Article

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Preparation, thermal stability and flame-retardant properties of halogen-free polypropylene composites

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Abstract

A flame retardant containing phosphorus and nitrogen was prepared. This halogen-free flame retardant was blended with polypropylene (PP) by hot melting to improve the flame-retardant capability and thermal stability of the composites. Fourier transform infrared spectroscopy, energy dispersive X-ray measurements, thermogravimetric analysis, limiting oxygen index (LOI) measurements, and UL-94 measurements were applied to characterize the structure and thermal and flame-retardant properties of the composites. When the flame-retardant concentration was 40 wt%, the LOI value of the composite was 40, passing the V-0 rating of the UL-94 test. The LOI and UL-94 data showed the composites have an excellent flame-retardant property. For a kinetic study of thermal degradation, Ozawa's method was applied to calculate the activation energies of pure PP and the composites. Analytical results indicate that the composites had higher values, meaning they have better thermal stability.

Keywords

polypropylene, flame retardant, halogen free, thermal stability, composite

1. Introduction

Polypropylene (PP), a widely used thermoplastic material in many applications, such as in building materials, automobiles, and electrical appliances, has excellent mechanical properties, a low density, good chemical resistance, and is easily processed. However, its inherent flammability limits its use in applications that require good flame retardancy. Most applications require a flame retardancy that can generally be obtained by adding flame-retardant additives. Thus, considerable effort has been expended to enhance the flame retardancy of PP over the recent decades.[1–6] Traditionally, halogen-containing compounds with antimony trioxide as a synergistic agent are the main flame retardants for PP; however, some compounds have limited use because they emit toxic gases and corrosive smoke during combustion. Halogen-free compounds are now regarded as promising flame retardants based on their environmentally friendly properties.[7–11]

This study synthesizes a novel flame retardant containing phosphorus and nitrogen to combine the benefits of both. Conventionally, two flame retardants were blended into a polymer matrix to achieve a synergistic effect on flame retardancy. However, this leads to poor dispersion of additives in the polymer matrix. Therefore, a single additive leads to good miscibility with the polymer matrix and good interface stability. At the same time, the amount of flame retardant added can be reduced further. The effects of this compound on flame retardancy and thermal stability are examined by thermogravimetric analysis (TGA),

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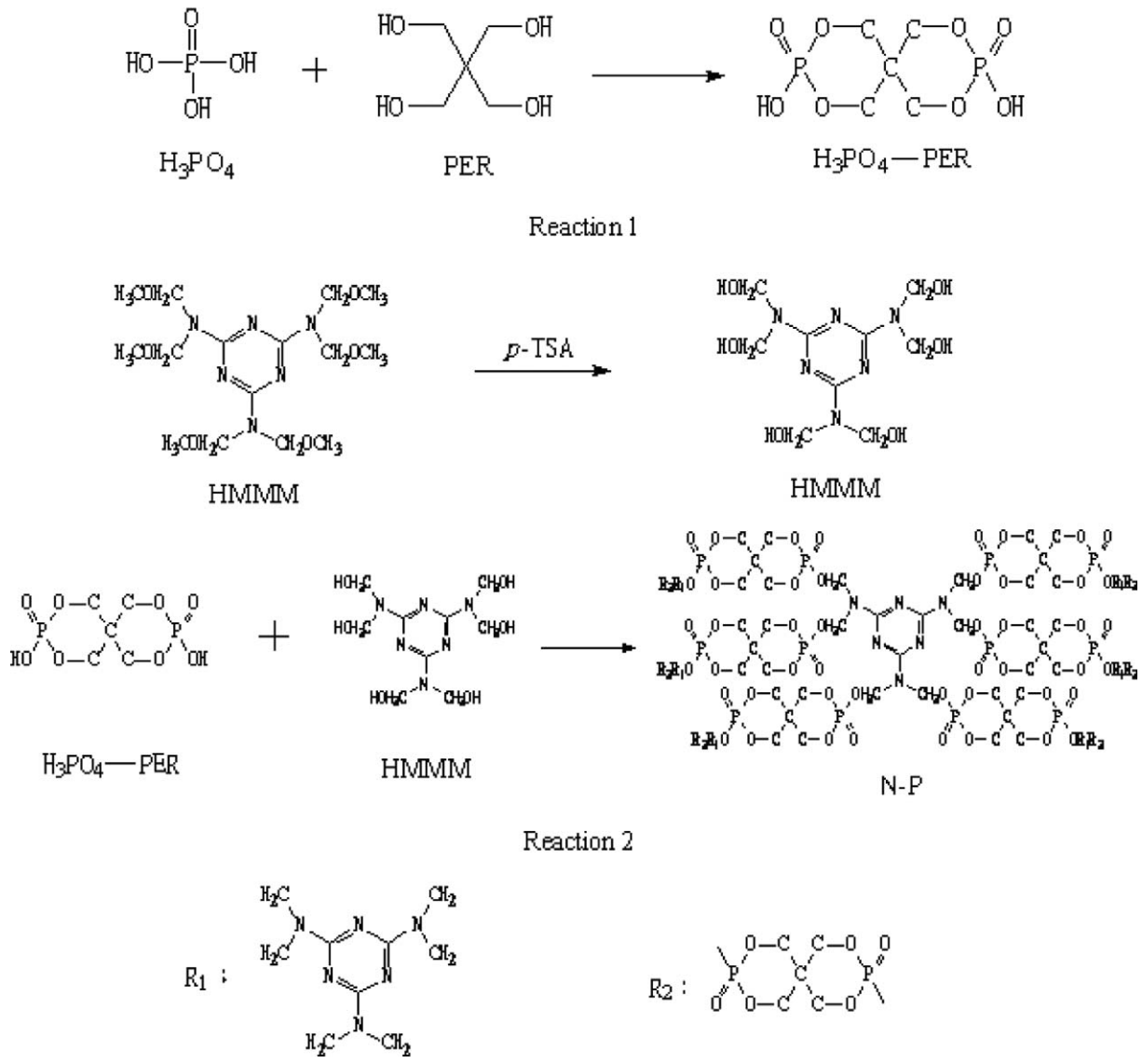

