

Compatibilization of Intumescent Flame Retardant/Polypropylene Composites Based on α -Methacrylic Acid Grafted Polypropylene

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ABSTRACT: A phosphoric acid–pentaerythritol–melamine copolymer was selected as an intumescent flame retardant (IFR). The influence of α -methacrylic acid grafted polypropylene (PP-*g*-MAA) on the properties and compatibility of IFR/PP composites was studied. The results obtained from mechanical tests and scanning electron microscopy showed that PP-*g*-MAA was a true coupling agent for IFR/PP blends, but it did not change the necessary flame retardancy. The cocrystallization between bulk PP and PP segments of PP-*g*-MAA was proved by wide-angle X-ray diffraction analysis. A flow test showed that the flow behaviors of composites in the melt were those of a pseudoplastic liquid and it was very small for PP-*g*-MAA and affected the rheological behavior of the PP/IFR composite. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 3128–3132, 2002; DOI 10.1002/app.10099

Key words: coupling agent; intumescent flame retardant; α -methacrylic acid; grafting; polypropylene

INTRODUCTION

The studies of a blend of intumescent flame retardant and polypropylene (IFR/PP) have attracted chemists, because intumescent materials have the advantages of low smoke, low toxicity, low corrosion, long life, no molten dropping, and being halogen free. The main problem of the preparation of IFR/PP is the incompatibility of the IFR filler and PP matrix, which yields a composition with poor properties. For this reason, the improvement of IFRs has attracted more and more attention from many researchers.^{1–4} Generally speaking, the IFR consists of three main components: an acid source, a carbon source, and a gas source. The ammonium polyphosphate–pentaerythritol–melamine system has been used exten-

sively for a long time. Ammonium polyphosphate is coated by melamine to show water repellency and microencapsulated by a self-extinguishing thermoplastic resin or aminoplast in order 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 the three main components of IFR coexist, it has good flame retardancy.

Some other studies showed that functionalized thermoplastics can be used to improve the compatibility of a hydrophilic filler and a hydrophobic thermoplastic matrix.⁵ According to the understanding of the principle of IFR, we selected phosphoric acid–pentaerythritol–melamine copolymer as the IFR, α -methacrylic acid grafted PP (PP-*g*-MAA) was chosen as a coupling agent for the IFR/PP composites, and the effect of PP-*g*-MAA on the properties and compatibilization mechanism of the IFR/PP composites were investigated.

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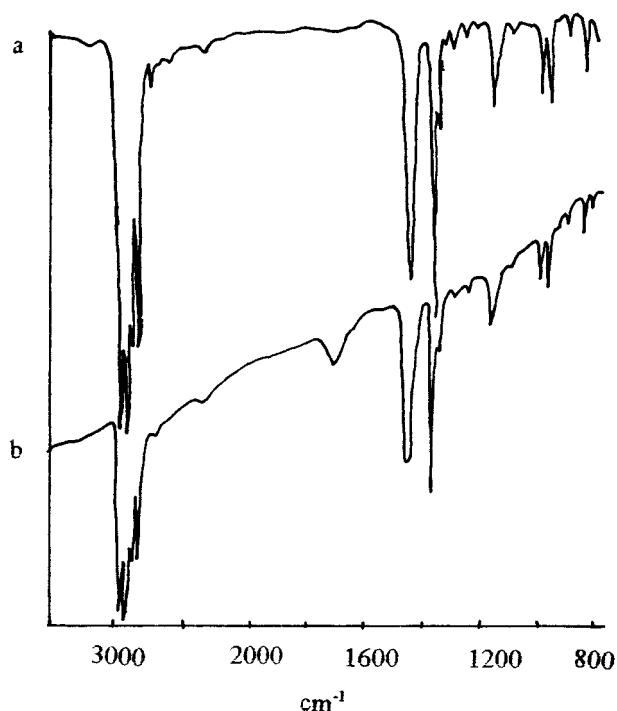


Figure 1 IR spectra of PP (spectrum a) and PP-g-MAA (spectrum b).

