

Structure and Properties of Polypropylene Composites Filled with Magnesium Hydroxide

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ABSTRACT: Silane and silicone oil modified superfine magnesium hydroxide (MH) was filled into polypropylene (PP) as a flame retardant. The PP and flame-retarded PP composites were studied for their mechanical properties and rheological behaviors by differential scanning calorimetry (DSC), polarizing optical microscopy (POM), limiting oxygen index (LOI), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). The results showed that the addition of MH improved flame retardancy of PP/MH composites, but seriously deteriorated mechanical properties of the composites. Surface treatment of MH could significantly improve tensile and impact strength of PP/MH composite because of its enhanced interfacial adhesion between MH and PP matrix. DSC results showed

that MH had heterogeneous nucleation effect on PP. Surface treatment of MH weakened its heterogeneous nucleation effect. POM results showed that the dispersion of MH particles played an important role in the crystalline morphology and spherulite size of PP crystals. TGA indicated that MH greatly enhanced the thermal stability of PP. The introduction of treatment agent further improved the thermal oxidative stability of the composite. According to LOI, silane-treated MH greatly enhanced flame retardancy of PP/MH composites. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4943–4951, 2006

Key words: polypropylene; magnesium hydroxide; surface treatment; crystallization; flame retardant; thermal stability

INTRODUCTION

Polypropylene (PP) is one of the universal polymers and has many advantages such as easy processability, corrosion resistance, and low cost. Its applications focus on interior decorations, furniture, insulation, electronics, architectural materials, and so on. It is known that PP is a highly combustible material. Its emission of smoke and poisonous gases during burning restricts its applications.¹ Therefore, it is important to improve the flame retardancy and reduce the emissions of smoke and poisonous gases. This could be achieved by the incorporation of additives. Traditionally, halogen-containing compounds, alone or in conjunction with antimony trioxide, are the main flame retardants (FR) of PP. However, it is more and more realized that those flame retardants would produce some problems, such as the corrosiveness, smoke emissions, and toxicity of the combustion products.^{2,3} Therefore, alternative halogen-free flame retardants (HFFR) such as metallic hydroxide, ex-

pandable graphite, and intumescent flame phosphorous-containing materials have attracted great attention of researchers.^{4–7}

Among the HFFR, magnesium hydroxide (MH) has been studied in detail and is the most popular replacement for halogen-based FR because of its high endothermic decomposition temperature (above 340°C) and low cost.^{8,9} The mechanisms of MH as a FR are quite different from that of a halogen-based FR. The heating-released water moisture during decomposition of MH dilutes the fuel supply present in the gas phase, and the decomposition products also insulate the underlying polymer matrix from the heat source.^{3,10} Therefore, the metallic hydroxides do not induce the smoke and corrosion problems. Nevertheless, one main disadvantage of the filler is the high levels (more than 60%) required to achieve the desired flame retardancy. Such high levels would cause a great decrease of mechanical properties and processability of composites.^{11,12} To minimize this effect, surface treatment of MH is an important way to improve compatibility. The character of the filler surface can be modified through use of different coatings to improve the boundary adhesion between the filler and polymer matrix. Typical coating agents containing hydroxyl groups are fatty acids, like stearic acid, and their salts, which can react with hydroxyl groups.^{13–15}

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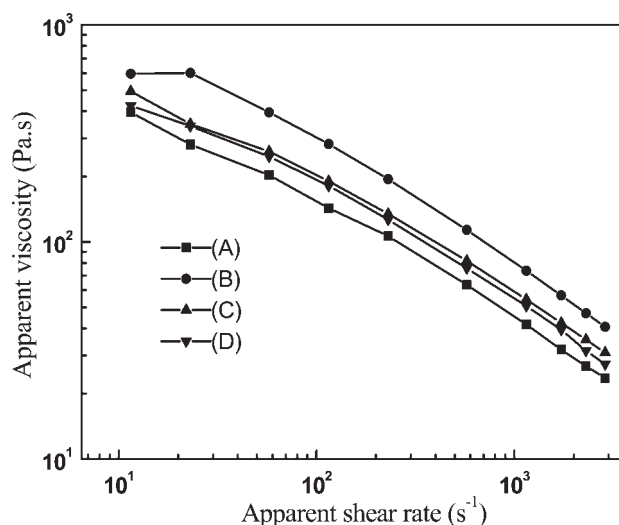


Figure 1 Effect of modifier on the apparent viscosity of PP and PP/MH (MH content: 100 phr by weight) composites at 210°C: (A) neat-PP, (B) no treatment, (C) 2 phr silane, and (D) 2 phr silicone oil.

Among these investigations on FR-filled polymers, much attention has been paid to the development of FR composites. However, rheological behaviors, crystallization behaviors, and mechanical properties of such material systems are paid less attention, especially for MH-filled PP composites. The aim of this work was to study the effects of surface treatment agent on MH powders modification, as well as the effect of surface modification of MH on the rheological behaviors, crystallization behaviors, mechanical properties, the flammability, and thermal stability of PP/MH composite.

