Thermal Properties of Polypropylene/Ionic Liquid Modified Clay Nanocomposites

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Polypropylene (PP)/ionic liquild modified clay nanocomposites were successfully synthesized *via in situ* polymerization based on Ziegler-Natta/clay compound catalyst. Wide angle X-ray diffraction (XRD) analysis proved clay layers were exfoliated into nanometer size in polypropylene matrix and the α-phase was the main crystal phase of polypropylene in the nanocomposites. The presence of clay enhanced the thermal stability of polypropylene materials, since the initial decomposition temperature of polypropylene/clay nanocomposites was evidently bigger than that of pure polypropylene. The crystalliztion temperature of nanocomposites was slightly higher than that of pure polypropylene due to nucleation ability of clay.

Key Words: Ziegler-Natta catalyst, Clay, Poly(propylene), Nanocomposites, Thermal properties.

INTRODUCTION

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

Polypropylene (PP), as one of the most widely used plastic, possesses a relatively high performance-to-price ratio. However, inferior properties of polypropylene, such as toughness, thermal stability and barrier properties, hinder its application as high performance materials and special materials. To prepare high-performance polypropylene composites for potential applications in the field of packaging and the automotive industry as a substitute of high performance engineering plastics, clay layers were hoped to scatter in polypropylene matrix by nanometer size, to exert rigidity, heat-resistant and dimension stability of the layers.

Three most common methods to prepare polypropylene/clay nanocomposites are solution blending[2,6], melt blending[7] and *in situ* polymerization[8]. Among these three methods, *in situ* polymerization is the most effective method to prepare exfoliated polypropylene/clay nanocomposites.

In previous work, one kind of Ziegler-Natta/ ionic liquild modified clay compound catalyst was prepared by chemical reaction and exfoliated polypropylene/clay nanocomposites were successfully prepared with this compound catalyst *via*

in situ polymerization. In this paper, Fourier transform infrared (FTIR) was used to clarify the dispersion of clay layers in polypropylene matrix. The dispersion of clay layers in polypropylene matrix was investigated by wide-angle X-ray diffraction (XRD) patterns. The thermal stability of polypropylene/clay nanocomposites was estimated by thermogravimetric analysis. The melting process and non-isothermal crystallization kinetics of polypropylene/clay nanocomposites were tested by differential scanning calorimetry.

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 diphenyldimethoxy silane (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) were 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: 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. The dispersion of clay layers in polypropylene matrix was

investigated by wide-angle X-ray diffraction (XRD) patterns. Wide-angle X-ray diffraction (XRD) analysis was performed on a Japan Rigaku D/max-2500 diffractometer. The interlayer spacing (d_{001}) of clay was calculated in accordance with Bragg equation: $2d \sin \theta = \lambda$. Thermogravimetric analysis (TGA) was performed with Perkin-Elmer TGA at a heating rate of 20 ºC/min under nitrogen atmosphere. 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) and melting enthalpy (ΔH_m) was determined in the second scan.

Preparation of polypropylene/clay nanocomposites: 1,3-Dihexadecane imidazolium iodine was synthesised and was used to modify clay according to He *et al.*[9]. Ziegler-Natta/ ionic liquild modified clay compound catalyst was prepared according to Wang *et al.*[10].

500 mL stainless autoclave was degassed and purified with propylene and then toluene, $AlEt_3$, DDS and the 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

Microstructure of the polypropylene/clay nanocomposites: Fig. 1 showed the FTIR spectra of the polypropylene/ clay nanocomposite. The dual kurtosis of Si-O stretching vibration of clay appear at 1095 and 1035 cm^{-1} and the bending vibration bands of Si-O-Fe and Si-O-Mg present itself at 463 and 515 cm^{-1}. The C-H bending vibration of polypropylene come forth at 1460 and 1375 cm^{-1}. The C-H symmetrical stretching and anamorphic vibration appear around 3000 cm^{-1}. Furthermore, appearing at 1639 and 1424 cm^{-1} is hydrocarbon absorption.
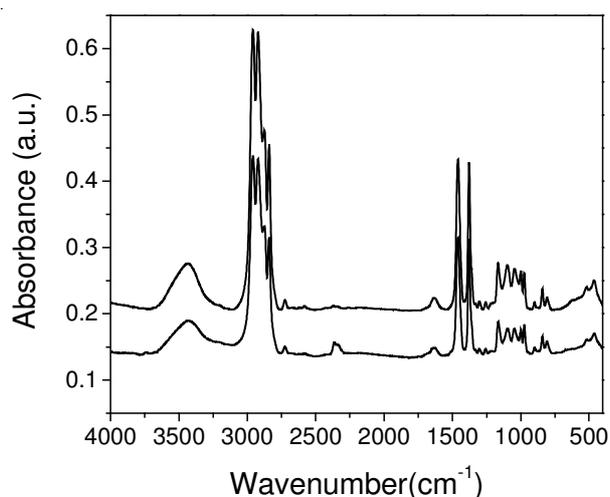

