Postprint: Effects of Two Maleic Anhydride-Grafted Polymers on the Properties of Intumescent Flame-Retardant Toughened Polypropylene Blend Composites

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Abstract

Polypropylene (iPP) was modified with intumescent flame retardant (IFR) and ethylene-octene copolymer (POE) to impart flame retardancy and toughening. The effects of two typical compatibilizers, polypropylene-grafted maleic anhydride (PP-g-MAH) and ethylene-octene copolymer-grafted maleic anhydride (POE-g-MAH), on the flame retardant and mechanical properties of the intumescent flame retardant toughened blend composite system were comparatively investigated. The results demonstrate that IFR can improve the flame retardant properties of polypropylene blends, but significantly deteriorates the mechanical properties of the material, whereas the incorporation of compatibilizers can simultaneously enhance both the flame retardant properties and mechanical properties of the composites. PP-g-MAH facilitates more uniform dispersion of IFR; the addition of 1 wt% PP-g-MAH reduces the average heat release rate, peak heat release rate, average specific extinction area, and total smoke release of the composite by 24%, 30%, 56%, and 46%, respectively, compared to the flame-retardant material without compatibilizer. Conversely, POE-g-MAH enables the composite to form an encapsulation structure, resulting in a significant improvement in impact strength; the addition of 5 wt% POE-g-MAH increases the impact strength of the composite by 93%.

Full Text

Preamble

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Effect of Two Maleic Anhydride Grafted Polymers as Modifiers on Intumescent Flame Retardancy and Mechanical Properties of Toughened Polypropylene Blend Composites

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Abstract

Intumescent flame retardant (IFR) and poly(ethylene-co-octene) (POE) were used to modify isotactic polypropylene (iPP) for flame retardancy and toughening. The effects of two typical compatibilizers—polypropylene grafted maleic anhydride (PP-g-MAH) and poly(ethylene-co-octene) grafted maleic anhydride (POE-g-MAH)—on the flame retardancy and mechanical properties of the intumescent flame-retardant toughened blend composites were investigated. The results show that while IFR can improve the combustion performance of polypropylene blends, it significantly reduces mechanical properties. The addition of compatibilizers simultaneously enhances both the flame retardancy and mechanical properties of the composites. PP-g-MAH promotes more uniform dispersion of IFR; adding 1% (mass fraction) PP-g-MAH reduces the average heat release rate, peak heat release rate, average specific extinction area, and total smoke release by 24%, 30%, 56%, and 46% respectively compared to the flame-retardant material without compatibilizer. POE-g-MAH enables the formation of an encapsulation structure in the composites, markedly improving impact strength—adding 5% POE-g-MAH increases the composite impact strength by 93%.

Keywords: composites, flame retardant and mechanical properties, blending and composites, compatibilizer

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Introduction

Polypropylene (PP) is a versatile general-purpose polymer material with good comprehensive properties. However, PP is highly flammable with a low limiting oxygen index (LOI) of 17-18, and it generates significant heat and melt dripping during combustion, necessitating the addition of flame retardants for practical applications. Intumescent flame retardant (IFR) is an environmentally friendly flame retardant primarily composed of nitrogen and phosphorus that produces minimal smoke and non-toxic gases during combustion while forming a protective char layer that prevents dripping, making it suitable for polyolefin flame retardancy [?]. IFR can be categorized into phosphorus-nitrogen based retardants and expandable graphite, with phosphorus-nitrogen types further divided into monomeric and compounded varieties. Among these, compounded IFRs have been commercialized and widely applied. However, using IFR to flame-retard PP substantially reduces mechanical properties, particularly impact strength [?, ?]. The side methyl groups on polypropylene molecular chains restrict chain rotation, resulting in inherently low toughness, and the addition of flame retardants further limits its application scope [?]. Therefore, it is necessary to simultaneously toughen PP materials while flame-retarding them to enhance overall performance.

