Studies on Compatibilization of Intumescent Flame-Retardant/PP Composites Based on Etched PP

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ABSTRACT: The phosphoric acid–pentaerythritol–melamine copolymer was selected as an intumescent flame retardant (IFR). The influence of dicromate acid–etching polypropylene (EPP) on the properties and compatibility of IFR/PP composites was studied. The results obtained from mechanical tests and SEM showed that EPP was a true coupling agent for IFR/PP blends, but without changing the necessary flame retardancy. The cocrystallization between bulk PP and PP segments of EPP was proved by WAXD analysis. Flow tests showed that the flow behavior of composites in the melt is that of a pseudoplastic liquid, which is almost insignificant for EPP affecting the rheological behavior of an IFR/PP composite. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 84: 522–527, 2002; DOI 10.1002/app.10261

Key words: coupling agent; intumescent flame retardant; polypropylene; dicromate acid–etched polypropylene

INTRODUCTION

In recent years the use of an intumescent flame retardant (IFR) as filler in thermoplastic is attracting more and more attention in research laboratories. Generally speaking, the IFR consists of three main components: the acid source, carbon source, and gas source. The ammonium polyphosphate–pentaerythritol–melamine system has been used extensively for some time. The main problem in the preparation of IFR/polypropylene (PP) composites is the incompatibility of the hydrophilic IFR filler and the hydrophobic PP matrix, which made for composites of poor properties. For this reason, improvement of IFR attracted the increasing attention of many researchers.[1–4] Ammonium polyphosphate was coated by melamine, to show water repellency, and was microencapsulated by self-extinguishing thermoplastic resin or aminoplast to improve the compatibility of IFR/PP. Unfortunately, it is impossible to solve these problems just by improving the compatibility considerations of composition of IFR with PP; because the three main components of IFR coexist, it must have good flame retardancy.

Previous studies showed that functionalized thermoplastics such as maleated polypropylene and methacrylic acid–grafted polypropylene can be used to improve the compatibility of hydrophilic filler and hydrophobic thermoplastic matrix.[6,7] However, its high cost limited widespread use. In this study a phosphoric acid–pentaerythritol–melamine copolymer was selected as IFR. EPP was chosen as a coupling agent for IFR/PP composites, and the effect of EPP on both the properties and the compatibilization mechanism of IFR/PP composite was investigated.

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EXPERIMENTAL

Materials

Polypropylene (T30S) was supplied by Tian-Jin United Chemical Co. (China). IFR [intumescent degree (ID) at 500°C is 110 cm^3/g, 200 mesh] was prepared by the reaction of 1.5 mol phosphorus pentoxide, 1 mol pentaerythritol, and 2.7 mol melamine, as previously reported.[5] Potassium dichromate and sulfuric acid were the chemical reagents, used as received.

Preparation of EPP

A fixed quantity of PP powder (diameter 0.62 mm), water solutions of 0.1 mol/L potassium dichromate, and 0.1 mol/L sulfuric acid were added in a flask under constant stirring at 60°C until the PP powder was immersed by water; the product was then filtered and dried at 100°C.

Equipment and Analysis Procedures

The morphology of the tensile fracture surfaces of the sample was observed with an Ammry 1000B scanning electron microscope (SEM), after being coated with gold. 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 an XCJ 40 impact test apparatus. The ease of ignition of the PP was studied according to GB 2408-80 horizontal standard using samples with dimensions 127 × 12.7 × 3.5 mm^3, with the Bunsen burner being ignited for 30 s; the combustion time, flame spread rate, and extinguish time were recorded. The IR spectra were recorded by an FTS-40 IR analyzer. The crystal structures of PP and EPP were measured with a Y-4Q X-ray diffractometer. Melt flow properties of the samples were measured on a Shimadzu KOKA rheometer (Shimadzu, Japan).