EXPERIMENTAL

Materials

Polypropylene used in this work was a commercial polymer PP-140, supplied by Baling Petrochemical (Hunan, China). Magnesium hydroxide, with an average particle size of 2.0–2.5 μm , was provided by Qindao Haida Chemical (Shandong, China). Silane coupling agent (2,3-epoxy propoxy propyltrimethoxysilane) was a commercial product from JinTan Eastchina Coupling Agent Factory (Jiangsu, China). Silicone oil (dimethyl silicone oil) was supplied by Chenguang Research Institute of Chemical Industry (Sichuan, China). Antioxidant 1010 (pentaerythritol tetra (β -(3,5-ditertbutyl-4-hydroxy phenyl) propionate)) is commercial auxiliary from Milan Chemical (Nanjing, China).

Preparation of samples

Modification of MH powders was proceeded according to the following steps. The MH powders were

dried at 110°C for 10 h to eliminate possible absorbed water on the surface of the powders. Then MH powders and treatment agent by the recipe were mixed in a high-speed mixer (Type SHR-10A; Jiangsu, China) at 100°C for 30 min. PP (dried at 80°C for 6 h) and untreated or treated MH were blended in a twin-screw extruder (Type TSE-40A/400-44-22, $L/D = 40$; Nanjing, China). The temperatures from hopper to die at six different zones are 175°C, 180°C, 190°C, 200°C, 210°C, and 215°C, respectively, and the screw speed is 160 rpm. The extrudate was cut into pellets and injection-molded (Type J80M3V; China) at 210°C into various specimens for test and characterization.

Measurements and characterization

Rheological behaviors

The rheological behaviors of melt extrudates were measured by high-pressure capillary rheometer (Rheograph 2002; Gottfert Co., Germany). L/D ratio is 30 and the experimental temperature is 210°C.

Differential scanning calorimetry analysis

It was carried out under dry nitrogen using a Perkin-Elmer Q 10 for measuring nonisothermal crystallization behaviors of PP and flame-retarded PP composites. Thermograms were recorded at a heating or cooling rate of 10°C/min. The degree of crystallinity (X_c) of composites was calculated from the following equation¹⁶:

$$X_c = \Delta H / (1 - \phi) \Delta H_{100}$$

where ΔH is the overall enthalpy of crystallization obtained from the integral area of the cooling thermo-

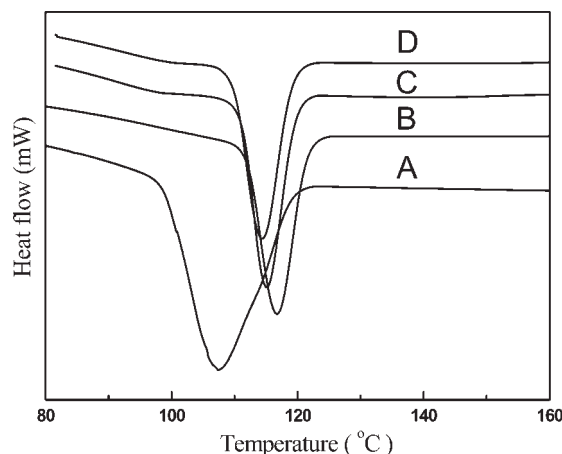


Figure 2 DSC crystallization exotherms of PP and its composites: (A) neat-PP, (B) PP/MH (100/100), (C) PP/MH/silane (100/100/2), and (D) PP/MH/silicone oil (100/100/2).

TABLE I
Nonisothermal Crystallization Parameters of PP and PP/MH Composites Containing Different Treatment Agents

Samples	T_{co} (°C)	T_p (°C)	ΔH_m (J g ⁻¹)	X_c (%)	Width (50%) (°C)
PP	122.3	107.3	90.3	43.2	11.5
PP/MH	124.5	117.1	43.2	41.3	7.0
PP/MH/silane	123.7	115.8	43.9	42.0	6.9
PP/MH/silicone oil	123.8	114.9	44.1	42.2	6.8

gram, ϕ is the volume fraction of MH in the composites, and ΔH_{100} is the enthalpy of PP of 100% crystallinity and was taken as 209 J/g.¹⁷

Polarizing optical microscopy

A polarizing optical microscope (POM) (Leitz Laborlux 12 Pols) was used to observe the crystal morphology. The samples were first annealed at 200°C for 5 min, and then quickly cooled to 110°C at a cooling rate of 90°C/min. The end images of the crystallization were recorded with an image processor.

Mechanical properties

The tensile test of samples was performed at room temperature with a crosshead speed of 50 mm/min

on a Material Test instrument (Model WDW-10C; Shanghai, China). The dimensions of specimens were 120 × 10 × 4 mm³.

Notched impact test was performed according to the Chinese regulation GB1048 on a drop weight impact tester (Model ZBC-4B; Shenzhen, China). The dimensions of specimens were 60 × 10 × 4 mm³. The notched depth is 2 mm and notch tip radius is 0.25 mm.

Fractography

The tensile and impact fracture surfaces of the samples were investigated by a scanning electron microscope (SEM) (Model HitachiX-650; Japan). Gold sputter coated samples were examined using a Cambridge Stereoscan 250 with an accelerating voltage of 10 kV.

