The Study of Morphology and Mechanical Properties of Compatibilized Polypropylene/Zinc Oxide Composites*

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Abstract
The paper studies the influence of compatibilizer (polypropylene-graft-maleic anhydride, PP-g-MA) on morphology and mechanical properties of polypropylene/zinc oxide composites. Polypropylene (PP) and zinc oxide (ZnO) composites were prepared by melt mixing technique in a twin screw extruder. The Young’s modulus and impact strength of the composites increased as ZnO loading increased, but the impact strength was decreased with the addition of the compatibilizer. The tensile strength of the composites before and after adding compatibilizer was almost the same with the pure PP. The dispersion of ZnO in the matrix polymer was investigated using scanning electron microscope (SEM). The results obtained show that the addition of a small of PP-g-MA compatibilizer during melt extrusion improved the dispersion of ZnO particles.

Key words: Polymer, Composites, Zinc Oxide, Morphology, Mechanical Properties

1. Introduction
The purpose of adding inorganic mineral fillers are used to fulfill a functional rule, such as increasing the stiffness, dimension stability, heat distortion temperature, hardness and toughening of the polymers [1-4]. The properties of particulate filled polymer composites depend on the particle size, shape, loading, dispersion and interfacial bonding [5-6]. The dispersion of fillers in polymer matrix has influence on the physical, mechanical, and thermal properties of polymers.

PP as one of the most important commodity polymers is widely used in technical applications. Because of its good processability, relatively high mechanical properties, great recyclability, and low cost. PP has found a wide range of applications in the household goods, packaging, and automobiles [7]. PP has no polar groups in the chain [4]. Efforts were made to improve the mixing of ZnO in PP by using functional oligomers as compatibilizer. Blending of PP with rigid inorganic particles is a promising approach to improve both stiffness and toughness of plastics simultaneously [8].

Thio et al. [9] used three types of CaCO₃ particle with average diameters of 0.07, 0.7 and 3.5 μm to toughen PP. It was reported that the 0.7 μm diameter particles improved Izod impact strength up to four times that of the unfilled matrix. The other particles, 0.07 and 3.5 μm, had either adverse or no effect on impact toughness due to their poor dispersion. Dispersion quality of particles played a crucial role in toughening efficiency. Gaymans et al. [10] reported that stearic acid coated particles showed a large positive effect on impact strength caused by the improved dispersion in PP. In addition, there was the use of compatibilizer to improve the dispersion of particles in the polymer matrix. Jie Ren et al.
[11] reported that PVC/VAc/OMMT nanocomposites show higher values of tensile strength, elongation at break and impact strength than PVC/OMMT nanocomposites, and nanocomposites containing more compatibilizer also display better mechanical properties.

Ma et al. [12] investigated the effects of nanoscale ZnO on the electrical and physical characteristics of the polystyrene (PS) nanocomposites. It was reported that the addition of ZnO nanopowder increased the flexural modulus and reduced the flexural strength. The silane coupling agents improved the flexural properties of the nanocomposites. The glass-transition temperatures and thermal degradation temperatures of the ZnO/PS nanocomposites increased with ZnO content. Chae et al. [13] prepared PS/ZnO nanocomposites by solution mixing and investigated the effects of ZnO nanoparticles on the physical properties of PS. They found that the thermal stability of PS was enhanced with increasing ZnO content.

In this work, we study the influence of compatibilizer (polypropylene-graft-maleic anhydride, PP-g-MA) on morphology and mechanical properties of PP/ZnO composites before and after adding PP-g-MA compatibilizer. Because of twin screw extruder is practically more convenient to compound polymer blends and composites in large batch sizes in the plastics industry thus we used a twin screw extruder to compound PP with ZnO and the compatibilizer. We use polypropylene-graft-maleic anhydride (PP-g-MA) as the compatibilizer.

2. Experimental

Materials

Pure PP (Mophen HP400K) and polypropylene-graft-maleic anhydride (PP-g-MA) as a compatibilizer were supplied by HMC Polymers Co, Ltd. and Creative Polymers Ltd., respectively. The melt flow rates of such materials are 4 dg/min and 120 g/10 min, respectively. Zinc oxide with a particle size about 135 nm purchased from S.R.LAB Co., Ltd. Zinc oxide is in form of a white powder.

Sample Preparation

Pure PP pellets, PP-g-MA pellets and ZnO particles were dried in an oven at 70 °C for 4 hrs before melt extrusion. The PP pellets and ZnO particles were melt-compounding with and without PP-g-MA compatibilizer in desired compositions in a twin screw extruder at temperatures in a range of 160-220 °C and a screw rotation rate of 50 rpm. The extrudates were palletized at the die exit. After compounding, the blends were compression molded into standard dumb-bell tensile bars and rectangular bars, the mold temperature was kept at 190 °C.

Tensile Test

Tensile tests were conducted according to ASTM D 638 with a universal tensile testing machine LR 50k from Lloyd instruments. The tensile tests were performed at crosshead speed of 50 mm/min. Each value obtained represented the average of five samples.

Charpy Impact Test

Charpy impact strength tests were performed according to D 6110-06 standard at room temperature. Each value obtained represented the average of five samples.

Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) were taken to study the morphology of the PP/ZnO composites and to evaluate the dispersion quality of the ZnO particles, the impact-fractured surfaces of the PP/ZnO composites obtained from impact test were
examined. All specimens were coated with gold before SEM observations.

