

Thermal and Crystallization Behavior of Engineering Polyblends. I. Glass Reinforced Polyphenylene Sulfide with Polyethylene Terephthalate*

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Synopsis

The thermal and crystallization behavior of blends of glass fiber reinforced polyphenylene sulfide (PPS) with polyethylene terephthalate (PET) has been reported. The blends showed two overlapping melting peaks and two separate crystallization peaks. The heat of crystallization of PPS was found to decrease continuously with increasing PET content, whereas the heat of crystallization of PET was found to increase with increasing PPS content. This indicates that the degree of crystallinity of PPS is reduced whereas that of PET is increased as a result of blending. It is interesting to note that the combined heats of fusion of the blends were marginally higher than those calculated by proportional additivity rule in spite of the drop in the heat of crystallization of PPS. The temperature onset of crystallization of PET in the blends shifted to higher temperature whereas there was no significant change in the crystallization temperature of PPS. The increase in the temperature of crystallization of PET indicates enhanced nucleation. The isothermal crystallization studies of the component polymers revealed that both the component polymers crystallized at a relatively faster rate in the blend. The crystallization rate of PPS was found to increase significantly with increasing PET content. A significant increase in the rate of crystallization of PET was also observed in the blends. The acceleration of crystallization rate of PET in the blends was more pronounced as compared to that of PPS. The acceleration in the PET crystallization rate was attributed to the presence of glass fibers and crystallized PPS.

INTRODUCTION

The technique of blending two polymers for obtaining a balanced combination of properties has been recognized as a cost-effective method to tailor-make materials to meet specific end-use requirements. The properties of the blends depend on the properties of the component polymers, their mutual compatibility/interaction in the solid phase, and the degree of mixing. The morphology of a molded part of a polyblend consisting of two crystallizable polymers can vary depending on the molding conditions and the relative rates and temperatures of crystallization of the component polymers. The constituent polymers can either crystallize at the same time or separately in a sequential manner, leading to different morphologies and hence different properties. Thus, in a blend of two semicrystalline polymers, the physical properties may be altered not only by the composition but also by changing

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their relative crystallization behavior. Therefore, it is important to study the effect of crystallization conditions on the crystallization behavior of the component polymers in the blend, in order to understand the structure development in melt processing.

The blends may consist of crystalline/amorphous or crystalline/crystalline components. Depending upon the difference in the melting points of the component polymers, the crystallization conditions would change. For example, if the difference in the melting points is small, both the polymers may crystallize over the same temperature range. On the other hand, if the melting point difference is significant, then one of the components would crystallize in the presence of the melt of the other component; whereas the second component in this case would crystallize in the presence of the solid phase of the other component. The presence of a second fluid or solid phase would influence the relative rate of crystallization and the degree of crystallinity, thereby modifying the morphology.

Martuscelli¹ has recently reviewed the effect of composition and crystallization conditions on the morphology and crystallization behavior of polymer blends. He has presented the results in terms of various parameters such as radial growth rate, overall rate of crystallization, equilibrium melting point, lamellar thickness, and long spacing. In case of compatible crystalline/amorphous blends, a decrease in the radial growth rate and a depression in melting point were observed with increasing content of the noncrystallizing component. In case of crystalline/crystalline blends, a decrease in radial growth rate, long spacing, and lamellar thickness were observed. In another study of blends of polycarbonate with polyesters, Paul and Barlow^{2,3} have reported a decrease in the crystallinity of the polyesters, namely, polybutylene terephthalate and polyethylene terephthalate. Escala and Stein⁴ have studied the crystallization behavior of polyethylene terephthalate/polybutylene terephthalate blends. They have reported that both the components crystallized separately according to their own crystal structure. However, a decrease in the crystallization rate was observed with increase in the amount of the second component. In a recent study of blends of poly-propylene with poly-1-butene, Siegmann⁵ has reported that the crystallization process of both components was significantly affected, resulting in a lower degree of crystallinity, depression in melting point, and a change in morphology from spherulitic to branched crystallites. Gupta et al.⁶ have reported an enhancement in nucleation, reduction in size of crystallites, and a lower degree of crystallinity in polypropylene when blended with high density polyethylene. The crystallization behavior of polyphenylene sulfide was found to be significantly affected by the presence of high density polyethylene melt, resulting in a lower degree of crystallinity and a narrower crystallite size distribution.⁷ Also in case of polyethylene terephthalate, the addition of polymethylmethacrylate increased the rate of crystallization of PET, leading to improved processibility at low mold temperatures, as reported by Nadkarni and Jog.⁸ Thus, it is established that the crystallization behavior and morphology of component polymers are considerably modified in polyblends.

This paper reports the results of thermal and crystallization studies of blends of glass-reinforced PPS with PET. Both these polymers have comparable melting points and crystallization temperatures. In terms of the relative

crystallization rates, PPS exhibits fast crystallization, whereas the crystallization of PET is sluggish.

EXPERIMENTAL

Materials. The glass fiber reinforced grade of polyphenylene sulfide, Ryton R-4 (40% fibers) supplied by Phillips Petroleum Co., and polyethylene terephthalate, clear grade Arnite A04 300, supplied by Cenka Plastics (India) were used for the preparation of the blends. The PET pellets were dried in vacuum oven at 120°C for 6 hrs before melt compounding.

Preparation of Blends. The blends were prepared by melt compounding in a Brabender Plasticorder mixer (PLE 330) at 285°C in nitrogen atmosphere, at a speed of 40 rpm with a residence time of 5 min. Five blends were prepared covering the entire range of PPS/PET compositions as per details summarized in Table I.

Thermal and Isothermal Crystallization Studies

The thermal characterization and crystallization studies were carried out using a Perkin Elmer DSC-2, Differential Scanning Calorimeter upgraded with Thermal Analysis Data Station (TADS). Indium was used as the reference sample for the calibration of temperature and energy scales.

