Introduction

Polymer/clay nanocomposite (PCN) technology, which offers superior mechanical, thermal, and barrier properties not achievable in conventional polymer composites, has been attracting increasing interests. A technological requirement involved in the process is the delamination of the silicate layers of clay, leading to their nanoscale dispersion in the polymer matrix. Although the PCN technology has been successfully employed to various thermoplastic[1-11] and thermoset polymer systems,[12, 13] it is still at the very early stage of development for polyolefin/clay systems. The technological difficulties with respect to polyolefin/clay nanocomposites principally result from the nonpolar chemical structures of polyolefins; intrinsically it is very difficult for inert polyolefins to penetrate into cation-containing stacked layers of clay and thereby separate them. Nevertheless, both melt intercalation and in-situ polymerization methods have been attempted for polyolefin/clay systems. Melt intercalation generally involves the addition of functionalized polyolefins, as was reported for the poly(propylene)/clay nanocomposite accomplished with the aid of maleic anhydride-functionalized poly(propylene).[13, 14] As for the in-situ polymerization method, it was recently reported that the polymerization of olefin using methylaluminoxane-activated transition-metal catalysts incorporated in between silicate layers caused their exfoliation.[15-19] Comparison of silicate dispersions showed that the in-situ polymerization method was more effective in nanocomposite formation than the melt intercalation method.[19]

In this study, we have developed an in-situ exfoliation method during ethylene polymerization by fixing a Ti-based Ziegler-Natta catalyst at the inner surface of montmorillonite. Both intercalated and non-intercalated montmorillonites have been used and their exfoliation characteristics have been examined. The fully exfoliated montmorillonite can be used as a master batch to prepare a polyolefin nanocomposite material.

Experimental Part

Materials

Natural sodium montmorillonite (Cloisite® Na⁺, MMT-Na) and organophilically modified montmorillonite (Cloisite® 30B, MMT-OH) supplied by Southern Clay Products Inc. were used as fillers. MMT-OH contains methyl tallow bis(2-
hydroxymethyl) quaternary ammonium (MT2EtOH) between the silicate layers with an MT2EtOH concentration of 90 meq/100 g. Both montmorillonites were dried in a vacuum oven for more than 24 h before treatment. Ethylene (Daelim Chemical Co., 99.9%) used as a polymerization monomer was dried through a column of molecular sieves 3 Å and deoxygenated with oxygen-trap before polymerization. Toluene was used as a solvent after it was dried over calcium hydride and sodium followed by distillation under reduced pressure. Titanium tetrachloride (TiCl4, 1 mol/L solution in toluene, Aldrich Chemical Co.) and triethylaluminium (Et3Al, 1.9 mol/L solution in toluene, Aldrich Chemical Co.) were used as received without further purification.

Catalyst Fixation onto Montmorillonite and Ethylene Polymerization

Fixation of the catalyst on the surface of montmorillonite and polymerization of ethylene were consecutively carried out in a 1 L high pressure glass reactor (Reaction Engineer, Korea) equipped with a magnetic drive. 5 g of dried montmorillonite were charged to the reactor and well dispersed in 200 mL of toluene. TiCl4 was then injected into the slurry. Typically, 0.9 mmol of TiCl4 were added, and fixation was performed at 30 °C. Then, typically, 36.0 mmol of Et3Al were introduced to activate TiCl4. The injection of ethylene started polymerization. The polymerization temperature varied between 30 and 50 °C, and polymerization pressure was fixed at 4 bar in all experiments. After predetermined reaction times, polymerization was quenched with a diluted HCl solution in methanol. The polymer was precipitated in methanol, separated by filtration, and dried in a vacuum oven.

