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Preparation and Characterization of Ionic Liquild Modified Montmorillonite and its Application in Poly(propylene)/Montmorillonite Nanocomposites

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Montmorillonite was organically modified with one kind of ionic liquild. Resulted organical modified montmorillonite was used to prepare a novel Ziegler-Natta/montmorillonite compound catalyst. Poly(propylene)/montmorillonite nanocomposites were synthesized with this argillaceous composite catalyst. Fourier transform infrared, wide angle X-ray diffraction (XRD) and thermogravimetric analysis (TGA) revealed that the 1-hexadecaneimidazolium cation was loaded in the galleries of the obtained ionic liquid montmorillonite. Thermogravimetric analysis result showed the thermal stability of ionic liquid montmorillonite was superior to montmorillonite. XRD patterns indicated that the d spacing of ionic liquid montmorillonite layers increased to 3.14 nm. XRD patterns of poly(propylene)/ montmorillonite nanocomposites showed that montmorillonite layers was dispersed in poly(propylene) matrix by nanometer size and that α-phase crystallite was the main crystallite of poly(propylene) in poly(propylene)/montmorillonite nanocomposites, no β-phase and γ-phase crystallite were observed in XRD patterns of poly(propylene)/montmorillonite nanocomposites.

Key Words: Ionic Liquild, Clay, Montmorillonite, Poly(propylene), Nanocomposites.

INTRODUCTION

Polymer/clay nanocomposites have recently received tremendous attention in both scientific and industrial communities due to their excellent properties, such as mechanical properties[1-3] and thermal stability and decreased gas/vapour permeability[4-6]. According to the dispersed state of clay layers in polymer matrix, polymer/clay nanocomposites are divided into three types *i.e.*, macroscopic two phase composite, intercalated nanocomposites and exfoliated nanocomposites that clay layers scattered uniformly in polymer matrix[7]. To exert rigidity, heat resistant and dimension stability of clay, the exfoliated nanocomposites were expected to obtain.

Montmorillonite (MMT), one kind of clay minerals, is a natural 2:1 phyllosilicate[8]. The montmorillonite crystal lattice consists of one central octahedral sheet of alumina and two external tetrahedral sheets of silica (in such a way that the oxygens from the octahedral sheet also belong to the tetrahedral sheets). These layers are about 1 nm-thin, 100 nm-broad and organize themselves to form stacks by a parallel manner with a regular van der Waals gap. Isomorphic substitution within the layers (for example, Al^{3+} replaced by Mg^{2+} or Fe^{2+}) generates a negative charges, so the layers' surface can adsorb cation[9] such as Na^+, Mg^{2+}, Ca^{2+}.

From the material point of view, MMT is only miscible with hydrophilic polymers. However, it is a great challenge for hydrophilic MMT layers to disperse homogeneously in hydrophobic polymer matrix, such as poly(ethylene) and poly(propylene). To improve the compatibility of hydrophobic polymers and hydrophilic MMT, many reseachers exchanged the alkali counter ions with cationic organic surfactants, such as alkyl ammoniums and nevertheless found alkyl ammonium surfactants not only accelerated the ageing and decomposition of polymer[10], but also led to the stacking recovery of the silicate layers[11].

In this work, 1-hexadecaneimidazolium iodine, one kind of ionic liquild, had been synthesized and organic modified MMT with this ionic liquid (ILMMT) was prepared by ionic exchange. A novel Ziegler-Natta/MMT compound catalyst was prepared by chemical reaction method and was used to prepare PP/MMT nanocomposites *via in situ* polymerization. Both Fourier transform infrared (FTIR) and Wide-angle X-ray diffraction (XRD) were used to clarify the microstructure of MMT and ILMMT. Thermogravimetric analysis (TGA) was carried out to estimate the thermal stability of ILMMT. The dispersion of MMT layers in poly(propylene) matrix and crystallite structure of obtained poly(propylene) were investigated by XRD patterns.

EXPERIMENTAL

Na⁺-MMT was supplied by Zhangjiakou Qinghe Chemical Factory with 90-100 mequiv/100 g cation exchange capacity

(CEC). Imidazole was purchased from Tianjin Fuchen Chemical reagent Co., 1-iodohexadecane (> 95 % purity) and diphenyl-dimethoxysilane (DDS, > 95 % purity) were purchased from Sigma Aldrich Co., tetrahydrofuran (THF), anhydrous ethanol and hexane were analytical reagent (AR) and purchased from Beijing Chemical Factory. 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. Toluene (analytical purity, Beijing Chemical Factory) was refluxed continuously over Na under argon for 24 h and withdraw from the still immediately before use. Triethyl aluminium ($AlEt_3$, analytical purity) was supplied by Yanshan Petrochemical Co. Propylene was supplied by Yanshan Petrochemical Co. Argon (extra pure grade, 99.99 % purity) was dried by passing it over a P_2O_5 column.

