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Preparation of exfoliated isotactic polypropylene/alkyl-triphenylphosphonium-modified montmorillonite nanocomposites via in situ intercalative polymerization

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Abstract

Alkyltriphenylphosphonium-modified montmorillonite(PMMT) was used to prepare $TiCl_4/MgCl_2/PMMT$ compound catalyst and exfoliated *i*-PP/PMMT nanocomposites were prepared by in situ intercalative polymerization of propylene with $TiCl_4/MgCl_2/PMMT$ catalyst. The catalytic efficiency of the above catalyst under optimum polymerization condition could reach as high as 1300 kg/(molTi h) and the combining of PMMT with Z–N catalyst do not change the stereo-regulation catalytic properties of the Z–N catalyst. The synthesized PP possessed high isotacticity, melting point and molecular weight. Wide angle X-ray diffraction (XRD) and transmission electron microscopy (TEM) examinations evidenced the nanocomposites obtained were exfoliated ones.

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1. Introduction

Polypropylene (PP), as one of the general plastics with high performance to price ratio, is expected to have improved toughness, enhanced modulus and barrier properties when filled with nanoclay or nanoparticles, and could be used in automobile and package fields as substitute for high performance engineering plastic. Compounding of PP and clay is an effective way to modify PP and the PP/clay nanocomposites with exfoliated structure are especially desirable for the nanoscale silicate layers dispersion in the PP matrix. However, it is difficult to prepare exfoliated PP/clay nanocomposites because of the incompatibility of hydrophobic PP and hydrophilic clay. Therefore, silicate layers are easily self-agglomerated during processing.

Generally speaking, melt blending [1–3], solution blending [4,5], and in situ polymerisation [6–10] methods have been used to prepare PP/clay nanocomposites, and in situ polymerization is an effective method to prepare exfoliated PP/clay nanocomposites compared with melt and solution blending methods. In order to improve the compatibility of clay and PP, alkyl-ammonium surfactants have been used to modify montmorillonite (AMMT). However, it was found that the thermal degradation of alkyl-ammonium surfactants at high processing temperature (200 ± 10 °C) not only accelerated the aging and decomposition of PP, but also led to the re-stacking of the silicate layers [11,12].

In our previous work, alkyl-imidazolium surfactant (Im) modified MMT (IMMT) was used to prepare novel Ziegler–Natta/IMMT compound catalyst. Exfoliated *i*-PP/montmorillonite nanocomposites with good thermal stability were successfully synthesized via intercalative polymerization [12], Our further study indicated that the imidazolium modified MMT had a little of negative effect on catalytic efficiency. Therefore, the objectives of these studies were not only to prepare exfoliated PP/clay nanocomposites, but also to find another kind of surfactant with high thermal stability, as well as little or no effect on the catalytic efficiency of catalyst.

In this paper, another surfactant alkyltriphenylphosphonium (Ph) with high thermal stability was used to modify MMT

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and $TiCl_4/MgCl_2$/PMMT heterogeneous compounding catalyst was prepared by chemical reaction method. It was found that the PP synthesized possessed relatively high isotacticity, melting point and molecular weight. The catalytic efficiency could reach as high as 1300 kg/(molTi h). Both XRD and TEM examinations evidenced that exfoliated PP nanocomposites were obtained.

2. Experimental

2.1. Materials and instruments

Na^+-MMT was supplied by Zhejiang Fenghong Clay Chemical Co. Ltd with about 90 mequiv./100 g CEC. 1-Iodohexadecane, phthalic anhydride and dipenyldimethoxylsilane (DDS) were purchased from Aldrich Com. Propylene (polymerization grade), titanium tetrachloride ($TiCl_{4,}$, >98% purity), triethyl aluminium ($AlEt_3$, >98% purity) were supplied by Yanshan Petrochemical Co. Anhydrous magnesium dichloride ($MgCl_2$, >98% purity) and CS catalyst were kindly supplied by Yingkou Science Chemical Co of China. 2-Ethyl hexanol and decane were purchased from Beijing Chemical Factory, dried with 5A molecule sieve and stored under argon before use. Toluene and heptane (analytical purity, Beijing Chemical Factory) was refluxed continuously over Na under argon for 24 h, and withdraw from the still immediately before use.