EXPERIMENTAL

Materials

The PP (T30S) was supplied by Tian-Jin Unite Chemical Co., and the MAA was a chemical reagent. The IFR was prepared by the reaction of 1.5 mol phosphorus pentoxide, 1 mol pentaerythritol, and 2.7 mol melamine as reported.⁶ The intumescent degree (ID) at 500°C was 110 cm³/g.

Preparation and Grafting Rate of PP-g-MAA^{7,8}

A fixed quantity of PP, xylene, and MAA were added to a flask and stirred under nitrogen until the temperature reached 120°C. When the solid

substance was dissolved, a solution of benzoyl peroxide 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. The precipitate was filtered first and then extracted with acetone by Soxhlet for 24 h to remove the polymer of MAA that could not be grafted to the PP. Finally the sample obtained was dried in a vacuum at 100°C for 72 h.

$$\text{grafting degree} = \frac{\Delta m(g)}{m(g)} \times 100\%$$

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

Equipment and Analysis Procedures

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

Preparation of Samples

The blending of the materials was done at 170–180°C in a two-roll mill. The IFR was added after the PP melted, and the mixing was carried out for

Table I Effect of PP-g-MAA Content on Properties

Composites	PP/IFR/PP-g-MAA	Horizontal Rate	Combustion Test Extinguish Time (s)	Tensile Strength (MPa)	Impact Strength (kJ m ⁻²)
PP	100/0/0		Burn	36	3.69
A	105/45/0	II	12	22.5	3.03
B	100/45/5	II	12	24.66	2.85
C	95/45/10	II	12	26.60	2.82
D	90/45/15	II	12	25.1	3.01

