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The selection reaction of homogeneous catalyst in soy-epoxide hydroxylation

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Abstract. Hydroxylation reaction of soy-epoxide has resulted soy-polyol; a prepolymeric material for polyurethane. The conversion and selectivity of soy-epoxide butanol based to hydroxylation was found higher than soy-ethylene glycol (EG) based. These reactions were performed by sulfur acid which commonly known as homogeneous catalyst. Conversion and selectivity of homogeneous catalyst compared to bentonite; a heterogeneous catalyst was lower as in fact the mixtures were more viscous. The catalysis were significantly effected to cell morphology. Foams were conducted by heterogeneous catalyst resulted an irregular form of windows while homogeneous catalyst are more ordered.

Keywords— polyurethane, conversion, selectivity, soybean, catalyst

1. Introduction

Increasing concerns about the environment and renewable resources are fueling a growing worldwide research effort which bringing significantly economic and scientific importance which impacted to reducing the dependence on fossil fuels which are rapidly being exhausted [1-2]. Vegetable oil-based products are well-known as being environment-friendly, abundant, cheap in cost, and excellent properties. The products can be developed and utilized for valuable polymeric materials [3-5].

Vegetable oils are part of larger family of chemical compounds known as fats or lipids, which made up predominantly of triesters of glycerol with fatty acids which can be processed into high value oleochemicals for various industries [6]. The composition of fatty acids contained in the vegetable oils determines the further use of oils; the conversion of oil seed crops into bioplastic could compete with plastics from petroleum chemicals [7-9]. Transformed of fatty acids into polyol through double bonds epoxidation and oxirane ring opening are used in many industries as an additives for polymers as well as composites [10], which have attracted attention for a multitude of plastic products, including polyurethanes [11-14]. The oils are characterized by their oxirane number and hydroxyl value.

Polyurethanes produced from vegetable oils; soybean-oil as well has presented some excellent properties such as hydrolytic and thermal stability. The preparation of polyols from oils have been the subject of many studies but limited attention has been paid to the effect of different alcohols to be used as the ring opening reagents for soy epoxide oil [15-16]. The hydroxyl groups are located in the middle of fatty acid chain resulting a significant steric hindrance to crosslinking. The method of using either electrophiles or nucleophiles, or catalyzed by either acids or bases. Epoxidation with peracetic acid is generally catalysed by soluble mineral acids like sulfur [17]. The reactions catalysed by clays



would be an alternatives which were carried under mild conditions. The separation of the spent catalyst is achieved by filtration, and the product is recovered by mere evaporation of solvent. Catalyst used in polyol production for discontinuous batch process for a common practice is sulfur acid [18]. The effectiveness of catalyst in promoting reaction to ethylene glycol (EG) and n-butanol were found 15.6% respectively at same condition [19].

The optimum conversion of epoxide to polyols of using homogeneous catalyst were found at the previous, by temperature 50C was 150 minutes of reaction, while at 60C was 90 minutes of reaction. The best oxirane number found at this conditions was 6.7 (%) [20].

This paper report works to find out the reaction conditions that allows the addition of different alcohols to epoxidized vegetable oils in maximizing selectivity with the used of homogeneous catalyst as well as heterogeneous in polyurethane synthesis. The reason of using EG and butanol, besides performing as chain extender it is also performed as source of hydroxyl others than soy-polyol.

2. Materials and Methods

2.1 Material specifications

Soy-oil based polyols used in this study were been synthesized in our laboratory using hydroxylation of epoxide methods. Sulfur acid catalysed were carried in the reaction in accordance to a known procedure to a peracetic acid *in situ* which generated from peroxide and acetic acid. The soybean-oil was purchased from grocery, is the product of Variatama Jakarta with specifications of acid value 0,024 mgr KOH/ gr sample, Iodine value 53,89 gram Iod/100 gr sample, and viscosity 443.007 cps.

3. Result and Discussion

3.1. Preparation of Flexible PU Foam

Hydroxyl groups were introduced by applying two-step methods involving epoxidation of unsaturated chain followed by epoxide ring opening. Chain extender (ethylene glycol, butanol) were taking part in the epoxidations and the amount of catalyst to be used is 1% (v/v). Bentonite was used as the comparative data. The role of these catalysts to polyurethane properties were evaluated.