Fig. 1. FTIR spectras of polypropylene/clay nanocomposites

Fig. 2 represents XRD patterns of polypropylene/clay composites and used to prove the microstructure of polypropylene/clay nanocomposites. No clay (001) diffraction peak displayed in XRD patterns of polypropylene/clay
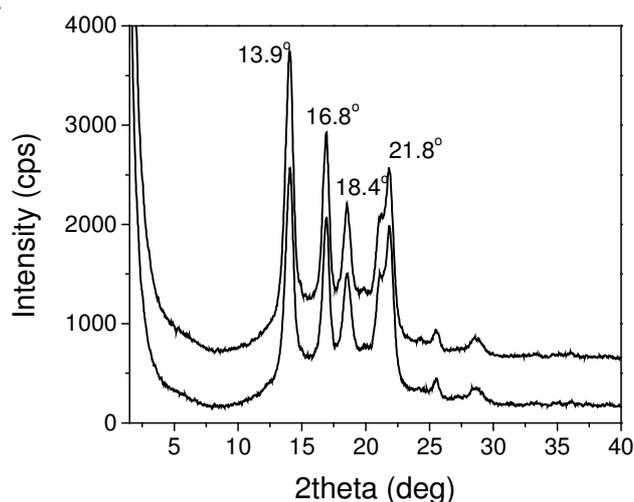

Fig. 2. XRD patterns of polypropylene/clay nanocomposites

nanocomposites, indicating that the average interlayer spacing of the clay was larger than 5.8 nm according to the Bragg equation. It indicated the silicate layers of clay were exfoliated during *in situ* intercalative polymerization. It could also be seen from Fig. 2 that the planes (110), (040), (130) and (111) of α-phase crystallite appear at 2θ = 13.9, 16.8, 18.4 and 21.8, respectively.

DSC results of polypropylene/clay nanocomposites: The DSC curves of pure polypropylene and polypropylene/ clay nanocomposites are given in Fig. 3. The data of thermal properties of polypropylene/clay nanocomposites were listed in Table-1. It can be seen in Table-1 that T_m of polypropylene/ clay nanocomposites is about 157.2-158.7 ºC, slightly smaller than 163.5 ºC of pure polypropylene, indicating an increase of the number of defects due to the presence of clay. It can also been seen in Table-1 that the crystalliztion temperature of nanocomposites is 118.2-119.9 ºC, which is slightly bigger than 116.8 ºC of pure polypropylene (Table-1), as shown in Table-1. This phenomenon may be due to the efficient nucleating effects of clay layers.

| TABLE-1						
DATA OF THERMAL PROPERTIES OF POLYPROPYLENE (PP)/CLAY NANOCOMPOSITES						
Run	T_m (ºC)	H_m (J/g)	T_c (ºC)	H_c (J/g)	$T_{0.01}$ (ºC)	$T_{0.1}$ (ºC)	Clay (%)
PP1	158.5	75.9	119.0	70.5	343.2	379.3	1.28
PP2	157.2	76.5	118.2	75.6	348.4	378.4	1.43
PP3	158.4	76.5	119.2	74.0	347.4	384.1	1.62
PP4	158.7	83.9	119.9	85.4	354.5	380.2	2.08
Pure PP	163.5	101.9	116.8	104.3	316.3	361	0

Thermal stability of polypropylene/clay nanocomposites: TGA was employed to determine the initial decomposition temperature (temperature at 1 wt. % weight loss $T_{0.01}$ and temperature at 10 wt. % weight loss $T_{0.1}$), as shown in Table-1. The $T_{0.01}$ and $T_{0.1}$ of polypropylene/clay nanocomposites were obviously larger than that of pure polypropylene. It indicated that the effect of clay on the thermal stability of the nanocomposites is much pronounced.

