Study on the Silicate Dispersion and Rheological Properties of PP/Starch-MB/Silicate Composites

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Abstract: Polypropylene (PP)/corn starch master batch (MB)/modified montmorillonite (silicate) composites with different silicate compositions of 1, 3, 5, and 7 wt% were prepared by melt compounding at 200 °C, using lab scale Brabender mixer. The thermal properties and silicate dispersion of the PP/MB/silicate composites were investigated by differential scanning calorimetry (DSC), thermogravimetric analyzer (TGA), X-ray diffraction (XRD), and transmission electron microscope (TEM). TGA curve indicated an increase in degradation temperature with the silicate amount. The dispersion of the silicate in PP/starch-MB matrix depended on the silicate composition. There was no remarkable change in silicate dispersion of the composite when maleic anhydride modified PP (MAH) was added. The rheological properties of the composites indicated increase in complex viscosity, shear thinning tendency, and viscous property with the silicate amount. These effects were confirmed by an oscillatory viscometer at 200 °C.

Keywords: PP/starch/silicate, nanocomposite, thermal property, rheological property

Introduction

Interest in biodegradable materials is increasing due to the environmental requirements on effective disposal of the polymers after use when it enters the waste stream. Corn starch is one of the biodegradable materials which have been concerned a lot of commercial applications [1-8]. However, the applications have several limitations due to relatively poor physical properties. Blends of polyolefin and starch have been studied by many researchers to improve their properties [1-3,6], but these blends also do not show sufficient physical properties.

There is much interest, scientifically and technologically, in nanocomposites of polymers with nanoscale layered silicates because these materials offer markedly improved properties as compared to the conventional polymer composites [9-17]. Further, these improvements are achieved at very low loadings of the inorganic component. Another field of interest with the polymer nanocomposite was that the melts possess unusual viscoelastic properties such as non-terminal dynamic moduli at low frequency and a high shear thinning tendency [18-20]. The rheology of polymer nanocomposites was not affected by the chemical nature of the polymer but rather by the physical structure of the hybrid. The silicate tactoids form a percolating network as a result of physical jamming, which then offers considerable resistance to deformation and hence the solid-like behavior [18].

Since polypropylene (PP) does not include any polar group in its backbone, it is thought that the homogeneous dispersion of the silicate minerals in PP is not realized. Initial attempts to create the nonpolar polymer/silicate nanocomposites by simple melt mixing were based on the introduction of a modified oligomer to mediate the polarity between the silicate surface and polymer [21-24]. One of the typical examples is PP/silicate nanocomposites system containing the PP which is modified by maleic anhydride (MAH) [22,23].

Although there have been considerable studies on the physical properties of the PP/corn starch master batch (MB) blends and polyolefin nanocomposites, little progress has been made in the effect of the silicate amount and MAH on the characterization and rheological properties of PP/MB/silicate composite. This is the reason that the study of the PP/MB/silicate nanocomposite on the
Table 1. Formulation and Thermal Properties of the PP/MB/silicate Composite

<table>
<thead>
<tr>
<th>Sample</th>
<th>PP/MB (wt%)</th>
<th>Silicate (wt%)</th>
<th>MAH (wt%)</th>
<th>Tm(°C)/ΔH (J/g)</th>
<th>Td (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP/MB</td>
<td>60/40</td>
<td>0</td>
<td>0</td>
<td>105.4/3.1</td>
<td>183.5</td>
</tr>
<tr>
<td>PP/MB-1</td>
<td>59.4/39.6</td>
<td>1</td>
<td>0</td>
<td>105.9/4.9</td>
<td>197.2</td>
</tr>
<tr>
<td>PP/MB-3</td>
<td>58.2/38.8</td>
<td>3</td>
<td>0</td>
<td>106.3/4.6</td>
<td>216.1</td>
</tr>
<tr>
<td>PP/MB-5</td>
<td>57/38</td>
<td>5</td>
<td>0</td>
<td>106.7/3.9</td>
<td>218.5</td>
</tr>
<tr>
<td>PP/MB-7</td>
<td>55.8/37.2</td>
<td>7</td>
<td>0</td>
<td>106.2/3.4</td>
<td>221.2</td>
</tr>
<tr>
<td>PP/MB-5/MAH</td>
<td>48/32</td>
<td>5</td>
<td>15</td>
<td>106.1/7.1</td>
<td>222.1</td>
</tr>
</tbody>
</table>

* The temperature at 3 wt% weight loss

physical properties is a topic of interest. Therefore, this study was carried out to determine the effects of silicate amount and MAH on the physical and rheological properties of PP/starch-MB/silicate composites. The PP/MB/silicate composites were accomplished with a laboratory-scale melt mixer and a systematic study was made on the effects of silicate amount and MAH on the physical properties.

