Synergistic Effect of Phosphorus, Nitrogen, and Silicon on Flame-Retardant Properties and Char Yield in Polypropylene

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ABSTRACT: In this study, several flame retardants (FRs), containing phosphorus, nitrogen, and silicon, were synthesized. These synthesized FRs were blended with polypropylene (PP) to obtain mixture samples. The flame-retardant properties of these mixture samples were estimated by the limiting oxygen index (LOI) value and thermal stabilities were characterized by thermogravimetric analysis. The LOI values of these samples were improved from 17.0 to 26.0 and the char yield increased from 0 to 27 wt %. A comparison of these samples, with respect to their LOI values and carbon yield, showed that the FRs, which simultaneously contained phosphorus, nitrogen, and silicon elements, can provide materials with the best flame-retardant properties, suggesting that there is a synergistic effect among the three elements on the flame-retardant properties and char yield when they are used in PP. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 854–860, 2005

Key words: flame retardance; char yield; thermogravimetric analysis (TGA); polypropylene (PP); synergistic effect

INTRODUCTION

Polypropylene (PP) is widely used in many aspects because it is easily processed into products of various shapes with strong tensile stress and high strain at break to meet the requirements of versatile and advanced applications. However, PP is easy to combust and drip when it is ignited, thus making it difficult to be used in some ways that require flame-retardant performance. To increase the flame-retardant property of the material, flame retardants (FRs) are often added to PP. Usually, FRs are classified into halogen-containing FRs and halogen-free FRs. Halogen-containing FRs can provide the material with effective flame-retardant properties, although their uses in polymers are limited because of their productions of toxic, corrosive, and halogen gases and the release of toxic, endocrine-disrupting chemicals during combustion. On the contrary, the halogen-free FRs are environmentally friendly because they generate fewer toxic substances during fire. They have been widely studied in recent years and are mostly used to replace halogen FRs. The common halogen-free FRs include organophosphorus compounds, nitrogen-containing compounds, and organosilicon compounds.[1–4]

Phosphorus-containing compounds are considered to be among the most effective flame retardants, as demonstrated in many recent studies.[5–9] This kind of FRs is characterized by a highly efficient degree of flame retardancy. Their products of decomposition are less toxic and corrosive, and do little damage to the environment during fire. By modifying their process of thermal decomposition, they can provide polymers with a flame-retardant characteristic.[7,9] Phosphorus-containing compounds decompose at a lower thermal temperature than that of basic polymers because of the weak bonds of phosphorate.[10] They can change the chemical reactions of decomposition, in favor of reactions yielding carbon rather than CO or CO_2. They form a surface layer of protective char during fire before the unburned structure materials begin to decompose.[3,10–13] The protective char could isolate the oxygen in the air and the heat away from the polymer matrix, holding back the decomposing molecule from transport onto the surface to be exposed to the fire.[10–13] However, FRs containing only phosphorus scarcely confer sufficient flame-retardant property to polymers to meet the application requirements.

The nitrogen-containing compounds are usually used as FRs with phosphorus-containing compounds. They produce incombustible gases without toxic smoke and fog when decomposing at high temperature. The gases can dilute the concentration of the oxygen near the flame and do no harm to the environment. The action of the evolved gases could foam the protective layer while heating. The foamed char layers serve as superior protective barriers to the main material against flame and heat.[14,15]

The silicon-containing compounds are considered to be one of the "environmentally friendly" flame-retardant materials. Their products do not pollute the environment during fire. They can concentrate onto the surface of the material during fire because of their low surface energy. Their products are silica carbon with high thermal stability during fire. Silica carbon can form a protective silica layer and protect the polymer residue from further thermal decomposition at high temperatures. Some studies in the literature reported that silicone-containing polymers [e.g., polydimethylsiloxanes (linear type)] were blended with other polymers, although the results showed that they themselves do not have sufficient flame-retardant properties to meet application requirements.[16–18]

Moreover, as mentioned above, any of phosphorus, silicon, and nitrogen elements could be used as an environmentally friendly flame-retardant element because their products are less toxic and generate less smoking and less-corrosive gases. They individually provide the material with limited flame-retardant properties, although they could be used alone as flame retardants. The FRs composed of two elements could provide polymers with better flame retardancy than those composed of one element, and the FRs composed of all three offer the best flame retardancy. When the FRs simultaneously contained the three flame-retardant elements, there is some synergistic effect among the three elements. The reason for the synergistic effect is that phosphorus offers the tendency of char formation, nitrogen foams the protective char, and silicon provides the thermal stability of the forming char during fire.[4,11,19–21] This article reports the investigation of the synergistic effect of the three elements on flame retardancy and char yield of polymers.

