



## Sustainable Rigid Polyurethane Foam from Partial Substitution with Bio-Based Polyol

Qusay N. Hussein and Harith H. Al-Moameri\*



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<sup>a</sup> Materials Engineering Department, College of Engineering, Mustansiriyah University, Baghdad, Iraq.

### Abstract

The marketplace has shifted for over decades towards biobased polyols manufactured from renewable feedstock to improve the industry's sustainability. As a result, the desire for biobased polyols has risen fast, creating the significant potential to convert biomass into polyurethane polyols. Bio-based polyol from expired sunflower oil was utilized as a partial substituent to the commercial polyol for making rigid polyurethane foam. Polyester polyol was synthesized via trans-esterification of glycerol followed by polycondensation with phthalic anhydride. The mechanical properties of the resulting foam were performed to identify the impact of this replacement. The SEM image shows deterioration in the foam cells in the substitution of over 30%. The 50 percent bio-based substitute, on the other hand, causes the cells to deteriorate. Foam density increases due to the long chain of the bio-based polyol. The greater density of the bio-based polyol than the commercial polyol is responsible for the increased foam density. The compressive strength values increase with the rise of the bio-based content. This increase was attributed to the increase in polyurethane flexibility. The minimum thermal conductivity was obtained in the 30% bio-based polyol substitution. At this value, the foam shows regular foam compared to higher substitution ratios. The results present a sustainable and eco-friendly source for polyurethane production.

Keywords: Sustainable; rigid; foam; bio-based; polyols; polyurethane; petroleum-based.

### 1. Introduction

PU (Polyurethanes) are considered essential and versatile industrial materials with various qualities, including good wear resistance, high mechanical strength, outstanding abrasion, and chemical resistance[1, 2]. PUs could be made from multiple raw materials and processed in various approaches. Raw material examples are soybean oil, orange oil, castor oil, sunflower oil, cardanol oil, and starch. They could be made into products with the required qualities used in various applications. Since Bayer et al. have invented PUs in the 1930s, there has been a growing interest in synthesizing such materials[3]. Therefore, PUs are considered one of the most heavily investigated and widely utilized polymers today. Consumer goods like furniture and bedding, footwear, vehicle seating, industrial paint, thermal insulation in walls, medical devices and packaging all employ PUs to some extent[4-6]. With producing almost 18 million tons in 2016, PU materials account for nearly 5% of the worldwide polymer market[7]. PU is a common

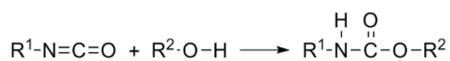
commodity polymer with high demand. Thermoplastics, elastomers, thermo-sets, and 1- or 2-component curable compositions are all members of the PU polymer family. Soft and rigid foams[8], solid rubbers[9], coatings and fibers[10], and sealants and adhesives are only a few of the uses for PUs[11]. A urethane group "NH(CO)O" is found in the base of the PUs. Yet, they might also include aromatic and aliphatic hydrocarbons, ethers, esters, urea, amides, and iso-cyanurate groups.[10, 12]

The isocyanate, which contains the isocyanate group "-N=C=O", and polyols having the hydroxyl group "-OH", are two crucial components in producing polyurethanes. Because an isocyanate group reacts with a hydroxyl group to form a urethane linkage, PUs are made through the polyol reaction with the isocyanate in the existence of the catalysts and other additive materials[13-15]. A generalized PU reaction has been exhibited in the following way.[16]

\*Corresponding author e-mail: [almoamerih@uomustansiriyah.edu.iq](mailto:almoamerih@uomustansiriyah.edu.iq); [almoamerih@gmail.com](mailto:almoamerih@gmail.com); (Harith H. Al-Moameri).

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Polyols containing hydroxyl groups are traditionally made into PUs by reacting with polyisocyanates. Petroleum-derived isocyanates and polyols are widely utilized in synthesizing PUs by related industries. Alternative pathways for PU synthesis are becoming increasingly important for reducing the dependence on finite petroleum resources and reducing the environmental effect. Factors like the steep rise in oil prices, concerns about global climate changes, and the worry of international crude oil exhaustion can all help accelerate the current trend toward the usage of renewable resources[17-19]. Other compelling advantages of employing renewable materials in the polymer sector include the abundant availability of bio-based materials at sensible prices, non-toxicity, and the potential to build industrially functional and scalable products without using petroleum-based monomers[17]. The newest emphasis on utilizing renewable materials from natural sources revitalized the interest in acknowledging the dedication to green chemistry concepts[1]

Vegetable oils are abundant in various nations and are renewable resources. Tri-glyceride molecules that have been made up of 3 fatty acids that have been joined by glycerol juncture make up the majority of such oils. Those fatty acids typically have “14 to 22” carbons and 0 to 3 double bonds for each fatty acid[20-22]. However, most vegetable oils lack hydroxyl groups required for PU reactions. Except for sunflower oil, most vegetable oils require chemical and physical modification for introducing hydroxyl groups. Sunflower oil was tested in several PU products because of its chemical structure’s natural presence of “hydroxyl groups” [23, 24]. the low cost[25].

