

Polyurethane Networks from Different Soy-Based Polyols by the Ring Opening of Epoxidized Soybean Oil with Poly(ethylene glycol)s

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Abstract

Epoxidized vegetable oils have drawn much attention in recent years, especially in the polymer industry as they are economical, available, environmentally friendly, non-noxious and renewable. Epoxidized soybean based polyols are a great alternative for the polyurethane industry in applications where hydrophobicity, hardness, flexibility, and mechanical and chemical resistance are needed: foams, coatings and floorings. In this study, PEG400-ESO soy-based polyols with a range of hydroxyl numbers based on epoxidized soybean oil (ESO) are prepared by oxirane ring opening with poly(ethylene glycol) (PEG400) having the molecular weight of 400g/mol in the presence of tetrafluoroboric acid catalyst. These epoxy ring opening reactions give a range of different structures, which when converted to polyurethanes imparted different properties to the final products. Rigid polyurethane foams are prepared by reacting with synthesized soy-based polyols and polymeric methylene diphenyl diisocyanate (MDI). The effects of reaction temperature and catalyst amount on the PEG400-ESO soy-based polyols were investigated by spectroscopic, chemical and physical methods.

Key words: Epoxidized soybean oils, soy-based polyols, polyurethane, polyethylene glycol

1. Introduction

The new interest in utilization of vegetable oils for industrial use is the result of the public awareness and insistence on sustainability and the need to save the environment. Vegetable oils have been successfully used for polyols in the polyurethane industry [1]. The production of urethane polymers is well known in the art. Urethanes are formed when isocyanate (NCO) groups react with hydroxyl (OH) groups. The most common method of urethane production is via the reaction of a petroleum derived polyol and an isocyanate, which forms the backbone urethane group. Polyester polyols and polyether polyols are the most common polyols derived from petroleum used in urethane production. Sole use of polyols derived from petrochemicals such as polyester or polyether polyols in forming urethane products such as elastomers and foams is disadvantageous for a variety of reasons. Petrochemicals are ultimately derived from petroleum. Accordingly, the petrochemicals are a nonrenewable resource. The production of a petroleum-derived polyol requires a great deal of energy, as oil must be drilled, extracted from the ground, transported to refineries, refined, and other wise processed to yield the polyol. These efforts add to the cost of polyols and to the disadvantageous environmental effects of its production.

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One difficulty with the use of vegetable oil-derived polyols to produce a urethane product is that conventional methods of preparing polyols from vegetable oils, such as soybean oils, do not produce polyols having a significant content of hydroxyl groups. Accordingly, it would be advantageous to develop a method to produce vegetable oil-based polyols having increased reactive hydroxyl groups over conventional polyols derived from a vegetable oil such as blown vegetable oil [2]. The epoxide ring-opening reaction is a widespread method for the functionalization of vegetable oils. Indeed, epoxidation of vegetable oils is an industrial process, mature, well controlled, and little expensive. Epoxide function allows to access different derivatives owing to the variety of nucleophiles used for epoxide ring opening. One or more alcohol functions are added on each aliphatic chain, based on the nucleophile used (Fig. 1). Epoxidized oils can undergo an accelerated alcoholysis with acid catalysts to yield hydroxylated oils. With monoalcohols, this process leads to the formation of polyols with secondary hydroxyl functions [3]. Thus, a very simple method consists in using water with acid catalyst to obtain a hydroxylated oil [4]. Moreover, alcohols such as methanol, ethylene glycol, butanol, or triethanolamine could be used as nucleophiles to open epoxide ring. Concerning catalysts, the most used are sulfuric acid, p-toluenesulfonic acid or tetrafluoroboric acid. Heterogeneous catalysts such as activated clays or ion exchange resins were also reported. [5, 6].

