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The application of a phosphorus nitrogen flame retardant curing agent in epoxy resin

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Abstract: In order to improve the compatibility of flame retardant and epoxy resin, a phosphorus nitrogen flame retardant curing agent poly(p-xylylenediamine spirocyclic pentaerythritol bisphosphonate) (PPXSPB) was synthesized. FTIR, ¹HNMR, and mass spectroscopy were used to identify the chemical structure of PPXSPB. Epoxy resin (E-44) and PPXSPB as the raw material, a series of thermosetting systems were prepared. The effects of PPXSPB on flame retardancy, water resistance, thermal degradation behavior, mechanical properties and the adhesive strength of EP/PPXSPB thermosets were investigated. The results show that with the increase of phosphorus content, the oxygen index and carbon residue of the system both increased significantly, and the heat release rate gradually decreased, which is of great significance in delaying the occurrence of fire. When the phosphorus content is 3.24% in EP/PPXSPB thermosets, EP-2 can successfully pass the UL94 V-0 flammability rating, the LOI value of EP-2 can reach 31.4%, the impact strength and tensile strength was 6.58 kJ/m² and 47.10 MPa respectively, and the adhesive strength was 13.79 MPa, the system presents a good overall performance.

Keywords: flame retardant; curing agent; synthesis; epoxy resin; property

1 Introduction

Epoxy resin has excellent mechanical properties, electrical properties, bonding properties and so on. So many advantages make it widely used in the electrical

and electronic, construction, chemicals, machinery, transportation, national defense construction, aerospace, optical instruments, sports equipment, and many other areas. In terms of its practical application, the epoxy resin is required to have better flame retardant properties, which have improved the development of the flame retardant epoxy resin (1-3).

Nowadays, the method of adding flame retardant by physical blending has still been widely used as its easy operation and low cost. Its flame retardant effects lessen rapidly as time passes by, especially in harsh environments, and because it is added as filler, it will have a certain impact on the mechanical properties of the material. Therefore, another method that incorporates flame retardant elements (P, N, Si, B, etc.) into polymer backbone or network chemical bonding is being extensively studied (4-7). Phosphorus-containing flame retardant curing agents, a part of reactive flame retardant, have drawn people's attention due to their advantages that they are halogen-free, low in toxicity and relatively efficient. There are many possibilities for phosphorus-containing chemical structures to be modified to adjust their different properties, such as ammonium polyphosphate (APP), 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), which are used as an intermediate in phosphorus-containing flame retardants. Many different flame retardants have been synthesized, most of which have good flame retardancy (8-11).

Phosphorus and nitrogen have been confirmed to have a synergistic effect during the burning process, which can improve the flame retardant effect (12-14). Thus a phosphorus nitrogen flame retardant curing agent was synthesized in this study, where the nitrogen in the form of amino groups is used as crosslinking groups, and a series of flame retardant epoxy resin systems were prepared. The flame retardancy of EP/PPXSPB thermosets was investigated by limiting oxygen index (LOI) and vertical burning test (UL94), the thermal degradation behavior was tested by thermal gravimetric analysis (TGA), and the mechanical properties were investigated by tensile strength and charpy impact strength tests and adhesive strength tests, respectively, and the scanning

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electron microscopy (SEM) was used to analysis the impact sections morphologies of EP/PPXSPB thermosets from impact tests and the char residues morphologies of the EP/PPXSPB thermosets.

2 Experimental

2.1 Materials

P-xylylenediamine (PXDA, chemically pure) were purchased from Shandong Xiya Chemical Reagent Co., Ltd. (Shandong, China), phosphorus oxychloride (POCl_3 , analytical reagent (AR)), 4-dimethylaminopyridine (DMAP, AR), Pentaerythritol (PER, AR), acetonitrile (AR), chlorobenzene (AR), and dichloromethane (CH_2Cl_2 , AR) were all purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). The EP resin (bisphenol A diglycidyl ether, trade name E-44, EP equivalent = 210-240 g/eq) was purchased from Jinan Zhuopu Chemical Technology Co., Ltd (Jinan, China).

