

Property of Polyurethane: from Soy-derived Phosphate Ester

Flora Elvistia Firdaus

Abstract—Polyurethane foams (PUF) were formed by a chemical reaction of polyol and isocyanate. The polyol was manufactured by ring-opening hydrolysis of epoxidized soybean oil in the presence of phosphoric acid under varying experimental conditions. Other factors in the foam formulation such as water content and surfactant were kept constant. The effect of the amount of solvents, phosphoric acid, and their derivatives in the foam formulation on the properties of polyurethane foams were studied. The properties of the material were measured via a number of parameters, which are water content of prepared polyol, polymer density and cellular structures.

Keywords— soy, polyurethane, phosphoric acid

I. INTRODUCTION

THE recent years, the price of crude oil has escalated raising many concerns over the stability and the sustainability of petroleum resources.^[1] The rising cost of crude oil also impacts the cost of polyurethane products, because majority of the raw materials, such as polyols and isocyanates used in foams are petroleum derivatives.^[2]

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. The oils are characterized by their hydroxyl values and fatty acid compositions. The modified oils have higher hydroxyl values and a lower unsaturated acids than regular unmodified oils. 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.^{[3]-[5]}

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%.^[6] 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.^[7]

Finding an alternative feedstock for polyurethane has become highly desirable for both economic and environmental

reasons. Natural oils have been shown to be a potential bio-renewable feedstock for polyurethane.^{[8]-[11]} A variety of chemical modifications of soy-epoxide are possible through the reactive oxirane functionality. By far the most predominant reaction of soy-epoxide is the ring-opening reactions with nucleophilic compounds. The reaction of nucleophile water with soy-epoxide produces compounds with multiple 1,2 diol structures, depending upon the oxirane content and the extent of hydrolysis. These soy-polyols have interesting properties and applications in a variety of fields.^[12-14]

Early research work has focused on synthesizing elastomers and rigid foams from entirely natural polyols which were proven to be successful. However, challenges remain in making flexible foams, the most significant polyurethane product, using entirely natural polyols.^[15]

In the present work, we focused on the study of ring opening reaction of ESBO in the presence of phosphoric acid, which is not only catalyzes the ring-opening hydrolysis reaction but also chemically combines and becomes a part of the polyol product. Besides eliminating the need for its removal from the reaction mixture, the presence of phosphate ester functionality will add value to the derived soy-polyols for many end use applications, such as in surfactants and coatings. We report some important findings of the study of ring-opening hydrolysis reaction of ESBO under varying experimental conditions.

II. EXPERIMENTAL PROCEDURES

A. Materials

The following are the equipment 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 were obtained from Merck Germany, Sulfuric Acid from Tedia Company, Inc., phosphoric acid from Harum sari. All solvents and reagents used in the study were of laboratory grade and were used as received.

The research was conducted to determine the effects of Phosphoric acid in the soy-epoxide hydroxylation to the property of polyurethane.

B. Ring-Opening Hydrolysis of Soy-epoxide

All the hydrolysis reactions reported in this study were carried out by the following general procedure, unless

Flora Elvistia Firdaus is with the Department of Chemical Engineering, Jayabaya University, Jl. Pulomas Kav 23 Jakarta-13210 Indonesia (corresponding author to provide phone: +62218583591; fax: +62218583591; e-mail: flora_elvistia@yahoo.com).

otherwise specified. The epoxide product was manufacture in three temperature conditions which are 50,60, and 70⁰C. To a 500-ml multi-neck reaction flask equipped with a mechanical stirrer, a thermometer, a water cooled condenser and a dropping funnel, a mixture of solvent epoxide alcohol. Phosphoric acid was charged up to 1.5 percentage of total volume. The mixture was brought to the reflux condition by heating at a slow rate under mechanical stirring. The temperature of the reaction mixture used was 70⁰C.

ESBO was dissolved in a portion of reaction solvent and added drop wise into the flask over a period of 120 min. After addition was complete, heating was continued and 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.

