

Halogen Free Flame Retardant Rigid Polyurethane Foam with a Novel Phosphorus–Nitrogen Intumescent Flame Retardant

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ABSTRACT: A novel phosphorous-nitrogen containing intumescent flame retardant, toluidine spirocyclic pentaerythritol bisphosphonate (TSPB), was synthesized and characterized by Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR). Flame retardant rigid polyurethane foams (TSPB-RPUF) were prepared by using TSPB. The flame retardancy of TSPB on rigid polyurethane foams (RPUF) was investigated by the limiting oxygen index (LOI), vertical burning test, thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and FTIR. The results showed TSPB exhibited better compatibility with RPUF and lesser negative influence on the mechanical properties of TSPB-RPUF. When the content of TSPB was 30 pph, the LOI of TSPB-RPUF could reach 26.5%, and a UL-94 V-0 rating was achieved. Furthermore, the TSPB-RPUF exhibited an outstanding water resistance that it could still obtain a V-0 rating after water soaking. TGA showed the charring ability of RPUF was relatively poor, However, the residual weight of TSPB-RPUF was improved greatly. SEM and FTIR indicated the intumescent chars formed from TSPB-RPUF were compact and smooth, which was a critical factor for protecting the substrate material from burning. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

KEYWORDS: flame retardance; foams; mechanical properties; polyurethanes; functionalization of polymers

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INTRODUCTION

Rigid polyurethane foam (RPUF) is widely used in industries and our daily lives due to its excellent properties. However, like the majority of organic materials, the RPUF is very flammable and releases toxic gases in the process of burning, which limits their further applications.^{1,2} The improvement of the fire behavior of the RPUF has currently been an important subject of many studies among the developments of new polymer foam materials.^{3,4} Traditionally, the main flame retardants for RPUF are the compounds containing halogen which endow the RPUF excellent flame retardation. But when burning, these kinds of retardants release a lot of toxic and corrosive gases, which pollutes environment, erodes instruments, and damages people's health.^{5,6} So, the flame retardant additives which have good flame retardant efficiency and hardly pollute environment are particularly needed.

In recent years, the phosphorus-nitrogen containing intumescent flame retardants (IFRs) have received considerable

attentions because it provides excellent fire protection with minimum of overall health hazard.^{7,8} The IFR system usually experiences an intense expansion and forms protective charred layers, thus well protecting the underlying material from the action of the heat flux or flame during combustion. Therefore, IFRs have been widely utilized in the flame retardation of RPUF and manifested good efficiency.^{9,10} However, traditional IFRs are mixtures, which are generally made of three constituents: inorganic acid sources (e.g., ammonium polyphosphate, etc.), carbonifics (e.g., pentaerythritol, graphite, etc.) and spumifics (e.g., melamine, etc.), and these additives are confronted with the problems of water solubility. Furthermore, they are not compatible with the RPUF matrix, which weakens the mechanical properties of the RPUF.^{11,12}

To overcome the disadvantages of traditional IFRs, the single intumescent flame retardant which chemically combines acid source, carbonization agent, and blowing agent into one molecule have been developed and proved to excellent nontoxic and

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smoke-suppressing halogen-free flame-retardant additives. These flame retardants present excellent flame retardancy and char forming ability in many polymeric materials, and have more slight damage for the mechanical properties of polymeric matrix.^{13,14} However, the application of these flame retardants in RPUF has few reports. Chen et al.¹⁵ prepared flame-retardant flexible polyurethane foam with phosphorus-nitrogen containing 2-carboxyethyl(phenyl)phosphinic acid melamine salt (CMA), and reported that the CMA-filled polyurethane foam had good flame retardance. When the content of CMA is 30 php, the LOI of the FPUF reaches 25.6%. But the CMA is water-soluble, as a result, the flame retardant composites are easily attacked by water and exuded, thus leading to a deterioration of the flame retardancy.

To overcome water solubility of the flame retardants and the deterioration of the mechanical properties of the foams caused by the incorporation of flame-retardant additives, a suitable flame retardant for RPUF should be used. For this purpose, a novel phosphorus-nitrogen containing single intumescent flame retardant, toluidine spirocyclic pentaerythritol bisphosphonate (TSPB), was synthesized and used as a flame-retardant additive for RPUF. The effects of this compound on the flame retardancy and water resistance were examined, and the influence on the compressive strength of the RPUF was also studied.

