

DISPERSION AND TENSILE BEHAVIOR OF POLYPROPYLENE/MONTMORILLONITE NANOCOMPOSITES PRODUCED VIA MELT INTERCALATION*

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Abstract Most of the articles on polymer nanocomposites focus on the importance of chemistry used to modify the surface of the clay, usually montmorillonite (MMT), and characterization of the nano-scale structure obtained. The role and importance of processing were also discussed recently. However, few papers concerning the correlation between morphology of MMT and mechanical properties were published. In order to understand the tensile behavior of PP/Montmorillonite (MMT) nanocomposites better, and to further improve the reinforcement efficiency, we first prepared the PP nanocomposites via direct melt intercalation using conventional twin-screw extrusion. The dispersion and tensile property of the composites were then investigated by SEM, XRD, TEM and a video-controlled tensile set-up. The macroscopic and microscopic dispersion of MMT in PP matrix was verified by XRD and TEM, combined with SEM. The tensile properties were obtained by video-controlled tensile set-up, which gives true stress-strain curve. It was found that a partly intercalated and partly exfoliated structure (also called incomplete exfoliation) existed in the system. Though the tensile strength of PP nanocomposites is not much improved in engineering stress-strain curves, more than 20% increase of true stress was found in a true stress-strain experiment at high true strain, which indicates that only oriented silicate layers can have a big effect on tensile properties. Not only orientation of silicate platelets but also the degree of exfoliation is a key factor to determine the reinforcement efficiency. The reinforcement efficiency of MMT has been discussed based on the “continuum” Halpin-Tsai equations. A good agreement was found between experimental data and theoretical prediction by changing N value (number of platelets per stack) which corresponding to different state of the dispersion of MMT in PP matrix.

Key words Polypropylene/Montmorillonite nanocomposites, Dispersion, Orientation, Tensile property

INTRODUCTION

Because of many advantages of polymer nanocomposites, they have been intensively investigated. These nanocomposites exhibit improved modulus, decreased thermal expansion coefficient, reduced gas permeability, increased solvent resistance, and enhanced ionic conductivity when compared to the pristine polymers. The enhanced properties are presumably due to the synergistic effects of nanoscale structure and improved interaction between the filler and the polymer.

Polymer melt intercalation of mica-type layered silicates (clay) is a viable approaches to synthesis of a variety of polymer-silicate nanocomposites. Since the possibility of direct melt intercalation was first demonstrated by Giannelis *et al.*^[1, 2], the melt intercalation method has become a mainstream technique for the preparation of intercalated polymer nanocomposites along side in situ intercalative polymerization. This method usually includes the following steps: (1) clay (in most cases montmorillonite is used) is first modified by cation

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exchange, and (2) mixed together with polymer matrix by a twin screw extrusion or a mixer. But because it is not thermodynamically spontaneous, the formation of nanocomposites by melt-intercalation needs to increase the interaction between polymer and silicate layers so that the melt intercalation process can occur. During the last few years, a number of polymer nanocomposites have been made through melt intercalation. They include polystyrene (PS)^[3, 4, 5], Nylon-6 (PA6)^[6], polypropylene (PP)^[7–18], polyethylene (PE)^[19–21], ethylene-vinyl acetate copolymers (EVA)^[22], poly(styrene-*b*-butadiene) copolymers (SBS)^[23], and poly(ethylene oxide) (PEO)^[24, 25]. Also some work have been done on the theoretical analysis of thermodynamics^[4, 26] and kinetics^[5, 27] involved in melt intercalation. The effect of melt processing conditions on the extent of exfoliation has been discussed recently, and the degree of dispersion was interpreted based on the residence time distribution in the extruder and the intensity of shear^[28].

