

Synthesis of phosphorus-containing flame-retardant antistatic copolymers and their applications in polypropylene

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ABSTRACT: By adjusting the molar ratios of antistatic monomer of octyl phenol ethylene oxide acrylate (denoted as AS), rigid monomer of methyl methacrylate (denoted as MMA), and flame-retardant monomer of 2-(phosphoryloxymethyl oxyethylene) acrylate (denoted as FR), a series of flame-retardant antistatic copolymers poly (octyl phenol ethylene oxide acrylate-co-methyl methacrylate-co-phosphoryloxymethyl oxyethylene acrylate) (denoted as AMF) were synthesized through radical polymerization. Among the obtained copolymers, two copolymers, AMF162 (the feed molar ratio of AS, MMA, and FR as 1 : 6 : 2) and AMF1104 (the feed molar ratio of AS, MMA, and FR as 1 : 10 : 4) with different concentrations were added into polypropylene (PP) to prepare PP-AMF162 and PP-AMF1104 series of composites. The thermal stability, limiting oxygen index, the antistatic property, and mechanical properties of PP composites were tested and analyzed. PP-AMF162 series composites have excellent antistatic effect. When the AMF162 content was equal to or <15 wt %, the impact strength of PP-AMF162 composites was higher than that of pure PP. The results indicated that copolymer AMF162 was a suitable flame-retardant and antistatic additive for PP. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41677.

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INTRODUCTION

With excellent mechanical properties, good chemical stability, easy forming process, and various forming methods, polypropylene (PP) has been widely used in industrial electronics, appliance, transportation, decoration materials, and other fields.^{1–6} However, the limited oxygen index (LOI) of PP is only 17–19%, and PP is prone to generate a great deal of molten drop and flame propagation during combustion.^{7–9} Moreover, because of the low polarity, low-water absorption, high-surface resistance, and high-volume resistance, PP products are prone to accumulate electrostatic charges, thus causing troubles, such as electric shocks and damages to electronic machines.^{10–12} The addition of flame-retardant or antistatic agents into PP is one of the common ways to improve the flame-retardant or antistatic capability of PP and widen the application scope of PP.

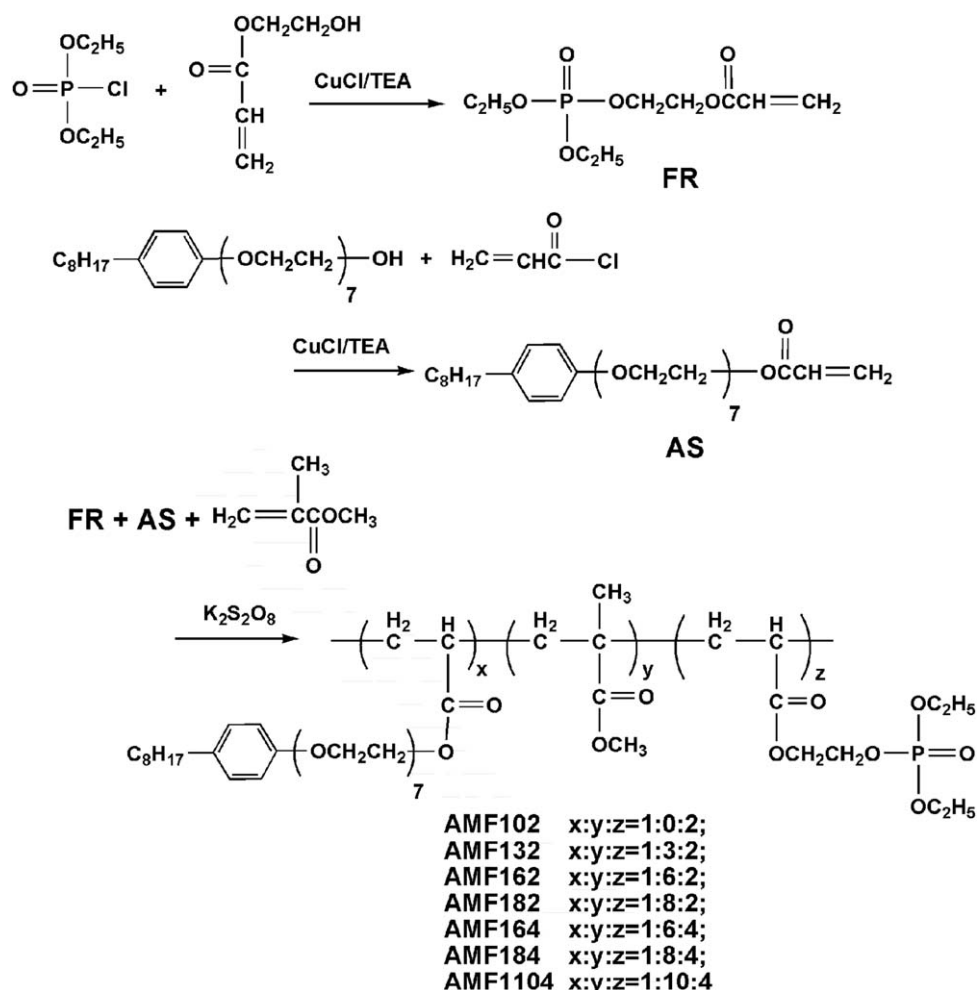
Traditionally, halogenated compounds are widely used to depress the flammability of PP. However, halogenated compounds can produce poisonous and corrosive smoke. In order to avoid the generation of toxic, corrosive, and halogenated gases and chemicals in combustion, it is necessary to adopt

halogen-free flame retardants in PP. Phosphorus-based flame retardants have been a major source of interest to replace halogen compounds because of their environmentally friendly by-products, low toxicity, and low production of smoke in fire.^{13–16} Compared to organic phosphorus small-molecule compounds, phosphorus-containing polymers have many advantages, such as good compatibility with the polymer substrate, migration resistance, and volatility.^{17,18} Therefore, phosphorus-containing polymers of flame retardants have broad application prospects in PP composites.

