

Preparation and Properties of Polyethylene/Montmorillonite Nanocomposites by *In Situ* Polymerization

Feng Yang,¹ Xuequan Zhang,² Haichao Zhao,¹ Bin Chen,² Baotong Huang,² Zhiliu Feng²

¹Department of Chemistry, Northeastern University, Shenyang 110006, China

²Polymer Engineering Laboratory, Changchun Institute of Applied Chemistry, Chinese Academy of Science, Changchun 130022, China

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ABSTRACT: Polyethylene (PE)/montmorillonite (MMT) nanocomposites were prepared by *in situ* coordination polymerization using a MMT/MgCl₂/TiCl₄ catalyst activated by Al(Et)₃. The catalyst was prepared by first diffusing MgCl₂ into the swollen MMT layers, followed by loading TiCl₄ on the inner/outer layer surfaces of MMT where MgCl₂ was already deposited. The intercalation of MMT layers by MgCl₂ and TiCl₄ was demonstrated by the enlarged interlayer spacing determined by WAXD. The nanoscale dispersion of MMT layers in the polyethylene matrix was characterized by WAXD and TEM. As a consequence, the crystallinity of the nanocomposite decreased

sharply, whereas the tensile strength was significantly improved compared to that of virgin polyethylene of comparable molecular weight. The confinement of the nanodispersed MMT layers to molecular chain and the strong interaction between the nanoscale MMT layers and the resin matrix were thought to account for the decrease of crystallinity and the remarkable enhancement of strength. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3680–3684, 2003

Key words: nanocomposites; montmorillonite; *in situ* polymerization; matrix; crystallization

INTRODUCTION

Great economic value of polyolefin/layered silicate nanocomposites is foreseen for applications in various areas; nevertheless, the preparation of such composites, although challenging, is still in its exploratory stage. Melting intercalation of an organically modified silicate with polyolefin is an approach receiving intensive attention^{1–3}; however, the steps of organically modifying the silicate, polarizing the polyolefin or its oligomers, and the chemical or physical deterioration of the virgin components during the mixing process may offset the benefits of the silicate to some extent. *In situ* polymerization is an alternative approach for preparation of polyolefin nanocomposites, which involves intercalation of a silicate by a metallocene or a Ziegler–Natta catalyst, followed by polymerization of an olefin.

In situ polymerization overrides entropic and enthalpic barriers associated with intercalating nonpolar polyolefin with polar silicates; the strongly polar nature of layered silicate is still to be considered for reactions involving metallocene or a Ziegler–Natta catalyst. The seemingly tolerant Brookhart catalyst to-

ward polarity and moisture was found to have a quite low activity in ethylene intercalation polymerization.⁴ To protect the active sites from the poisonous inner surface of the silicate, Tudor et al.⁵ first treated the layered silicate with a large amount of methylaluminoxane (MAO), and then immobilized the metallocene catalyst on the MAO-modified silicate. Unfortunately, *in situ* polymerization with this catalyst gave only propylene oligomers of low activity. Although a polyethylene nanocomposite with superior mechanical properties was prepared by a similar method by Alexandre et al.,⁶ the much lower catalytic activity resulting from the chemically complicated layer surface of the layered silicate and the large amount of MAO needed could be barriers to practical applications. Heinemann et al.⁷ prepared polyethylene nanocomposites through ethylene homo- and copolymerization in the presence of layered silicates treated by various quaternary alkylammonium cations. Although the method was proved to be capable of nanocomposite formation, reinforcement by the silicate was not observed compared to high-density polyethylene homopolymer.

Preparation of polyolefin nanocomposites by *in situ* polymerization, using a typical Ziegler–Natta catalyst, has the advantage of using industrial catalysts, the most cost-effective among coordination catalysts. Qi et al.⁸ prepared PP/MMT nanocomposites with improved dynamic mechanical properties and thermal

Correspondence to: X.-Q. Zhang (xqzhang@ciac.jl.cn).

