

Polymerization of Ethylene Glycol and Soy-epoxide Derived Phosphate Ester for Polyurethane Foam

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Abstract

Polyurethane foams (PUF) were substantially manufactured from isocyanate TDI: MDI (70:30) and polyol; a ring-opening hydrolysis mechanism of epoxidized soybean oil with ethylene glycol (EG) in the presence of o-phosphoric acid 85 %. The amount of phosphoric acid, and their derivatives were found to be significantly effected in replacing petroleum polyol until 100 %.

Keywords: polymerization, soybean oil, ethylene glycol, phosphoric acid, polyurethane foam

1. Introduction

Polyurethane foams manufacturing rely significantly on petroleum and its derivatives as major reactants for the production of polyols. Depleting oil resources and dependence on using renewable resources has led to concerns over the price of raw materials used to manufacture polyurethanes. This can reduce dependence on petroleum derived materials (Guo et al., 2007; John et al., 2002).

The use of nonrenewable petrochemical based feedstock has led to search for vegetable oil-based alternatives, a great deal of research effort has been and is still devoted to the development of innovative technologies using renewable resources (Narine et al., 2007).

The preparation of polymers from renewable resources is of significant economic and scientific importance. Vegetable oils have a number of excellent properties that can be utilized in reproducing valuable polymeric materials. Soybean is a preferred feedstock for developing new industrial oil product applications due to its relatively unreactiveness in polymer formulations. The fatty composition in percentage by weight are (16:0) 17.75 %; (18:0) 3.15 %; (18:1) 23.2 %; (18:2) 55.5 % and (18:3) 6.31 % (Casado, 2009). This oil can be functionalized by hydroxylation of the carbon-carbon double bonds with peroxy acids or alcoholysis with triol like glycerol or triethanolamine to reach a hydroxyl value which is useful for flexible foam production (Barret et al., 1993; Heidbreder, 1999; Firdaus, 2012).

Replacement of substantial parts of polyol and isocyanate with soybean oil derived epoxide is economically significant. The oxirane ring cleavage has high reactivity, it makes epoxide versatile as chemical intermediates and as end product (Knothe & Derksen, 1999).

The modified epoxide soybean oil (ESBO); a vegetable oil polyols can be used as a replacement for conventional polyols, reacting with isocyanates to produce flexible slabstock polyurethane foam (PUF), elastomer and coating (Narine et al., 2007; Narine et al., 2007; Aneja, 2002).

O-Phosphoric acid (o-H₃PO₄) has been extensively used in the preparation of phosphate ester for rigid polyurethane (Dwan'Isa et al., 2003; Zhong et al., 2001).

Guo and co workers have reported phosphoric acid content addition to the reactants has made soy polyols have tunable hydroxyl content and phosphate ester functionally can control the type and amount of polar solvent. Phosphoric acid does not only catalyzed ring opening reaction of soy epoxide with water but chemically become part of the polyol product (Cracknell & Moore, 1995; Sato et al., 2001).

Early research work has focused on synthesizing polyurethane foams from entirely natural polyols which were proven to be successful (Firdaus, 2012). In the present work, we focused on the study the effect of phosphoric acid in the polyurethane synthesis to properties of the foam.

2. Experimental Procedures

2.1 Materials

The following are equipments and materials required for the experiment; Soybean oil of RBD (Refined, Bleached, Deodorized) was supplied by Salim Ivomas with viscosity of 65.5278 cps, acid value was 0.024 mgr KOH/ sample. Hydrogen peroxide was obtained from Brataco Chemika, several other reagents; acetic acid was obtained from Merck Germany, Sulfuric Acid from Tedia Company, Inc., phosphoric acid, and ethylene glycol from Harum sari. All solvents and reagents used in the study were of laboratory grade and were used as received.

2.2 Ring-opening Hydrolysis of Soy-epoxide

Soy derived phosphate ester were obtained from hydrolysis of soy epoxide which were manufactured from three different temperature; 50°C, 60°C, and 70°C. Phosphoric acid was charged up to 1.5 percentage of total volume.