The thermal parameters were obtained from the DSC scans of the sample heated at 10°C/min. up to 300°C, cooled at 10°C/min. to 50°C and then reheated at 10°C/min to 300°C. The melting parameters of the blend samples were determined from the reheating scans, since these would represent morphologies of samples crystallized from the melt under identical cooling rates. It may be noted that the first heating scans of the as-compounded samples cannot be compared in view of the different and uncontrolled quench conditions encountered by the different samples. The heat of crystallization was calculated from the cooling scans. These values of heat of fusion and heat of crystallization were corrected for glass fiber content in order to obtain the values of the heat of fusion and crystallization of the component polymers.

The isothermal crystallization studies were carried out over a wide range of temperatures of crystallization. The sample was heated to 300°C and held at that temperature for two minutes to destroy any residual nuclei. The sample was then cooled at 160°C/min. to a predetermined temperature of crystalliza-

TABLE I
Composition of PPS/PET Blends

Blend composition PPS/PET by weight %	100/0	90/10	75/25	50/50	25/75	10/90	0/100
PPS	60	54	45	30	15	6	—
PET	—	10	25	50	75	90	100
Glass Fiber	40	36	30	20	10	4	—
Blend Composition by volume %							
PPS	100	88.3	71.5	45.6	21.8	8.5	0
PET	0	11.7	28.5	54.4	78.2	91.5	100

tion, T_c , at which the exothermic crystallization peak was recorded on time base. The total crystallization time, t_c , was calculated from the width of the exothermic peak. The details of the experimental technique are discussed in earlier publications by the authors.⁷⁻⁹

RESULTS AND DISCUSSION

Melting Behavior of the Blends

The DSC scans of the blends were used to determine a number of parameters signifying the melting and nonisothermal crystallization behavior of the components in the blends. The melting parameters include the onset of melting (T_1), melting peak temperatures (T_2 , T_3), completion of melting (T_4),

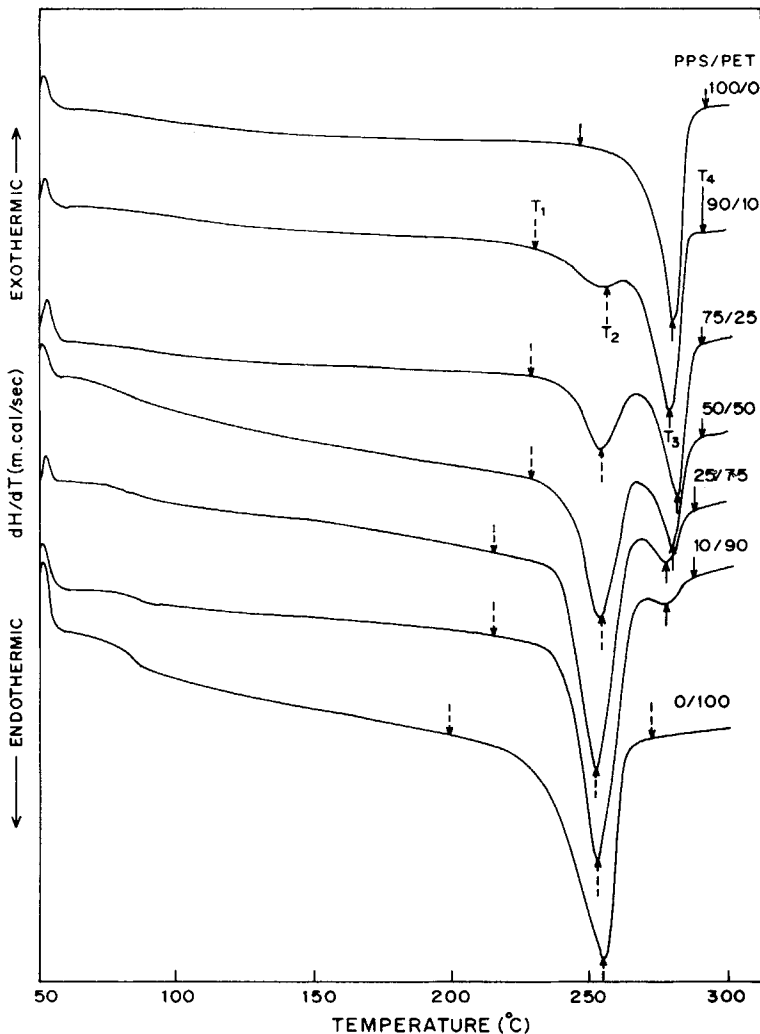


Fig. 1. DSC scans of PPS/PET blends in reheating mode (Heating rate = $10^\circ C/min$).

melting temperature range, and heat of fusion determined from the reheating scans. The onset of crystallization (T_5 , T_8), crystallization peak temperature (T_6 , T_9), completion of crystallization (T_7 , T_{10}), and heat of crystallization were determined from the cooling scans. The DSC scans of the component polymers and the blends in the heating and cooling mode are shown in Figures 1 and 2 respectively, wherein the nomenclature for the thermal parameters is also indicated.

The blends exhibit overlapping melting peaks in the heating scan and two distinct crystallization peaks in the cooling scan. The data on the melting behavior of the blends are summarized in Table II. The calculated heat of fusion for the blends was computed by using proportional additivity rule on the basis of actual weight percentages of the polymers, excluding glass fibers,

