



Effect of compatibilizers on thermal stability and mechanical properties of magnesium hydroxide filled polypropylene composites

Hao Shen, Yuhai Wang, Kancheng Mai*

Key Laboratory for Polymeric Composites and Functional Materials of Ministry of Education, Material Science Institute, College of Chemistry and Chemical Engineering, Zhongshan (Sun Yat-sen) University, Guangzhou 510275, China

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ABSTRACT

Effect of different compatibilizers and magnesium hydroxide (MH) on morphology, thermal stability and mechanical properties of polypropylene (PP) composites were investigated in this study. Two different types of compatibilizers namely, polypropylene grafted-maleic anhydride (PP-g-MA) and ethylene-octene copolymer grafted-maleic anhydride (POE-g-MA) were used in this study. The results indicated that the degradation of PP/MH composites contained two steps: decomposition of MH and degradation of macromolecular. MH particles acting as physical barrier improved the thermal stability of PP, especially in oxygen. POE-g-MA enhanced it furthermore. Introduction of PP-g-MA or POE-g-MA to PP/MH composites resulted in considerable improvement in mechanical properties. The addition of PP-g-MA was most effective in increasing the tensile strength, while addition of POE-g-MA greatly increased the impact strength of PP/MH composites.

Morphological investigation revealed that the improvement was attributed to the formation of encapsulation structure in these compatibilized PP/MH composites.

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1. Introduction

Polypropylene (PP) is a most common commodity plastic, which is of practical use in many areas. However, the poor flame resistance hinders its practical application in many fields. Magnesium hydroxide (MH) is a good flame retardant for its high decomposition temperature and smoke suppressibility, and widely used in thermoplastics, such as polypropylene, polyethylene, polystyrene, ethylene vinyl acetate, polyamide [1–7]. Compounding PP with MH was an effective way to improve the flame resistance of PP [8,9]. Tai and Li [10] investigated the flammability performance of PP composite filled with bromine-antimony (BR) and magnesium hydroxide-based flame retardant (FR). They found that 60 wt% of MH was needed in order to achieve the same degree of flammability as the composite containing only 30 wt% of BR. To be effective in flame-retardant capability, high MH filler loading is often necessary.

However, MH has highly polar hydrophilic surfaces, whereas PP is non-polar and hydrophobic. When they compound each other, interfacial adhesion between the filler surface and the matrix is poor. Polymer modification with polar molecules (such as PP-g-MA

and POE-g-MA) is an efficient way to enhance interfacial adhesion, widely used in polyolefin-based composites [11–16]. The polar groups are then able to interact with functional groups on the inorganic filler, while the long hydrocarbon tails are able to anchor to the polymer matrix through physical entanglements and van der Waals interactions. A bridge between the filler and the matrix is thereby established [17].

In this study, PP-g-MA and POE-g-MA as compatibilizers were used to enhance interfacial interaction between PP matrix and MH particles. They have the same polar groups but different backbones. The same polar groups will result in the same interfacial interaction between MH and compatibilizer, while different backbones will result in different compatibility with PP and interfacial interaction between MH and PP. Our previous study [18] indicated that the crystallization and melt behaviors of PP depended upon the interfacial interaction between MH and PP. In the present work, the effect of PP-g-MA and POE-g-MA on morphology, thermal stability and mechanical properties of PP/MH composites was investigated. We aimed to figure out the thermal degradation mechanism of compatibilized and uncompatibilized PP/MH composite in different atmosphere, which will be helpful to understand the effect of MH and compatibilizers on thermal stability of PP. The objective of this study also aimed to obtain composites with both high impact strength and tensile strength, through selection of suitable compatibilizers.

* Corresponding author. Tel.: +86 20 84115109; fax: +86 20 84115109.
E-mail address: cesmkc@mail.sysu.edu.cn (K. Mai).