Polymer blending and compounding can combine the advantages of multiple polymers and compensate for the mechanical property degradation caused by flame retardants. To achieve high-performance polypropylene, this study selected poly(ethylene-co-octene) (POE) as a toughening agent for PP, a commercial compounded IFR as the flame retardant, and PP-g-MAH and POE-g-MAH as compatibilizers to improve interfacial compatibility. Although numerous studies have investigated polypropylene flame retardancy [?], reports on flame-retardant polypropylene blends remain limited [?, ?]. While adding compatibilizers has become a conventional practice in composite systems, few studies have specifically examined how compatibilizer type affects the comprehensive properties of flame-retardant toughened blend composites. This paper investigates the influence of adding two typical compatibilizers on the flame retardancy and mechanical properties of the composite system.

1.1 Raw Materials

iPP (S1003, industrial grade); POE (Engage 8150); POE-g-MAH (GR-216); PP-g-MAH (GPM200A); IFR (industrial grade, JLS-PNP1D); silane coupling agent (KH-161); xylene (analytical grade).

1.2 Sample Preparation

Prior to experiments, the IFR was modified using phenyltrimethoxysilane coupling agent (KH-161) at a dosage of 5‰ (mass fraction) of the total IFR. According to the formulations in Table 1 , appropriate amounts of raw materials were weighed and mixed uniformly. The mixture was then fed into a TSSJ-2S twin-screw extruder for melt extrusion. The temperature profile from feed zone to die was 170°C, 190°C, 200°C, and 195°C, with an extrusion speed of 100 r/min. The extrudate was pelletized to obtain granules, which were left to stand under dry conditions for 24 hours to stabilize the system components. The granules were then injection-molded using a high-pressure injection molding machine at 40 MPa injection pressure and 205°C, with 8 s holding time and 10 s cooling time. Different molds were used to prepare specimens for limiting oxygen index, vertical burning, tensile, and impact tests. For cone calorimetry tests, dried granules were compression-molded on a plate vulcanizing machine at 190°C and 15 MPa for 5 minutes, then cooled to 120°C and held for 10 minutes to produce test plates.

1.3 Performance Testing

Combustion Performance Testing
The limiting oxygen index (LOI) was measured using an HC-2CZ oxygen index instrument according to GB/T 2406.2-2009 "Plastics—Determination of burning behavior by oxygen index—Part 2: Ambient-temperature test." Specimen dimensions were 80 mm × 10 mm × 4 mm (10 specimens per group). Cone calorimetry was performed using a UKS001 cone calorimeter at a heat flux of 35 kW/m^2 according to ASTM E-1354. Plate dimensions were 10 mm × 10 mm × 3 mm (3 specimens per group).

Mechanical Performance Testing
Tensile properties were tested using an INSTRON 3365 universal testing machine according to ISO 527-1BA (6 specimens per group). Impact properties were tested using an XJC-250 electronic pendulum impact tester on specimens measuring 80 mm × 10 mm × 4 mm with V-notches machined using a RAY-RAN RR3700 automatic notching machine, following GB/T 1843-2008 "Plastics—Determination of Izod impact strength" (6 specimens per group). Testing temperature was 20°C.

Microstructure Characterization
A JSM 6700F scanning electron microscope was used at 5 kV working voltage and 10 A current. Impact fracture surfaces were etched in xylene solution at 30°C for 72 hours to remove the POE component from the composites.

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2 Results and Discussion

2.1.1 Limiting Oxygen Index (LOI) and Vertical Burning Performance

Table 1 lists the formulations, LOI values, and mechanical test results for pure iPP, iPP/POE material, and iPP/POE/IFR composites. Pure iPP has an LOI of only 17.8, making it highly flammable in air. The iPP/POE blend shows an improved LOI of 20.0. With 20% IFR addition, the iPP/POE/IFR composite reaches an LOI of 27.0, achieving a flame-retardant rating. Adding compatibilizers further increases the LOI to 28.8.