EXPERIMENTAL

Materials

Phosphorus oxychloride ($POCl_3$) was purchased from Tingxin Chemical Industry Corp. of China (Shanghai, China). 2,2-Dimethyl-1,3-propanediol (neopentyl glycol), potassium hydroxide (KOH), tetraethoxysilane (TEOS), and trichoromethane ($CHCl_3$) were acquired from Shanghai Chemical Agent Corp. The α,ω-dihydroxide polydimethsiloxane (PDMS) was received from Shanghai Resin Industry Corp., and N-β-(aminoethyl)-γ-aminopropyl methyl dimethoxysilane (HD-103) was obtained from Shanghai Yehao Chemical Industry Corp. The polypropylene used here was Novatel H57541 [melt index (GB 368283): 2 g/10 min; density: 0.918 g/cm^3], supplied by Japan Polychem Corp. (Tokyo, Japan).

Synthesis of PSiN flame retardant

Neopentyl glycol (104 g, 1 mol) and 300 mL $CHCl_3$ were charged to a 500-mL three-neck round-bottom flask with a stirrer, dropping funnel, and rubber pipe to transport the hydrogen chloride into the KOH solution. Phosphorus oxychloride (153.6 g, 1 mol) was added slowly by drops and the temperature was kept at about 0°C during the process. After $POCl_3$ had been added, the temperature was increased to 20–40°C where it was kept for 2 h. Then $CHCl_3$ was removed to obtain a white solid. Later, the obtained product, which is neopentyl glycol phosphonyl chloride (PCII), was heated in the oven under vacuum for 8 h at 60°C.

PDMS and HD-103 were mixed at various ratios with KOH, used as a catalyst in the three-neck round-bottom flask with a stirrer, under nitrogen, when the temperature was controlled between 80 and 100°C. After 2 h, 1 to 5 mL water was added to the flask when the opaque liquid in the flask changed to transparent. After 1 h, the by-products were removed under vacuum for 6 h at around 80°C. The product obtained was labeled Si—N.

PCII was dissolved in $CHCl_3$. The solution was added to the three-neck round-bottom flask with a stirrer while the temperature was controlled at 18–25°C. The Si—N was also dissolved in $CHCl_3$ and the solution was added slowly to the flask with the nitrogen stream to release HCl. When the solution had been added, the temperature was kept at 18–25°C for 2 h. The temperature was then increased to 120°C and the solvent was removed under vacuum for several hours. The flame retardants, which contained phosphorus, nitrogen, and silicon—labeled PSiN—were obtained. The various PSiN compounds, which contained the three elements, were obtained by synthesis with various ratios of PDMS, HD-103, and PCII. The PDMS and PCII were used as flame retardants, containing only silicon or phosphorus. The Si—N was used as a silicon- and nitrogen-containing flame retardant. The flame retardant containing P and Si was obtained by blending PDMS and PCII at room temperature.

PP and flame retardants were mixed in a Haake Rheocord 90 internal mixer (Haake, Bersdorff, Germany) to obtain mixtures that were subsequently pressed into sheets of suitable thickness to obtain samples that contained synthesized FRs.

