Role of interfacial interaction on the crystallization behavior and melting characteristics of PP/Nano-CaCO₃ composites modified with different compatibilizers

Yuhai Wang₁,², Hao Shen¹,³, Gu Li¹, Kancheng Mai¹*

¹Key Laboratory of Polymeric Composites and Functional Materials, the Ministry of Education, Materials Science Institute, School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou, 510275, People's Republic of China; fax: +86-20-84115109, e-mail: cesmko@mail.sysu.edu.cn
³School of Engineering, Sun Yat-sen University, Guangzhou, 510006, People’s Republic of China.

(Received: 21 March, 2009; published: 21 May, 2010)

Abstract: PP/nano-CaCO₃ composites with different interfacial interaction were prepared by addition of compatibilizers with the same polar groups but different backbones. The non-isothermal and isothermal crystallization behavior of PP/nano-CaCO₃ composites was investigated using differential scanning calorimetry (DSC). The results indicated that the interfacial interaction between PP and nano-CaCO₃ increased the crystallization temperature and crystallization rate of PP due to the heterogeneous nucleation of nano-CaCO₃. The interfacial interaction between nano-CaCO₃ and compatibilizer further increased the crystallization temperature and crystallization rate of PP and induced the formation of β-crystal of PP due to the synergistic effect of heterogeneous nucleation between nano-CaCO₃ and compatibilizer. This synergistic effect of heterogeneous nucleation between nano-CaCO₃ and compatibilizer depended on the interfacial interaction between compatibilizer and PP matrix. The increased compatibility between compatibilizer and PP matrix favoured the heterogeneous nucleation between nano-CaCO₃ and compatibilizer.

Introduction

Inorganic particles have been widely used to produce polypropylene (PP) composites not only due to reducing the cost but also due to improving the mechanical properties, thermal stability and flame retardant characteristics of PP. Of these inorganic particles, calcium carbonate (CaCO₃) is most commonly used mainly for its availability in readily usable form and low cost. Therefore, The PP composites filled by micro- and nano-CaCO₃ have been extensively studied [1-21]. The incorporation of fillers can lead to changes in crystallization and morphology of PP, and further affects the mechanical properties of PP composites. Thus, many studies have focused on the crystallization and melting behaviour of PP/CaCO₃ composites.

Many investigations reported that the addition of CaCO₃ markedly increased crystallization temperature of PP due to the heterogeneous nucleation effect of CaCO₃ particles [8-21]. The heterogeneous nucleation effect was related to the crystal category, particle shape, particle size and content of CaCO₃ [8, 15, 16, 20]. Mai et al. [8] found that high content of nano-CaCO₃ induced a greater
heterogeneous nucleation effect and increased the crystallization degree of PP. Weon et al. [13] reported that addition of nano-CaCO₃ reduced the size of spherulites of PP and induced the formation of β-phase crystallites, which led to a more ductile PP matrix and improved the impact strength of PP. Similar result was observed by Mai et al. [12].

The surface treatment of CaCO₃ could change the heterogeneous nucleation effect of CaCO₃ on PP. It is found that nano-CaCO₃ particles treated with nonionic modifier increased the crystallization rate of PP matrix [12]. Similar result was obtained when surface was modified with an aluminiate coupling agent [11]. Shanks et al. [21] found that CaCO₃ treated with silicone was more effective in increasing the crystallization degree of PP than that treated with titanate. However, a contrary result was found by Supaphol et al. [18] that surface treatment of CaCO₃ particles by stearic acid reduced the ability for CaCO₃ particles to nucleate the PP matrix. In recent years, macromolecular compatibilizers have been used to improve the interface interaction between CaCO₃ and PP. Mai et al. [10] found that the PP-g-AA could improve the heterogeneous nucleation effect of nano-CaCO₃ and further increased the crystallization temperature of PP. Avella et al. [15, 16] also demonstrated that addition of PP-g-MA enhanced the heterogeneous nucleation ability of nano-CaCO₃ particles by improving the interfacial interaction between CaCO₃ particles and PP.

