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Preparation of Ziegler-Natta/Ionic Liquild Modified Clay Compound Catalyst and its Catalysis During Preparation of Poly(propylene)/Clay Nanocomposites

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Ziegler-Natta/ionic liquid modified clay compound catalyst was prepared with dibutylphthalate as internal donor. Poly(propylene)/clay nanocomposites were synthesized with this compound catalyst in combination with triethyl aluminium as cocatalyst and dipenyldimethoxylsilane as an external donor by *in situ* intercalative polymerization. The stereospecificity of compound catalyst didn't fall down sharply because of the existence of clay and *bis*alkylimidazolium. Catalytic efficiency of compound catalyst could rise by pretreatment of compound catalyst. Poly(propylene) obtained in composites was high isotacticity poly(propylene). Both wide angle X-ray diffraction (XRD) analysis and transmission electron microscopy (TEM) images showed clay layers were exfoliated into nanometer size in poly(propylene) matrix.

Key Words: Ziegler-Natta catalyst, Ionic liquild, Clay, Poly(propylene), Nanocomposites, *In situ* polymerization.

INTRODUCTION

Poly(propylene) (PP), as one of the most widely used plastic, possesses a relatively high performance-to-price ratio. However, inferior properties of poly(propylene), such as toughness[1], thermal stability and barrier properties[2], hinder its application as high performance materials and special materials. Clay is one of abundant phyllosilicate resources[3]. To improve the properties of poly(propylene), clay layers were hoped to scatter uniformly in poly(propylene) matrix, to exert its rigidity, heat-resistant and dimension stability. Three most common methods to prepare poly(propylene)/clay nanocomposites are solution blending, melt blending and *in situ* polymerization[4].

In previous work, 1,3-dihexadecane imidazolium iodine had been synthesized to improve the compatibility of clay and poly(propylene). Organic clay modified with this ionic liquid was prepared by ionic-exchange and poly(propylene)/clay composites were prepared by solution blending[5]. However, the polymerization is an effective method to prepare exfoliated poly(propylene)/clay nanocomposites compared with solution blending[6]. In this paper, one Ziegler-Natta/clay compound catalyst was prepared by chemical reaction and poly(propylene) /clay nanocomposites were prepared with this compound catalyst *via in situ* polymerization. The catalytic efficiency and the catalytic stereospecificity of compound catalyst for propylene polymerization were studied. The microstructure of poly(propylene) /clay nanocomposites was investigated systematically.

EXPERIMENTAL

Na^+-MMT was supplied by Zhangjiakou Qinghe Chemical Factory, the cation exchange capacity is 90-100 mequiv/100 g. Imidazole was purchased from Tianjin Fuchen Chemical reagent Co. 1-Iodohexadecane (95 % purity) and diphenyldimethoxylsilane (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 ($TiCl_4$, analytical purity) was supplied by Beijing Yili fine chemicals limited Co. Triethyl aluminium ($AlEt_3$), dibutylphthalate (DBP) and propylene were supplied by Yanshan Petrochemical Co. Toluene and heptane (Beijing Chemical Factory) were refluxed continuously over Na under argon for 24 h and withdrawn from the still immediately before use.

Detection method: Wide-angle X-ray diffraction (XRD) analysis was performed on a Japan Rigaku D/max-2500 diffractometer with CuK_α radiation ($\lambda = 0.1540$ nm) at a generator voltage of 40 kV and generator current of 100 mA. Scaning was performed in a step of 0.02º at a speed of 2º/min. The interlayer spacing (d_{001}) of clay 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. Differential scanning calorimetry (DSC) was conducted using a Perkin-Elmer DSC-7 thermal analyzer under nitrogen atmosphere with a heating rate of 10 ºC/min in a temperature range of 40-200 ºC for dynamic scanning and melting temperature (T_m) was determined in the second scan. Thermogravimetric analysis (TGA) was performed with Perkin-Elmer TGA at a heating rate of 20 ºC/min under nitrogen atmosphere. Isotactic index (II) was carried out in boiling normal heptane using Soxhlet's extractor.

