Preparation and properties of a novel flame retardant polyurethane quasi-prepolymer for toughening phenolic foam

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ABSTRACT: A novel phosphorus- and nitrogen-containing polyurethane quasi-prepolymer (PNPUQP) was synthesized and incorporated into phenolic foam (PF) in different ratios in order to improve the toughness. The structure of PNPUQP was confirmed by Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR). The effects of PNPUQP on the flame retardant properties, thermal stability and mechanical properties of modified PF were investigated. The results suggested that the addition of 3 wt % PNPUQP increased the toughness of PF and improved the flame retardancy. The investigation on the morphology of PF and modified PF by scanning electron microscope (SEM) certified the good toughness of the PNPUQP on PF. Additionally, the thermal properties of the foams were investigated by thermogravimetric analysis (TGA) under N_2 atmosphere. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42424.

INTRODUCTION

Polymer foams have been widely used as insulating material in civil construction due to the good thermal insulation, mechanical strength and affordable cost, so polymer foams have attracted more and more attentions in recent years. Among them, phenolic foam (PF) plays a dominant role due to its excellent fire properties, low water absorption, low flammability combustion, low smoke density and toxicity. Therefore, PF has been widely used in a broad range of applications, especially in construction.[1–8] However, PF is considerably brittle because they consist of lots of benzene rings, which limits its applications.[9–12] Thus, some research is required to improve the toughness of PF for their comprehensive applications.[13]

Over the past decades, several methods, such as inter-fillers, fiber reinforcement and chemical modification, ect. have been employed to deal with the brittleness of PF.[14] Among these methods, chemical modification is found to be an effective method to improve toughness. In general, chemicals with long and flexible molecular chains are introduced into the rigid backbone of PF to reduce brittleness by chemical reaction.[8,15] Nor-

mally, the toughening agents are characterized with long chains and active groups that can react with hydroxymethyl and hydroxyl in phenolic resin. At present, the frequently used toughening agents are polyether,[8] polyurethane prepolymer,[15] epoxy resin,[16] cardanol,[17] etc. Among these toughening agents, polyurethane prepolymer has been widely used to toughen PF owing to its flexible polyether chains and high reactivity of isocyanate groups. However, polyurethane prepolymer has side effects on the flame retardancy of PF. Thus, the enhancement of the flame retardant of polyurethane prepolymer for their comprehensive applications in toughness of PF is necessary.[13] For this reason, flame retardant and eco-friendly polyurethane prepolymer containing phosphorus, nitrogen or silicon, etc, have attracted much attention in recent years.[2,18–20]

Yuan, Xing *et al.*, used 10-(2,5-dihydroxyphenyl)-9, 10-dihydro-9oxa-10-phosphaphenanthrene-10-oxide (DOPO-BQ) to synthesize phosphorus-containing polyurethane prepolymer (PPUP) as toughening agent. Although this agent lowered the limiting oxygen index (LOI), especially at a high content of PPUP, it still exhibited better flame retardance than the conventional
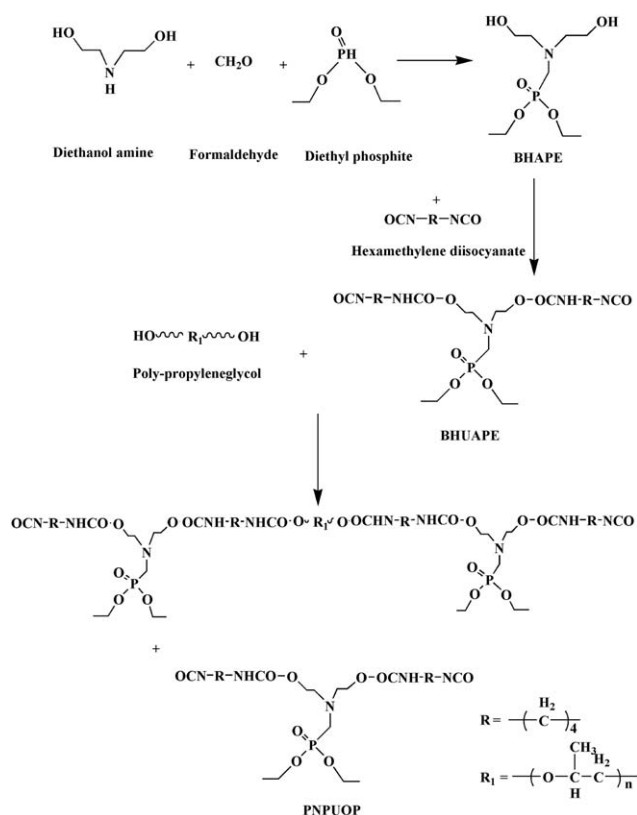
Scheme 1. Synthesis route and structure of PNPUQP.

