J Mater Sci (2007) 42:4350–4355
DOI 10.1007/s10853-006-0692-5

Fabrication and characterization of PE/MMT nanocomposites via copolymerization of ethylene and in situ formed α-olefins

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Received: 4 June 2006 / Accepted: 18 July 2006 / Published online: 28 February 2007

Abstract An iron-based ethylene oligomerization catalyst, $\{[(2\text{-ArN}=\text{C(Me)})_2\text{C}_5\text{H}_3\text{N}]\text{FeCl}_2\}$(Ar = 2-$CH_3$-4-$OCH_3$($C_6H_4$)) (Fe-Cat.) was synthesized and PE/MMT nanocomposites were prepared successfully employing the obtained catalyst supported on MMT and *rac*-Et(Ind)$_2$ZrCl$_2$ (Zr-Cat.) with ethylene as the single monomer and MAO the cocatalyst. The iron-based catalyst could oligomerize ethylene to α-olefins and they copolymerized with ethylene the same time to form PE/MMT nanocomposites in the interlayer of MMT under *rac*-Et(Ind)$_2$ZrCl$_2$. The catalytic system was of high polymeric activities towards ethylene copolymerization and produced branched PE matrix. Characterization of the resultant PE/MMT nanocomposites was performed with ^{13}C nuclear magnetic resonance (NMR), X-ray diffraction (XRD), transmission electron microscopy (TEM), differential scanning calorimeter (DSC), and thermogravimetric analysis (TGA) etc. Also investigated were the mechanical properties of the resulting PE/MMT nanocomposites.

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Introduction

Polymer nanocomposites are a class of hybrid materials composed of an organic polymer matrix that is imbedded with inorganic particles, which have at least one dimension in the range of 1–100 nm [1]. Dramatically improved thermal, physical, electronic and optical properties have been discovered due to the addition of only a few weight percent of the inorganic modifier [1–3]. Due to the synergistic effects resulted from the inexpensive layered silicate or clay, the synthesis and characterization of polymer nanocomposites have aroused great interests [4]. However, such nanocomposites are usually confined to polar polymers and not suitable for nonpolar polyolefin. So the synthesis of polyolefin/clay nanocomposites remains a scientific challenge. There is till now three methods in the preparation of PE/MMT and PP/MMT nanocomposites. The first method is the melt intercalation of a polymer into an organically modified silicate [5]. The second is the solution blending in which an organic-modified clay is dispersed in polyolefin resin dissolved in an organic solvent to form intercalated polyolefin/clay nanocomposite [5]. The last yet most convenient strategy receiving increasing attention involves a silicate that is intercalated by an initiator or catalyst [6], and, upon the introduction of a monomer, an intercalated or exfoliated polymer nanocomposite is formed. It must be noted that conventional method does not work well without using organic silicates and cannot produce PE/MMT nanocomposites, of which the polymer matrix is the copolymer of ethylene and α-olefins generated from ethylene oligomerization by MMT-supported iron-based catalyst, hence needing no comonomers added from outside. There have been reports about the synthesis of PE/MMT nanocomposite by copolymerization of ethylene with in situ produced ethylene oligomers under a dual functional catalyst system intercalated into MMT layer [7, 8].

In this paper, the preparation of PE nanocomposites, different from that before, is investigated for the first time by employing the combination of an iron-based ethylene oligomerization catalyst supported on MMT and homogeneous metallocene *rac*-Et(Ind)$_2$ ZrCl$_2$. By means of this fabrication methodology, the interlayer spacing of MMT (d_{001}) was increased significantly after the fixation of ethylene oligomerization catalyst in between layers of MMT, and, the ethylene oligomer (α-olefins) formed in situ from MMT-supported iron-based diimine complex-catalyzed ethylene oligomerization expanded further the layer distance of MMT and formed an intercalated ethylene oligomer-MMT nanocomposite. Finally, exfoliated PE/MMT nanocomposites were prepared after the copolymerization of ethylene and α-olefins intercalated between layers of MMT with *rac*-Et(Ind)$_2$ZrCl$_2$ as the copolymerization catalyst.