Antistatic polymers are a class of permanent antistatic agents, which can eliminate static charges by forming a continuous conducting network inside the plastic matrix, and have many advantages, including long-lasting antistatic effects, less dependence on environment humidity, superior thermal stability, fine compatibility with polymer materials, and little effect on mechanical properties of polymer materials.^{19–21} Adding an appropriate amount of antistatic polymer into the polymer matrix is one of the effective methods to improve the antistatic properties of the polymer matrix.

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Scheme 1. Synthesis routes of monomers and copolymers.

The antistatic and flame-retardant properties of PP composites were widely studied.^{7–12} However, the synthesis of polymers with both flame retardant and antistatic properties as well as their applications in PP composites was seldom reported.²² For the PP applications in many cases, such as coal, chemical, rubber, and powder processing industries, PP should have both the antistatic property and flame-retardant property. To prepare PP composites with both antistatic property and flame-retardant property, a series of flame-retardant antistatic copolymers poly (octyl phenol ethylene oxide acrylate-co-methyl methacrylate-co-phosphoryloxymethyl oxyethylene acrylate) (donated as AMF) were synthesized through a radical polymerization. Two properly selected copolymers, AMF162 (the feed molar ratio of AS, MMA, and FR as 1 : 6 : 2) and AMF1104 (the feed molar ratio of AS, MMA, and FR as 1 : 10 : 4) with suitable forming properties were added into polypropylene (PP) according to different concentrations to prepare PP-AMF162 and PP-AMF1104 series of flame-retardant antistatic composites. By adjusting the addition ratios of the flame retardant monomer of 2-(phosphoryloxymethyl oxyethylene) acrylate (FR), antistatic monomer of octyl phenol ethylene oxide acrylate (AS), and polar monomer of methyl methacrylate (MMA), the

flame-retardant, antistatic, and mechanical properties of the resulting copolymers can be tuned.

EXPERIMENTAL

Materials and Measurement Methods

¹H NMR spectra were recorded on Varian Inova 400 (Varian, America) in deuterated chloroform solution at 298 K. Elemental analysis was performed on FlashEA 1112 elemental analysis instrument (Elementar Co.). Fourier Transform-Infrared (FT-IR) analysis was conducted with a Fourier-Transform infrared spectroscopy (Va Rong Biochemical Instrument, China). All the FT-IR specimens were prepared as follows: powder samples were mixed with KBr powder and then pressed into a tablet or liquid specimens. DSC curves were recorded at a heating rate of 10°C min⁻¹ in nitrogen atmosphere on a NETZSCH-DSC200PC differential scanning calorimeter (Netzsch-Gerätebau GmbH, German) (Netzsch-Gerätebau GmbH, German). The thermogravimetry (TG) curves were recorded on a Netzschsta409P (Netzsch-Gerätebau GmbH, German) with a heating rate of 10°C min⁻¹ in air atmosphere. LOI was measured according to GB 2406.2–2009 (China) with a DRK304B oxygen index meter (Federer Instrument Co., China). The sample size in the experiment was 100 × 10 × 4 mm³. The

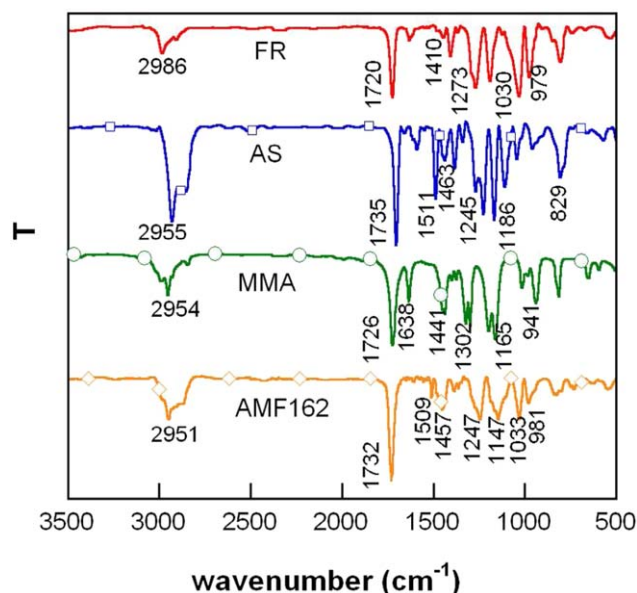


Figure 1. FT-IR spectra of monomers of FR, AS, MMA and copolymer of AMF162. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

volume resistivity (ρ_v) and surface resistivity (ρ_s) of PP composites were detected with a ZC36 high resistance micro-current meter (Shanghai Precision Scientific Instrument Co., China). The sample size was $77.9 \text{ mm} \times 2.7 \text{ mm}$ (diameter \times height). Testing environment temperature is $25 \pm 2^\circ\text{C}$ and the relative humidity is $65 \pm 5\%$. The average of three measurements was used as the result of each sample. Charpy unnotched impact test of PP composites was performed according to GB/T 1043.1–2008 (China) with a JJ-20 memory impact testing machine (Changchun Intelligent Equipment Co., China). The sample size was $100.0 \times (10.0 \pm 0.5) \times (4.0 \pm 0.3) \text{ mm}^3$. A JSM 7001F scanning electron microscope (SEM) was used to observe the brittle fracture surface

