Polyethylene/MMT nanocomposites prepared by in situ polymerization using supported catalyst systems

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Abstract

A polyethylene/montmorillonite (MMT) nanocomposite was prepared by in situ polymerization method using MMT-supported methylaluminoxane (MAO) cocatalyst and/or Cp2ZrCl2 catalyst. The catalyst components had been supported on the unmodified MMT-Na and modified commercial product, Cloisite 25A. With XRD it was found that the layered silicate gallery of Cloisite 25A was exfoliated by incorporating MAO cocatalyst and zirconocene catalyst while the d-spacing of MMT-Na was less changed. The in situ polymerization of ethylene was carried out to prepare the nanocomposite by using the supported MMT, and the fully exfoliated product was obtained with Cloisite 25A. The decomposition temperature of the obtained nanocomposite increased up to 258°C, but the melting temperature was not improved much.

Keywords: Polyethylene; MMT; Nanocomposites; In situ polymerization

1. Introduction

In recent years, polymer/clay nanocomposite have attracted great interest, both in industry and in academy, because they often exhibit remarkable improvement in material properties compared to virgin polymer or conventional micro- and macro-composites [1–3]. Preparation of good products of polymer matrix nanocomposites is a challenging area that draws considerable efforts. Researchers have tried a variety of processing techniques including melt mixing, in situ polymerization and other approaches to make polymer nanocomposites having better interaction between the filler and matrix [4].

Polyolefins such as polyethylene (PE) and polypropylene (PP) are major plastics in world-wide polymer industry. These commodity polymers have been produced with the organometallic coordination catalysts such as heterogeneous Ziegler–Natta type and homogeneous metallocene type catalysts. In recent years, special interests have been devoted to discover an effective immobilization method of the metallocene catalyst on either organic or inorganic materials for the commercial applications [5,6].

Due to the lack of polar group in polyolefins, many efforts have been attempted to improve the dispersion of inorganic fillers such as clay, silica, alumina, etc. into polyolefin matrix for the preparation of effective polyolefin nanocomposites [7–9].

In this article, we described the preparation of a variety of zirconocene/methylaluminoxane (MAO)-supported montmorillonite (MMT)s and the in situ polymerization of ethylene to form PE/MMT nanocomposites. The chemical composition and d-spacing of supported MMT were analyzed, and the dispersion and thermal properties of the obtained PE/MMT nanocomposites were examined.
2. Experimentals

2.1. Materials

The used clays were the unmodified MMT-Na and modified Cloisite 25A (Southern Clay Products, USA) and all experiments were performed in nitrogen atmosphere. The zirconocene catalyst of bis(cyclopentadienyl)zirconium dichloride (Cp2ZrCl2, TCI, Japan) and the modified MAO (MMAO, Type-3A, Al=5.9 wt% in toluene, Akzo Nobel, USA) cocatalyst were used as received. Ethylene (E) monomer was received from Korea Petrochem. Ind. Co., Korea. Toluene (Duxsan Chem. Co., Korea) was distilled with sodium–benzophenone complex.

2.2. Supporting procedure

After being vacuum-dried at 40 °C for 5 days, the clay (1.67 g/L) of MMT-Na or Cloisite 25A was suspended in toluene under nitrogen atmosphere and then MMAO solution (0.29 mol/L g of clay) was added with vigorous stirring at room temperature. After 24 h, the precipitated solid was washed several times with fresh toluene to remove the unreacted MMAO. The obtained MMAO-supported clays were noted as MMT-M and 25A-M, respectively.

In addition, MMT-M and 25A-M (1.58 g/L) were treated with Cp2ZrCl2 toluene solution (2.1×10−4 mol/L g of clay) under nitrogen atmosphere at room temperature. To remove the unsupported zirconocene after 24 h, the treated clays were washed with toluene and the double-supported MMT-MZ and 25A-MZ were obtained, respectively.

