Effect of Montmorillonoite Modification and Maleic Anhydride-Grafted Polypropylene on the Microstructure and Mechanical Properties of Polypropylene/Montmorillonoite Nanocomposites

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ABSTRACT: Two types of modified montmorillonite (MMT) were achieved using octadecylamine as the modifying agent by the methods of dry process and wet route. Polypropylene (PP)/MMT nanocomposites were prepared using the melt mixing technique and employing maleic anhydride-grafted polypropylene (PP-MA) as the compatibilizer. The modification of montmorillonite was characterized by fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and scanning electron microscope (SEM). The effect of MMT modification and PP-MA on the microstructure and properties of PP/MMT nanocomposites was investigated by SEM, differential scanning calorimeter (DSC), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), and polarizing microscopy. The results show that organic montmorillonite modified by wet process (WOMMT) has a large d-spacing increment; whereas montmorillonite modified by dry process (DOMMT) shows little d-spacing increment. Furthermore, the mechanical properties of composites incorporating WOMMT are better than that containing DOMMT. As a third component, the addition of PP-MA benefits the formation of exfoliated structure and the dispersion of MMT in PP matrix, and hence, enhances the physical properties of the nanocomposite. With the presence of PP-MA, the highly dispersed MMT increases the number of spherulite crystals, enhances the melting enthalpy, improves the thermal stability, and induces the desired tiny crazes more effectively. MMT increases the storage modulus (E') and glass-transition temperature (T_g) of PP because of the stiffness of MMT layers, but PP-MA decreases them owing to its high melt flow index, both of which were in favor of improving the physical properties. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 3952–3960, 2013

INTRODUCTION

Scientific research on preparation and characterization of polymer/clay nanocomposites has grown continuously in the last few years with the general aim of developing new polymeric materials with improved characteristics. Polypropylene/clay nanocomposites probably receive the highest interest because of excellent cost-performance ratio of this polymer and high versatility.[1]

Polypropylene (PP) is one of the fastest growing classes of thermoplastics. This growth is ascribed to its appealing combination of low cost, low density, and high heat distortion temperature.[2] To upgrade its properties to match the profile of a typical engineering thermoplastic, proper fillers or reinforcements are incorporated into the PP matrix.[3] PP-based composite applications have consequently received wide spread use, such as in the automobile, cable, and packaging industries. Because of the feasibility of preparing polymer/clay nanocomposites with the con-

ventional melt-mixing technology,[4] the development of PP/clay nanocomposites has been greatly inspired.[5–9]

Silicate clay like MMT has been used as reinforcing materials for polymer composites owing to its high aspect ratio and unique intercalation/exfoliation characteristics. Nanocomposite of polymer–montmorillonite was obtained by widely used formation method-melt compounding[10] and extrusion just before injection. However, MMT particles are easily agglomerated in polypropylene, because MMT exhibits hydrophilic characteristics and shows an affinity for hydrophilic (polar) polymers.[11] For nonpolar PP, the naturally hydrophilic MMT has to be organically modified with organic surfactant.

In order to achieve good distribution, the naturally hydrophilic MMT is organically modified by means of exchanging the interlamellar metallic ions of the clay by alkyl ammonium salt surfactant and its interlayer spacing increases. So PP chains could diffuse into MMT interlayer and the intercalated or even

exfoliated structures were formed in the composite.[12] Preparation of organophilic montmorillonite (OMMT) plays a crucial role in the formation of the structure and property of PP.[13] In the previous literatures, the usually employed intercalation agent is the long chain ammonium ions, such as dimethyl dihydrogenated tallow quaternary ammonium ion, methyl tallow bis-2-hydroxyethyl quaternary ammoniumion,[14] dodecyl ammonium chloride,[13] undecyl ammonium chloride,[1] and stearyl ammonium chloride.[15] The intercalation modification of MMT could be successfully achieved by employing these long chain ammonium ions. After the modified OMMT or commercially available OMMT has been incorporated into PP, the analysis of microstructure, thermoanalysis, and dynamic mechanical analysis of these nanocomposites were deeply investigated; whereas the mechanical strength of them was hardly emphasized. In addition to ammonium ions surfactant, the long chain primary amine like octadecylamine, one of the potential modifiers, was also used for MMT modification. According to the reports,[16–18] montmorillonite was modified with octadecylamine by forming ammonium salt of octadecylamine in acidic solution. However, a limited increment in d-spacing or inhomogeneous interlayer distances of OMMT was observed and the impact strength of polypropylene was negatively affected by the addition of this OMMT, indicating that the preparation of OMMT using octadecylamine should be improved.

As the stratagem of employing organic MMT improves the affinity between the polymer matrix and MMT only to a limited extent,[14] the addition of extra compatibilizers are required to improve the compatibility between PP and OMMT.[19] PP-MA exhibits the affinity for both organic montmorillonite and PP to form nanocomposites. Therefore, PP-MA could play an important role in promoting the formation of PP/organoclay nanocomposites.

The main idea of this work is to obtain OMMT with large and homogeneous d-spacing using octadecylamine and develop the PP/OMMT nanocomposites with good mechanical strength. Two kinds of OMMT were prepared using octadecylamine by the methods of dry process and wet route, respectively. The influence of the obtained OMMT and PP-MA on the structure and properties of PP were studied. The mechanical properties of PP/OMMT composites were determined through tensile, flexural, and izod impact tests. The crystal structure and the thermal properties of these composites were evaluated by polarizing microscope, DSC, TGA, and DMA.

EXPERIMENTAL

Materials

Polypropylene (Model No. EPS30R, melting point = 160∼170°C, specific gravity = 0.90 g/cm³, melt flow index = 2.0 g/10 min) was provided by Sinopec Mao Ming Petrochemical in Guang Dong. Na⁺ type montmorillonite (Na-MMT) was supplied by Zhejiang San Ding Technology Co. Ltd. in Zhejiang of China. Commercial grade of PP-MA with a melt flow index = 100g/10 min, was obtained from High Polymer Material Co. Ltd. in Nanjing. Octadecylamine was used to modify Na-MMT, supplied by Melist Plastic Technical Limited Company.

