Nucleation and Crystallization of PET Droplets Dispersed in an Amorphous PC Matrix

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Received 12 June 1997; accepted 3 April 1998

ABSTRACT: The present work compares the nucleation and crystallization process of poly(ethylene terephthalate) (PET) in bulk and when it is finely dispersed in a poly-carbonate (PC) matrix. Two types of 80/20 PC/PET immiscible blends were prepared by twin-screw extrusion at different screw rotation rates in order to produce fine dispersions of PET. The results indicate that the finer the dispersion, the greater the inhibition of the crystallization of the PET droplets. These results are explained by demonstrating (through self-nucleation experiments) that a fractionated crystallization process was developed in the dispersed PET, since the number of PET particles was much greater than the number of heterogeneities originally present in the bulk polymer. The dispersion of PET into droplets also affects its crystallization rate during isothermal crystallization at high temperatures and its reorganization capacity during heating. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1725–1735, 1998

Key words: poly(ethylene terephthalate); bisphenol-A polycarbonate; fractionated crystallization; self-nucleation; blends

INTRODUCTION

The crystallization of polymers in confined spaces is produced in many immiscible blends and multicomponent systems, such as block copolymers with crystallizable blocks. The ability and extent of crystallization within such microphases can affect the processing and bulk properties of the system.

It is generally acknowledged that bisphenol-A polycarbonate (PC) and poly(ethylene terephthalate) (PET) blends are immiscible for compositions where PC constitutes the major phase and where transesterification reactions during processing have been avoided.^{1–3} The effect of blending on the crystallinity of PET has been the subject of several investigations.⁴⁻⁷ These studies have reported that the crystallinity of PET tends to decrease, and in some cases to disappear, as the PC content in the blend increases. In a recent report, Reinsch and Rebenfeld⁷ found that the degree of crystallinity of the PET component in PC/PET blends was significantly depressed in blends with PC contents greater than 60%. Furthermore, two distinct crystallization exotherms were observed for the PET component in these blends when dynamically cooled from the melt in a differential scanning calorimeter. The results were attributed to the highly constrained growth that should occur in a high-content PC blend, where, according to these authors, cocrystallization between PC and PET could be responsible for the low-temperature exotherms or the formation of a different crystal superstructure.

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Contract grant sponsor: Consejo Venezolano de Investigaciones Científicas y Tecnológicas (CONCIT), Proyecto Nuevas Tecnologías-BID; contract grant number: NM-43.

Contract grant sponsor: Decanato de Investigación y Desarrollo, Universidad Simón Bolívar; contract grant number: DID-G02.

Journal of Applied Polymer Science, Vol. 70, 1725-1735 (1998)

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The results of Reinsch and Rebenfeld⁷ for the crystallization of PET in the PC/PET blends are very similar to those found in the literature when a crystallizable polymer is finely dispersed in an immiscible matrix.^{8–18} The crystallization of the dispersed component of an immiscible binary blend sometimes starts at greater undercoolings than is common for the bulk polymer. This phenomenon is known as fractionated crystallization and occurs when the number of heterogeneities originally present in the bulk polymer is much smaller than the number of dispersed polymer droplets.^{8,18}

For this work we used differential scanning calorimetry (DSC) to study the nucleation and crystallization processes of PET dispersed in an immiscible PC matrix, at two different extrusion rates. We compared the behavior of bulk PET with that of dispersed PET in the blends under dynamic crystallization conditions. The self-nucleation process and the isothermal crystallization behavior of the blends were also studied in comparison with bulk PET. To minimize the miscibility of the polymers and increase the degree of dispersion, a PC/PET blend with an 80/20 weight (by weight-composition ratio) was chosen.

EXPERIMENTAL

Materials

A bisphenol-A polycarbonate Lexan grade HF1110-111 (MFI 1.2 g/10 min), and a PET Kodapak grade 7352 (MFI 22.0 g/10 min) were used. The polymers were dried under vacuum for 24 h at 110°C prior to mixing.

Blend Preparation

For the preparation of the blends, a Haake biconic counterrotating twin-screw extruder was used, with an L/D ratio of 13. The 80/20 PC/PET blend was extruded at two different screw-rotating speeds, 10 and 40 rpm. The extrusion was performed for all dry materials with the following temperature profile (four temperature zones can be programmed from hopper to die): 250, 270, 290, and 280°C. The estimated residence time was 2 min 40 s for the 10-rpm blend and 1 min 35 s for the 40-rpm blend.