Preparation of $MgCl_2$/DBP/$TiCl_4$/clay compound catalyst: 1,3-Dihexadecane imidazolium iodine was synthesised and was used to modify clay according to ref.[5].

$MgCl_2$, iso-octanol and decane were added into a 150-mL flask equipped with a mechanical stirrer and nitrogen inlet/outlet, the mixture was kept stirring for 2 h at 130 ºC, followed by the addition of dibutylphthalate. The organically modified clay (dispersed in 50 mL toluene) was added to the $MgCl_2$/DBP solution at 60 ºC and stirred for 24 h and then filtrated. After that, excess $TiCl_4$ was added dropwise into the $MgCl_2$/DBP/clay mixture. The mixture was allowed to react at 100 ºC for 3 h, filtered and excess $TiCl_4$ was added into the reactor. The reaction was continued for another 3 h and then the slurry was filtered and washed with hexane for 6 times. After removing solvent, $MgCl_2$/DBP/$TiCl_4$/clay compound catalyst solid powder was obtained.

Preparation of poly(propylene)/clay nanocomposites: 500 mL stainless autoclave was degassed and purified with propylene and then toluene, $AlEt_3$, DDS and the pre-treated catalyst slurry or catalyst powder were added successively to start polymerization. After predetermined reaction time, polymerization was quenched with diluted hydrochloric solution of ethanol. The composites were washed with ethanol several times, filtered and dried in a vacuum oven at 70 ºC for 8 h.

RESULTS AND DISCUSSION

Preparation and characterization of the 1,3-dihexadecane-imidazolium-modified clay: 1,3-Dihexadecane imidazolium iodine was synthesized and used as surfactant for clay. The surfactant containing two long alkyl tails can not only render clay surface hydrophilic to organophilic, but also can enlarge the interlayer spacing. Organically modified clay was prepared *via* ion-exchange procedures and characterized by XRD. Fig. 1 shows that the (001) diffraction peak of clay shifts to $2\theta = 2.47º$ from $2\theta = 7.16º$ of dried clay, indicating the d-spacing of clay increasing to 3.57 nm from 1.23 nm according to the Bragg equation: $2d \sin \theta = \lambda$. Besides, the secondary and the tertiary reflection appear at $2\theta = 5.04º, 7.53º$.

Preparation and characterization of the compound catalyst: Generally speaking, producing poly(propylene) uses metallocene catalysts[7], Ziegler-Natta catalysts[8,9] or late transition metal catalysts[10]. Metallocene catalysts and the cocatalyst alkyl aluminoxane show high-cost and poly(propylene) produced has many stereospecific defects. Poly(propylene) synthesized with late transition metal catalysts shows less favourable 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 poly(propylene) with higher stereospecificity and higher relative molecular mass. In this work, $MgCl_2$/DBP/$TiCl_4$/clay compound catalyst was prepared by chloride scorified method, with anhydrous $MgCl_2$ powder as material. Toluene slurry of organically modified clay was added to $MgCl_2$ solution with DBP as an internal donor and the mixture was stirred at 70 ºC for 24 h, which was enough long to $MgCl_2$/DBP solution intercalating into the galleries of clay. Then $TiCl_4$ reacted with $MgCl_2$/DBP and $MgCl_2$ crystal came into being *in situ* inside the clay interlayers.