Polypropylene is one of the most widely used polyolefin polymers. Since it does not include any polar group in its backbone, the homogeneous dispersion of the hydrophilic clay layers in polypropylene is very difficult. PP/montmorillonite nanocomposites was first reported by Kato *et al.* in 1997^[7–10]. Since then, many research groups have devoted attention to PP/layered silicate nanocomposites^[11–18] due to their promising applications. In general, the clay is modified with alkylammonium to facilitate its interaction with PP. However, the organically modified clay does not disperse well in the still too hydrophobic non-polar polypropylene. In order to improve the interaction between polypropylene and the modified silicates layers, a polar functional polymer (such as maleic anhydride-modified PP, PP-MA) is introduced to mediate the polarity. Hasegawa^[8] and Reichert^[11] compared the influence of compatibilizer functionality, and found that there are two important factors involved achieving the exfoliated and homogeneous dispersion of the layers in PP matrix: (1) relatively high PP-MA content (typically 22 wt%), (2) sufficient polar functionalization of PP-MA chains (acid value = 26 mg KOH/g for $M_w = 40,000$). By adding PP-MA as a compatibilizer, we also have successfully prepared well-ordered intercalated PP/MMT nanocomposites via direct melt intercalation in a twin-screw extruder^[13].

So far, most of the work is focused on the preparation and characterization of polypropylene nanocomposites. Some mechanical properties were also reported, but few publications correlating the dispersion and mechanical properties are seen. Compared with Nylon 6/MMT nanocomposites, PP/MMT nanocomposites show much less enhanced mechanical properties. For example, Nylon-6/MMT nanocomposite with a 4.2 wt% MMT content shows a change of heat-distortion temperature from 62°C to 152°C, and the yield strength, tensile modulus, flexural strength, and flexural modulus have all been very much improved^[6]. While for PP/MMT nanocomposites, less than 10% increase of tensile strength was noted^[7, 11, 13]. It is not clear so far why the mechanical property of PP/MMT nanocomposites is much lower than what is expected from the concept and idea of nanoscale reinforcement. We noted that all the reported tensile strengths were obtained from a nominal stress-strain curve. This nominal stress-strain curve does not give much valuable information due to the inhomogeneity of the deformation process, *i.e.* the formation of the neck. For an in-depth study of the mechanism of reinforcement, we thus need a true stress-strain curve that is recorded under constant strain. We also understand that the efficiency of reinforcement depends mainly on the aspect ratio (defined as diameter/thickness) of fillers. The higher the aspect ratio, the larger the reinforcement will be. Since the aspect ratio is directly related to the dispersion of MMT in PP matrix, in this work, we concentrated our attention first on the dispersion of MMT in PP matrix by using XRD, SEM and TEM, and then to tensile properties by using Instron, video-controlled uniaxial tensile test. The purpose of this paper is not to develop a way to further improve the exfoliation, nor to investigate the effect of nano-particles on PP crystal morphology. Our purpose is to establish the relation between dispersion and tensile property of PP/MMT nanocomposites, and to understand better the reinforcement efficiency. Both the orientation of silicate platelets and degree of exfoliation are found to be two key factors in determining the reinforcement efficiency of PP/MMT nanocomposites.

EXPERIMENTAL

Materials

The materials used for the preparation of the PP/MMT nanocomposites are listed in Table 1. The dioctadecyl

dimethylammouium bromide (C-18) is an alkylammonium salt used for cation exchange. PP-MA in which maleic anhydride group is randomly grafted on a PP backbone was used as a “compatibilizer”.

Table 1. Raw materials used in the experimentals

Name	Characterization	Suppliers
Sodium montmorillonite	Cation exchange capacity: 68.6 mmol/100 g MMT	Renshou, Sichuan, China
Diocetadecyl dimethylammonium bromide (C-18)		Zhongli Co., China
Polypropylene 1300	Melt index: 1.0 g/10 min	Yan Shan Co., China
Maleic anhydride-modified PP (PP-MA)	MA: 0.6 wt%	Chengguang Research Institute, China

Preparation of Organically Modified MMT

50 g Sodium montmorillonite was dispersed in 1000 mL hot water using a stirrer. The dioctadecyl dimethylammonium bromide (C-18) (25 g) was dissolved in hot water (300 mL) and then poured into the montmorillonite-water solution under vigorous stirring for 2 h. The product was washed three times with water and filtered, then dried in vacuum at 100°C for several hours. It is termed OMMT. The interlayer spacing of pure and treated MMT was measured by X-ray diffraction.

