



Research article

Use of different epoxide ring openers and volumes of epoxidized palm oil to modify palm oil into biopolyol

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Abstract

Importance of the work: Epoxide ring openers and the volume of epoxidized palm oil are the most influential factors on the hydroxyl number.

Objectives: To investigate the effects of three types of epoxide ring opener and varying volumes of epoxidized palm oil on the production of biopolyol.

Materials & Methods: This study used 10 mL, 20 mL or 30 mL of epoxidized palm oil reacted with 30 mL of different epoxide ring openers (ethylene glycol, propylene glycol and distilled water) and added 1% sulfuric acid catalyst at 50°C for 1 hr. Biopolyol was characterized based on the hydroxyl number and Fourier-transform infrared spectroscopy (FTIR).

Results: The optimum results for biopolyol as raw material for flexible polyurethane foam were a mixture of 10 mL of epoxidized palm oil with 30 mL of ethylene glycol, based on mean $\pm$ SD values for: hydroxyl number (99.37 ± 7.27 mg KOH/g), acid number (1.19 ± 0.1 mg KOH/g), viscosity at 30°C (46.10 ± 6.45 cP) and density at 30°C (0.906 ± 0.009 g/mL) and a clear yellow color. A wave number of 3332.05/cm in the FTIR represented the alcohol group (hydroxyl) in the polyol sample.

Main finding: Ethylene glycol successfully produced biopolyol according to the specified criteria as a suitable raw material for flexible polyurethane foam with a hydroxyl number of less than 100 mg KOH/g and an acid number of less than 2 mg KOH/g.

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Introduction

The primary raw material for polyurethane is petroleum polyol (Amezúa-Arranz et al., 2023). Petroleum is a non-renewable natural resource; consequently, its availability is decreasing daily. Meanwhile, the human demand for polyurethane products is increasing. Every day, various polyurethane products are used, including in heating systems, cars, furniture, bedding, refrigerators, textile additives and building insulation (Dutta, 2018; Furtwengler and Avérous, 2018). Thus, it has become increasingly attractive to study methods of obtaining renewable and more environmental-friendly polyols derived from natural resources to replace petroleum polyols (Huo et al., 2019; Ghasemlou et al., 2019; Kurańska et al., 2020).

Biopolyol can be sourced from starches, agricultural wastes, sawdust and vegetable oils (Dodangeh et al., 2020). Polyols derived from vegetable oils can make elastomers and flexible foams, though the latter can only be produced from polyols with a hydroxyl number of less than 100 mg KOH/g (Dutta, 2018). Palm oil is a vegetable oil with potential as a raw material for polyols (Prociak et al., 2018). The advantages of palm oil are its abundant availability, low price and its content of unsaturated fatty acids with double bonds that can be converted to biopolyols through epoxidation reactions and using epoxide ring openers (Gurgel et al., 2021). However, the weakness of palm oil polyols is that they have more secondary OH groups than primary OH groups, making them less reactive with isocyanates to form flexible polyurethane foam (Prociak et al., 2018). Palm oil polyols have a hydroxyl number exceeding 100 mg KOH/g. Several researchers have produced palm oil polyols with high hydroxyl numbers, such as 102 mg KOH/g and 128 mg KOH/g (Prociak et al., 2018), 155 mg KOH/g (Pillai et al., 2016), 115.2 mg KOH/g (Ng et al., 2017), 148.7–223.9 mg KOH/g (Hoang and Kim, 2015) and 150–156 mgKOH/g (Polaczek et al., 2021). The hydroxyl number of polyols exceeding 100 mg KOH/g is only suitable for producing semi-rigid and rigid polyurethane foams (Peyrton and Avérous, 2021). However, the epoxide ring openers and epoxidized palm oil volume affect the hydroxyl number and the primary OH group content in biopolyol (Petrovic et al., 2003). An important study was conducted to obtain palm oil polyols with a hydroxyl number of less than 100 mg KOH/g and more primary OH groups. Fig. 1 shows the synthesis of the palm oil polyols with epoxide ring openers from DEG and water.

Based on the description above, the present study was conducted to examine the synergistic effects of epoxide ring openers and the volume of epoxidized palm oil in generating polyols with hydroxyl numbers less than 100 mg KOH/g.

Materials and Methods

The materials used in the research were commercial palm oil brand Sari Murni, H₂O₂ 50% (Bratachem), acetic acid 100% (Merck), sulfuric acid 98% (Smart Lab), ethylene glycol (Bratachem), propylene glycol (Bratachem), sodium bicarbonate (Merck) and HBr (Merck), KOH (Merck). The research design used was exploratory and consisted of two treatment factors and was repeated three times. The first factor was the type of epoxide ring opener (distilled water, ethylene glycol, propylene glycol). The second factor was the volume of epoxidized palm oil (10 mL, 20 mL, 30 mL). The test result data were averaged and then presented in tables and graphs.