To a 500-ml multi-neck reaction flask equipped with mechanical stirrer, thermometer, water cooled condenser and dropping funnel, soy based soy epoxide was dissolved in a portion of reaction solvent and added drop wise into the flask over a period of 120 minutes. After addition was completed, the reaction sample was periodically tested for the acid value and the percentage of the oxirane content. Reaction was stopped after 6 h. The product was purified to remove unreacted acid by washing with distilled water using a separatory funnel, followed by drying over anhydrous sodium sulphate (Figure 1).

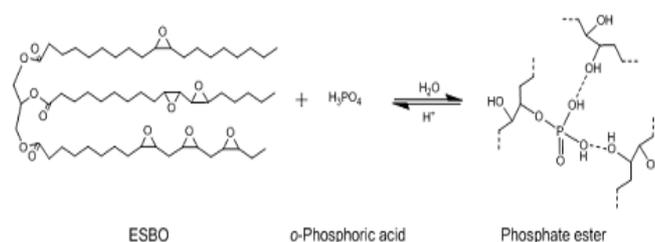


Figure 1. Schematic of phosphate ester formation

2.3 Concentration of Phosphoric Acid

The acid-catalyzed nature, the amount of phosphoric acid are used is expected to have significant effect to product characterizations. A series of reactions with varying amounts of o-phosphoric acid 85 % were investigated, whereas the concentration of phosphoric acid are 0.5 %, 1.0 %, and 1.5 % (v/v).

The compositions in the formulation were listed in (Table 1). As expected, higher concentrations of phosphoric acid gave essentially complete ring-opening in a progressively shorter reaction time. With increasing phosphoric acid content, the products not only showed higher final acid values it progressively increased during the course of reaction. This might be due to the progressive hydrolysis of higher phosphate esters to lower esters. High residual acidity is an undesirable polyol property, it will have a significant impact on polyurethane foam synthesis as it competes with hydroxyls to react with isocyanates and consumes catalyst.

Table 1. Concentration of Phosphoric acid in polyol synthesis

Ratio of	Designated	EG(ml)	H3PO4		
			0.5 % (v/v) ml	1.0 % (v/v) ml	1.5 % (v/v) ml
			I	II	III
1:01	A	4.26	0.145	0.28	0.4
1:05	B	21.3	0.23	0.46	0.7
1:07	C	29.8	0.27	0.55	0.8
1:09	D	38.34	0.315	0.63	0.9

After optimization, the polyol chosen to be proceed as the material for polyurethane synthesis was the product synthesized using 1.0 % (v/v) phosphoric acid.

2.4 Preparation of PU Foam (PUF)

A foaming procedure was used in this study detailed in (Table 2). The foam were prepared by adding TDI (2,4):MDI (4,4') (70:30) to the polyol blend, which consisted of surfactant, and distilled water. The mixtures were vigorously mixed (stirring at 1000 rpm using high speed mixer for 1 minute), then were poured into an open glass mold. At the creamy stage (the mixture turning creamy), which was rose freely in an open mould. The foams were removed from the mould and allowed to postcure for one day at room temperature before cut into the test specimens.

Table 2. Formulation of flexible polyurethane foam

	PUF 1	PUF 2	PUF 3	PUF 4
TDI:MDI (70:30)	5	5	1	5
Soy Polyol	8	0	10	10
Petro Polyol*	0	10	0	0
EG**	4	0	0	0
Si	2	2	2	2
Water	1	1	1	1

* Petro polyol was used as a control

** EG as chain extender

The polyurethane was design in four formulations. Polyurethane 3 (PUF3) was chosen as a control variable because ethylene glycol were inserted in the foam synthesis. PUF1, PUF2 and PUF3 using soy derived phosphate, but in PUF1 ethylene glycol were inserted in the foam synthesis.

