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Synthesis and Characterization of Novel Castor Oil-Based Polyol for Potential Applications in Coatings

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Abstract: In this study, three sorts of polyols were successfully synthesized from castor oil using a Dean-Stark quick, eco-friendly and high-efficiency method. For this purpose, castor oil was epoxidized in the presence of two types of catalysts including γ-alumina and formic acid, named as ECO_{Al} and ECO_F, respectively. Epoxidized castor oils were then characterized by use of hydrogen nuclear magnetic resonance (H-NMR) and oxirane oxygen content analysis. The relative percentages of conversion double bond to oxirane were obtained 96% and 74% for ECO_{Al} and ECO_F, respectively. Ring opening reaction of ECO_{Al} was performed by two types of saponified castor oil as well as castor oil in a system equipped with Dean–Stark apparatus. The synthesized polyols were characterized by attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), gel permeation chromatography (GPC), differential scanning calorimetry (DSC), viscometer and OH number evaluation. The material obtained in this research is a candidate to be intended in synthesis of polyurethane for coating applications.

Keywords: Castor oil; dean-Stark; polyol; epoxidation

1 Introduction

After replacing water with petroleum solvents and producing water-based polymers, the researchers attempted to replace other petroleum components of polymer products with renewable materials. In fact, concerns regarding petroleum depletion and the growing cost of oil, as well as the environmental impact of nonrenewable, petrochemical resources, have led to an increased interest in alternative, sustainable, environmentally friendly materials based on renewable resources in various industries, including the polymer industry [1]. Renewable resources, such as cellulose, starch, vegetable oil, and sugar, are examples of materials used in the polymer industry [2-5]. Among these materials, vegetable oils such as castor [6-8], canola [9,10] and soybean oil [10-13] are most used as a polyol in the synthesis of polyurethane, because they are inexpensive, readily available and renewable resource.

Vegetable oils are triglycerides of saturated and unsaturated fatty acids. The six most common fatty acids are palmitic (C16:0), stearic (C18:0), oleic (C18:1), linoleic (C18:2), linolenic (C18:3), and ricinoleic (C18:1 OH), acids (in this notation, the first number represents the number of carbon atoms, the second number represents the number of carbon-carbon double bond, and OH represents hydroxyl groups in the fatty acid) [14]. Castor oil is one of the most important triglycerides, which is a viscous, pale yellow, non-volatile and non-drying oil [15] that Because of its medicinal value has been known since ancient days [16]. This vegetable oil has peculiar characteristics, such as its fatty acid composition (90% of ricinoleic acid). This acid has 18 carbon atoms with one hydroxyl in carbon 12 [17]. Its unique structure makes it a very useful vegetable oil in various industries. Castor oil-based polyol, in addition to

its use in polyurethane synthesis, can be used as plasticizer in poly (vinyl chloride) (PVC)-based materials [18]. Also, acylated derivatives of castor oil could be used as biolubricant [19].

In order to produce vegetable oil-based polyol, the hydroxyl groups should be introduced through appropriate chemical modifications on either the carbon-carbon double bonds or the ester functionally present in triglycerides [20]. Almost all synthetic routes such as epoxidation followed by oxirane ring-opening [21], hydroformylation followed by hydrogenation [22], ozonolysis [10,23] and transesterification [24] start from one of these two functional moieties [21].

Epoxidation of vegetable oils, followed by oxirane ring-opening is one of the most common methods to introduce the hydroxyl groups on the carbon-carbon double bonds. In all reported studies, after the opening of the oxirane ring, two further steps include rotary evaporation and drying in a vacuum oven overnight were used to remove impurities.

Epoxidation is performed using an oxidizing agent, usually hydrogen peroxide, in the presence of a catalyst. The use of soluble mineral acids, such as H_2SO_4 [25], as a catalyst leads to the production of harmful byproducts and requires extra steps to remove these byproducts. As a result, in the industry, time and cost of production increase. Also, the use of organic acids, such as formic acid [26], as a catalyst does not have high efficiency. In recent years, the use of heterogeneous catalysts has been considered due to the lack of production of harmful byproducts, high efficiency and also its ability to be reused. Among these catalysts, γ-alumina due to low prices has been more attention [27,28]. In this study, two types of catalysts including γ-alumina and formic acid were used and their efficiency was compared.

Typically, the compounds containing active hydrogen atoms, such as carboxylic acids [29,30], hydrohalic acids [31] and alcohols [32,33] used to ring-opening reactions.