Polyurethane was prepared using formula by fixing molar ratio of epoxide to chain extenders [1:1]; [1:3]; [1:5]; [1:6] and [1:10] then adding TDI (2.4): MDI (4.4') (80:20) into polyols. The mixtures were vigorously mixed to surfactant and distilled water, which then poured into an open glass mould. The foams removed from the mould and allowed to postcure for one day at room temperature. Oxirane number indicates the epoxide ring has completely reacted in hydroxylation reaction resulted hydroxyl.

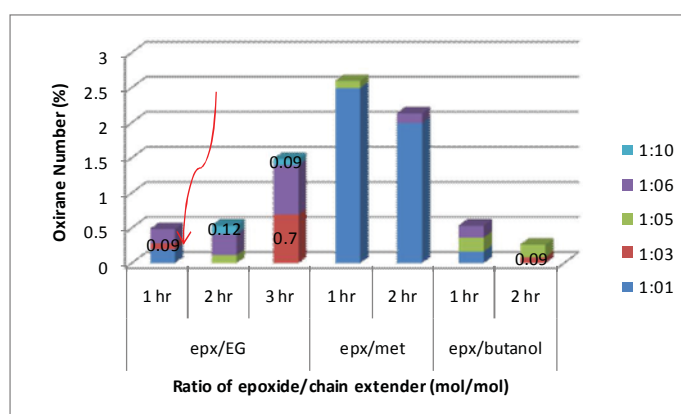


Figure 1. Time of reaction Optimization

The reduction of oxirane number of polyol would be caused by increasing hydroxyl value. As can be seen in figure 1. The lowest oxirane number was achieved at concentration of epoxide/ethylene glycol (1:3) at 1 hour and three hour reaction and also at two hour for ratio of epoxide/butanol. Concentration (1:3) was used as based formula for proceed reactions. Hydroxyl value of butanol using sulfur and bentonite are 549.7 mgr KOH/gr and 710 mgr KOH/gr respectively, as compared to EG was 308.5 mgr KOH/gr. High hydroxyl value would cause high consumes of catalyst if further processed to urethane foams.

One of the apparent differences between butanol and EG, which butanol has secondary hydroxyls while EG has only primary hydroxyls. Selecting of polyols for foaming it is well understood that primary hydroxyl are preferred for molded foam process, because the speed up gelling reaction.

3.2. The Catalytic Studies

The effect of polymerization catalyst is illustrated in Figure 1, keeping the weight of sulfur acid at constant for the whole reactions. The product results were compared to as if it is being catalysed by bentonite.

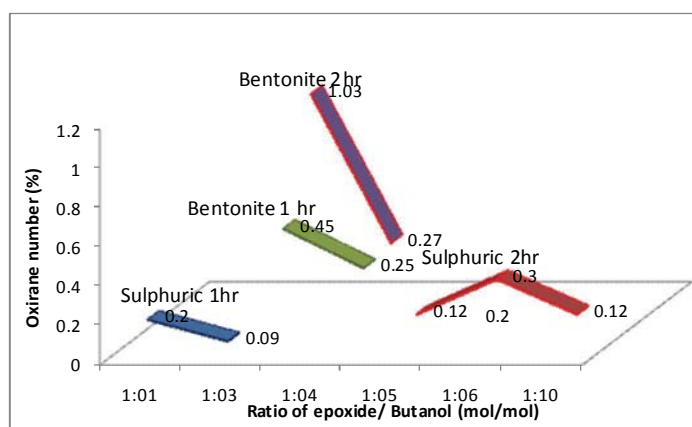


Figure 2. Comparative catalysis existence of epoxidation

Results of the epoxidation of fatty acid catalyzed by H_2SO_4 are displayed in figure 2 and figure 3, with the temperature of $60 \pm 0.5^\circ C$. These figures have clearly explained the conversion and selectivity of epoxidation using butanol are higher than EG.