EXPERIMENTAL

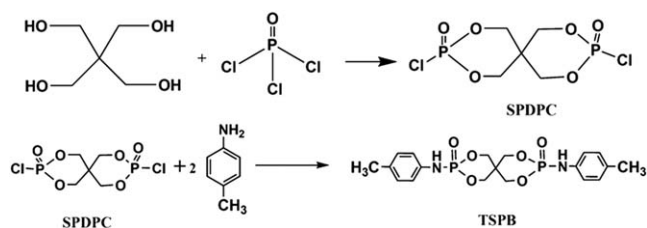
Materials

All the starting materials and solvents were commercially available and were used without further purification. The pentaerythritol was obtained from Shanghai Lingfeng Chemical Plant. Phosphorus oxychloride, acetonitrile, triethylamine, paratoluidine of A.R. grade were from Beijing Tingxing Chemical Plant.

A polyether polyol 4110 were purchased from Gao Qiao Petro. (Shanghai, China), in which typical hydroxyl number is 450 mg KOH equiv g⁻¹; viscosity (25°C) is 3.283 Pa·s; functionality is 4.1; number average molecular weight is 550 g mol⁻¹. Silicone glycol copolymer (SGC), a surfactant was purchased from Shanghai Chemical Reagent (Shanghai, China). Dibutyltin dilaurate (DBDT), a tin catalyst with a density of 1.052 g cm⁻³ and an Sn content of 18 wt % and triethylamine, amine catalyst were purchased from Sichuan Chemical Reagent (Sichuan, China). 4,4'-Diphenylmethane diisocyanate (MDI), -NCO content by weight, 30%, viscosity (25°C), 0.220 Pa·s, was purchased from Yantai Wanhua Polyurethane (Shandong, China). Distilled water, blowing agent, self-preparing.

Synthesis of Spirocyclic Pentaerythritol Bisphosphonate Disphosphoryl Chloride

Pentaerythritol (0.05 mol) and phosphorus oxychloride (50 mL) were mixed in a 250 mL glass flask equipped with a circumference condenser and tail gas absorber. Under stirring, the mixture was heated up to 80°C gradually and maintained 6 h with the protection of nitrogen, then the reaction temperature up to 110°C until no HCl gas was emitted. The raw product was filtered and purified with dichloromethane and ethanol sequentially, then dried to constant weight at 60°C. The white solid powder was obtained (yield: 80%). In addition, the unreacted POCl₃ was recycled to avoid environmental problems.



Scheme 1. Synthesis of TSPB.

Synthesis of Toluidine Spirocyclic Pentaerythritol Bisphosphonate

SPDPC (14.85 g, 0.05 mol) and triethylamine (10.12 g 0.1 mol) were added in a glass flask and dispersed by acetonitrile (50 mL), the solution of p-toluidine (0.1 mol) in acetonitrile (10 mL) was then dropwise below 25°C under stirring. After 1 h, the mixture was stirred and gradually heated to 60°C with nitrogen protection. The reaction system would be cooled after 4 h, and the product obtained was filtered and washed with water, and then was purified by recrystallization from acetonitrile and then dried to constant weight at 50°C in vacuum oven. The pale yellow solid powder was obtained (yield: 82.3%; MP: 176–178°C). The synthesis route was shown in Scheme 1.

Preparation of Flame-Retardant RPUF with TSPB

The flame-retardant RPUF samples were prepared by the one-pot and free-rise method. Polyols 4110, distilled water, catalysts (DBDT and triethylamine), surfactant (SGC), and flame retardant (TSPB) were well mixed in a 1 L beaker. Next, MDI was added into the beaker with vigorous stirring for 10 s. The mixture was immediately poured into an open mold (300 × 200 × 150 mm³) to produce free-rise foam. The foam was cured for 168 h under ambient conditions. The formulations of RPUF were shown in Table I.

Measurements

Structural Characterization of TSPB. IR spectroscopy was applied with a Vector-22 FTIR spectrometer using KBr pellets. ¹H-NMR spectra were recorded on a Bruker AV II-400 MHz spectrometer, using tetramethylsilane (TMS) as a reference and DMSO-d₆ as a solvent.

