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# Characterization of polyurethane produced by polyol synthesized from corn oil

## Mısır yağından sentezlenen poliolden üretilen poliüretanın karakterizasyonu

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**Abstract**
In this study, biopolyol has been synthesized from corn oil by epoxidation, hydroxylation, neutralization, and purification processes. The rheological properties of both corn oil and polyol obtained from corn oil have been compared. When the variation of viscosity with temperature is examined, it is seen that corn oil-based polyol is more viscous than corn oil. Accordingly, it is thought that the molecular structure of the biopolyol changes, and its molecular weight increases. According to the results obtained, the hydroxyl number of the synthesized polyol is determined as approximately 160 mg KOH/g polyol by the analytical method. The produced polyols have been prepared for polyurethane production after being characterized physically and chemically. The production of polyurethane sponge with a suitable process and method has been realized according to the purpose of use. The approximate density of the produced polyurethane was 40 kg/m$^3$ and the thermal conductivity coefficient was found to be 0.026 W/m·K. Also, Taguchi method has been used in experimental studies to determine an efficient and economical process in both the polyol synthesis and the polyurethane production.

**Keywords:** Corn oil, Polyol, Polyurethane, Rheology**,** Characterization.

**Özet**
Bu çalışmada mısır yağından epoksilleme, hidroksilleme, nötralizasyon ve saflaştırma işlemiyle biopoliol sentezlenmiştir. Mısır yağından elde edilen poliol ve mısır yağının reolojik özellikleri karşılaştırılmıştır. Viskozitenin sıcaklıkla değişimi incelendiğinde mısır yağı esaslı poliolün mısır yağına göre daha viskoz olduğu görülmektedir. Buna göre biopoliolün moleküler yapısının değiştiği ve molekül ağırlığının arttığı düşünülmektedir. Elde edilen sonuçlara göre sentezlenen poliolun hidroksil sayısı yaklaşık 160 mg KOH/g poliol olarak analitik yöntemle tayin edilmiştir. Üretilen plioller, fiziksel ve kimyasal olarak karakterize edildikten sonra poliüretan üretimi için hazırlanmıştır. Kullanım amacına göre poliüretan süngerin uygun bir proses ve yöntemle üretimi gerçekleştirilmiştir. Üretilen poliüretanın yaklaşık yoğunluğu 40 kg/m$^3$ ve ısıl iletkenlik katsayısı 0.026 W/m·K olarak bulunmuştur. Ayrıca deneysel çalışmalarda hem poliol sentezinde hem de poliüretan üretiminde verimli ve ekonomik bir süreç belirlemek amacıyla Taguchi yöntemi kullanılmıştır.

**Anahtar kelimeler:** Mısır yağı, Poliol, Poliüretan, Reoloji, Karakterizasyon.

## 1. Introduction

Today, the use of biopolymer raw materials is becoming more and more widespread. In particular, the synthesis of bioraw materials can be realized by using renewable resources and wastes. For example, polyol, which is the raw material of polyurethane, is obtained from vegetable oils instead of petrochemical sources. Studies have shown that triglycerides in the structure of vegetable oils are suitable for polyol production.

The mechanical properties of high-density and rigid polyurethane foams have been studied in the literature [1]. The determination of mechanical, structural, and morphological properties of polyurethane foams is an important research topic [2]. In the current studies, soybean oil-based polyol was obtained by applying epoxidation and hydroxylation steps to soybean oil. The properties of soy-based polyol and polyurethane were examined and their characterizations were made.

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Besides, the variation of viscosity, density, and molecular weight of polyol obtained from soybean oil with temperature was determined [3].

As a result of the modification of vegetable oils, both the double bonds in their molecules are broken and their molecular weights increase. For these reasons, an increase in the viscosity of polyols synthesized from vegetable oils can be observed compared to vegetable oils. Also, when the rheological properties of vegetable oils and polyols obtained from them are examined, it has been determined that the viscosity values decrease as the temperature increases [5-7].

It has been observed that the heat transfer coefficients of castor oil-based polyurethane materials are lower than commercial polyurethane materials. From TGA curves, it has been determined that the thermal stability of castor oil-based polyurethane materials is better than the polyurethanes produced from the commercial polyol. From the mechanical strength test results, it was observed that the mechanical properties of castor oil-based materials were weakened compared to the commercial product [4].

