ABSTRACT

In situ polymerization of ethylene was used to prepare silica/PE parent material (46.8 wt% of SiO₂), which was then blended with PE (and PP) to synthesize silica/polyolefin nanocomposites (a two-step method), such as PE05, PE10, and PE20 (or PP05, PP10, and PP20), whose silica contents were 0.5 wt%, 1.0 wt%, and 2.0 wt%. For comparison, silica/polyolefin nanocomposites with 2.0 wt% of SiO₂ were also prepared via blending method (PE20M and PP20M). TEM, TGA and tensile test characterization results showed that the nanocomposite prepared via the two-step method behaved better than that prepared via blending method, as for nanosilica dispersion, thermal stability, crystallinity, and tensile mechanical properties. For example, the dispersion of nanosilica particles in PE20 was better than that in PE20M. The temperatures of maximum weight loss rate (Tₚ), crystallinity and strength of PE20 were 472°C, 68.3% and 28.3 MPa that were improved compared with those of PE20M, which were 430°C, 66.3% and 26.3 MPa, respectively. Furthermore, the two-step method could utilize minimum amount of in situ polymerization product to produce maximum amount of nanocomposite. All these findings have shown that the two-step method can easily and cheaply produce silica/polyolefin nanocomposites with high quality.

INTRODUCTION

In recent years, nanoparticles/polymer composites have attracted much attention, because they usually exhibit far better performance properties than the traditional organic/inorganic composites, and they can be used for plastics, rubbers, fibres, coating, etc. [1-4]. Polyolefins as one of the most consumed resins, especially polyethylene (PE) and polypropylene (PP), are widely used in diverse applications, such as packaging, ornament, agriculture, and etc. However, the use of PE and PP is restricted because of their several drawbacks, including poor heat resistance, low strength among many others. Nanosilica with huge surface area and low cost is widely used to reinforce polyolefin composites, such as their heat resistance, low strength, optical properties, etc. [5-9]. But the synthesis of silica/polyolefin nanocomposites is particularly challenging. There are two principal strategies investigated to date. The first one is the melt...
mixing of polyolefin with silicates [10-12]; the second is the in situ polymerization of olefin via a catalyst supported on inorganic materials [13-16]. However, the process of in situ polymerization of polyolefin, especially PE and PP, is very complex and expensive.

In this paper, the in situ polymerization method and blending method were combined to prepare silica/PE and silica/PP nanocomposites, known as “two-step method” i.e., in situ polymerization of ethylene was used to pretreat nanosilica. The treated nanosilica was then blended with polyolefin to prepare silica/polyolefin nanocomposites. Therefore, a two-step method was utilized with minimum amount of in situ polymerization product to produce maximum amount of nanocomposites. The cost to prepare nanocomposites via a two-step method was lower than that of in situ polymerization. Besides, the two-step method might take advantage of the high quality of in situ polymerization method in the synthesis of nanocomposites, that are of high quality and have good performance in nanosilica dispersion, thermal stability and tensile mechanical properties, etc. For comparison, silica/polyolefin nanocomposites were also prepared via blending method.

EXPERIMENTAL

Materials

PE and PP were supplied via Luoyang Petrochemical Co., Ltd. (China). The melt flow index (MFI) of PE and PP measured under standard test conditions were 2.1 g/10min and 2.5 g/10min, and the densities of the solid state were 0.918 g/cm³ and 0.921 g/cm³. Nanosilica was purchased via Zhejiang Zhoushan Nanomaterial Co. (China), the particle size ranged from 20 nm to 25 nm, before use it was heated at 150°C under vacuum for 2 days and then cooled to room temperature under N₂ atmosphere. Bis(cyclopentadienyl)zirconium dichloride (Cp₂ZrCl₂, Boulder Scientific Company), methylaluminoxane (MAO: 10 wt% in toluene, Ethyl Corporation) and ethylene (polymerization grade, Liaoyang Chemical Corporation) were used. Toluene was dried over 4 Å molecular sieves for 10 days, then refluxed over Na/K alloy for at least 8 h and distilled.