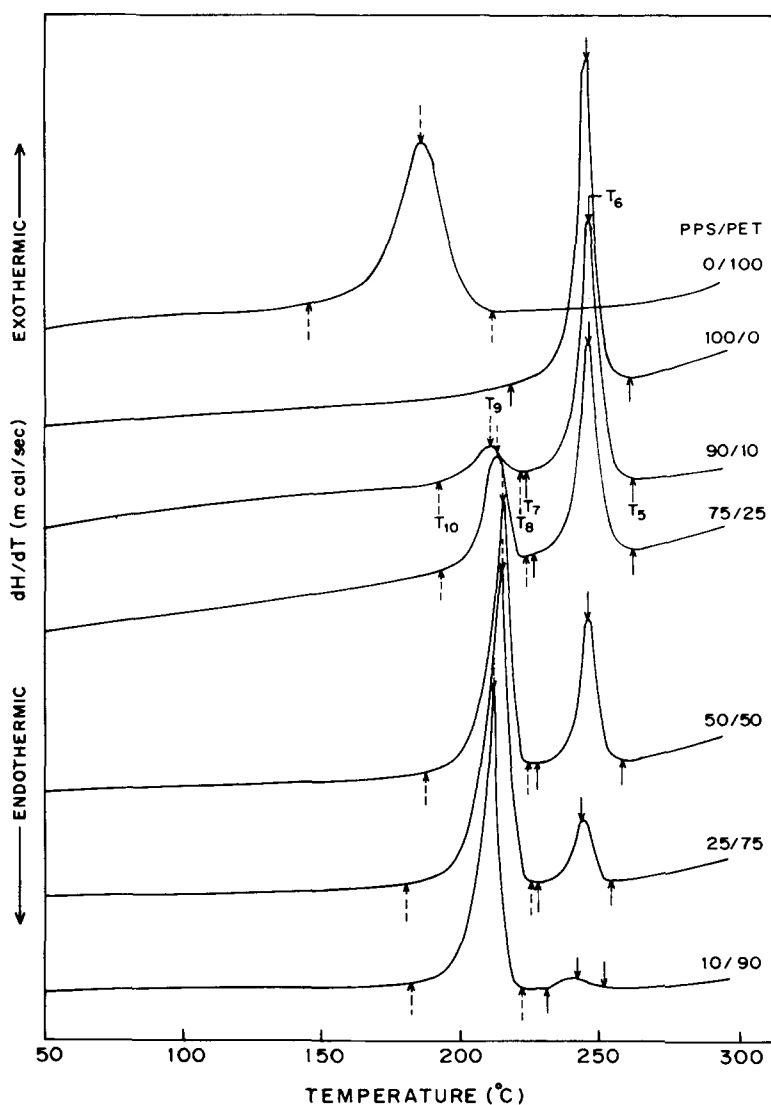


Fig. 2. DSC scans of PPS/PET blends in cooling mode (Cooling rate = $10^{\circ}\text{C}/\text{min}$).

TABLE II
Melting Behavior of PPS (R-4)/PET Blends

Sr. No.	Blend composition PPS/PET weight %		Melting parameters from the DSC reheating scans							Heat of fusion ΔH_f^* (Cal/g)
	With glass fibers	Without glass fibers	Onset of melting	Peak Temperature PET	Peak Temperature PPS	Completion of melting	Peak width	Exptl. (Cal/g)		
			T_1 (°C)	T_2 (°C)	T_3 (°C)	T_4 (°C)	$T_4 - T_1$ (°C)			
1	100/0	—	247.0	—	280.0	293.0	46.0	9.2	—	
2	90/10	84/16	230.0	254.0	279.0	291.0	61.0	10.3	9.2	
3	75/25	64/36	229.0	254.0	281.0	291.0	62.0	10.1	9.3	
4	50/50	38/62	228.0	254.0	280.0	290.0	62.0	10.1	9.4	
5	25/75	17/83	214.0	252.0	277.0	287.0	73.0	10.3	9.4	
6	10/90	6/94	215.0	252.0	282.0	287.0	72.0	10.3	9.5	
7	0/100	—	199.0	255.0	—	273.0	74.0	9.5	—	

* ΔH_f calculated excluding glass fibers

as given below:

$$\Delta H_{f(50/50)} = 0.38(\Delta H_{f(\text{PPS})}) + 0.62(\Delta H_{f(\text{PET})})$$

The variation of the onset of melting, peak temperature, and completion of melting for PPS and PET phases in the blends is illustrated in Figure 3. The onset of melting for PPS could not be determined experimentally as the two melting peaks are overlapping.

The melting peak temperatures for both PPS and PET and the temperature at completion of melting for PPS do not vary significantly with composition. However, the onset of melting for PET in the blends is considerably higher than virgin PET. The onset of melting for PET homopolymer was observed at 199°C, whereas in the blends, the onset of melting varied from 214

