

Polypropylene–Intumescent Flame-Retardant Composites Based on Meleated Polypropylene as a Coupling Agent

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ABSTRACT: The phosphoric acid-pentaerythritol-melamine copolymer, which is composed of three main components of intumescent flame retardant (IFR) and has optimal intumescent degree, was selected as IFR. The influence of meleated polypropylene (PP-*g*-MAH) on the properties and compatibility of IFR polypropylene (PP) composites were studied. The results obtained from mechanical tests, rheological behavior of composites, and scanning electron microscope showed that PP-*g*-MAH was a true coupling agent for IFR/PP blends and did not change the necessary flame retardancy. The cocrystallization between bulk PP and PP segments of PP-*g*-MAH was also proven by WAXD analysis. Flow test showed that the flow behaviors of composites in the melt are those of a pseudoplastic and it is very small for PP-*g*-MAH affecting rheological behavior of the PP/IFR composite. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 257–262, 2002

Key words: coupling agent; intumescent flame-retardant; maleic anhydride; grafted polypropylene; polypropylene; rheological behavior

INTRODUCTION

In recent years, the use of intumescent flame retardant (IFR) as a filler in thermoplastic has attracted more and more attention in research laboratories. Generally speaking, the IFR consists of three main components: the acid source, the carbon source, and the gas source. The ammonium polyphosphate-pentaerythritol-melamine system had been used extensively in the past. The main problem of preparing of IFR/polypropylene (PP) composites is the incompatibility of hydrophilic IFR filler and hydrophobic PP matrix, which yields poor properties. For this reason, the improvement of IFR attracted more and more atten-

tion from many researchers.^{1–4} Ammonium polyphosphate was coated by melamine to show water repellency and self-extinguishing thermoplastic resin or aminoplast microencapsulated ammonium polyphosphate composition was used to improve the compatibility of IFR/PP. Unfortunately, it is impossible to solve the problems only by improving the compatibility of part of the composition of IFR with PP, because only if the three main components of IFR coexist, it has good flame-retardancy.

Some other studies showed that functionalized thermoplastics such as meleated polypropylene (PP-*g*-MAH) can be used to improve the compatibility of hydrophilic filler and hydrophobic thermoplastic matrix.⁵ According to the understanding of the principle of IFR, in this article, phosphoric acid-pentaerythritol-melamine copolymer was selected as IFR; PP-*g*-MAH was chosen as a coupling agent for IFR/PP composites, and the effect of PP-*g*-MAH on the properties and com-

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patibilization mechanism of IFR/PP composite was investigated.

EXPERIMENTAL

Materials

Polypropylene (T30S) was supplied from Tian-Jin Unite Chemical Co. (Tin Jin, China). Phosphorus pentoxide, pentaerythritol, melamine, xylene, maleic anhydride (MAH), acetone, and benzoyl peroxide (BPO) are all chemical reagent (China).

Preparation of IFR

IFR was prepared by the reaction of phosphorus pentoxide, pentaerythritol, and melamine as reported.⁶ The mixture of phosphorus pentoxide and pentaerythritol was stirred while the temperature was raised to and held at 130°C for about 2 h. Melamine was added in small portions with stirring as the temperature was raised to 200°C over a period of about 1 h. The temperature was held at 200–220°C for 2–3 h; during this time, with the crosslinking occurring in the product, the mixture became very viscous and difficult to stir. After the reaction was finished and the sample was adequately cooled, the IFR was removed from the flask and pulverized, after being screened through a 200-mesh sieve. The resulting product was kept to be used.

Next, 0.2–0.5 g IFR was weighted accurately and held at 500°C for 10 min in a muffle furnace. By measuring the variation of the volume before being heated and after, the intumescent degree (ID) could be calculated from the following equation:

$$ID = \frac{\text{Volume changes } \Delta V \text{ (cm}^3\text{)}}{\text{Sample mass } M \text{ (g)}}$$

Preparation and Grafting rate of PP-g-MAH^{7,8}

The fixed quantity of PP, xylene, and MAH were added in a flask and continued to be stirred under the conditions of nitrogen until the temperature reached to 120°C. When the solid substance was solved, the solution of BPO in acetone was added. The reaction was held at 120°C for 2 h under the protection of nitrogen; then, the product was precipitated by pouring it into acetone. After being filtered first, the precipitation was Soxhlet-extracted with acetone for 24 h to remove MAH that could not be grafted to PP. Finally, the ob-

tained sample was dried in a vacuum at 100°C for 72 h:

$$\text{Grafting rate} = \frac{\Delta m(\text{g})}{m(\text{g})} \times 100\%$$

where Δm is the mass changes, and m is the mass of PP.