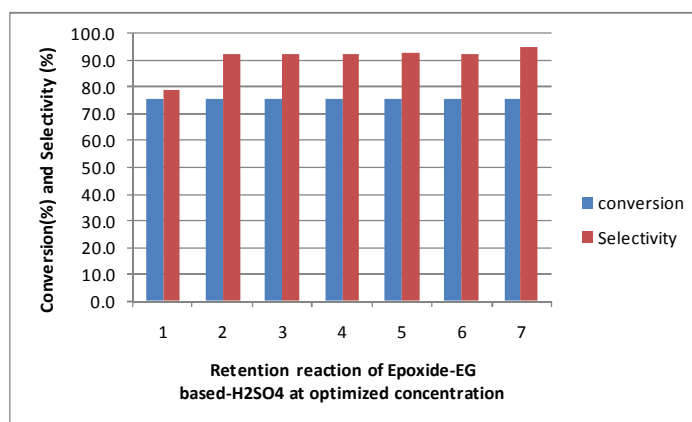


Figure 3. Epoxidation of EG- based with H_2SO_4

The glycols produced as the result reaction of water to epoxide, its formation were favoured by a lower crosslinking. Butanol although has high crosslinking will gives poor selectivity due to glycol formation. The low selectivity were assumed to happened with the decrease of cross-linking.

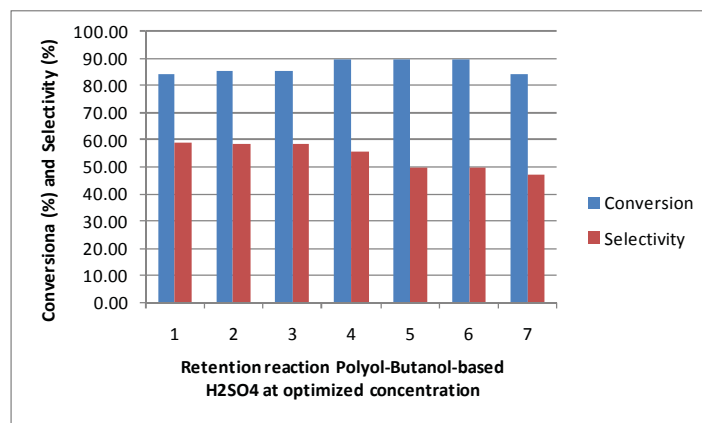


Figure 4. Epoxidation of Butanol-based with H₂SO₄

The viscosity of polyol butanol-based using sulfur acid catalyst were 569.43 cps while viscosity of polyol EG-based using sulphuric acid were 30.55 [21], logically viscous mixture will find difficulties in the reactions, but referred to this founding the viscosity seems is not effected to conversions and selectivity. For α and β branched alcohols it was possible to improve the selectivity that shown in figure 4. Less complex alcohols it was possible to obtain 100% selectivity at 100% conversion.

The hydroxyl value of polyol butanol-based using sulphuric acid is 549.65 mgr KOH/gram and as compared to hydroxyl value of polyol butanol-based using betonite catalyst is 710.91 mgr KOH/gram. These differences are met of reactivity and selectivity of the catalyst itself.

3.3. Characterization and Property Measurement of Polyurethane (PU) Foam

The obtained PU foams were characterized by using density measurement, the foams were cut into specimens with dimension of 1x1x1 cm. The specimens were accurately weighed using equation, density = mass/ volume. The density for each foam was ascertained using average value. Many factors and conditions can influence the foaming process of flexible cellular polyurethanes.

Natural oils polyols are significantly different from petroleum-derived polyols, the hydroxyls located in the center of polyol chains. Compared to mostly petroleum-derived polyols, which have either primary hydroxyls and secondary hydroxyls with only one covalent bond removed from the chain ends while for natural oil converted from single oil molecule are most likely to be 5-8 covalent bonds removed from the chain ends, this stated as disadvantages for natural polyol with respect to gelling reaction.

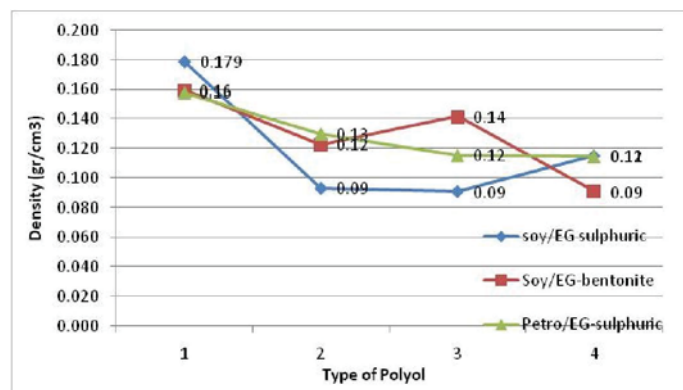


Figure 5. The density of different type of PU Foam

However the theoretical review can be voided to the finding of bentonite as displayed in figure 5. According to Chan-tu there are relationships between foams density and hydroxyl value, foams are made from vegetable oil-based polyols with hydroxyl value below 100 mgr KOH/gram, or polyol mixture having OH_m lower than 292 usually shrank within days of storage [22].