The titanium content of the catalysts was measured using a spectrophotometer at a wavelength of 410 nm. Differential scanning calorimetry (DSC) was conducted using a Perkin–Elmer DSC-7 thermal analyzer under a nitrogen atmosphere with a heating rate of 10 °C/min in a temperature range of 50–200 °C for dynamic scanning, and T_m was determined in the second scan. Thermogravimetric analysis was performed with Perkin–Elmer TGA at a heating rate of 20 °C/min under nitrogen atmosphere. Isotactic index (II) was carried out in boiling heptane for 10 h using Soxhlet's extractor. The molecular weight and its polydispersity of PP were measured by GPC (Waters Alliance GPC2000) in 1,2,4-trichlorobenzene at 150 ± 0.05 °C. Wide-angle X-ray diffraction (XRD) analysis was performed on a Japan Rigaku D/max-2500 diffractometer with Cu K_α radiation ($\lambda = 0.1504$ nm) at a generator voltage of 40 kV and generator current of 100 mA. Scanning was in 0.02° steps at a speed of 2°/min. The interlayer spacing (d_{001}) of MMT was calculated in accordance with Bragg equation: $2d \sin \theta = \lambda$. Transmission electron microscopy (TEM) was carried out on a Jeol JEM2010 transmission electron microscope using an acceleration voltage of 100 kV. Samples for TEM were prepared by embedding of powder composites in epoxy resin Epon 812 in a capsule and microtomed into ultrathin sections.

2.2. Synthesis of hexadecyl-triphenylphosphonium iodide

A precise amount of triphenylphosphonium was placed into a 500 mL flask with reflux condenser under the argon atmosphere, then a precise amount of 1-iodohexadecane was added to the flask. The reactants were left stirring for approximately 14 h at 80 °C. The resulted solid was washed with hexane for three times and then dried under vacuum at 50 °C for 24 h.

The preparation procedures of PMMT and Ziegler–Natta/PMMT catalyst are as described in Ref. [12]. The titanium contents of the compound catalyst was 1.3 wt%.

2.3. Polymerization of propylene

The Ziegler–Natta/PMMT catalyst was pre-treated with toluene firstly before initiation polymerizations. 500 mL stainless autoclave was degassed and purified with propylene, and then toluene, $AlEt_3$, DDS and the pre-treated catalyst slurry or powder were added successively to start polymerization. After predetermined reaction time, polymerization was quenched with diluted HCl solution of ethanol. The polymer was washed with ethanol several times, filtered, and dried in a vacuum oven at 70 °C for 10 h. Neat PP and PP/IMMT nanocomposites were synthesized by CS catalyst and Ziegler–Natta/IMMT catalyst, respectively.

3. Results and discussion

3.1. Preparation and characterization of alkyltriphenylphosphonium-modified montmorillonite

Alkyltriphenylphosphonium (Ph) surfactant with high thermal stability was synthesized and used as surfactant for clay. Ph-modified montmorillonite (PMMT) was prepared via ion-exchange procedures and characterized by XRD. Fig. 1 shows that the (001) diffraction peak of PMMT shifts to $2\theta = 2.64°$ from $2\theta = 9.05°$ of dried Na-MMT, indicating the *d*-spacing of PMMT increasing to 3.34 nm. Another two diffraction peaks appeared at $2\theta = 5.32$ and 8.0°, respectively, which were assigned to the secondary and tertiary diffraction peaks. To the best of our knowledge, the special volume effect of Ph containing three phenyl groups and one long alkyl tail might benefit the enlargement of interlayer spacing. The thermal stability of PMMT and surfactant itself were measured and TGA was employed to determine the initial decomposition temperature (temperature at 1% weight loss $T_{0.01}$ and temperature at 10% weight loss $T_{0.1}$), and the maximum decomposition temperature (T_{max}), as shown in Table 1. It was found that the $T_{0.01}$ of PMMT was much higher than that of both AMMT and IMMT and could reach as high as 310 °C. Once Ph was intercalated into the interlayers of MMT, the organic modified MMT exhibit higher thermal stability compared to its organic salt, which was due to the barrier properties of silicate layers. However, it was found that the T_{max} value of PMMT was higher than that of AMMT, but lower than that of IMMT. The TGA results indicate that the PMMT can bear higher temperature for the initial decomposition, however, the decomposition proceeds much quickly compared with that of IMMT if the decomposition begins.