polyurethane prepolymer toughening agent.[15] Yang et al. synthesized phosphorus- and silicon-containing polyurethane prepolymer by the chemical reaction of phenyl dichlorophosphate with hydroxy-terminated polydimethylsiloxane and toluene-2,4-diisocyanate. The LOI value was found to improve, which resulting from the synergistic effect of phosphorus and silicon.[2] In addition to the phosphorus-silicon synergism, phosphorus-nitrogen synergism has been demonstrated in some papers. However, there have been few literature reports concerning the use of PNPUQP as flame retardant toughening agent in PF.[21]

In this work, a novel polyurethane quasi-prepolymer containing phosphorus and nitrogen elements was designed and synthesized for the tougheness of PF. The structure of the PNPUQP was characterized by Fourier transform infrared spectra (FTIR), ^{1}H nuclear magnetic resonance (^{1}H NMR) and ^{31}P nuclear magnetic resonance (^{31}P NMR) respectively. In order to explore the effect of PNPUQP on the properties of PF, a series of PF with different loadings of PNPUQP toughening agents were then prepared. The flame properties, thermal stability, and mechanical properties of the PF were investigated.

EXPERIMENTAL

Materials
Diethanolamine, formalin (37% in water), diethyl phosphite (DEPP), hexamethylene diisocyanate (HDI), Dibutyltindilaurate (DBTDL), Ethyl acetate (analytical grade) were purchased from Nanjing Chemical Ragents Co. Ltd (Jiangsu, China), Poly-propyleneglycol (PPG; molecular weight of 2000 g mol^{-1}) was

supplied by Haian Petrochemical Plant (Jiangsu, China) and dried at 110°C under vacuum for 1 h before used. Resol-type phenolic resin (made in lab, viscosity, 25°C, 3000∼4000 mPa·S, solid content: ≥75%), Other reagents were used as received without further purification.

Synthesis of BHAPE (N, N-Bis (2-hydroxyethyl)-aminomethylphosphonic acid diethylester)
The BHAPE was prepared according to the previous report and illustrated in Scheme 1[1] Diethanolamine (10.5 g, 0.1 mol) and formalin (8.1 g, 37% in water) were added into a three-necked flask equipped with thermometer, reflux condenser and mechanical stirrer at 35°C. The mixture was stirred at 45°C for 2 h and heated to 80°C to remove the generated water during the reaction under vacuum. DEPP (13.8 g, 0.1 mol) was then added into the above flask after the temperature was cooled to at 60°C. The mixture was then stirring for another 2 h at 60°C, the BHAPE was obtained after dried in a vacuum at 100°C.

Synthesis of BHUAPE (N, N-Bis (2-hydroxyethyl urethane) aminomethylphosphonic acid diethylester)
HDI (16.8 g, 0.1 mol) and a proper portion of catalyst (0.1 wt % DBTDL) were dissolved in 30 mL of dried Ethyl acetate and charged into a four-necked round-bottomed flask equipped with mechanical stirrer, dropping funnel and nitrogen inlet. The mixture was stirred and heated slowly to 70°C under N$_2$ atmosphere. Then a solution of BHAPE (12.75 g, 0.05 mol) and 20 mL of dried ethyl acetate was slowly added into to the above flask within 30 min, and the mixture was kept stirring for 2 h. The obtained product was referred as BHUAPE.

Synthesis of PNPUQP
PPG (25 g, 0.0125 mol) was dissolved in 20 mL of dried Ethyl acetate, and the mixture was added dropwise into the above flask within 30 min. The mixture was then stirred for another 2 h. After the reaction was completed, the solvent was evaporated at reduced pressure, a yellow viscous PNPUQP was obtained. The synthesis route was illustrated in Scheme 1.

Preparation of Phenolic Foams
The PFs were prepared by a one-shot process, where all the ingredients were mixed simultaneously and allowed to cure at 70°C for 2 h.[22] The procedure was described as: Firstly, a certain proportion of resol-type phenolic resin, phosphoric acid (neutralizing agent), tween 80 (surfactant), PNPUQP (toughening agent), and curing agent (p-toluenesulfonic acid : phosphoric acid : sulphuric acid : water = 0.5 : 1 : 3 : 2.5 by weight) were added into a 500 mL plastic beaker at room temperature. The mixture was stirred immediately with high-speed mechanical mixer for 60 s. Then, n-pentane (blowing agent) was added into the mixture and stirred for 10 s. Finally, the obtained viscous mixture was poured into a foaming mould quickly, and cured at 70°C for 2 h. The foam sample was cut precisely and used for characterization including the fire, mechanical, and other testings. The compositions of PFs were summarized in Table I. Other samples were prepared by the similar procedure.

