Research Article

Microstructure and Thermal Properties of Polypropylene/Clay Nanocomposites with $\text{TiCl}_4/\text{MgCl}_2/\text{Clay}$ Compound Catalyst

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Polypropylene (PP)/clay nanocomposites were synthesized by in situ intercalative polymerization with $\text{TiCl}_4/\text{MgCl}_2/\text{clay}$ compound catalyst. Microstructure and thermal properties of PP/clay nanocomposites were studied in detail. Fourier transform infrared (FTIR) spectra indicated that PP/clay nanocomposites were successfully prepared. Both wide-angle X-ray diffraction (XRD) and transmission electron microscopy (TEM) examination proved that clay layers are homogeneously distributed in PP matrix. XRD patterns also showed that the α phase was the dominate crystal phase of PP in the nanocomposites. Thermogravimetric analysis (TGA) examinations confirmed that thermal stability of PP/clay nanocomposites was markedly superior to pure PP. Differential scanning calorimetry (DSC) scans showed that the melt temperature and the crystallinity of nanocomposites were slightly lower than those of pure PP due to crystals imperfections.

1. Introduction

Since the nylon-6/clay nanocomposites with some excellent properties [1–4], such as enhanced mechanical properties [1, 2], increased heat distortion temperature, and decreased gas/vapor permeability [3], were successfully prepared by Toyota researchers in the late 1980s [4], many researchers from both academic and industrial labs have been focused on the polymer/clay nanocomposites [5–8].

Polypropylene (PP), as one of the most widely used plastics, possesses a relatively high performance-to-price ratio. However, inferior properties of PP, such as toughness [9], thermal stability, and barrier properties [10], hinder its application as high performance materials and special materials. Clay is one of very abundant phyllosilicate resources [11]. To improve PP properties, clay layers were hoped to disperse uniformly in PP matrix, exerting its rigidity, heat resistance, and dimension stability. However, it is difficult to prepare exfoliated PP/clay nanocomposites because of the incompatibility of hydrophobic PP and hydrophilic clay.

In order to improve the compatibility of clay and PP, surfactants have been used to modify clay [12]. However, It was found that some surfactants at the PP processing temperature not only accelerated the aging and decomposition of PP [13], but also led to the restacking of the silicate sheets [14]. Therefore, the design of surfactants with higher thermal stability is becoming more and more crucial.

In our previous work, 1-hexadecane-3-methylimidazolium bromine with relatively high thermal stability had been designed and synthesized as clay modification surfactants. Organically modified clay was used to prepare $\text{TiCl}_4/\text{MgCl}_2/\text{clay}$ compound catalyst by chemical reaction method and PP/clay composites were successfully synthesized by intercalative polymerization. Effects of polymerization conditions, such as temperature and time, on activity and catalytic stereospecificity of compound catalyst were studied in detail [15].

In this paper, the microstructure and thermal properties of PP/clay nanocomposites were studied at length. Fourier transform infrared (FTIR) was used to clarify the dispersion

of clay layers in PP matrix. The dispersion of clay layers in PP matrix was investigated by wide-angle X-ray diffraction (XRD) patterns and transmission electron microscopy (TEM). The thermal stability of PP/clay nanocomposites was estimated by thermogravimetric analysis (TGA). The melting process and nonisothermal crystallization kinetics of PP/clay nanocomposites were tested by differential scanning calorimetry (DSC).

2. Experimental

2.1. Materials. Clay was supplied by Zhangjiakou Qinghe Chemical Factory with 90~100 mmol/100 g cation exchange capacity (CEC). 1-Methylimidazole, 1-bromohexadecane (>95% purity), and diphenyldimethoxysilane (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 was withdrawn from the still immediately before use. Triethylaluminum (AlEt_3) and propylene were supplied by Yanshan Petrochemical Co. Argon (99.99% purity) was dried by passing it over a P_2O_5 column.

