Material Behaviour

Non-isothermal crystallization kinetics of polypropylene/silicon nitride nanocomposites

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1. Introduction

In recent years, silica nanoparticle filled polypropylene (PP) and PP blends have been studied widely. Mechanical property improvement is the major subject in such a research field [1–5]. It is well known that the intrinsic properties of semi-crystalline polymer material, including the mechanical properties, are determined by the microstructure of the final products, which is in turn dependent on the thermal or mechanical history that the material experiences during processing. Because the practical processes usually proceed under non-isothermal crystallization conditions, it is necessary to explore the non-isothermal crystallization kinetics of PP nanocomposites [6,7]. However, there are not as many reports on the non-isothermal crystallization behavior of PP/silica nanocomposites as there are on the mechanical properties [8–10]. Especially, there is no report on the non-isothermal crystallization kinetics of PP/silicon nitride (Si3N4) nanocomposites.

Si3N4 is a ceramic material with high strength and toughness. It has been used in many industrial applications, such as engine components, bearings, springs, high temperature automobile components and cutting tools [11]. Si3N4 nanoparticles exhibit high-potential for the reinforcement of polymers. In a recent report, high strength Nylon-6 composite fibers have been manufactured by adding Si3N4 nanorods and spherical shaped nanoparticles [12]. Si3N4 nanoparticles have also been used for enhancing the thermal conductivity of polyethylene composites [13] and the wear resistance of polymer materials [14].

In this work, the crystallization kinetics of PP nanocomposites containing Si3N4 at various amounts, from 1 wt % to 5 wt %, was studied under non-isothermal conditions by DSC analysis. Avrami and Ozawa equations, along with the method proposed by Mo et al. were applied to obtain the non-isothermal crystallization kinetics of the PP/Si3N4 nanocomposites. Moreover, the nucleation activity of the nanoparticles on the polymer matrix was explored. Finally, the effective energy barrier of non-isothermal crystallization was calculated as a function of the relative degree of crystallinity using an isoconversional approach.
2. Experimental details

2.1. Materials

Commercially available isotactic polypropylene was supplied by Anqing Petrochem Group (Anqing, China) with a melt flow index (MFI) of 7 g/10 min at 230 °C. The Si3N4 nanoparticles used was supplied by Hefei Kaier Nanotechnology (Hefei, China) with a diameter not more than 20 nm. Before use, the Si3N4 nanoparticles were treated with silicone coupler KH-560.

2.2. Specimen preparation

Nanocomposites containing 1, 2, 3, 4 and 5 wt% Si3N4 nanoparticles were prepared by melt mixing on a twin screw extruder (model SJSH-35) with L/D 30 (D = 35 mm) and injected into standard tensile test specimens on an injection molder (model HTL90-F5B). Specimens used in crystallization kinetics analysis were cut from the injected samples.

2.3. Apparatus and experimental procedures

A Metro-Toledo DSC 822e differential scanning calorimeter (DSC) was used for calorimetric investigations of the non-isothermal crystallization of PP/Si3N4 nanocomposites. About 5 mg of each sample was placed in a DSC pan and heated at a rate of 80 °C/min from ambient temperature to 210 °C, and held at this temperature for 3 min to remove all memory of previous thermal and mechanical history. After that, the sample was cooled to 50 °C at a preset rate. The constant cooling rates R used were set as 2.5, 5, 10, 20 °C/min.

3. Results and discussion

3.1. Non-isothermal crystallization analysis

Fig. 1 shows typical DSC curves of heat flow as a function of temperature at different cooling rates for plain PP and PP/Si3N4 nanocomposites with 2 wt% Si3N4 nanoparticles. The values of the crystallization temperature $T_p$, the half-life $t_{1/2}$, and the half width of the crystallization peaks $\Delta T_1$ for all specimens are collected from the cooling curves and listed in Table 1. Here, the crystallization temperatures $T_p$s are those corresponding to the exothermic peak maxima, the half-life $t_{1/2}$ is the time taken for 50% of the total crystallization to occur. The results shown in Table 1 indicate that the crystallization temperature of PP nanoparticles used was supplied by Hefei Kaier Nanotechnology (Hefei, China) with a diameter not more than 20 nm. Before use, the Si3N4 nanoparticles were treated with silicone coupler KH-560.