Characterization

The FTIR spectroscopy was performed by use of a Perkin–Elmer Paragon 1000 (Perkin Elmer Cetus Instruments, Norwalk, CT). The limiting oxygen index (LOI) values were measured on a Stanton–Redcroft LOI FTA II–type instrument (Fire Testing Technology, East Grinstead, UK) according to ASTM D 2863. The
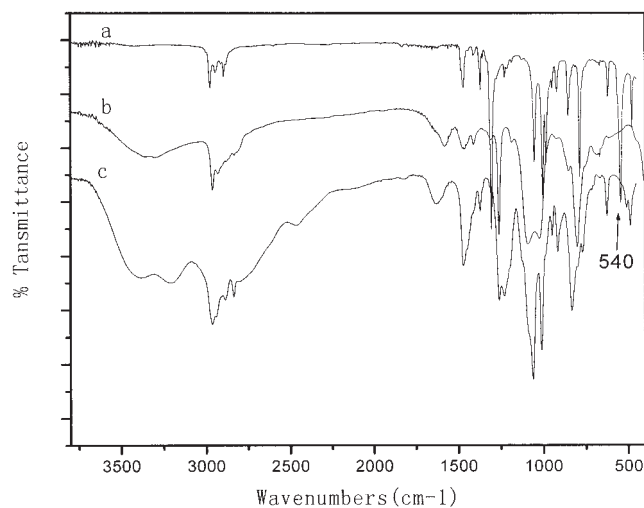
Figure 1 FTIR spectra of the synthesized flame retardant: (a) PCII; (b) Si-N; (c) PNSi.

thermogravimetric analysis (TGA) was performed using a Perkin–Elmer 7 Series Thermal Analyzer at a heating rate of 20°C/min under a nitrogen atmosphere, and the temperature ranged from room temperature to 800°C.

RESULTS AND DISCUSSION

Figure 1 presents the FTIR spectra of the synthesized compounds. Curve (a) is the FTIR spectrum of PCII and the absorptions are observed at 2900–2980 cm^{-1} for –CH$_2$–and –CH$_3$, 1300 cm^{-1} for P=O, 1000–1100 cm^{-1} for P—O—C,[22] and 540 cm^{-1} for P—Cl.[23] Curve (b) is the FTIR spectrum of the synthesized Si—N. The absorptions are observed at 3100–3400 cm^{-1} for –NH– and –NH$_2$–, 2800–3000 cm^{-1} for –CH$_2$– and –CH$_3$, 1260 and 1000–1100 cm^{-1} for Si—O—Si, and 800 cm^{-1} for Si—C.[24] Curve (c) is the FTIR spectrum of one of the synthesized FR composed of phosphorus, nitrogen, and silicon. The absorptions are: 3300–3400 cm^{-1} for –NH–, 2800–3000 cm^{-1} for –CH$_2$– and –CH$_3$, 1260

and 1000–1100 cm^{-1} for Si—O—Si, 1200–1230 cm^{-1} for P=O, and 1000–1100 cm^{-1} for P—O—C. The absorption of the PCII at 540 cm^{-1} is not observed in the FTIR curve of the PSiN, which suggests that the P—Cl chemical bonds disappeared and the new chemical bonds were formed.

These obtained FRs were blended with PP at a total amount of 30 wt % additive, which was kept constant. All the samples are presented in Table I. The percentage of oxygen in the O$_2$ and N$_2$ 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. The flame retardancy of the samples increases with their increasing LOI values. The LOI values of these samples are shown in Table I, and the contents of the three kinds of flame-retardant elements in the material are also presented here. As shown in Table I, the LOI values increased from 17.0 to 26.0 with the various FRs at the same total loading. The maximal enhancement reaches 44.4%. For the compounds with only phosphorus or silicon flame-retardant elements, the enhancement of LOI value is limited, as shown by samples P–Si-1 and P–Si-2 in Table I. However, the LOI values could be slightly increased when the compounds contained two flame-retardant elements: the silicon and the nitrogen elements or the phosphorus and the silicon elements, which are shown by the P–Si-3, P–Si-4, and P–Si-5 in Table I. When the FRs are composed of three flame-retardant elements at the same time, the LOI values increased further with the same total weight loading, which improved to 26.0 when the flame retardant contained 4.4 wt % of phosphorus, 2.0 wt % of silicon, and 1.0 wt % of nitrogen, as shown by P–Si-7 in Table I.

