

PREPARATION, THERMAL STABILITY AND FLAME RETARDANT PROPERTIES OF HALOGEN-FREE POLYPROPYLENE COMPOSITES

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Abstract

In this study, flame retardant which contained phosphorus and nitrogen was successfully prepared. The kind of halogen free flame retardant was blended with polypropylene (PP) by hot melt to improve the flame retardant and thermal stability of the composites. Fourier transform infrared spectroscopy (FTIR), energy dispersive X-ray (EDX), thermogravimetric analysis (TGA), limiting oxygen index (LOI) and UL-94 were used to characterize the structure, thermal and flame retardant property of the composites. When the concentration of flame retardant was 40 wt %, the LOI value of composite was 40 and passed V-0 rating of UL-94 test. LOI and UL-94 data showed the composites possess excellent flame retardant property.

1 Introduction

Polypropylene (PP) is a widely used thermoplastic material because of its excellent mechanical properties, low density, good chemical resistance and ease of processing. It is used in many fields, such as building materials, automobile, electrical appliance and so on. However, its inherent flammability has limited its widespread applications in some fields where good flame retardancy is required. Most of the applications require the flame retardancy that can generally be obtained by adding flame retardant additives. Thus great efforts have been made to enhance the flame retardant property of PP in the past several decades [1-6]. Traditionally, halogen-containing compounds with antimony trioxide as a synergistic agent are the main flame retardants of PP, but some of them are limited in use because of the evolution of toxic gases and corrosive smoke during combustion. Now halogen-free compounds are regarded as promising flame retardants due to their environmentally friendly properties [7-11].

The purpose of this study is to synthesize novel flame retardant containing phosphorus and nitrogen that concentrates all of the two elements in itself. The single additive leads to a good miscibility with polymer matrix and good interface stability, at the same time, the addition amount of the flame retardant would decrease much more. Effects of this compound on the flame retardancy and thermal stability were examined by TGA, LOI and UL-94 measurement.

2 Experimental

2.1 Materials

Pentaerythritol (PER) was obtained from the Acros Organics Co., Janssens Pharmaceuticaan, Geel, Belgium. Phosphoric acid was obtained from the Union Chemical Works Ltd, Taiwan. Hexamethoxymethylmelamine (HMMM) was supplied by the Cytec Industries Inc., Taiwan. p-Toluenesulfonic acid (p-TSA) was purchased from the Showa Chemical Co. Ltd, Japan. Polypropylene (PP) with M.W. 135,700, m.p. =180°C was supplied as pellets by Chi-Mei Plastics Company, Taiwan.

2.2 Preparation of flame retardant containing nitrogen and phosphorus (N-P)

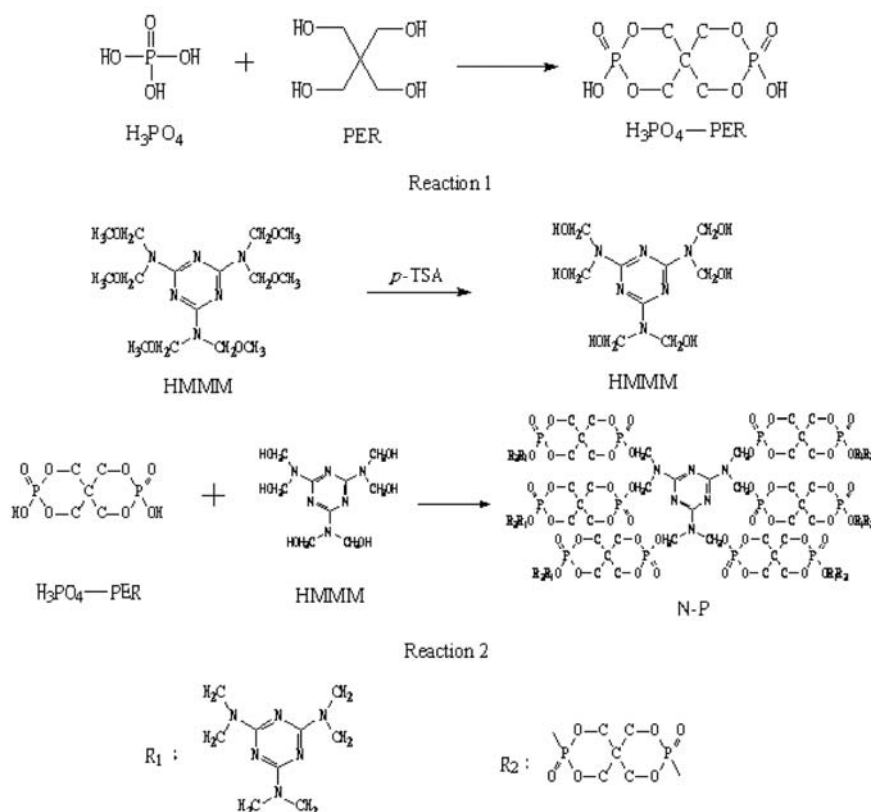
8.5 g H₃PO₄ and 5.86 g PER (equivalent weight ratio=1:1) were added into the sample bottle and stirred mechanically at 120°C for 4 hours to form H₃PO₄-PER. 5.64 g HMMM and 0.17 g p-TSA were poured into H₃PO₄-PER at 120°C for 3 hours to produce flame retardant, N-P.