Scheme 1. Reaction scheme of N-P.

limiting oxygen index (LOI) measurements and UL-94 measurements. To kinetically analyze thermal degradation, Ozawa's method is applied to calculate the activation energies of pure PP and that of the composites and to determine whether the thermal stability of the composites is enhanced.

2. Experimental details

2.1 Materials

Pentaerythritol (PER) was obtained from the Acros Organics Co., Janssens Pharmaceuticalaan, 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. PP with M.W. 135,700, m.p. = 180°C, was supplied as pellets by Chi-Mei Plastics Company, Taiwan.

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

In total, 8.5 g H_3PO_4 and 5.86 g PER (equivalent weight ratio = 1:1) were added to a sample bottle and stirred mechanically at 120°C for 4 h to yield H_3PO_4-PER. Then, 5.64 g HMMM and 0.17 g *p*-TSA were mixed with the H_3PO_4-PER at 120°C for 3 h to generate the flame retardant containing nitrogen and phosphorus (N-P).

2.3 Preparation of PP/N-P composites

All samples were mixed with 50 g batches of PP with the desired amounts of N-P for 8 min at 180°C using a

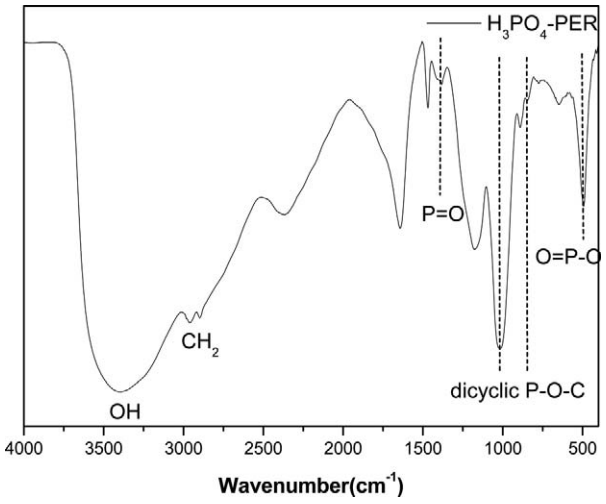

Figure 1. The *Fourier transform infrared* spectra of PER and H_3PO_4.

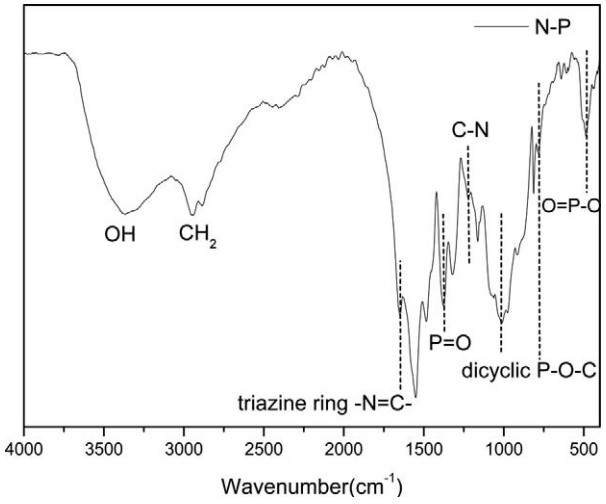

Figure 2. The Fourier transform infrared spectra of N-P.