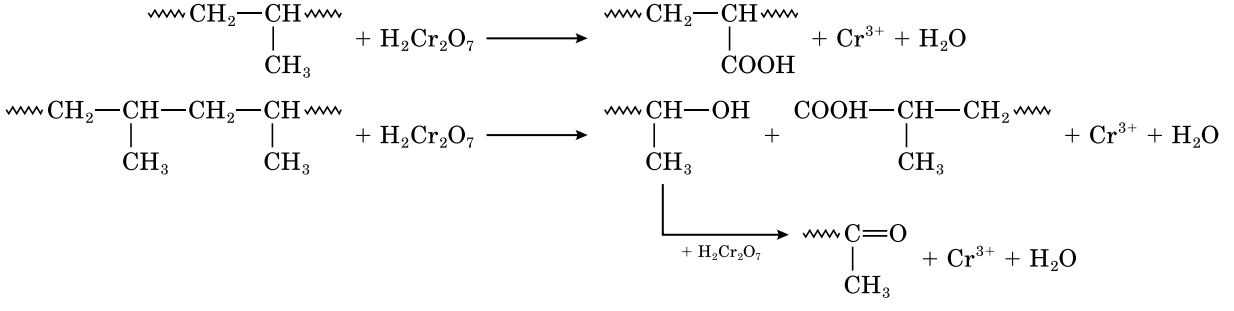
Preparation of Samples

The blending of materials was done at 170–180°C in a two-roll mill; IFR was added after the 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

Characterization of EPP

In the IR spectra of EPP [Fig. 1(b)], the band at 1730 cm^{-1} of the C═O implied the oxidizing reaction of PP with dichromate acid. However, the reaction does not take place only at the $-CH_3$ branch; some C—C bonds can also break, as can be seen from Figure 2. The EPP's apparent viscosity (η_a) decreased because the etching reaction decreased the molecular weight. The reaction is represented as follows:



Furthermore, the characteristic peak of PP did not change either before or after being etched. Some absorption peaks, such as 1368 cm^{-1} of the CH_3 side group and 947 and 975 cm^{-1} related to the crystallization, were still retained.

Effect of EPP on Properties of the 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 for composite sample B in Table I, the addition of 45 g of IFR in 105 g PP could provide good flame retardancy, intumescence, and no dripping, although the mechanical properties, especially tensile strength, decreased drastically. To improve the compatibility, part PP of the composites was substituted by EPP. As seen in Table I, composites C, D, E, F, and G produced a significant

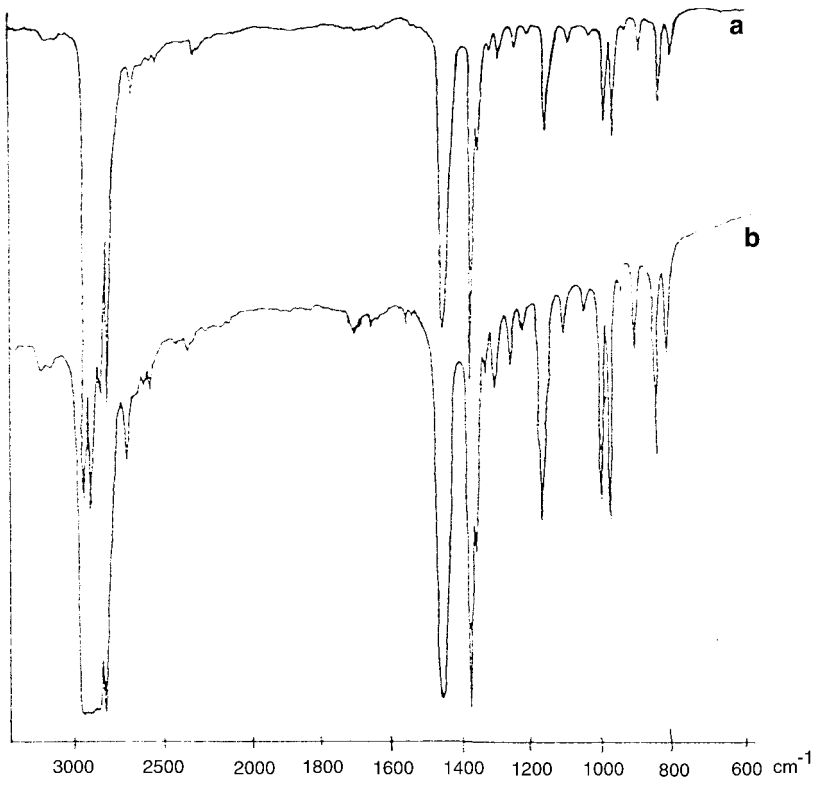


Figure 1 IR spectra of PP (a) and EPP (b).

