

A Novel Polyurethane Prepolymer as Toughening Agent: Preparation, Characterization, and Its Influence on Mechanical and Flame Retardant Properties of Phenolic Foam

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ABSTRACT: A novel phosphorus- and silicon-containing polyurethane prepolymer (PSPUP) was synthesized by the chemical reaction of phenyl dichlorophosphate with hydroxy-terminated polydimethylsiloxane (HTPDMS) and subsequently with toluene-2,4-diisocyanate. The structure of PSPUP was confirmed by Fourier transform infrared spectroscopy and ¹H nuclear magnetic resonance. Afterward, a series of phenolic foams (PF) with different loadings of PSPUP toughening agent were prepared. The apparent density and scanning electron microscopy results showed that the addition of PSPUP can increase the apparent density of phenolic foam. The compressive, impact and friability test results showed that the incorporation of PSPUP into PF dramatically improved the compressive strength, impact strength, and reduced the pulverization ratio, indicating the excellent toughening effect of PSPUP. The limiting oxygen index of PSPUP modified phenolic foams remained a high value and the UL-94 results showed all samples can pass V0 rating, indicating the modified foams still had good flame retardance. The thermal properties of the foams were investigated by thermogravimetric analysis under air atmosphere. Moreover, the thermal degradation behaviors of the PF and PSPUP/PF were investigated by real-time Fourier transform infrared spectra. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: foams; mechanical properties; thermal properties; flame retardance

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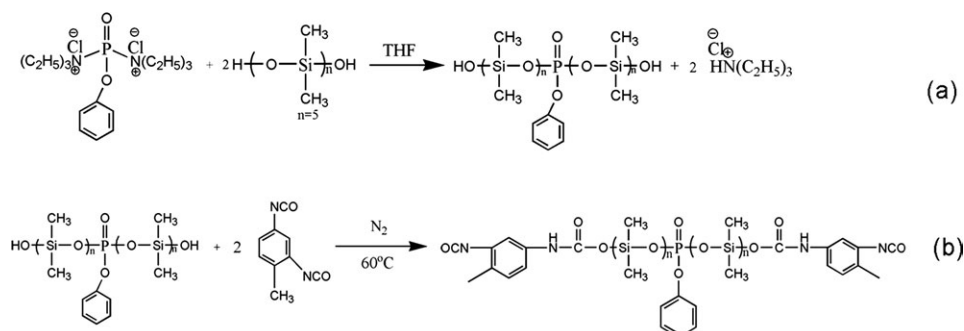
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INTRODUCTION

Phenolic foam (PF) has aroused a great deal of interest in recent years, due to its low thermal conductivity, excellent fire proof performance, and low generation of toxic gas during combustion.^{1–4} Replacing polyurethane foams⁵ and polystyrene foams⁶ which have high flammability with phenolic foam for building thermal insulation materials is the development trend. However, the largest weakness of phenolic foam is its brittleness and powdering, which restricts its wide applications.⁷ Therefore, studying the toughening technology of phenolic foams is particularly necessary.

Over the past few decades, many methods have been developed to improve the toughness properties of phenolic foam, mainly including three categories⁸: chemical modification,⁹ inert fillers,⁷ and fiber reinforcement.¹⁰ Among them, chemical modification has attracted extensive attention for its notable toughening effect.

Typically, the toughening mechanism of chemical modification is introducing flexible chains (such as polyether, polysiloxane) into the rigid backbone of phenolic resin. To introduce the flexible molecular chain into phenolic resin, there must be active groups which can react with resin in both ends of molecular chain of toughening agent. Normally, the active groups include epoxy, hydroxy, amino, and isocyanate. The associated toughening agents are epoxy-terminated polyether,¹¹ polyethylene glycol,¹² amine-terminated polyether,¹³ polyurethane prepolymer,¹⁴ and so on. Among these compounds, polyurethane prepolymer has been spotlighted due to its high reactivity of isocyanate groups. However, the excellent fire retardant performance of phenolic foam itself will be deteriorated after the addition of these toughening agents. Therefore, the toughening agents, which own the function of toughness and flame retardance simultaneously is expected to be the ideal toughening modifier.



Scheme 1. The schematic synthesis route of PSPUP.

Traditionally, halogen-containing compounds are widely used to prepare flame retardants for polymer materials due to their high flame retardant efficiency. However, halogen-containing compounds can generate toxic smoke and corrosive products during combustion, which is harmful to the environment and human beings.^{15,16} So, halogen-free fire retardants have attracted much attention, such as the compounds containing phosphorus, silicon, and so on. Phosphorus-containing compounds are considered to be one of the most effective halogen-free flame retardants,^{17–19} mainly acting on condensed phase flame retardant mechanism. Silicon-containing compounds are also one kind of popular flame retardants due to the high temperature resistance of silica products formed during thermal degradation process, which can cover the surface of char and form a protective silica layer.^{20,21}

In this work, a novel phosphorus- and silicon-containing polyurethane prepolymer (PSPUP) was prepared via the chemical reaction between phenyl dichlorophosphate, hydroxy-terminated polydimethylsiloxane and toluene-2,4-diisocyanate. Then a series of phenolic foams (PF) with different loadings of the polyurethane prepolymer toughening agent were prepared. The physical, thermal, flame-retardant properties and thermal oxidative degradation process of the PF/PSPUP hybrids were investigated.