Preparation of PP/MMT Nanocomposites

OMMT and PP-MA were melt-mixed with PP at 200°C using a twin screw extruder. The temperature of the extruder was maintained at 160°C, 190°C, 210°C, 210°C and 195°C from hopper to die. The screw speed was 110 r/min. The resulting pellets were compression-molded into sheets around 0.4 mm thickness at a temperature of 180°C. The melt sheets were kept at this temperature for 10 min for completing the polymer chain relaxation before they were transferred quickly to room temperature. Samples with the standard “dog bone” shape were obtained with the aid of a stamp for tensile testing. The specimens for XRD were also cut from the melt-pressed sheet.

Characterization of the Dispersion of MMT in PP Matrix

The disperisibility of silicate layers in the composites was evaluated by using XRD, SEM and TEM. XRD analysis was performed by using a Rigaku Denki RAD-B instrument with Cu-K α ($\lambda = 0.154$ nm) radiation at room temperature. The basal spacing of the montmorillonite was estimated from the (001) peak in the XRD pattern. For SEM investigation, the samples were fractured in liquid nitrogen. The fractured surfaces were then gold coated and investigated in a JEOL JSM-5900LV SEM instrument, using an acceleration voltage of 20 kV. For TEM measurement, ultrathin sections with a thickness of 100 nm were prepared at -80°C using a diamond knife. The measurement was performed on a LEO 912 Omega apparatus at 120 kV.

Tensile Properties

The tensile strength and tensile modulus were measured using an Instron 4301 tensile testing machine at a speed of 50 mm/min and 5 mm/min, respectively. According to the procedure developed by G'Sell^[29, 30], true stress-strain curves were measured on the Instron equipped with a video-control that maintained a constant local strain rate in the narrowest part of the specimen. The neck profile is registered with the aid of a CCD camera. Assuming a constant sample volume during the stretching, the local strain in the center of the neck can be derived from the minimum diameter. The true stress and strain are continuously registered with the aid of the video camera connected to a computer via a frame grabber.

RESULTS AND DISCUSSION

The Dispersion of MMT in Composites

To have the overall macroscopic review of MMT dispersion in PP, we begin with the result of SEM. This is shown in Fig. 1. Some primary MMT particles are observed with a size of 100–200 nm and are quite homogeneously dispersed in PP matrix. Due to the low resolution of SEM, one does not know whether the

observed particles have an intercalated-structure or an exfoliated structure in the remaining area. So other evidential experiments are needed. XRD and TEM are two preferential methods to characterize the dispersion of MMT in nanocomposites. Figure 2 shows the XRD profiles of MMT and OMMT. The peaks correspond to the (001) reflections of the clay (the interlayer gallery height). The basal spacing of the OMMT increases from 1.47 nm for the pure MMT, to 1.9 nm. Figure 3 shows the XRD profiles of samples with different OMMT content after melt-mixing with PP, the peak of OMMT was further extended to 3.3 nm, suggesting that the intercalation of PP into the gallery indeed takes place. There exists a clear regular layered structure, demonstrated by the presence of d_{001} and higher-order diffraction peaks. It should be noted that the interlayer gallery is independent of the MMT loading, as evidenced from the constant peak position. This independence of the gallery height on MMT loading was also found in PS-based nanocomposites^[3, 4].