Brabender mixer. The resulting mixtures were then compression-molded at 185°C into 3-mm-thick sheets under a pressure of 9 MPa for 10 min. The sheets were then cut into suitable sizes for fire testing.

2.4 Reaction schemes

The novel composite materials were prepared as described in Scheme 1.

2.5 Fourier transform infrared spectroscopy

The Fourier transform infrared (FTIR) spectra of reaction products were recorded using a Nicolet Avatar 320 FTIR spectrometer (USA). Thin films were prepared using the solution-casting method. A minimum of 32 scans were signal-averaged with a resolution of 2 cm^{-1} in the 4000–400 cm^{-1} range.

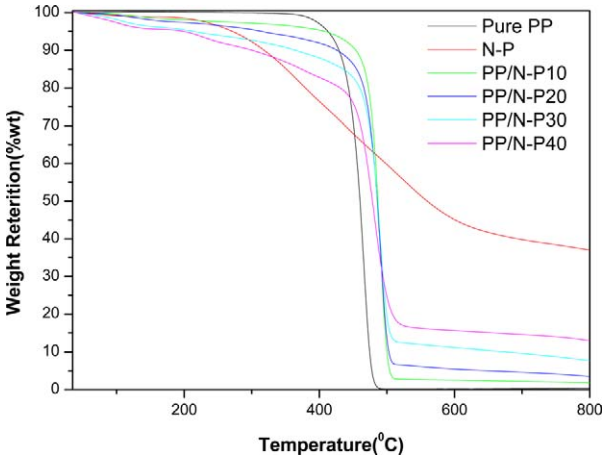

Figure 3. Thermogravimetric analysis of PP/N-P with various contents (wt%).

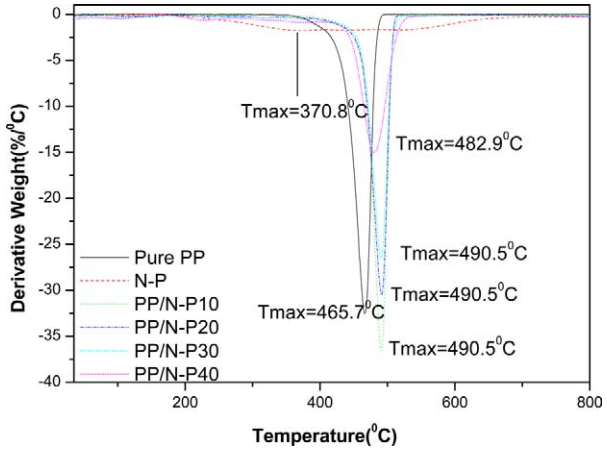

Figure 4. Derivative curves of PP/N-P composites with various contents (wt%).

2.6 Thermal stability test

TGA was conducted using a thermogravimetric analyzer (PerkinElmer TGA 7) by heating samples from room temperature to 800°C at various heating rates under an inert gas flow. The flow of nitrogen gas, the inert gas, was increased at approximately 100 ml/min, and the sample mass in the alumina pan was measured from an initial mass of 6–10 mg.[12–16] Measurement results were used to assess the thermal stability of samples and calculate the activation energy of thermal degradation.

2.7 Limiting oxygen index

The LOI is defined as the minimum fraction of O_2 in a mixture of O_2 and N_2 that will just support flaming combustion.

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

Sample No.	T_{d5} (°C)	T_{max} (°C)	R_{max} (wt%/°C)	IPDT (°C)	Char (wt%)
Pure PP	416	465.7	–32.3	456	0.4
N-P	271	370.8	–1.8	1177	37.2
PP/N-P10	416	490.5	–36.7	496	1.9
PP/N-P20	325	490.5	–30.5	512	3.5
PP/N-P30	231	490.5	–26.6	556	7.7
PP/N-P40	204	482.9	–15.0	615	12.9

R_{max}: Maximum thermal degradation rate

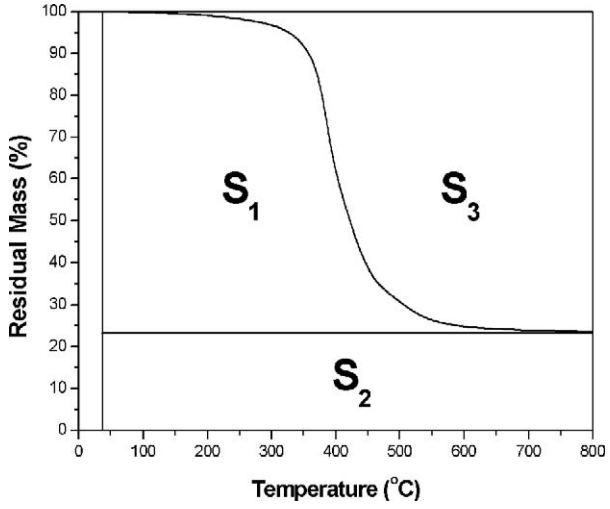

Figure 5. Schematic representation of S_1, S_2, and S_3 for A^* and K^*.