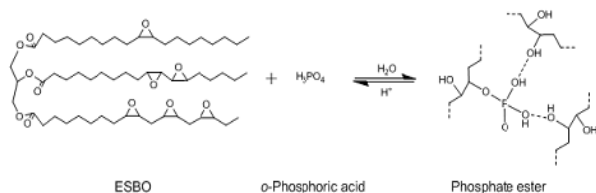


Fig. 1 Schematic of Phosphate Ester Formation

C. Concentration of Phosphoric Acid

In this reaction the acid-catalyzed nature, the amount of phosphoric acid used is expected to have significant effect on the reaction time and the characteristics of the product. A series of reactions with varying amounts of o-phosphoric acid 85% were investigated, whereas the concentration were 0.5%, 1.0%, and 1.5% (v/v). The polyol used in the synthesis was manufactured from epoxide route which was the result from epoxidation of unsaturated fatty acid with temperature reaction respectively are 50, 60, and 70⁰ C, then continue to alcoholysis reaction with temperature of 70⁰C. The composition in the formula listed in (table I).

TABLE I
CONCENTRATION of PHOSPORIC ACID in POLYOL SYNTHESIS

Ratio of Epoxide%/alc.	Designated	EG(ml)	H ₃ PO ₄		
			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

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, but acid values progressively increased during the course of the reaction. This might be due to the progressive hydrolysis of higher phosphate esters to lower esters. One interesting observation here are the comparison of density as a function of

phosphoric acid content.

D. Preparation of PU Foam

The procedure for the preparation of a flexible polyurethane foam involves ongoing process at the interfacial level as well as within bulk.

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 min), then were poured into an open glass mold. To investigate the effect of catalyst content on the properties of the PUF, the quantities of all components listed (table II).

TABLE II
FORMULA for POLYURETHANE SYNTHESIS

	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

At the creamy stage (the mixture turning creamy), which was rose freely in an open mould. The foam was removed from the mould and allowed to postcure for one day at room temperature before cut into the test specimens.

III. RESULTS AND DISCUSSION

The viscosity of the products decrease with increasing of phosphoric acid. This can primarily be attributed to (a) decreased tendency for oligomerization reaction due to higher acid concentration and (b) presence of increasing amount of higher phosphate esters. The sample obtained from the reaction containing 0.5% phosphoric acid exhibits higher density. These characteristics can be attributed to the significantly lower oligomerization and lower phosphate esters in this case. We believe that the reason for this significant drop in oligomerization, despite higher acid concentration, is due to the rapid consumption of oxirane groups in formation of phosphate esters. The high hydroxyl value justifies the fact that excessive oxirane groups are not lost in oligomerization as can be seen in fig 2.

A. Characterization and Property of Soy Polyol

The phosphoric acid content constitute into three variable concentrations, which are I (0.5% v/v); II (1.0% v/v) and III (1.5% v/v).

The polyol result from the synthesis with ratio of epoxide/alc were 1:1(A); 1:5(B); 1:7 (C) and 1:9 (D).

The average of polyols oxirane number under same operation conditions whereas synthesized using o-H₃PO₄ 85% with concentration which are 0.5% > 1.5% > 1.0% (v/v). The

0.5% (v/v) is assumed to be the optimized concentration of H_3PO_4 in the reaction.

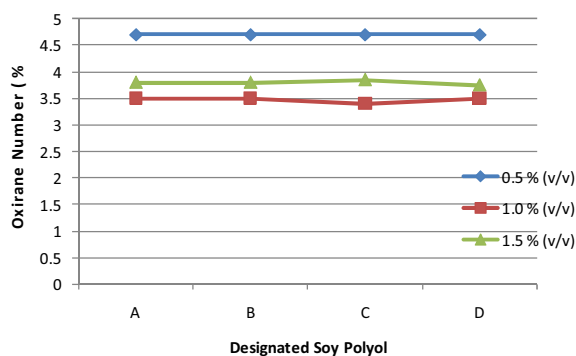


Fig 2 Concentration of Phosphoric acid to soy polyol oxirane number

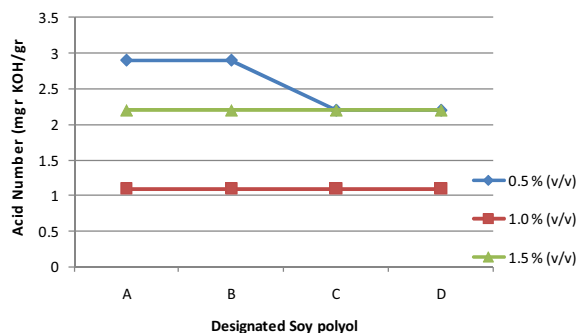


Fig. 3 Acid number of polyol was measured, with the amount of phosphoric acid made at 0.5%, it can be seen the greater acid number occur at molar ratio of epoxide to alcohol at 1:1 (mol/mol); which were in the range of 2.0-2.8%.