2.3 Preparation of PP /N-P composites

All samples were mixed as 50 g batches of PP with the desired amounts of N-P for 8 min at 180°C using Brabender mixer. The resulting mixtures were then compression molded at 185 °C into sheets (3 mm thickness) under a pressure of 9 MPa for 10 min. The sheets were cut into suitable size specimens for fire testing.

2.4 Reaction schemes

The novel composites materials were prepared as described in scheme 1 :



Scheme 1. Reaction scheme of the N-P

3. Results and Discussion

3.1 Characterization of flame retardant

Reaction 1 of scheme 1 presents the reaction between H_3PO_4 and PER to form the H_3PO_4 -PER. Figure 1 shows the FT-IR spectra of PER and H_3PO_4 . The region of $3500\text{--}3300\text{ cm}^{-1}$ corresponds to the absorption bands of -OH. The peaks at 839 and 1020 cm^{-1} are attributed to the -P-O-C- bonds [12-15]. The peak at 1390 cm^{-1} is associated with the bending mode of -P=O. The band at 476 cm^{-1} is assigned to the bending mode of O=P-O- group [16]. The peaks between 2980 and 2875 cm^{-1} can be assigned to -CH₂- bands. The phenomena confirm the reaction between PER and H_3PO_4 .

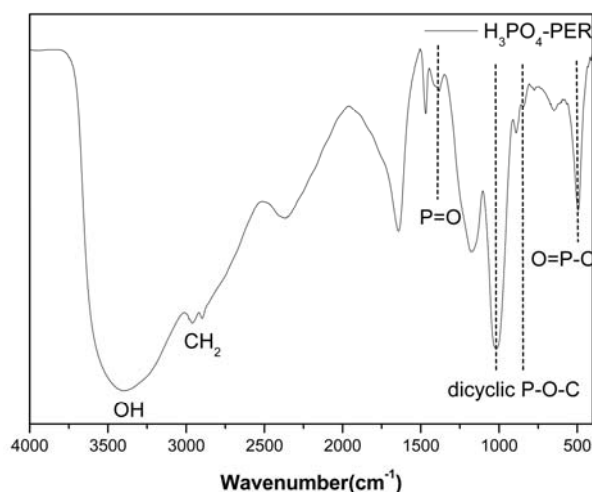


Figure 1 The FT-IR spectra of PER and H_3PO_4 .

Reaction 2 of scheme 1 presents the reaction between H_3PO_4 -PER and HMMM to form the N-P flame retardant. Figure 2 presents the FT-IR spectra of N-P. The peak at 1500 cm^{-1} can be assigned to -N=C- in the triazine ring. The peak at 800 cm^{-1} is attributed to the skeleton vibration of the triazine ring of HMMM [17-18]. The characteristic peaks also can be found in the figure. The intensity of -OH functional group of H_3PO_4 -PER decreases obviously, it means H_3PO_4 -PER had reacted with HMMM to form N-P flame retardant.

