

# Biobased Polyols Using Thiol-Ene Chemistry for Rigid Polyurethane Foams with Enhanced Flame-Retardant Properties

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**ABSTRACT:** Biobased polyol was synthesized using 1-thioglycerol and limonene, an extract of orange peel, via thiol-ene chemistry as an alternative to petrochemical-based polyol for preparation of rigid polyurethane foams (RPFs). Fire-retardant polyurethane foams were prepared by addition of different amounts of dimethyl methyl phosphonate (DMMP) in the polyol. The effect of DMMP on the properties of RPFs was studied. All the biobased RPFs maintained a regular cell structure with uniform cell distribution and over 90% of closed cell. The RPFs showed excellent compressive strength of ~230 kPa without addition of DMMP. These RPFs almost retained their specific compressive strength even when 2 parts by weight (pbw) of DMMP was added but with significant improvement in fire retardancy. Horizontal burning test of RPFs containing only 2 pbw of DMMP showed reduction in burning time by ~83% compared to the neat sample. Weight loss during the burning test for the control sample was nearly 50% and this was reduced significantly by addition of 2 pbw of DMMP to merely 7%. TGA analysis indicated that the improved flame retardancy could be attributed to the release of DMMP at the temperature range of 100 °C to 250 °C.

**KEYWORDS:** Biobased polyol, flame-retardant foam, polyurethanes, rigid foam, thiol-ene reaction

## 1 INTRODUCTION

Polyurethane is a versatile material which can be used for various industrial applications in the form of rigid PU foams, flexible PU foams, thermoplastic, elastomer, coating and adhesive [1–4]. Among them, rigid polyurethane foams have emerged as a prime candidate for thermal insulation and filling material in the construction industry due to their low thermal conductivity, high compressive strength and high closed-cell structure [5–7]. Polyurethane foams are prepared by reacting diisocyanates with compounds containing two or more hydroxyl groups (polyol) in the presence of blowing agent, catalyst and surfactant [8]. Currently, starting chemicals for polyurethane and many other polymers are obtained from petrochemical feedstock. However, environmental, political and

economic issues have led scientists to search for alternative sources of raw materials. Recently, the use of plant-derived chemicals as starting materials for polymers has gained considerable attention due to their sustainable and renewable nature [9, 10]. In particular, chemicals derived from soybean oil, castor oil, starch and cellulose offer a wide variety of starting materials for the synthesis of polyols [11–14].

Limonene is another biobased material which can be used to synthesize polyols for the preparation of polyurethane foams [15]. Limonene is an extract of orange peel, a sustainable and renewable chemical generated from the residues from the citrus industry [16]. Limonene has been used for several other industries as a starting material for fragrances, flavors and pharmaceuticals [16, 17]. The monocyclic terpene structure of limonene offers several synthesis routes for polymerization. For example, low molecular weight polylimonene and copolymer of limonene-maleic anhydride have been previously synthesized utilizing Ziegler catalyst system and radical polymerization method, respectively [18, 19]. The presence of

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internal and external alkene functional groups in the terpene structure opens the thiol-ene synthesis route for limonene with thiol compound [20]. Janes *et al.* have synthesized the thiols of limonene,  $\alpha$ -pinene,  $\alpha$ - and  $\gamma$ -terpinene, terpinolene, 3-carene and pulegone by reacting them with hydrogen sulfide using thiol-ene reaction [21]. Marvel and Olson exploited thiol-ene reaction to prepare dithiol from thioacetic acid and limonene, later polymerizing it with limonene to obtain a copolymer [22]. There have been other applications of thiol-ene reaction to modify the properties of plant-derived materials such as improving the wear and friction resistance of the vegetable oils [23–25], crosslinking and oligomerization of vegetable oil with polyfunctional thiols [26–29]. Also, as a synthesis route to obtain renewable monomers from fatty acids for polyesters and polyanhydride [30–32]. Recently, our group photochemically grafted the 1-thioglycerol and glycerol-1-allylether onto alkene groups of limonene and limonene dimercaptan, respectively, to synthesize biobased polyols using thiol-ene reaction [15]. Subsequently, biobased polyols were used for the preparation of polyurethane foams. Physical and mechanical properties of the biobased polyurethanes were found to be comparable to polyurethanes from a commercial polyol.

The main disadvantage of the polyurethane is low flame retardancy due to the predominant presence of carbon, hydrogen and oxygen in its structure. The highly porous and combustible nature of polyurethane foams further facilitate the flame spread rate [33]. High flammability of polyurethane foams restricts some of its valuable applications [34]. Therefore, many studies have been conducted to improve the flame-retardant properties of polyurethanes. For example, phosphorous-, nitrogen-, aluminum- and expandable graphite-containing compounds were used as flame-retardant additives in polyurethane [35–40]. Among them, phosphorous compounds were found to be effective additive flame retardant. In the present work, limonene-based polyol was synthesized and dimethyl methyl phosphonate (DMMP) was incorporated into it in order to enhance the flame-retardant properties of biobased rigid polyurethane foams (RPFs). Further, morphological, structural and mechanical properties of RPFs were characterized. The effect of DMMP as a flame retardant in biobased polyurethanes was studied.

## 2 EXPERIMENTAL

### 2.1 Materials

Limonene, 1-thioglycerol and 2-hydroxy-2-methylpropionophenone were obtained from Sigma-Aldrich for

the synthesis of limonene polyol (LTG). Commercially available polyol, soybean oil-based X-210 (OH content of 210 mg KOH/g) was received from Cargill and sucrose-based polyether Jeffol SG-520 (OH content of 520 mg KOH/g) was received from Huntsman. Isocyanate, Rubinate M (polymeric methylenediphenyl diisocyanate, NCO content of 31%) was supplied from Huntsman. For the preparation of rigid polyurethane foams, catalysts DABCO T-12 and NIAx A-1 were purchased from Air Products and OSi Specialties, respectively. Silicone surfactant (Tegostab B-8404) was purchased from Evonik. Distilled water was employed as the blowing agent. Dimethyl methyl phosphonate from Sigma-Aldrich was used as the additive flame retardant.

### 2.2 Synthesis of Limonene Polyol

One-step thiol-ene chemistry was used for the synthesis of polyol based on limonene and 1-thioglycerol. In typical synthesis, 23.8 g of limonene was added into 37.8 g of 1-thioglycerol (1:2 molar ratio of limonene to 1-thioglycerol). The thiol-ene reaction was carried out at room temperature for 8 h under 365 nm ultraviolet radiation in the presence of 1.5 g of 2-hydroxy-2-methylpropionophenone as the photoinitiator. The reaction was carried out under constant stirring using magnetic stirrer at 300 rpm.

### 2.3 Characterization of Limonene Polyol

The synthesized polyol was characterized using various techniques. The phthalic anhydride/pyridine (PAP) method (ASTM-D 4274) was used to determine the hydroxyl number of the polyol. Gel permeation chromatography (GPC) was performed using a system by Waters (Milford, MA, USA). GPC was composed of four 300  $\times$  7.8 mm phenogel 5  $\mu$  columns with different pore sizes of 50, 102, 103 and 104 Å. Eluent solvent was tetrahydrofuran (THF) and eluent rate was 1 ml/min at 30 °C. The FT-IR spectrum of the polyol was recorded using a Shimadzu IR Affinity-1 spectrophotometer at room temperature. Viscosity was measured by using an AR 2000 dynamic stress rheometer (TA Instruments, USA) at 25 °C with shear stress increasing from 1 to 2000 Pa linearly. The rheometer was equipped with a cone plate having an angle between 2° and a cone diameter of 25 mm.