A number of investigations indicated that surface treatment significantly influenced the crystallization behavior of PP/CaCO₃ composites due to changing the interfacial interaction between CaCO₃ particles and PP matrix. When modified by polar macromolecular compatibilizer, a core–shell structure with particles encapsulated by compatibilizer would be formed in polymer matrix, resulting in the formation of two interfaces: the interface between particles and compatibilizer as well as the interface between compatibilizer and polymer matrix. The physical and mechanical properties of polymer composites depend not only on the interfacial interaction between the filler and the compatibilizer but also on the interfacial interaction between the polymer and the compatibilizer. In order to investigate the effect of the interfacial interaction between the polymer and the compatibilizer on crystallization and mechanical properties of PP/nano-CaCO₃ composites modified by compatibilizers, three compatibilizers with same MA groups (PP-g-MA, POE-g-MA and EVA-g-MA) were used to modify the PP/nano-CaCO₃ composites. These compatibilizers were chosen because they had the same polar group but different backbones. The same polar groups in these compatibilizers should associate with nano-CaCO₃ particles, resulting in the same interfacial interaction between compatibilizers and particles, but the different long backbones in these compatibilizers have different compatibility with the polymer matrix, and this would result in different interfacial interaction between compatibilizer and PP matrix. In this paper, the effect of different interfacial interaction on the crystallization behavior of PP/nano-CaCO₃ composites has been reported.

**Results and discussion**

**Non-isothermal crystallization of PP in PP/nano-CaCO₃ composites modified with different compatibilizer**

The compositions of prepared materials are listed in Table 1. The components are in weight ratio. Figure 1 shows the non-isothermal crystallization curves of PP and PP/nano-CaCO₃ composites at several cooling rates. It is found that the
crystallization peak of the specimens shifts to lower temperature with increasing cooling rate. The crystallization curves of modified PP/nano-CaCO$_3$ composites are found to have a similar tendency in nature (figure not shown here).

**Tab. 1.** The compositions for PP/nano-CaCO$_3$ composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PP (wt%)</th>
<th>CaCO$_3$ (wt%)</th>
<th>PP-g-MA (wt%)</th>
<th>POE-g-MA (wt%)</th>
<th>EVA-g-MA (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PP-10</td>
<td>90</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PP-10a</td>
<td>85</td>
<td>10</td>
<td>5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PP-10b</td>
<td>85</td>
<td>10</td>
<td>-</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>PP-10c</td>
<td>85</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>5</td>
</tr>
</tbody>
</table>

**Fig. 1.** DSC crystallization curves of PP (a) and PP-10 (b) at different cooling rates.

**Fig. 2.** DSC crystallization curves of PP and its composites at the cooling rate of 10 °C/min (a) and 20 °C/min (b).

The crystallization curves of PP and its composites at the cooling rate of 10 °C/min and 20 °C/min are shown in Figure 2. From these curves, it can be seen that the addition of nano-CaCO$_3$ particles and compatibilizers significantly change the crystallization behaviour of PP. The onset crystallization temperatures ($T_{c,\text{on}}$) and the peak crystallization temperatures ($T_{c}$) against cooling rate are shown in Figure 3. It can be seen that addition of nano-CaCO$_3$ particles increases the $T_{c}$ about 3-6 °C at
different cooling rates, indicating that nano-CaCO$_3$ can act as nucleating agent of PP. Many other nanoparticles were also found to have nucleation effect for PP crystallization [22, 23].

Previous investigation [24] showed that addition of PP-g-MA slightly increases the crystallization temperature ($T_c$) of PP matrix, while addition of POE-g-MA and EVA-g-MA decreases the $T_c$ of PP matrix.

It can be seen from Figure 3 that addition of PP-g-MA further increases the $T_c$ of PP in PP/nano-CaCO$_3$ composite, the $T_c$ of PP-10a is about 8-10 °C higher than that of PP at different cooling rates. This suggests that there exist a synergism of heterogeneous nucleation of PP-g-MA and nano-CaCO$_3$ for PP crystallization. Addition of POE-g-MA slightly increases the $T_c$ of PP in PP/nano-CaCO$_3$ composite, the $T_c$ of PP-10b is about 5-6 °C higher than that of PP at different cooling rates, which is lower than that of PP-10a. This indicates that there also exist a synergism of heterogeneous nucleation of POE-g-MA and nano-CaCO$_3$ for PP crystallization, but is weaker than that of PP-g-MA and nano-CaCO$_3$. However, addition of EVA-g-MA reduces the $T_c$ of PP in PP/nano-CaCO$_3$ composite. The $T_c$ of PP-10c is even lower than that of PP at different cooling rates, indicating that addiction of EVA-g-MA retards that heterogeneous nucleation of nano-CaCO$_3$ for PP crystallization.