EXPERIMENTAL

Materials

Phenyl dichlorophosphate (PDCP) was provided by Huiyuan Chemical Industry Corporation (Zhengzhou, China) and freshly distilled before use. Triethylamine (TEA) was obtained from the Sinopharm Chemical Reagent (Shanghai, China), and purified by distillation. Tetrahydrofuran (THF) using as solvent was refluxed with sodium, and then distilled before use. Toluene-2,4-diisocyanate (TDI), phosphoric acid, and *p*-toluenesulfonic acid (*p*-TSA) were standard laboratory reagents and purchased from Sinopharm Chemical Reagent. *n*-pentane, used as blowing agent, was obtained by Tianjing Guangfu Chemical Research Institute (Tianjing, China). Hydroxy-terminated polydimethylsiloxane (HTPDMS, $M_n = 400$) was supplied by Wuxi Quanli Reagent Chemical Factory (Jiangsu, China) and dried at 100°C under vacuum for 3 h. Resol-type phenolic resin (viscosity, 25°C: 2500–3000 mPa S⁻¹, solid content: 75%) was supplied by Shandong Haiguan Chemical Technology (Shandong, China).

Modified silicon oil (colorless transparent liquid) using as defoaming agent was obtained from commercial sources and used as received.

Synthesis of Phosphate Ester-Containing Siloxane Oligomer (PESO)

PDCP (21.1 g, 0.1 mol) was dissolved in 40 mL dry THF in a 100-mL conical flask fitted with a magnetic stirrer. Then, triethylamine (21.25 g, 0.21 mol) was added into the above mixture and the system was cooled to 0°C and stirred for 20 min. Meantime, HTPDMS (84 g, 0.21 mol) was dissolved in 100 mL dry THF in a 500-mL three-neck flask equipped with a nitrogen inlet, a dropping funnel, a calcium chloride dry tube and a mechanical stirrer. The mixture of PDCP, TEA and THF was added dropwise to the above flask at 0°C using an ice bath, and kept at 0°C for 4 h with constant agitation under nitrogen. Finally, the mixture was heated to room temperature, stirred for another 10 h. The triethylamine hydrochloride salt by-product was removed by filtration. Then the solution was rotary evaporated to remove the solvent and the unreacted reactants. A viscous liquid was obtained and named PESO. The synthesis route was illustrated in Scheme 1(a).

Synthesis of Phosphorus, Silicon-Containing Polyurethane Prepolymer (PSPUP)

TDI (10.45 g, 0.06 mol) and TEA (0.003 mol %) were introduced into a 250-mL three-neck flask with a magnetic agitator, flux condenser, dropping funnel, and nitrogen inlet. After the mixture was saturated with nitrogen atmosphere under vigorous magnetic stirring, a mixture of PESO (28.14 g, 0.03 mol) and THF (40 mL) was slowly dropped into the above flask within 2 h at 60°C. Finally, the mixture was maintained at 60°C and stirred for another 10 h. Afterward, the solution was rotary evaporated to remove the solvent. A white viscous liquid was obtained and named PSPUP. The synthesis route was illustrated in Scheme 1(b).

Preparation of the Samples of Phenolic Foam

A certain percentage of resol-type phenolic resin, silicon oil (defoamer), and PSPUP (toughening agent) were added into a 500-mL plastic beaker at room temperature, and then stirred with high-speed mechanical mixer for about 25 s. The mixture was then mixed with *n*-pentane (foaming agent) and curing agent (phenol sulfonic acid : phosphoric acid : water = 2 : 1 : 2), and stirred at high speed for 30 s. The obtained viscous

Table I. The Composition and Apparent Density of Phenolic Foam Samples

Sample no.	Resol (g)	Foaming agent (g)	Curing agent (g)	Defoamer (g)	PSPUP (g)	Apparent density (kg m ⁻³)
PF	150	15	15	6	0	32.6
PSPUP-2%-PF	150	15	15	6	3	43.1
PSPUP-3%-PF	150	15	15	6	4.5	48.9
PSPUP-5%-PF	150	15	15	6	7.5	60.2

mixture was poured into a foaming mould quickly, and cured at 80°C for 2 h. The sample was cut precisely and used for the fire and mechanical testing. The composition of toughness phenolic foams was listed in Table I. Other samples were prepared in the same procedures.

Measurements and Characterization

¹H nuclear magnetic resonance (NMR) spectra was recorded on an AVANCE 400 Bruker spectrometer at room temperature with chloroform-*d* as the solvent.

Fourier transform infrared (FTIR) spectroscopy was obtained at 4 cm⁻¹ resolution and averages of spectra were obtained from at least 16 scans in the standard wavenumber range of 400–4000 cm⁻¹ by Nicolet 6700 spectrometer (Nicolet Instrument Company, USA) using KBr pellets.

