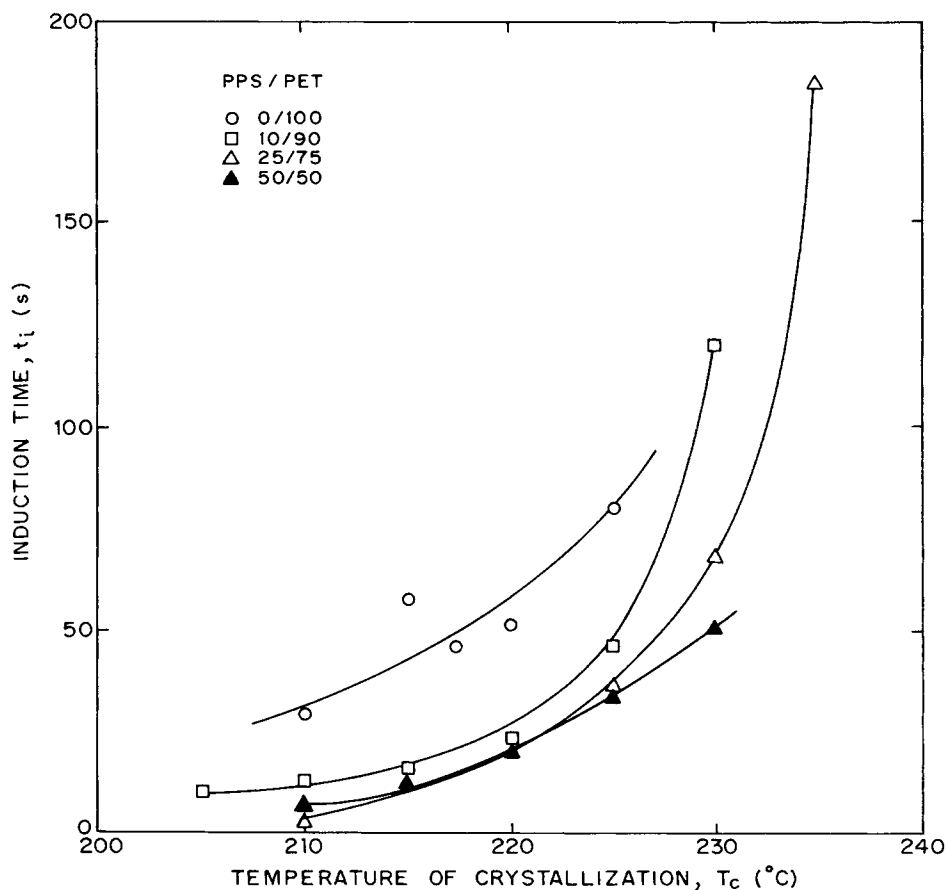
Over the temperature range of PPS crystallization (230–260°C), the PET is in the form of a supercooled melt exhibiting greater order than in its melt at temperatures above 256°C. In view of the aromatic chain structure and polar linkages in both PPS and PET, greater secondary molecular interactions would be expected in their blends. The low values

Table V Crystallization Rate Constant, $k \times 10^{-4}$ (s⁻ⁿ) for PPS in the Blends

No.	Temperature of Crystallization T_c (°C)	Blend Composition PPS/PET (w/w)			
		100/0	90/10	75/25	50/50
1	260	—	0.10	0.13	0.23
2	255	0.26	0.46	1.00	0.32
3	250	2.40	5.40	13.7	4.30
4	245	23.0	57.00	80.0	31.0
5	240	49.0	71.00	320.0	43.0
6	235	84.0	200.0	415.0	62.0
7	230	130.0	—	—	—

of the interaction parameter ($\chi_{12} = 8 \times 10^{-4}$) computed from the solubility parameters of PPS and PET suggest the possibility of secondary interactions in these blends. These factors would lead to an increase in the local ordering (“nematic alignment”) of the polymer chains in the molten state of the blends. Takahashi et al. observed such a phe-

nomenon in PVDF/PMMA blends, in which chemical interactions between the component polymers are known to exist.²⁵ They have made an attempt to quantify the order parameter (defined as the number of monomer units arranged parallel to each other) that increases dramatically in these blends. This implies that the local ordering can be induced


Figure 12 Variation of induction time (t_i) with the temperature of crystallization (T_c) for PET in the blends.

by intermolecular interactions. The presence of such local ordering would therefore facilitate the nucleation of PPS, as evidenced by a decrease in the induction time for PPS in the presence of PET.

Isothermal Crystallization of PET in the Blends

The isothermal crystallization of PET in the blends was studied over a temperature range of 210–235°C, whereas the isothermal crystallization temperature range for virgin PET was 210–225°C. Thus, the highest temperature at which PET crystallization could be detected and recorded under given experimental conditions shifted by as much as 10°C as a result of blending with PPS. This dramatic shift clearly indicates that the nucleation of PET is facilitated by the presence of PPS.