Characterization
Fourier Transform Infrared (FTIR) Spectroscopy. FTIR spectra of samples were recorded on a FTIR in a range of wave

Table I. The Compositions of Samples

Sample no.	Resol (g)	Defoamer agent (g)	Curing agent (g)	Foaming agent (g)	PNPUQP (g)
PF	90	6	13.5	5	0
PNPUQP-2%-PF	88.2	6	13.5	5	1.8
PNPUQP-3%-PF	87.3	6	13.5	5	2.7
PNPUQP-5%-PF	85.5	6	13.5	5	4.5
PNPUQP-8%-PF	82.8	6	13.5	5	7.2

numbers from 4000 to 400 cm^{-1}, using attenuated total reflection Fourier transform infrared (ATR-FTIR) method on a Nicolet (USA) IS10 instrument.

Nuclear Magnetic Resonance Spectroscopy (NMR) Analysis. Nuclear magnetic resonance (NMR) measurement was performed on an AVANCE 400 Bruker spectrometer at room temperature. The solvent was CDCl$_3$.

Limiting Oxygen Index Testing (LOI). LOI testing was carried out with a JF-3 oxygen index instrument (Jiangning Analysis Instrument Factory, Jiangsu, China), the test was measured according to ASTM D2863. The samples used for the test were 120 $\times$ 10 $\times$ 10 mm^3.

Thermogravimetric Analysis (TGA). Thermogravimetric analyses was performed using a TGA Q500 (TA Instruments) instrument. About 4 mg of each sample was scanned from 30 to 800°C at a heating rate of 10°C min^{-1} under nitrogen gas at a flow rate of 100 mL min^{-1}.

Scanning Electron Microscopy (SEM). PF foams were investigated with a scanning electron microscope (SEM) FEI Quanta 200. The specimens were mounted on an aluminum stub and sputter coated with a thin layer of gold to avoid electrostatic charging during examination

Apparent Density Testing. The apparent density of PFs was measured according to ASTM D1622. The size of specimen was 30 $\times$ 30 $\times$ 30 mm^3 (length $\times$ width $\times$ thickness), and the average values of five foams was recorded.

Compression and Flexural Testing. The compressive and flexural properties were tested with a CMT4000 universal testing machine (Shengzhen, China) according to ASTM D1621-94 and GB/T8812-2007, respectively. At least three samples were tested to obtain average values.

RESULTS AND DISCUSSION

Synthesis and Characterization of BHAPE, BHUAPE, and PNPUQP

As shown in Scheme 1, the novel PNPUQP was synthesized by a three-step process. BHAPE was synthesized via the Mannich reaction. Then the esterification between BHAPE and HDI was carried out to obtain BHUAPE. Followed by the last step that the esterification reaction performed between BHUAPE and PPG 2000, the PNPUQP was obtained.

The chemical structure of BHAPE, BHUAPE, and PNPUQP were characterized by FTIR, ^{1}H NMR and ^{31}P NMR, respec-

tively. The FTIR spectrum of BHAPE, BHUAPE, and PNPUQP are shown in Figure 1. The characteristic absorption peaks of BHAPE at 3401 cm^{-1}, 1220 cm^{-1}, and 1018~960 cm^{-1}, corresponding to the —OH stretching, the P=O stretching and the stretching vibration of P—O—C, respectively, are clearly observed[1]. For BHUAPE and PNPUQP, the esterification reaction led to the disappearance of absorption peak at 3401 cm^{-1} corresponding to —OH group and the generation of new peaks at 3312 cm^{-1} and 3336 cm^{-1} that attributed to the absorption of N—H groups. Additionally, the strong absorption peaks at 2269 and 1719 cm^{-1}, corresponding to isocyanate bond and urethane bond, respectively, are remarkable present. The above analysis confirms the successful synthesis of PNPUQP.