2.2 Synthesis

2.2.1 Synthesis of the SPDPC (pentaerythritol diphosphate diphosphoryl chloride)

PER (13.61 g, 0.10 mol), POCl_3 (46.01 g, 0.30 mol), and chlorobenzene (150 mL) were introduced into a 500 mL, three-neck and round-bottom glass flask equipped with a condenser, a dry N_2 inlet, a thermometer, a magnetic stirrer, and a gas absorber. DMAP (0.13 g, 0.0011 mol) as catalyst was also added into the glass flask. The mixture was stirred at 60°C for 2 h and 80°C for 6 h. Then mixture continued to react at 95°C until no large amount of HCl gas was spilled over. All reactions were carried

out under dry N_2 atmosphere. The crude product was washed with CH_2Cl_2 and ethanol sequentially, and then dried it at 80°C for 12 h under vacuum until its quality does not change. The obtained white solid powder was SPDPC. Yield: 26.34 g (88.9%). Scheme 1a is the reaction formula.

2.2.2 Synthesis of the PPXSPB

PXDA (57.20 g, 0.42 mol) and acetonitrile (230 mL) were introduced into a 500 mL four-neck and round-bottom glass flask equipped with a magnetic stirrer, reflux condenser, thermometer, and dry nitrogen inlet. The mixture was heated to 60°C under N_2 atmosphere and stirred until PXDA dissolved completely. Then SPDPC (59.18 g, 0.2 mol) was added. The reaction was stirred under 60°C for 2 h. Then the reaction continued at 75°C for 6 h. The mixture was filtered hot to remove excessive PXDA and acetonitrile, the crude product was washed successively for 3 times with acetonitrile, and then vacuum-dried at 70°C for 12 h, and PPXSPB was the obtained white powder. Yield: 86.3 g (87.0%). Scheme 1b is the reaction formula.

2.3 Preparation of flame-retarded EP resin

PXDA was used as a pure sample curing agent which was used to compare with the flame retardant curing agent PPXSPB. The curing process of all flame retardant epoxy resin composites was under the same conditions. The mass ratios of all components are listed in Table 1. The mixture was stirred continuously by high speed disperser for 20 min at 90°C . When the mixture was mixed well, degassed it under vacuum for 30 min, then the mixture was poured into a preheated mold at 119°C . The samples were cured for 2 h at 119°C , 3 h at 146°C and then post-cured for 2 h at 178°C .

Scheme 1: Synthesis route of SPDPC (a) and PPXSPB (b).

Table 1: EP/PPXSPB flame retardant systems.

Sample	E-44 (g)	PPXSPB (g)	PXDA (g)	P (%)
EP-0	100	0	25	0
EP-1	100	30	0	2.77
EP-2	100	35	0	3.12
EP-3	100	40	0	3.42

Note: The phosphorus content is calculated as: “P% = (PPXSPB mass / total mass of the system) × 12.01 wt% × 100%”. (12% is the mass fraction of P in the PMXSPB, and phosphorus content is determined by ammonium molybdate spectrophotometric method)

2.4 Characterization

Phosphorus content was determined by 721 digitally visible spectrophotometer (Sanghai Jinghua, China) according to the GB/T11893-89, potassium persulfate was used as the oxidant to digest the solid sample.

FTIR analysis was performed using a Thermo Nicolet NEXUS-470 (Ramsey, Minnesota, USA) spectrometer by an attenuated total reflectance method. Each sample was scanned from 4000 to 400 cm⁻¹.

¹HNMR spectra and ³¹PNMR were recorded on an AVANCE III 500MHz spectrometer (Bruker, Switzerland). The chemical shifts relative to that of DMSO-*d*₆ were recorded.

The molecular weight was determined by microTOF-Q 125 (Bruker Customer, Germany), with the sample dissolved in methanol.

Thermogravimetric analysis (TGA) were performed on a STA449C/41G thermal analyzer (NETZSCH, Germany). The mass of PPXSPB was 5 mg, and EP-0, EP-1, EP-2, EP-3 were the same, 4.5 mg. Each sample was tested from 30 to 800°C at a heating rate of 10°C/min under N₂ or air atmosphere.

