## Antinucleating Action of Polystyrene on the Isothermal Cold Crystallization of Poly(ethylene terephthalate)

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ABSTRACT: The effect of polystyrene (PS) on the kinetics of the cold crystallization of poly(ethylene terephthalate) (PET) was thoroughly investigated. The PET/PS blends were essentially immiscible, as observed by dynamic mechanical thermal analysis, which showed two distinct glass-transition temperatures, and by scanning electron microscopy. The neat PET and its blends were isothermally cold-crystallized at various temperatures, and the kinetic parameters were determined with the Avrami approach. PET and its blends presented values of the Avrami exponent close to 2, and the kinetic constant increased with the crystallization temperature increasing. For all the crystallization temperatures studied, the presence of only 1 wt % PS significantly reduced the rate of cold crystallization of PET. A further increase in the PS concentration did not show any significant influence. The blends presented higher values of the activation energy

## INTRODUCTION

It is a common sense that poly(ethylene terephthalate) (PET) is nowadays one of the most important polymers, being used in a variety of products, including packaging for mineral water, soft drinks, and cosmetics as well as durable consumer products such as those used in electronics. For some applications, materials with special characteristics and improved properties may be necessary. One of the desirable properties of PET bottles is transparency. Early crystallization of PET during the injectionblow-molding process, called cold crystallization, may induce haze or even opacity, causing a change in appearance and making the blow-molding stage unfeasible (which is mostly important for processing). This is the reason that the rate of crystallization during both the cooling stage of the preform injection molding and the heating stage of the preform for cold crystallization, which was estimated from Arrhenius plots. The equilibrium melting temperature of neat PET was determined on the basis of the linear Hoffman-Weeks extrapolative method to be ~ 255°C. This value decreased in the presence of PS, and this suggested limited solubility between PET and PS. From the spherulitic growth equation proposed by Hoffman and Lauritzen, the nucleation parameter was obtained, and it was shown to be higher for the neat PET than for the blends. Moreover, a transition of regimes (I  $\rightarrow$  II) was observed in both PET and its blends. From the investigations conducted here, it is clear that PS in small amounts causes a reduction in the rate of PET crystallization, acting as an antinucleating agent. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 1884–1895, 2009

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before blowing must be low. On the other hand, a higher level of crystallinity in the finished product is required for PET bottles to withstand hot filling processes. In summary, a (semi)crystalline polymer is necessary, but the rate of crystallization should not be too high. To obtain a compromise between these two requirements, the PET grade for bottles is usually a copolymer in which the comonomer makes crystallization slightly more difficult.<sup>1</sup> However, different contents and types of comonomers may be necessary to acquire the desired crystallization properties with respect to the processing conditions and product characteristics. This is not very easy to reach from the market point of view on account of cost and versatility reasons. The main point is that a new grade requires a different polymerization setup.

To fulfill the conditions described previously for controlling the rate of PET crystallization, an interesting approach would be the development of an additive that could be added before processing. If this additive interfered with the crystallization of PET but not with the polymer's mechanical and physical properties, then a great achievement would be obtained. Blending an amorphous polymer with a crystallizable polymer may cause a dramatic effect on the thermodynamic and kinetic parameters of the crystallization of the polymer.<sup>2,3</sup> This appears to be a

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useful route for controlling the crystallization rate of a crystalline polymer, but usually high contents of the second constituent are added, also affecting the physical and mechanical properties. In the current study, low amounts of polystyrene (PS) were added in an attempt to reduce the rate of cold crystallization of PET. If this is achieved, the heating stage during blow molding may have a wider operating window, which could reduce the amount of scrap in bottle factories. To achieve a systematic control of crystallization, it is essential that the crystallization kinetics be investigated in detail. This article reports the isothermal cold crystallization kinetics of PET and PET/PS blends and examines the changes in the crystallization kinetics and morphology. The kinetics of the cold crystallization of PET, because of its practical importance, has attracted a lot of attention from the scientific community, and some of the published work will be reviewed throughout the text.

#### **EXPERIMENTAL**

#### Materials

PET (bottle grade) was supplied by Rhodia-Ster S.A. (Sao Paulo, Brazil) (Rhopet S78) with an intrinsic viscosity of 0.78 dL/g and a weight-average molecular weight of 48,000 g/mol. A general-purpose injectionmolding grade of PS was purchased from Dow (Sao Paulo, Brazil) with the trade name of Styron 649D. The thermal transition temperatures of the polymers are shown in Table I, and their chemical structures are shown in Figure 1.