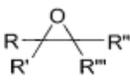
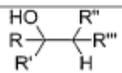
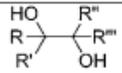
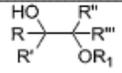
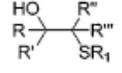
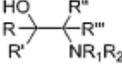
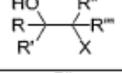
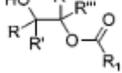
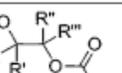
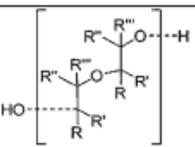
Substrate	Reactant	Product	Reference
	H ₂		29
	H ₂ O		2-7
	HOR ₁		8-18
	HSR ₁		19
	HNR ₁ R ₂		1, 20, 21
	HX, X=Cl, Br		22, 23
	HOC(O)R ₁		24-28, 30
	Carbonatation + HNR ₁ R ₂		31
	Polymerization		32

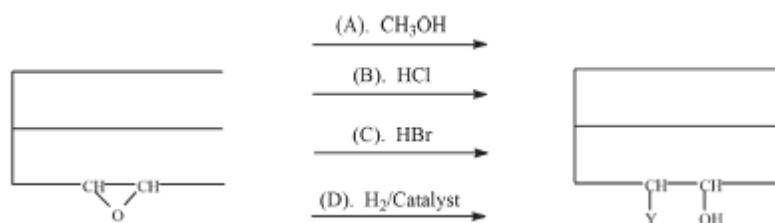
Figure 1. Summary of the possible reactions leading to alcohol from epoxidized vegetable oils [3].

Petrovic and coworkers recently developed methods for preparing soy polyols from epoxidized soybean oil (ESO) and for further reacting these with diisocyanates to form PUs. Such materials have applications as rigid materials or as foams for insulation, carpet backing, and so forth. Liu and coworkers prepared soft to rigid composites of polyamine-cured ESO with fillers and fibers. Shogren prepared citric acid cured ESO resins for use as coatings and showed that these disintegrate over time during soil burial [7]. Although many types of vegetable oils have been tested and reported for polyol and PU applications, soybean oil (SBO) is the most promising for partially replacing petroleum to make polyols because of its volume and price stability. Many innovative chemical and/or biological approaches are possible for converting SBO into polyols, but limited attention has been paid to the effects of different alcohols of low molecular weights, used as ring-opening reagents with ESO, on the properties of polyols and resulting PUs [8]. Vegetable oil polyols have to satisfy some structural requirements in order to compete with petrochemical polyols, such as the right functionality, molecular weight, and OH number. Functionality of most flexible polyols is around 3 and molecular weights between 3000 and 6000 (OH numbers = 56 - 28 mg KOH/g, respectively). Higher OH numbers usually increase the cost of the formulation due to a higher isocyanate consumption. Vegetable oils have molecular weights below 1000 and cannot be easily transformed into triols of the given molecular weights. Besides, hydroxyl groups are usually introduced at the positions of double bonds, i.e., they are not terminal as in petrochemical polyols [9]. Number average functionality can be measured directly, but for the weight average functionality one should know the distribution of functional species in the polyol. Technically one can measure the effective weight average functionality of the component A, f_{aw} , from the gel point, p , determined with a two-functional isocyanates at stoichiometric ratio:

$$p_{ac} = \sqrt{\frac{1}{f_{aw} - 1}}$$

This method is not precise at higher functionalities due to imprecision in gel point determination, as well as due to cyclization reactions, which are not taken into account in expression [10].

In this study, a couple of polyols with a range of hydroxyl (OH) numbers based on ESO were prepared by oxirane ring opening with polyethylene glycol. The general scheme for the epoxy group conversions is given in Figure 2.



Where $Y = \text{OHCH}_3, \text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}, \text{Cl}, \text{Br}, \text{H}$

Figure 2. Formation of polyols from epoxidized soybean oil [11].

All these polyols have relatively high functionality (about 4) and OH numbers (around 150 mg KOH/g) and are more suitable for rigid applications. If however lower hydroxyl numbers and reduced functionality is desired, then the heterogeneity of the functional species would be more pronounced and the amount of non-functional material increased. All polyols were fully characterized with Fourier transform infrared (FTIR) spectrometry and by the measurement of the OH number. The objective of this work was to synthesize PU resins from polyols reacted with polymeric methylene diphenyl diisocyanate (MDI).

2. Materials and Method

2.1. Materials

ESO with 6.2 % oxygen content and an iodine value of 1.62 g of I/100 g of oil were kindly provided by Plastifay Co., Ltd. (Istanbul, Turkey). Tetrafluoroboric acid (48%) was provided by Acros Organics, and Polyethylene Glycol 400 was provided by J. T. Baker. They were used as supplied.