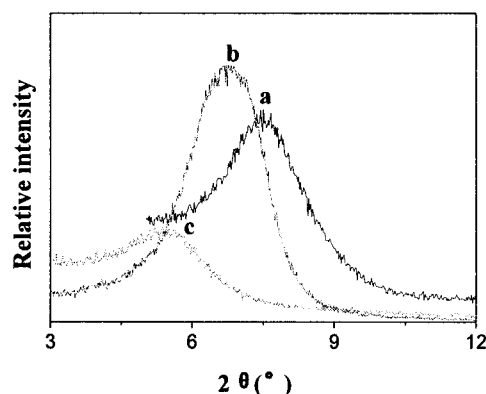


Figure 1 WAXD patterns of (a) MMT, (b) MMT/MgCl₂, and (c) MMT/MgCl₂/TiCl₄ catalyst.

properties using a MMT/MgCl₂/TiCl₄ catalyst, although polymerization results were not reported.

It is well known that MgCl₂ dissolves in alcohols forming MgCl₂·*n*ROH complexes in homogeneous solution. Montmorillonite can swell in alcohols.⁹ When MMT is immersed in a MgCl₂/alcohol solution, MMT can be swelled, thus allowing the diffusion of MgCl₂·*n*ROH complexes into the spacing between the MMT layers. After removal of the alcohol, MgCl₂ as microcrystallites may well deposit on/between the surfaces of layered MMT. In this study, MgCl₂ was first deposited on the layer surfaces of MMT, then MMT/MgCl₂/TiCl₄, similar to a typical high-activity Ziegler–Natta catalyst, was prepared by loading TiCl₄. During the ethylene polymerization process, the layers of MMT could be exfoliated by polymerization force and polyethylene/MMT nanocomposite produced *in situ*.

EXPERIMENTAL

Materials

Cloisite Na⁺ (supplied by Southern Clay) was used after being soaked in a muffle furnace at 400°C for 6 h. Titanium tetrachloride (TiCl₄) was obtained from Beijing Zhonglian Chemical Co. (China). Anhydrous magnesium dichloride (MgCl₂) was supplied by Yingkou Chemical Co. (China). Hexane (supplied by Qimei Co.) as solvent was refluxed and distilled over Na/K alloy before use. *n*-Butanol (A. R. Beijing Chem Factory, China) was dried over molecular sieves and

distilled before use. Triethylaluminum [Al(Et)₃; Aldrich, Milwaukee, WI] was used as received. Polymerization-grade ethylene from Liaoyang Petrochemical Co. (China) was used without further purification.

Preparation of clay/MgCl₂/TiCl₄ catalyst

To the MgCl₂/*n*-butanol homogeneous solution, a calculated amount of Cloisite Na⁺ was added under a nitrogen atmosphere at 60°C. After vigorous stirring for 2 h, excess *n*-butanol was removed by evacuation. The solid was treated with excess TiCl₄ at 60°C for 2 h, after which the suspension was filtered. The precipitate was washed with hexane five times, followed by vacuum drying. A soil-yellow solid was obtained as catalyst. The composition of catalyst was analyzed by inductively coupled plasma–atomic emission spectroscopy (ICP–AES) to be Ti, 1.98 wt % and Mg, 7.5 wt %.

Polymerization of ethylene

Ethylene polymerization was carried out in a 200-mL glass reactor equipped with a mechanical stirrer. After heating and evacuating alternately for about 1 h, the reactor was filled with ethylene to a pressure of 0.01 MPa. Hexane (100 mL), Al(Et)₃, and catalyst ([Al]/[Ti] = 20M ratio) were introduced into the reactor in succession. The polymerization was controlled at 50°C, with an ethylene pressure of 0.01 MPa for a given time, and then terminated with acidified ethanol. The polymerization product was washed with ethanol several times and then dried in vacuum at 60°C for 24 h.