Experimental

Materials and Fabrication of the Composites
Polypropylene (PP) used in this study was PP from Daehan petrochemical of Korea with a melt index = 3.2 g/10 min and a density = 0.9 g · cm⁻³. Corn starch master match (MB) with a melt index = 3.5 g/10 min and a density = 1.1 g · cm⁻³ was used. The modified montmorillonite (Closite silicate, abbreviation: silicate) supplied by Southern Silicate Products was used, which was ion-exchanged with dimethyl dihydrogenate tallow ammonium ions (Tallow was composed pre-dominantly of octadecyl chains with smaller amount of lower homologues. The approximate composition was C₁₈ 65 %, C₁₆ 30 %, and C₁₄ 5 %). Maleic anhydride modified PP (MAH, 0.6 % wt% maleic anhydride grafted, Aldrich) with a melt index = 150 g/10 min and a density = 0.95 g · cm⁻³ were used. All chemicals were used without further purification.

Several types of the PP/starch MB composites with different compositions of the organically modified silicate were prepared by melt compounding at 200 °C, using Brabender mixer with the chamber size of 50 cm³. The PP weight percent of PP/starch MB blend was 60. Screw speed was 60 rpm and the mixing time was 5 min for all the cases. Formulations are summarized in Table 1.

Measurements
FT-IR was used to confirm the chemical structure of the PP/MB/silicate/MAH composites. The FT-IR spectra were recorded on a Bomen-MB-100 FT-IR spectrometer with a 4 cm⁻¹ resolution. DSC and TGA were carried by using Shimadzu TA Instruments (TA50). Heating rates were fixed at 20 °C · min⁻¹ and all measurements were run under an atmosphere of dry nitrogen. X-ray diffraction (XRD) was carried out by using Rigaku X-ray generator (Cu Kα radiation with λ = 0.15406 nm) at room temperature. The diffractograms were scanned in 2θ ranges from 1.2 to 20° at a rate of 2° · min⁻¹. Transmission electron microscope, Pillops CM20, was used to observe the dispersibility of the silicate in hybrids using an acceleration voltage of 120 kV. An ultra-thin section of 70 nm in thickness was prepared by an ultra-microtome Leica EM FCS. Rheological properties was monitored using an oscillatory viscometer (Physica, Rheo-Lab MC 120) in a parallel plate type of geometry (12.5 mm in radius) at 200 °C. Disk-shaped samples were molded at 200 °C by a laboratory hot press under about 2 MPa and dried in a vacuum oven for 24 h at 80 °C before the test. The samples were diameter in 25 mm and thickness was 2 mm. The gap between the plates was 1.2 mm.

Results and Discussion

Characterization of the PP/MB/Silicate Composites
Figure 1 shows the FT-IR spectra of PP/MB/silicate composites with or without MAH. The peak at 3500 cm⁻¹ of the PP/MB indicates the -OH group of starch MB. It is also found that new peaks appear at 1780 cm⁻¹ (C = O) in the PP/MB with MAH compared to the PP/MB without MAH. New peak indicate that MAH has been successfully blended in PP/MB matrix.

Figure 2 shows DSC and TGA thermograms of the PP/MB/silicate composites with different compositions of silicate. The degradation temperature of PP/MB blend without silicate at 3 wt% loss was about 183.5 °C. When the silicate is loaded to PP/MB matrix, the degradation temperature of the PP/MB/silicate composite increased from 183.5 to 218.5 °C. This may result from the thermal barrier property of silicate platelets in the PP/MB matrix. The melting temperature shifts to higher value but no remarkable change in the melting enthalpy displays as the silicate amount increases. Thermal properties of the com-
Figure 1. FT-IR spectrum of the PP/MB blends with MAH.

Figure 2. TGA and DSC thermograms of the PP/MB/silicate composites.

Figure 3. XRD patterns for the PP/MB/silicate composites.

The interlayer distance is determined by the diffraction peak in the X-ray method, using the Bragg equation:

\[ 2d_{001} \sin \theta = \lambda \]

