Non-isothermal crystallization kinetics of isotactic polypropylene nucleated with nucleating agent bicyclic [2,2,1] heptane di-carboxylate

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Abstract: Bicyclic [2,2,1] heptane di-carboxylate (commercial product name: HPN-68) is a novel nucleating agent with high nucleation efficiency for isotactic polypropylene (iPP). In this paper, the non-isothermal crystallization kinetics of virgin iPP and iPP nucleated with HPN-68 were investigated by means of a differential scanning calorimeter (DSC). The Caze method was used to analyze the non-isothermal crystallization kinetics. The results show that addition of HPN-68 can increase the crystallization peak temperature ($T_p$) of iPP greatly under the same cooling rate. Under non-isothermal conditions, the addition of HPN-68 changes the spherulite growth pattern of iPP. For virgin iPP, the growth pattern is mainly spontaneous nucleation followed by three-dimensional spherulite growth, while for iPP nucleated with HPN-68, the growth pattern is mainly heterogeneous nucleation followed by three-dimensional spherulite growth.

Keywords: crystallization kinetics; nucleating agent; isotactic polypropylene; bicyclic [2,2,1] heptane di-carboxylate

Introduction

Isotactic polypropylene (iPP) is one of the most important thermoplastic polymers owing to its low manufacturing cost and rather versatile properties. Moreover, i-PP is a polymorphic polymer and has at least four modifications, namely, $\alpha$, $\beta$, $\gamma$, and smectic, all sharing a threefold conformation but with different orientations and packing of the polymer chains in the crystal lattice [1-5]. The difference in the crystallography is the manner in which the chains are packed in the unit cell. The intrinsic architecture and extrinsic parameters affect mostly through their influence on crystallization behaviors and morphological features, which are probably the most important factors affecting the final physical properties of iPP. Therefore, controlling the growth rate and tailoring the proportion of different polymorphs are extremely important for iPP applications. Addition of nucleating agents into iPP is an effective method to improve mechanical and optical properties which are related to crystallization and morphology [6-16]. Bicyclic [2,2,1] heptane di-carboxylate (commercial product name: HPN-68) is a novel nucleating agent which was developed by Milliken Chemical in recent years. Compared to conventional nucleating agents such as MDBS and ADK NA-11, the nucleating agent HPN-68 can greatly increase crystallization rate of iPP, so that the particles have fewer deflection in molding and shorter molding cycle period. However, there are few papers systematically reporting crystallization behaviors and nucleation mechanism of HPN-68 in iPP. From a technological point of view, non-isothermal crystallization...
conditions approach more closely the industrial conditions of polymers processing, so that the study of crystallization of polymers under non-isothermal conditions is of great practical importance. In this paper, non-isothermal crystallization kinetics of iPP nucleated with HPN-68 was studied by using the Caze method to obtain some crystallization parameters and nucleation parameters, and the objective was to explain the nucleation mechanism of this type of nucleating agent in iPP, so as to provide some theoretical foundations for developing novel and highly active nucleating agents and to provide some experimental data for processing of iPP.

Results and discussion

The non-isothermal crystallization of virgin iPP and iPP nucleated with HPN-68 were carried out by DSC with cooling rates from 2.5^°C/min to 40^°C/min. The thermograms of virgin iPP and iPP nucleated with HPN-68 are reported in Fig 1. With increasing of cooling rate, crystallization peak temperature of iPP (T_p) shifts to lower temperature. With the addition of nucleating agent HPN-68, T_p of iPP is increased greatly. When the cooling rate is 10^°C/min, T_p of iPP nucleated with HPN-68 is increased from 118.7^°C of virgin iPP to 133.3^°C.

**Fig. 1.** DSC cooling curves of virgin iPP (a) and iPP nucleated with HPN-68 (b) under non-isothermal crystallization.

**Fig. 2.** Relative crystallinity of virgin iPP (a) and iPP nucleated with HPN-68 (b) at different cooling rate.
By means of integrating the partial areas under the DSC endotherm, we can obtain the values of the crystalline weight fraction \(X_w(T)\) (Fig. 2).

Crystallization half-time \(t_{1/2}\) can be obtained from Fig. 2 by using equation 
\[
t = \frac{T_0 - T}{\Phi}
\]
(where \(t\) is crystallization time, \(T_0\) is onset crystallization temperature, \(T\) is crystallization temperature and \(\Phi\) is cooling rate). The results are listed in Tab. 1.

