

PREPARATION OF POLYPROPYLENE/CLAY NANOCOMPOSITES BY *in situ* POLYMERIZATION WITH $\text{TiCl}_4/\text{MgCl}_2$ /CLAY COMPOUND CATALYST*

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Abstract $\text{TiCl}_4/\text{MgCl}_2$ /clay compound catalyst was prepared by chemical reaction. Exfoliated polypropylene (PP)/clay nanocomposites were synthesized by *in situ* polymerization with this compound catalyst. Effects of polymerization temperature, polymerization time, propylene pressure, solvent consumption and pre-treat time of catalyst on catalyst activity and catalytic stereospecificity were studied. Under optimal conditions, activity of the nano-compound catalyst is about 88.3 kg/(mol Ti·h). Isotacticity of PP obtained in the nanocomposites is in the range of 89%–99%, and its melting temperature is about 159°C. The weight-average molecular weight of PP can reach $6.7 \times 10^5 - 7.8 \times 10^5$, and the molecular weight distribution is between 7.7 and 7.9.

Keywords: Polypropylene; Clay; Stereospecificity; Nanocomposite; Nano-compound catalyst.

INTRODUCTION

Polypropylene (PP), as one of the most widely used plastics with a relatively high performance-to-price ratio, is expected to have improved mechanical and barrier properties when it is filled with nanoclay or nanoparticles. Compounding of PP and clay is an effective way to modify PP. According to the dispersed state of clay layers in PP matrix, PP/clay nanocomposites are divided into three types: macroscopic two-phase composites, intercalated nanocomposites and exfoliated nanocomposites. Among them, PP/clay nanocomposites with exfoliated structure are especially desirable for uniform dispersion of the nanoscale silicate layers in the PP matrix.

Solution blending^[1, 2], melt blending^[3–6] and *in situ* polymerization^[7–14] methods have been used to prepare PP/clay nanocomposites. *In situ* polymerization is an effective method to prepare exfoliated PP/clay nanocomposites compared with melt blending and solution blending. Generally speaking, PP is produced with metallocene catalysts^[7, 8], Ziegler-Natta catalysts^[9–11] or late transition metal catalysts^[12]. Metallocene catalysts and the cocatalyst alkyl aluminosilane show high-cost and PP produced has many stereospecific defects. PP synthesized with late transition metal catalysts shows less favorable catalyst activity and relative molecular mass. By comparison, Ziegler-Natta type catalyst shows low-cost, low sensitive to impurities, at one time, and can synthesize PP with higher stereospecificity and higher relative molecular mass.

In this work, 1-hexadecane-3-methylimidazolium bromine organically modified clay was used to prepare a

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novel $\text{TiCl}_4/\text{MgCl}_2/\text{clay}$ compound catalyst by chemical reaction method, and exfoliated stereospecific PP/clay nanocomposites were successfully synthesized by intercalative polymerization. Effects of polymerization conditions, such as temperature and time on activity and catalytic stereospecificity of compound catalyst and the physical characteristics of PP obtained were studied.

EXPERIMENTAL

Materials and Instruments

Clay was supplied by Zhangjiakou Qinghe Chemical Factory with 90–100 mequiv/100 g cation exchange capacity (CEC). 1-Methylimidazole, 1-bromohexadecane (> 95% purity) and dipenyldimethoxysilane (DDS, > 95% purity) were purchased from Sigma-Aldrich Co. Anhydrous magnesium dichloride (MgCl_2 , > 95% purity) was kindly supplied by Yingkou Science Chemical Co. Titanium tetrachloride (TiCl_4) was supplied by Beijing Yili Fine Chemicals Limited Co. Toluene (Beijing Chemical Factory) was refluxed continuously over Na under argon for 24 h, and withdrawn from the still immediately before use. Triethyl aluminium (AlEt_3) was supplied by Yanshan Petrochemical Co. Propylene was supplied by Yanshan Petrochemical Co. Argon (99.99% purity) was dried by passing it over a P_2O_5 column. Iso-octanol and *n*-decane were purchased from Beijing Chemical Factory, dried with 0.5 nm molecule sieve and stored under argon before use.