#### **Blend** preparation

Before being mixed, the polymers were dried in an oven with forced air circulation. PET was dried at 120°C for 6 h to prevent hydrolysis during the processing,<sup>5–7</sup> and PS was dried at 80°C for 14 h to remove moisture.<sup>5,8</sup> The mixture was conducted in a System 90 torque rheometer from Haake-Büchler (Waltham, MA, USA) coupled with a Rheomix 600 internal mixer and operating with roller-type rotors. The mixing was performed at 265°C and 60 rpm for 10 min with 50 g of material. After compounding, the melt was quickly quenched in a water–ice bath to obtain amorphous blends.

TABLE I Thermal Transition Temperatures of PET and PS

| Polymer | $T_g$ (°C) | $T_c$ (°C) | $T_m$ (°C) |  |  |
|---------|------------|------------|------------|--|--|
| PET     | 70         | 124        | 250        |  |  |
| PS      | 94         |            |            |  |  |

The data were taken from Wellen et al.<sup>4</sup>



Figure 1 Chemical structures of PET and PS.

#### Dynamic mechanical thermal analysis (DMTA)

A DMA 983 apparatus (TA Instruments, Kyoto, Japan) was used for measurements of the loss factor (tan  $\delta$ ). This was done under nitrogen, and the temperature ranged from -20 to  $200^{\circ}$ C at  $2^{\circ}$ C/min with a frequency of 1 Hz.

#### Differential scanning calorimetry (DSC)

DSC measurements were carried out with a Shimadzu DSC-50 (Kyoto, Japan). The isothermal cold crystallization was achieved by the quick heating (~  $100^{\circ}$ C/min) of the samples from room temperature to the target isothermal crystallization temperature ( $T_c$ ). The exothermic output was registered as a function of time as long as no variation in the baseline was observed. The target  $T_c$  values ranged from 110 to 160°C. If, during the experiment, the crystallization started before the target temperature was reached, the measurement was discarded. The kinetic parameters of isothermal cold crystallization were obtained with the Avrami approach,<sup>9</sup> which is described later.

#### Scanning electron microscopy (SEM)

SEM analyses were carried out with an SSX 550 Superscan from Shimadzu. The samples were fractured in liquid nitrogen and coated with gold to prevent the accumulation of charges.<sup>10</sup>

### **RESULTS AND DISCUSSION**

#### **DMTA** measurements

One of the most common ways of determining miscibility in a polymer blend is the analysis of the glass-transition temperatures ( $T_g$ 's) of the components in the mixture. When the  $T_g$  values of the components are not shifted with respect to the original values, the blend is considered immiscible, whereas the observation of only one  $T_g$  in an intermediate position denotes miscibility. When partial miscibility occurs, the values of  $T_g$  are shifted with respect to each other.<sup>11</sup> The samples studied here were analyzed with DMTA, which is the most accurate technique for  $T_g$  determination. The DMTA curves for PS, PET, and a blend with 15 wt % PS are presented in Figure 2, which shows that the  $T_g$ 's of PET and PS in the blends are located close to their original



Figure 2 DMTA thermograms of PS, PET, and a blend with 15 wt % PS.

values; this indicates that the polymers form a twophase mixture. The second peak in the PET thermogram (at  $\sim 140-150^{\circ}$ C) might be an artifact of the sample analysis due to, for instance, sample slippage at the grips.

#### Isothermal cold crystallization

The DSC scans for the isothermal cold crystallization of the neat PET and its blends with PS are shown in Figure 3. The exotherms are shifted to shorter times with increasing  $T_{cr}$  evidencing an increase in the crystallization rate of PET. Similar behavior was reported in a previous study of extruded PET foils subjected to cold crystallization.<sup>12,13</sup> This behavior results from an increase in the molecular mobility with increasing temperature, which facilitates crystalline ordering.<sup>14</sup>



Figure 3 Selected DSC exotherms for the isothermal cold crystallization of PET and PET/PS blends.

