Preparation and Properties of Polypropylene Filled with Organo-Montmorillonite Nanocomposites

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ABSTRACT: Organo-Montmorillonite (Org-MMT)/maleic anhydride grafted polypropylene (PP-*g*-MAH)/polypropylene nanocomposites have been prepared by melt blending with twin-screw extruder. The mechanical properties of the nanocomposites and the dispersion of Org-MMT intercalated by the macromolecular chain were investigated by transmission electron microscopy and mechanical tests. The crystal properties of the nanocomposites have been tested by a differential scanning calorimeter. The thermal properties of the nanocomposites were investigated by thermo gravimetric analysis. The results show that not only the impact property but also the tensile property and the bending modulus of the system have been increased evidently by the added Org-MMT. The Org-MMT has been dispersed in the matrix in the nanometer scale. With the addition of the Org-MMT, the melting point and the crystalling point of the nanocomposites increased; the total velocity of crystallization of the nanocomposites also increased. Thermal stability of the nanocomposites is increased by the filled Org-MMT. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 2875–2880, 2006

Key words: PP; Org-MMT; nanocomposites; intercalated; thermal stability; crystallinity

INTRODUCTION

Increasing the impact toughness of polymers or composites that are used as structural materials has attracted considerable interest. The traditional, successful toughening method involves the use of elastomer for toughening the plastic. At the same time, the added elastomer decreases the tensile properties and bending modulus of the composites. It is commonly known that the use of elastomer such as ethylene-propylene rubber, ethylene-propylene-diene terpolymers and ethylene-1-octylene copolymer toughens the polypropylene (PP) matrix. Hence, much research has been carried out on this theme in the past 10 years. The main mechanism is that elastomer particles may play the role of craze-inducing agent, and cause shear yielding of the surrounding matrix and terminate the propagation of cracks.

In the past, the inorganic particles were always filled in the polymer as fillers, e.g., $CaCO_3$, talc powder, and so on. Now, the nanomaterials such as nanoinorganic particles can be filled in the composites as reinforcements because of their superior physical and mechanical properties.[1,2]

Nanomaterials (nanolamella) have attracted substantial attention because of their superior physical and mechanical properties, when compared with those of the micro- and macromaterials filled in polymer. Such nanocomposites have high potential for application as functional materials, but there has been a strong restriction on the polymers that are used for nanocomposites. Thus far, only polar polymers, such as PA6,[3,4] PVA,[5] and PI,[6] have been used successfully. This is because they can intercalate between montmorillonite layers easily, from which the nanocomposites are derived. PP is one of the most widely used polymers, and so it is important to increase the properties of PP to extend the use scale of PP. PP/clay hybrids have necessarily been studied. However, PP, which is a nonpolar polymer, has never been used successfully for nanocomposites despite strong demand from the practical point of view. To synthesize nonpolar polymer nanocomposites, researchers have usually used maleic anhydride or vinyl benzyl chloride modified nonpolar polymers,[7,8,9] which can make polar functional adducts with the nonpolar polymer, which can easily intercalate the organo-modified montmorillonite.[10,11]

In this work, the Organo-Montmorillonite (Org-MMT)/maleic anhydride grafted polypropylene (PP-

Sample	PP (wt PHR)	Masterbatch (wt PHR)
1	100	0
2	99	2
3	98	4
4	97	6
5	95	10

MAH)/polypropylene (PP) nanocomposites were prepared by melt intercalation blending. In this way, the PP-MAH was used as the compatibilizer because of its polarity. The mechanical, crystallization, and thermal properties of the nanocomposites were investigated.

EXPERIMENTAL

Materials

PP (4220), whose melting index is less than 0.7 g/10 min, was supplied as pellets by Yanshan Petrochemical Company, China. The organo-montmorillonite (Org-MMT) was provided by Feng-hong Clay Chemical Material Company Limited, ZheJiang, China. PP-MAH was supplied by the Dow Chemical Company.

