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# Synthesis of Novel Biobased Polyol via Thiol-Ene Chemistry for Rigid Polyurethane Foams

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**ABSTRACT:** The objective of this research is to prepare rigid polyurethane (PU) foams from α-phellandrene, a biobased compound. Two types of polyols were synthesized by reacting α-phellandrene with 2-mercaptoethanol and α-thioglycerol via thiol-ene chemistry route. The completion of the reaction was identified by using FTIR. PU foams from α-phellandrene polyols and commercial polyol were compared with regard to foam characteristics and properties. All the PU foams showed apparent density of 28–39 kg/m$^3$ with closed-cell content above 90%. The highest glass transition temperature of 229 °C and compressive strength of 220 kPa were observed for the polyol synthesized by reacting α-phellandrene and α-thioglycerol, due to the higher number of hydroxyl functionalities. The type of polyol also had an influence on thermal stability and foam reactivity. The PU foams from α-phellandrene polyol had lower onset degradation temperature. However, this was improved upon blending with commercial polyol. Foam reactivity was the highest in the polyol consisting of primary hydroxyl groups. This study establishes the preparation of biobased polyols from α-phellandrene for the preparation of rigid PU foam which could be suitable for thermal insulation.

**KEYWORDS:** Biobased polyol, α-phellandrene, polyurethanes, rigid foam, thiol-ene reaction

## 1 INTRODUCTION

Polyurethane (PU) is an important class of polymers, which manifests versatile properties suitable for a wide range of industrial applications [1–3]. Rigid and flexible foams are the two major polyurethane products. Elastomers, paints, sealants, and adhesives are among other typical uses for polyurethane [4]. Rigid polyurethane foams represent one of the most efficient thermal insulators and are extensively used in the construction industry as a thermal barrier because of their low thermal conductivity, light weight, high compression strength, and good adhesion [5, 6]. Also, rigid PU foams can be commonly found as an insulation layer in pipes, tanks, refrigerators, boats, and aircrafts [7, 8]. The rigid foam structure of PU is formed by trapping the gas generated by a blowing agent inside solid PU matrix. Insulation properties of rigid PU foams depend on the thermal conductivity of gas and solid PU, which are governed by the properties of the blowing agent, closed-cell structure, and cell size [9, 10]. The excellent thermal insulation performance of rigid PU foams is due to the very low thermal conductivity of gas, and gas occupies nearly 96% of the total volume of rigid PU foams [11].

Currently, the starting chemicals for polyurethane and most other polymers are accrued from petroleum feedstocks. Increasing concerns over environmental issues and scarcity of petroleum resources have motivated the search for alternative starting raw materials for polyurethane. Extensive research has been focused on synthesizing plant-derived isocyanates [12, 13] and polyols [14–17], two starting chemicals of polyurethane, to replace the conventional petrochemical-based chemicals. So far, various plant-derived materials have been explored for the synthesis of polyol for polyurethane because of their sustainability, availability, value addition to the agricultural products, and commercial competitiveness. However, most plant oils require the incorporation of hydroxyl functional group to undergo reaction with isocyanate for the preparation of PU. Epoxidation [18–20], hydroformylation [21–23],

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ozonolysis [24, 25], and transesterification [26–28] are among the commonly utilized synthesis routes to modify the unsaturation of the triglyceride or fatty acids. These synthesis processes involve multistep reactions or expensive catalysts. Recently, thiol-ene coupling has been attracting interest as a viable option to functionalize the unsaturated compounds via free radical addition of thiol to the double bonds [29]. Presently, thiol-ene coupling reaction is being used to alter the chemical structure of plant oils for various applications. Hydroxy thio-ether derivatives of vegetable oils were obtained by thiol-ene coupling to improve the wear and friction resistance of the vegetable oils [30–32]. Thiol-ene coupling is an effective reaction for crosslinking and oligomerization of vegetable oils with polyfunctional thiols under UV irradiation [33–35]. Notably, renewable monomers based on fatty acids have been synthesized by thiol-ene reaction. Subsequently, monomers were polymerized to polyesters and polyandries. These polymers exhibited fast degradation in hydrolytic condition, indicating their suitability for biomedical applications [36–38]. Recently, thiol-ene reaction has been utilized to synthesize biobased polyol, grafting 1-thioglycerol and limonene dimercaptan onto double bonds of limonene and glycerol-1-allylether, respectively. This thiol-ene coupling showed the characteristics of "click" reaction such as high yield of polyol, unsophisticated reaction conditions and relatively short reaction time [39–41].

α-Phellandrene is a monoterpene with two endocyclic carbon double bonds. It is the main constituent of several essential oils, extracted from plants such as Peruvian pepper (*Schinus molle* L.) [42], eucalyptus [43, 44], piper [45, 46], fennel [47, 48], false fennel (*Ridolfia segetum* L. Moris) [49, 50] and dill (*Anethum graveolens* L.) [51, 52]. α-Phellandrene inherently has a strong aroma and is often incorporated into fragrances [53]. In addition, α-phellandrene contains essential oil capable of inhibiting microbial growth [54, 55]. For the first time, we report the use α-phellandrene to synthesize biobased polyols via thiol-ene chemistry for the preparation of rigid PU foam. This article studies the effect of the structural difference between the two polyols in terms of foam reactivity, cell morphology, thermal, and mechanical properties. We also compare the synthesized polyols with a commercial counterpart in the search for a potential industrial application.

## 2 EXPERIMENTAL

### 2.1 Materials

α-Phellandrene (≥ 85%, Sigma-Aldrich), α-thioglycerol (TCI), 2-mercaptoethanol (Acros Organics) and 2-hydroxy-2-methylpropiophenone (TCI) were used as received for the synthesis of biobased polyol. A commercially available Jeffol SG-360, a sucrose/glycerine-based polyether polyol with an OH content of 360 mg KOH/g (Huntsman), was selected as the control polyol. The Rubinate M (polymeric methylenediphenyl diisocyanate, NCO content of 31%) was purchased from Huntsman. The following chemicals were utilized for the preparation of polyurethane foams: DABCO T-12 (Air Products) and NIAX A-1 (OSi Specialties) were used as the catalyst, and silicone surfactant (Tegostab B-8404) was purchased from Evonik. Distilled water was used as blowing agent.