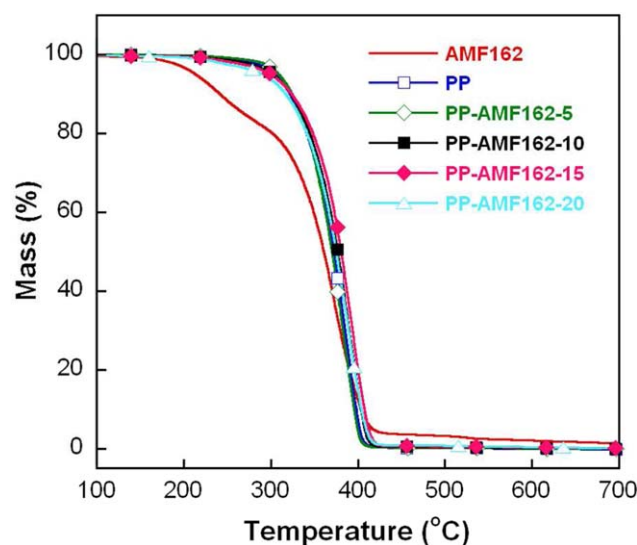


Figure 2. TG curves of PP-AMF162 series of composites with a heating rate of $10^\circ\text{C min}^{-1}$ at air atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

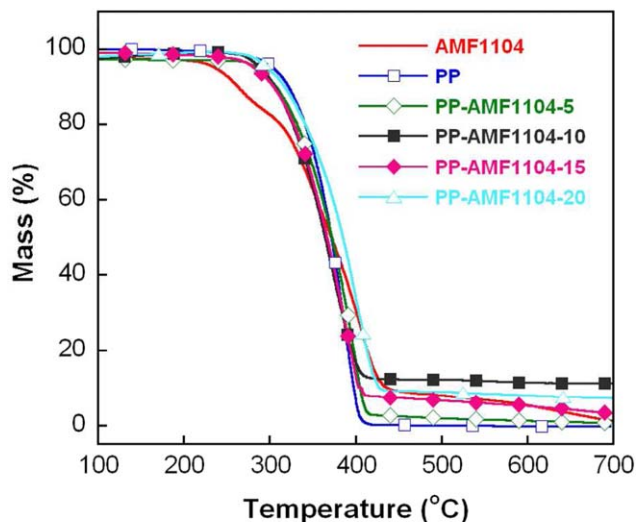


Figure 3. TG curves of PP-AMF1104 series of composites with a heating rate of $10^\circ\text{C min}^{-1}$ at air atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

morphology of the PP/AMF composites. The wide angle X-ray diffraction (WAXD) analyses were performed using an X'pert powder diffractometer in the reflection mode. Cu-K α radiation was used at 20 kV and 40 mA. The analyses were performed at angles of 5° to 45° and the scan step was 0.052 (in 2θ) with a counting time of 20 s per step.

Diethyl chlorine and acryloylchloride were obtained from Shanghai Redchemical Co. Hydroxyethyl acrylate and CuCl were obtained from Aladdin-Reagent Database Inc. Octyl phenol ethoxylates was obtained from Nantong Chen Run Chemical Co. MMA and PP were obtained from Tianjin Kemiou Chemical Reagent Co. All solvents were carefully dried and purified in a nitrogen flow.

Synthesis of Flame-Retardant Monomer of FR

Hydroxyethyl acrylate (7.2 g, 62.0 mmol), triethylamine (6.24g, 61.8 mmol), CuCl (0.1g, 1.0 mmol), and ether (80 mL) were successively added into a 250-mL three-necked flask and cooled to 0°C in an ice bath. Diethyl chlorophosphate (11.0 g, 68.2 mmol) diluted with 20 mL ether was added dropwise within 1 h. Then the reaction mixture was warmed to room temperature and stirred for 24 h. The reaction mixture was filtered. Then the filtrate was washed with saturated brine and dried with anhydrous magnesium sulfate. The solvent was removed through evaporation under a reduced pressure to yield a pale-yellow liquid, the product FR (13.28 g, 83%). EI-MS: 275.31 ($M + \text{Na}^+$). $^1\text{H NMR}$ (400 MHz, CDCl_3 , δ): 6.43–6.47 (d, 1H), 6.09–6.17 (m, 1H), 5.85–5.88 (d, 1H), 4.26–4.36 (d, 4H), 4.09–4.13 (m, 4H), 1.31–1.35 (m, 6H). IR (CH_2Cl_2 , ν , cm^{-1}): 2986 (CH_3), 2918 (CH_2), 1728 ($\text{C}=\text{O}$), 1635, 1410 ($-\text{CH}=\text{CH}_2$), 1273 ($\text{P}=\text{O}$),²³ 1192 ($\text{C}-\text{O}-\text{C}$), 1030, 979 ($\text{P}-\text{O}-\text{C}$).¹⁹