Equipment and Analysis Procedures

After being coated with gold, the morphology of the tensile fracture surfaces of the sample was observed with a Ammry 1000B scanning electron microscope (SEM). The tensile strengths were measured following the GB 1843 standard by an LJ-3000N test apparatus and the impact strengths were measured following the GB 1040 standard by a XCJ 40 impact test apparatus. The ease of ignition of the PP was studied according to GB 2408-80 horizontal standard by using samples with dimensions of 127 × 12.7 × 3.5 mm³. With the Bunsen burner ignited for 30 s, the flame spread rate and extinguish time (ET) were recorded. Melt flow properties of samples were measured on a Shimadzu Koka rheometer. The IR spectra were recorded by a FTS-40 IR analyzer.

Preparation of Samples

The blending of materials was done at 170–180°C in a two-roll mill. IFR was added after PP had melted, and the mixing was carried out for 10 min. After being mixed, the blends were removed for compression molding at 170°C for 10 min. Finally, the composites were cooled to room temperature by cool pressing.

RESULTS AND DISCUSSION

The Choice of IFR

One property of the IFR is intumescent. Only if it is intumescent, can it be used as IFR. Therefore, the intumescent property of IFR, which was composed of different compositions, was studied first (Fig. 1). When the content of phosphorus, an acid source, and pentaerythritol, a carbon source, did not change, with melamine content being increased, the ID increased first. Then it kept constant at a higher ID in some scope, and finally, decreased rapidly. So, it is impossible to obtain a stable increase of ID only by increasing phosphorus content. Experiments show that only if the

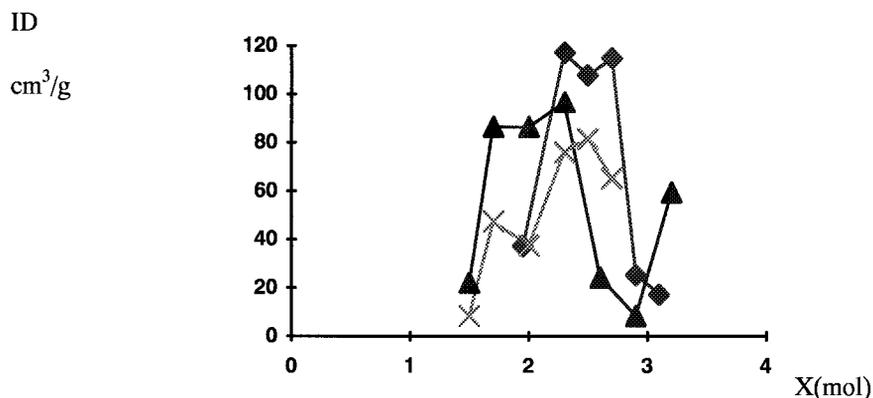


Figure 1 The ID of IFR versus melamine content. (◆) P_2O_5 : pentaerythritol : melamine = 1.5 : 1 : X; (▲) P_2O_5 : pentaerythritol : melamine = 1.0 : 1 : X; (×) P_2O_5 : pentaerythritol : melamine = 2.0 : 1 : X.

three main components of IFR coexist at an appropriate proportion will it have optimal ID. The appropriate proportions are P_2O_5 : pentaerythritol : melamine = 1 : 1 : 1.7–2.3, 1.5 : 1 : 2.3–2.7, and 2 : 1 : 2.3–2.7 (mol). Here, the one composed of 1.5 : 1 : 2.7 was selected as IFR-ID: 500°C, 110 cm^3/g .