The limiting oxygen index (LOI) test was carried out with an HC-2 oxygen index meter (LOI analysis instrument company, Jiangning County, China). The test was measured according to ASTM D2863. The samples used for the test were 100 × 10 × 10 mm³.

The vertical burning test was conducted by a CZF-II horizontal and vertical burning tester (Jiang Ning Analysis Instrument Company, China). The specimens which used were 130 × 12.7 × 3 mm³ according to UL94 test ASTM D3801 standard.

Thermogravimetric analysis (TGA) was carried out using a Q5000IR (TA Instruments) thermo-analyzer instrument at a linear heating rate of 20°C min⁻¹ under an air flow. The weight of all samples was kept within 3–10 mg in an open Pt pan and heated from room temperature to 700°C.

Scanning electron microscopy (SEM; KYKY1010B, Shanghai Electron Optical Technology Institute, China) was used to study the cellular structure of phenolic foams, which was obtained by thin sectioning. The slices were adhibitted on the copper plate and then coated with gold/palladium alloy.

Real time Fourier transform infrared spectra (RT-FTIR) was recorded using the Nicolet 6700 FT-IR spectrophotometer equipped with a ventilated oven having a heating device. The samples were ground with KBr powder, pressed into a tablet, placed into the oven, and heated at a raised rate of about 10°C min⁻¹.

The compressive properties were tested with a WSM-20KB universal testing machine (Changchun, China) according to GB/T 8813-2008. At least three samples were tested to obtain average values.

Weighing measurements were used to monitor how much the weight loss after friction. Fixed a sand paper (220 mesh,) on horizontal tabletop firstly, then put the foam sample (base area: 50 mm × 50 mm) which load with 200 g weight on the sand paper. Finally, pulled the foam sample back and forth 30 times evenly with a constant force. The single-pass shift distance is 250 mm. The pulverization ratio is determined as follows:

$$\text{Pulverization ratio} = \frac{M_1 - M_2}{M_1} \times 100\%$$

where *M*₁ and *M*₂ are the weights of the foam samples before and after friction process, respectively.

Charpy unnotched impact strength was evaluated with a JJ-20 mnemonic impact tester (Changchun Intelligent Instrument

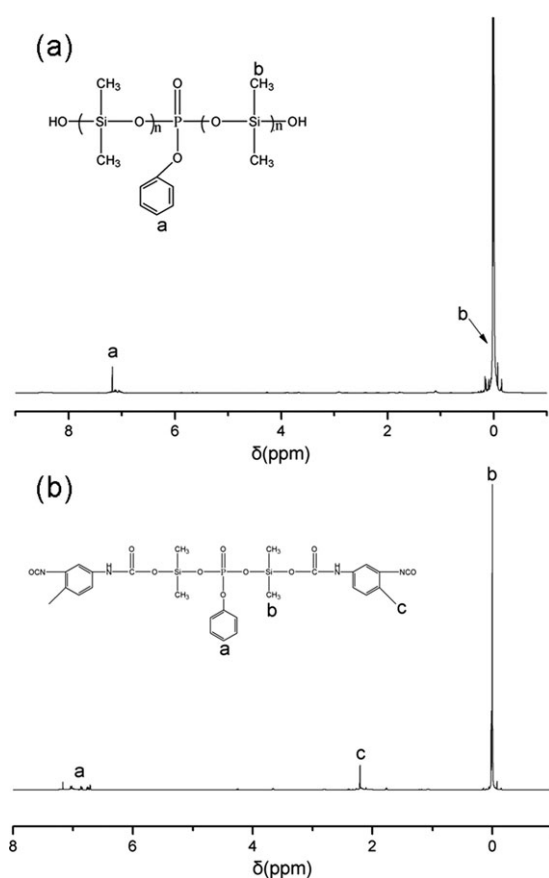


Figure 1. ¹H NMR spectra of PESO (a) and PSPUP (b) in CDCl₃.

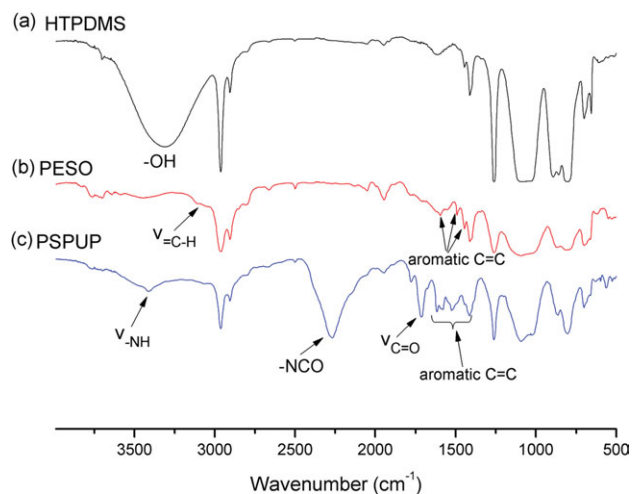


Figure 2. FTIR spectrum of HTPDMS (a), PESO (b) and PSPUP (c). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CO. LTD., China) according to ISO179-1: 2000. The sample dimensions were $130 \times 15 \times 10 \text{ mm}^3$. Ten specimens of each sample were tested and the average values are reported.