Synthesis of Antistatic Monomer of AS

Octyl phenol ethoxylates (13.6 g, 27 mmol), triethylamine (5.0 g, 49.5 mmol), CuCl (0.1 g, 1.0 mmol), and dichloromethane

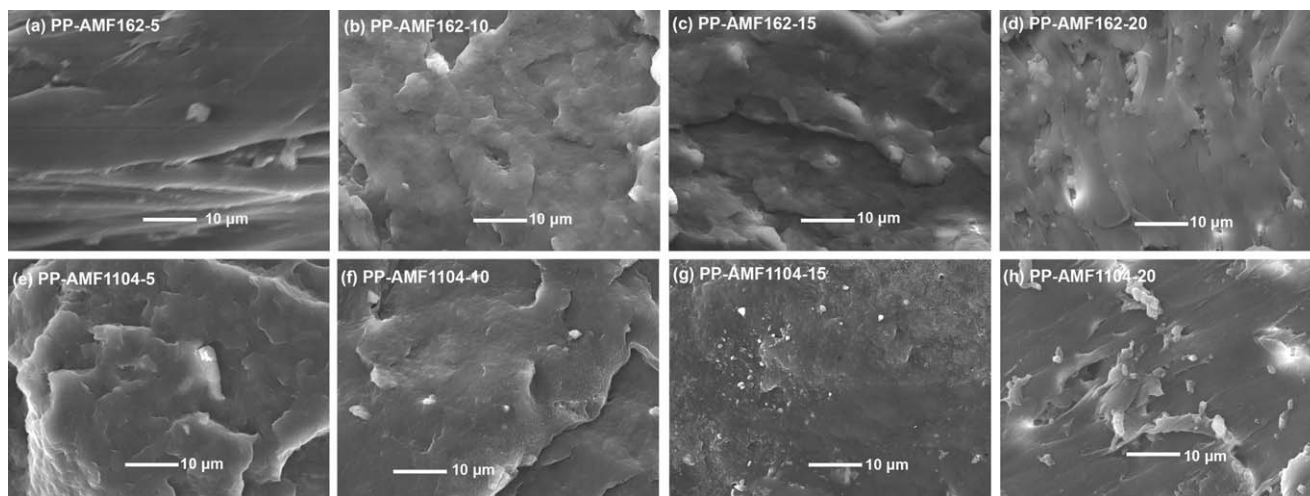


Figure 4. SEM micrographs of PP/AMF composites (15KV, $\times 2000$).

(100 mL) were successively added into the 250-mL three-necked flask and cooled to 0°C in an ice water bath. Then, acryloylchloride (5.3 g, 49.0 mmol) diluted with 20 mL dichloromethane was added dropwise within 1 h. The reaction mixture was stirred for 15 min at 0°C , warmed to room temperature and then stirred for 24 h. The reaction mixture was filtered. The filtrate was removed through evaporation under a reduced pressure. The crude product was purified by column chromatography [silica gel, chloroform/isopropanol (10 : 1)] to yield a pale yellow liquid (6.57 g, 43%). ^1H NMR (400 MHz, CDCl_3 , δ): 6.80–6.82 (d, 2H), 6.40–6.50 (m, 2H), 6.11–6.18 (m, 1H), 5.92–5.94 (d, 1H), 5.82–5.85 (d, 1H), 3.65–3.84 (m, 28H), 1.68 (s, 2H), 1.32 (s, 12H), 0.69 (s, 3H). IR (CH_2Cl_2 , ν , cm^{-1}): 2955 (CH_3), 2878 ($-\text{CH}_2$), 1735 ($\text{C}=\text{O}$), 1614, 987 ($-\text{CH}=\text{CH}_2$), 1511, 1463 ($\text{C}=\text{C}$ in benzene ring), 1245, 1065 ($\text{Ar}-\text{O}-\text{C}$), 1186 ($\text{C}-\text{O}-\text{C}$), 829 ($\text{C}-\text{H}$ in benzene ring).

General Preparation Method of Copolymers of AMF

The copolymers were prepared by free radical polymerization. In the N_2 atmosphere, deionized water, various monomers (FR, AS, and MMA) were successively added into a 250-mL four-necked flask and stirred mechanically for 30 min. Then a certain amount of initiator ($\text{K}_2\text{S}_2\text{O}_8$) was added into the reaction mixture, which was heated to 70°C for 24-h reaction. After the reaction, the reaction mixture was cooled to room temperature and filtrated. The obtained solid was washed with hot water for several times and then dried for 24 h under vacuum conditions at 50°C .

AMF102: AS (3.41 g, 6 mmol), FR (3.0 g, 12 mmol), and $\text{K}_2\text{S}_2\text{O}_8$ (0.29 g) were added. The product is a dark yellow viscous solid (5.5 g, 86%). IR (CH_2Cl_2 , ν , cm^{-1}): 1511, 1477 ($\text{C}=\text{C}$ in benzene ring), 1255 ($\text{P}=\text{O}$), 1158 ($\text{C}-\text{O}-\text{C}$), 1027, 979 ($\text{P}-\text{O}-\text{C}$).