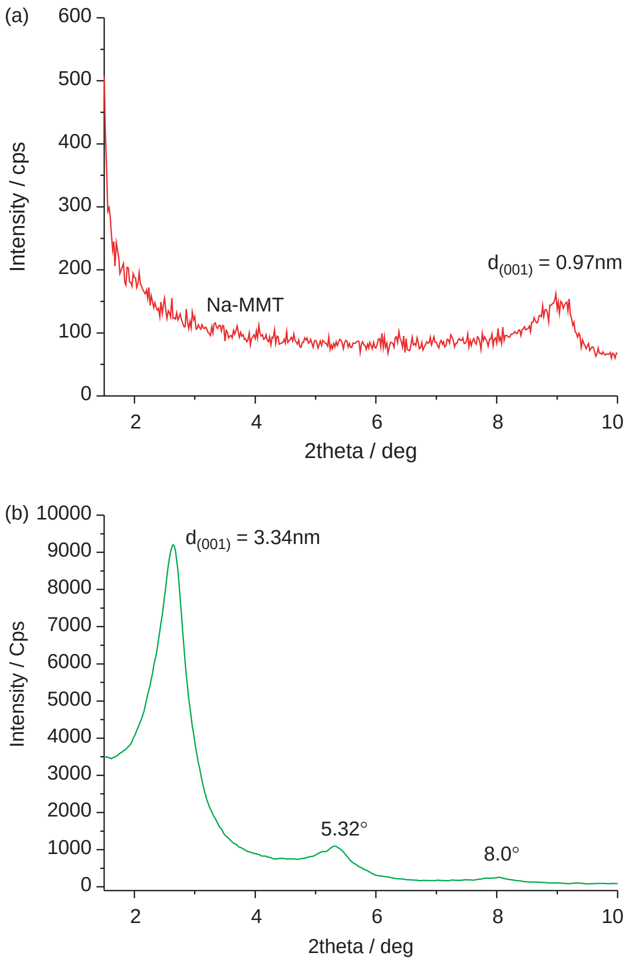

Fig. 1. XRD patterns of Na^+-MMT (a) and PMMT (b).