The limiting oxygen index (LOI) is used to indicate the concentration (volume fraction) of oxygen in a mixture of oxygen and nitrogen when it is just capable of supporting its combustion. LOI test was carried out according to the GB/T2406-1993. The LOI was measured using a JF-3 LOI chamber (Jiangning Analytical Instrument Factory, Nanjing, China), and according to the ASTM D2863 standard, the sample dimensions were 130 × 6.5 × 3.0 mm³.

The vertical burning tests (UL94) were measured by a CZF-3 instrument (Jiangning Analytical Instrument Factory, Nanjing, China), and according to the ASTM D3801 testing procedure, the sample dimensions were 130 × 13.0 × 3.0 mm³. The vertical burning categories are shown in Table 2 according to EN 60695-11-10:1999.

For each set of five test specimens from the two conditional treatments, calculate the total afterflame time for the set t_f in seconds, using the following equation:

Table 2: Vertical burning categories.

Criteria	Category (see note)		
	V-0	V-1	V-2
Individual test specimen afterflame time (t_1 and t_2)	≤ 10s	≤ 30s	≤ 30s
Total set afterflame time t_f for any conditioning	≤ 50s	≤ 250s	≤ 250s
Individual test specimen afterflame plus afterglow time after the second application ($t_2 + t_3$)	≤ 30s	≤ 60s	≤ 60s
Did the afterflame and/or afterglow progress up to the holding clamp?	No	No	No
Was the cotton indicator pad ignited by flaming particles or drops?	No	No	Yes

Note: If the test results are not in accordance with the specified criteria, the material cannot be categorized by this test method. Use the horizontal burning test method described in clause 8 to categorize the burning behavior of material.

$$t_f = \sum_{i=1}^5 (t_{1,i} + t_{2,i}) \quad (1)$$

where:

t_f – the total afterflame time, in seconds;

$t_{1,i}$ – the first afterflame, in seconds, of the i^{th} test specimen;

$t_{2,i}$ – the second afterflame, in seconds, of the i^{th} test specimen.

The standard sample for LOI and vertical burning was dried to constant weight at 70°C, weighed and recorded as W_0 ; it was placed in distilled water at 70°C for 168 h, and dried it at 70°C to constant weight, recorded as W_1 . The immersed samples were subjected to LOI and vertical burning tests. The mobility of the flame retardant in EP/PPXSPB flame retardant systems is calculated according to the formula:

$$M\% = \frac{W_0 - W_1}{W_0} \times 100\% \quad (2)$$

Cone calorimeter test was carried out according to the ISO 5660-1 standard on a FTT cone calorimeter (Fire Testing Technology Co. Ltd. UK). Specimens with sheet dimensions of 100 × 100 × 3.0 mm³ were irradiated at a heat flux of 35 kW/m². Each sample was tested at least twice.

The tensile strength tests were performed according to the International Organization for Standardization ISO 527-2 standards using a TCS-2000 electric tensile tester (Gotech testing machines Inc., Taiwan), and the tests were performed at a speed of 10 mm·min⁻¹ at room temperature.

Charpy impact tests were performed according to ISO 179-1 standard using a GT-7045-MDL Charpy impact tester (Taiwan). All of the listed results are the mean of five samples. The dumbbell sample dimension of tensile tests was 200 mm × 20 mm × 4 mm, and the size of the stretched part is 60 mm × 10 mm × 4 mm. The sample dimension of Charpy impact tests was 80 mm × 10 mm × 4 mm.

Scanning electron microscopy (SEM) testing by an S-3400N instrument (Hitachi, Japan) was used to investigate the combustion residues of burned samples from cone calorimeter tests.

The adhesive strength tests were performed according to GB/T 7124-2008 using electronic universal testing machine RGD-5 (Shenzhen, China). The stretching rate was 10 mm/min, Iron substrate 100 mm × 25 mm × 5 mm, sizing area of 12.5 mm × 25 mm, curing conditions of 119°C/2 h + 146°C/2 h + 178°C/2 h. The data was taken as the mean of five samples.