Figure 3 shows that the cold crystallization peak of the neat PET at a given temperature occurred in a shorter time interval in comparison with the blends with PS, suggesting that the presence of PS reduced the tendency of PET crystallization. Moreover, the crystallization exotherms of the blends with 15 or 20 wt % PS were similar to those of the blends with only 1 wt % PS (see also the kinetic data reported later). This means that the addition of larger amounts of PS does not have a significant influence in reducing the rate of the cold crystallization of PET. A similar trend was reported previously when atactic polypropylene (PP) was added to isotactic PP and a reduction in the rate of crystallization was observed, regardless of the type and amount of atactic PP.15-19 The authors argued that the atactic molecules acted like noncrystallizable impurities, disturbing the crystallization of PP.

In this work, the reduction of the crystallization rate of PET in the presence of PS can be associated with the solubility between the polymers. Although the PET/PS blends are essentially immiscible, as shown in Figures 2 and 12 (the latter of which is shown with the SEM analyses), it is possible that a very small fraction of PS molecules is actually soluble in the amorphous phase of PET. This consideration is based on the concept of solubility, in which traces of a component can be soluble in a medium even without a homogeneous mixture being formed (where the solute is present in larger proportions).<sup>2,11</sup> In the case of PET/PS mixtures, the solubility limit of PS in PET must be low (certainly <1 wt %, as shown later in Fig. 12), but even so, it can hinder the crystallization of PET. The existence of a low solubility limit explains the only slight influence of higher concentrations of PS on the crystallization kinetics of PET. In other words, when the solubility limit is reached, additional molecules of PS just segregate to the borders of the crystallization zone and do not interfere with the crystallizability of PET. In a recent article, Schababerle and Mitchell<sup>20</sup> investigated the effect of PS on the cold crystallization behavior of PET when the blend was produced by cryogenic mechanical attrition. Although the process of blend preparation was different from the process followed here and the amount of PS was much higher, similar results were obtained for the displacement of  $T_c$ . Using laser scanning confocal fluorescent microscopy, they showed that PS was not detected in the crystal phase of PET.<sup>20</sup>

Another aspect that can contribute to reducing the crystallization rate of the blends is the higher glass temperature ( $T_g$ ) of PS with respect to PET (Table I). Because  $T_g$  is related to the mobility of the polymer segments, the presence of PS causes an increase in the energy for the transport of the crystallizable chains of PET toward the growing crystals, and as a



Log t (s)

**Figure 4** Evolution of  $X_t$  with *t* during the isothermal cold crystallization of PET and blends with 1 wt % PS.

result, the crystallization of PET becomes more difficult in the presence of PS.<sup>21,22</sup>

From the DSC scans shown in Figure 3, the evolution of the relative crystallinity with crystallization time *t* was calculated, and the curves for PET and for the blend with 1 wt % PS are illustrated in Figure 4. All the isotherms presented a sigmoidal form characterizing a phase transformation without discontinuities, which is typical in polymers. The variations that occurred during solidification were marked by differences in the nucleation and crystalline growth rates, without much difference in the morphological growth.<sup>23-25</sup> It can also be observed in Figure 4 that the evolution of the relative crystallinity in the blends shifted to longer times in comparison with PET, and this indicates that PS decreases the crystallization rate of PET. These results might be associated with the presence of a fraction of noncrystallizable molecules of PS in the PET phase.<sup>15,16</sup>

From the isotherms shown in Figure 4, the parameters  $t_{0.01}$  and  $t_{0.99}$  (i.e., the times to reach 1 and 99% relative crystallinity, respectively) were calculated, and the results are displayed in Figure 5. The blends



**Figure 5** Effect of  $T_c$  on  $t_{0.01}$  and  $t_{0.99}$  of PET and PET/PS blends.

with 1 or 15 wt % PS presented higher values of  $t_{0.01}$  and  $t_{0.99}$  in comparison with the neat PET at all temperatures. It can also be observed that the addition of larger amounts of PS did not contribute to a subsequent increase in  $t_{0.01}$  or  $t_{0.99}$ , and the blend with 15 wt % PS presented values similar to those obtained with the blends with only 1 wt % PS.

