

## Research on properties of rigid polyurethane foam with heteroaromatic and brominated benzyl polyols

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**ABSTRACT:** Rigid polyurethane foams (RPUFs) were prepared with specific heteroaromatic and brominated benzyl polyols. The mechanical properties and thermal stability were studied using dynamic mechanical analysis (DMA) and thermogravimetric analysis (TG). The limiting oxygen index (LOI) was used to investigate the flame retardancy of the RPUFs. The results showed that the glass transition temperature ( $T_g$ ) of the RPUF prepared by heteroaromatic polyol was 182°C, demonstrating an improved thermal stability for this specific heteroaromatic polyol. Brominated benzyl polyol exhibited less negative influence on mechanical properties of the RPUFs at the same time of improving the flame retardancy. The LOI values increased with an increase in the brominated polyol content to 27.5%, and the char-forming ability of the RPUF improved; the char residue rate reached 12.6% at 700°C, but it was only 6.2% without the flame retardant. Scanning electron microscope (SEM) and energy-dispersive spectrometry (EDS) verified that the mechanism of flame retardancy was due to a synergistic effect of the gas phase and the condensed phase. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 42349.

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### INTRODUCTION

Rigid polyurethane foams (RPUFs) have been widely used as structural materials and insulation materials in recent years<sup>1–3</sup> because of their excellent properties, such as low thermal conductivity, low density and high abrasion resistance. However, their low thermal stability and high flammability, primarily due to the presence of biuret, allophanate, urethane and urea groups into their structure,<sup>4,5</sup> restricted their applications. The life and property security is threatened, which results of the release of toxic smoke, such as HCN and CO, when they are exposed to fire.<sup>6–8</sup> Hence, it is important to improve the properties to increase the popularity of RPUFs.<sup>9–12</sup>

Levchik and Weily<sup>13</sup> presented a review about thermal decomposition, combustion and flame retardancy of polyurethanes. It was pointed out that thermal decomposition of polyurethanes usually started at the thermally weakest links, such as biuret, urethanes and isocyanurate group. So the introduction of heat resistant groups can be used to improve the thermal stability of RPUFs.

Generally, the heteroaromatic structure, such as isocyanurate<sup>14,15</sup> and benzene ring,<sup>16</sup> possesses larger cohesive energy and steric hindrance, which leads to higher decomposition temperature. So it can significantly improve the thermal stability of the

RPUF. Masiulianis and Zielinski<sup>17</sup> introduced a heteroaromatic structure into the main chain of polyurethane. The thermal stability was obviously improved because the overall performance remained unchanged, and the thermal degradation temperature could reach up to 500°C. Wang and Shi<sup>18</sup> improved the thermal stability of polyurethane by introducing an isocyanurate structure, and the thermal decomposition temperature increased ~23°C. In addition, the introduction of the rigid structure, such as heteroaromatic and benzene ring, increases the cross-linking density and intermolecular forces of polymers to some extent, greatly limits the movement of molecular chain. Therefore, the glass transition temperature of polymers increases and then the thermal stability is improved.

However, the RPUF without flame retardant is flammable and the toxic gases released during its burning are harmful to the human health and environment. The traditional method of preparing flame-retardant RPUF was to incorporate flame retardant additives into polyols and physically disperse to the final material. Although this technique is convenient for the RPUF to achieve flame retardancy, bonding flame retardant groups into the RPUF backbone has attracted much attention recently.<sup>19</sup> Using a reactive flame retardant has the advantage of permanent in the flame retardancy, which lead to the acquirement that a

much smaller amount of flame retardant is acquired to reach a certain degree of flame retardancy. Consequently, a much smaller influence is brought upon the physical and mechanical properties of RPUF.<sup>20</sup>

A series of organo-cyclic phosphorus compounds were synthesized in an attempt to find an efficient flame retardant by Hoang.<sup>21</sup> Thermogravimetric analysis results revealed that cyclic phosphorus compounds synthesized in the study showed better thermal stability and flame retardancy with a much lower loading, which demonstrated that heterocyclic structure can significantly improve the flame retardancy of polymers. A dihydroxyl cyclotriphosphazene was synthesized and was used to prepare new cyclotriphosphazene-containing polyurethanes,<sup>22,23</sup> the result demonstrated that the incorporation of cyclotriphosphazene moiety increased the thermal stability and flame retardancy of polyurethanes.

In this work, a heteroaromatic polyol was used as a matrix resin to improve the thermal stability and flame retardancy of RPUFs. Additionally, a brominated flame-retardant polyol with a benzene ring structure was added to improve the flame retardancy. The thermal stability, the dynamic mechanical performance and the mechanical properties of flame-retardant RPUFs were studied.

## EXPERIMENTAL

### Materials

MDI (methane diphenyl diisocyanate) is produced by Huntsman Corporation, whose commercial designation is 5005 with average functionality 2.6–2.7, and characterized by NCO % = 30.75, viscosity to 25°C = 220 mPa s.