FTIR spectra were analyzed with a Perkin-Elmer System 2000 Fourier transform infrared in a wave number range of 4000–400 cm^{-1} . FTIR spectra were obtained on samples mixed with KBr and molded into pellicle. XRD analysis was performed on a Japan Rigaku D/max-2500 diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 0.1540 \text{ nm}$) 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°/min. The interlayer spacing (d_{001}) of clay was calculated in accordance with the Bragg equation: $2d \cdot \sin \theta = \lambda$. TEM was carried out on a Jeol JEM 2010 transmission electron microscope using an acceleration voltage of 100 kV. Samples for TEM were prepared by molding into specimens at 200°C and turned into ultrathin membrane by plasma cutting. TGA was performed with Perkin-Elmer TGA at a heating rate of 20°C/min under nitrogen atmosphere. DSC was conducted using a Perkin-Elmer DSC-7 thermal analyzer under nitrogen atmosphere with a heating rate of 10°C/min in a temperature range of 40–200°C for dynamic scanning, and melting enthalpy (ΔH_m) and melting temperature (T_m) were determined in the second scan. The crystallinity (X_c) was calculated with the following equation:

$$X_c = \Delta H_m \times \frac{100\%}{[\Delta H^* \times (1 - \text{wt.}\%(\text{MMT}))]}, \quad (1)$$

where ΔH^* is melting enthalpy of PP whose crystallinity is 100%, equal to 240.5 J/g [8].

2.2. Synthesis of $\text{TiCl}_4/\text{MgCl}_2$ /Clay Compound Catalyst. Synthesis of 1-hexadecane-3-methylimidazolium bromine, preparation of organically modified clay, and preparation of $\text{TiCl}_4/\text{MgCl}_2$ /clay compound catalyst are as described in [15].

2.3. Preparation of PP/Clay Nanocomposites. 2000 mL stainless autoclave was degassed and purified with propylene, and then toluene, AlEt_3 , DDS, and the pretreated catalyst slurry or powder were added successively to start polymerization. After predetermined reaction time, polymerization was quenched with diluted hydrochloric solution of ethanol. Composites (PP1 and PP2) were washed with ethanol three times, filtered, and dried in a vacuum oven at 70°C for 8 h.

3. Results and Discussion

3.1. Characterization of PP in PP/Clay Nanocomposites. PP was synthesized with $\text{TiCl}_4/\text{MgCl}_2$ /clay compound catalyst in combination with AlEt_3 as cocatalyst and DDS as an external donor in the slurry phase batch process. Some atactic activity centres can turn inactive because of DDS as an external donor in the slurry polymerization [16]. PP obtained in PP/clay nanocomposites might be stereospecific PP. Isotactic index (I.I) of PP was carried out as follows: 1–2 g dried PP/clay nanocomposites were wrapped with the filter paper. The package was extracted with boiling normal heptane for 10 h in Soxhlet's extractor and was dried in a vacuum oven until its mass was constant. Isotactic index was calculated with the following equation:

$$\text{I.I} = (w_3 - w_1) \times \frac{100\%}{(w_2 - w_1)}, \quad (2)$$

where w_1 is the weight of the dried filter paper, w_2 is the weight of PP/clay nanocomposites and the filter paper, and w_3 is the weight of package after being extracted and dried. On average, the I.I value of PP obtained in composites was 94%, which was close to I.I of PP synthesized by the commercial CS-2 catalyst (98%), indicating that PP obtained is high isotacticity PP.

3.2. Structure Characterization of the PP/Clay Nanocomposites. To prove clay in the resulting PP matrix, an infrared dichroism technique was carried out. Figure 1 shows the FTIR spectra of the PP/clay nanocomposites. The absorption bands at 1460 cm^{-1} and 1375 cm^{-1} are C–H bending vibration of PP. The broad peak around 3000 cm^{-1} is C–H symmetrical stretching and anamorphic vibration. It also can be seen that dual kurtosis of Si–O stretching vibration of clay appears at 1095 cm^{-1} and 1035 cm^{-1} , and bending vibration bands of Si–O–Fe and Si–O–Mg appear at 463 cm^{-1} and 515 cm^{-1} . The results revealed that the PP/clay composites were successfully prepared.