The dependence of  $T_c$  on the half-time of crystallization ( $t_{0.5}$ ) is shown in Figure 6(a).  $t_{0.5}$  is a more widely used parameter for evaluating the kinetics of crystallization, representing the time to reach 50% relative crystallinity under a given experimental condition.<sup>14</sup>  $t_{0.5}$  decreases with increasing  $T_c$ , and this can be associated with a decrease in the polymer viscosity, which facilitates chain mobility. The viscosity can affect the nucleation rate as well as the crystal growth rate.<sup>26</sup> Figure 6 also indicates that the development of the crystallinity of PET in the blend with PS was slower than that of the neat PET; this agrees with the crystallization exotherms of Figure 3 and the isotherms of Figure 4. The parameter  $t_{0.5}$  was used to determine crystallization rate  $C_{0.5}$ , which was taken as the inverse of  $t_{0.5}$ . Figure 6(b) shows that  $C_{0.5}$  increases linearly with  $T_c$  for PET and the PET/PS blends, and the values obtained for PET are considerably higher than those for the blends. This is consistent with previous results and again indicates that PS reduces the cold crystallization rate of PET.

A decrease in the crystallization rate of PET has been previously observed in different systems, such as poly(ethylene terephthalate-*co*-benzimidazole), PET/polycarbonate, PET/Vectra A 900, PET/poly (ether imide), and PET/poly(vinylidene fluoride),<sup>27–31</sup> and it has been related to aspects such as an increase in the melt viscosity, molecular segregation of the second component, limited solubility among the components, an increase in the activation energy for isothermal crystallization, and a decrease in the crystallizability of PET. Schababerle and Mitchell<sup>20</sup> considered the reduction in the rate of PET crystallization in the presence of PS to be due



**Figure 6** Effect of  $T_c$  on  $t_{0.5}$  and  $C_{0.5}$  of PET and PET/PS blends.

to the enhancement of a rigid amorphous phase that retarded the growth of PET crystals. In comparison with the results shown here, a significant difference is that in the cases reported in the literature, the concentration of the second component was reasonably high: between 10 and 50 wt %. The use of only 1 wt % PS to reduce the rate of cold crystallization of PET to a degree similar to what was obtained with much higher concentrations highlights the importance of this investigation. At this concentration, no significant effects on the mechanical and optical properties of PET were detected.<sup>4</sup> In addition, the procedures for the industrial application of these blends in the manufacture of bottles and thermoformed products, for example, are quite simple and require no change in comparison with the processing of neat PET. It is possible that even lower amounts of PS could lead to similar results in reducing the crystallization rate of PET, and this is a topic for further study.

## Kinetics of isothermal cold crystallization: the Avrami theory

Because the relative degree of crystallinity at crystallization time t ( $X_t$ ) increases with t, following an Sshaped curve, the Avrami equation can be used to analyze the isothermal cold crystallization kinetics of PET and its blends as follows<sup>9,32,33</sup>:

$$1 - X_t = e^{-Kt^n} \tag{1}$$

where n is the Avrami exponent, which is dependent on the nature of the nucleation and growth geometry of the crystals, and K is the crystallization rate constant, which depends on the nucleation and growth rates.

For practical purposes, eq. (1) can be rewritten in its double logarithmic form:

$$Log[-Ln(1 - X_t)] = Log K + n Log t$$
(2)

Accordingly, Avrami parameters *n* and *K* can be obtained from the slope and intercept, respectively, of a plot of  $\text{Log}[-\ln(1 - X_t)]$  versus Log t.

Avrami plots for PET and for the blend with 1 wt % PS obtained with different  $T_c$  values were built from the crystallization isotherms of Figure 4 and are shown in Figure 7. Some kinetic curves presented a linear stage followed by a nonlinear one at the end of the crystallization process, and this indicated that in these cases the crystallization occurred in two stages. Crystallization in two stages is a well-known phenomenon and frequently happens because of the interference among crystals at the end of the primary crystallization; this is called secondary crystallization.<sup>34,35</sup> In this work, two-stage behavior was detected for some compositions (nor-



**Figure 7** Examples of Avrami plots for the isothermal cold crystallization of PET and blends with 1 wt % PS.

mally those containing PS) and  $T_c$  values, but the data (*n* and *K*) were taken just from the main crystallization process, that is, the first stage. Crystallization has been observed by several authors in different polymer systems, including poly(ether ether ketone),<sup>36</sup> PET/poly(ether imide),<sup>37</sup> PET,<sup>38</sup> poly(phenylene sulfide),<sup>39</sup> poly(methylene terephthalate),<sup>40</sup> poly(butylene terephthalate),<sup>41</sup> poly(trimethylene terephthalate),<sup>42</sup> PP,<sup>43</sup> nylon 11,<sup>44</sup> poly(ethylene terephthalate),<sup>45</sup> syndiotactic PS,<sup>46</sup> PET/polycarbonate,<sup>47</sup> and nylon 11/nylon 66.<sup>48</sup>

