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Synergization of silicone with developed crosslinking to soybased polyurethane foam matrix

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Abstract. Flexible polyurethane foam obtained from reaction of soybased polyol with TDI:MDI (80:20), and surfactant. The goal of this research is to determine the synergization effect of silicone with low molecular alcohols; methanol and ethylene glycol (EG) in soy-polyurethane formula on holding moisture of foams to density, foam solutions capacity, and cellular morphology. The optimized of polyol was achieved by ratio of epoxide/methanol 1:6 (mol/mol), and epoxide/EG 1:3 (mol/mol). It was found silicone surfactant can minimize solution absorbency in polyurethane foam matrix.

Keywords- soy polyurethane, surfactant, moisture, crosslinking

1. Introduction

Some research has explored and used various technological innovations as an effort to save environment as to respond the fears of supply of non-renewable natural resources to using renewables material [1]-[2]. Agricultural resources as one of many renewables has gaining attention of researchers for the environmental awareness and their potential to replace petroleum derivatives [3].

Polyurethanes (PUR) are the result of the exothermal reaction between a polyisocyanate and molecule containing two or more alcohols groups (-OH). Flexible properties owned by soft segmented with the percentages is higher than hard segment. It occured when ratio of polyol to isocyanate is greater than 1. Polyols will perform as soft segment while isocyanates forming hard segment. PUR products has range of wide spectrum from straight-chain polymers to thermosetting plastics. The structure and properties of polyurethane depends on density, hard and soft segments, and chemical compositions [4]-[11].

The flexible foam can be made as necessary by adding a chain extender, polyol derived from a short chain polyhydroxy defined as low molecular hydrocarbons, if not using chain extenders it can be added polyhydroxy initiator [12]. Chain extender are generally low molecular weight of reactant which produces hard segment in polyurethane, this believed as the result from an increased intermolecular association or bonding induced. The addition of small amount of water leads to the formation of urea linkages, which result in crosslinking. A component can be added to the prepolymer reaction to develop crosslinking, which can effect to the increasing the number of OH sites with which isocyanate can react and have reactive group [13].

The use of natural oils as raw materials for PUR production, multiple hydroxyl functionalities are required. By reacting epoxidised oils with low molecular weight or polyfunctional alcohols or acids. Unsaturated fatty acids in vegetable oil are plays an important role from the intermediates to final

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product. Fatty acid in soybean oil are constitute of palmitic acid 11%, stearic acid 4%, oleic acid 23%, linoleic acid 54%, and linolenic 8%. The combination of polyols, di isocyanate, and low molecular chain extender gives a multitude forms which suitable for extremely different practical applications [14]-[15].

Some advantages of using vegetable oils are having low toxicity, soluble, and high purity. Advantages possessed of using vegetable oils, because are easily to be reshaped and tailormade, which can be made according to market needs. Based on the previous research the optimized oxirane number was 6.7% [16]-[17]. The optimized formulation were then implemented to the proceeded steps.

This research was conducted an assessment of different polyurethane foam products synthesized from combinations of two low molecular weight alcohols; methanol represented as monol, and ethylene glycol represented as diol with a silicone surfactant inclusion. Furthermore, studied its role in holding the amount of solutions of an undisturbed foam which then verified to petrochemical-based polyurethane.

2. Materials and Methods

Soy polyol synthesis. Fifteen ml of soy-epoxide (oxirane number 6.7 mgr KOH/gr sample which processed from soybean oil with specification of kinematic viscosity 443.007 cps; Iodine value 53.89 gr Iod/100 gram sample) was mixed to methanol with ratio (1:1; 1:3; 1:5 and 1:6) (mol/mol), and fifteen ml of soy-epoxide was also mixed to EG with ratio (1:1; 1:3; 1:5;1:6 and 1:10) (mol/mol) in two designated time; 1 hour and 2 hours for methanol and 1 hour, 2 hours, and 3 hours for EG with the concentration of acid catalyst 1% (v/v) and temperature 117^{0} C. The products obtained was neutralized, decantated, and filtered. The average number of –OH groups can lead to a certain controlled amount sites to develop crosslinking, which has the effect of increasing the number OH which then can react to isocyanate.

In making polyols from two route reactions; for methanol-based are namely as (M1;M2;M3 and M4) and EG based (EG1; EG2; EG3; EG4 and EG5). The products from each route are optimized before manufactured to polyurethanes namely as (PUR1) and (PUR2).

Overall, this determination is to identify which of these route of reaction will result the best property to PUR products. The expected oxirane number in polyol synthesis is the lowest among other compositions, which were conducted in triplo in a stable average number.

PUR synthesis. PUR were made by mixing soy-polyol, TDI: MDI (80:20), surfactants, and blowing agent, distilled water. The mixture is then poured into the glass mold, after a couple of minutes being completely dried and safe to be appointed from the molding.

2.1.Method of Analysis

- Oxirane number: specify a group of oxirane oxygen obtained from the titration using HBr in glacial acetic acid.
- Foam Density test: the sample that had been prepared in a particular dimension was weighed using an analytical balance, and then calculate the volume of dimension.

