

# Effect of Blending on the Crystallization Behavior of PET

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## SYNOPSIS

The crystallization of poly(ethylene terephthalate) (PET) in its blends with other thermoplastics such as poly(phenylene sulfide) (PPS), high-density polyethylene (HDPE), poly(methyl methacrylate) (PMMA), aromatic polyamide, and a co-polyester is reported. The nonisothermal crystallization and melting behavior of PET in its blends has been discussed. Because of differences between the melting/softening points of these polymers and the melting point of PET, the crystallization of PET takes place in the presence of solidified PPS in PET/PPS blends and in presence of the molten phase of the second component in the remaining blends. The observed changes in the melting and crystallization behavior are explained on the basis of the effect of the physical state of the second component. The results of the isothermal crystallization studies are consistent with these studies. The changes in the overall crystallization rate could be further explained in terms of the nucleation and growth processes occurring during the crystallization of PET using the isothermal crystallization data.

## 1. INTRODUCTION

Poly(ethylene terephthalate) (PET) is a versatile polymer used in synthetic fibers, films, blow-molded containers, and injection-molded engineering components. The properties of melt-processed articles of PET can be modified by blending it with a variety of crystalline and amorphous polymers. The investigations on PET blends reported in the published literature pertain to the blends of PET with polyolefins,<sup>1</sup> polyamides,<sup>2-6</sup> polyarylate,<sup>7</sup> poly(methyl methacrylate),<sup>8</sup> polycarbonate,<sup>9-11</sup> and poly(ester carbonate).<sup>12</sup> The main property improvements sought by blending PET with these polymers include higher heat-distortion temperature, better impact resistance, and improved moldability.

In the case of crystalline blends, the crystallization behavior of the component polymers in the blend is influenced by their relative amounts, chemical compatibility, and the level of dispersion

achieved in the compounding process. Also, the melting points and the temperature range of crystallization of the component polymers determine the physical conditions of crystallization. Thus, if the melting points are comparable, depending upon the crystallizability of the individual component polymers, the polymers may crystallize concurrently or sequentially. On the other hand, if the melting-point difference is significant, the high-melting polymer would crystallize in the presence of the molten phase of the low-melting polymer, whereas the low-melting polymer would crystallize in the presence of the solidified first component.

The present paper reports a differential scanning calorimetric investigation of the thermal and crystallization behavior of PET in its blends with crystalline polymers such as poly(phenylene sulfide) (PPS) and high-density polyethylene (HDPE) and amorphous polymers such as poly(methyl methacrylate) (PMMA), aromatic polyamide (T), and co-polyester (PETG). The objective of the investigation was to elucidate the relative effects of the various factors governing the extent and direction of change in the crystallization rate and morphology of PET. These factors include miscibility, melting temperatures of the component polymers, and their relative melt viscosities and chemical compatibility.

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## 2. EXPERIMENTAL

The polymers used for the present studies were all commercial grades. Their thermal properties are summarized in Table I. The melting point and the glass transition temperatures of the polymers were determined using differential scanning calorimetry at a heating rate of 10°C/min.

The blends were prepared by melt-compounding on a Brabender Plasticorder Model PLE 330 in a batch-type roller mixer. The polymers were dried at 120°C for 6 h in a vacuum oven prior to compounding. The compounding was done in nitrogen atmosphere at temperatures of 280–285°C for 5 min and a rotor speed of 40 rpm. Five blend compositions were prepared, covering the entire range for each blend system, except for PET/PMMA, for which only three PET-rich compositions were made. The neat PET was also subjected to the identical processing in the Brabender batch mixer in order to nullify the effects of thermal history.

The nonisothermal and isothermal crystallization studies were carried out using a Perkin-Elmer DSC-2C equipped with a thermal analysis data station (TADS). The thermal parameters were obtained from the cooling and reheating scans for the crystallization and melting behavior. The details of the experimental procedure are reported elsewhere.<sup>13,14</sup>

The isothermal crystallization studies for PET were carried out over a wide range of crystallization temperatures (180–230°C). The sample was heated to 300°C, and after a dwell time of 2 min at 300°C, it was cooled at 160°C/min to a predetermined crystallization temperature. The exothermic crystallization peak was then recorded. The total crystallization time,  $t_c$ , was determined from the width of the exothermic crystallization peak recorded at each temperature of crystallization. The induction time,  $t_i$ , signifying the time required for initiating

homogeneous nucleation of PET, was also determined from the isothermal crystallization peaks.