The LOI test was performed according to the testing procedure of the ASTM D 2836 Oxygen Index Method with a test specimen bar 7–15 cm long, 6.5 ± 0.5 mm wide, and 3.0 ± 0.5 mm thick. Sample bars were suspended vertically and ignited using a Bunsen burner. The flame was removed and the timer was started. The oxygen concentration was increased when the flame on the specimen was extinguished before burning for 3 min or when 5 cm of the bar was burned away. The oxygen content was adjusted until the limiting concentration was determined.

2.8 Vertical burning test

The vertical burning test was conducted inside a fume hood. Samples were held vertically with tongs at one end and burned at the free end. Samples were exposed to the ignition source for 10 s, and were then were allowed to burn above cotton wool until both the sample and cotton wool were extinguished. Observable parameters were recorded to determine fire retardancy. The UL 94 test classifies materials as V-0, V-1, and V-2 according to the time period needed before self-extinction and the occurrence of flame dripping after the ignition source is removed. The V-0 classification is the most ambitious and desired classification.

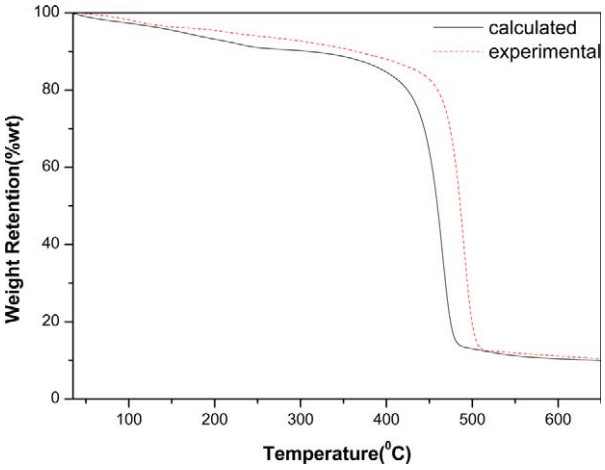

Figure 6. Comparison of experimental and calculated thermogravimetric analysis curves for PP/N-P 30.

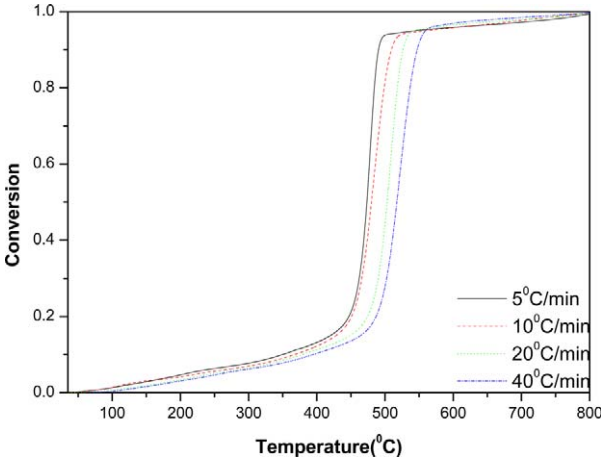

Figure 7. Typical conversion curves of PP/N-P30.

2.9 Energy dispersive X-ray

Energy dispersive X-ray (EDX) measurements were conducted using scanning electron microscope (SEM) EDX mapping (JEOL JSM 840A Japan). The white points in Figure 10 denote P atoms.

3. Results and discussion

3.1 Characterization of flame retardant

Reaction 1 of Scheme 1 was the reaction between H_3PO_4 and PER to form H_3PO_4-PER. Figure 1 shows the FTIR spectra of PER and H_3PO_4. The region of 3500–3300 cm^{-1} corresponds to -OH absorption bands. Peaks at 839 and 1020 cm^{-1} were attributed to the -P-O-C- bonds.[16–19] The peak at 1390 cm^{-1} was associated with the bending mode of -P=O. The band at 476 cm^{-1} was assigned to the bending mode of the O=P-O- group.[20] Peaks between 2980

Table 2. The calculated activation energy of thermal degradation by Ozawa's method.