Limiting Oxygen Index Test. The LOI test was performed using an HC-2 oxygen index test instrument in terms of the standard

Table I. Formulations of Flame-Retardant RPUF Containing Different TSPB Contents

Material	php ^a
Polyols 4110	100
DBDT	0.26
Triethylamine	0.46
SGC	2.0
distilled water	0.4
TSPB	0-30
MDI	150

^a Parts per hundred of polyol by weight.

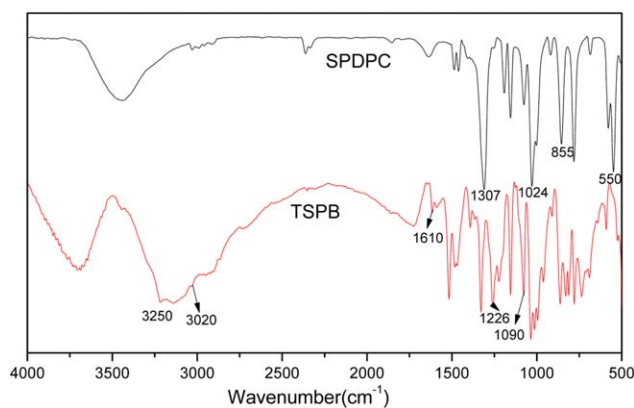


Figure 1. FTIR spectra of SPDPC and TSPB. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

LOI test, ASTM D 2863-97. The specimens for measurement were cut to a size of $127 \times 10 \times 10 \text{ mm}^3$.

Vertical Burning Test. The vertical burning tests were performed with a CZF-5 vertical burning instrument according to ASTM D 3801-96. The specimens for measurement were machined into sheets of $127 \times 13 \times 10 \text{ mm}^3$.

Thermogravimetric Analysis. Thermogravimetric analysis (TGA) was done in a TG-209F3 thermal analyzer at a scanning rate of $10^\circ\text{C}/\text{min}$ under N_2 , 4 mg samples were heated under nitrogen from room temperature to 700°C .

Scanning Electronic Microscopy Observation. Scanning electronic microscopy (SEM, SU-1500) was used to investigate the surface of residues of the flame retardant RPUF. The residue samples for SEM were obtained after combustion in their limiting oxygen concentration. SEM graphs of the residual char samples were recorded after gold coating surface treatment.

Mechanical Property Measurement. The compressive strength was measured with a universal electronic tensile machine (Shimadzu, Japan) with compression rate of $2 \text{ mm}/\text{min}$ according to ASTM D 1621-94.

Water Resistance Test. The samples were put in distilled water at 70°C and kept at this temperature for 168 h. The treated samples were subsequently taken out and dried in a vacuum oven at 80°C to constant weight. The weight of the sample was measured before water soaking and after drying. The migration percentage was calculated as the following equation:

$$\text{Migration percentage } (M) = \frac{W_0 - W}{W_0} \times 100\% \quad (1)$$

where W_0 is the initial weight of the samples before water soaking, and W is the remaining weight of the samples after water soaking and drying. Moreover, the flame resistance of the composites was also evaluated by the change of LOI values and UL-94 rating after the water treatment.

RESULTS AND DISCUSSION

Chemical Structure of TSPB

The FT-IR spectra of SPDPC, TSPB are shown in Figure 1. There are some characteristic peak for SPDPC: 1307 cm^{-1}

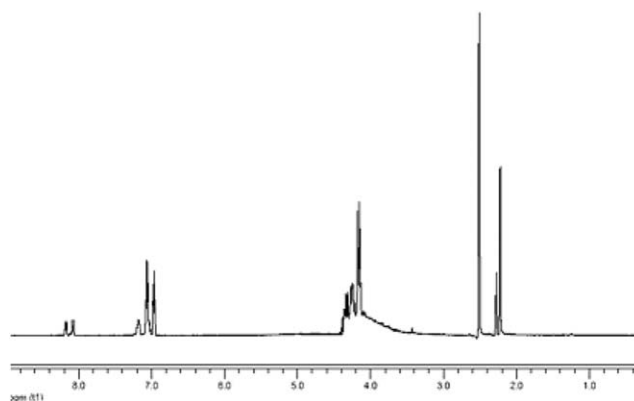


Figure 2. $^1\text{H-NMR}$ spectrum of TSPB.