The titanium content of the catalysts was measured using a spectrophotometer at a wavelength of 410 nm. Wide-angle X-ray diffraction (XRD) analysis was performed on a Japan Rigaku D/max-2500 diffractometer with Cu K_α radiation ($\lambda = 0.1540$ nm) at a generator voltage of 40 kV and generator current of 100 mA. Scanning was performed in a step of 0.02° at a speed of $2^\circ/\text{min}$. The interlayer spacing (d_{001}) of clay was calculated in accordance with Bragg equation: $2d \cdot \sin \theta = \lambda$. Differential scanning calorimetry (DSC) was conducted using a Perkin-Elmer DSC-7 thermal analyzer under nitrogen atmosphere with a heating rate of 10 K/min in a temperature range of 40–200°C for dynamic scanning, and melting temperature (T_m) was determined in the second scan. Isotactic index (I.I) was measured in boiling normal heptane using a Soxhlet's extractor. Weight-average molecular weight and polydispersity of PP were measured by gel permeation chromatography (Waters Alliance GPC2000) in 1,2,4-trichlorobenzene at $(150 \pm 0.5)^\circ\text{C}$.

Synthesis of 1-Hexadecane-3-methylimidazolium Bromine

Equimolar quantities of 1-methylimidazole and 1-bromohexadecane were placed into a 500 mL flask with reflux condenser under the argon atmosphere. Then the reactor was degassed and sealed under vacuum. The reactants were left stirring for approximately 7 days at 120°C. The resulted solid was recrystallized from dry acetonitrile and washed by hexane for 3 times and then dried under vacuum overnight. The yield was 84 wt%.

Preparation of Organically Modified Clay

The surfactant (twice the CEC of clay) was dissolved in ethanol at 50°C and the surfactant solution was added to a 10 wt% aqueous suspension of montmorillonite under vigorous stirring. The mixture was stirred for 8 h at 60°C, then the products were collected by filtration, washed with hot ethanol, and paper filtered until no bromide anions were detected. The organically modified clay was dried at 80°C under vacuum for 24 h. The yield was 89 wt%.

Synthesis of $\text{TiCl}_4/\text{MgCl}_2/\text{Clay}$ Compound Catalyst

10 mL *n*-decane was added to 6 g dry MgCl_2 in a 150 mL flask equipped with a mechanical stirrer and nitrogen inlet/outlet, and the solution was stirred at 130°C for 1 h. 20 mL *iso*-octanol was added into the solution and the solution was stirred for another 1 h, then $\text{MgCl}_2 \cdot \text{ROH}$ was obtained. 2.5 g of dried clay were charged to the $\text{MgCl}_2 \cdot \text{ROH}$ and well dispersed in 200 mL toluene. TiCl_4 was then injected into the slurry, stirring for approximately 1 h at 60°C. The resulted solid was washed with hexane for three times and then dried under vacuum. The titanium contents of the compound catalyst was 2.44 wt%.

Synthesis of Exfoliated PP/Clay Nanocomposites

500 mL or 2000 mL stainless autoclave was degassed and purified with propylene, and then toluene, AlEt_3 ,

DDS and powder catalyst or the pre-treated catalyst slurry were added successively to start polymerization. After predetermined reaction time, polymerization was quenched with diluted hydrochloric solution of ethanol. Composites was washed with ethanol three times, filtered and dried in a vacuum oven at 70°C for 8 h.

RESULTS AND DISCUSSION

Characterization of Clay and the Compound Catalyst

Clay is one of 2:1 layered silicates. There are negative charges on the inner surface of the gallery duo to isomorphous replacement. The galleries are normally occupied by such metal cations as Na^+ and Ca^{2+} . The interlayer distances are expanded by ion exchange reaction with different organic cations, which not only render clay surface hydrophilic to orgnophilic, but also enlarge the interlayer spacing to permit the entry of MgCl_2 and the monomer. Clay, organically modified clay and compound catalyst were characterized by XRD. Figure 1(a) shows that the (001) diffraction peak of clay shifts to $2\theta = 2.48^\circ$ from $2\theta = 7.19^\circ$ of dried clay, indicating the d -spacing of clay increasing to 3.47 nm from 1.20 nm according to the Bragg equation: $2d \cdot \sin\theta = \lambda$. Besides, the secondary and the third reflection appear at $2\theta = 5.08^\circ$, 7.51° .

$\text{MgCl}_2\cdot\text{ROH}$ solution is intercalated into the galleries of clay. Subsequently, it reacts with TiCl_4 . Then MgCl_2 crystal separates out *in situ* inside the interlayers and $\text{Mg}-\text{Cl}-\text{Ti}$ chemical bond forms. Compound catalyst gives a very broad dispersive peak at 6.15° , shown in Fig. 1(b), indicating the order stacking of clay was destroyed due to *in situ* separating out of MgCl_2 crystals during the synthesis of compound catalyst.