The density was determined using the dimensions and the weight of the foam.

RESULTS AND DISCUSSION

Synthesis and Characterization of Phosphorus- and Silicon-Containing Polyurethane Prepolymer (PSPUP)

Scheme 1(a, b) shows the synthetic route of PESO and PSPUP, respectively. It can be clearly seen that PESO was synthesized by the reaction of PDCP with HTPDMS, and then PSPUP was synthesized by the reaction of PESO and TDI. The chemical structure of these two compounds was characterized by ^1H NMR and FTIR. As can be seen from Figure 1(a), the chemical shift at 0 ppm is attributed to the hydrogen atoms of methyl attached to siloxane backbone. Aromatic signals appear at 7.3–7.1 ppm and the hydroxy proton appears at 2.9 ppm. From Figure 1(b), the methyl protons attached to siloxane backbone and the aromatic signals were also observed at 0 ppm and 7.3–7.1 ppm, respectively. The methyl protons attached to aromatic ring appear at 2.2 ppm.

Figure 2(a–c) shows the FTIR spectra of PDMS, PESO, and PSPUP, respectively. From Figure 2(a), the most significant absorption can be observed at 3314 , 2963 , and 1262 cm^{-1} corresponding to O–H stretching vibration, C–H asymmetrical

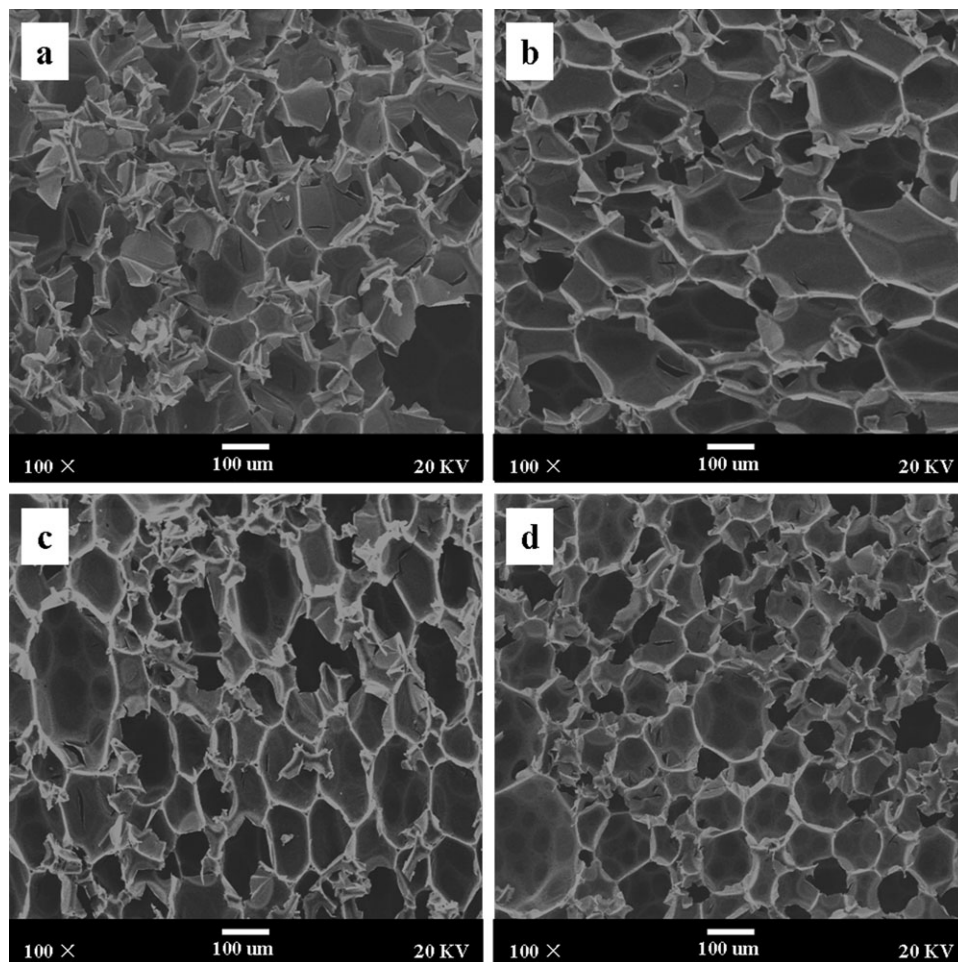


Figure 3. SEM images of pure phenolic foams (a), and phenolic foams with 2 wt % (b), 3 wt % (c), 5 wt % (d) PSPUP.

