

SYNTHESIS AND CHARACTERIZATION OF POLYPROPYLENE/MONTMORILLONITE NANOCOMPOSITES VIA AN *in-situ* POLYMERIZATION APPROACH

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Abstract Polypropylene/montmorillonite (PP/MMT) nanocomposites were prepared by *in-situ* polymerization using a MMT/MgCl₂/TiCl₄-EB Ziegler-Natta catalyst activated by triethylaluminum (TEA). The enlarged layer spacing of MMT was confirmed by X-ray wide angle diffraction (WAXD), demonstrating that MMT were intercalated by the catalyst components. X-ray photoelectron spectrometry (XPS) analysis proved that TiCl₄ was mainly supported on MgCl₂ instead of on the surface of MMT. The exfoliated structure of MMT layers in the PP matrix of PP/MMT composites was demonstrated by WAXD patterns and transmission electron microscopy (TEM) observation. The higher glass transition temperature and higher storage modulus of the PP/MMT composites in comparison with pure PP were revealed by dynamic mechanical analysis (DMA).

Keywords Polypropylene, Nanocomposite, *in-situ* Polymerization

INTRODUCTION

Polymer layered silicate nanocomposites (PLSNs) have attracted considerable interest during the recent past few years^[1–10]. The importance of such composites is due to the strong synergistic effects between the polymer and the silicates, which may result in enhanced electrical, optical, mechanical and thermal properties as compared with their conventional microcomposite counterparts.

Synthesis of PP/MMT nanocomposites becomes an active field in industrial and academic research. Most recent studies have been focused on preparing PP/MMT nanocomposites by a melt intercalative compounding process using a functionalized polypropylene as compatibilizer^[11–16]. Although the dispersed morphology of the clay particles, the excellent mechanical properties^[14, 15] and the rheological behaviors^[16] of the intercalated PP/MMT nanocomposites were investigated, this method usually suffers from a number of drawbacks. The steps of modifying the silicate to render highly hydrophilic montmorillonite organophilic by ion exchange with various organic cation molecules, polarizing the polyolefin or its oligomers and the chemical or physical deterioration of the virgin components during the melt process may offset the benefits of the silicate to some extent. An alternative way of making PP/MMT nanocomposites is to use *in-situ* polymerization in which the silicate is intercalated with a catalyst, and upon introduction of a monomer the layered silicate tends to disperse itself into the resin by the driving force of the polymerization reaction. O'Hare and coworkers^[17, 18] have reported the intercalation of synthetic layered silicates with metallocene catalyst after treating the silicates with methylaluminoxane and the polymerization with this catalyst only yielded propylene oligomers. In these papers, no composite characterization was provided. Preparation of polypropylene nanocomposite by *in-situ* polymerization using a typical Ziegler-Natta catalyst has technological advantages, but few reports have been

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found in the open literature^[19].

In this paper, we report the preparation of polypropylene/MMT nanocomposites by *in-situ* polymerization using a MMT/MgCl₂/TiCl₄-EB Ziegler-Natta catalyst. The layer structures of MMT both in the catalyst and in the PP/MMT composites are discussed, and the dynamic mechanical properties of the composites are investigated as well.

EXPERIMENTAL

Materials

Sodium montmorillonite (MMT), Southern Clay product, was dried at 400°C for 2 h before use. Anhydrous MgCl₂ was kindly supplied by Yingkou Xiangyang Science Chemical Co. Ethyl benzoate (EB), titanium tetrachloride (TiCl₄), dimethoxy(diphenyl)silane (DDS), triethylaluminum (TEA) and ethanol (EtOH) were commercial products. Hexane and heptane were dried over 0.4 nm molecular sieves and distilled over potassium-sodium alloy before use. Propylene, polymerization-grade from Liaoyang Chemical Corporation, was used without further treatment.

Preparation of MMT/MgCl₂/TiCl₄-EB Catalyst

A hexane solution of MgCl₂/EtOH in a molar ratio of EtOH/MgCl₂ = 6 was stirred at 60°C until a transparent solution was formed. A calculated amount of MMT was introduced into the system, and stirred at 60°C for 2 h. The slurry was filtered, washed with hexane for several times and finally dried by evacuation, giving a MMT/MgCl₂ solid. To MMT/MgCl₂ solid, purified heptane was added, and TiCl₄ and EB in a calculated amount were introduced at 98°C with vigorous stirring. The reaction continued for 2 h, then the slurry was filtered, washed with hexane at 60°C several times, and finally dried by evacuation.