Synthesis of epoxidized palm oil

The synthesis was based on the method of Neswati and Nazir (2021). Palm oil (200 mL) was heated at 50–55°C with 47% acetic acid (0.3 mol) in a 250 mL necked flask equipped with a stirrer and then concentrated sulfuric acid catalyst (98%) amounting to 1% of the total oil amount was added with continual stirring at 200 revolutions per minute.

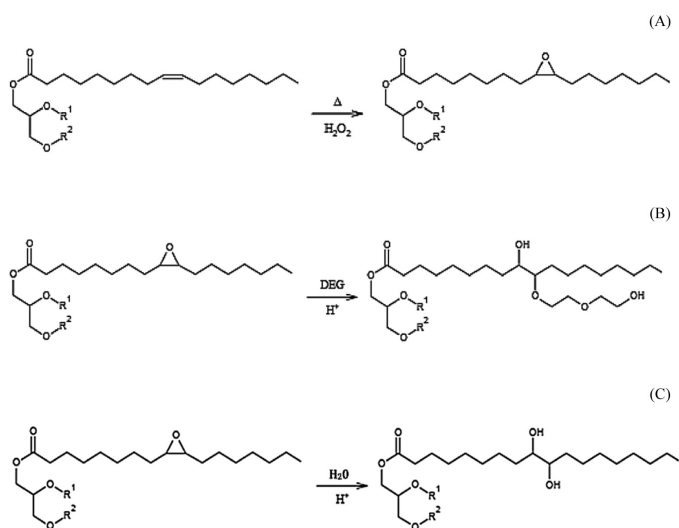


Fig. 1 (A) Oxidation reaction of palm oil with hydrogen peroxide; (B) epoxide ring opening reaction of epoxidized palm oil using diethylene glycol (DEG); (C) epoxide ring opening reaction of epoxidized palm oil using water (Prociak et al., 2018)

Then, 50% hydrogen peroxide (H_2O_2 , diluted) of 1.7 mol was added gradually (while stirring and maintaining the temperature at 50–55°C). After adding the H_2O_2 , the temperature was held at 50°C for 1 hr. The epoxidized oil was separated using a separating funnel; then, a saturated sodium bicarbonate solution was added until the pH was neutral, followed by washing twice with hot distilled water. Then, the washing water was separated using a separatory funnel. Sodium sulfate solution was added to absorb the remaining water and then filtered. The epoxidized palm oil obtained was slightly cloudy yellow.

Epoxide ring opening reaction

The epoxide ring opening reaction followed Abdullah (2012). Epoxidized palm oil was reacted with the epoxide ring openers; then, a sulfuric acid catalyst (1% of the total reactants) was added at 50°C for 1 hr. After the reaction had been stopped, the product was cooled to room temperature and hexane was added, with a reaction-to-product ratio of 1:1, after which NaHCO_3 was added dropwise until the pH was neutral. Then, the solution was washed with distilled water to remove the remaining epoxide ring openers, catalysts and epoxy oil that had not reacted. Next, the mixture was poured into a separating funnel, where the top layer was an organic layer containing a yellow-colored product, while the bottom layer was a clear residue of the reactants (ring-opening compounds). Finally, a rotary vacuum evaporator purified the top layer (organic layer) at 80°C to remove hexane (solvent).

Hydroxyl number

The hydroxyl number analysis procedure followed ASTM D4274-99 (American Society for Testing and Material, 2000). The polyol sample of 5.61 g was dissolved in the esterification reagent for 15 min at 98°C. Then, distilled water was added while thoroughly stirring. After adding phenolphthalein indicator, the solution was titrated with 0.5 N sodium hydroxide until it turned pink. The hydroxyl number (milligrams of KOH per gram) was calculated using Equation 1:

$$\text{Hydroxyl number} = \frac{(X - Y) \times N \times 56.1}{\text{Sample}} \quad (1)$$

where X is the NaOH solution needed to titrate the sample, Y is the NaOH solution needed to titrate without sample (= 98 mL), N is the normality of the NaOH solution (= 0.5 N) and the sample weight is in grams.

Acid number

The acid number analysis procedure was carried out based on ASTM D974-14^{e2} (American Society for Testing and Material, 2016). Samples were diluted in 100 mL of isopropyl alcohol, toluene and 0.5 mL of phenolphthalein solution. Next, the samples were titrated with 0.1 M KOH solution until the orange color changed to green. The acid number (milligrams of KOH per gram) was calculated using Equation 2:

$$\text{Acid number} = \frac{(X - Y) M \times 56.1}{\text{Sample}} \quad (2)$$

where X is the KOH solution needed to titrate the sample, Y is the KOH solution needed to titrate without sample (98 mL), M is the molarity of the KOH solution (0.1 M) and the sample weight is in grams.

Statistical analysis

The data were analyzed using two-way analysis of variance and Duncan's post hoc test in the IBM Statistical Package for the Social Sciences (SPSS) software version 16 (SPSS Inc.; Chicago, IL, USA). All tests were considered significant at $p < 0.05$.