improvement of the mechanical properties; the tensile strength increased significantly, particularly for composite F, which had the maximum tensile strength value. The loss of impact strength of the blends was negligible. Meanwhile, their flame retardancy also increased. Tensile strength values of composites G and H are lower than that of composite F because the etching reaction decreased the molecular weight of PP. In a word, the mechanical properties of PP/IFR composites can be significantly improved by EPP.

Effect of EPP on Rheological Behavior of Composites

A Koka (Shimadzu) 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/cm^2. A plot of apparent viscosity ln η_a versus apparent shear rate ln γ_w is given in Figure 2.

Figure 2 shows the influence of the addition of IFR and EPP on the flow properties of PP melt. Because the etching reaction decreased the molecular weight of PP, the EPP's apparent viscosity (η_a) obviously decreased. The addition of IFR results in an increase of the η_a of composites. It is worth noting that the five overlapping lines show that only a very small amount of PP substituted

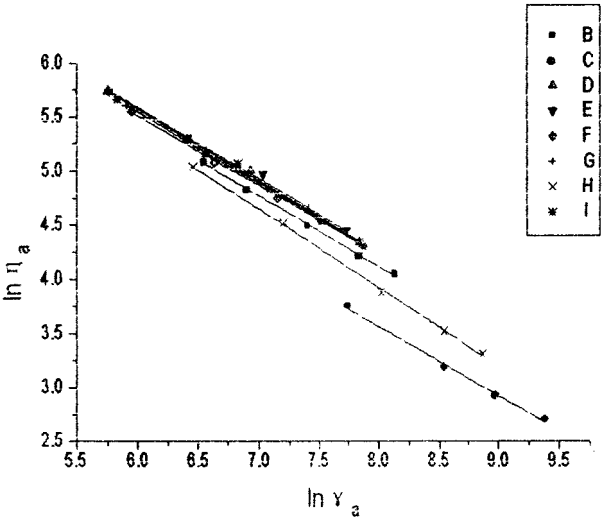


Figure 2 The rheological behavior of PP/IFR/EPP composites (180°C): B, 100/0/0; C, 0/0/100; D, 99/45/6; E, 96/45/9; F, 93/45/12; G, 90/45/15; H, 87/45/18; I, 105/45/0.

Table I Effect of EPP Content on Properties

Composite Sample	PP/IFR/EPP	Horizontal Combustion Test		Tensile Strength (MPa)	Impact Strength (kJ m^{-2})
		Extinguish Rate	Time (s)		
A	100/0/0	Burn and dripping	—	36	3.69
B	105/45/0	II and no dripping	12	22.5	3.03
C	102/45/3	II and no dripping	12	23.10	2.71
D	99/45/6	II and no dripping	10	24.06	2.62
E	96/45/9	II and no dripping	4	24.89	3.28
F	93/45/12	I and no dripping	2	26.40	2.57
G	90/45/15	I and no dripping	3	25.85	2.62
H	87/45/18	I and no dripping	0	22.91	2.58

by EPP (≤15%) can affect the rheological behavior of PP/IFR composite, although the viscosity of EPP was lower than that of PP. This phenomenon implies that EPP might have improved the interfacial adhesion of PP and IFR. When EPP was 18%, the viscosity of the whole system decreased, which indicates that only part of EPP played the role of improving the adhesion of PP and IFR.