![Fig. 3.](image)

**Fig. 3.** The onset crystallization temperature (a), peak crystallization temperature (b) of PP and its composites as a function of cooling rate.

*The melting characteristics of PP in non-isothermal crystallized PP/nano-CaCO$_3$ composites modified with different compatibilizers*

The DSC melting curves of the specimens crystallized at various cooling rates are shown in Figure 4. It can be seen that the melting peak shifts to lower temperature with the increase of cooling rates. For PP-10a and PP-10b, the peaks at about 150 °C corresponding to β-crystal of PP are observed. At the same time, the intensity of melting peaks at about 150 °C increases with increasing cooling rates. This indicates that fast cooling rate favours the formation of β-crystal of PP in PP/nano-CaCO$_3$ composite modified by PP-g-MA or by POE-g-MA. However, there are no melting peaks of β-crystal in neat PP, PP-10 and PP-10c. It is suggested that the formation of β-crystal of PP is induced by the synergistic effect of nano-CaCO$_3$ particle and compatibilizer, but it also depends on the compatibility between PP matrix and compatibilizer.
Fig. 4. DSC melting curves of the specimens crystallized at different cooling rates: (a) PP; (b) PP-10; (c) PP-10a; (d) PP-10b and (e) PP-10c.

Non-isothermal crystallization kinetics of PP in PP/nano-CaCO₃ composites modified with different compatibilizers

Three methods have been widely adopted to describe the non-isothermal crystallization process, namely Jeziorny equation, Ozawa equation and Mo’s method.
Jeziorny equation was obtained from Avrami equation, which was applied to describe the isothermal crystallization process of polymers. The double logarithmic form of Avrami equation is [25]:

\[
\log [-\ln (1 - X(T))] = \log Z_t + n \log t
\]

(1)

where \(X(T)\) is the relative crystallinity at the crystallization time of \(t\), \(Z_t\) and \(n\) are the crystallization kinetic constant and Avrami exponent, respectively.

**Tab. 2.** Non-isothermal crystallization kinetic parameters of PP and its composites.

<table>
<thead>
<tr>
<th>Samples</th>
<th>(X(T)) (%)</th>
<th>10</th>
<th>30</th>
<th>50</th>
<th>70</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>(F(T))</td>
<td>5.16</td>
<td>6.99</td>
<td>8.27</td>
<td>9.64</td>
<td>12.0</td>
</tr>
<tr>
<td></td>
<td>(\alpha)</td>
<td>1.18</td>
<td>1.20</td>
<td>1.21</td>
<td>1.23</td>
<td>1.26</td>
</tr>
<tr>
<td>PP-10</td>
<td>(F(T))</td>
<td>5.50</td>
<td>6.89</td>
<td>7.87</td>
<td>8.96</td>
<td>11.0</td>
</tr>
<tr>
<td></td>
<td>(\alpha)</td>
<td>0.99</td>
<td>1.01</td>
<td>1.03</td>
<td>1.06</td>
<td>1.11</td>
</tr>
<tr>
<td>PP-10a</td>
<td>(F(T))</td>
<td>4.81</td>
<td>6.32</td>
<td>7.30</td>
<td>8.43</td>
<td>10.6</td>
</tr>
<tr>
<td></td>
<td>(\alpha)</td>
<td>1.08</td>
<td>1.06</td>
<td>1.07</td>
<td>1.10</td>
<td>1.14</td>
</tr>
<tr>
<td>PP-10b</td>
<td>(F(T))</td>
<td>5.83</td>
<td>7.13</td>
<td>8.07</td>
<td>9.16</td>
<td>11.1</td>
</tr>
<tr>
<td></td>
<td>(\alpha)</td>
<td>0.92</td>
<td>0.95</td>
<td>0.97</td>
<td>1.00</td>
<td>1.04</td>
</tr>
<tr>
<td>PP-10c</td>
<td>(F(T))</td>
<td>5.67</td>
<td>7.37</td>
<td>8.52</td>
<td>9.72</td>
<td>11.8</td>
</tr>
<tr>
<td></td>
<td>(\alpha)</td>
<td>1.06</td>
<td>1.07</td>
<td>1.08</td>
<td>1.10</td>
<td>1.14</td>
</tr>
</tbody>
</table>