**Tab. 1.** Non-isothermal crystallization kinetics parameters for virgin iPP and iPP nucleated with HPN-68.

<table>
<thead>
<tr>
<th>(\Phi, ^\circ\text{C/min})</th>
<th>(T_p, ^\circ\text{C})</th>
<th>(a)</th>
<th>(T_p, ^\circ\text{C})</th>
<th>(t_{1/2}, \text{s})</th>
<th>(n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>124.4</td>
<td>-0.90</td>
<td>124.1</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>121.9</td>
<td>-0.88</td>
<td>122.1</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>118.7</td>
<td>-0.78</td>
<td>119.0</td>
<td>44</td>
<td>3.82</td>
</tr>
<tr>
<td>20</td>
<td>115.0</td>
<td>-0.75</td>
<td>114.8</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>110.2</td>
<td>-0.74</td>
<td>110.0</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>138.9</td>
<td>-1.40</td>
<td>139.1</td>
<td>118</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>136.5</td>
<td>-1.38</td>
<td>136.5</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>133.3</td>
<td>-1.02</td>
<td>133.5</td>
<td>43</td>
<td>3.28</td>
</tr>
<tr>
<td>20</td>
<td>129.6</td>
<td>-0.88</td>
<td>129.4</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>125.5</td>
<td>-0.80</td>
<td>125.6</td>
<td>14</td>
<td></td>
</tr>
</tbody>
</table>

*a determined from Fig. 1; \(^{b}\) calculated from the Caze method.

Now \(X_w(T)\) can be converted into \(X_v(T)\) by the following relation [17]:

\[
X_v(T) = \frac{X_w(T) \rho_a}{\rho_c} \frac{\rho_a}{1 - (1 - \rho_a/\rho_c) X_w(T)}
\]

(1)

where \(\rho_a\) and \(\rho_c\) are the bulk densities of the amorphous phase and the crystallized phase, respectively.

**Fig. 3.** Plots of \(\ln[\ln(1 - X_v(T))]\) vs. \(T\) for virgin iPP (a) and iPP nucleated with HPN-68 (b).

For iPP, the density of the amorphous phase is \(\rho_a=0.852\), and that of the crystallized phase is \(\rho_c=0.935\). So plots of \(\ln[\ln(1 - X_v(T))]\) vs. \(T\) can be obtained (Fig. 3) and
there is good linear relationship between them. The values of a and –aT_p can be determined from the slope and intercept of each straight line, and the results are also listed in Tab. 1.

Straight lines can be obtained from plots of obtained T_p vs. lnφ/a under different cooling rates (Fig. 4), and the Avrami exponents of virgin iPP and iPP nucleated with HPN-68 can be determined from the slope of each straight line. The results are also listed in Tab.1.

![Fig. 4. Plots of T_p vs. lnφ/a for virgin iPP and iPP nucleated with HPN-68.](image)

For iPP, the Avrami exponent is 3.82 close to 4, which indicates that in virgin iPP the crystal growth pattern is mainly spontaneous nucleation followed by three-dimensional spherulite growth. Of course, impurities such as catalyst residues and dusts existing in virgin iPP can act as heterogeneous nuclei and therefore heterogeneous nucleation will also occur in virgin iPP. Such combination of heterogeneous nucleation and spontaneous nucleation causes non-integer Avrami exponent. While the Avrami exponent of iPP nucleated with HPN-68 is 3.28 close to 3, which indicates the crystal growth pattern of iPP nucleated with HPN-68 is mainly heterogeneous nucleation followed by three-dimension spherulite growth. Particles of nucleating agents HPN-68 in iPP will become heterogeneous nucleus of iPP so that it will change the crystal growth pattern of iPP.

**Conclusions**

Non-isothermal crystallization kinetics of iPP nucleated with a novel nucleating agent HPN-68 has been investigated by adopting the Caze method. Under the same cooling rate, addition of HPN-68 can increase the crystallization peak temperature (T_p) of iPP greatly. The Caze method is successfully employed to deal with the non-isothermal crystallization kinetics. Under non-isothermal conditions, the addition of HPN-68 changes the spherulite growth pattern of iPP. For virgin iPP growth pattern is mainly spontaneous nucleation followed by three-dimension spherulite growth, while for iPP nucleated with HPN-68, the growth pattern is mainly heterogeneous nucleation followed by three-dimension spherulite growth.
Experimental part

Materials

iPP powders T30S with a MFR of 2.5 g/10 min and tacticity of 95%, supplied by SINOPEC Jiujiang Company (China), were used in this work. Nucleating agent bicyclic [2,2,1] heptane di-carboxylate (commercial product name: HPN-68, melting point is above 300 °C) whose chemical structure shown in scheme I was provided by Milliken Chemical.