Experimental part

All manipulations involving air- and/or moisture-sensitive compounds were carried out under argon atmosphere using drybox procedures or standard Schlenk techniques. *rac*-Et(Ind)$_2$ZrCl$_2$ and MAO (1.4 mol/L solution in toluene) were purchased from Aldrich Company and Albemarle Company, respectively. Ethylene of polymerization grade was generously offered by Yanshan Petro. Chem. Co. Toluene was dewatered over sodium/benzophenone and degassed. MMT, particle size 40–70 μm and cation exchange capacity (CEC) 90–100 mmol/100 g, was generously provided by Zhangjiakou Qinghe Chem. Plant. All other chemicals were commercially obtained and used as received.

Preparation of {[(2-ArN= C(Me))$_2$C$_5$H$_3$N]FeCl$_2$} (Ar=2-CH$_3$-4-OCH$_3$(C$_6$H$_4$))

2,6-Diacetylpyridine (0.5 g, 3.06 mmol) and 4-oxymethyl-2-methylaniline (1.7 mL, 12.24 mmol) were added to a round-bottom flask with 30 mL of 1,2-dichloroethane. A stirbar and 5 drops of 97% formic acid were added, and the solution was stirred for 48 h at 50 °C. After removing the solvent in vacuo the resulting viscous oil was washed with cold methanol prior to the formation of a yellow solid, which was confirmed to be the desired ligand after filtration isolation and identification by ^{1}H NMR The pre-catalyst complexes were formed by addition of the ligand to FeCl$_2$·4H$_2$O in THF.

Ligand (C$_{25}$H$_{27}$N$_3$O$_2$) ^{1}H NMR (CDCl$_3$): $\delta = 8.26$ (d, Py-*m*-H), 8.02 (t, Py-*p*-H), 6.99 (d, Aryl), 6.72 (m, Aryl), 3.79 (s, Aryl–OCH$_3$), 2.83 (s, N=C–CH$_3$), 2.34 (s, Aryl–CH$_3$). Elemental Analysis: Calc (%): C = 74.8, H = 6.73, N = 10.47, O = 7.98, Found (%): C = 74.25, H = 6.72, N = 10.20, O = 7.69.

Preparation of MMT-supported Fe-Cat

To a 500 mL three-necked flask with magnetic stirring, dried and air free, 30 g of MMT and 150 mL of MAO were added at 50 °C and reacted for 8 h. After removing the solvent and unreacted MAO, 0.036 g of Fe-Cat. and 120 mL of toluene were added to the flask under the same conditions as that of the first step. Removal of the unsupported {[(2-ArN =C(Me))$_2$ C$_5$H$_3$N]FeCl$_2$}(Ar=2-CH$_3$-4-OCH$_3$(C$_6$H$_4$)) by washing with toluene and drying under vacuum at 50 °C gave rise to an MMT-supported ethylene copolymerization catalyst. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES POEMS TJA Co.) indicates that Fe content is 0.2 wt‰, based on the total weight of the immobilized catalyst.

Preparation of PE/MMT nanocomposites

Ethylene copolymerization was conducted in a 2 L stainless steel autoclave. Before each run, the autoclave was heated up to 90 °C under vacuum for 4 h and cooled down to room temperature. After transferring 0.7 L of hexane to the reactor, a prescribed amount of MAO/MMT-supported Fe-Cat. suspension in hexane was added and the autoclave was heated to required temperature while raising ethylene pressure to 0.7 MPa. The autoclave reactor was cooled down to room temperature after 15 min and the ethylene pressure was slowly lowered to be atmospheric. About 10 μmol of *rac*-Et(Ind)$_2$ZrCl$_2$ in toluene was transferred into the autoclave with 0.3 L of hexane, the reactor was maintained at the same temperature and ethylene pressure as those of the first step to perform the copolymerization of ethylene with α-olefins produced in situ from the first step, a process proceeded all the time until the copolymerization was terminated after 2 h. The polymers were precipitated in 5 wt% acidified ethanol, washed with ethanol, and dried to constant weight under vacuum.