### 2.2 Synthesis of α-Phellandrene-Derived Polyol

α-Phellandrene-based polyol was synthesized by reacting 27.13 g of α-phellandrene with 36.65 g of α-thioglycerol (1:2 molar ratio of α-phellandrene and α-thioglycerol) in the presence of 2.85 g of 2-hydroxy-2-methylpropiophenone as the photoinitiator. The photochemical reaction was carried out at room temperature for 8 h under 365 nm ultraviolet radiations. The synthesized polyol was named AP-TG. The same synthesis route was adopted to synthesize AP-ME-TG polyol (1:1:1 molar ratio of α-phellandrene, 2-mercaptoethanol and α-thioglycerol).

### 2.3 Characterization of α-Phellandrene-Derived Polyol

The synthesized polyols were characterized using various techniques. The phthalic anhydride/pyridine (PAP) method (ASTM D4274) was used to determine the hydroxyl number of the polyols. The FTIR spectrum of polyol was recorded using a Shimadzu IRAffinity-1 FTIR spectrophotometer at room temperature. Viscosity was measured by using an AR 2000 dynamic stress rheometer (TA Instruments) at 25 °C.

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

Biobased polyol and/or commercial polyol, catalysts, silicone surfactant and blowing agent were thoroughly premixed in an open plastic container. Pre-weighted diisocyanate was added to the above mixture and vigorously stirred about 10 seconds. The homogenous mixture was allowed to rise freely at room temperature. Once the rising of the PU foam started, cream time, tack-free time and rise time were recorded. All PU foams were kept under ambient conditions for 7 days to complete the curing process. The detailed formulation of the RPFs is given in Table 1. The amount of diisocyanate

  

**Table 1** Formulations by weight (g) used for synthesis of RPFs.

| Ingredients | F-J | F-AP-TG | F-AP-ME-TG | F-AP-TG-J | F-AP-ME-TG-J |
|---|---|---|---|---|---|
| AP-TG | 0 | 20.00 | 0 | 10.00 | 0 |
| AP-ME-TG | 0 | 0 | 20.00 | 0 | 10.00 |
| Jeffol SG-360 | 20.00 | 0 | 0 | 10.05 | 10.03 |
| Tegostab B-8404 | 0.40 | 0.40 | 0.40 | 0.41 | 0.40 |
| Niax A-1 | 0.11 | 0.12 | 0.12 | 0.12 | 0.12 |
| DABCO T-12 | 0.04 | 0.03 | 0.03 | 0.03 | 0.03 |
| Water | 0.80 | 0.81 | 0.80 | 0.81 | 0.80 |
| Rubinate M | 30.78 | 44.58 | 38.80 | 35.62 | 34.30 |

(Rubinate M, index 105) in each formulation was based on equivalent weight of polyols and distilled water:

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

where $w_i$, $w_p$, $w_{pc}$ and $w_{water}$ are the weights of isocyanate, polyols, commercial polyols and water, respectively. $Ew_i$, $Ew_p$ and $Ew_{pc}$, are the equivalent weights of isocyanate, biobased polyol, and commercial polyol, respectively. $Ew_{water}$ (= 9) is the hydroxyl equivalent weight of water.

## 2.4 Characterization of Rigid Polyurethane Foams

Morphology, microstructural and physical properties of the fabricated RPFs were studied according to the standard procedures. The apparent density of foams was determined according to ASTM D1622. Cylindrical shaped foam with a diameter of about 46 mm and a height of about 30 mm was cut from the top of the PU foam block and weighed to calculate the density. Closed-cell content of the same cylindrical shaped specimens was determined from gas displacement method (ASTM 6226) by using an Ultrapycnometer, UltraFoam 1000. Compressive strength was measured using the specimens with dimensions of ~ 50 mm × 50 mm × 25 mm from a Q-Test 2-tensile machine (MTS, USA) in accordance with the ASTM 1621 standard procedure. Specimens were subjected to a compressive force parallel to the foam rise direction at a rate of 30 mm/min. Compressive strength was calculated as the force required to reach 10% of strain divided by the surface area of the specimen. Cell morphology of the PU foams was analyzed using a G2 Pro scanning electron microscope (SEM) from Phenom-World, Netherlands. The PU foams were subjected to sputter gold coating prior to the imaging to avoid the accumulation of electrostatic charge on the surface.

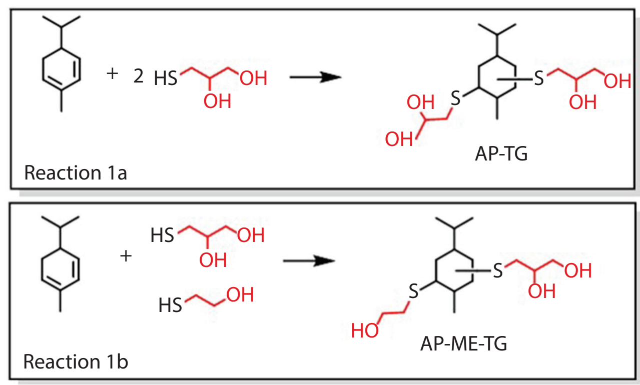


**Figure 1** The chemical structures of the synthesized α-phellandrene bio-based polyols.

Thermogravimetric analysis (TGA) was performed using a TGA Q500 (TA Instruments, USA) from room temperature to 600 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. For dynamic mechanical analysis (DMA), specimens with the dimensions of ~ 15 mm × 6 mm × 2 mm were prepared from the PU foams and tested in tension mode using a DMA 2980 (TA Instruments, USA). Heating rate and mechanical vibration frequency were set at 3 °C/min and 10 Hz (amplitude: 15 µm), respectively, to record the storage modulus and loss modulus.