Results and Discussion

Epoxide is a cyclic ether with a three-membered ring. The three-membered ring has a very high strain in the epoxide molecule, which makes the epoxide more reactive to nucleophilic substitution than other ethers. The acid catalyst aids the opening of the epoxide ring by providing an OH group on the carbon atom that undergoes nucleophilic attack. This catalyst is essential, especially if the nucleophile is weak, such as water or alcohol (Marcovich et al., 2017). The selection of a suitable nucleophilic reagent greatly affects the functionality of the polyol and the type of polyurethane product produced.

Hydroxyl number

The hydroxyl number (in milligrams of KOH per gram) indicates the weight in milligrams of potassium hydroxide required to neutralize the free acetic acid produced during the acetylation of the hydroxyl group (Alagi et al., 2016). The hydroxyl group of the biopolyol is influenced by the type of epoxide ring-opening compound used. Water is the cheapest epoxide ring-opening compound and has two secondary

hydroxyl groups. Epoxide ring-opening compounds, with secondary and primary hydroxyl groups, have two or more hydroxyl groups, such as ethylene glycol, diethylene glycol or 1,2 propanediol (Kurańska et al., 2020). Secondary hydroxyl groups form soft segments in flexible polyurethane foam (Coman et al., 2021). Therefore, different epoxide ring-opening agents will produce polyols with varying hydroxyl numbers (Prociak et al., 2018).

The analysis of variance shows that the volumes of epoxidized palm oil and types of epoxide ring opener have no significant effects on the hydroxyl number ($p = 0.8006$ and 0.9632 , respectively) (Fig. 2). Furthermore, the interaction between these two factors also shows no significant effect ($p = 0.8379$). It's worth noting that polyurethane flexible foam raw material requires a biopolyol hydroxyl number of less than 100 mg KOH/g . While statistically, the type of epoxide ring opener and the volume of epoxidized palm oil are not significantly related with the hydroxyl number of palm oil polyols, variation in hydroxyl number values do impact the characteristics of the resulting polyurethane foam.

Ethylene glycol is a diol used in the polymer industry, with 20 mL epoxidized palm oil with ethylene glycol producing the polyol with the highest hydroxyl number (136.10 mg KOH/g) compared to 10 mL epoxidized palm oil (99.37 mg KOH/g) and 30 mL (90.54 mg KOH/g). Using 10 mL and 30 mL epoxidized palm oil produced polyols with hydroxyl numbers less than 100 mg KOH/g . The petrochemical polyols that synthesize flexible polyurethane foam have hydroxyl numbers of 28–56 mg KOH/g (Chan et al., 2021).

The 30 mL epoxidized palm oil mixture with an ethylene glycol ring opener produced a polyol with a lower hydroxyl number (90.54 mg KOH/g) than with 10 mL and 20 mL but with a higher viscosity and a lower acid number. The higher the volume of epoxidized oil in the system, the greater the free fatty acids. According to Borowicz et al. (2020), epoxidized oil contains free fatty acids, which could undergo side reactions with ring openers, resulting in low hydroxyl numbers of polyols. The low hydroxyl number was caused by an oligomerization reaction increasing the unreacted diethylene glycol content and viscosity (Polaczek et al., 2022). High viscosity will negatively affect the polyurethane foam formation process. Furthermore, unreacted glycol would separate from the biopolyol and form an immiscible phase (Borowicz et al., 2020). The opening of the epoxy/epoxide ring caused side reactions in the ethylene glycol. Ionescu (2016) explained that systemic side reactions could react with free fatty acids, deactivating the free OH group and producing a low hydroxyl number in a biopolyol. In addition, the side reaction reduced the number of bio-polyol

acids, which reflected the final product's free fatty acid content. Furthermore, Paciorek-Sadowska et al. (2018) stated that the oligomerization of bio-polyol molecules was a side reaction that affected the efficiency of the epoxide ring opening reaction (a glycol chain inserted into the biopolyol molecule). This side reaction produced a dimer of two fat molecules linked by a glycol chain or a fat molecule cyclization product.

According to Petrovic et al. (2000), it was advisable to add alcohol in excess at the hydroxylation stage (epoxide ring opening reaction) to prevent polymerization and the formation of products with a higher viscosity. This statement was consistent with the current results that ring-opening compounds in the 10 mL of epoxidized palm oil produced polyols with higher hydroxyl numbers and lower viscosity.

