Thermal and Crystallization Behavior of Alloys of Polyphenylene Sulfide and High-Density Polyethylene

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Synopsis

The thermal and crystallization behavior of alloys of two semicrystalline thermoplastics, namely, polyphenylene sulfide (PPS) and high-density polyethylene (HDPE) were studied by differential scanning calorimetry (DSC). The presence of a second component in the alloy was found to influence the nonisothermal crystallization process of both the component polymers. The crystallization temperature of PPS in the DSC cooling scan is significantly affected, whereas there is little variation in case of HDPE in the composition range studied. The morphological changes observed in both PPS and. HDPE are similar. These include larger crystallite size, a narrower crystallite size distribution, and a lower degree of crystallinity in the alloys as compared to the homopolymers. The isothermal crystallization of the component polymers in the alloys is significantly different from that of the homopolymer. The composition dependence of the overall rate of isothermal crystallization is explained in terms of the competing processes of nucleation and crystal growth. The results show that blending of a high melting polymer with a low melting polymer accelerates the crystallization of the high melting polymer, even at low levels of about 10% of the lower melting component.

INTRODUCTION

The technique of alloying polymers has given the polymer scientist and engineer an effective tool to tailor make materials for achieving specific balanced combinations of physical properties, processing characteristics, and cost. The cost effectiveness of high-priced engineering thermoplastics can be improved by alloying them with lower cost bulk polymers without adversely affecting their thermal and mechanical performance. For example, alloying of high-density polyethylene (HDPE) with Nylon can lead to improved toughness without adversely affecting the high filler acceptibility of Nylons; compounds of Nylon/HDPE alloys with molybdenum sulfide are used in bearing applications. The alloying of polyphenylene oxide (PPO) with polystyrene (PS) improves processibility of the high-performance polymer. The combination of polyethylene terephthalate (PET) with acrylic has resulted in materials with better warp resistance and easier moldability. Such engineering thermoplastic alloys are steadily replacing metals in a variety of applications, mainly because of the high productivity and design flexibility offered by the process of injection molding.

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The properties of an injection-molded part are influenced by its morphology. In case of semicrystalline polymers the morphology is influenced by the crystallization behavior of the polymer.[1] In any multicomponent system, such as alloys of two semicrystalline polymers (Nylon 66/HDPE) or in alloys of a semicrystalline and an amorphous polymer (PET/acrylic), the crystallization behavior of the component polymers is affected by the presence of the other phase. Even if the polymers are thermodynamically miscible, crystallization results in phase segregation unless the polymers can form isomorphic blends. Thus, the morphological features such as degree of crystallinity, domain shape, and size are affected by the relative rates of crystallization of the component polymers. A knowledge of the crystallization behavior of the thermoplastic blend is therefore necessary for effective manipulation of properties and for specifying the molding conditions.

The thermal and crystallization behavior of the constituents of polymer blends are influenced by their relative amounts, miscibility, and dispersion level. The dispersion level is affected by the technique and conditions of compounding. Although there is considerable published literature on the thermal and crystallization behavior of polymer blends,[2-16] a majority of the investigations involve solution blending. Whereas investigations on melt-compounded polymer alloys would be technologically more relevant. The few investigations on melt-blended alloys[5,8-13] confirm that the crystallization of component polymers is affected by the presence of a second phase. Gupta et al.[10] have reported that addition of small amounts of (5-25%wt) of high-density polyethylene (HDPE) resulted in an enhanced rate of nucleation of polypropylene and a reduction in the crystallite size. This is confirmed by Teh,[11] who observed a decrease in the spherullitic size of polypropylene when blended with low-density polyethylene (LDPE). Siegmann[8,9] has also reported that the crystallization of poly-1-butene was significantly affected by polypropylene over the whole range of composition. The incorporation of ethylene propylene copolymer and polyisobutylene in PP resulted in an enhanced nucleation rate and a decrease in the average size of spherullites as reported by Martuscelli et al.[14]

The references concerning the thermal and crystallization behavior are summarized in Table I. The investigations are aimed at studying the miscibility of two phases by determination of glass transition temperature,[2,4-6,12] the effect of composition on degree of crystallinity,[6-11,14] and structure property relationships.[9,10] The crystallization behavior has been investigated in terms of the size of crystallites,[10,11,14] the crystallization temperature in DSC scans,[2,8-10,13] and spherullitic growth rate studies.[14,15] However, little published literature exists on the crystallization rate and crystallizability of polymers in melt-compounded thermoplastic blends.