The present work reports for the first time the synthesis three types of castor oil-based polyols using a short, eco-friendly and high-efficiency method. Epoxidation and ring opening reactions were successfully accomplished in succession. The Dean-Stark system was used to remove impurities, which resulted in the elimination of additional equipment and additional steps. Properties of obtained polyols were investigated by ATR-FTIR, GPC, DSC, viscometer and OH number evaluation.

2 Experimental

2.1 Materials and Instruments

Castor oil was purchased from Paras Chemical Industries. Hydrogen peroxide (30%), formic acid, and hydrochloric acid (37%) were bought from Merck, Germany. γ-alumina and ethyl acetate were purchased from Sigma-Aldrich. Sodium bicarbonate and potassium hydroxide were bought from PubChem. All materials were analytical grades and used as received without further purification. In this study, the Dean-Stark system was employed after epoxidation stage.

2.2 Epoxidation of Castor Oil

Castor oil, hydrogen peroxide (30%) as the oxidizing agent and catalyst either γ-alumina or formic acid were loaded into a 500 ml three-necked round-bottom flask, equipped with a mechanical stirrer and nitrogen flow. This flask was then immersed in glycerin and heated up to 85°C while stirring vigorously. The molar ratio of the reaction mixture was prepared as follows:

The molar ratio of hydrogen peroxide to double bonds in triglyceride was set in 1.8:1. The molar ratios of hydrogen peroxide to γ-alumina and formic acid were also set in 1:0.3 and 1:1, respectively. It should be noted that the high amount of peroxide has a negative effect on the stability of epoxy group. The reaction mixture was stirred for 4 hours. The aqueous solution of sodium bicarbonate and ammonia was used to adjust the pH of reaction of 2 to 7. After neutralization of the mixture, ethyl acetate (1.5 times of the castor oil weight) and water (equivalent to the weight of castor oil) were added to the reaction mixture. After 5 minutes, silica gel was incorporated into the mixture in order to have two phases separated immediately. The upper and lower phases were respectively opaque-oily and transparent, as illustrated in

Fig. 1. These phases were then manually separated using a filter. The solid content of the oily phase was 45% to 50%. In fact, this phase was the epoxidized castor oil, consisting of water and ethyl acetate as the impurity. Due to the use of the Dean-Stark system in the next step of reaction, further purification and drying were not required. Based on the catalyzer employed, the as-prepared epoxidized castor oil is herein after referred to either ECO_{Al}, catalyzed by γ-alumina, or ECO_F, catalyzed by formic acid. In virtue of higher efficiency of ECO_{Al} than ECO_F, it was employed to synthesize polyol in the next step of reaction.


Figure 1: The phase separation in bilayers after adding silica gel at the end of the epoxidation process

2.3 Saponification of Castor Oil

Fatty acid existing in castor oil can be obtained by either saponification or fractional distillation of hydrolyzed castor oil. In saponification process, amount of saponifying agent deeply affects the efficiency of process. In this study, potassium hydroxide was employed as saponifying agent in two different molar ratio, either equal to or in excess of the stoichiometry. The saponified triglycerides were named as SCO_{Eq} and SCO_{Ex}. Briefly, castor oil and an aqueous solution of potassium hydroxide were heated at 55°C and neutralized by diluted hydrochloric acid. After neutralization, ethyl acetate and silica gel were added into the mixture and two phases formed were manually separated.

2.4 Ring Opening Reaction of ECO_{Al}

Ring opening reaction of ECO_{Al} was performed by means of not only the saponified castor oils (SCO_{Eq} and SCO_{Ex}) but also castor oil. The molar ratio of epoxy group to carboxyl group had been set at 1.2:1. The entrance of round-bottom flask had been equipped with a Dean-Stark system. In fact, the Dean-Stark system removes impurities like water and ethyl acetate from the mixture of reaction. As a result, this system will not require additional equipment such as rotary evaporation or steps like overnight in a vacuum oven. This is the first attempt to use Dean-Stark system for producing vegetable oil-based polyol. The schematic of the Dean-Stark system is illustrated in Fig. 2.
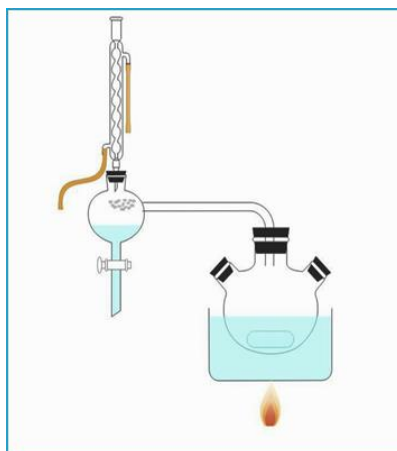
Figure 2: The schematic of a Dean-Stark system