Preparation of OMMT

Method 1, preparation of organic montmorillonite by dry process (DOMMT): DOMMT were prepared by mixing 10g of Na-MMT

Table I. Nominal Weight Compositions of the Composites Under Study

S.no.	Compositions	Parts
(1)	PP	100
(2)	PP/WOMMT	98/2
(3)	PP/PP-MA/DOMMT	94/3/3
(4)	PP/PP-MA/WOMMT	98/1/1
(5)	PP/PP-MA/WOMMT	96/2/2
(6)	PP/PP-MA/WOMMT	94/3/3
(7)	PP/PP-MA/WOMMT	92/4/4
(8)	PP/PP-MA/WOMMT	90/5/5

and 0.4g of octadecylamine in a tumble mixer directly under vigorous stirring at 80°C for 2 hours. The obtained DOMMT was crushed into powder with particle size of less than 40 μm.

Method 2, preparation of organic montmorillonite by wet route (WOMMT): Octadecylamine was dissolved in 250 mL of hot distilled water (80°C) under stirring and subsequently concentrated hydrochloric acid, HCl (34 mmol), was added until octadecylamine(34 mmol) was completely dissolved. Then, 10g of Na-MMT was dispersed in this solution evenly along with vigorous stirring for 6 hours to obtain WOMMT. Finally, the WOMMT was filtered and washed several times with hot distilled water (80°C) until no free chloride ion was detected in the filtrate by 0.1 N AgNO₃. The dried WOMMT was crushed into powder with particle size of less than 40 μm.

Nanocomposites Preparation

PP/MMT nanocomposites were prepared using SHJ-20 twin-screw extruder (diameter = 22 mm, L/D = 40) in the corotating mode. A barrel temperature profile was selected from 160°C at the polymer feeding to 180°C at the end. The screw rotation speed was fixed at 100 rpm. Under these conditions, the melt temperature measured at the die never exceeded 200°C. The formulation of PP/MMT nanocomposites was shown in Table I. For comparison purposes, pure PP was also melt-extruded as the reference material.

Characterization

Fourier transform infrared spectroscopy (FTIR) spectra were recorded by Avatar370 FTIR spectrophotometer with wave number range of 4000–370 cm⁻¹ and X-ray diffraction (XRD) analysis was carried out on a Philips PW-1830 apparatus. X-ray unit operating at 40 kV and 30 mA was used to carry out the experiments at room temperature. The X-ray source was CuK$_\alpha$ radiation with a wavelength of 0.154 nm. The diffractograms were scanned in the 2θ range from 2° to 30° at a rate of 1.2°/min. The morphology of the Na-MMT, DOMMT, and WOMMT and PP/MMT composites were observed by Quanta200 scanning electron microscopy (SEM) with metal spraying for 3 minutes used 10 mA.

Mechanical properties were carried out with a universal testing machine (CMT4106) at room temperature according to ASTM D 638-10. Tensile test was performed at a crosshead speed of 50 mm/min. For flexural test, a three-point bending configuration was selected with a support span length of 64 mm and a crosshead speed of 5 mm/min. Izod impact test was carried out
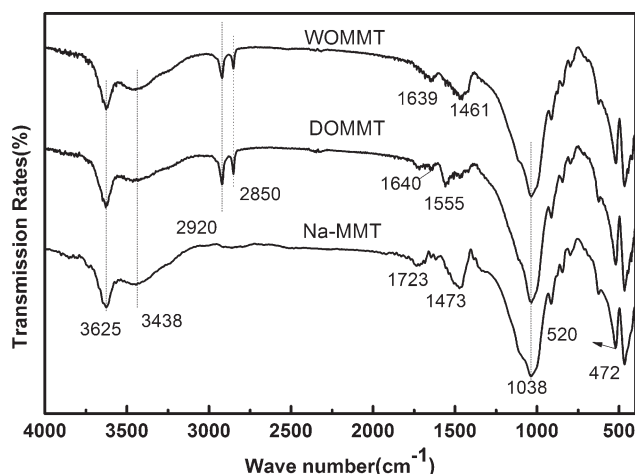
Figure 1. FTIR spectra of Na-MMT, DOMMT, and WOMT.

Figure 2. X-ray patterns of Na-MMT, DOMMT, and WOMMT.

on notched specimens using a Pendulum Hammer Impact XJU-22 according to ASTM D 256-02 with a impact speed of 3.46 m/s. Five samples were prepared and tested to get the mean value at each point.

The crystal morphology of the pure PP and PP/MMT nanocomposites was studied by OLYMPUS polarizing microscopic. These samples were heated at 220°C for 5 minutes to eliminate thermal history, and then cooled fast to 140°C under isothermal crystallization for 20 minutes.

Dynamic mechanical analysis (DMA) testing was carried out using DMA/SDTA861 METTLER equipment, with the testing configuration in the shear mode. Specimens of $6 \times 5 \times 2$ mm^3 were employed. A dynamic force of 5N at 1 Hz was applied in the range of temperature from -50 to 150°C, employing a heating rate of 3°C/min.