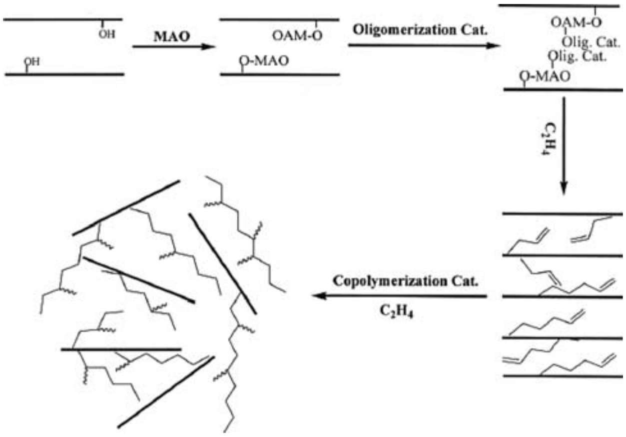
Characterization

^{13}C NMR analysis was performed on Bruker AM-300 operating at 120 °C and 75 MHz. The polymer solutions were prepared in *o*-dichlorobenzene in a sample tube with diameter of 5 mm. The deuterated solvent was used to provide the internal lock signal. The chemical shifts were referenced internally to methylene carbon of main chain backbone resonance, which was taken as 30.00 ppm from Me_4Si. Spectra were taken with a 45° flip angle, an acquisition time of 0.983 s and a delay of 3.0 s. A differential scanning calorimetry (DSC) analysis was carried out on a Perkin–Elmer DSC-7 operating under ultrahigh-purity nitrogen. The PE sample (≈4 mg) was heated to 150 °C at a rate of 10 °C/min, it was then cooled to 50 °C at 10 °C/min. Subsequently, a second heating cycle was conducted at a heating rate of 10 °C/min. X-ray powder diffraction (XRD) data were collected on a Rigaku D/max 2400 diffractormeter (Japan) using CuK_α radiation of wavelength 0.154 nm. Diffraction data were recorded between 1 and 10°. The interlayer spacing (d_{001}) of MMT was calculated in accordance with Bragg equation: $\lambda = 2d{\cdot}\sin\theta$. An AVS-300 viscometer (Shott Co) was employed to measure the viscosity of polyethylene in decahydronaphthalene at 135 ± 0.1 °C and Viscosity-average molecular weight (M_η) of PE was calculated from $[\eta]$ according to the equation: $[\eta] = 2.3 \times 10^{-4}\, M_\eta^{0.82}$ [8]. PE/MMT samples were deposited on a sample holder and sputtered with gold and transmission electron microscopy (TEM) images were obtained with a HITACHI H-800 electro microscope operated at an accelerated voltage of 100 kV. All of the ultrathin sections (<80 nm) were microtomed by Leica Microsystems Ltd.. Thermal gravimetric analysis (TGA) was performed in air on a Perkin–Elmer 7 series system from 50 to 750 °C at a heating rate of 10 °C/min. Samples for tension testing were prepared on a CS-183 MINI MAX injection molding machine and tested on Instron-1122 device.

Results and discussion

The most difficult problem to tackle in the preparing of PE/MMT nanocomposites is to anchor either ethylene polymerization or copolymerization catalysts onto the interlayer of MMT. Based on and quite different from previous research work [6, 7], Fe-Cat., capable of oligomerizing ethylene to α-olefins, was efficiently immobilized into MMT layers as shown in Scheme 1. MAO played great roles in modifying MMT and bridging Fe-Cat. onto its interlayer spacing.

The TEM photograph of the resultant PE/MMT materials (Fig. 1) showed that the MMT layers were dispersed in the PE matrix and exfoliated nanocomposite were formed.