The impurities began to exit from the system at 77°C, which is the same Boiling point of ethyl acetate. Last of all, in order to produce polyol, the reaction mixture of the round-bottom flask was heated in a glycerin bath at 170°C for 5 hours. The obtained polyols from the reaction of ECO_{Al} with SCO_{Eq}, SCO_{Ex} and castor oil were named as $PSCO_{Eq}$, $PSCO_{Ex}$ and PCO, respectively. The solids content of all samples was over 99%.

3 Characterization

AOCS official method Cd 9-57 and standard test method D4274-99 were used to determine oxirane oxygen content (concentration of oxirane groups) of epoxidized castor oils and OH group of polyols, respectively. H-NMR spectra were recorded on a 400 MHz Bruker instrument using $CDCl_3$. The spectroscopic analysis of H-NMR were used to obtain from the number of carbon−carbon double bonds in the castor oil and epoxy groups in the epoxidized castor oils.

The molecular weights of all specimens were measured using a gel permeation chromatography (GPC Agilent 1100) equipped with refractive index detector (RID). The viscosity of synthesized polyols was measured using Brookfield Viscometer (DV-II, Spindle 5, 25°C). Glass transition temperatures of polyols were measured by differential scanning calorimetry (DSC 6 Pyris-PerkinElmer) at a heating rate of 10°C min^{-1} from -50°C to +150°C. The attenuated total reflectance-Fourier transform infrared spectra (ATR-FTIR) of CO, ECO_{Al} and polyols were recorded using spectrophotometer with a resolution of 4 cm^{-1} (TENSOR 27, Bruker) in the range of 4000 cm^{-1} to 400 cm^{-1} using KBr pellet.