The crystallization and melting investigations of the samples were determined with a TA Q2000 DSC analyzer in nitrogen gas with the heating rate of 10°C/min. The thermal stability of the samples was characterized using a thermogravimetric analyzer (TA Q2000) in the air environment at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

The Characterization of WOMMT and DOMMT

FTIR Analysis. The FTIR spectra of Na-MMT, DOMMT, and WOMMT are illustrated in Figure 1. These three kinds of MMT have the same characteristic transmission bands at 3625, 3438, 1038, 520, and 472 cm^{-1} .The bands at 3625 cm^{-1} and 3438 cm^{-1} are attributed to the asymmetric stretching vibration and symmetric stretching vibration of the structural –OH groups. The strong band at 1038 cm^{-1} is corresponding to the Si-O stretching vibration, and the sharp peaks at 520 and 472 cm^{-1} are assigned to Si-O bending vibration. Compared with the spectrum of Na-MMT, the appearance of the new peaks at 2920 and 2850 cm^{-1} in the spectra of DOMMT and WOMMT, associated with the asymmetric stretching vibrations of the –CH$_3$, –CH$_2$, and –CH bonds, provides evidence of the organic modification process, which were in good agreement with the previous investigations.[12,16] The bending-in-plane vibrations of the –OH groups are characterized by a broad band at 1723 cm^{-1}
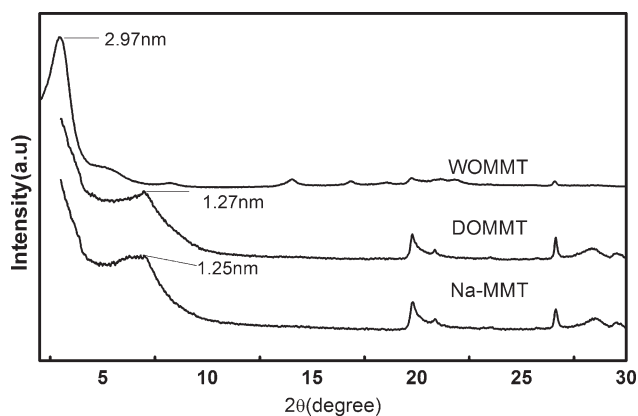
and 1473 cm^{-1} in the spectrum of Na-MMT, but these two bands shift slightly and become weaker in the FTIR spectra of the samples modified with octadecylamine, implying the removal of some structural hydroxyl groups from O-H sites.[20]

XRD Analysis. Figure 2 represents the XRD patterns of Na-MMT, DOMMT, and WOMMT. The typical XRD reflection of Na-MMT related to the basal spacing (d001) between the clay platelets appears at $2\theta = 7.02°$, corresponding a basal spacing of 1.25 nm. It can be noted that the d001 diffraction peak of DOMMT has shifted to $2\theta = 6.95°$, which corresponds to d-spacing of 1.27 nm. The reflection of a sharp d001 diffraction peak of WOMMT is observed at $2\theta = 2.97°$ with basal spacing of 2.97 nm. The increment in d-spacing indicates that octadecylamine group has successfully intercalated into the interlayer of Na-MMT, and the d-spacing of the WOMMT is greater than that reported by Balakrishnan et al.[16]

According to Figure 2, the interlayer spacing increases from 1.25 nm of Na-MMT to 2.97 nm of WOMMT, a significant increase of 137.6%; whereas the d-spacing increment of DOMMT is only 1.6% (from 1.25 nm to 1.27 nm). Therefore, octadecylamine groups have successfully homogeneously intercalated into the interlayer of Na-MMT using wet route, but few octadecylamine groups have entered into the interlayer using dry process. According to FTIR and XRD results as studied, it can be concluded that Na-MMT is modified by adsorbing octadecylamine on the MMT surface employing the modification method of dry process, whereas it is modified by the intercalation of dodecylamine ammonium in its interlayers using wet route.

SEM Analysis. SEM results provide important information about the morphology of all the MMT samples. The SEM photograph of Na-MMT in Figure 3(a) illustrates that the distinct blocky structure with thick plate was observed. The SEM results [Figure 3(b and c)] of MMT modified with octadecylamine show that the physical appearance of the clay particles changes significantly. The blocky bulk of Na-MMT is replaced by ponysize granular particles of DOMMT, [Figure 3(b)], shedding light on the effect of the surfactant on the macroscopically dispersion of MMT. The surface of Na-MMT is coated by the long chain of octadecylamine, so the dispersion degree is improved as the result of lowered surface energy. Figure 3(c) indicates that the thin smooth flakes of WOMMT are detected and the grain boundaries steadily
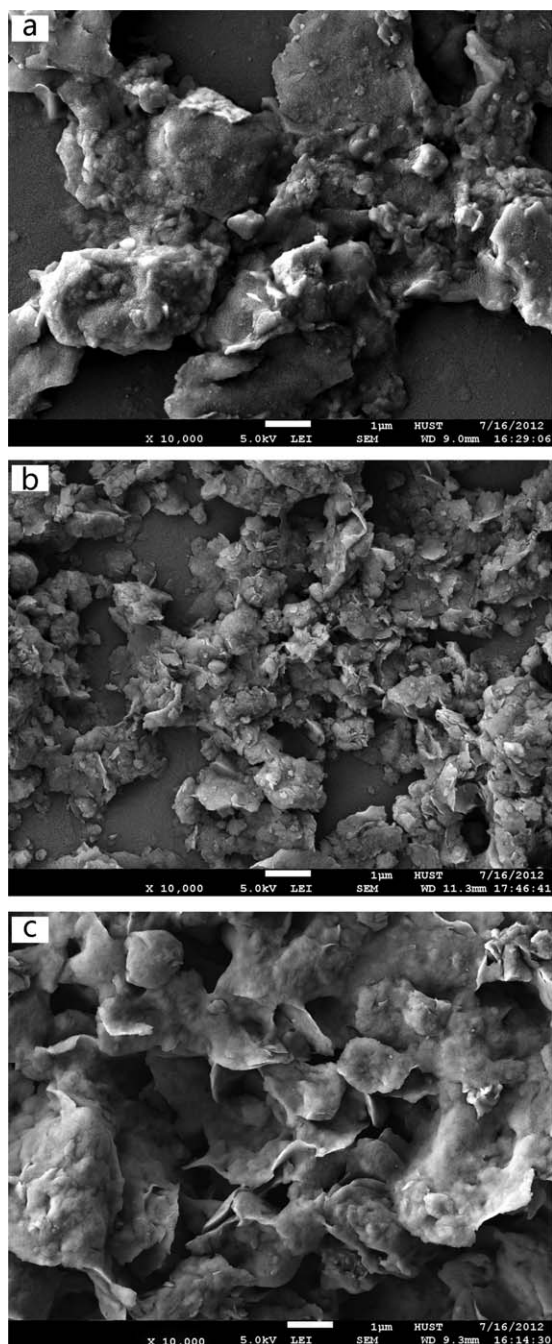
Figure 3. SEM images of (a) Na-MMT, (b) DOMMT, and (c) WOMMT.