Fourier transform infrared (FTIR) spectra was analyzed with a Perkin-Elmer system 2000 Fourier transform infrared in a wave number range of 4000-400 cm^{-1}. FTIR spectras were obtained on samples mixed with KBr and molded into pellicle. Thermogravimetric analysis (TGA) was performed with Perkin-Elmer TGA at a heating rate of 20 °C/min under nitrogen atmosphere. 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 0.02° at a speed of 2°/min. The interlayer spacing (d_{001}) of clay was calculated in accordance with Bragg equation: $2d \sin \theta = \lambda$.

Synthesis of 1-hexadecaneimidazolium iodine: A solution of imidazole in THF was placed into a 500 mL flask with reflux condenser under the argon atmosphere. After 1-iodohexadecane was added dropwise at room temperature, the mixture was reflux for approximately 8 h. Then THF was removed using coevapourating. The resulted sample was rinsed with distilled *n*-hexane and dried under vacuum overnight at 40 °C.

Preparation of ionic liquild modified montmorillonite: 1-Hexadecane imidazolium iodine (twice the CEC of MMT) was dissolved in ethanol at 50 °C and the 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. The products were washed with hot ethanol till no iodine anions were measured using Ag^+ ions. The organical MMT modified with the ionic liquid (ILMMT) was dried at 80 °C under vacuum for 24 h.

Synthesis of Ziegler-Natta/MMT compound catalyst: $MgCl_2$, isooctanol 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 °C, followed by the addition of dibutylphthalate. ILMMT (dispersed in 50 mL toluene) was added to the above $MgCl_2·ROH$ solution at 60 °C and stirred for 24 h and then filtrated. After that, excess $TiCl_4$ was added dropwise into the $MgCl_2·ROH$/MMT mixture. The mixture was allowed to react at 100 °C for 3 h, the mixture was 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 six times. After removing solvent from the solid portion, Ziegler-Natta/ MMT compound catalyst solid powder was obtained.

Preparation of PP/MMT nanocomposites: 500 mL stainless autoclave was degassed and purified with propylene and then toluene, $AlEt_3$, DDS and catalyst powder were added successively to start polymerization. After predetermined reaction time, polymerization was quenched with diluted hydrochloric solution of ethanol. The PP/MMT nanocomposites was washed with ethanol several times, filtered and dried in a vacuum oven at 70 °C for 8 h.

RESULTS AND DISCUSSION

FTIR analysis of ionic liquild modified montmorillonite: Fig. 1 shows the FTIR spectra of MMT and ILMMT.
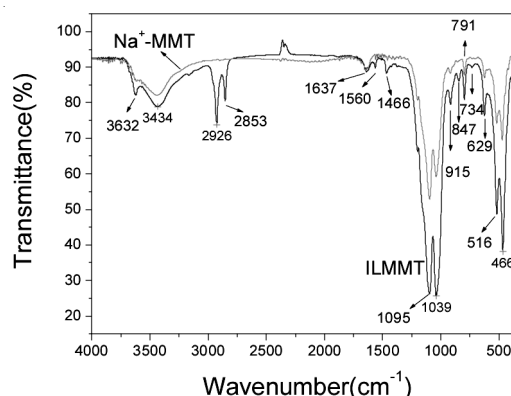

Fig. 1. FTIR Spectras of Na+-MMT and ILMMT

It could be seen that dual kurtosis of Si-O stretching vibration of MMT appeared at 1095 and 1039 cm^{-1} and bending vibration bands of Si-O and Al-O appeared at 466 and 516 cm^{-1}, respectively. Compared with the spectra of Na^+ MMT and ILMMT, the absorption bands at 2926 and 2853 cm^{-1} were characteristic absorptions of organic ionic liquild, which were C-H asymmetrical stretching vibration and deformation stretching vibration, respectively. It could simultaneously be seen that the stretching vibration bands of C=C stretching vibration of imidazolium appeared at 1466 and 1560 cm^{-1} and bending vibration band at 847 cm^{-1}. Furthermore, the wide absorption bands at 3434 and 1637 cm^{-1} were due to the stretching vibration and deformation vibration of water, respectively.

XRD measurement of organically modified montmorillonite: However, the XRD analysis is a powerful technique to prove ionic liquild loaded into interlayer of MMT. Fig. 2 shows XRD patterns of Na^+ MMT and ILMMT. The pattern of ILMMT shows that the (001) diffraction peak of montmorillonite shifts to $2\theta = 2.81°$ from $2\theta = 7.04°$ of Na^+ MMT, indicating the dspacing of layers increases to 3.14 nm from 1.25 nm according to the Bragg equation. Besides, the secondary reflection appears at $2\theta = 6.22°$.