In this study, polyol, the raw material of polyurethane, has been synthesized from corn oil by economical methods. After examining the physical and chemical properties of the obtained biopolyol, it has been used in the production of polyurethane. The unique aspect of this research is both the synthesis of bioraw materials and the production of polyurethane foam with the raw material obtained. The mechanical properties, thermal conductivity coefficient, density, thermal stability, and surface morphology of polyurethane produced from corn oil-based polyol have been evaluated.

## 2. Materials and Methods

### 2.1. Materials

The corn oil used has 30 % monounsaturated, 57 % polyunsaturated, and 13 % saturated fat. Besides, the density of corn oil at room temperature is 910 $kg/m^3$ and its viscosity is 74 cp. Refined corn oil used in experimental processes has a density of 910 $kg/m^3$ at 25 °C, a refractive index of 1.45, an iodine index of 105, and a saponification number of 170. The density of the used filler ($CaF_2$) is 3180 $kg/m^3$, and the particle diameter is below about 5 μm. Hydrogen peroxide ($H_2O_2$) 30 %, methanol ($CH_3OH$) 99.5 %, acetic acid ($CH_3COOH$) 80 %, sulfuric acid ($H_2SO_4$) 95–98 % were supplied from Merck. Toluene diisocyanate, triethylenediamine, silicon, and tin octoate have been obtained from Ravago Petrochemicals.

### 2.2. Experimental method

In this research, biopolyol has been synthesized from corn oil by epoxidation, hydroxylation, purification, and neutralization processes. After using optimum amounts of corn oil and acetic acid in PID-controlled reactor (Figure 1), hydrogen peroxide was added dropwise. Hydroxylation of the synthesized epoxy-corn oil was achieved with the help of methanol. This process was carried out using certain amounts of methanol, water, and sulfuric acid. In the last stage, impurities such as water and methanol were recovered with the help of a vacuum rotary evaporator. After this stage, the neutralization process was carried out again and the phases were separated from each other with the help of a separating funnel to obtain the biopolyol [11].

**Figure 1.** Polyol synthesis system (PID) from corn oil

In the production of polyurethane, it was mixed with corn oil-based polyol filler ($CaF_2$) for 5 minutes at a mixing speed of 750 rpm. After adding certain proportions of water, silicon, and amine mixture to the polyol, TDI was added and mixed at 1500 rpm for 2 minutes. After pouring the mixture into the prepared molds, it was waited for 24 hours to cure. Then the physical characterization of the polyurethane was done.

## 3. Results and Discussions

### 3.1. Rheological properties of corn oil and its polyol

The rheological properties of corn oil in Figure 2 and corn oil-based polyol in Figure 3 at different temperatures are shown. Corn oil-based polyol has higher viscosity and shear stress than corn oil. This change can occur due to the increase in both the molecular weight and the molecular chain length. When the rheological properties of corn oil and polyol obtained from corn oil were examined, it was determined that the temperature increase decreased the viscosity. Besides, shear-thinning behavior has been observed in both corn oil and polyol obtained from corn oil. Fluids with such rheological behavior (non-Newtonian) show pseudoplastic behavior [8].