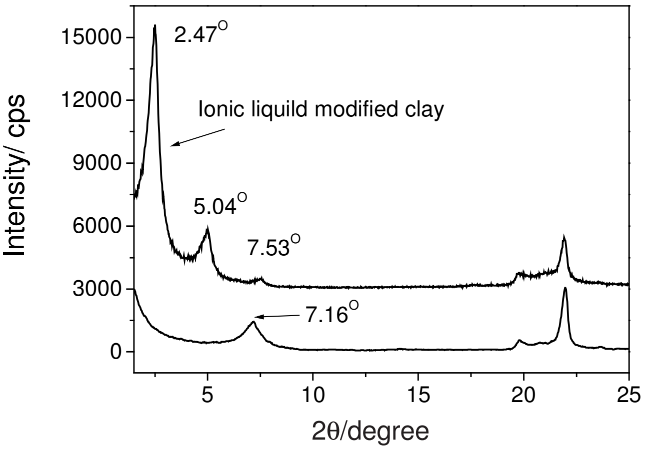

Fig. 1. XRD spectra of clay and ionic liquild modified clay

The active components for propene polymerization were $TiCl_4$ and $MgCl_2$ in the compound catalyst. However, double-alkyl-imidazolium and clay might have certain negative influence on the activity. To investigate the catalytic efficiency (CE) of the compound catalyst, polymerization conditions were varied as shown in Table-1. As it is well known that the $MgCl_2$/DBP/$TiCl_4$ compound lied inside the interlayers of clay, so it will be difficult for cocatalyst $AlEt_3$ to react with $TiCl_4$ and to create active catalytic centers. The compound catalyst was thereby pre-treatment that toluene slurry of compound catalyst was stirred for 1-36 h. It could be seen from Table-1 that the pre-treatment time of catalyst had some benefit on the catalytic efficiency (Run PP5, PP6). However, excess long-time pre-treatment might lead to the inefficiency of some titanium because of the impurity (Run PP7, PP11 and PP12). It is due to that the rate of chain propagation falls at lower temperature and that clay and double-alkyl-imidazolium quicken the deactivation rate of compound catalyst at higher temperature. Lower and higher polymerization temperature make against the enhancement of the catalytic efficiency. It can be seen from Table-1, that the catalytic efficiency distinctly increase with increasing temperature (PP4 and PP5). Pre-treatment on this coumpound catalyst didn't alter the trend (PP7 and PP8) at the same temperature. But when the temperature continued to increase, the catalytic efficiency wound decrease (PP9 and PP10). Moreover, effect of Al/Ti molar ratio on catalytic efficiency of compound catalyst was less (Run PP6, PP13 and PP14). The effect of polymerization time on catalytic efficiency of compound catalyst is very evident. It can be seen that the catalytic efficiency reaches a maximum (104.6 kg/(mol h)) at 2 h (Run PP1-PP9).

The role of internal electron donor is to improve compound catalytic stereospecificity. Dibutylphthalate (DBP) and ethyl benzoate (EB) are two common internal electron donors with

TABLE-1
POLYMERIZATION PERFORMANCE OF THE COMPOUND CATALYST

Run	Al/Ti molar ratio	Temperature (ºC)	Time (h)	Propylene pressure (mPa)	Pre-treat time (h)	Catalytic efficiency (kg/(mol h))	Yield (%)
PP1	50	60	1.0	0.6	0	89.8	91
PP2	50	60	1.5	0.6	0	82.8	95
PP3	50	60	2.0	0.6	0	104.6	91
PP4	100	60	2.0	0.5	0	46.6	94
PP5	100	40	2.0	0.5	0	37.0	91
PP6	100	40	2.0	0.5	1	47.1	82
PP7	100	40	2.0	0.5	11	39.9	80
PP8	100	60	2.0	0.5	11	46.1	84
PP9	100	70	2.0	0.5	11	43.1	92
PP10	100	80	2.0	0.5	11	32.9	89
PP11	50	60	2.0	0.5	14	37.4	94
PP12	50	60	2.0	0.5	36	34.3	88
PP13	80	40	2.0	0.5	1	50.3	84
PP14	150	40	2.0	0.5	1	49.5	84