2.3. Polymerization

With continuous flow of E under atmospheric pressure, the in situ polymerization was carried out by three methods. At first, the polymerization was initiated with addition of Cp2ZrCl2 toluene solution (5.5×10−5 mol/L) in the presence of MMT-M (\([\text{Al}]=5.2×10^{-3}\) mol/L) or 25A-M (\([\text{Al}]=5.4×10^{-3}\) mol/L) to obtain the PE composites of PE/MMT-1 or PE/25A-1, respectively (Method 1). Without any addition of catalyst components, the polymerization was tried only with MMT-MZ (\([\text{Al}]=5.3×10^{-3}\) mol/L; \([\text{Zr}]=0.2×10^{-5}\) mol/L) or 25A-MZ (\([\text{Al}]=7.2×10^{-3}\) mol/L; \([\text{Zr}]=8.0×10^{-5}\) mol/L) and the prepared composite was noted as PE/MMT-2 or PE/25A-2, respectively (Method 2).

Finally, E was polymerized with MMT-MZ (\([\text{Al}]=5.3×10^{-3}\) mol/L; \([\text{Zr}]=0.2×10^{-5}\) mol/L) or 25A-MZ (\([\text{Al}]=7.2×10^{-3}\) mol/L; \([\text{Zr}]=8.0×10^{-5}\) mol/L) and additional MMAO cocatalyst (0.1 mole/L) to prepare composite of PE/MMT-3 or PE/25A-3, respectively (Method 3).

After certain times, the polymerization was terminated by the addition of acidic ethanol, and then the product was filtered and dried in the vacuum oven (40 °C) for 48 h.

2.4. Characterization

The Al and Zr contents of the supported MMT-M or 25A-M and the double-supported MMT-MZ or 25A-MZ were measured with Inductively Coupled Plasma Mass Spectrometer (ICP-MS, Plasmaquad 3, VG Elemental Ltd, England). The modifier contents of Cloisite 25A and 25A-M as well as 25A-MZ were estimated from nitrogen contents obtained with Elemental Analysis (Fisons, EA 1108, Italy). The d-spacings of the supported clays and the obtained nanocomposites were examined with X-ray diffractometer (XRD, X’pert PRO MRD, Philips, The Netherlands). The melting temperature (\(T_m\)) and maximum decomposition temperature (\(T_{\text{dm}}\)) as well as clay content of nanocomposites were determined by using a differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA, Thermal Analysis 2000, Dupont, USA) with heating rate of 20 °C/min under nitrogen atmosphere. With transmission electron microscopy (TEM, H-7600, 110 kV, Hitachi, Japan), the dispersion of MMT in nanocomposites was observed.

3. Results and discussion

3.1. Structure of supported MMT

First of all, it was found that the composition of modified MMT, Cloisite 25A was changed during the supporting procedure as shown in Table 1. Remarkably more than 90% of modifier was removed by supporting MMAO cocatalyst on Cloisite 25A. On the other hands, the modifier content of 25A-MZ was not changed much in supporting Cp2ZrCl2 catalyst on 25A-M. This result suggested strongly that most of the amine modifier in clay had been removed by MMAO probably due to its high reactivity.

The amounts of supported MMAO cocatalyst and Cp2ZrCl2 catalyst on the unmodified and modified clays were analyzed and the results were given in Table 2. It turned out that a very small portion (<1%) of the added MMAO was actually supported to obtain MMT-M and 25A-M. MMAO content of 25A-M was slightly higher than

| Modifier | CH3 | CH3 - N+ - CH2 CH2 CH2 CH2 CH2 | CH3 |
|----------|-----|--------------------------------|-----|
|          | 1   | 1                              | 1   |
|          |     | HT *                           | CH3 |
| Modifier contents (wt%) | 34.0 | 3.9 | 2.5 |

HT, hydrogenated tallow (~65% C18, ~30% C16, ~5% C14).
that of MMT-M. In addition, the amounts of supported MMAO were changed less during the double-supporting process with Cp2ZrCl2 to produce MMT-MZ and 25A-MZ. Meanwhile, the Cp2ZrCl2 content of MMT-MZ was much less than that of 25A-MZ under this experimental condition.