($\text{P}=\text{O}$), 1024 cm^{-1} ($\text{P}-\text{O}-\text{C}$), 855 cm^{-1} ($\text{P}-\text{O}$), 550 cm^{-1} ($\text{P}-\text{Cl}$), which is consistent with the literature.¹⁶ In the FTIR spectra of TSPB, the absorption peaks at 3250 cm^{-1} , ($-\text{NH}$), 3029 cm^{-1} ($\text{C}-\text{H}$), 1610 cm^{-1} ($\text{C}=\text{C}$), 1226 cm^{-1} ($\text{P}=\text{O}$), 1022 cm^{-1} ($\text{P}-\text{O}-\text{C}$), 1085 cm^{-1} ($\text{P}-\text{N}$) are found. The stretching vibration absorption of $\text{P}=\text{O}$ in SPDPC appeared at 1307 cm^{-1} has shifted to 1226 cm^{-1} in TSPB due to the formation of $\text{O}=\text{P}-\text{N}$, and the disappearance of the peak at 550 cm^{-1} ($\text{P}-\text{Cl}$), which indicates that TSPB is a new compound. The $^1\text{H-NMR}$ spectrum of TSPB is shown in Figure 2. The peaks of H: 2.19–2.31 ppm ($-\text{CH}_3$ in the toluidine), 4.11–4.41 ppm ($-\text{CH}_2$ in the spiral structure), 6.95–7.13 ppm (benzene ring) 8.07–8.23 ppm ($\text{P}-\text{NH}-$) confirm the final structure of TSPB.

Thermal Stability of TSPB

Figure 3 shows the TGA and DTG thermograms of TSPB and RPUF. TGA results show that TSPB starts decomposition at 182.5°C and has a residue of 42% at 700°C in N_2 . The high char weight indicates that TSPB is an efficient char-forming agent. DTG result indicates that TSPB has a major weight-loss stage at 259.3°C , which can be assigned to the intumescent char formation.¹⁶ The RPUF starts decomposing at 275.2°C and has a major weight-loss stage at 342.3°C . Compared to the TGA and DTG data of TSPB and RPUF, the TSPB degrades earlier than RPUF and forms intumescent char before RPUF decomposes quickly, which indicates TSPB is a suitable flame retardant for RPUF matrix.

Cell Morphology of Flame Retardant RPUF with TSPB

It is known that the cell structure of foam can greatly affect the mechanical properties of RPUF. The effect of TSPB on the cell morphology of the polyurethane foam was studied in comparison with virgin polyurethane foam. Figure 4 shows scanning electron micrographs of the virgin RPUF (A), RPUF with TSPB (B). The micrograph of RPUF filled with 30 pph TSPB shows undamaged cell morphology as virgin RPUF. This result indicates TSPB has good miscibility with RPUF matrix. At the same time, it is observed that the size of the cell of RPUF filled with 30 pph TSPB decreases comparison with the RPUF, it is well understood that TSPB existed as hard particles in the foam and high amounts of TSPB particles will lead to the foam shrinkage.¹⁷