where \( d_{001} \) is the interplanar distance of (001) diffraction face, \( \theta \) is the diffraction position and \( \lambda \) is the wavelength. There is no detectable change in interlayer spacing of the composites according to the silicate content. The interlayer spacing of silicate, PP/MA-1, PP/MA-3, PP/MA-5, PP/MA-7, PP/MA-5/MAH, and silicate are 3.87, 3.90, 3.91, 3.96, 3.98, and 2.31 nm, respectively. Compared to the interlayer spacing of the silicate, the X-ray patterns of the composites showed clearly that the interlayer spacing increased. This fact reveals that the silicates are dispersed homogeneously in the PP/MB matrix. It is well known that MAH is important thing to the silicate dispersion in the PP/silicate composites. The effects of MAH on the interlayer spacing of the silicate in PP/MB matrix were investigated. However, there was no detectable change in the interlayer spacing of the composite with MAH. No effect of MAH on the silicate dispersion can be interpreted by the fact that the polarity of starch MB in PP/MB composites enhances already the dispersion of silicate in PP/MB matrix. In order to confirm the nanoscale dispersion of silicate, the morphology of the composite was observed by transmission electron microscopy (TEM). In Figure 4, the dark lines are the silicate layers. Each layer of silicate is dispersed in the composite. TEM photos showed the similar tendency in interlayer spacing of the composites. From these results, it is found that the polarity of starch MB is an important factor to improve the dispersion of silicate in the PP/MB composites.
Table 2. The Summary for Rheological Properties of PP/MB/silicate Composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>aViscosity Ratio</th>
<th>bSlopes</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP/MB</td>
<td>11.45</td>
<td>1.219</td>
</tr>
<tr>
<td>PP/MB-1</td>
<td>11.72</td>
<td>1.231</td>
</tr>
<tr>
<td>PP/MB-3</td>
<td>12.29</td>
<td>1.248</td>
</tr>
<tr>
<td>PP/MB-5</td>
<td>12.69</td>
<td>1.261</td>
</tr>
<tr>
<td>PP/MB-7</td>
<td>12.96</td>
<td>1.289</td>
</tr>
<tr>
<td>PP/MB-5/MAH</td>
<td>12.19</td>
<td>1.238</td>
</tr>
</tbody>
</table>

aViscosity ratio = \( \eta_{1 \text{rad/sec}} / \eta_{100 \text{rad/sec}} \).
bSlopes calculated by linear regression of plot \( \log G' \) against \( \log G'' \).

The Rheological Properties of PP/MB/Silicate Composites

The rheological properties in molten state are very sensitive to change of network structure as a result of physical jamming of silicate. Oscillatory measurements were used to observe the effects of the silicate on rheological properties of PP/MB blend. The complex viscosities and dynamic modulus obtained for PP/MB/silicate composites before and after loading MAH are shown in Figure 5. The measured temperature and strain were 200 \(^\circ\)C and 5 %, respectively. All data presented in this paper was verified to be in the linear regime at 200 \(^\circ\)C and 5 % strain. The complex viscosities of the composites without MAH showed a monotonic increase at all frequency ranges with increasing silicate concentration as shown in Figure 5(a). The shear sensitivity increased also with the silicate concentration. The shear sensitivity data are summarized in Table 2. The similar behaviors were observed for the silicate-based nanocomposites [18,19,25,26]. The silicate layers would form network locally despite the exfoliation of a composite due to the highly anisotropic nature of the layered silicates. That is, flow-induced alignment of network in the composite results in increase in complex viscosity and shear thinning tendency [27-29]. Compared to PP/MB/MAH blend, the complex viscosity of the PP/MB-5/MAH composite increased dramatically at low frequency region. However, the flow curve displayed similar pattern to the PP/MB-5 composite. Figure 5(b) showed the storage and loss modulus as a function of frequency. There was no detectable change in storage (\( G' \)) versus loss (\( G'' \)) modulus. The storage and loss modulus indicates an elasticity and viscous property in molten state, respectively.

To investigate the effect of the silicate on the modulus further, the plot of log \( G' \) against log \( G'' \) was made for the PP/MB/silicate composites as shown in Figure 6.
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Figure 6. Plots of $G'$ vs. $G''$ and tan $\delta$ ($G''/G'$) of the PP/MB/silicate composites. Solid lines indicate linear regression.

There is a completely different pattern (shift toward right) for the composites. Moving toward right, of course, indicates decrease in elasticity. The linear regression of the plot of log $G'$ against log $G''$ is one of the useful methods to measure the shear sensitivity. The slopes of linear regression are summarized in Table 2. Tan $\delta$ indicates the ratio of loss and storage modulus in molten state. The tan $\delta$ increased with the silicate amount and it means to decrease in elastic property. The decrease in elastic property was postulated that flow-induced alignment of the silicate occurs at higher strain. It is well-known that flow-induced alignment can alter the rheological properties in their molten state [18,27-30].

The mechanical properties of the composites were measured on an Instron tensile machine (Instron 4502). To investigate the effect of silicate on the tensile strength, the fibers were prepared by spinning the composites through a capillary die at 200 °C. The tensile strength of the composite without silicate was 1.21 g/d. On the other hand, the strength of the composite with 5 wt% silicate was 1.34 g/d.

Conclusion

The X-ray pattern showed clearly a new basal reflection peak with very weak intensity at lower angle than the peak of the silicate. This fact reveals that the polarity of starch is one of the factors to enhance the silicate dispersion and dispersed homogeneously in the PP/MB matrix. The modified PP does not significantly affect the silicate dispersion of the PP/MB/silicate composites. As the silicate concentration increased, the PP/MB/silicate composites showed an increase in complex viscosity, shear sensitivity and viscous property. The increase in shear sensitivity can be interpreted by the fact that the silicate form a percolating network as a result of physical jamming, which then offers considerable resistance to deformation and hence the solid-like behavior. Large amplitude dynamic data showed a slight decrease in the storage modulus and it was postulated that flow-induced alignment of the silicate occurs at higher strain.

Acknowledgments

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References

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