Activation energy $E\alpha$ (kJ/mole)		
α	Pure PP	PP/N-P30
0.1	133.3	155.2
0.2	151.9	194.1
0.3	162.3	202.0
0.4	166.1	199.3
0.5	167.7	200.4
0.6	164.4	196.7
0.7	170.4	196.1
0.8	174.2	190.4
0.9	174.9	182.5
Average $E\alpha$	162.8	190.7

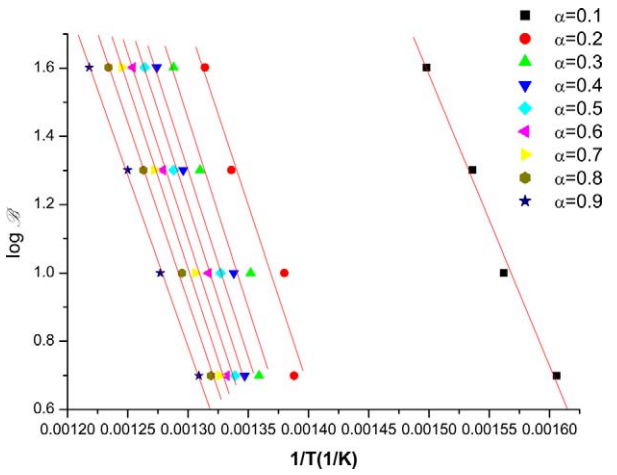

Figure 8. Typical Ozawa plots for the thermal degradation of PP/N-P30 composites.

and 2875 cm^{-1} were assigned to -CH_2- bands. These phenomena confirm the reaction between PER and H_3PO_4.

Reaction 2 of Scheme 1 was the reaction between H_3PO_4-PER and HMMM to form the N-P flame retardant. Figure 2 shows the FTIR spectra of N-P. The peak at 1500 cm^{-1} was assigned to –N=C– in the triazine ring. The peak at 800 cm^{-1} was attributed to the skeleton vibration of the tranzine ring of HMMM.[21,22] Characteristic peaks are also identified in this figure. The intensity of the -OH functional group of H_3PO_4-PER decreased markedly, meaning that H_3PO_4-PER reacted with HMMM to form the N-P flame retardant.

3.2 Thermal stability of composites

TGA, a commonly used technique for rapid determination of the thermal stability of different materials, also indicates the decomposition of polymers at various temperatures. Figures 3 and 4 and Table 1 show TGA, derivative of thermalgravimetry (DTG), and the thermal properties of PP/N-P composites with various contents from room temperature to 800°C in a nitrogen atmosphere. The thermal degradation behavior of PP had only one peak of PP backbone decomposition at 466°C, and the maximum decomposition rate was very fast (32.3%/°C) (Figure 4 and Table 1). For the composite containing 40 wt%, the maximum decomposition rate decreased to 15.0%/°C, indicating that the formed char can slow down the speed of thermal degradation. For the PP/N-P composites, the initial decomposition temperatures (IDTs) at which weight loss was 5 wt% are shown as T_{d5} (Table 1), noted as IDT, and were lower than that for pure PP due to the decomposition of N-P at lower temperatures. When samples were heated under a nitrogen atmosphere, the phosphorus-containing groups decomposed to dehydrate the char source-containing groups before the PP matrix began degrading.[23,24] After the IDTs, the degradation process of PP was retarded by N-P, and depended on the N-P loading. This phenomenon may be attributed to the formation of a char with increased stability. No char residue existed in PP at temperatures exceeding 500°C. The char yields of PP/N-P composites increased as the N-P components increased, meaning that the thermal stability of composites is better than that of pure PP resin at high temperatures. The temperature at which the maximum decomposition rate of PP occurred was 466°C, while those at which the maximum decomposition rate of PP/N-P composites appeared were 483–491°C (Table 1), which were shifted to a high temperature. This is likely attributed to the fact that endothermic reactions occurred during the N-P charring process, and a char layer formed by the flame retardant prevented heat from transferring into inside of the PP/N-P system.

The integral procedure decomposition temperature (IPDT), as proposed by Doyle,[25] involves the volatile parts of polymeric materials and is used to estimate the inherent thermal stability of polymeric materials.[26,,27] IPDT was calculated from

$$\mathrm{IPDT}(^{\circ}\mathrm{C}) = A^{*}K^{*}(T_f - T_i) + T_i \quad (1)$$

$$A^{*} = (S_1 + S_2)/(S_1 + S_2 + S_3) \quad (2)$$

$$K^{*} = (S_1 + S_2)/S_1 \quad (3)$$

where A^* is the area ratio of total experimental curve defined by the total TGA thermogram, T_i is the initial experimental temperature, and T_f is the final the initial experimental temperature. Figure 5 shows a representation of S_1, S_2 and S_3 for calculating A^* and K^*. We use Equation (1) to calculate the IPDT of N-P. The result is 1177°C for N-P, which is flame retardant in this study. This means that N-P possesses excellent thermal stability. It is helpful to promote thermal stability of the composites. The IPDT of pure PP was 456°C and the IPDTs of composites were higher than that of pure PP (Table 1). The IPDT values of the composites increased as the amount of additive increased. The thermal stability of composites increased