3.2. Preparation of the compounding catalyst and polymerization investigation of the catalyst

$TiCl_4/MgCl_2$/PMMT compound catalyst was prepared by chemical reaction method as described in Ref. [12]. The organic surfactant used in PMMT was expected to play two key roles, one is acting as compatilizer of clay and PP, the other is enlarging the interlayer spacing, which would benefit the entrance of $MgCl_2$. ROH solution into the interlayers and then in situ generation of $MgCl_2$ crystals inside the interlayers. However, what we considered is whether the surfactant in organically modified MMT still lied in the final compound catalyst. The TGA analysis shows that char content in catalyst was 55.1 wt% at 700 °C, which meant that the organic compound content was about 44.9 wt%. Therefore we can conclude that the surfactant was still in the compound catalyst. It is well known that $TiCl_4$ supported on the $MgCl_2$ crystals could be transferred to the active center by alkyl substitution and deoxidization reactions with co-catalyst $Al(Et)_3$, and then initiate the coordination polymerization of propylene monomer. As surfactants for clay modification, both Ph and alkylimmidazolium (Im) ion-exchanged into the galleries of clay are cationic compounds, which might destroy the active catalytic species and thereby decrease the catalytic efficiency. However, the volume barrier of Ph is bigger than that of Im, which might reduce its negative effect on the active catalytic species. To investigate the catalytic efficiency (CE) of the compound catalyst, polymerization conditions were varied as shown in Table 2. Samples (PP1–PP8) were prepared from $TiCl_4/MgCl_2$/PMMT, PP9 was prepared form CS industrial catalyst, and PP10 was prepared from $TiCl_4/MgCl_2$/IMMT. It can be seen from Table 2 that the pre-treatment time of catalyst do have some effect on the CE, no pre-treatment (PP1) or excess long pre-treatment (PP3) on the catalyst did not have any positive effect on the CE. As we all known, the MMT is in the form of aggregation in which the $MgCl_2$–$TiCl_4$ crystals might be embedded. Therefore, it will be difficult for some embedded titanium to react with co-catalyst and then transfer to active catalytic centers. However, excess long-time pre-treatment might lead to the inefficiency of some titanium because of the impurity. The polymerization temperature play an important role on the CE and the CE value could reach as high as 1300 kg/(molTi h) at 70 °C. In our study, the $TiCl_4/MgCl_2$/PMMT compound catalyst showed unusually high CE compared with that of $TiCl_4/MgCl_2$/IMMT.

Table 1
TGA results for Ph, PMMT and AMMT

Modified clay	$T_{0.01}$ (°C)	$T_{0.1}$ (°C)	T_{max} (°C)	Char at 600 °C (%)
Ph	285.3	312.4	338.3	0
PMMT	310.9	343.7	345.5	65.2
IMMT	267	410	422	78.3
AMMT	104	281	273	70.3

3.3. Characterization of the PP/PMMT nanocomposites

PP/PMMT nanocomposites were obtained by slurry polymerization. Typical physical properties of PP/PMMT composites are also listed in Table 2. The results indicated that high isotacticity PP could be produced. The isotactic index values (II) of PP obtained in composites could reach as high as 99% and varied from 96–99%. The melting points of PP composites was about 163 °C. The cold crystallization temperature for PP/PMMT nanocomposites was higher than that of pure PP, which could be attributed to the effect that MMT layers act as nucleating agent for PP. The above results showed that chemical environmental of the active catalytic species in the compound catalyst were similar to that of the industrial catalyst and the Ph had little effect on the active species. The molecular weight of PP in these composites varied typically from 250,000 to 620,000, and the polymerization temperature could affect the molecular weight of PP distinctly. The decrease in polymerization temperature leads to the increase in the molecular weight of PP. The MWD of PP was in the 4.6–6.2 range, showing that the active complex were multi-sites (Fig. 2). Both the molecular weight and MWD of PP synthesized by the combined catalyst could be comparable to that of PP9 synthesized by the industrial CS catalyst.