3 Results and discussion

3.1 Structural characterization

The structure of PPXSPB was characterized by FTIR, ¹HNMR, and mass spectroscopy. Figure 1 was the FTIR spectra of SPDPC and PPXSPB, as is shown in spectra of PPXSPB, the absorption peak of P=O appears at 1245 cm⁻¹, 1022 cm⁻¹ and 1074 cm⁻¹ are the absorption peaks of P–O–C and P–N (15), respectively. Compared with SPDPC, the spectrum of PPXSPB shows the absorption peaks at 3380 cm⁻¹ is attributed to the stretching vibration absorptions of –NH₂. The absorption peak at 838 cm⁻¹

Figure 1: FTIR spectra of SPDPC and PPXSPB.

is attributed to the bending vibration absorptions of –Ph. The absorption peaks at 1598 cm⁻¹ is assigned to the variable angle vibration of –NH (16), and the absorption peak of P=Cl at 547 cm⁻¹ disappeared.

Figure 2 was the ¹HNMR (a) and ³¹PNMR (c) spectra of PPXSPB and the ³¹PNMR (b) spectrum of SPDPC. As is

Figure 2: ¹HNMR (a) and ³¹PNMR (c) spectra of PPXSPB and ³¹PNMR (b) spectra of SPDPC.

Figure 3: Mass spectrum of PPXSPB.

shown in Figure 2a, the signal at 2.50 ppm is attributed to the DMSO- d_6 protons. The chemical shift of protons (b), (g) of methylene between $-NH_2$ and the aromatic ring is at 3.9 ppm, and methylene proton adjacent to P-O can be observed at 3.34 ppm. The chemical shifts of $-NH_2$ adjacent to the aromatic ring is at 4.22 ppm, the chemical shifts of the protons (c), (d), (e) and (f) of the aromatic ring were observed at 7.15-7.56 ppm. The protons (h) of $-NH$ between $-P=O$ and the aromatic ring is shown at 8.07 ppm. The ^{31}P NMR is shown in Figure 2c, the signal at 6.45 ppm is attributed to the P proton, compared with Figure 2b, the signal at 6.45 ppm disappeared, which proves that SPDPC has completely reacted.

The mass spectrum of PPXSPB is shown in Figure 3. The m/z values 232.1, 429.1, 497.2, 609.1, 789.2 are correspond to $1/13 M_8H^+$, $1/2M_2H^+$, MH^+ , $1/2 M_3H^+$, $1/2M_4H^+$, respectively, while M is the repeating unit of PPXSPB.

3.2 Thermal stability of PPXSPB and EP/PPXSPB composite

Figure 4a is the TG and DTG curves of PPXSPB in air atmosphere. Epoxy resin will decompose at about 200°C in air (17), while PPXSPB starts to decompose at 250~300°C, which proves that it can adapt to the processing temperature of epoxy resin and may delay the decomposition of epoxy resin to some extent. The residual carbon content is 56.5% at 600°C, this indicates that it has good char formation, which may have potential promotion effect on the flame retardancy of the material (18-21).

In order to study the thermal properties of the material degradation process, the thermal decomposition (TGA under nitrogen) and thermo-oxidate decomposition (TGA under air) of EP/PPXSPB composited are investigated.

The TG and DTG curves of EP/PPXSPB composited with different contents of PPXSPB in nitrogen and in air are shown in Figures 4b and 4c. It can be seen that the initial decomposition temperature of the EP/PPXSPB system is slightly lower than that of the pure epoxy resin in the atmosphere of both air and nitrogen. This is perhaps due to the larger steric hindrance of PPXSPB which leads to low crosslink density of the EP/PPXSPB systems (22,23). As is shown in Figures 4b and 4c, the char yields around 480°C under air atmosphere are higher than which under nitrogen atmosphere. However, at 600°C and 800°C, the result is reversed where the char yield is lower in N_2 atmosphere. So we can infer that an oxidative environment promotes the formation of a char layer earlier, it helps the substrate to fully oxidize and degrade at high temperatures.

However, it is noted that the residual carbon yield of the cured epoxy resin increases as phosphorus increases. The residual char yield of EP-1, EP-2, and EP-3 are 23%, 25%, and 27% respectively, while the residual char yield of EP-0 is only 5%. It means that the PPXSPB can improve the carbonization characteristics of the epoxy resin during combustion. As a result, it can be concluded that the phosphorus and nitrogen in the EP/PPXSPB system have a synergistic effect in the condensed phase to promote charring of epoxy resin (24,25).