Polyol-1 is a heteroaromatic polyether polyol based on isocyanurate with an –OH terminal group (polyether polyol of 1, 3, 5-tris (2-hydroxyethyl) isocyanurate (THEIC) derivate). The hydroxyl value is 319 mgKOH g<sup>-1</sup>, the functionality is 3, and the average molecular weight is 530 g mol<sup>-1</sup>.

Polyol-2 is a polyether polyol based on tetrabromobisphenol with an –OH terminal group (brominated flame-retardant polyol). The content of bromine (Br) is 41.29%, the hydroxyl value is 150 mgKOH g<sup>-1</sup>, and the functionality is 2. The average molecular weight is 770 g mol<sup>-1</sup>.

Polyol-3 is an aromatic polyester polyol based on polyethylene terephthalate with an aromatic content of 31%. Its hydroxyl value is 315 mgKOH g<sup>-1</sup>, the functionality is 2, and its viscosity at 25°C is 13,000~23,000 mPa s. The average molecular weight is 360 g mol<sup>-1</sup>.

Polyol-4 is a polyol based on phthalates with an –OH terminal group. The hydroxyl value is 390–430 mgKOH g<sup>-1</sup>, the average functionality is ~3.3, and it has an average molecular weight of 450 g mol<sup>-1</sup>.

Polyol-5 is a sucrose polyether polyol, whose hydroxyl value is 500 mgKOH g<sup>-1</sup>. The functionality is 5, the average molecular weight is 560 g mol<sup>-1</sup>, and its viscosity at 25°C is 5800 mPa s.

Polyol-6 is a sucrose polyether polyol, whose hydroxyl value is 380 mgKOH g<sup>-1</sup>. Its functionality is 6, the average molecular weight is 890 g mol<sup>-1</sup>, and the viscosity at 25°C is 11,250 mPa s.

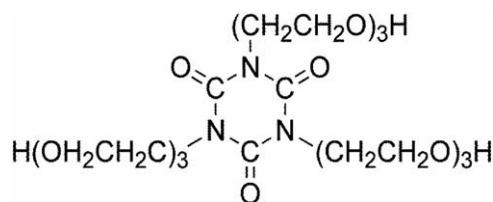


Figure 1. Structure of THEIC derivate polyether polyol (Polyol-1).

Triethylenediamine and stannous octoate were used as catalysts.

HCFC-141b (dichlorofluoroethane) was used as blowing agents and polysilicone was used as foam stabilizer.

### Sample Preparation

THEIC (261 g, 1 mol) was dissolved in ethylene glycol monomethylether at 80°C, and then, triethylamine (5.25 g, 1 wt %) was added into the reaction system as a catalyst. After the THEIC was completely dissolved, epoxyethane (264 g, 6 mol) was slowly added to the solution and participated in the reaction. The product was then subjected to vacuum dehydration, and the structure of the product is shown in Figure 1.

The tetrabromophthalic anhydride (464 g, 1 mol) was mixed with diethylene glycol (106 g, 1 mol) in a flask and stirred. The mixture was warmed up to 110°C and kept for 3~5 h, and then, it turned into a yellow transparent solution. After the solution was vacuum dehydrated for 1 h, propylene oxide was slowly added drop wise, until the acid value was less than 0.8 mgKOH g<sup>-1</sup>. The structure of the product is shown in Figure 2.

The foams were prepared using a hand mixing technique. The isocyanate was added to the formulated polyol (i.e., the mixture of polyols, catalysts, surfactant, flame retardant and blowing agents); then, the mixture was mixed for 10 s and allowed to stand and foam up. After the preparation, the foams were kept in an oven at 70°C for 24 h to complete the polymerization reaction. The parameters for preparing RPUFs from the different types of polyols are shown in Table I, and the formulations for the flame-retardant RPUFs containing different flame retardants are displayed in Table II.

### Characterization

Thermogravimetric analysis (TGA) was performed using a TG analyzer (NETZSCH, Germany) at a heating rate of 10°C min<sup>-1</sup> from 30 to 800°C under a dynamic nitrogen flow of 30 mL min<sup>-1</sup>.

The flame retardancy of the RPUFs was characterized by the limiting oxygen index (LOI) measurement (according to the GB/T 2406-2009) using a HC900-2C oxygen index instrument (Nanjing HAS Analysis Instrument, China) at room

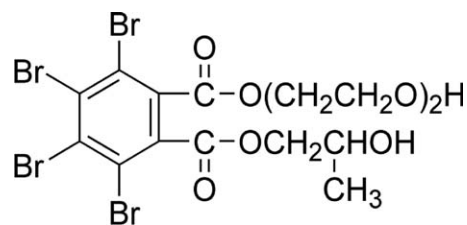


Figure 2. Structure of brominated benzyl polyol (Polyol-2).