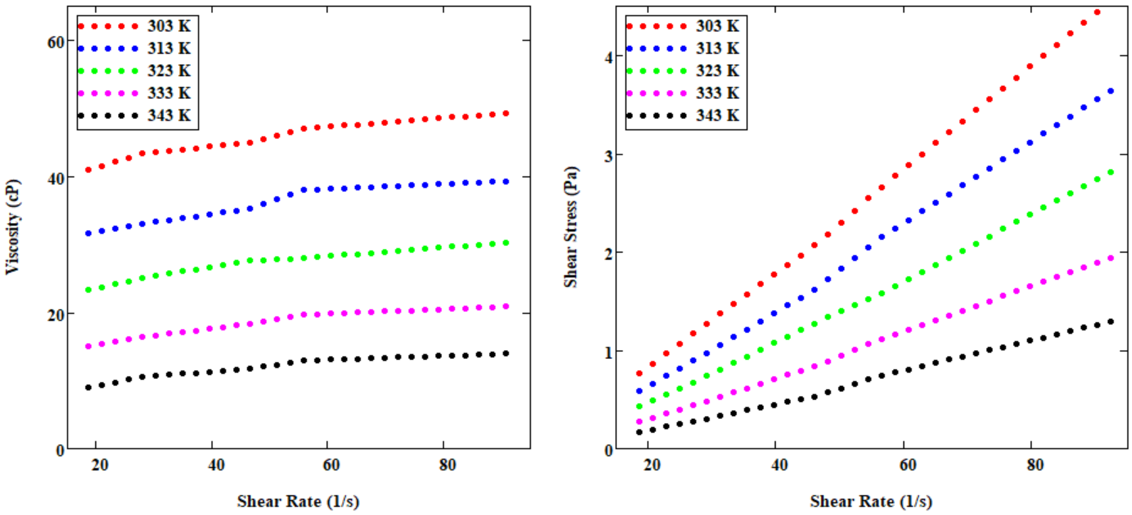


**Figure 2**. Variation of viscosity and shear stress of corn oil with shear rate at different temperatures

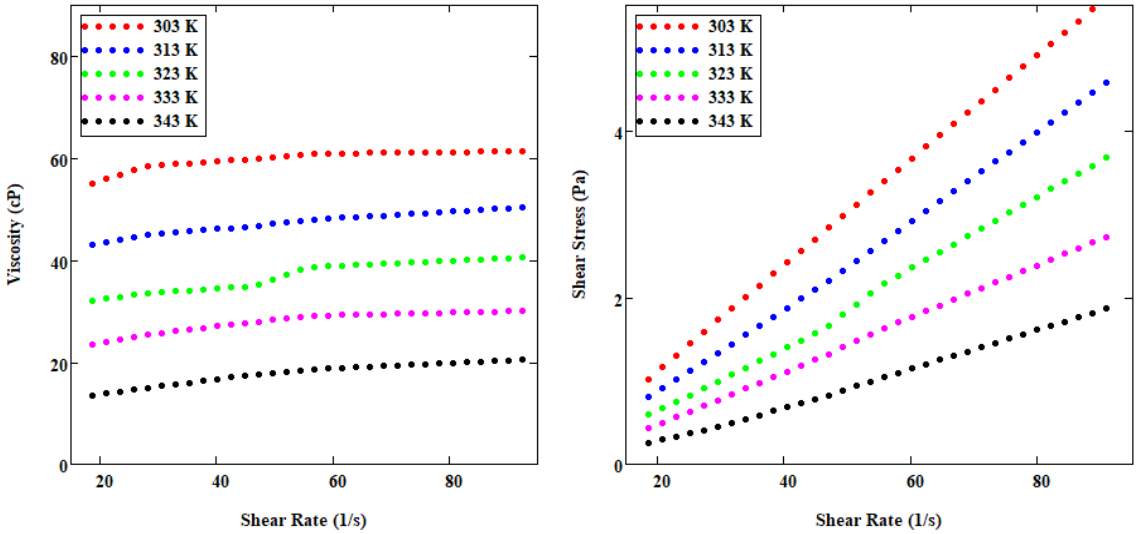


**Figure 3.** Variation of viscosity and shear stress with shear rate of corn oil-based polyol

## 3.2. FTIR spectra of corn oil and polyol

Corn oil-based polyol has been synthesized by changing the structure of refined corn oil. The chemical bond structure of both corn oil and synthesized polyurethane have been determined by FTIR spectrophotometer. In particular, the presence of hydroxyl bonds in the structure of the corn oil-based polyol indicates that the modification is successful. Figure 4 shows 1236-1099 $cm^{-1}$ C-O ester groups, 1647 $cm^{-1}$ C=C cis-olefins, 1745 $cm^{-1}$ ester carbonyl groups of triglycerides, 3009 $cm^{-1}$ C-H bonds, 2923-2855 $cm^{-1}$ $CH_2$ groups vibration stresses in FTIR spectra of corn oil.