In the case of the blends studied here, it is possible that the second stage in the Avrami plots is also related to the molecular segregation of the PS (noncrystallizable) molecules, which contributes to the decrease in the crystalline growth rate. Similar behavior was previously observed in blends such as poly(ethylene oxide)/poly(ether sulfone),<sup>49</sup> linear polyethylene/low-density polyethylene,<sup>50</sup> polyhydroxybutyrate/poly (hydroxybutyrate hydroxyvalerate),<sup>51</sup> syndiotactic PS/

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| the First Stage of Isothermal Crystallization |                  |         |      |                              |              |         |            |                              |              |         |      |                              |
|---|------------------|---------|------|------------------------------|--------------|---------|------------|------------------------------|--------------|---------|------|------------------------------|
|   | PET              |         |      | 1 wt % PS                    |              |         | 15 wt % PS |                              |              |         |      |                              |
| Т   | t <sub>0.5</sub> |         | K    | t <sub>0.5</sub>             |              |         | K          | t <sub>0.5</sub>             |              |         | K    |                              |
| (°C)  | Experimental     | eq. (3) | п    | $(10^{-3}  \mathrm{s}^{-1})$ | Experimental | eq. (3) | п          | $(10^{-3}  \mathrm{s}^{-1})$ | Experimental | eq. (3) | п    | $(10^{-3}  \mathrm{s}^{-1})$ |
| 110   | 1.10             | 0.98    | 1.93 | 0.204                        | _            | _       | _          | _                            | _            | _       |      | _                            |
| 115   | 0.84             | 0.81    | 1.94 | 0.306                        |              | _       | _          |                              | —            | _       | _    |                              |
| 120   | 0.80             | 0.72    | 1.88 | 0.380                        |              | _       | _          |                              | —            | _       | _    |                              |
| 125   | 0.56             | 0.627   | 2.01 | 0.466                        |              | _       | _          |                              | —            | _       | _    |                              |
| 130   | 0.50             | 0.51    | 2.00 | 0.732                        | 1.54         | 1.56    | 2.02       | 0.076                        | —            | —       | —    | —                            |
| 135   | 0.42             | 0.427   | 1.97 | 1.091                        | 1.13         | 1.11    | 1.96       | 0.160                        | 1.09         | 0.92    | 1.88 | 0.241                        |
| 140   | 0.35             | 0.35    | 1.98 | 1.518                        | 0.88         | 0.88    | 1.99       | 0.250                        | 0.99         | 1.05    | 2.10 | 0.137                        |
| 145   | 0.32             | 0.30    | 1.87 | 2.316                        | 0.78         | 0.89    | 2.10       | 0.226                        | 0.95         | 0.89    | 2.02 | 0.189                        |
| 150   | 0.30             | 0.29    | 1.90 | 2.317                        | 0.60         | 0.60    | 2.00       | 0.526                        |              |         | 1.95 | 1.189                        |
| 155   | —                |         |      |                              | 0.58         | 0.62    | 2.01       | 0.454                        | 0.51         | 0.55    | 1.98 | 0.910                        |
| 160   | _                | —       | —    |                              | 0.46         | 0.51    | 2.12       | 0.678                        | —            | —       | 1.98 | 1.458                        |

TABLE IIParameters of the Isothermal Cold Crystallization of PET and PET/PS Blends:  $t_{0.5}$  and Avrami Parameters n and K for<br/>the First Stage of Isothermal Crystallization

 $t_{0.5}$  was obtained experimentally (Fig. 4) and with eq. (3).

isotactic PS, and syndiotactic PS/atactic PS,<sup>52</sup> in which the amount of segregated molecules showed a dependence on the cooling/heating conditions during crystallization.

From the Avrami plots (Fig. 7), the parameters nand K were determined, and the results are shown in Table II and Figure 8. *n* presented values close to 2 for PET and for the blends, and this is associated with a disklike growth generated by heterogeneous nucleation.<sup>9,32,33</sup> Similar values of *n* were previously obtained for PET<sup>53–55</sup> and PET/poly(ethylene oxide) blends.<sup>45</sup> The values of kinetic parameter Kincreased progressively with increasing  $T_c$  (Fig. 8) as a result of the higher molecular mobility. In Figure 8, it can also be observed that the blends had much lower values of K than the neat PET because of the reduction of the crystallization rate in the presence of noncrystallizable molecules, as discussed previously. For example, when the samples were submitted to isothermal crystallization at 150°C, PET presented a K value of  $2.32 \times 10^{-3} \text{ s}^{-1}$ , whereas the blends with 1 and 15 wt % PS presented values of  $0.53 \times 10^{-3}$  and  $1.12 \times 10^{-3}$  s<sup>-1</sup>, respectively. For this temperature, a decrease in the cold crystallization rate of PET of approximately 80% in the blend with 1 wt % PS and of approximately 50% in the blend with 15 wt % PS was observed. These results are consistent with those shown in Figure 6.

