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Synthesis, characteristic of a novel additive-type flame retardant containing silicon and its application in PC/ABS alloy

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Abstract A novel flame retardant (DPA–SiN) containing phosphorus, nitrogen and silicon elements at the same time was synthesized. 9-(9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide)-propanoic acid (DPA) synthesized through simple addition reaction of 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and acrylic acid (AA) was introduced into N-β-(aminoethyl)-γ-aminopropyl methyl dimethoxysilane/dimethylsiloxane copolymer (SiN) to form a novel flame retardant (FR). The structure of DPA and DPA–SiN were characterized by Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) spectroscopy. After blend with PC/ABS, the flame-retardant properties of the PC/ABS/DPA–SiN blends are estimated by Limiting Oxygen Index (LOI) values and CONE Calorimeter, while thermal stabilities are investigated through Thermo Gravimetric Analysis (TGA). The morphological structures of the char formed after PC/ABS/DPA–SiN burnt in LOI test were investigated by Scanning Electron Microscopy (SEM).

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Introduction

To control the flammability of polymers, the most commonly used method is the addition of flame retardant (FR) additives, among which halogenated compounds are the most widely used. However, use of halogen based FRs has given rise to some environmental concerns. Thus, a lot of emphasis has been laid to develop halogen-free FRs. The common halogen-free FRs include Magnesium hydroxide ($Mg(OH)_2$), aluminum hydroxide ($Al(OH)_3$), organophosphorus compounds, nitrogen-containing compounds, and organosilicon compounds [1–4].

Seeking for new fire retardants, organophosphorus compounds have proved to be good FRs for polymeric materials. Upon heating intumescent fire-retardant systems, a layer of foamy carbonaceous char is produced, which protects the polymer surface from the flames. This layer acts as a physical barrier that hinders the transfer of heat from the flame to the material [5, 6].

The cyclic phosphorus group, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, has received notable attention in research owing to its attractive properties. DOPO was widely incorporated into polymers for improving the polymers' FR properties and thermal stability [7, 8]. It may be attributed to the cyclic O=P–O chain being more thermaly stable than the open O=P–O chain. Moreover, incorporation of DOPO groups into polymers also brought improved organosolubility to the polymers, due to the DOPO group's bulk structure and polarity [9–11].

Beside organophosphorus compounds, those with nitrogen and silicon are classed as environmental friendly FRs too, for the less toxic and more innocuous products they generate. As demonstrated in some recent studies, when these three FR elements exist at the same time, the

FR system could offer better flame retardancy to the matrix material [12, 13].

Like many other polymeric materials, the flammability of Polycarbonate/Acrylonitrile–butadiene–styrene copolymer (PC/ABS) alloys limits its application in many fields. And the mostly used FR additive in PC/ABS is Tetrabromobisphenol A, which should be replaced by halogen-free FRs [14–18]. In our study, a new environmental friendly flame-retardant in which phosphorus, nitrogen and silicon elements exist at the same time was synthesized through a simple method. The cyclic phosphorus group DOPO was incorporated into the FR. This FR was applied in PC/ABS to improve the fire performance.

This article reports the synthesis of a novel halogen-free FR and the investigation of its affection on the FR properties and thermal behavior of PC/ABS.

Experiments

Materials

9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was purchased from Shandong Mingshan Quick-lvfine Chemicalci. Ltd.

Acrylic acid (AA) obtained from Shanghai Zhenxing Chemical Industry Corporation was used as received.

The N-β-(aminoethyl)-γ-aminopropyl methyl dimethoxysilane (HD-103) was obtained from Shanghai Yehao Chemical Industry Corporation.

The α,ω-dihydroxide polydimethsiloxane(PDMS) was received from Shanghai Resin Industry Corporation.

Acetone was acquired from chemical reagents Co. Ltd of China National Pharmaceutical Group Corporation. Potassium hydroxide (KOH), chloroform ($CHCl_3$), and hexamethyldisioxane were acquired from Shanghai Resin Industry Corporation.