Figure 4. The effect of MMT on the mechanical properties of composites: (1) pure PP, (3) PP/PP-MA/DOMMT and (6) PP/PP-MA/WOMMT nanocomposites. Each bar represents the mean ± SD of five experiments.

disappear in comparison with Na-MMT,[20] implying that WOMMT layers are exfoliated as the intercalation of octadecylamine, which is consistent with the result of XRD.

Mechanical Properties and Structure Characteristics of Nanocomposites

Mechanical Properties. Figure 4 shows the mechanical properties of PP, PP/PP-MA/DOMMT and PP/PP-MA/WOMMT nanocomposites, displaying the effect of clay modification on the strengths of PP/MMT nanocomposites. The tensile property and the impact strength of the PP/PP-MA/DOMMT composite are lower than that of PP/PP-MA/WOMMT composites. This indicates that
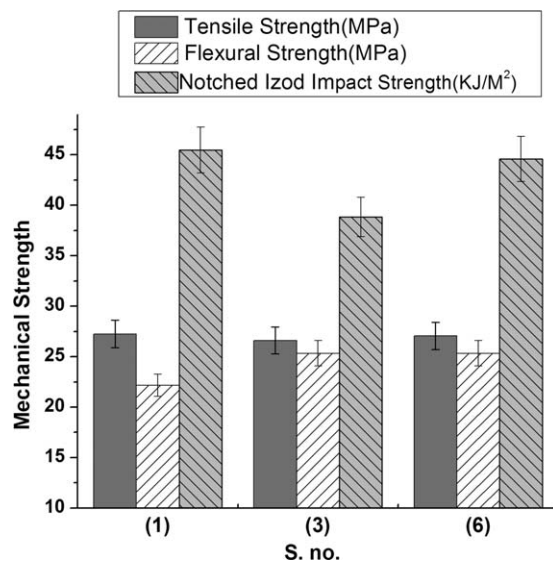
compared with DOMMT, the formation of intercalated or exfoliated structure of WOMMT in PP matrix increases the strength property of the composite, for the strong interaction between the exfoliated clay platelets and polymeric matrix can prevent the crack from propagating. But the notched izod impact strength of PP/PP-MA/WOMMT is lower than that of pure PP. This can be explained that the addition of WOMMT may be slightly large, and thus, some undesired agglomeration of WOMMT exists in PP matrix, which damages the notched izod impact strength by inducing stress concentration when the samples experience a sudden impact. In Figure 4, the flexural properties of the two composites are much higher than that of PP. According to the literatures,[13,21] this may be ascribed to the difference in the deformation mode and the alignment of the silicate layers in the polymer matrix. The silicate layers of organoclay may align predominantly parallel to the melt flow direction during injection molding.[22]

Figure 5 shows the mechanical properties of the PP, PP/WOMMT, and PP/PP-MA/WOMMT nanocomposites. It can be observed that the tensile strength of the PP/WOMMT composites is low in comparison to that of other samples, indicating that the presence of WOMMT cannot effectively improve the tensile strength of PP without the addition of PP-MA. This may be attributed to the undesired dispersion of WOMMT and a poor interaction between clay and polymeric matrix.[13] It also can be seen that the addition of OMMT decreases the impact strength of PP/MMT composites. The reduction in the impact strength may be related to the immobilization of the macromolecular chains by the clay particles, which limits their ability to adapt to the deformation and make the material more brittle. In addition, the aggregates of silicate layers produce the site of stress concentration and act as a microcrack initiator.[23] However, the presence of compatibilizer helps to form better exfoliated structure of MMT in the PP/MMT nanocomposites. According to Masenelli-Varlot et al.[24] and Fornes et al.,[25] when the clay particles are exfoliated fully, a higher aspect ratio and a larger interfacial area of MMT
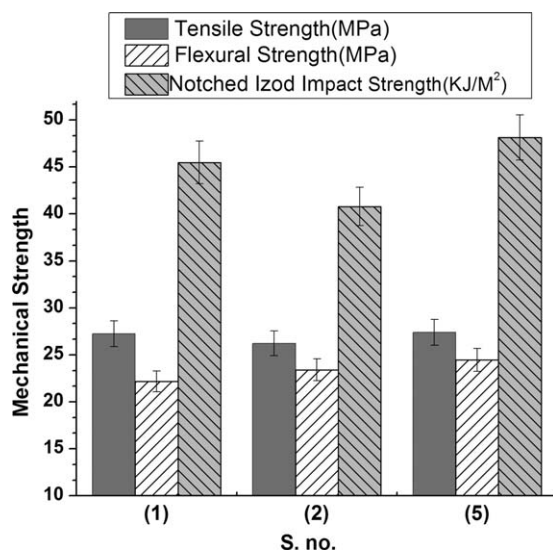
Figure 5. The effect of PP-MA on the mechanical properties of composites: (1) pure PP, (2) PP/WOMMT and (5) PP/PP-MA/WOMMT nanocomposites. Each bar represents the mean ± SD of five experiments.

Figure 6. The effect of WOMMT content on the mechanical properties of composites: (1) pure PP, (4)-(8) PP/PP-MA/WOMMT nanocomposites with different MMT content (1–5 wt %). Each bar represents the mean ± SD of five experiments.

are achieved, both of which make the force pass from PP matrix to the silicate layers much more effectively and thus improve the mechanical properties.[9] So, the addition of PP-MA as the third component increases the mechanical strength, highlighting that PP/MMT nanocomposites could not be achieved without the inclusion of the compatibilizers.

From the results as discussed earlier, it is obvious that WOMMT has higher commercial value and PP/PP-MA/WOMMT nanocomposites are worth studied deeply. In order to get better properties of PP/PP-MA/WOMMT composites, the proper addition of OMMT and PP-MA is investigated as follows.

