CRYSTALLIZATION OF (POLYETHYLENE TEREPHTALATE) (PET) IN PET/POLYOLEFINS BLENDS.

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Nonisothermal crystallization kinetics of polyethylene terephtalate/polyethylene (PET/PE) blends with or without compatibilizer (EGMA) were studied using DSC at various cooling rates. The Ozawa theory and a method developed by Mo and coworkers were employed to describe the nonisothermal crystallization process of blends. The results show that Mo method is successful in describing the nonisothermal kinetics, while Ozawa theory is not accurate to interpret the whole process of nonisothermal crystallization.

Introduction

Poly(ethylene terephtalate) (PET) and polyolefins (HDPE, LDPE, PP, etc) are thermoplastics largely used as packaging materials (bottles, films, containers, etc). So, they represent an important part of domestic wastes. Consequently, recycling techniques have become a crucial economical and scientific challenge. In France, collecting systems have been developed and give an important flow of polymer blends which must be treated. Although techniques used for sorting materials are increasingly efficient, these methods are very expensive. Thus, post-consumer polymer blends may be very interesting and cost-effective from an economical viewpoint.

For thermodynamical considerations, most of polymers are not miscible but many scientific studies show the interest of chemical compatibilizers for non-miscible blends. Particularly PET and PE are non-miscible polymers but this polymer blend can be compatibilized by maleic anhydride grafted polyolefins (PE-g-MA, PP-g-MA, etc) or block copolymers as ethylene-glycidyl methacrylate (E-GMA) [1-6].

The physical and mechanical properties of plastic materials depend on the polymer microstructure and generally increase with degree of crystallinity. However, PET has a low crystallization rate compared to polymer such as polyethylene or polypropylene [7,8]. So, cooling rates encountered during injection molding of plastic parts freeze the microstructure in a non optimal state, which prevents from having good intrinsic properties of the polymer. Thus, a variety of inorganic or organic substances, known as nucleating agents, are commonly added to improve PET’s crystallization rate [9]. Nevertheless, it has been shown that polypropylene is effective as a nucleating agent for PET [10]. Although the presence of polyolefin in recycled PET could be a drawback for the morphology and interfacial adhesion, it could be also very interesting to improve crystallization of PET.

In this study, nonisothermal crystallization kinetics of PET/PE and PET/PE/EGMA blends has been investigated in order to evaluate the effect of polyethylene, with or without compatibilizing agent, on the crystallization behavior of PET. Furthermore, the kinetics are analyzed using theoretical approaches of Ozawa and Mo and coworkers.

Experimental

Materials

The polyethylene terephtalate used in this work was a recycled PET obtained from beverage bottles (irregular shapes and sizes of flakes). The polyethylene was a virgin polymer supplied by Polymeri Europa (Riblène FL20). PET/PE blend was compatibilized with commercial ethylene glycidyl methacrylate (EGMA) copolymer containing 8% mol. of GMA produced by Atochem (Lotader AX8840). Before use, recycled PET was carefully dried under vacuum at 120°C for 8h.

Blend preparation

PET/PE blends (80/20 by weight percentage) with and without compatibilizer (PET/PE/EGMA 80/18/2 and 80/13/7 by weight percentage) were carried out in a single-screw extruder (Kaufman). The barrel temperature settings ranged from 240 to 280°C. The extruder was equipped with a mixing zone regulated at 270°C. The extrudate was cooled in water and pelletized.
Characterization

The morphology of the blends was studied by scanning electron microscopy Philips SEM 505. Tensile fracture surfaces of the blends were examined. The samples were coated with gold before analysis. The crystallization behavior of polymer blends was studied with differential scanning calorimetry (DSC Q100, TA Instruments) with a sample weight between 5 and 6 mg under a nitrogen atmosphere. The temperature and melting enthalpy were calibrated with standard indium. In order to erase the previous thermal history, the samples were encapsulated into aluminium pans and were heated to 270°C and kept at this temperature for 3 min. Then, they were cooled to room temperature at constant cooling rates (λ) of 5, 10 and 50°C/min. These samples were then heated to 270°C at a heating rate of 10°C/min to record the melting behavior. Each measurement was repeated 4 time.

