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# The Production of Vegetable Oil-Based Polyols and Modelling of Rheological Properties

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**Ercan Aydoğmuş**[1,*], **Müge Gür**[1], **Fethi Kamışlı**[1]

[1]Fırat University, Department of Chemical Engineering, 23119, Elazığ/Turkey

**Abstract:** In this study, some vegetable-oil based polyols were produced from the different vegetables oils with the catalysts. The produced polyols compared with commercial polyols in terms of rheological properties such as viscosity, temperature, shear stress, shear rate. The rheological properties of the polyols were modelling with general equations based on experimental data. Canola, cotton, linseed, corn, hazelnut and soybean oils were used in the production of polyols. The polyol production was accomplished by oxygen bonding to the structure followed by hydroxyl bonding by breaking the double bonds in the oil. These steps were, respectively, the steps of epoxidation, hydroxylation and purification. In this study, variations of viscosities of soybean oil, cottonseed oil, corn oil, hazelnut oil, canola oil, linseed oil-based polyols and commercial polyols were determined a function of temperature. It is known that the viscosity of the fluid decreases as temperature increases. The tested polyols showed Newtonian and non- Newtonian fluids behavior at certain temperature range. According to the experimental data; the linear and non-linear regression were made to determine coefficients of regression in the model equations.

**Keywords:** Vegetable oil; polyols; rheological properties; modelling.

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***Corresponding author. E-mail:** ercanaydogmus@firat.edu.tr

## INTRODUCTION

When the polyurethane produced from petroleum-based polyols is compared with that produced from vegetable oil-base polyols, a smaller amount of isocyanate is used for the production of polyurethane from vegetable oil polyols. The polyurethane produced from the vegetable oil-base polyols has a lower compression resistance [1].

Wood powder was added as filler to the polyurethane derived from castor oil-based polyol. The polyurethane of the swelling time was compared with commercial polyols, and castor oil-based polyols. Effective thermal conductivity of the castor oil-based polyurethane material was compared to that of commercial polyurethane material and it was observed that the effective thermal conductivity for the polyurethane produced from vegetable oil-base polyols had a lower value. Increasing the filler has negative impact on the effective heat transfer coefficient. Density of polyurethane material was found to be between 36 and 39 kg/m$^3$. TGA value of the thermal stability of the castor oil-based polyurethane material was found to be more commercially polyol product [2].

The goal of this study is to determine the rheological properties of different oil-based polyols and choose the best model complying with experimental data and the viscosity to each waste vegetable oil based-polyols are measured at different temperatures (25, 30, 35, 40, 45 and 50 °C) by using a rotary viscometer (Brookfield DV-II). Samples were sheared with several different rotational speeds at an increasing order. One of the most important parameters required in the design of technological processes in polyurethane industries is the viscosity of raw materials. Data obtained for apparent viscosity and rotational speed were used to describe the flow behavior by the model equations both in the forward and backward - measurement.

The polyols are produced from the waste vegetable oils in three consecutive steps which are epoxidation, hydroxylation and purification. The temperature of the system is kept under the control using a thermostat. When it is reached to the desired reaction temperature, the peroxides are added into the vegetable oils in acidic medium by the aid of dropping funnel in the certain time.

After the reaction is completed, the mixture is taken into separatory funnel and after for a while the mixture separates in two phases with the upper phase of the epoxidized vegetable oil. After the epoxidation step, neutralization with water and the hydroxylation starts. Especially hydroxylation with alcoholysis is frequently preferred in the production of polyols. The purification process is carried with rotary evaporator to get rid of impurities such as water, heptane and etc. The polyols produced from the vegetable oil are used in the production of polyurethane by checking the number of hydroxyl. The structures of the hydroxyl compounds were investigated with the FTIR spectrometer. The polyurethane was produced from the different vegetable oil-based polyols and commercial polyols. The characteristic properties of the polyurethane such as thermal conductivity, the structures of porosity, density were determined. The polyurethane produced from the different vegetable oils is compared one another in terms of thermal properties.