Figure 6 shows the mechanical properties of the PP and PP/PP-MA/WOMMT nanocomposites along with different proportion of PP-MA/WOMMT. With the increase of PP-MA and WOMMT, no obvious difference of the tensile properties is observed, but the flexural properties increase obviously, and notched izod impact strength firstly increases and then decreases. When the ratio of PP/PP-MA/WOMMT is 96:2:2(S. no. (5)), its comprehensive performance is most excellent. The tensile strength, flexural strength, and notch impact strength of composites increase by 0.15%, 10.33%, and 5.85%, respectively, with respect to pure PP.

This work suggests that proper addition of MMT can increase the flexural properties and impact strength of PP. These improvements should be attributed to the good dispersion of OMMT and the interfacial compatibility between PP and OMMT in the presence of the compatilizer PP-MA. The drop in impact strength of the composites with higher MMT content is caused by the agglomeration of MMT in the PP matrix.[14,26,27] Excessive dosage of inorganic rigid particles used make particles so close that they cause macromatrix cracks propagation, and hence, negatively affect mechanical property. Proper MMT content also causes stress concentration in PP matrix, but the good dispersion of OMMT with the better exfoliated layers absorbs a certain amount of deformation energy by triggering matrix
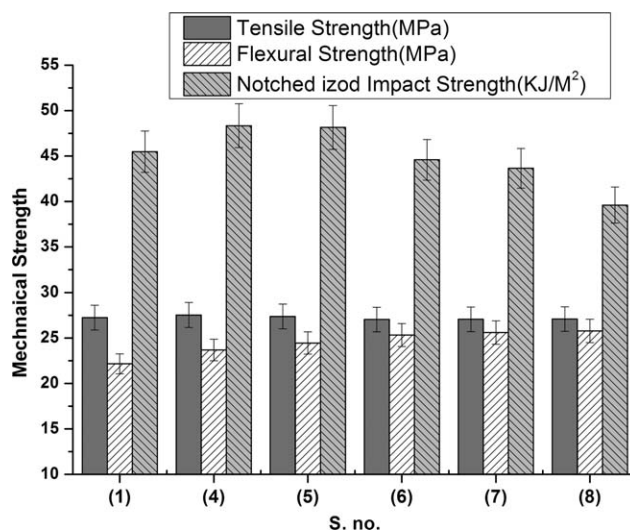
crazing or shear zone. Consequently, the nanocomposites with lower WOMMT content have higher mechanical properties.

SEM Analysis. Figure 7 shows SEM images of the fracture surface of the nanocomposites. For the nanocomposite without compatibilizer [Figure7(a and b)], aggregated OMMT particles were observed, highlighting the poor dispersion of OMMT in the PP matrix and the weak interaction between OMMT and PP matrix. There exist the destructive cracks and cavities corresponding to the location of aggregated MMT particles that have detached from the PP matrix during the fracture because the adhesive energy between PP and OMMT is much lower than the clay fracture energy.[9] These destructive cracks and cavities cause stress concentration and macro cracks propagation; hence, the impact strength of the composite is negatively affected by the poor dispersed OMMT. Figure 7(c) shows that a few big particles are detected on the fracture surface of nanocomposite, although it contains compatibilizer PP-MA, and in Figure 7(d), it is observed that the fracture surface is smooth and characterless. This indicates that the surface modification of DOMMT hardly increases the affinity between the polymer matrix and MMT and barely induced tiny crazes. Figure 7(e and f) is showing the good dispersion of the nanoclay in nanocomposites,[2] furthermore, a lot of tiny crazes rather than destructive cracks are observed, which can enhance the mechanical properties of the composites.