### 2.4 Preparation of Rigid Polyurethane Foams (RPFs)

Rigid polyurethane foams were prepared using limonene polyol, commercial polyols (X-210 & SG-520)

and a blend of limonene polyol/commercial polyol (50/50 w/w ratio). Equivalent weight of isocyanate to polyol and distilled water was calculated based on the following equation:

$$w_i = Ew_i \left( \frac{w_p}{Ew_p} + \frac{w_{pc}}{Ew_{pc}} + \frac{w_{water}}{Ew_{water}} \right) \quad (1)$$

where  $w_i$ ,  $w_p$ ,  $w_{pc}$  and  $w_{water}$  are the weights of isocyanate, limonene polyol, commercial polyol and water, respectively;  $Ew_i$ ,  $Ew_p$  and  $Ew_{pc}$  are the equivalent weights of isocyanate, limonene polyol and commercial polyol, respectively; and  $Ew_{water} = 9$ , which is the hydroxyl equivalent weight of water. RPFs were prepared according to the following procedure. Polyol, catalysts, surfactant, blowing agent and fire retardant (DMMP) were mixed thoroughly to obtain a homogenized mixture using a high speed (6,000 rpm) mechanical stirrer. The effect of DMMP loading was studied by adding 0, 2, 4, and 6 parts by weight (pbw) to polyol. The detailed formulations are given in Table 1. After thorough mixing, isocyanate was added and the mixture was again stirred for several seconds. Finally, the mixture was allowed to rise at room temperature. Foams were kept at room temperature for 7 days to complete the curing process.

## 2.5 Characterization of Rigid Polyurethane Foams

Physical properties, fire-retardant characteristics and morphology of RPFs were determined by the following standard procedures. The apparent density of foams was determined according to the standard

test method for apparent density of rigid cellular plastics (ASTM D 1622). Closed-cell content of the foams was determined according to ASTM 2856 standard method by using Ultrapycnometer, Ultrafoam 1000. Cylindrical shape specimens of 45 mm × 30 mm (diameter × height) were used for both density and closed-cell content calculations. The compressive strength at 10% strain was measured according to ASTM 1621 standard method for all the RPF samples by using a Q-Test 2-tensile machine (MTS, USA). The specimen sizes were 50 mm × 50 mm × 25 mm (length × width × height). Compressive force applied was parallel to the direction of the foam rise with a strain rate of 30 mm/min. Microstructure and morphology of the foams were observed using a Phenom G2 Pro scanning electron microscope (Netherlands). Before imaging, rectangular shape samples were cut with a sharp blade and attached with conductive carbon tape. Samples were gold sputtered to avoid the charging effect during imaging. Thermal stability of RPFs was studied using thermogravimetric analysis (TGA) on a TA instrument (TGA Q500). Heating was carried out under nitrogen at a rate of 10 °C/min. Dynamic mechanical analysis (DMA) was performed on a TA instrument (TA 2980) which was operated on tension mode on a rectangular shape specimen (15 mm × 6 mm × 2 mm). Heating rate and mechanical vibration frequency were set as 3 °C/min and 10 Hz (amplitude: 15 μm), respectively. Fire-retardant properties of RPFs were studied according to the test method for horizontal burning characteristics of cellular polymeric materials (ASTM D 4986-98). Specimens of 150 mm × 50 mm × 12.5 mm were exposed to flame for 10 s. Burn time and weight difference (before and after the burn) were observed.

**Table 1** Formulation of rigid polyurethane foams\*.

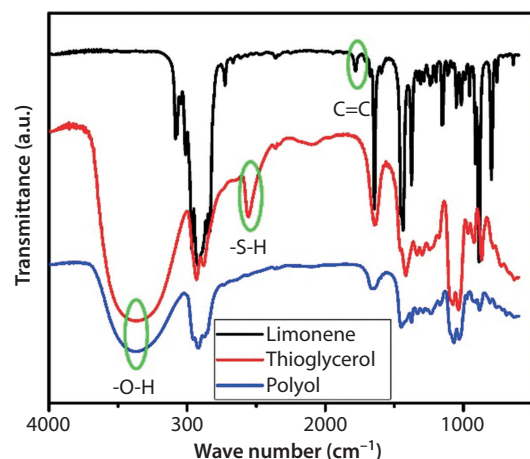
Ingredient	0pbw-L/X	2pbw-L/X	4pbw-L/X	6pbw-L/X	0pbw-L/S	2pbw-L/S	4pbw-L/S	6pbw-L/S	2pbw-L	2pbw-X	2pbw-S
LTG	10	10	10	10	10	10	10	10	20	0	0
X-210	10	10	10	10	0	0	0	0	0	20	0
SG-520	0	0	0	0	10	10	10	10	0	0	20
NIAX A-1	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Water	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
DABCO T-12	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Tegostab B8404	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Isocyanate	31.2	31.2	31.2	31.2	38.4	38.4	38.4	38.4	39.5	22.9	37.2
DMMP	0	2	4	6	0	2	4	6	2	2	2

\*pbw- parts by weight

### 3 RESULTS AND DISCUSSION

#### 3.1 Synthesis of Limonene Polyol

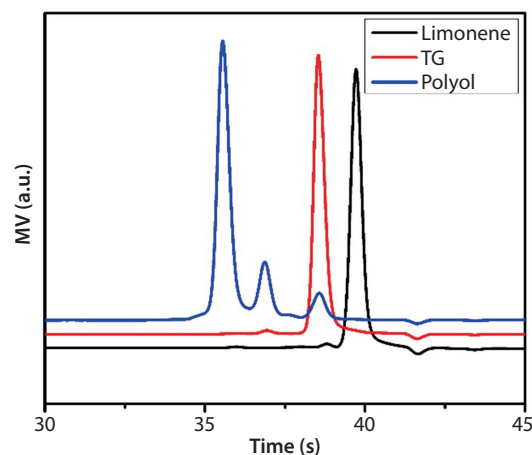
The infrared spectra of the synthesized limonene polyol and its starting materials are shown in Figure 1. The appearance of a broad peak around  $3400\text{ cm}^{-1}$  in limonene polyol indicates the presence of alcohol ( $\text{-OH}$  stretching) group. This indicates the reaction between 1-thioglycerol and limonene. The peak around  $2550\text{ cm}^{-1}$  is the characteristic peak of  $\text{S-H}$  stretching of 1-thioglycerol. The disappearance of this peak in the FT-IR spectrum of the limonene polyol suggests that the reaction has been carried out. In addition, alkene group ( $\text{C}=\text{C}$  stretching) around  $1700\text{ cm}^{-1}$  in limonene has disappeared in the synthesized polyol. This further confirms the completion of the free radical initiated reaction between thiol and alkene groups of 1-thioglycerol and limonene, respectively, as shown in Figure 2. The thiol-ene reaction presented a single-step, cost-effective chemical route to hydroxy functionalize the limonene for the synthesis of polyols, compared to the tedious synthesis processes and expensive catalyst involved with the previously reported chemical route for the synthesis of polyol from plant materials [41].