The neat PET was processed at somewhat different conditions. It was extruded on a Davenport melt flow indexer at 290°C with a load of 5.0 Kgf and an estimated residence time of 3 min. This treatment was performed in order to produce a thermal history in the neat PET similar to that in the blends. It was not possible to use temperatures higher than 250°C in the first extrusion zone of the Haake extruder. This meant that under the temperature profile used for the blends, the generated torque with neat PET was higher than the maximum allowed in the extruder because partially melted PET was being conveyed through the first extrusion zone until the second was reached (the second zone was at 270°C, as indicated above). This problem was not present in the blends because only 20% PET was used.

Thermal Analysis

The thermal analysis was performed with a Perkin–Elmer DSC7 under an ultrahigh-purity nitrogen atmosphere. The equipment was calibrated with indium and tin standards. The sample weight varied between 14.0 and 16.5 mg. The unmixed blends were prepared using equivalent weights of pure PC and pure PET in the same DSC pan but separated by aluminum foil. In this way the individual response of each polymer, according to its weight ratio, was evaluated without any effect associated with mixing.

Dynamic DSC Experiments

In order to perform a preliminary evaluation of the thermal behavior of the samples, dynamic heating and cooling scans were recorded at 10°C/ min. The as-extruded samples were first heated in the differential scanning calorimeter to record the first melting run, up to 290°C. Then a cooling run was registered, down to 50°C, followed by a second heating run.

Self-Nucleation Experiments

The procedure suggested by Fillon and colleagues¹⁹ to study self-nucleation behavior in the calorimeter was closely followed. The following consecutive steps were applied to the samples:

- 1. The samples were first melted, up to 290°C for 3 min, to erase all previous thermal history.
- 2. The sample was then cooled to 50°C, at 10°C/min, with the aim of creating a "standard thermal history."
- 3. The sample was again heated at the same



Temperature [°C]

Figure 1 Partial or complete melting domains according to Fillon and colleagues¹⁹ for the self-nucleation of semicrystalline polymers. (See Experimental section.)

rate up to a temperature denoted T_s , or self-nucleating temperature.

- 4. The sample was held at T_s for 5 min.
- 5. A cooling scan of the sample was recorded from T_s down to 50°C.
- 6. Finally, a heating scan of the sample up to 290°C was recorded to register the material's melting behavior.

The value of the chosen T_s is very important because it determines whether the polymer undergoes complete melting (domain I), only selfnucleation (domain II), or a combination of selfnucleation and annealing of the unmelted crystals (domain III). The different partial melting domains are shown in Figure 1, as depicted by Fillon and coworkers.¹⁹ For further details on the molecular consequences of self-nucleation refer to the work of Fillon and associates.¹⁹

Isothermal Crystallization

The isothermal crystallization process was also carried out in the differential scanning calorimeter. The samples were first heated to 290°C for 3 min to erase all previous thermal history, and then were quenched (at a nominal rate of 200°C/min) to the isothermal crystallization temperature (T_c) . The samples were held at T_c for a constant period of 40 min. Finally, a heating scan from T_c up to complete melting was recorded at 10°C/min.

Morphological Examination

A Phillips scanning electron microscope model SEM505 was used to observe the morphology of

the prepared blends. Small extruded fragments were submerged in liquid nitrogen for 15 min and then fractured with a guillotine. The fractures were made on the longitudinal extrusion axis as well as on the transversal axis. Finally, the fracture surface was treated with gold and vanadium.

The particle size was obtained directly from the micrographs, measuring 500 particles per blend. After the measurements were completed, the mean number radius (\bar{r}_n) , the mean volume radius (\bar{r}_v) , and the size dispersion were calculated according to the following expressions²⁰:

$$\bar{r}_n = \frac{\sum n_i r_i}{N} \tag{1}$$

$$\bar{r}_v = \frac{\sum n_i r_i^4}{\sum n_i r_i^3} \tag{2}$$

$$D = \frac{\bar{r}_v}{\bar{r}_n} \tag{3}$$

where n_i is the number of particles of radius r_i , N is the total number of particles, and D is the size dispersity.