3. Results and Discussion

The viscosity values were observed to have increased and oxirane number decreased as well. This was attributed to ring opening reaction of oxirane groups in soy-epoxide and simultaneous formation of soy epoxide- ethylene glycol. The resulting increase viscosity and consumption of oxirane oxygen content linearly to the amount of phosphoric acid were mainly attributed to the complexation of the main products which were suggested. A high viscosity polyol product of using 1.5 % phosphoric acid compared to 1.0 % phosphoric acid indicates a higher degree of oligomerization or complexation between soy epoxide and ethylene glycol of the products decrease with increasing of phosphoric acid. Viscosity is significantly related to hydroxyl content or otherwise the oxirane number, which generally increase with increase hydroxyl content, and reduce in oxirane number. This can be primarily attributed to decreased tendency for oligomerization reaction due to lower acid concentration.

3.1 Characterization and Property of Soy polyol

The phosphoric acid content was made in three variable concentrations; 0.5 % v/v; 1.0 % v/v and 1.5 % v/v. The Soy-Phosphate Ester results from ratio of epoxide/ethylene glycol 1:1; 1:5; 1:7 and 1:9 (mol/mol). Concentration 0.5 % (v/v) of H₃PO₄ in the synthesis occurred as the highest oxirane number of polyol products (Figure 2).

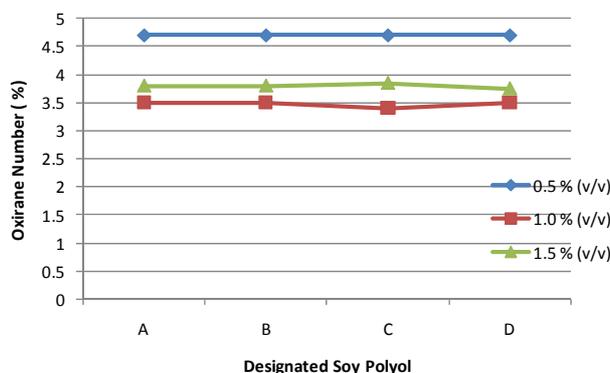


Figure 2. Concentration of phosphoric acid to soy polyol oxirane number

The acid number of polyol products using three combinations of phosphoric concentration is tolerable, because they are under value of 10 mgr KOH/ g polyol (Kiatsimkul, 2007) (Figure 3).

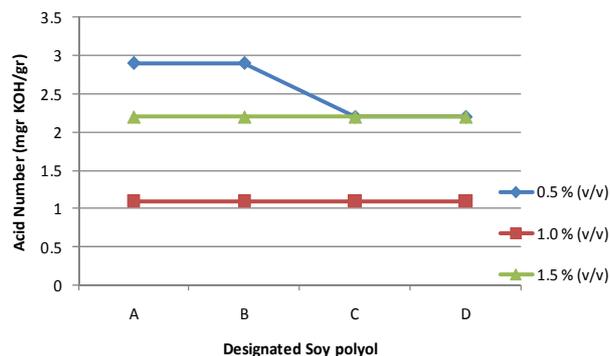


Figure 3. The effect concentration of phosphoric acid to polyol acid number

The excess of water content in the polyol using phosphoric is still remain as a big question mark. It is clearly be seen that the polyol using phosphoric acid has more water content comparing to using sulfuric; which though can be neglected. Because in practically polyol has to be water removed by evaporation before proceed to the further reactions (Figure 4).

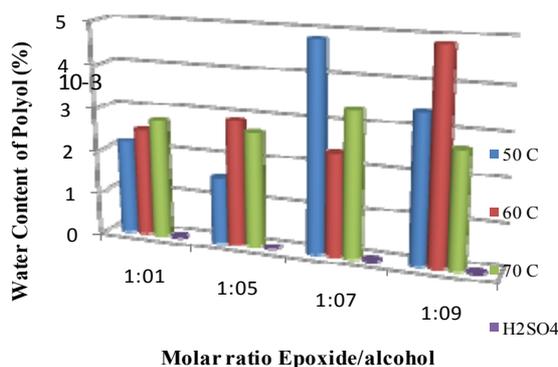


Figure 4. Comparative polyol product to water content

*H₂SO₄ was used as a comparison

3.2 Characterization of Polyurethane Foam

3.2.1 Density

The obtained PU foams were characterized by using density measurements, the foams were cut into specimens with dimension of 1cm x1cm x1cm. The specimens were accurately weighed to determine their densities using the equation, density = mass/volume.