Propylene glycol is one of the alcohols classified as a chiral diol and used as a polymeric material with very low toxicity (Kaur et al., 2024). The mixture of 20 mL of epoxidized palm oil with propylene glycol produced a polyol with a low hydroxyl number (81.64 mg KOH/g) and a higher viscosity (Fig. 2), because propylene glycol not only played a role in adding OH groups to the epoxide ring opening reaction but could also cause side reactions. The epoxide ring opening reaction can occur with molecules other than propylene glycols (Polaczek et al., 2021). According to Allauddin et al. (2016), the formation of products from oligomerization side reactions was obtained from newly formed OH groups and existing epoxy groups, resulting in a biopolyol with a low hydroxyl number and increased viscosity. These reactions increased the product's molecular weight and thickness, while decreasing the hydroxyl number of the biopolyol. The mixture with 30 mL of epoxidized palm oil and propylene glycol yielded a polyol with a higher hydroxyl number (126.16 mg KOH/g) and a lower viscosity.

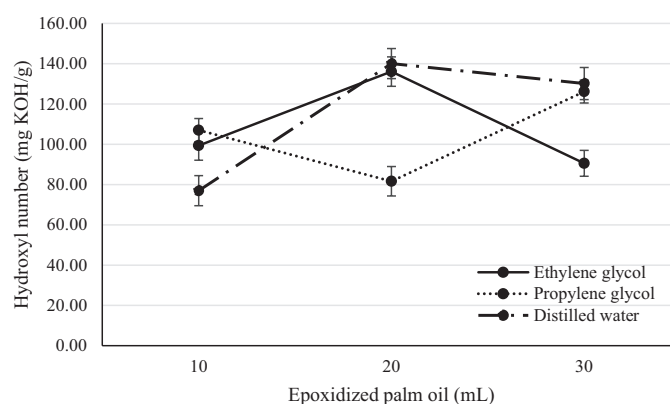


Fig. 2 Hydroxyl number of biopolyol resulting from various types of epoxide ring opener and different volume of epoxidized palm oil, where values are shown as mean $\pm$ SD ($n = 9$), and error bars represent SD.

According to Petrovic et al. (2000), distilled water is essential in the epoxide ring-opening reaction. The distilled water reacts with the epoxide ring of the epoxidized palm oil to form two hydroxyl groups per epoxy group (epoxide) to increase the hydroxyl content of vegetable oil-based polyols. In the current study, 10 mL of epoxidized palm oil with distilled water produced a polyol with the lowest hydroxyl number (76.96 mg KOH/g) and the highest viscosity (102.07 cP). The distilled water volume, at three times more than the amount of epoxidized oil, caused hydrolysis side reactions that produced free fatty acids. The high content of free fatty acids could react with the molecules making up the system so that the free OH groups became deactivated, causing the hydroxyl number of the biopolyol to be low (Ionescu, 2016). However, 20 mL of epoxidized palm oil with distilled water produced a polyol with the highest hydroxyl number (140.04 mg KOH/g). The ability of distilled water to add OH groups to the epoxide ring of epoxidized oil was greater than with propylene glycol and ethylene glycol. Epoxidized palm oil exceeding 20 mL produced a biopolyol with a lower hydroxyl number. The weakness of the epoxide ring-opening compound in the water produced a biopolyol that only had secondary hydroxyl groups. Hence, the reaction of the biopolyol with the isocyanate became slower, which could slow foam gel formation and foam development (Allauddin et al., 2016; Marcovich et al., 2017).

The epoxide ring opener compounds that comply with the requirements of polyols as raw materials for making flexible polyurethane foam must have a hydroxyl number of less than 100 mg KOH/g, an acid number of less than 2 mg KOH/g and a low viscosity (Firdaus, 2014; Ionescu, 2016). The Dow Chemical Company has produced commercial polyol with a hydroxyl number of 56 mg KOH/g as a raw material for flexible polyurethane foam (The Dow Chemical Company, 2022). The biopolyol hydroxyl number from the current research was higher (99.37 mg KOH/g) than the polyol hydroxyl number produced by Dow. However, the hydroxyl number of palm oil polyols from the current study was lower than the hydroxyl number of palm oil polyols from research by Prociak et al. (2018) that reported 102 mg KOH /g and 128 mg KOH /g. Therefore, the biopolyol must be mixed with commercial polyol derived from petroleum to produce flexible polyurethane foam.

Dutta (2018) stated that the epoxide ring opening of palm oil with propylene glycol would have a secondary OH and was less reactive than the polyols formed from ethylene glycol ring openers. Ethylene glycol has a primary OH

that was more reactive than a secondary OH group; thus using ethylene glycol as an epoxide ring opener compound increased the reactivity of palm oil polyols when reacted with toluene diisocyanate (TDI) in the polyurethane flexible foam synthesis process (Kurańska and Malewska, 2021). These criteria could be met by polyols obtained from 10 mL of oil epoxidized with ethylene glycol.