Processing stability of polypropylene/clay nanocomposites: Fig. 4 shows the XRD patterns of polypropylene/clay

(a)

(b)
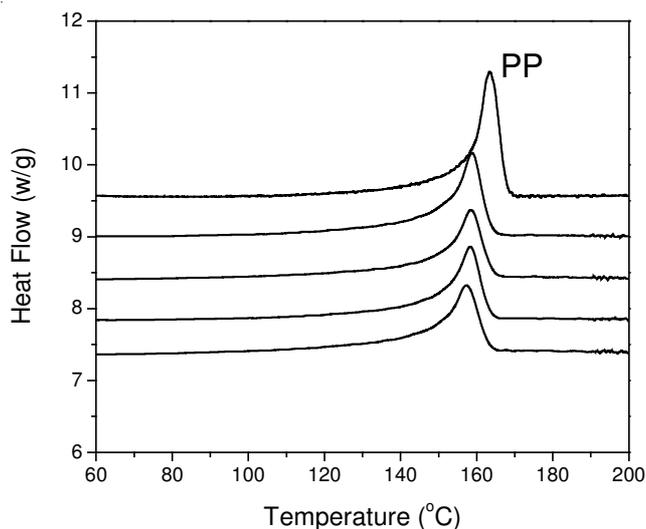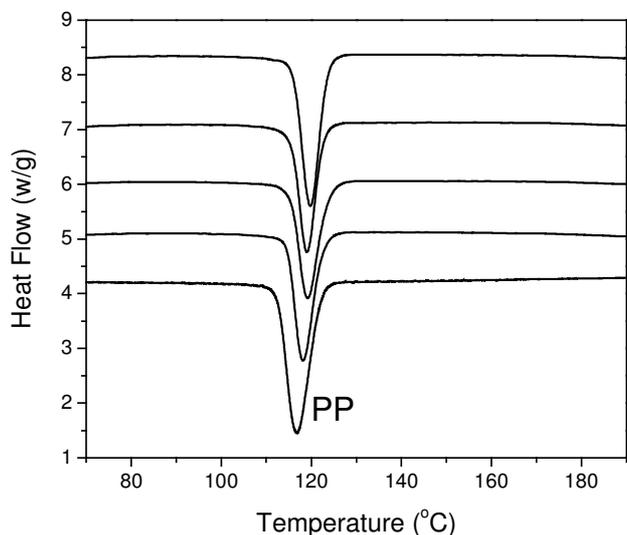
Fig. 3.   DSC scaning of pure polypropylene and polypropylene/clay nanocomposites (a) DSC heating thermograms; (b) DSC cooling thermograms
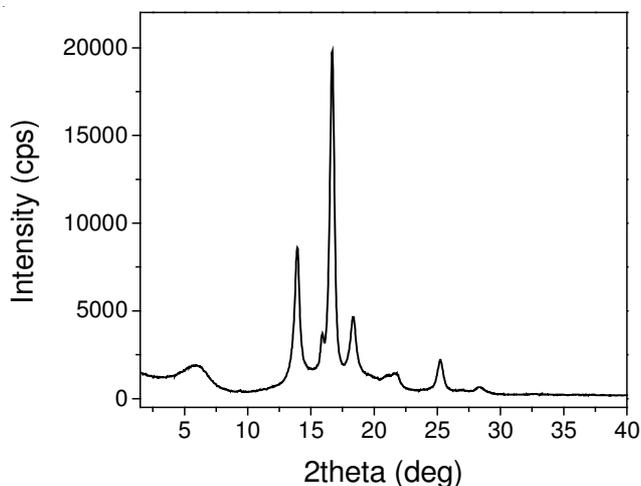

Fig. 4.   XRD patterns of polypropylene/clay nanocomposites after processing

nanocomposites after processing at 200 ºC for 10 min under certain shear rate. As shown in Fig. 4, (001) diffraction dispersion peak of clay was distinctly observed. It indicated stacking of silicate layers. At the same time, the plane (040) of α-phase crystallite markedly boost up and the plane (300) of β-phase crystallite came forth slightly at 2θ = 16.0.

Conclusion

Polypropylene/clay nanocomposites were successfully synthesized by *in situ* intercalative polymerization with Ziegler-Natta/ionic liquild modified clay compound catalyst. XRD examinations proved clay layers scattered in polypropylene matrix by the nano-meter and the α-phase was the dominate crystal phase of polypropylene in the nanocomposites. DSC scans showed the crystalliztion temperature of nanocomposites was slightly bigger than that of pure polypropylene due to the efficient nucleating effects of clay layers. TGA proved that the thermal stability of polypropylene/clay nanocomposites rose noticeably, in comparison the initial decomposition temperature of polypropylene/clay nanocomposites with that of pure polypropylene. The aggregation of clay layers was found after processing at 200 ºC for 10 min, but it could be avoided by shortening the shear time in acordence with previous work[8,11].

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