4 Results and Discussion
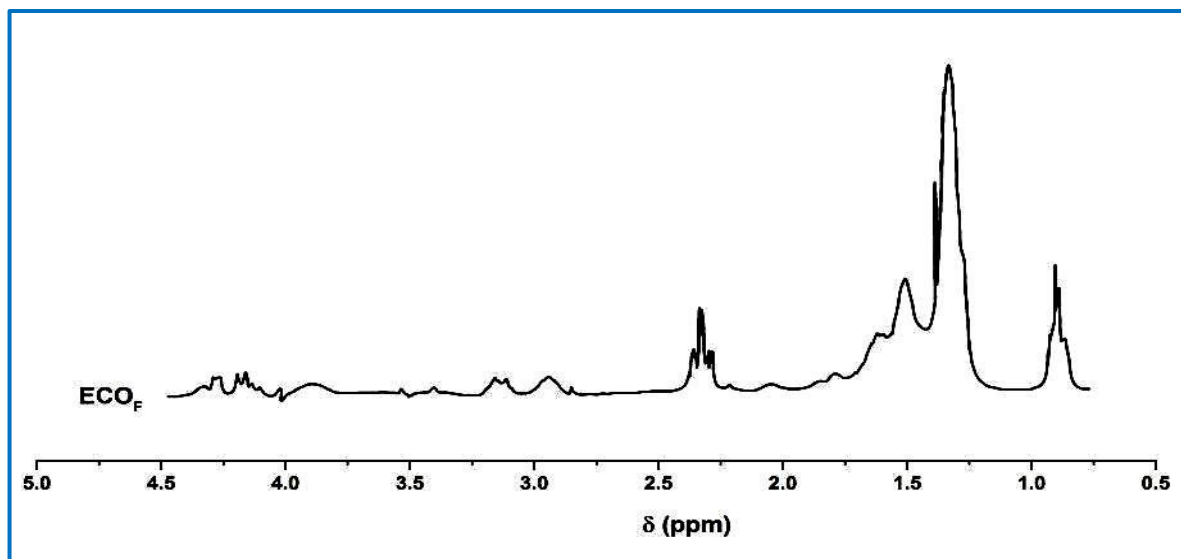
4.1 H-NMR of Epoxidized Castor Oils

H-NMR spectra of castor oil and epoxidized castor oils (ECO_{Al} and ECO_F) are shown in Fig. 3. As can be seen, the H-NMR spectra of castor oil show several peaks between 4.06-4.28 ppm and 5.2-5.25 ppm belonging to the existence of $-CH_2$ and -CH groups in glycerol. Furthermore, the peak of C-H attached to the hydroxyl group appears at 3.52-3.6 ppm. The peak at 5.28-5.5 ppm which belongs to the presence of C=C bond in castor oil disappeared after epoxidation and the peak of epoxy group observed at 2.9-3.2 ppm.
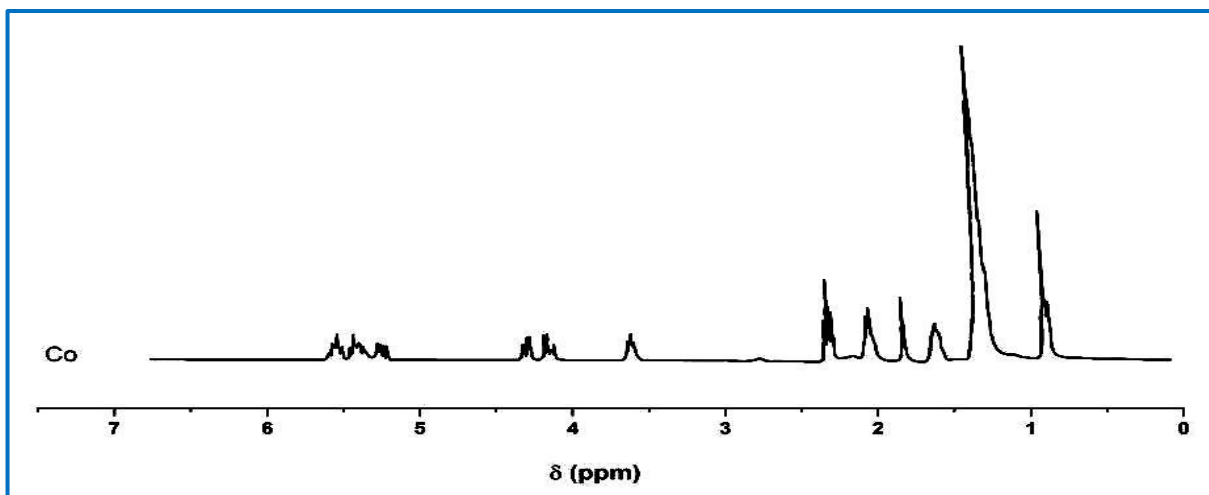
(a)
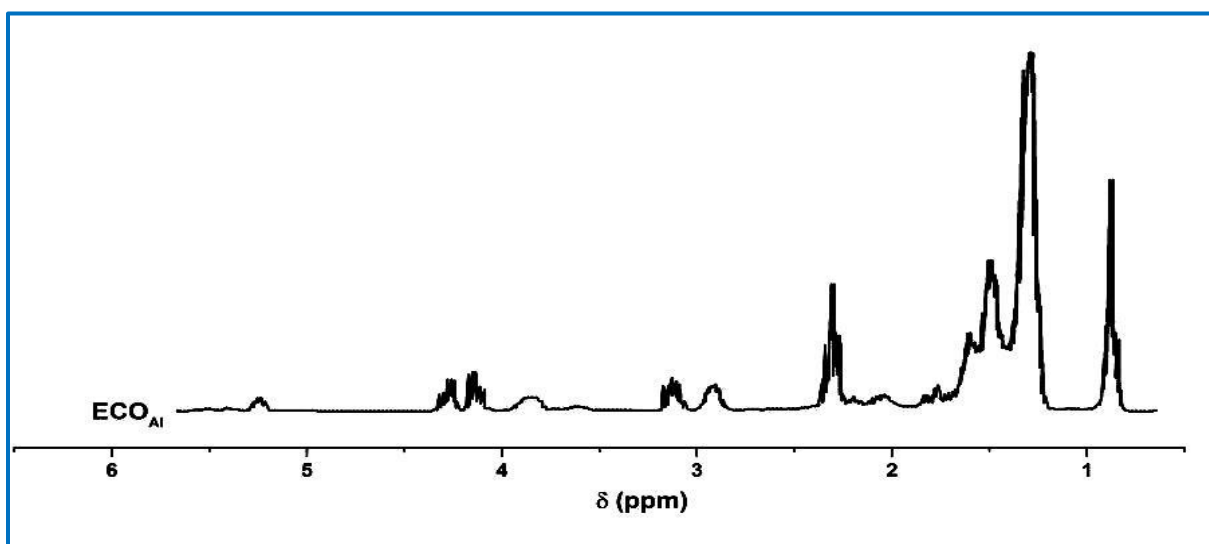
(b)