Pure iPP exhibits the highest tensile strength at 39.1 MPa but low impact strength of only 2.0 kJ/m^2. Blending with POE substantially improves toughness while maintaining tensile strength. This is because POE contains flexible, coiled octene chains that can deform and absorb significant impact energy upon impact, while also initiating crazing in the material [**?**]. However, adding flame retardant reduces tensile strength to 24.5 MPa and decreases impact strength from 18.5 kJ/m^2 for the blend to 4.6 kJ/m^2 for the composite. With small amounts of compatibilizer, IFR-c1 shows a 43% increase in impact strength to 6.6 kJ/m^2 compared to IFR-0, while IFR-c5 further improves impact strength to 8.9 kJ/m^2. The mechanical properties are primarily affected by IFR particle dispersion in the matrix. IFR exists as a solid during compounding and has different polarity from the iPP matrix, resulting in poor compatibility, easy agglomeration, weak interfacial bonding, and void formation between phases, which degrades mechanical properties. Compatibilizer addition enhances interfacial adhesion, reduces IFR agglomeration and void formation, and decreases IFR particle size, thereby improving mechanical properties.

2.1.2 Heat Release Characteristics

Table 2 presents cone calorimetry results for pure iPP and its composites. After adding flame retardant, all composites show earlier time to ignition (TTI) than iPP/POE, while peak heat release rate (PHRR) and mean heat release rate (MHRR) decrease significantly. With compatibilizers, heat release is further reduced compared to IFR-0. Figure 1 [Figure 1: see original paper] shows the heat release rate curves. Pure iPP and iPP/POE exhibit similar HRR curves, burning rapidly and intensely with a sharp peak reaching 640-660 kW/m^2 immediately after ignition, followed by gradual decline. With 20% IFR, IFR-0 shows dramatically different combustion behavior divided into three stages: (1) heating and ignition (0-140 s), where the char layer formed by IFR covers the material surface, blocking heat and gas transfer, causing HRR to rise sharply then slow down around 150 kW/m^2; (2) stable combustion (140-600 s) with relatively constant HRR due to protective char layer; and (3) char layer rupture (600-1000 s), where HRR rises again after the char breaks, reaching a second peak of 344.6 kW/m^2 around 800 s before declining as fuel is exhausted.

For compatibilized flame-retardant toughened polypropylene, the three-stage combustion process persists. The maximum PHRR occurs in the later combustion stage. After ignition under radiant heat, the flame retardant forms an expanded char layer, significantly reducing the HRR growth rate compared to iPP and iPP/POE. However, as combustion continues, surface char rupture causes HRR to rise again. Compared to IFR-0, IFR-c1 and IFR-p1 show significantly reduced HRR in the third stage, with minimal differences in the first two stages. This is because the char layer formed during combustion is more uniform and dense, resisting rupture in the later stage and providing better protection

(Figure 2 [Figure 2: see original paper] and Figure 3 [Figure 3: see original paper]). IFR-p1 exhibits a PHRR of 240.6 kW/m^2, representing decreases of 64%, 30%, and 24% compared to iPP/POE, IFR-0, and IFR-c1, respectively, while its MHRR of 152.9 kW/m^2 decreases by 57%, 44%, and 14%. Thus, PP-g-MAH further reduces combustion hazards more effectively than POE-g-MAH. However, composites with 5% compatibilizer show reduced flame retardancy compared to those with 1%, particularly IFR-c5, possibly due to the poor thermal stability of maleic anhydride grafted polymers themselves.