Acid number

The presence of residual acids in polyols reduced the activity of tertiary amine catalysts that were involved in the polyol-isocyanate reaction (Ionescu, 2016). The acid number is calculated based on the percentage of free fatty acids to measure the mass of potassium hydroxide (KOH) in milligrams needed to neutralize 1 g of the chemical substance in the polyol (Enderus and Tahir, 2017; Vicentini-Polette et al., 2021). Furthermore, Ionescu (2016) stated that the acid number needed to be known to correct the hydroxyl number of a polyol because in the epoxide ring opening reaction process, sulfuric acid was used as a catalyst, with other acids being produced as products from side reactions. Gurgel et al. (2021) stated that if water was in the system, the epoxide ring opening reaction could coincide with the hydrolysis reaction to produce free fatty acids.

The results for the different epoxide ring openers and volumes of epoxidized palm oil were significantly ($p < 0.05$) different. Table 1 indicates there was interaction ($p = 0$) with both factors. The combination of the epoxide ring openers and the volumes of epoxidized palm oil influenced the acid number of the biopolyol. Different properties of the epoxide ring openers had different side reactions in producing free fatty acids during hydroxylation.

The concentration of ethylene glycol used as an epoxide ring opener was 99.8%, meaning it contained around 0.2% water. This water caused a hydrolytic reaction to produce free fatty acids.

Table 1 Biopolyol acid number resulting from various types of epoxide ring opener and varying volume of epoxidized palm oil

Epoxide ring opener	Epoxidized palm oil (mL)		
	10	20	30
Ethylene glycol	1.19±0.10 ^{cA}	1.19±0.10 ^{bA}	1.04±0.21 ^{bA}
Propylene glycol	4.84±0.46 ^{aA}	2.83±0.28 ^{aB}	1.94±0.21 ^{aC}
Distilled water	2.16±0.28 ^{bA}	2.46±0.18 ^{bA}	1.94±0.38 ^{aA}

Values (mean±SD) in same column with different lowercase superscripts, and in same row with different uppercase superscripts are significantly ($p < 0.05$) different.

The mixtures with 10 mL and with 20 mL epoxidized palm oil with propylene glycol yielded the same acid number (1.19 mg KOH/g). A combination of 30 mL epoxidized palm oil with ethylene glycol produced biopolyol with a lower acid number (1.04 mg KOH/g). However, this low acid number was accompanied by high viscosity and a low hydroxyl number of the biopolyol, indicating that the 30 mL epoxidized palm oil with ethylene glycol had caused side reactions between the free fatty acids and the system, resulting in a lower biopolyol acid number.

The highest acid number was obtained from 20 mL epoxidized palm oil with propylene glycol (4.84 mg KOH/g), while the lowest acid number was obtained from 30 mL epoxidized palm oil with ethylene glycol (1.04 mg KOH/g). The maximum acceptable acid number for polyester polyol is 2 mg KOH/g (Ionescu, 2016).

The propylene glycol used as the epoxide ring opener was 99.8% pure, with 0.2% water. The hygroscopic characteristic of propylene glycol caused the water content in the system to increase. Table 1 shows that the higher the volume of oxidized palm oil in the system (10 mL, 20 mL, and 30 mL), the lower the remaining propylene glycol to attract water in the environment so that the free fatty acids produced are lower and affect the lower acid number, namely 4.84 mg KOH/g; 2.83 mg KOH/g; and 1.94 mg KOH/g.

Mixing 10 mL of epoxidized oil with distilled water produced a biopolyol with a lower acid number (2.16 mg KOH/g), a lower hydroxyl number and high viscosity. Gurgel et al. (2021) stated that water in the system could cause a hydrolytic reaction to produce free fatty acids. This encouraged side reactions between the designed compound and free fatty acids, which in turn caused a decrease in the biopolyol acid number and was reflected in the free fatty acid content in the final product (Ionescu, 2016). A mixture of 20 mL epoxidized palm oil with distilled water produced a higher acid number (2.46 mg KOH/g) and hydroxyl number but with a lower viscosity, indicating that a hydrolytic reaction also followed the epoxide ring opening reaction. The acid number of the biopolyol was higher.

A biopolyol with an acid number of less than 2 mg KOH/g was obtained from 30 mL epoxidized palm oil with propylene glycol, from 30 mL epoxidized palm oil with distilled water, from 10 mL epoxidized palm oil with distilled water and from both 20 mL and 30 mL epoxidized palm oil with ethylene glycol. Peyrton and Avérous (2021) stated that the polyol system's high acidity could reduce the amine catalyst activity used to synthesize flexible polyurethane foam. The biopolyol produced from 10 mL of an epoxidized palm oil compound

with ethylene glycol was the best treatment because side reactions did not occur; in addition, it had a hydroxyl number lower than 100 mg KOH/g. Ethylene glycol is a ring opener compound with a primary OH group that increases the reactivity of biopolyol to isocyanate in the synthesis of flexible polyurethane foam (Kurańska and Malewska, 2021).