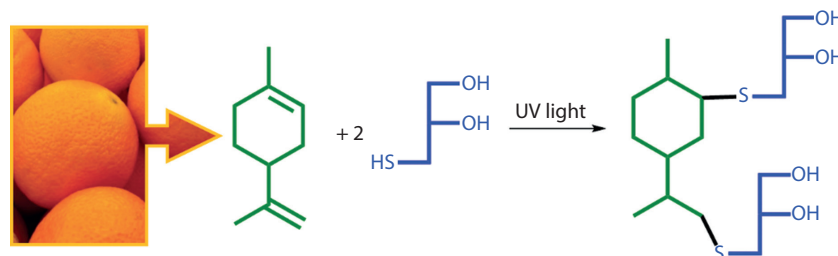
**Figure 1** FT-IR spectra of limonene, 1-thioglycerol and limonene polyol.

#### 3.2 Characteristics of Limonene Polyols

The hydroxyl number and viscosity of the limonene polyol were determined to be  $569\text{ mg KOH/g}$  and  $12\text{ Pa.s}$ , respectively. The GPC curves of limonene-based polyol and its starting materials (limonene and 1-thioglycerol) are shown in Figure 3. Overlay of the GPC curves further confirms that the majority of the limonene and 1-thioglycerol has been reacted to form limonene polyol. It can be seen in the GPC curve of the polyol that there is only a negligible amount of 1-thioglycerol residue. This suggests that the thiol-ene chemistry between limonene and 1-thioglycerol can be utilized successfully to synthesize the limonene polyol. Two peaks in the GPC curve for the synthesized limonene polyol at 35.5 min and 36.9 min retention times were observed. These correspond to the two different types of molecular species in the synthesized polyol. Retention peak at 35.5 min represents the higher molecular weight polyol species due to the addition of 1-thioglycerol to both the internal and terminal double bond of the limonene. Retention peak at 36.9 min might be the monoaddition of 1-thioglycerol to terminal double bond as a result of the reactivity difference in exocyclic and endocyclic unsaturation of the limonene [42].



**Figure 3** GPC spectra of limonene, 1-thioglycerol (TG) and limonene polyol.



**Figure 2** Synthesis of limonene polyol using thiol-ene chemistry.

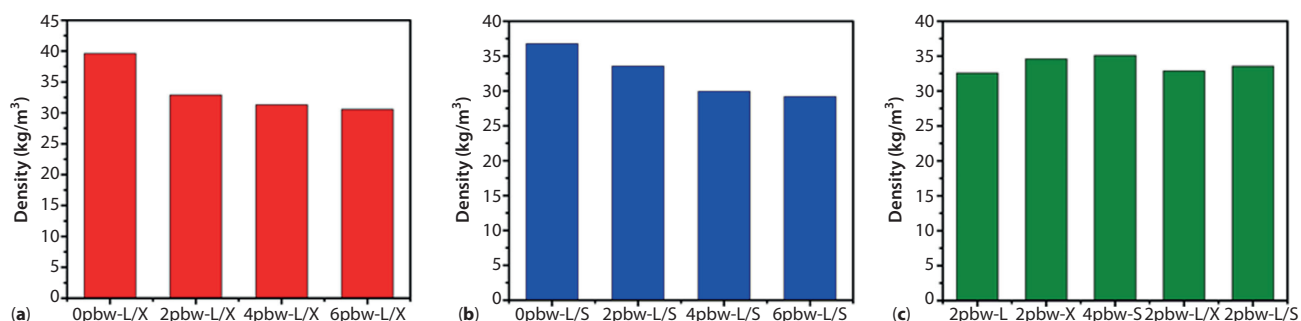
### 3.3 Properties of Rigid Polyurethane Foams

Figure 4a,b shows the effect of DMMP concentration on the density of RPFs prepared using LTG-X 210 and LTG-SG 520 (50:50 w/w). It is observed that the density of the RPFs decrease with the increase in DMMP amount. For example, for RPFs prepared using LTG-X 210 the density decreases approximately by  $10 \text{ kg/m}^3$  with increasing concentration of DMMP from 0 pbw to 6 pbw. Similar behavior was observed for the RPFs prepared using LTG-SG 520. Figure 4c compares the densities of RPFs containing 2 pbw of DMMP prepared using LTG (2pbwL), X 210 (2pbwX), SG 520 (2pbwS) and their 50/50 blends (2pbwL/X, 2pbwL/S). Densities of all the foams were around  $35 \text{ kg/m}^3$ , which comply with the densities of the typical industrial RPFs ( $20\text{--}50 \text{ kg/m}^3$ ) [43].

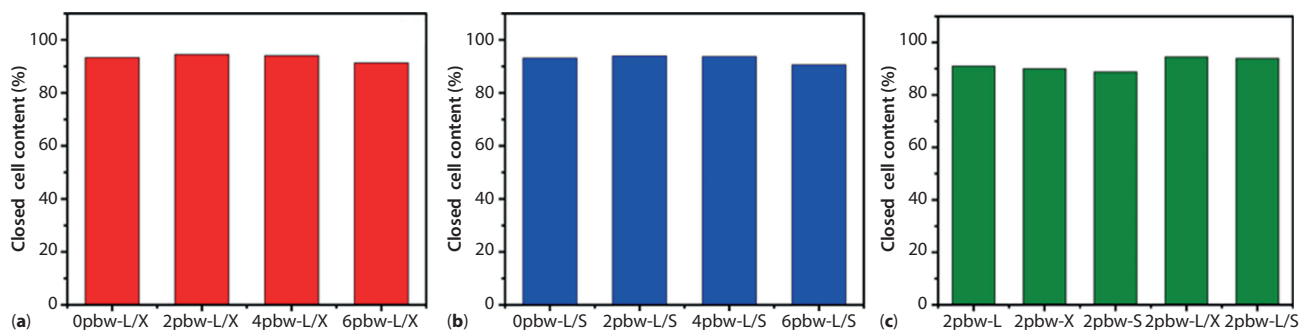
Closed-cell content (CCC) is another important property of RPFs that should be considered. The CCC of all the polyurethane foams based on limonene and commercial polyol blends was above 90% even for the higher concentration DMMP (Figure 5a,b). This suggests that the RPFs prepared using limonene polyol blends may

serve as a better thermal insulator due to the higher CCC percentage which restricts the airflow through the foams. Figure 5c compares the CCC of RPFs containing 2 pbw of DMMP prepared using LTG (2pbwL), X 210 (2pbwX), SG 520 (2pbwS) and their 50/50 blends (2pbwL/X, 2pbwL/S). As observed, the CCC of all the foams was above 90%. The comparable CCC for the RPFs with and without DMMP suggests that addition of DMMP does not disturb the foaming process. The closed-cell content of our prepared polyurethane foams was higher than those made using polyether polyol for flame-retardant polyurethanes [44].