It is well known that the dispersion of filler in polymer matrix is a key for the enhancement of mechanical properties of polymer composites. Generally, it is difficult to achieve a good dispersion of inorganic filler in a thermoplastic. And this problem is even worse as the nanoparticles are used due to the strong tendency of filler agglomeration.[14] However, in our work, under the conditions of adding PP-MA, not only does the clay disperse uniformly in the matrix but also it combines well with the matrix, which is evidenced by the absence of destructive cracks.[28] When the material subjects to a sharp blow, tiny crazes in the high stress zones is induced by the exfoliated silicate layers to absorb some of the
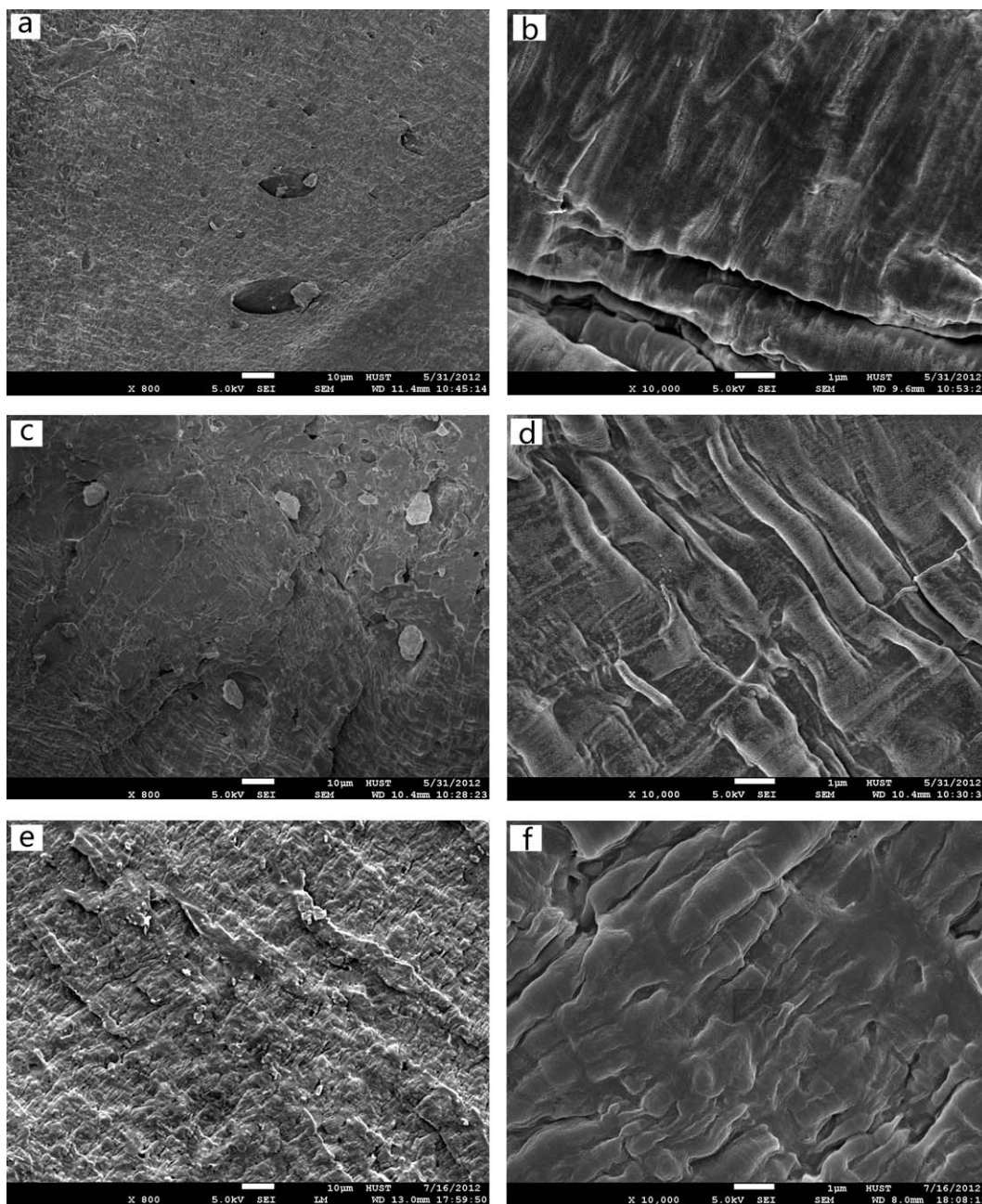
Figure 7. SEM images fracture surface of PP/WOMMT (a×800 and b×10000), PP/PP-MA/DOMMT (c×800 and d×10000) and PP/PP-MA/WOMMT nanocompasites (e×800 and f×10000).

impact energy.[2] So, the improvement of dispersion of MMT can strengthen the interfacial interactions of the polymer molecules that lead to an enhancement in impact properties.

Polarizing Microscopic Analysis

PP/PP-MA/WOMMT nanocomposites have better mechanical properties than raw PP as studied previously, which is closely relevant to its micro structure. In order to find out the connection between microstructure and mechanical properties, the isothermal crystallization morphologies of samples were characterized by a polarizing optical microscope. Figure 8 shows the images of pure PP, PP/WOMMT and PP/PP-MA/WOMMT nanocomposites with 2 wt % OMMT. As shown in Figure

8(a), for pure PP, perfect and big spherulites are observed. The addition of OMMT increases the amount of spherulites and reduces the dimension of the spherulite [Figure 8(b)], which can be ascribed to the nucleation effect of OMMT because the dispersed exfoliated layers of OMMT act as the nucleus in the nanocomposite. Figure 8(c) shows that the presence of compatibilizer further increases the amount of spherulite. The spherulite distributes so dense that the spherulites junction are obscure. Compatibilizer improves the dispersion of OMMT in the PP matrix, resulting in a large number of nucleuses and thus causing a large number of spherulites in the limited space. On the contrary, compatibilizer enhances the interfacial
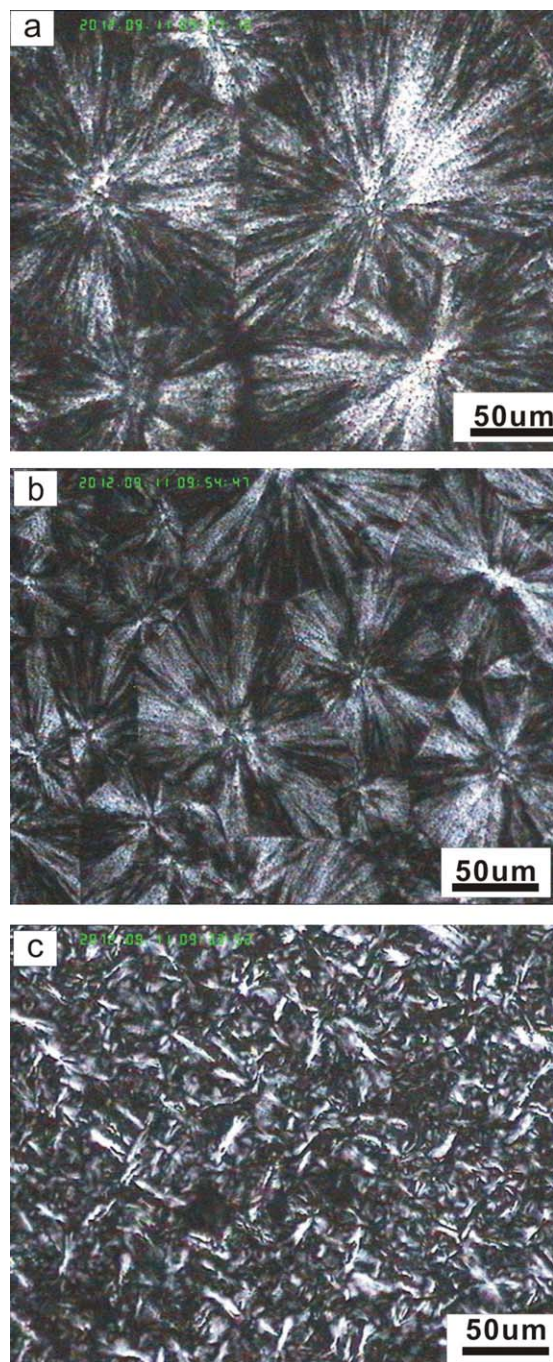
Figure 8. Morphologies of (a) pure PP, (b) PP/WOMMT and (c) PP/PP-MA/WOMMT under a polarizing microscope. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

interaction between PP matrix and OMMT, which benefits the assembling of PP molecule on the basis of exfoliated layers of OMMT. As these smaller spherulites can enhance the impact toughness of the PP, the addition of proper MMT and PP-MA benefit the mechanical properties of PP as described before.