The soy epoxide-ethylene glycol has a foam density in the range of 0.154-0.33 gr/cm³. The concentration of phosphoric affected to foam density, which in sequentially 1.5 % (v/v) > 1.0 % (v/v) > 0.5 % (v/v) (Figure 5). An increased of density may be governed by the rate of reaction of the polyol and isocyanate that makes polyurethane network after curing optimum. A faster reaction would result a denser crosslinked three dimensional polyurethane network, which gives a higher foam density.

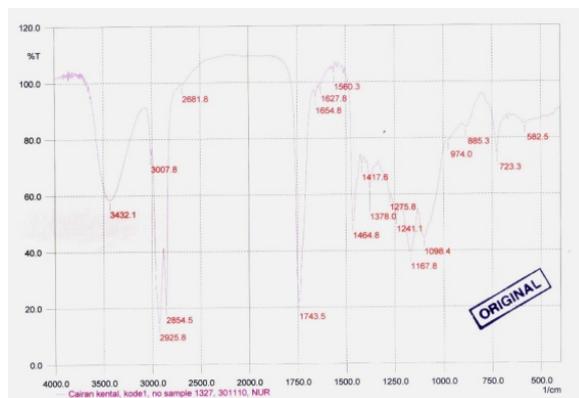


Figure 5. The FTIR spectra of soy derived phosphate

3.2.2 Fourir Transform Infrared Spectroscopic Analyses

The functionality groups present in polyol samples are aliphatic ester with OH terminal groups. The wavenumbers were CH_2 and CH_3 deformation at 1465 cm^{-1} ; phosponate at 1242 cm^{-1} (strong); phosphate at 1171 cm^{-1} (strong); hydroxide at 1418 cm^{-1} (medium intensity, OH bending in plane); phosphate at 1099 cm^{-1} (strong); hydroxide at 1378 cm^{-1} ; phosphate ester at 723 cm^{-1} .

3.2.3 Cell Morphology

SEM micrograph was used to take images of cured solid polyurethane foams. The formula PUF1, PUF2, PUF3, and PUF4 (Figure 6). The addition of ethylene glycol is seems not to be significantly effected to micrograph of polyurethane. The homogeneous voids in PUF4 does not state automatically as the best in elasticity, otherwise randomized open cell of PUF3 is the fair in elasticity among three other formulas which is 71.42 %.

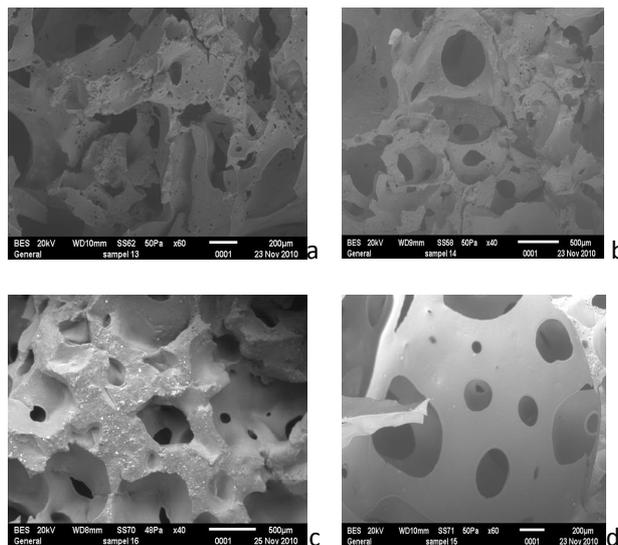


Figure 6. SEM images of PUF a. PUF- 1 b. PUF- 2 c. PUF- 3 d. PUF-4

4. Conclusion

Phosphate ester were derived from polymerization of soy epoxide by mixing soy epoxide oil to 0.5 % v/v; 1.0 % v/v, and 1.5 % v/v o-phosphoric acid at 50°C , 60°C , and 70°C . The optimized condition were chosen from the characterization of products obtained were 1.0 % v/v o-phosphoric acid at 70°C . The products were homogeneous, low acid value, and ready to replace petroleum polyol.