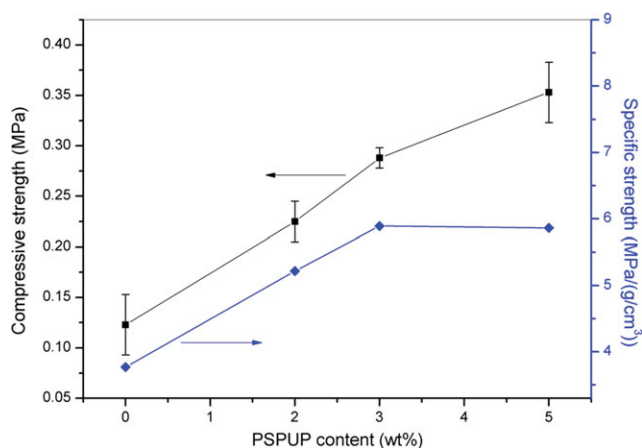
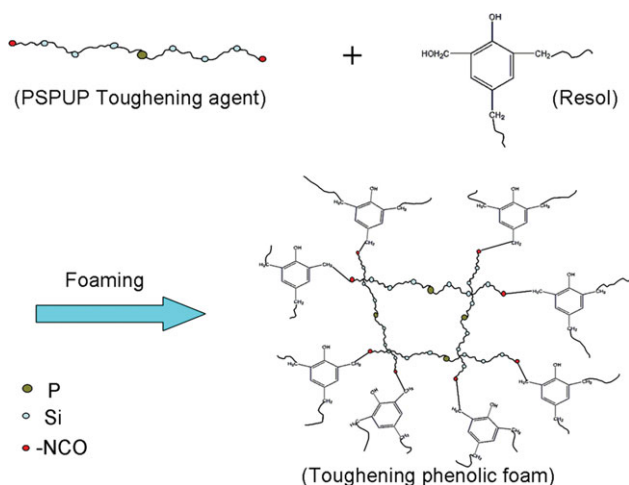


Figure 4. Compressive strength and specific strength of PSPUP/PF systems. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

stretching vibration, and $-\text{CH}_3$ bending vibration of PDMS, respectively. The strong $\text{Si}-\text{O}-\text{Si}$ stretching absorption at $1085-1024\text{ cm}^{-1}$ is characteristics of the siloxane backbone.²² Comparing Figure 2(b) with Figure 2(a), it can be seen that the FTIR spectra change after the reaction between HTPDMS and PDCP. The most obvious change is the reduction of absorption peak intensity of $\text{O}-\text{H}$ stretching vibration and its shifting to 3450 cm^{-1} . The absorption band at around 3099 cm^{-1} is attributed to stretching vibration of $=\text{C}-\text{H}$ groups on aromatic ring.^{23,24} The absorptions at 1596, 1491, and 1445 cm^{-1} are attributed to the skeletal vibration of aromatic ring. From Figure 2(c), the absorptions at 3413, 1713, and 1525 cm^{-1} are attributed to the $\text{N}-\text{H}$ stretching vibration, $\text{C}=\text{O}$ stretching vibration and $\text{N}-\text{H}$ deformation vibration, respectively. The characteristic absorption peak of $-\text{NCO}$ group occurs at 2268 cm^{-1} .²⁵ The above results confirmed the structure of PSEO and PSPUP as shown in Scheme 1.



Scheme 2. The toughening schematic of phenolic foam. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Apparent Density and Microstructure of Phenolic Foams

As is well known, light weight and good mechanical strength phenolic foam is the ideal foam material in the field of exterior-wall insulation material. So, it is important to enhance the physical properties of phenolic foam by modification.

As listed in Table I, the apparent density of phenolic foam samples increases after the addition of PSPUP, which is mainly due to the high reaction activity of isocyanate groups on both ends of PSPUP molecular chains. Isocyanate groups can react with hydroxymethyl of resol rapidly during the mixing process.²⁶ Therefore, the addition of PSPUP into phenolic foaming system increases the viscosity of resol matrix and restricts the movement of resol resin under the force provided by the gasification of n-pentane. The microstructure of the phenolic foams was observed by SEM (Figure 3). Figure 3(a) shows the microstructure of pure phenolic foam, the foam cells are not very uniform, and there are many fragment attached to the cell walls. After adding 2 and 3 wt % of PSPUP into phenolic foam, the shape of foam cells is ellipsoid-like, and the size of the cells is gradually reduced, as show in Figure 3(b, c). When the amount of PSPUP is increased to 5 wt %, the shape of cells is relatively spherical and the average size of the cells is further reduced.

Compression Properties

The results of compressive strength measurements are given in Figure 4. The black curve shows that the compressive strength of phenolic foam modified with 5 wt % PSPUP significantly increases by 187% (from 0.123 to 0.353 MPa) compared to that of neat phenolic foam. This significant improvement may be attributed to the increased apparent density. As for the specific strength curve (the blue curve), the specific strength of PSPUP/PF systems also has a growing tendency. Phenolic foam modified with 3 wt % PSPUP (48.9 kgcm^{-3}) exhibits the greatest specific strength. The specific strength²⁷ is known as the strength-to-weight ratio, which can properly reflect the quality of structural material. The increased compressive strength and specific strength of PSPUP/PF systems indicated that the addition of PSPUP improved the toughness of PSPUP/PF systems significantly. The toughening mechanism is illustrated in

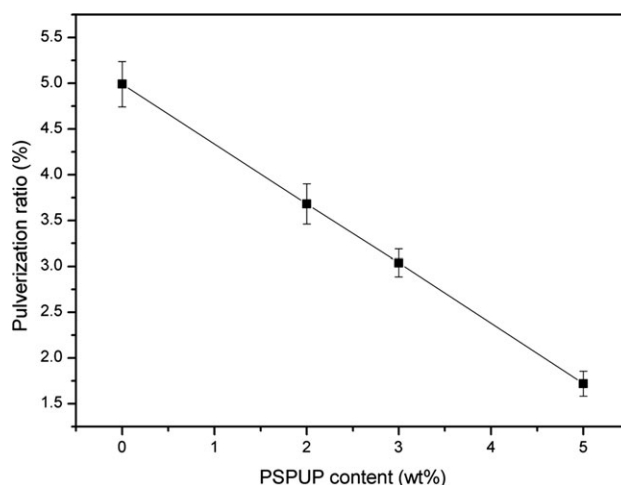


Figure 5. Pulverization ratio of PSPUP/PF systems.