Characterization of PP-g-MAH

In the IR spectra of PP-g-MAH [Fig.2(b)], the band at 1730 cm^{-1} of C=O implied the grafting

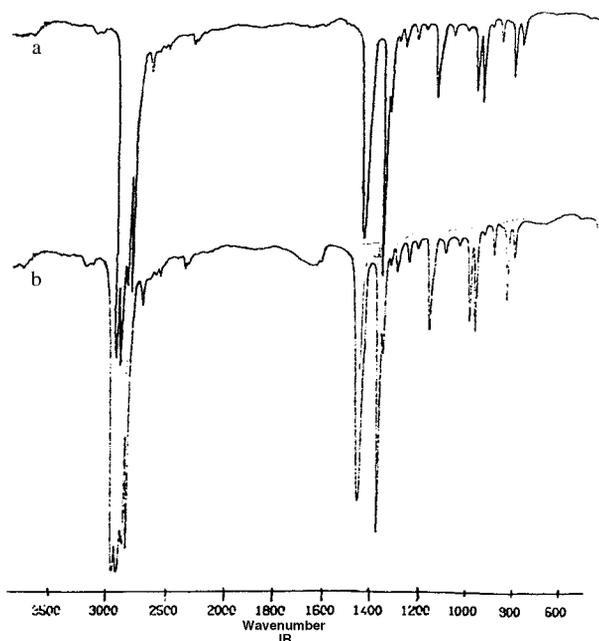


Figure 2 IR spectra of PP and PP-g-MAH. (a) PP; (b) PP-g-MAH.

reaction of PP with MAH. In addition, the character peak of PP did not change before and after being grafted. Some absorption peaks, such as 1368 cm^{-1} of CH_3 side group, and 947 and 975 cm^{-1} concerning the crystallization, were still retained. By being calculated, the grafting degree is about 1.5%. As can be seen from Figure 3, the apparent viscosity (η_a) of PP-g-MAH decreased, because some C—C bonds can break by the grafting reaction, the molecular weight of PP decreased.

Effect of PP-g-MAH on Properties of the Composites

Because of the poor compatibility of PP and IFR, it is nearly impossible to prepare the IFR/PP

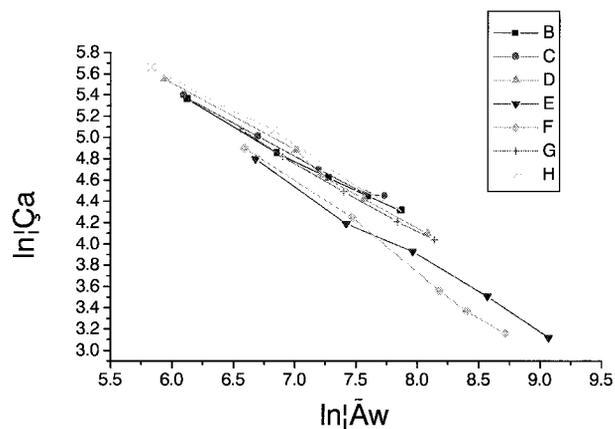


Figure 3 The rheological behavior of PP/IFR/PP-g-MAH composites (180°C). (B) 99/45/6; (C) 96/45/9; (D) 93/45/12; (E) 90/45/15; (F) 0/0/100; (G) 100/0/0; (H) 105/45/0.

Table I Effect of PP-*g*-MAH Content on Properties

Composites	Sample (PP/IFR/PP- <i>g</i> -MAH)	Horizontal Combustion Test Rate	ET (s)	Tensile Strength (MPa)	Impact Strength (KJ m ⁻²)
PP	100/0/0	Burn and dripping	—	36	3.69
A	105/45/0	II and no dripping	12	22.5	3.03
B	99/45/6	II and no dripping	5	24.71	3.33
C	96/45/9	II and no dripping	3	27.51	3.30
D	93/45/12	I and no dripping	1	26.45	3.01
E	90/45/15	I and no dripping	0	25.89	3.23

blends with good mechanical properties. As seen in Table I, composite A, by adding 45 g IFR in 105 g, PP could provide good flame-retardancy, but the mechanical properties, especially tensile strength, decreased drastically. To improve the compatibility, part PP of the composites was substituted by PP-*g*-MAH. As seen in Table I, composite B produced a significant improvement of the mechanical properties, and the tensile strength increased to a great extent, Composite C especially, had the maximum value of tensile strength. Meanwhile, the flame retardancy and the impact strength values of the blend composite almost remained unchanged. The tensile strength of the composites D and E are lower than that of C, because the graft reaction decreases the molecular weight of PP. In a word, the mechanical properties of PP/IFR composites can be significantly improved by PP-*g*-MAH.