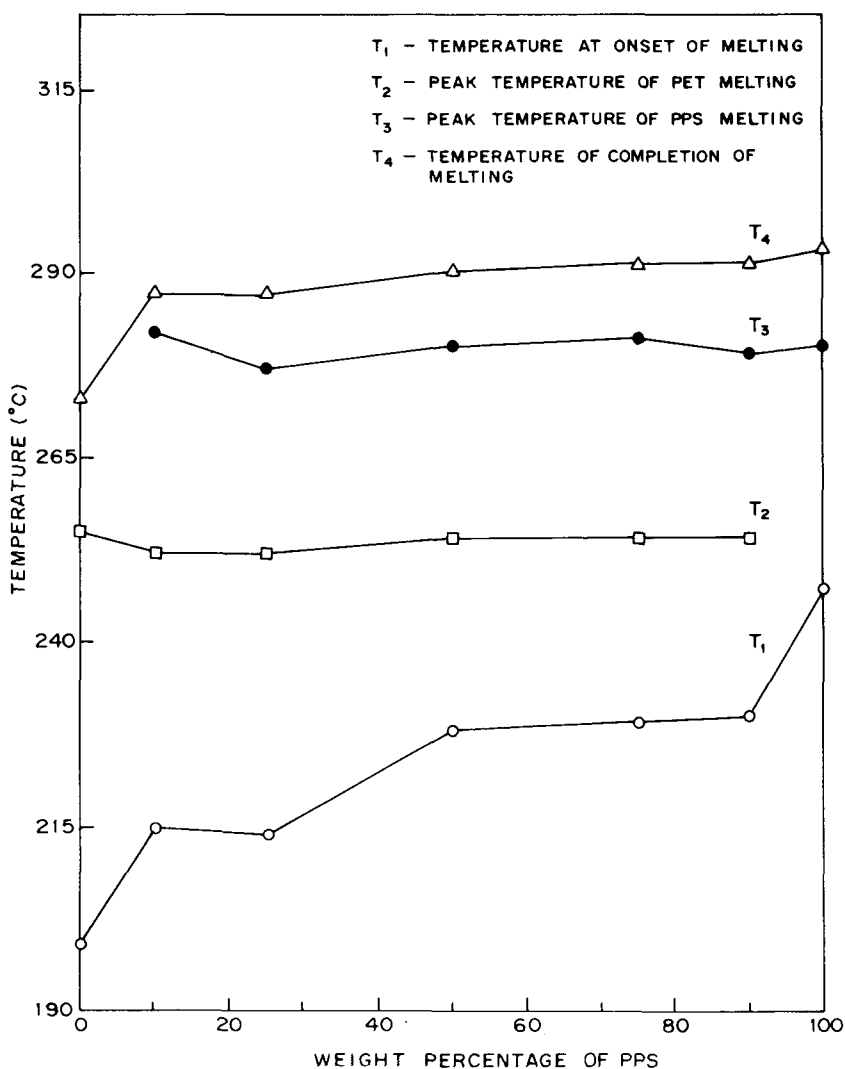


Fig. 3. Melting parameters for PPS/PET blends.

to 230°C. It was also observed that for PPS rich blends the onset of melting was about 15°C higher than the PET rich blends. This increase in onset of melting may be attributed to an increase in the crystallite size of PET in the blends.

The melting range, which is the temperature difference between the completion and onset of melting (T_4-T_1), is narrower in the blends as compared to the theoretical value. Theoretically the combined melting range should have been from 199°C (onset of melting for PET) to 293°C (completion of melting for PPS), that is, 94°C. But the observed combined melting range for the blends varied from 61–73°C indicating a narrower crystallite size distribution in the blends.

Figure 4 shows the variation of heat of fusion for the blends with composition. The heats of fusion for the constituents in the blends as calculated from the area under the combined melting peak are about 10% higher than those obtained by the additivity rule. However, the total degree of crystallinity is insensitive to the blend composition as indicated by their comparable heats of fusion in the range of 10 cal/g. The marginal increase of about 10% in the overall crystallinity can be explained on the basis of the heterogeneous nucleation provided by the glass fibers and already crystallized PPS to a moderately crystallizing PET phase. Thus, during the controlled cooling, PET

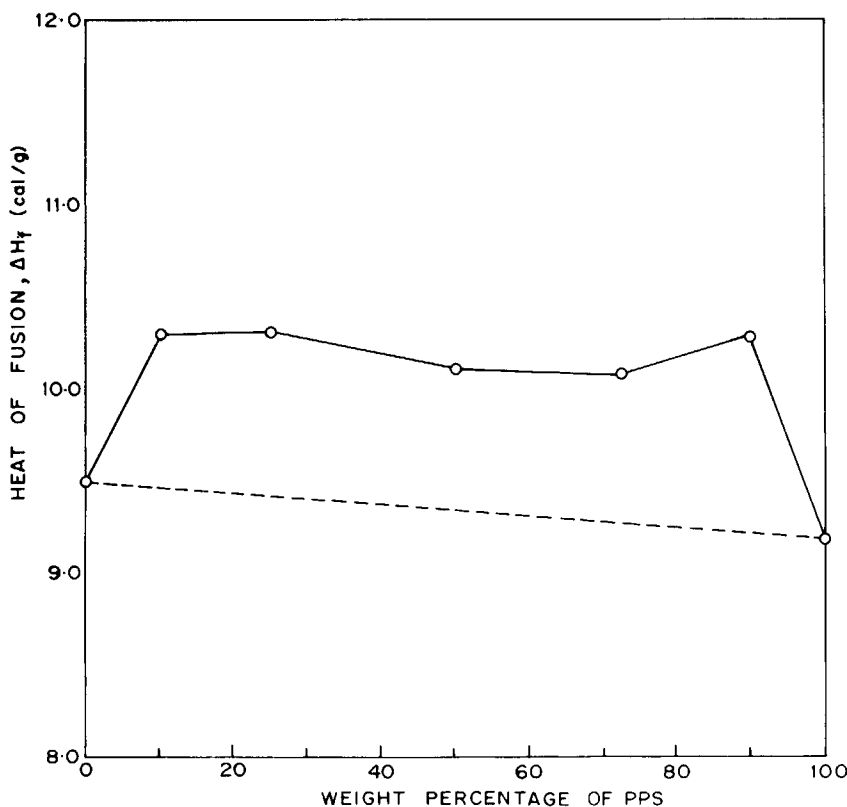


Fig. 4. Heat of fusion of PPS/PET blends; --- calculated — experimental values.

TABLE III
Nonisothermal Crystallization Behavior of PPS(R-4) in the Blends

Sr. No.	Blend composition PPS/PET Weight %	Crystallization parameters for PPS(R-4) from the DSC cooling scans							Heat of crystallization* ΔH_c (cal/g)
		Onset T_5 (°C)	Peak T_6 (°C)	Completion T_7 (°C)	Peak Width $T_5 - T_7$ (°C)	Degree of supercooling $\Delta T = T_3 - T_5$ (°C)			
1	100/0	260.0	244.0	216.0	44.0	20.0		10.2	
2	90/10	260.0	246.0	223.0	37.0	19.0		9.8	
3	75/25	260.0	245.0	225.0	35.0	21.0		9.3	
4	50/50	258.0	244.0	226.0	32.0	22.0		8.9	
5	25/75	253.0	242.0	226.0	27.0	24.0		7.8	
6	10/90	253.0	237.0	227.0	26.0	29.0		5.1	
7	0/100	—	—	—	—	—		—	

*Per gram of PPS in the blend (excluding glass fibers)