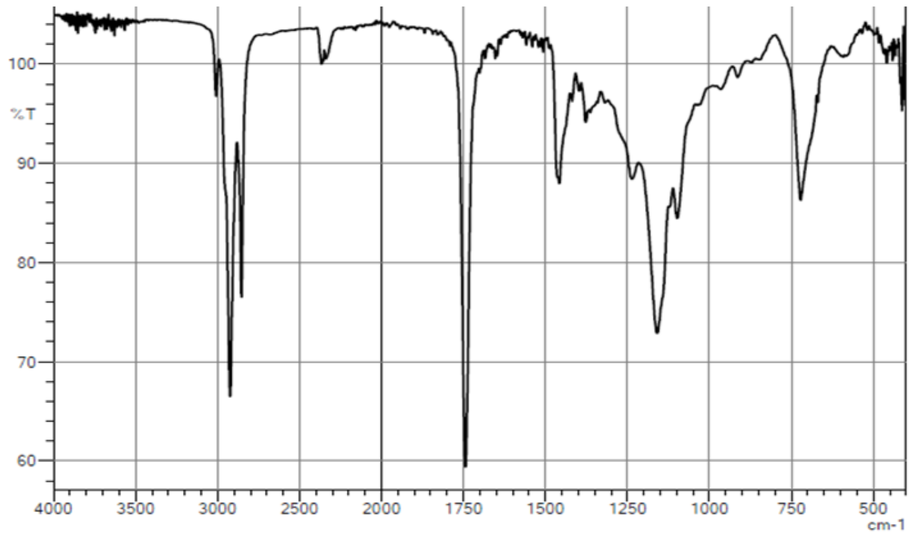


**Figure 4.** FTIR spectra of corn oil

In FTIR spectra in Figure 5, 3498 $cm^{-1}$ OH stretching vibrations, 3293 $cm^{-1}$ NH stretching vibrations, 2970 $cm^{-1}$ CH asymmetric stretching vibrations, 2866 $cm^{-1}$ CH symmetrical stretching vibrations, 2273 $cm^{-1}$ N=C=O stretching vibrations, 1720 $cm^{-1}$ C=O stretching vibrations, 1535 $cm^{-1}$ NH bending vibrations, 1452 $cm^{-1}$ CH shear vibrations, 1223 $cm^{-1}$ CN and 1094 $cm^{-1}$ CO stretching vibrations are shown.

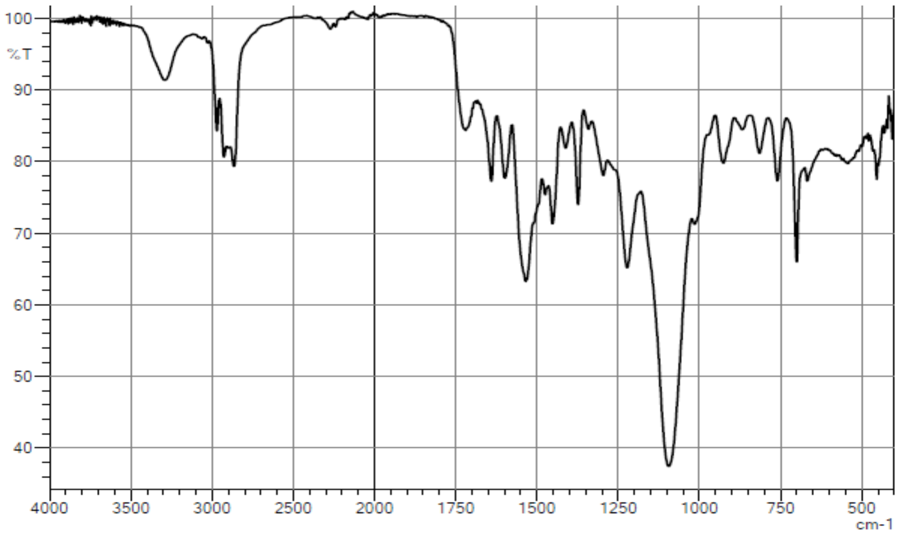


**Figure 5.** FTIR spectra of polyurethane derived from corn oil-based polyol

## 3.3. Tensile test of polyurethane produced from corn oil-based polyol

Standard samples have been prepared for polyurethane and measurements are made in the tensile test device. Samples were prepared in standard molds with the cross-sectional area (a = 20 mm, b = 10 mm, and A = 200 $mm^2$) and length (L = 100 mm). The applied preload, the tensile speed of 10 mm/minute, the stress ($\sigma$ = N/$mm^2$), and the elongation ($\varepsilon$ = mm) of the sample were determined. The polyurethane obtained from corn oil-based polyol was cut into standard sizes and prepared for the tensile test. A force of 10 mm/minute was applied to the standard sample with an initial length of 100 mm and a cross-sectional area of 200 $mm^2$ (20 mm·10 mm). The maximum stress reached up to about 100 kPa. As seen in Figure 6, approximately 75 % elongation was observed in the standard sample relative to its initial length. The tensile test started with a preload of 5 N and the maximum force was measured as approximately 20 N.