## 3. RESULTS AND DISCUSSION

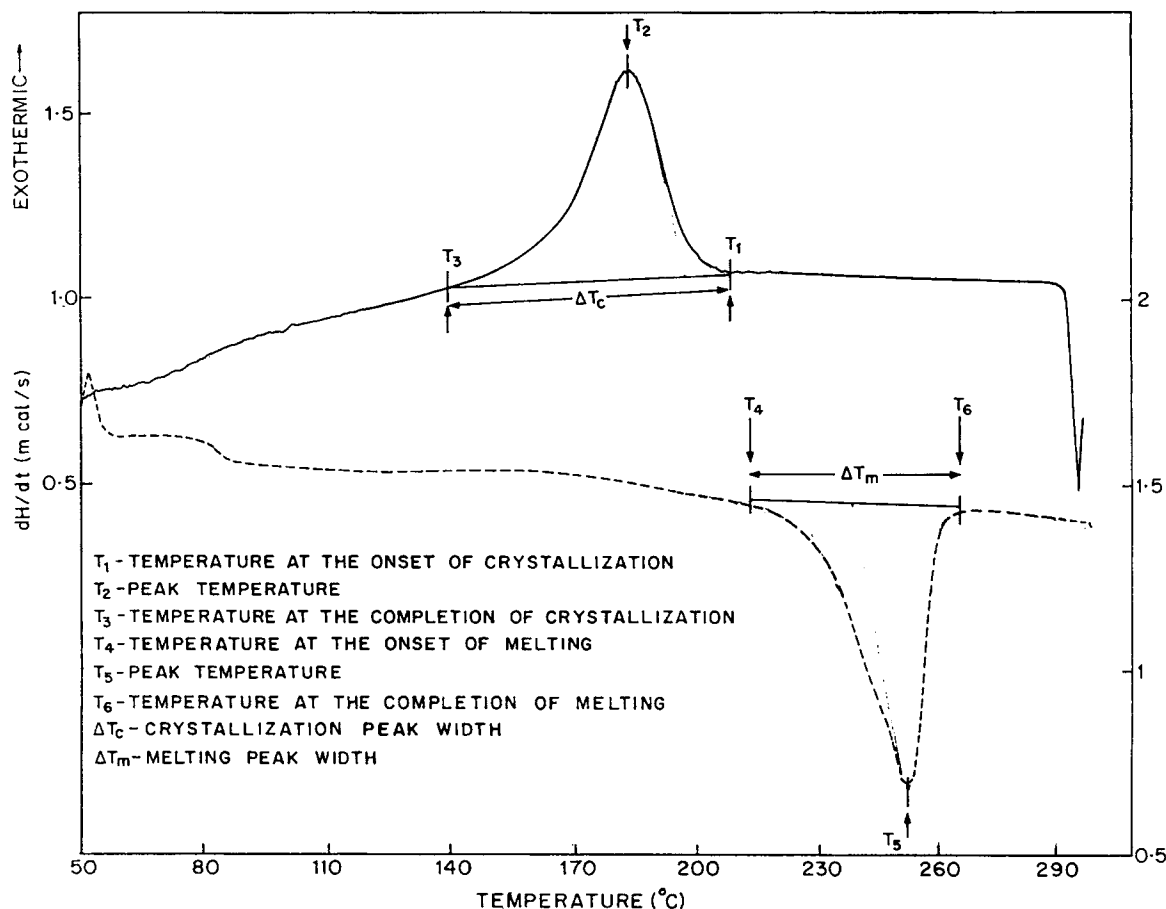
### 3.1. Nonisothermal Crystallization

The various crystallization parameters determined from the cooling scans of the blends are schematically illustrated in Figure 1. A shift in the temperature at the onset of crystallization would signify modification of the nucleation process. The changes in the crystallization peak width and the heat of crystallization would relate to the effect of blending on rate of crystal growth and degree of crystallinity, respectively. The normal temperature range for crystallization of PET from quiescent melt is 170–210°C. Thus, in its blends with PPS, the PET crystallizes in the presence of solidified PPS, whereas in blends with HDPE, PMMA, co-polyester, and aromatic polyamide, the PET crystallization takes place in the presence of the superheated or supercooled melt of the second component.

The composition dependence of the crystallization parameters for PET in the blends are shown in Figures 2–4. The variation of the temperature at the onset of crystallization of PET with volume fraction ( $V_f$ ) of the second component in the blends is shown in Figure 2. It is observed that PET crystallizes at a higher temperature over the entire composition range in its blends with PPS, while marginal changes were observed in its blends with HDPE, PMMA, and aromatic polyamide. However, it crystallizes at a lower temperature in case of PET/PETG blends. Thus, the nucleation of PET was found to be facilitated in its blends with PPS, whereas it was retarded in its blends with co-polyester. The increase in the temperature at onset of

**Table I** Thermal Parameters of Polymers Used for Blending

Polymer	Trade Name and Grade	Melting Point (°C)	Glass Transition Temperature (°C)	Supplier
PET	ARNITE A04300	256	70	Cenka Plastics (India)
Copolyester	KODAR(PETG) A-150	265	87	Eastman Kodak (USA)
Amorphous polyamide	TROGAMID T	—	138	Dynamit Noble (Germany)
PPS	RYTON (V-1)	280	93	Phillips Petroleum (USA)
HDPE	HOSTALENE GM7745F	130	—	Polyolefins Industries Ltd. (India)
PMMA	ACRYPOL-876G	—	87	GSFC (India)



**Figure 1** Crystallization and melting parameters for PET determined from the cooling and heating scans, respectively.

PET crystallization was the most significant in PET/PPS blends because of the heterogeneous nucleation due to solidified PPS. The presence of molten HDPE, PMMA, and aromatic polyamide does not bring about significant changes in the nucleation of PET.

The temperature at the onset of PET crystallization was found to be almost independent of the composition in PET/HDPE blends, whereas it varied with composition in PET/T and PET/PPS blends. In PET/T blends, the onset temperature dropped initially and then increased almost linearly with increasing volume fraction of *T* beyond  $V_f$  of 0.25. On the other hand, in PET/PPS blends, the onset temperature showed a significant increase up to a volume fraction of 0.25 followed by a gradual decrease with increasing volume fraction of PPS. These differences in the composition dependence of the onset temperature may be explained in terms of the differences in the phase morphologies that are being investigated and will be reported separately.

The PET/PETG blends exhibited a single crystallization peak in the DSC cooling scans, for both the components. The temperatures at the onset of crystallization in these blend compositions were found to be lower than those of PET (220°C) and PETG (219°C).

The PET crystallization peak width, which is indicative of the overall crystallization rate, varied with the volume fraction of the second component, as shown in Figure 3. The crystallization peak width for PET in blends was comparable to that of neat PET for the PET-rich blend compositions (up to 20% of the second component) except for PET/PMMA and PET/PETG, suggesting little change in the crystallization process of PET. However, the crystallization peak width decreased almost linearly with increasing amounts of the second component in PET/PPS, PET/HDPE, and PET/T blends, suggesting an acceleration of the crystallization of PET. In case of PET/PETG blends, the crystallization peak width showed higher values. It should

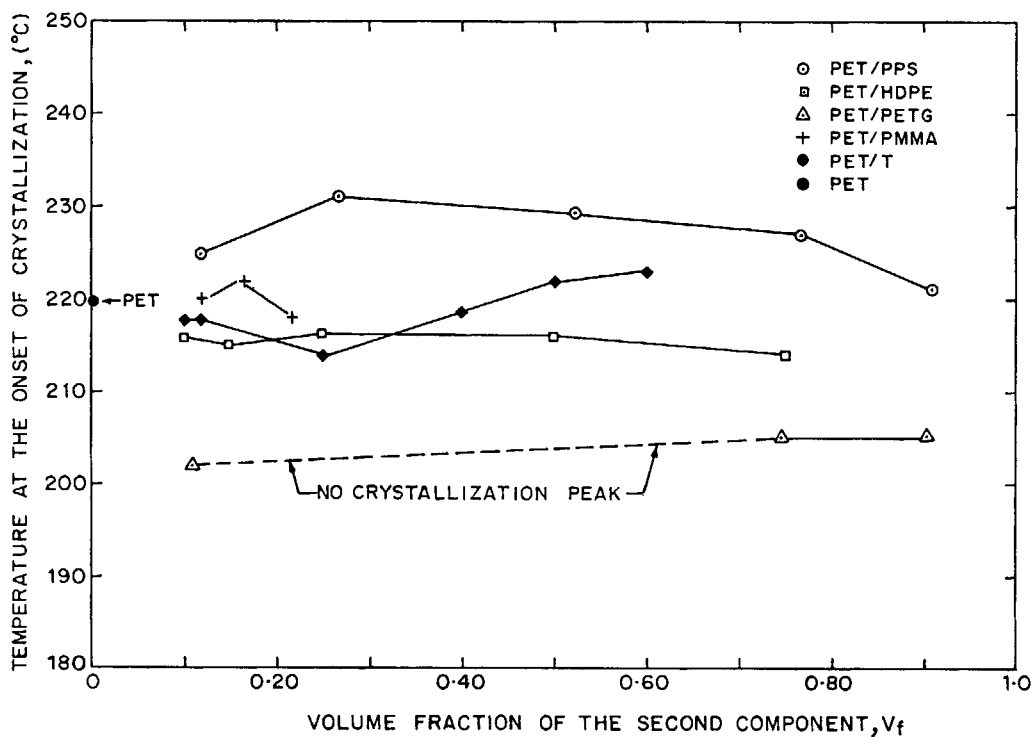


Figure 2 Variation of the temperature at the onset of crystallization for PET in its blends with PMMA, HDPE, PETG, PPS, and T.