**Table I.** Parameters of Different RPUFs

Materials	Sample 1 (pbw)	Sample 2 (pbw)	Sample 3 (pbw)
Polyol-1	100	-	-
Polyol-3	-	58	-
Polyol-4	-	42	-
Polyol-5	-	-	50
Polyol-6	-	-	50
Triethylenediamine	0.8	0.8	0.8
Stannous octoate	0.2	0.2	0.2
Polysilicone	1.0	1.0	1.0
HCFC-141b	23.0	23.0	23.0
MDI	125	125	125

Sample 1 was the RPUF prepared by heteroaromatic polyether polyol. Sample 2 was the RPUF prepared by aromatic polyester polyol. Sample 3 was the RPUF prepared by sucrose polyether polyol.

temperature. The size of the specimen was  $150 \times 10 \times 10 \text{ mm}^3$  (length  $\times$  width  $\times$  thickness).

The morphology and elemental content of the solid residues collected at the end of the LOI were investigated using an S-3400N scanning electron microscope (SEM) instrument (Hitachi, Japan) after gold-sputtering. The accelerating voltage was 20 kV.

The dynamic mechanical analysis (DMA) was performed using a NEZSCH 242 apparatus from NETZSCH (Germany), which was carried out from room temperature to 200°C at a heating rate of 3°C min<sup>-1</sup> at 1 Hz.

The mechanical properties of the samples were evaluated at 23°C using a SUN 500 universal testing machine (GALDABINI Corp., Italy). The compression strength is 10% of the compressive stress of the relative deformation, according to the GB 8813-1988.

## RESULTS AND DISCUSSION

### Characteristics of the RPUFs with a Heteroaromatic Polyol as the Matrix Resin

The heteroaromatic polyols derived from THEIC have many advantages, such as enhanced stiffness, improved thermal stabil-

ity and so on, due to their specific heteroaromatic structures. In this work, it was selected as the matrix resin to improve the properties of the RPUFs. DMA and TG were investigated to determine the performance.

The peak value of loss tangent ( $\tan \delta$ ) is the most important criterion for the glass transition temperature ( $T_g$ ), and it is usually used to examine the thermal stability of materials. As observed in Figure 3, the  $T_g$  of the RPUF prepared by heteroaromatic polyether was 182°C, while it was 175°C for aromatic polyester and 167°C for sucrose polyether. Thus, the  $T_g$  of RPUF prepared with heteroaromatic polyol was significantly higher than that for normal polyol, which may be related to the stable structure of the heteroaromatic polyol. The structure of the heterocycle and benzene ring can improve the thermal stability of polymers because of their conjugated effects, but the resonance energy of a heterocycle (82 kcal mol<sup>-1</sup>) is much higher than that of benzene ring (36 kcal mol<sup>-1</sup>). Thus, the  $T_g$  of the RPUF with heteroaromatic polyether was higher than the RPUF with aromatic polyester.

However, the hydroxyl content in the polyols has little effect on the thermal stability of the RPUFs.<sup>24</sup> The crosslinking density of foams increases with an increase in the polyol functionality; more heat and energy is needed to destroy the crosslinking branched chain when the foam has a higher functionality. Therefore, the thermal stability was improved as the  $T_g$  of the foams increased, and we conclude that heteroaromatic polyols can improve the thermal stability of polymers.

Additionally, as shown in Figure 4 and Table III, the initial decomposition temperature of the RPUF based on the pure heteroaromatic polyether polyol is 330°C, which was higher than that for ordinary RPUFs (250–320°C). Thus, we conclude that heteroaromatic polyether polyols can also improve the flame retardancy of RPUFs.

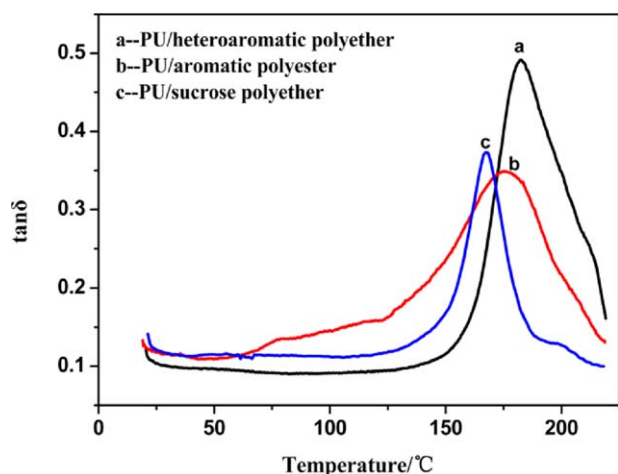
In summary, the thermal stability of the heteroaromatic polyether polyol is much better than that of the aromatic polyester or the sucrose polyether polyol. Thus, the heteroaromatic polyether polyol was selected as the matrix resin to synthesize the RPUFs, and the physical properties and flame retardancy were studied.