## EXPERIMENTAL

### Material, Methods, and Modelling

In this study, a system consisting of a three necked balloon joe, thermometer, water bath, magnetic stirrer, condenser and funnel was used for the epoxidation reaction, which is the first step of obtaining polyols from vegetable oils used as raw materials. A three-necked balloon was used at the atmospheric pressure with a magnetic stirrer to heat the water bath to 325 – 330 K. A condenser system was attached to the ball of three necks and a thermometer is placed with the help of plugs. The refined oil was placed in the amount determined in a three-necked balloon with the aid of a funnel. Acetic acid, sulfuric acid and heptane were added to the system with the necessary optimizations. Hydrogen peroxide was added dropwise to the system after reaching a temperature of 325 K, and the epoxidation step was carried out in 4 hours. After the reaction was completed, the epoxy-oil is separated off with the separating funnel. Since the epoxy-oil was acidic, the pH value was raised by washing with pure water. Neutralization was also achieved using a basic ion exchange resin. In the experimental system, the hydroxylation was carried out by adding the certain amounts of methanol, water and acetic acid to the three necked balloon. The mixture was heated to the boiling temperature of the methanol while it was stirred. When the boiling temperature was reached, epoxy-oil was added to the three necked balloon. Hydroxylation proceeded for about 2 hours. Neutralization was performed again after this step. In the last step, impurities such as water, methanol, heptane were removed by using vacuum evaporator. The hydroxyl value of the obtained polyol was determined according to ASTM D 4274 D method.

The viscosities of the polyols produced from different the vegetable oils were measured by using a rotary viscometer (Brookfield DV-II) at different temperatures (25, 30, 35, 40, 45 and 50 °C). Samples were sheared with several different rotational speeds (2.5, 5, 10, 20, 30 and 50 rpm) at an increasing order. The obtained data for apparent viscosity and rotational speed were used to describe the flow behavior by the model equations.

Brookfield rotational viscometer (Model DV-II, Brookfield Engineering Laboratories) equipped with spindle 21 was used to measure viscosities of produced and commercial polyols. Enough samples nearly 8 mL in the beaker were used for immersing the groove on the spindle with guard leg. Temperature was kept constant at a desired value using thermostatically controlled electrical system. Shear rate ($\dot{\gamma}$) and shear stress ($\tau$) were read from viscometer directly. Shear stress and shear rate can also be calculated by using Eq. (1), (2) and (3).

$$\dot{\gamma} = \beta.N \qquad \textbf{(Eq. 1)}$$

$$\tau = \mu.\dot{\gamma} \qquad \textbf{(Eq. 2)}$$

$$\tau = \mathrm{K}.(\mu)^{\delta} \qquad \textbf{(Eq. 3)}$$

Where; $N$ is rotational speed (rpm), $\tau$ is shear stress (Pa), $\mu$ is the apparent viscosity (mPa.s), $\mathrm{K}$ is the consistency coefficient (mPa.s), $\delta$ is flow behavior index and $\beta$ is coefficient (dimensionless).

The viscosity of a blend as a function of temperature can be calculated using one of the equations given below. Here all the equations given below are used to determine how the viscosity depends on temperature. In order to choose the best model for each blend, $R^2$ is calculated for each model.