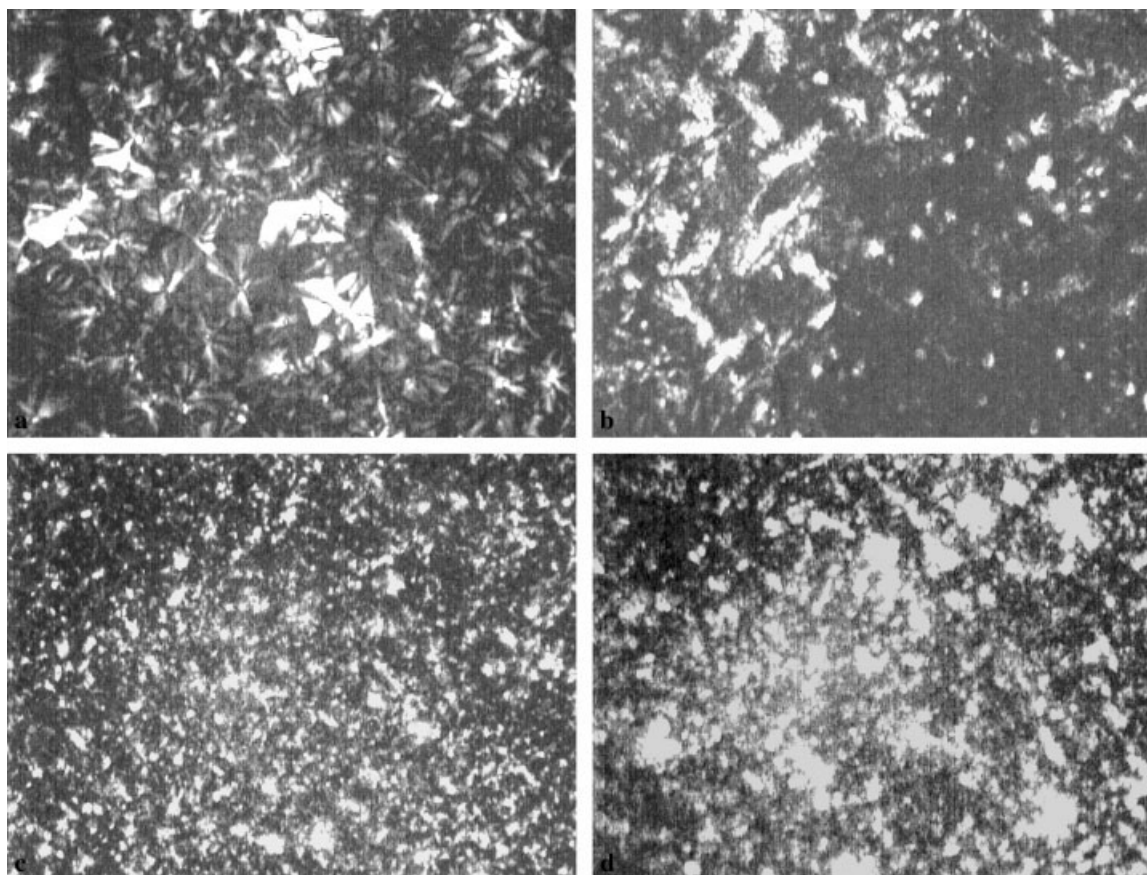


Figure 3 POM photos of PP and its composites: (A) neat-PP, (B) PP/MH (100/100), (C) PP/MH/silane (100/100/2), and (D) PP/MH/silicone oil (100/100/2).

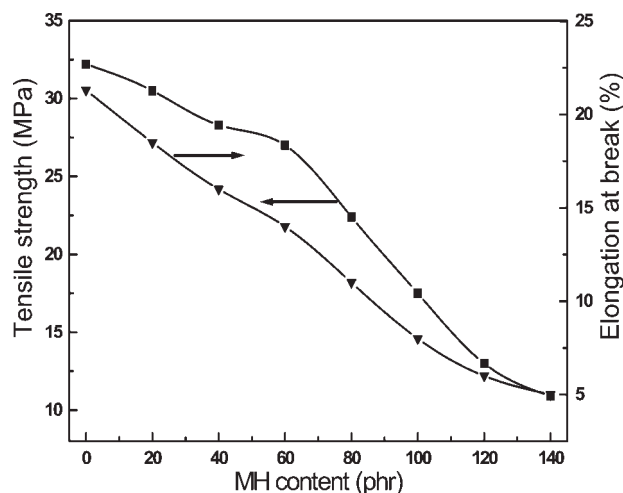


Figure 4 Effect of MH content on the tensile properties of PP/MH composites.

Limiting oxygen index

The LOI value was measured using a limiting oxygen index instrument (Type JF-3; Jiangning Analysis Instrument Factory, Nanjing, China) on sheets $100 \times 10 \times 4 \text{ mm}^3$ according to the standard oxygen index test ASTM D2863-77. The LOI value is calculated according to the equation given below:

$$\text{LOI} = \frac{[\text{O}_2]}{[\text{O}_2] + [\text{N}_2]} \times 100\%$$

where $[\text{O}_2]$ and $[\text{N}_2]$ are the concentration of O_2 and N_2 , respectively.