(c)

Figure 3: H-NMR Spectra of (**a**) Castor oil, (**b**) epoxidized castor oil catalyzed by γ-alumina, (**C**) epoxidized castor oil catalyzed by formic acid

4.2 Effect of Catalyst Type on Epoxidation Efficiency

Each iodine molecule (M_w = 254 g mol^{-1}) neutralizes a double bond in the molecular structure of castor oil (M_w = 928 g mol^{-1}). By calculation, the number of castor oil's carbon-carbon double bonds in the H-NMR and also using Equation reported by the American Oil Chemists' Society, the iodine value of castor oil 83.5 (g I/100 g) was obtained.

The theoretical concentration of oxirane groups in epoxidized castor oil was found to be 5 wt% and the experimental concentration of oxirane groups in ECO_{Al} and ECO_F were calculated to be 4.8 wt% and 3.7 wt%, respectively. Therefore, the relative percentage conversions to oxirane for ECO_{Al} and ECO_F were found to be 96% and 74%, respectively. As a result, the relative percentage conversion to oxirane using γ-alumina catalyst was greater than the formic acid catalyst.

4.3 ATR-FTIR of ECO_{Al} and Polyols

ATR-FTIR spectra of castor oil, ECO_{Al} and polyols ($PSCO_{Eq}$, $PSCO_{Ex}$ and PCO) depicted in Fig. 4, successfully confirms the epoxidation reaction and synthesis of polyols. The FTIR spectra of castor oil show several absorption peaks which can be related to -CH_2 (asymmetric stretching), -CH_2 (symmetric stretching), C-O-C and C = O groups, assigned at 2934 cm^{-1}, 2844 cm^{-1}, 1160 cm^{-1} and 1745 cm^{-1}, respectively. The OH groups of castor oil display a broad peak at 3380 cm^{-1}. The peaks at 1645 cm^{-1} and 3008 cm^{-1} can be ascribed to stretching vibration of C = C and = C-H, respectively. After the epoxidation reaction, the peak belonging to the unsaturated carbon group (C = C) disappeared and an additional peak belonging to epoxy groups revealed at 843 cm^{-1}. By performing the ring opening reaction, the peak of epoxy group disappeared and the intensity of the peak belonging to hydroxyl groups increased, indicating that the epoxy ring is opened and the hydroxyl group is formed.
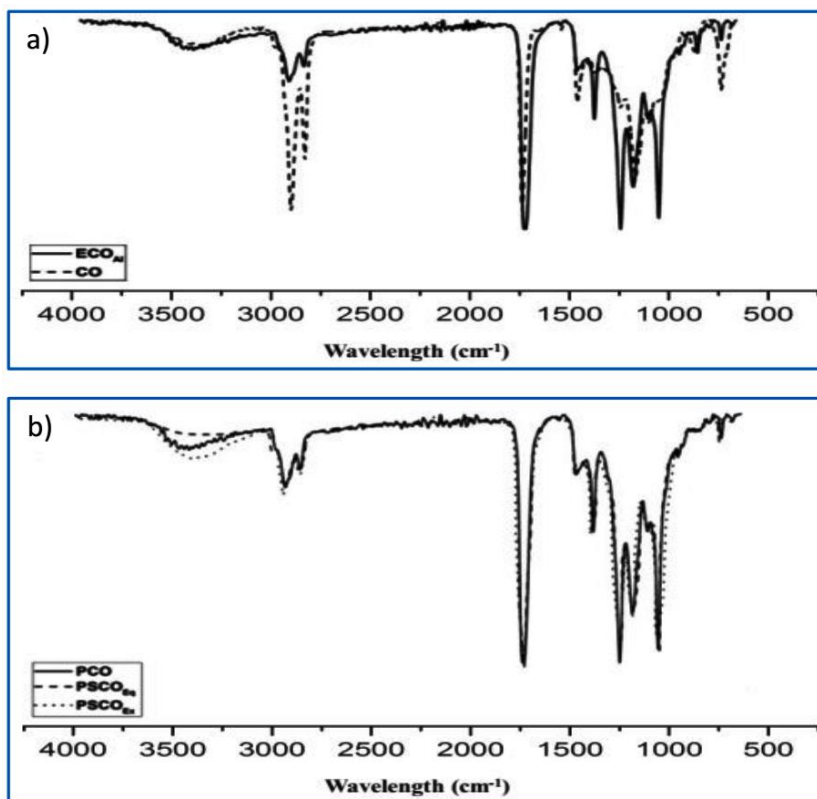
Figure 4: The Spectra of (**a**) Castor oil, epoxidized castor oil catalyzed by γ-alumina (**b**) polyols obtained from the reaction of ECO_{Al} with SCO_{Eq}, SCO_{Ex}, and castor oil