When applied to describe the non-isothermal crystallization process, Jeziorny pointed out that the value of rate parameter \(Z_t\) in Avrami equation should be adequately corrected [26]. Assuming constant or approximately constant \(R\), the final form of the parameter characterizing the kinetics of non-isothermal crystallization is given as follows:

\[
\ln Z_c / (\ln Z_t) = R
\]

(2)

Ozawa derived an equation which double logarithmic form is [27]:

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

(3)

where \(R\) is the cooling rate, \(K(T)\) is a function related to the overall crystallization rate, and \(m\) is the Ozawa index, which is somewhat similar to the Avrami exponent and depends on the type of nucleation and growth dimensions.

Mo and co-workers [28] proposed a different equation by combining the Avrami and Ozawa equations, giving rise to the relationship between cooling rate \(R\) and crystallization time \(t\) at a given relative crystallinity:

\[
\log Z_t + n \log t = \log K(T) - m \log R
\]

(4)

\[
\log R = \log F(T) - \alpha \log t
\]

(5)

where the kinetic parameter, \(F(T) = [K(T) / Z_t]^{1/m}\), has a definite physical and practical meaning, the smaller the value of \(F(T)\) is, the higher the crystallization rate becomes. The Mo exponent \(\alpha\) is the ration of the Avrami exponent \(n\) to the Ozawa exponent \(m\), that is, \(\alpha = n/m\).

Here, we use Mo’s method to describe the non-isothermal crystallization behaviour of PP/nano-CaCO₃ composites. At a given relative crystallinity, the plots of \(\log R\) against \(\log t\) of PP/nano-CaCO₃ composite are given in Figure 5. A series of almost parallel lines for various temperatures are obtained, indicating that the Mo’s equation is
suitable to describe the non-isothermal crystallization behaviour of PP and PP/compatibilizer/CaCO$_3$ composites. Many other papers [29, 30] also indicated that Mo’s equation could be applied to describe non-isothermal crystallization process.

![Plots of log R versus log t for PP and its composites: (a) PP; (b) PP-10; (c) PP-10a; (d) PP-10b and (e) PP-10c.](image)

**Fig. 5.** Plots of log R versus log t for PP and its composites: (a) PP; (b) PP-10; (c) PP-10a; (d) PP-10b and (e) PP-10c.

The values of $F(T)$ and $a$ can be obtained from the slopes and intercepts of the straight lines, respectively, tabulated in Table 2. It can be observed that the values of $F(t)$ increased systematically with increasing the relative degree of crystallinity and the values of $a$ increased slightly. Besides, at the same $X(T)$, the values of $F(T)$ for these specimen ranges as: PP-10c $\geq$ PP $>$ PP-10b $\geq$ PP-10 $>$ PP-10a. This means that the crystallization rate is PP-10a $>$ PP-10 $\geq$ PP-10b $>$ PP $\geq$ PP-10c. It also
indicated that nano-CaCO$_3$ particles have a heterogeneous nucleation effect on PP crystallization, increasing the crystallization rate of PP. Addition of PP-g-MA promotes and addition of EVA-g-MA decreases the heterogeneous nucleation of nano-CaCO$_3$ particles. These results were in agreement with the crystallization behaviour discussed above.

*Isothermal crystallization and melting characteristics of PP in PP/nano-CaCO$_3$ composites modified with different compatibilizers*

Representative isothermal crystallization curves of PP in PP/nano-CaCO$_3$ composite at different temperatures are shown in Figure 6 and the data is shown in Table 3. As anticipated by the nucleation-controlled crystal growth theory, the time needed to complete crystallization is longer for the specimens crystallized at higher crystallization temperature ($T_c$) [31]. Similar trends are observed for the modified composites (not shown here).