Thermogravimetric analysis

TGA of samples (about 8 mg) was carried out in air atmosphere with a flow rate of 30 mL/min in a tem-

perature range from 30°C to 600°C at a scanning rate of 10°C/min by a Perkin-Elmer Q 50 thermogravimetric analyzer. Experimental error is about $\pm 5^\circ\text{C}$ and $\pm 1 \text{ wt } \%$ for thermal degradation temperature and residue, respectively.

RESULTS AND DISCUSSION

Rheological behaviors

The flow curves of PP and flame-retarded PP composites are shown in Figure 1. The apparent viscosities of PP, PP/MH, PP/MH/silane, and PP/MH/silicone oil composites decrease with increasing shear rate. This indicates that the melts of PP and flame-retarded PP composites are pseudoplastic fluids. From Figure 1, it can be seen that MH has great effect on the apparent viscosity of PP at 210°C, indicating that the difference in apparent viscosities of PP and PP/MH composite is very large. The incorporation of MH increases the apparent viscosity of PP. But for the PP/MH/silane and PP/MH/silicone oil composites, the apparent viscosities are much lower than that of PP/MH composite at the same shear rate. The reason is that surface energy of the treated filler decreases, and thus the treatment agent increases dispersion of primary MH particles in PP matrix and these well-dispersed MH particles are responsible for the lower viscosity of the composites. All these can reduce resistance of molecular chains, reducing the apparent viscosities of composites.⁶

Crystallization behaviors

The DSC exotherms of neat-PP, PP/MH, PP/MH/silane, and PP/MH/silicone oil composites under nonisothermal crystallization conditions were measured at a cooling rate of 10°C/min, and the results

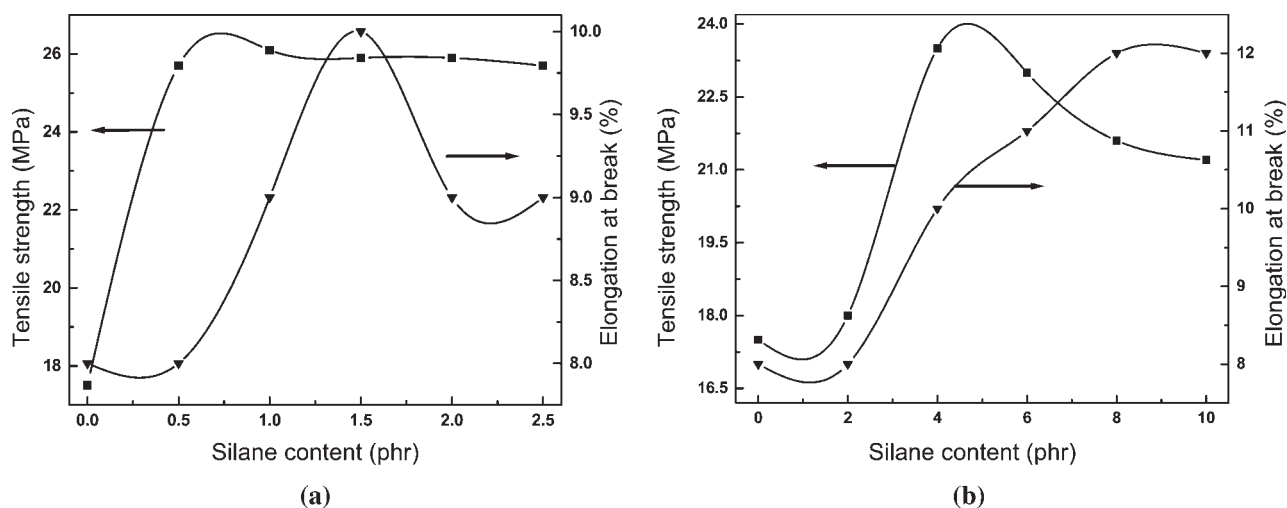


Figure 5 Effect of modifier on tensile properties of PP/MH (100/100) composite.