The MMT/TiCl₄-EB catalyst was prepared by directly loading TiCl₄ and EB on MMT in heptane at 98°C, followed by the steps of filtering, washing and drying.

The MgCl₂/TiCl₄-EB catalyst for preparation of isotactic polypropylene as a reference was prepared according to the literature^[20].

Preparation of PP and PP/MMT Composites

Polymerization was carried out in a 2 L steel reactor at 70°C for 1 h under a propylene pressure of 0.8 MPa with heptane as solvent, TEA as cocatalyst and dimethoxy(diphenyl)silane (DDS) as external donor.

Characterization

The Ti and Mg loadings of the catalyst were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Plasma-Spec (I) instrument. A Perkin-Elmer TGA-7 thermal gravimetric analyzer was used to measure MMT content in the composites. Wide-angle X-ray diffraction (WAXD) was used to measure the layer spacing of the MMT both in the catalyst and in the PP/MMT composites using a D/max 2000PC apparatus with Cu-K radiation. Transmission electron microscopy (TEM) observation was performed on a Hitachi H-800EM instrument. Samples were compression-molded into sheets at 180°C, then cut into ultrathin films at -150°C using a LKB2088 microtome. The molecular weight of polypropylene was determined by gel permeation chromatography (GPC) with a Waters 410 GPC. A Metravib MAK-04 Viscoanalyzer dynamic mechanical thermal analyzer (DMA) was used to measure the dynamic mechanical properties of the samples at 11 Hz. The samples were heated from -70°C to 150°C at a heating rate of 3 K/min.

RESULTS AND DISCUSSION

Catalyst Structure Analysis

The characteristics of MMT, such as layered structure with a layer thickness of 1 nm, high surface area and the capability of swelling in alcohol^[21], suggest its use as a component of MgCl₂/TiCl₄-type catalysts. Based on these considerations, in this work, MMT was first immersed in a homogeneous MgCl₂/EtOH heptane solution, where

the complex of $\text{MgCl}_2 \cdot n\text{EtOH}$ was able to diffuse into the swelled interlayers of MMT by chemical or physical absorption. Then, MgCl_2 was reformed after removal of EtOH from the system. By loading TiCl_4 and the internal donor EB, the MMT/ MgCl_2 / TiCl_4 -EB catalyst with intercalated structure was formed.

On using the *in-situ* polymerization approach, intercalation of catalyst components into the MMT layers was essential for obtaining composites with the MMT layers nano-scale dispersed in the polymer matrix. WAXD diffraction patterns (Fig. 1) clearly showed continuously enlarged layer spacing of MMT when the catalyst components were intercalated successively into the layers of MMT. As shown in Fig. 1, the pristine MMT had a strong 001 peak at $2\theta = 7.64^\circ$ corresponding to an interlayer spacing of 1.15 nm, while with intercalation of MgCl_2 , the 001 peak shifted to $2\theta = 6.34^\circ$ corresponding to an interlayer spacing of 1.39 nm, and finally with intercalation of TiCl_4 -EB, it shifted to $2\theta = 5.18^\circ$ corresponding to an interlayer spacing of 1.71 nm. The continuous enlarged interlayer spacing of MMT by successivel intercalation of the catalyst components is schematically shown in Scheme 1.

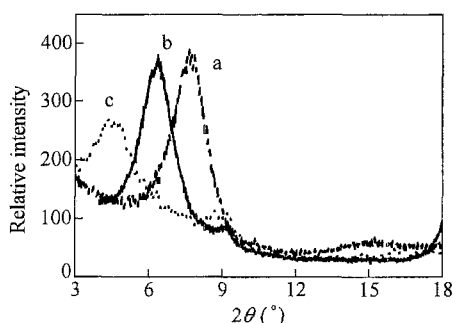
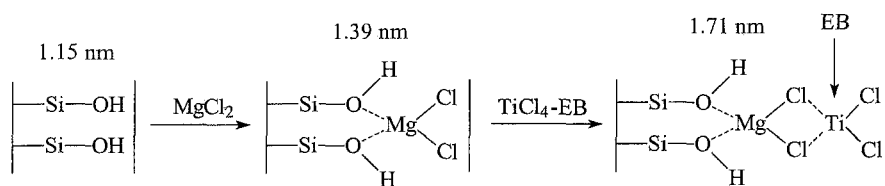