2.2 Characterization

The hydroxyl value determinations were carried out according to the ASTM D 4274 standard test method. The sample is acetylated with a solution of acetic anhydride in pyridine in a pressure bottle at 98°C. The excess reagent is hydrolyzed with water and the acetic acid is titrated with standard sodium hydroxide solution. The hydroxyl content is calculated from the difference in titration of the blank and sample solutions. Acid number in polyols is determined according to ILL 003/3-01-27. Acid number is expressed as the number of milligrams of potassium hydroxide required to neutralize the acidity of one gram sample. Acid number is important to correct the value of hydroxyl number in order to obtain the real value for OH. For some polyols, such as polyester polyols or reactive flame retardants, the maximum acidity accepted is around 2 mg KOH/g. The water content of the polyol was determined using the Karl Fischer Titrator model Metrohm KFT 701 series (ASTM D4672-00(2006) e1: Standard Test Methods for Polyurethane Raw Materials: Determination of Water Content of Polyols) while the viscosity of the polyol was determined using the Brookfield digital viscometer model DV-I (ASTM D4878-88: Standard Test Methods for Polyurethane Raw Materials- Determination of Viscosity of Polyols). The viscosity of the polyol is important in determining the flowability of the polyurethane resin in the foaming process where it is advantageous in the material consumption. The Fourier Transform Infrared Spectroscopy (FTIR) spectra were recorded on a FTIR spectrometer (IR Prestige-20, Shimadzu, Japan).

2.3 Preparation of PEG400-ESO Polyols

The polyols were prepared by complete epoxy ring opening in ESO with polyethylene glycol in the presence of a tetrafluoroboric acid catalyst at 100°C. The polyol synthesized was made by mixing the epoxide soybean oil (ESO) with polyethylene glycol-400 (PEG400) in stoichiometric molar ratio. The ratio of ESO/PEG400 was at 1:1 (mol/mol) under 100°C temperatures.

The concentration of the catalyst was 0.2 wt.% of the total weights of the reaction mixture. PEG400 and the catalyst were added to a 500-mL, five-necked glass reactor equipped with a refluxing column, a mechanical stirrer, and a thermometer. The reactor was heated with a water bath. ESO was then added to the mixture of the refluxing PEG400 and the catalyst. The reaction mixture was kept at 100°C for 24 hours for the first sample PEG400-ESO-1. Second sample is PEG400-ESO-2 was prepared at 110°C for 24 hours. And the last sample PEG400-ESO-3 was prepared at 100°C for 24 hours in the presence of a double amount of tetrafluoroboric acid. After cooling to room temperature to avoid hydroxylation during the neutralization process, ammonia (30%) was added to neutralize the catalyst and dried over molecular sieve. The OH numbers of the polyols were determined according to the ASTM D 4274 standard test method. The sample is acetylated with a solution of acetic anhydride in pyridine in a pressure bottle at 98°C. The excess reagent is hydrolyzed with water and the acetic acid is titrated with standard sodium hydroxide solution. The hydroxyl content is calculated from the difference in titration of the blank and sample solutions.

2.4 Synthesis of PU foams with PEG400-ESO polyols

PUs were prepared via the mixing of the PEG400-ESO polyols -these mixture include, chain extenders, *crosslinkers*, *catalysts*, stabilisers, anti-oxidants, processing aids, colorants, *flame-retardants*, adhesion promoters- with polymeric methylene diphenyl diisocyanate (MDI). The polyol and the isocyanate components were stirred for 10 seconds and PU foams were obtained.

3. Results

The PEG400-ESO polyols are prepared by ring opening from ESO.

3.1. Properties of Polyols from ESO

3.1.1 The effect of Polyols OH number

The OH numbers, viscosities, water contents, and acids of the polyols are presented in Table I. Acid number is important to correct the value of hydroxyl number in order to obtain the real value for OH. For some polyols, such as polyester polyols or reactive flame retardants, the maximum acidity accepted is around 2 mg KOH/g. A special characteristic of all polyols is the fact that practically all of them are liquid at room temperature or at low temperatures (40-60°C). This fact is a really important technological advantage, because the high MW polyurethane polymer is obtained using only low viscosity liquid intermediates, which are very easy to process. The viscosity gives an indication of the processability of a polyol. The water content value determinations were carried out according to the ASTM D 4878 standard test method.