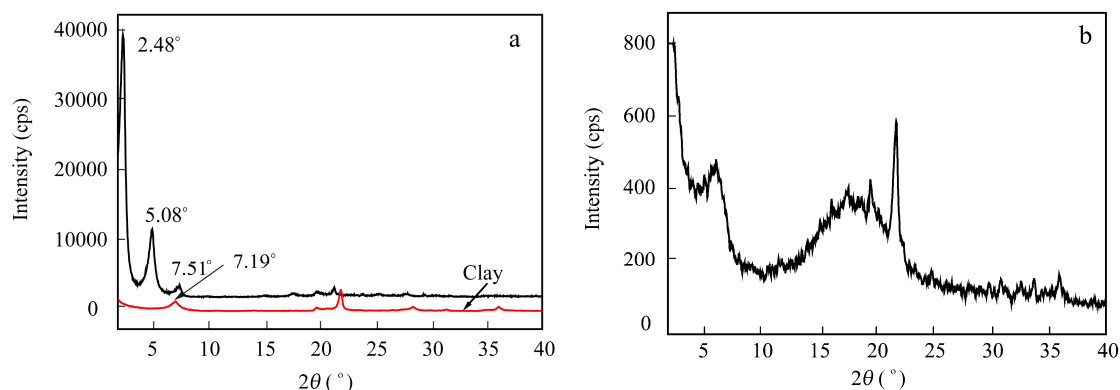


Fig. 1 XRD spectra of clay and $\text{TiCl}_4/\text{MgCl}_2/\text{clay}$ compound catalyst
a) Clay and organically modified clay; b) $\text{TiCl}_4/\text{MgCl}_2/\text{clay}$ compound catalyst

Effect of Polymerization Conditions on the Catalytic Activity of Compound Catalyst

The active components for propene polymerization were TiCl_4 and MgCl_2 in the compound catalyst. Alkylimidazolium and clay had certain negative influence on the activity. Results of propylene *in situ* polymerization with $\text{TiCl}_4/\text{MgCl}_2/\text{clay}$ composite catalyst are summarized in Table 1. As shown in Table 1, activity of compound catalyst is apparently lower than that of the commercial catalyst CS-2 under the same condition (Run PP1 and PP2). This is due to that polarity impurities in clay and imidazolium cation compound make the catalyst poisoning. But from the view point of nanocomposites, the lower catalytic activity makes higher content of clay in nanocomposites. When the activity is $68.3 \text{ kg}/(\text{mol Ti}\cdot\text{h})$, the amount of clay is 1.0 wt% (Run PP2). Otherwise, the amount of clay reaches 1.9 wt%, when the activity is $27.6 \text{ kg}/(\text{mol Ti}\cdot\text{h})$ (Run PP3).

Effect of polymerization time

Polymerization time has an important influence on the catalyst activity, which distinctly decreases with increasing time (PP2 and PP4 in Table 1). The reason is that the kinetic behavior of propylene polymerization reaction assumes a mode of attenuating.

Effect of propylene pressure

Effect of propylene pressure on the compound catalyst activity is summarized in Table 1 (PP2, PP5 and PP6). Increasing of propylene pressure can improve the catalytic activity of composite catalysts. When the propylene pressure is 0.6 MPa, the composite catalyst activity reaches a maximum (68.3 kg/(mol Ti·h)). It is the reason that the higher the pressure of propylene is, the more the propylene amount dissolved in the solvent is, as a result, the collision probability of propylene molecules with active sites and the reaction rate increase.

Table 1. Results of propylene *in situ* polymerization with TiCl₄/MgCl₂/clay compound catalyst

Run	Temperature (°C)	Time (h)	Propylene pressure (MPa)	Pre-treat time (h)	Catalytic activity [kg/(mol Ti·h)]	I.I (%)	T _m (°C)	Clay (%)
PP1 ^a	60	2	0.6	–	430	98	163	–
PP2	60	2	0.6	–	68.3	89	158.5	1
PP3	60	2	0.4	–	27.6	94	158.7	1.9
PP4	60	1.5	0.6	–	79.6	99	159.2	0.9
PP5	60	2	0.5	–	37.4	94	160	1.4
PP6	60	2	0.3	–	31.2	90	159.3	1.68
PP7 ^b	60	2	0.5	–	46.8	94	159	1.2
PP8	50	2	0.6	–	53.2	96	157.5	1.1
PP9	70	2	0.6	–	49.2	95	158	1.2
PP10	60	2	0.6	1	88.3	95	158	0.6
PP11	60	2	0.6	13	50.2	96	158.3	1

^a CS-2 catalyst; ^b 200 mL heptane as solvent

Effect of solvent consumption

With increasing the amount of solvent, the compound catalyst activity decreased (Run PP5 and PP7 in Table 1). It is possible that increasing solvent may introduce more impurities, and more catalyst active sites turn inactive.