3.3 Water resistance and flame resistance of EP/PPXSPB composite

The flame retardant and water resistance of the cured epoxy resins are listed in Table 3. As shown in Table 4, the LOI value of pure EP is only 18.0%, with the increase of phosphorus content, the LOI value of EP-1, EP-2 and EP-3 are increased to 28.8%, 31.4%, and 32.2%, respectively, which is due to the overall flame retardancy of the N-P synergistic flame retardant system (26,27). After immersion in water at 70°C for 168 h, the

Figure 4: The TG and DTG curves of PPXSPB (a) and EP/PPXSPB composites (b,c): (a) in air atmosphere, (b) in nitrogen atmosphere, (c) in air atmosphere.

system shows a lower flame retardant migration rate. This is mainly due to the fact that PPXSPB forms a large number of chemical bond connections with epoxy, and the compatibility is greatly improved, thereby preventing the migration of the flame retardant to the surface of the material.

3.4 The cone calorimeter test

The fire hazard of materials is essentially a combination of thermal hazard and the smoke hazard. Therefore, it is necessary to analyze the combustion characteristics of materials that cause thermal hazards and smoke hazards

under fire conditions. Using the cone calorimeter is an effective way to measure these indicators. The heat release rate (HRR) is one of the most important effective evaluation parameters for thermal hazards in fire behavior, and the

smoke produce rate (SPR) reflects the smoke hazard when the material is burning.

As is shown in Figures 5a-c, the peak heat release rate (PHRR), total heat release (THR) and smoke produce

Table 3: Thermal analysis data of PPXSPB and EP/PPXSPB composites.

Samples	Temperature of weight loss (°C)				Residue (%)			
	T _{5%} (N ₂)	T _{5%} (Air)	T _{max} (N ₂)	T _{max} (Air)	600°C (N ₂)	600°C (Air)	800°C (N ₂)	800°C (Air)
PPXSPB	/	290	/	320	/	59.1	/	9
EP-0	330	317	353	345	24.4	4.9	24.2	0.2
EP-1	295	300	326	314	28.8	22.5	26.0	1.5
EP-2	292	297	329	309	30.7	25.5	28.9	2.1
EP-3	292	295	321	307	31.0	27.2	29.2	2.8

Table 4: Flame retardance and water resistance of different simples.

Sample	t ₁ (s)	t ₂ (s)	UL94	LOI%	Dripping	M%	t ₁ ' (s)	t ₂ ' (s)	UL94 (after water immersion)	LOI% (after water immersion)	Dripping (after water immersion)
EP-0	45	39	Burning	18.0	No	0.02	49	39	Burning	18	No
EP-1	9	8	V-0	28.8	No	0.11	20	12	V-1	28.0	No
EP-2	7	5	V-0	31.4	No	0.18	9	7	V-0	30.5	No
EP-3	7	4	V-0	32.2	No	0.27	9	4	V-0	31.0	No

Figure 5: HRR (a), THR (b), and SPR (c) curves of EP/PPXSPB composites.

rate (SPR) of EP/PPXSPB composites are all lower than that of EP-0. This means that it can provide longer time for human escapes in the event of a fire. From the trend of HRR curve we can infer that after the flame retardant system begins to burn, the surface of the system rapidly forms a layer of carbon under the catalysis of the produced phosphoric acid, thereby causing a small decrease of HRR at the beginning of combustion.

SEM and digital images of the char residues after cone calorimeter test are revealed in Figure 6, combined with the residue which is showed in Table 5, it is obvious that after burning, EP-0 has only a small amount of residue, while the char of EP-2 was fully expanded and covered with small bubbles containing non-combustible gas. The surface of the system is heated to form an expanded carbon layer. On the one hand, external radiant heat is difficult to transfer to the inside, reducing the heat absorption value of the internal material and reducing the pyrolysis rate (28). On the other hand, it increases the time required for

thermal degradation to release flammable volatiles. At the same time, the non-combustible gas released by the ruptured bubbles, such as NH_3 , H_2O , etc., takes away the heat required for combustion, and the carbon layer formed on the surface can retard the contact speed of the material interior with oxygen to some extent, thereby delaying the burning of the materials (29).