3. Experimental Results and Discussion

Tensile Properties

The trend in variation of the tensile strength of PP/ZnO composites is presented in Fig. 1. The values of tensile strength did not change much by adding 0.5 – 8 wt% of ZnO. It is shown that the ZnO content did not improve on tensile strength of PP that the specimens prepared by compression molding. It is well known that the tensile strength of a particulate composite is usually reduced with filler content following a power law in the case of a poor filler/matrix bonding. That means, the strength of the composite cannot be greater than that of the unfilled version because the filler particles do not bear any fraction of the external load [14].

The Young’s modulus of the composites increased after adding ZnO, as shown in Fig. 2. For the low ZnO contents, the Young’s modulus increased slowly with increasing ZnO content. For the high ZnO contents, the Young’s modulus increased fast with increasing ZnO content.

![Fig. 1 Tensile strength of PP and PP/ZnO composites.](image)

Table 1 shows the values of Young’s modulus and the tensile strength for PP/ZnO composites (4 wt% of ZnO) before and after adding PP-g-MA compatibilizer. It can be seen that Young’s Modulus increased after adding PP-g-MA, while the values of tensile strength did not change with PP-g-MA content. The PP-g-MA had no effect on the tensile strength.

Impact properties

Fig. 3 indicates that impact strength shows same tendency with Young’s modulus with increase in ZnO content. It can be seen that impact strength increased after adding ZnO. It was interesting that, when the ZnO content was low, the impact strength of PP composites increased. When the ZnO was high, the impact strength decreased. It was that, when high content was incorporated, the dispersion of ZnO was very difficult, because particle with high surface energy were easy to agglomerate [15]. The agglomerates could decrease the impact strength.
Fig. 2 Young’s modulus of PP and PP/ZnO composites.

Table 1 Mechanical properties of PP/ZnO composites and compatibilized composites.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Young’s modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
</tr>
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<tbody>
<tr>
<td>Pure PP</td>
<td>1311.69</td>
<td>32.82</td>
</tr>
<tr>
<td>4% ZnO/PP</td>
<td>1375.84</td>
<td>32.28</td>
</tr>
<tr>
<td>4% ZnO/PP + 1% PP-g-MA</td>
<td>1448.25</td>
<td>32.99</td>
</tr>
<tr>
<td>4% ZnO/PP + 3% PP-g-MA</td>
<td>1394.16</td>
<td>33.09</td>
</tr>
</tbody>
</table>

Fig. 3 Impact strength of PP and PP/ZnO composites.

The impact strength values of PP/ZnO composites before and after adding PP-g-MA are listed in Table 2. It shows that the impact strength decreased with increasing of PP-g-MA content. With the addition of PP-g-MA, the interfacial bonding between the ZnO
particles and the matrix was highly improved, thus the crack was not initiated at the interface, but at the ZnO particles, when the impact occurred [16]. The PP-g-MA is more brittle than the PP polymer, and this causes decreased impact strength in the composite.

Table 2 Impact strength of PP/ZnO/PP-g-MA composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Impact strength (mJ/mm²)</th>
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<tbody>
<tr>
<td>4 % ZnO/PP</td>
<td>3.037</td>
</tr>
<tr>
<td>4 % ZnO/PP + 1 % PP-g-MA</td>
<td>2.934</td>
</tr>
<tr>
<td>4 % ZnO/PP + 3 % PP-g-MA</td>
<td>2.837</td>
</tr>
</tbody>
</table>

Morphological Characteristics

The morphologies of fracture surface of impact specimen of composites filled with ZnO particles were examined by SEM. Fig. 4(a-f) show the micrographs of the fracture surface of impact sample of PP composites filled with 0.5, 1.0, 2.0, 4.0 and 8.0 wt% of ZnO, respectively. It was observed that the dispersion of ZnO particles was relatively good, only few aggregated existed as shown in Fig. 4(b-e), except Fig. 4(f) shows the ZnO particles formed many aggregates. The ZnO aggregates may be influence on the mechanical properties of PP composites.

The dispersion of nanoparticles in PP melt depends on both extrinsic and intrinsic variables. Extrinsic variables include screw configuration, extrusion temperature, screw speed, etc [8]. Intrinsic variables include compatibility between PP and ZnO. In our work, we chose the addition of PP-g-MA compatibilizer to improve the compatibility between PP and ZnO and the dispersion of ZnO particles.
The effect of PP-g-MA compatibilizer on the dispersion of the PP/ZnO composites was studied by use of SEM. Fig. 5 shows micrographs of 4.0 wt% of ZnO/PP after adding 1.0 wt% and 3.0 wt% of PP-g-MA, respectively. It can be seen the dispersion of ZnO after adding PP-g-MA compatibilizer was uniformly dispersed in polypropylene matrix and formed less aggregates as shown in Fig. 5(a-b). With the addition of PP-g-MA, the interfacial bonding between ZnO particles and the matrix polymer were improved. The results show that the PP-g-MA compatibilizer enhanced the interaction between ZnO and PP matrix.

4. Conclusions

PP/ZnO composites before and after adding PP-g-MA compatibilizer were prepared by melt compounding in a twin screw extruder. The dispersion quality of ZnO particles in PP and compatibility between PP and ZnO were improved by adding PP-g-MA compatibilizer. The Young’s modulus and impact strength of the composites increased as ZnO loading increased, but the impact strength was decreased with the addition of the compatibilizer.
The tensile strength of the composites before and after adding compatibilizer was almost the same with the pure PP.

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References