2.1.3 Smoke Generation and Toxicity Characteristics

To evaluate real fire hazards, smoke release must be assessed, including total smoke release (TSR), average CO yield (av-COY), average CO_2 yield (av-CO_2Y), average specific extinction area (av-SEA), peak CO yield (p-COY), peak CO_2 yield (p-CO_2Y), and peak specific extinction area (p-SEA). Table 3 presents smoke release data from cone calorimetry. Adding 20% IFR increases smoke release compared to iPP and iPP/POE, while compatibilizers mitigate this negative effect. IFR-c1 shows TSR and av-SEA decreasing to 1861.6 m^2/m^2 and 551.9 m^2/kg, respectively—21% and 31% lower than IFR-0. IFR-p1 achieves even lower TSR of 1264.7 m^2/m^2, representing decreases of 36%, 26%, 46%, and 32% compared to pure iPP, iPP/POE, IFR-0, and IFR-c1, respectively, while av-SEA decreases by 45%, 48%, 56%, and 36%. Regarding toxic gases, CO yield shows no significant change with IFR addition, while CO_2 yield decreases somewhat. Adding 1% compatibilizer further reduces av-CO_2Y, p-COY, and p-CO_2Y compared to IFR-0, decreasing fire hazard. However, 5% compatibilizer does not improve smoke toxicity, with IFR-c5 actually increasing smoke generation.

2.2 Morphology of Intumescent Char Layer and Composites

Macroscopic morphologies of residual char after cone calorimetry are shown in Figure 2 [Figure 2: see original paper]. IFR-0 produces limited char expansion with irregular, fragmented char showing undulating structures and poor surface coverage. IFR-c1 maintains similar overall morphology but with denser, more continuous char. Composites with PP-g-MAH show more pronounced char expansion with more uniform and dense residual char (Figures 2c and 2e).

Microstructures of char surfaces from cone calorimetry are shown in Figure 3 [Figure 3: see original paper]. IFR-0 fails to form a continuous, dense intumescent char structure. With compatibilizers, IFR-c1 and IFR-c5 show relatively more continuous char, though IFR-c5 shows reduced continuity compared to IFR-c1. IFR-p1 and IFR-p5 exhibit continuous, stable char surfaces with numerous wrinkled structures containing vesicles that can trap volatile flammable gases (Figures 3c and 3e). This stable, uniform wrinkled structure enhances heat and gas barrier capabilities, providing better material protection and improved flame retardancy.

Phase structures of composite impact fractures are shown in Figure 4 [Figure 4: see original paper], revealing micro-voids formed by etched POE domains in the iPP matrix. In IFR-0 (Figures 4a and 4a1), IFR disperses extremely unevenly in the iPP matrix with severe agglomeration and weak interfacial bonding, creating voids where IFR particles have detached. This indicates that rigid IFR particles act as impurities, impairing impact energy absorption and reducing mechanical properties. With compatibilizers, POE domain size decreases significantly and IFR dispersion improves markedly. As shown in Figures 4b-4e, IFR agglomeration decreases and particle size reduces. At 5% compatibilizer content, IFR particles become fully or partially encapsulated, forming tighter interfacial bonding that can absorb impact energy through interfacial displacement and deformation, thereby improving toughness. Comparing Figures 4b vs 4c and 4d vs 4e, PP-g-MAH provides more uniform IFR dispersion, enabling formation of more uniform, dense char layers during combustion and thus better flame retardancy. However, since rigid IFR particles cannot buffer and absorb impact energy through elastic deformation, the impact strength improvement is less significant. Conversely, POE-g-MAH, as a compatibilizer for the toughening modifier POE, alters POE polarity, causing IFR to preferentially disperse in POE-rich regions and form a "core-shell" structure [**?**], which further enhances impact toughness. More IFR particles remain on the fracture surface in POE-g-MAH composites, while most IFR particles detach under impact in PP-g-MAH composites, explaining why POE-g-MAH more significantly improves impact toughness.

Conclusion

IFR improves flame retardancy but severely reduces the mechanical properties of toughened blends. Compatibilizer addition promotes more uniform IFR dispersion with reduced particle size and stronger interfacial bonding, generating more continuous and dense char layers during combustion. This reduces heat release, smoke production, and toxic gas yields, particularly the peak heat release rate. More importantly, compatibilizers significantly improve the mechanical properties of flame-retardant toughened blend composites, compensating for the detrimental effects of IFR. PP-g-MAH enables more uniform IFR dispersion and forms char layers with abundant wrinkled structures, substantially improving flame retardancy while maintaining mechanical properties. POE-g-MAH promotes encapsulation of IFR by POE, forming a typical "core-shell" structure that markedly enhances impact toughness.

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