Table 2
Physical properties of PP/MMT nanocomposites

Run	PP1	PP2	PP3	PP4	PP5	PP6	PP7	PP8	PP9	PP10
Surfactant	Ph	Ph	Ph	Ph	Ph	Ph	Ph	Ph	–	Im
Pre-treat. time of catalyst (h)	0	1.5	24	312	336	336	1	1	0	0
Propylene pressure (MPa)	0.5	0.5	0.5	0.3	0.3	0.3	0.3	0.3	0.6	0.5
Al/Ti molar ratio	100	100	100	100	100	100	100	100	50	100
T (°C)	60	60	60	80	70	40	70	40	60	60
t (h)	2	2	2	1	0.5	0.5	1	1	2	2
CE (kg/(molTi h))	178	977	201	185	360	321	1300	826	860	72
MMT (wt%)	0.8	0.15	0.7	1.48	1.53	1.72	0.21	0.33	0	0.7
T_m (°C)	161	163	163	162.7	163	161	161	163	163	160
ΔH_m (J/g)	105.5	93.4	91	108.8	107.4	89.5	94.5	97	100	88.2
T_c (°C)	120	117	121	122.3	124.8	122	121	121.5	117.2	119
ΔH_c (J/g)	−106.1	−97.6	−90	−103.8	−102.8	−86.2	−88.9	−97.5	−99	87.9
$T_{0.01}$ (°C)	273	278	287	273	292.6	295.4	281	285	290	316
$T_{0.05}$ (°C)	312	309	325	310	329.4	334.7	312	310	329	372
T_{onset} (°C)	360	341	372	341	385.9	388.6	358	342	353	425
II (%)	98.2	95.9	98	98	97.1	96.6	99.1	96.2	99	90
M_w ($\times 10^{-4}$)	–			25.79	46.12		54.97	60.9	51.7	
MWD				5.01	6.13		4.60	5.08	6.18	

The thermal decomposition temperature including $T_{0.01}$, $T_{0.05}$, and T_{onset} of these PP/PMMT materials was investigated by using TGA. It was found that the initial decomposition temperature $T_{0.01}$ of the PP/PMMT nanocomposites synthesized in this work approached to that of the neat PP, and even higher than that of neat PP.

The in situ formed polymer chains in the interlayers and the reaction heat were expected to contribute to the exfoliation of silicate layers. The XRD patterns for PP/PMMT composites are shown in Fig. 3. It was found that the XRD curves of those PP/PMMT composites displayed no (001) diffraction peaks from the MMT, indicating that the average interlayer spacing of the MMT in PP/PMMT nanocomposites was larger than 5.8 nm according to the Bragg equation. TEM measurements indicated that the silicate layers with 5–15 nm thickness and 100–200 nm length are dispersed uniformly in the whole PP matrix. Micron-sized clays are scarcely observed in the PP matrix, as shown in Fig. 4. It can be concluded from both TEM and XRD measurements that exfoliated *i*-PP/MMT nanocomposites were prepared by in situ polymerization method. The completely homogeneous dispersion of nanoparticles in the PP matrix is critical for the enhancement of the performance of PP nanocomposites.

Generally speaking, α-phase crystallite is the mainly crystallite formed in neat PP. While γ-phase crystallite in neat PP is only formed in some special cases such as isothermal crystallization under very high pressure [13] and crystallization of very low molecular weight fraction [14]. The enhancement of the formation of γ-phase crystallite in neat PP takes place when the chainfolding in lamellae becomes be more difficult as reported by Kressler et al. [15], or as Nam et al. reported the formation of γ-phase crystallite in PP/MMT nanocomposites at high MMT content (4–7.5 wt%) [3]. In our study, it can be seen from Fig. 3 that the diffraction peaks at $2\theta = 13.9$, 16.8, 18.4 and 21.7° corresponded to the planes (110), (040), (130) and (111) of α-phase crystallite, respectively. α-Phase crystallite

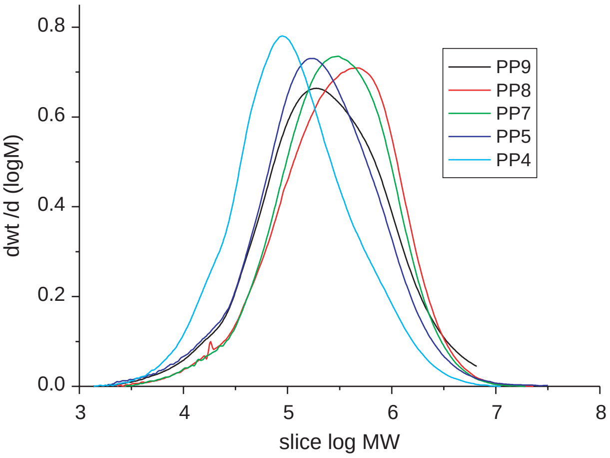

Fig. 2. GPC curves of PP samples.