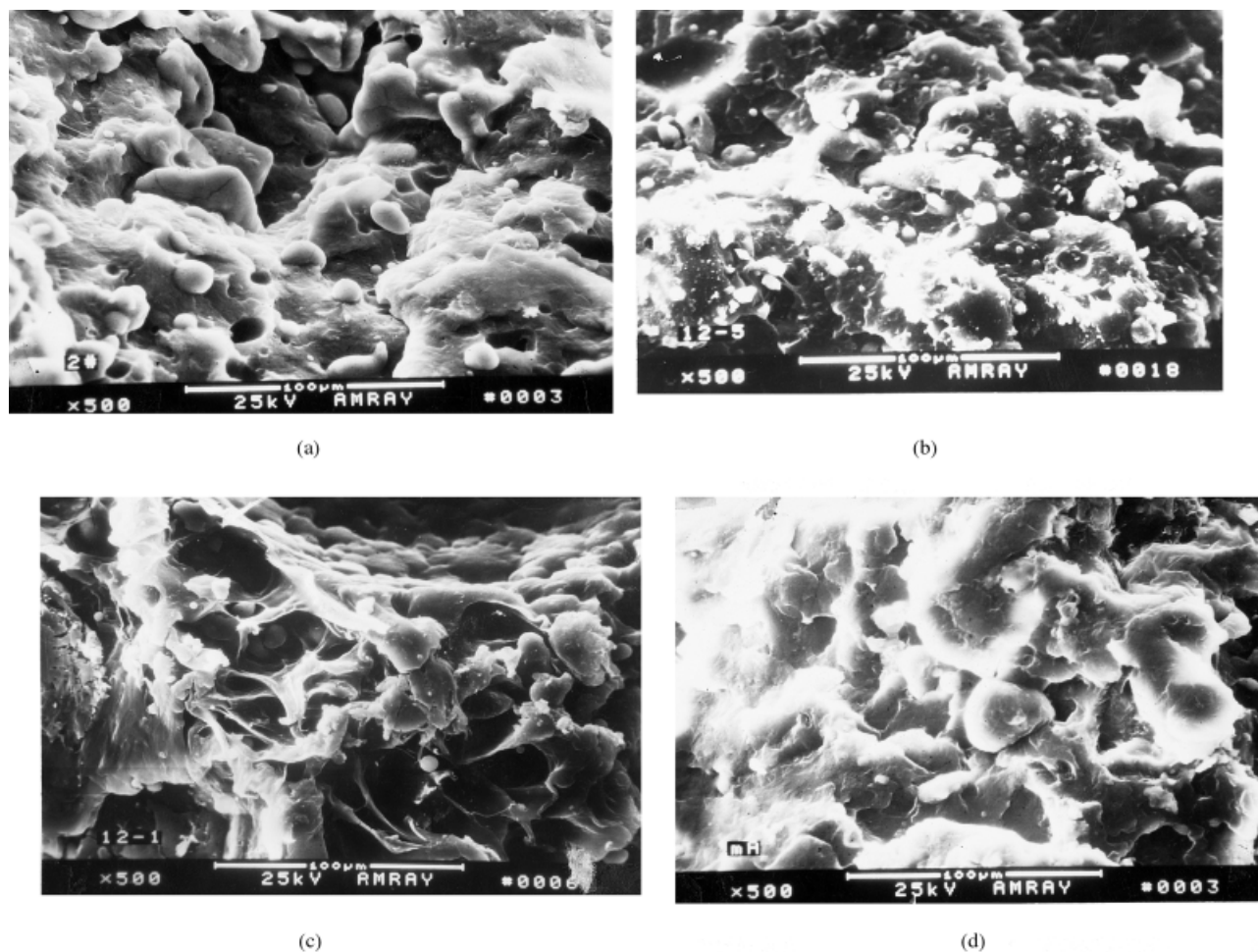


Figure 2 A SEM micrograph of the fracture surface of the IFR/PP composite: (a) composite A, (b) composite B, (c) composite C, and (d) composite D.

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

Characterization of PP-*g*-MAA

In the IR spectra of PP-*g*-MAA (Fig. 1, spectrum) the band at 1730 cm^{-1} of C=O implied the grafting reaction of PP with MAA. In addition, the characteristic peak of PP did not change before and after being grafted. Some absorption peaks, such as 1368 cm^{-1} of the CH_3 side group and 947 and 975 cm^{-1} concerning the crystallization,⁸ were still retained. The grafting degree was calculated as 2.5%.

Effect of PP-*g*-MAA on Properties of Composites

Because of the poor compatibility of PP and IFR, it is nearly impossible to prepare the IFR/PP blends with good mechanical properties. As seen in Table I, composite A with 45 g of IFR in 105 g PP could provide good flame retardancy, but the mechanical properties, especially the tensile strength, decreased drastically. In order to improve the compatibility, part of the PP of the composites was substituted by PP-*g*-MAA. 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 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 composite D is lower than that of C,

because the graft reaction decreases the molecular weight of the PP.

In short, the mechanical properties of PP/IFR composites can be significantly improved by PP-g-MAA.

SEM Analysis

The tensile fracture surface of the composite sample, which contained IFR, was studied by SEM, and the results are shown in Figure 2. As seen from Figure 2(a), composite A shows poor wetting of the IFR by the PP matrix and the fracture occurs in the interface of the IFR and PP because of insufficient adhesion between the IFR and PP. In Figure 2(b) composite B shows partial wetting of the IFR by the PP matrix; in Figure 2(c,d) composites C and D show the fracture occurs in the matrix material, and the IFR is covered by a layer of the PP matrix.

The facts mentioned above illustrated that the presence of PP-g-MAA not only enhanced the adhesion of IFR and PP but also improved the compatibility of the two phases. Thus, it could lead to better mechanical properties.

Compatibilization Mechanism of PP-g-MAA

As is well known, a coupling agent affects the compatibilization by interacting with both the filler and the matrix, thus forming a link between the components. It is shown that PP-g-MAA had an excellent compatibilizing effect on IFR/PP composites; as to the essence of the compatibilization of this type, we think that the PP segments of PP-g-MAA formed miscible blends with the bulk PP through cocrystallization. On the other

Table II Crystal Parameters of PP and PP-g-MAA

Sample	<i>hkl</i>	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-g-MAA	110	14.06	0.630	60
	040	16.93	0.524	
	130	18.48	0.480	
	111	21.27	0.418	
	131	21.73	0.409	