The induction time analysis was carried out for PET crystallization and the temperature dependence of induction time for PET crystallization is shown in Figure 12. It is observed that the induction time for PET crystallization decreases dramatically as a result of blending with PPS. It is observed that as the amount of PPS in the blends increases the induction time required to initiate PET crystallization decreases. This effect was observed to be predominant at higher crystallization temperatures (nucleation-controlled region) rather than at lower

temperatures. This is to be expected in view of the heterogeneous nucleation mode. The induction time required to initiate PET crystallization was found to level off when the PET content in the blend was more than 30% by weight.

The temperature dependence of the crystallization half-time ($t_{0.5}$) for PET in the blends is shown in Figure 13. The curves of $t_{0.5}$ vs. T_c were observed to shift to shorter times and higher temperatures, confirming the faster crystallization of PET. The crystallization rate constants for PET at different temperatures are summarized in Table VI. These data also confirm the acceleration of PET crystallization in the blends.

A similar increase in the isothermal crystallization rate for PET in its blends with poly(methyl methacrylate) (PMMA) has been observed by Nadkarni and Jog.²³ This has been attributed by the authors to the enhancement in the nucleation of PET. However, in the PET/PMMA blends, the crystallization of PET takes place in the presence of molten PMMA, whereas in the present investigation, the increase in the rate of PET crystallization is due to heterogeneous nucleation provided by the already-solidified PPS.

Thus, in summary, it can be concluded that the crystallization behavior of both PPS and PET were found to be modified as a result of blending. Both

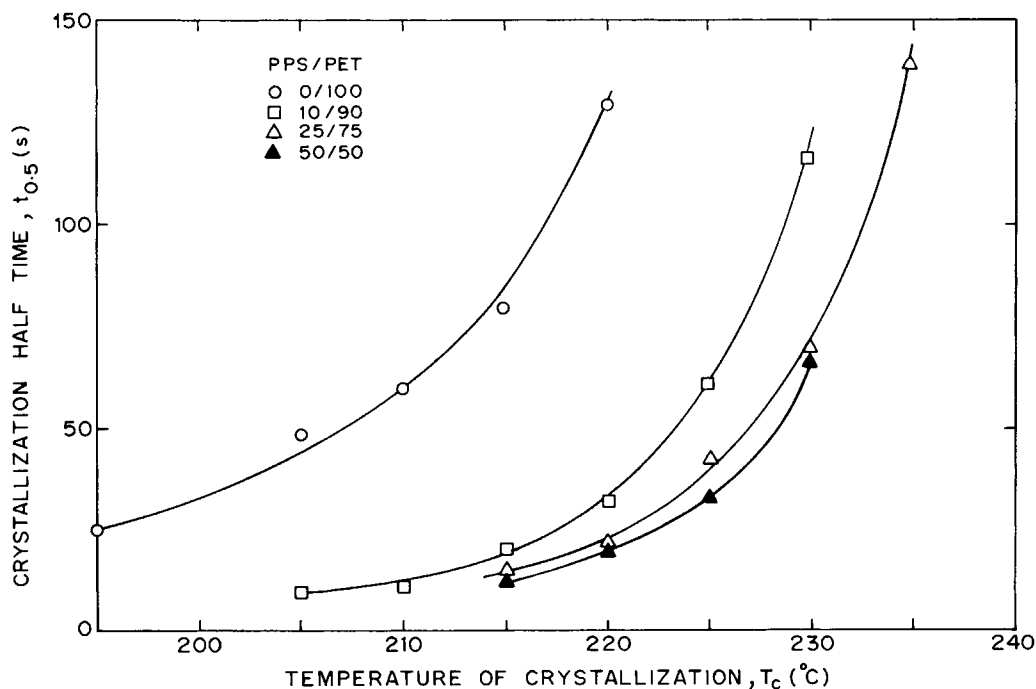


Figure 13 Variation of crystallization half-time ($t_{0.5}$) with the temperature of crystallization (T_c) for PET in the blends.

Table VI Crystallization Rate Constant, $k \times 10^{-4}$ (s⁻ⁿ) for PET in the Blends

No.	Temperature of Crystallization T_c (°C)	Blend Composition PPS/PET (w/w)			
		0/100	10/90	25/75	50/50
1	235	—	—	0.27	—
2	230	—	1.00	1.30	1.10
3	225	—	2.00	8.70	7.80
4	220	—	4.50	—	57.0
5	215	—	44.0	85.0	78.0
6	210	0.62	89.0	31.0	—
7	205	1.78	197.0	—	—
8	200	0.87	—	—	—
9	195	2.77	—	—	—
10	190	4.50	—	—	—

PPS and PET were found to crystallize at a faster rate in the presence of the other component. However, the extent of acceleration in the rate of crystallization for PET was observed to be more pronounced as compared to that for PPS. This has been explained on the basis of heterogeneous nucleation provided by the already-crystallized PPS. As a result, the blends exhibited a marginally higher degree of crystallinity in comparison to the values computed from the proportional additivity rule.

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