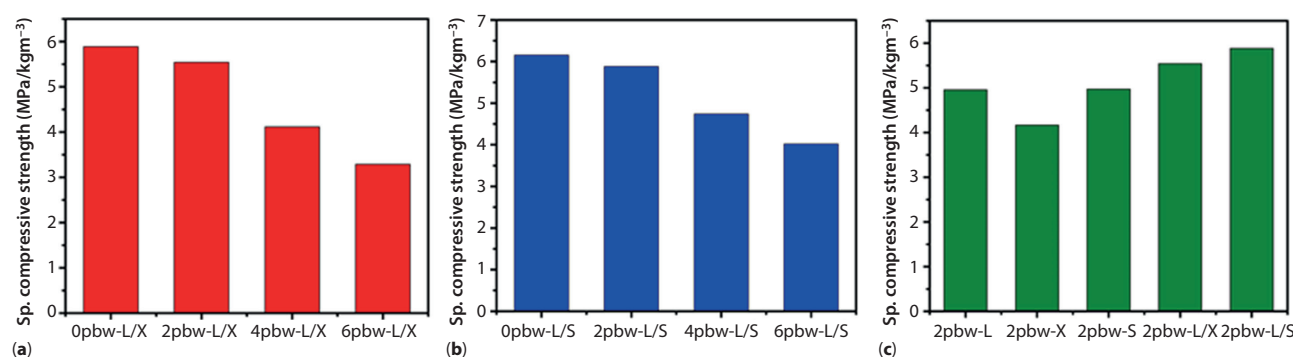
The effect of the variation in density on compressive strength was eliminated by calculating the specific compressive strength (compressive strength/density) for all the foams, as presented in Figure 6. The compressive strength of the RPFs synthesized using limonene polyol is comparable to the compressive strength of polyurethanes prepared using commercial polyether-based polyol [45]. The highest compressive strengths of 233 and 226 kPa were observed for neat (without DMMP) polyurethane foams 0pbw-L/X and 0pbw-L/S, respectively. In contrast, the specific strength of 0pbw-L/S was 4% higher



**Figure 4** Density of the rigid polyurethane foams for (a) LTG/X210 blend having different amounts of DMMP, (b) LTG/SG520 blend having different amounts of DMMP, and (c) limonene, X210, SG520 and their blends with 2 pbw of DMMP.



**Figure 5** Closed-cell content of the rigid polyurethane foams having different amounts of DMMP for (a) LTG/X210 blend, (b) LTG/SG520 blend, and (c) limonene, X210, SG520 and their blends with 2 pbw of DMMP.



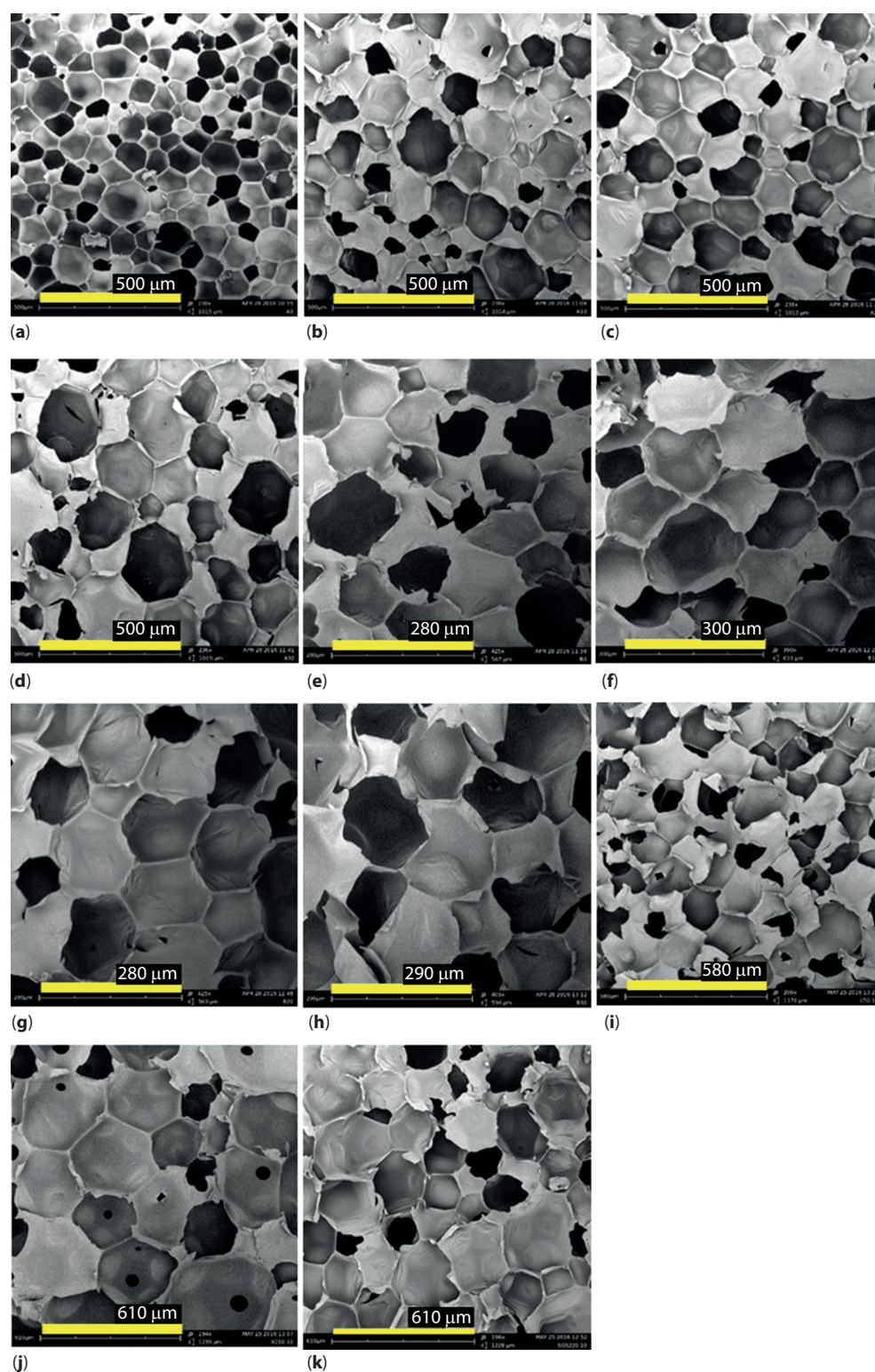
**Figure 6** Specific compressive strength of rigid polyurethane foams with the DMMP quantity for (a) LTG/X210 blend, (b) LTG/SG520 blend, and (c) compressive strength of RPFs based on limonene, X210, SG520 and their blends with 2 pbw of DMMP.

than that of 0pbw-L/X. The higher specific compressive strength of the L/S blends was due to the superior hydroxyl numbers of the SG-520 polyol which provide a maximum crosslinking density to the polyurethane network [46]. Specific compressive strength of RPFs seems to not be affected by the addition of low concentration of DMMP. For example, the specific compressive strength of both 0pbw-L/X and 0pbw-L/S RPFs was reduced by approximately 5% when 2 pbw of DMMP was added. However, the continuous addition of DMMP from 2 pbw to 6 pbw, significantly reduced the specific compressive strength (nearly by 30% in both types of RPFs). Decrease of the mechanical properties can be attributed to the release of lower molecular weight acidic substances released due to the reaction between polyether polyol and DMMP. As a result, concentration of plasticizer increases and this influences the change in properties [47]. It is further noted that RPFs based on limonene polyol have similar compressive strength to the commercial polyol-based RPFs (Figure 6c). However, when they are blended with commercial polyol, RPFs showed further enhancement in the compressive strength.