Theoretical background

The relative crystallinity $x_{rel}$ as a function of time is defined through the following equation:

$$x_{rel} = \frac{\int_{t_1}^{t_\infty} \frac{dH_c}{dt} \, dt}{\int_{0}^{\infty} \frac{dH_c}{dt} \, dt} = \frac{A_0}{A_\infty}$$

(1)

where $t_1$ and $t_\infty$ are the times at which crystallization starts and ends, and $A_0$ and $A_\infty$ the areas under the normalized DSC curves.

The absolute crystallinity $\chi\%$ is defined as:

$$\chi\% = \frac{\Delta H_f}{\Delta H_{f0}} \times 100$$

(2)

where $\Delta H_f$ and $\Delta H_{f0}$ are the melting enthalpies of sample and 100% crystallized sample ($\Delta H_{f0}$ PET = 117.6 J/g [11]). $\Delta H_f$ is determined by the integral area of a DSC heating curve, and the absolute crystallinity, $\chi\%$ is a decreasing function of the cooling rate.

The Avrami theory [12,13] has been widely used for the interpretation of the isothermal kinetic crystallization:

$$x_{rel} = 1 - \exp[-k(T)t^n]$$

(3)

where $x_{rel}$ is the relative degree of crystallinity at time $t$; the Avrami exponent, $n$, is a mechanism constant with a value depending on the type of nucleation and the growth dimension, and $k(T)$ is a growth rate constant involving both nucleation and growth rate parameters.

Considering the nonisothermal character of the process, the cooling rate ($\lambda$) is the factor that needs to be considered. Ozawa [14] extended the Avrami equation to the nonisothermal condition by incorporating the cooling rate:

$$1 - x_{rel} = \exp\left(\frac{-\kappa(T)}{\lambda^m}\right)$$

(4)

In the logarithmic form Eq.4 can be rewritten as:

$$\ln[-\ln(1-x_{rel})] = \ln \kappa(T) - m \ln(\lambda)$$

(5)

where $\lambda$ is the cooling rate, $\kappa(T)$ a function related to the overall crystallisation rate that indicates how fast crystallization proceeds and $m$, the Ozawa exponent that depends on the dimension crystal growth.

During the nonisothermal crystallization process, the relationship between crystallization $t$ and temperature $T$ is given by:

$$t = \frac{(T_0 - T)}{\lambda}$$

(6)
where \( T \) is the temperature at time \( t \), \( T_0 \) is the initial temperature when crystallization begins \((t=0)\). As the degree of crystallinity is related to the cooling rate \( \lambda \) and the crystallization time \( t \) (or temperature \( T \)), the relationship between \( \lambda \) and \( t \) can be built up at a given degree of crystallinity. Consequently, Mo and coworkers [15] established a new kinetic equation of nonisothermal crystallization by combining Avrami equation and Ozawa equation:

\[
\ln k(T) + n \ln t = \ln \kappa(T) - m \ln \lambda \quad (7)
\]

and further rewritten as:

\[
\ln \lambda = \ln F(T) - \alpha \ln t \quad (8)
\]

where the kinetic parameter \( F(T) = [k(T)/k]^{1/m} \) refers to the cooling rate that needs to be selected within a unit of crystallization time when the measured system amounts to a certain degree of crystallinity, and \( \alpha \) is the ratio of the Avrami exponent \( n \) to the Ozawa exponent \( m \) \((\alpha = n/m)\). Consequently, \( \alpha \) depends on the dimension crystal growth. Thus, at a given degree of crystallinity, the values of \( \alpha \) and \( F(T) \) can be obtained from the plot \( \ln \lambda \) versus \( \ln t \) by fitting linear slopes and determining intercepts of the lines, respectively.

**Results and Discussion**

*Morphological characterization of the blends*

SEM micrographs of PET/PE and PET/PE/EGMA blends are shown in figure 1. Without compatibilizer, the blend (figure 1.a) shows a dispersed PE phase with irregular shapes and sizes in a PET matrix. Holes induced by strain and break and consequently by the pull-out of droplets reveal the poor interfacial adhesion between PE and PET. The addition of compatibilizer is characterized by regular shapes and relatively uniform sizes of PE droplets (figure 1.b). That phenomenon is further increased when more compatibilizer is used. The blend containing 7% wt. of E-GMA (figure 1.c) shows a great decrease of the number of PE droplets which suggests the blend has been compatibilized.