Although there are many advantages in using the heteroaromatic polyether polyol, it cannot yet improve the pyrolysis of

**Table II.** Formulations of Flame-Retardant RPUF Containing Different Flame Retardant Contents

Materials	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7
Polyol-1	100	90	70	50	30	10	-
Polyol-2	-	10	30	50	70	90	100
Triethylenediamine	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Stannous octoate	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Polysilicone	1.0	1.0	1.0	1.0	1.0	1.0	1.0
HCFC-141b	23.0	23.0	23.0	23.0	23.0	23.0	23.0
MDI	125	125	125	125	125	125	125

Sample 1–7 was RPUFs prepared by different contents of reactive flame retardant polyol, adding amount was 0, 10, 30, 50, 70, 90, and 100%, respectively.



**Figure 3.**  $\tan \delta$  as a function of temperature for RPUFs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

RPUFs without a flame retardant. Therefore, the flame retardancy of RPUFs was modified via adding brominated flame-retardant polyol as the reactive flame retardant. The brominated flame-retardant polyol also exhibited an improved compatibility with the matrix resin and less negative influence on the mechanical properties of the RPUFs.

#### Thermal Stability of the Flame-Retardant RPUFs

The influence of brominated benzyl polyol on the thermal stability of the RPUFs was studied using TG analyzer in a nitrogen atmosphere. The TG and the DTG curves of the RPUFs with different brominated benzyl polyol contents are presented in Figure 4, and the detailed results are given in Table III.

As depicted in Figure 4, the thermal degradation of the RPUFs primarily occurred in two stages, and the trend for the initial stage was the same. As shown in the DTG curves, the initial decomposition temperature reduced slightly with the addition of the brominated benzyl polyol, but the mass loss rate of the flame-retardant RPUFs was significantly lower than that of the RPUF without the flame retardant at 330–550°C. The mass loss

rate was 24% for the flame-retardant RPUF, and it was 33% for the RPUF without flame retardant.

This phenomenon may be related to the chemical bond in the molecular chain. Because the bond energy and the activation energy of the thermal degradation of the C-Br bonds are significantly lower than those of the C-H and C-C bonds, thus, the initial decomposition temperature decreased, and weight loss decreased with the addition of the brominated benzyl polyol. And the release of Br may change the surface structure of the material and produce the first peak in the TG curve.

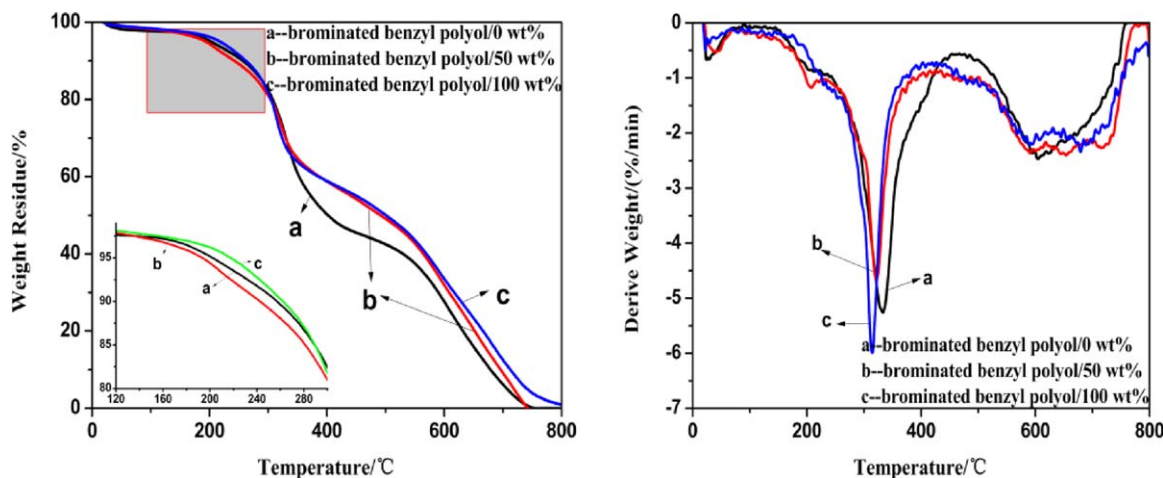
Additionally, as shown in TG curves and detailed in Table III, the char residue of the flame-retardant RPUF can reach 12.6% at 700°C, while that of pure RPUF was only 6.2%. Thus, an increased amount of char residues was obtained when the brominated benzyl polyol loading was increased. This is mainly related to the high-carbon content of the benzene ring in the brominated benzyl polyol, which increased the residues after burning. The increasing protective chars remained and resisted to even higher temperatures, shielded the underlying polymers from the attack of oxygen and radiant heat. Therefore, the brominate benzyl polyol can effectively enhance the flame retardancy of the RPUF.

#### Dynamic Mechanical Properties of the Flame-Retardant RPUFs

DMA was used to measure the  $T_g$  and to characterize the thermal stability from a different perspective. DMA is a precise technique that provides information about the relationship between the strain and stress of materials.<sup>25–27</sup> Generally, the storage modulus ( $E'$ ), loss modulus ( $E''$ ) and loss tangent ( $\tan \delta$ ) along with the change of temperature under different frequency can be obtained from the DMA spectra.