The present paper reports the thermal behavior and isothermal crystallization rate of polyphenylene sulfide (PPS) and high-density polyethylene (HDPE) in PPS/HDPE alloys at three different compositions. The crystallization behavior of the components in the alloys is compared to their behavior in the virgin polymer phase. The technique of differential scanning calorimetry (DSC) is used for investigating the isothermal crystallization kinetics. PPS is an engineering plastic with excellent mechanical, thermal, and electrical properties. The cost effectiveness of molding grade of PPS can be further enhanced by alloying it with HDPE without significantly affecting its excep-

TABLE I
Summary of Investigations on Thermal and Crystallization Behavior of Blends

Sr. no.	Ref. no.	Blend constituents	Compounding technique	Scope of investigation
1	2	PVDF/PMMA	Co-precipitation	Compatibility studies by T_g measurement (DSC)
				Crystallization temperature measurement (DSC)
2	3	PVDF/isotactic PEMA	Co-precipitation	LCST behavior and crystallization by DSC
3	4	Polyester/Polycarbonate	Solution casting	Miscibility studies by T_g measurement (DSC)
4	5	Polystyrene-co-alkyl alcohol/polycarbonate	Melt blending	Miscibility studies by T_g measurement (DTA)
5	6	Phenoxy/aliphatic polyester	Solution casting	Miscibility studies by T_g measurement
				Crystallinity by measuring heat of fusion (DSC)
6	7	LDPE/Polycaprolactone	Coprecipitation	Crystallinity measurement by DSC
				Morphology by optical microscopy
7	8, 9	PP/Poly-1-butene	Melt blending	Crystallization temperature by DSC
				Degree of dispersion by dynamic mechanical analysis
				Crystallinity measurement by WAXD
8	10	PP/HDPE	Melt blending	Crystallization temperature by DSC
				Crystallinity by heat of fusion measurement
9	11	LDPE/PP	Melt blending	Crystallinity measurement by DSC and WAXD
				Morphology by polarized light microscopy
10	12	PET/PC	Melt blending	Glass transition behavior by DTA
11	13	PP/thermoplastic rubber	Melt blending	Crystallization temperature by DSC
12	14	Isotactic PP/EPM and PIB	Solvent blending	Microphase structure by electron microscopy
				Radial growth rate measurements by optical polarizing microscopy
				Crystallinity measurement by DSC
13	15, 16	PEO/PMMA	Solution casting	Spherulitic growth rate measurement by hot stage microscopy

DSC = Differential scanning calorimetry, DTA = differential thermal analysis, WAXD = wide-angle X-ray diffraction.

tional chemical and thermal resistance. Blending with HDPE is also expected to give an alloy material with improved toughness. Understanding the thermal and crystallization behavior of such alloys is relevant to their processing and product development.

EXPERIMENTAL

Polyphenylenesulfide (PPS), Ryton Grade R-4, supplied by Phillips Petroleum (USA) was used. The R-4 grade of Ryton is a pelletized resin containing 40% glass fibers and is recommended for injection molding. The glass fiber

content in Ryton R-4 was confirmed by thermogravimetric analysis (TGA) from the amount of residue left.

High-density polyethylene (HDPE), Hostalene-grade GF 7745, supplied by Polyolefin Industries Ltd. (India) was used for blending with PPS.

The blends were prepared on a Brabender plasticorder mixer, model PLE 330 at 280°C and a speed of 40 RPM for 5 min under nitrogen atmosphere.

Three alloy compositions were prepared with PPS/HDPE weight ratio of 90/10, 75/25, and 50/50.

The thermal characterization and the crystallization kinetics studies were carried out on a Perkin Elmer DSC-2 differential scanning calorimeter. The thermal characterization data were obtained at a heating and cooling rate of 10°C/min. The heats of fusion and crystallization were calculated by peak area measurement and the values were corrected for weight percentage of the polymer as well as the glass fiber content.