RESULTS AND DISCUSSION

Morphology

Figure 2 shows a micrograph of a cryogenically fractured 80/20 PC/PET blend (prepared at 40



Figure 2 Morphology of an 80/20 PC/PET blend, prepared by twin-screw extrusion in the melt at 40 rpm. The white horizontal line represents 10 μ m.

Table I Particle Dimensions, Particle Size	
Dispersity, and Volumetric Particle Density in	n
the 80/20 PC/PET Blends Prepared at the	
Indicated Extrusion Rates	

Screw Rotation	\bar{r}_n	$ar{r}_v$	D	Particle
Rate (rpm)	(µm)	(μ m)		Number (cm ³)
40 10	$\begin{array}{c} 0.51 \\ 1.07 \end{array}$	$\begin{array}{c} 1.21 \\ 1.67 \end{array}$	$2.38 \\ 1.56$	$2.39 imes 10^{10}\ 9.07 imes 10^{9}$

 r_n , mean number radius; r_v , mean volume radius; D, size dispersity.

rpm). The dispersion of PET in the PC matrix is very good. Extensive observations of the extruded cylinders fractured along the radius and perpendicular to it revealed the spherical nature of the PET inclusions in the PC matrix. The morphology of the blend prepared at 10 rpm was qualitatively similar to that shown in Figure 2.

Table I shows the results of the measurements of mean particle sizes and particle size dispersity of the blends; and it is easy to see that the higher the screw speed, the finer the resulting mean particle size. Figure 3 shows the distribution of particle size for the two blends. It can be seen that the mean particle size is smaller for the blend prepared using a higher screw rotation rate, even if the dispersity of droplet sizes is greater. This is a consequence of the higher deformation rates applied in the preparation of this blend (the 40rpm blend) as compared with the blend prepared at 10 rpm. The lower shear rates applied at 10 rpm may also allow more coalescence after droplet formation than at 40 rpm, therefore causing a broadening of the full particle size distribution curve. The particle density is higher in the 40rpm blend than in the 10-rpm blend. This result will have important repercussions for the crystallization behavior of the finely dispersed PET.

Thermal Behavior of Bulk PET and Dispersed PET in the PC/PET Blends

Figure 4 shows the heating and cooling scans for neat PET and for the unmixed 80/20 PC/PET blend. After the fusion of the crystalline material at 290°C, the cooling scan of PET shows a distinctive crystallization exotherm [i.e., Fig. 4, curve (b)], with an enthalpy of 20.8 J/g. Curve (c) shows the subsequent heating scan, where a very small cold crystallization exotherm at around 175°C can be appreciated, indicating that the material did not crystallize fully during the previous cooling at 10°C/min. The melting endotherm [curve (c)] possesses a higher enthalpy of fusion (36.9 J/g) than the crystallization enthalpy associated with the exotherm of curve (b). This means that the crystallinity of the polymer increased during the scan, partly by the cold crystallization mentioned and partly by partial melting and recrystallization. The glass transition temperature (T_g) of PET can also be seen in curve (c) at around 70°C.

The DSC scans corresponding to the unmixed blend behavior are presented in Figure 4 on curves (d-f). The first heating run of the unmixed blend shows a very clear T_g for PC (80% by weight in this sample) and the melting endotherm of PET. During the cooling scan [curve (e)], the crystallization exotherm of PET can be seen for the unmixed blend just before the T_g of PC. In the subsequent heating run [curve (f)] the characteristic endothermic jump of the T_g of PC is followed by the melting of PET. Since the PET content is only 20%, neither the $T_{\rm g}$ of PET nor the very small cold crystallization of PET is visible in curve (f). As expected with an unmixed blend, the behavior is simply a superposition of the weighted response of each individual component. This would be the behavior to be observed during DSC scans if the blend were totally immiscible and the morphology of the blend had no influence on the nucleation and crystallization of the PET component.



Figure 3 Particle size distribution for the PET component in the two 80/20 PC/PET blends.

The thermal behavior of the melt-mixed blends is shown in Figure 5. The first heating of the as-extruded sample, the cooling run from the melt, and the subsequent heating scan are presented for the two blend extrusion speeds used.

