

Studies of Polypropylene–Intumescent Flame-Retardant Composites Based on Etched Polypropylene as a Coupling Agent

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ABSTRACT: The ammonium polyphosphate (APP)–pentaerythritol (PT)–melamine (M) system was selected as an intumescent flame retardant (IFR). The influence of dichromic acid–etched polypropylene (EPP) on the properties and compatibility of IFR/polypropylene (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 seg-

ments of EPP was confirmed by WAXD analysis. Flow tests showed that the flow behavior of composites in the melt is that of a pseudoplastic liquid, which is significant for EPP's effect on the rheological behavior of IFR/PP composite. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1388–1391, 2004

Key words: coupling agent; intumescent; flame-retardant; polypropylene; etched polypropylene

INTRODUCTION

Generally speaking, an intumescent flame retardant (IFR) consists of three main components: the acid source, carbon source, and gas source. The ammonium polyphosphate–pentaerythritol–melamine (APP–PT–M) system has been extensively used 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 induces poor properties in composites. For this reason, improvement of IFRs has been the focus of increasing attention of many researchers.^{1–4} APP was coated by M to confer water repellency, and was microencapsulated by self-extinguishing thermoplastic resin or aminoplast to improve the compatibility of IFR/PP. Some other studies showed that functionalized thermoplastics can be used to improve the compatibility of hydrophilic filler and hydrophobic thermoplastic matrix.^{5–7} According to our understanding of the principle of compatibilization, in this article, APP–PT–M system was selected as the 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 Unite Chemical Co. (China). APP (Chang-Feng Chemical Co. Ltd., Shi-Fang City, China) and PT and M (both supplied by Gaocheng Chemical Co., Shijiazhuang, China) are all 200 mesh. EPP was prepared as previously reported.⁸

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 $127 \times 12.7 \times 3.5 \text{ mm}^3$; 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 Koka rheometer (Shimadzu, Kyoto, Japan). A Shimadzu DT-40 thermal analyzer was used for TG and DTA experiment at a rate of $10^\circ\text{C}/\text{min}$ with a programmed temperature controller.

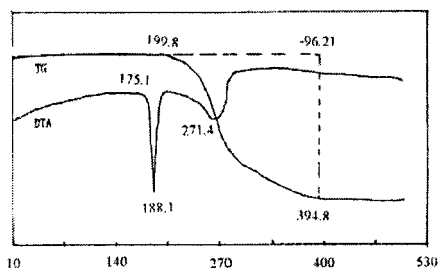


Figure 3 Thermal analysis curve of pentaerythritol.

Effect of EPP on rheological behavior of composites

A Kaka (Shimadzu) flow tester was used to investigate the rheological behavior of the composites. The experimental temperature was fixed at 180°C with experimental loads of 60, 50, 40, 30, 20, and 10 kg/cm². A plot of apparent viscosity $\ln \eta_a$ versus apparent shear rate $\ln \dot{\gamma}_w$ 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) (line C) obviously decreased. The addition of IFR did not change the η_a of composite B (line D) as the shear rate $\dot{\gamma}_w$ increase, which could be the result of PT's melting. Figure 3 shows results of the thermal analysis of PT: the TG and DTA curves show that PT's melting point is 175–190°C, which is also the blend temperature of the IFR/PP system, thus causing problems in the processibility of IFR/PP system.

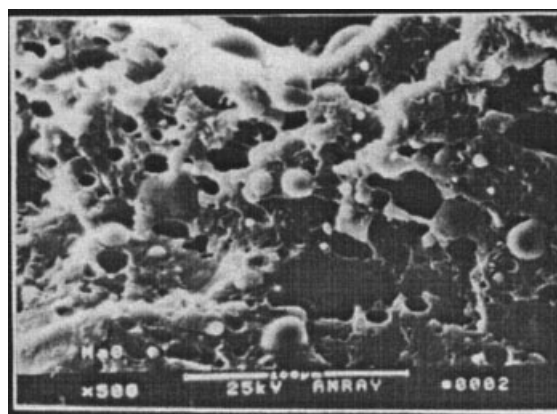
It is worth noting that three lines (lines E, F, and G) show that PP substituted by EPP significantly affects the rheological behavior of PP/IFR composites. The apparent viscosity of melts ($\ln \eta_a$) decreased as the shear rate ($\ln \dot{\gamma}_w$) increased, although the viscosity of composite B did not change as the shear rate $\dot{\gamma}_w$ increased. This phenomenon implies that EPP might have reacted with PT. When the content of EPP was at 12.5%, the viscosity of the whole system increased, which indicates that EPP improved the adhesion of PP and IFR.

In addition, the results of Figure 2 showed that the apparent viscosity of the PP/IFR/EPP melt ($\ln \eta_a$) decreased as the shear rate ($\ln \dot{\gamma}_w$) increased, demonstrating linearity. This phenomenon implied that the melt is a pseudoplastic liquid and has good processibility.

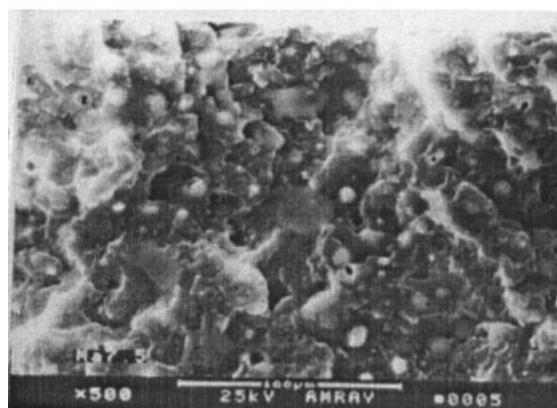
SEM analysis

The tensile fracture surfaces of composite samples containing IFR were studied by SEM, the results of which are shown in Figure 4. As seen in Figure 4(a), the SEM tensile fracture surface of composite B shows

poor wetting of IFR by the PP matrix, and fracture occurred in the interface of IFR and PP, attributed to the insufficient adhesion between IFR and PP. The SEM tensile fracture surface of composite D in Figure 4(b) shows partial wetting of IFR by the PP matrix. The



a



b



c

Figure 4 SEM micrographs of fracture surface of IFR/PP composites: (a) composite B; (b) composite C; (c) composite E.

SEM tensile fracture surface of composite E in Figure 4(c) shows that the fracture occurred in the matrix material, and the IFR was covered by a layer of PP matrix.

The preceding observations illustrated 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 that EPP had an excellent compatibilization effect on IFR/PP composites. With respect to 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 abundance of $-NH_2$ (M) and $-OH$ (PT) groups on the surfaces of IFR and the polar portion ($-COOH$) of EPP. It is reasonable to propose that EPP can react with IFR through an amino link or a ester link, which we were not able to study with infrared spectroscopy or other characterization methods. Given the complex characteristic of IFR and the insignificant amount of the polar portion of EPP, it is a difficult problem to be solved. However, the rheological behavior of the composites implies that EPP might have reacted with PT. 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 components 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 crystallites of PP and EPP existed in the α -crystal form, characterized by nearly the same crystal parameters (see Ma et al.⁸).

CONCLUSIONS

EPP is a true coupling agent for intumescent flame-retardant/polypropylene composites and can improve their compatibility, thus increasing the mechanical properties of the composites without adversely changing the necessary flame retardancy. It also has a significant effect on the rheological behavior of IFR/PP composite. PP/IFR/PP composites are characterized by good processibility.

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