Table 1. Properties of Polyols from ESO

	PEG400-ESO-1	PEG400-ESO-2	PEG400-ESO-3
Reaction time (h)	24	24	24
Reaction temperature(°C)	100	110	100
OH number (mg KOH/g)	167	146	169
Viscosity (cPa)	3850	3500	5500
Water content (ppm)	2.12	4.01	3.10
Acid (mg KOH/g)	6.15	6.06	6.54

Hydroxyl value of polyol is important for quality control in production of polyurethane. In this study, samples of PEG400-ESO-1 and PEG400-ESO-2 showed that increasing temperature was obtained low OH numbers in polyol. Accordingly the results there still were double bonds in the polyol molecules, and this may result in the rubbery properties of PU. We had purposed to arrive rigid PU foams since the beginning of experimentals. Table 2 shows us technical requirements for polyols used in polyurethane flexible and rigid foam industry. PEG400-ESO polyols had a lower hydroxyl number (OH number is 167 mg KOH/g) than the petroleum-based polyol, (OH number is around 300 mg KOH/g). According to the Petrovic's and coworkers' study most of polyols with OH numbers of about 200 and less give semi-rigid polyurethanes of moderate or low crosslinking density when crosslinked with a diisocyanate [9].

Table 2. Technical requirements for polyols used in polyurethane industry [12].

Classification	Flexible Foam/ Elastomer	Rigid/ Structural Foam
Molecular Weight	1000 to 6500	400 to 1200
Hydroxyl Value	28 to 160	250 to 1000
Functionality	2.0 to 3.0	3.0 to 8.0

3.1.2 The effect of Polyols viscosity value

The other important properties of polyols are a viscosity. In this study we have realized that increasing temperature gave the lower viscosity results. The other comparison is between PEG400-ESO-1 and PEG400-ESO-3. The temperature was set in stone for two polyol samples, and the catalyst value was increased for third, PEG400-ESO-3, polyol. Increasing catalyst caused to increase the viscosity of PEG400-ESO-3. The increase in viscosity for these monomers can be related to the increase in molecular weight and polarity. OH number did not change nearly. Table 2 shows the technical requirements for both flexible and rigid foams. Our samples provided good functionality but the low OH number.

3.1.3 Tensile strength results of PU foams

Table 3 shows the tensile stress-stain values are 55 KPa, 57 KPa, and 56KPa for PEG400-ESO-1, PEG400-ESO-2, and PEG400-ESO-3 PU foams, respectively. In general, all of these PU foams are brittle in nature. Tensile strength values of these materials are fairly small and similar for all PU foams. The tensile strength behavior of these new vegetable oil-based materials demonstrates properties characteristic of polymers ranging from hard and brittle to relatively soft and ductile plastics. Typically, polymers prepared from the more unsaturated vegetable oils possess better mechanical properties.

Table 3. Tensile strength results for polyurethane foams

	PEG400-ESO-1	PEG400-ESO-2	PEG400-ESO-3
Tensile Strength [KPa]	55	57	56

4. Discussion

ESO-PEG is derived from ESO with an oxygen content of 6.31% by oxirane ring opening with PEG. The PEG400, ESO, and sample of polyols a chain of fatty acid with carboxylic acid group displays intense C=O stretching bands of acids absorb at 1740 cm^{-1} as shown in Fig. 3. The ESO characteristic peaks at 822.4 cm^{-1} (indicated by an arrow), attributed to the epoxy group, disappeared after the epoxy group opening reaction. Also, there were new characteristic absorption peaks at $3,480\text{ cm}^{-1}$ in the spectrum of PEG400-ESO-1. The C-H stretches at 2922 and 2854 cm^{-1} . Two bands arising from C-O stretching and O-H bending appear in the spectra of ESO and polyols near $1156\text{-}1241$ and $1460\text{-}1378\text{ cm}^{-1}$ respectively. Both of these bands involve some interactions between C-O stretching and in plane C-O-H bending. The C-O-H bending band near $1460\text{-}1378\text{ cm}^{-1}$ is of moderate intensity and occurs in the same region as the CH_2 scissoring vibration of the CH_2 group adjacent to the carbonyl.