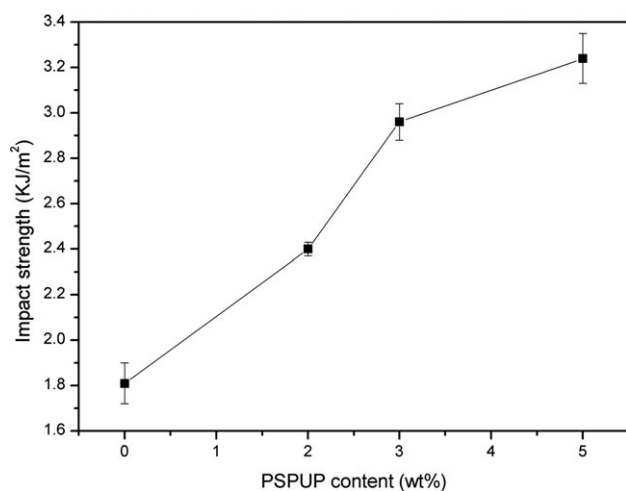


Figure 6. Impact strength of PSPUP/PF systems.

Scheme 2. First, the PSPUP molecular chains have excellent flexibility due to the flexible Si—O—Si structure. Second, the high-activity —NCO group in the ends of PSPUP can react with hydroxymethyl of resol rapidly during the foaming process, so the flexible PSPUP molecular chains are chemically bonded to the rigid phenolic structure.

Friability Properties

Efflorescence always being a serious drawback of phenolic foam, many researchers^{28–30} have focused on reducing the powdering of phenolic foams. The friability test results of the PSPUP modified phenolic foams are shown in Figure 5. With the increasing of PSPUP content, the pulverization ratio of PSPUP/PF systems shows a linear decline. Moreover, the phenolic foam with 5 wt % PSPUP exhibits the minimal pulverization ratio (1.72%). These results indicate that the addition of PSPUP significantly reduces the friability of phenolic foam. This phenomenon also can be explained by the introduction of flexible PSPUP molecular chains into the rigid phenolic structure, thus the modified phenolic foam cells can not be easily damaged during the friction process. So, the pulverization ratio of PSPUP/PF systems shows a linear decline with the increasing of PSPUP content.

Impact properties

To further explain and support the toughening efficiency of the toughening agent, the impact properties of phenolic foam samples are investigated. The results are showed in Figure 6. A gradually increasing impact strength trend of modified phenolic foam samples can be seen obviously with slightly increasing PSPUP content, indicating that the introduction of PSPUP can

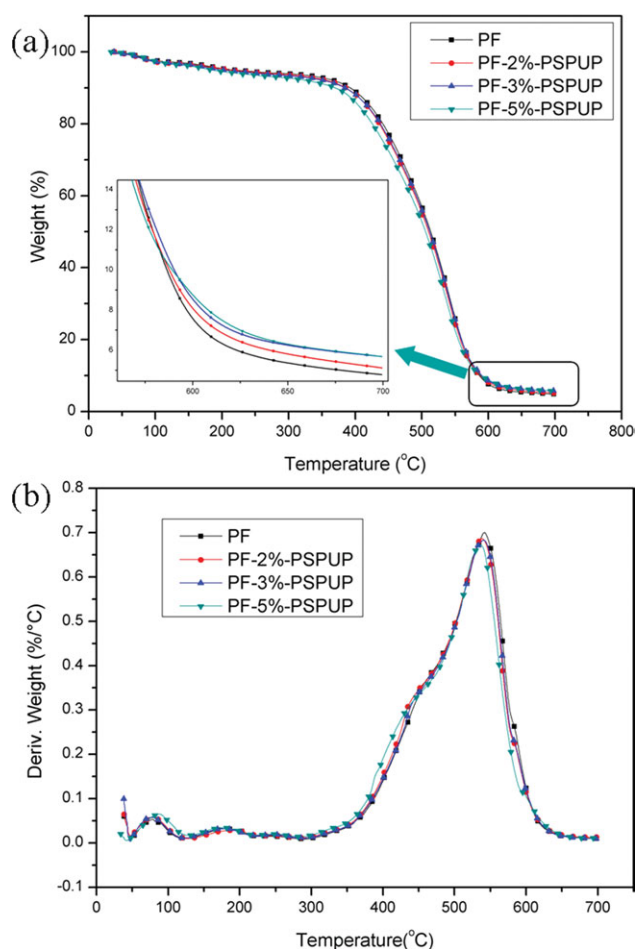


Figure 7. TGA (a) and DTG (b) curves of PF and PSPUP/PF foams with different PSPUP content in air atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

assuredly improve the shock resistance of phenolic foam, and further showing the high toughening efficiency of PSPUP.