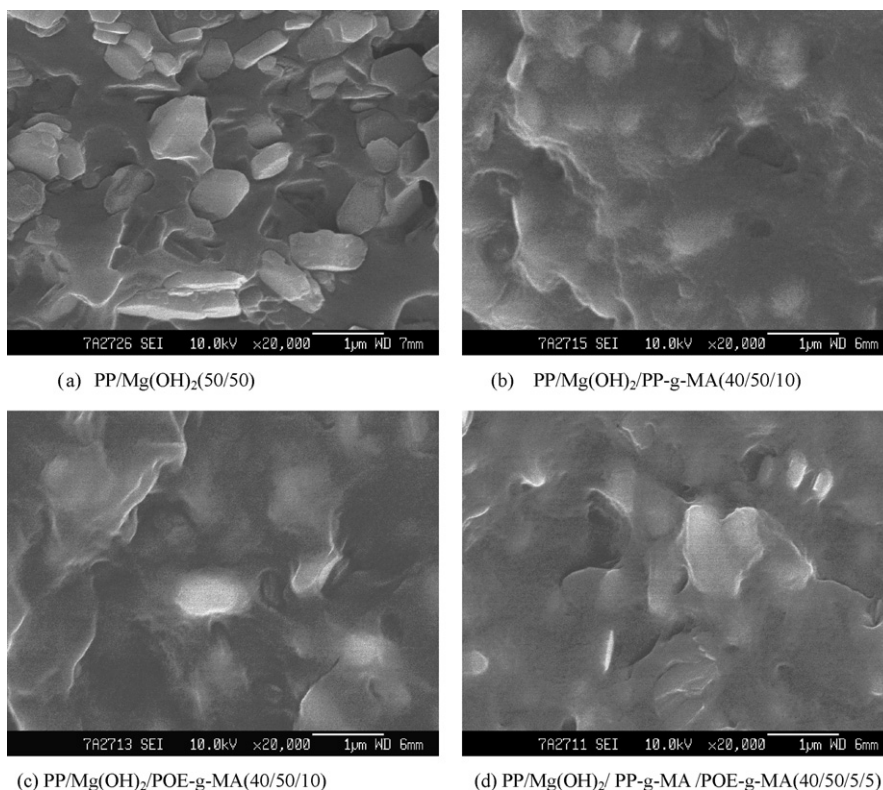


Fig. 1. SEM cryo-fractographs of PP/MH composites modified with different compatibilizer (20,000 \times). (a) PP/Mg(OH)₂ (50/50), (b) PP/Mg(OH)₂/PP-g-MA (40/50/10), (c) PP/Mg(OH)₂/POE-g-MA (40/50/10) and (d) PP/Mg(OH)₂/PP-g-MA/POE-g-MA (40/50/5/5).

2. Experimental

2.1. Materials

A commercial grade of iPP homopolymer (HP500N) was supplied by Basell. MH was high purity untreated grade (around 1.0 μm), supplied by Foshan Jinge Firefighting materials Co. PP-g-MA (containing 1.0 wt% of MA) and POE-g-MA (containing 1.1 wt% of MA) were supplied by Guangzhou Lushan Chemical Materials Co. More materials detail can be seen in our previous study [18].

2.2. Preparation

PP blends with two kinds of grafted macromolecules, PP/MH composites and its composites modified by different compatibilizers were prepared using a Berstoff ZE25A corotating twin-screw extruder ($L/D=40$, $D=35.5$ mm) with a temperature profile of 200/190/200/200/220/210/200 $^{\circ}\text{C}$ and a rotating speed of 250 rpm. The compositions for the binary PP/compatibilizer, PP/MH50 and ternary PP/compatibilizer/MH composites are 80/20, 50/50 and 40/10/50, respectively.

2.3. Characterization

The phase morphology of both binary and ternary PP composites was observed by a JSM-6330F scanning electron microscope (SEM). All specimens were obtained by cryogenic fracture.

Thermogravimetric analysis was carried out with a TA Q10 thermogravimetric analyzer using 4–5 mg samples. The samples were heated from room temperature to 600 $^{\circ}\text{C}$ in a 50 ml/min flow of N₂ or O₂ at scanning rate of 10 $^{\circ}\text{C}/\text{min}$.

Before testing, all specimens were conditioned at 25 $^{\circ}\text{C}$ and 50% relative humidity for 3–5 days. Tensile properties were charac-

terized using a Hounsfield THE 10K-S testing machine according to ASTM D 638. Charpy impact strength tests of notched specimens were carried out according to standard ISO 179-1993(E) using Advanced Pendulum Impact Tester (ATLAS)-type testing machine. Five samples were tested from each compound and the average results were recorded.

3. Results and discussion

3.1. Phase morphology

Phase morphologies of PP/MH50 and PP/MH/compatibilizer composites are presented in Fig. 1. The micro-particles seen in Fig. 1(a) were MH. The SEM micrograph showed that PP was the continuous matrix in which the MH particles were dispersed. Obviously the dispersion of MH particles was less uniform. Some of the MH particles agglomerate together, and poor compatibility resulted in a distinct interface between PP matrix and MH particles.