Polycarbonate (PC) used here was supplied by Dow Chemical Co with a melt index(GB 368283) of 20 g/10 min and a density of 0.918 g/cm^3.

Acrylonitrile Butadiene Styrene (ABS) used here was PA757 supplied by Chimei Corporation with a melting index (GB 368283) of 2 g/10 min and a density of 0.918 g/cm^3.

Synthesis of substrate characteristics

Synthesis of DPA

DOPO (21.6 g, 0.1 mol) and AA (7.2 g, 0.1 mol) were introduced into a three-neck and round-bottom 250 mL glass flask equipped with a nitrogen inlet, a reflux condenser, and a mechanical stirrer. The mixture was stirred and heated slowly to 80 °C for about 20 min until DOPO was dissolved completely in AA. The mixture was stirred at a constant rate over a period of 6 h under a nitrogen gas atmosphere. The temperature was maintained at 70 °C during the addition. The mixture then became thick due to the precipitation of the formed DPA. After being cooled to room temperature, the mixture was dissolved in acetone. Chloroform was used as precipitating agent. After adding chloroform into the solution, the product separated out. The ivory white powder was collected by filtration, and dried under reduced pressure. FTIR (KBr, cm^{-1}): 2,800–3,000 (–CH_2,–CH_3); 1,729 (C=O); 1,200 (C–O); 922 (P–O– Ph); 1,595 (P–Ph).

Synthesis of SiN

PDMS (7.4 g, 0.1 mol), HD-103 (20.6 g, 0.1 mol), and catalyst (KOH) were introduced into a 250 mL three-neck and round-bottom glass flask, while the temperature of the mixture was controlled between 80 °C and 100 °C. Two hours later, 1 mL water was added into the flask, and another hour later, the by-product were removed at around 80 °C under reduced pressure for 6 h. The product obtained was called N-β-(aminoethyl)-γ-aminopropyl methyl dimethoxysilane/dimethylsiloxane copolymer (SiN). FTIR (KBr, cm^{-1}): 3,200–3,340 (–NH_2,–NH–); 2,884–2,963 (–CH_2–,–CH_3); 1,260 (Si–CH_3); 1,000–1,100 (Si–O–Si); 800 (Si–C).

Synthesis of DPA–SiN

DPA (28.8 g, 0.1 mol) and acetone (200 mL) were introduced into a 500 mL three- neck and round-bottom glass flask with stirrer. The mixture was stirred and heated to 70 °C for about 1 h until DPA was dissolved completely in acetone. SiN (23.4 g, 0.1 mol) was dissolved in 100 mL acetone, and dropped slowly into the DOPO-AA solution. When the solution was added, the temperature remained at 20 ~ 40 °C for 2 h. Then the temperature was raised to 100 °C and the solvent was removed from vacuum. The flame retardant (DPA–SiN) containing phosphorus, nitrogen, and silicon was obtained. FTIR (KBr, cm^{-1}): 3,400 (–NH–); 2,884–2,963 (–CH_2–,–CH_3); 1,260 Si–CH_3, P=O); 1,235 (P=O); 1,000 ~ 1,100 (Si–O–Si, P–O–C); 800 (Si–C).

Preparation of PC/ABS/DPA–SiN Composites

PC and ABS pallets were dried at 80 °C in a vacuum for 5 h. Then PC, ABS, and DPA–SiN were mixed in a HAAKE Rheocord 90 internal mixer at 215° for 6 min.

The mixtures were pressed into sheets of suitable thickness. The compositions of PC/ABS/ DPA–SiN composites are summarized in Table 2.

Characterization

The Fourier transform infrared spectroscopy (FTIR) was performed by a Perkin–Elmer Paragon 1000. The spectra of the liquid sample were obtained as smeared on KBr plates and solid samples were recorded as pressed KBr pallets.