Melting and Crystallization Behaviors

The melting behaviors of pure PP, PP/WOMMT, and PP/PP-MA/WOMMT nanocomposites were investigated by DSC. Figure 9 shows the DSC heating thermograms of these samples. Table II
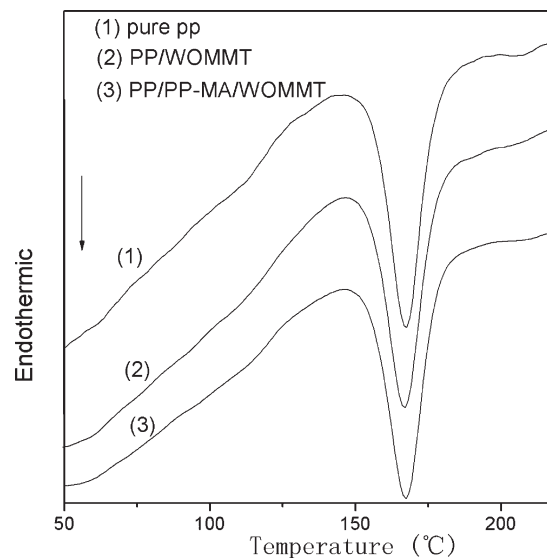

Figure 9. DSC heating curves of pure PP, PP/WOMMT and PP/PP-MA/WOMMT.

lists the corresponding melting peak temperature (T_m), the melting enthalpy value (ΔH_c), and the crystallinity (C_m) of them. In Figure 9, the melting peak temperatures of PP/WOMMT and PP/PP-MA/WOMMT nanocomposites alter slightly with respect to that of pure PP. According to the literature,[14] this may be attributed to the fact that the addition of WOMMT and the further addition of PP-MA cannot greatly influence the structure and stability of the PP crystals. The melting enthalpy values, determined from DSC heating thermograms, increases with the addition of WOMMT and the presence of PP-MA. The melting enthalpy is mainly dominated by the crystallinity of PP: the higher the crystallinity, the larger the melting enthalpy. The crystallinity of these samples could be roughly evaluated by the eq. (1) and the calculated results are listed in Table II. The high crystallinity of WOMMT-included composites indicates that WOMMT addition is beneficial to the crystallization of PP, demonstrating the nucleating efficiency of WOMMT and the increased nucleation effectiveness after the addition of compatibilizers.

$$C_m = \Delta H_m / \Delta H_0 \qquad (1)$$

Where ΔH_m is the melting enthalpy value of the sample, ΔH_0 is the melting enthalpy value of PP with the crystallinity of 100% and the value of ΔH_0 is 209 J/g.

Thermal Stability

The thermal stabilities of pure PP, PP/WOMMT and PP/PP-MA/WOMMT composites are evaluated by TGA (Figure 10). The PP/PP-MA/WOMMT composites show the best thermal stability with the lowest total weight loss, followed by PP/WOMMT composites, and then pure PP. For pure PP, PP/WOMMT, and PP/PP-MA/WOMMT composites, the decomposition temperatures at 10% weight loss determined from the TGA scans are 310.1°C, 315.5°C, and 321.9°C, respectively. Therefore, the addition of WOMMT and the further addition of PP-MA can effectively enhance the thermal stability of PP. The enhancement of the thermal stability are attributed mostly to the intercalated or exfoliated structure of WOMMT in PP matrix, for WOMMT platelets not only obstacle oxygen and

Table II. Typical Thermal Data of the Samples from DSC Scans

samples	T_m (°C)	ΔH_m (J/g)	C_m (%)
PP	167.7	30.2	14.4
PP/WOMMT	167.6	32.0	15.3
PP/PP-MA/WOMMT	167.3	32.5	15.6

T_m, the melting peak temperatures; ΔH_m, melting enthalpy (J/g); C_m, crystallinity
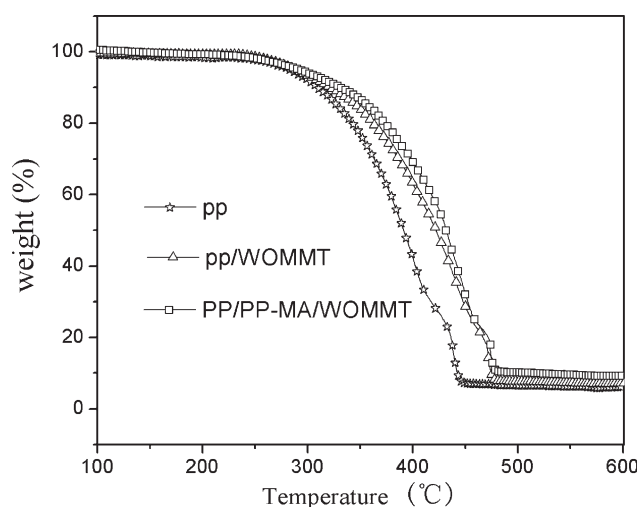
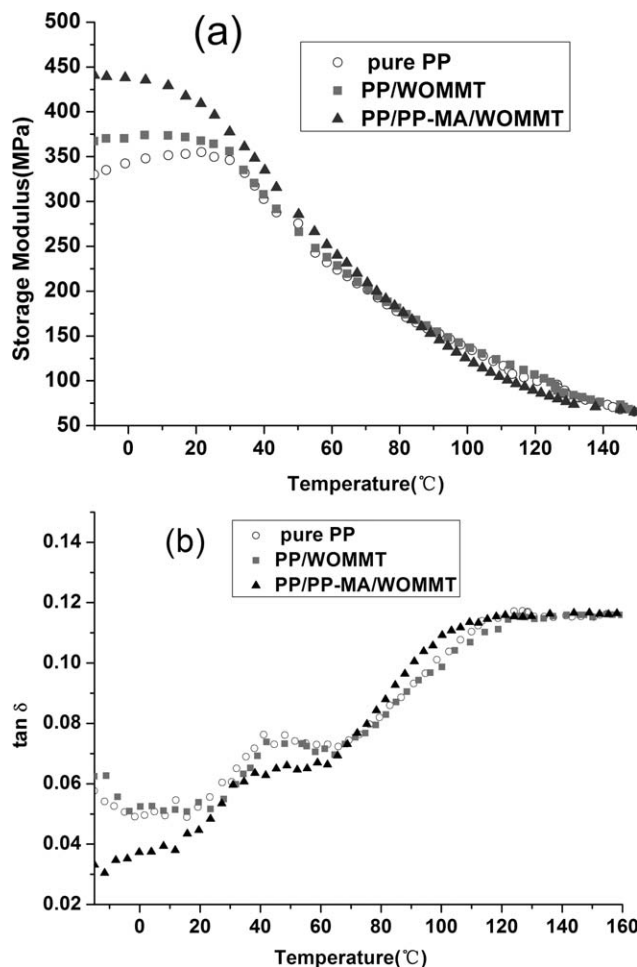**Figure 10.** TGA thermograms of pure PP, PP/WOMMT and PP/PP-MA/WOMMT.