Density = M/W where

(1)

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M: mass specimen (gram)

V: volume of specimen (cubic cm)

• Foam water capacity: measures the amount of solution held in foam matrix to specimen not less than 10 cc.

Water Capacity (%) = $[W_w/w_d]$ *100 (2)

IOP Conf. Series: Materials Science and Engineering **58** (2014) 012023 doi:10.1088/1757-899X/58/1/012023

• Hydroxyl number (OH number): a number arising from a wet analytical method; milligrams of KOH equivalent to the hydroxyl content in one gram of polyol hydroxyl compound.

	OH number = 56.1×1000 /equivalent weight	(3)
•	Density Distribution (%) = [max. density-min. density/average density]x 100	(4)

- Solution Percentages (%) = $[W_w W_d/W_d] *100$ (5)
- % oxirane reduction = 6.7% (optimized oxirane)- $Ox_c / 6.7\% \times 100$ (6) where:

Ox_c; the current oxirane number

3.Result and Discussion

A. Synthesis of Polyol.

Hydroxylation groups have been introduced from two-step synthesis which involving epoxidation of unsaturated sites with a mixed of peroxide with acetic acid; followed by epoxy ring opening with mono functional and difunctional alcohol.

The oxirane number occured from polyol methanol-based for 1 hour reaction was in the range of 0.11-2.47% with the range percentages of oxirane number reduction was 63-95%; the oxirane number for 2 hour reaction was 0.14-1.95% with range percentages of oxirane reduction was 71-90% but it has reached hydroxyl number to 579 mgr KOH/gr sample as compared to palm oil-based polyol with same method is 70-130 mgr KOH/gr [18]. The graph can be seen in figure 1.



Figure 1. Soy-polyol synthesized from soy-epoxide hydroxylation with methanol as a source for develop cross linkers. It was made in four formula. The graph illustrates relationship between the percentages reduction of soy-polyol oxirane number referred to optimized epoxide oxirane number 6.7% to the formation of -OH sites in soy-polyol determined by hydroxyl number

While, oxirane number of polyol EG-based for 1 hour reaction was in the range 0.09-0.2 % with oxirane reduction 90-98%; for 2 hour reaction was 0.08-0.3% with oxirane reduction 96-99%, and for 3 hour reaction was 0.1-0.7% with oxirane reduction 90-99% as can be seen in figure 2.



Figure 2. Soy-polyol synthesized from soy-epoxide hydroxylation with EG as a source for develop cross linkers. It was made in five formula. The graph illustrates relationship between epoxide oxirane number referred to optimized epoxide oxirane number 6.7% to the percentages reduction of oxirane number after soy-polyol formation

The high percentage reduction of oxirane number of EG compared to methanol, does not concerted to the high hydroxyl number. The hydroxyl number of EG was 309 mgr KOH/ gr sample as can be seen in figure 3. This indicates the developed cross link of methanol-based is higher than EG-based, and caused to the high –OH sites to methanol-based.



Figure 3. Soy-polyol synthesized from soy-epoxide hydroxylation with EG as a source for develop cross linkers. It was made in five formula. The graph illustrates relationship between the (%) reduction of soy-polyol oxirane to the formation of -OH sites in soy-polyol determined by hydroxyl number

Using EG in the second stage of the method it is possible to obtain soy-based polyols with primary and secondary hydroxyl groups. The aliphatic β -OH in EG has effected to hydroxyl number of polyol, referred to steric hindrance during hydroxylation reaction which in methanol only have aliphatic α -OH.

B. PUR Characterization

Densitv

The 1 ml amount of silicone in PUR formulation is seems not to be significantly effected to apparent density of the foam. The volume molding relates to the space free rising of the foam which caused to lowering density. Overall, foams molding with volume 500 mLgives density and density distribution are lower than volume 250 mL.

Type of PUR	Density	Density	
	(gr/cm3)	Distribution (%)	
Without Silicone			
Methanol (250)	0.12	74	
EG (250)	0.10	15	
Synthetic (250)	0.13	33	
With Silicone			
Methanol (250)	0.07	16	
Methanol (500)	0.06	11	
EG (250)	0.07	11	
EG (500)	0.06	17	

Table 1 The Apparent Density of dry molded soy-PUR

*Amount of silicone is 1 ml

The molding were designed in 250 mL and 500 mL

Solution Capacity to PUR matrix

The absorbency of foam matrix its seems does relate to density distributions. The high density distribution in the foam matrix more distance between the open cellular. Water capacity for 250 mL molded PUR is higher than 500 mL molded PUR. The addition of silicone in PUR formula has made to the low foam matrix water capacity.

The immersion of etanol (Et-OH) 96% into foam matrix has made a significant effect to using silicone and without silicone in PUR formulation; with silicone the foam matrix has the capacity to hold the Et-OH solutions over 100%. It was found in the general pore diameter for methanol-based PUR was 7.8 mm and EG-based PUR was 5 mm.