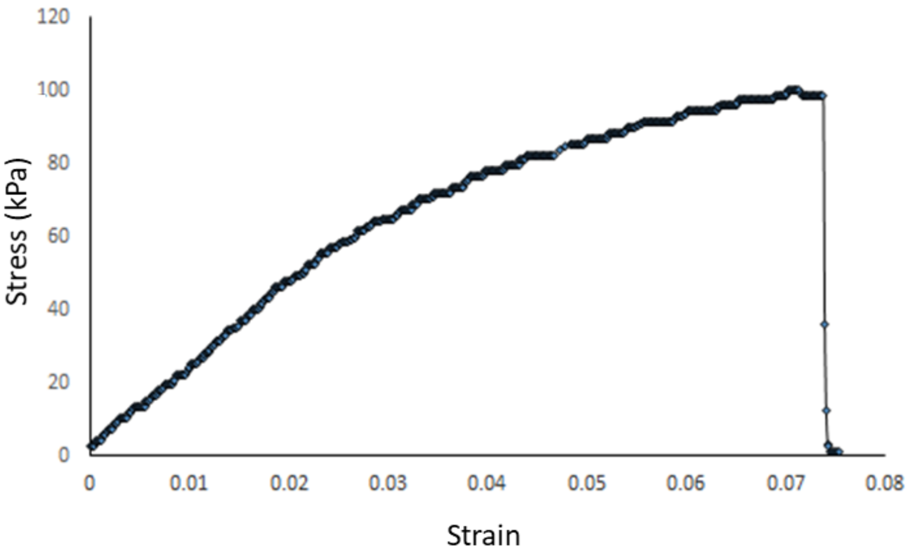


**Figure 6.** Deformation of corn oil-based polyurethane due to applied force

### 3.4. SEM image of polyurethane

SEM image and EDX data of polyurethane obtained from corn oil-based polyol are given in Figure 7. As seen here, carbon is 66.89 wt.%, oxygen 26.61 wt.%, nitrogen 3.28 wt.%, fluorine 2.98 wt.% and tin 0.23 wt.%. Catalysts used in EDX data may be slightly removed. After the conditions are optimized, there is no significant change in the amount of catalyst used. Compounds such as $CaF_2$, which are called fillers and additives, have been used to increase the density, non-flammability, and thermal stability of polyurethane. Before the reaction, the additives must be mixed or mixed homogeneously with the polyol. Use of the additive more than 30 g per 100 g of vegetable oil-based polyol: It affects the mechanical strength, thermal conductivity coefficient, and pore structure negatively.

Besides, the high use of additives increases the number of closed cells and makes breathing between cells difficult. The more regular the pore structure of the obtained polyurethane, the lower the thermal conductivity coefficient. As the porosity and the number of independent cells increase, the insulation property of polyurethane improves. Especially when the SEM images are examined, the surface morphology and pore structure of the polyurethane can be determined [9].