In the ratio of 1:7 and 1:9 the acid number range from 1.7-2.1%. (Fig 3) Overall the temperature reaction during the synthesis also impacted to acid number of polyol products, as can be seen in fig 4.

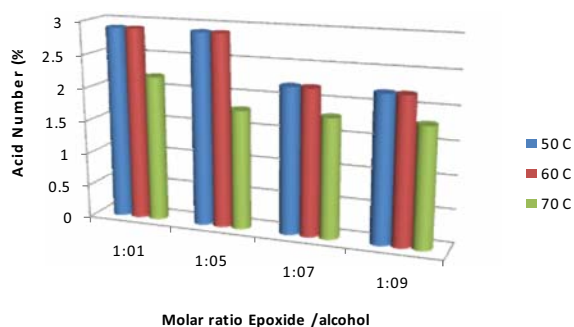


Fig. 4 The effect of reaction temperature on acid number

The relationship between phosphoric concentration in the mixture to the density seems to be significantly affected to density of foams. However, it is clearly evident the concentration of phosphoric at 0.5% (v/v) result the density as

high as 0.3 gr/cm^3 but decrease to 0.2 gr/cm^3 and 0.16 gr/cm^3 with 1.0% (v/v) and 1.5% (v/v). The concentration of phosphoric affected to flexibility of foam, which in sequence $1.5\% \text{ (v/v)} > 1.0\% \text{ (v/v)} > 0.5\% \text{ (v/v)}$.

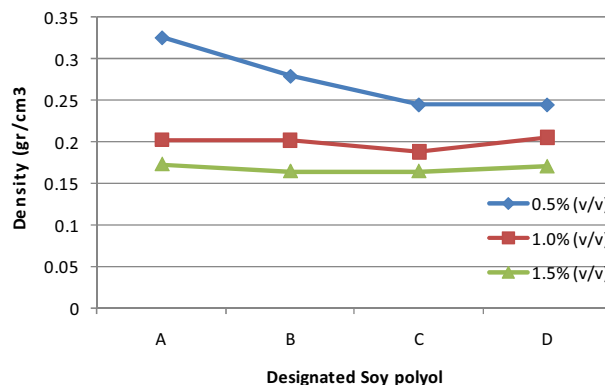


Fig 5 Phosphoric Acid to Density of Polyurethane

This research have tried to link water content of polyol which have done at the previous work using sulfuric acid as catalyst. It is clearly be seen the polyol using phosphoric acid has more water content than using sulfuric catalyst; which though can be neglected. In practically all the polyol has to be water removed by evaporation.

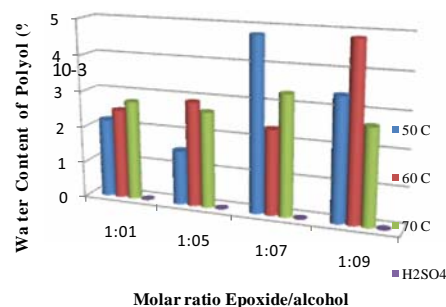


Fig 6 Comparative polyol product

The above figure illustrate the comparison of polyol product which were manufacture from three temperature conditions which are 50, 60, and 70°C in the presence of H_3PO_4 and compared to H_2SO_4 .

B. Characterization PU Foam

The obtained PU foams were characterized by using density measurement, the foams were cut into specimens with dimension of $1\text{cm} \times 1\text{cm} \times 1\text{cm}$. The specimens were accurately weighed to determine their densities using the equation, density = mass/ volume. The density for each foam was ascertained using average value.