Effect of polymerization temperature

Effect of polymerization temperature is listed in Table 1. It can be seen that the the compound catalyst activity reaches a maximum (68.3 kg/(mol Ti·h)) at 60°C (Run PP2, PP8 and PP9 in Table 1). The rate of chain propagation falls at lower temperature, otherwise clay and imidazolium quicken the deactivation rate of compound catalyst at higher temperature. So lower or higher polymerization temperatures make against the enhancement of the compound catalyst activity.

Effect of pre-treat time of catalyst

As we all known, clay is in the form of aggregation in which the MgCl₂/TiCl₄ 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. It can be seen from Table 1 that the pre-treatment time of catalyst do have some benefit on the catalytic activity (Run PP2, PP10). However, excess long-time pretreatment might lead to the inefficiency of some titanium because of the impurity (Run PP11).

Compound Catalytic Stereospecificity for Propylene Polymerization

As shown in Table 1, the isotactic index (I.I) of PP obtained in composites varies from 89% to 99% (Run PP2–PP11), which is close to I.I of PP synthesized by the commercial CS-2 catalyst (98%). The results indicate that PP obtained is high isotacticity PP. It is also deduced that stereospecificity of compound catalyst doesn't fall down sharply because of the existence of clay and alkylimidazolium.

Weight-average Molecular Weight and Molecular Weight Distribution of PP Synthesized

GPC curves of PP synthesized by the compound catalyst are shown in Fig. 2. The weight-average molecular weight of PP obtained in composites varies typically from 6.7×10^5 to 7.8×10^5 . Molecular weight distribution of PP is in the 7.7–7.9 range. These results indicate that PP obtained has higher molecular weight and broad molecular weight distribution, which can be comparable to those of PP1 synthesized by the commercial CS-2 catalyst^[9], showing that the active complexes were multi-sites.

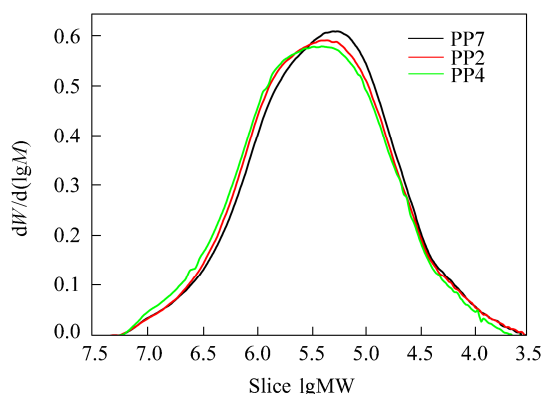


Fig. 2 GPC curves of PP synthesized with $\text{TiCl}_4/\text{MgCl}_2/\text{clay}$ compound catalyst

CONCLUSIONS

$\text{TiCl}_4/\text{MgCl}_2/\text{clay}$ compound catalyst was prepared by chemical reaction. Under optimal polymerization conditions: Al/Si molar ratio 10, Al/Ti molar ratio 50, 60°C , 0.6 MPa, 2 h, pre-treat time of catalyst 1 h and heptane as solvent, activity of the compound catalyst is about $88.3 \text{ kg}/(\text{mol Ti}\cdot\text{h})$. In comparison with the commercial CS-2 catalyst, the compound catalytic activity evidently decreased. But from the view point of nanocomposites, the higher catalytic activity makes against higher content of clay in nanocomposites. Isotacticity of PP synthesized by the compound catalyst is in the range of 89%–99% and its melting temperature is about 159°C . Weight-average molecular weight of the PP can reach 6.7×10^5 – 7.8×10^5 and the molecular weight distributions are between 7.7 and 7.9. Exfoliated isotactic PP/clay nanocomposites were synthesized successfully *via in situ* polymerization method with $\text{TiCl}_4/\text{MgCl}_2/\text{clay}$ compound catalyst.

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