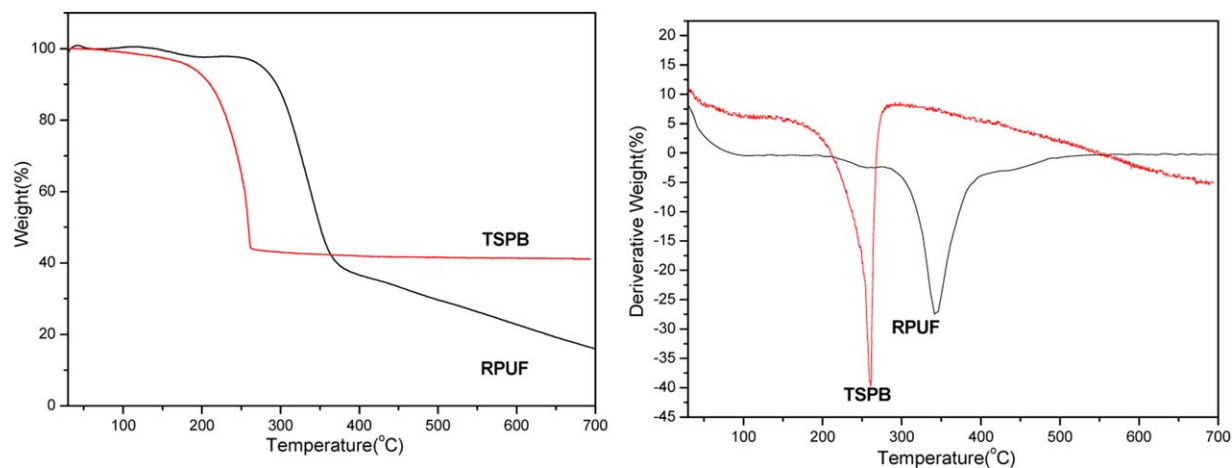


Figure 3. TGA and DTG curves of TSPB and RPUF. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Mechanical Properties of Flame Retardant RPUF with TSPB

The densities of flame retardant RPUF are shown in Table II. Foam density depends on the amount of blowing agent. We chose distilled water as the blowing agent and the amount is

kept constant. It can be seen that there is a increase in foam density with the increase of TSPB contents, which is probably due to the increase of TSPB particles embedded in the cell wall leads to decrease cell size.¹⁸

The effect of TSPB on the compress strength of the RPUF is studied. In general, incorporation of filler into RPUF causes inferior mechanical properties,¹⁹ Meng et al.²⁰ prepared flame-retardant RPUF based on the blended intumescent flame retardants EG/APP, which the optimal ratio was 1 : 1 by weight. When 15 wt % EG/APP was added into RPUF, the compressive strength of RPUF decreased by about 40%. For TSPB, it is clear from Table II that the compressive strength of filled RPUF decreases with reference to neat RPUF. For TSPB(30)-RPUF, the compressive strength decreases from 0.38 to 0.26 MPa, decrease by 31.6%. In comparing with EG/APP, TSPB has lesser negative influence on the mechanical properties of RPUF. This probably because the cell structure of the foam containing 30 pph TSPB is not destroyed, as shown in Figure 4. The result further confirms that there is better compatibility between TSPB and RPUF.

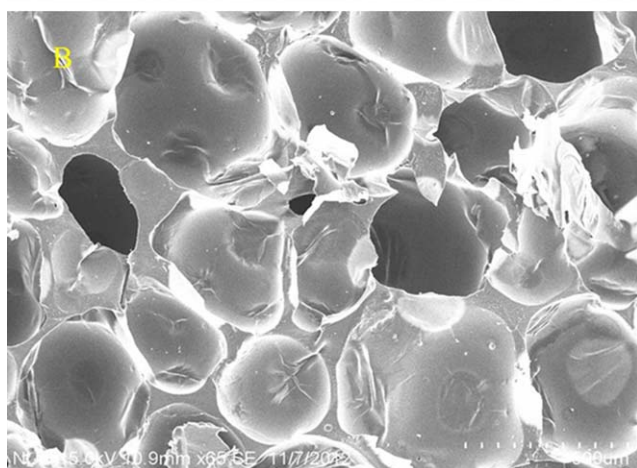
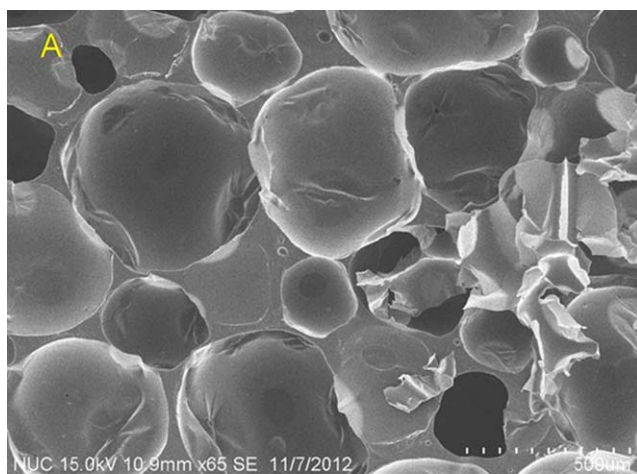


Figure 4. SEM images of (A) RPUF, (B) RPUF filled with 30 pph TSPB. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Flame Retardancy and Water Resistance of the TSPB-RPUF