The preparation of Org-MMT intercalated PP-MAH

To get a good dispersibility of the Org-MMT, the masterbatch was prepared. PP-MAH and PP were melt-mixed with Org-MMT using a twin-screw extruder (PE-20, Keya Company Limited, Nanjing, JiangShu, China). The temperatures of the extruder were ordinal: 140, 185, 205, and 200°C. The mixing weight ratio of PP-MAH, PP, and Org-MMT was 1:1:2.

The preparation of PP/Org-MMT nanocomposites

The pellets of PP/Org-MMT nanocomposites were prepared using the twin-screw extruder. The PP and the masterbatch were mixed as per ratio. Table I shows the mixing weight ratio of PP to the masterbatch. The nanocomposites were prepared using the single-screw extruder (SJ-30, Beijing Plastic Engineering Company Limited, Beijing, China), the temperatures of which were ordinal (160, 190, 205, and 200°C).

Mechanical properties of the nanocomposites

The impact strength of the nanocomposites was measured by Charpy pendulum impact testing machines (XJJ-5, ChengDe JinJian Testing Machine Company, HeBei, China.) at room temperature. The tensile (testing speed, 50 mm/min) and the flexural (testing speed, 10 mm/min) properties were recorded by Instron universal testing machine (Instron 1185, Instron Company, England) at room temperature.

Evaluation of dispersibility of the Org-MMT in PP matrix

The dispersion of the Org-MMT was evaluated by transmission electron microscopy (TEM). TEM specimens were cut at −90°C using an ultra microtome (LKB-5, Switzerland) with a diamond knife. TEM images were obtained by Hitachi H-800 (Japan) with the acceleration voltage of 200 kV.

Thermal stability

The samples were analyzed by thermogravimetric analysis (TGA), using a Netzsch STA-449c thermal analyzer (Netzsch, Germany) under nitrogen flow from 50 to 800°C at the rate of 10.00°C/min. The T_g curves are shown in Figure 5. Both the 5% loss temperature ($T_{-5\%}$) and the maximum weight loss temperatures (T_{max}), and char residue at 800°C are listed in Table III.

Crystallinity of the matrix

The samples were analyzed by the differential scanning calorimeter (DSC) using a DSC-2 (Perkin–Elmer, USA) under nitrogen heat from 50 to 230°C at the rate of 10.00°C/min to get the melting curve, and allowed to stand for 5 min at 230°C, and at last cooled from 230 to 50°C at the rate of 10.00°C/min to get the crystalling curve. The melting and the crystallinity properties are shown in Tables IV and V.
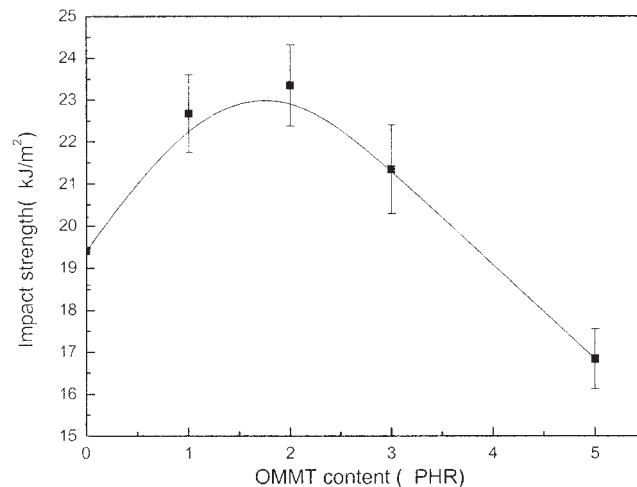