![DSC thermograms of non-isothermal crystallization for the PP composites with 2 wt% Si3N4 at various cooling rates.](image)

**Table 1**
The crystallization temperature ($T_p$), the half-width of the peak ($\Delta T_1$), $t_{1/2}$ and crystallinity for plain PP and PP/Si3N4 nanocomposites at different cooling rates.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Plain PP</th>
<th>PP/Si3N4 (1 wt%)</th>
<th>PP/Si3N4 (2 wt%)</th>
<th>PP/Si3N4 (3 wt%)</th>
<th>PP/Si3N4 (4 wt%)</th>
<th>PP/Si3N4 (5 wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5 K/min</td>
<td>$T_p/°C$</td>
<td>122.4</td>
<td>122.1</td>
<td>125.9</td>
<td>122.9</td>
<td>122.9</td>
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<tr>
<td></td>
<td>$\Delta T_1/°C$</td>
<td>4.2</td>
<td>3.7</td>
<td>3.5</td>
<td>3.6</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>$t_{1/2}/min$</td>
<td>2.93</td>
<td>2.95</td>
<td>2.86</td>
<td>2.81</td>
<td>2.93</td>
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<td>5 K/min</td>
<td>$T_p/°C$</td>
<td>119.3</td>
<td>118.6</td>
<td>122.6</td>
<td>119.6</td>
<td>119.5</td>
</tr>
<tr>
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<td>$\Delta T_1/°C$</td>
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<td>3.8</td>
<td>4.1</td>
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<tr>
<td></td>
<td>$t_{1/2}/min$</td>
<td>1.76</td>
<td>1.52</td>
<td>1.47</td>
<td>1.45</td>
<td>1.54</td>
</tr>
<tr>
<td>10 K/min</td>
<td>$T_p/°C$</td>
<td>114.9</td>
<td>115.2</td>
<td>119.0</td>
<td>115.8</td>
<td>115.7</td>
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<td></td>
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<td>4.5</td>
<td>4.6</td>
<td>4.5</td>
<td>4.5</td>
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<tr>
<td></td>
<td>$t_{1/2}/min$</td>
<td>1.0</td>
<td>0.84</td>
<td>0.78</td>
<td>0.86</td>
<td>0.90</td>
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<tr>
<td>20 K/min</td>
<td>$T_p/°C$</td>
<td>110.3</td>
<td>111.4</td>
<td>114.5</td>
<td>112.3</td>
<td>112.0</td>
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<td>4.89</td>
<td>5.86</td>
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</tr>
<tr>
<td></td>
<td>$t_{1/2}/min$</td>
<td>0.60</td>
<td>0.50</td>
<td>0.44</td>
<td>0.52</td>
<td>0.51</td>
</tr>
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</table>
changes with cooling rate and addition of Si$_3$N$_4$ nanoparticles. As the cooling rate increases, the $T_p$s moves to higher temperature. The sharpness of the crystallization peaks, as measured by $\Delta T_p$, is higher for the PP/Si$_3$N$_4$ nanocomposites than for plain PP. The values of $t_{1/2}$ of PP nanocomposites are less than that of plain PP. All these results indicate that the addition of Si$_3$N$_4$ nanoparticles can increase the crystallization rate of PP.

However, the $T_p$s of PP nanocomposites does not increase with the Si$_3$N$_4$ nanoparticle content monotonically. For the PP nanocomposites with 2 wt% Si$_3$N$_4$ nanoparticles, the $T_p$ increment is the largest, about 4 °C. The increment of $T_p$ is smaller for the other PP nanocomposite. Usually, it is about 1–2 °C. It seems that the nucleation effect of Si$_3$N$_4$ is not as strong as for other inorganic nanoparticles, such as SiO$_2$ [8], CaCO$_3$ [15] and Talc [16].