Ethylene Polymerization

Ethylene polymerizations were carried out in a 1.5-L glass reactor. Dried toluene (1000 mL), treated nanosilica (10.0 g), MAO (Al/Zr = 1500) and catalyst (10 μmol) were added to the reactor alternately. The polymerization reaction was initiated via introducing ethylene into the reactor under stirring. Temperature (60°C) and partial pressure of ethylene (1.2 atm) were kept constant during the reaction. The polymerization was terminated via adding acidified ethanol in an hour. The product was isolated via filtration and washed with ethanol. The polymer was then air-dried under ambient conditions and then dried at 60°C under vacuum for 1 day. Finally, a white powder (20.6 g) was obtained.

Nanocomposites Preparation

Blending process of PE (or PP) was carried out at 135°C (or 175°C) for 10 min in a mixer under the atmospheric environment. Scheme I exhibits the processes of blending method and two-step method.

Characterization

Field emission scanning electron microscope (FESEM, A TMX 840) was used to observe the sample surface. All samples were sputtered with gold to endure high voltage within examination via FESEM. Differential scanning calorimetry (DSC) measurements were conducted on Perkin-Elmer DSC-7 at a heating rate of 10°C/min from 25°C to 150°C under a nitrogen atmosphere. Thermal gravimetric analysis (TGA) was carried out on a Perkin-Elmer TGA-7 Series Thermal Analysis System at a heating rate of 10°C/min from 50°C to 700°C under nitrogen gas. Transmission electron microscope (TEM) micrographs of the silica/polyolefin nanocomposites were obtained from a Hitachi H-600 apparatus (Hitachi Corporation, Japan). Samples were prepared via ultramicrotome at room temperature, giving sections of nearly 100 nm in thickness. No further staining was used to improve its contrast. Tensile test was performed on a universal testing machine (CMT-4204, Shenzhen SANS Test Machine Co. Ltd., China) with an extension rate of 100 mm/min at 50% relative humidity at 20°C.
RESULTS AND DISCUSSION

FESEM micrographs of nanosilica particles (Figure 1) show that the average diameter size of nanosilica particles was about 30 nm (Figure 1b), and the nanosilica primary particles agglomerated to form micrometer-scale particles (Figure 1a). In situ polymerization of ethylene was then carried out in the presence of nanosilica particles to prepare PE modified nanosilica (PMS). Its TGA curve (Figure 2) showed that the silica content of PMS was 46.8% (obtained at 600°C).

PMS was then used as nanosilica source for the preparation of silica/PE and silica/PP nanocomposites via blending method. For comparison, silica/PE and silica/PP nanocomposites were also prepared via direct blending of PE and PP with nanosilica particles. The blending parameters and silica contents of silica/polyolefin nanocomposites are listed in Table 1, which shows that the silica contents of PE05, PE10, PE20, PE20M, PP05, PP10, PP20, and PP20M were 0.50 wt%, 1.00 wt%, 2.00 wt%, 2.00 wt%, 0.50 wt%, 1.00 wt%, 2.00 wt%, and 2.00 wt%, respectively.

TEM micrographs of PE05 and PE20 (Figures 3a and 3b) show that most of the nanosilica particles are separated into nanosilica primary particles, and they are dispersed evenly in the polymer matrix, similar to that of PP20 (Figure 3c), showing that the dispersions of nanosilica particles in the silica/polyolefin nanocomposites via two-step method are good. TEM micrograph of PE20M (Figure 3d) shows that most of
the nanosilica particles have still agglomerated to form large particles, indicating that the dispersion of nanosilica particles in the silica/polyolefin nanocomposite via blending method has been inefficient, which was because the nanosilica used in the two-step method was pretreated via an in situ polymerization before blending, and the in situ polymerization process could well separate nanosilica agglomerates into nanosilica primary particles [17-19].