Figure 1 Mechanical properties of the impact strength of pure PP and nanocomposites.
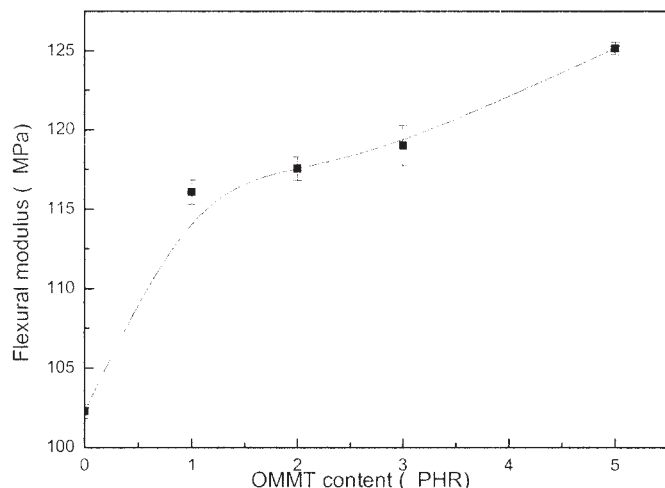
Figure 2 Mechanical properties of the flexural modulus of pure PP and nanocomposites.

Figure 3 Stress–strain curve of pure PP and nanocomposites.

RESULTS AND DISCUSSION

Mechanical properties of PP/clay hybrids

Figure 1 shows the changes in the curve of the impact strength of the nanocomposites with the addition of the Org-MMT. It shows that when Org-MMT was added from 0 to 3.5 phr, the impact properties of the nanocomposites increased. When Org-MMT was added more than 3.5 phr, the impact properties of nanomcomposties decreased. When Org-MMT (2 phr) was added, the impact strength of nanocomposite is at the maximum, which is about 1.21 times than that of pure PP.

Figure 2 shows the changes in the curve of the bending modulus of the nanocomposites with the addition of the Org-MMT. It shows that with the addition of Org-MMT, the bending modulus has evidently increased. The bending modulus of pure PP is 102.3 MPa; when Org-MMT (1 phr) is added, the bending modulus reaches 116.1 MPa, and so the bending modulus of the nanocomposite is 1.14 times more than that of pure PP; when Org-MMT (5 phr) is added, the bending modulus of the nanocomposite reaches 125.2 MPa, which is 1.23 times more than that of pure PP.

Ordinarily, when the matrix is toughened by the elastomer, the bending modulus of the system will decrease which is an unavoidable problem. However, using nanoparticles to toughen the matrix can evidently increase the toughness and stiffness at the same time, which is the peculiarity and advantage of the nanoparticles.

Figure 3 shows the stress–strain curve of the nanocomposites. It shows that with the addition of the Org-MMT, the extension at break ratio of the hybrid dramatically increases. However, the tensile yield strength of the system is basically not changed.

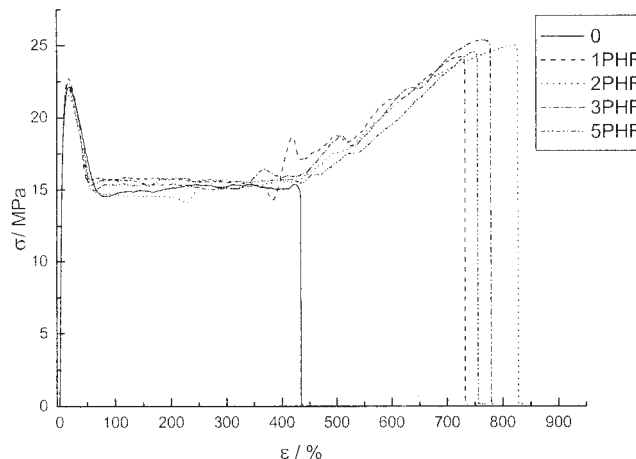Table IIshows the tensile properties of the nanocomposites and the pure PP. It shows that with the addi-

tion of the Org-MMT, the tensile strength of nanocomposites increased evidently.