Figure 2 presents the LOI values versus the weight concentration of phosphorus-containing compounds in the PP/PSiN blend samples with the same total loading of 30 wt % obtained FRs. The curve AEFGB indicates that the LOI values of the samples containing three flame-retardant elements simultaneously change

TABLE I
Different Components and LOI Values of Samples

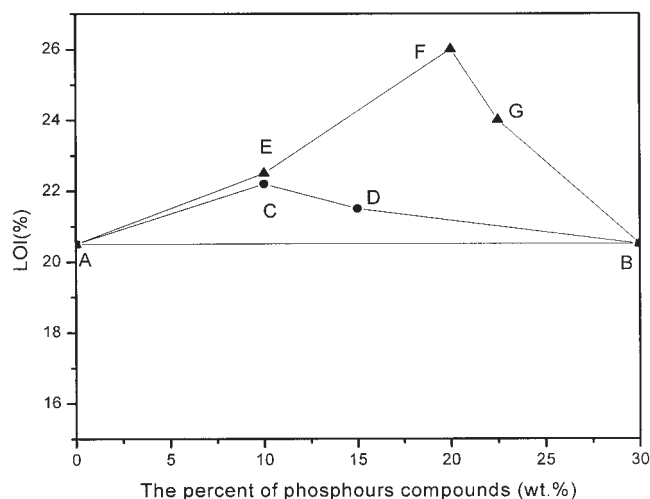| Sample	PP (wt %)	Phosphorus compounds (wt %)	Phosphorus (wt %)	Silicon compounds (wt %)	Silicon (wt %)	Nitrogen compounds (wt %)	Nitrogen (wt %)	LOI value	Δ LOI value
P–Si-0	100	0	0	0	0	0	0	17.0	—
P–Si-1	70	0	0	30	11.1	0	0	20.5	3.5
P–Si-2	70	30	6.6	0	0	0	0	20.5	3.5
P–Si-3	70	0	0	30	4.7	30	4.7	21.0	4.0
P–Si-4	70	10	2.2	20	7.6	0	0	22.2	5.2
P–Si-5	70	15	3.3	15	5.7	0	0	21.5	4.5
P–Si-6	70	10	2.2	20	5.6	20	1.5	22.9	5.9
P–Si-7	70	20	4.4	10	2.0	10	1.0	26.0	9.0
P–Si-8	70	22.5	5.0	7.5	1.5	7.5	0.7	24.0	7.0

Figure 2 Plots of LOI value versus wt % of phosphorus compounds in the samples: (A) P–Si-1; (B) P–Si-2; (C) P–Si-4; (D) P–Si-5; (E) P–Si-6; (F) P–Si-7; (G) P–Si-8.

with the concentration of phosphorus. The LOI value of sample P–Si-1 without phosphorus is 20.5 on the curve as shown in Figure 2. It can be improved with increasing concentration of phosphorus. When the concentration of the phosphorus-containing compound is increased to 20 wt %, it achieves a maximum of 26.0. After that, the LOI values decrease with increasing amounts of phosphorus compounds. The reason for this is that other compounds that contained silicon or nitrogen elements decreased too much. The y-coordinate values of curve ACDB indicate that the LOI values of these phosphorus- and silicon-containing samples change with the weight percentage of phosphorus. They increase with increasing loading of phosphorus-containing FRs in the samples, as shown by the curve. When the concentration of phosphorus-containing FRs reaches 10 wt %, the LOI values on the curve achieve a maximum of 22.2. After that, the LOI values begin to decrease. The y-coordinate values of the plots on the curve AB indicate the LOI values gained by the theoretic addition of the contribution of phosphorus and silicon elements according to the ratio. However, the curve ACDB is above the line AB, as shown by Figure 2, which indicates that the LOI values on the line are larger than those on the line beneath it. This shows that the FRs containing two flame-retardant elements can simultaneously confer larger LOI values to the samples than those of the theoretical addition by the two FRs, respectively, when the loading of phosphorus FRs remains the same; an identical scenario pertains to FRs that contain three flame-retardant elements at the same time, suggesting a synergistic effect among the three elements on the flame retardancy in PP.