Hydrogen Nuclear Magnetic Resonance (^{1}H NMR), Phosphorus Nuclear Magnetic Resonance (^{31}P NMR), and Carbon Nuclear Magnetic Resonance (^{13}C NMR) were performed by Mercuryplus 400 (400 MHz) NMR spectrometer with dimethyl sulfoxide as a solvent.

Limiting oxygen index (LOI) values were measured on a Stanton–Redcroft LOI FTA α type instrument according to ASTM D2863. The percentage of oxygen in the O_2 and N_2 mixture, just sufficient to sustain the flame, was taken as LOI. The sample size is 100*6.5*3 mm^3.

Cone calorimeter was used to investigate the combustion behavior under ventilated conditions including time to ignition (TTI), heat release rate (HRR), total heat released (THR), effective heat of combustion (EHC), mass loss rate (MLR), specific extinction area (SEA), smoke density, carbon monoxide, and carbon dioxide evolution; samples' mass loss was determined by cone calorimeter in accordance with the procedure described as ASTM standard method. The hest flux used was 35 kW/m^2. All samples (100*100*3 mm^3) were measured in a horizontal position.

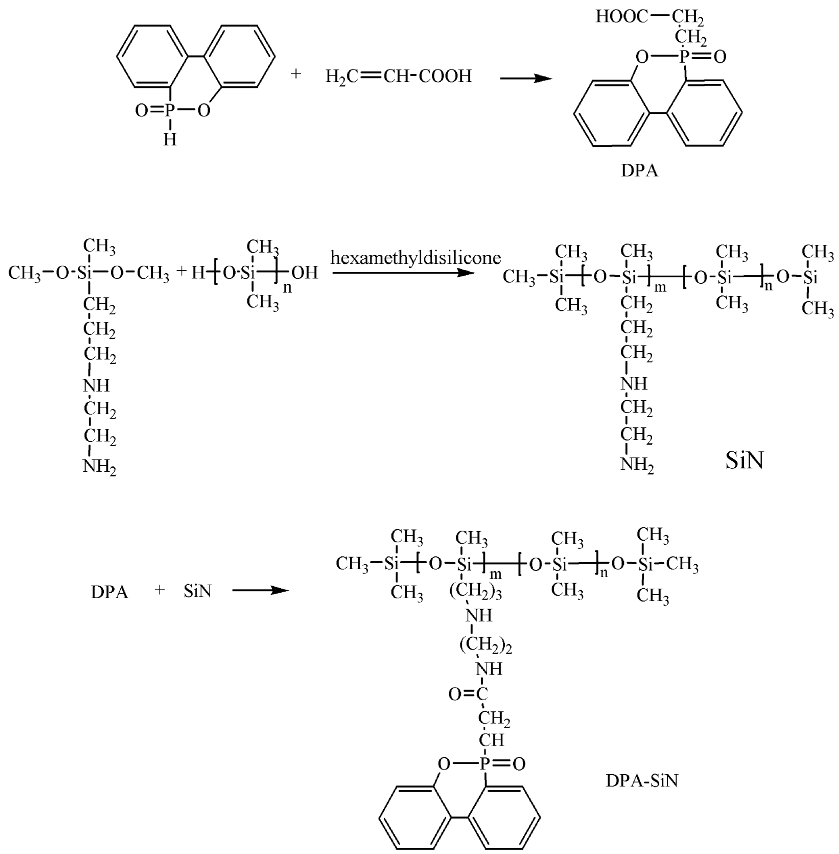
The thermo gravimetric analysis (TGA) was performed by a Perkin–Elmer 7 Series Thermal Analyzer at a heating rate of 20 °C /min in a nitrogen atmosphere, and the temperature ranged from room temperature to 800 °C. The sample weight used was around 3–5 mg.

Scanning electron microscopy (SEM, Hitachi S520) was used to investigate the morphology of the char layer of samples being tested after the LOI test. The sample was coated with gold to make the surface conductible.