Curve (a) in Figure 5 shows the DSC heating run of the as-extruded blend prepared at 40 rpm, where a better dispersion was obtained. Upon increasing temperature, the T_g of the PET component can be seen at around 75°C, followed by a superposition of PET cold crystallization exotherm and the T_g of the PC component at 145°C. At higher temperature (251°C) the melting endotherm of the PET component can be clearly observed. As will become apparent later, the relatively high crystallinity developed by the PET component is due to the crystalline memory effect present on this component, as a result of the molecular orientation achieved during extrusion.²¹

After all crystalline memory had been erased by holding the sample in the melt at 290°C for 3 min, the 80/20 PC/PET blend showed almost no noticeable crystallization upon cooling at 10°C/ min [curve (b) in Fig. 5]; as opposed to the behavior of pure PET [curve (b) in Fig. 4] or the PET



Figure 4 DSC scans of bulk PET: (a) First heating scan of the heat-treated sample (see the Experimental section), (b) cooling scan after 3 min at 290°C, and (c) subsequent heating scan after the cooling in (b). DSC scans of the unmixed 80/20 PC/PET blends: (d) First heating scan, (e) cooling scan after 3 min at 290°C, (f) subsequent heating scan after the cooling in (e).



Figure 5 DSC scans of the 40-rpm 80/20 PC/PET blend: (a) First heating scan of the as-extruded sample, (b) cooling scan after 3 min at 290°C, and (c) subsequent heating scan after the cooling in (b). DSC scans of the 10-rpm 80/20 PC/PET blend: (d) First heating scan of the as-extruded sample, (e) cooling scan after 3 min at 290°C, and (f) subsequent heating scan after the cooling in (e).

component in the unmixed blend [curve (e) in Fig. 4]. The cooling scan of the melt-mixed sample only shows, very clearly, the vitrification of the excess component (PC) and at lower temperatures the vitrification of the minor component (PET), which is difficult to appreciate in Figure 5. The difficulties that the dispersed PET component has in crystallizing during cooling at 10°C/min are also evidenced in the subsequent heating run [curve (c) in Fig. 5]. It can be seen that during heating, the material is capable only of very limited crystallization during the scan (cold crystallization) and therefore a very noisy and broad melting endotherm is observed, corresponding to the fusion of a very small amount of crystals formed during the scan ($\Delta H_m = 2.2$ J/g).

The melt-mixed sample prepared at 10 rpm showed a behavior qualitatively similar to the blend prepared at higher mixing speeds, but it was capable of crystallizing more during the cooling [curve (e), Fig. 5] as well as during the heating [curve (f), Fig. 5, $\Delta H_m = 5.7$ J/g]. It should be remembered that the PET droplet size was higher in this blend where the dispersion was not as good as in the blend prepared with a higher mixing speed in the melt.

We believe that the peculiar difficulties that dispersed PET droplets find in crystallizing, as opposed to the bulk material, are connected to the degree of dispersion. The phenomenon is similar to the fractionated crystallization exhibited by many polymers when they are finely dispersed into droplets.^{8,11-18} The bulk PET contains a number of heterogeneous nuclei which are responsible for nucleation and crystallization at the lowest undercoolings possible (which will be denoted "type A" heterogeneities) depending on the cooling rate from the melt (i.e., for PET the dynamic peak crystallization temperature upon cooling from the melt at 10°C/min will be around 175°C; see Fig. 4). When the polymer is dispersed in fine droplets, the number of droplets could be much greater than the number of available type A heterogeneities. As a matter of fact, the number of dispersed particles $(10^9-10^{10} \text{ particles/cm}^3)$ is very high (see Table I) as compared with the usual number of type A heterogeneities in molten PET $(10^6 \text{ heterogeneities/cm}^3; \text{ see Ref. 22})$. This means that many PET droplets will not contain any type A heterogeneity; therefore, the polymer inside the droplet cannot crystallize at the same undercooling, and will crystallize at larger undercoolings only if another type of heterogeneity (say, "type B," active at larger undercoolings) is present or by creating its own nuclei in a homogeneous crystallization process that usually occurs at the largest possible undercooling.⁸ Because these nucleation events are time-dependent, and given the relatively low crystallization rate of PET, it is possible that at the cooling rate used here the crystallization could be almost completely suppressed (as in the 40-rpm blend) or only partially suppressed (as in the 10-rpm blend). The differences in the ability to crystallize upon cooling could then be due to the degree of dispersion in the blend.