The above phenomena may be explained as follows. When the samples, consisting of phosphorus, nitro-

gen, and silicon elements simultaneously, are ignited, the temperature of the material near the flame is elevated. The silicon-containing compounds melt and begin to transport to the surface of the material because of their low glass-transition temperature and low surface energy. Phosphorus-containing compounds start to decompose and the protective phosphorus–carbon layer begins to form as a result of the weak phosphorate 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. They do not devote themselves to burning and the gases could dilute the concentration of the oxygen near the surface of material as well as foam the carbon layer during fire.[11] The phosphorus-containing carbon layer is easily foamed by the products of the nitrogen-containing compounds during fire, thus showing a superior property of insulation to heat transfer and of reducing the production of combustible gases. The carbon layer might decompose further during the processing of burning. High-temperature thermal stability can be increased with the addition of the silicon-containing compounds because their products are silicon dioxide, which cannot be oxidized further. If the flame-retardant elements were used as individual FRs in the material, it could offer only one kind of retardant function during fire. The phosphorus–carbon layer would be burned without the protection of the silicon dioxide layer, and the nitrogen- and silicon-containing compounds could not alone afford the protective carbon layer to meet the requirements in the fire. However, when they are simultaneously used in the same material, their functions for flame-retardant property are correlated and affect each other. This suggests that, among the three flame-retardant elements on flame retardancy, there is a synergistic effect when they are used in PP. The results of the LOI values are shown in Table I and Figure 2.

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 shows the TGA thermograms of PSiN, from room temperature to 800°C, in nitrogen atmosphere. There is only one stage in the curve. The initial decomposition temperature (IDT) is defined as the 5% weight loss.[4] The IDT, the temperature of 10% weight loss, the temperature of the rapid weight loss before 800°C, and the char yield at 800°C in nitrogen are summarized in Table II. The slope of the curve indicates the velocity of the weight loss of the mate-
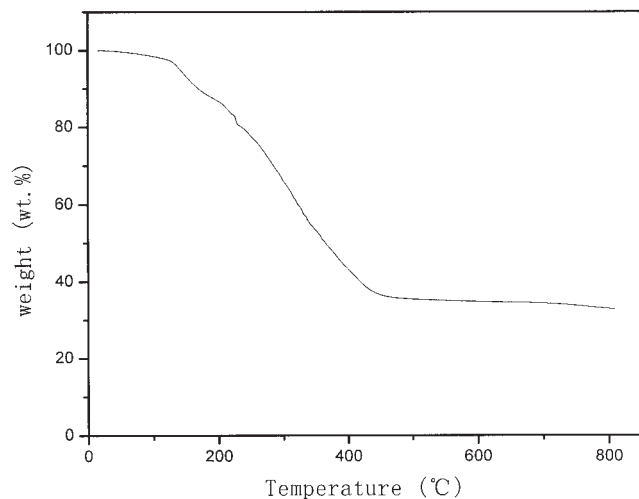
Figure 3 TGA thermogram of the flame retardant in nitrogen.

Figure 4 TGA thermograms of materials with different flame retardants in nitrogen: (d) P–Si-1, the silicon-containing compounds; (e) P–Si-3, the nitrogen- and silicon-containing compounds; (f) P–Si-2, the phosphorus-containing compounds.

rial, as shown in Figure 3. The velocity of weight loss increases with increasing value of the slope for the curve. The rate of decomposition for PSiN is relatively slow. The degradation temperature range is between 141 and 440°C. The slope remains almost the same until about 440°C, after which the velocity of weight loss slows down. The reason for the comparatively slow rate during the decomposition may be that the phosphorus–carbon layer is formed. Finally, there is no visible rapid weight loss between 500 and 800°C, which suggests that there is no further decomposition in the temperature range. The last residue is 33 wt % because of the formation of phosphorus-containing carbon.