 $t_{0.5}$ , defined as the time at which the relative crystallinity is 50 wt % complete, can also be determined from the measured kinetic parameters as follows:

$$\mathbf{t}_{0.5} = \left(\frac{\mathrm{Ln2}}{K}\right)^{1/2} \tag{3}$$

The calculated values of  $t_{0.5}$  from eq. (3) for several  $T_c$  values are listed in Table II, and the results

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are quite consistent with those obtained from the experimental curves of Figure 4. This also indicates that the Avrami analysis can be satisfactorily employed to describe the first stage of the isothermal cold crystallization of PET.<sup>56</sup>

#### Activation energy for cold crystallization

The crystallization process of PET is assumed to be thermally activated, and then crystallization parameter *K* can be approximately described by the Arrhenius equation<sup>36,40,44,56,57</sup>.

$$K^{1/n} = K_o \exp\left(-\frac{\Delta E}{RT_c}\right) \tag{4}$$



**Figure 8** Effect of  $T_c$  on K of PET and blends with PS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



**Figure 9** Arrhenius plots for the determination of the activation energy of the isothermal cold crystallization of PET and PET/PS blends.

where  $K_o$  is a temperature-dependent pre-exponential factor; R is the gas constant; and  $\Delta E$  is the total activation energy, which consists of the transport activation energy and the nucleation activation energy.

 $\Delta E$  can be determined from the slope of the plots of 1/n Ln K versus  $1/T_c$ . These plots are shown in Figure 9 for PET and PET/PS blends. The value of  $\Delta E$  for the first stage of the cold crystallization of PET was 48.7 kJ/mol. The literature presents a wide range of values for the activation energy of PET crystallization, 83-300 kJ/mol, depending on the crystallization modes (cold or from the melt), molar mass, comonomers, and polymerization conditions.<sup>55,58-61</sup> Wide variations from grade to grade could result from different values of this property. The activation energies of the blends with 1, 15, and 20 wt % PS were 61.5, 67.3, and 70.0 kJ/mol, respectively. The higher values of  $\Delta E$  for the blends indicate that cold crystallization is thermodynamically less favorable. A larger amount of energy should be supplied for the occurrence of crystallization, and this agrees with the results shown previously throughout this article.

## Equilibrium melting temperature $(T_m^{0})$

A study of the melting behavior was conducted with DSC for PET and PET/PS blends previously subjected to isothermal cold crystallization, and selected melting endotherms are given in Figure 10. The melting behavior of PET seemingly did not change in a significant way with the addition of PS at the different  $T_c$  values investigated. Because polymer melting occurs in a wide interval of temperatures on account of the different sizes and perfection of the crystals, the value of the melting temperature ( $T_m$ ), taken as the peak of the curve, is not a truly intrinsic property of the material. For that purpose,  $T_m^0$  was determined. This represents the stability of crystals of infinite size and, therefore, constitutes a better parameter for evaluating the differences in the thermal stability for several compositions.<sup>62</sup>

According to a theoretical consideration by Hoffman and Weeks,<sup>63</sup>  $T_m^0$  can be obtained in a plot of  $T_m$  versus  $T_c$  as the intersection of the resulting straight line with the line  $T_m = T_c$ , and the dependence of  $T_m$  on  $T_c$  is given by

$$T_m = T_m^0 \left( 1 - \frac{1}{2\beta} \right) + \frac{1}{2\beta} T_c \tag{5}$$

where  $\beta$  is the thickening ratio. In other words,  $\beta$  is the ratio of the thickness of the mature crystallites  $(l_c)$  to the thickness of the initial ones  $(l_c^*)$ ; therefore,  $\beta$  is equal to  $l_c/l_c^*$ , which is supposed to be always greater than or equal to 1.