Further evidence that the lack of nuclei is the reason for the crystallization difficulties of the PET droplets is provided in the next section, where controlled self-nucleation experiments support this view.

On the other hand, in a related phenomenon, it has been reported that the PET possesses 3×10^6 nuclei/cm³ when it is cooled from the melt to a particular crystallization temperature (where $T_c > T_g$), and 3×10^{11} nuclei/cm³ when it is heated from the amorphous state to the same T_c , in view of a self-seeding mechanism.²² This phenomenon of a higher quantity of nuclei present during the heating run could explain why, even in dispersed



Figure 6 DSC cooling scans at 10°C/min of bulk PET after 5 min at the indicated T_s temperatures.

PET droplets, the polymer shows a greater tendency to crystallize at lower temperatures (cold crystallization) during the heating run and therefore exhibits a small fusion endotherm in the heating scan.

Self-Nucleation Experiments

The cooling scans after self-nucleation for 5 min at previously chosen self-seeding temperatures (T_s) in a wide temperature range for PET are shown in Figure 6. The chosen temperature range encompassed all three self-nucleation domains described in the experimental section and Figure 1. The DSC scans corresponding to the lowest T_s temperatures used (231, 240, and 245°C) exhibited no crystallization exotherm at all because the fraction of crystals melted at T_s is too low. As T_s increased, a progressively higher fraction of crystals melted at T_s and recrystallized upon cooling at increasingly lower temperatures. When T_s was 290°C or higher, the time spent at that temperature was enough to erase all crystalline memory of the material, therefore the material needs greater undercooling in order to crystallize. This is the typical behavior of the majority of semicrystalline polymers when they are in domain I, according to Fillon and coworkers.¹⁹ After 5 min



Figure 7 DSC heating scans of bulk PET after previous crystallization (Fig. 6) from the indicated T_s temperatures.

at this T_s (290°C), bulk PET crystallizes at a lower temperature and up to a lower degree than when it is self-nucleated at lower T_s in domain II.

The identification of the different domains depending on the T_s used is easier when the subsequent heating scans are examined. Figure 7 shows such heating scans after the cooling presented in Figure 6. For those samples treated at T_s temperatures between 231 and 258°C, the heating scan shows complex endotherms that are composed of two signals: the endotherm that corresponds to the fusion of the crystals that were annealed at T_s , and that of the fusion of the crystals formed during cooling (and altered during the heating scan by partial melting and recrystallization processes). All these samples are clearly under domain III.

The transition from domain III to domain II is achieved at 258°C because at T_s values greater than this, only self-nucleation occurs (domain II), as indicated by the absence of higher-temperature melting endotherms; whereas at values lower than or equal to this temperature, both self-nucleation and annealing take place (domain III). The samples treated at 260 and 262°C are therefore under domain II and the final sample, treated at 290°C, is under domain I, as explained above.

When a similar self-nucleation procedure was applied to the PC/PET blends, the self-seeding temperature range was shortened in view of the intrinsic differences in the melting range of the pure PET and the PET component in the blend (compare Fig. 4 with Fig. 5); so the maximum T_s applied for self-nucleation behavior in domain II was 258°C. Higher T_s temperatures induced a transition to domain I (i.e., complete melting). Such behavior also indicates that it is more difficult to induce self-nucleation in the dispersed PET droplets than in bulk PET because lower T_s temperatures must be used.

Figures 8 and 9 show the cooling and subsequent heating after self-nucleation for the 40-rpm 80/20 PC/PET. Apart from the appearance of the step attributed to the T_g of the PC component (in both heating and cooling scans), the self-nucleation behavior of the PET component in the blend is very similar, at least qualitatively, to that of pure PET. The quantitative differences in behavior are due to the morphological restrictions imposed by the fine dispersion of the PET in the PC matrix. For instance, the development of crystallinity in the dispersed PET component at high T_{i} (from 251 to 258°C) was smaller than in bulk PET (see discussion of Fig. 12, below). The behavior of the 10-rpm blend was also qualitatively similar. Further comparisons between the blends and the homopolymer are made below.