# 3 RESULTS AND DISCUSSION

## 3.1 Synthesis of α-Phellandrene Biobased Polyol

Thiol-ene coupling is a useful reaction for hydroxy functionalization of unsaturated terpenes. The synthesis of α-phellandrene polyol proceeds through free radical addition of thiol group into the two internal double bonds of α-phellandrene, as shown in Figure 1. Free radicals in thiol groups are generated from the photoinitiation of 2-hydroxy-2-methylpropiophenone

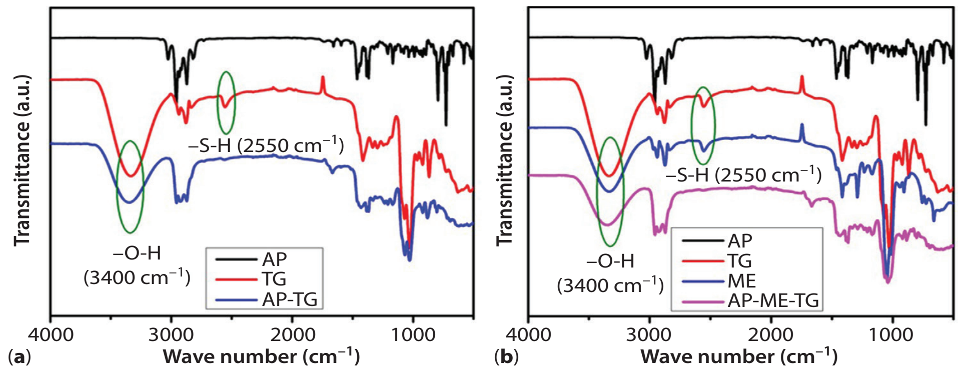


**Figure 2** FTIR spectra of the starting materials and their polyols using (**a**) AP and TG and (**b**) AP, TG and ME.

**Table 2** Foaming parameters and PU foam characteristics.

| Ingredients | F-J | F-AP-TG | F-AP-ME-TG | F-AP-TG-J | F-AP-ME-TG-J |
|---|---|---|---|---|---|
| Cream time (s) | 13 | 11 | 7 | 11 | 10 |
| Rise time (s) | 62 | 40 | 35 | 45 | 48 |
| Tack-free time (s) | 107 | 71 | 62 | 80 | 84 |
| Density (kg/m$^3$) | 37.5 | 33.7 | 28.3 | 36.7 | 39.0 |
| Closed cell content (%) | 94 | 92 | 91 | 95 | 95 |
| Compressive strength at 10% strain (kPa) | 200 | 220 | 160 | 228 | 231 |
| Specific compressive strength [kPa/(kg/m$^3$)] | 5.33 | 6.53 | 5.65 | 6.21 | 5.92 |
| Glass transition temperature/$T_g$ (°C) | 183 | 229 | 205 | 218 | 196 |

by UV radiation [17]. Functionality of the resultant polyols varied depending on which thiol compound (α-thioglycerol or 2-mercaptoethanol) reacted with the α-phellandrene.

The FTIR spectra of synthesized polyols and starting chemicals are shown in Figure 2a and 2b. The broad and strong peaks at 3400 cm$^{-1}$ correspond to the –O-H stretching. These peaks in AP-TG and AP-ME-TG polyols would be the result of the reaction between alkene group of α-phellandrene and thiol compounds. This reaction is further confirmed by the disappearance of the peaks at 2550 cm$^{-1}$ for –S-H stretching from the synthesized polyols. The –S-H groups in α-thioglycerol and 2-mercaptoethanol have been converted to the –S-R by thiol-ene reaction. The peak at 3050 cm$^{-1}$ in α-phellandrene is attributed to the –C–H stretching of alkene. This peak has shifted to the 2950 cm$^{-1}$ resembling the –C–H stretching of an alkane, after the addition of thiol group to α-phellandrene. These observations reveal that the thiol-ene reaction between α-thioglycerol and 2-mercaptoethanol, and α-phellandrene has been accomplished.

## 3.2 Properties of α-Phellandrene Biobased Polyol

The hydroxyl numbers of the AP-TG and AP-ME-TG polyols were 554 and 500 mg KOH/g, respectively. These values comply with the commonly required hydroxyl number for the preparation of rigid polyurethane foam, which is in the range between 300 and 650 mg KOH/g [56]. The viscosity at 25 °C of the AP-TG and AP-ME-TG were determined to be 0.616 and 0.157 Pa.s, respectively.

## 3.3 Properties of Rigid Polyurethane Foams

Measurement of the foaming parameters (cream time, rising time and tack-free time) for the PU foam formation allows the determination of the reactivity of PU foaming process. The foaming parameters for the five different PU foams are listed in Table 2. The PU foam based on 100% AP-ME-TG polyol is the most reactive system with the shortest cream time, rising time and tack-free time. In contrast, slow reaction times were recorded for the AP-TG polyol-based PU foam (F-AP-TG). The reactivity difference in PU systems can be attributed to the structural variation of the two synthesized polyols. AP-ME-TG polyol consisted of primary and secondary hydroxyl groups due to the addition of both α-thioglycerol and 2-mercaptoethanol. However, AP-TG polyol only contained secondary hydroxyl groups, which are less reactive towards the isocyanate compared to the primary hydroxyl groups in AP-ME-TG polyol.

  

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Apparent density and closed-cell content of rigid PU foams are displayed in Table 2. Density of all the foams was in the range of 28–39 kg/m$^3$, which satisfies the commonly requested density of 20–50 kg/m$^3$ for the rigid PU foams [11]. A higher percentage of closed-cell content is desired in rigid PU foams to be used as thermal insulation material. All the α-phellandrene-based foams consisted of closed-cell content above 90% and were comparable to the PU foam based on commercial polyol. Closed-cell content was further enhanced when α-phellandrene polyols were blended with the commercial polyol.