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References

- Aneja, A. (2002). *Structure property relationships of flexible polyurethane foams*, Dissertation. Virginia Polytechnic institute and state university, p.11.
- Barret, L. W., Sperling, L. H., & Murphy, C. J. (1993). Naturally functionalized triglyceride oils in interpenetrating polymer networks. *J. Am. Oil Chem. Soc.*, 70(5), 523-534. <http://dx.doi.org/10.1007/BF02542588>
- Casado, U., Marcovich, N. E., Anguren, M. I., & Mosiewicki, M. A. (2009). High strength composite based on Tung oil polyurethane and wood flour: effect of filler concentration on the mechanical properties. *J. Polymer Engineering and Science*, 49, Brookfield center, 713-721.
- Cracknell, R. B., & Moore, A. J. (1995). Patent Application 5414103, USPTO, USA.
- Dwan'Isa, J. P. L., Mohanty, A. K., Misra, M., Drzal, L. T., & Kazemizadeh, M. (2003). Novel Biobased Polyurethanes Synthesized from Soybean Phosphate Ester Polyols: Thermomechanical Properties Evaluations. *Journal of Polymers and the Environment*, 11(4), 161-168. <http://dx.doi.org/10.1023/A:1026004431534>
- Firdaus, F. E. (2012). The Type of Catalyst to Physical Properties of Soy- Based Polyurethane. *J. Chem. Chem. Eng.*, 6. David Publishing, 96-100.
- Firdaus, F. E. (2012). Role of Silicone on Molded Flexible Polyurethane from Soy Oil. *International Journal of Chemistry*, 4(1), 45-49. <http://dx.doi.org/10.5539/ijc.v4n1p45>
- Guo, Y., Hardesty, J., Mannari, V., & Massingil, J. (2007). *J. of the American Oil Chemist Society*, 84, 929.
- Heidbreder, A., Höfer, R., Grützmacher, R., Westfechtel, A., & Blewtt, C. W. (1999). Oleochemical products as building blocks for polymers. *Fett/Lipid*, 101(11), 418-424.
- John, J., Bhattacharya, M., & Turner, R. B. (2002). Characterization of polyurethane foams from soybean oil. *J. Appl. Polym. Sci.*, 86, 3097-3107. <http://dx.doi.org/10.1002/app.11322>
- Kiatsimkul, P., Suppes, G., & William, R. Sutterlin. (2007). Production of new soy-based polyols by enzyme hydrolysis of bodied soybean oil. *Industrial Crops and Products*, 25(2), 202-209. <http://dx.doi.org/10.1016/j.indcrop.2006.10.001>
- Knothe, G., & Derksen, J. T. P. (1999). *Recent development in the synthesis of fatty acid derivatives*. AOCS, Champaign. <http://dx.doi.org/10.1201/9781439832073>
- Narine, S. S., Kong, X., Bouzidi, L., & Sporns, P. (2007). Physical properties of polyurethanes produced from polyols from seed oils: I. Elastomers. *J. Am. Oil Chem. Soc.*, 84(1), 55-63, <http://dx.doi.org/10.1007/s11746-006-1006-4>
- Narine, S. S., Kong, X., Bouzidi, L., & Sporns, P. (2007). Physical properties of polyurethanes produced from polyols from seed oils: II. Foams. *J. Am. Oil Chem. Soc.*, 84, 65-72. <http://dx.doi.org/10.1021/bm8001478>
- Sato, S., Crielo Bueno, R., Bueno, A., & Bueno De, A. W. (2001). Patent Application 6274750, USPTO, USA.
- Zhong, B., Shaw, C., Rahim, M., & Massingil, J. (2001). *Journal of Coatings Technology*, 73, 53.