Results and discussion

Synthesis of DPA–SiN

The synthesis route for DPA–SiN was presented in Scheme 1. According to previous reports, DOPO having an active hydrogen atom (–P(O)–H) could react with double bond groups [19–21], which suggests that it can also react with AA. The product of the reaction was characterized by FTIR as shown in Fig. 1 (curve DPA). As the addition



Scheme 1 The synthesis route for DPA–SiN

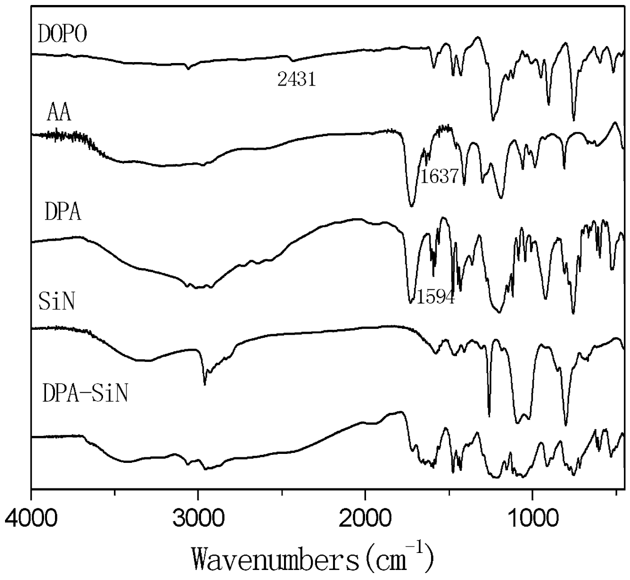


Fig. 1 FTIR of DOPO, AA, DPA, SiN, and DPA–SiN

reaction between DOPO and AA proceeded, the distinctive absorption at 2,431 cm^{-1} for –P–H (curve DOPO) and 1,637 cm^{-1} for –C=C (curve AA) in FTIR spectra disappeared. The structure of the compound was also characterized by means of NMR spectroscopy. The ^{31}P NMR spectrum of DPA is shown in Fig. 2. Only one specific absorption peak at 37.5 ppm can be observed in the ^{31}P NMR spectrum of DPA while DOPO has an absorption peak at 16 ppm. The ^{1}H NMR spectra of DPA shown in Fig. 3 further demonstrates the structure of DPA: the chemical shifts at 7 ~ 8 ppm resulted from the eight aromatic hydrogens of the biphenol section; the chemical shift at about 12.3 ppm was from the carboxylic acid hydrogen (H_c); and chemical shifts at around 2.0 ~ 2.5 ppm could be assigned to H_b, while the chemical shifts at 1.5 ppm was assigned to H_a. Figure 4 shows the ^{13}C NMR spectra of the compound DPA with all assignments.