Characterization

The Ti and Mg loadings of the catalyst were determined by ICP–AES on a Plasma–Spec (I) instrument. The molecular weights of samples were measured by gel permeation chromatography (GPC) at 135°C on a PL–GPC 220 with dichlorobenzene as the solvent using polystyrene calibration. Wide-angle X-ray diffraction (WAXD) was used to measure the interlayer spacing of MMT on a D/max 2000PC instrument with Cu–K_α radiation. The dispersion of MMT in the composites was observed by transmission electron microscopy (TEM) on a Hitachi H-800 (Hitachi, Ibaraki, Japan). The specimens were ultrathin-sectioned using an

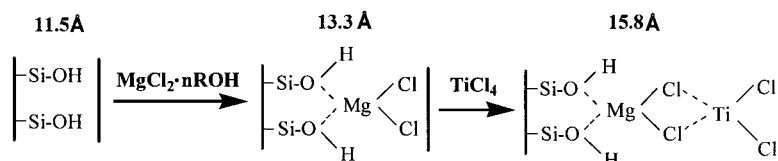


Figure 2 Scheme of intercalated catalyst.

TABLE I
Results of Polymerization^a

Sample	Time (min)	Activities (kg PE/mol Ti h ⁻¹)	Clay content (wt %)	M_w ($\times 10^{-6}$) (g/mol)	M_w/M_n
PE-0	—	—	0	1.3	—
PE-1	180	280	0.08	1.1	3.9
PE-2	150	291	0.13	1.1	3.9
PE-3	120	320	0.16	1.2	3.8
PE-4	90	472	0.22	1.0	4.3
PE-5	60	641	0.56	0.9	5.2
PE-6	45	748	0.67	0.8	7.8

^a Polymerization conditions: Al(Et)₃ as cocatalyst; [Al]/[Ti] = 20, hexane as solvent; polymerization temperature, 50°C.

LKB 2088 microtome (LKB Ultrascan XL, Bromma, Sweden). The thermal behavior of the samples was measured on a Perkin–Elmer DSC-7 differential scanning calorimeter (Perkin Elmer Cetus Instruments, Norwalk, CT) at a scanning rate of 10°C/min. Measurement of the mechanical properties was made on an Instron-1121 electronic tester at a drawing speed of 50 cm/min. The samples were heat-molded into sheets at 210°C and then cut into pieces of dimension 20.0 × 3.85 × 0.65 mm.

RESULTS AND DISCUSSION

Structure and properties of the MMT/MgCl₂/TiCl₄ catalyst

The key factor in preparation of polyolefin/layered MMT nanocomposites by *in situ* polymerization is that the catalyst species can intercalate into the MMT layers efficiently without sacrificing the high catalytic activities of the catalyst.

Figure 1 shows the WAXD patterns of MMT, MMT/MgCl₂, and the MMT/MgCl₂/TiCl₄ catalyst. The procedures of immersing MMT into MgCl₂BuOH solution for a certain time, followed by removal of BuOH, increased the interlayer spacing of MMT from the original 11.5 Å to 13.3 Å, and finally to 15.8 Å after loading TiCl₄. The continuous swell of interlayer spacing of MMT indicated the continuous intercalation of catalyst ingredients into the layers of MMT and that the catalyst was formed in the spacing of neighboring layers of MMT. The possible reactions are schematically shown in Figure 2.

In typical highly active Ziegler–Natta catalysts, MgCl₂ is an essential component in promoting the activity and polymerization behavior of the catalyst. Additionally, on one hand, it may form a single molecular layer along the inner surfaces of MMT layers, avoiding the formation of non/low active species (Si–O–Ti), resulting from the reaction of –OH on the MMT layer surface with TiCl₄,¹⁰ while on the other hand increasing the MMT interlayer spacing, preliminarily making TiCl₄ easier to intercalate into MMT layers.