Table 2 and Figure 3 show the mechanical properties of the rigid PU foams. The effect of the density difference in five PU samples was eliminated by comparing the specific compressive strength (i.e., compressive strength at 10% strain divided by the density of the rigid PU foam). The highest specific compressive strength of 6.53 kPa/(kg/m$^3$) was observed in F-AP-TG foam, which is 13% higher than specific compressive strength of F-AP-ME-TG foam. Correspondingly, specific compressive strength of F-AP-TG-J foam was 5% higher than that of F-AP-ME-TG-J foam. Therefore, it is evident that polyol synthesized solely by reacting α-thioglycerol with α-phellandrene is more suitable to prepare mechanically stable, rigid PU foams, because it gives the polyol with the highest hydroxyl functionality and the PU network with maximum crosslinking density. Zlatanic and coworkers studied the effect of hydroxyl number on the properties of PU. They observed that tensile strength and flexural modulus linearly increased with increment of hydroxyl number [57]. Furthermore, mechanical properties of rigid PU foams based on α-phellandrene polyols were better than the rigid PU foam based on commercial polyol.

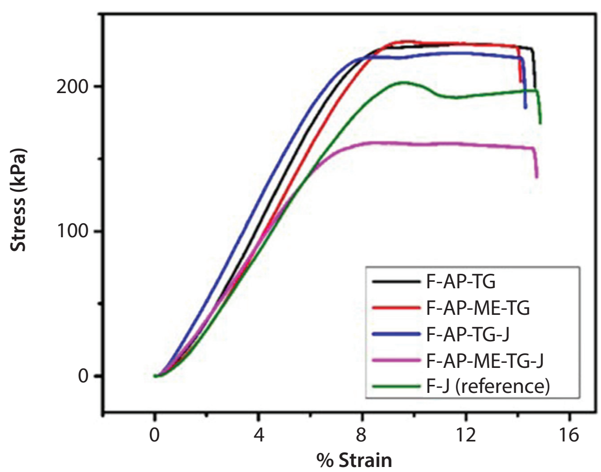


**Figure 3** Compressive strength plots for various rigid PU foams.

Cell structure and morphology of the PU foams were studied using the SEM images shown in Figure 4. The SEM images suggest that PU foams are mainly composed of closed cells. This observation is in good agreement with the measured closed-cell content of above 90% in Table 2. The PU foams prepared from AP-ME-TG polyol (Figure 4, F-AP-ME-TG and F-AP-ME-TG-J) consist of regularly shaped closed cells with stable pentagonal or hexagonal faces and uniform cell size distribution compared to the microstructure of AP-TG polyol-based PU foams (Figure 4, F-AP-TG and F-AP-TG-J).

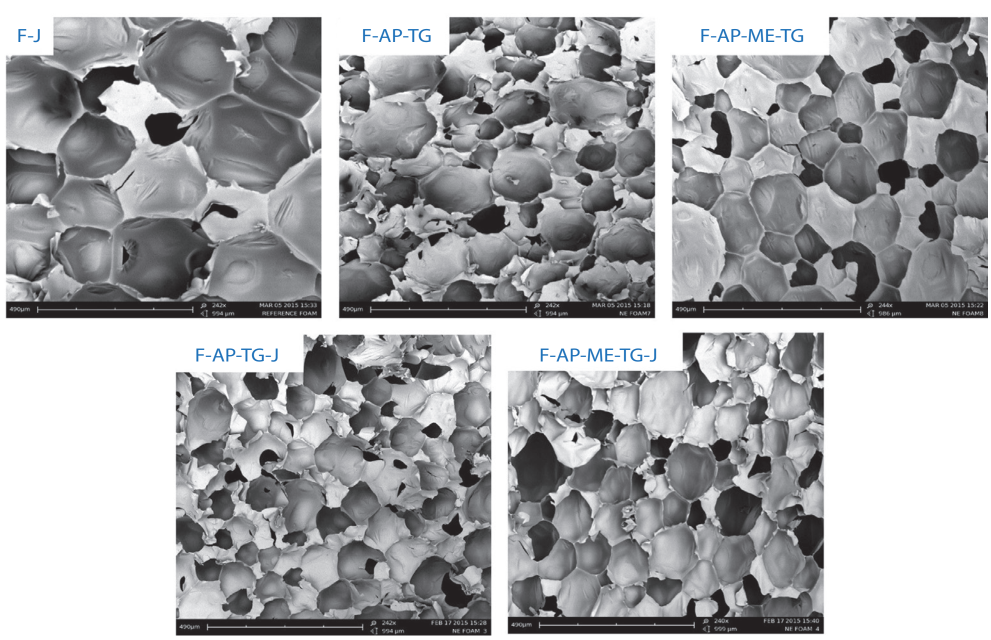


**Figure 4** SEM images of rigid PU foams.

 

Thermal stability of rigid PU foams was studied using thermogravimetric curves under nitrogen atmosphere and corresponding derivative (DTGA) curves (Figure 5). The DTGA curves revealed two distinct degradation phases. The first degradation phase is related to the dissociation of urethane bond in the temperature range of 230–370 °C; and is then followed by a second degradation phase around 500 °C, due to the C-C bond cleavage. The thermal stability of PU foams F-J, F-AP, and F-AP-ME-TG can be distinguished by the number of peaks and characteristics of the peaks associated with the first degradation phase. Three peaks were observed for PU foams based on AP-TG and AP-ME-TG polyols, albeit with different weight losses. Whereas, PU foam based on Jeffol SG-360 showed only two peaks for the