Characterization

IR spectra were measured on a Nicolet Magna-IR Spectrometer 750 using KBr pellets. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC7 under a nitrogen atmosphere with a heating rate of 10 °C/min in a temperature range of 50 to 200 °C. Wide-angle X-ray diffraction (WAXD) was performed on a Mac Science M18XHF using CuKα radiation (λ = 1.5406 Å) with a scanning rate of 2 °/min. Samples for transmission electron microscopy (TEM) were prepared using an ultramicrotome with a diamond knife and observations were carried out on a Jeol JEM-100CXII. Scanning electron microscopy (SEM) observations were carried out on a Hitachi S-2500C microscope with samples being coated with gold in a sputter coater. The molecular weight of polyethylene (PE) was determined on a Waters 150C gel permeation chromatography (GPC) equipped with two Waters Styragel® columns (HT4 and HT5) using o-dichlorobenzene as the solvent at 140 °C and a column flow rate of 0.3 mL/min. For the separation of PE from powdery PE/montmorillonite composite, Soxhlet extraction was conducted using o-dichlorobenzene as the solvent. Standard polystyrene (Polymer Laboratories) was used for GPC calibration.

Results and Discussion

The fixation of the catalyst in between the silicate layers of montmorillonite is the most important step in producing in-situ polymerized nanocomposites. It clearly depends on the concentration of reactive sites on the surface of montmorillonite for chemically anchoring catalysts. Another important parameter could be the interlayer distance of the silicate layers that determines the ease of catalyst approach to reactive sites. We have selected MMT-OH as a supporting medium among various kinds of modified montmorillonites since it offers a high concentration of reactive hydroxyl groups as well as a wide interlayer distance of 18.8 Å. Scheme 1 shows the TiCl4 fixation mechanism between the silicate layers of MMT-OH. The quantitative determination of saturation concentrations of TiCl4 fixed on the surface of MMT-Na and MMT-OH was conducted by reacting excessive amounts of TiCl4 with the montmorillonites and measuring the fixed amount of Ti by means of inductively coupled plasma (ICP). Saturation concentrations for MMT-Na and MMT-OH were 23.4 mmol/100 g and 75.4 mmol/100 g, respectively. MMT-OH has a higher saturation value because it contains higher amounts of hydroxyl groups than MMT-Na.

Table 1 summarizes the experimental conditions for catalyst preparation and subsequent polymerization results. In order to avoid free unsupported TiCl4 on the surface of montmorillonites, the amount of TiCl4 added for polymerization varied within the saturation concentration of TiCl4 fixed at each montmorillonite based on ICP results. As shown in the table, catalyst activity expressed in kg · PE/mol · Ti · h is relatively low. This low catalyst activity can be explained with the kinetic results typical of the composites prepared from MMT-OH (PE/MMT-OH), which show a rapid decrease in polymerization rate as illustrated in Figure 1 by the amount of ethylene in standard cm3/min (scm) injected during polymerization. The fast decrease in polymerization rate probably resulted from the deactivation of titanium catalyst by the dangling hydroxyl groups present in MT2EtOH, which did not participate in the TiCl4 fixation reaction. This might also play an important role in controlling the molecular weight of the synthesized polymer. The catalyst activity was significantly dependent on the Al/Ti molar ratio as shown in Figure 2. Catalyst activity increased with increasing the Al/Ti molar...
ratio. Et₃Al plays a major role in reducing TiCl₄ for initiating the polymerization. In this experimental system, however, it is presumed that it also reacted with the hydroxyl groups of MT₂EtOH, to some extent resulting in a prohibition of catalyst deactivation by MT₂EtOH. This probably contributed to the increase in catalyst activity with an increase in the Al/Ti molar ratio.

Typical melting temperatures, degrees of crystallinity, and molecular weights of the in-situ polymerized composites are listed in Table 2. The degree of crystallinity was measured by means of DSC, using the ratio of fusion enthalpies of product to folded-chain PE. For the determination of molecular weight, PE was extracted for 48 h from the powdery PE/montmorillonite composite. PEMMT-OH had lower molecular weight than the composite prepared from MMT-Na (PEMMT-Na). This might support the easy catalyst deactivation by the hydroxyl groups of MT₂EtOH as mentioned above.

Table 1. Experimental conditions for in-situ polymerization of ethylene using MMT-OH and MMT-Na fillers, and corresponding polymerization results. (The amount of filler used in the polymerization was 5 g, and ethylene pressure was fixed to 4 bar.)