From the above observations, it was considered that MMAO cocatalyst was supported by the reaction to hydroxyl group of layer surface [10]. The removal of amine modifier could be understood by the reaction of oxygen atoms of MMAO with the ammonium ions to form the zwitterions of alkoxide anion/ammonium cation as suggested by Barren [11]. According to his interpretation the zwitterion can be transferred to a non-hydrogen bonded intermediate and will presumably then undergo the rapid alkane elimination to yield amine. It might be reasonable to assume that this amine could be liberated from the MMT by the formation of Lewis acid–base adduct from the interaction between aluminum atom of MMAO and nitrogen atom of amine.

For confirming the incorporation of MMAO into gallery of MMT, the structures of MMT-Na and Cloisite 25A before and after supporting MMAO and Cp2ZrCl2 were examined with XRD, and the obtained diffraction patterns are given in Fig. 1. As shown in Fig. 1, the d-spacing of MMT-Na increased less (up to only 0.25 nm) while Cloisite 25A was almost exfoliated by incorporating MMAO and Cp2ZrCl2.

From this observation, it could be suggested that the MMAO was supported on MMT-Na by the reaction with surface hydroxyl group, while ca. 20% additional MMAO was incorporated into the gallery of Cloisite 25A by the replacement of organic modifier for the intercalation of MMT. The additional MMAO incorporation into gallery of 25A-M as mentioned above may be understandable on the basis of the fact that the Cp2ZrCl2 content of 25A-MZ was much higher than that of MMT-MZ as shown in Table 2.

### 3.2. In situ polymerization behaviors

In the presence of the clays supported with MMAO cocatalyst (MMT-M, 25A-M) and double-supported with MMAO followed by Cp2ZrCl2 catalyst (MMT-MZ, 25A-MZ), the in situ polymerizations of E were carried out by three methods (described in Section 2.3) to obtain the corresponding nanocomposites such as PE/MMT-1, PE/MMT-2, and PE/MMT-3 as well as PE/25A-1, PE/25A-2, and PE/25A-3, respectively.

The experimental results of catalyst activity and clay content of PE/MMT nanocomposites are given in Fig. 2. As observed in Fig. 2(a), the modified Cloisite 25A support was concluded to produce more polymers than the unmodified clay MMT-Na irrespective of polymerization methods.

### Table 2

| Clay (g/L) | Added MMAO (mol/L) | Supported MMAO (×10³ mol/L) | Supported/added MMAO (%) | Added Cp2ZrCl2 (×10⁴ mol/L) | Supported Cp2ZrCl2 (×10⁵ mol/L) | Supported/added Cp2ZrCl2 (%) |
|-----------|-------------------|----------------------------|--------------------------|-----------------------------|--------------------------------|-----------------------------|
| MMT-M     | 1.67              | 0.29                       | 1.9                      | 0.65                        | –                              | –                           |
| 25A-M     | 1.67              | 0.29                       | 2.3                      | 0.80                        | –                              | –                           |
| MMT-MZ    | 1.58              | –                          | 2.0                      | –                           | 2.1                            | 0.07                        |
| 25A-MZ    | 1.58              | –                          | 2.7                      | –                           | 2.1                            | 0.3                         |

g (in unit); g of clay.

![Fig. 1. X-ray diffraction patterns of MMT-Na (a) and Cloisite 25A (b) before and after supporting MMAO and Cp2ZrCl2.](image-url)
For Cloisite 25A, the Method 3 exhibited the highest catalyst activity among the attempted polymerization methods. In the case of MMT-Na, it hardly obtained PE with MMT-MZ because the \( \text{Cp}_2\text{ZrCl}_2 \) content of MMT-MZ was too small to initiate the polymerization even with a very high mole ratio of \([\text{MMAO}]/[\text{Cp}_2\text{ZrCl}_2]\).