$E'$  was used to characterize the ability of the materials to resist thermal mechanical deformation. The variations of  $E'$  as a function of temperature for the flame-retardant RPUFs are shown in Figure 5.

As observed in Figure 5, the values of  $E'$  increased first and then decreased, and the transition point is denoted as  $T_g$ .



**Figure 4.** TG and DTG curves of flame-retardant RPUFs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Table III.** Results Obtained by TG and DTG Analysis for RPUFs

Sample	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	$T_{\max 1}$ (°C)	$T_{\max 2}$ (°C)	$C_{700^\circ\text{C}}$ (%)
a	202.02	256.96	401.86	333.34	604.31	6.15
b	193.49	242.39	491.42	321.54	600.63	9.16
c	217.26	261.93	500.73	314.75	607.36	12.58

$T_{5\%}$ ,  $T_{10\%}$ , and  $T_{50\%}$  represent temperatures at 5, 10, and 50% weight loss, respectively.  $T_{\max 1}$  and  $T_{\max 2}$  represent maximum degradation temperatures in first and second stage, respectively.

Moreover, the  $E'$  of the RPUF prepared by brominated benzyl polyol was higher than that of the RPUF without the flame retardant for the application temperature range. The values of  $E'$  are associated with the structure of the materials, thus, the RPUF was not easily thermally deformed because the stiffness structural content increased with the addition of the brominated benzyl polyol. Additionally, the stress increased because the movement of the atoms in the material accelerated with the increasing temperature, but the molecular chains were frozen below  $T_g$ , resulting in an almost unchanged strain. Thus, the  $E'$  increased below  $T_g$ . The crosslinking density of the RPUF prepared by 50 wt % brominated benzyl polyol was higher than that of 100 wt % brominated benzyl polyol because of its higher functionality; thus, its strain was lower, and its  $E'$  was correspondingly higher. An energy barrier existed for molecular chain to break the frozen status. When the temperature approached and exceeded  $T_g$ , the barrier was broken and the molecular chain rearranged, which led to a rapid drop in  $E'$ . Narine *et al.*<sup>28</sup> also concluded that the storage modulus decreased with an increase in temperature because of the molecular mobility, which further verified our conclusion.

Generally,  $E''$  is defined as the characterization of energy loss in the form of heat during the deformation. The curves of  $E''$  for flame-retardant RPUFs with different added amounts of bromi-

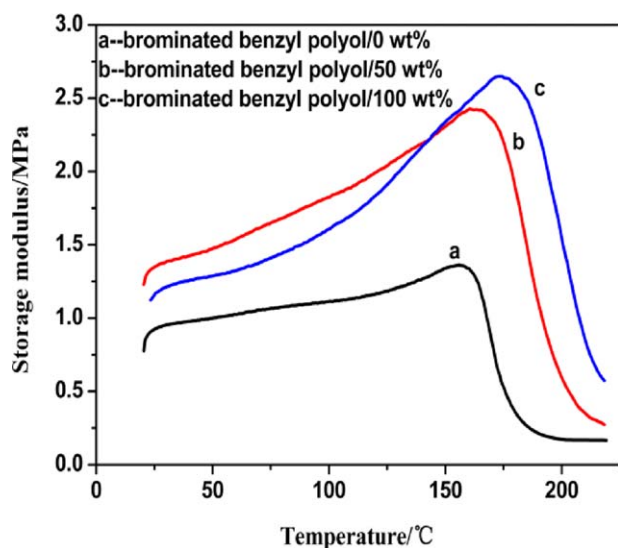
nated benzyl polyol as a function of temperature are shown in Figure 6.

$E''$  exhibited the same trend as  $E'$ , reaching the maximum at  $T_g$  and dropping apparently above  $T_g$ . Additionally, the peak ( $T_g$ ) of  $E''$  shifted to a higher temperature, and the intensity of the peak increased with an increasing amount of brominated benzyl polyol.

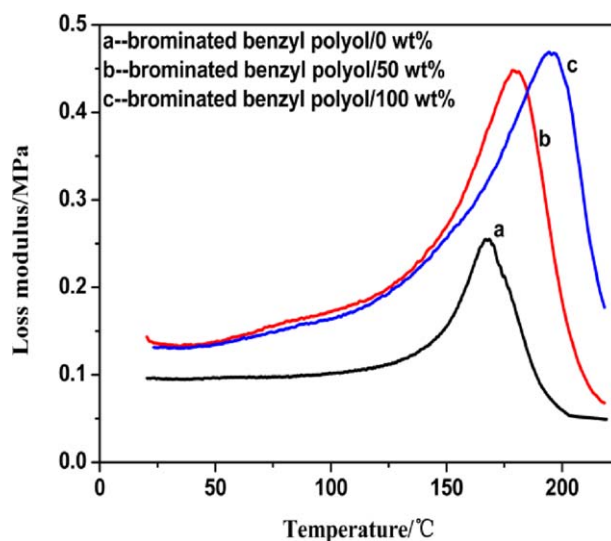
$E''$  characterizes the energy loss due to internal friction, and the molecular chain segment moves more easily as the temperature increases. Thus, the largest resistance of the molecular chain segment movement was observed when the glass transition occurred. In addition, the  $E''$  of the RPUF prepared by brominated benzyl polyol was much larger than that of the RPUF without flame retardant.