Viscosity at 30°C

Viscosity is a critical property of polyols, with preheating being required to facilitate dispensing, mixing and filling the mold due to a high viscosity (Kurańska and Malewska, 2021). Palm oil polyol has more secondary OH than primary OH groups. Ionescu (2016) explained that polyols containing more secondary OH groups than primary OH groups had lower reactivity, so the viscosity increased very slowly during the reaction. Conversely, polyols that had more primary OH groups than secondary OH groups would have higher reactivity. The viscosity increased very rapidly during the reaction; industry prefers low-viscosity polyols to make the production process easier (Ionescu, 2016).

The 20 mL epoxidized palm oil mixture with ethylene glycol produced the lowest polyol viscosity (39.53 cP). Ethylene glycol had the highest polyol viscosity in the epoxidized palm oil with 30 mL (50.40 cP), due to the ratio of epoxidized palm oil-to-ethylene glycol exceeding the optimum limit, which caused side reactions that produced products with high molecular weights.

The 10 mL epoxidized palm oil mixture with propylene glycol yielded a very low viscosity biopolyol (Fig. 3).

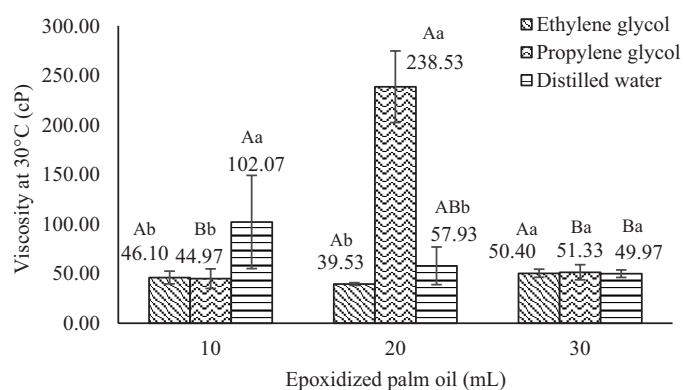


Fig. 3 Viscosity of biopolyol resulting from various types of epoxide ring opener and varying volume of epoxidized palm oil, where different lowercase letters above the bars indicate significant difference ($p < 0.05$) among means within each volume of epoxidized palm oil, and different uppercase letters indicate significant differences ($p < 0.05$) among means within each type of epoxide ring opener; error bars represent SD.

Having excessive epoxide ring openers avoided side reactions that increased the viscosity of the biopolyol (Petrovic et al., 2000). The highest biopolyol viscosity occurred with the 20 mL epoxidized palm oil with propylene glycol (138.53 cP). Propylene glycol reacted with the water or acid residues in the epoxidized oil to form hydroxyl and acetoxy compounds. After the mixture had been created, it reacted with the epoxide ring present in the epoxidized oil to form a dimer so that the viscosity of the polyol increased and the hydroxyl number decreased (Petrović et al., 2002). However, 30 mL of epoxidized oil with propylene glycol produced a biopolyol with a high hydroxyl number and a lower viscosity.

The results for the epoxide ring openers and volumes of epoxidized palm oil were significantly ($p < 0.05$) different. Fig. 3 indicates the significant interaction ($p = 0.0002$) of both factors. The differences in the biopolyol viscosity were due to the combination of the epoxide ring openers and the volumes of epoxidized palm oil.

Distilled water resulted in the highest polyol viscosity in epoxidized palm oil containing 10 mL (102.07 cP). Excessive distilled water caused a hydrolytic reaction to produce high-free fatty acids. The free fatty acids reacted with each other to form fatty acid dimers, which had a high molecular weight and thus, the viscosity of the biopolyol increased. The mixtures with 20 mL and 30 mL epoxidized oil with distilled water produced biopolyols with viscosities of 57.93 cP and 49.97 cP, respectively, resulting in lower biopolyol viscosity. The more epoxidized oil used, the greater the opportunities for the distilled water to add hydroxyl groups. In addition, the hydrolysis reaction could be suppressed, so the amounts of free fatty acids were also low. These free fatty acids and biopolyols formed hydrogen bonds with the distilled water, causing lower viscosity. Ifa et al. (2018) stated that water acted as a diluent.

Density at 30°C

The current study applied the classical method to determine the density by using a pycnometer at constant temperature (Ionescu, 2016). Polyols with a high viscosity have a higher molecular weight and a high density (Abdullah, 2012).

Fig. 4 shows that neither the types of epoxide ring openers ($p = 0.1145$) nor the volumes of epoxidized palm oil ($p = 0.1454$) significantly affected the density of biopolyol. Furthermore, the interaction between these factors also showed no significant effect ($p = 0.3549$). The variation in density values determines the types of polyurethane foam.

Therefore, this parameter is essential for discussing the influence of both the epoxide ring opener and the volume of the epoxidized palm oil.

The mixtures of 10 mL and 20 mL epoxidized palm oil with ethylene glycol produced the lowest density polyols (0.906 g/mL and 0.899 g/mL, respectively). Excessive ethylene glycol avoided side reactions that formed high molecular weight products. The ethylene glycol produced its highest polyol density with the 30 mL epoxidized palm oil (0.913 g/mL). This condition encouraged polymerization side reactions to produce a higher density biopolyol.