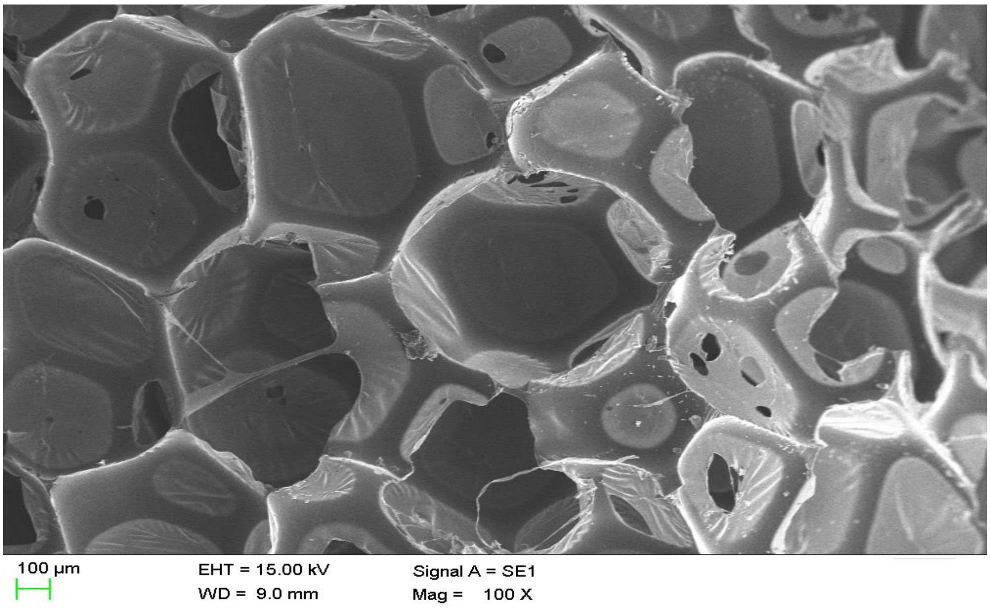


**Figure 7.** SEM image of polyurethane obtained from corn oil-based polyol

### 3.5. Thermogravimetric analysis (TGA) of polyurethane

TGA analyzes have been carried out at a nitrogen gas flow rate of 100 mL/min, starting at 20 °C, with a heating rate of 10 °C/min, using an alumina crucible up to a temperature of 600 °C. TGA curve of polyurethane produced with polyol synthesized from corn oil is shown in Figure 8. When TGA curve of the polyurethane obtained from corn oil-based polyol is examined, it is seen that physical impurities are removed in the first region. It is seen that the chemical decomposition of polyurethane started at a temperature of approximately 275 °C. The thermal degradation behavior of the polymer occurred rapidly in the second region. After the temperature of 400 °C (third region), thermal decomposition structures are observed more slowly.

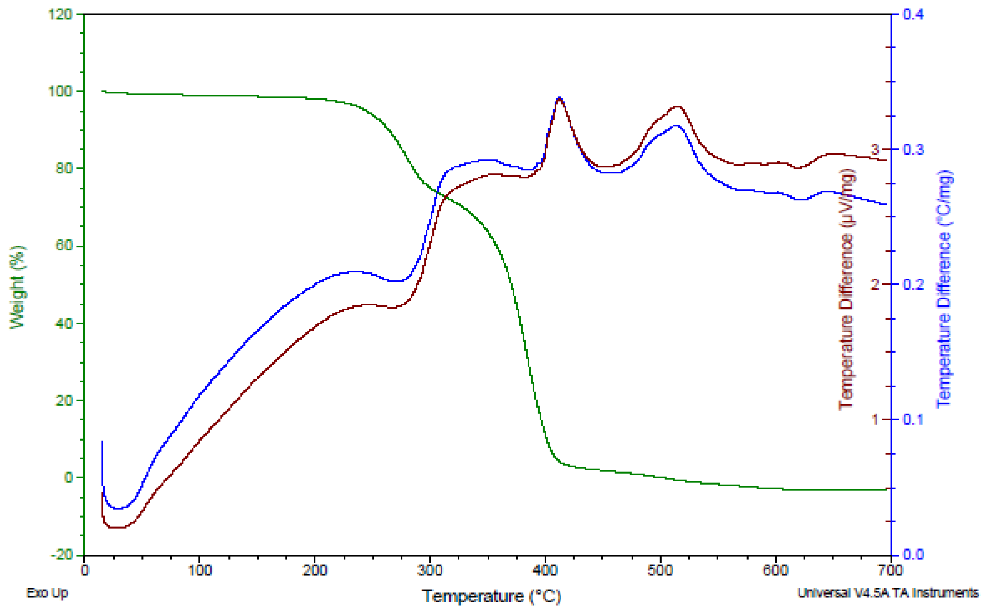


**Figure 8.** TGA curve of polyurethane produced from corn oil-based polyol

## 4. Conclusions

In this study, biopolyol has been synthesized from corn oil, and its physical and chemical characterization is carried out. In FTIR results, it is seen that the double bonds in the vegetable oil are broken and hydroxyl is attached to the structure [10]. The viscosity of corn oil and polyol obtained from corn oil decreased with temperature. However, the viscosity and shear stress values of the bipolyol obtained with the modification were higher than the corn oil. This result, it is thought that corn oil is caused by the change in both the chemical bond structure and the molecular chain length. In addition, the hydroxyl number of the synthesized polyol was determined as approximately 160 mg KOH/g polyol. Polyurethane production has been carried out using biopolyol, catalysts, and initiators. The obtained polyurethane has a density of about 40 kg/m$^3$ and a thermal conductivity value of 0.026 W/m·K. Besides, the use of filling material in polyurethane at a high rate has been weaken both the pore structure and mechanical properties. Experimental conditions have been optimized to determine an efficient and economical method for polyol synthesis and polyurethane production.

## 5. Acknowledgments

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## 6. Author Contribution Statement

In this study, Author 1 contributed making the design, literature review, contributed to forming the idea, the analysis of the results; Author 2 contributed to checking the spelling and checking in terms of content.

## 7. Ethics Committee Approval and Conflict of Interest

There is no need for an ethics committee approval in the prepared article. There is no conflict of interest with any person/institution in the prepared article.

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