The  $\tan \delta$  curves for different amounts of the brominated benzyl polyol as a function of temperature for the RPUFs are shown in Figure 7.

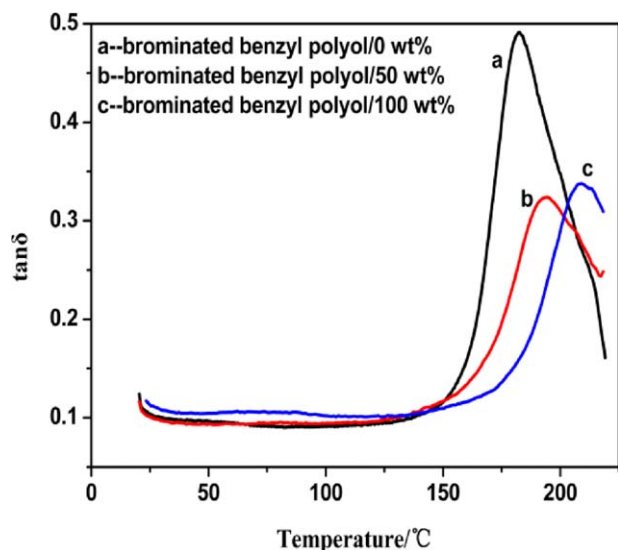
The values of  $\tan \delta$  increased with an increase in temperature, and then decreased when the temperature was above a certain value. In addition, the  $T_g$  value of the RPUF prepared with the THEIC derivate polyether polyol (a) was  $\sim 182^\circ\text{C}$ , and that of the RPUF modified by the brominated benzyl polyol (c) was  $209^\circ\text{C}$ . So that the  $\tan \delta$  value of the RPUF shifted to a higher temperature as the brominated benzyl polyol content increased.



**Figure 5.**  $E'$  as a function of temperature for RPUFs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 6.**  $E''$  as a function of temperature for RPUFs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 7.**  $\tan \delta$  as a function of temperature for RPUFs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

This phenomenon may be related to the stiffness of the benzene ring structure. The molecular chain of the benzene ring exhibits low flow ability with an increasing amount of structural stiffness, and it converts to a glassy state at higher temperatures. Additionally, the  $T_g$  value mainly depends on crosslinking, intermolecular attraction and steric hindrance. Thus, the steric hindrance and the conjugated effect of the benzene ring in the brominated benzyl polyol can also increase the  $T_g$  of the RPUF with an increasing amount of the brominated benzyl polyol. Additionally, Nielsen and Landel<sup>29</sup> suggested that the incorporation of fibers or fillers into the polymer matrices restricted the mobility of polymer chains and therefore increased the glass transition temperature. Therefore, the  $T_g$  value increased when the polymer system was added to the sticky brominated benzyl polyol, which restricted the mobility of the polymer chains.

#### Mechanical Properties of the Flame-Retardant RPUFs

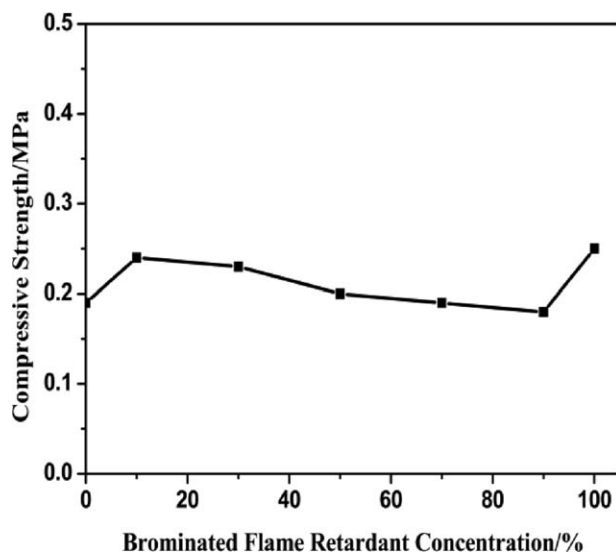
Typically, the compressive strength is measured to verify the effect on the mechanical properties of RPUFs modified by brominated benzyl polyol. The effect of brominated flame retardant concentration on the compressive strength of the flame-retardant RPUFs is shown in Figure 8.

As shown in Figure 8, the compressive strength did not change much with the increasing amount of brominated benzyl polyol, which indicates that the addition of brominated benzyl polyol exhibited almost no effect on the mechanical properties of the flame-retardant RPUFs.