4.4 Properties of Saponified Castor Oils and Polyols

Tab. 1 illustrates the properties of saponified castor oils and polyols. As can be seen, the viscosity of SCO_{Eq} is higher than SCO_{Ex}, which can be attributed to the higher hydrogen bonding and molecular weight. In order to make a comparison between the as-prepared polyols in terms of viscosity, it can be said that as both of $PSCO_{Eq}$ and $PSCO_{Ex}$ have higher hydroxyl groups than PCO. Therefore, expected that they possess higher viscosity by virtue of having higher hydrogen bonding interactions, but results revealed that the higher molecular weight of PCO eclipses this effect and results in the highest viscosity for PCO. Moreover, the higher viscosity of PCO can also be ascribed to the fact that ring opening of epoxide is carried out by hydroxyl groups of fatty acid chain, instead of primary hydroxyls, which leads to an increase in not only the density of cross-links but also the viscosity of PCO.

Comparison of viscosity between $PSCO_{Eq}$ and $PSCO_{Ex}$ sheds some light on the fact that the influence of hydrogen bonding in $PSCO_{Ex}$ is more pronounced than the influence of molecular weight in $PSCO_{Eq}$. In other words, hydrogen bonding and molecular weight compete with each other in order to control the viscosity of the mixture.

The values of glass transition temperature (Tg) of polyols are given in Tab. 1, which is the temperature in the midpoint of the inclined region. Generally, augmentation of hydroxyl groups leads to the increment of the formation of hydrogen bonds and cross-link density. Therefore, the chain mobility decreases and Tg increases. With respect to the low Tg of PCO compared to $PSCO_{Eq}$ and $PSCO_{Ex}$, it is also worth mentioning that castor oil can potentially employ not only as a crosslinker but also as a chain lubricant to facilitate the movement of chains. A slight difference in Tg of samples $PSCO_{Eq}$ and $PSCO_{Ex}$ can be attributed to the reopening reaction of $PSCO_{Ex}$, which is mainly carried out through the primary hydroxyls.

Table 1: Properties of saponified castor oils and polyols

Sample	OH concentration (mg KOH g⁻¹)	Average molecular weight (g mol⁻¹)	OH number	Viscosity (mPa.s)	Tg (°C)
SCO$_{Eq}$	179	386.2	1.23	450	-
SCO$_{Ex}$	186	316.9	1.05	360	-
PSCO$_{Eq}$	429	811	6.2	1800	-6.5
PSCO$_{Ex}$	491	776.9	6.8	2500	-6.9
PCO	58	2675.2	2.76	11200	-37

5 Conclusions

In this study, epoxidation of castor oil was performed by two different catalysts, either γ-alumina or formic acid. The relative percentages of conversion double bond to oxirane were found to be 96% and 74% for γ-alumina and formic acid respectively. The next step was saponification of castor oil using saponifying agent at two different amounts, either equal to the stoichiometry or in excess of the stoichiometry. Then to prepare of polyols, the epoxidized castor oil, which catalyzed by γ-alumina, was reacted with two types of saponified castor oil and also castor oil. In this step, Dean-Stark system was employed, which will not require additional equipment such as rotary evaporation or steps like overnight in a vacuum oven. The OH number of saponified castor oil-based polyol in excess of the stoichiometry was obtained more than the sample equal to the stoichiometry. The OH number of castor oil-based polyol was lower than that of prepared from other samples, it was greater than other samples in terms of molecular weight. Formation of hydrogen bonds, influenced by OH number, along with molecular weight affected the viscosity of polyols, each of which may overcome one another, depending on its severity. Although in the castor oil, performing reaction using hydroxyl group in fatty acid chain increased the cross-link density, but since castor oil acted as a chain lubricant, so castor oil-based polyol had the lowest Tg.

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