In addition, the results of Figure 2 show that the apparent viscosity of the melt (ln η_a) decreases as the shear rate (ln γ_w) increases, demonstrating linearity. This phenomenon implied that the PP/IFR/EPP melt is a pseudoplastic liquid, such that the IFR/PP composite has fine processibility.

SEM Analysis

The tensile fracture surfaces of composite samples containing IFR were studied by SEM, the results of which are shown in Figure 3. As seen in Figure 3(a), the SEM tensile fracture surface of

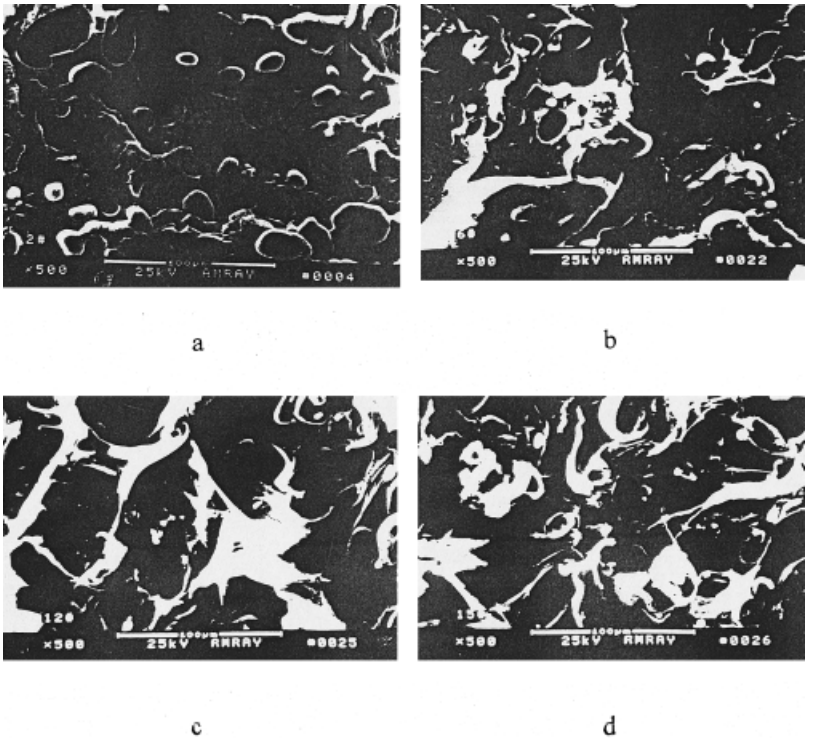


Figure 3 SEM micrograph of fracture surface of IFR/PP composite: (a) composite B; (b) composite D; (c) composite F; (d) composite G.

Table II Crystal Parameter of PP and EPP

Sample	2θ (°)	d_{hkl} (nm)	X_c (%)
PP	14.12	0.627	
	17.02	0.521	52
	18.53	0.479	
	21.15	0.420	
	21.83	0.407	
EPP	13.76	0.644	
	16.59	0.534	53
	18.020	0.492	
	20.747	0.428	
	21.067	0.422	
	21.617	0.411	

composite B 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. The SEM tensile fracture surface of composite D in Figure 3(b) shows partial wetting of IFR by the PP matrix. The SEM tensile fracture surfaces of composites F and G in Figures 3(c) and 3(d), respectively, show that the fracture occurred in the matrix material and the IFR was covered by a layer of PP matrix.

The preceding observations illustrate that the presence of EPP not only enhanced the adhesion of IFR and PP but also improved the compatibility of the two phases, thus leading to better mechanical properties.

Compatibilization Mechanism of EPP

It is well known that a coupling agent affects compatibilization by interacting with both the filler and the matrix, thus forming a link between the components. It is shown here that EPP had an excellent compatibilization effect on IFR/PP composites. Concerning the essence of the compatibilization of this type, on one hand, it is thought that the PP segments of EPP formed miscible blends with the bulk PP through cocrystallization; on the other hand, one could consider the abundant $-NH_2$ groups on the surfaces of IFR (melamine in excess) and the polar part (–COOH) of EPP. It is reasonable to propose that EPP can react with IFR through an amino link, which cannot be studied with infrared spectroscopy or other characterization methods. Given the complex characteristics of IFR and the insignificant amount of the polar part of EPP, it is a difficult problem to be solved. Results of the compatibilization mechanism of EPP are discussed next.