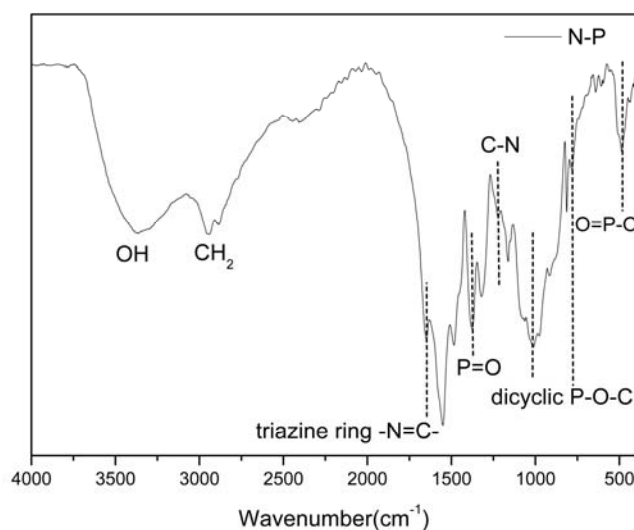


Figure 2. The FT-IR spectra of N-P

3.2 Thermal stability of composites

Thermogravimetric analysis (TGA) is one of the commonly used techniques for rapid evaluation of the thermal stability of different materials, and also indicates the decomposition of polymers at various temperatures. Figure 3, 4 and Table 1 show TGA, DTG and thermal properties of PP/N-P composites with various contents from room temperature to 800°C in nitrogen atmosphere. The thermal degradation behaviour of PP showed only one peak of PP backbone decomposition at 466 °C, and the maximum rate of decomposition was very fast (32.3 %/°C). For the composite containing 40 wt%, the maximum rate of decomposition decreased to 15.0 %/°C. It means that the formed char can slow down the speed of thermal degradation. For PP/N-P composites, the initial decomposition temperatures (IDT) at which the weight loss exhibits 5 wt%, noted as IDT, are lower than that for pure PP because the decomposition of N-P occurred at lower temperature. When the samples were heated under nitrogen atmosphere, the phosphorus-containing groups decompose to dehydrate the char source-containing groups before PP matrix began to degrade [19-20]. After IDT, the degradation process of PP is retarded with N-P, depending on the loading of N-P. This phenomenon might be attributed to the formation of more stable char. There is no char residue remaining in PP over 500 °C. The char yields of the PP/N-P composites increase with increasing N-P components. It means the thermal stability of composites is better than that of pure PP resin during high temperature period. The main decomposition peak of PP took place at 466 °C, while the main decomposition peak of PP in PP/N-P composites system appeared at 483 ~ 491 °C. This was probably attributed to the fact that the endothermic reactions took place in N-P charring process and char layer formed by flame retardant prevented heat from transferring into inside of PP/N-P system.

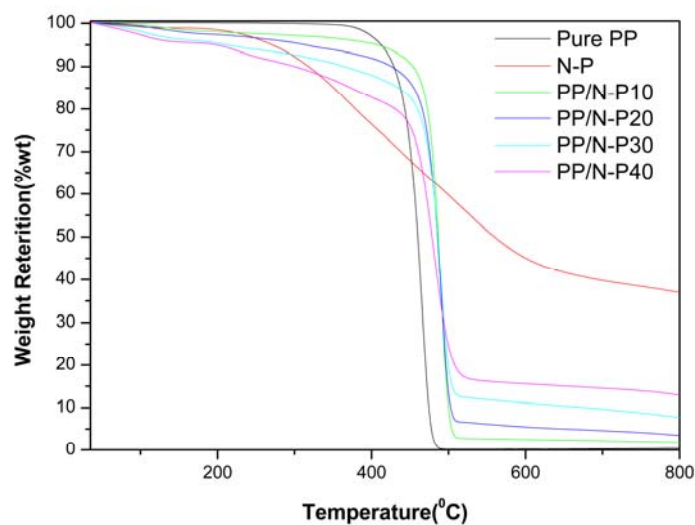


Figure 3 TGA of PP/N-P with various contents (wt%)