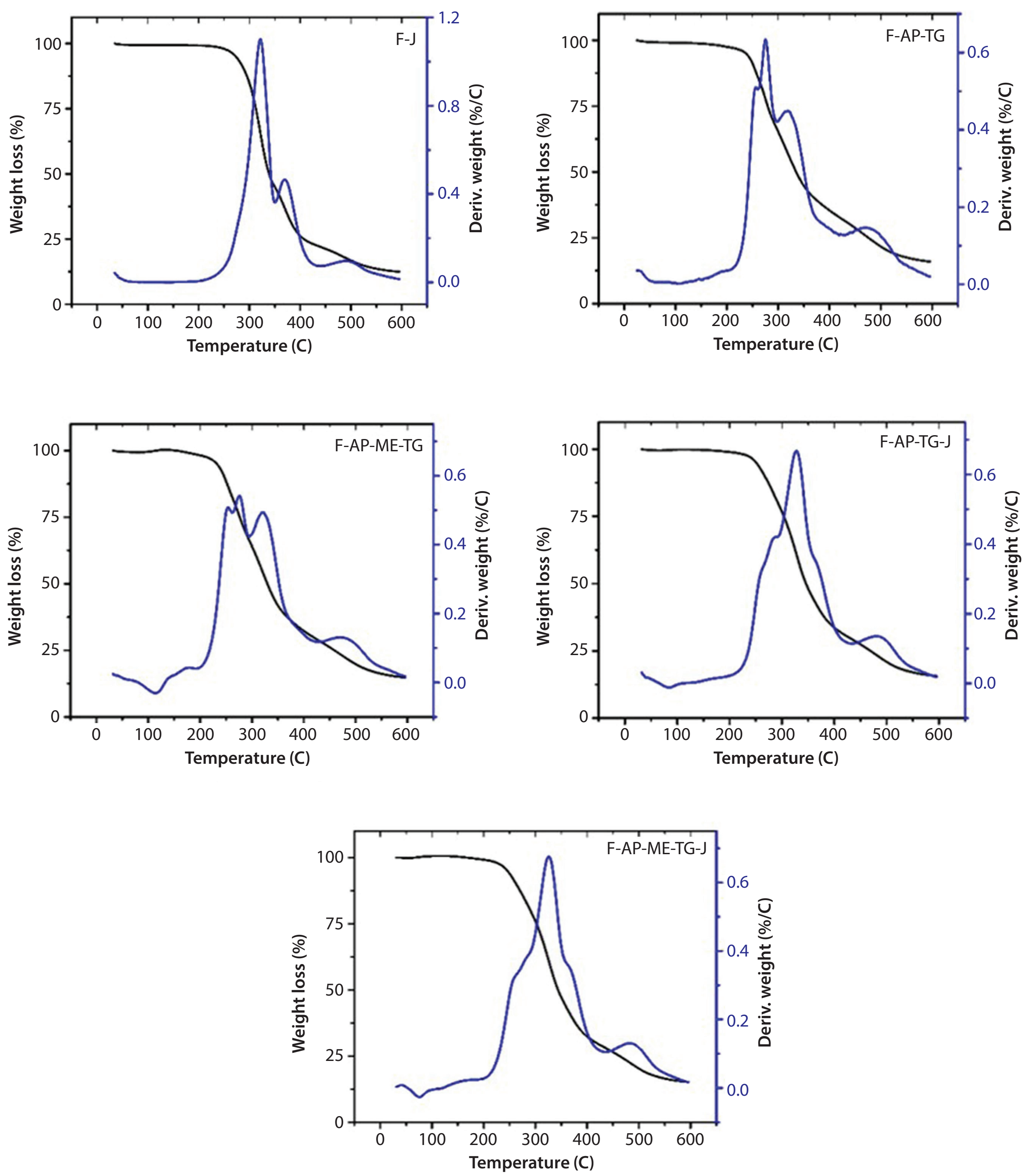


**Figure 5** TGA and DTGA curves of rigid PU foams.

  