TABLE IV
Nonisothermal Crystallization Behavior of PET in the Blends

Sr. No.	Blend Composition PPS/PET Weight %	Crystallization parameters for PET from the DSC cooling scans						Heat of crystallization* ΔH_c (cal/g)
		Onset T_8 ($^{\circ}\text{C}$)	Peak T_9 ($^{\circ}\text{C}$)	Completion T_{10} ($^{\circ}\text{C}$)	Peak Width $T_8 - T_{10}$ ($^{\circ}\text{C}$)	Degree of supercooling $\Delta T = T_2 - T_8$ ($^{\circ}\text{C}$)		
1	100/0	—	—	—	—	—	—	—
2	90/10	221.0	210.0	191.0	30.0	33.0	8.1	8.1
3	75/25	222.0	212.0	189.0	33.0	32.0	9.4	9.4
4	50/50	224.0	214.0	186.0	38.0	30.0	10.6	10.6
5	25/75	224.0	213.0	180.0	44.0	28.0	10.6	10.6
6	10/90	221.0	209.0	175.0	46.0	31.0	10.5	10.5
7	0/100	211.0	186.0	145.0	66.0	44.0	7.7	7.7
8	35% glass filled PET	224.0	215.0	191.0	33.0	39.0	9.0	9.0

*Per gram of PET in the blend.

develops a considerable amount of crystallinity, as indicated by the increased heat of fusion for the blends in the reheating scans.

In summary, the melting behavior of the blends indicates the presence of larger crystallites with a narrower distribution and an increased degree of crystallinity of the component polymers in the blends.

Nonisothermal Crystallization

The parameters characterizing the nonisothermal crystallization behavior of the component polymers in the blends are summarized in Tables III and IV. With reference to Table III, it is clear that the nonisothermal crystallization behavior of PPS is not altered significantly by blending, in terms of the onset and peak temperatures of crystallization, except for PET rich compositions. The degree of supercooling ΔT , for PPS ($T_3 - T_5$), is comparable for all the blend compositions except for PPS/PET 10/90 where PET forms a major phase, thereby retarding the crystallizing ability of PPS (without glass fibers this composition is 6/94 of PPS/PET). However, the crystallization peak width, which is the temperature range over which PPS crystallizes in the blends ($T_5 - T_7$), decreases linearly with increasing PET content, from 44°C to 26°C (Fig. 5). This is indicative of narrowing down of the temperature range of crystallization for PPS in the presence of molten PET. The heat of

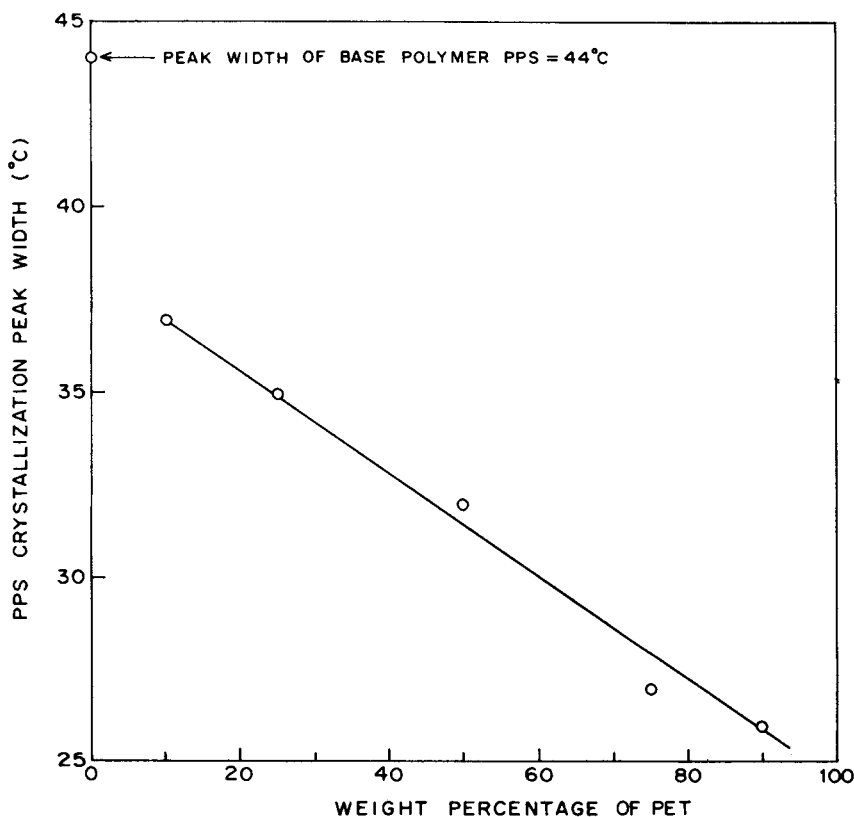


Fig. 5. PPS crystallization peak width against weight percentage of PET.

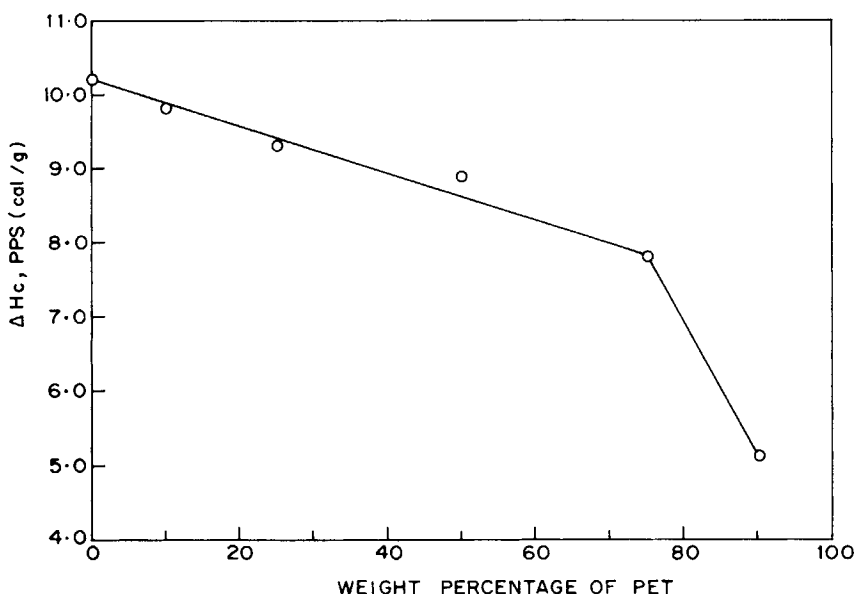


Fig. 6. Heat of crystallization for PPS against weight percentage of PET.