Scheme 1 Schematic formation of PE/MMT nanocomposite

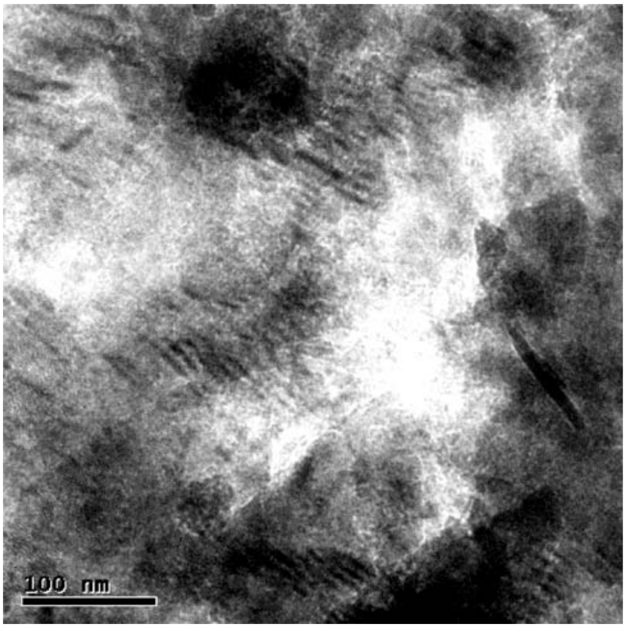


Fig. 1 TEM image of PE/MMT nanocomposite P4

Obvious from Fig. 2 is that the interlayer spacing (d_{001}) of pristine MMT increases from 1.3 nm ($2\theta = 6.41°$, Fig. 2a) to 2.0 nm ($2\theta = 4.44°$, Fig. 2b) after ethylene oligomerization catalyst is fixed onto the interlayer spacing of MMT, indicating that the modification of MAO on MMT plus the supporting of the oligomerization catalyst make MMT layers intercalated to such an extent that almost delamination occurs. As the introduction of ethylene monomer into MMT-supported Fe-Cat., the formation of α-olefins intercalated further into layers of MMT (Fig. 2c) and the characteristic diffraction peak of MMT moved to a much lower angle of $2\theta = 2.22°$ ($d_{001} = 4.0$ nm). Eventually the architecture of an exfoliated PE/MMT nanocomposite was built up once the copolymerization of ethylene and in situ-formed α-olefins is carried out

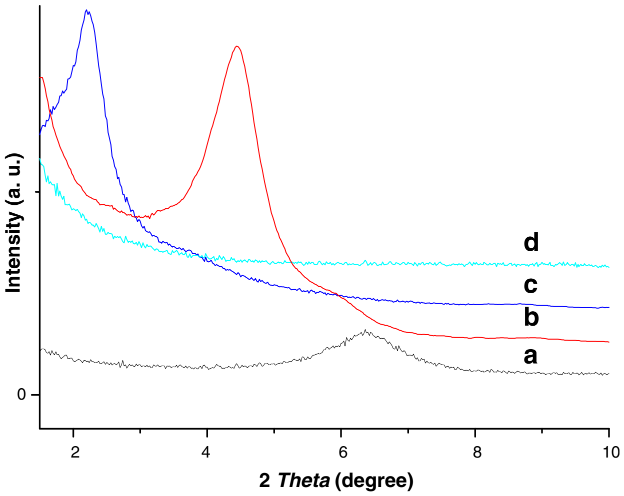


Fig. 2 XRD patterns of (**a**) pristine MMT; (**b**) MMT-supported Fe-Cat.; (**c**) ethylene oligomer/MMT; (**d**) PE/MMT nanocomposites

with *rac*-Et(Ind)$_2$ZrCl$_2$ and the characteristic diffraction peak of MMT did not appear any longer (Fig. 2d).

Figures 2 and 3 and Table 1 also show that the dispersion state of MMT layers relates to not only MMT content in the composites but also polymerization conditions, the two factors correlating with each other. As the polymerization temperature and the molar ratio of Fe to Zr went up the polymerization activity increased, embodying "comonomer effect", and exfoliated PE/MMT nanocomposites were obtained.