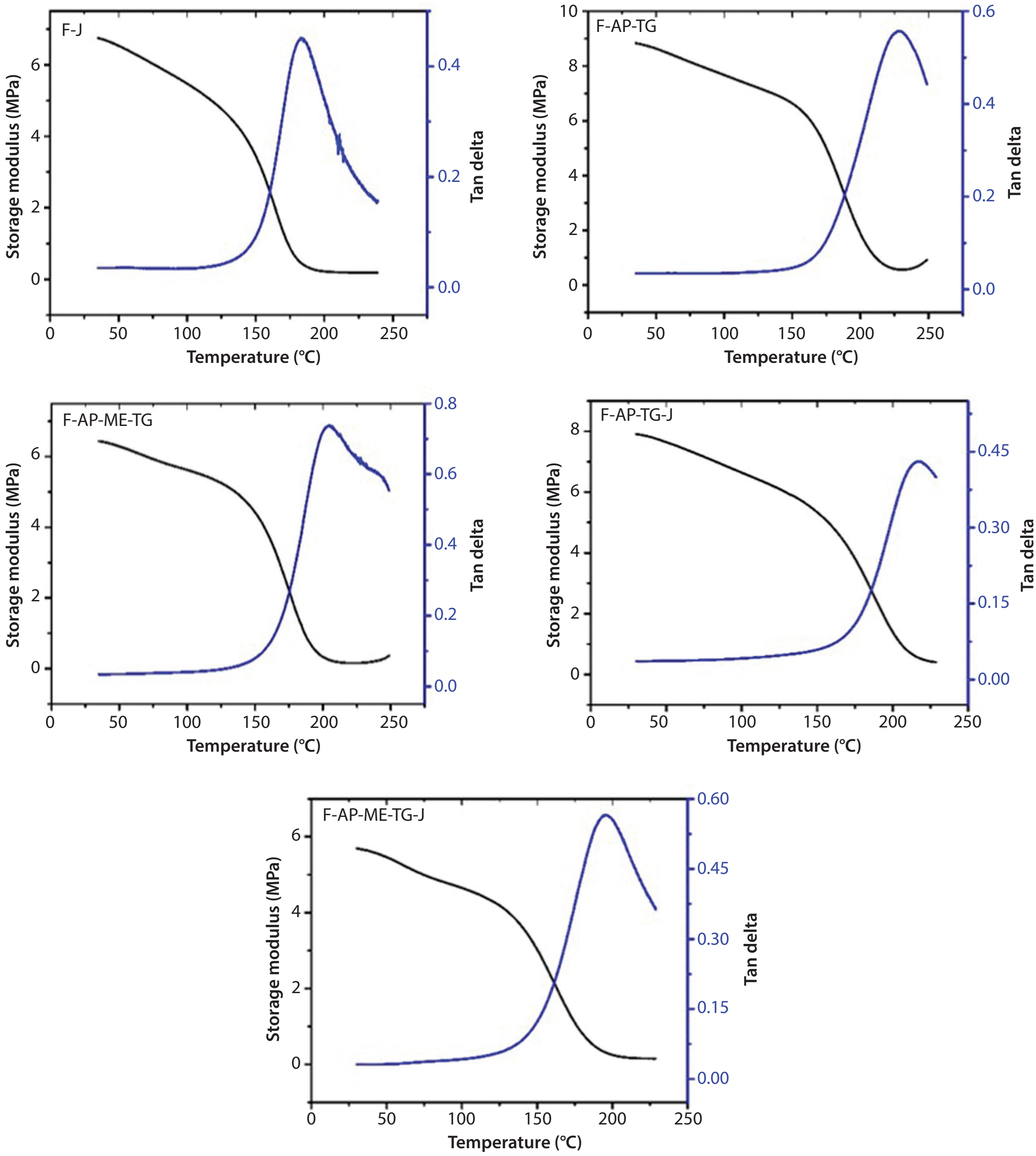


**Figure 6** Storage moduli and tan δ curves of rigid PU foams.

considered temperature range. These observations might be attributed to the difference in the bond energies imparted by the different polyol structures [58]. The highest onset degradation temperature of 266 °C was observed in rigid PU foam based on Jeffol SG-360, followed by onset degradation temperature of 234 and 228 °C for PU foams based on polyol AP-TG and AP-ME-TG, respectively. Onset degradation temperature of α-phellandrene polyol-based PU foams was increased to 238 and 235 °C by replacing 50% with commercial polyol, indicating improved thermal stability of blended rigid PU foams.

Dynamic mechanical analysis was utilized to determine the storage modulus and the glass transition temperature ($T_g$) of rigid PU foams. As seen in Figure 6, storage modulus gradually decreases until 150 °C, and then exhibits a sharp drop which is associated with the glass transition of the PU samples. The maximums of the tan δ curves in Figure 6 were reported as the $T_g$ and presented in Table 2. The $T_g$ of PU foams consisting of a single polyol follow the trend of hydroxyl number. The highest $T_g$ of 229 °C was obtained for the PU foam based on polyol AP-TG which also has the highest hydroxyl number, followed by the $T_g$ and hydroxyl number of polyol AP-ME-TG and Jeffol SG-360. This agrees with the previous reports, where they found that $T_g$ increases as the hydroxyl number increases due to the higher crosslinking density [56,59].

## 4 CONCLUSION

Two novel biobased polyols were successfully synthesized from the α-phellandrene via photoinitiated thiol-ene reaction. It was found that these polyols are suitable for the preparation of rigid PU foams by providing an alternative to the petrochemical-based monomers currently used for the synthesis of rigid PU foams. Rigid PU foams from biobased polyols exhibited superior sp. compressive strength and blending with commercial polyol improved the closed-cell content and thermal stability. We also showed that type and functionality of the polyols can affect the properties of the PU foams. Polyol with primary hydroxyl groups is highly reactive. Specific compressive strength and glass transition temperature increase with the increase of hydroxyl functionality. This opens a method to control the properties of PU foams by changing the thiol compound, especially for the PU foam-based structural application where high strength is desired. High mechanical properties, excellent closed-cell content, cell morphology, and density suggest that these foams are ideal for thermal insulation to conserve the energy required for heating and cooling in households as well as in industries.