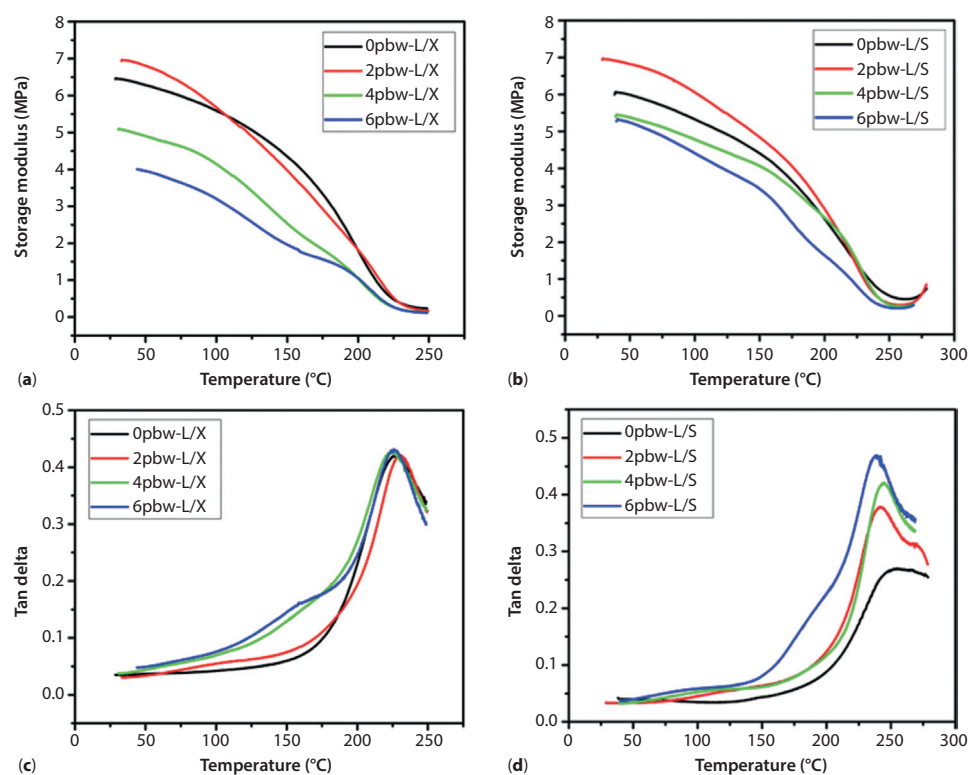
The microstructure and cell size distribution of the RPFs were studied using scanning electron microscopy (SEM). The SEM images of the polyurethane foams are shown in Figure 7. As seen in the SEM images, all the polyurethane foams had a polygon-shaped closed-cell structure which is in good agreement with the above 90% closed-cell content measured from the gas pycnometer. Shape of the cell structure and cell size were uniformly distributed across the foams. Comparison of the SEM images of RPFs without DMMP (Figure 7a,e) and RPFs with DMMP (Figure 7b-d; 7f-h) revealed that average cell size increased with the incorporation of fire retardant. For example, the average cell size of the polyurethane foams 0pbw-L/X, 2pbw-L/X, 4pbw-L/X and 6pbw-L/X was observed as 100, 150, 150 and 175  $\mu\text{m}$ , respectively. On the other hand, the

foams 0pbw-L/S, 2pbw-L/S, 4pbw-L/S and 6pbw-L/S showed cell size of about 30, 150, 160 and 170  $\mu\text{m}$ , respectively. This increase in cell size with the addition of flame retardant might be attributed to the plasticizing effect of DMMP.

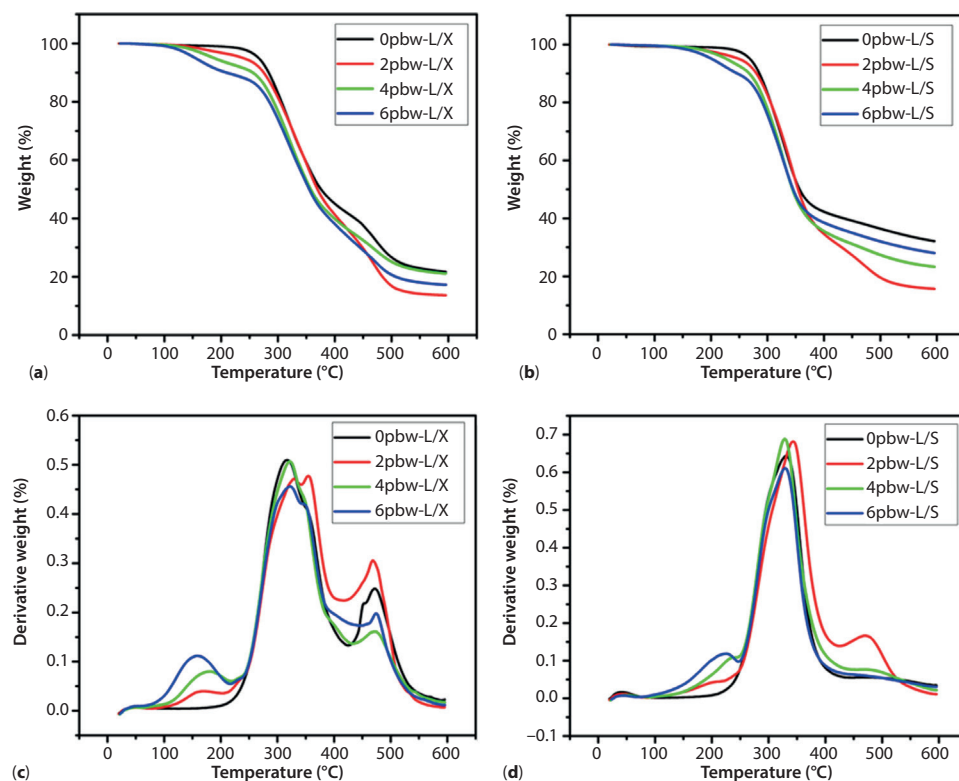
Storage modulus and glass transition temperatures ( $T_g$ ) of RPFs were determined using dynamical mechanical analysis (Figure 8). The maximum of tan delta was reported as the glass transition temperature of the RPFs. The  $T_g$  of the L/X and L/S blends was around 228  $^{\circ}\text{C}$  and 242  $^{\circ}\text{C}$ , respectively. The  $T_g$  is affected by the crosslinking density. An increase in crosslinking density increases the  $T_g$ ; therefore, higher  $T_g$  was observed for the L/S blends. Thermal stability of pure RPFs and DMMP containing RPFs were analyzed and illustrated in Figure 9. According to the TGA and DTGA curves, there are two and three thermal transitions in pure RPFs and DMMP containing RPFs, respectively. This suggests that the incorporation of flame retardant has changed the thermal stability of polyurethane foams. The first transition peak for all the DMMP-containing samples appeared in the temperature range of 100  $^{\circ}\text{C}$  to 250  $^{\circ}\text{C}$ . On the other hand, pure RPFs without DMMP did not show any significant change in weight in a similar temperature range. This weight loss in flame retardant containing RPFs can be attributed to the volatilization of DMMP [48]. It is also observed that increase of DMMP percentage increased the initial weight loss in flame-retardant polyurethane foams. For example, an increase of the DMMP quantity in RPFs from 2 pbw to 6 pbw, increased the weight loss by 8% in both L/X and L/S samples. The main degradation phase in RPFs was observed between 250–400  $^{\circ}\text{C}$ . Significant weight loss (around 50% and 65% for sample L/X and L/S, respectively) in this temperature range might be due to the depolymerization of polyisocyanates and polyols after the cleavage of polyurethane main chain. As a result, some combustible gas products are generated [49].