excellent qualities. The distance between the coordination oxygen atoms of DBP is longer, so the coordination bond between magnesium and oxygen easily arises in $MgCl_2$ (110) crystalline planes. It can prevent the formation of atactic activity centres. Poly(propylene) was synthesized using $MgCl_2$/DBP/$TiCl_4$/clay compound catalyst in combination with $AlEt_3$ as cocatalyst and DDS as an external electron donor in slurry polymerization. Some atactic activity centres can turn inactive because of DDS as an external donor. But in the $MgCl_2$/DBP/$TiCl_4$/clay-$AlEt_3$/DDS activated system, clay had some influence in catalytic stereospecificity. As shown in Table-1, yield of poly(propylene) obtained in composites varies from 80-95 %, which is close to yield of poly(propylene) synthesized by the commercial CS-2 catalyst. It indicated that poly(propylene) obtained was stereospecific poly(propylene) and the stereospecificity of compound catalyst didn't fall down sharply because of the existence of clay and *bis*alkylimidazolium.

Microstructure of poly(propylene)/clay nanocomposites: According to the dispersed state of clay layers in poly(propylene) matrix, poly(propylene)/clay nanocomposites are divided into three types: macroscopic two-phase composite, intercalated nanocomposites and exfoliated nanocomposites. XRD and TEM were used to prove the microstructure of poly(propylene)/clay nanocomposites. XRD patterns of poly(propylene)/clay composites are shown in Fig. 2. XRD patterns display no clay (001) diffraction peak, indicating that the average interlayer spacing of the clay in poly(propylene)/clay nanocomposites is larger than 5.8 nm according to the Bragg equation. The silicate layers of clay were fully exfoliated during *in situ* intercalative polymerization. However, the TEM analysis is a powerful technique to present the extent of clay dispersion. Samples for TEM were prepared by embedding of powder composites in epoxy resin and microtomed into ultrathin sections. As shown in Fig. 3, TEM patterns showed that the clay layers were well dispersed in the whole poly(propylene) matrix. The average thickness of the clay layers dispersed in poly(propylene) matrix was less than 10 nm, corresponding to about 5 silicate layers of stacking. It can be concluded from TEM measurements that exfoliated poly(propylene)/clay nanocomposites were prepared by the *in situ* polymerization method.

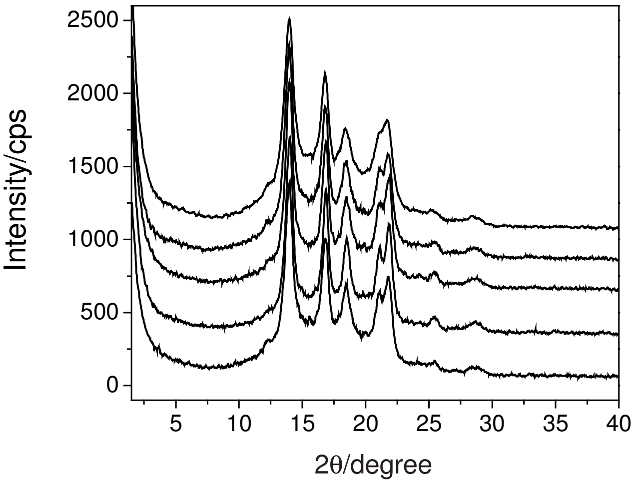

Fig. 2. XRD spectra of poly(propylene)/clay nanocomposites

Fig. 3. TEM image of poly(propylene)/clay nanocomposites

Conclusion

$MgCl_2$/DBP/$TiCl_4$/clay compound catalyst was prepared by chloride scorified method. Poly(propylene)/clay nanocomposites were synthesized with this compound catalyst in different polymeriziton condition, with triethyl aluminium as cocatalyst and dipenyldimethoxylsilane as an external donor. Under optimal polymerization conditions, catalytic efficiency of the compound catalyst is about 104.6 kg/ (mol h). Pretreatment of compound catalyst was benefit on catalytic efficiency. The existence of clay and *bis*alkylimidazolium had slight influnce in catalyic stereospecificity of compound catalyst. The isotacticity of poly(propylene) synthesized by compound catalyst was in the range of 80-95 %. Both XRD and TEM examinations proved clay layers scattered in poly(propylene) matrix by the nano-meter.

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