The highest density of biopolyol occurred with the 20 mL epoxidized palm oil with propylene glycol (0.907 g/mL), as shown in Fig. 4. This was due to the propylene glycol reacting with the water or acid residues that were still present in the epoxidized oil to form hydroxyl and acetoxy compounds. It reacted with the epoxide ring in the epoxidized oil to create a dimer so that the polyol density increased, while the hydroxyl number decreased (Petrović et al., 2002).

The use of 10 mL epoxidized palm oil with distilled water produced a biopolyol with a high viscosity. A high viscosity indicated that the biopolyol contained molecules with a high molecular weight and that the biopolyol had a high density (0.908 g/mL). The higher the level of epoxidized palm oil, the lower the biopolyol viscosity. A low viscosity indicated that the biopolyol had a low molecular weight and low density. Epoxidized palm oil amounts of 20 mL and 30 mL with distilled water produced biopolyols with lower polyol densities. The free fatty acids were carboxylic acids bonded with water through hydrogen bonds so that the viscosity of the polyols was low.

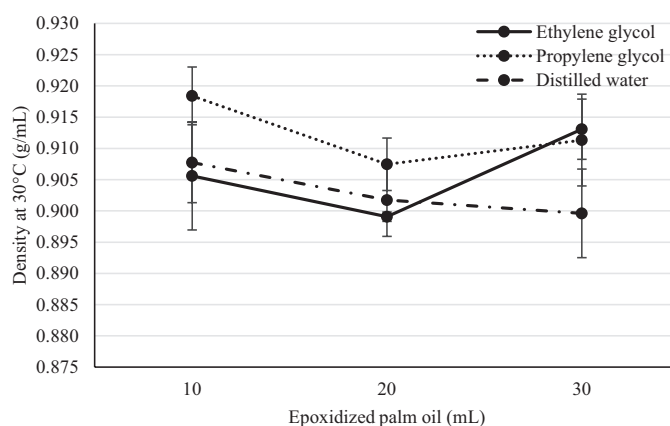


Fig. 4 Density of biopolyol resulting from various types of epoxide ring opener and varying volume of epoxidized palm oil, where values are mean $\pm$ SD ($n = 9$) and error bars represent SD.

Color

The color of the polyol was determined by the vegetable oil used. According to Ionescu (2016), polyols have colors ranging from yellow to brown. The brighter color of polyols increases the commercial value and indicates that the product has not degraded during synthesis.

In the current study, the color of the biopolyols produced in all treatments was a clear yellow (Fig. 5). The biopolyol made from each treatment had only slightly different chemical characteristics, so there were no striking color differences because the ring-opening reaction took place at a low temperature (50°C) and in a short time (1 hr), so that the resulting biopolyol did not degrade and become brown.

Fourier-transform infrared spectroscopy

The biopolyol with a hydroxyl number (99.37 mg KOH/g) less than 100 mg KOH/g and with the lowest acid number (1.19 mg KOH/g) was the best treatment. FTIR was used to analyze the mixture of 10 mL of epoxidized oil with ethylene glycol. The criteria for the raw material for flexible

polyurethane foam were a biopolyol with a hydroxyl number of less than 100 mg KOH/g and an acid number of less than 1.1 mg KOH/g (Kurańska and Malewska, 2021). The purpose of testing using FTIR was to determine the functional groups in the biopolyol at specific wave numbers.

The FTIR spectra in Fig. 6 show a wave number of 2922.54/cm (A), 2922.28/cm (B), and 2922.48/cm (C) indicating an aliphatic C-H group (CH₃ methyl group), with the wave number at 3332.05/cm (A), 3364.81/cm (B),

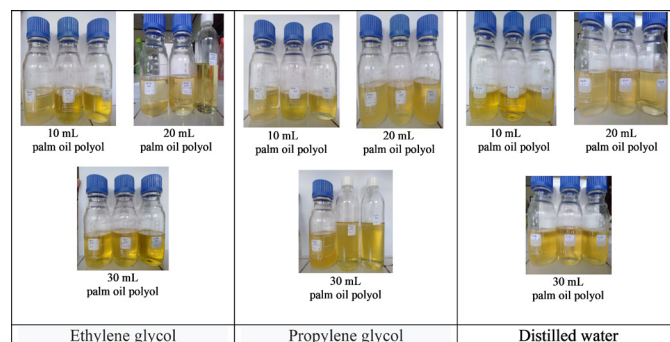


Fig. 5 Color of biopolyols resulting from various types of epoxide ring opener and varying volume of epoxidized palm oil