Crystalline melting temperatures ($T_m$), and crystallinities of polyolefin and silica/polyolefin nanocomposites are listed in Table 2. Table 2 shows that the addition of nanosilica into polyolefin had little effect on $T_m$. For example, $T_m$ of PE and silica/PE nanocomposites were very close, ranged from 132ºC to 135ºC. Besides, the addition of nanosilica into polyolefin led to the increase of crystallinity, because the silica particles are known to

![Figure 2. TGA curve of PMS.](image)

![Figure 3. TEM photos of: (a) PE05, (b) PE20, (c) PP20, and (d) PE20M.](image)
nucleate the polymer crystallization, increasing its crystallinity [20,21]. For example, crystallinities of PE05, PE10, PE20, and PE20M were 68.6%, 69.1%, 68.3%, and 66.3%, higher than that of pure PE, which was 63.1%. Furthermore, PE20M (or PP20M) had higher crystallinity than PE05, PE10, and PE20 (or PP05, PP10, and PP20), because the former had fewer silica particles (most of the nanosilica particles in the former agglomerated), showing the advantage of two-step method in producing nanocomposite with high crystallinity.

TGA curves of PE and silica/PE nanocomposites are shown in Figure 4. From Figure 4, it can be found that the temperatures of maximum weight loss rate ($T_p$) of PE05, PE10, and PE20 were 463ºC, 464ºC, and 472ºC, respectively, obviously higher than that of LLDPE, which was only 416ºC, indicating the great effect of the addition of nanosilica particles into the polymer matrix on the thermal stability of polymer, and the thermal stability of the composites increased along with the increase of silica content. Furthermore, $T_p$ of PE20M was 430ºC, higher than that of LLDPE, PE20M.

Table 1. Blending parameters and silica contents of silica/polyolefin nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PMS (g)</th>
<th>polyolefin (g)</th>
<th>Yield (g)</th>
<th>Silica contenta (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE05</td>
<td>0.80</td>
<td>69.2 (PE)</td>
<td>70</td>
<td>0.50</td>
</tr>
<tr>
<td>PE10</td>
<td>1.50</td>
<td>68.5 (PE)</td>
<td>70</td>
<td>1.00</td>
</tr>
<tr>
<td>PE20</td>
<td>3.00</td>
<td>67.0 (PE)</td>
<td>70</td>
<td>2.00</td>
</tr>
<tr>
<td>PE20Mb</td>
<td>0.00</td>
<td>68.6 (PE)</td>
<td>70</td>
<td>2.00</td>
</tr>
<tr>
<td>PP05</td>
<td>0.80</td>
<td>69.2 (PP)</td>
<td>70</td>
<td>0.50</td>
</tr>
<tr>
<td>PP10</td>
<td>1.50</td>
<td>68.5 (PP)</td>
<td>70</td>
<td>1.00</td>
</tr>
<tr>
<td>PP20</td>
<td>3.00</td>
<td>67.0 (PP)</td>
<td>70</td>
<td>2.00</td>
</tr>
<tr>
<td>PP20Mc</td>
<td>0.00</td>
<td>68.6 (PP)</td>
<td>70</td>
<td>2.00</td>
</tr>
</tbody>
</table>

(a) Calculated from $W_{PMS}/W_{product} \times 46.8%$; (b,c) silica resource was nanosilica, in which 1.40 g of nanosilica was used.