Figure 2 displays the ^{1}H NMR spectra of BHAPE, BHUAPE and PNPUQP, respectively. Figure 2(a) shows the NMR spectrum of BHAPE. The protons of the —CH$_3$ in BHAPE were in the range of 1.2~1.3 ppm. The peaks at 3.96~4.12 ppm were assigned to the protons of P—O—CH$_2$, —CH$_2$ adjacent to tertiary amine nitrogen and —P=O were in the ranges of 2.7~2.8 ppm and 2.9~3.0 ppm, respectively. The protons of —CH$_2$— near to hydroxyl appeared at 3.46~3.72 ppm and the primary hydroxyl band observed at 4.1~4.4 ppm[1]. After reaction with HDI, the proton signal of hydroxyl in the range of 4.1~4.4 ppm disappeared and new signals corresponding to —N—CH$_2$ and —NH
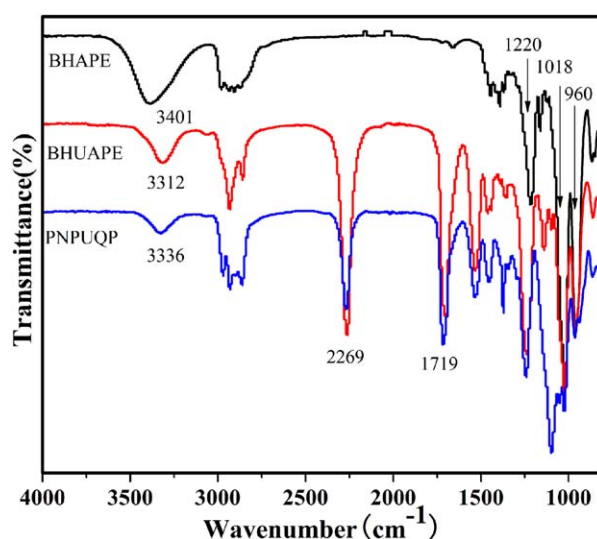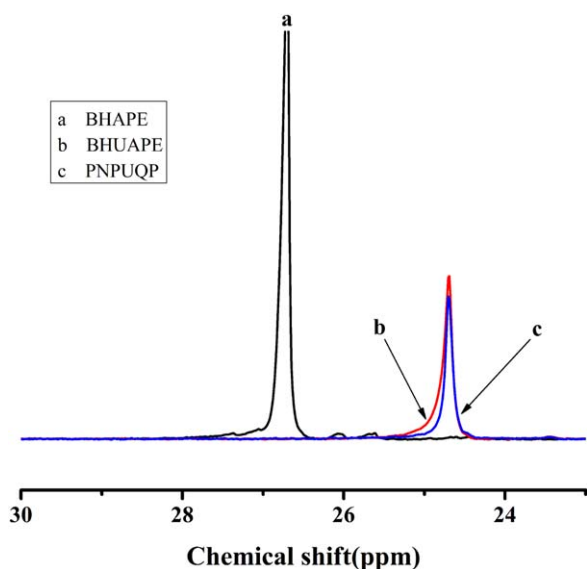

Figure 1. FTIR spectra of BHAPE, BHUAPE and PNPUQP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
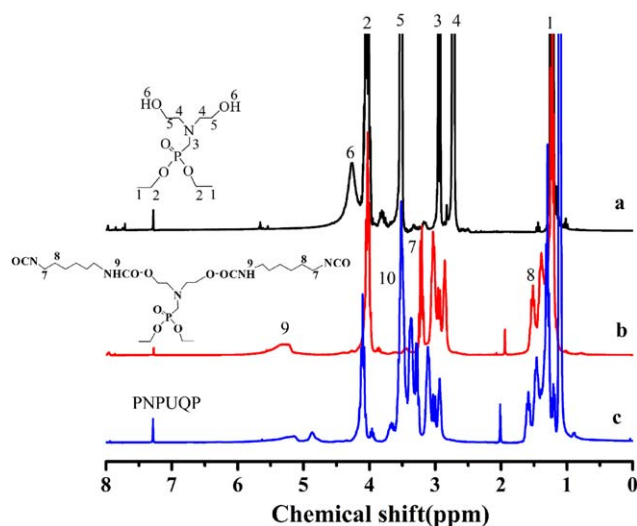
Figure 2. ^{1}H NMR spectra of BHAPE, BHUAPE, and PNPUQP. [Color figure can be viewed in the online issue, which is available at wileyonline-library.com.]

appeared at 3.16∼3.28 ppm and 5.14∼5.70 ppm, indicating that the reaction between the hydroxyl group of BHAPE and isocyanate group [Figure 2(b)]. As shown in Figure 2(c), the ^{1}H NMR spectra of PNPUQP has similar signals with BHUAPE, the different characterized signal corresponding to O—CH in PPG-2000 appeared at 3.43∼3.62 ppm.

The ^{31}P NMR spectra of BHAPE, BHUAPE, and PNPUQP are shown in Figure 3. It can be observed that the BHAPE spectrum exhibit the peaks between 26.3 and 27.8 ppm corresponding to the phosphorus signals from P=O and P—O—C groups. When reacted with HDI and PPG-2000, the phosphorus signals of BHUAPE and PNPUQP both move to 24.3∼25.5 ppm. These results further confirm the successful synthesis of the BHUAPE and PNPUQP.