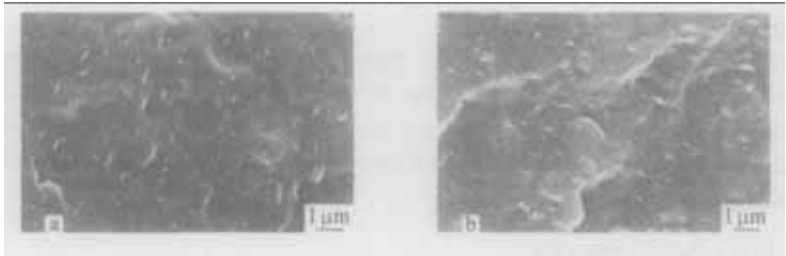


Fig. 1 SEM microphotograph of the fractured surface of PP/MMT nanocomposites
a) 5 wt% MMT content; b) 10 wt% MMT content

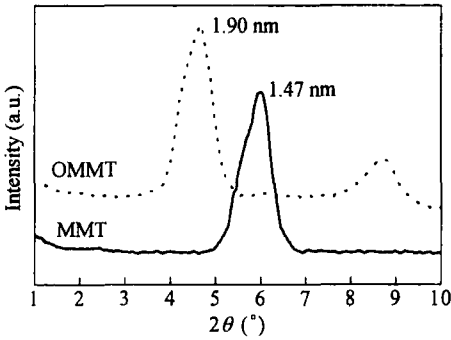


Fig. 2 XRD profiles of MMT before and after treatment with dioctadecyl dimethylammonium bromide
a) MMT; b) OMMT

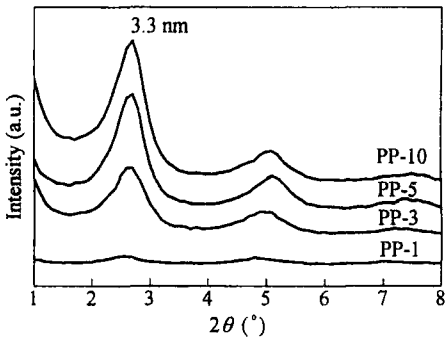


Fig. 3 XRD profiles of different content of MMT after melt-mixing with PP

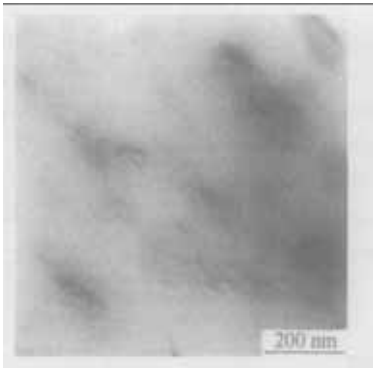


Fig. 4 TEM microphotograph of PP/OMMT nanocomposite 5 wt% MMT content

Nevertheless, XRD can not tell us any information about the exfoliation of MMT, because no peak appears in the XRD profile if exfoliation occurs. In order to verify further the dispersion of the silicate layers in PP/OMMT, a TEM experiment was conducted. Shown in Fig. 4, as an example, is the TEM microphotograph of PP/OMMT nanocomposites with OMMT content of 5 wt%, where the dark lines are the cross sections of silicate layers. Most of the silicate layers are dispersed uniformly in the polypropylene matrix with sizes of only 5–10 nm, indicating most of the silicate layers are exfoliated. But in some areas, intercalated layers with a size of 50–100 nm are also observed. Combined together with the results of SEM, XRD and TEM, it can be concluded that an exfoliated and intercalated structure co-exists (also called incomplete exfoliation) in the composites.

True Stress-Strain Curves from Video-controlled Tensile Experiment

Having the general picture of the dispersion of MMT in PP matrix, we proceed to understand the tensile behavior. In the great majority of the known results of the studies of the tensile properties of PP/MMT nanocomposites, an engineering load-extension curve was registered under a condition of constant cross-head speed. Figure 5(a) gives a typical nominal stress-strain relationship of the composites. Here, the nominal stress σ_{nom} , and the nominal strain ε_{nom} are defined as

$$\sigma_{\text{nom}} = \frac{F}{A_0} \quad (1)$$

$$\varepsilon_{\text{nom}} = \frac{\Delta L}{L_0} \quad (2)$$

where F is the load applied, A_0 and L_0 are the original cross-section area and length, and ΔL is the change in length. One finds a yield maximum after a nearly linear region at low deformations, followed by a necking and the growth of the neck indicated by a stress plateau. Only 2–3 MPa increase of the yield maximum which is called also tensile strength, is observed from 35 MPa of pure PP to 37–38 MPa of the nanocomposites. A slight decrease of the yield maximum of the composites as MMT content increases from 1 wt% to 10 wt% may be due to the fact that dispersion becomes worse when MMT content is getting higher.