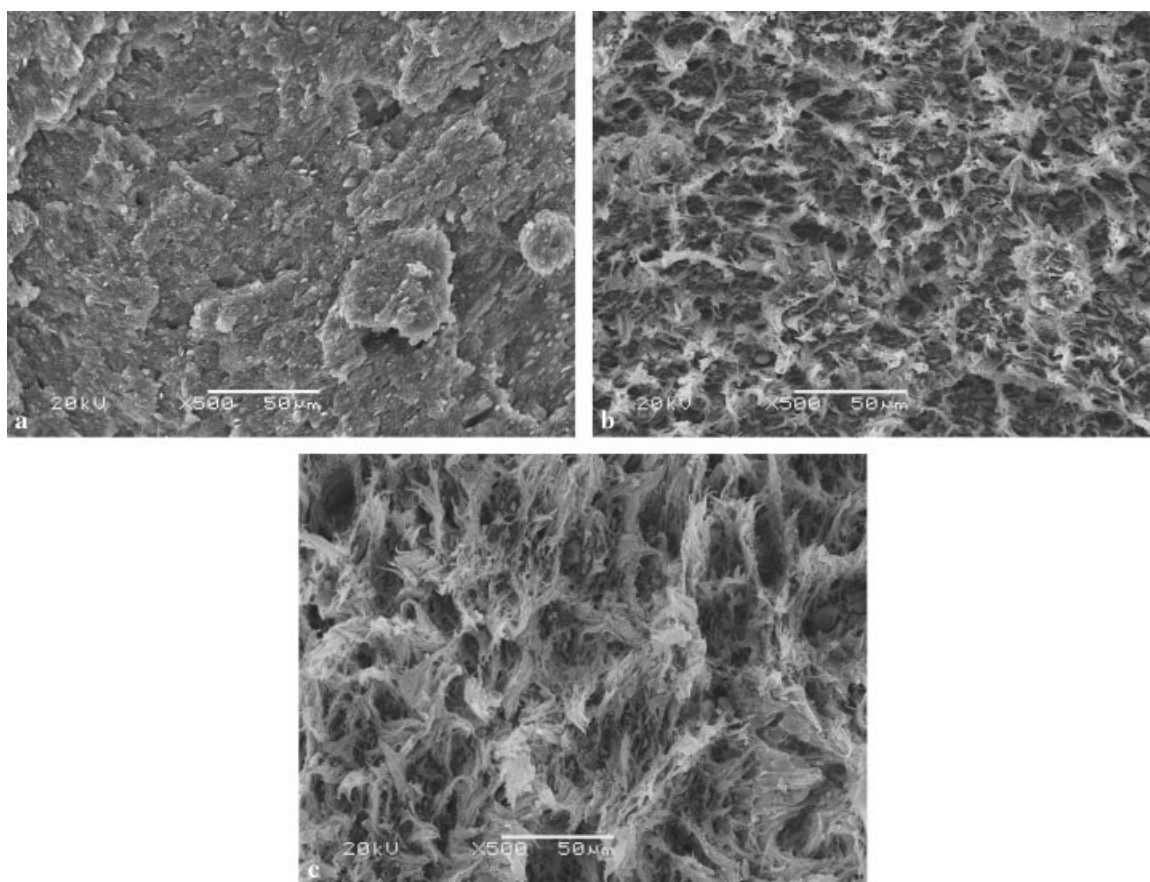


Figure 6 The tensile fracture surfaces of the PP/MH (100/100) composites with and without treatment: (A) no treatment, (B) 2 phr silane modified, and (C) 8 phr silicone oil modified.

are presented in Figure 2. The onset temperature (T_{co}), the peak temperature (T_p) of the exotherm, and the crystallinity degree (X_c) are commonly used to describe the nonisothermal crystallization process of polymers.^{18,19} The T_{co} , T_p , X_c and the half-height peak width values of PP and its composites are shown in Table I. It can be seen from Figure 2 that only one exothermic peak can be observed for each curve between 90°C and 160°C. For neat-PP, an exothermic crystallization peak appears at about 107.3°C. However, T_p of the exotherm of PP/MH composite (curve B) shifts to higher temperature (117.1°C) in comparison with that of neat PP (curve A). The reason for the increase of T_p may be attributed to the heterogeneous nucleation effect of MH in the composites. The nucleation action of MH can also shorten the whole crystallizing time, exhibiting a decrease in the half-height peak width according to DSC cooling scan. The addition of MH also causes a reduction of ΔH_m of PP, indicating the decrease of its crystallinity. Similar result was obtained in other work.²⁰ The T_{co} and T_p of the exotherm of PP/MH composite containing different treatment agents (curve C and D) shift to lower temperature compared with those of the composite without treatment

agent. The introduction of surface treatment agents leads to a small increase of crystallinity and slight decrease of half-height peak width. Obviously, the surface treatment agents are coated on the surface of MH particles and weaken heterogeneous nucleation effect of MH on PP.

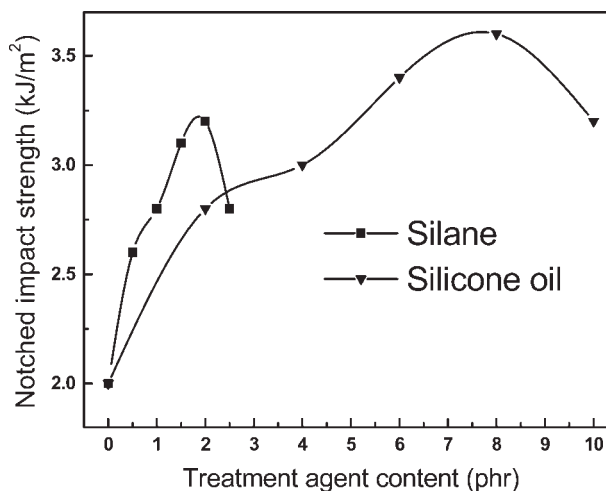


Figure 7 Effect of modifier on impact strength of PP/MH (100/100) composite.