Dispersibility of PP/clay hybrids

Figure 4 shows the TEM image of nanocomposites filled with 2 and 5 phr Org-MMT. Figure 4(a,c) are magnified 10,000 times. Figure 4(b,d) are magnified 200,000 times. Figure 4(a,c) show that the Org-MMT has been dispersed in the polymer matrix in the nanometer scale. Because, only the dispersion occurred in the twin-screw extruder and the blending time was transitory, some of the Org-MMT existed as aggregates. The dispersion of Org-MMT of nanocomposites filled with 2 phr is better than that of nanocomposites filled with 5 phr. Upon addition of the Org-MMT, the reuniting chance of the nanolamella increased, which caused the dispersion of Org-MMT to decrease.

The nanocomposites were extruded by the single-screw extruder, so that the lamellar aggregates had an orientation along with the direction of the shearing force.

Figures 4(b) and 4(d) show that the macromolecular chain has intercalated the interlaminar of the Org-

TABLE II
Tensile Properties of the Nanocomposites and the Pure PP

Sample	Tensile strength (MPa)	Extension at break ratio (%)	Tensile yield strength (MPa)
1	15.4 ± 0.97	434 ± 22	22.1 ± 0.30
2	24.2 ± 1.03	732 ± 32	22.7 ± 0.32
3	25.0 ± 1.33	827 ± 31	21.6 ± 0.27
4	25.4 ± 1.39	778 ± 30	22.4 ± 0.29
5	24.5 ± 1.26	731 ± 24	22.5 ± 0.44

(a)

(b)

The ratio of Org-MMT/PP is 2/100

(c)