The isothermal crystallization data were obtained by heating the sample to 300°C under N_2, holding it there for 3–5 min, and then cooling at 320°C/min to a predetermined crystallization temperature at which the exothermic crystallization peak was recorded. The total crystallization time was determined as the time required from the onset of the peak till a steady baseline was obtained. The isothermal crystallization time measurements were carried out over a wide range of temperatures from 200°C to 240°C for PPS and from 80°C to 120°C for HDPE. The details of the experimental procedure and analysis are reported by the authors in an earlier paper.[17]

RESULTS AND DISCUSSION

The heating and cooling scans of the alloys, obtained by differential scanning calorimetry were used to determine a number of parameters signifying the thermal and crystallization behavior. These include the temperature of the onset of melting, melting peak temperature, melting temperature range (width of the melting peak), and heat of fusion from the heating scans; and the temperature of onset of crystallization, crystallization peak temperature, and heat of crystallization from the cooling scans. The degree of supercooling, ΔT, was calculated as the difference between the melting peak temperature and the temperature of onset of crystallization in the cooling scan.

The DSC scans of the component polymers and alloys are reported in Figures 1 and 2. The alloys manifest two melting peaks and two crystallization peaks as expected. The thermal data are summarized in Tables II and III.

THERMAL BEHAVIOR OF PPS IN THE ALLOYS

The melting peak temperature of PPS in the alloys is marginally higher than that of virgin PPS, although the degree of crystallinity of PPS in the alloys is considerably lower than that of the virgin polymer, as indicated by the heats of fusion (Figure 1 and Table II). This conclusion is also supported by the gradual decrease in the heat of crystallization of PPS in the alloys (Table II). This is probably due to the larger crystallite size and narrower crystallite size distribution of PPS in the alloys. The temperature of onset of PPS melting is significantly higher for the alloys, indicating a larger crystallite size. The PPS melting temperature range is also considerably narrower for
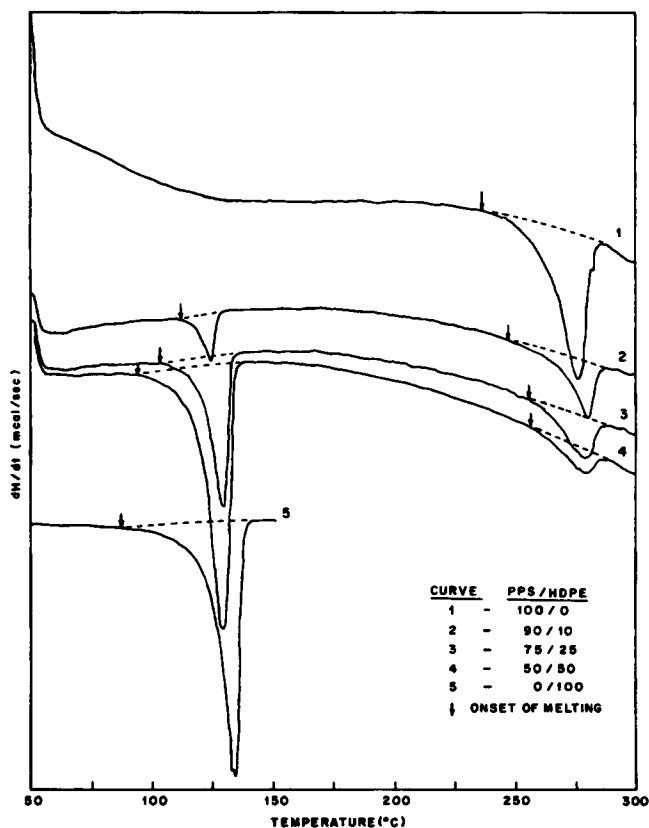
Fig. 1.   DSC scans of the component polymers and alloys in heating mode.

the alloy compositions relative to virgin PPS, suggesting a narrower crystallite size distribution.

Thus, the presence of even 10% (by weight) of HDPE alters the crystallinity and morphology of PPS.