![Fig. 6. DSC curves of PP (a) and PP-10 (b) isothermally crystallized at different temperatures.](image)

Figure 7 shows the DSC curves of PP and its composites isothermally crystallized at 128 °C and 130 °C. It can be seen that the time needed to complete the
crystallization ranges as: PP-10c ≥ PP >> PP-10 > PP-10b > PP-10a. That is to say, the crystallization rate of these specimens is PP-10a > PP-10b > PP-10 >> PP ≥ PP-10c. It also indicated that nano-CaCO₃ particles have a heterogeneous nucleation for PP crystallization, increasing the crystallization rate of PP. Addition of PP-g-MA promotes the heterogeneous nucleation of nano-CaCO₃ particles and addition of EVA-g-MA decreases the heterogeneous nucleation of nano-CaCO₃ particles. These results were in agreement with the non-isothermal crystallization behaviour discussed above.

![Fig. 8. DSC melting curves of PP-10a (a) and PP-10b (b) crystallized at different temperatures.](image)

Figure 8 shows the melting curves of PP-10a and PP-10b crystallized isothermally at different temperatures. The melting temperatures are listed in Table 3. It can be seen that the melting temperatures increase with the increase of crystallization temperatures because the perfection of PP crystals at high crystallization temperature. The small peaks at about 152 °C are corresponding to the melting of β-crystal of PP, and the intensity of these peaks seems to decrease with increasing the crystallization temperatures. This indicates that high crystallization temperatures restrict the formation of β-crystal of PP.

**Isothermal crystallization kinetics of PP in PP/nano-CaCO₃ composites modified with different compatibilizers**

Generally, isothermal crystallization of polymers can be described by Avrami equation (equation (1)). Here, the exponent \( n \) is a mechanism constant, which depends on the type of nucleation and growth process; \( Z_t \) is a composite rate constant involving both nucleation and growth rate parameters. The larger is the value of \( Z_t \), the higher the crystallization rate becomes. When plot \( \log [-\ln (1-X(T))] \) straight against \( \log t \), the values of \( n \) and \( Z_t \) can be obtained from the slopes and intercepts of the straight lines, respectively, tabulated in Table 3. From Table 3, it can be seen that the values of \( n \) lie between 2.4 and 3.0 for all the specimens at different crystallization temperature, indicating heterogeneous nucleation and tridimensional growth of PP crystals [32]. This suggests that addition of nano-CaCO₃ particles and compatibilizers does not modify the type of nucleation and growth process of PP. However, addition of nano-CaCO₃ particles and compatibilizers significantly influences the nucleation and growth rate of PP. The value of \( Z_t \) for these specimens
ranges as: PP-10a > PP-10b > PP-10 >> PP ≥ PP-10c. These results are in agreement with those discussed above. When plot log \( Z_t \) against \( T_c \), it can be observed that log \( Z_t \) increases straight with the decrease of crystallization temperatures \( (T_c) \) (Figure 9).