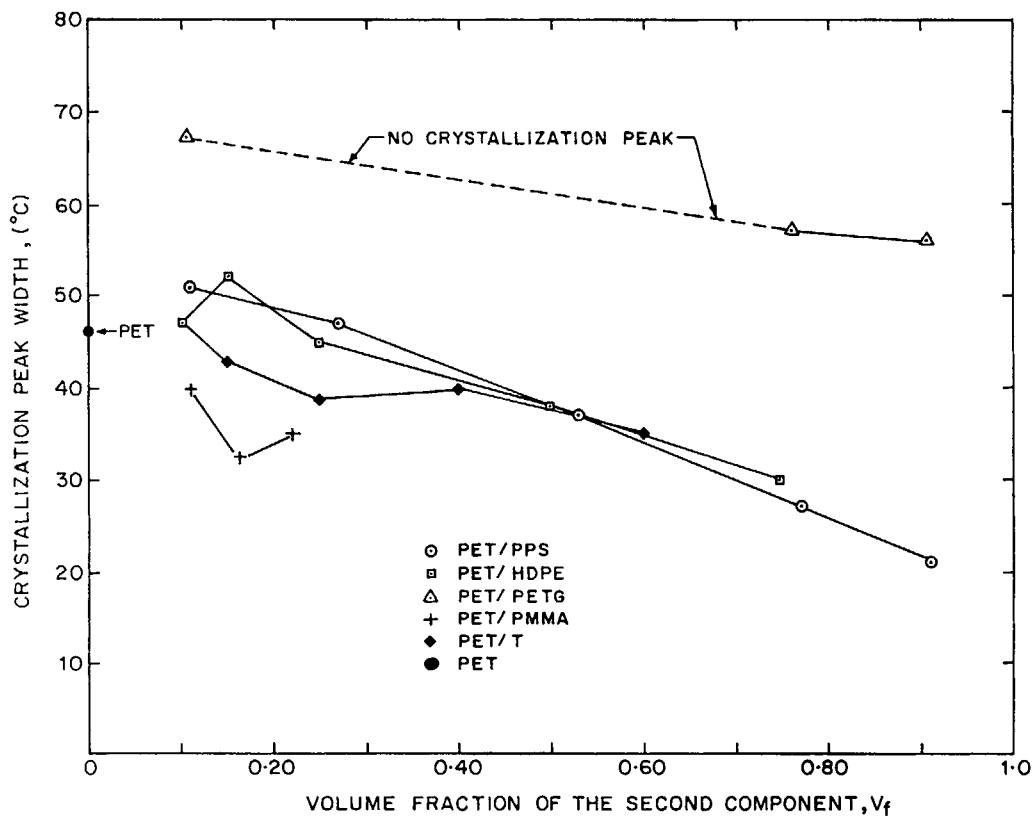


Figure 3 Variation of crystallization peak width of PET with blend composition.

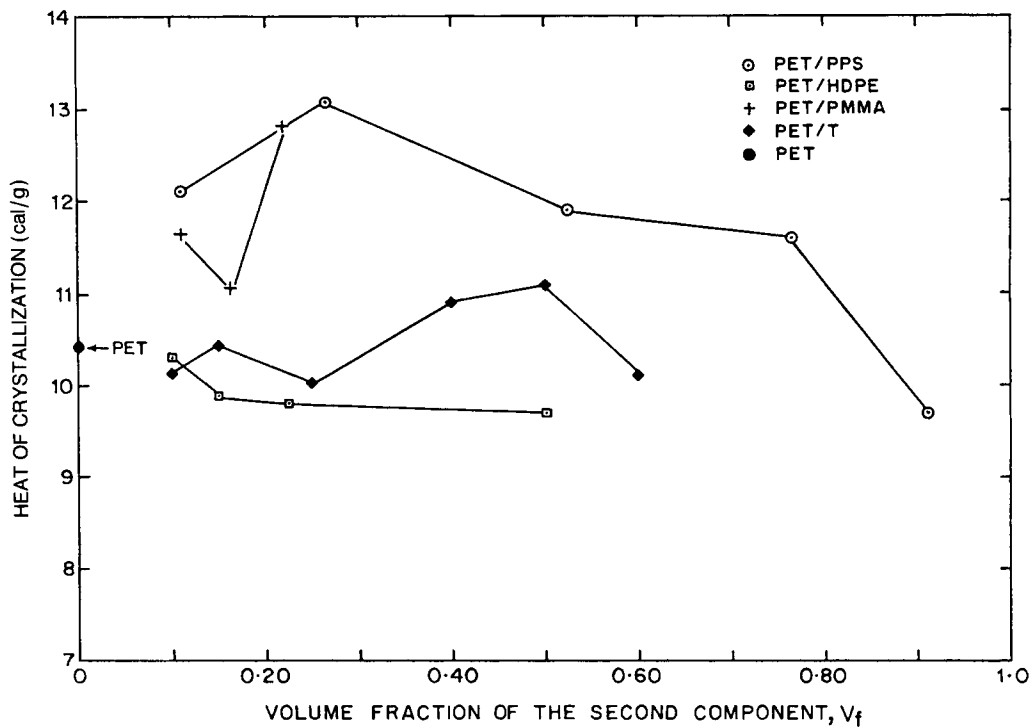


Figure 4 The composition dependence of heat of crystallization of PET in the blends.