crystallization for PPS in the blends decreases with increasing PET content (Fig. 6). It may be noted here that the heat of crystallization for PPS in 10/90 PPS/PET composition is considerably lower because of PET being the major phase (94% excluding glass fibers).

Referring to Table IV it is observed that the nonisothermal crystallization behavior of PET gets altered significantly. The onset temperature of crystallization for base polymer PET is 211°C. In the blends, the onset of crystallization for PET increases considerably and varies between 221 to 224°C. This can be attributed to the heterogeneous nucleation provided by the glass fibers and the already solidified PPS in the blend. The degree of supercooling ($\Delta T = T_2 - T_8$) required for PET crystallization varies between 28–33°C in all the blend compositions and is considerably less than that for PET homopolymer ($\Delta T = 44^\circ\text{C}$).

This conclusion is supported by the fact that the degree of supercooling for glass fiber reinforced PET (35% glass fibers) is comparable. The dependence of peak width on the blend composition is shown in Figure 7. The significant decrease in the crystallization peak width ($T_8 - T_{10}$) from 66°C to 31°C as a result of blending can be attributed to the heterogeneous nucleation of PET. The heat of crystallization for PET in the blends shows a considerable increase as compared to the homopolymer.

The PET crystallization is known to involve a slower homogeneous nucleation step followed by the growth process. In case of its blends with PPS, the glass fibers and the already solidified PPS can act as heterogeneous nuclei, thereby facilitating PET crystallization in the blends. Thus, PET in the blends exhibits higher crystallinity as indicated by the higher heats of crystallization and fusion, and faster crystallization rate as indicated by narrower peak widths.

In summary, the blending of PPS with PET modifies the crystallization behavior of both the components. The extent of modification is not significant

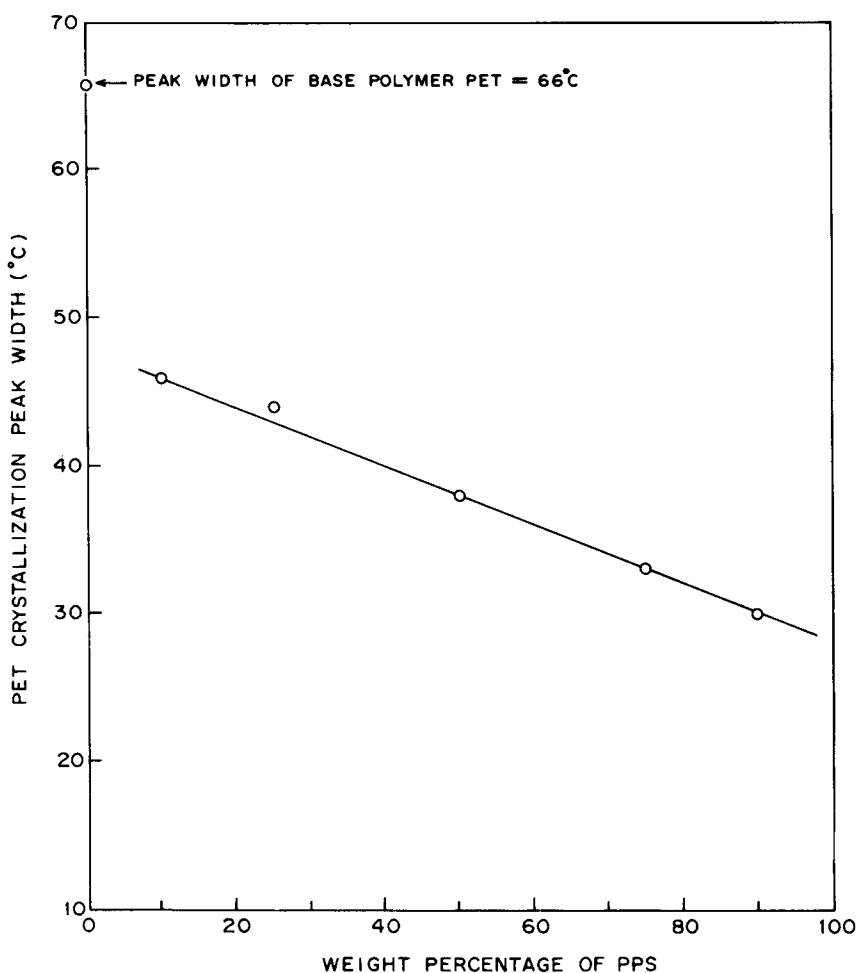


Fig. 7. PET crystallization peak width against weight percentage of PPS.

for PPS, whereas the crystallization behavior of PET gets modified considerably.

Isothermal Crystallization of PPS in the Blends

The onset of crystallization of PPS takes place at a temperature around 255°C comparable to the melting point of PET. Therefore, PPS crystallization would occur in the presence of molten PET. The effect of PET melt on the isothermal crystallization behavior of PPS was further investigated.

The isothermal crystallization of PPS was studied over a temperature range of 230°C to 260°C. The variation of crystallization time, t_c , with temperature of crystallization, is shown in Figure 8. The crystallization time for PPS could be measured only for three, PPS rich blend compositions. Referring to Figure 8 at a particular crystallization temperature, the crystallization time for PPS in the blends is less than that of virgin PPS. The crystallization time was found to decrease considerably with increasing PET content (Fig. 9). It may be noted that the compositions of relevance are the volume compositions.