While addition of PP-g-MA or POE-g-MA changed this situation, seen in Fig. 1(b)–(d). Whether PP-g-MA or POE-g-MA used as compatibilizer, the MH particles were all embedded in PP matrix. Almost none isolated MH particles appeared on the fractured surfaces. Compared with PP/MH50 composite, addition of PP-g-MA or POE-g-MA as compatibilizers substantially improved the interfacial adhesion between MH particles and PP matrix. After modification with maleic anhydride, the non-polar polymer (such as PP and POE) always obtained higher polarity, which resulted in a higher affinity for polarity fillers. The maleic anhydride group (MAH) might interact with the $-\text{OH}$ on the surface of MH particle, dragging compatibilizers around with MH particles. This resulted in the formation of an encapsulation structure of compatibilizers surrounding MH particles [19].

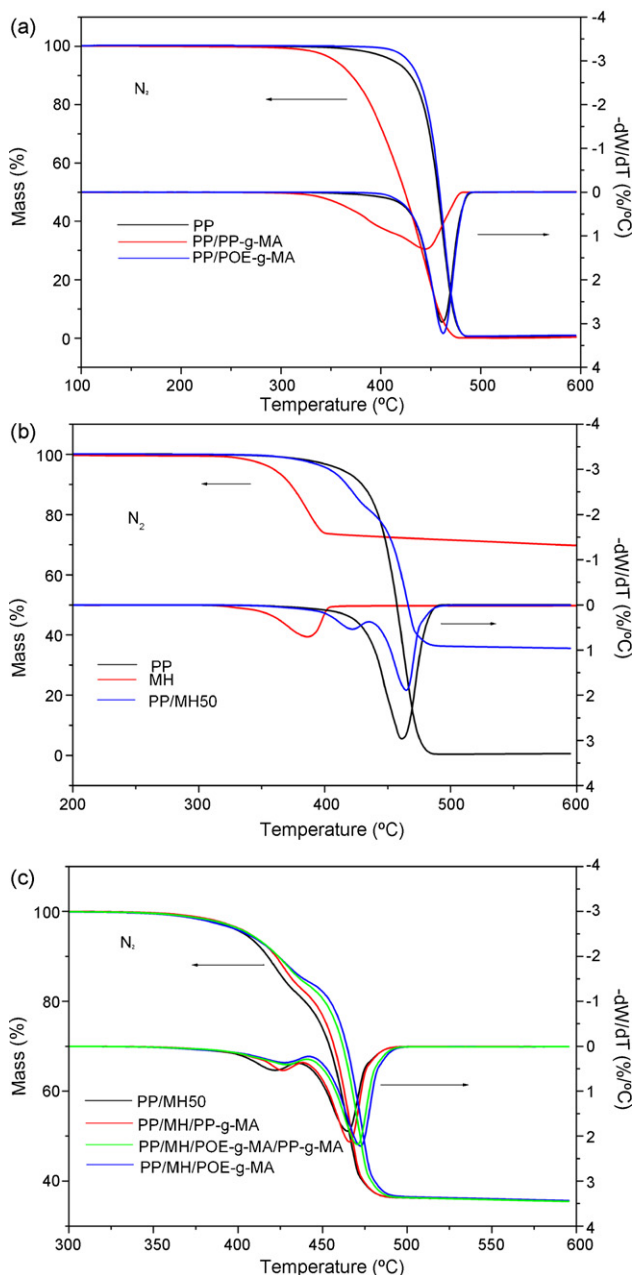


Fig. 2. TGA and DTG curves of PP, PP/compatibilizer blends (a), PP/MH composites (b) and compatibilized PP/MH composites (c) at a heating rate of 10 °C/min in N₂ atmosphere.

3.2. Thermal stability

The effect of MH particles and compatibilizers on the thermal stability of the composites was studied by means of thermogravimetric experiments, carried out in both inert and oxidative conditions. This analysis can effectively assist in the determination of the degradation mechanisms, as well as predict the thermal stability of the polymers.