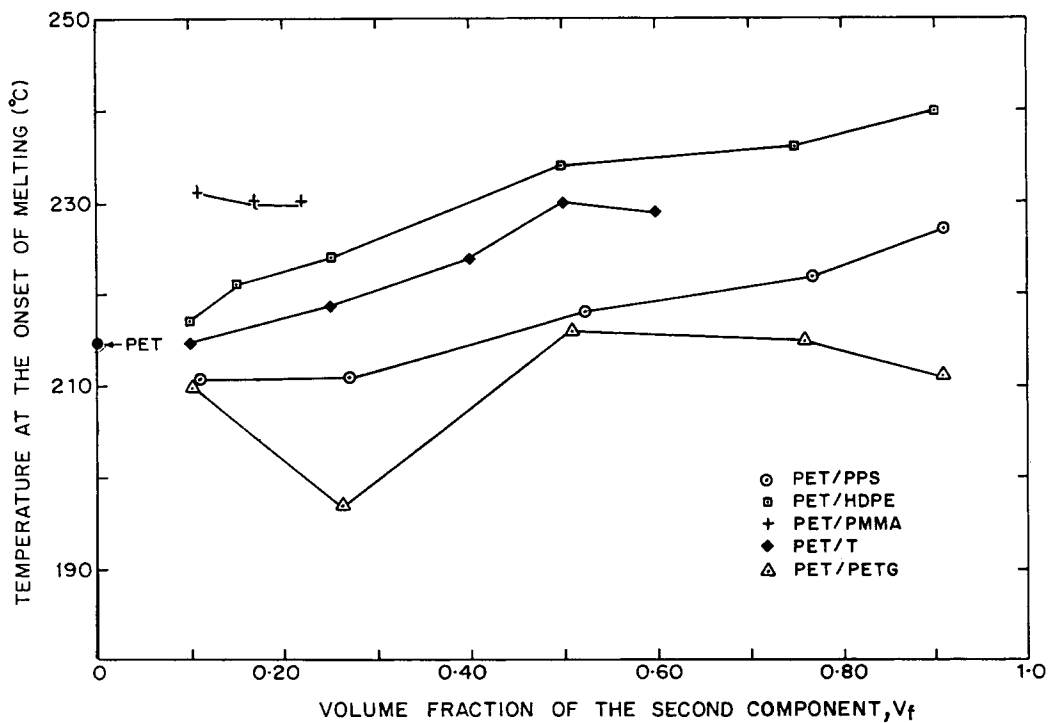


Figure 5 Variation of temperature at the onset of melting with blend composition.

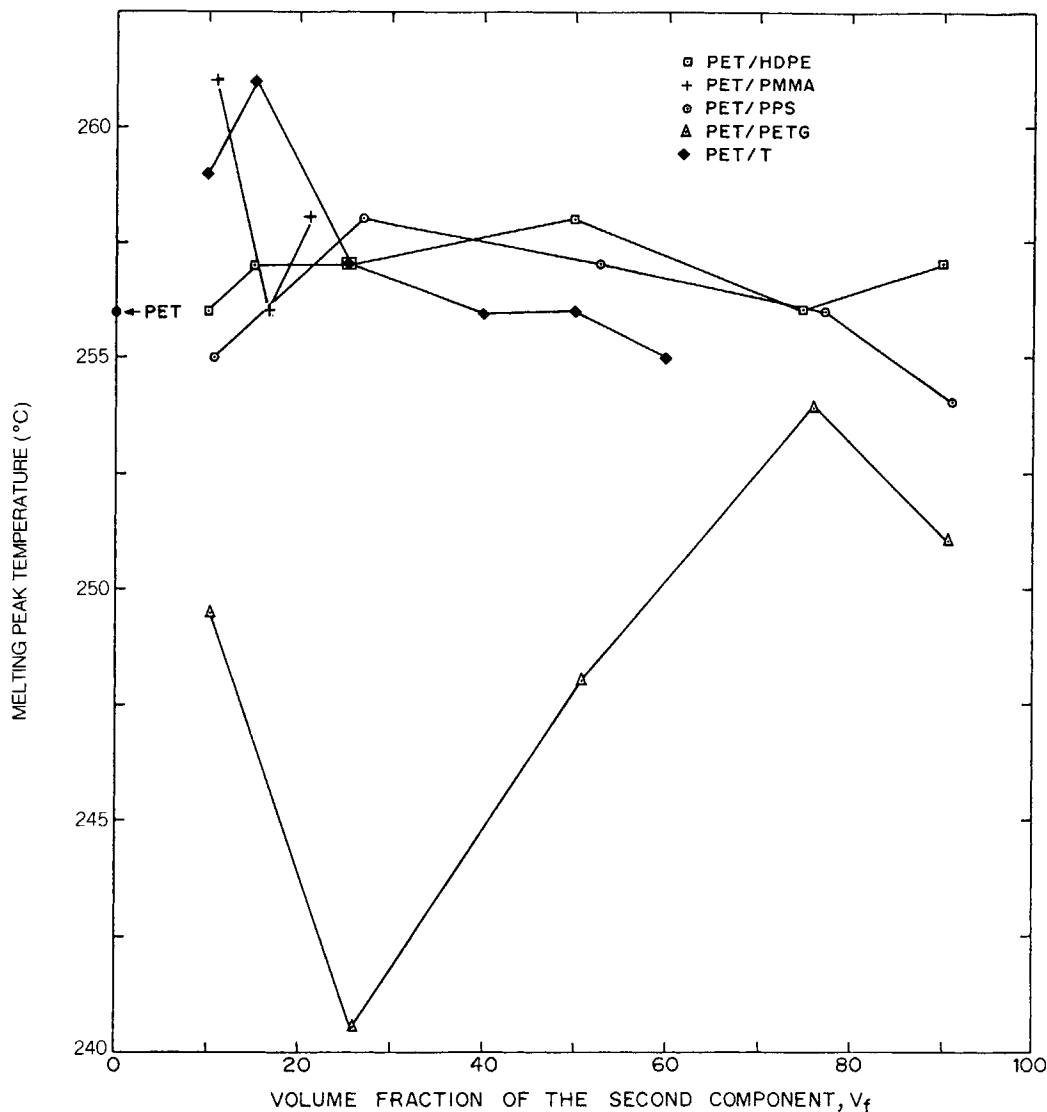


Figure 6 Variation of PET melting peak temperature with blend composition.

be noted here that both PET and PETG crystallize over the same temperature range and, hence, no definite conclusion can be drawn about the crystallization process of PET in its blends with PETG.

The variation of the heat of PET crystallization (per gram of PET in the blend), which represents the extent of crystallization, was found to be different for various blends (Fig. 4). The increase was found to be most pronounced in PET/PPS and PET/PMMA blends for PET-rich compositions. In PET/PPS blends, the heat of crystallization was found to decrease from 13 cal/g to about 10 cal/g as the PPS fraction increased from 0.25 to 0.9, exhibiting a maximum at a volume fraction of 0.3 of PPS. In PET/T blends, the heat of crystallization was found to be comparable to that of neat PET at

low-volume content of T (up to 25%) and it exhibited a maximum at around 50% volume composition of T. However, marginal changes were observed in PET/HDPE blends, with almost no composition dependence.