Table I shows the polymerization data with the

MMT/MgCl₂/TiCl₄ catalyst. The catalyst shows fairly good activity up to 748 kg PE/molTi h⁻¹, behaving like the normal MgCl₂-supported Ziegler–Natta catalysts.

It is possible to obtain PE/MMT nanocomposites of different clay content by changing the polymerization conditions, such as polymerization temperature, ethylene pressure, and [Al]/[Ti] molar ratio. However, the molecular weight of the final product may be altered as well, which is undesirable if one wishes to examine the influence of MMT content on the physical properties of the composites. From Table I, one can notice that the molecular weight of the composites does not alter significantly, with the polymerization time, which remains around 1 × 10⁶ g/mol on average, in the case of a lack of chain transfer reagent. Therefore, as shown in Table I, changing the polymerization time is a simple and efficient way to obtain PE/MMT composites of different MMT content having comparable molecular weight.

Structure of PE/MMT nanocomposites

Figure 3 shows WAXD patterns of the original MMT and PE/MMT composites. The (001) peak of the MMT

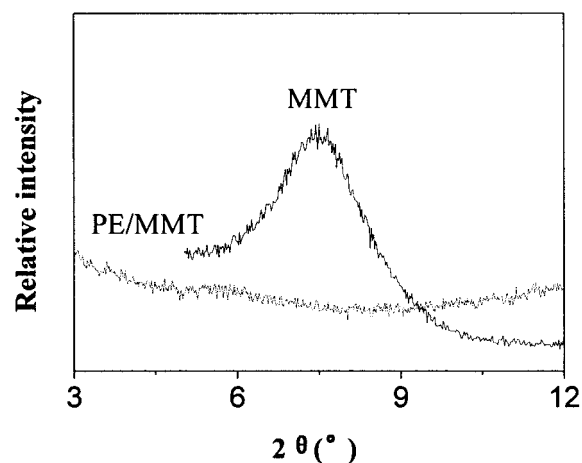


Figure 3 WAXD patterns of MMT and the PE/MMT nanocomposite.

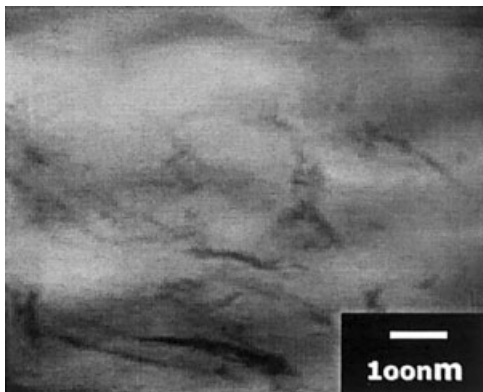


Figure 4 TEM microphotography of PE/MMT nanocomposite.

in the composite shifted from the original $2\theta = 7.6$ to $2\theta = 5.8$ and became significantly diffused, indicating that both intercalation and exfoliation could have occurred.¹¹ Exfoliation structure was confirmed by TEM microphotography (Fig. 4), with MMT layers dispersed in the PE matrix in a single layer or in stacks of a few layers.

Thermal analysis of PE/MMT nanocomposites

DSC curves of PE/MMT composites with different MMT contents are shown in Figure 5 and Figure 6. The melting temperatures and crystallization temperatures of the composites were observed to be almost the same as those of the virgin polymer with the comparable molecular weight. Nevertheless, the heat of fusion, corresponding to crystallinity, decreased sharply (Fig. 6). WAXD patterns also show that the crystalline structure is not different from that of virgin polymer. It seems that the composites have two different components having different crystallizabilities, one having the same crystallization behavior as that of PE, and the other almost unable to crystallize. The failure of crystallization of PE chains is attributed to the confinement of PE

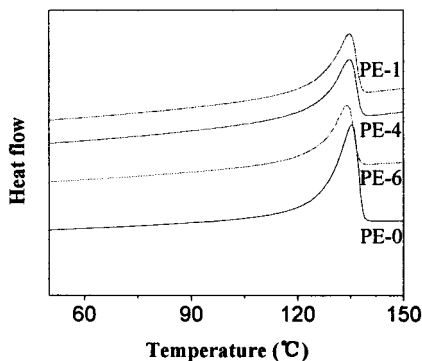


Figure 5 DSC heating thermograms of PE and PE/MMT nanocomposites.