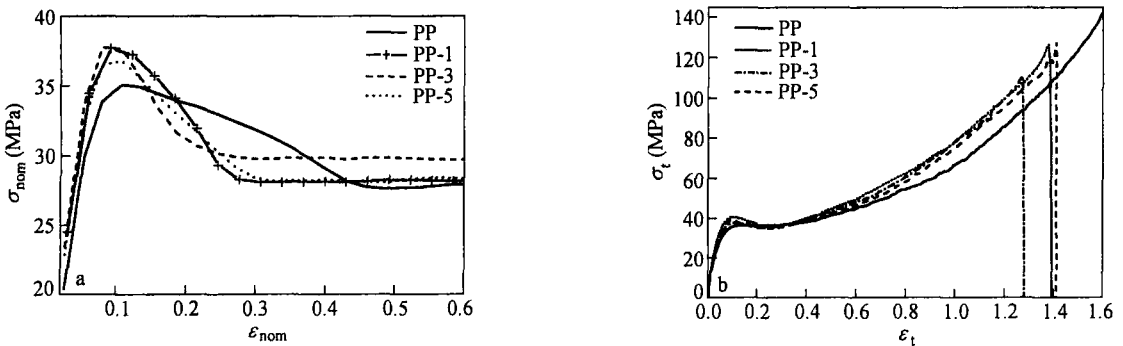


Fig. 5 The engineering stress-strain curves (a) and true stress-strain (b) of PP/MMT nanocomposites

The tensile deformation is inhomogeneous after the yield maximum due to the neck. The formation of a neck strongly affects the measured stress-strain curves. It is difficult to compare the deformation behavior of different samples merely based on the engineering stress-strain curves. In fact, the formation of a neck complicates the analysis of the deformation behavior. This nominal stress-strain curve does not give much valuable information due to the inhomogeneity of the deformation process, *i.e.* the formation of the neck. We do not know the change of stress with the increase of deformation after the formation of the neck. For a better understanding of reinforcement efficiency of the PP nanocomposites, a true stress-strain curve is thus needed and which is recorded under a constant strain rate. True stress is defined by

$$\sigma_t = F/A \quad (3)$$

in which A is the true cross section at different time.

And the true strain is defined by

$$\varepsilon_t = \int_{L_0}^L \frac{dL_i}{L_i} = \ln \frac{L}{L_0} = \ln \lambda \quad (4)$$

where λ denotes the extension ratio. The true stress-true strain curves which are shown in Fig. 5(b) were measured by video-controlled uniaxial tensile testing under a constant strain rate. The same sample as used in obtaining Fig. 5(a) curves was stretched at constant Hencky strain rate of $5 \times 10^{-3} \text{ s}^{-1}$. Comparing Fig. 5(b) with Fig. 5(a), the first observation is that the stress maximum in the engineering stress-strain curve, which is characteristic for a necking sample, has disappeared. The true stress-true strain curve represents a result without the effect of neck. It is possible to compare the true stress at different deformation based on this technique. There is no change of the true stress at low strain. A large increase of the stress, however, is observed at high strain. This may be ascribed to the increased orientation of MMT along the stretching direction as the strain is increased. For comparison, some true stresses at selected true strains are listed in Table 2. An increase of the stress by 20% is obtained at $\varepsilon_t = 1.38$ by adding only 1 wt% MMT to PP. Again, the decreased true stress at high MMT loading is caused by the worse dispersion of MMT in PP matrix when MMT content is getting higher. To follow the orientation change with ε_t during stretching, the deformed sample was examined by WAXS experiments. Employing a Mini-Instron (Rheometric Scientific Mini Mat 2000), samples could be kept under stress during the exposure. Figure 6 collects some WAXS diagrams registered for PP nanocomposite (MMT = 3 wt%) at three deformations (ε_t) under load. Starting from the non-deformed state at $\varepsilon_t = 0$, the isotropic intensity distribution of PP is observed, with five circles in WAXS patterns associated with different lattice planes of PP. One also finds a weak circle near to the center, resulting from the {001} diffraction of MMT. As ε_t increases to 0.6, the orientation of silicates layers starts, as indicated by the intensity change of {001} diffraction of MMT, but not very much orientation is seen for PP. At $\varepsilon_t = 1.2$, however, the circles of PP become spots, due to the orientation of PP chain along the drawing direction, as we expected. Meanwhile, one only observes two broad spots (two strings) in the meridian for MMT, which suggests that all the silicate layers (intercalated or exfoliated) are highly oriented along the drawing direction. This corresponds to the large increase of true stress at large true strain. So the orientation of silicate layers is very important for improving the reinforcement efficiency.