AMF132: AS (3.41 g, 6 mmol), MMA (1.8 g, 18 mmol), FR (3.0 g, 12 mmol), and $\text{K}_2\text{S}_2\text{O}_8$ (0.37 g) were added. The product is a dark yellow viscous solid (6.7 g, 81%). IR (CH_2Cl_2 , ν ,

cm^{-1}): 1512, 1451 ($\text{C}=\text{C}$ in benzene ring), 1243 ($\text{P}=\text{O}$), 1139 ($\text{C}-\text{O}-\text{C}$), 1032, 977 ($\text{P}-\text{O}-\text{C}$).

AMF162: AS (3.41 g, 6 mmol), MMA (3.6 g, 36 mmol), FR (3.0 g, 12 mmol), and $\text{K}_2\text{S}_2\text{O}_8$ (0.44 g) were added. The product is a yellow solid of moderate hardness (7.5 g, 75%). IR (CH_2Cl_2 , ν , cm^{-1}): 1509, 1457 ($\text{C}=\text{C}$ in benzene ring), 1247 ($\text{P}=\text{O}$), 1147 ($\text{C}-\text{O}-\text{C}$), 1033, 981 ($\text{P}-\text{O}-\text{C}$).

AMF182: AS (3.41 g, 6 mmol), MMA (4.8 g, 48 mmol), FR (3.0 g, 12 mmol), and $\text{K}_2\text{S}_2\text{O}_8$ (0.49 g) were added. The product is a pale yellow solid of high hardness (8.6 g, 77%). IR (CH_2Cl_2 , ν , cm^{-1}): 1520, 1459 ($\text{C}=\text{C}$ in benzene ring), 1254 ($\text{P}=\text{O}$), 1152 ($\text{C}-\text{O}-\text{C}$), 1030, 971 ($\text{P}-\text{O}-\text{C}$).

AMF164: AS (3.41 g, 6 mmol), MMA (3.6 g, 36 mmol), FR (6.0 g, 24 mmol), and $\text{K}_2\text{S}_2\text{O}_8$ (0.56 g) were added. The product is a pale yellow viscous solid (10.2 g, 78%). IR (CH_2Cl_2 , ν , cm^{-1}): 1510, 1455 ($\text{C}=\text{C}$ in benzene ring), 1254 ($\text{P}=\text{O}$), 1155 ($\text{C}-\text{O}-\text{C}$), 1026, 973 ($\text{P}-\text{O}-\text{C}$).

AMF184: AS (3.41 g, 6 mmol), MMA (4.8 g, 48 mmol), FR (6.0 g, 24 mmol), and $\text{K}_2\text{S}_2\text{O}_8$ (0.60 g) were added. The product is a pale yellow viscous solid (11.5 g, 81%). IR (CH_2Cl_2 , ν , cm^{-1}): 1518, 1457 ($\text{C}=\text{C}$ in benzene ring), 1242 ($\text{P}=\text{O}$), 1148 ($\text{C}-\text{O}-\text{C}$), 1028, 980 ($\text{P}-\text{O}-\text{C}$).

AMF1104: AS (3.41 g, 6 mmol), MMA (6.0 g, 60 mmol), FR (6.0 g, 24 mmol), and $\text{K}_2\text{S}_2\text{O}_8$ (0.65 g) were added. The product is a yellow solid of moderate hardness (12.8 g, 83%). IR (CH_2Cl_2 , ν , cm^{-1}): 1512, 1453 ($\text{C}=\text{C}$ in benzene ring), 1246 ($\text{P}=\text{O}$), 1141 ($\text{C}-\text{O}-\text{C}$), 1032, 976 ($\text{P}-\text{O}-\text{C}$).

Preparation of PP/AMF Composites

After the PP, AMF162 and AMF1104 were dried at 75°C for 12 h, according to different mass fractions (5, 10, 15, and 20%), AMF162 or AMF1104 was respectively evenly mixed with PP. The mixture was melt for 15 min at about 180°C on an open mill and then the mixed sample was pressed into cylindrical or rectangular specimens with certain size by hot pressing