Thermal Stability

Figure 7 shows the (a) TGA and (b) DTG curves of pure PF and phenolic foams with various contents of PSPUP at the linear heating rate of $20^{\circ}\text{C min}^{-1}$ under air atmosphere, and the corresponding values are listed in Table II. From the DTG curve, it can be seen that there are three DTG peaks located approximately at 80, 180, and 540°C , which are mainly due to the evaporation of water, the dehydration of further curing and the degradation of phenolic resin, respectively.³¹ All modified phenolic foams present the similar degradation behavior to that

Table II. TGA Data in Air of Phenolic Foam Samples

Sample no.	$T_{-5\%}$ ($^{\circ}\text{C}$)	$T_{-10\%}$ ($^{\circ}\text{C}$)	$T_{-50\%}$ ($^{\circ}\text{C}$)	T_{max} ($^{\circ}\text{C}$)	Char residue (%) at 700°C
PF	217.3	392.5	513.4	541	4.79
PSPUP-2%-PF	210.9	386.1	510.3	537	5.14
PSPUP-3%-PF	199.2	384.8	512.0	541	5.69
PSPUP-5%-PF	185.1	370	505.7	536	5.69

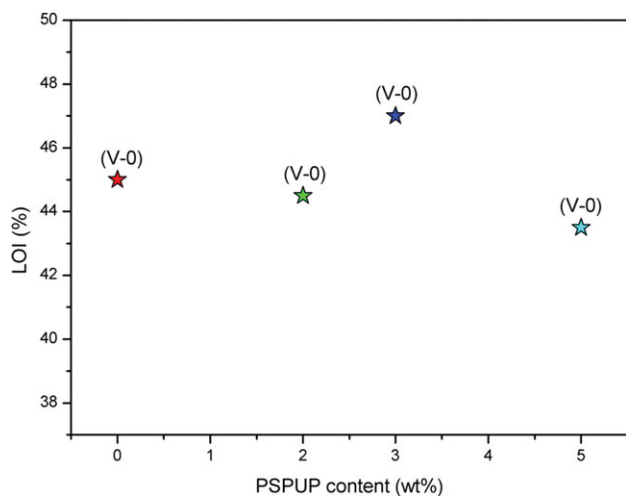


Figure 8. UL-94 results and LOI curves of the foam systems. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of neat PF, but the main difference is the degradation temperature. Compared with neat PF, the modified phenolic foams have slightly lower degradation temperatures ($T_{-5\%}$ and $T_{-10\%}$ listed in Table II), and the temperature of the maximum DTG peaks (T_{max}) is also slightly shifted to lower temperature. Moreover, a slight increase of char residue at 700°C is observed by the incorporation of PSPUP into phenolic foams. These results indicate that the incorporation of PSPUP basically maintains the excellent thermal stability of phenolic foam.

Fire-Resistant Behavior

UL-94 vertical burning test³² and limiting oxygen index (LOI)³³ were used to evaluate the fire-resistant behavior of PF and PF/PSPUP systems, as shown in Figure 8. It is clear that all samples can pass the V0 rating, indicating the modified foams still remain the good flame retardance. The LOI value of pure PF is 45%. The phenolic foam sample which modified by 3% PSPUP content exhibits the highest LOI value 47%. When the content of PSPUP is 2 and 5%, the LOI values decrease slightly to 44.5 and 43.5%, respectively. Although the methyl groups of polysiloxane are flammable, the phosphorus and silicon elements endow the PSPUP toughening agent with good fire retardance, thereby remain the excellent flame retardance of phenolic foam.

Thermal Oxidative Degradation

To further investigate the thermal oxidative degradation process of pure PF and PSPUP/PF systems under the air atmosphere, PF and 3 wt % PSPUP/PF were chosen for measuring the changes in spectra of dynamic FTIR, as shown in Figure 9(a, b), respectively. The assignment of dynamic FTIR spectra of PF and 3 wt % PSPUP/PF sample is presented in Table III.³⁴ It can be noticed that with increasing temperature the —OH stretching band at 3391 cm^{-1} shifts toward higher wavenumbers because changes take place in the hydrogen bonding and the number of OH groups decreases. Also, the intensity of —OH band at 1380–1350 cm^{-1} decreases. At around 180°C, two new peaks appearing at 1650 and 1740 cm^{-1} , which are attributed to carbonyl groups and carboxylic acids, formed together with

quinones after oxidation of the methylene bridges.³⁵ When the temperature increases to 300 and 400°C, the peak at 1740 cm^{-1} has become much stronger. While the temperature rises up to 540°C, it is found that most of absorption peaks disappear, indicating that the main decomposition happens at this stage. This is consistent with the TGA results.