Because there were great amount of α-olefins formed in the oligomerization step much copolymer of ethylene with in situ produced α-olefins over Zr-Cat. led to not only high activity as 1.64×10^7 g mol Zr^{-1} h^{-1} but also low molecular weights of polyethylene. DSC and ^{13}C NMR analyses also confirm that the polyethylene matrix in the nanocomposites is ethylene copolymers with melting temperatures around 125 °C (Fig. 3P6) and branching degree of 40 CH$_3$/1,000 CH$_2$ (Fig. 4).

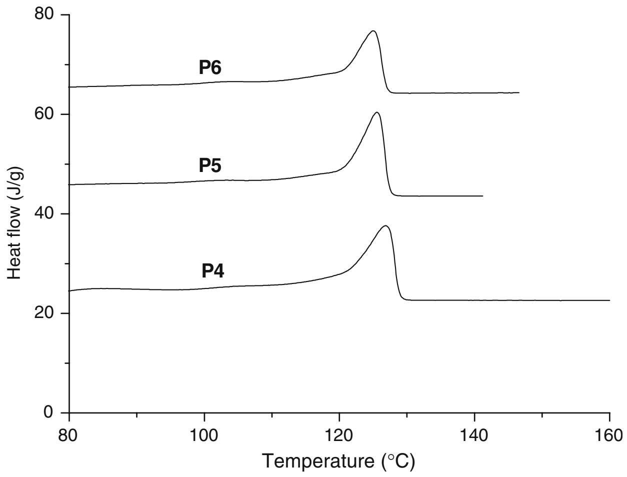


Fig. 3 DSC traces of PE/MMT nanocomposites (P4, P5, and P6 in Table 1)

Table 1 Data of ethylene copolymerization over MMT-supported Fe-Cat/Zr-Cat

Run	Zr μmol	Fe/Zr mol/mol	T_p^c °C	Activity 10^6 g mol Zr^{-1}·h^{-1}	M_η 10^4 g mol^{-1}
P0[a]	10	6	70	20.3	5.56
P1[a]	10.1	6	60	2.34	2.69
P2[a]	10.3	6	70	13.6	2.16
P3[a]	9.9	6	80	16.4	1.89
P4[b]	10.2	2	60	5.30	2.14
P5[b]	10.3	2	70	8.12	1.13
P6[b]	9.8	2	80	6.11	1.26

Reaction conditions: [a] MAO/Fe (mole ratio) = 2,000; [b] MAO/Zr (mole ratio) = 1,000; [c] polymerization temperature; ethylene pressure = 0.7 MPa; solvent = 1 L hexane; copolymerization time = 2 h

As shown in Table 1, high copolymerization activity can be reached due to the employment of single activator MAO to MMT-supported Fe-Cat. and homogeneous Zr-Cat.. Reason for this is that little interference exists within the two catalysts, so "comonomer effects" can be observed [9]. Also can be seen from Table 2 is that the onset temperature of thermal decomposition (T_{onset}) of PE/MMT nanocomposite rised by 36 °C compared with neat polyethylene, embodying the improving effects of MMT layers on the thermal stability of the resulting polyethylene matrices. Reason for this is that the dispersed layered sheets of MMT formed tortuous pathway for oxygen and volatile degradation products to permeate through it [10].

Now that copolymer of ethylene and α-olefins are of excellent properties, the comprehensive properties of polyethylene can surely be bettered by combining with MMT in the nanocomposites through polymerization process. Systematic investigations on other properties of PE/MMT nanocomposites such as impermeability, heat deformation temperature and dynamic mechanical behaviors etc. are well under way.

Data in Table 2 show that the mechanical and thermal properties were improved. The tensile strength, compared with 22.3 MPa of low-density polyethylene (LDPE), increases by about 50% with the increment of MMT and tends to go up as MMT content increases. Also improved was the Young's modulus of the PE/MMT nanocomposites which increased form 0.68 GPa of polyethylene to 1.21 GPa of the as-fabricated polymer-montmorillonite nanocomposites, fully exhibiting the reinforcement effects of the nano-dispersed MMT layers on polymer matrix [11].