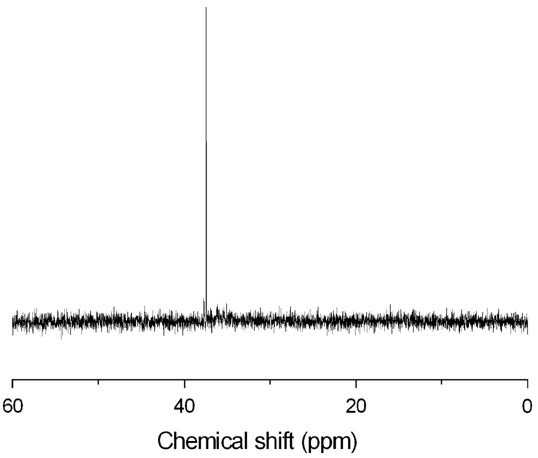


Fig. 2 ^{31}P NMR of DPA in DMSO

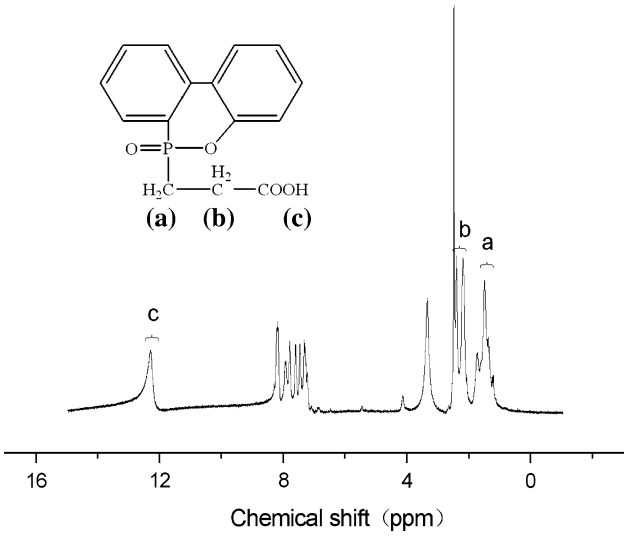


Fig. 3 ^{1}H NMR of DPA in DMSO

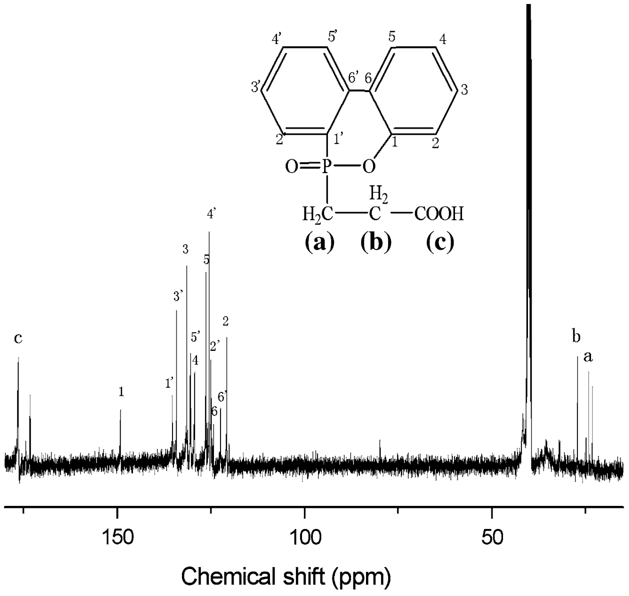


Fig. 4 ^{13}C NMR of DPA in DMSO

The –COOH group in DPA could react with the $-NH_2$ group in SiN via neutralization reaction. The FTIR analysis on DPA–SiN is shown in Fig. 1. From the ^{31}P NMR spectura of DPA–SiN presented in Fig. 5, only one specific absorption peak at 42.5 ppm can be observed.

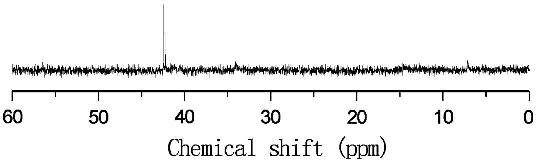


Fig. 5 ^{31}P NMR of DPA–SiN in DMSO

Application of DPA–SiN in PC/ABS

Flammability test by LOI and cone calorimeter

The compositions of the samples and corresponding LOI values are listed in Table 1. As shown in Table 1, The LOI value of unmodified PC/ABS is 21.0%. The LOI value increases with the increasing content of DPA–SiN. The LOI value of blend-3 which contains 2.2 wt.% of phosphorus, 2.4 wt.% of silicon, and 1.2 wt.% of nitrogen with a DPA–SiN loading amount of 30% is 27.0%.

The traditional method of measuring and predicting the hazard of materials is based on the determination of a variety of properties measured independently by different small-scale apparatuses. The cone calorimeter provides a means of measuring simultaneously, a number of different parameters in the same test. It has been claimed that the rate of heat released by a product is the most important property predicting hazard in a fire situation, and the assumption is that the HRR is a measure of the intensity of a fire. The cone calorimeter testing is a useful small-scale test since it is able to determine HRR associated with a variety of other parameters [22–24].