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## REFERENCES

1. H. Somarathna, S. Raman, K. Badri, A. Mutalib, D. Mohotti, and S. Ravana, Quasi-static behavior of palm-based elastomeric polyurethane: For strengthening application of structures under impulsive loadings. *Polymers (Basel)* **8**(5), 202–222 (2016).
2. Z.S. Petrović and J. Ferguson, Polyurethane elastomers. *Prog. Polym. Sci.* **16**(5), 695–836 (1991).
3. M. Szycher, *Handbook of Polyurethanes*, CardioTech International Inc., Woburn, MA, US (1999).
4. E. Ciecierska, M. Jurczyk-Kowalska, P. Bazarnik, M. Kowalski, S. Krauze, and M. Lewandowska, The influence of carbon fillers on the thermal properties of polyurethane foam. *J. Therm. Anal. Calorim.* **123**(1), 283–291 (2016).
5. M. Thirumal, D. Khastgir, N.K. Singha, B.S. Manjunath, and Y.P. Naik, Effect of foam density on the properties of water blown rigid polyurethane foam. *J. Appl. Polym. Sci.* **108**(3), 1810–1817 (2008).
6. 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. Crops Prod.* **74**, 1–8 (2015).
7. W.J. Seo, H.C. Jung, J.C. Hyun, W.N. Kim, Y.-B. Lee, K.H. Choe, and S.-B. Kim, Mechanical, morphological, and thermal properties of rigid polyurethane foams blown by distilled water. *J. Appl. Polym. Sci.* **90**(1), 12–21 (2003).
8. W.J. Seo, J.H. Park, Y.T. Sung, D.H. Hwang, W.N. Kim, and H.S. Lee, Properties of water-blown rigid polyurethane foams with reactivity of raw materials. *J. Appl. Polym. Sci.* **93**(5), 2334–2342 (2004).
9. A. Prociak, J. Pielichowski, and T. Sterzynski, Thermal diffusivity of rigid polyurethane foams blown with different hydrocarbons. *Polym. Test.* **19**(6), 705–712 (2000).
10. H. Lim, S.H. Kim, and B.K. Kim, Effects of silicon surfactant in rigid polyurethane foams. *Express Polym. Lett.* **2**(3), 194–200 (2008).
11. T. Widya and C. Macosko, Nanoclay modified rigid polyurethane foam. *J. Macromol. Sci. Part B Phys.* **44**(6), 897–908 (2005).
12. L. Hojabri, X. Kong, and S.S. Narine, Fatty acid-derived diisocyanate and biobased polyurethane produced from vegetable oil: Synthesis, polymerization, and characterization. *Biomacromolecules* **10**(4), 884–891 (2009).
13. G. Çaylı and S. Küsefoğlu, Biobased polyisocyanates from plant oil triglycerides: Synthesis, polymerization, and characterization. *J. Appl. Polym. Sci.* **109**(5), 2948–2955 (2008).
14. N. Mahmood, Z. Yuan, J. Schmidt, and C. (Charles) Xu, Depolymerization of lignins and their applications for the preparation of polyols and rigid polyurethane foams: A review. *Renew. Sustain. Energy Rev.* **60**, 317–329 (2016).
15. P.K.S. Pillai, S. Li, L. Bouzidi, and S.S. Narine, Metathesized palm oil polyol for the preparation of improved bio-based rigid and flexible polyurethane foams. *Ind. Crops Prod.* **83**, 568–576 (2016).
16. G. Lligadas, J.C. Ronda, M. Galiá, and V. Cádiz, Plant oils as platform chemicals for polyurethane synthesis: Current state-of-the-art. *Biomacromolecules* **11**(11), 2825–2835 (2010).
17. 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**(1), 38–79 (2012).
18. J.-P.L. Dwan'isa, A.K. Mohanty, M. Misra, L.T. Drzal, and M. Kazemizadeh, Novel soy oil based polyurethane composites: Fabrication and dynamic mechanical properties evaluation. *J. Mater. Sci.* **39**(5), 1887–1890 (2004).

  

19. A. Guo, Y. Cho, and Z.S. Petrović, Structure and properties of halogenated and nonhalogenated soy-based polyols. *J. Polym. Sci. Part A Polym. Chem.* **38**(21), 3900–3910 (2000).
20. M. Ionescu, Z.S. Petrović, and X. Wan, Ethoxylated soybean polyols for polyurethanes. *J. Polym. Environ.* **18**(1), 1–7 (2010).
21. A. Guo, D. Demydov, W. Zhang, and Z.S. Petrović, Polyols and polyurethanes from hydroformylation of soybean oil. *J. Polym. Environ.* **10**(1/2), 49–52 (2002).
22. T.H. Khoe, F. Otey, E.N. Frankel, and J.C. Cowan, Polyurethane foams from hydroxymethylated fatty diethanolamides. *J. Am. Oil Chem. Soc.* **50**(8), 331–333 (1973).
23. C.K. Lyon, V.H. Garrett, and E.N. Frankel, Rigid urethane foams from hydroxymethylated castor oil, safflower oil, oleic safflower oil, and polyol esters of castor acids. *J. Am. Oil Chem. Soc.* **51**(8), 331–334 (1974).
24. P. Tran, D. Graiver, and R. Narayan, Ozone-mediated polyol synthesis from soybean oil. *J. Am. Oil Chem. Soc.* **82**(9), 653–659 (2005).
25. Z.S. Petrovic′, W. Zhang, and I. Javni, Structure and properties of polyurethanes prepared from triglyceride polyols by ozonolysis. *Biomacromolecules* **6**(2), 713–719 (2005).
26. S.D. Desai, J.V. Patel, and V.K. Sinha, Polyurethane adhesive system from biomaterial-based polyol for bonding wood. *Int. J. Adhes. Adhes.* **23**(5), 393–399 (2003).
27. Z.S. Petrović, I. Cvetković, D. Hong, X. Wan, W. Zhang, T. Abraham, and J. Malsam, Polyester polyols and polyurethanes from ricinoleic acid. *J. Appl. Polym. Sci.* **108**(2), 1184–1190 (2008).
28. R. Tanaka, S. Hirose, and H. Hatakeyama, Preparation and characterization of polyurethane foams using a palm oil-based polyol. *Bioresour. Technol.* **99**(9), 3810–3816 (2008).
29. G.B. Bantchev, J.A. Kenar, G. Biresaw, and M.G. Han, Free radical addition of butanethiol to vegetable oil double bonds. *J. Agric. Food Chem.* **57**(4), 1282–1290 (2009).
30. 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. Coatings Technol.* **166**(2), 141–152 (2003).
31. B.K. Sharma, A. Adhvaryu, and S.Z. Erhan, Synthesis of hydroxy thio-ether derivatives of vegetable oil. *J. Agric. Food Chem.* **54**(26), 9866–9872 (2006).
32. B.K. Sharma, A. Adhvaryu, and S.Z. Erhan, Friction and wear behavior of thioether hydroxy vegetable oil. *Tribol. Int.* **42**(2), 353–358 (2009).
33. M. Black, and J.W. Rawlins, Thiol-ene UV-curable coatings using vegetable oil macromonomers. *Eur. Polym. J.* **45**(5), 1433–1441 (2009).
34. 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**(6), 1646–1653 (2010).
35. J. Samuelsson, M. Jonsson, T. Brinck, and M. Johansson, Thiol-ene coupling reaction of fatty acid monomers. *J. Polym. Sci. Part A Polym. Chem.* **42**(24), 6346–6352 (2004).
36. C. Lluch, G. Lligadas, J.C. Ronda, M. Galià, and V. Cadiz, "Click" synthesis of fatty acid derivatives as fast-degrading polyanhydride precursors. *Macromol. Rapid Commun.* **32**(17), 1343–1351 (2011).
37. O. Türünç and M.A.R. Meier, Fatty acid derived monomers and related polymers via thiol-ene (click) additions. *Macromol. Rapid Commun.* **31**(20), 1822–1826 (2010).
38. O. Türünç, M.A.R. Meier, Thiol-ene vs. ADMET: A complementary approach to fatty acid-based biodegradable polymers. *Green Chem.* **13**(2), 314–320 (2011).
39. R.K. Gupta, M. Ionescu, D. Radojcic, X. Wan, and Z.S. Petrovic′, Novel renewable polyols based on limonene for rigid polyurethane foams. *J. Polym. Environ.* **22**(3), 304–309 (2014).
40. R.K. Gupta, M. Ionescu, X. Wan, D. Radojcic, and Z.S. Petrović, Synthesis of a novel limonene based Mannich polyol for rigid polyurethane foams. *J. Polym. Environ.* **23**(2), 261–268 (2015).
41. C.K. Ranaweera, M. Ionescu, N. Bilic, X. Wan, P.K. Kahol, and R.K. Gupta, Biobased polyols using thiol-ene chemistry for rigid polyurethane foams with enhanced flame-retardant properties. *J. Renew. Mater.* DOI: 10.7569/JRM.2017.634105 (2017).
42. B. Marongiu, A.P.S. Porcedda, R. Casu, and P. Pierucci, Chemical composition of the oil and supercritical $CO_2$ extract of *Schinus molle* L. *Flavour Fragr. J.* **19**(6), 554–558 (2004).
43. S.-S. Cheng, C.-G. Huang, Y.-J. Chen, J.-J. Yu, W.-J. Chen, and S.-T. Chang, Chemical compositions and larvicidal activities of leaf essential oils from two eucalyptus species. *Bioresour. Technol.* **100**(1), 452–456 (2009).
44. M. Gilles, J. Zhao, M. An, and S. Agboola, Chemical composition and antimicrobial properties of essential oils of three australian eucalyptus species. *Food Chem.* **119**(2), 731–737 (2010).
45. L. Jirovetz, G. Buchbauer, M.B. Ngassoum, and M. Geissler, Essential oils from Cameroon using solid-phase microextraction–gas chromatography, solid-phase microextraction–gas chromatography–mass spectrometry and olfactometry. *J. Chromatogr. A* **976**, 265–275 (2002).
46. A. Martins, L. Salgueiro, R. Vila, F. Tomi, S. Cañigueral, J. Casanova, A. Proença da Cunha, and T. Adzet, Essential oils from four piper species. *Phytochemistry* **49**(7), 2019–2023 (1998).
47. N. García-Jiménez, M.J. Pérez-Alonso, and A. Velasco-Negueruela, Chemical composition of fennel oil, *Foeniculum vulgare* Miller, from Spain. *J. Essent. Oil Res.* **12**, 159–162 (2000).
48. R. Piccaglia and M. Marotti, Characterization of some Italian types of wild fennel (*Foeniculum vulgare* Mill.). *J. Agric. Food Chem.* **49**(1), 239–244 (2001).
49. Z. Fleisher and A. Fleisher, Volatiles of leaves and flowers of *Ridolfia Segetum* L. Moris. Aromatic plants of the holy land and the Sinai. Part XII. *J. Essent. Oil Res.* **8**(2), 189–191 (1996).
50. B. Marongiu, A. Piras, S. Porcedda, E. Tuveri, and A. Maxia, Comparative analysis of the oil and supercritical $CO_2$ extract of *Ridolfia Segetum* (L.) Moris. *Nat. Prod. Res.* **21**(5), 412–417 (2007).
51. B. Faber, K. Bangert, and A. Mosandl, GC-IRMS and enantioselective analysis in biochemical studies in dill (*Anethum graveolens* L.). *Flavour Fragr. J.* **12**(5), 305–314 (1997).