**Figure 7** SEM images of rigid polyurethane foams (a) 0pbw-L/X, (b) 2pbw-L/X, (c) 4pbw-L/X, (d) 6pbw-L/X, (e) 0pbw-L/S, (f) 2pbw-L/S, (g) 4pbw-L/S, (h) 6pbw-L/S, (i) 2pbw-L, (j) 2pbw-X, and (k) 2pbw-S.



**Figure 8** Variation of storage modulus in (a) 0pbw-L/X to 6pbw-L/X, (b) 0pbw-L/S to 6pbw-L/S, and tan delta in (c) 0pbw-L/X to 6pbw-L/X, (d) 0pbw-L/S to 6pbw-L/S with temperature for various RPFs.



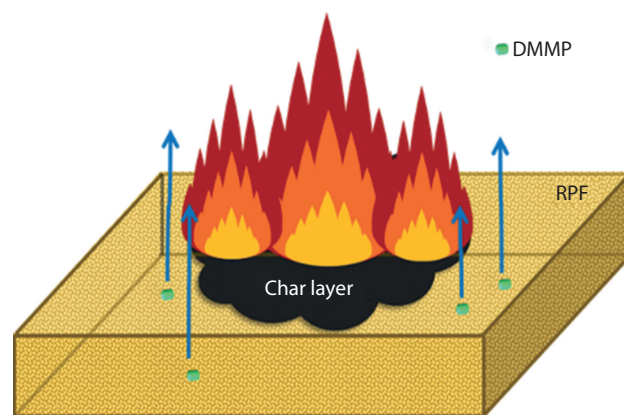
**Figure 9** The TGA curves of RPFs in (a) 0pbw-L/X to 6pbw-L/X, (b) 0pbw-L/S to 6pbw-L/S. DTGA curves of RPFs (c) 0pbw-L/X to 6pbw-L/X, (d) 0pbw-L/S to 6pbw-L/S.

Thermal stability of RPFs can be correlated to the burning test results, as shown in Figure 10a–c. Neat RPFs continued to burn for 110 s after the removal of the ignition source. However, RPFs with DMMP stopped burning after 19 s (Figure 10a,b). This enhanced flame-retardant property of DMMP can be explained as follows. Under heating, DMMP releases the phosphorous-containing compound into the gaseous phase. These phosphorous compounds quench the combustible products released during the decomposition of polyurethane foams [44]. In addition, the formation of char layer also helps to prevent further burning. The flame-retardant mechanism of DMMP is further illustrated in Figure 11. An increase of DMMP quantity from 2 pbw to 6 pbw decreases the burning time by 5 s, which is due to the release of higher amounts of phosphorus compound into the gaseous phase. Weight loss during the burning was also recorded and shown in Figure 10d–f. The RPFs without any flame retardant showed considerable loss of weight. However, addition of even only 2 pbw of DMMP has reduced the weight loss by almost 40%. This indicates that the DMMP acts as an effective flame retardant in limonene-based polyurethane foam. Reference RPFs with 2 pbw of flame retardant showed comparable burning time and weight loss (Figure 10c,f), suggesting the suitability of DMMP as a flame retardant for

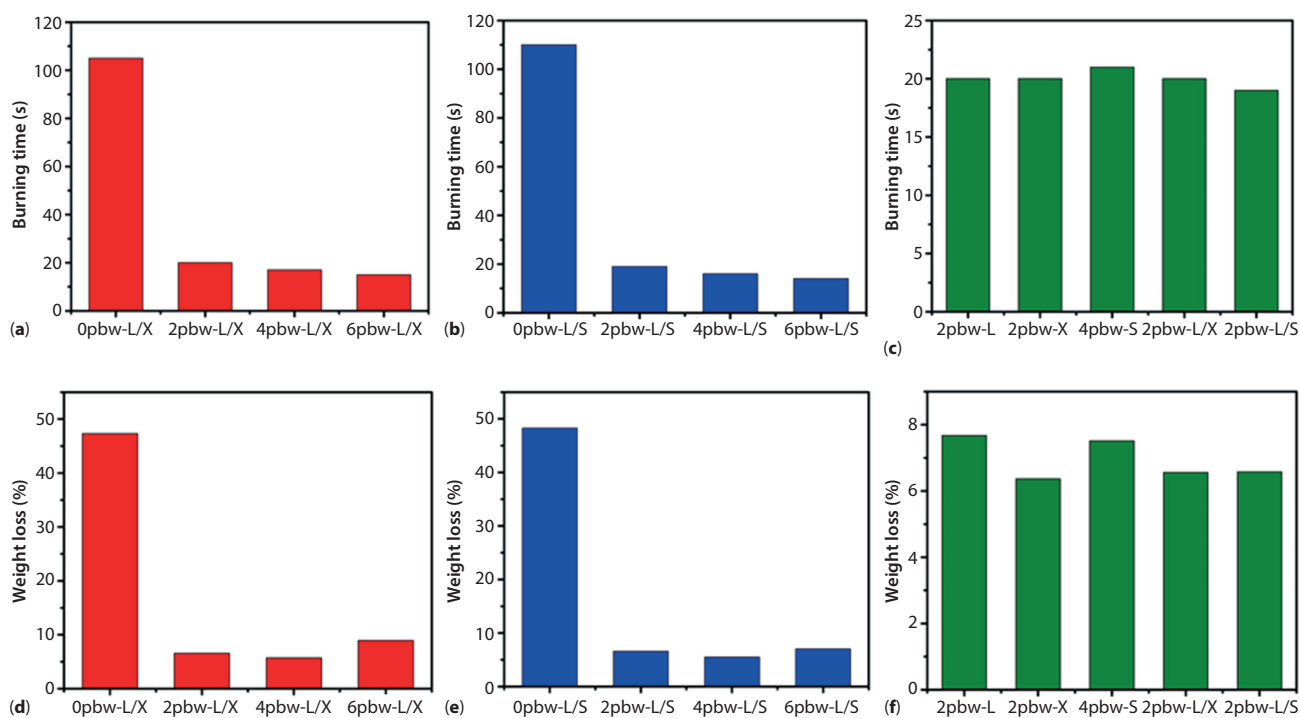
different types of polyurethane compounds. The digital photographs of the polyurethane foams after the burning test are shown in Figure 12. As seen in the images, the addition of DMMP significantly reduces the burning of the polyurethane foams.

#### 4 CONCLUSION

Limonene, an extract of orange peel, was reacted with 1-thioglycerol using photochemically activated



**Figure 11** Flame-retardant mechanism of DMMP in RPFs.



**Figure 10** Burning time of RPFs (a) 0pbw-L/X to 6pbw-L/X, (b) 0pbw-L/S to 6pbw-L/S and (c) reference RPFs with 2pbw of DMMP. Weight loss during the burning test of RPFs (d) 0pbw-L/X to 6pbw-L/X, (e) 0pbw-L/S to 6pbw-L/S, and (f) reference RPFs with 2pbw of DMMP.