Kirpluks et al. [26] developed high-quality rigid polyurethane (PU) foam thermal insulation products using second-generation bio-based feedstocks. It was found that esterification methods with various polyfunctional alcohols “such as diethylene glycol and trimethylolpropanes” were employed to make high-functionality bio-polyols, such as diethanolamine and triethanolamine. Foam compositions for thermal insulation made of stiff polyurethane foam were created by mixing four high-function biopolyols with a tall oil esterified biopolyol. The bio-polyol and physical blowing agent: c-pentane content was enhanced by response surface modeling. The biobased rigid PU foam compositions outperformed their

petrochemical counterparts in terms of thermal insulation.

EPUU elastomers with an isocyanate index of 1.07 were synthesized by Mizera et al. [26] using polyols derived from rapeseed oil at a 20 or 50 weight percent concentration. Isopropanol (RO) and diethylene glycol were used to generate the bio-polyols. EPUUs manufactured from poly(ethylene adipate) were the subject of this investigation to examine how biopolyols influenced their thermal and mechanical properties. According to the biopolyol used, the number of hydrogen bonding and degree of phase separation in EPUUs differed. When bio-polyol concentration is increased, hydrogen bonds between stiff materials are reduced.

The present study used locally available expired sunflower cooking oil (Al-Dar) to produce bio-polyol. The current research novelty is in using expired sunflower oil. The bio-based polyol was used to substitute the commercial petroleum oil for making polyurethane rigid polyurethane foam. The bio-based polyol was used to substitute the commercial polyol by 10%, 20%, 30%, 40%, and 50%. Several tests were conducted to investigate the efficiency of the produced foam.

## 2. Experimental procedure

### 2.1. Materials

Sunflower oil that had been bleached, refined, and deodorized was provided from a local market. General Drug House (P) Ltd, India, provided the glycerol (99.5%, analytical grade) and the phthalic anhydride (98%, analytical grade). Sigma Aldrich provided the calcium oxide (90%). Polyurethane formulas included Dow Chemical’s REANIN1801OC and Huntsman Company’s polymeric Methylene diphenyl diisocyanate (PMDI). Experiments were carried out using an isocyanate index of 1.1. Data on polyol and PMDI characteristics may be found in Table 1. “Polyethermodified polysiloxane” copolymer was the surfactant utilized. One percent “Triethylene diamine” and “Bis(2-dimethylaminoethyl) ether” in dipropylene glycol were added as catalysts to di-propylene glycol as a solution. All studies used the same quantity of surfactants and catalysts.

**Table 1.**

PMDI and polyol characteristics.

Property	REANIN17 01OC	PMDI
Density (gcm <sup>-3</sup> )	1.07-1.10	1.203
Avg. MWt	731	345
Polymer functionality	4.51	2.71
OH# (mgKOH.g <sup>-1</sup> )	105-210	-
Water content	1.21%	-
Equivt. wt.	165	135
Viscosity, mPas@25°C)	250-450	165-235
NCO content (wt %)	-	32.2
Vapor Pressure(mmHg@25°C)	-	Less than 10
Cp (gcal.g <sup>-1</sup> @ 25°C)	-	0.4

## 2.2. Polyol preparation

for producing monoacylglycerides, glycerol transesterification regarding sunflower oil has been conducted in a 1000mL flask equipped with the condenser, magnetic stirrer, thermometer with omega controller, and heater. The reactor was charged with 99.50 g of glycerol, 300 g of sunflower oil, and 0.20 g of calcium oxide as catalysts. The mixture was heated to 220°C in a closed Parr reactor with steady mechanical stirring for two hours. Phthalic anhydride has been added to the monoglyceride mix at 10 to 20% to make the polyester polyol. The polycondensation reaction was conducted in a round bottom 1000mL flask with the condenser, thermometer, and magnetic stirrer. Also, reaction time was changed between 3 and 5 hours, while the reaction temperature was varied between 130°C and 180°C. Figure 1 shows a suggested reaction approach for forming polyester polyol from the CMG and divalent acid. As a design of the experiment, a central composite design was used, with temperature, acid loading, and reaction time as variables.