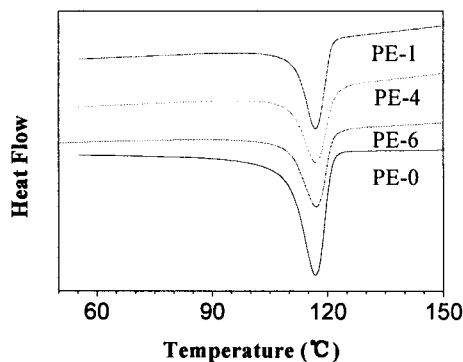


Figure 6 Crystallization thermograms of PE and PE/MMT nanocomposites.

molecular chains by the MMT layers (see Fig. 7). The chain segments are rooted in the MMT layers, which work as a heavy “tail,” and PE near the “tail” is difficult to crystallize.

The xylene-extraction experiments using a Soxhlet extractor show that over 50 wt % of the composites are nonextractable, indicating the strong interaction between MMT layers and PE molecular chains.

Tensile properties of PE/MMT nanocomposites

Figure 8 shows the tensile profiles of PE/MMT composites of different MMT contents. With increasing MMT content, the tensile strength increases monotonically and the tensile elongation increases as well. The tensile strength of the composite with MMT content of 0.7 wt % increases over 65% compared with that of virgin PE. We suggest that the enhanced properties of the material by the MMT result from the enhancement of the amorphous region. The confinement of the MMT layers to the molecular movement makes the amorphous region of the material more rigid and stiff, and the PE/MMT nanocomposite behaves like a miscible mixture of crystalline PE and rigid amorphous PE.

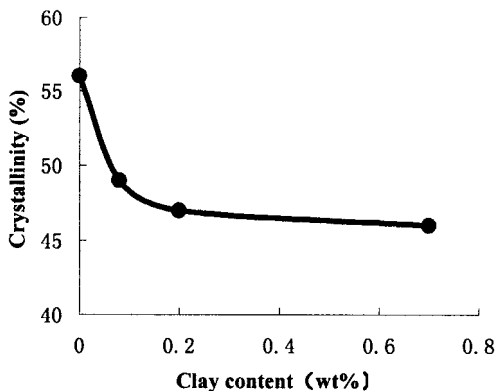


Figure 7 Crystallinity of PE in PE/MMT nanocomposites.

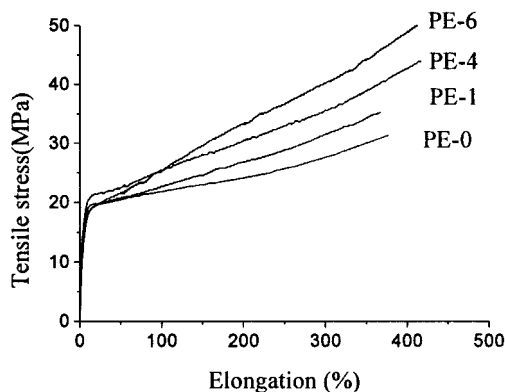


Figure 8 The tensile profiles of PE/MMT nanocomposites.

CONCLUSIONS

PE/MMT nanocomposites with superior tensile properties were prepared by *in situ* intercalative polymerization. WAXD and TEM analyses indicate the occurrence of exfoliation. DSC results show that the melting temperature and crystallization temperature of the nanocomposites are almost the same as those of the virgin PE, whereas the crystallinity decreases sharply with the increase of clay content. We suggest that the

improved tensile strength and decreased crystallinity are attributable to the confinement of clay layers, restricting the movement of PE molecular chains, and the strong interaction between clay and the matrix.

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