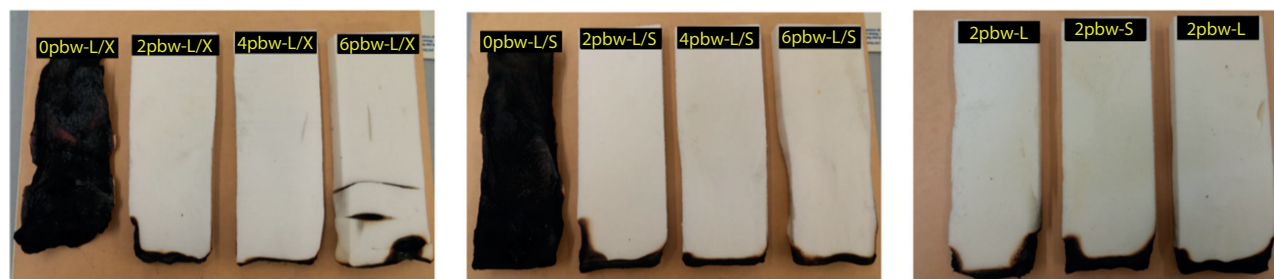


Figure 12 Digital photographs of the foam after burning test.

thiol-ene chemistry to successfully synthesize biobased polyol. We showed that biobased polyol is suitable for preparation of rigid polyurethane foam with uniform cell morphology, high closed-cell content and excellent mechanical properties. Incorporation of DMMP significantly enhanced the flame-retardant behavior of RPFs. Addition of 2 pbw DMMP to the pure RPF reduced the burning time from 110 s to 20 s. Further increment of DMMP concentration slightly improved the flame-retardant properties. However, addition of DMMP reduces the mechanical properties of the prepared foams. It was found that 2 pbw of DMMP was the optimum quantity of fire retardant, which exhibited balanced fire resistance and mechanical properties for the considered polyurethane foam matrix. Analysis of thermal stability and burning behavior of RPFs indicated that the decomposition products of DMMP may retard the combustion of polyurethane in gaseous phase. Our study suggests that limonene polyol can be used for the preparation of rigid polyurethane foams. Addition of a small amount of DMMP in RPFs significantly reduced the fire hazard.

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## Author Contributions

RKG and CKR conceived the project and designed the experiments. CKR performed all the synthesis and prepared polyurethane foams. All the characterizations were performed by CKR. NB helped for flammability and mechanical testing. CKR prepared the first draft of the manuscript. All the authors reviewed and commented on the manuscript.

## REFERENCES

1. S. Oprea, V.-O. Potolinca, and V. Oprea, Synthesis and properties of new crosslinked polyurethane elastomers based on isosorbide. *Eur. Polym. J.* **83**, 161–172 (2016).
2. C.S. Carriço, T. Fraga, and V.M.D. Pasa, Production and characterization of polyurethane foams from a simple mixture of castor oil, crude glycerol and untreated lignin as bio-based polyols. *Eur. Polym. J.* **85**, 53–61 (2016).
3. N.V. Gama, B. Soares, C.S.R. Freire, R. Silva, C.P. Neto, A. Barros-Timmons, and A. Ferreira, Bio-based polyurethane foams toward applications beyond thermal insulation. *Materials & Design* **76**, 77–85 (2015).
4. J. Bernardini, P. Cinelli, I. Anguillesi, M.-B. Coltelli, and A. Lazzeri, Flexible polyurethane foams green production employing lignin or oxypropylated lignin. *Eur. Polym. J.* **64**, 147–156 (2015).
5. A.R. Kakroodi, M. Khazabi, K. Maynard, M. Sain, and O.-S. Kwon, Soy-based polyurethane spray foam insulations for light weight wall panels and their performances under monotonic and static cyclic shear forces. *Ind. Crop Prod.* **74**, 1–8 (2015).
6. G. Zhang, B. Wang, L. Ma, L. Wu, S. Pan, and J. Yang, Energy absorption and low velocity impact response of polyurethane foam filled pyramidal lattice core sandwich panels. *Composite Structures* **108**, 304–310 (2014).
7. D.B. Morris and B. Fogg, Rigid polyurethane foam: Refrigerator cabinet design and construction. *Int. J. Refrig.* **2**, 105–112 (1979).
8. M. Ionescu, *Chemistry and Technology of Polyols for Polyurethanes*, Rapra Technology, Shrewsbury, UK (2005).
9. X. Kong, G. Liu, H. Qi, and J.M. Curtis, Preparation and characterization of high-solid polyurethane coating systems based on vegetable oil derived polyols. *Prog. Org. Coat.* **76**, 1151–1160 (2013).
10. L. Montero de Espinosa and M.A.R. Meier, Plant oils: The perfect renewable resource for polymer science?! *Eur. Polym. J.* **47**, 837–852 (2011).
11. S. Husić, I. Javni, and Z.S. Petrović, Thermal and mechanical properties of glass reinforced soy-based polyurethane composites. *Compos. Sci. Technol.* **65**, 19–25 (2005).