3.2.1. N₂ condition

The TGA and DTG curves (N₂ condition) of all studied samples are presented in Fig. 2a–c. It seems that PP and PP/compatibilizer blends show a single step of degradation (Fig. 2a) during the thermal degradation process. Pure PP begins to decompose at

about 400 °C, completing at temperatures up to 480 °C, with no residue remaining. PP/POE-g-MA shows almost the same degradation behavior as pure PP, while the presence of PP-g-MA shifts the degradation temperature of PP to lower temperature, indicating the poor thermal stability of PP-g-MA. It is suggested that the degradation of pure PP in nitrogen is mainly the decomposition of macromolecular, with a complex radical chain mechanism, including initiation reactions, propagation reactions and termination reactions. The following products of thermal degradation under vacuum of PP have been reported: C₂H₄, C₃H₆, C₄H₁₀, C₄H₈, pentene, etc. [20].

From Fig. 2b, we can see that MH began to decompose at about 340 °C, and complete at 400 °C. There was no overlapping region between the pure PP and MH. Pure PP began to decompose after the decomposition of MH completed. The thermal degradation of PP/MH50 showed two steps, while the weight loss of first step and second step are 15.7 and 50.2%, respectively. These are almost consistent with the amount of the composition of PP/MH50 composite. From the degradation of pure PP and MH, we can conclude that the first step would correspond to MH decomposition and the second step would correspond to PP degradation. It is noted that the degradation temperature of MH in the composite is significant higher than that of pure MH, suggesting that the presence of PP delayed the decomposition of MH. Although the degradation process of PP/MH50 composite started at low temperature due to the decomposition of MH, the addition of MH shifted the degradation temperature of PP (second step) to higher temperature.

For PP/MH/compatibilizer composite, the degradation processes of these composites also show two steps (see Fig. 2c). Addition of compatibilizer enhanced the thermal stability of PP/MH composites, shifting the TGA curves to higher temperature. The first step of MH decomposition all delayed in these compatibilized PP/MH composites, especially in the presence of POE-g-MA. This would attribute to the formation of encapsulated structure in PP/MH composites modified by POE-g-MA. The surrounded POE-g-MA at the surface of fillers would hinder the release of H₂O after MH decomposition. At the same time, the thermal stability improvement at second step in the presence of compatibilizers would attribute to some inactivation of the centers active in the main chain decomposition by interaction with the filler or by prevention of the unzipping degradation from occurring through physical and chemical grafting points built up between polymer chains and filler particles [21]. Therefore, the PP/MH composites modified by compatibilizers exhibited higher degradation temperatures than that of PP/MH composite.

3.2.2. O₂ condition

Fig. 3a–c illustrated results of thermogravimetric analysis performed in the O₂ atmosphere. For pure PP, almost 90% mass loss happened at the range of 220–320 °C. Addition of PP-g-MA shifted the TGA curves of PP to low temperature, while addition of POE-g-MA shifted it to high temperature (see Fig. 3a). PP/POE-g-MA blend showed higher thermal stability than PP/PP-g-MA in O₂ atmosphere as the same as in N₂ condition. Differently, the main degradation of PP in oxygen atmosphere is thermal oxidation. The process has been reported [22]: on the surface of sample, PP macromolecules are degraded into volatile oligomers by well-known fragmentation process, then some propylene monomer units take part in peroxidation in positions opposing methyl groups which finally leads to double bonds between adjacent carbons in the main chain. The presence of oxygen accelerated the degradation of PP.

However, addition of MH largely improved the thermal stability of PP in oxygen (see Fig. 3b). The TGA curve of PP/MH50 composite shows two steps of degradation process. Comparing with MH and pure PP, we found that the first step of degradation (weight loss