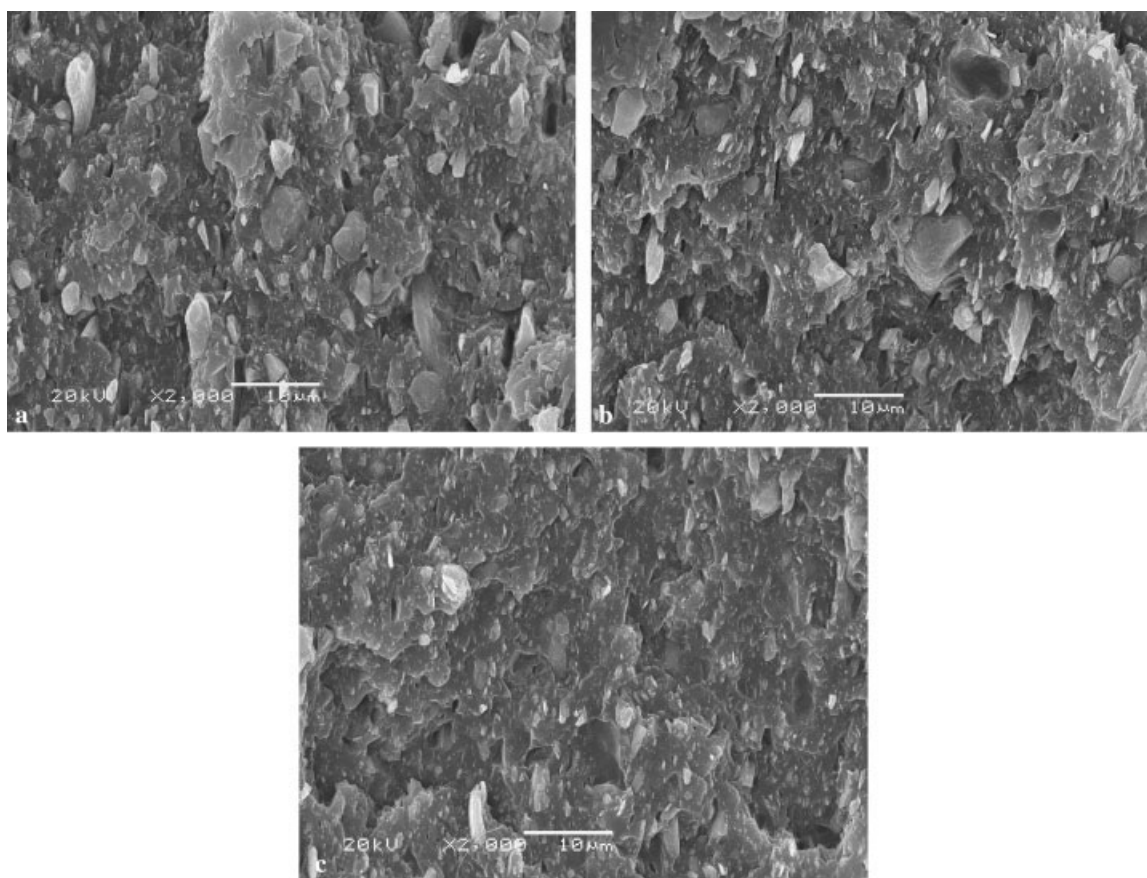


Figure 8 The impact fracture surfaces of the PP/MH (100/100) composites with and without treatment: (A) no treatment, (B) 2 phr silane modified, and (C) 8 phr silicone oil modified.

POM observation is used to characterize the crystallization of polymer and its composites. Figure 3 shows the crystalline morphologies of neat-PP, PP/MH, PP/MH/silane, and PP/MH/silicone oil composites at 110°C. It is apparent that the crystals of neat PP show perfect spherulite structure [Fig. 3(A)]. MH particles in conventional PP/MH composite act as heterogeneous nucleating agent. It can be also seen that the spherulite crystal structure of PP disappears and its crystal size distribution is very wide. Surface treatment improves the dispersion of MH in PP matrix and enhances adhesion between MH and PP matrix. This suggests that crystalline morphology and crystals distribution of PP would change. Figure 3(c,d) show that incorporation of silane and silicone oil further reduces the spherulite size of PP. Moreover, crystals disperse well and crystal final size is very small.

Mechanical properties

In general, the addition of FR causes a decrease in the mechanical properties of polymers.²¹ To assess the effect of MH on mechanical properties of PP, tensile properties and impact strength were mea-

sured. The effect of MH content on the tensile properties of PP/MH composites is shown in Figure 4. It can be seen that the tensile strength and the elongation at break decrease with increasing MH content. The observed reduction in the tensile properties is

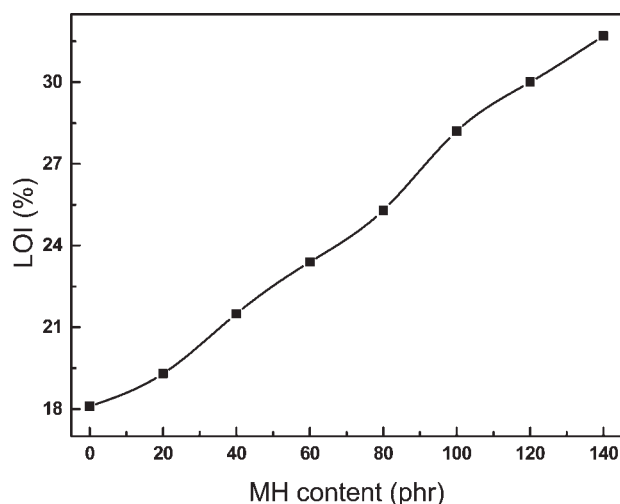


Figure 9 LOI of PP and PP filled with various amounts of MH.