Samples listed in Table 1 are tested by cone calorimeter and the results are summarized in Table 2. Figure 6 shows the HRR of PC/ABS blends as a function of time. Both the peak and average HRR values of DPA–SiN modified PC/ABS are strongly reduced in comparison with the virgin PC/ABS. It can be observed that Blend-3 has the lowest peak HRR which is 50% lower than that of virgin PC/ABS, and the average HRR of Blend-3 is 153 kW/m^2 which is 40% lower than that of virgin PC/ABS. The EHC of PC/ABS blends also decreases with the increasing content of DPA–SiN. Lower HRR and EHC of DPA–SiN modified PC/ABS indicate that as a flame retardant DPA–SiN has some activity in PC/ABS. Time to ignition measures the time to achieve sustained flaming combustion at particular cone irradiance. The TTI of unmodified PC/ABS alloy is 47 s, while DPA–SiN modified PC/ABS is about 30 s. The unexpected reduction in TTI of modified PC/ABS is due to the early decomposition of DPA–SiN before it could play its own role in the material [25]. Figure 7 shows the relationship between the mass and time investigated by cone calorimeter. DPA–SiN modified PC/ABS decomposed before PC/ABS, and had a high char yield than PC/ABS at the end of cone calorimeter test. These accord with the

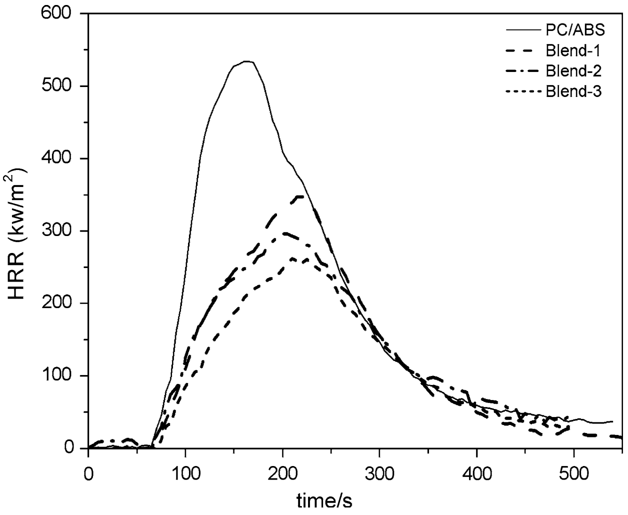


Fig. 6 HRR of PC/ABS, Blend-1, Blend-2, and Blend-3

Table 1 The different components and LOI values of samples

Sample	PC (wt.%)	ABS (wt.%)	DPA–SiN (wt.%)				LOI (vol%)
			Total	Phosphorus	Silicon	Nitrogen	
PC/ABS	70	30	0	0	0	0	21.0
Blend-1	63	27	10	0.7	0.8	0.4	21.5
Blend-2	56	24	20	1.4	1.6	0.8	24.0
Blend-3	49	21	30	2.2	2.4	1.2	27.0

Table 2 Cone calorimetric data measured with an irradiance of 35 kW/m^2

Sample	PC/ABS	Blend-1	Blend-2	Blend-3
Initial mass/g	32.7	32.9	32.7	29
TTI/s	47	30	30	32
Flameout/s	549	250	270	269
Average HRR/(kW/m^2)	252.39	196.75	181.23	152.64
Peak HRR(kW/m^2)	534.00	347.39	296.25	262.10
EHC(MJ/kg)	22.43	12.96	12.82	10.49
THR(MJ/m^2)	81.3	43.3	43.7	34.9
Char yield (%)	6.7	12.0	11.8	12.0