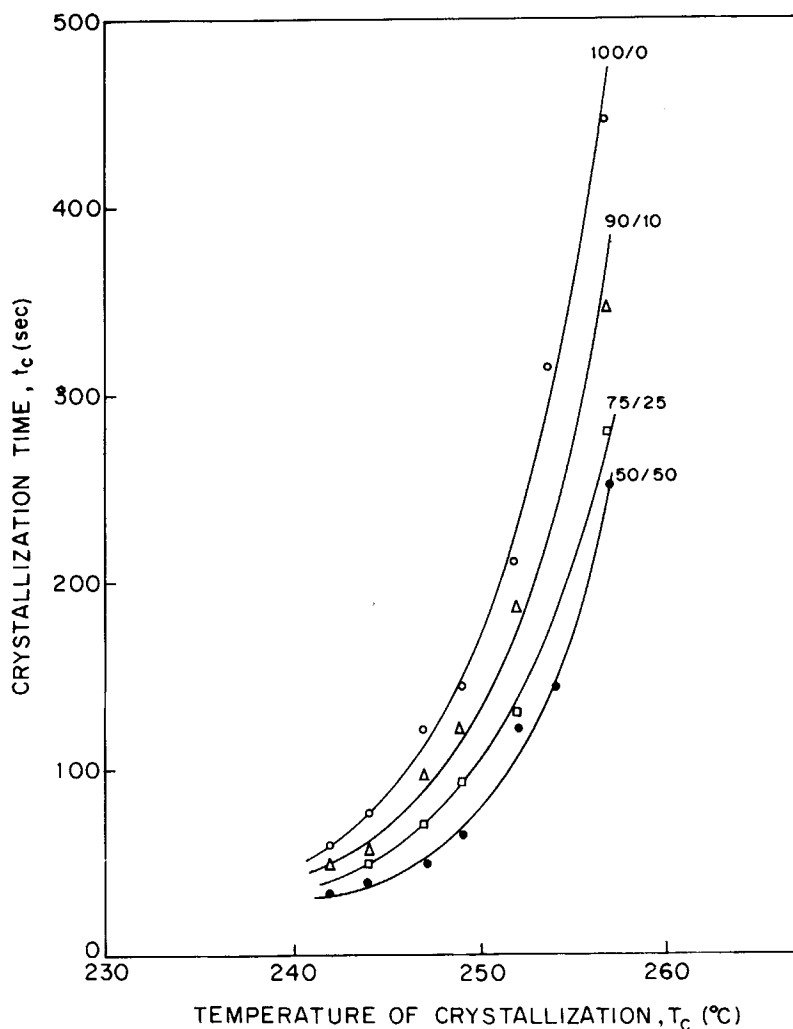


Fig. 8. Variation of isothermal crystallization time, t_c , with temperature of crystallization, T_c , for PPS in PPS/PET blends.

Thus, the crystallization rate of PPS is accelerated to a small extent by the presence of PET melt and the extent of acceleration is composition dependent. These results are consistent with the nonisothermal crystallization behavior.

Isothermal Crystallization of PET in the Blends

The isothermal crystallization of PET in the blends was investigated over a temperature range of 200° to 230°C. It can be seen that the t_c versus T_c curves (Fig. 10) are shifted by blending to significantly higher temperatures and lower crystallization times, even at 10% addition of PPS. The crystallization time progressively decreases with increasing amount of PPS in the blends. The PET crystallization time decreases considerably with increasing amount of PPS (Fig. 11). The reduction in the crystallization time may be

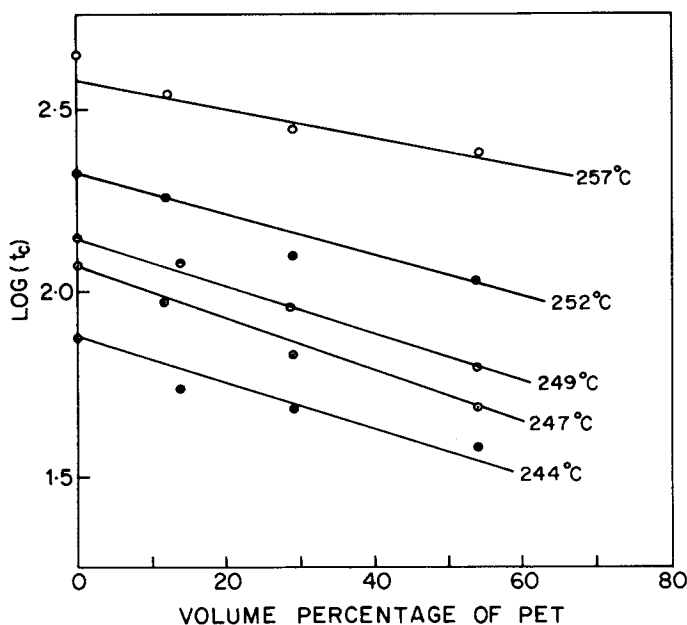


Fig. 9. Dependence of isothermal crystallization time on composition at different temperatures of crystallization for PPS in PPS/PET blends.

attributed to the acceleration of the crystallization rate due to enhanced nucleation since PET crystallizes in the presence of crystallized PPS. PPS crystallites besides glass fibers can act as heterogeneous nuclei, thereby accelerating the crystallization process. As a result, PET crystallization takes place at progressively higher temperatures with increasing PPS content. These results are consistent with nonisothermal behavior which showed an increase in the temperature onset of crystallization of PET with increasing amounts of PPS. Crystallization at higher temperatures would lead to better crystal perfection and probably larger crystallite size. This contention is supported by the fact that the PET in the blends exhibited a significantly higher temperature at onset of melting, indicating larger crystallite size and better crystal perfection. Also, the extent of acceleration in crystallization due to blending is more pronounced for PET than for PPS. This is to be expected since the virgin PET grade is unfilled and hence its crystallization involves slower homogeneous nucleation step.