**Tab. 3.** DSC results of isothermal crystallization of PP and its composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_c ) (°C)</th>
<th>( t_p ) (min)</th>
<th>( T_m ) (°C)</th>
<th>( Z_t \times 10^n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>122</td>
<td>1.25</td>
<td>164.9</td>
<td>46.13 ( \times 10^2 )</td>
</tr>
<tr>
<td></td>
<td>124</td>
<td>1.77</td>
<td>165.5</td>
<td>11.62 ( \times 10^2 )</td>
</tr>
<tr>
<td></td>
<td>126</td>
<td>2.59</td>
<td>166.1</td>
<td>2.15 ( \times 10^2 )</td>
</tr>
<tr>
<td></td>
<td>128</td>
<td>3.51</td>
<td>167.2</td>
<td>0.51 ( \times 10^2 )</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>5.55</td>
<td>167.8</td>
<td>0.17 ( \times 10^2 )</td>
</tr>
<tr>
<td>PP-10</td>
<td>126</td>
<td>1.65</td>
<td>166.9</td>
<td>23.65 ( \times 10^2 )</td>
</tr>
<tr>
<td></td>
<td>128</td>
<td>2.15</td>
<td>167.6</td>
<td>6.80 ( \times 10^2 )</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>2.82</td>
<td>168.4</td>
<td>1.89 ( \times 10^2 )</td>
</tr>
<tr>
<td></td>
<td>132</td>
<td>3.95</td>
<td>169.3</td>
<td>3.99 ( \times 10^2 )</td>
</tr>
<tr>
<td></td>
<td>134</td>
<td>6.21</td>
<td>170.3</td>
<td>0.11 ( \times 10^2 )</td>
</tr>
<tr>
<td>PP-10a</td>
<td>128</td>
<td>1.20</td>
<td>166.2</td>
<td>91.29 ( \times 10^2 )</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>1.52</td>
<td>166.9</td>
<td>22.88 ( \times 10^2 )</td>
</tr>
<tr>
<td></td>
<td>132</td>
<td>2.04</td>
<td>167.7</td>
<td>4.69 ( \times 10^2 )</td>
</tr>
<tr>
<td></td>
<td>134</td>
<td>2.80</td>
<td>167.8</td>
<td>2.02 ( \times 10^2 )</td>
</tr>
<tr>
<td></td>
<td>136</td>
<td>3.55</td>
<td>166.8</td>
<td>0.45 ( \times 10^2 )</td>
</tr>
<tr>
<td>PP-10b</td>
<td>126</td>
<td>1.44</td>
<td>166.0</td>
<td>27.70 ( \times 10^2 )</td>
</tr>
<tr>
<td></td>
<td>128</td>
<td>1.85</td>
<td>166.7</td>
<td>9.22 ( \times 10^2 )</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>2.51</td>
<td>167.4</td>
<td>2.44 ( \times 10^2 )</td>
</tr>
<tr>
<td></td>
<td>132</td>
<td>3.49</td>
<td>168.2</td>
<td>0.68 ( \times 10^2 )</td>
</tr>
<tr>
<td></td>
<td>134</td>
<td>4.89</td>
<td>169.3</td>
<td>0.21 ( \times 10^2 )</td>
</tr>
<tr>
<td>PP-10c</td>
<td>124</td>
<td>1.95</td>
<td>164.6</td>
<td>7.32 ( \times 10^2 )</td>
</tr>
<tr>
<td></td>
<td>126</td>
<td>2.45</td>
<td>165.5</td>
<td>2.68 ( \times 10^2 )</td>
</tr>
<tr>
<td></td>
<td>128</td>
<td>4.09</td>
<td>166.2</td>
<td>0.33 ( \times 10^2 )</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>5.95</td>
<td>167.0</td>
<td>0.19 ( \times 10^2 )</td>
</tr>
<tr>
<td></td>
<td>132</td>
<td>8.85</td>
<td>168.3</td>
<td>0.04 ( \times 10^2 )</td>
</tr>
</tbody>
</table>

\( T_c \), the isothermal crystallization temperature; \( t_p \), the crystallization peak time; \( T_m \), the melting peak temperature of the isothermally crystallized specimen; \( Z_t \) and \( n \) are the isothermal crystallization kinetic parameters obtained from equation (1).

According to Turnbull and Fisher, the crystallization rate of the polymer could be described as follows [33, 34]:

\[
G = G_0 \exp(-\Delta F / kT_c)\exp(-\Delta \Phi / kT_c)
\]