![SEM micrographs of PET/PE 80/20](image)

![SEM micrographs of PET/PE/EGMA 80/13/7](image)

*Figure 1 – SEM micrographs of fractured tensile specimens of PET/PE 80/20 (a), PET/PE/EGMA 80/18/2 (b) and PET/PE/EGMA 80/13/7 (c).*
Nonisothermal crystallization kinetics

The effects of PE and compatibilizer on the crystallization behavior of PET are quantitatively analyzed through nonisothermal DSC experiments. The crystallization exotherms of pure PET and PET in blends with and without compatibilizer at different cooling rates give some useful data for describing their nonisothermal crystallization behavior, such as the crystallization peak temperature $T_c$ and the half-time of crystallization $t_{0.5}$. The values of these parameters are given in Table 1. It clearly appears from Table 1 that $T_c$ shifts, as expected, to a lower temperature when the cooling rate increases, which is attributed to the lower time scale that does not allow the polymer to crystallize absolutely [16].

The presence of polyethylene in PET also leads to a significant increase in $T_c$. In addition, the same phenomenon is reported for compatibilized blends and $T_c$ reaches a maximum value when 2% wt. of E-GMA is added to the blend. However, the 7% wt. compatibilized blend has the lowest value of $T_c$ among the blends. This implies that the polyethylene is an efficient nucleating agent to increase the rate of crystallization of PET. On the other hand, this effect is all the more marked as the blend contains a small quantity of compatibilizer.

Table 1 also shows the half-time crystallization values of pure PET and PET in blends with and without compatibilizer. The half-time crystallization, $t_{0.5}$, is a function of the relative degree of crystallinity. Thus, as expected, the crystallization half-time increases with increasing cooling rate. Furthermore, it appears that the value of half-time crystallization for PET in blends at various cooling rates is lower for pure PET and reaches a minimum value for the blend compatibilized with 2% wt. of E-GMA. The same phenomenon has been observed by Yuan and al. [17] on polypropylene-clay nanocomposites. These authors state the clay nanoparticles are efficient nucleating agent to increase the PP crystallization rate. So, polyethylene and particularly polyethylene with 2% wt. act as a nucleating agent for the PET. Little droplets of PE act as nucleation center but the number of PE droplets in blend compatibilized with 7% wt. of EAGMA is so low that it inhibits the nucleating effect.

**Table 1** – Crystallization peak temperature $T_c$ and half-time of crystallization $t_{0.5}$ of pure PET and PET in blends with and without compatibilizer.

<table>
<thead>
<tr>
<th>PET/PE/EGMA</th>
<th>100/0/0</th>
<th>80/20/0</th>
<th>80/18/2</th>
<th>80/13/7</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$ (°C/min)</td>
<td>$T_c$ (°C)</td>
<td>$t_{0.5}$ (min)</td>
<td>$T_c$ (°C)</td>
<td>$t_{0.5}$ (min)</td>
</tr>
<tr>
<td>5</td>
<td>203</td>
<td>4,41</td>
<td>207</td>
<td>3,22</td>
</tr>
<tr>
<td>10</td>
<td>195</td>
<td>2,81</td>
<td>200</td>
<td>1,81</td>
</tr>
<tr>
<td>50</td>
<td>159</td>
<td>0,61</td>
<td>166</td>
<td>0,58</td>
</tr>
</tbody>
</table>

Figure 2 shows the results for pure PET and PET in blends with and without compatibilizer according to Ozawa’s method.
In this study, the Ozawa plots of pure PET and blends show changing slopes, indicating that the parameter m is not constant with temperature during the crystallization process. So, the cooling function $\kappa(T)$ cannot be determined from the plots in figure 2. This suggests that the Ozawa equation is not appropriate to describe the nonisothermal crystallization. The same behavior has been observed by Eder and al. [18] on polyethylene, in which most of crystallization is attributed to secondary crystallization. This makes us suggesting that Ozawa’s equation does not account for secondary crystallization.

The method developed by Mo and coworkers is also employed to describe the nonisothermal crystallization. This method has been successfully used on polyolefin blends [19]. At a given crystallinity, the plot of $\ln \lambda$ versus $\ln t$ will give a straight line with an intercept of $\ln F(T)$ and a slope of $\alpha$. As shown in figure 3, plotting $\ln \lambda$ versus $\ln t$ of PET/PE blends with and without compatibilizer yields a linear relationship at a given $x_{rel}$, and the values of $F(T)$ and $\alpha$ are reported in table 2.