Figure 3. ^{31}P NMR spectra of BHAPE, BHUAPE, and PNPUQP. [Color figure can be viewed in the online issue, which is available at wileyonline-library.com.]
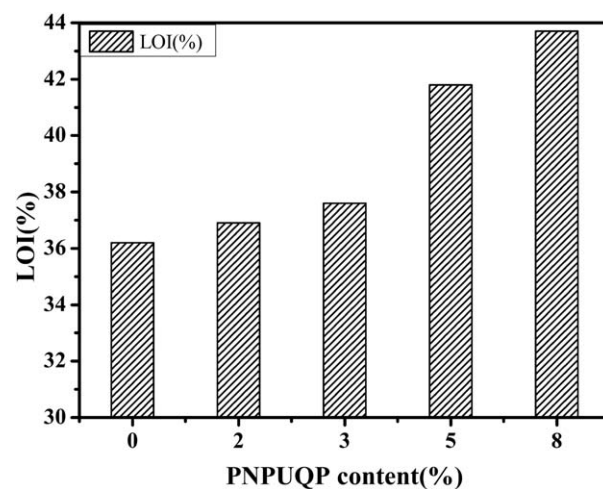
Figure 4. Dependence of LOI values of foams versus PNPUQP content.

Flame Properties

According to ASTM D2863-97, LOI is considered as an important parameter reflecting the flammability of polymeric materials. Compared with conventional foam material, PF exhibit a
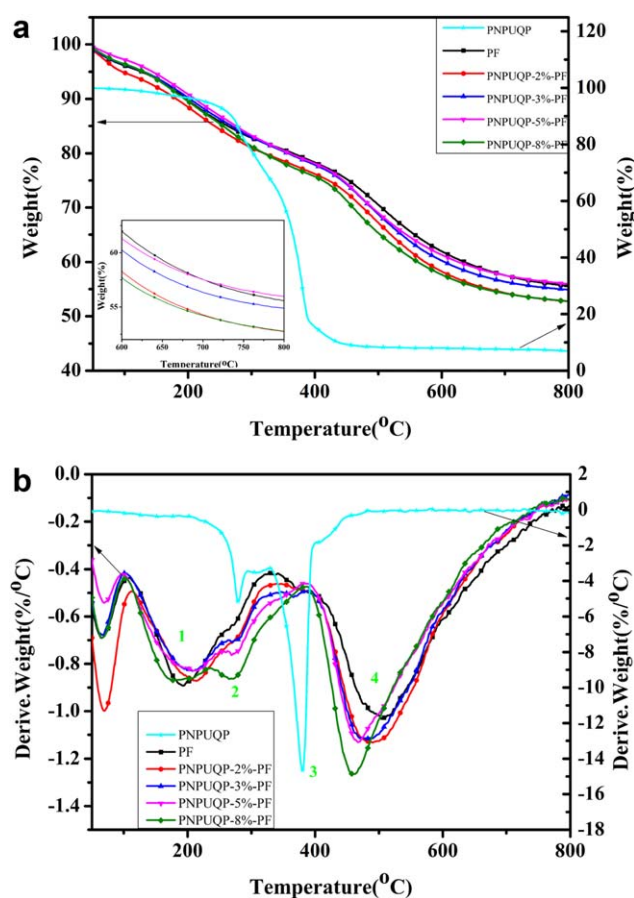
Figure 5. (a) TGA curves of PNPUQP, PF, and PNPUQP/PF foams with differentPNPUQP content in N₂ atmosphere. (b) DTG curves of PNPUQP, PF and PNPUQP/PF foams with different PNPUQP content in N₂ atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Some TGA Date of Pure PNPUQP, PF, and Toughened Foams

Sample no.	$T_{-5\%}$(°C)	T_{max} (°C)				Residue at 800°C (%)
		Step 1	Step 2	Step 3	Step 4	
PNPUQP	229	–	279	380	–	6.9
PF	126	192	–	–	504	55.6
PNPUQP-2%-PF	96	207	279	–	491	52.7
PNPUQP-3%-PF	130	208	277	–	483	54.9
PNPUQP-5%-PF	144	210	273	–	467	56
PNPUQP-8%-PF	129	175	265	–	462	52.8

high LOI value as it have a large number of benzene rings, as well as the high proportion of carbon atoms that easily carbonized at high temperature.[8] The LOI values of pure PF and toughened foams are summarized in Figure 4. When the loadings of PNPUQP increase from 0 to 8 wt %, the LOI values of toughened foams are found to increase drastically from 36.2 to 43.7. These results indicate that the introduction of PNPUQP can enhance the flame retardancy of PF. The phosphorus and nitrogen elements are introduced into the backbone of PNPUQP, resulting in the increase in LOI value of toughened foams. In these cases, phosphorus acts as an acid source, which strengthens the char formation ability and accelerates the char formation process in the condensed phase. Nitrogen acts as gas source, which produces nonflammable gases near foam to protect the underlying material while heating.[1,5,23,24]

Thermal Stability

The thermal stability and thermal degradation of PNPUQP, pure foam and toughened foams are investigated by TGA. The TGA curves mainly include the release of decomposition products and the formation of chars.[13,25] Figure 5 shows the TGA and derivative thermogravimetric (DTG) curves of the PNPUQP, pure PF and toughened foams at the linear heating rate of 10°C min^{-1} from room temperature to 800°C under N$_2$ atmosphere, and some decomposition data are summarized in Table II.