$$\mu_{Linear} = a.T + b \qquad \textbf{(Eq. 4)}$$

$$\mu_{Exponential} = c.\exp(d.T) \qquad \textbf{(Eq. 5)}$$

$$\mu_{Power} = e.T^{f} \qquad \textbf{(Eq. 6)}$$

$$\mu_{Logarithmic} = g.\ln(T) + h \qquad \textbf{(Eq. 7)}$$

$$\mu_{Polynomial} = i.T^{2} + j.T + k \qquad \textbf{(Eq. 8)}$$

$$\mu_{Suggested} = \exp(-T) + m.T + n \qquad \textbf{(Eq. 9)}$$

## FIGURES AND TABLES

**Table 1:** Comparison of vegetable oil based polyols with model equations.

| **MODELS** | **Correlation Coefficients** | Soybean Polyols | Cotton Polyols | Corn Polyols | Hazelnut Polyols | Canola Polyols | Linseed Polyols |
|---|---|---|---|---|---|---|---|
| **Linear** | **a** | -9,6579 | -7,9912 | -1,9308 | -5,8209 | -2,1367 | -4,4974 |
| | **b** | 3058,5 | 2508,7 | 643,23 | 1793,2 | 707,18 | 1355,3 |
| | **$R^2$** | 0,9702 | 0,9855 | 0,9588 | 0,9567 | 0,9296 | 0,9929 |
| **Exponential** | **c** | $2.10^{6}$ | $5.10^{16}$ | $2.10^{10}$ | $4.10^{18}$ | $1.10^{9}$ | $5.10^{37}$ |
| | **d** | -0,109 | -0,113 | -0,065 | -0,131 | -0,056 | -0,283 |
| | **$R^2$** | 0,7668 | 0,7897 | 0,8920 | 0,7809 | 0,9653 | 0,9066 |
| **Power** | **e** | $6.10^{82}$ | $7.10^{85}$ | $4.10^{51}$ | $1.10^{97}$ | $2.10^{44}$ | $4.10^{208}$ |
| | **f** | -32,56 | -33,85 | -20,11 | -38,55 | -17,19 | -83,91 |
| | **$R^2$** | 0,7542 | 0,7809 | 0,8773 | 0,7717 | 0,9593 | 0,9044 |
| **Logarithmic** | **g** | -2906 | -2400 | -601,1 | -1721 | -663,2 | -1335 |
| | **h** | 16736 | 13798 | 3492,4 | 9862,8 | 3848,3 | 7619,5 |
| | **$R^2$** | 0,9667 | 0,9830 | 0,9600 | 0,9524 | 0,9404 | 0,9935 |
| **Polynomial** | **i** | -0,095 | -0,105 | 0,006 | -0,144 | 0,039 | 0,132 |
| | **j** | 47,629 | 55,433 | -5,377 | 79,46 | -26,51 | -82,93 |
| | **k** | -5576,5 | 7025,3 | 1179,4 | -10842 | 4465,6 | 12991 |
| | **$R^2$** | 0,979 | 0.995 | 0.961 | 0.987 | 0.994 | 0.998 |
| **New (Suggested)** | **m** | -9,65795 | -7,97888 | -1,93083 | -5,82090 | -2,13662 | -4,49741 |
| | **n** | 3058,480 | 2505,030 | 643,2298 | 1793,152 | 707,1342 | 1355,300 |
| | **$R^2$** | 0,9996 | 0,9997 | 0,9998 | 0,9998 | 0,9997 | 1,0000 |