(d)
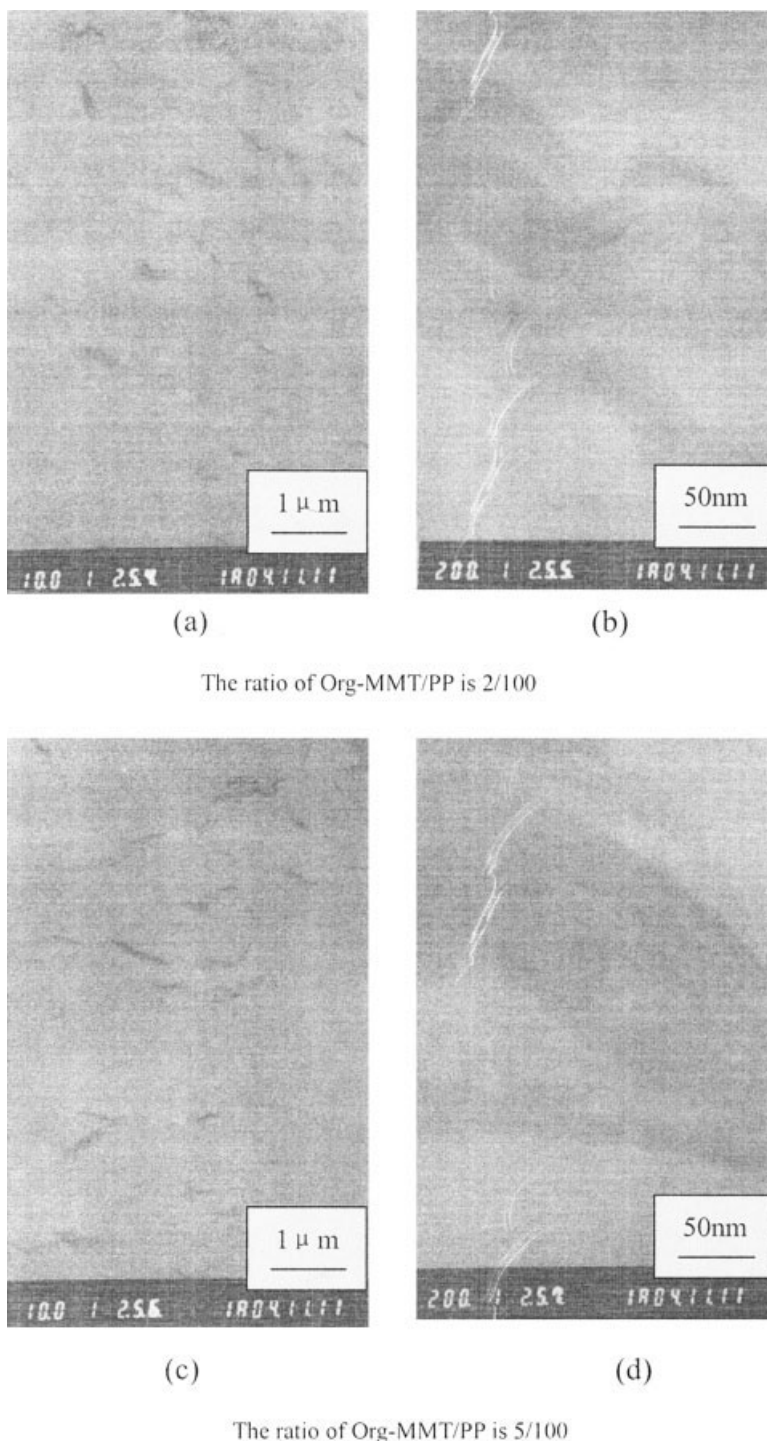
The ratio of Org-MMT/PP is 5/100

Figure 4 The photo TEM of the nanocomposites.

MMT. Due to the shear flow in melt extrusion, the lamellar body of Org-MMT is flexural in the matrix.

Thermal degradation

Thermal stability is an important property in which the nanocomposite morphology plays an important role. The PP/clay hybrids were analyzed by TGA. The T_g curves are shown in Figure 5. The onset loss temperature(T_{onset}), the 5% loss temperature ($T_{-5\%}$), the maximum weight loss temperatures (T_{max}), and char residue at 800°C are listed in Table III. Figure 5 shows that the thermal stability of nanocomposites is evidently better than that of pure PP.

Table III reveals that PP/clay nanocomposites show good thermal stability. When filled with Org-MMT,
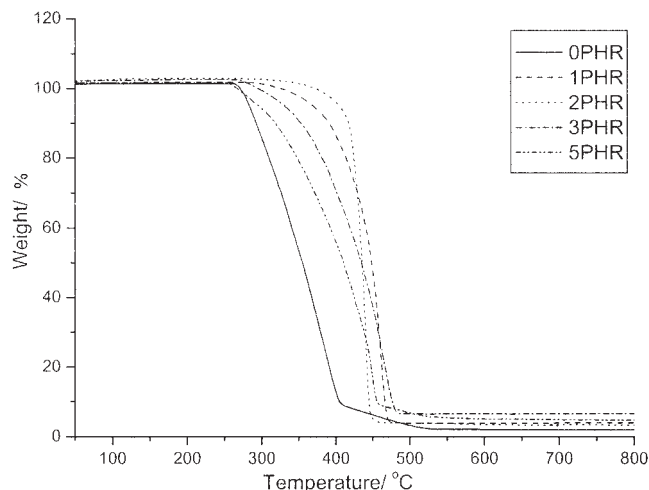
Figure 5 the T_g curves for the pure PP and Org-MMT/PP nanocomposites

the thermal gravimetric loss temperature of nanocomposites was higher than that of pure PP. When 2 phr Org-MMT was filled, the loss temperature (5%) was 395.1°C, which was 112.1°C higher than that of pure PP. The probable reasons may be that in nanocomposites the intimate contact between the polymer molecules and the inorganic crystalline layers has decreased the activity of the macromolecules, which need more energy to activate, and at the same time, due to an ablative reassembling of the silicate layers which may occur on the surface of the nanocomposites creating a physical protective barrier on the surface of the material. Volatilization might also be delayed by the labyrinth effect of the silicate layers dispersed in the nanocomposites. Thus it can be seen that the Org-MMT and the preparation methods have an influence on thermal stability.