It can be found that Pure PNPUQP mainly showed two stages of weight loss. The first stage decomposition of pure PNPUQP took place from about 230 to 300°C (279°C is the maximum-rate degradation temperature) with a weight loss about 17%, which is can be assigned to the decomposition of urethane bond. The second stage, occurred from around 320 to 400°C (380°C is the maximum-rate degradation temperature) where the mass loss reached about 55%, which is related to the

decomposition of PNPUQP hydrocarbon chains. Both the pure PF and toughened foams have three similar decomposition steps. The decomposition temperature below 100°C (about 8% mass loss), which mainly due to the evaporation of water, blowing agent and some other small molecules products in the foam. In the temperature ranging from 100 to 250°C, most of the chemical bonds begin to breakdown and the maximum weight loss temperatures (T_{max}) of this step occur at around 193°C. This may be due to the degradation of surfactant (Tween 80) and some curing agents in the foam. The degradation of phenolic resin is found in the temperature ranging from about 330–800°C and have the T_{max} at 504°C.[3,8] Compared with pure PF, one step occurring between 230°C and 400°C in the modified PFs is attributed to the degradation of PNPUQP.

As shown in Figure 5, it can be noted that the degradation temperature of toughened PF is lower than that of pure PF, and the temperature of the maximum DTG peaks (T_{max}) is also slightly shifted to lower temperature.[2] With the increase of PNPUQP content, the thermal stability of toughened PF is found to reduce, which is consistent with the earlier report.[26] This phenomenon is probably due to the lower stability of polyurethane section in PNPUQP.[23]

Furthermore, from Table II, it can be seen that the char residue of at 800°C for PNPUQP is only 6.9%, while the char residue of pure PF is 55.6%. The addition of PNPUQP has little changes compared the pure PF. There are mainly two competitive factors which affect the char residue of modified PF. On the one hand, the increase of less stable urethane segments with the increase of PNPUQP content results in reducing the thermal stability of PF and the char residue. On the other hand, the increase of phosphorus element with the increase of PNPUQP content, which acts as a char-forming catalyst during the decomposition process and yields more char at higher

Table III. Mechanical Properties of Pure PF and Modified Foams

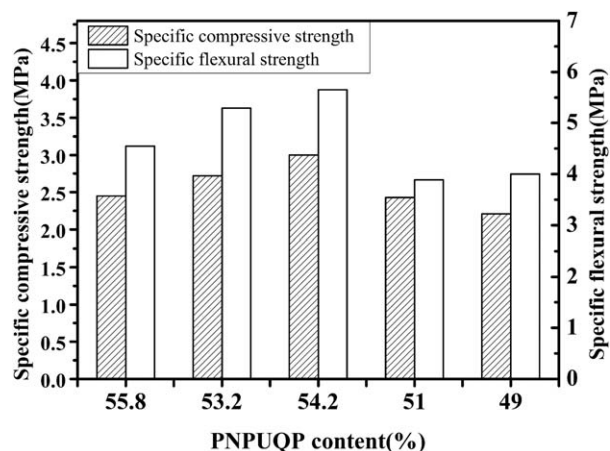| Sample no.	Compressive strength (MPa)	Flexural strength (MPa)	Apparent density (Kg•m^{-3})
PF	0.1365	0.2539	55.8
PNPUQP-2%-PF	0.1433	0.2812	53.2
PNPUQP-3%-PF	0.1632	0.2913	54.2
PNPUQP-5%-PF	0.1239	0.1985	51
PNPUQP-8%-PF	0.1081	0.199	49

Figure 6. Specific strength for pure and modified foams.

temperature, this can improve the drawback (lower thermal stability) for foam modified with polyurethane prepolymer.[8,23,26,27] This indicates that adding an adequate addition of PNPUQP basically maintains the excellent thermal stability of PF.

Mechanical Properties

The mechanical properties are characterized by universal testing machine according to the ASTM D1621-94 and GB/T8812-2007 standards. The mechanical properties of the pure PF and toughened foams including compress strength, flexural strength and apparent density are summarized in Table III, It is well known that the type and amount of blowing agent affect the apparent density of foam.[15] In this work, n-pentane was used as blowing agent and its concentration was kept constant. It can be seen from Table III that adding PNPUQP into pure foam can reduce the apparent density. This may be due to the fact that the increasing contents of PNPUQP in the system, resulting in the increase of the isocyanate groups that can react with water and produce lots of bubbles which also act as blowing agent.[4]