<table>
<thead>
<tr>
<th>No.</th>
<th>Filler</th>
<th>TiCl₄ mmol</th>
<th>Al/Ti</th>
<th>Temperature °C</th>
<th>Catalyst efficiency kg·PE/mol·Ti·h</th>
<th>2θ/d (WAXD) ° deg/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MMT-OH</td>
<td>0.45</td>
<td>20</td>
<td>30</td>
<td>5.7</td>
<td>5.04/17.59</td>
</tr>
<tr>
<td>2</td>
<td>MMT-OH</td>
<td>0.67</td>
<td>20</td>
<td>30</td>
<td>11.8</td>
<td>no peak</td>
</tr>
<tr>
<td>3</td>
<td>MMT-OH</td>
<td>0.9</td>
<td>20</td>
<td>30</td>
<td>16.9</td>
<td>no peak</td>
</tr>
<tr>
<td>4</td>
<td>MMT-OH</td>
<td>0.9</td>
<td>50</td>
<td>30</td>
<td>21.5</td>
<td>no peak</td>
</tr>
<tr>
<td>5</td>
<td>MMT-OH</td>
<td>0.9</td>
<td>100</td>
<td>30</td>
<td>49.6</td>
<td>no peak</td>
</tr>
<tr>
<td>6</td>
<td>MMT-OH</td>
<td>0.9</td>
<td>50</td>
<td>50</td>
<td>47.2</td>
<td>no peak</td>
</tr>
<tr>
<td>7</td>
<td>MMT-OH</td>
<td>0.9</td>
<td>100</td>
<td>50</td>
<td>80.0</td>
<td>no peak</td>
</tr>
<tr>
<td>8</td>
<td>MMT-Na</td>
<td>0.45</td>
<td>20</td>
<td>30</td>
<td>9.8</td>
<td>8.76/10.09</td>
</tr>
<tr>
<td>9</td>
<td>MMT-Na</td>
<td>0.9</td>
<td>20</td>
<td>30</td>
<td>60.0</td>
<td>6.24/14.15</td>
</tr>
</tbody>
</table>

a) Wide-angle X-ray diffraction (WAXD) results, indicating scattering angle 2θ and the corresponding basal spacing value d.
b) No peak denoted the complete disappearance of the basal peak appearing for pristine MMT-OH.

Figure 3 shows WAXD patterns of pristine MMT-Na, MMT-OH, and the composites obtained from in-situ polymerization of ethylene for individual montmorillonites. For the WAXD observation of composites, dried powdery reaction products were directly used without further processing. Scattering angle 2θ values for pure
MMT-Na and MMT-OH were 7.52° and 4.68°, respectively, which correspond to a basal spacing of 11.7 and 18.8 Å. The WAXD curve of PEMMT-OH displays the complete disappearance of the basal peak, indicating that silicate layers of MMT-OH were fully exfoliated during polymerization. On the other hand, in the case of PEMMT-Na, a slight shift to a low scattering angle of MMT-Na is observed. A complete disappearance of the basal peak could however not be investigated even though polymerization was performed with increased TiCl4 concentrations fixed on MMT-Na. This indicates that ethylene polymerization predominantly occurred outside the silicate layers of MMT-Na.

After the confirmation of exfoliation for PEMMT-OH, we were interested in the critical concentration of supported titanium catalyst above which exfoliation of MMT-OH can occur. Table 1 lists the various reaction conditions where exfoliation of MMT-OH was successfully achieved. Since the exfoliation of MMT-OH depends on the number of growing polymer sites as well as on the molecular weight of the synthesized polymer, the critical concentration sensitively varies with reaction parameters, such as temperature, pressure, Al/Ti molar ratio, etc. At 30°C and a Al/Ti molar ratio of 20, the critical Ti concentration was approximately 0.134 mmol/g · MMT-OH, which is 17.8% of saturation concentration of Ti fixed for MMT-OH.