**Figure 1.** polyol preparation

## 2.3. Foaming process

The petroleum polyol, vegetable oil-based polyol made from Expired Sun Flower oil (bio polyol), surfactant, catalysts, and blowing agent (i.e. B-side materials) have been added through the weighing in various proportions of 0%, 10%, 20%, 30%, 40%, and 50% into 500mL disposable plastic cup and mixing with petroleum polyol at 2000 rpm for 10 seconds. For 120 seconds, the mix has been left to degas. Isocyanate (A-side material) was quickly added in a 1:1 ratio, and stirring was continued at 2000 rpm for another 5 seconds. The mixtures were poured into a wooden mold of 11.40x11.40x21.60 cm, lined with aluminium foil. A thermometer connected to a data logger monitored and recorded the reaction temperature. The foaming procedures are depicted in Figure 2.

**Figure 2.** Experimental setup and foam samples.

The thermos scientific Nicolet<sup>TM</sup> iS50 FT-IR was used to identify the functional groups in the bio-based polyol. At a scan rate of 32/s, a wavenumber range of 4,000 to 400cm<sup>-1</sup> was scanned. Scanning electron microscopy “FEI Quanta 600” was used to investigate the morphology of foam cells in reinforced stiff polyurethane foams. Using a razor blade and conductive carbon tape, we cut the foams into 10x10x1mm slices. At an 80x magnification, the samples were imaged under the influence of strong acceleration voltages (up to 5 kV). The cellular foam structure was discovered to run perpendicular to the free-rise direction..

All samples' foam density was measured by cutting the foams into regular shapes and measuring the weight and volume. The compressive strength of the PU foams has been determined based on ASTM D16216 (equivalent to ISO 8447). An ELE Digital Elect 2000 devise was used for measuring the compressive strength of foam samples. The PU foam compressive strength has been determined based on ASTM D16216 (equivalent to ISO 8447). An ELE Digital Elect 2000 devise was used for measuring the

compressive strength of the foam samples. QTM-500 determined the thermal conductivity according to ASTM C1113-99. Foam samples of 10x10x10 cm were tested. The probe the stick sensor on the specimen surface and press the start key. The results of measurements will appear based on the characteristics of the material.

### 3. Results and discussion

The broad absorption bands at  $3340\text{ cm}^{-1}$  in the FTIR spectra of polyester biobased polyol shown in Figure 3 suggest the existence of terminal hydroxyl groups. The presence of phthalic esters in the oil-based polyol is confirmed by a wide band at  $1281\text{ cm}^{-1}$ , corresponding to C=O stretching [27, 28]. The methylene and methyl bands were found at  $2850\text{--}2920\text{ cm}^{-1}$ . In addition, the ester carbonyl bands were discovered in the  $1720\text{ cm}^{-1}$  range. The existence of hydroxyl and ester carbonyl absorption bands in the oil-based polyol's FT-IR spectra confirms the production of the hydroxyl group. [29, 30]

SEM images were taken to the rigid polyurethane foams prepared to foam the substitution of the commercial polyol with bio-based polyol. The SEM

images present the cell size, orientation, and shape of the foam cells. The SEM images were taken to the control, 30%, and 40% bio-based content, as shown in Figure 4. SEM image of the control shows big cell size with deterioration compared to the foams after adding the bio-based polyol. The 30% bio-based substitution show uniform cell with regular size. However, the 50% bio-based substitution show deterioration in the cells. This deterioration is attributed to the lower functional group of the bio-based polyol.

The impact of bio-based content on the reaction temperature is illustrated in Figure 5. The control's maximum reaction temperature is achieved (0% bio-based polyol). In addition, it shows a faster reaction rate at the earlier stages of the reaction. The 10% bio-based content show close results of reaction temperature to the control. The increase of the bio-based polyol content decreases the reaction rate and the maximum reaction temperature. The 40% and 50% bio-based content show a slower reaction rate and maximal temperature of the reaction due to the mass transfer limitation due to the higher viscosity of the bio-based polyol.