Fig. 1 X-ray diffraction patterns of (a) MMT, (b) MMT/ MgCl_2 and (c) MMT/ MgCl_2 / TiCl_4 -EB



Scheme 1

It was worth while to consider whether TiCl_4 was supported on MgCl_2 microcrystallites or on the layer surface of MMT, the latter having been confirmed as having very low activity with regard to the olefin polymerization^[22]. To clarify our suspicion, the binding energies (E_b) of $\text{Ti}_{2p_{3/2}}$ in the three catalysts measured by XPS analysis were investigated. As tabulated in Table 1, the E_b values of $\text{Ti}_{2p_{3/2}}$ in MMT/ MgCl_2 / TiCl_4 -EB were almost the same as in MgCl_2 / TiCl_4 -EB, but lower than in MMT/ TiCl_4 -EB, indicating that the chemical environment of Ti species in MMT/ MgCl_2 / TiCl_4 -EB is the same as in MgCl_2 / TiCl_4 -EB, but different from that in MMT/ TiCl_4 -EB. From this observation, it can be concluded that the Ti species in MMT/ MgCl_2 / TiCl_4 catalyst is mainly supported on the MgCl_2 , probably through a Cl bridge, instead of on the layer surface of MMT^[23].

Polymerization

By varying the polymerization conditions, PP/MMT composites with different MMT contents were obtained (Table 2). As shown in Table 2, the activity of the MMT/ MgCl_2 / TiCl_4 -EB was comparable to that of the general type Ziegler-Natta catalyst, (MgCl_2 / TiCl_4 -EB), further confirming that TiCl_4 was mainly supported on MgCl_2 . Even though, the isotactic index (I.I.) of the composites was lower than that of general PP, probably due to the complicated chemical or physical properties of the MMT layer surface. Intensive studies are progressing to

promote the I.I. of the composites.

Table 1. Results of XPS analysis

Samples	Binding energy E_b in eV		
	Mg _{2s}	Cl _{2p}	Ti _{2p3/2}
MgCl ₂ /TiCl ₄ -EB	51.2	199.0	458.2
MMT/TiCl ₄ -EB	—	198.6	459.2
MMT/MgCl ₂ /TiCl ₄ -EB	51.1	199.5	458.1

Table 2. The polymerization results^a

Samples	Catalyst	[Al]/[Ti] molar ratio	[Ti]/[DDS] molar ratio	Activity (10 ⁻⁵ g/mol · Ti · h)	I.I. ^b (wt%)	M_w 10 ⁻⁴	MMT ^c (wt%)
PP-0	MgCl ₂ /TiCl ₄ -EB ^{d1}	40	4	1.7	97	14.6	—
PP-1	MMT/MgCl ₂ /TiCl ₄ -EB ^{d2}	20	4	2.4	87	13.9	1.1
PP-2		30	4	3.1	85	15.3	0.8
PP-3		40	4	1.1	89	15.7	2.4
PP-4	MMT/TiCl ₄ -EB ^{d3}	40	4	trace	—	—	—

^a Polymerization was performed in a 2 L reactor under a propylene pressure of 0.8 MPa with 1000 mL hexane as solvent, TEA as cocatalyst. The Ti contents of the different catalyst are 2.5% (d1), 1.9% (d2) and 0.2% (d3), respectively.

^b Isotactic index was measured by extraction with boiling heptane for 8 h

^c MMT content was measured by TGA.

Analysis of the PP/MMT Composites

X-ray diffraction pattern (Fig. 2) of the PP/MMT composite showed no diffraction peak in the 3–10° angle region, indicating the loss of a layered structure and thus possibly the exfoliation of the MMT layers. As discussed above, the catalyst components were loaded within the interlayer spacing, and during polymerization the growing PP chains tended to disjoin the MMT layers, resulting in the ultimate destruction of the layered organization.