In PPS/HDPE alloys, crystallization of PPS would take place in the presence of molten HDPE, because of the large difference in the melting points of the two polymers (PPS: 280°C, HDPE: 130°C). Referring to the crystallization parameters in Table II, it is apparent that the crystallization of PPS is accelerated in the presence of HDPE. The degree of supercooling required for initiating crystallization is progressively lowered with increasing amount of HDPE. The specific gravity of Ryton R-4 is 1.6, whereas that of HDPE is 0.95. Therefore, the compositions of the PPS/HDPE alloys in terms of volume are 84/16, 64/36, and 37/63 corresponding to the weight ratios of 90/10, 75/25, and 50/50 respectively. Thus, for the 50/50 weight ratio, HDPE is the major component. However, even in this case, where HDPE melt would be the major domain- (space) filling component, it appears that the nucleation of PPS is accelerated, since the degree of supercooling is 24°C versus 43°C for the virgin polymer. Thus the nucleation of PPS is facilitated in the HDPE melt. However, with increasing amount of HDPE, the crystal growth may be impeded.
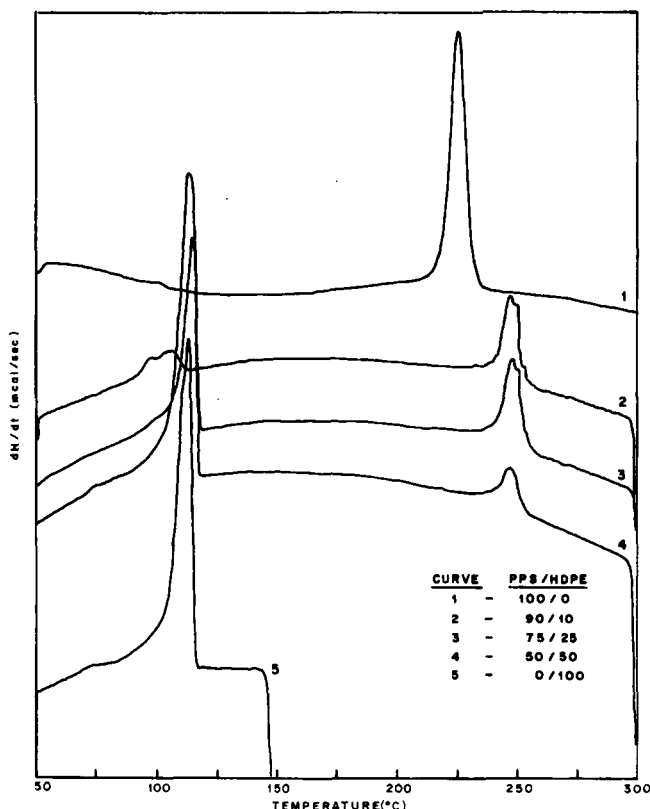
Fig. 2.   DSC scans of the component polymers and alloys in cooling mode.

In summary, alloying of PPS with HDPE reduces its degree of crystallinity even at 10 wt% (16 vol%) level. However, the onset of crystallization of PPS is facilitated in presence of HDPE melt. The crystallization of PPS in molten HDPE leads to a narrower crystallite size distribution and a larger crystallite size. However, extent of this morphological change is reduced with increasing volume of HDPE.

THERMAL BEHAVIOR OF HDPE IN THE ALLOYS

In the case of HDPE in the alloys, the crystallization from the molten phase takes place in the presence of solidified PPS particles which would act as heterogeneous nuclei. Unlike PPS, the degree of crystallinity of HDPE is reduced only when HDPE is the minor component (in terms of volume fraction). Thus, the heat of fusion of the 50/50 PPS/HDPE alloy is comparable to that of virgin HDPE, whereas it is lower for the 75/25 and 90/10 PPS/HDPE compositions. (Table III). Also, the heat of crystallization, ΔH_c, is comparable to that of virgin HDPE in case of PPS/HDPE (50/50) alloy, while it is lower for 75/25 and 90/10 alloys.

The temperature of onset of HDPE melting progressively increases and the melting range decreases with increasing amount of PPS. (Refer to Figure 1, curves 5,4,3, and 2 represent progressively increasing amount of PPS.) These

TABLE II
Thermal Behavior of PPS in the Alloys

	Composition PPS/HDPE		Melting				Crystallization			
	By weight	By volume	Onset °C	Peak °C	Peak width °C	H_f cal/g	Onset °C	Peak °C	H_c cal/g	Degree of super cooling T, °C
1.	100/0	100/0	235	276	50	7.8	235	225	7.5	43
2.	90/10	84/16	245	280	39	5.6	254	248	5.7	26
3.	75/25	64/36	254	280	30	5.0	255	248	4.7	25
4.	50/50	37/63	255	279	29	5.0	255	246	5.6	24

TABLE III
Thermal Behavior of HDPE in the Alloys

	Composition PPS/HDPE		Melting				Crystallization			
	By weight	By volume	Onset °C	Peak °C	Peak width °C	ΔH_f cal/g	Onset °C	Peak °C	ΔH_c cal/g	Degree of super cooling ΔT, °C
1.	0/100	0/100	88	130	50	31.9	118	112	32.0	12
2.	50/50	37/63	94	129	39	32.1	118	113	31.1	11
3.	75/25	64/36	103	130	31	25.9	119	115	25.2	11
4.	90/10	84/16	113	125	16	22.3	113	106	22.2	12

Note: The values of ΔH_f and ΔH_c are corrected for 40% glass fibers, and for the respective weight fractions of the polymers.

observations indicate that, in the presence of PPS, HDPE crystallites have a larger crystallite size and a narrower crystallite size distribution relative to virgin HDPE. The HDPE melting peak temperatures of the alloys are comparable to virgin HDPE, except for the 90/10 composition where it is lower.