Interaction Between EPP and PP

Cocrystallization is the driving force of compatibilization between crystalline/crystalline compo-

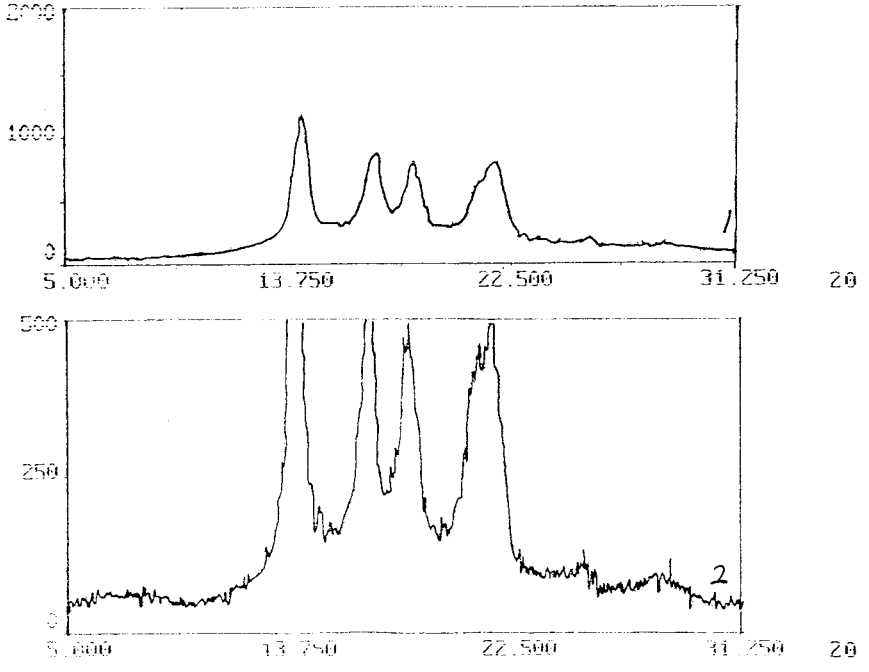


Figure 4 The crystallinity of PP (1) and EPP (2).

nents of the same kind. The crystal structures of PP and EPP were measured with a wide-angle X-ray diffractometer. The results showed that all the crystalline PP and EPP existed in a crystal form, characterized by nearly the same crystal parameters (see Table II and Fig. 4).

CONCLUSIONS

EPP is a true coupling agent for intumescent flame-retardant/polypropylene composites and can improve the compatibility of polypropylene and intumescent flame retardant, thus increasing the mechanical properties of the composites without adversely changing the necessary flame retardancy. It also has only a slight effect on rheological behavior of the IFR/PP composite; the PP/IFR/EPP composites have fine processibility.

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REFERENCES

1. Iwama, M.; Yoda, Y.; Takenaga, M. Jpn. Kokai Tokyo Koho JP 08 67,769.
2. Ookawa, K.; Suzuki, H.; Yoda, Y.; Iwama, M. Jpn. Kokai Tokyo Koho JP 08 67,768.
3. Cipolli, R.; Oriani, R.; Masarati, E.; Nucida, G. Eur. Pat. Appl. EP 544,352.
4. Liao, K.; Lu, Z.; Ni, Y. Polym Mater Sci Eng 1999, 15, 100.
5. Bost, H. W. U.S. Pat. 4,072,643, 1978.
6. Ma, Z.-L.; Zhao, M.; Hu, H.-F.; Ding, H.-T.; Zhang, J. J Appl Polym Sci, to appear.
7. Ma, Z.-L.; Liu, Y.-F.; Hu, H.-F.; Niu, H.-J.; Ding, H.-T.; Zhang, J. J Appl Polym Sci, to appear.