The compressive strength and flexural strength at first increase with the addition of PNPUQP until a maximum in compressive strength and flexural strength reach. However, with the further increase in PNPUQP content, the compressive strength and flexural strength start to decrease. The highest compressive strength and flexural strength value of toughened foams
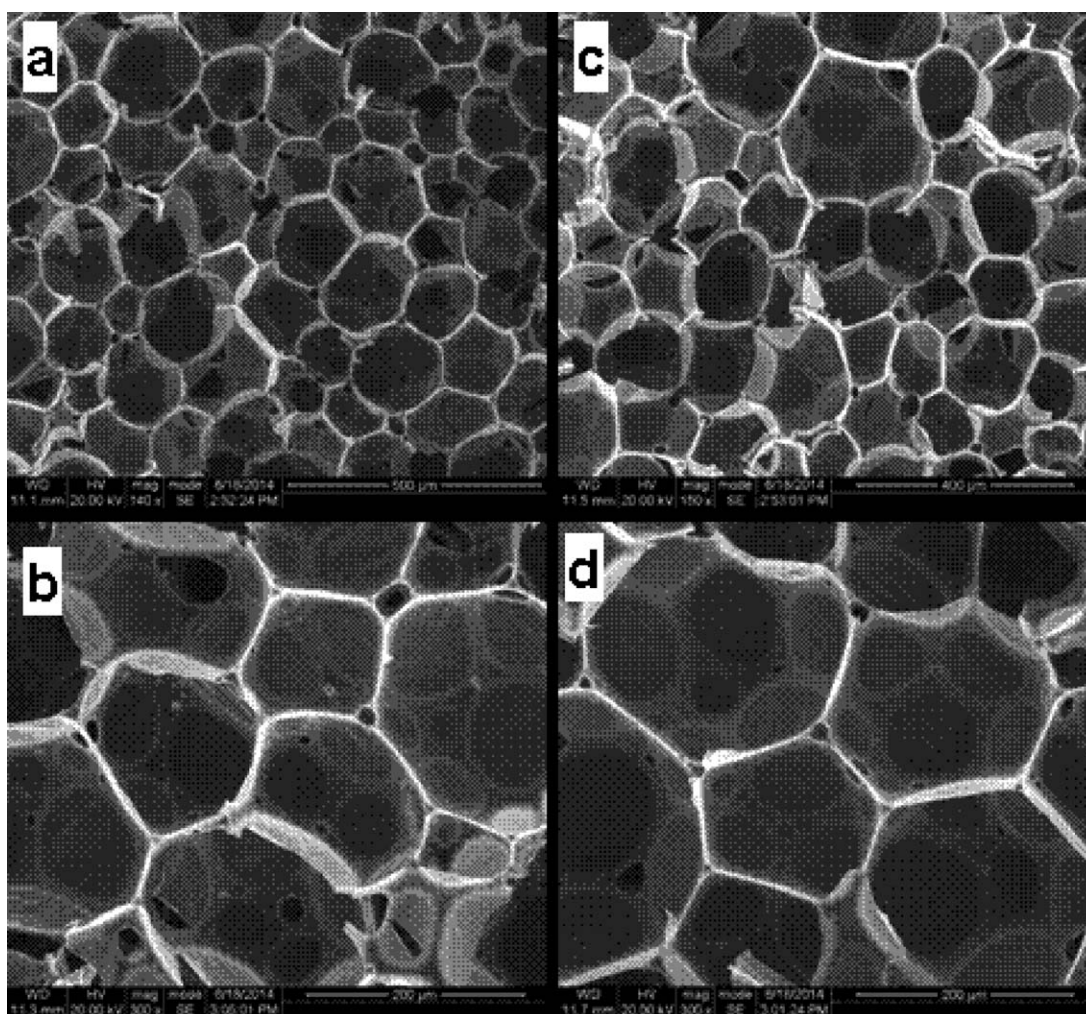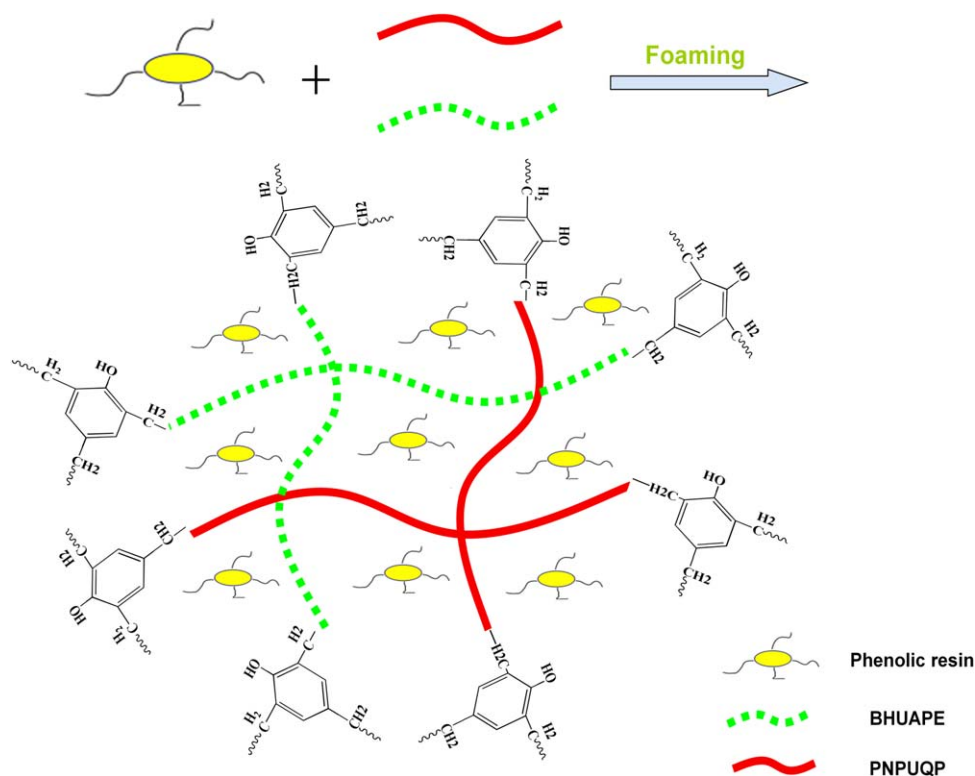