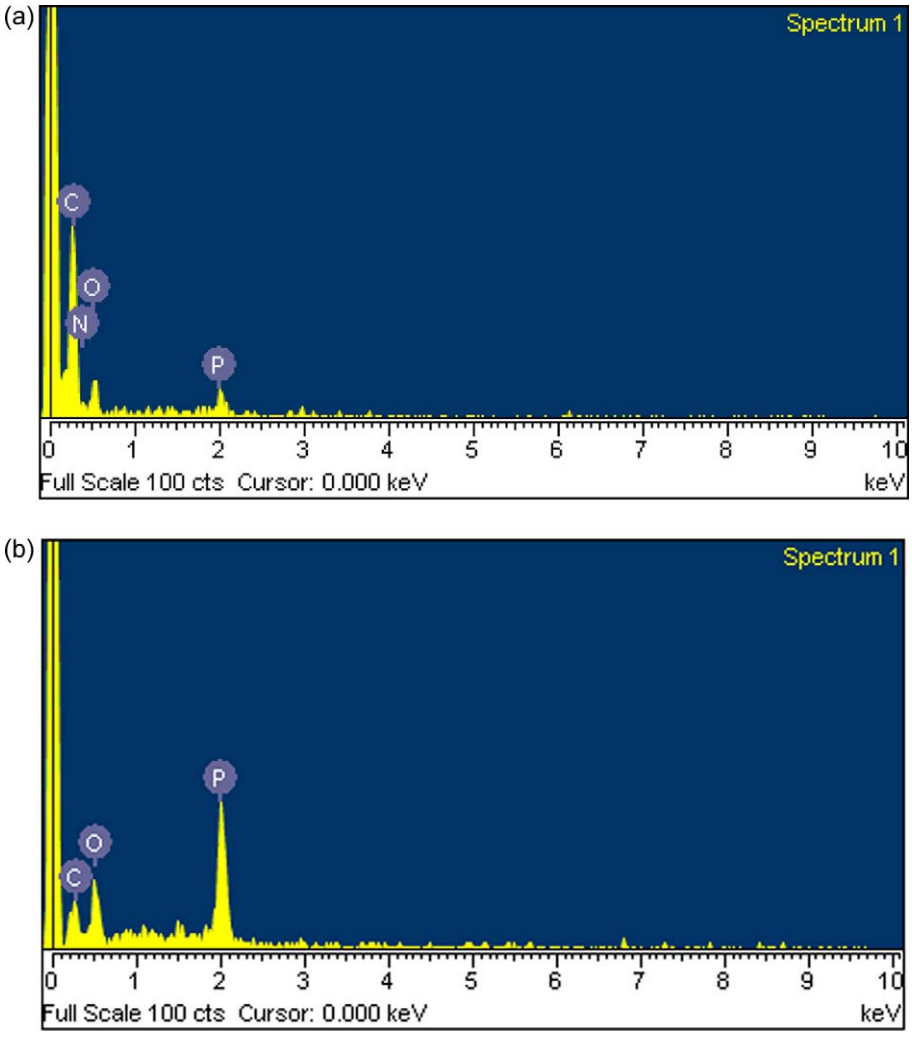

Figure 9. Energy dispersive X-ray measurements of the PP/N-P30 composite (a) before combustion (b) after combustion.

as N-P content increased, indicating that inorganic components enhanced the thermal stability of pure PP.

Figure 6 shows experimental and calculated TGA curves for the PP/N-P30 composite. The calculated data (M) are a linear combination of TGA curves of individual components in a 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 represents a non-interactive phenomenon between PP and N-P. The thermal decomposition behavior differed from expectations based on the decomposition behavior of the mixture by comparing experimental and calculated thermograms, which is probably responsible for the flame-retardant effect. According to the experimental curve (Figure 6), the amount of char from experimental data was higher than that of the calculated curve during the entire thermal degradation process. The PER played the role of char formerly. The catalyst during the combustion period was H_3PO_4. This is important evidence indicating that N-P interacted with the polymer matrix, because the flame-retardant formulation generated a significant amount of solid residue compared with that of the calculated mixture formulation.[28] All these experimental results demonstrate that the N-P flame retardant is an excellent char-forming agent and significantly contributes to the fire retardancy of resin.

Thermal degradation is a chemical reaction. The activation energy of thermal degradation is typically utilized to investigate the energy barrier for thermal decomposition and to quantify the thermal stability of materials. Studying the activation energy of thermal degradation is also used to classify the thermal stability of materials.