XRD was used to prove the dispersion of clay sheets in PP matrix. Figure 2 shows XRD patterns of PP/clay composites. The XRD patterns display no (001) diffraction peak from the clay, indicating that the average interlayer spacing of the clay in PP/clay nanocomposites is larger than 5.8 nm according to the Bragg equation and indicating that the silicate layers of clay are fully exfoliated during in situ intercalative polymerization. At the same time, it could be seen from Figure 2 that the diffraction peaks at $2\theta = 13.9$, 16.8, 18.4, and 21.8 corresponded to the planes (110), (040), (130), and (111) of α -phase crystallite, respectively. α -phase

TABLE 1: Thermal properties of PP/clay nanocomposites.

Run	T_m (°C)	H_m (J/g)	T_c (°C)	H_c (J/g)	$T_{0.01}$ (°C)	$T_{0.05}$ (°C)	T_{onset} (°C)
PP0	162.8	100	117.2	98	298.6	330	379
PP1	158.7	82.7	116.5	82.3	308.8	343.6	443.2
PP2	160.0	80.8	118.3	80.3	323.0	366.3	452.3

FIGURE 1: FTIR spectra of PP/clay nanocomposites.

FIGURE 2: XRD patterns of PP/clay nanocomposites.

crystallite was still the main crystallite of PP in PP/clay nanocomposites. Diffraction peaks of β -phase and γ -phase crystallite were not observed in XRD patterns of PP/clay nanocomposites. This conclusion agreed with former work, and the dominate crystal phase of PP did not change because of the change of imidazolium and the existence of clay [8].

However, TEM is a powerful technique to prove the extent of silicate dispersion. Figure 3 shows TEM image of PP/clay nanocomposites. The TEM micrograph showed that the silicate layers were well dispersed in the whole PP

FIGURE 3: TEM image of PP/clay nanocomposites.

matrix. The average thickness of the clay layers was less than 20 nm, corresponding to about 10 silicate layers of stacking. It could be concluded from TEM measurements that exfoliated PP/clay nanocomposites were prepared via in situ polymerization.

3.3. Thermal Properties of PP/Clay Nanocomposites. DSC is a technique used to study what happens to the nanocomposites when they are heated. Figure 4 shows DSC curves of PP/clay nanocomposites and pure PP, and Table 1 lists the data of thermal properties of PP/clay nanocomposites. It can be seen in Figure 4 and Table 1 that the melting temperature (T_m) of PP/clay nanocomposites is about 160°C, slightly lower than 162.8°C of pure PP, indicating an increase of crystals imperfections because of the presence of clay layers. The degree of crystallization (X_c) of PP/clay nanocomposites was lower than that of pure PP, as shown in Table 1, which also proved the existence of crystals imperfections. However, the crystallization temperature (T_c) of nanocomposites was 116.5°C to 118.3°C, close to 117.2°C of pure PP (PP0).

Thermal stability of PP/clay nanocomposites was measured by using TGA. Figure 5 shows the TGA curves of PP/clay nanocomposites and pure PP. The initial decomposition temperature (temperature at 1 wt.% weight loss $T_{0.01}$ and temperature at 5 wt.% weight loss $T_{0.05}$) and the maximum decomposition temperature (T_{onset}) were shown in Table 1. In comparison of the thermal decomposition temperature of PP/clay nanocomposites (PP1 and PP2) with that of pure PP (PP0), the thermal stability of PP/clay nanocomposites was much higher than that of pure PP. In a word, the effect of

FIGURE 4: DSC curves of pure PP and PP/clay nanocomposites: (a) DSC heating thermograms; (b) DSC cooling thermograms.

FIGURE 5: TGA curves of pure PP and PP/clay nanocomposites.

clay on the thermal stability of the nanocomposites was much pronounced.

4. Conclusions

PP/clay composites were successfully synthesized by in situ intercalative polymerization with $\text{TiCl}_4/\text{MgCl}_2/\text{clay}$ compound catalyst, in accordance with FTIR spectra. XRD patterns and TEM image showed that clay layers in composites were exfoliated into nanometer size and dispersed uniformly in the PP matrix. The clay enhanced the thermal stability of PP materials. PP obtained in the nanocomposites had high isotacticity. The effect of clay on melting temperature and the crystallization temperature of PP/clay nanocomposites was slight.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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