The degree of supercooling required for initiating nonisothermal crystallization of HDPE is surprisingly not affected by the presence of PPS.

Thus the presence of PPS has an effect on the morphology of HDPE. The degree of HDPE crystallinity is affected when HDPE is the minor component (volume basis). Whereas the DSC cooling scans do not indicate any significant change in the nonisothermal crystallization behavior of HDPE in the alloys.

ISOTHERMAL CRYSTALLIZATION OF PPS IN THE ALLOYS

The thermal behavior of PPS in the alloys is markedly different from that of virgin PPS. It indicates that both the crystallizing ability and crystalline morphology of PPS are affected by the presence of HDPE melt. The effect of alloying on the crystallization behavior of PPS has been further elucidated by studying the isothermal crystallization of PPS in the melt-compounded alloys, and comparing it to the isothermal crystallization behavior of virgin PPS (Ryton R-4), reported earlier by the authors.[17]

The isothermal crystallization was studied over a temperature range of 200–245°C. The crystallization time, t_c, was determined from the width of the isothermal crystallization peak recorded on the DSC scan with time base (Fig. 3). The variation of the isothermal crystallization time, t_c, with the crystallization temperature, T_c, is shown in Figure 4. At a given temperature, the crystallization time of PPS is reduced due to alloying with HDPE for those compositions wherein PPS forms the major component (volume ratio of 84/16 and 64/36). Whereas in the PPS/HDPE alloy composition of 37/63 by volume, the overall crystallization of PPS in the alloy is retarded.
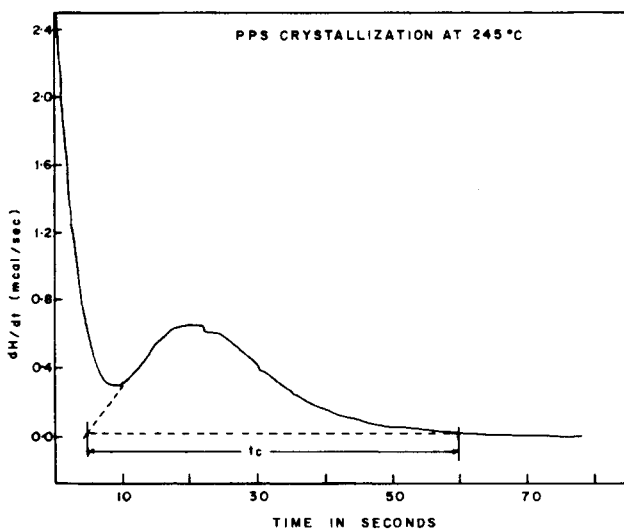

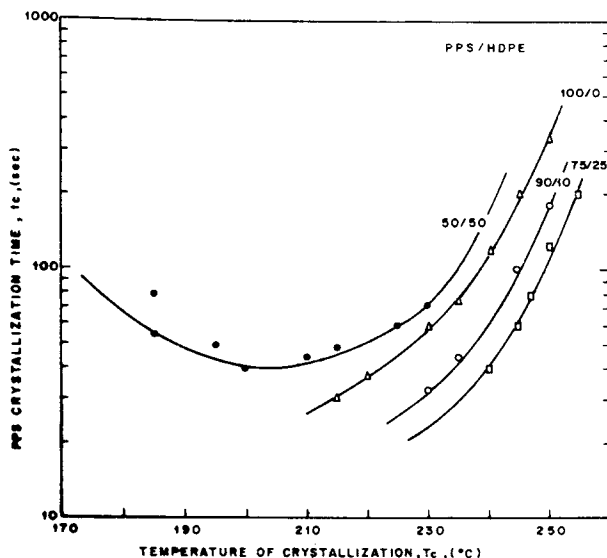Fig. 3.   Typical isothermal crystallization peak of PPS in the alloy.

Fig. 4. Isothermal crystallization time, t_c of PPS in the alloys.