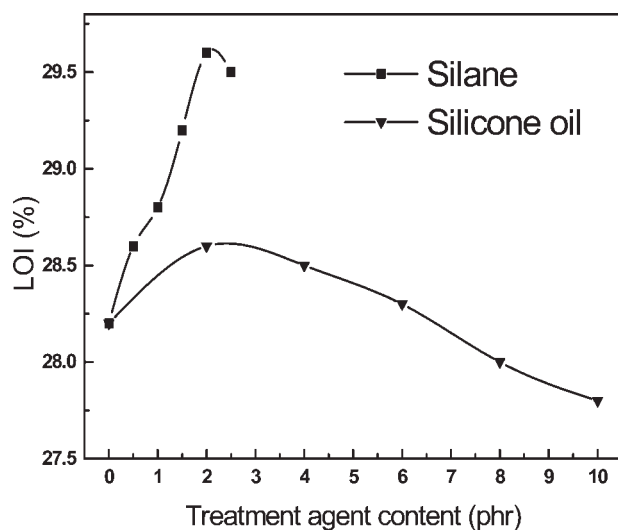


Figure 10 Effect of treatment on LOI of PP/MH (100/100) composite.

mainly due to the poor compatibility between the filler and the matrix in PP/MH composite. The surface modification of filler is the main way for the property improvement of the composites. As shown in Figure 5, the tensile strength and elongation at break of the composites with treatment agent are much higher than those of the composite without treatment agent at the same MH content. The tensile strength of the PP/MH/silane and PP/MH/silicone oil composites is about 6–8 MPa higher than that of the PP/MH composite, increasing by ~34–45%. Mechanical properties improvement of the composites indicates that the incorporation of treatment agent enhances compatibility between the filler and PP matrix.

Figure 6 shows SEM micrographs of the tensile fracture surfaces for the PP/MH, PP/MH/silane, and PP/MH/silicone oil composites. For the composite without surface treatment agent [Fig. 6(A)], a very smooth fracture surface was observed. This indicates that the composite is very brittle. However, for the composites with modified MH [Fig. 6(b,c)], a lot of PP fibrils were observed. These PP fibrils are remnants of the cold-drawn PP ligaments between the rigid MH particles. Toughening distortion of PP matrix takes place.

The notched impact strength of PP/MH, PP/MH/silane, and PP/MH/silicone oil composites is shown in Figure 7. The impact strength for PP/MH composite is very low. For the PP/MH composites with treatment agent, the impact strength increases with the increase of treatment agent content, and passes through a maximum. Then their impact strengths get reduced.

Figure 8 is the SEM micrographs of the impact fracture surfaces of PP/MH, PP/MH/silane, and PP/MH/silicone oil composites. Compared with unmodified

MH particles, MH particles treated with silane and silicone oil [Fig. 8(b,c)] become more and more smaller, and MH particles distribution in PP matrix is narrower. Moreover, MH particles are better attached to the PP matrix. It is ascribed to the enhanced interfacial adhesion between the filler and matrix by the surface treatment of MH, and then the composites become more ductile.

Flame retardancy

The limiting oxygen index (LOI) is widely used to evaluate flame retardancy of polymer materials. Figure 9 shows the LOI data obtained from the PP composites with different content MH. It can be seen from Figure 9 that the LOI of PP/MH composite increases as the MH content increases. This means that higher oxygen density is required to initiate and sustain combustion of the samples after the addition of MH into PP. The LOI value of PP composites is 28.2 at 100 phr (50% by weight) of MH, whereas the corresponding values at 140 phr (58.3% by weight) is 31.7, as shown in Figure 9. The results illustrate the low flame-retardant efficiency of MH in the PP system. Higher loading of MH is necessary to provide adequate flame retardance. Considering the practice application, we use the total amount 100 phr of MH additive as a reference formulation.

Figure 10 displays the changes of LOI values for the composites with treatment agent content. The results show that the LOI increases with increasing treatment agent content. However, the LOI decreases with further increasing treatment agent content. These data illustrate that the coating of MH with appropriate content of modifiers greatly improves the flame retardance of PP/MH composite, espe-

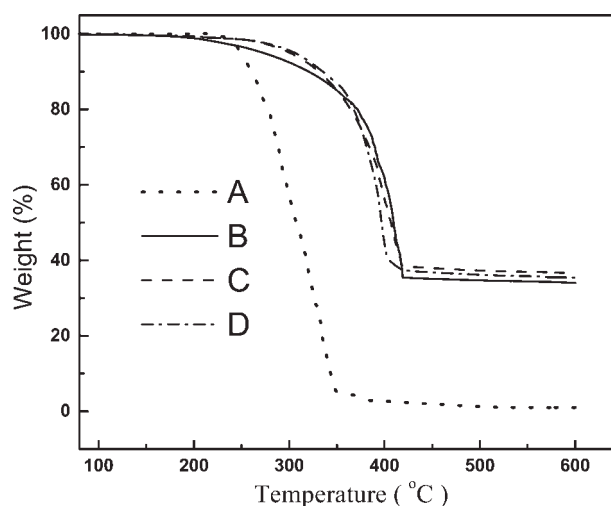


Figure 11 The TGA curves of PP and flame retarded PP composites in air: (A) neat-PP, (B) PP/MH (100/100), (C) PP/MH/silane (100/100/2), and (D) PP/MH/silicone oil (100/100/2).