The degree of conversion, α, is defined as the ratio of actual weight loss to total weight loss, $\alpha = \frac{m_0 - m}{m_0 - m_\infty}$, where m is the actual weight at time t (or at temperature T); m_0 is initial weight; and m_∞ is weight at the end of isothermal or non-isothermal experiments. Consequently, the rate of degradation, $d\alpha/dt$, depends on the temperature and weight of a sample, as given by Equation (4):

Table 3. Composition for PP/N-P30 composite before and after combustion from energy dispersive X-ray measurements.

	Before combustion		After combustion	
Element	Weight%	Atomic%	Weight%	Atomic%
C	60.40	66.82	33.04	41.75
N	11.40	10.81	9.40	10.18
O	25.58	21.25	43.31	41.08
P	2.62	1.12	14.25	6.98

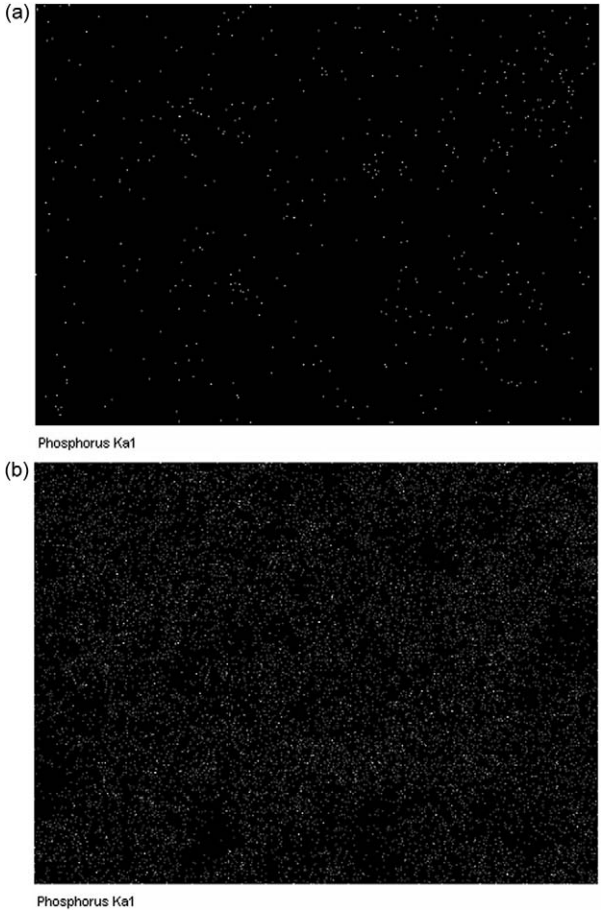

Figure 10. P-mapping of PP/N-P30 composite fractured surface (a) before combustion (b) after combustion.

$$d\alpha/dt = k(T) \times f(\alpha) \tag{4}$$

where $k(T)$ is the rate constant and $f(\alpha)$ is a conversion function.

If $k(T) = A \exp(-Ea/RT)$ and $f(\alpha) = (1-\alpha)^n$, Equation (4) can then be expressed as

$$d\alpha/dt = A\exp(-E_a/RT)(1-\alpha)^n \tag{5}$$

where A is the pre-exponential factor; Ea is activation energy; R is the gas constant; T is absolute temperature, and n is the reaction order:

$$\frac{d\alpha}{(1-\alpha)^n} = \left[\frac{A\exp(-Ea/RT)}{\beta}\right]dT \tag{6}$$

where β is the heating rate

Ozawa's method[29] considers several TGA curves obtained at various heating rates (β). The degree of conversion, α, is defined as the ratio of actual weight loss to total weight loss. From the isoconversion curve, apparent activation energies are calculated from the slopes of lines using the expression

$$Ea = -slope \times {}^{R}/_{0.457} \tag{7}$$

Figure 7 shows the relationship between conversion degree and thermal degradation temperature. The formed char protects the polymer from further degradation. Figure 8 presents Ozawa plots of log β versus $1/T$ for each α value of the composites. Table 2 shows the calculated activation energy of thermal degradation of pure resin and composites using Ozawa's method. Average activation energies of the composites exceeded that of pure PP. These phenomena reveal that incorporating flame retardant into the matrix material promoted the thermal stability of the resin. In composite materials, the thermal degradation process of phosphorus and nitrogen may change. An opposite effect of phosphorus and nitrogen on the activation energy was observed for hybrids degrading in nitrogen. Introducing nitrogen into the formulations increased their activation energies of degradation and phosphorus decreased activation energies. The low activation energy of the hybrid containing phosphorus was due to the weak P-O bonds.[30]

3.3 Combustion behavior of composites

Figure 9 shows the EDX measurements of the PP/N-P30 composite, and Table 3 shows EDX data for the PP/N-P30 composite before and after combustion. Nitrogen-containing compounds are commonly used as flame retardants for phosphorus-containing compounds. These nitrogen-containing compounds produce incombustible gases without toxic smoke or fog when decomposing at high temperatures. The gases emitted can dilute the oxygen concentration near a flame and do no harm the environment. The action of evolved gases can produce protective foam when heated. The foamed char layers are superior

Table 4. The flame retardance of the PP/N-P composites by UL-94 and limiting oxygen index (LOI) values.