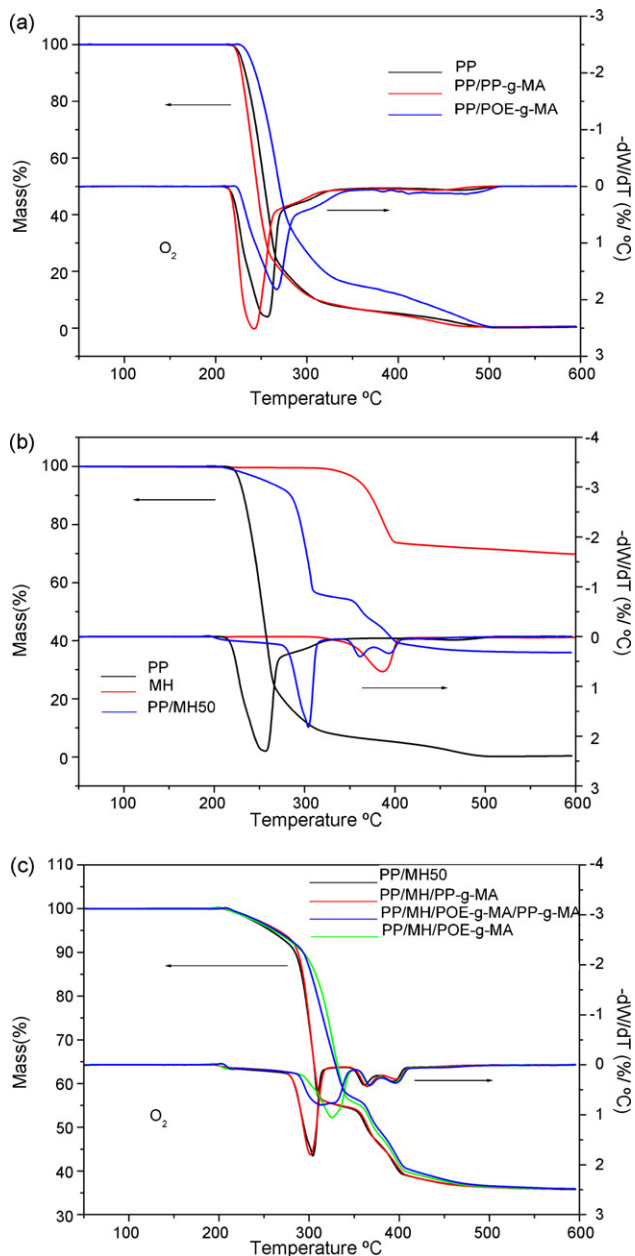


Fig. 3. TGA and DTG curves of PP, PP/compatibilizer blends (a), PP/MH composites (b) and compatibilized PP/MH composites (c) at a heating rate of 10 °C/min in O₂ atmosphere.

almost 50%) corresponded to thermal oxidative degradation of PP, which was improved by the introduction of MH particles. But the second step of degradation (weight loss almost 15%) corresponding to thermal decomposition of MH changed slightly (see Fig. 3b DTG curves).

For the compatibilized PP/MH composites, it can be observed from Fig. 3c that the presence of POE-g-MA further enhanced the thermal stability of PP in PP/MH composites. However, addition of PP-g-MA shows little effect on the thermal stability of PP in PP/MH composites.

The experimental results indicated that the thermal degradation of PP in O₂ atmosphere was different from that in N₂ atmosphere, but the decomposition temperature of MH did not change either in O₂ or N₂. Under O₂ atmosphere, the thermal oxidative degradation of PP starts before the thermal decomposition of MH, so MH can still act as a physical barrier, reducing oxygen diffusion towards the bulk and hindering the exit of the volatile degradation gases from the PP, just like the effect of clay [22]. So the thermal stability of PP significantly improved with addition of MH in O₂ atmosphere. But the thermal decomposition of MH occurred before the thermal degradation of PP under N₂ atmosphere, which reduced the effect of physical barrier of the inorganic filler. So the improvement of thermal stability in MH filled PP composites is limited.

3.3. Mechanical properties

Just like thermal stability, mechanical properties also determine the use of material. In this study, the effect of compatibilizers on tensile and impact properties of PP/MH composites is discussed below. For binary blends of PP/compatibilizer, incorporation of compatibilizers (either PP-g-MA or POE-g-MA) mildly decreased the tensile strength of PP, while PP/PP-g-MA showing higher tensile strength than PP/POE-g-MA (see Fig. 4a). In contrast, the addition of PP-g-MA or POE-g-MA into PP caused increase of impact strength (see Fig. 4b), especially in PP/POE-g-MA. The elastomer-toughening effect of POE-g-MA led to much higher impact strength of PP. The tensile strength and impact strength both decreased with the incorporation of MH. The main reason would attribute to the poor interfacial adhesion between PP matrix and MH particles, which was also confirmed by above SEM observation.