where \( G \) is the crystallization rate, \( G_0 \) is a pre-exponential factor, \( \Delta F \) is the transport activation energy and \( \Delta \Phi \) is the nucleating activation energy. Obviously, isothermal crystallization rate of polymers basically depends on two energetic terms. One is the activation energy (\( \Delta F \)) required for transportation of the chain molecules across the melt-crystalline interface. The other is the free energy (\( \Delta \Phi \)) required for the formation of a nucleus of critical size, which contains enthalpic and entropic terms. The value of \( \Delta F \) depends on the variation of \( T_g \) of PP in the composites. The specimen with a lower \( T_g \) possess a higher molecular mobility and a lower \( \Delta F \) value at the same crystallization temperature. Therefore, the crystallization rate of specimens with lower \( T_g \) will be faster if the influence of \( \Delta \Phi \) term is negligible [35]. However, the \( T_g \) of PP,
PP-10, PP-10a, PP-10b and PP-10c are 21.2 °C, 21.5 °C, 20.6 °C, 19.7 °C and 20.0 °C, respectively. The difference of \( T_g \) is less than 2 °C and the influence of \( \Delta F \) term can be neglected at the same \( T_c \). Therefore, the influence of \( \Delta \Phi \) term should play a dominant role in controlling the isothermal crystallization of PP in its composites. As discussed above, addition of nano-CaCO\(_3\) increases the crystallization rate of PP. It is believed that nano-CaCO\(_3\) particles act as nucleation agent, decrease the value of \( \Delta \Phi \) term, which resulted in the easy formation of nucleus of critical size and increased the crystallization rate of PP. When modified with compatibilizers, the interaction between the compatibilizers and nano-CaCO\(_3\) has higher heterogeneous nucleation for PP crystallization and decrease the value of \( \Delta \Phi \) term, resulting in the increased crystallization rate of PP. However, the crystallization rate of PP in modified composites is dependent of the interfacial interaction between PP matrix and compatibilizer.

**Fig. 9.** Log \( Z_t \) versus \( T_c \) for PP and its composites crystallized at different temperatures.

*Interfacial interaction in PP/nano-CaCO\(_3\) composites modified with different compatibilizers*

The above experimental results indicate that the PP/nano-CaCO\(_3\) composites modified with different compatibilizers exhibits different crystallization behaviour and melting characteristics of PP. It is suggested that there exist different interfacial interaction in PP/nano-CaCO\(_3\) composites with and without compatibilizers.

1. **Interfacial interaction between PP and nano-CaCO\(_3\) particles:** This interfacial interaction generally increases the crystallization rate and crystallization temperature of PP due to the heterogeneous nucleation of nano-CaCO\(_3\) particles.

2. **Interfacial interaction between compatibilizer and nano-CaCO\(_3\) particles:** Because of compatibilizer with the same polar groups, it is considered the interfacial interaction between compatibilizer and nano-CaCO\(_3\) particles is basically the same. The chemical reaction between polar groups (MA) of compatibilizer and nano-CaCO\(_3\) particles in this interface may lead to the formation of carboxylate salts [17] with more heterogeneous nucleation. The carboxylate salts acting as a more effective nucleating agent further increases the crystallization temperature and crystallization rate of PP and induces the formation of \( \beta \)-crystal of PP.
It is found that the heterogeneous nucleation of carboxylate salts in the interface between compatibilizer and nano-CaCO₃ particles increases the temperature domain of β-crystal crystallization. Various investigations [36-38] indicated that there exists a temperature range (generally in the range 130-105 °C) for the formation of β-crystal. As shown in Figure 8, the intensity of β-crystal decreases with increasing the crystallization temperature. However, the melting peak of β-crystal can be detected even when crystallized at 138 °C. Non-isothermal crystallization also indicates that the melting peaks of β-crystal are detectible even until the crystallization starts above 140 °C (the $T_c^{on}$ of PP-10a and PP-10b at 1 °C/min is 144.4 °C and 141.3 °C respectively). Therefore, it is suggested that the heterogeneous nucleation of carboxylate salts extended the critical temperature for the formation of β-crystal.

(3) **Interfacial interaction between PP and compatibilizer**: Because of nano-CaCO₃ particles encapsulated by compatibilizer, addition of different compatibilizer with different backbones results in the formation of different interfacial interaction between compatibilizer and PP matrix. The heterogeneous nucleation of carboxylate salts in the interface between compatibilizer and nano-CaCO₃ particles depends on the compatibility between PP and compatibilizer. For the composites modified by crystallizable PP-g-MA, the heterogeneous nucleation of carboxylate salts in the interface between compatibilizer and nano-CaCO₃ particles can pass through the highly miscible interface layer due to the good compatibility between PP matrix and PP chains in PP-g-MA, increasing the crystallization temperature and crystallization rate of PP and inducing the formation of β-crystal of PP. For the composites modified by POE-g-MA, the partial miscible interface layer between PP and POE chains in POE-g-MA weakens the heterogeneous nucleation of carboxylate salts. For the composites modified by EVA-g-MA, the poor compatibility between PP and EVA in EVA-g-MA due to distinct discrepancy in polarity retards the heterogeneous nucleation of carboxylate salts, resulting in the decreased crystallization temperature and crystallization rate of PP.