The heat of crystallization for PET could not be determined separately in the PET/PETG blends since the observed peak represents a combined peak for both PET and PETG. However, if the heat of crystallization is calculated using the rule of additivity, the experimentally observed heats of crystallization of the combined peak are considerably lower than the calculated values. This indicates that both the polymers in this blend do not crystallize to the same extent as they do in their virgin forms. Also, the crystallization peaks are observed only for

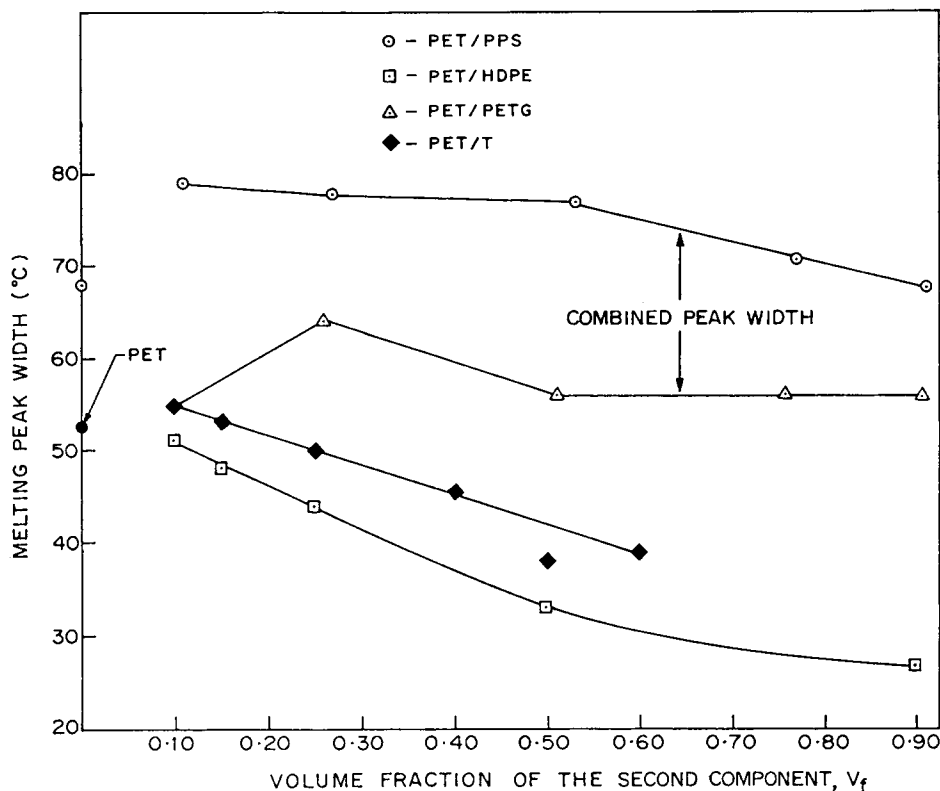


Figure 7 Variation of PET melting peak width with blend composition.

three blend compositions, containing 10, 75, and 90% of PETG. Nonisothermal crystallization peaks were not observed in the intermediate compositions, indicating suppression of crystallization over this composition range. Thus, the nonisothermal crystallization studies indicated a strong influence of blending on the crystallization of PET in PET/PETG blends.

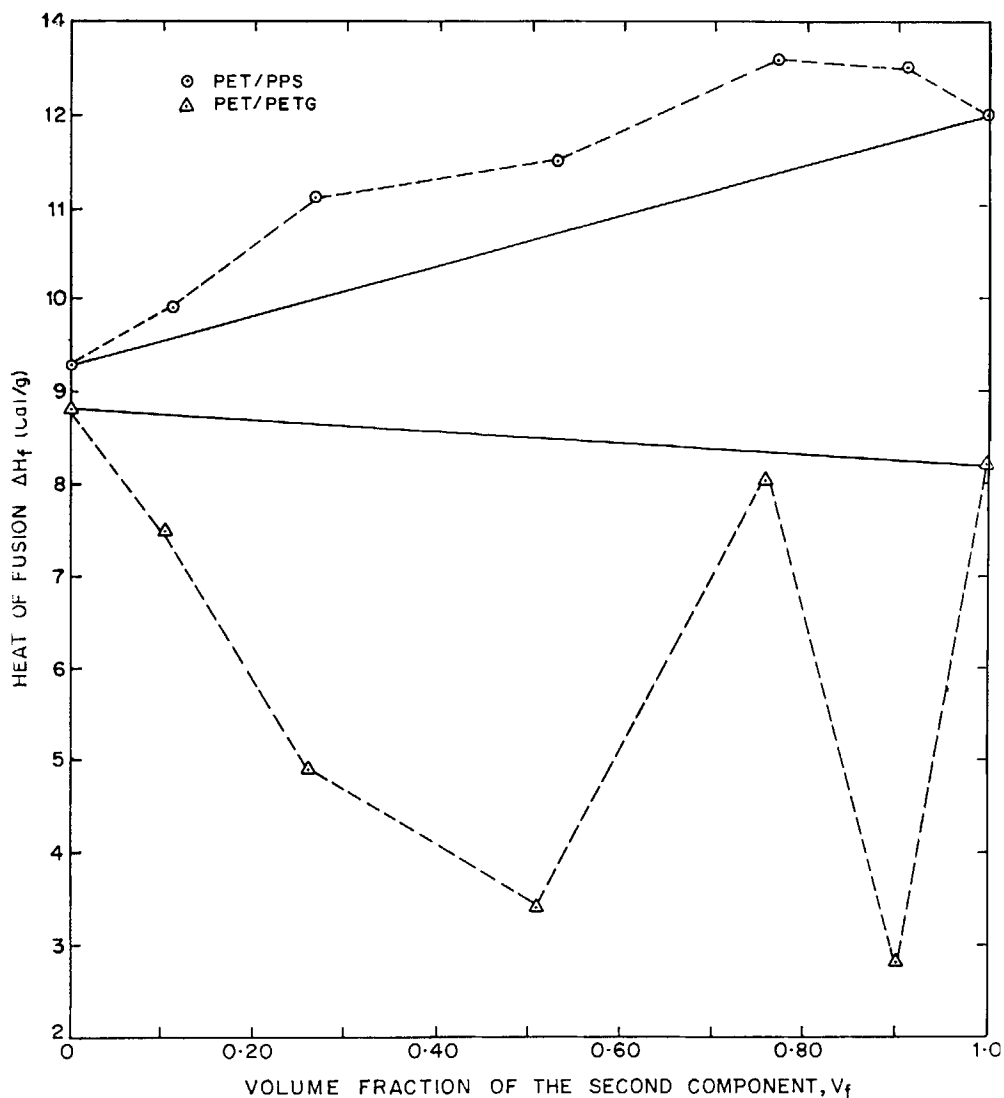
### 3.2. Melting Behavior

The melting behavior of PET in the blends was studied in order to elucidate the effect of blending on the morphology of PET in the blends. The effect of the second component on the morphology of PET may be analyzed in terms of certain characteristic melting parameters (Fig. 1). These parameters are the temperature at the onset of melting relating to the least stable (thinnest or most imperfect) crystallites; the melting peak width, relating to the distribution of crystallite stability; and the heat of fusion, representing the degree of crystallinity.