In Figure 4, curve (d) shows the TGA thermogram of the sample P–Si-1 with the silicon-containing FR. It has two stages of decomposition for the sample. The IDT is 408°C. The maximum temperature is 480°C because of where the slope of the line arrives at the maximum. When the temperature is at about 520°C, the second stage begins. In this stage, the velocity of
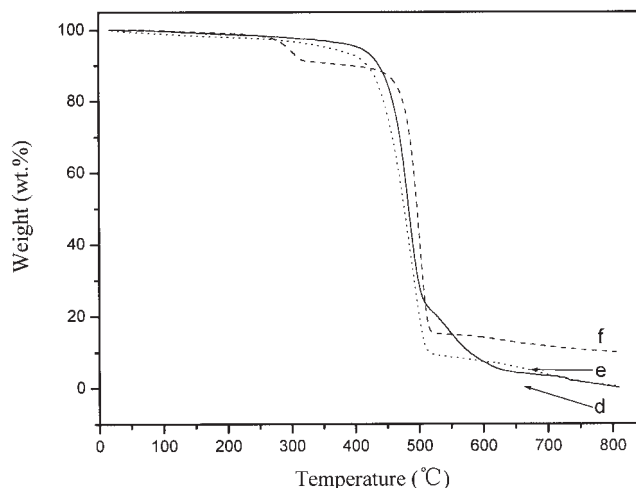
weight loss slows down because the silicon-containing compounds form silicon dioxide, which cannot decompose further. The weight loss in the first stage is 67 wt %, and in the second stage it is 28 wt %. The continuous weight loss, without anything remaining in the end, is a result of the products of the silicon dioxide lost in the airstreams of nitrogen, which suggests that only the silicon compound does not provide enough carbon to protect the unburned material during fire, although its products could not promote burning. Curve (e) is the TGA thermogram of sample P–Si-3, which contains both nitrogen and silicon elements and has only one stage of decomposition. The first stage begins at about 408°C. The weight loss of the sample is about 88 wt % in this temperature range. There is hardly any weight loss between 500 and 800°C. The reason is that the concentration of the silicon element in P–Si-3 is less than that of P–Si-1, and the nitrogen-containing compound could produce ammonia gas to speed the velocity of the weight loss of silicon dioxide before the temperature reaches 500°C. There is no residue of P–Si-1 or P–Si-3 when the temperature reaches 800°C, as shown in Figure 4, which shows that neither the silicon nor the nitrogen element can afford a continuous protective carbon layer to remain in the polymer during flame; it also suggests that the thermal stability of the compound with nitrogen and silicon is not better than the compound with only the silicon flame-retardant element.

There are two decomposition stages in the TGA curve of the sample P–Si-2, as shown by curve (f) in Figure 4. The first stage begins at 250°C for the decomposition of the phosphorus-containing compound in the material. The IDT of phosphorates is low be-

TABLE II
Temperatures of Various Decompositions and Char Yield in N_2 at 800°C

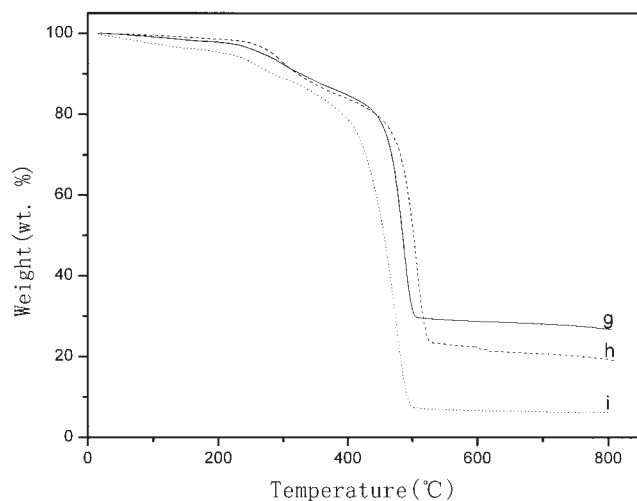| Sample	Temperature of 5% weight loss (°C)	Temperature of 10% weight loss (°C)	Temperature of the rapid weight loss (°C)	Char yield at 800°C in N_2 (wt %)
PNSi	141	170	—	33
P–Si-1	400	434	480	0
P–Si-2	290	390	500	10
P–Si-3	360	420	480	0
P–Si-6	212	284	467	6
P–Si-7	268	328	484	27
P–Si-8	284	323	500	19

Figure 5 TGA thermograms of materials with phosphorus-, nitrogen-, and silicon-containing FRs in nitrogen atmosphere: (g) P–Si-8; (h) P–Si-7; (i) P–Si-6.