Table 2. True stress at selected true strain

ε_t		0.1	0.2	0.4	0.6	0.8	1.0	1.27	1.38
σ_t (MPa)	PP	35.7	36.2	38.1	44.8	54.3	66.9	93.7	106.3
	PP-1	40.5	37.0	39.8	49.6	62.5	78.1	107.3	126.4
	PP-3	37.7	35.3	39.4	48.2	60.6	78.3	110.4	—
	PP-5	38.7	35.3	38.6	46.6	58.1	75.3	104.2	119.9

The Effect of Incomplete Exfoliation on Tensile Modulus

Compared with tensile strength or true stress, tensile modulus is a more well-defined property. Over years, several theories have been developed to predict the tensile modulus of composites^[31–33]. Among them, the “continuum” Halpin-Tsai Equations are practically useful to predict the modulus of nanocomposites based on the layered filler. According to this theory, in a completely exfoliated system, we have:

$$\frac{E_{\text{composite}}}{E_{\text{matrix}}} = \frac{1 + 2A_f\eta\phi}{1 - \eta\phi}$$

where A_f is the aspect ratio of the platelet (assuming a disk-like platelet, A_f is defined as diameter divided by thickness). ϕ is the volume fraction of platelets in the composites and η is given by:

$$\eta = \frac{E_r - 1}{E_r + 2A_f}$$

where E_r is the ratio of the platelet to the matrix modulus.

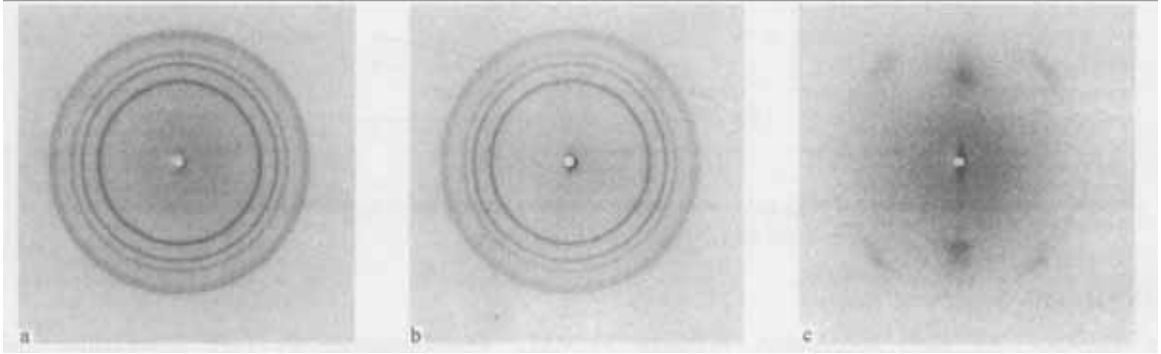


Fig. 6 WAXS diagrams PP/MMT nanocomposites (3 wt% MMT content) measured for indicated strain during stretching under load

a) $\varepsilon_t = 0$; b) $\varepsilon_t = 0.6$ and c) $\varepsilon_t = 1.3$

For an incomplete exfoliation system (like our system), the modified Halpin-Tsai Equations proposed by Bicerano^[32] can be used, which considers the system as a composite. The composite consists of a matrix and pseudoparticles which are incompletely exfoliated stacks of individual platelets.