It is hypothesized that the homogeneous nucleation of PPS is enhanced in the presence of molten HDPE. The number average molecular weight of molding grade of PPS is about 21,000.[18] The HDPE grade used in the present work is a blow-molding grade with melt flow index (MFI) of 1.6 g/10 min, corresponding to a number average molecular weight in the range of 70,000–85,000 as per manufacturer's product brochure. Since the number average molecular weight of HDPE (addition polymer) is significantly higher than that of PPS (condensation polymer), the HDPE melt would constrain the mobility of PPS polymer chains, thereby increasing the probability of forming extended or strained PPS chain segments that can act as homogeneous nuclei. On the other hand, the HDPE melt would also retard crystal growth by restricting the diffusion of PPS chains to the nuclei. The retarding influence on crystal growth would be more prominent for alloy compositions wherein HDPE is the major phase (by volume). Since the overall rate of crystallization is a combined effect of the rates of nucleation and crystal growth, the crystallization time of PPS is reduced in the PPS/HDPE alloy compositions of 84/16 and 64/36 (by volume) compared to virgin PPS, whereas it is higher in the 37/63 PPS/HDPE (by volume) alloy compared to virgin PPS.

The isothermal crystallization time versus temperature curves for the PPS-rich alloy compositions are also shifted to higher temperatures relative to virgin PPS. That is to say that a lower degree of supercooling is required to initiate crystallization of PPS in these alloys. Thus, the crystal growth of PPS in the alloy would take place at a higher temperature leading to larger crystallite size, improved crystal perfection, and narrower crystallite size distribution. These conclusions are supported by the thermal characterization (DSC) results. The observed lower degree of crystallinity of PPS in the alloys relative to virgin PPS may be attributed to the retarding influence of HDPE melt on chain diffusion and crystal growth.

ISOTHERMAL CRYSTALLIZATION OF HDPE IN THE ALLOYS

The isothermal crystallization of HDPE in the virgin pellets and in alloys was investigated over a temperature range of 80–120°C. The variation of the crystallization time, t_c, with the temperature is shown in Figure 5. At any temperature, the crystallization time of HDPE is reduced progressively with increasing amount of PPS in the alloy. The reduction in crystallization time for the blends is attributed to the presence of solidified PPS particles that can act as heterogeneous nuclei. Figure 6 shows a typical isothermal crystallization peak for HDPE in the 50/50 PPS/HDPE alloy. The crystallization process clearly exhibits two overlapping peaks indicating two different crystallization processes, probably corresponding to homogeneous and heterogeneous nucleation, whereas the isothermal crystallization of virgin HDPE exhibits a single peak. A similar behavior is observed for PPS/HDPE blends
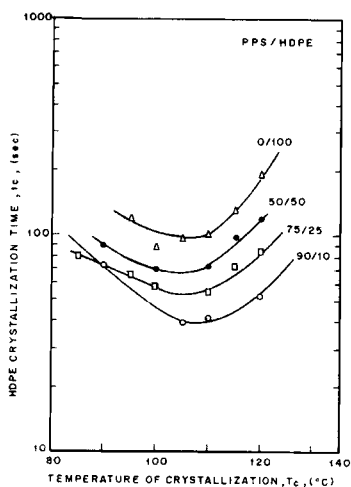

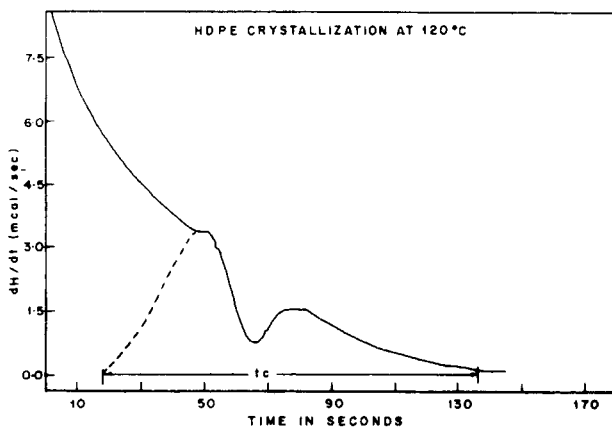Fig. 5.   Isothermal crystallization time, t_c of HDPE in the alloys.