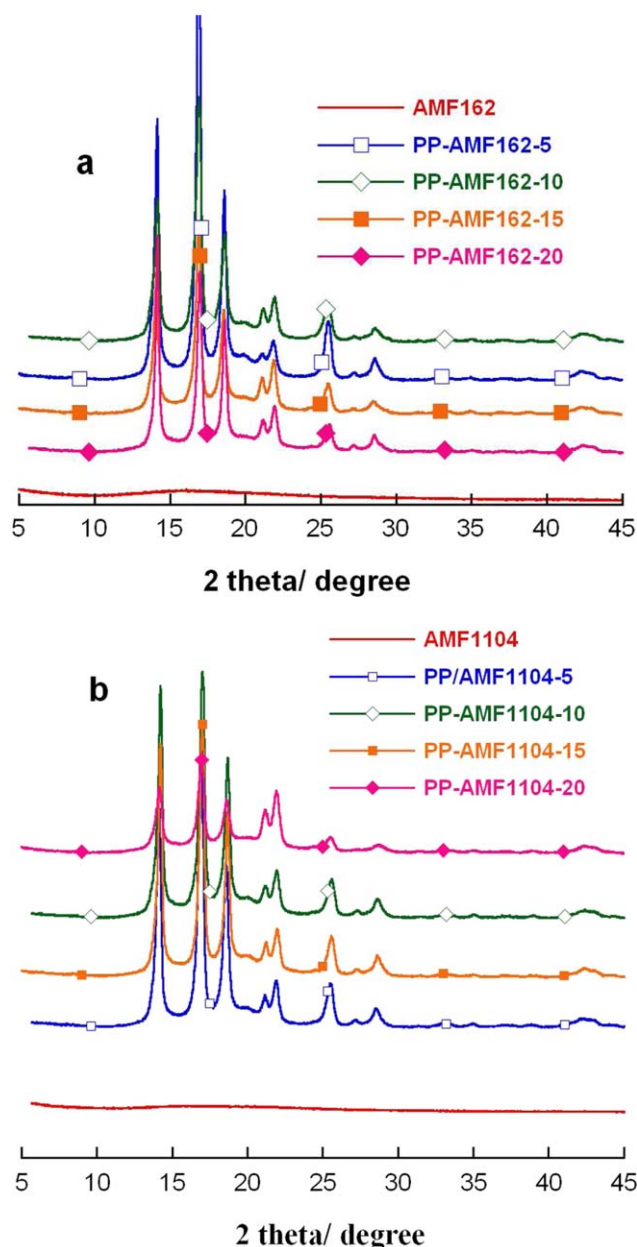


Figure 5. WAXD patterns of (a) AMF162 and PP/AMF162 serial composites, (b) AMF1104 and PP/AMF1104 serial composites in a range of 5–45°. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

for 10 min at 185°C under 10 MPa on a flat vulcanizing machine.

RESULTS AND DISCUSSION

Synthesis, Characterization, and Thermal Properties of the Copolymers

The synthesis routes of the monomers and copolymers are shown in Scheme 1. A series of copolymers were synthesized according to a radical polymerization method by adjusting the molar ratios of antistatic monomer of AS, retardant monomer of FR, and hard monomer of MMA. The molar ratio of FR and AS of 1 : 2 yielded the product of copolymer AMF102, which

was a viscous solid and not suitable for molding. Then the rigid monomer MMA was added into the reaction mixture and a series of copolymers, AMF132, AMF162, AMF182, AMF164, AMF184, and AMF1104 were synthesized. Among these resulting copolymers, AMF132, AMF164, and AMF184 have a high viscosity and are not suitable for molding. AMF162 and AMF1104 are solid and can be easily added to the PP. Thus, AMF162 and AMF1104 were used as flame-retardant antistatic additives to prepare the PP/AMF composites. For the resulting copolymers, their molecular weight and molecular weight distribution were not tested due to the poor solubility in common organic solvents. FT-IR spectra of all the copolymers were similar. Therefore, the infrared spectrum of the copolymer AMF162 (Figure 1) was analyzed as an example. The infrared spectra of monomer FR, AS and MMA were showed in Figure 1 to analyze the infrared spectrum of the copolymer AMF162. The absorption peaks at 1511 and 1477 cm^{-1} corresponds to the C=C stretching vibration of the benzene ring. The absorption peak at 1255 cm^{-1} is assigned to P=O stretching vibration. Absorption peaks at 1027 cm^{-1} and 979 cm^{-1} are attributed to P—O—C stretching vibration. The absorption peak at 1158 cm^{-1} is the C—O—C absorption peak. The copolymer AMF162 contains an ether bond with antistatic function, as well as a phosphate group with the flame-retardant property.

The DSC curves of the copolymers were shown in Supporting Information, Figure S1. With the increase of MMA content, T_g of copolymers increases gradually (Supporting Information, Table SI). From the DSC curves, only one T_g can be observed for each polymerized product. So we can roughly determine the polymerized product is a copolymer not mixtures. The thermal stabilities of the resulting copolymers were investigated by TG analysis (Supporting Information, Figure S2). All the copolymers have two decomposition processes. The first stage may involve the rupture of P—O—C bond and the second stage is ascribed to the decomposition of the copolymer main chain. With the increase of the MMA content, T_{onset} (extrapolated onset decomposition temperature) and $T_{50\%}$ (50% mass decomposition temperature) are gradually increased (Supporting Information, Table SI). The results indicated that the copolymers have moderate thermal stabilities.

Preparation and Thermal Properties of PP/AMF Composites

To study the effects of the contents of AMF162 and AMF1104 on the properties of PP-AMF162 and PP-AMF1104 composites, we prepared two series of composites PP-AMF162 and PP-AMF1104, in which the mass fractions of AMF162 and AMF1104 were 5, 10, 15, and 20%, respectively. PP-AMF162 series composites were denoted as PP-AMF162-5, PP-AMF162-10, PP-AMF162-15, and PP-AMF162-20. PP-AMF1104 series composites were recorded as PP-AMF1104-5, PP-AMF1104-10, PP-AMF1104-15, and PP-AMF1104-20.