It appears that the variation of $\alpha$ for both pure PET and blends is small. This indicates that the method of Mo and coworkers is successful in describing the nonisothermal process of pure PET and PET/PE blends with and without compatibilizer. The value of $F(T)$ systematically increases with the relative crystallinity for pure PET and PET/PE blends. In addition, $F(T)$ has a maximum value for the blend compatibilized with 2% wt. of E-GMA. This confirms that adding 2% wt. of E-GMA to the polymer blend is the best way to improve crystallization rate of PET.

### Table 2 – Nonisothermal crystallization kinetic parameters for pure PET and blends with and without compatibilizer at different relative degrees of crystallinity.

<table>
<thead>
<tr>
<th>xrel (%)</th>
<th>$\alpha$</th>
<th>$F(T)$</th>
<th>$\alpha$</th>
<th>$F(T)$</th>
<th>$\alpha$</th>
<th>$F(T)$</th>
<th>$\alpha$</th>
<th>$F(T)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.09</td>
<td>23.9</td>
<td>1.39</td>
<td>19.89</td>
<td>1.18</td>
<td>14.53</td>
<td>1.68</td>
<td>19.94</td>
</tr>
<tr>
<td>40</td>
<td>1.1</td>
<td>27.93</td>
<td>1.39</td>
<td>24.71</td>
<td>1.19</td>
<td>18.53</td>
<td>1.64</td>
<td>25.97</td>
</tr>
<tr>
<td>60</td>
<td>1.12</td>
<td>32.41</td>
<td>1.37</td>
<td>29.67</td>
<td>1.14</td>
<td>22.12</td>
<td>1.63</td>
<td>32.2</td>
</tr>
<tr>
<td>80</td>
<td>1.06</td>
<td>38.35</td>
<td>1.27</td>
<td>37.41</td>
<td>1.09</td>
<td>27.67</td>
<td>1.53</td>
<td>41.56</td>
</tr>
</tbody>
</table>
Melting and crystallization behaviors of PET in blends with and without compatibilizer

Table 3 gives some parameters of DSC heating curves, such as melting peak temperature and absolute degree of crystallinity of pure PET and PET in blends with and without compatibilizer, obtained at a heating rate of 10°C/min.

Table 3 – Melting peak temperature \( T_m \) and absolute degree of crystallinity \( \chi \% \) of pure PET and PET in blends with and without compatibilizer.

<table>
<thead>
<tr>
<th>PET/PE/EGMA</th>
<th>( T_m (°C) )</th>
<th>( \chi % (%) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0/0</td>
<td>241</td>
<td>32</td>
</tr>
<tr>
<td>80/20/0</td>
<td>242</td>
<td>35</td>
</tr>
<tr>
<td>80/18/2</td>
<td>249</td>
<td>37</td>
</tr>
<tr>
<td>80/13/7</td>
<td>245</td>
<td>33</td>
</tr>
</tbody>
</table>

It is clear that both the melting peak temperature \( T_m \) and the absolute degree of crystallinity increase with the addition of polyethylene and reach a maximum value for the blend compatibilized with 2% wt. of E-GMA. This is in agreement with the results of the nonisothermal kinetics of crystallization. PE and particularly in presence of 2% wt. of E-GMA allows to improve the crystallization of PET whereas adding 7% wt. of compatibilizer inhibits the crystallization process.

Conclusion

The nonisothermal crystallization behavior of pure PET and his blends with PE compatibilized or not with EGMA was studied by DSC. The kinetic studies suggest that the addition of PE leads to an increase of the crystallization peak temperature. This parameter reaches a maximum value with 2% wt. of EGMA and decreases with 7% wt. of EGMA. In addition, the halftime of crystallization decreases with the addition of PE, reaches a minimum value for the blend compatibilized with 2% wt. of EGMA and increases with 7% wt. of EGMA.

Kinetic models based on Ozawa and modified Avrami–Ozawa (method Mo and coworkers) were used to analyze the nonisothermal crystallization behavior. Ozawa’s method failed to provide an adequate description of the nonisothermal crystallization of PET and its blends. However, the method proposed by Mo and coworkers successfully described the nonisothermal crystallization process of PET and its blends. Moreover, the melting behavior of PET and its blends has also been investigated. The absolute degree of crystallinity increases with the addition of PE and reaches a maximum value for the 2% wt. EGMA compatibilized blend but decreases for the 7% wt. EGMA compatibilized blend. Thus, PE and particularly with a little quantity of EGMA (2% wt.), acts as a nucleating agent of PET whereas adding 7% wt. of EGMA in the blend leads to an inhibitor effect.

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