In Figure 10, the peak crystallization temperature is plotted as a function of the self-seeding



Figure 8 DSC cooling scans at 10°C/min of the 40-rpm 80/20 PC/PET blend after 5 min at the indicated T_s temperatures.



Figure 9 DSC heating scans of the 40-rpm 80/20 PC/PET blend after previous crystallization (Fig. 6) from the indicated T_s temperatures.

temperature for bulk PET and dispersed PET droplets in both types of blend. This figure illustrates that the self-nucleation procedure qualitatively affects both bulk PET and dispersed PET droplets in the same way. It is noteworthy that the maximum achieved self-nucleation temperature is lower as the degree of dispersion of PET is increased. This result is probably related to the intrinsic difficulties experienced by PET when it is dispersed into droplets; we present further consequences of droplet crystallization below. At con-



Figure 10 Crystallization temperature as a function of the self-nucleation temperature for bulk PET, and the PET component in the 40-rpm and 10-rpm 80/20 PC/PET blends.



Figure 11 Melting temperature as a function of selfnucleation temperature for bulk PET and the PET component in the 40-rpm 80/20 PC/PET blend. (Data from Figs. 6–9.)

stant T_s values, bulk PET always crystallizes at slightly higher T_c than the blends.

In Figure 11, the values of all the melting peaks after self-nucleation treatments (see Figs. 6-9) are plotted as a function of the self-seeding temperatures for bulk PET and for dispersed PET (in the 40-rpm 80/20 PC/PET blend). Most samples in Figures 6-9 exhibit complex endotherms with two maxima. The melting point of the crystals of bulk PET that were annealed at T_s (labeled T_{m_1} in Fig. 11) increases linearly with annealing temperature (i.e., T_s) with a correlation coefficient of 0.9902. However, the melting point of the crystals that were formed during cooling from T_s (labeled T_{m_2} in Fig. 11) does not vary appreciably with self-seeding temperature (their T_m is approximately 252°C in most cases). This invariance of T_{m_2} indicates that these lamellae suffered partial melting and recrystallization during the heating runs of Figures 7 and 9, a well-known process in PET.²³⁻²⁷ A very similar situation was encountered for the PET dispersed into droplets in the 40-rpm blend. The melting peak of the annealed crystals correlates with T_s linearly with a correlation coefficient of 0.9968, whereas that of the crystals formed during cooling and reorganized during the heating scan does not vary sensibly with T_s . It is very interesting to note that the melting point of the crystals reorganized during the scan tends to be higher in bulk PET than in dispersed PET. This is another consequence of the morphological restrictions imposed by the confinement of PET into fine droplets. The results for the 10-rpm blend were analogous to those obtained for the 40-rpm blend.



Figure 12 Crystallization enthalpy as a function of self-nucleation temperature for bulk PET and the PET component in the 80/20 PC/PET blends. Symbols: squares, bulk PET; circles, PET component in the 10-rpm 80/20 PC/PET blend; triangles, PET component in the 40-rpm 80/20 PC/PET blend.

The variation of the enthalpy of crystallization upon cooling from T_s , as a function of the selfseeding temperature, exhibits an expected trend, as shown in Figure 12. The crystallinity degree increases with T_s very rapidly since the fraction of crystals previously melted at T_s also increases with increasing temperature.

The maximum value of crystallization enthalpy achieved by dispersed PET in the self-nucleated 40-rpm blend is significantly lower ($\approx 50\%$) than those observed for dispersed PET in the 10-rpm blend or for bulk PET. This must be due to the lower amount of self-nuclei generated in the PET contained within the 40-rpm blend, because it did not contain many crystals to partially melt at T_s . When the blend dispersion is not so fine (i.e., in the 10-rpm blend) the self-nucleation procedure can be as effective as in bulk PET, therefore yielding the same final crystallinity value.

Figure 12 also shows the enthalpy of crystallization for bulk PET and for dispersed PET in the blends after all the crystalline memory has been erased (i.e., at $T_s = 290$ °C). In this case, the degree of dispersion has a major effect in determining the amount of crystals formed at that cooling rate (10°C/min).