	N-P (wt%)				UL-94			
Sample No.	Total	P	N	P+N	Ranking	Dripping	LOI	ΔLOI
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

[a]No/Yes corresponds to the first/second flame application.

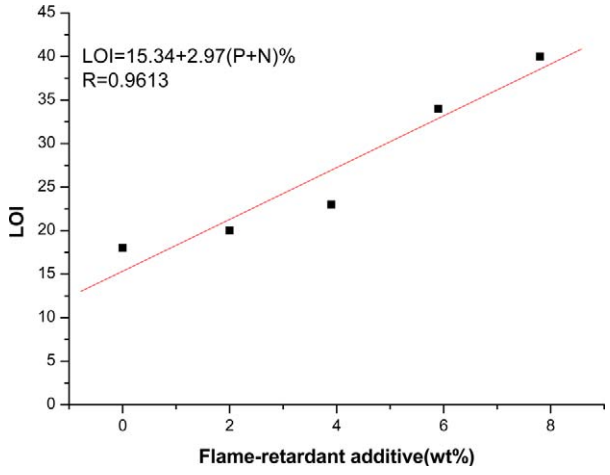

Figure 11. Limiting oxygen index (LOI) values versus the contents of phosphorus and nitrogen of N-P.

barriers that protect the main material against flame and heat.[31,32] Compared with the composite before combustion (Figure 9(a)), the concentration of phosphorus in the composite was high because phosphorus formed a carbonaceous char, preventing further thermal degradation of the PP resin after combustion (Figure 9(b)). Figure 10 shows the P-mapping of the PP/N-P30 composite's fractured surface before and after combustion. The distribution of phosphorus atoms in the char of N-P30 was much denser than that of N-P30 before combustion, indicating that the char layer contains many phosphorus components, and it can enhance char formation. These phenomena agree with EDX data.

3.4 Flame-retardant property of composites

Table 4 lists the LOI values and UL-94 test results for PP/N-P composites. The percentage of oxygen in the O_2 and N_2 mixture, barely sufficient to sustain a flame, was taken as the LOI value. The LOI value can be applied to estimate the flame-retardant properties of a material. The LOI values of PP/N-P composites were higher than that of pure PP resin, and the UL-94 ratings of composites improved significantly. The PP/N-P30 and PP/N-P40 composite samples passed the V-0 rating (short burning time and no dripping) (Table 4). PP is a thermoplastic that drips during combustion, resulting in the spread of a fire. Clearly, N-P flame retardants eliminate dripping and thereby increase fire safety. Notably, PP is easily flammable and its LOI value is only 18 (Table 4). When the N-P concentration was 20 wt%, the LOI value was 23, indicating that the composite is self-extinguishing. When the N-P concentration was 30 wt%, the LOI value of composites was 34, higher than 26. This reveals that the composite is a flame retardant. Figure 11 presents the LOI values of the PP/N-P composites, which increased as the N-P content increased. A linear relationship existed between LOI values and the amount of flame-retardant components (N+P wt%). From ΔLOI data, we conclude that the N-P flame retardants greatly improved the flame-retardant property of composites. These phenomena can be explained as follows. Phosphorus-containing compounds start decomposing and, due to weak phosphate bonds, the protective phosphorus-carbon layer begins to form. The carbon layer can hold back flammable gases during pyrolysis arriving at a fire, and isolate heat from the unburned matrix. The nitrogen-containing compound in the sample decomposed to produce ammonia or other molecules. The high heat-insulating and heat-resistant products and incombustible ammonia gases from the thermal degradation of melamine markedly influence reduction of the flammability of a material.[33]

4. Conclusions

The PP/flame-retardant composites containing nitrogen and phosphorus were prepared. The structure of the flame retardant was characterized by FTIR spectroscopy. The thermal stability of PP composites exceeded that of pure resin based on TGA, T_{d5}, and IPDT results. Activation energies of composites, determined using Ozawa's method, were higher than that of resin during thermal degradation. The LOI and UL-94 reveal distinct synergistic effects for the flame-retardant property. Incorporating nitrogen and phosphorus into the resin promoted the thermal stability and flame-retardant property of PP.

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