$$\frac{E_{\text{composite}}}{E_{\text{matrix}}} = \frac{1 + 2A_f' \eta' \phi'}{1 - \eta' \phi'} \quad \eta' = \frac{E_r' - 1}{E_r' + 2A_f'}$$

$$A_f' = \frac{A_f}{\hat{N}} \left(\frac{1}{1 + (1 - 1/\hat{N}) \frac{s}{t}} \right)$$

$$E_r' = E_r \left(\frac{1}{1 + (1 - 1/\hat{N}) \frac{s}{t}} \right) + \frac{(1 - 1/\hat{N}) \frac{s}{t}}{1 + (1 - 1/\hat{N}) \frac{s}{t}} \quad \phi' = \phi \left(1 + (1 - 1/\hat{N}) \frac{s}{t} \right)$$

$$\hat{N} = N + (1 - N) \left(\frac{s}{t} \right) \left(\frac{\phi}{1 - \phi} \right)$$

where N is the number of platelets per stack, and s/t is the ratio of platelet spacing to platelet thickness in a stack, for well-exfoliated platelets, $N = 1$. Figure 7 shows the theoretical tensile modulus at different N together with experimental data in the PP nanocomposites, the aspect ratio ($A_f = 200$) and $s/t (= 2)$ are chosen based on XRD and TEM results. At 1 wt% MMT content, the experimental tensile modulus is nearly equal to that predicted by the theory with $N = 2$, suggesting that the system most likely has a exfoliated structure. With increase of MMT content, the experimental data fit the theoretical prediction only at high N values. For example, $N = 12$ for 3 wt% MMT, $N > 12$ for 5 wt% MMT. The increase of N suggesting a worse dispersion of MMT in PP matrix as MMT content is increased, is in good agreement with experimental observation. It also should be noted that N is just an average value, not necessary meaning that all the MMT particles have the same morphology. This result indicates that both N and s/t play important roles in determining the tensile modulus, and only completely exfoliated silicate layers can significantly improve the tensile modulus. In other word, the intercalated morphology makes little contribution to the tensile modulus. Thus the ratio of exfoliation to intercalation is a key to determine the tensile modulus of PP nanocomposites.

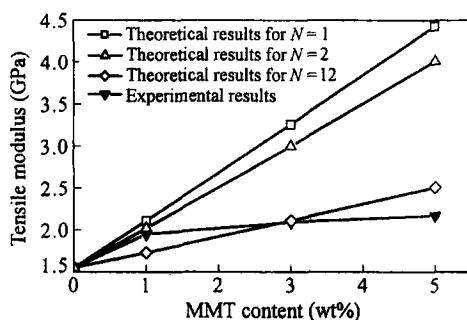


Fig. 7 The theoretical tensile modulus at different N together with experimental data in the PP nanocomposites

CONCLUSION

In summary, we have successfully prepared PP/MMT nanocomposites by melt intercalation using organomontmorillonite and the conventional twin-screw extrusion compounding process. There exists a partly intercalated and partly exfoliated structure in the system. The ratio of exfoliation to intercalation plays an important role in determining the tensile modulus of PP nanocomposites and only completely exfoliated silicate layers can significantly improve the tensile modulus. The modified Halpin-Tsai Equations can be well used to predict the tensile modulus of PP/MMT nanocomposites. In addition to the degree of exfoliation of MMT, the orientation of silicate platelets is another key factor to achieve a good tensile enhancement. Without the orientation, not very much improvement of tensile strength and true stress is observed, and nearly 20% increase of true stress is obtained at high strain due to a change of the orientation of silicate platelets along the stretching direction.

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