Effect of PP-*g*-MAH on Rheological Behavior of Composites

A kaka flow tester was used to investigate the rheological behavior of composites. The experimental temperature was fixed at 180°C with experimental loads of 80, 70, 60, 50, and 40 kg/cm². A plot of apparent viscosity $\ln \eta_a$ versus apparent shear rate $\ln \dot{\gamma}_w$ is given in Figure 3.

Figure 3 shows the influence of the addition of IFR and PP-*g*-MAH on the flow properties of PP melt. Because of the grafting reaction decrease of the molecular weight of PP, the apparent viscosity of PP-*g*-MAH (η_a) decreased obviously (line F). The addition of IFR results in an increase of the η_a of composites (line H). The four lines (lines B, C, D, and H) overlap, which is very small for PP substituted by PP-*g*-MAH (≤ 12 part), and affect the rheological behavior of the PP/IFR composite, although the viscosity of PP-*g*-MAH was lower than that of PP. This phenomenon implies that

PP-*g*-MAH might have improved the interfacial adhesion of PP and IFR. When PP-*g*-MAH was 15 part (line E), the viscosity of the whole system decreased, which indicates that only part of the PP-*g*-MAH played a role in improving the adhesion of PP and IFR.

In addition, the results of Figure 3 showed that the apparent viscosity of melt ($\ln \eta_a$) decreased as the shear rate ($\ln \dot{\gamma}_w$) increased and showed linearity. This phenomenon implied that the PP/IFR/EPP melt is a pseudoplastic liquid. Therefore, the PP/IFR composite has fine processibility.

SEM Analysis

The tensile fracture surface of the composite sample, which contained IFR, was studied by SEM. The results are shown in Figure 4. As seen from Figure 4 (a), composite A showed poor wetting of IFR by the PP matrix, and the fracture occurred in the interface of IFR and PP, because of the insufficient adhesion between IFR and PP. Figure 4 (b), composite B, showed partial wetting of IFR by the PP matrix; Figure 4 (c, d), composite D and E, showed that the fracture occurred in the matrix material. The IFR were covered by layer of PP matrix.

The facts mentioned above illustrate that the presence of PP-*g*-MAH not only enhanced the adhesion of IFR and PP but also improved the compatibility of the two phases; so it led to better mechanical properties.

Compatibilization Mechanism of PP-*g*-MAH

As we all know, a coupling agent affects compatibilization by interacting with both the filler and the matrix, thus forming a link between the components. It is shown that PP-*g*-MAH had an excellent compatibilizing effect on IFR/PP composites. As to the essence of the compatibilization of