The microscopic differences between the two composites of PEMMT-OH and PEMMT-Na are obvious from a comparison of the morphologies by means of electron microscopy as illustrated in Figure 4. Pristine montmorillonites MMT-Na and MMT-OH are stacked aggregates of polygonal structure, whose sizes range between approximately 2 and 5 μm. Both PEMMT-OH and PEMMT-Na are composed of finely dispersed particles, but the particle size distribution of PEMMT-OH is more uniform than that of PEMMT-Na. PEMMT-OH shows particle sizes smaller than pristine MMT-OH, probably because of the fragmentation of original aggregates. Since the size of each particle in PEMMT-OH is in accord with the basic dimension of the flat plate of montmorillonite, we speculate that each particle corresponds to the stacked sheets of silicate layer, which are exfoliated with PE like a stretched accordion fold. In the case of PEMMT-Na, particles smaller than 1 μm can be observed, which are loosely secured on large particles. These are most likely PE particles that are polymerized at the external surface of the stacked layer.

In order to investigate the micro-dispersion of montmorillonites in PEMMT-OH, TEM observations were carried out. For the preparation of TEM samples, PEMMT-OH samples were dry-blended with commercial high-density PE (HDPE, Yuhwa Co., M = 280000, Tm = 132.4°C) and processed in a sheet at a temperature lower than 200°C. In order to confirm the retention of the exfoliated state of PEMMT-OH after processing, the dispersion state of montmorillonite in the processed sheet was again investigated by means of WAXD analysis. Interestingly, it was observed that, depending on the processing conditions, stacking recovery of montmorillonites occurred as shown in Figure 5. The appearance of a basal peak at a 2θ value of about 6.0° was observed, but the extent of stacking was sensitively dependent on the processing conditions. Processing of PEMMT-OH through a twin-screw extruder (PRISM®) gave more serious stacking recovery than compression, which indicates that stacking recovery relies on the mixing conditions during processing.

Figure 6 shows the TEM micrograph of the PEMMT-OH composite (8 wt.-% of MMT-OH) processed into a sheet in a compression where the stacking of montmorillonites was minimized. The thread-like dark lines in the figure denote discrete silicate layers. The silicate layers are in disordered state and well dispersed in the whole HDPE matrix. Any dispersion of micron-sized clays is scarcely observed in the whole matrix. However, we
Figure 4. SEM images of (a) pristine MMT-OH, (b) pristine MMT-Na, (c) PEMMT-OH, and (d) PEMMT-Na. For PEMMT-OH and PEMMT-Na samples, see Table 2.

Figure 5. WAXD patterns of (a) powdery PEMMT-OH (20.5 wt.-% of MMT-OH) before processing, (b) compression-molded PEMMT-OH in a sheet diluted with HDPE (5 wt.-% of MMT-OH), and (c) twin screw-extruded PEMMT-OH in a sheet diluted with HDPE (5 wt.-% of MMT-OH).
could observe that thick dark lines are intermingled whose maximum thickness is approximately less than 15 nm corresponding to about 10 silicate layers of stacking. We think that the WAXD results of the processed PEMMT-OH in Figure 5 reveals the stacked part of montmorillonites. Since the surface of montmorillonite is hydrophilic while the HDPE matrix is very hydrophobic, the stacking recovery of montmorillonites is thermodynamically indispensable during processing. A more detailed study on the mechanism of stacking recovery and its relation to processing conditions is needed, however, we believe that the rate of stacking recovery during processing is deeply related with the method of fixing the catalyst. This deserves a high mark in our future work.

**Conclusion**

PE/montmorillonite nanocomposites were successfully prepared by performing in-situ Ziegler-Natta polymerizations of ethylene using the intercalated montmorillonite MMT-OH. Wide interlayer distance and abundant hydroxyl groups of MMT-OH facilitated the fixation of TiCl4/ Et3Al inside the interlayer space, and subsequent polymerization induced a complete exfoliation of the layered silicates. In order to provide the interlayer surface with appropriate expansion force needed for exfoliation, the concentration of catalyst fixed at the inner surface of MMT-OH was properly controlled. Even though the powdery PEMMT-OH obtained from in-situ polymerization showed complete exfoliation, its subsequent processing involving the melting of PEMMT-OH induced the stacking recovery of montmorillonites to some extent depending on the processing conditions.

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