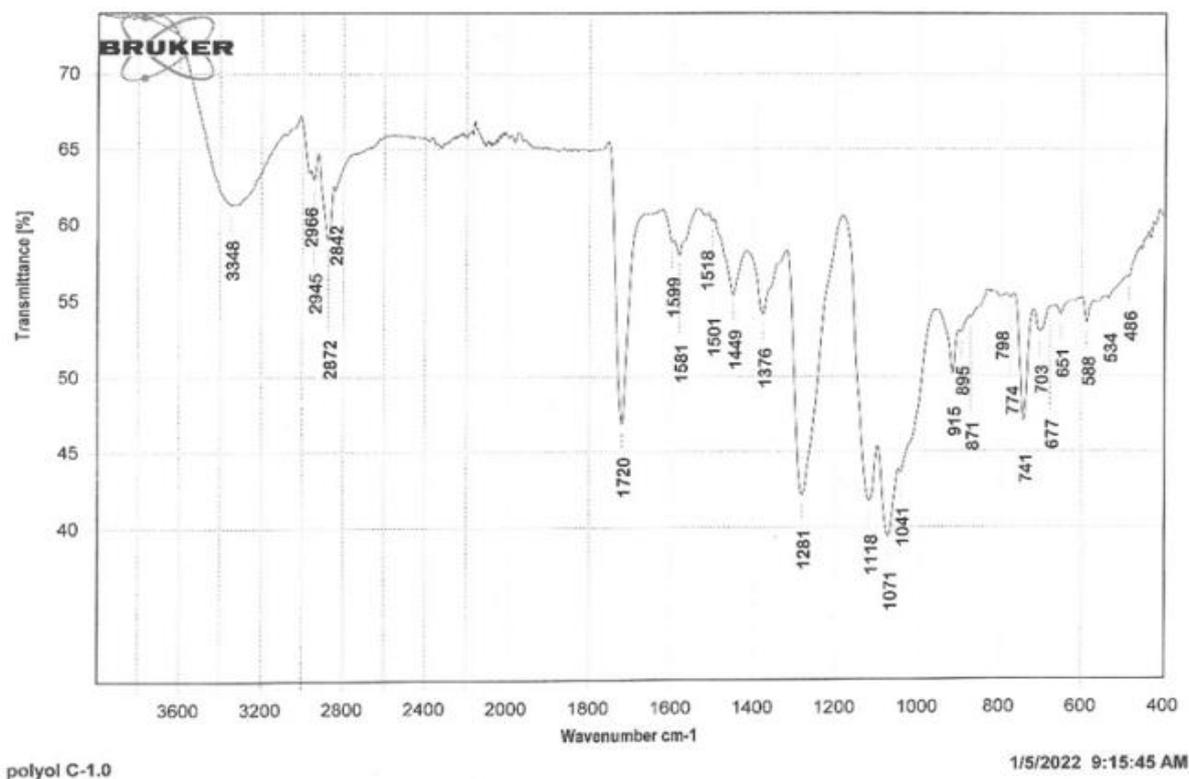


Figure 3. FTIR results of the bio-based polyol.

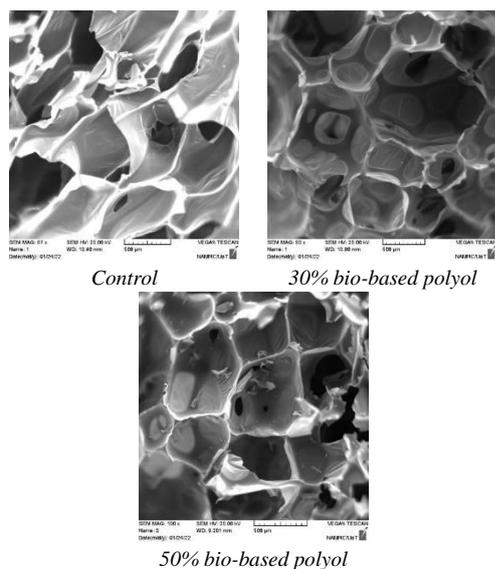


Figure 4. SEM images of foam samples.

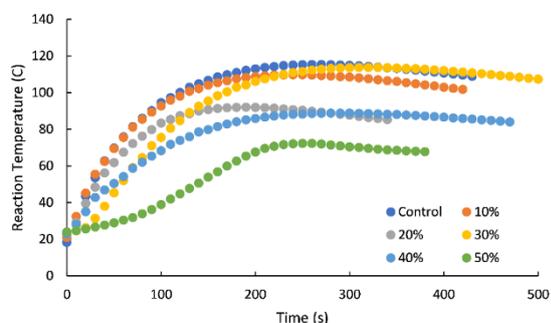


Figure 5. Impact of bio-based content on the rigid polyurethane reaction temperature.

