Towards balanced strength and toughness improvement of isotactic polypropylene nanocomposites by surface functionalized graphene oxide

Rui-Ying Bao, Jun Cao, Zheng-Ying Liu, Wei Yang*, Bang-Hu Xie, Ming-Bo Yang

College of Polymer Science and Engineering, Sichuan University, State Key Laboratory of Polymer Materials Engineering, Chengdu, 610065, Sichuan, China

In order to observe the effect of functionalization of GO on the crystallization behavior of iPP, the isotherm crystallization behaviors of pure iPP and iPP composites with 0.1% GO and GO-D were investigated. The sample was melted at 200 °C for 2 min to remove the thermal history. Then, it was cooled to the desired crystallization temperature \( T_c = 132, 128 \) and 126 °C) at 100 °C/min for an isothermal crystallization period of 20 min.

Fig. S1 shows isothermal crystallization exotherms for pure iPP and iPP composites with 0.1% GO and GO-D at various crystallization temperatures of 132, 128 and 126 °C. Compared to that of pure iPP, the crystallization peak for iPP composites with GO-D become sharper and shifted to the shorter time side at various \( T_c \), indicating that the crystallization rate of iPP is enhanced by GO-D; However, slightly weak crystallization peak for iPP composites with GO can be observed.

* Corresponding author. Tel.: + 86 28 8546 0130; fax: + 86 28 8546 0130.

E-mail address: weiyang@scu.edu.cn (W Yang)
Fig. S1 isothermal crystallization exotherms for pure iPP and iPP composites with 0.1% GO and GO-D at various crystallization temperatures of (a) 132, (b) 128 and (c) 126 °C.

Fig. S2 shows relative crystallinity ($x_t$) as a function of time for pure iPP and iPP composites with 0.1% GO and GO-D at various crystallization temperatures. Relative crystallinity development is directly proportional to the evolution of heat released during the crystallization process. This relationship is depicted as

$$x_t = \frac{\int_0^\infty (dH / dt)dt}{\int_0^\infty (dH / dt)dt}$$

(1)
Fig S2 Relative crystallinity as a function of time for pure iPP and iPP composites with 0.1% GO and GO-D at various crystallization temperatures of (a) 132, (b) 128 and (c) 126 °C.

Isothermal crystallization kinetics of pure iPP and iPP composites can be described by the classical Avrami equation as follows:

\[ 1 - x_t = \exp(-kt^n) \]  

where \( x_t \) is the relative crystallinity, \( n \) is the Avrami exponent that is normally an integer between 1 and 4, \( k \) is the overall crystallization rate constant, and \( t \) is the crystallization time. Applying logarithmic properties to both sides of Eq. (2), the following equation can be obtained:
\[ \log[-\ln(1-x_t)] = n \log t + \log k \]  

(3)

Fig. S3 Avrami plots for pure iPP (a) and iPP composites with 0.1% GO (b) and GO-D (c) at various crystallization temperatures.

Table S1. Crystallization kinetics parameters of pure iPP and iPP composites at various crystallization temperatures.

<table>
<thead>
<tr>
<th>sample</th>
<th>iPP</th>
<th>0.1%GO</th>
<th>0.1%GO-D</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(K) (min(^{-n}))</td>
<td>(n)</td>
<td>(t_{1/2}) (min)</td>
</tr>
<tr>
<td>132°C</td>
<td>1.02\times10^{-2}</td>
<td>2.4</td>
<td>5.59</td>
</tr>
<tr>
<td>128°C</td>
<td>6.73\times10^{-2}</td>
<td>2.6</td>
<td>2.45</td>
</tr>
<tr>
<td>126°C</td>
<td>1.66\times10^{-2}</td>
<td>2.9</td>
<td>1.57</td>
</tr>
</tbody>
</table>
The values of k and n can be calculated from the linear fitting of \( \log[-\ln(1-X_t)] \) versus \( \log t \). Fig. S3 shows the Avrami plots for pure iPP and iPP composites at various crystallization temperatures. Crystallization kinetics parameters were obtained from the Avrami plots, and are summarized in Table S1. Crystallization half-time (\( t_{1/2} \)), defined as the time spent from the onset of the crystallization to the point where the crystallization is 50% completed, has been normally used in the analysis of crystallization kinetics and is taken as a measure of the overall rate of crystallization. As shown in Table S1, the overall crystallization rate reflected by \( k \) is coincident with that of \( t_{1/2} \). Obviously, GO has a slight hindering effect on the crystallization of iPP, while GO-D shows a promotion effect. The value of \( t_{1/2} \) for 0.1 wt% GO-D modified iPP is the shortest at the selected crystallization temperature, while that for 0.1 wt% GO modified iPP is slightly longer than that of pure iPP. The enhanced heterogeneous nucleating ability of GO-D is related to its improved dispersion as well as the compatibility between GO-D and iPP matrix.

![SEM images](image)  
Fig. S4 SEM images of impacted surface of iPP composites with 0.5 wt% GO-N at low and high magnification.

As can be seen in Fig 4, GO-D is better exfoliated and shows stronger interactions with iPP
matrix, which can help to absorb iPP molecular chains effectively and provide more nucleating sites. It should be mentioned that GO-N modified iPP has more than one crystal form, it is not reasonable to discuss its isothermal crystallization. However, the enhanced nucleating ability due to the improved dispersion should be similar to that of GO-D.