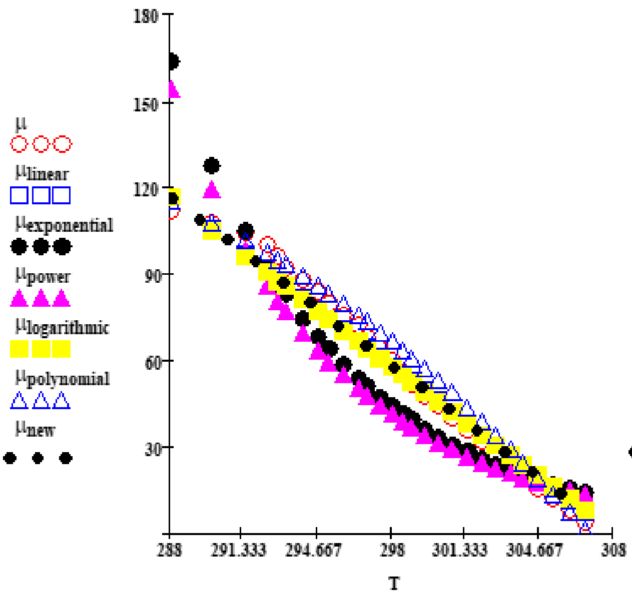

**Figure 1:** Hazelnut oil-based polyols

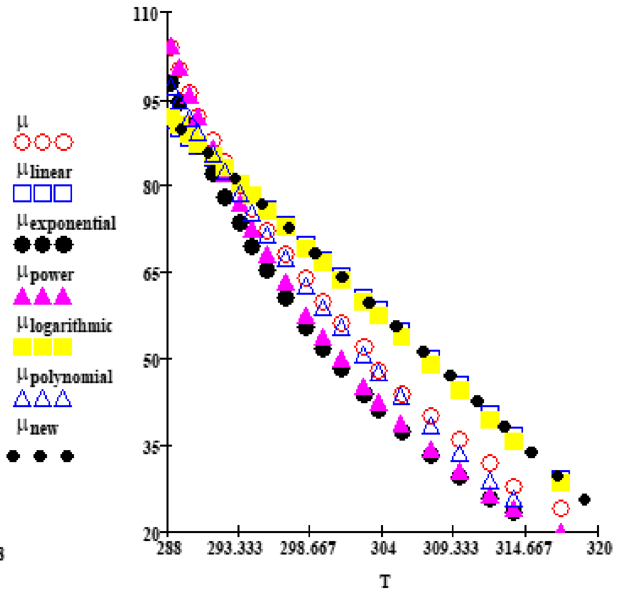

**Figure 2:** Canola oil-based polyols

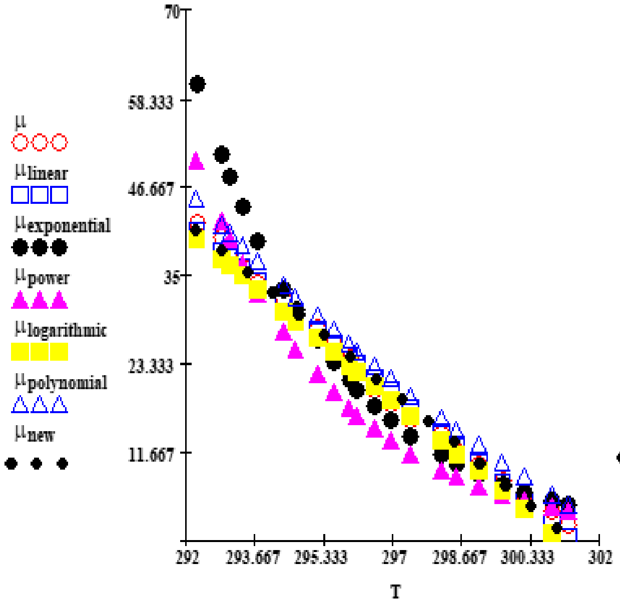

**Figure 3:** Linseed oil-based polyols

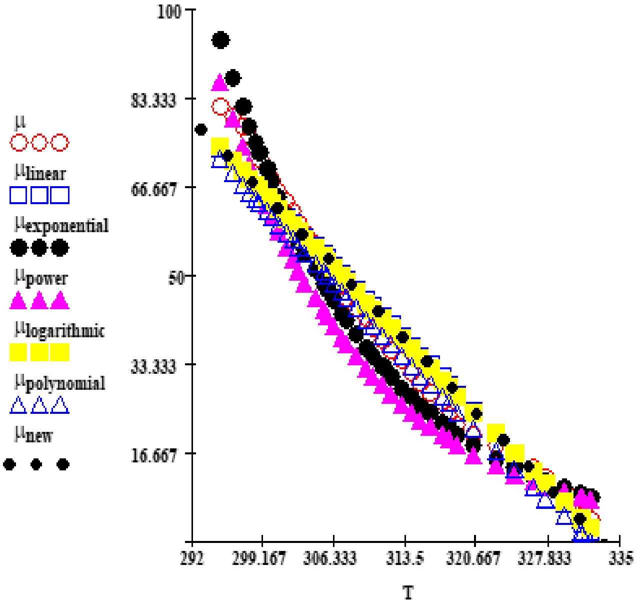

**Figure 4:** Corn oil-based polyols

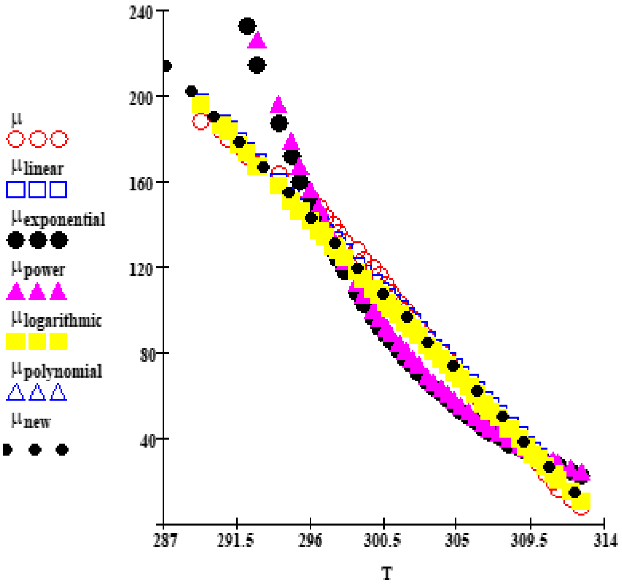

**Figure 5:** Cottonseed oil-based polyols

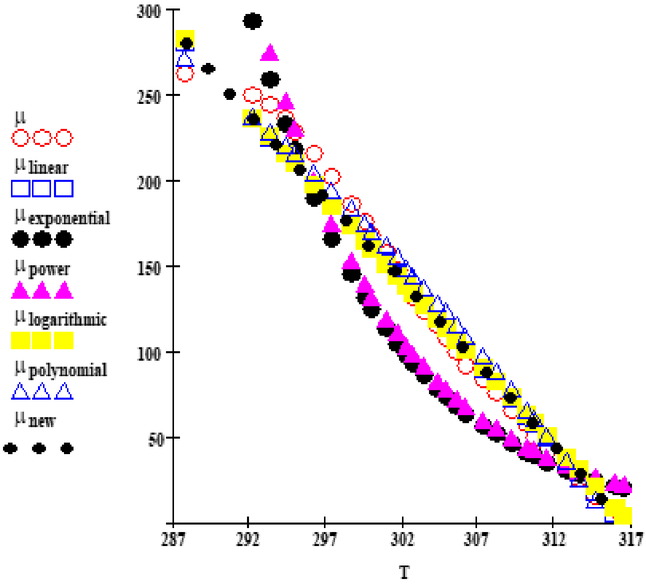

**Figure 6:** Soybean oil-based polyols

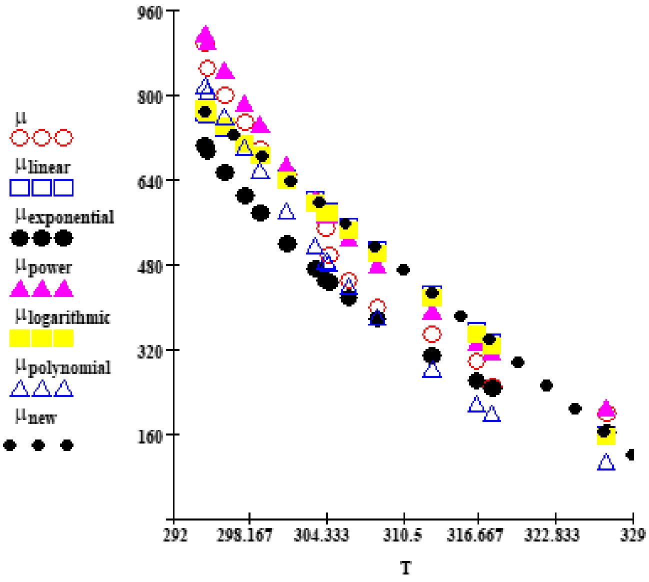

**Figure 7:** Commercial polyols

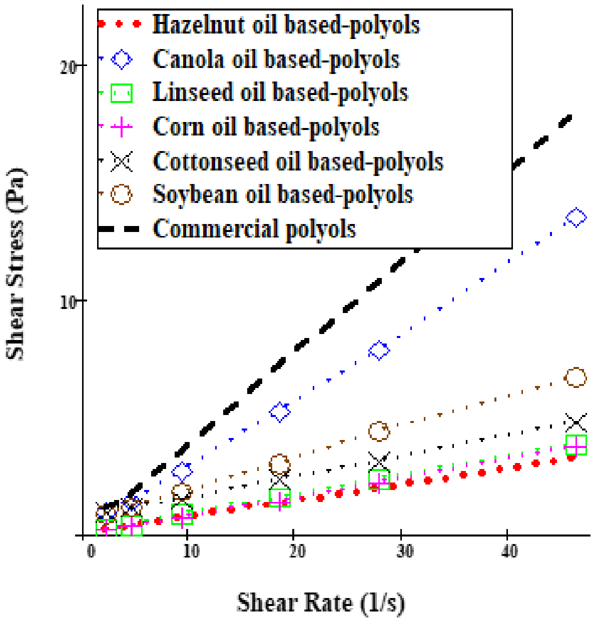

**Figure 8:** Shear stress vs. shear rate

## RESULTS AND DISCUSSION

In this study, the temperature dependence of the viscosity of the vegetable oil-based polyols; model equations compared with experimental data. In Figures: 1, 2, 3, 4, 5, 6 and 7; the variations of apparent viscosities of polyols as a function of temperature were examined by using various model equations which were compared with experimental results. Operating temperatures of the assay were measured by raising temperature stepwise in a water bath. The viscosities of vegetable oil-based polyols were measured by different rotational speeds at an increasing order. According to the experimental results regression coefficients of model equations (4), (5), (6), (7), (8) and (9) were determined.