In addition to polymerization methods as well as the initial clay loading, it was possible to control the ratio of PE and clay by varying the polymerization time. For the same initial clay and catalyst loading, the increment of the polymerization time decreased the amount of clay in the final product as shown in Fig. 2(b). The above three variables can be used to effectively control the ratio of PE and clay, which is important if such system is chosen to prepare a master batch of hybrid PE-clay for subsequently blending with other polymers. The polymerization temperature can also affect the clay content in the final product because the catalyst activity decreases with lowering of the polymerization temperature.

The clay content in the final product was determined by TGA, which agreed closely with the clay amount calculated using the values of initial clay loading and polymer yield.

### 3.3. Characterization of PE/MMT nanocomposite

The degree of dispersion of filler into polymer matrix is important for good physical properties and was classified into intercalation and exfoliation, etc. [12].

The dispersion of clay in the PE/MMT-Na composites obtained with Method 1 for different polymerization times was studied by XRD and the patterns are given in Fig. 3. For the unmodified MMT-Na, the \( d \)-spacing of nanocomposite product was slightly larger than that of MMT-Na itself (Fig. 1(a)) and less affected by polymerization times.

On the contrary, the PE/25A nanocomposite was intercalated irrespective of polymerization methods and the diffraction peak disappeared at longer polymerization time as shown in Fig. 4. It was concluded that the in situ polymerization of Method 3 might be suitable for the preparation of PE/clay exfoliated nanocomposite.

The MMT dispersion in nanocomposite obtained with the in situ polymerization of E was probed using TEM. As shown in Fig. 5, the silicate layers are thin enough to produce less diffraction pattern during TEM analysis. There was, however, some indication of partial exfoliation of silicate layer evidenced by the presence of clusters of silicate layers. If the layered silicate would not been exfoliated during the supporting procedure and in situ polymerization, the clusters of silicate at micrometer size range would be present.

The thermal properties of PE/clay nanocomposites obtained for 2 h were measured using TGA and DSC as shown in Fig. 6. From the differential curves of TGA of Fig. 6(a), it was observed that \( T_{\text{md}} \) of PE/MMT-1 nanocomposite was ca. 25°C higher than that of PE.
For PE/25A-1 nanocomposite, $T_{md}$ was ca. 15 °C lower than that of PE and the organic modifier was decomposed at ca. 300 °C, which was confirmed with Cloisite 25A ($T_{md}$=320 °C) itself. It appeared that the presence of alkyl ammonium modifier in Cloisite 25A contributed to the degradation of polymer matrix as well [13].

Fig. 4. X-ray diffraction patterns of PE/Cloisite 25A nanocomposites prepared with various polymerization methods for different polymerization times (h).

Fig. 5. TEM image of PE/25A-1 (2 h) nanocomposite.

Fig. 6. TGA (a) and DSC (b) curves of PE and PE/clay nanocomposites.
In contrast, it was concluded that $T_m$ of PE/clay nanocomposite estimated by DSC was found to be almost same as that of PE itself as shown in Fig. 6(b).

4. Conclusion

For the preparation of catalyst-supported clays, the unmodified MMT-Na and modified Cloisite 25A were supported with MMAO cocatalyst followed by Cp$_2$ZrCl$_2$ catalyst, respectively. With analysis of the supported clays, it was found that the $d$-spacing of the layered silicate gallery of clay increased by the incorporation of MMAO cocatalyst and Cp$_2$ZrCl$_2$ catalyst, and especially for Cloisite 25A the most parts of organic amine modifier were eliminated by MMAO. PE/clay nanocomposites were prepared by the in situ polymerizations of E with supported clay in various methods. The most effective method for the preparation of nanocomposite was found to be the in situ polymerization of E with 25A-MZ and additional MMAO cocatalyst. The exfoliation of layered silicate in nanocomposite was estimated by XRD and TEM. The thermal properties of PE/clay nanocomposite were not improved much.

From the above observations, it was considered that the supporting process allowed the MAO cocatalyst and zirconocene catalyst to react with clay surface and enter into the clay galleries followed by the formation of the active sites for E polymerization. The formation of polymer inside the galleries might lead to the exfoliation of the layered silicate in polymer matrix.

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