We have tried to analyse the data using outlier test, the possibility of existence density data of soy/EG using sulfur at 0.09 and 0.179, and for soy/EG using bentonite at 0.12 are not in the range distribution to the rest data by using Grubbs's (G) equation [23]. ($X_{suspect}$) values are considered to be at the extremes of the data, \bar{x} ; mean of the data, and s standard deviation.

$$G = \frac{|x_{suspect} - \bar{x}|}{s} \quad (1)$$

For soy/EG sulfur the $x_{suspect}$ was 0.09 with $G_{suspect}$ 0.7156 and $x_{suspect}$ 0.179 with $G_{suspect}$ 1.44 and for soy/EG bentonite the $x_{suspect}$ was 0.12 with $G_{suspect}$ 0.1142. G value then compared to tables of critical for G at $\alpha = 0.05$, If $G_{suspect} > G_{critical}$ then the suspect can be rejected. From this investigation all of the $G_{suspect} < G_{critical}$. It means that all previously $x_{suspect}$ data are in the range of foam density.

The density of using heterogeneous is seem to be much promising. It works in the surface acidity which promotes to an optimum hydroxylation reaction. Although surface area of catalyst are very critical to determine the catalytic site, but it was suitable for the soy-polyol synthesis.

3.4. Cell Morphology

SEM micrograph using of cured solid polyurethane were examined and the average cell diameter are shown in figure 5 a,b and figure 6 a,b. The foam occurred by homogeneous (sulfur) catalyst at previous hydroxylation has large average cell size with widen cell size distribution. However the cell was in ordered form. Using heterogeneous (bentonite) catalyst in the synthesis has resulted an irregular form.

The hydroxyl value are related to gelling reaction, using heterogeneous is found to be higher than homogeneous. In extreme case the slow gelling reaction could cause foam to collapse during curing. The selectivity obtained using bentonite is poor, value below 40% is implied to incompleteness of soybean-oil conversions. The foaming process evidently did not change, however the final morphology unveiled by the characterization study.

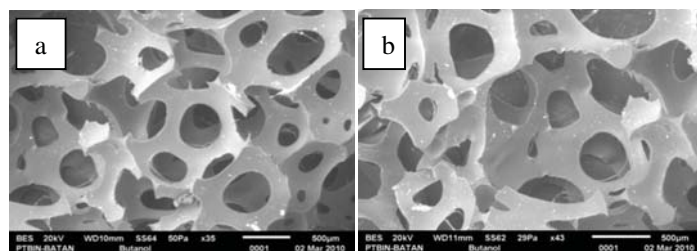


Figure 5 a,b Images of Polyurethane foam using H₂SO₄ catalyst

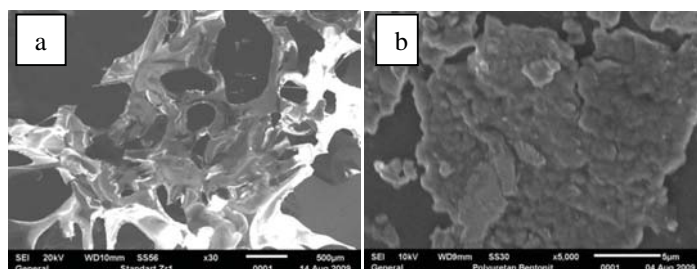


Figure 6 a,b Images of Polyurethane foam using bentonite catalyst

Conclusions

It is found the type of catalyst in polyol synthesis are effected to density, cell morphology, and to other properties of polyurethane as well. The aim of using alcohols in the polyol synthesis are synergize to the optimum existence of catalysis. Catalyst performance in natural oil can void the doubt of using soy-based for future polyurethane manufacture, which can replace petro-based polyol.

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