The FTIR spectrum of 3 wt % PSPUP/PF sample from Figure 9(b) shows very similar features to that of PF. The characteristic peaks of PSPUP are not obvious because its characteristic bands probably coincide with the characteristic bands of the PF matrix. It is worth noting that the intensities of most peaks at both of 450 and 540°C are weaker than that of pure PF, meaning that the presence of PSPUP can catalyze the thermal degradation of PF and the formation of char.

CONCLUSION

In this work, we successfully synthesized a novel phosphorus- and silicon-containing polyurethane prepolymer (PSPUP), to modify the phenolic foams. The physical properties, thermal

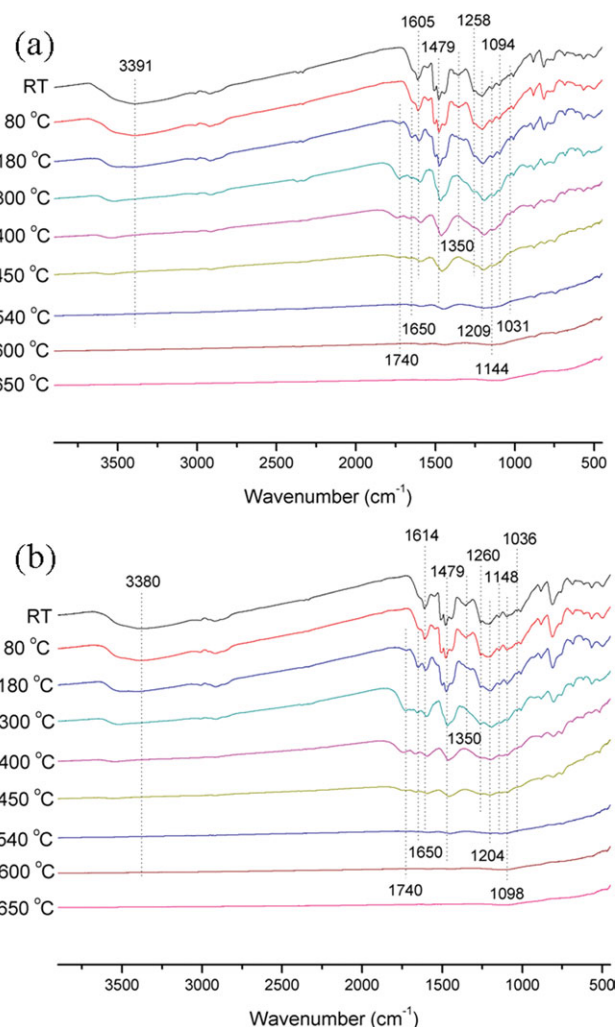


Figure 9. Real time FTIR spectra of PF (a) and 3 wt % PSPUP/PF sample (b) at different pyrolysis temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Assignment of FTIR Spectra of PF and 3 wt % PSPUP/PF Sample

Wavenumber (cm ⁻¹)	Assignment
PF	
3391	Phenolic O—H stretch
3100–2800	C—H stretching
1740	Tetra-substitute benzene ring C—C stretch
1650	Carbonyl C=O stretch
1605, 1510, 1479	C—C stretching vibration of aromatic ring
1442	aliphatic CH ₂ scissor bending
1384, 1356	Phenolic O—H in-plane deformation
1258	Biphenyl ether C—O stretch
1209	Phenolic C—O stretch
1094	Si—O—Si stretch
1031	P—O stretch
PSPUP-3%-PF	
3380	Phenolic O—H stretch
3100–2800	C—H stretching
1740	Tetra-substitute benzene ring C—C stretch
1650	Carbonyl C=O stretch
1614, 1512, 1479	C—C stretching vibration of aromatic ring
1442	aliphatic CH ₂ scissor bending
1384, 1356	Phenolic O—H in-plane deformation
1260	Biphenyl ether C—O stretch
1204	Phenolic C—O stretch
1098	Si—O—Si stretch
1036	P—O stretch

stability, flame-retardant properties and thermal oxidative degradation process of phenolic foams modified by PSPUP were studied. Results showed that the addition of PSPUP increased the apparent density of phenolic foam. Compressive, impact and friability test results showed that the incorporation of PSPUP into PF improved compressive strength, specific strength, impact strength and reduced the pulverization ratio of PF/PSPUP, such as the compressive strength of 5 wt % PSPUP/PF sample significantly increases by 187%, the 3 wt % PSPUP/PF sample exhibits the greatest specific strength, and the 5 wt % PSPUP/PF sample exhibits the minimal pulverization ratio (1.72%) compared to that of neat phenolic foam (4.99%). Though the LOI values of PF/PSPUP systems partly showed a reduction, the samples still remained the excellent flame retardance, with all samples passing V0 rating in UL-94 test. TGA results showed that the PF/PSPUP samples possessed slightly lower initial degradation temperatures and a slight increase of char residue at 700°C. The RT-FTIR results indicated the thermal oxidative degradation process of pure PF and PSPUP/PF, which included the dehydration, oxidation, and crosslinking reactions. The flexible Si—O—Si chain structures and rich flame

retardant elements (Si, P, N) content of PSPUP contribute an excellent toughening effect to phenolic foam without a considerable deterioration of the fire-retardant properties.

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