Figure 7. SEM micrographs of pure foam (a: 150×, b: 300×) and PF modified with 3 wt % PNPUQP (c: 150×, d: 300×).

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

obtained by the addition of 3 wt % of PNPUQP are 0.1632 MPa and 0.2913 MPa, which increase by 19.5% and 14.7% in contrast to that of pure foam. These results indicate that adding an adequate addition of PNPUQP into pure foam can enhance mechanical properties compared with pure foam.[28] The reason for the improved mechanical properties can be explained by that the flexible urethane and ether structure in PNPUQP molecular chains afford the toughness of the phenolic forms. Most of importance, the high-activity isocyanate group in the ends of PNPUQP allow the formation of covalent bond by esterification reaction with hydroxymethyl of resol during the foaming process, which making the phenolic forms more flexible.[2] However, when the dosage of PNPUQP excess 3 wt %, the mechanical properties of modified foams decrease. This phenomenon can be attributed to the fact that with the introduction of PNPUQP, the increase in the viscosity of the system lead to the difficulty in the mixture of resin, defoamer, curing agent, foaming agent and PNPUQP within the limited time, resulting in the increase of the cell of PF and the decrease in the mechanical properties of modified foams.[15]

To eliminate the influence of foam apparent density on the compressive strength and flexural strength, a specific compressive strength and flexural strength (strength/density) are used for comparison. As shown in Figure 6, the specific compressive strength and flexural strength first increase and then decrease along with increasing foam density. When the dosage of PNPUQP is up to 3 wt %, the specific compressive strength and flexural strength reach the maximum values of 3.0 MPa/g cm^{-3} and 5.65 MPa/g cm^{-3}.[4,15] The results further indicate that the modified

foam with 3 wt % PNPUQP can improve the toughness of the PF. The mechanical properties of foam have a certain relationship with the cellular structures of foam. Therefore, the microstructure of PFs is observed by SEM (Figure 7). It can be seen that the modified foam has similar cellular structures with pure foam, indicating that appropriate incorparation of PNPUQP do not result in significant changes in cellular structures.

From the above analysis, it can conclude that modified foam with 3 wt % PNPUQP is the best one according to the mechanical properties of toughened foams as compared to the pure foam. The toughening schematic is illustrated in Scheme 2.

CONCLUSION

In this work, a novel phosphorus- and nitrogen-containing polyurethane quasi-prepolymer (PNPUQP) was synthesized through Mannich and esterification reaction, and a series of modified foams were obtained by PNPUQP in various ratios. The chemical structure of BHAPE, BHUAPE and PNPUQP were confirmed by FTIR, ^{1}H NMR and ^{31}P NMR. The results showed that the PNPUQP improved the compressive strength, flexural strength, specific strength and reduced the apparent density. The compressive strength and flexural strength of modified foams with 3 wt % PNPUQP content were increased by 19.5% and 14.7%. The modified foam with 3 wt % PNPUQP content exhibited the greatest specific strength in compression and flexibility, as compared to the pure foam. And the SEM micrograph further certified the similar result. The as-prepared modified foams exhibited a significant increase in the LOI

values, suggesting an enhancement in the flame retardancy. The TGA was used to investigate the thermal degradation of foams, demonstrating that the PNPUQP/PF samples possessed slightly lower degradation temperatures and basically kept the similar char residue at 800°C.

ACKNOWLEDGMENTS

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