From the endotherms of Figure 10, the  $T_m^0$  values of PET and PET/PS blends were calculated, and the obtained values are summarized in Table III.



**Figure 10** Melting endotherms of PET and PET/PS blends after isothermal cold crystallization at different temperatures.

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| Composition | $T_m^0$ (°C) | $\Delta H_m$ (J/g) | <i>X<sub>c</sub></i> (wt %) |  |  |
|-------------|--------------|--------------------|-----------------------------|--|--|
| PET         | 255          | 31.04              | 26                          |  |  |
| 1 wt % PS   | 250          | 28.14              | 24                          |  |  |
| 15 wt % PS  | 246          | 29.60              | 25                          |  |  |
| 20 wt % PS  | 248          | 29.40              | 25                          |  |  |

Examples of these plots and calculations are easily found in the literature.<sup>64</sup>  $T_m^0$  of PET was approximately 255°C, which is within the range of values found in the literature (245–310°C).<sup>27,31,37,42,61,65–68</sup> Such remarkable discrepancies in the values of  $T_m^0$ can be attributed to two main factors. First, there are different ways of estimating  $T_m^0$ . Some authors<sup>69,70</sup> have employed the fundamental Thomson-Gibbs equation, which considers the depression of  $T_m$  that an infinitely thick crystal will suffer when it is divided by the thickness of the lamellae  $(l_c)$ . Other authors<sup>1,42,71</sup> have used the most common method of Hoffman and Weeks. A third method is an optical microscopy approach used to observe the melting behavior. Second, high- $T_m$  polymers such as PET may show multiple melting endotherms, and this often gives rise to controversies with respect to which one is the most appropriate melting point.<sup>56</sup>

The results given in Table III show that the  $T_m^0$  values of the blends were clearly lower than those of the neat PET. The small but clear variation in this parameter indicates that PS molecules are actually disturbing the crystallization of PET, making the crystals less stable. This indicates that there is some solubility among the polymers, as speculated previously to explain the reduction in the crystallization rate of PET in the presence of PS (Figs. 6 and 8). Not surprising, one of the methods that is used to evaluate the miscibility of blends based on a semicrystal-line polymer and an amorphous polymer is the depression of  $T_m$  of the crystallizable component.<sup>3,11</sup>

From the melting endotherms of Figure 10, the melting enthalpy ( $\Delta H_m$ ) values of the neat PET and the blends were also calculated, and the results are given in Table III, together with the crystallinity degree ( $X_c$ ), which was calculated as follows:

$$X_{\rm c} = \frac{\Delta H_m}{\Delta H_m^0} \tag{6}$$

where  $\Delta H_m^{0}$  is the melting enthalpy of the crystals (117.65 J/g).<sup>72,73</sup>

The values of the PET crystallinity showed just small variations in the presence of PS. This is a good result because in many applications a high degree of crystallinity is an important requirement. It is also worth mentioning that the mechanical properties of the blends were not different from those obtained

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with the neat PET, as shown in a previous article.<sup>4</sup> This is highly relevant from a technological point of view given that the addition of only 1 wt % PS will reduce industry scrap through a wider processing window and, at the same time, make feasible products with good thermal, mechanical, and optical properties.

# Crystal growth and nucleation rate parameter analysis

The crystal growth rate (*G*) was analyzed with the Lauritzen–Hoffman equation:

$$G = G_o \exp\left[-\frac{U^*}{R(T_c - T_\infty)}\right] \exp\left[-\frac{K_g}{T_c(T_m^o - T_c)f}\right]$$
(7)

where  $G_o$  is a temperature-independent pre-exponential factor (µm/min);  $U^*$  is the activation energy for the transportation of segments of molecules (J/mol); R is the universal gas constant (J/mol K);  $T_{\infty}$  is the temperature at which the molecules are motionless [ $T_{\infty}(K) = T_g - 30$  K (a temperature below which the polymer chain movement ceases)];  $K_g$  is the nucleation constant; and f is a factor compensating for the temperature dependence of the fusion enthalpy, that is,  $f = 2T_c/(T_c + T_m^0)$ 

The first exponential term in eq. (7) contains the contribution of the diffusion process to the growth rate, and the second one is the contribution of the nucleation process.