Thermogravimetric analysis of organically modified montmorillonite: To evaluate the thermal stability of the ILMMT, thermogravimetric analysis was carried out after vacuum drying at 80 °C for 8 h and the results were shown in Fig. 3. The mass loss corresponding to the release of water molecule between the silicate sheets was as small as 0.4 % below 230 °C. It was revealed that 1-hexadecaneimidazolium

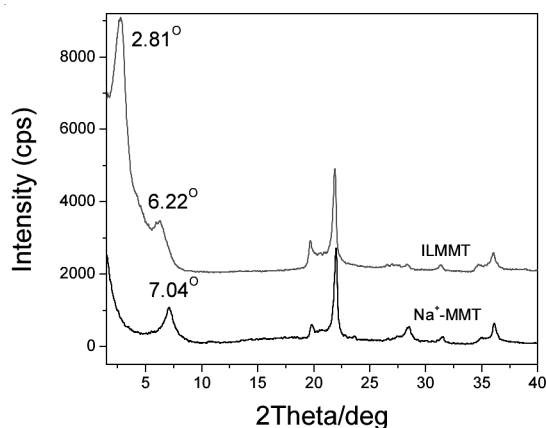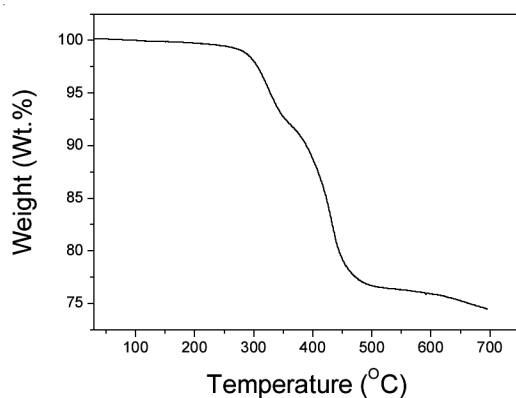Fig. 2. XRD patterns of Na⁺-MMT and ILMMT

Fig. 3. Thermogravimetric result of ILMMT

Fig. 4. XRD images of PP/MMT nanocomposites

cation intered into clay layers instead of Na⁺ because Na⁺ made it easy that the hydration water in the interlayer space of the respective montmorillonite samples formed H-bonds with the clayoxygen plane[13]. Otherwise, the temperature (230 ℃) is feckly the same as the processing temperature of poly(propylene). TG analysis also show that char content in ILMMT was 74.5 wt. % at 700 ℃, which meant that the ionic liquid cation content was about 25.5 wt. %.

Ionic liquid montmorillonite degraded in two main steps at 322 ℃ (T_{onset}) and 432 ℃ (T_{onset}), as shown in Fig. 3. The first stage weight loss is found to be 0.42-8.14 % from 231-364 ℃. This weight loss is due to decomposition of imidazolium. The second stage weight loss is 8.18-23.69 % from 365-545 ℃. The weight loss in this region is attributed to both degradation of the hexadecane chain and removal of structural hydroxy water in ILMMT.

XRD patterns of PP/MMT nanocomposites: XRD patterns for PP/MMT composites are shown in Fig. 4. XRD patterns of PP/MMT nanocomposites displayed no (001) diffraction peak from montmorillonite, indicating that the average interlayer spacing of the montmorillonite in PP/MMT nanocomposites was larger than 5.8 nm according to the Bragg equation. At the same time, it can be seen from Fig. 4 that the diffraction peaks at 2θ = 13.9, 16.8, 18.4 and 21.78 corresponded to the planes (110), (040), (130) and (111) of α-phase crystallite, respectively. α-Phase crystallite was still the 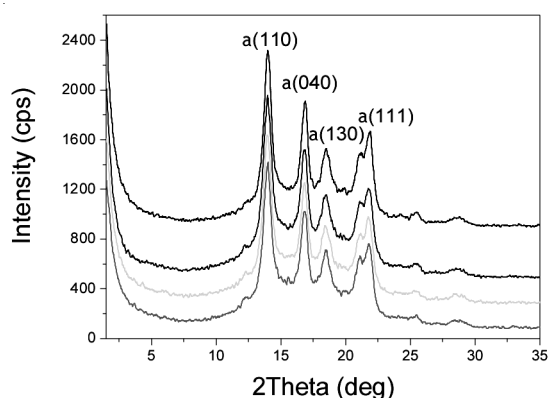main crystallite of PP in PP/MMT nanocomposites. Diffraction peaks of β-phase and γ-phase crystallite were not observed in XRD patterns of PP/MMT nanocomposites.

Conclusion

Montmorillonite was modified with 1-hexadecaneimidazolium iodine. FTIR revealed that the ionic liquild was loaded in the galleries of the resulting ILMMT. XRD patterns indicated that the d-spacing of ILMMT layers increasing to 3.14 nm from 1.25 nm of MMT. TG results show that the mass loss was very small below the processing temperature of PP and the thermal stability of ILMMT was superior to MMT. ILMMT was used to prepare a novel Ziegler-Natta/MMT compound catalyst and PP/MMT nanocomposites were synthesized *via in situ* polymerization. XRD patterns of PP/MMT nanocomposites showed that MMT layers was dispersed in PP matrix by nanometer size and that α-phase crystallite was still the main crystallite of PP in PP/MMT nanocomposites.

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