The Production of Polyurethane from Waste Vegetable Oil-Based Polyols and Modelling of Rheological Properties

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Abstract

Polyols in polyurethane production is of great importance. The future will increase the production of polyols from renewable sources. The result of the reduction of fossil fuels will be important in the use of renewable resources. Especially important alternative which will expand polyols production from vegetable oils. Polyols derived from vegetable oil will be produced by epoxidation, hydroxylation and purification.

In this study, the waste vegetable oil based polyols were produced the polyurethane with the catalysts. The thermal conductivity, density and mechanical properties of polyurethane were investigated. Also the produced polyols compared with commercial polyols with rheological properties as viscosity, temperature, shear stress, shear rate. The rheological properties of the polyols were modelling with developed equations based on experimental data.

Key Words: Waste Vegetable Oil, Polyols, Polyurethane, Rheological Modelling.

1. Introduction

Polyurethane, low thermal conductivity, easy to use, flexibility, high mechanical strength, it is preferred in many fields. Polyols are the most important of the polyurethane industry. But the world's oil supply is decreasing rapidly with each passing day. Therefore, an inquiry from renewable sources that can replace the petroleum-based polyol. The common view is that the natural plant and animal oils of alternative raw materials.

Studies in the literature have epoxidized oil-based polyether polyol instead of soy-based polyols were produced using the vegetable oil.

Compared to petroleum-based polyols in polyurethane production from vegetable oil polyol produced with a smaller amount of isocyanate used. The polyurethane produced with the polyol produced from vegetable oil decreased compression resistance [8].

The polyurethane material in the work they added crystallized calcium carbonate and silica particles. It has been shown to becomes smaller the size of filler by adding the closed spherical cells. Mechanical properties of polyurethane materials were modeled. Moreover, the effect of the particle size of the filler was investigated [11].
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. Increasing the filler had negative impact on the effective thermal conductivity. Effective thermal conductivity compared to commercial polyurethane material of the castor oil-based polyurethane material has been found to be lower. Increasing the filler has negative impact on the effective heat transfer coefficient. Density polyurethane material has been found to be between 36 and 39 kg/m³. TGA value of the thermal stability of the castor oil-based polyurethane material has been found to be more commercially polyol product [12].

Boron organic compounds were used as filler in polyurethane production. Boron organic based - polyurethane compounds was observed that decrease with the increase friability. Boron organic compounds rates were seen to increase with the increase of compressive strength. The softening temperature has been found that increasing the content of boron organic compounds fell from 230 °C to 180 °C [16].

2. Material and Method

The polyols were produced from the waste vegetable oils in three steps which were epoxidation, hydroxylation and purification. The temperature of the system was kept under the control every steps. When it was reached to the desired reaction temperature, the peroxides added into the vegetable oils in acidic medium by the aid of dropping funnel in the certain time. After the reaction was completed, the mixture was taken for a while the mixture was separated in two phases with the upper phase of the epoxidized vegetable oil. After the epoxidation step, neutralization with water and the hydroxylation was starting. Especially hydroxylation with alcoholysis preferred frequently in the production of polyols. The purification process was being carried with rotary evaporator to get rid of impurities such as water, heptane and etc. The polyols produced from the vegetable oil was being used in the production of polyurethane by checking the number of hydroxyl. The structure of the hydroxyl compounds was investigated with the FTIR spectrometer. In pre-trials the polyols used for the production of polyurethane were produced vegetable oil-based polyols.

After the reaction was completed, the mixture was taken into separatory funnel and after for a while the mixture was separated in two phases with the upper phase of the epoxidized vegetable oil. After the epoxidation step, neutralization with water and the hydroxylation was starting. Especially hydroxylation with alcoholysis preferred frequently in the production of polyols. The purification process was being carried with rotary evaporator to get rid of impurities such as water, heptane and etc. The polyols produced from the vegetable oil was being used in the production of polyurethane by checking the number of hydroxyl. The structures of the hydroxyl compounds were investigated with the FTIR spectrometer. In pre-trials the polyols used for the production of polyurethane were produced vegetable oil-based polyols. The polyurethane produced from the different resources is being compared one another in terms of thermal properties. The thermal properties of the polyurethane produced from the vegetable oils have improved by trying to use different type of catalyst. The improvement in the thermal properties of polyurethane is quite important in terms of energy efficiency since polyurethane was used for insulation in the building.
Polyurethane catalysts help to improve the mechanical and thermal properties and are asked to contribute to the economy by reducing dependence on foreign raw materials towards polyol synthesized from vegetable oil. It also created to compare the actual results with theoretical models and the damage to the environment of raw materials used in production are intended to minimize.