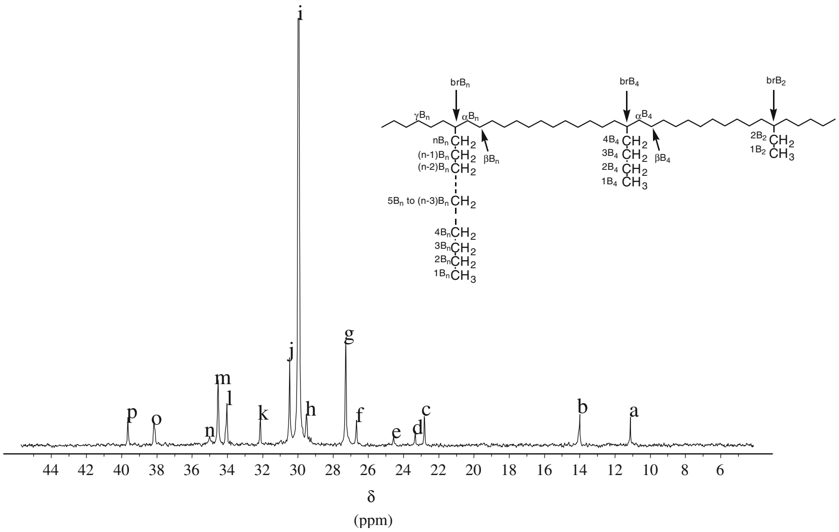


Fig. 4 ^{13}C NMR spectrum of PE/MMT nanocomposite (P6 in Table 1)

Table 2 Mechanical properties of the obtained PE/MMT nanocomposites

Run	T_m °C	T_{onset} °C	σ_b MPa	ε_b %	Young's modulus GPa	d_{001} nm	MMT wt%
P0	120	410	22.3	1021	0.68	–	0
P1	128	446	32.1	868	1.08	>6	1.9
P2	126	420	33.5	820	1.19	>6	1.74
P3	125	426	32.6	891	1.13	>6	1.44
P4	127	417	30.5	693	1.05	>6	3.62
P5	126	413	33.1	728	1.21	>6	2.36
P6	125	416	32.1	672	1.12	>6	3.14

Notes: σ_b: Tensile strength; ε_b: elongation at break

Conclusion

PE/MMT nanocomposites can be prepared employing a dual functional catalytic system comprising MMT-supported iron-based diimine ethylene oligomerization catalyst and metallocene catalyst *rac*-Et(Ind)$_2$ZrCl$_2$, which is capable of copolymerizing ethylene and in situ formed α-olefins in the same reactor using MAO as the only activator and hexane the solvent. Both catalysts in the system are activated by MAO, hence reduce interference with each other and reach high polymerization activities. {[(2-ArN=C(Me))$_2$C$_5$H$_3$N]FeCl$_2$} (Ar=2-CH$_3$-4-OCH$_3$(C$_6$H$_4$)) is effectively intercalated in between layers of MAO-treated MMT without much loss in catalytic activity and increases the interlayer spacing of MMT accordingly. The ethylene oligomer formed in situ with MMT-supported Fe-Cat. expands further the layer distance of MMT and eventually gives rise to exfoliated PE/MMT nanocomposite after the copolymerization of ethylene and in situ-formed α-olefins under the catalysis of *rac*-Et(Ind)$_2$ ZrCl$_2$/MAO. Because the tortuous path originating from irregular exfoliated MMT layers the decomposed small volatile molecules, upon heating and even combustion, are difficult to pass through, the resultant PE/MMT nanocomposites are more thermally stable, exhibiting an increase of ca. 30 °C in the onset temperature of thermal decomposition. Also improved is the tensile strength and Young's modulus of the resultant PE/MMT nanocomposites.

Acknowledgements The authors gratefully thank National Natural Science Foundation of China (Nos. 50573081, 50103012) for its financial support.

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