The stiffness of the benzene ring increases with a higher content of brominated polyol, preventing the molecular chain from rotating freely. Thus, the deformation of the polymer is difficult at the macro level, the compress strength of the flame-retardant RPUFs changed little.

#### Fire Behavior of the Flame-Retardant RPUFs

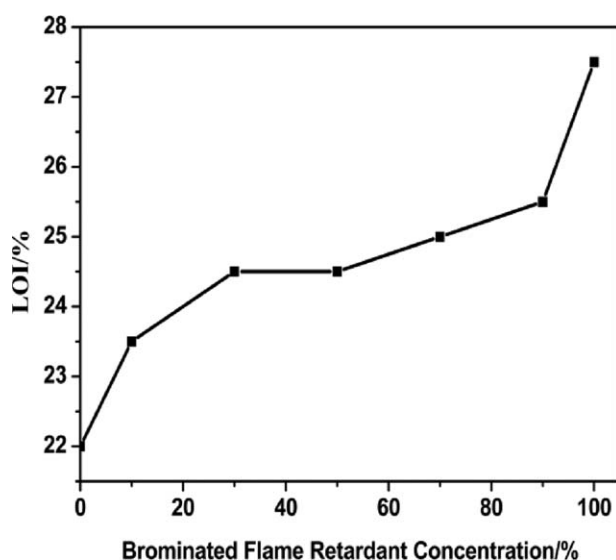
The LOI of the RPUFs with the brominated flame retardant polyol was tested, and the results are provided in Figure 9.



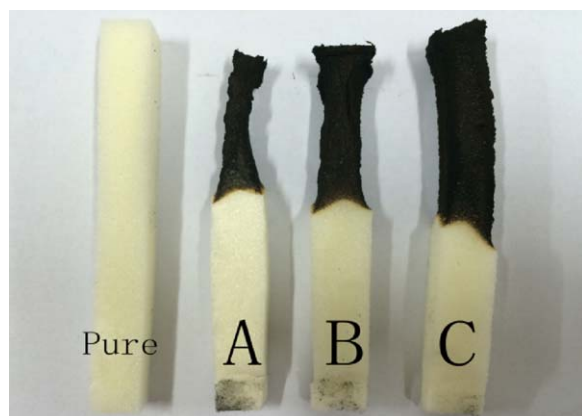
**Figure 8.** Effect of brominated polyol concentration on compressive strength of flame-retardant RPUFs.

As shown in Figure 9, all the RPUFs modified with the brominated benzyl polyol had higher LOI values than the original RPUF. The LOI values of the flame-retardant RPUFs increased with increasing brominated polyol content and eventually reached 27.5%; however, the LOI value of RPUF without the flame retardant was only 22%. It can be concluded that brominated benzyl polyol has an excellent flame retardant effect.

The bromine content increases with an increase in the brominated benzyl polyol; more bromine compounds release hydrogen halide, which can dilute the oxygen concentration surrounding the matrix, leading to an increase in the LOI. So bromine compounds capture the flammable free radicals and prevent further combustion. Additionally, the LOI value of the RPUF reached a maximum when it was completely prepared by



**Figure 9.** Effect of brominated polyol concentration on LOI of flame-retardant RPUFs.



**Figure 10.** Surface macroscopic morphology images: (A) RPUF with source resin, (B) RPUF with 50% flame retardant polyether, and (C) RPUF with 100% flame retardant polyether. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

brominated benzyl polyol, which was substantially larger compared with the original RPUF.