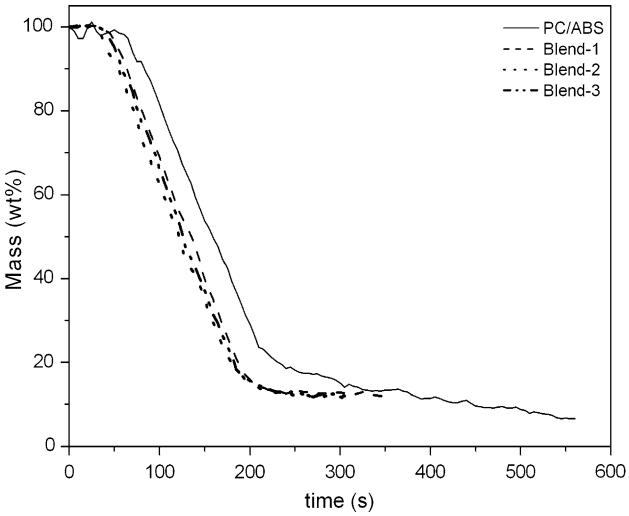


Fig. 7 Mass loss (cone calorimeter) of PCABS, Blend-1, Blend-2, and Blend-3

result from TGA well, which will be discussed in the following part.

From the LOI test and cone calorimeter results which are discussed above, it is clear that the flame retardancy of PC/ABS is enhanced by incorporation of DPA–SiN.

Thermal stability of DPA–SiN and DPA–SiN modified PC/ABS by TGA

The thermal stability and decomposition behaviors of DPA–SiN were estimated by TGA. Figure 8 presents the TGA of PC/ABS, DPA–SiN, and DPA–SiN modified PC/ABS from 100 °C to 800 °C in N_2, and the thermal stability factors are given in Table 3. The initial decomposition temperature (IDT) is defined as the temperature at which the weight loss of sample reaches 5 wt.% [26]. $T_{10\%}$ is the temperature when the weight loss of the sample is 10%, and T_{max} is the temperature when the weight loss rate of the sample reaches its maximum. C is referred as the char residue at 800 °C.

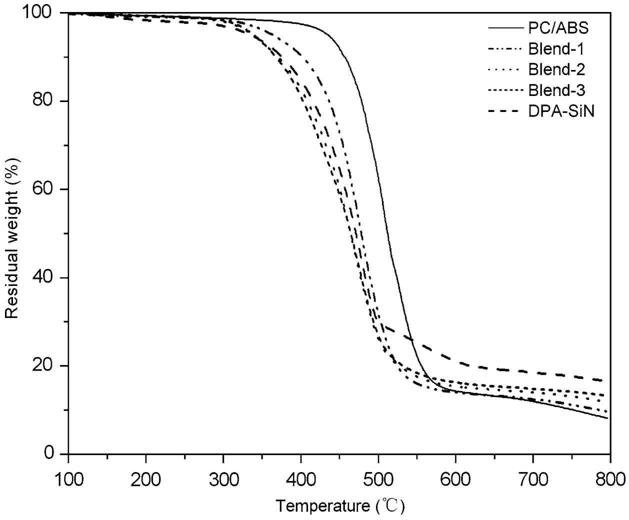


Fig. 8 TGA of DPA–SiN, PCABS, Blend-1, Blend-2, and Blend-3 in N_2

Table 3 The thermal stability parameter of samples in N_2

Sample	IDT (°C)	$T_{10\%}$ (°C)	T_{max} (°C)	800 °C (wt.%)
PC/ABS	435	457	505	8.2
Blend-1	364	403	476	9.7
Blend-2	337	370	470	11.8
Blend-3	338	366	474	13.2
DPA–SiN	334	375	479	16.4

There is only one stage in the TGA curve of DPA–SiN. The IDT of DPA–SiN is 334 °C, higher than the processing temperature of PC/ABS alloy (usually around 250 °C). This suggests DPA–SiN could be used in PC/ABS alloy. The weight loss of DPA–SiN increases slowly with the increasing temperature until 375 °C, where the weight loss is 10 wt.%. After that, the weight loss rate increases gradually and reaches its maximum at 479 °C. Very slow weight loss rate and small amount of weight loss are observed in the temperature region of 510 ~ 600 °C. At last, the char yield of DPA–SiN at 800 °C in nitrogen is 16.4 wt.%. The IDT of DPA–SiN is relatively higher than many other phosphates, the high thermal stability of the P–O–C bond in this compound may be attributed to the O=P–O group being protected by phenylene groups [5]. After the cleavage of the O=P–O pendant group at around 510 °C, the DOPO-containing FR exhibits its thermal stability at 510 ~ 600 °C, and at temperature higher than 700 °C weight loss occurs due to char oxidation [21].