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Type of PUR	Density	Water	Foam Water	Et-OH 96%	Foam Et-OH 96%
	(gr/cm3)	in Foam (%)	Capacity (%)	in Foam (%)	Capacity (%)
Without Silicone					
Methanol (250)	0.12	87	231	0.20	0.09
EG (250)	0.10	89	189	0.19	0.09
Synthetic (250)	0.13	(-)	(-)	0.06	0.06
with Silicone					
Methanol (250)	0.07	7	107	0.07	100.07
Methanol (500)	0.06	14	114	0.11	100.11
EG (250)	0.07	17	117	0.07	100.07
EG (500)	0.06	18	118	0.15	100.15

Table 2. PUR foam matrix to the capacity of holding solutions

*The conditions was made for undisturbed foam matrix

Solutions used; 4 drops of water and 4 drops of Et-OH 96% in the foam dimension (1cmx1cmx1cm)

The justification of the result above confirmed by P foam cell morphology using SEM (figure 5). Visible cavities (void) generated by the methanol-based PUR2 is larger and comparable to EG-based PUR. It was found in the general pore diameter for methanol-based PUR was 7.8 mm and EG-based PUR was 5 mm.



Figure 4. Cell Morphology of a. Methanol-based PUR 40x μ m and b. EG-based PUR 45x 500 μ m

Conclusion

The present results confirmed the high percentages reduction of epoxide oxirane number occurred during polyol synthesis does not brought to the conclusion to the high hydroxyl number. The developed cross linking existence from low molecular alcohol are depends on the –OH group location during the hydroxylation reactions.

According to the research founding, silicone surfactant are effective in lowering foam imbibe to water to either methanol-based PUR or EG-based PUR, but this does not valid to Et-OH 96%.

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Acknowledgement

The authors gratefully acknowledge to the support of the Indonesia Department of Higher Education (Dikti-Kementerian Pendidikan dan Kebudayaan Republik Indonesia) as funding the research.

References

- [1] Narine, Kong, Bouzidi dan Sporns, Physical properties of polyurethane produsced from polyol seed oils; elastomers. J Amer Oil Chem Soc 84: 2007, pp. 55-63
- [2] Guidoti *et.al*, Heterogenous catalytic epoxidation of fatty acid nd methl esters on titanium grafted silicas, Green Chem, 5, 2003, pp. 421-424
- [3] Chuajulit S, Sangpakdee T, Saravari O (2007), J Met Mater Miner 17(1), pp.17-23.
- [4] Kong and Narine 2007. Physical properties of polyurethane plastic sheets produced from polyols from canola oil biomacromolecules 8; 2007, pp. 2203-2209
- [5] Hanson and Larock, Soybean oil divinilbenzene thermosetting polymers: synthesis, structure, properties and their realtionships. Pollymer 42(4):2001, pp. 1567-1579
- [6] Petrovic, Cevalos, Javni, Schaefer, and Justice 2005. Soy oil based segmented polyurethanes. J Polym Phys 43(22):2005, pp. 3178-3190
- [7] Petrovic, Zhang, and Javni 2005. Structure and properties of polyurethane prepared from triglycerides polyols by ozonolysis. Biomacromolecules 6(2):2005, pp. 713-719
- [8] Zlatanic, Petrovic, and Dusek, Structure and properties of triolein based polyurethane networks, Biomacromolecules, 3: 2002, pp. 1048-1056
- [9] Lligadas, Ronda, Galia and Cadiz, Polyurethane networks from fatty acid based aromatic triols: synthesis and characterization. Biomacromolecules 8:2007, 1858-1864
- [10] Andjelkovic and Larock, Novel rubbers from cationic copolymerization of soybean oils and dicyclopentadiene 1: synthesis and characterization. Biomacromolecules 7:2006, pp. 927-936
- [11] Guner, Yagci, and Erciyes 2006. Polymers from triglyceride oils. Prog Polym Sci 31: 2006, pp. 633-670
- [12] Aneja, Structure Property Relationships of flexible Polyurethane Foams. Dissertation. 2000, Virginia Polytechnic Institute.
- [13] Thomson T., Design and Applications of Hydrophilic Polyurethanes Technomics Publishing Company, Inc., USA, 2000, p.7-8
- [14] Wang, T.L, Hsiech, Polym J, 29 1996, p.839
- [15] Bauman, H., Bühler, M., Fochen, H., Hirisnger, F. Zoebelien Angew, H., Chem. Int. Ed Engl., 27, 1998, pp.41-62
- [16] Flora, F.E, Optimization of Soy Epoxide Hydroxylation to Properties of Prepolymer polyurethane, Proceeding International Conference on Applied Science Engineering and Information Technology, ISSN 2010-3778, Waset v81 2011, Singapore, p. 189
- [17] Flora, F.E, Silicone on Blending Vegetal Petrochemical Based Polyurethane, Proceeding International Conference on Applied Chemistry, ISSN 2010-3778, Waset 65, 2010, Tokyo, p.350
- [18] Patent US 2008293913 A1