Form density was measured for all samples, as shown in Figure 6. The volume and weight of plastics that make up foam matrix and gases that have been trapped in foam cells determine the density of the plastic foam. As indicated, the bio-based polyol replaced the commercial polyol in 0 to 50 %, resulting in a considerable change in foam density. The results show that the density of the rigid polyurethane foam increases by increasing the bio-based polyol percentage. This increase in foam density is attributed to the higher density of the bio-based polyol than the commercial polyol.

Figure 7 exhibits the compressive strength of PU foams made from different contents of the bio-based polyols. The results show that increasing the bio-based content increases the compressive strength of the resultant rigid PU foam. The increase in the compressive strength of the low bio-based content has been attributed to more regular foam cells that withstand the compression load. Beyond the 30% bio-based content, the foam is becoming more flexible due

to the long chains of the bio-based oil, which increases the compression load.

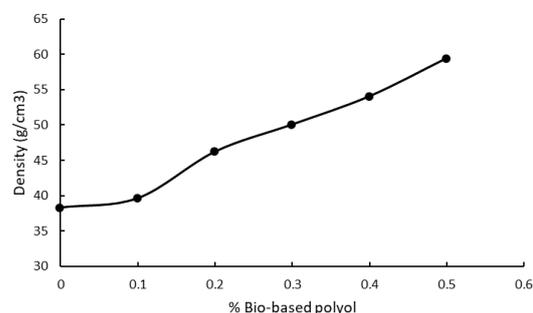


Figure 6. Impact of bio-based content on rigid polyurethane density.

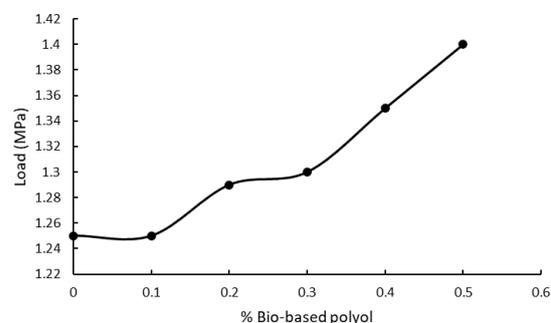


Figure 7. Impact of bio-based content on compressive strength of the rigid polyurethane.

Figure 8 also exhibits the impact of replacing REANIN1801OC with 0 to 50% of the bio-based polyol on the thermal conductivity of rigid PU foams. The results show that increasing the bio-based content decreases the thermal conductivity of foams up to 30% substitution. This decrease is attributed to the uniform foam cells. When the bio-based polyol content exceeded 30%, the solid structure of the PU may have weakened to the point where foam cells were more open, trapping fewer gases inside foams. This rise corresponds to the foams' SEM images.

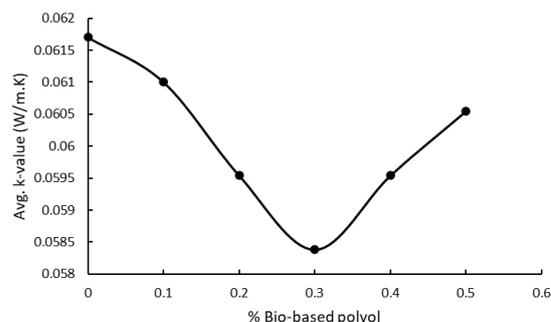


Figure 8. Impact of bio-based content on thermal conductivity of rigid polyurethane.

#### 4. Conclusions

The tendency into using bioresources to make polymers has prompted manufacturers to develop novel monomers. Polyester polyol was effectively synthesized from the expired sunflower oil by glycerol transesterification followed by a subsequent polycondensation reaction with phthalic anhydride. The reacting isocyanates were used to make polyurethane (PU) foams with varied substitutions of the commercial polyol with bio-based polyol. The commercial polyol was substituted with 10%, 20%, 30%, 40%, and 50% vegetable bio-based polyols synthesized from expired sunflower oil. FTIR identified the presence of the alcohol group in the synthesized bio-based polyol. The thermal and mechanical properties of the resulting foam were measured for the resulting rigid polyurethane foam. Thermal conductivity, density, SEM, reaction temperature, and compressive strength were performed. The results showed that increasing the bio-based polyol increases the density and the compressive strength of the resulting foam. However, the 30% bio-based substitution provides the best thermal insulation. The SEM images verified these results.

#### 5. Nomenclature

EPUU	ureaurethane elastomers
MK	diethylene glycol
PU <sub>s</sub>	Polyurethanes
RO	isopropanol

#### 6. Acknowledgement

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