The DSC curves of PP, PP/AMF162 and PP/AMF1104 serials composites were shown in Supporting Information, Figure S3. Compared with neat PP, T_g of PP/AMF composites has little change because PP and AMF1104 or AMF162 have approximate T_g , the melting temperature (T_m) slightly reduces, and the crystallization temperature (T_c) slightly increases with the

increase of the AMF1104 or AMF162 content. The percentage crystallinity of the pure PP and PP phase in PP/AMF composites were calculated according to the approximate calculation formula $X_c (\%) = \Delta H_c / (\Delta H_0 \cdot w)$. Wherein, X_c is the percentage crystallinity of PP. ΔH_c is enthalpy of crystallization, ΔH_0 is enthalpy of complete crystallization of PP, and w is PP content in PP/AMF composites. For PP/AMF162 composites and PP/AMF1104 composites, X_c of PP slightly reduces compared with pure PP (Supporting Information, Table SII). Figures. 2 and 3 show the TG curves of PP, PP-AMF162 serial and PP-AMF1104 serial composites in air, respectively. The initial decomposition temperatures of AMF162 and AMF1104 are lower than that of PP, and the temperatures for 50% mass loss of AMF162 and AMF1104 are almost the same to that of PP. When AMF162 or AMF1104 was added into PP, the initial decomposition temperatures of PP/AMF composites were slightly lower than that of PP and the temperatures for 50% mass loss were almost identical to that of PP. For PP/AMF1104 composites, carbon residue has no rule because the AMF distribution in thermal analysis samples maybe uneven due to the worse compatibility of AMF1104 with PP with the increase of AMF1104 content. Overall, PP/AMF composites have high thermal stability. AMF162 and AMF1104 hardly affect the thermal stability of PP composites.

Morphology of PP/AMF Composites

The dispersion of AMF162 or AMF1104 in PP matrix is investigated by SEM. The cryo-fractured surfaces of PP/AMF162 blend and PP/AMF1104 blend are shown in Figure 4. For PP/AMF162 serials composites, AMF162 (white parts in the micrograph) is distributed with tiny particles in the PP when the AMF162 content is low. When the AMF162 content is 20 wt %, AMF162 forms many aggregates in PP. AMF162 is polar, leading to its aggregation in the process. The SEM images for PP/AMF1104 serials composites have similar images with those of PP/AMF162 serials composites. The results indicate that the miscibility of AMF with PP becomes worse with the increase of AMF content in PP.

WAXD Analysis

Figure 5 shows the WAXD patterns of AMF162, AMF1104, PP-AMF162, and PP-AMF1104 serial composites over a range of 5–45°. No features of AMF162 and AMF1104 are visible in the patterns, only reflections of PP phases can be observed,

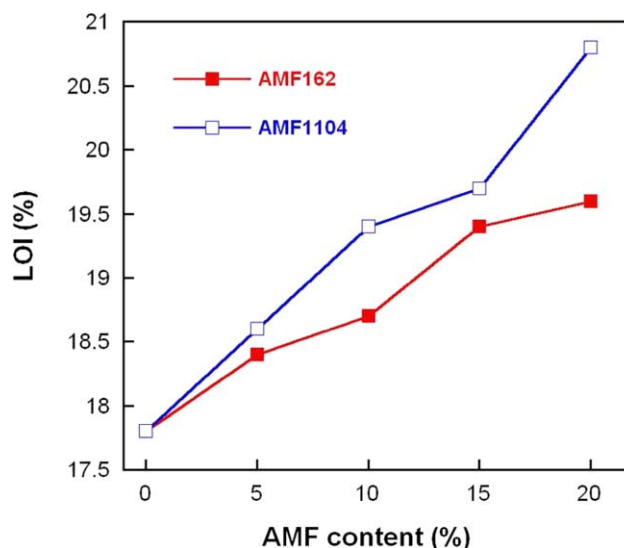


Figure 6. The curves of LOI variation with AMF162 and AMF1104 content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

which indicates that AMF162 and AMF1104 are amorphous and the crystalline phases of PP/AMF composites are ascribed to PP (α -crystal, crystalline peaks at about 14°, 17°, 18.5°, 21°, and 21.8°) (Supporting Information, Table SII).

Limiting Oxygen Index (LOI) of PP/AMF Composites

Figure 6 shows the curves of LOI variation with the contents of AMF162 and AMF1104. The LOI of PP composite is higher than that of pure PP. Moreover, with the increases of the contents of AMF162 and AMF1104, the LOI of PP-AMF composite is rising. The LOI of pure PP is 17.8%. The LOI of PP-AMF162 is 19.7% when the AFM162 content is 20 wt %. The LOI of PP-AMF1104 is 20.8% when the AFM1104 content is 20 wt %. The LOIs of PP-AMF1104 series composites are higher than that of PP-AMF162 series because the molar ratio of the flame retardant of FR in AMF1104 is higher than that in AMF162. Compared with pure PP, flame retarding effect of PP/AMF composites is not significant, mainly because the content of flame retardant unit in the copolymer AMF is relatively low and the charring source wasn't added in PP/AMF composites.