#### Char-Forming Properties of the Flame-Retardant RPUFs

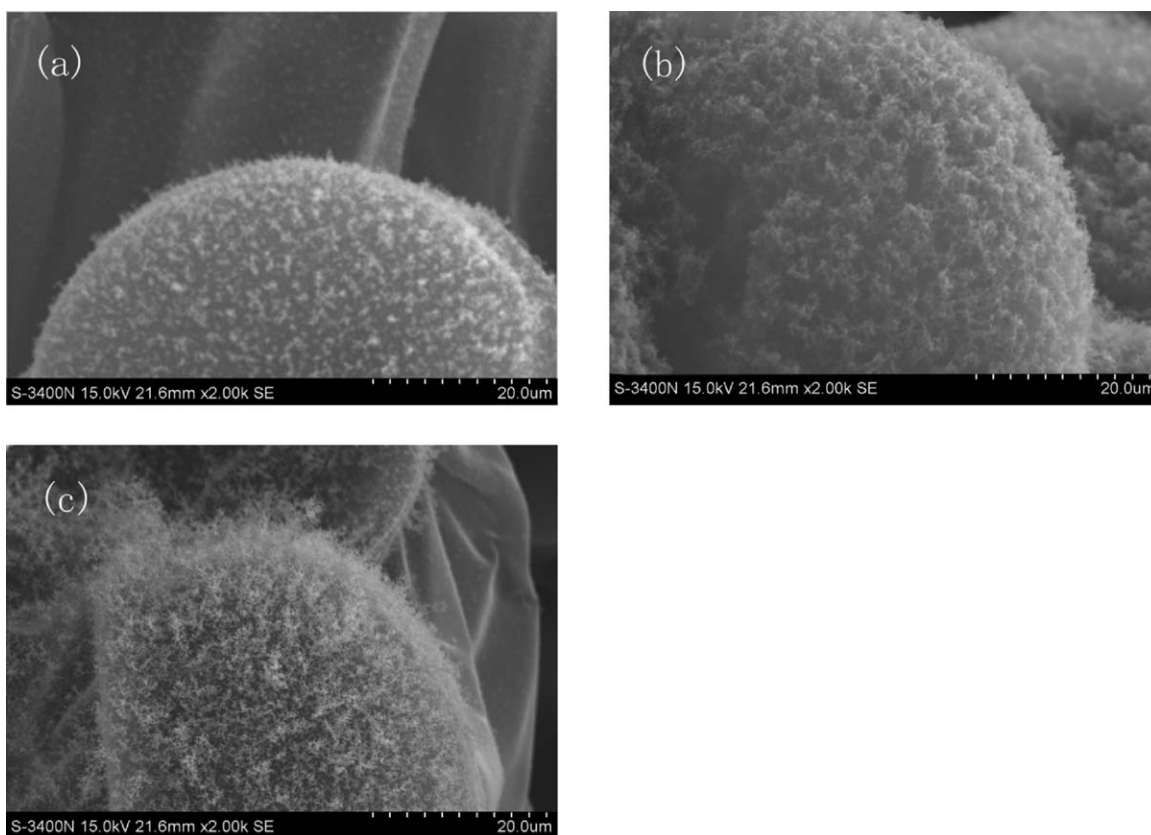
A stable char layer was generated on the surface of the RPUFs during the burning process, and it could play an important role in the flame retardancy of polymers. The surface macroscopic morphology is shown in Figure 10, and the morphology of the

**Table IV.** Element Content of Different Residues from EDS

Sample	C/wt %	O/wt %	C/O
a	68.26	30.66	2.23
b	77.44	21.15	3.66
c	78.90	20.26	3.89

char layer was subjected to SEM scanning (Figure 11) to verify the flame retardant mechanism of the brominated polyol. The elemental content of the different residues was found using energy-dispersive spectrometry (EDS), and is shown in Table IV.

As displayed in Figure 10, a char layer coated the surface of the RPUFs and expanded with the increase in the brominated benzyl polyol, which was also observed in the SEM images shown in Figure 11(a–c) in the microscopic scale. The hydrogen bromide caused swelling the char layer upon escaping from the matrix. At the same time, the hydrogen bromide released from the matrix diluted the flammable gas in the gas phase and restricted further thermal degradation. Alternatively, the char yield increased with an increasing amount of brominated polyol, as shown in Table IV, which is mainly related to the high carbon content of the benzene ring in brominated benzyl polyol that increased the residues after burning. The char layer in the condensed phase can retard the release of combustible gases, hinder the oxygen entering the condensed phase from



**Figure 11.** SEM images of (a) RPUF with source resin, (b) RPUF with 50% flame retardant polyether, and (c) RPUF with 100% flame retardant polyether.

participating in the oxidative degradation and even reduce the heat flow back to the polymer matrix, preventing further thermal degradation.

## CONCLUSION

The influence of specific heteroaromatic and brominated benzyl polyols on the mechanical properties, thermal stability, and flame retardancy of RPUFs was investigated. The flame-retardant RPUFs with the brominated benzyl polyol increased thermal stability and flame retardancy over the RPUF without the flame retardant.

Specifically, the  $T_g$  of the RPUF prepared by heteroaromatic polyol was 182°C, while that of the RPUF prepared by the common polyol was only 167°C, demonstrating the improved thermal stability of the heteroaromatic polyol. Additionally, the incorporation of the brominated benzyl polyol not only influenced the initial decomposition temperature but also improved the char yield of the flame-retardant RPUFs at high temperatures. The DMA suggested that the  $T_g$  of flame-retardant RPUF (209°C) is much higher than that of the RPUF without the flame retardant (182°C) because of the increasing content of the rigid benzene group. The storage modulus and the loss modulus showed the same trend as the  $T_g$ , and they also verified the trend of the compressive strength. The LOI values of the flame-retardant RPUFs increased with increasing amounts of the brominated benzyl polyol, and they eventually reached 27.5%; however, that of the RPUF without the flame retardant was only 22%. Thus, brominated benzyl polyol can significantly improve the flame retardancy of the RPUFs. The SEM images displayed the intumescent phenomenon of the char layer caused by hydrogen bromide, and the EDS showed that the char yield increased with an increasing amount of brominated benzyl polyol. This indicated that the mechanism of brominated benzyl polyol involved a synergistic effect of the gas phase and the condensed phase.

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