Fig. 6.   Typical isothermal crystallization peak of HDPE in the alloy.

with compositions (90/10) and (75/25). However, the extent of crystallization has been found to change with composition. In case of HDPE crystallization, the amount of PPS does not have an adverse effect on the crystallization process, as the PPS phase is already solidified and it does not affect the mobility of HDPE chains in the melt even when PPS is the major phase.

CONCLUSIONS

It is concluded that both the crystallization behavior and the morphology of the component polymers, in the present case PPS and HDPE, are affected by the presence of the other phase in the alloy. The relative amounts of the two polymers in the alloy also influence the crystallization process.

The morphological changes observed in both PPS and HDPE are similar. These include a larger crystallite size, a narrower crystallite size distribution, and a reduced degree of crystallinity relative to the virgin polymers.

Figure 7 depicts the variation of isothermal crystallization time of PPS with the volume percentage of HDPE in the alloy at three temperatures of crystallization. It is seen that the isothermal crystallization time of PPS is reduced in the presence of molten HDPE for alloy compositions wherein PPS forms the major phase (by volume), whereas the overall crystallization rate is retarded beyond HDPE volume fraction of about 35–40%. It is hypothesized that the presence of HDPE melt accelerates nucleation but retards crystal growth of PPS. The retarding influence on crystal growth would be more pronounced in alloy compositions rich in HDPE. Therefore, the crystallization time of PPS exhibits a minimum with respect to the HDPE volume fraction.

On the other hand, the isothermal crystallization time of HDPE decreases gradually with the volume fraction of PPS in the alloy, as shown in Figure 8. This is attributed to the presence of solidified PPS particles in the crystalliz-
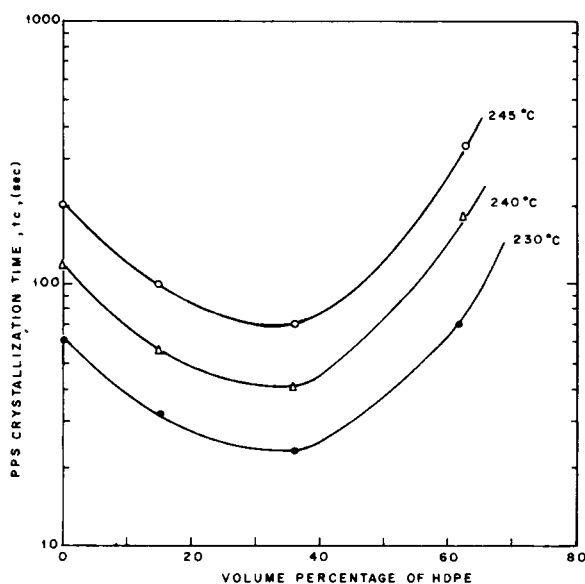

Fig. 7.   Variation of isothermal crystallization time of PPS with HDPE volume percentage.
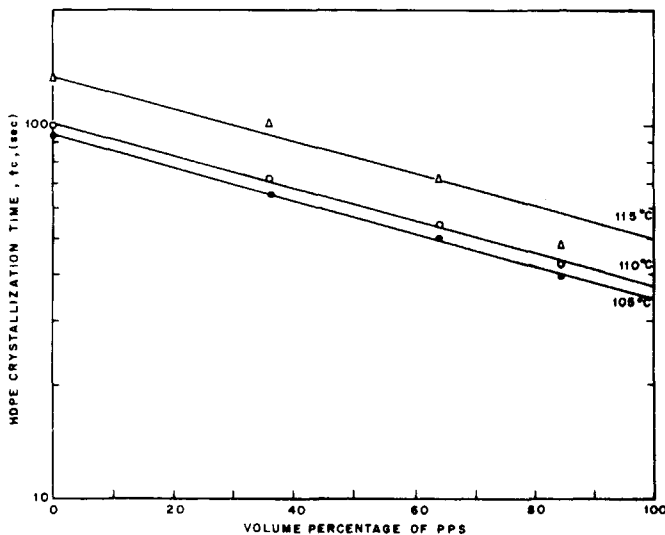
Fig. 8. Variation of isothermal crystallization time of HDPE with PPS volume percentage.

ing melt of HDPE, which can act as heterogeneous nuclei and accelerate the crystallization.

The major process implication of the present study is that the crystallization of high-melting engineering polymers may be accelerated by blending them with small quantities of a low-melting polymer. The accelerated crystallization would be helpful in lowering the mold temperature and shortening the mold cycle. The type of nucleating polymer (lower melting) may be chosen on the basis of chemical and thermal compatibility considerations.

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