Table I. The ρ_v , ρ_s , and Charpy Unnotched Impact Strength of PP and PP/AMF Composites

Samples	ρ_v (Ω cm)	ρ_s (Ω)	Charpy unnotched impact (KJ m^{-2})
PP	1.25×10^{15}	1.54×10^{15}	20.42 ± 0.15
PP-AMF162-5	2.55×10^{13}	6.60×10^{14}	30.64 ± 0.21
PP-AMF162-10	1.71×10^{12}	9.39×10^{13}	26.98 ± 0.17
PP-AMF162-15	2.17×10^{11}	1.69×10^{13}	23.57 ± 0.25
PP-AMF162-20	6.02×10^{10}	9.23×10^{12}	15.48 ± 0.27
PP-AMF1104-5	7.86×10^{14}	7.42×10^{14}	25.47 ± 0.19
PP-AMF1104-10	2.91×10^{14}	5.93×10^{14}	19.77 ± 0.30
PP-AMF1104-15	3.59×10^{13}	4.0×10^{14}	16.50 ± 0.24
PP-AMF1104-20	6.12×10^{12}	1.33×10^{14}	11.80 ± 0.18

Antistatic Properties of PP/AMF Composites

Table I shows the effect of the content of copolymers (AMF162 and AMF1104) on the ρ_V and ρ_S of series composites (PP-AMF162 series and PP-AMF1104 series). The ρ_V and ρ_S of pure PP were $1.25 \times 10^{15} \Omega \cdot \text{cm}$ and $1.54 \times 10^{15} \Omega$, respectively. With the increase of the content of AMF162, the ρ_V and ρ_S of the PP-AMF162 series composites decrease gradually. When the AMF162 content is 20 wt %, the ρ_V of the PP-AMF162 series composites is decreased to $6.02 \times 10^{10} \Omega \cdot \text{cm}$, which is five orders of magnitude less than that of pure PP. The ρ_S of the PP-AMF162 series composites is decreased to $9.23 \times 10^{12} \Omega$, which is three orders of magnitude less than that of pure PP. The higher the antistatic agent AMF162 content is, the better the antistatic properties of PP-AMF162 series composites are. With the increase of the content of antistatic agent AMF162, the content of the antistatic unit increases in the matrix, resulting in improved antistatic properties. Similarly, with the increase of the content of AMF1104, the ρ_V and ρ_S of the PP-AMF1104 series composites decrease gradually. However, the ρ_V and ρ_S of PP-AMF162 series samples were significantly lower than those of PP-AMF1104 series samples. The antistatic effect of the resulting antistatic agent AMF is mainly attributed to the ether bond in AS unit. The content of AS unit in copolymer AMF162 is almost two times of that in copolymer AMF1104. Therefore, the antistatic effect of PP-AMF162 series samples is better than that of PP-AMF1104 series composites. According to the military handbook DOD-HDBK-263,^{24,25} the antistatic material has a ρ_S between 10^9 and $10^{14} \Omega \cdot \text{sq}$. Therefore, the PP/AMF162 samples have reached the antistatic material requirement.

Mechanical Properties of PP/AMF Composites

Table I listed the Charpy unnotched impact strengths of PP, PP-AMF162 series and PP-AMF1104 series composites. With the increase of the content of AMF162, the impact strengths of the samples firstly increase and then decrease slowly. The impact strength of pure PP is 20.42 KJ m². When AMF162 content is 5 wt %, the impact strength of PP-AMF162-5 reaches its maximum value, 30.64 KJ m². The impact strengths of PP-AMF162-10 and PP-AMF162-15 are lower than that of PP-AMF162-5, but still higher than that of pure PP. When the AMF162 content is increased to 20 wt %, the impact strength of the sample is significantly decreased to only 15.48 KJ m². When the content of AMF162 is low, AMF162 has good miscibility with PP, which can improve the impact strengths of PP composites. The miscibility of AMF with PP becomes worse with the increase of AMF content in PP, which leads to the decrease of impact strength. Similarly, with the increase of the content of AMF1104, the impact strengths of the samples firstly increase and then decrease slowly. When AMF1104 content is 5 wt %, the impact strength of PP-AMF1104-5 reaches its maximum value of 25.47 KJ m². The impact strengths of PP-AMF1104-10, PP-AMF1104-15, and PP-AMF1104-20 are lower than that of pure PP.

CONCLUSIONS

By adjusting the molar ratios of antistatic monomer of AS, flame-retardant monomer of FR, and rigid monomer of MMA, a series of phosphorus-containing flame-retardant antistatic copolymers were synthesized through radical polymerization.

Then PP-AMF162 series and PP-AMF1104 series composites were prepared respectively by adding the copolymers AMF162 and AMF1104 into PP according to different mass fractions of 5, 10, 15, and 20 wt %, respectively. With the increases of the contents of AMF162 and AMF1104 in PP, the LOIs of PP composites increase gradually. The flame retardant effect of AMF on PP is unsatisfactory, mainly because of the low content of flame retardant unit and lack of charring source in PP/AMF composites. When AMF162 content in PP is 20 wt %, ρ_V of PP composite is $6.02 \times 10^{10} \Omega \cdot \text{cm}$, which is five orders of magnitude lower than that of pure PP, indicating that PP composites have good antistatic effect and meet the requirements of industrial applications. Flame-retardant antistatic copolymer of AMF162 has little effect on the mechanical properties of PP composites. When the AMF162 content is equal to or <15 wt %, impact strength of PP-AMF162 composites was higher than that of pure PP. AMF162 copolymer is a suitable flame-retardant antistatic additive for PP composites and has potential application in PP. We will test and analyze other mechanical properties of PP-AMF composites and study the structural design of new flame-retardant antistatic copolymers in the next work.

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