The Avrami equation is widely applied for the non-isothermal crystallization of polymers [17–19]. It assumes that the relative degree of crystallinity develops with the crystalline time $t$,

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

where the exponent $n$ is a mechanism constant, which depends on the type of nucleation and growth process; $X_t$ is the relative degree of crystallinity at time $t$; $Z_t$ is a composite rate constant involving both nucleation and growth rate parameters. Considering the non-isothermal character of the process investigated, Jeziorny pointed out that the value of rate parameter $Z_t$ should be adequately corrected [20]. Assuming constant or approximately constant $R$, the final form of the parameter characterizing the kinetics of non-isothermal crystallization is given as follows:

$$\ln Z_c = (\ln Z_t)/R$$

By using the Avrami equation, the plots of $\ln[-\ln(1-X_t)]$ versus $\ln t$ are shown in Fig. 2. As it can be seen, straight lines are obtained in every sample (correlation coefficient $R > 0.998$). The values of $n$ and $\ln Z_c$ determined from the slope and intercept of the initial linear portion in Fig. 2, are listed in Table 2. The average values of the Avrami exponent for plain PP and PP nanocomposites were 4.4, 4.5, 4.3, 4.4, 4.6 and 4.6, respectively. The values of the rate parameter $Z_c$ increase with increasing the cooling rate $R$.

The overall non-isothermal crystallization kinetics of plain PP and PP/Si$_3$N$_4$ nanocomposites was also studied using the Ozawa formalism [21]. This is based on the equation

$$\ln[-\ln(1-X(T))] = K(T) - m \ln R$$

where $X(T)$ is the volume fraction of material crystallized at temperature $T$, $R$ is the constant cooling rate, $m$ is an Ozawa exponent that depends on the crystal growth and nucleation mechanism, and $K(T)$ is the cooling crystallization function.

Fig. 3 shows the results of Ozawa analysis for plain PP and PP/Si$_3$N$_4$ nanocomposites. A series of lines are obtained for different temperatures. This indicates that the Ozawa equation is not appropriate for describing the non-isothermal crystallization behavior of plain PP and PP nanocomposites in this work. Unlike results in the literature [22–24], almost no linear plots could be obtained.

By combining the Avrami and Ozawa equation together, Mo et al. proposed a new method to analyze the non-isothermal crystallization of polymers [25].

$$\log R = \log F(T) - \alpha \log t$$

where the parameter $F(T) = [K(T)/Z_t]^{1/m}$ refers to the value of cooling rate, which has to be chosen at unit
crystallization time when the measured system amounts to
a certain degree of crystallinity; $\alpha$ is the ratio of the Avrami
exponent $n$ to the Ozawa exponent $m$.

Apparently, non-isothermal crystallization analysis by
Mo’s method is suitable for PP/Si$_3$N$_4$ nanocomposites.
Perfect linear relationship between $\log R$ and $\log t$ can be
obtained for plain PP and PP nanocomposites, which is
shown in Fig. 4. The kinetic parameters $F(T)$ and $\alpha$ for PP
and PP/Si$_3$N$_4$ nanocomposites are listed in Table 3. For each
specimen, the $\alpha$ values change slightly with the relative
degree of crystallinity and the content of Si$_3$N$_4$ in PP. For
each specimen, the $F(T)$ value increases as the relative
crystallinity increases.

3.2. Non-isothermal crystallization kinetics

Nucleation activity $\phi$ is a measurement of the work
decrement of three-dimensional nucleation with the
addition of a foreign substrate. The value of $\phi$ ranges from
0 to 1, the stronger the activity of the foreign substrates, the
lower the $\phi$ value should be. According to Dobreva and
Gutzow [26,27], the nucleation activity of foreign
substrates in polymer melts can be calculated from the
ratio:

$$\phi = \frac{B'}{B}$$

where $B'$ stands for the parameter during heterogeneous
nucleation, while $B$ stands for that in homogeneous
nucleation. $B$ and $B'$ can be experimentally determined
from the slope of the following equation:

$$\ln R = \text{Constant} - \frac{B}{\Delta T^2_p}.$$  

where $\Delta T_p$ represents the supercooling ($\Delta T_p = T_m - T_p$).