52. L. Jirovetz, G. Buchbauer, A.S. Stoyanova, E.V. Georgiev, and S.T. Damianova, Composition, quality control, and antimicrobial activity of the essential oil of long-time stored dill (*Anethum graveolens* L.) seeds from Bulgaria. *J. Agric. Food Chem.* **51**(13), 3854–3857 (2003).
53. T. Jagella and W. Grosch, Flavour and off-Flavour Compounds of Black and White Pepper (*Piper nigrum* L. ). *Eur. Food Res. Technol.* **209**(1), 16–21 (1999).
54. R. Singh, V. Ahluwalia, P. Singh, N. Kumar, O. Prakash Sati, and N. Sati, Antifungal and phytotoxic activity of essential oil from root of *Senecio amplexicaulis* Kunth (Asteraceae) growing wild in high altitude-Himalayan region. *Nat. Prod. Res.* **30**(16), 1875–1879 (2016).
55. S.K.S. Al-Burtamani, M.O. Fatope, R.G. Marwah, A.K. Onifade, and S.H. Al-Saidi, Chemical composition, antibacterial and antifungal activities of the essential oil of *Haplophyllum tuberculatum* from Oman. *J. Ethnopharmacol.* **96**(1), 107–112 (2005).
56. V.B. Veronese, R.K. Menger, M.M. Forte, and C.L. de C. Petzhold, Rigid polyurethane foam based on modified vegetable oil. *J. Appl. Polym. Sci.* **120**(1), 530–537 (2011).
57. A. Zlatanic, 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. Part B Polym. Phys.* **42**, 809–819 (2004).
58. S.S. Narine, X. Kong, L. Bouzidi, and P. Sporns, Physical properties of polyurethanes produced from polyols from seed oils: II. Foams. *J. Am. Oil Chem. Soc.* **84**(1), 65–72 (2007).
59. T.W. Pechar, S. Sohn, G.L. Wilkes, S. Ghosh, C.E. Frazier, A. Fornof, and T.E. Long, Characterization and comparison of polyurethane networks prepared using soybean-based polyols with varying hydroxyl content and their blends with petroleum-based polyols. *J. Appl. Polym. Sci.* **101**, 1432–1443 (2006).

  