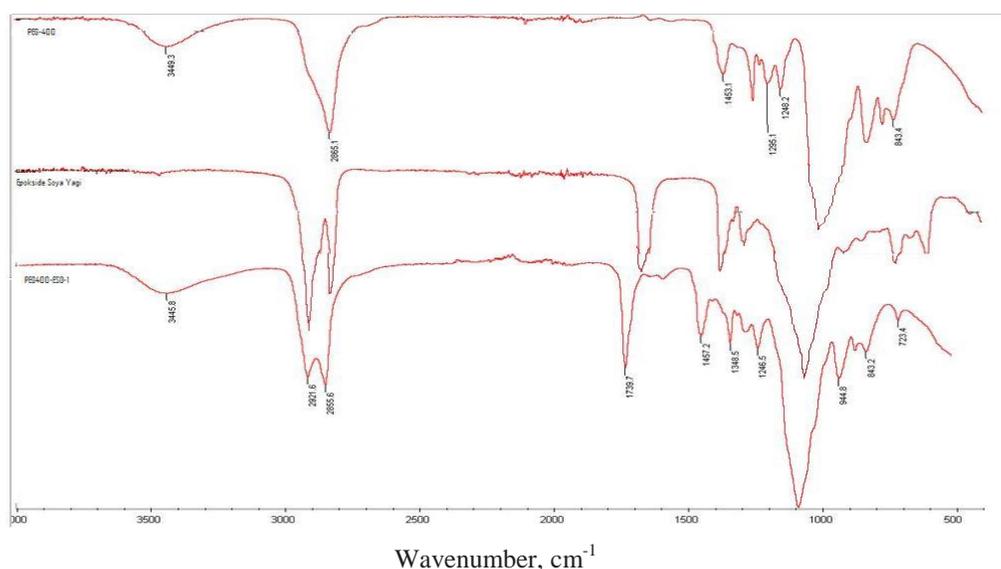
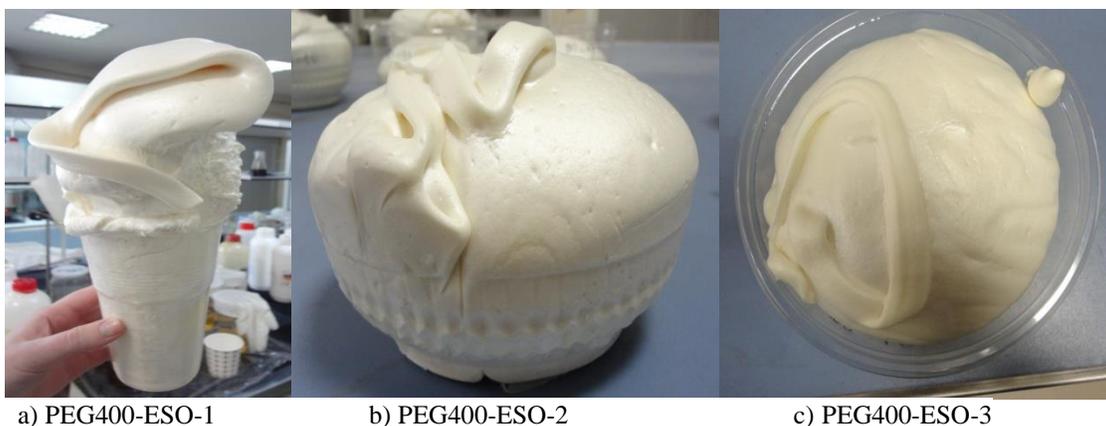


Figure 3. FTIR spectrums of PEG 400, epoxidized soybean oil, and PEG400-ESO-1 polyol

PU foams were prepared via the mixing of the PEG400-ESO polyols with polymeric methylene diphenyl diisocyanate (MDI). These PU foams were prepared for spray PU foams applications. Spray polyurethane foam (SPF) is an effective insulation and air sealant material. Spray foam insulation saves on energy costs and lowers utility bills. At this stage we specified PU foams of cream time, gel time, and handling time. The results were shown in Table 4. According to Table 4, the main goal arrived to obtain PU foams in a short time. PEG400-ESO-1 foam was obtained in a short time from the others foam samples. But three PU foams have an acceptable time intervals. We displayed photo of the PU foams in Figure 4.