C. Cell Morphology

SEM micrograph was used to take images of cured solid polyurethane foams PUF1, PUF2, PUF3, and PUF4 as it shown in fig 7. The addition of ethylene glycol to the

polyurethane formula seems to be effected to the micrograph, which the sample present s a homogeneous pattern of fracture with no pull out. It seems the absent of ethylene glycol in the formula does not result significant difference of the cell. The shapes of the cells on fig 7d are spherical with many windows. The spherical cells are found to be closed cells.

Fig. 7 SEM images of PUF a. PUF 1 b. PUF 2 c. PUF 3 d. PUF4

IV. CONCLUSION

The polyol based on soybean could be used as one of the raw material for preparing polyurethane foam. The synthesis of polyol using phosphoric catalyst. The prepared polyol was reacted with TDI:MDI (70:30) in the presence of chemical blowing; H₂O and surfactant. The PUF obtained exhibited densities in the range 0.2-0.33 gr/cm³. The results of the morphology by SEM revealed that the cells of these foams were opened cells. Concentration 0.5 % of phosphoric acid can not accelerate the perfect nucleation.

ACKNOWLEDGMENT

The authors gratefully acknowledge the support of the Indonesia Department of higher education as funding the research.

REFERENCES

- [1] Energy Information Administration, world Crude oil Process: <http://tonto.eia.doe.gov/dnav/pet/hist/wtotusaw.htm>, accessed on April 11th, 2008
- [2] ICIS Chemical Business Americas Oct. 30th, 270(16), 2006, p. 4343
- [3] A.P. Singh, Viscoelastic changes and cell opening of reacting polyurethane foams from soy oil. *J. Polym Eng Sci* 44, 2004, 1977-1987
- [4] S.S Narine, X Kong, L. Bouzidi, P. Sporns, Physical properties of polyurethanes produced from polyols from seed oils: I. Elastomers. *J Am Oil Chem Soc* 84: 2007, 55-63
- [5] S.S Narine, X Kong, L. Bouzidi, P. Sporns, Physical properties of polyurethanes produced from polyols from seed oils: II.Foams *J Am Oil Chem Soc* 84: 2007, 65-72
- [6] A.Aneja, "Structure property relationships of flexible polyurethane foams, Dissertation, Virginia Polytechnic institute and state university, 2002, p.11
- [7] U.Casado, N.E Marcovich, M.I. Anguren, M.A. Mosiewicki, High strength composite based on tung oil polyurethane and wood flour: effect of filler concentration on the mechanical properties, *J. Polymer engineering and science*, vol.49, Brookfield center, 2009, pp. 713-721
- [8] L.W. Barret, L.H. Sperling, C.J Murphy, Naturally functionalized triglyceride oils in interpenetrating polymer networks, *J. Am.Oil Chem. Soc.*, 70(5), 1993, pp. 523-534
- [9] A. Heidbreder, R.Höfer, R. Grützmacher, A. Westfechtel, C.W. Blewtt, Oleochemical products as building blocks for polymers, *Fett/ Lipid*, 101(11), 1999, pp. 418-424
- [10] Z.S Petrovic, W. Zhang, I. Javni, Structure and properties of polyurethane prepared from triglyceride polyols by ozonolysis. *Biomacromolecules*, 6(2), 2005, pp. 713-719
- [11] T. Roloff, U. Erkens, R. Höfer, Polyols based on renewable feedstocks:
- [12] Guo A, Javni I, Petrovic C, Rigid polyurethane foams based on soybean oil, *J. Appl Polym Sci* 77, 2000, pp.467-473
- [13] Petrovic ZS, Guo A, Javni A, Zhang W; Optimization of composition of soy-based polyols for rigid polyurethane foams. Annual technical conference society of plastic engineers, 58th 3, 2000, pp. 3732-3736
- [14] Gruber B, Hofer R, Kluth H, Meffert A; Polyols on the basis of oleochemical raw materials. *Fat Sci Technol* 89, 1987, pp.147151
- [15] E.F. Flora, Silicone on blending Vegetal Petrochemical Based Polyurethane, *Journal of World Academy of Science Engineering and Technology*, 65, 2010, pp. 349-352