12. M.A. Corcuera, L. Rueda, B. Fernandez d'Arlas, A. Arbelaiz, C. Marieta, I. Mondragon, and A. Eceiza, Microstructure and properties of polyurethanes derived from castor oil. *Polym. Degrad. Stab.* **95**, 2175–2184 (2010).
13. S.J. Lee and B.K. Kim, Covalent incorporation of starch derivative into waterborne polyurethane for biodegradability. *Carbohydr. Polym.* **87**, 1803–1809 (2012).
14. J.L. Rivera-Armenta, T. Heinze, and A.M. Mendoza-Martínez, New polyurethane foams modified with cellulose derivatives. *Eur. Polym. J.* **40**, 2803–2812 (2004).
15. R.K. Gupta, M. Ionescu, D. Radojic, X. Wan, and Z.S. Petrovic, Novel Renewable Polyols Based on Limonene for Rigid Polyurethane Foams. *J. Polym. Environ.* **22**, 304–309 (2014).
16. M. Firdaus, L. Montero de Espinosa, and M.A.R. Meier, Terpene-Based Renewable Monomers and Polymers via Thiol-Ene Additions. *Macromolecules* **44**, 7253–7262 (2011).
17. R.T. Mathers, K.C. McMahon, K. Damodaran, C.J. Retarides, and D.J. Kelley, Ring-Opening Metathesis Polymerizations in d-Limonene: A Renewable Polymerization Solvent and Chain Transfer Agent for the Synthesis of Alkene Macromonomers. *Macromolecules* **39**, 8982–8986 (2006).
18. M. Modena, R.B. Bates, and C.S. Marvel, Some low molecular weight polymers of d-limonene and related terpenes obtained by Ziegler-type catalysts. *J. Polym. Sci. Part A: General Papers* **3**, 949–960 (1965).
19. T. Doiuchi, H. Yamaguchi, and Y. Minoura, Cyclocopolymerization of d-limonene with maleic anhydride. *Eur. Polym. J.* **17**, 961–968 (1981).
20. K. Griesbaum, Problems and Possibilities of the Free-Radical Addition of Thiols to Unsaturated Compounds. *Angew. Chem. Int. Edit.* **9**, 273–287 (1970).
21. J.F. Janes, I.M. Marr, N. Unwin, D.V. Banthorpe, and A. Yusuf, Reaction of monoterpenoids with hydrogen sulphide to form thiols and epi-sulphides of potential organoleptic significance. *Flavour. Fragr. J.* **8**, 289–294 (1993).
22. C.S. Marvel and L.E. Olson, Polyalkylene sulfides. XIII. Polymers from 4-vinyl-1-cyclohexene and d-limonene. *J. Polym. Sci.* **26**, 23–28 (1957).
23. U. Bexell, M. Olsson, M. Johansson, J. Samuelsson, and P.-E. Sundell, A tribological study of a novel pre-treatment with linseed oil bonded to mercaptosilane treated aluminium. *Surf. Coat. Technol.* **166**, 141–152 (2003).
24. B.K. Sharma, A. Adhvaryu, and S.Z. Erhan, Synthesis of Hydroxy Thio-ether Derivatives of Vegetable Oil. *J. Agric. Food Chem.* **54**, 9866–9872 (2006).
25. B.K. Sharma, A. Adhvaryu, and S.Z. Erhan, Friction and wear behavior of thioether hydroxy vegetable oil. *Tribol. Int.* **42**, 353–358 (2009).
26. M. Black and J.W. Rawlins, Thiol-ene UV-curable coatings using vegetable oil macromonomers. *Eur. Polym. J.* **45**, 1433–1441 (2009).
27. C. Lluch, J.C. Ronda, M. Galià, G. Lligadas, and V. Cádiz, Rapid Approach to Biobased Telechelics through Two One-Pot Thiol-Ene Click Reactions. *Biomacromolecules* **11**, 1646–1653 (2010).
28. J. Samuelsson, M. Jonsson, T. Brinck, and M. Johansson, Thiol-ene coupling reaction of fatty acid monomers. *J. Polym. Sci. Polym. Chem.* **42**, 6346–6352 (2004).
29. M. Comí, G. Lligadas, J.C. Ronda, M. Galià, and V. Cádiz, Synthesis of castor-oil based polyurethanes bearing alkene/alkyne groups and subsequent thiol-ene/yne post-modification. *Polymer* **103**, 163–170 (2016).
30. C. Lluch, G. Lligadas, J.C. Ronda, M. Galià, and V. Cádiz, “Click” synthesis of fatty acid derivatives as fast-degrading polyanhydride precursors. *Macromol. Rapid Commun.* **32**, 1343–1351 (2011).
31. O. Türlüç and M.A.R. Meier, Fatty acid derived monomers and related polymers via thiol-ene (click) additions. *Macromol. Rapid Commun.* **31**, 1822–1826 (2010).
32. O. Turunc and M.A.R. Meier, Thiol-ene/ADMET: a complementary approach to fatty acid-based biodegradable polymers. *Green Chem.* **13**, 314–320 (2011).
33. M. Zammarano, R.H. Krämer, R. Harris, T.J. Ohlemiller, J.R. Shields, S.S. Rahatekar, S. Lacerda, and J.W. Gilman, Flammability reduction of flexible polyurethane foams via carbon nanofiber network formation. *Polym. Adv. Technol.* **19**, 588–595 (2008).
34. R. Benrashid and G.L. Nelson, Synthesis of new siloxane urethane block copolymers and their properties. *J. Polym. Sci. Polym. Chem.* **32**, 1847–1865 (1994).
35. L. Fengjiao, D. Xuejia, and S. Yu, Properties of Rigid Polyurethane Foams Produced by the Addition of Phosphorus Compounds. *Am. J. Mater. Res.* **1**, 14–19 (2014).
36. W. Xing, H. Yuan, P. Zhang, H. Yang, L. Song, and Y. Hu, Functionalized lignin for halogen-free flame retardant rigid polyurethane foam: preparation, thermal stability, fire performance and mechanical properties. *J. Polym. Res.* **20**, 1–12 (2013).
37. A. König, U. Fehrenbacher, T. Hirth, and E. Kroke, Flexible Polyurethane Foam with the Flame-retardant Melamine. *J. Cell. Plast.* **44**, 469–480 (2008).
38. A. König, A. Malek, U. Fehrenbacher, G. Brunklaus, M. Wilhelm, and T. Hirth, Silane-functionalized Flame-retardant Aluminum Trihydroxide in Flexible Polyurethane Foam. *J. Cell. Plast.* **46**, 395–413 (2010).
39. A. Gharehbaghi, R. Bashirzadeh, and Z. Ahmadi, Polyurethane flexible foam fire resisting by melamine and expandable graphite: Industrial approach. *J. Cell. Plast.* **47**, 549–565 (2011).
40. M.-J. Chen, C.-R. Chen, Y. Tan, J.-Q. Huang, X.-L. Wang, L. Chen, and Y.-Z. Wang, Inherently flame-retardant flexible polyurethane foam with low content of phosphorus-containing cross-linking agent. *Ind. Eng. Chem. Res.* **53**, 1160–1171 (2013).
41. M. Desroches, M. Escouvois, R. Auvergne, S. Caillol, and B. Boutevin, From vegetable oils to polyurethanes: Synthetic routes to polyols and main industrial products. *Polym. Rev.* **52**, 38–79 (2012).
42. P.A. Wilbon, F. Chu, and C. Tang, Progress in renewable polymers from natural terpenes, terpenoids, and rosin. *Macromol. Rapid Commun.* **34**, 8–37 (2013).

43. H.J.M. Grunbauer, J. Bicerano, P. Clavel, R.D. Daussin, H.A. de Vos, M.J. Elwell, H. Kawabata, H. Kramer, D.D. Latham, C.A. Martin, S.E. Moore, B.C. Obi, V. Parenti, A.K. Schrock, R. van den Bosch, *Polymeric Foams: Mechanisms and Materials*, CRC Press, Boca Raton, FL (2004).
44. F. Feng and L. Qian, The flame retardant behaviors and synergistic effect of expandable graphite and dimethyl methylphosphonate in rigid polyurethane foams. *Polym. Compos.* **35**, 301–309 (2014).
45. W. Xi, L. Qian, Y. Chen, J. Wang, and X. Liu, Addition flame-retardant behaviors of expandable graphite and [bis(2-hydroxyethyl)amino]-methyl-phosphonic acid dimethyl ester in rigid polyurethane foams. *Polym. Degrad. Stab.* **122**, 36–43 (2015).
46. A. Zlatanić, C. Lava, W. Zhang, and Z.S. Petrović, Effect of structure on properties of polyols and polyurethanes based on different vegetable oils. *J. Polym. Sci. Polym. Phys.* **42**, 809–819 (2004).
47. F. Liu, X. Ding, and Y. Su, Properties of rigid polyurethane foams produced by the addition of phosphorus compounds. *Am. J. Mater. Res.* **1**, 14–19 (2014).
48. A. Lorenzetti, M. Modesti, S. Besco, D. Hrelja, and S. Donadi, Influence of phosphorus valency on thermal behaviour of flame retarded polyurethane foams. *Polym. Degrad. Stab.* **96**, 1455–1461 (2011).
49. S. Duquesne, M. Le Bras, S. Bourbigot, R. Delobel, G. Camino, B. Eling, C. Lindsay, T. Roels, and H. Vezin, Mechanism of fire retardancy of polyurethanes using ammonium polyphosphate. *J. Appl. Polym. Sci.* **82**, 3262–3274 (2001).