With reference to Figure 10, it can be seen that the isothermal crystallization behavior of the blends is similar to the glass filled PET. The enhanced nucleation in the PPS/PET blends may be attributed to the presence of both glass fibers and solidified PPS.

Thus it may be concluded that the crystallization of both the component polymers is affected by the presence of the other phase in the blend. There is considerable drop in the heat of crystallization of PPS with increasing PET content. On the other hand, the blending with PPS significantly increases the heat of crystallization of PET. Since the increase in the heat of crystallization of PET is greater than the drop in the heat of crystallization of PPS, the reheating scans of the melt crystallized blends showed a marginal increase in

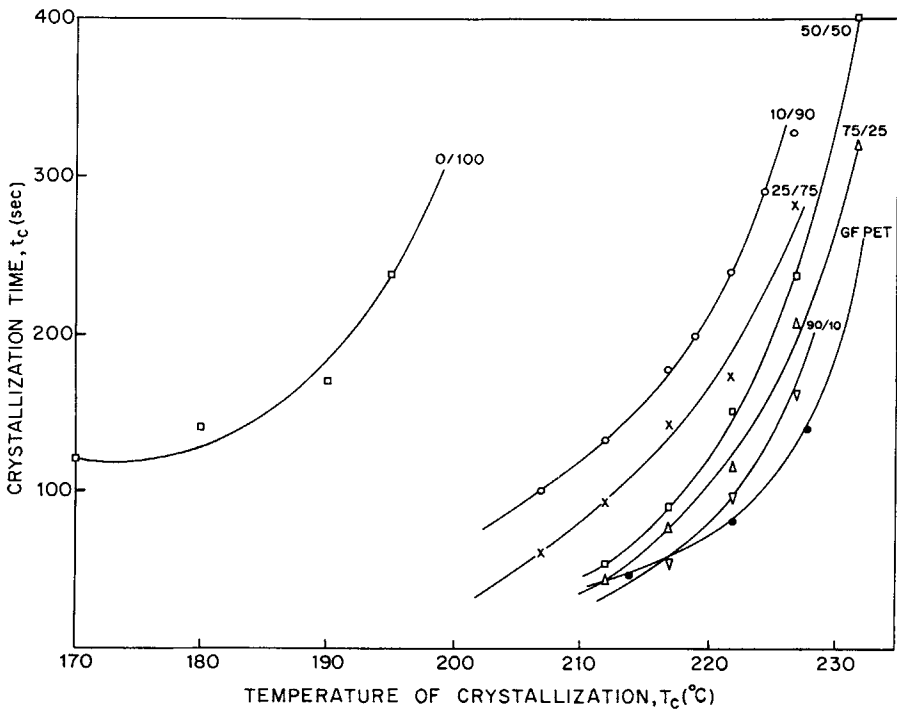


Fig. 10. Variation of isothermal crystallization time t_c with temperature of crystallization, T_c , for PET in PPS/PET blends.

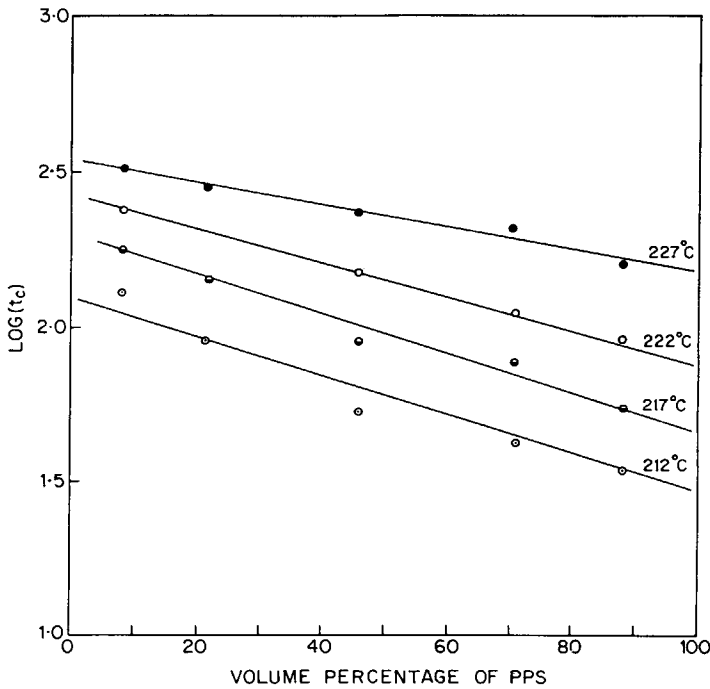


Fig. 11. Dependence of isothermal crystallization time on composition at different temperatures of crystallization for PET in PPS/PET blends.

the heat of fusion. Thus blending increases the degree of crystallinity of PET whereas the degree of crystallinity of PPS is reduced. It was observed that the isothermal crystallization rates of the component polymers are also accelerated as a result of blending. The isothermal crystallization time versus temperature curves for the polymers in the blend shift to higher temperatures and shorter times compared to the virgin polymers. The extent of acceleration of the crystallization process depends on the blend composition. Since the crystallization of the component polymers in the blend takes place at relatively higher temperatures compared to the virgin polymers, it would lead to a narrower crystallite size distribution and bigger crystallite size. This conclusion is supported by the higher temperatures at onset of melting and narrower melting peaks observed in the reheating scans of the blends.

In PPS/PET blends, PPS is crystallizing in the molten PET. The effect of molten phase on the degree of crystallinity, crystallization rate, and morphology of PPS observed in the present investigation are consistent with the earlier findings in PPS/HDPE blends.⁷

In order to distinguish the relative effects of PPS particles and glass fibers on PET crystallization, studies are being conducted on the blends of unfilled PPS with PET.

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