3.5 Tensile strength, impact strength and adhesive strength of EP/PPXSPB composite

The tensile strength, impact strength and adhesive strength properties of different samples are shown in Table 6. The tensile strength and impact strength properties of EP/PPXSPB composite are reduced than EP-0. On the one hand, compared with the liquid curing agent used in EP-0, the solid curing agent used in this EP/PPXSPB composite

Figure 6: SEM and digital images of the char residues after cone calorimeter test: (a) EP-0, (b) EP-0, (c) EP-0 magnification: 200 $\times$, (d) EP-2, (e) EP-2, (f) EP-2 magnification: 200 $\times$.

Table 5: Cone calorimeter data of EP/PPXSPB composites.

Samples	TTI (s)	PHRR (kW/m ²)	avHRR (kW/m ²)	THR (MJ/m ²)	avEHC (MJ/kg)	avMLR (g/s)	TSR (m ² /m ²)	Residue (%)
EP-0	79	785.54	335.44	92.25	23.20	0.128	3216.37	10.27
EP-1	80	409.57	176.07	68.27	16.85	0.092	3003.04	25.83
EP-2	81	344.52	146.06	65.00	16.29	0.075	2746.96	32.34
EP-3	81	339.80	145.50	63.40	16.06	0.067	2549.81	32.50

Table 6: Tensile strength, impact strength and adhesive strength of EP/PPXSPB composite.

Sample	P%	Tensile strength (MPa)	Impact strength (kJ/m ²)	Adhesive strength (MPa)
EP-0	0	64.97 ± 0.97	7.11 ± 0.91	13.0 ± 0.69
EP-1	2.88	35.21 ± 0.87	4.86 ± 0.45	11.62 ± 0.34
EP-2	3.24	47.10 ± 0.71	6.58 ± 0.68	13.79 ± 0.65
EP-3	3.56	40.21 ± 0.99	5.92 ± 0.72	12.88 ± 0.59

is less likely to be evenly dispersed. During the mixing of the flame retardant system, some of the PPXSPB did not uniformly disperse, resulting in a slight agglomeration phenomenon, so that some PPXSPB cannot bond well with the epoxy resin and cause a slight gap in the system (30). Eventually, if there is external force contact, the system is unevenly stressed, and it is more prone to brittle fracture. On the other hand, steric hindrance is also one of the causes of the deterioration of the mechanical properties of the material. Larger steric hindrance of PPXSPB reduces the reactivity of PPXSPB, and some unreacted PPXSPB acts as a filler, thereby reducing the crosslink density of the system.

As for the adhesive strength of different samples, the adhesive strength of EP-2 increase 6% than that of EP-0. The main reason for this phenomenon is that the two curing agents have different internal stresses in the curing process. It is known that the use of a liquid curing agent will cause a certain degree of volume shrinkage of the curing system. When the internal stress is large, the adhesive strength will be significantly reduced. In addition, the stress distribution around the adhesive end or adhesive gap is not uniform, the resultant stress also increased the possibility of cracks appear. While PPXSPB is a solid curing agent, PPXSPB can partially act as filler during curing process, so the volume shrinkage of the cured product was reduced (31). At the same time, when the cured material containing the filler subject to the stress, the stress will be uniformly transferred to the surface of the filler particles. The filler takes most of the stress and played a role in the uniform distribution of stress. So there is a higher adhesive strength. However, too much excessive PPXSPB is equivalent to add an excessive amount of filler into the system. Excessive filler will reduce the degree of crosslinking of the system, and result in a decrease in adhesive strength.

4 Conclusions

A phosphorus-nitrogen flame-retardant curing agent PPXSPB was successfully synthesized. The impact of

PPXSPB on the properties of the epoxy resin (E-44) was discussed. The results show that with the increase of phosphorus content, the flame retardant effect of the system is getting better and better. As a reactive flame retardant curing agent, it has excellent water resistance and is difficult to migrate. When the phosphorus content is 3.24%, the comprehensive performance of the system is best. The LOI value is 31.4%, impact strength is 6.58 kJ/m², tensile strength is 47.10 MPa and the adhesive strength is 13.79 MPa.

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