Table III lists the LOI and UL-94 test results of the samples with different mass ratio of TSPB. It can be seen that pure RPUF shows low flame retardancy, the LOI value is 17%, and

Table II. Mechanical Properties of RPUF with and without TSPB

Sample	TSPB content (pph)	Density (kg/m ³)	Compress strength (MPa)
RPUF	0	50.3	0.38
TSPB(5)-RPUF	5	52.7	0.37
TSPB(10)-RPUF	10	56	0.35
TSPB(15)-RPUF	15	58.3	0.33
TSPB(20)-RPUF	20	63.4	0.29
TSPB(25)-RPUF	25	67.2	0.28
TSPB(30)-RPUF	30	68.7	0.26

Table III. LOI and UL-94 Results of the Samples Before and After Water Soaking

Samples	Before soaking		After soaking		M (%)
	LOI	UL-94 rating	LOI	UL-94 rating	
RPUF	17.0	No rating	17.0	No rating	0
TSPB(5)-RPUF	18.5	No rating	17.5	No rating	0.43
TSPB(10)-RPUF	21.5	No rating	20.5	No rating	0.84
TSPB(15)-RPUF	22.5	No rating	21.5	No rating	1.20
TSPB(20)-RPUF	24.0	No rating	23.5	No rating	1.48
TSPB(25)-RPUF	25.5	V-1	25.0	V-1	1.71
TSPB(30)-RPUF	26.5	V-0	26.0	V-0	1.93

the UL-94 test classed no rating. However, the flame retardancy is significantly improved with the further addition of TSPB. When the amount of TSPB reaches up to 30 pph, the LOI value was increased from 17 to 26.5%, and the UL-94 result was improved from no rating to V-0 rating. The results indicate that TSPB(30)-RPUF has excellent flame retardant effect.

Table III also presents the migration percentages and the flame retardation changes of the samples after soaking. It can be clearly seen TSPB-RPUF has a very low migration percentages, which demonstrate TSPB has excellent water resistance. In Table III, It can be concluded the water soaking has less impact on the flame retardancy of the TSPB-RPUF. In spite of the slight decline in the LOI values after water treatment, a good maintaining of the UL-94 rating was observed. For instance, the LOI value of TSPB(30)-RPUF was 26.5%, whereas the value was still as high as 26% after soaking, and the UL-94 test could still obtain a V-0 rating.

Thermal Stability of TSPB-RPUF

Figure 5 shows the TGA and DTG thermograms of pure RPUF and RPUF with various TSPB contents. Only one step decomposition around 350–500°C is found for pure RPUF and its composites under nitrogen. The detailed TGA and DTG data are summarized in Table IV. RPUF decomposes at 275.2°C, leaving negligible char at 700°C. Compared to the RPUF, The $T_{5\%}$ in TGA curve of TSPB(20)-RPUF and TSPB(30)-RPUF are lower, which is related to the thermal stability of TSPB in this temperature range. The decrease of T_{max} was attributed to the decomposing of TSPB and formation of polyphosphoric acid, which will degrade reaction activation energy of flame-retardant RPUF as a strong Lewis acid catalyst.¹⁹ At high temperatures, TSPB(30)-RPUF has high char yields, 47.4% at 700°C, in comparison with the RPUF, 15.1% at 700°C. The high yield of residual char indicates that TSPB is an effective charring agent. As we know, the protective chars can be resistant to even higher temperatures and shield the underlying polymers from attack from oxygen and radiant heat.¹⁶ Therefore, the addition of TSPB can enhance effectively the flame retardancy of the RPUF.

Morphology and FTIR Analysis of Char Residue

To further clarify the flame retardant mechanism, the morphology of the char residues for the TSPB-RPUF was observed.