The goal of this study was to determine the rheological properties and modeling for polyols 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 the viscosity of raw materials. Data obtained from apparent viscosity and rotational speed were used to describe the flow behavior by the model equations both in the forward (increasing shear rate) and backward (decreasing shear rate) - measurement.

3. Mathematical Model

Brookfield rotational viscometer (Model DV-II, Brookfield Engineering Laboratories) equipped with different spindles 21 - 28 were used. Enough samples in a 8 - 12 mL beaker were used to immerse the groove on the spindle with guard leg. Temperature is maintained using thermostatically controlled electrical system. Shear rate (α) and shear stress (τ) were calculated using the apparent viscosity (μ) and speed (N: rpm) in the following equations:

\[ \alpha = 0.209N \]  \hspace{1cm} (1)
\[ \tau = \mu \cdot \alpha \]  \hspace{1cm} (2)
\[ \tau = k \cdot (\alpha)^n \]  \hspace{1cm} (3)

Where; N is rotational speed (rpm), \( \tau \) is shear stress (Pa), \( \mu \) is the apparent viscosity (mPa.s), \( k \) is the consistency coefficient (mPa.s) and \( n \) is flow behavior index (dimensionless).

\[ \mu_{\text{linear}} = A \cdot T + B \]  \hspace{1cm} (4)
\[ \mu_{\text{exponential}} = C \cdot \exp(D \cdot T) \]  \hspace{1cm} (5)
\[ \mu_{\text{power}} = E \cdot T^F \]  \hspace{1cm} (3)
\[ \mu_{\text{logarithmic}} = G \cdot \ln(T) + H \]  \hspace{1cm} (4)
\[ \mu_{\text{polynomial}} = I \cdot T^2 + J \cdot T + K \]  \hspace{1cm} (5)
Figure 1: Polyols produced from canola oil; the effect of temperature on viscosity, comparison with model equations, the change of shear rate ($\alpha$) and shear stress ($\tau$).

Figure 2: Polyols produced from corn oil; the effect of temperature on viscosity, comparison with model equations, the change of shear rate ($\alpha$) and shear stress ($\tau$).
Figure 3: Polyols produced from cottonseed oil; the effect of temperature on viscosity, comparison with model equations, the change of shear rate (α) and shear stress (τ).

Figure 4: Polyols produced from soybean oil; the effect of temperature on viscosity, comparison with model equations, the change of shear rate (α) and shear stress (τ).

Figure 5: Polyols produced from hazelnut oil; the effect of temperature on viscosity, comparison with model equations, the change of shear rate (α) and shear stress (τ).
4. Results and Discussion

Several types of polyurethane structures were produced with the waste vegetable oil based polyols. The effective thermal conductivity in these structures was measured. The influences of the thermal conductivity of polyurethane, the gasses, the porosity, the size and spatial distribution of pores on the effective thermal conductivity of these structures were analyzed. The results indicated that the effective thermal conductivity of the polyurethane measured between 0.020 W/mK and 0.030 W/mK. Effective thermal conductivity was measured TLS 100 instrument with used method of ASTM D5334.

Waste vegetable oil based polyols in different ratios were added into the petroleum-based polyols. Our experiments produced polyurethane mechanical properties decreased with increasing waste vegetable oil based polyol ratios. In experimental studies of the polyols derived from vegetable oil
by looking at the number of hydroxyl bonds, and optimizations was made. Waste vegetable oil-based polyols increases in the number of hydroxyl polyurethane bonding is stronger. Polyurethane was, density between. The density of the polyurethanes that produced waste vegetable oil-based polyols were between 18 kg/m³ and 55 kg/m³.

In addition, the temperature dependence of the viscosity of the vegetable oil-based polyol; model equations and compared with experimental data. Figures: 1, 2, 3, 4, 5, 6 and 7; the temperatures in the polyols as shown in the variation of absolute viscosity were compared with model equations and experimental datas. Operating temperatures of the assay were measured by raising temperature stepwise in a water bath. According to the experimental datas; model equation (1), (2), (3), (4), (5), (6) and (7) with the help of mathematical model, was determined.

In this study, Soybean oil, cottonseed oil, corn oil, hazelnut oil, canola oil, linseed oil-based polyols and commercial polyols change of viscosity with temperature were observed. It is known that the viscosity of the fluid decreases as temperature increases. Working in polyols showed Newtonian and non-Newtonian fluids behavior at certain temperature range. According to the experimental data; The model equations were consistent mathematical model comparing the linear and non-linear it has been determined by regression.

References