At the same filler loading, addition of PP-g-MA or POE-g-MA into PP/MH composites all led to considerable improvement in tensile strength and impact strength (see Fig. 4a–b). PP-g-MA was more effective for increasing the tensile strength of PP/MH, the tensile strength of PP/MH/PP-g-MA is close to pure PP, even higher than that of PP/PP-g-MA blend. The order of tensile strength from high to low in PP/MH/compatibilizers composites is PP/MH/PP-g-MA > PP/MH/POE-g-MA/PP-g-MA > PP/MH/POE-g-MA. While POE-g-MA was more effective for increasing the impact strength of PP/MH composites, the order of impact strength in

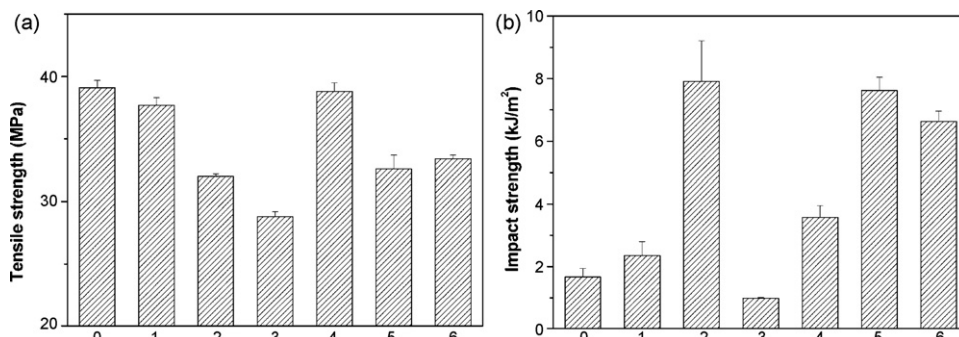


Fig. 4. Mechanical properties of PP composites. 0: PP; 1: PP/PP-g-MA; 2: PP/POE-g-MA; 3: PP/MH50; 4: PP/MH/PP-g-MA; 5: PP/MH/POE-g-MA; 6: PP/MH/PP-g-MA/POE-g-MA.

PP/MH/compatibilizers composites is contrast to the order of tensile strength. It is noted that PP/MH composites modified with PP-g-MA and POE-g-MA exhibited high tensile strength and impact strength at the same time.

From above SEM observation, we knew that an encapsulation structure was formed in the PP/MH composites modified with PP-g-MA or POE-g-MA. In these encapsulation structures, there exist two kinds of interfaces: interface between PP and compatibilizer, and interface between compatibilizer and MH. Obviously, the interfacial adhesion between compatibilizer and MH is stronger than that of between PP and compatibilizer due to the strong interaction between polar groups (MA) of compatibilizers and –OH on the MH. Therefore, the interface between PP and compatibilizer in compatibilized PP/MH composites might determine the mechanical properties. For the PP/MH composites modified with PP-g-MA or POE-g-MA, the same interfacial interactions between MH and compatibilizer, and different interfacial interaction between PP matrix and compatibilizer are obtained. The interfacial interaction between PP matrix and compatibilizer is dependent of the compatibility between PP and compatibilizer. The compatibility between PP and PP chain of PP-g-MA is higher than that between PP and POE chain of POE-g-MA. Therefore, the tensile strength of PP/MH composites modified with PP-g-MA is higher than that of PP/MH composites modified with POE-g-MA. But the impact strength of PP/MH composites modified with POE-g-MA is higher than that of PP/MH composites modified with PP-g-MA due to the toughening of POE. An optimum balance of tensile strength and impact strength are obtained for PP/MH composites modified by PP-g-MA and POE-g-MA.

4. Conclusions

In this paper, the morphology, thermal stability and mechanical properties of PP blends with compatibilizers and PP/MH composites modified with compatibilizers were investigated. Addition of high loading of MH particles improved the thermal stability of PP, especially in oxygen atmosphere but decreased the mechanical properties due to the poor adhesion between PP matrix and MH particles. The introduction of PP-g-MA or POE-g-MA to PP/MH

composites improves the interfacial interaction between MH particles and PP matrix, which resulted in considerable improvement in mechanical properties. The addition of PP-g-MA was most effective for increasing the tensile strength, while addition of POE-g-MA greatly increased the impact strength of PP/MH composites. An optimum balance of tensile strength and impact strength are obtained for PP/MH composites modified by PP-g-MA and POE-g-MA.

This study also gave us an understanding of the relationship between interface structure and mechanical properties in the ternary PP/compatibilizer/filler composites. As the filler particles were surrounded by the compatibilizers, the PP-filler interface changed to PP–compatibilizer interface and compatibilizer–filler interface. Due to the presence of chemical interaction, the compatibilizer–filler interface is always stronger than the former. So the mechanical properties of PP/compatibilizer/filler composites depend on the nature of PP–compatibilizer interface.

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