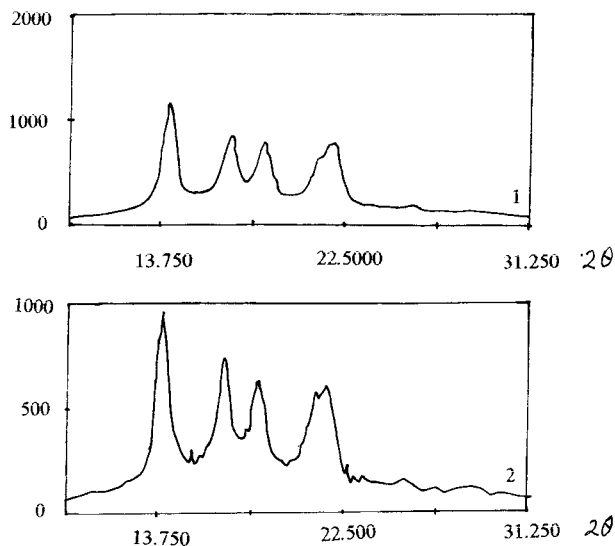


Figure 3 The crystallinity of PP (spectrum 1) and PP-g-MAA (spectrum 2).

hand, considering the abundant NH_2 groups on the surfaces of IFR (melamine in excess) and the polar part of PP-g-MAA (MAA), it is reasonable for us to propose that PP-g-MAA can react with IFR through an amino link, which cannot be studied with IR spectroscopy or any other characterization method. Because the IFR situation is complicated and the amount of MAA in the PP-g-MAA is minor, it is a difficult problem to solve. The following is our study of the compatibilization mechanism of PP-g-MAA.

Interaction between PP-g-MAA 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-MAA were measured with a wide-angle X-ray diffractometer. The results demonstrated that all the crystalline parts of PP and PP-g-MAA existed in an α -crystal form and had the same lattice parameters (Table II, Fig. 3). After being grafted, the PP-g-MAA crystallinity is increased, because the $-\text{COOH}$ group plays a core part in the crystallization.

Effect of PP-g-MAA on Rheological Behavior of Composites

A koka flow tester was used to investigate the rheological behavior of the composites. The experimental temperature was fixed at 180°C with experimental loads of 80, 70, 60, 50, and 40 kg/cm^2 .

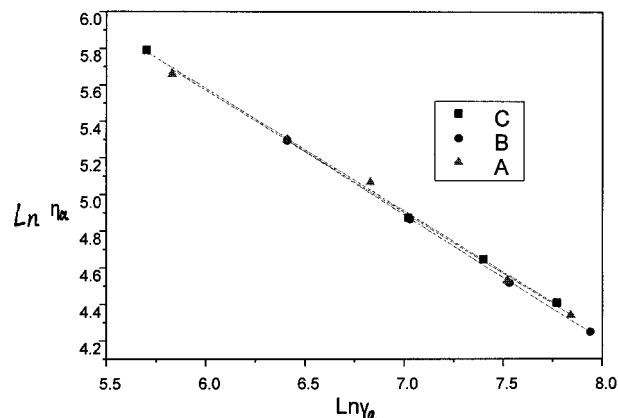


Figure 4 The rheological behavior of PP/IFR/PP-*g*-MAA composites (180°C): (▲) 105/45/0 PP/IFR/PP-*g*-MAA, (●) 100/45/5 PP/IFR/PP-*g*-MAA, and (■) 95/45/10 PP/IFR/PP-*g*-MAA.

A plot of the apparent viscosity ($\ln \eta_a$) versus the apparent shear rate ($\ln \gamma_a$) is given in Figure 4.

As seen in Figure 4, the η_a decreased with an increasing γ_a . It was shown that the flow behaviors of composites in the melt are those of a pseudoplastic liquid and showed linearity. Thus, the PP/IFR composite has fine processability. The overlap of three line shows it is very small for PP-*g*-MAA, affecting the rheological behavior of the PP/IFR composite.

CONCLUSION

PP-*g*-MAA is a true coupling agent for PP/IFR composites. It can improve the compatibility of PP and the IFR and hence increase the mechanical properties of the composites, but not change the necessary flame retardancy. It is very small and affects the rheological behavior of PP/IFR composite also. The PP/IFR/PP-*g*-MAA composites have fine processability.

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