Plots of $\ln R$ versus $1/\Delta T^2_p$ for plain PP and all PP/Si$_3$N$_4$
nanocomposites are shown in Fig. 5. As it can be seen,
straight lines are obtained in every sample (correlation
coefficient > 0.995). The values of $B$ and $B'$ for the plain PP
and the nanocomposites can be calculated from the slopes
of these lines. These values together with their corre-
sponding 95% confidence intervals are $0.951 \pm 0.032$,
$0.888 \pm 0.068$, $0.757 \pm 0.044$, $0.894 \pm 0.073$, $0.887 \pm 0.072$
and $0.790 \pm 0.094$ for the plain PP and the nanocomposites.

Table 2

<table>
<thead>
<tr>
<th>Samples</th>
<th>Avrami parameters</th>
<th>Cooling rate (K/min)</th>
</tr>
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<tr>
<td></td>
<td>$n$</td>
<td>2.5</td>
</tr>
<tr>
<td>Plain PP</td>
<td>lnZt, lnZc</td>
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<tr>
<td></td>
<td>lnZt, lnZc</td>
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</tr>
<tr>
<td></td>
<td>$\ln Zc$</td>
<td>-1.92</td>
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<td>PP/Si$_3$N$_4$</td>
<td>(1 wt%)</td>
<td>4.6</td>
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<tr>
<td></td>
<td>$\ln Zt$</td>
<td>-5.32</td>
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<tr>
<td></td>
<td>$\ln Zc$</td>
<td>-2.13</td>
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<td>PP/Si$_3$N$_4$</td>
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<td>4.7</td>
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<tr>
<td></td>
<td>$\ln Zt$</td>
<td>-5.34</td>
</tr>
<tr>
<td></td>
<td>$\ln Zc$</td>
<td>-2.14</td>
</tr>
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<td>PP/Si$_3$N$_4$</td>
<td>(3 wt%)</td>
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<tr>
<td></td>
<td>$\ln Zt$</td>
<td>-4.78</td>
</tr>
<tr>
<td></td>
<td>$\ln Zc$</td>
<td>-1.91</td>
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<tr>
<td>PP/Si$_3$N$_4$</td>
<td>(4 wt%)</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td>$\ln Zt$</td>
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<td>$\ln Zc$</td>
<td>-2.12</td>
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<td>PP/Si$_3$N$_4$</td>
<td>(5 wt%)</td>
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<td></td>
<td>$\ln Zt$</td>
<td>-6.15</td>
</tr>
<tr>
<td></td>
<td>$\ln Zc$</td>
<td>-2.46</td>
</tr>
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</table>

Fig. 3. Ozawa plots of $\ln[1-\ln(1-X(T))]$ vs. $\ln R$ for non-isothermal crystallization of (a) the plain PP and (b) the PP/2 wt% Si$_3$N$_4$ nanocomposite.
with 1, 2, 3, 4 and 5 wt% silica, respectively. Then, the nucleation activity is computed from $f = \frac{B^*}{B}$. The effect of the amount of the Si$_3$N$_4$ nanoparticles on the activity is presented in Fig. 6. From these results, it can be seen that the $f$ values for PP nanocomposites are all lower than that of plain PP, indicating that Si$_3$N$_4$ nanoparticles are acting effectively as a nucleation agent in the PP matrix. However, the nucleation activity of Si$_3$N$_4$ nanoparticles is not like that of nano-SiO$_2$ reported earlier [8]. The nucleation efficiency does not increase continuously with the increase of nanoparticle content. Instead, the strongest nucleation effect appears as the Si$_3$N$_4$ nanoparticle content reaches 2 wt%. Lower or higher Si$_3$N$_4$ content all results in weaker nucleation effect. Such a result agrees well with the observation of the crystallization temperature $T_p$ in Section 3.1.

Beyond the nucleation activity, it is also interesting to evaluate the effective energy barrier, $\Delta E$, for the non-isothermal crystallization process of polymer nanocomposites. The differential isoconversional method of Friedman [28] is one of the most appropriate methods for evaluating the effective energy barrier:

$$\ln \left( \frac{\text{d}X}{\text{d}t} \right)_{X_i} = \text{constant} - \frac{\Delta E}{RTX_i}$$

where $\text{d}X/\text{d}t$ is the instantaneous crystallization rate as a function of time at a given conversion $X$. According to this

### Table 3

Values of $a$ and $F(T)$ versus degree of crystallinity based on Mo's treatment for PP and PP/Si$_3$N$_4$ nanocomposites.