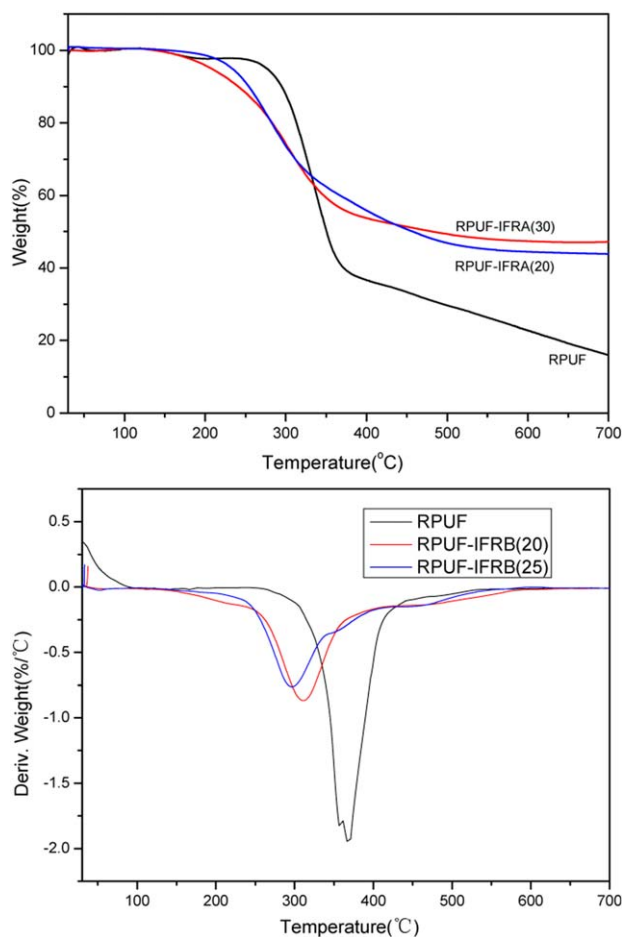


Figure 5. TGA and DTG curves of TSPB-RPUF. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6 shows the SEM micrographs of the residues for the TSPB(30)-RPUF and RPUF after LOI test. From the intersection surface of the char from TSPB(30)-RPUF, it can be seen the outer surface of the char is compact and smooth, however, the inner surface of the char is loose and exists incomplete burned polyurethane residues, which indicates outer compact char can inhibit effectively underlying polyurethane to flame. Further observe the morphology of the char residues of the TSPB(30)-RPUF and RPUF under the condition of magnification 500 times, there is a compact and continuous swollen t-char covered on the composite, which can effectively prevent both heat and mass transfer. In contrast, the char layer of RPUF is rather

Table IV. Data of TGA and DTG Thermograms of RPUF with Various TSPB Additions

Samples	$T_{5\%}$ (°C)	T_{max} (°C)	Char residue at 700°C (%)
RPUF	275.2	367	15.1
TSPB(20)-RPUF	233.8	332	43.4
TSPB(30)-RPUF	211.2	303	47.4

$T_{5\%}$: 5% weight loss temperature. T_{max} : Maximum weight loss temperature.