**Conclusions**

PP/nano-CaCO₃ composites with different interfacial interaction were prepared by addition of compatibilizers with the same polar groups but different backbones. The non-isothermal and isothermal crystallization and melting behaviour of PP/nano-CaCO₃ with different interfacial interaction were investigated using differential scanning calorimetry. The results indicated that the interfacial interaction between PP and nano-CaCO₃ increased the crystallization temperature and crystallization rate of PP due to the heterogeneous nucleation of nano-CaCO₃. The interfacial interaction between nano-CaCO₃ and compatibilizer with different polar group further increase the crystallization temperature and crystallization rate of PP and induce the formation of β-crystal of PP due to the formation of carboxylate salts with more heterogeneous nucleation. The different backbones of compatibilizer result in the formation of different interfacial interaction or the compatibility between compatibilizer and PP matrix. The heterogeneous nucleation of carboxylate salts in the interface between compatibilizer and nano-CaCO₃ particles depends on the compatibility between compatibilizer and PP matrix. The good compatibility between PP-g-MA and PP matrix favoured the heterogeneous nucleation of carboxylate salts. The partial compatibility between POE-g-MA and PP matrix weakened the heterogeneous nucleation of carboxylate salts. The poor compatibility between EVA-g-MA and PP matrix retarded the heterogeneous nucleation of carboxylate salts.
Experimental part

Materials
Polypropylene (EPS30R), ethylene content 2.87 %, MFI=2.1 g/10 min (2.16 kg at 230 °C), was supplied by Dushanzi Petroleum Chemical, China. Polypropylene grafted with maleic anhydride (PP-g-MA), grafting ratio 1.0 %, MFI>15 g/10 min (2.16 kg at 230 °C); ethylene-octene copolymer grafted with maleic anhydride (POE-g-MA), grafting ratio 1.1 %, MFI=0.72 g/10 min (2.16 kg at 230 °C); ethylene-vinyl acetate copolymer grafted with maleic anhydride (EVA-g-MA), grafting ratio 1.0 %, MFI=2.46 g/10min (2.16 kg at 230 °C). The compatibilizers were provided by Guangzhou Lushan Chemical Materials Co. China. Nano-CaCO3 (CC), with particle size: 70-90 nm, was obtained from Shiraishi Kogyo Kaisha LTD, Japan.

Sample preparation
All materials were dried in an oven at 60 °C for 12 h. PP/nano-CaCO3 composites with and without compatibilizers were prepared using a Berstoff ZE25A corotating twin-screw extruder. The blending temperature was set at 200 °C. All the materials were simultaneously added into the extruder after previous mixing.

Characterization
The crystallization behaviour of the specimens was examined using differential scanning calorimetry (DSC) (Perkin–Elmer DSC-7) under nitrogen atmosphere. The heat flow and temperatures of DSC were calibrated with standard materials, indium and zinc. The weights of the specimens ranged from 4 mg to 5 mg.

For non-isothermal crystallization study, the samples were heated rapidly to 220 °C and melted for 3 min to erase the thermal history and then cooled down to 50 °C at constant cooling rates of 1, 2, 5, 10, 15 and 20 °C/min, respectively. The crystallized specimens were reheated at rate of 10 °C/min to investigate the corresponding melting behaviours. For isothermal crystallization study, all the specimens were heated rapidly to 220 °C and melted for 3 min to erase the thermal history and then rapidly cooled down at 200 °C/min to different designed crystallization temperatures (Tc) for 30 min. The crystallized specimens were heated at rate of 10 °C/min to investigate the corresponding melting behaviours.

Acknowledgements
The project was supported by Natural Science Foundation of China (Grant No. 50573094, 50873115) and Project of Science and Technology of Guangdong Province, China (Grant No. 0711020600002).

References