Figure 11. DMA spectra of of PP, PP/WOMMT and PP/PP-MA/WOMMT nanocomposites. (a) Storage modulus (E') and (b) tan δ curves.

heat permeability into the PP matrix but also slow the escape of decomposed smaller molecules from the PP matrix during the heating.[14] The thermal stability of PP can be improved more effectively by adding WOMMT together with PP-MA because the presence of PP-MA can increase the dispersion of WOMMT as well as the formation of intercalated or exfoliated platelets.

Dynamic Mechanical Analysis

Figure 11(a) shows the storage modulus (E') as a function of temperature for PP, PP/WOMMT, and PP/PP-MA/WOMMT nanocomposites. PP/WOMMT composite show the higher storage modulus than PP over the whole temperature range from −10 to 150°C. The improvement of the storage modulus of PP/ MMT composite is probably caused by the stiffness of MMT layers dispersed in the PP matrix.[1,22] PP/PP-MA/WOMMT composite displays the highest values of E' at the temperature below 80°C but the lowest E' value above 80°C .This result is different from other reports[1,16] that demonstrated the improvement of storage modulus given by the presence of clay particles in the PP matrix over the

measured range of temperature. At the temperature below 80°C, the enhancement of E' for PP/PP-MA/WOMMT composites with compatibilizer included is ascribed to the nanoscaled dispersion of layered clays. The presence of the compatibilizer PP-MA increases the dispersion of the layered clays in PP matrix, promotes the formation of exfoliated layers of the reinforcing clay particles and improves interface interaction of the PP matrix and clay particles. The dispersed clays, especially the exfoliated layers, hinder the movement of PP molecular chain and thus increase the storage modulus of the composite. However, PP-MA used in this study has much higher melt flow index, leading to the decrease of the storage modulus of the composite at high temperature. Therefore, PP/PP-MA/WOMMT composite shows higher E' value at low temperature but lower E' value at higher temperature.

Table III. Effect of WOMMT on the E' and T_g of PP Nanocomposites

	E' (MPa)				T_g (°C)	tan δ
	0°C	40°C	80°C	120°C		
PP	371.7	307.1	175.6	100.5	40.7	0.0781
PP/ WOMMT	342.9	302.2	180.1	107.2	41.8	0.0775
PP/PP-MA/WOMMT	437.4	335.9	179.3	88.6	37.6	0.0641

Figure 11(b) depicts the tan δ as a function of temperature for PP, PP/WOMMT, and PP/PP-MA/WOMMT nanocomposites. One peak is observed from 38°C to 45°C, which is assigned to the glass transition temperature (T_g) of PP. Moreover, it is interesting that the glass transition temperature T_g of PP is higher than that of PP/PP-MA/WOMMT but lower than PP/ WOMMT as shown in Table III. Compared with pure PP, the glass transition temperature of PP/OMMT composite is high; showing a good agreement with the previous studies on conventional clay-filled polymers,[1] where adding filler resulted in higher glass transition temperature. The glass transition temperature of composite when compared with the neat polymer increases because the filler influences the PP molecular movement of the nanocomposites. However, PP/PP-MA/WOMMT nanocomposites has the low T_g value, which may be associated with the addition of high melt flow index of PP-MA that exhibits high mobility of molecules at lower temperature.

CONCLUSIONS

Two types of organic Na-MMT (DOMMT and WOMMT) were obtained using octadecylamine by the methods of dry process and wet route. Organic modification of Na-MMT was confirmed from XRD, FTIR, and SEM data. The results indicate that only by wet route could the intercalated structure of modified Na-MMT be achieved. The composite incorporating the WOMMT modified by wet route is better than that containing DOMMT modified by dry process. The compatibilizer PP-MA, as the third component, effectively increases the mechanical properties of the PP/MMT by enhancing the high dispersion degree of WOMMT that induces the formation of tiny crazes. For PP, PP/WOMMT, and PP/PP-MA/WOMMT, the size of spherulite crystals decrease and the amount of spherulite increase in order, for the dispersed clay and exfoliated layers of MMT could act as the nucleating agent. The addition of WOMMT and the further addition of PP-MA enhance the melting enthalpy value, the crystallity, and thermal stability of PP. DMA results illustrate that the presence of clay particles increases the storage modulus of PP and the glass transition temperature, whereas the addition of compatibilizer with high melt flow index exhibites the opposite function.

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