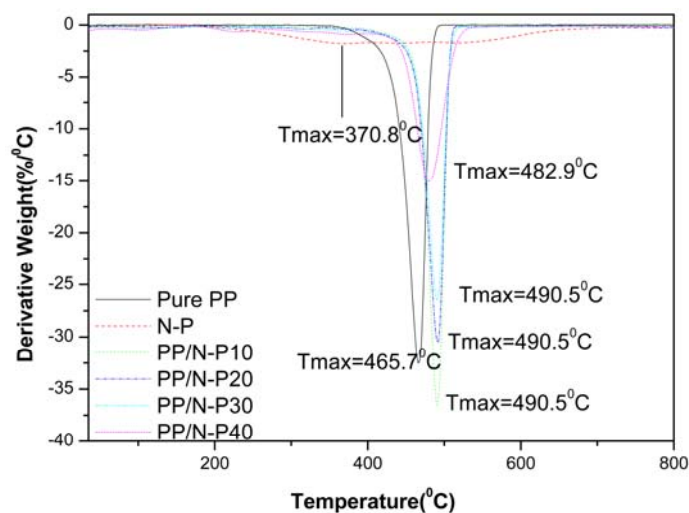


Figure 4 Derivative curves of PP/N-P composites with various contents (wt%)

Sample No.	T_{d5} (°C)	T_{max} (°C)	R_{max} (wt%/°C)	T_g (°C)	IPDT (°C)	Char (wt%)
Pure PP	416.2	465.7	-32.3	20.8	456	0.4
N-P	270.5	370.8	-1.8	—	1177	37.2
PP/N-P10	416.2	490.5	-36.7	19.3	496	1.9
PP/N-P20	324.6	490.5	-30.5	18.3	512	3.5
PP/N-P30	231.1	490.5	-26.6	17.8	556	7.7
PP/N-P40	204.3	482.9	-15.0	17.5	615	12.9

* R_{max} : Maximum thermal degradation rate

Table 1. Thermal properties of PP/N-P composites

The integral procedure decomposition temperature (IPDT) proposed by Doyle [21] involves the volatile parts of the polymeric materials and is used to estimate the inherent thermal stability of the polymeric materials [22-23]. From Table 1, the IPDT of pure PP was 456 °C and the IPDTs of composites were higher than that of pure PP. The thermal stability of the composites increased with the N-P contents. The inorganic components improve the thermal stability of pure PP.

Figure 5 shows the experimental and calculated TGA curves for PP/N-P30 composite. The calculated data (M) is a linear combination of the TGA curves of the individual components of the mixture,

$$M = 70\% \times A + 30\% \times B$$

where A and B are the TGA data of neat PP and pure N-P, respectively. Thus M is representative of a non-interacting phenomenon between PP and N-P. The thermal decomposition behaviour differs from the expectation based on the decomposition behaviour of the mixture by comparing experimental and calculated thermograms, which is probably responsible for the flame retardant effect. According to the experimental curve in Figure 5, it was found out that the amount of char from the experimental data was higher than that of the calculated curve during the whole thermal degradation process. PER played the role of char former. H_3PO_4 was used as the catalyst during the combustion period. This is important evidence that N-P interacts with polymer matrix because the flame retardant formulation gives significant amount of solid residue compared with the calculated formulation of the

mixture [24]. All the above-mentioned results well demonstrated that the N-P flame retardant was an excellent char-forming agent and had significant contribution to the fire retardancy of resin.