The thermal stability factors given in Table 3 indicate that DPA–SiN modified PC/ABS blends have lower IDT compared to PC/ABS. The relatively lower IDT of DPA–SiN modified PC/ABS blends are due to the early decomposition of DPA–SiN as discussed above. The char yield of the blends at 800 °C increase as the content of DPA–SiN increases, and the data reveal that DPA–SiN contributes to the charring process of PC/ABS during the thermal decomposition.

Not only the amount, but also the thermal stability of the formed char plays an important role in the fire performance [27]. As shown in Fig. 8, from about 510 °C, the char of DPA–SiN modified PC/ABS blends have better stability than PC/ABS. It indicates that the addition of DPA–SiN improves the thermal stability of the char layer of the alloy above 510 °C. The reason for this fact should be that after

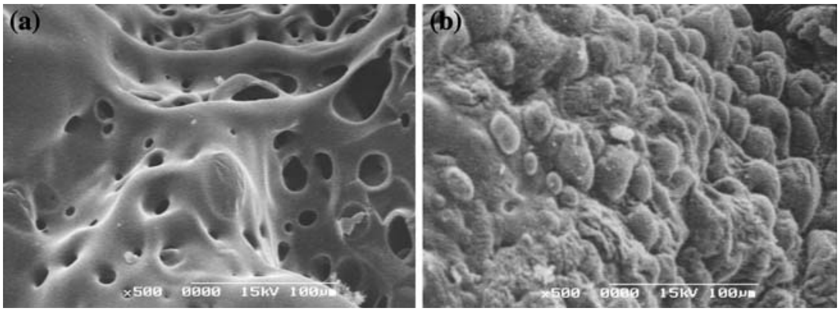


Fig. 9 SEM of the intumescent char: (**a**) for the inner surface; (**b**) for the outer surface of the char layer

the cleavage of the O=P–O pendant group at around 510 °C, the char formed acts as a protective layer for the rest residue. As discussed above, the addition of DPA–SiN changes the thermal behavior of PC/ABS, and these changes offer PC/ABS with flame retardancy.

Morphology of the char of PC/ABS/ DPA–SiN after the LOI test

The SEM micrographs in Fig. 9 show the morphological structures of the char of DPA–SiN modified PC/ABS blends formed after the LOI test. The morphology of the inner surface of the char layer is shown in Fig. 9a. Cells are formed by the gases in the process of heating. The morphology of the outer surface of the char is shown in Fig. 9b. The outer surface is compact and smooth. The char layer, which has a swollen inner structure as well as a close and compact outer surface, provides a barrier to resist the transfer of heat and mass during a fire.

Conclusions

A novel flame retardant (DPA–SiN) has been synthesized; the chemical structures of DPA and DPA–SiN have been characterized by FTIR and NMR. The incorporation of DPA–SiN into PC/ABS improves the LOI value of PC/ABS from 21.0 vol% to 27.0 vol% with 2.2 wt.% of phosphorus. At this loading amount, the HRR, THR and EHC are reduced to about half of unmodified PC/ABS; TGA result reveals that the addition of DPA–SiN changes the thermal behavior of PC/ABS to offer it with flame retardancy, DPA–SiN helps PC/ABS to form more stable char layer during thermal decomposition. Comparing with unmodified PC/ABS, char yield of Blend-3 at 800 °C in nitrogen is improved from 8.2 wt.% to 13.2 wt.%. The morphological structure of char formed by DPA–SiN modified PC/ABS blends indicates that the char layer could swell well to form a barrier to resist the transfer of heat and mass during a fire. The qualitative contribution provided by the FRs to PC/ABS is evident.

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