Table 4. The Cream, Gel, and Handling Time Values of PU foams

PU Foams	Cream time (s)	Gel time (s)	Handling time (s)
PEG400-ESO-1 foam	5	7	8
PEG400-ESO-2 foam	7	8	10
PEG400-ESO-3 foam	6	8	10



a) PEG400-ESO-1

b) PEG400-ESO-2

c) PEG400-ESO-3

Figure 4. Images of PU foams prepared from PEG400-ESO polyols

Conclusions

Vegetable oils offer a variety of new structures in polyols depending on the method of synthesis, resulting in polyurethane foams with new properties, suitable for a range of applications. Currently, vegetable oil polyols must be used in conjunction with petrochemical polyols in rigid foams, but they could be used as sole polyols in other applications. In this work, a series of polyols with a range of OH numbers based on ESO were prepared by oxirane ring opening with poly(ethylene glycol) (PEG400) having the molecular weight of 400g/mol in the presence of tetrafluoroboric acid catalyst. These epoxidized soybean oil based polyols have been reacted with MDI to give PU foams with different crosslink densities. The PU foams prepared from polyols with OH numbers greater than 150 mg of KOH/g were glassy, whereas those prepared from polyols with OH numbers less than 150 were rubbery. The tensile strength of the PU foams did

not increase with the OH number increasing or decreasing. This could be caused by the low reduced crosslinking density of the resins due to the lower OH value of the polyols. The effects of reaction temperature and catalyst amount on the PEG400-ESO soy-based polyols were investigated by spectroscopic, chemical and physical methods. The advantages of these PU foams are their low cost, availability from a renewable natural resource, and possible biodegradability.

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References

- [1] Petrović, Z., S., Cvetković, I., Vegetable oil-based hyperbranched polyols in flexible foams. *Contemporary Materials*, III-1, 2012, 63-71.
- [2] Geiger, E.J., Becker, N.M., Lemars, Armbruster, L.A., US Patent No. 7,989,647 B2: US Patent and Trademark Office.
- [3] Desroches, M., Escouvois, M., Auvergne, R., Caillol, S., Boutevin, B., From vegetable oils to polyurethanes: Synthetic routes to polyols and main industrial products. *Polym. Rev.* 2012, 52, 38–79.
- [4] Dwanisa, J.P.L., Mohanty, A.K., Misra, M., Drzal, L.T., Kazemizadeh, M., Novel soy oil based polyurethane composites: Fabrication and dynamic mechanical properties evaluation. *J. Mater. Sci.* 2004, 39, 1887–1890.
- [5] Erhan, S.Z., Adhvaryu, A., Liu, Z., US Patent 6583302, 2003.
- [6] Lathi, P.S., Mattiasson, B., Green approach for the preparation of biodegradable lubricant base stock from epoxidized vegetable oil. *Appl. Catal. B: Environ.* 2007, 69, 207–212.
- [7] Wang, C., Yang, L., Ni, B., Shi, G., Polyurethane Networks from Different Soy-Based Polyols by the Ring Opening of Epoxidized Soybean Oil with Methanol, Glycol, and 1,2-Propanediol, 2009, 114, 125–131.
- [8] Zhang, L., Structure-Property Relationship of Polyurethane Flexible Foam Made from Natural Oil Polyols, 2008.
- [9] Petrovic, Z.S., Polyurethane from Vegetable Oils, *Polymer Reviews*, 2008, 48:1, 109-155.
- [10] Holcapek, M.; Jandera, P.; Zderadicka, P.; Hrubá, L. “Characterization of triacylglycerol and diacylglycerol composition of plant oils using high-performance liquid chromatography Atmospheric pressure chemical ionization mass spectrometry”, *J. Chromatogr. A*, 2003, 1010, 195–215.
- [11] Guo, A., Cho, Y.J., Petrovic, Z.S., Structure and properties of halogenated and non-halogenated soy-based polyols, *J. Polym. Sci. Part A: Polym. Chem.* 2000, 38, 3900–3910.
- [12] Badri, K.H., Biobased Polyurethane from Palm Kernel Oil-Based Polyol, Chapter 20, 2012.