The dispersion of MMT layers in the PP/MMT composite was directly observed by TEM (Fig. 3). A few nanometric particles can be clearly seen in Fig. 3, evidencing the occurrence of partial exfoliation. It should be pointed out that the samples had been compression-molded into sheets at 180 °C, then cut into ultrathin films for TEM observation. Therefore, Fig. 3 showed the dispersion of the MMT layers having been deformed to some extent. The dispersion of MMT layers in the nascent polymer particles, which may record information regarding departing neighbouring MMT layers from each other during polymerisation process, will be the subject of future work.

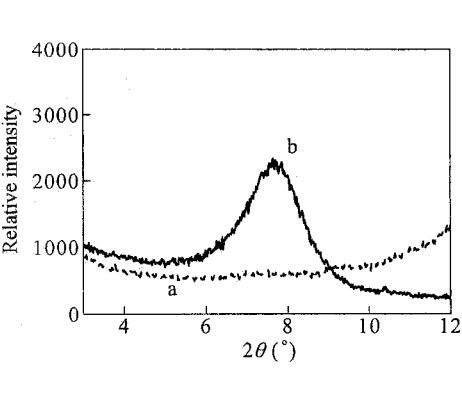


Fig. 2 X-ray diffraction patterns of (a) MMT and (b) PP-3 nanocomposite

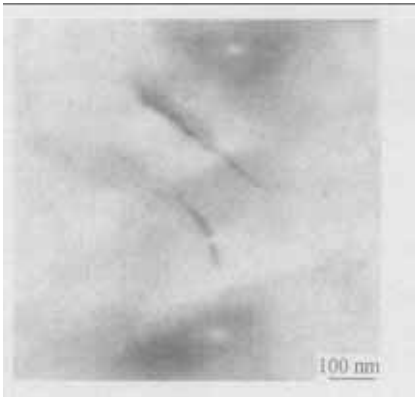


Fig. 3 TEM image of PP-3 nanocomposite

Dynamic Mechanical Properties of the PP/MMT Nanocomposites

Figures 4 and 5 show the plots of storage modulus and relative storage modulus ($E'_{\text{PP/MMT}}/E'_{\text{PP}}$) against temperature, respectively. As compared to PP without MMT (PP-0), the PP/MMT composites have higher storage modulus below the temperature of around 80 °C (Fig. 5), implying the improved mechanical strength of the composites. At above 80 °C, the enhancement effect of MMT on the composite materials is no longer observable, the lower isotactic index of PP in the composites might weaken the benefits of MMT to some extent, preventing the composites from gaining better high temperature performance.

Figure 6 illustrates the dependence of $\tan\delta$ on the MMT content for the nanocomposites and pure PP. The glass transition temperatures (T_g s) of the composites raise 3–5 °C, as compared to PP. This means that the molecular chains of PP in the composites become more rigid and stiff, due to the strong interaction between the molecular chains and the nano-scale dispersed MMT layers, which could be the inherent reason for the improved storage modulus and higher T_g s of the composites.