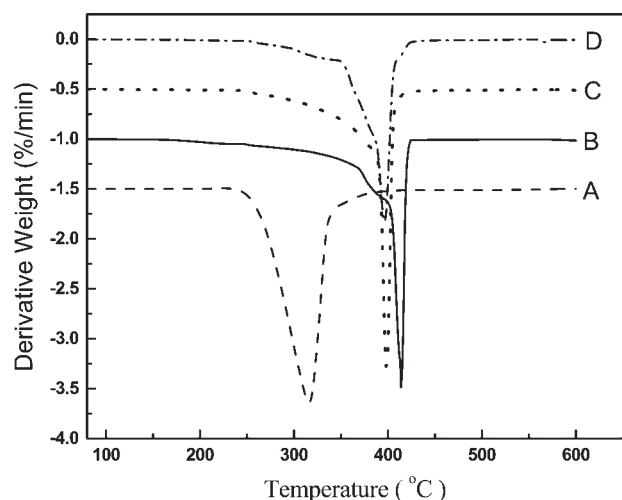


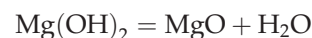
Figure 12 The DTG curves of PP and flame retarded PP composites in air: (A) neat-PP, (B) PP/MH (100/100), (C) PP/MH/silane (100/100/2), and (D) PP/MH/silicone oil (100/100/2).

cially for silane treatment agent. Moreover, the LOI of the composites with silane is higher than that of corresponding composites with silicone oil.

Thermogravimetric analysis

TGA is widely used to study the thermal stability of polymer and its composites. TGA and DTG curves of PP and flame-retardant PP composites in air atmosphere are shown in Figures 11 and 12, respectively. The neat PP undergoes completely thermal oxidative degradation at temperature up to 420°C, and there is no residue at the end of the degradation. However, the flame-retarded PP composites show better thermal oxidative stability than neat PP and have about 35–37% residue left after the degradation. It can be also found that the thermal weight loss of PP-treated MH composites is lower than that of PP-untreated MH composite at below 360°C. While the thermal weight loss of the modified MH-filled PP composites is high than that of the nontreated MH-filled PP composite in the temperature range of 360–410°C. The possible reason is that the aggregated and poor-dispersed untreated MH particles in the composites would delay the decomposition of MH with releasing water, which restrains thermal degradation of PP.

The residue of PP-treated MH composites is higher than that of PP-untreated MH composites after degradation at 500°C, which indicates that the addition of treated MH into PP results in the increase of the thermal oxidative stability. The TGA results are summarized in Table II. Flame resistance can also be evaluated from the residue after pyrolysis of the composites. Van Krevelen²² found a linear relationship between LOI and char residue in halogen-free flame-retarded polymers. Increasing residue formation can hold up the release of combustible carbon-containing gases, and decrease the exothermicity induced by pyrolysis reactions as well as the thermal conductivity of the surface of burning materials.²³ According to the following equation:



The MgO content in the residue is a constant at 500°C and the decomposition products also insulate the underlying polymer matrix from the heat source.¹⁰ Therefore, the residue reflects the eventual char residue at the same condition. Table II shows the residue data after degradation of PP-untreated MH and PP-treated MH composites at 500°C. As compared with that of PP-untreated MH composites, the residue after degradation of PP-treated MH composites at 500°C is higher, which is responsible for the enhancement of their flame retardancy. Figures 9 and 10 indicate higher LOI in the PP-treated MH composites.

CONCLUSIONS

Compared with untreated MH, treated MH improved processing behavior of the PP/MH composites. DSC results indicated that MH had heterogeneous nucleation effect on PP. However, surface modifier weakened heterogeneous nucleation effect of MH. The mechanical tests showed that MH alone seriously deteriorated the mechanical properties of the composites. It was evident that treated MH greatly improved mechanical properties of PP/MH composite. SEM analysis showed that the incorporation of treatment agent into the PP/MH composite dramatically enhanced interface adhesion of the composites due to the improvement of the compatibility between MH and PP matrix. TGA revealed that PP/MH composites with and without surface

TABLE II
Thermal Stability and Degradation Data of PP and Flame-Retarded PP

Sample	$T_{5\%}$ (°C)	$T_{20\%}$ (°C)	$T_{50\%}$ (°C)	T_p (°C)	Residue at 500°C (%)
PP	233.5	263.0	292.2	316.2	1.1
PP/MH	272.1	371.2	409.9	414.8	34.7
PP/MH/silane	300.1	364.2	406.9	401.7	37.3
PP/MH/silicone oil	305.2	367.4	397.8	396.6	36.2

treatment agent had better thermal stability than neat PP. A higher residue was obtained from PP filled with treated MH composites, which resulted in an enhancement in the flame retardance, reflecting the increase of LOI.

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