Equation (7) is usually rearranged into a log form:

$$\log G + \frac{U^{*}}{2.3R(T_{c} - T_{\infty})} = \log G_{o} - \frac{K_{g}}{2.3T_{c}(\Delta T)f}$$
(8)

According to Caminiti et al.,<sup>39</sup> the bulk crystallization rate, normalized for n, may be assumed to be proportional to G:

$$G \propto K^{1/n}$$
 (9)

The spherulitic growth rate assumes the following form:

$$\log K^{1/n} + \frac{U^*}{2.3R(T_c - T_{\infty})} = \log G_o - \frac{K_g}{2.3T_c(\Delta T)f}$$
(10)

The plot of the left-hand side of eq. (10) versus  $1/(T_c\Delta Tf)$  gives a straight line, from which  $-K_g$  is obtained (Fig. 11). From this figure, it is clear that both the neat PET and the blend with 1 wt % PS present two crystalline growth regimes. For low  $T_c$  values, regime II is observed when nucleation is the dominant process, and for high  $T_c$  values, regime I is observed, with the crystalline growth being the dominant process.<sup>74</sup>  $K_g$ , determined from the plots of Figure 11, has the following values: for PET,  $K_{gI}$ 



**Figure 11** Plot of Log  $G + U^*/2.3R(T_c - T_g + 30)$  versus  $1/(T_c\Delta Tf)$  for PET and a blend with 1 wt % PS.

=  $6.08 \times 10^4 \text{ K}^{-2}$  and  $K_{gII} = 1.67 \times 10^5 \text{ K}^{-2}$ , and for the blend with 1 wt % PS,  $K_{gI} = 3.18 \times 10^4 \text{ K}^{-2}$  and  $K_{gII} = 0.69 \times 10^5 \text{ K}^{-2}$ . Because regime II occurs at low temperatures at which nucleation is the dominant process, it is easily understood that  $K_{gII}$  is greater than  $K_{gI}$ . It can also be observed that both  $K_{gI}$  and  $K_{gII}$  are higher for the neat PET, and this means that during the isothermal cold crystallization, the neat PET presented a higher tendency for nucleus formation with respect to the blend with PS.

The nucleation rate of a semicrystalline polymer such as PET depends partly on the viscosity at  $T_c$ and mainly on the energy barrier to form stable nuclei for further crystal growth. The presence of a second, immiscible phase in a polymer blend can reduce or raise the energy barrier because of the negative or positive contribution of interfacial energy, which facilitates or makes more difficult the formation of nuclei.<sup>26</sup> In PET/PS blends, even though there was no significant variation in the viscosity, an expressive increase of the activation energy for the cold crystallization of PET was observed when PS was added, contributing to the low values observed in the nucleation parameters. The ultimate result is a slow crystallization rate of PET in the blends, as shown before in Figures 3, 6, and 8. From these results, it is clear that PS reduces the rate of cold crystallization of PET by reducing the nucleation rate. It turns out that PS is actually an antinucleating additive to PET, acting in the opposite way of nucleating agents, which accelerate the rate of crystallization of semicrystalline polymers.

### SEM

The morphology of PET and the blends with 1 and 15 wt % PS was examined with SEM; Figure 12 shows a two-phase structure composed of the PET matrix, and nearly spherical particles of PS can be clearly noticed. It can also be observed in the SEM images that the polymers PET and PS present low interfacial adhesion because PS particles were taken out of the PET matrix. The average diameters of



**Figure 12** SEM images of (a) PET and (b) a blend with 1 wt % PS.

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dispersed domains of PS in the blends were 0.8 and 2.4  $\mu$ m for the 1 and 15 wt % blends, respectively. According to Favis and Willis,<sup>75</sup> blends with a mobile interface (immiscible blends) coalesce very easily, and the size of the domains is highly dependent on the composition.

#### CONCLUSIONS

In this study, the isothermal cold crystallization of PET and PET/PS blends was analyzed with DSC, and the Avrami equation was used in the determination of the kinetic parameters. The main conclusions are as follows:

- The PET/PS polymer blends formed predominantly two-phase mixtures, as observed by DMTA and SEM. The depression of the melt equilibrium temperature of PET with the addition of PS, on the other hand, indicated the occurrence of limited solubility between the blend components.
- The presence of PS, even at low concentrations (1 wt %), significantly reduced cold crystallization constant *K* of PET.
- The activation energy for the isothermal crystallization of PET was higher for the blends as a result of the more difficult crystallization.
- The values of *K*<sub>g</sub> were lower for the blends with PS, indicating that this is actually an antinucleating additive to PET.

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