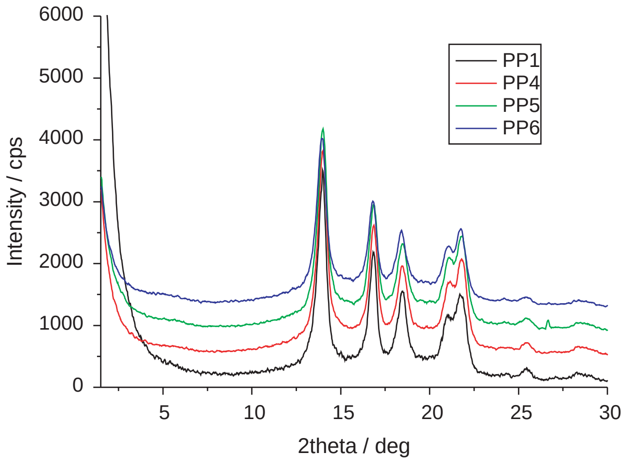

Fig. 3. XRD patterns of PP/MMT nanocomposite.

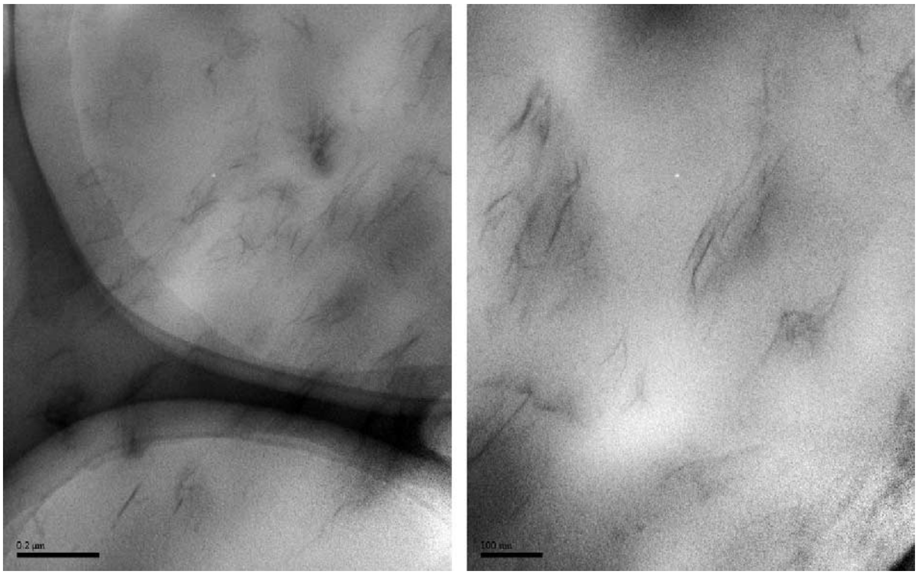

Fig. 4. TEM images of sample PP5.

was still the main crystallite for PP/PMMT nanocomposites with less than 2 wt% clay content. Diffraction peaks of γ-phase crystallite were not observed in XRD patterns of PP/PMMT nanocomposites in our study.

4. Conclusions

It can be concluded that exfoliated PP/PMMT nanocomposites with improved thermal stability were prepared successfully via in-situ polymerization method with Ziegler–Natta/PMMT compound catalyst. The effect of polymerization conditions on catalytic activity and other catalytic properties were studied. It was found that the catalytic efficiency of the above catalyst under optimum polymerization condition could reach as high as 1300 kg/(molTi h) and the combining of PMMT with Z–N catalyst do not change the catalytic properties of the Z–N catalyst. The PP synthesized possessed relatively high isotacticity and molecular weight, which are important for PP materials. Both XRD and TEM results confirmed that the silicate layers of MMT were well dispersed in the whole *i*-PP matrix on the scale of nanometer. α-Phase crystallite was the main crystallite formed in PP/PMMT nanocomposites.

Acknowledgements

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