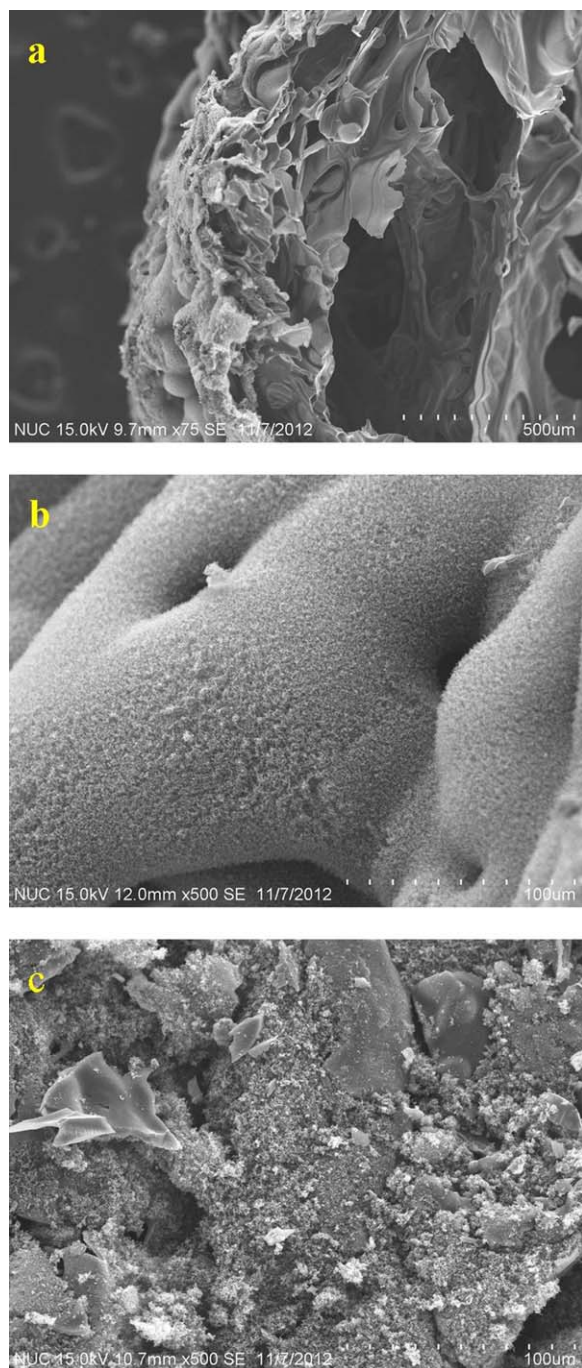


Figure 6. The SEM micrographs of the residues: the intersection surface of the char from TSPB(30)-RPUF(a), the surface of the char from TSPB(30)-RPUF(b), the surface of the char from RPUF(c). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

incompact and broken up, which might be the reason for its unsatisfied flame retardant property.

The FTIR spectrum of the intumescent residual char for TSPB(30)-RPUF is given in Figure 7. As can be seen, in the outer char of TSPB(30)-RPUF, The 1600 cm^{-1} were attributed to the characteristic peak of C=C of aromatic ring,²¹ 1020 and 1180 cm^{-1} attributed to the characteristic peaks of P—O—C

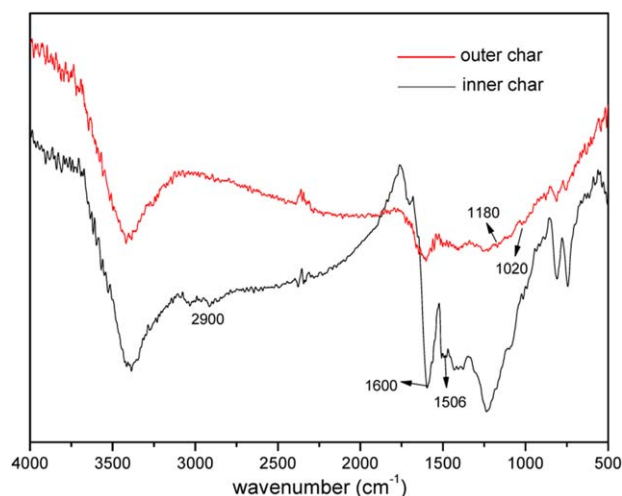


Figure 7. FTIR spectra of the residual char of TSPB(30)-RPUF. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and O=P—O—P=O.^{16,22} The FTIR spectra results show that TSPB in the polyurethane matrix produces phosphoric and polyphosphoric acids during thermal degradation, which acts as the dehydration agents and accelerates the formation of the heat resistant carbonaceous char by carbonization.²¹ In the inner char of TSPB(30)-RPUF, at 1600 , 1020 , and 1185 cm^{-1} the characteristic peaks of C=C, P—O—C and O=P—O—P=O appears; however, at 2900 and 1506 cm^{-1} the absorption peaks of C—H and benzene ring in polyurethane are retained, which means there are incomplete burned polyurethane residues. The results indicate outer compact char can protects the polyurethane from burning, as Figure 6 showed.

CONCLUSIONS

A novel phosphorus-nitrogen containing single intumescent flame retardant, toluidine spirocyclic pentaerythritol bisphosphonate (TSPB), was synthesized and characterized by FTIR and $^1\text{H-NMR}$. TSPB exhibited favorable compatibility with polyurethane and lesser negative influence on the mechanical properties of the flame-retardant RPUF. Particularly TSPB exhibited much lower water solubility and excellent flame retardant performance. When the content of TSPB was 30 pph, the LOI value of the TSPB(30)-RPUF was 26.5%, and the UL-94 test reached a V-0 rating. Furthermore, the composite exhibited an outstanding water resistance and it could still obtain a UL-94 V-0 rating after soaking in 70°C water for 168 h. TGA results showed that the onset decomposing temperature of the TSPB-RPUF decreased but the char yields increased. The SEM and FTIR results indicated that TSPB-RPUF could form a compact and thermostable char residue, which could effectively protect the substrate material from burning.

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