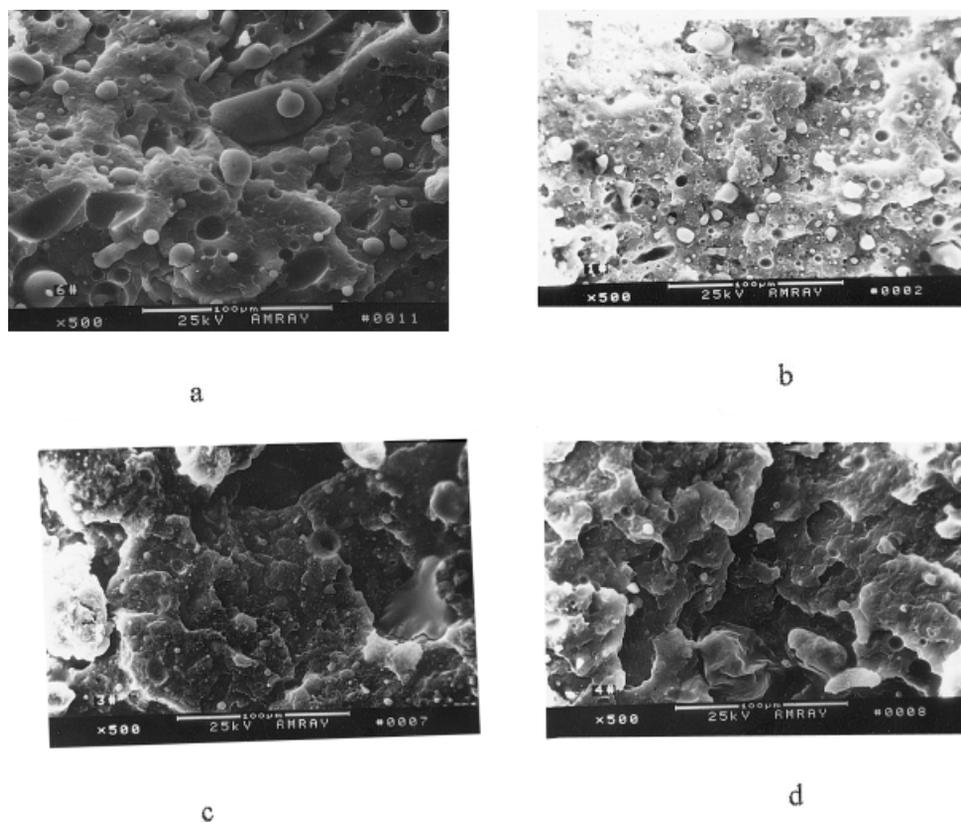


Figure 4 SEM micrograph of fracture surface of IFR/PP composites. (a) Composite A; (b) composite B; (c) composite D; (d) composite E.

this type, we think that the PP segments of PP-*g*-MAH formed miscible blends with the bulk PP through cocrystallization. On the other hand, considering of the abundant —NH_2 groups on the

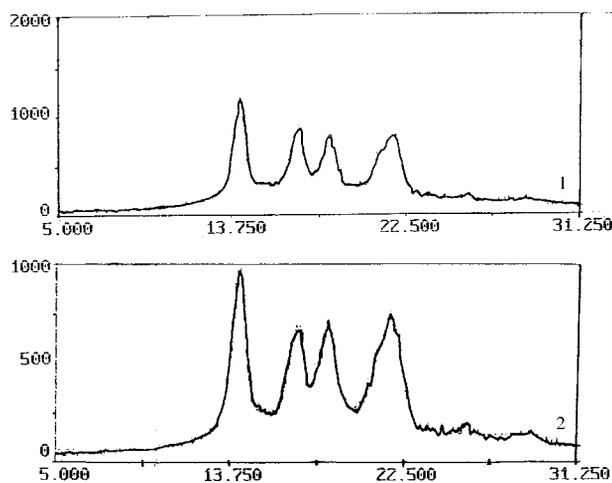


Figure 5 The crystallinity of PP and PP-*g*-MAH. (1) PP; (2) PP-*g*-MAH.

surfaces of IFR (melamine in excess) and the polar part of PP-*g*-MAH (MAH), it is reasonable for us to propose that PP-*g*-MAH can react with IFR through an amino link, which cannot be studied with infrared spectroscopy or other characterization methods. Because the situation of IFR is complicated and the MAH amount of PP-*g*-MAH is minor, it is a difficult problem to be solved. The following is our study of the compatibilization mechanism of PP-*g*-MAH.

The Interaction Between PP-*g*-MAH and PP

Cocrystallization is the driving force of compatibilization between crystalline/crystalline components of the same kind. The crystal structures of PP and PP-*g*-MAH were measured with a wide-angle X-ray diffractometer. The results demonstrated that all the crystallinity of PP and PP-*g*-MAH existed in α -crystal form and had the same lattice parameters (Table II and Fig. 5). After being grafted, PP-*g*-MAH crystallinity increased, because the —COOH group plays a core in the crystallization.

Table III Crystal Parameter of PP and PP-*g*-MAH

Sample	hkl	2θ (°)	d_{hkl} (nm)	X_c (%)
PP	110	14.12	0.627	52
	040	17.02	0.521	
	130	18.53	0.479	
	111	21.15	0.420	
	131	21.83	0.407	
PP- <i>g</i> -MAH	110	14.22	0.623	57
	040	17.14	0.517	
	130	18.686	0.474	
	111	21.22	0.419	
	131	21.79	0.408	

CONCLUSIONS

- (1) Adding 45 g of IFR that has optimal ID, composed of P_2O_5 : pentaerythritol : melamine = 1.5 : 1 : 2.7 in 105 g PP, could prepare good flame-retardancy composition.
- (2) PP-*g*-MAH is a true coupling agent for polypropylene-intumescent flame retardant composites. It can improve the compatibility of polypropylene and intumescent flame retardant and increase the

mechanical properties of the composites, and it does not change the necessary flame retardancy.

- (3) The compatibilization mechanism in the PP segments of PP-*g*-MAH cocrystallize with the bulk PP.
- (4) The flow behaviors of composites in the melt are those of a pseudoplastic.

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