The variation of the temperature at the onset of melting with volume fraction of the second component is illustrated in Figure 5. The temperature

at the onset of melting was found to increase significantly with increasing amounts of the second component. The extent of change was more pronounced for PET/HDPE, PET/PMMA, and PET/T blends and was less for PET/PPS and PET/PETG blends. The increase in the temperature at the onset of melting indicates that the stability of the least-stable crystallites in the system has been increased by blending. It is likely that this relates to an overall increase in the crystallite thickness. The higher thickness of crystallites in the case of PET/HDPE, PET/T, and PET/PMMA blends could be the result of facilitated crystal growth since the crystallization of PET takes place in presence of the molten phase of the second component. However, in PET/PPS blends, this effect is not as significant, which may be attributed to the heterogeneous nucleation provided by the solidified PPS phase.

The melting peak temperature for PET in its blends with HDPE and PPS were found to be comparable with that of neat PET and did not show significant composition dependence. The melting peak temperatures for PET in PET/T and PET/PMMA were higher (6–7°C) in compositions con-



**Figure 8** The composition dependence of heat of fusion of PET in the blends (PET/PPS, PET/PETG).

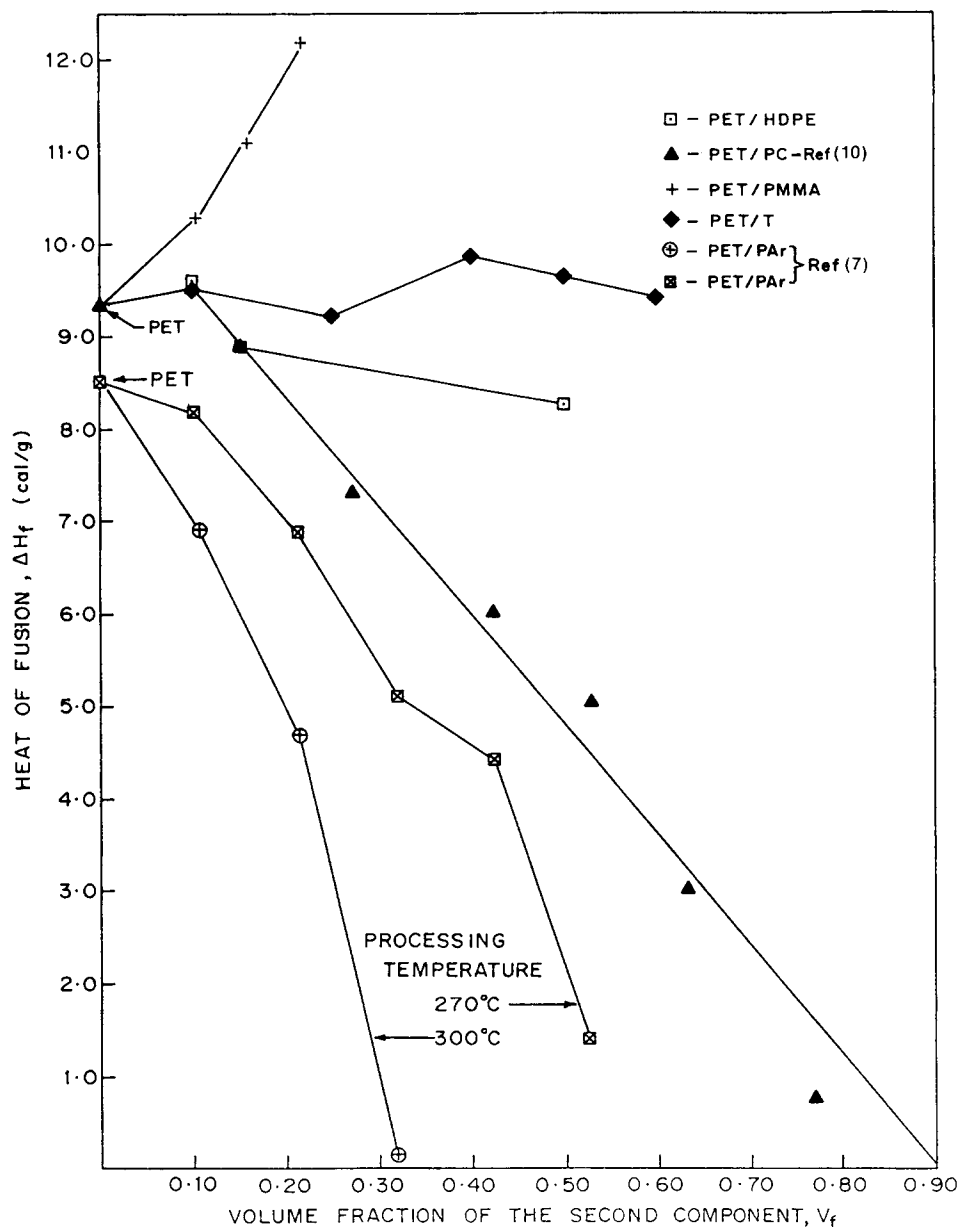
taining about 10% of the second component. However, in case of blends with PETG, the melting-point depression was observed for PET as illustrated in Figure 6, suggesting miscibility of the component polymers. Similar trends related to the melting-point depression have been reported by Kimura et al.<sup>15,16</sup> in case of blends of polyesters with polyarylates. The comparable values of the melting points of PET with marginal composition dependence in its blends with HDPE, PPS, PMMA, and T indicate that the component polymers do not exhibit miscibility.

The melting range for PET could be measured only in PET/HDPE and PET/T blends. In PET/PPS and in PET/PETG blends, as the component polymers exhibited overlapping melting peaks, the melting peak width for PET in the blend could not

be determined separately. The composition dependence of melting peak width of PET is shown in Figure 7. It is observed that the melting peak was narrower in the blends relative to virgin PET and the peak width decreased with increasing amount of the second component in PET/HDPE and PET/T blends. These observations suggest that the crystallite-size distribution of PET becomes narrower as a result of blending in these two blends.