In Table III, the char residue of nanocomposites tends to increase, compared with that of the polymer matrix. The char residue of pure PP is 0.69 wt %, because the condition is under nitrogen, which leads to part of the polymer carbonized.

Crystallinity of the matrix

Polypropylene is a crystal polymer, and so the study on the crystallinity properties of the composite is very important. Table IVshows the fusion point and the absorbing enthalpy of the nanocomposites and the pure PP and Table Vshows the crystallinity properties of the nanocomposites and the pure PP.

From Table IV, it is evident that the melting point of the hybrid has increased by the added Org-MMT. The absorbing enthalpy of the composites displays that the added Org-MMT can normally decrease the crystallinity of the nanocomposites.

In Table V, the t_{onset} means the beginning point of the crystallization; t_p means the peak temperature of the crystallization; Δt, which is $t_{onset} - t_p$, can be attributed to the total velocity of crystallization. If the numerical value is small, the total velocity of crystallization is fast. ΔH is the releasing enthalpy of the nannocomposties and the pure PP.

From Table V, it is seen that the beginning crystalling temperature and the peak temperature of the nanocomposites have been higher than the pure PP. Δt of the nanocomposites has been decreased, which means that the total velocity of crystallization is less than the pure PP. ΔH of the nanocomposites has also been decreased, which means that the crystallinity of the nanocompostes is lower than pure PP.

It can be explained that PP-g-MAH and Org-MMT acting as heterogeneous nucleating agents during crystallization of PP from melt are inclined to absorb macromolecule segments, owing to the carboxyl group included in PP-g-MAH which exhibits strong polarity, and the interlayers of Org-MMT have spacious superficial area, and consequently their movements were constrained and initiate to crystallize. When the polymer crystallizes, it will release heat, and

TABLE IV
The Melting Point of the Nanocomposites and the Pure PP

Sample	t_p (°C)	ΔH (J/g)
1	142.5	64.8
2	143.1	67.1
3	143.9	62.2
4	143.7	62.2
5	143.7	60.4

TABLE III
Thermal Properties of the Nanocomposites and the Pure PP

Sample	T_{onset} (°C)	$T_{-5\%}$ (°C)	T_{max} (°C)	Char residue at 800°C (wt %)
1	294.6	283.0	383.8	0.69
2	429.5	368.8	462.0	1.30
3	425.4	395.1	441.6	2.04
4	391.6	330.2	468.6	3.95
5	393.9	295.3	449.8	3.69

TABLE V
The Crystallinity of the Nanocomposites and the Pure PP

Sample	t_{onset} (°C)	t_p (°C)	Δt ($t_{onset} - t_p$) (°C)	ΔH (J/g)
1	105.8	101.9	3.9	66.1
2	106.1	102.3	3.8	64.8
3	106.1	102.1	4	65.2
4	106.2	102.5	3.7	63.0
5	106.6	103.1	3.5	64.1

so the enthalpy can explain the change of crystallinity. The acceleration of the crystallization and the higher crystalling point induce the lower crystallinity.

CONCLUSIONS

PP-based nanocomposites were prepared by melting-blend intercalation, with a twin-screw extruder. As nonpolar PP macromolecule could hardly intercalate between the interlayers of Org-MMT, introducing PP-g-MAH is necessary for preparing PP/PP-g-MAH/ Org-MMT nanocomposite. The mechanical properties of the nanocomposites increases. The nanocomposites structure is demonstrated by TEM. Thermal stability of PP/clay hybrids has been analyzed by TGA, which shows that Org-MMT has increased the thermal stability of nanocomposites. The crystal properties of the composite have been tested by DSC, which shows that Org-MMT can have a heterogeneous nucleus effect on pure PP, which results in a decrease of crystallinity and an increase of the total velocity of crystallization. This work also shows that PP/clay nanocomposites can be prepared in ordinary machines, which provides a general concept for manufacturing polymer nano-composites by direct melting-blend intercalation.

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