It is worth emphasizing once again the difference between bulk PET and the dispersed PET droplets in the blends. For the 40-rpm blend, the dispersed PET was unable to crystallize upon cooling from 290°C (Figs. 5 and 12); however, bulk PET can crystallize under identical conditions (Figs. 4 and 12). The self-nucleation experiments presented above demonstrate that the reason behind this difference is the lack of enough heterogeneous nuclei. Once the nuclei have been provided by self-seeding (Fig. 8), the droplets can crystallize. However, in the 40-rpm blend, not all droplets crystallize because the crystallinity degree achieved is lower in the dispersed PET in this blend than that achieved by bulk PET (Fig. 12). We have previously shown that the use of suitable nucleating agents can also provide a way of eliminating the fractionated crystallization phenomenon of isotactic polypropylene or branched polyethylene dispersed in several immiscible matrices.^{11,14,15,17}

Isothermal Crystallization

Because the experiments shown in previous sections of this work indicated that PET experienced difficulties in crystallizing dynamically when it is dispersed in an immiscible PC matrix, some isothermal crystallization experiments were performed to explore the differences in this case with bulk PET.

Figure 13 presents heating DSC scans from T_c to 290°C of bulk PET samples after isothermal



Figure 13 DSC heating scans of bulk PET after previous isothermal crystallization at the indicated temperatures for 40 min.



Figure 14 DSC heating scans of the PET component in the 40-rpm 80/20 PC/PET blend after previous isothermal crystallization at the indicated temperatures for 40 min.

crystallization at the indicated crystallization temperatures for 40 min (i.e., 200, 205, 210, 215, and 220°C). These DSC heating curves exhibit a complex endotherm with three identifiable maxima, as opposed to the fusion scans of samples crystallized dynamically. The melting signal is composed of three components: (1) a low-temperature endotherm whose fusion peak is located approximately 10°C higher than T_c , (2) an intermediate endotherm that is shifted to higher temperatures as T_c increases, and (3) a high-temperature endotherm. These maxima will be referred to as peaks I, II, and III, respectively, in increasing temperature order.

Previous works have attributed peak I to the fusion of the crystals formed by the secondary crystallization process,²⁸ and it is dependent on crystallization time and temperature.^{23–26} The intermediate peak II can be assigned to the fusion of crystals formed by primary crystallization at T_c .^{25,26} Finally, peak III is probably due to the fusion of the crystals reorganized during the DSC scan by a partial melting–recrystallization process,^{23–27} as discussed earlier in the dynamic crystallization experiments. This is why this peak is independent on T_c and is located at around 250°C, similar to the peak labeled T_{m_2} in Figure 11 (discussed in the previous section; see also Fig. 7).

For the 40-rpm blend (Fig. 14), the situation is

qualitatively similar for almost all of the chosen crystallization temperatures. However, some important differences can be appreciated. Peak I is barely detected at T_c 215°C and has completely disappeared at T_c 220°C. This behavior probably reflects the increasing difficulties of PET to undergo secondary crystallization at high T_c when it is finely dispersed in a PC matrix.

Figure 15 shows the variation of the enthalpy of fusion as a function of isothermal crystallization temperature, where the highest value is for the bulk PET. It can also be observed that the dispersed polymer tends to decrease its degree of crystallization as T_c increases. At 220°C the degree of crystallinity achieved strongly depends on the degree of dispersion. The dispersion of PET in the blends explains this behavior, because the absence of enough heterogeneous nuclei for all the dispersed PET particles makes the isothermal crystallization process difficult.

CONCLUSIONS

When PET is dispersed into fine particles within an immiscible matrix, its crystallization capability is reduced. In dynamic crystallization experiments, the finer the degree of dispersion achieved, the greater the suppression of crystallization in the droplets as compared with the bulk polymer. This phenomenon is due to the lack of enough heterogeneous nuclei to provoke heterogeneous nucleation events at the usual undercooling for all the droplets produced in the dispersion, since the number of dispersed particles is much greater than the number of heterogeneous nuclei present in bulk PET.



Figure 15 Fusion enthalpy as a function of the crystallization temperature for bulk PET and the PET component in the 80/20 PC/PET blends.

The dispersion of PET into droplets also affects its crystallization rate during isothermal crystallization at high temperatures and its reorganization capacity during heating scans in DSC.

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