![Chemical structure of nucleating agent HPN-68.](image)

Scheme I. Chemical structure of nucleating agent HPN-68.

Sample preparation and DSC analysis

The iPP powders and nucleating agents (0.2 wt%) were mixed in a high-speed mixer for 5 min. Then the mixture was extruded by a twin-screw extruder and was pelletized. The pellets were used for subsequent DSC analysis. Temperatures in seven zones of the extruder are 190 °C, 210 °C, 210 °C, 220 °C, 220 °C, 205 °C and 195 °C, respectively. Rotation speed of both screws was 170 r/min.

The crystallization behaviors were investigated under non-isothermal conditions by using a Perkin Elmer Pyris 1 DSC (Perkin Elmer Company, USA). All DSC operations were carried out under a nitrogen environment. Samples weights were between 2-3 mg and all samples were heated to 200 °C and held in the molten state for 5 min to erase their thermal history. Non-isothermal crystallization experiments were carried out by cooling the samples from 200 °C to 50 °C by using different cooling rates. The exotherms were recorded with the cooling rates 2.5, 5, 10, 20 and 40 °C/min, respectively.

Theory of crystallization

The Avrami equation has been proposed to analyze the isothermal crystallization of polymers:

\[ 1 - X_t = \exp(-Z_t t^n) \]  

(3)

where \( n \) is the Avrami exponent, \( Z_t \) is the Avrami rate constant and \( X_t \) is the relative crystallinity at temperature \( T \), defined by

\[ X_t = \frac{X_t(t)}{X_t(\infty)} = \frac{\int_0^t \frac{dH(t)}{dt} \, dt}{\int_0^\infty \frac{dH(t)}{dt} \, dt} \]  

(4)

where \( \frac{dH(t)}{dt} \) represents the heat flow, \( X_t(t) \) and \( X_t(\infty) \) denote the absolute crystallinity at time \( t \) and at the termination of the crystallization process, respectively.
The Avrami equation has been extended by Ozawa [18] from the theory of Evans for isothermal crystallization to develop a simple method to study the non-isothermal experiment. The general form of Ozawa theory is written as follows:

\[ X_v(T) = 1 - \exp\left(-\frac{K_T}{\phi^n}\right) \]  \hspace{1cm} (5)

where \( K_T \) is the cooling crystallization function, \( \Phi \) is the cooling rate and \( n \) is the Ozawa exponent that depends on the dimension of the crystal growth. But there is a main hypothesis in Ozawa method that \( n \) is independent of temperature and only a limited number of \( X_v \) data are available for the foregoing analysis, as the onset of crystallization varies considerably with the cooling rate. In addition, the equation is valid exclusively for primary crystallization before crystal growth impingement takes place at high transformation [19].

Caze et al [17] put forward a new method to modify Ozawa equation. They have assumed an exponential increase of \( K_T \) with \( T \) upon cooling. On this basis, the temperatures at the peak and the two inflection points of the exotherm with skew Gaussian shape are linearly related to \( \ln\Phi \) in order to estimate the exponent \( n \).

On the basis of the findings on the crystallization behavior of poly(ethylene terephthalate) and PP [19], Kim et al proposed:

\[ \ln K_T = a(T - b) \]  \hspace{1cm} (6)

where \( a \) and \( b \) are empirical constants. If the extreme point of the pertinent \( \frac{\partial X_v(T)}{\partial T} \) curve occurs at \( T=T_p \) (crystallization peak temperature), i.e. \( \left( \frac{\partial^2 X_v(T)}{\partial T^2} \right)_{T_p} = 0 \), we have:

\[ K_T(T_p) = \phi^n \]  \hspace{1cm} (7)

Combining equations (5), (6) and (7) yields:

\[ \ln[-\ln(1 - X_v(T))] = a(T - T_p) \]  \hspace{1cm} (8)

Hence, a linear plot of \( \ln[-\ln(1 - X_v(T))] \) against \( T \) would result in the constant \( a \) and the product \( -aT_p \) from the gradient and intercept, respectively. At \( T=T_p \) obtained from the foregoing algorithm, equations (6) and (7) lead to:

\[ T_p = \frac{n \ln \phi}{a} + b \]  \hspace{1cm} (9)

As such, parameter \( n \) can be obtained from the linear plot of \( T_p \) against \( \ln\Phi/a \) in accordance with equation (9).

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**References**