<table>
<thead>
<tr>
<th>Samples</th>
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<th>30</th>
<th>50</th>
<th>70</th>
<th>90</th>
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<tr>
<td>Plain PP</td>
<td>$a$</td>
<td>1.4</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.4</td>
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<tr>
<td></td>
<td>$F(T)$</td>
<td>5.95</td>
<td>8.55</td>
<td>10.31</td>
<td>12.09</td>
<td>15.07</td>
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<td>PP/Si$_3$N$_4$ (1 wt%)</td>
<td>$a$</td>
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<td>1.1</td>
<td>1.1</td>
<td>1.1</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>$F(T)$</td>
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<td>7.08</td>
<td>8.24</td>
<td>9.44</td>
<td>11.42</td>
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<td>PP/Si$_3$N$_4$ (2 wt%)</td>
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<td>1.2</td>
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<td>$F(T)$</td>
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<td>6.87</td>
<td>8.17</td>
<td>9.53</td>
<td>11.79</td>
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<td>1.3</td>
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<td>12.23</td>
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<td>5.50</td>
<td>7.55</td>
<td>8.91</td>
<td>10.28</td>
<td>12.58</td>
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<td>7.03</td>
<td>8.13</td>
<td>9.25</td>
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**Fig. 4.** $\log R$ vs. log t from the Mo’s equation for non-isothermal crystallization of (a) plain PP and (b) PP/Si$_3$N$_4$ nanocomposites (2 wt%).

**Fig. 5.** Plots of $\ln R$ versus $1/\Delta T_p^2$ for plain PP and all PP/Si$_3$N$_4$ nanocomposites.

**Fig. 6.** Variation of nucleation activity ($f$) with silica content, for the PP/Si$_3$N$_4$ nanocomposites.
method, the $X_t$ function obtained from the integration of the experimentally measured crystallization rates is initially differentiated with respect to time to obtain the instantaneous crystallization rate, $dX/dt$. Furthermore, by selecting appropriate degrees of crystallinity (i.e. from 0.02 to 0.975) the values of $dX/dt$ at a specific X are correlated to the corresponding crystallization temperature at this X, i.e. $T_x$. Then by plotting $\ln(dX/dt)$ with respect to $1/T_x$, a straight line must be obtained with a slope equal to $E_x/R$. Supaphol et al [24,29] also applied the isothermal method of Friedman to determine the effective barrier of poly(terephthalate).

Fig. 7 is the plots of $\ln(dX/dt)$ vs. $1/T_x$ for the PP at different relative degrees of crystallinity. The $\Delta E$ values obtained from the slopes determined from Fig. 7 are plotted in Fig. 8. Generally, the $\Delta E$ value for plain PP and PP nanocomposites increases monotonically with increasing conversion degree. This suggests that, as the crystallization progresses, it is more difficult for the polymer to crystallize. As crystallization proceeds, diffusion of the crystallizing molecular segments from the melt to the growth front will be deterred by the rejected molecular segments [18]. For a given conversion degree, the $\Delta E$ value of PP/Si3N4 nanocomposites is less than PP/Si3N4 nanocomposites, which is in turn less than plain PP. Such a result is different from the earlier report for PP/SiO2 nanocomposites, in which the effective energy barrier of nanocomposites was higher than the plain PP [8].

4. Conclusions

The non-isothermal crystallization kinetics and nucleation activity of filler in PP/Si3N4 nanocomposites was determined by DSC analysis. The Averami equation and Mo’s method can describe the non-isothermal crystallization behavior of PP/Si3N4 nanocomposites well, while the Ozawa equation is not applicable here. Crystallization temperature ($T_p$) of PP nanocomposites with 2 wt% Si3N4 is the highest, indicating that the crystallization rate is the highest at this Si3N4 content. Nucleation activity of Si3N4 nanoparticles is also the strongest when Si3N4 nanoparticles content reaches 2 wt%. Lastly, analysis of the effective energy barrier of crystallization of PP nanocomposites shows that the $\Delta E$ value increases with the relative conversion degree. For a given relative degree of crystallinity, the $\Delta E$ value of PP/Si3N4 nanocomposites increases as the nanoparticle content increases.

References