cause of the weak chemical bonds in phosphorates. The weight loss of this stage was 10 wt %, but the loading of FR is 30 wt %, because some additives change into char to remain in the material and others do not decompose. There is a relatively stable area between 310 and 460°C. The temperature of the second stage is from 460 to 510°C resulting from the decomposition of the polymer matrix. The weight loss is at 75 wt % in the 50°C region, where most of the polymer would have decompounded, which is similar to curves (d) and (e) in Figure 4. The final residue remaining is 10 wt % for the formation of phosphorus-containing carbon that does not decompose in the nitrogen atmosphere. The flame-retardant property of P–Si-2 is estimated by the LOI value, as shown in Table I. It is improved by the addition of the phosphorus-containing compounds for the formation of protective carbon during fire; however, the LOI values of P–Si-1 and P–Si-3 are also increased without the formation of the protective carbon layer by the addition of the silicon compounds. This suggests that the LOI value could be increased with or without the protective layer, and also shows that the flame-retardant mechanism of the silicon and the phosphorus element might be different from each other.

Figure 5 shows the TGA thermograms of the samples with FRs that contain phosphorus, nitrogen, and silicon elements at the same time. All of these TGA curves include two stages of decomposition and all have some amount of final residue. The rates of weight loss in the first stage are smaller than those in the second stage. There is a slight weight loss in these samples before 300°C. The IDT curves (d) and (e), which are the TGA thermograms of P–Si-7 and P–Si-8, respectively, are at about 280°C. The first stages of both curves begin at 230°C. Both of the second stages

begin at 450°C, but sample P–Si-7 ends at about 500°C and sample P–Si-8 ends at 520°C. Weight losses of the first stage for both P–Si-7 and P–Si-8 are near 20 wt %, and those of the second stage are 57 and 50 wt %, respectively, as shown in Figure 5. The residue for sample P–Si-7 is 27 wt % and that for P–Si-8 is 19 wt %, as shown in Figure 5 and summarized in Table II. Curve (i) presents the TGA thermogram of sample P–Si-6, which is similar to the curves of P–Si-7 and P–Si-8, although it is always beneath the other two curves and the residue is 6 wt %. When the sample simultaneously contains the three elements, as shown in Tables I and II, the LOI values are improved with increasing amounts of the char residue. The flame-retardant property of sample P–Si-7 is superior to that of samples P–Si-6 and P–Si-8 because the amount of P–Si-7 is the largest among them, as shown by Figure 5 and Table II, with different ratios of the three flame-retardant elements. This suggests that there is a synergistic effect of the phosphorus, nitrogen, and silicon elements in the same compounds on forming the protective carbon, and the synergistic effect correlates with the ratio of the three elements.

The reason for this phenomenon may be explained as follows. When the samples are heated and ignited, the silicon-containing FRs concentrate to the surface of the material as a result of its low surface energy. The phosphorus-containing FRs decompose to form the continuous and protective carbon layer, to resist the transport of heat and mass. The silicon dioxide formed by the silicon-containing compounds during fire is not ignited and can be fixed in the material by the liquid phosphorus-containing carbon in the flame. The amino gas produced by the nitrogen-containing compounds foam the carbon layer because the carbon layer is liquid when it initially formed during fire. The silicon-containing carbon with foam performs better at holding back the transport of heat and mass than does the carbon layer only containing phosphorus. At the same time, this kind of layer has a superior high-temperature stability for containing silicon dioxide. As shown by Table I, Table II, and Figure 5, there is strong correlation between the char yield and the LOI values: the greater the yield, the greater the LOI value. All these factors suggest that there is a synergistic effect among the three flame-retardant elements, and thus both the LOI value and the char yield of materials are increased.

CONCLUSIONS

The FRs composed of phosphorus, nitrogen, or silicon element can provide materials with flame-retardant properties. The flame retardance would be improved further when the samples included FRs that simultaneously contained two of these elements. The best flame-retardant properties and highest char yield of

the samples are obtained by adding FRs that simultaneously include the three flame-retardant elements (PSiN). There is a synergistic effect of the three elements on flame retardancy and char yield in PP. The LOI value of the sample P–Si-7, with 30 wt % loading of PSiN, can be increased to 26.0, that is to say the LOI value is increased by 44.4 wt %, and the char yield can be increased from zero to 27% because of the synergistic effect on them.

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