Table 2. Results of DSC characterization.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_m$ (ºC)</th>
<th>$\Delta H_f$ (J/g)</th>
<th>Crystallinitya (%)</th>
<th>Sample</th>
<th>$T_m$ (ºC)</th>
<th>$\Delta H_f$ (J/g)</th>
<th>Crystallinityb (%)</th>
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</thead>
<tbody>
<tr>
<td>PE</td>
<td>132</td>
<td>188</td>
<td>63.1</td>
<td>PP</td>
<td>167</td>
<td>83.4</td>
<td>40.3</td>
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<tr>
<td>PE05</td>
<td>134</td>
<td>202</td>
<td>67.6</td>
<td>PP05</td>
<td>169</td>
<td>96.9</td>
<td>46.6</td>
</tr>
<tr>
<td>PE10</td>
<td>134</td>
<td>209</td>
<td>69.3</td>
<td>PP10</td>
<td>170</td>
<td>95.8</td>
<td>45.8</td>
</tr>
<tr>
<td>PE20</td>
<td>135</td>
<td>208</td>
<td>68.3</td>
<td>PP20</td>
<td>170</td>
<td>97.6</td>
<td>46.2</td>
</tr>
<tr>
<td>PE20M</td>
<td>134</td>
<td>202</td>
<td>66.3</td>
<td>PP20M</td>
<td>170</td>
<td>93.4</td>
<td>44.2</td>
</tr>
</tbody>
</table>

(a) Calculated from $K \times \Delta H_f/\Delta H_f100\%$, $\Delta H_f100\% = 298$ J/g, $K_{PE} = 1$, $K_{PE05} = 0.995$, $K_{PE10} = 0.99$, $K_{PE20/PE20M} = 0.98$;
(b) calculated from $K \times \Delta H_f/\Delta H_f100\%$, $\Delta H_f100\% = 207$ J/g, $K_{PP} = 1$, $K_{PP05} = 0.995$, $K_{PP10} = 0.99$, $K_{PP20/PP20M} = 0.98$.

Figure 4. TGA curves of PE, PE05, PE10, PE20, and PE20M.
which further confirmed that the addition of nanosilica could increase the thermal stability of LLDPE. However, $T_p$ of PE20M was obviously lower than those of PE05, PE10, and PE20. The reason was that the dispersion of nanosilica particles in PE20M was worse than those in PE05, PE10, and PE20, which affected the full role played by nanosilica. PP and PP nanocomposites were also characterized via TGA. TGA results showed that $T_p$ of PP05, PP10, PP20, and PE20M were 408°C, 411°C, 416°C, and 398°C, higher than that of PP (387°C), showing the great improvement of PP thermal stability via the addition of nanosilica particles. These showed that silica/polyolefin nanocomposites prepared via two-step method had higher thermal stability than those prepared via blending method.

The tensile test results of PE, PP, and their nanocomposites are listed in Table 3. From Table 3, it can be found that the tensile mechanical properties of silica/PE and silica/PP nanocomposites were higher than those of pure PE and PP [2], and they increased along with the raised silica content as the silica content was not higher than 2 wt%. For example, the strength, modulus, and elongation of PE05 were 25.9 MPa, 297 MPa, and 903%, respectively, larger than those of pure PE, which were 24.3 MPa, 282 MPa, and 900%, respectively. As the silica content in the nanocomposites increased to 1.0 wt% (PE10) and 2.0 wt% (PE20), their strengths increased to 26.5 MPa and 28.3 MPa, modulus increased to 303 MPa and 317 MPa, elongation increased to 960% and 1030%, respectively. In addition, due to the better dispersion of nanosilica particles in the polymer matrix, the tensile mechanical properties of PE20 (or PP20) were better than those of PE20M (or PP20M) at the same silica content, for example, strength, modulus, and elongation of PP20 were 35.5 MPa, 623 MPa, and 49.9%, respectively, while those of PE20M were 34.3 MPa, 592 MPa, and 48.3%, respectively.

**CONCLUSION**

In summary, silica/polyolefin nanocomposites prepared via two-step method has demonstrated the advantage of those prepared via blending method in nanosilica dispersion, thermal stability, crystallinity, tensile mechanical properties, etc. Besides, the two-step method could utilize minimum amount of in situ polymerization product to produce maximum amount of nanocomposite and take advantage of the simplicity of blending method in preparing nanocomposite. Simply the two-step method could easily and cheaply produce a large amount of nanocomposite with high quality.

**ACKNOWLEDGEMENT**

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