In present study, variations of viscosities of soybean oil, cottonseed oil, corn oil, hazelnut oil, canola oil, linseed oil-based polyols and commercial polyols were determined a function of temperature. As expected that the viscosity of the fluid decreases as temperature increases. The tested polyols showed Newtonian and non- Newtonian fluids behavior at certain temperature range.

As can be seen in Figures (1), (2), (3), (4), (5), (6) and (7) the viscosities of all types polyols irrespective of their production sources decrease substantially with increasing temperature. Heating may rupture molecular entanglement and bonds, which may stabilize the molecular structure and reduce the effect of molecular volume in the vegetable oil-based polyols. In other words, as temperature increases, thermal energy of molecules increase and molecular distance develops due to reduction of intermolecular forces, hence viscosity of the fluid decreases.

When thermal energy of molecules increases, molecular entanglement aligns easily and molecular structure stabilizes quickly since the molecules with high thermal energy move over one another easily.

As can be seen in Figure 8 the highest viscosity belongs to the commercial polyols while the lowest viscosity belongs to the polyol obtained from the raw hazelnut oil. The viscosities of polyols from high to low can be put in order as $\mu_{commercial} > \mu_{canola} > \mu_{soybean} > \mu_{cottonseed} > \mu_{Linseed} > \mu_{corn} > \mu_{hazelnut}$, here $\mu_{commercial}$, $\mu_{canola}$, $\mu_{soybean}$, $\mu_{cottonseed}$, $\mu_{Linseed}$, $\mu_{corn}$ and $\mu_{hazelnut}$ denote the viscosities of commercial polyol and polyols obtained from raw canola oil, soybean oil, cottonseed oil, linseed oil, corn oil and raw hazelnut oil, respectively. Furthermore, it can be seen that all types of polyols show almost Newtonian behavior.

The regression coefficients and correlation coefficients of each model equation for each polyol obtained from different vegetable oils are given Tables 1., high values of R-squared were obtained for polynomial model irrespective of polyols obtained sources. Moreover, the new (suggested) model has the highest values for R-squared.

In addition, density of vegetable oil based-polyols was measured to be 880 and 910 kg/m$^3$.

The petroleum-based polyols and vegetable-based polyols have different hydroxyl numbers. The hydroxyl numbers of vegetable-based polyols were optimized by varying temperature, reaction time and catalyst.

The model equations and experimental data were compared with one another in terms of the temperature dependent-apparent viscosities of vegetable oil-based polyols. According to the experimental data; the linear and non-linear regression were made to determine coefficients of regression in the model equations.

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