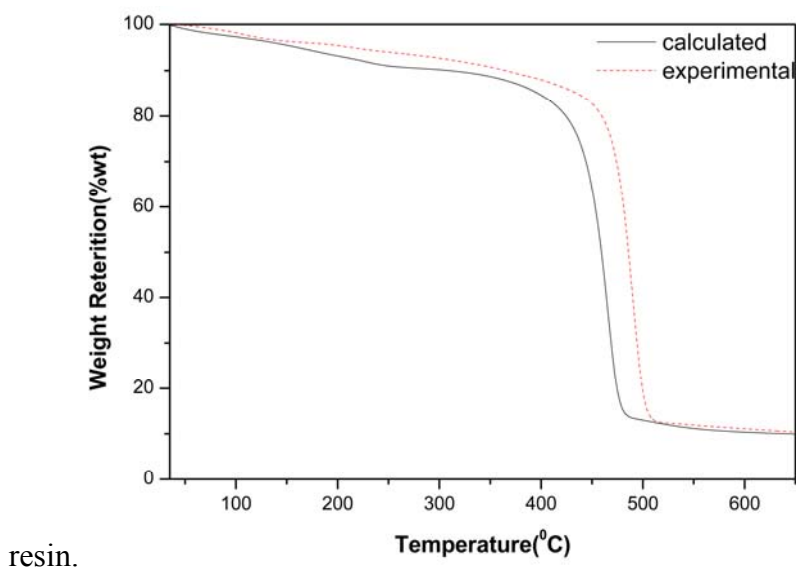


Figure 5 Comparison of experimental and calculated TGA curves for PP/N-P 30.

3.3 Flame retardant property of composites

The LOI values and UL-94 testing results of the PP/N-P composites are presented in Table 2. The percentage of oxygen in the O₂ and N₂ mixture, just sufficient to sustain the flame, is taken as the limiting oxygen index (LOI). The LOI value could be used to estimate the flame-retardant properties of material. It can be seen that the LOI values of PP/N-P composites are higher than that of pure PP resin and the UL-94 ratings of the composites are improved significantly. The samples of the PP/N-P30 and PP/N-P40 composites can pass the V-0 rating (short burning time and no dripping) shown in Table 2. PP is one kind of thermoplastic, it easily happens to drip during the combustion period. This will result in the spread of fire. Obviously, the N-P flame retardants can improve the dripping phenomena and raise the fire safety property. From Table 2, PP is easily flammable and its LOI is only 18. When N-P was 20 wt %, LOI reached 23. It means the composite is self-extinguishing level. When N-P concentration was 30 wt %, the LOI value of composite was 34, which was more than 26. It revealed the composite is flame retardant level. Figure 10 presents those LOI values of the PP/N-P composites increase with the increase with N-P contents. There is linear relationship between LOI and amounts of flame retardant components (N+P wt %). From Δ LOI data, we conclude that the N-P flame retardants can greatly improve the flame retardant property of composites. The above phenomena may be explained as follows. Phosphorus-containing compounds start to decompose and the protective phosphorus-carbon layer begins to form as a result of the weak phosphate bonds. The carbon layer could hold back the flammable gases of pyrolysis to arrive at the fire, and isolate the heat away from the unburned matrix. The nitrogen-containing compound in the sample decomposes to produce ammonia or other molecules. The high heat-insulating, heat-resistant products and incombustible ammonia gases from the thermal degradation of melamine have a substantial influence on reducing the flammability of material.

Sample No.	N-P (wt%)				UL-94		LOI	Δ LOI
	Total	P	N	P+N	Ranking	Dripping		
Pure PP	0	0	0	0	Fail	Yes	18	0
N-P 10	10	1.4	0.6	2	Fail	Yes	20	2
N-P 20	20	2.7	1.2	3.9	Fail	No/Yes ^a	23	5
N-P 30	30	4.1	1.8	5.9	V-0	No/No	34	16
N-P 40	40	5.4	2.4	7.8	V-0	No/No	40	22

^aNo/Yes corresponds to the first/second flame application.

Table 2. The flame retardance of the PP/N-P composites by UL-94 and LOI values.

4. Conclusions

PP/flame retardant containing nitrogen and phosphorus composites were prepared successfully. The structure of flame retardant was characterized using FTIR spectroscopy. The thermal stability of PP composites exceeds that of pure resin from TGA, T_{d5} and IPDT. LOI and UL-94 revealed distinct synergistic effects for flame retardant property. Incorporating nitrogen and phosphorus into the resin promoted the thermal stability and flame retardant property of PP.

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