In the case of PET/PPS and PET/PETG blends, the component polymers exhibited overlapping melting peaks. The combined heat of fusion of the two component polymers (per gram of blend) varied with the blend composition as shown in Figure 8. These experimental values may be compared to the computed values of the combined heats of fusion of





**Figure 9** The composition dependence of heat of fusion of PET in its blends with HDPE, PMMA, T, PC, and polyarylate.

the component polymers, after normalizing for their respective weight fractions. Thus, in PET/PPS blends, it is observed that the blends exhibited marginally higher values of heats of fusion over the entire composition range, indicating that the components crystallized to a greater extent as a result of blending. Thus, the overall crystallization of the component polymers, namely, PPS and PET, is facilitated as a result of blending.

The PET/PETG blends exhibited lower heats of fusion than those calculated by the rule of additivity,

indicating that the crystallization process of the component polymers is suppressed as a result of blending. These blends also exhibited a melting-point depression. The melting point of the blends varied from 236 to 253°C, whereas the melting points of PET and PETG are 256 and 265°C, respectively.

In the other three blend systems, namely, PET/PMMA, PET/T, and PET/HDPE, the heats of fusion of PET could be determined separately as shown in Figure 9. In PET/PMMA blends, the increase in the heat of fusion was significant, indicat-

**Table II Comparison of PET Blend Systems**

Blend System	Miscibility	$T_g$ of Second Component (°C)
PET		70
PET/T		138
PET/polyarylate	Miscible <sup>a</sup>	187
PET/PMMA		87
PET/PPS		93
PET/polycarbonate	Partially miscible	149
PET/PETG		87
PET/HDPE	Immiscible	-110

<sup>a</sup> On the basis of single glass transition temperature.

ing a higher degree of crystallinity of PET in the blends relative to virgin PET. The heat of fusion of PET in PET/T blends were comparable with no composition dependence. These results are consistent with the heat of crystallization data for PET/PMMA and PET/T blends. In the case of PET/HDPE blends, the heat of fusion of PET in the blends was found to be marginally lower than that of virgin PET.

Thus, the degree of crystallinity of PET decreased only in the PET/PETG blends. These results are similar to the reported retardation of PET crystallization and lowering of its degree of crystallinity in its miscible blends with polycarbonate and polyarylates,<sup>7,9-11</sup> as shown in Figure 9. The decrease in the crystallinity in these blends was attributed to the possibility of chemical interaction and changes in the glass transition temperature of PET in the different miscible blend systems. The data on the glass transition temperatures are summarized in Table II. In the miscible blends of PET with polymers having higher glass transition temperatures, the  $T_g$  of the blend would be higher than that of PET, thereby reducing the temperature range of PET crystallization and retarding the crystallization process. The reported lowering of the crystallinity of PET in its blends with polycarbonate and polyarylate has been attributed to their high glass transition temperatures.

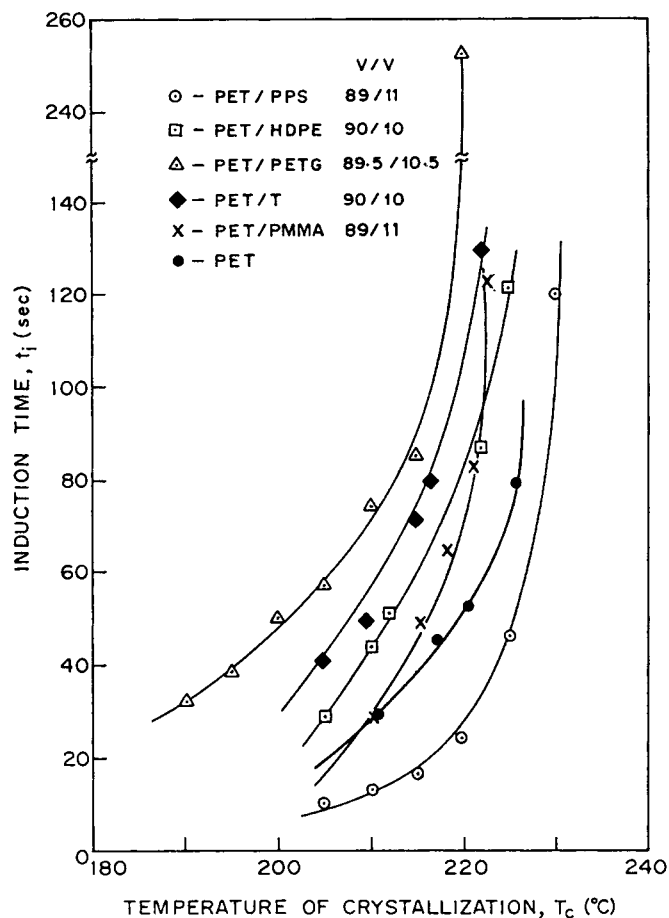
### 3.3. Isothermal Crystallization

The isothermal crystallization behavior of PET in the blends with HDPE, PPS, PETG, and amorphous polyamide was investigated at low concentration (about 10 vol %) of the second component over a temperature range of 190–230°C.

The induction time  $t_i$  is defined as the time required for initiation of the crystallization process at

a particular temperature of crystallization. The variation of the induction time with the temperature of crystallization is shown in Figure 10 for PET in its virgin form and in PET/HDPE, PET/T, PET/PPS, and PET/PETG for compositions containing low amounts (about 10%) of the second component. The induction time for crystallization in the blends was longer than that for virgin PET over the entire range of crystallization temperatures, indicating retarded nucleation except in PET/PPS blends. This change in PET/PPS blends has been attributed to the heterogeneous nucleation of PET in the presence of solidified PPS. The induction times for PET in its blends with HDPE, PMMA, and aromatic polyamide were found to be in a narrow band. In these blends, PET would crystallize by homogeneous nucleation. Thus, the presence of molten phase of second component appears to suppress the nucleation of PET in the blends. These results are consistent with the results of the nonisothermal crystallization studies, wherein PET was found to crystallize with higher degrees of supercooling in the blends relative to virgin PET. In case of PET/PETG blends, similar results relating to the retardation of nucleation was the most pronounced. However, since both the polymers are crystallizing over the same range of temperature, no definite conclusions can be drawn about PET crystallization.