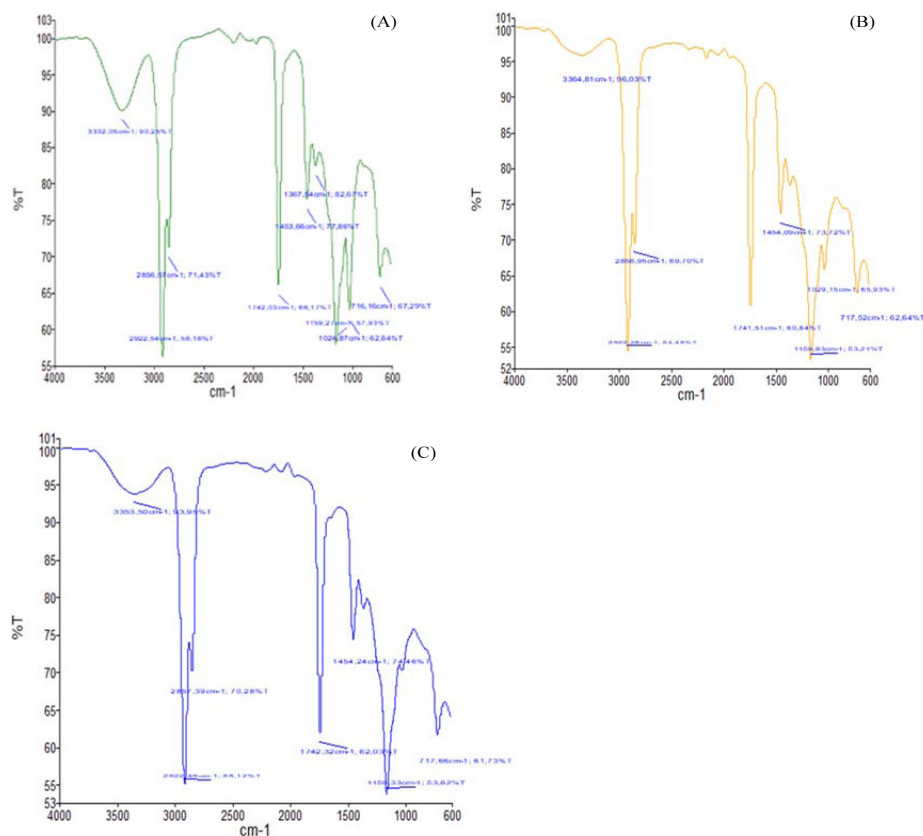


Fig. 6 FTIR spectra of 10 mL of palm oil polyol with 30 mL of epoxide ring opener in ethylene glycol (A), propylene glycol (B), and distilled water (C)

and 3353.50/cm (C) representing the alcohol group (hydroxyl) in the polyol sample. Figure 6 A shows that there is a sharp absorption peak at wave number 3332.05/cm, meaning that the use of ethylene glycol as an epoxide ring opener produces palm oil polyols with higher primary OH than propylene glycol and distilled water. Ifa et al. (2018) reported the presence of a double bond group 2 (C=C) at wave numbers 1550–1670/cm. There were no C=C groups in the polyol samples, indicating that the triglyceride double bonds had been converted to polyols via an epoxidation reaction, followed by a ring-opening reaction. C-O stretching with alcohol groups occurred at wave number 1159.27/cm (A), 1159.92/cm (B), and 1159.22/cm (C).

Primary and secondary hydroxy groups would be formed during the epoxide ring opening reaction. This group was named after its position in the triglyceride chain (Prociak et al., 2018). The primary OH group was in the polyol samples at wave number 3332.05/cm (A), 3364.81/cm (B), and 3353.50/cm (C), while the secondary OH group was at wave number 1159.27/cm (A), 1159.92/cm (B), and 1159.22/cm (C). Based on this, it was possible to conclude that palm oil polyols contained more secondary OH groups, as evidenced by the sharp peaks. When polyols with secondary hydroxyl groups reacted with isocyanates, their reactivity was three times lower than that of primary groups (Polaczek et al., 2021).

At wave number 1742.03/cm (A), 1741.51/cm (B), and 1742.32/cm (C) the polyol sample contained a carbonyl group (C=O). This demonstrated that the carbonyl group was not oxidized, unlike the alkene group (double bond).

Adding different epoxide ring-opening compounds resulted in palm oil polyols with varying properties. Flexible polyurethane foams are made from polyols with hydroxyl values less than 100 mg KOH/mg (Peyrton and Avérus, 2021). According to the findings, the hydroxyl value of biopolyol could be produced from epoxidized palm oil amounts of 10 mL and 30 mL with ethylene glycol, from an epoxidized palm oil amount of 20 mL with propylene glycol and with an epoxidized palm oil amount of 10 mL with distilled water. Adding excess epoxidized palm oil prevented polymerization and the formation of a product with a higher viscosity. An epoxidized palm oil amount of 10 mL with ethylene glycol produced a biopolyol with a lower acid number. This study produced biopolyols that met the flexible polyurethane foam raw material criteria.

Conflict of Interest

The authors declare that there are no conflicts of interest.

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