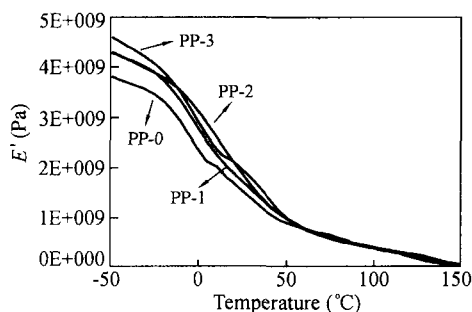


Fig. 4 DMA plots of storage modulus against temperature

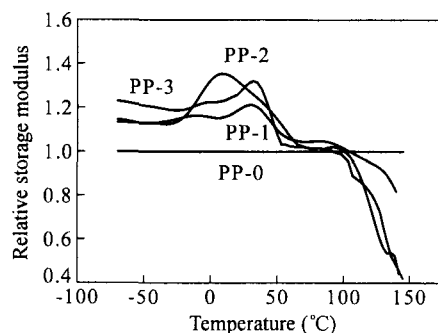


Fig. 5 Relative dynamic storage modulus as a function of temperature

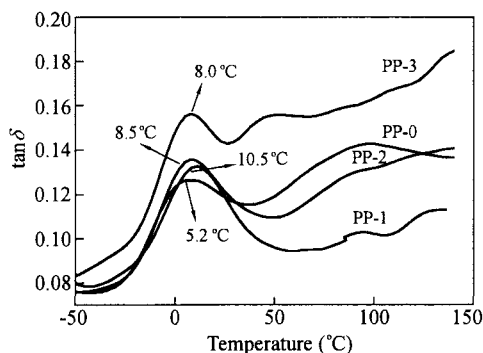


Fig. 6 DMA plots of $\tan\delta$ against temperature

CONCLUSION

PP/MMT nanocomposites were prepared by *in-situ* polymerization using a MMT/MgCl₂/TiCl₄-EB Ziegler-Natta catalyst. The intercalated structure of MMT layers in the catalyst was confirmed by gradually enlarged layer spacing of MMT with the successive intercalation of the catalyst components. XPS analysis proved that TiCl₄ was mainly supported on MgCl₂ instead on the surface of MMT.

The exfoliated structure of MMT layers in the PP matrix of PP/MMT composites was cross-checked using WAXD and TEM. Higher T_g s and higher storage modulus of the PP/MMT composites in comparison with the pure PP were revealed by DMA. The more rigid polypropylene molecular chains, owing to the strong interaction between the molecular chains and the nano-scale dispersed MMT layers, are claimed to be the inherent reason for

the improved storage modulus and higher T_g s of the composites.

REFERENCES

- 1 Messersmith, P.B. and Stupp, S.I., *J. Mater. Res.*, 1992, 7: 2559
- 2 Okada, A. and Usuki, A., *Mater. Sci. Eng.*, 1995, 3: 109
- 3 Giannelis, E.P., *Adv. Mater.*, 1996, 8: 29
- 4 Novak, B.M., *Adv. Mater.*, 1993, 5: 422
- 5 Komarneni, S.J., *Mater. Chem.*, 1992, 2: 1219
- 6 Wang, Z. and Pinnavaia, T.J., *Chem. Mater.*, 1998, 10: 3769
- 7 Li, Q., Zhao, Z.D., Ou, Y.C., Qi, Z.N. and Wang, F.S., *Acta Polymeric Sinica (in Chinese)*, 1997, (2): 188
- 8 Ke, Y.C., Wang, L. and Qi, Z.N., *Acta polymeric Sinica (in Chinese)*, 2000, (12): 768
- 9 Burnside, S.D. and Giannelis, E.P., *Chem. Mater.*, 1995, 7: 1597
- 10 Armand, M.B., *Adv. Mater.*, 1994, 6: 2216
- 11 Kato, M., Usuki, A. and Okada, A., *J. Appl. Polym. Sci.*, 1997, 66: 1781
- 12 Hasegawa, N., Kawasumi, M., Kato, M., Usuki, A. and Okada, A., *J. Appl. Polym. Sci.*, 1998, 67: 87
- 13 Kawasumi, M., Hasegawa, N., Kato, M., Usuki, A. and Okada, A., *Macromolecules*, 1997, 30: 6333
- 14 Hasegawa, N., Okamoto, H., Kato, M. and Usuki, A., *J. Appl. Polym. Sci.*, 2000, 78: 1981
- 15 Hasegawa, N., Okamoto, H., Kato, M., Tsukigase, A. and Usuki, A., *Macromol. Mater. Eng.*, 2000, 280: 76
- 16 Galgali, G., Ramesh, C. and Lele, A., *Macromolecules*, 2001, 34: 852
- 17 Tudor, J., Willington, L., O'Hare, D. and Royan, B., *Chem. Commun.*, 1996, 2031
- 18 Tudor, J. and O'Hare, D., *Chem. Commun.*, 1997, 603
- 19 Ma, J., Qi, Z.N. and Hu, Y.L., *J. Appl. Polym. Sci.*, 2001, 82: 3611
- 20 Galli, P., Barbe, P.C. and Noristi, L., *Angew. Makromol. Chem.*, 1984, 120: 73
- 21 Thorez, J., in: "Practical Identification of Clay Minerals, a Handbook for Teachers and Students in Clay Mineralogy", Elsevier, Amsterdam, 1976, p.361
- 22 Rong, J.F., Jing, Z.H., Li, H.Q. and Sheng, M., *Macromol. Rapid. Commun.*, 2001, 22: 329
- 23 Liu, H.L. and Xiao, S.J., *Makromol. Chem.*, 1993, 194: 421