The dependence of the total crystallization time ( $t_c$ ), on the temperature of crystallization ( $T_c$ ), is illustrated in Figure 11 for blends containing low amounts of second component (about 10% by volume). The  $t_c$  vs.  $T_c$  curves shifted to higher temperatures and shorter crystallization times in PET/PMMA and PET/PPS blends, while an opposite trends were observed in PET/T, PET/HDPE, and PET/PETG blends. The shift in the  $t_c$  vs.  $T_c$  curves is about 12–15°C for PET/PPS blends, wherein PET crystallization occurs through a heterogeneous



**Figure 10** The variation of induction time  $t_i$  with temperature of crystallization  $T_c$  for PET in the blends.

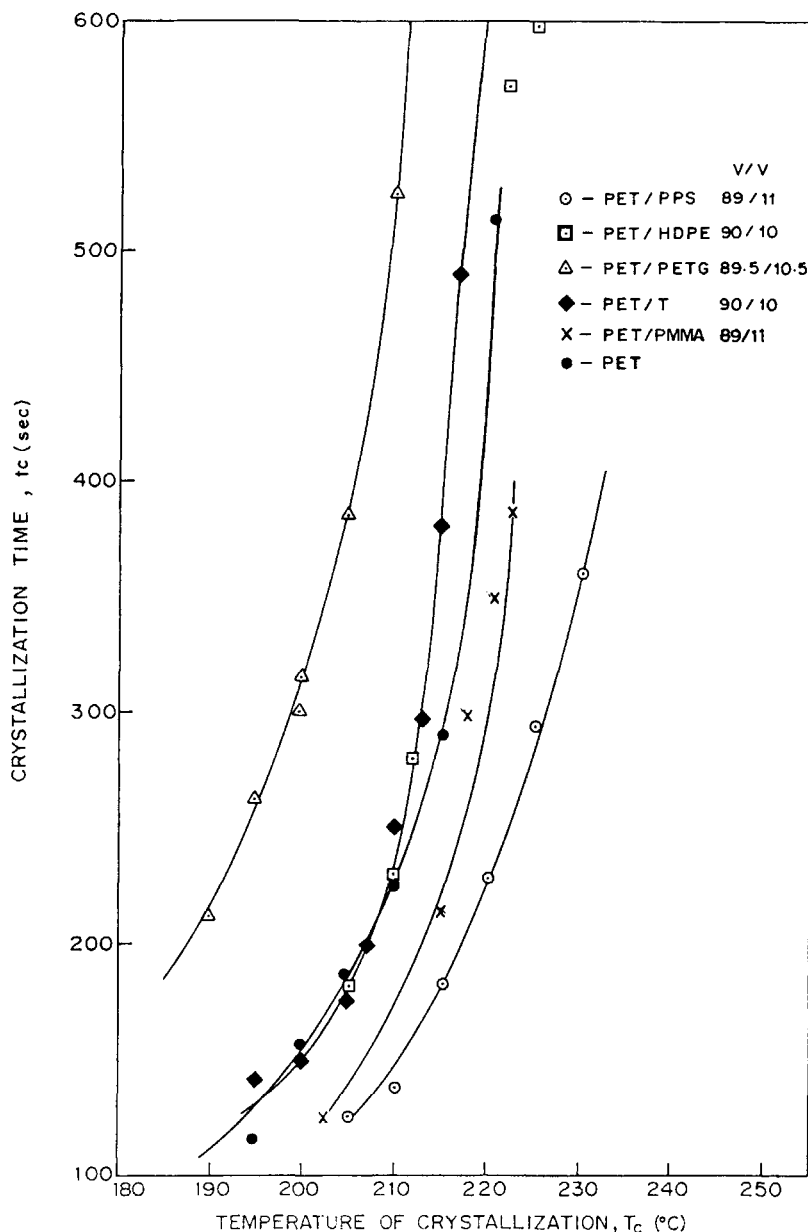
nucleation mode. It is interesting to note here that the  $t_c$  vs.  $T_c$  curves for PET/HDPE and PET/T could be represented by a single curve. Thus, the addition of about 10% by volume of HDPE and aromatic polyamide have comparable effects on the overall crystallization behavior of PET. The maximum retardation of PET crystallization was observed in PET/PETG blends.

#### 4. SUMMARY AND CONCLUSIONS

It is known that the crystallization behavior of a polymer becomes modified in a blend because of the presence of the other component. However, the results of the present investigation clearly indicate that the direction and extent of the modification depend not only on the physical state (solid or molten) of the second component but also on other factors such as chemical compatibility and relative melt

viscosities of the two component polymers. Thus, the observed changes in the crystallization behavior of PET in its blends with PPS, HDPE, PETG, PMMA, and aromatic polyamide are quite different.

The nonisothermal crystallization studies showed that the PET crystallization is facilitated by the presence of the solidified PPS in PPS/PET blends, as indicated by an increase in the onset temperature of crystallization by 6–10°C and also by narrowing of the crystallization peak width. The degree of crystallinity of PET was significantly increased in the blends except in the extreme PPS-rich composition 90/10 PPS/PET. On the other hand, blending of PET with PETG had a clear retarding influence on PET crystallization. No nonisothermal crystallization peaks were observed at intermediate blend compositions, whereas the crystallization peak width was considerably broadened in the 90/10, 25/75, and 10/90 PET/PETG blends. The degree of crystallinity in the blends was also significantly reduced as compared to virgin PET. These blends ex-



**Figure 11** The variation of crystallization time  $t_c$  with temperature of crystallization  $T_c$  for PET in the blends.

hibited melting-point depression, implying partial miscibility of the component polymers.

The trends observed in the nonisothermal crystallization of PET in the other blends were not very clear. It appears that the overall crystallization rate of PET is accelerated in its blends with PMMA and the polyamides, as indicated by narrowing of the crystallization peak width, whereas it is adversely affected in the PET/HDPE blends. The crystallinity of PET was found to increase in the blends with PMMA, whereas it decreased slightly in the PET/

HDPE blends; the crystallinity in the PET/T blends was comparable to that of virgin PET.

The isothermal crystallization studies provided greater insight, since the effects of blending on nucleation and growth could be resolved by following the crystallization process over a time interval. Thus, in the PET/PPS blends, both the nucleation and crystal growth of PET are accelerated, whereas both these processes are clearly retarded in the PET/PETG blends, confirming the findings of the nonisothermal studies. It is interesting to note that the

nucleation of PET appears to be retarded by the presence of molten PMMA, HDPE, and the polyamide, yet the growth process is accelerated in the PET/PMMA blends and only marginally affected in the PET/HDPE and PET/T blends.

The observed differences in the extent of modification of PET crystallization behavior in the different blends may be attributed to the differences in the chemical interactions and the phase morphologies. The effect of the relative melt viscosities of component polymers at compounding conditions on the phase morphologies of the different blend systems and the influence of phase morphology on PET crystallization are being investigated, and these studies will be reported separately.

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