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Silicone on Blending Vegetal Petrochemical Based Polyurethane

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Abstract**—**Polyurethane foam (PUF) is formed by a chemical reaction of polyol and isocyanate. The aim is to understand the impact of Silicone on synthesizing polyurethane in differentiate volume of molding. The method used was one step process, which is simultaneously caried out a blending polyol (petroleum polyol and soybean polyol), a TDI (2,4):MDI (4,4') (80:20), a distilled water, and a silicone. The properties of the material were measured via a number of parameters, which are polymer density, compressive strength, and cellular structures. It is found that density of polyurethane using silicone with volume of molding either 250 ml or 500 ml is lower than without using silicone.

Keywords**—**soybean, petro, silicone, polyurethane

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I. Introduction

IN 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 flexible foams are petroleum derivatives.[2]

Polyurethane Foam (PUF) are been utilized in a variety of applications such as foams, elastomers, adhesives, coating, and sealant. Flexible polyurethane foam, are manufactured by the controlled expansion of a gas during the polymerization process. They are designed to be open-celled, the completion of foam expansion, which allow the free movement of a gas within the foam cells.[3]-[4]

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. [5]-[8] .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.[9]-[11]

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, (16:0) 17.75%; (18:0) 3.15%; (18:1) 23.2%; (18:2) 55.5% and (18:3) 6.31%.[12] 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.[13] However, the SEM images of entirely soybean polyol provided show large amounts of closed cells.[11] Replacing part of petroleum polyol with soybean oil-derived polyol found improvements in foam load properties without concerning in the number of open cells.[14]

The soft phase of polyurethane foam is usually a polyfunctional alcohol or polyol phase glycols such as ethylene glycol is commonly used for chain extension to form hard segments. Low molecular weight diol chain extender plays a very important role in polyurethane.Without a chain extender, polyurethane formed by directly reacting diisocyanate and polyol generally has very poor physical properties and often does not exhibit microphase separation.[15]

Surfactants as one of reagent was used in the PU synthesis plays a crucial role in influencing at the interfacial level as well as within the bulk. The interfacial processes come into play as early as when the initial bubbles are formed in the liquid Silicone based surfactants.[16] The properties of the foam mainly depend on the type of polyol such as hydroxyl value, type and amount of surfactant, and blowing agent.[17]

II. Experimental Procedures

Materials

Soybean oil of RBD (Refined, Bleached, Deodorized) was obtained from PT Variatama Jakarta with Iodine value of 53,89 gram Iod/100 gr sample, viscosity was 65,5278 cps, acid value was 0,024 mgr KOH/ sample. Hydrogen Peroxide was obtained from PT Brataco Chemika, several other reagents; Acetic Acid were obtained from Merck Germany, Sulphuric Acid from Tedia Company, Inc., Butanol and Ethylene Glycol from PT Harum Sari. All materials were used as received without further purification.

The research was conducted to determine the effects of silicone to the physical and chemical properties of polyurethane foam.

Preparation of soy Polyol

Hydroxyl groups have been introduced through two-step synthesis involving epoxidation of the unsaturated sites with acetic acid and hydrogen peroxide, followed by epoxy ring opening with mono alcohol; methanol, butanol, and polyfunctional alcohol; ethylene glycol.

The experiments were carried out in a 500 ml three necked round bottom flask which were equipped with a thermometer, mechanical stirrer. The whole appratus was placed in a waterbath to maintain the temperature at range 110 ± $0{,}5^0$C which was measured inside the flask, and also inside the water bath. The obtained product was allowed to cool to room temperature, and its chemical structure was analysed by using an FTIR spectrophotometer. The oxirane value was determined based on ASTM D1652-9, hydroxyl value was determined based on ASTM D 4274-95, and the viscosity was determined using ASTM D 445-06. The length of reactions are 1 hour and 2 hour.

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Soy polyol series 1 and series 2

Soy polyol series 1 and series 2 are products of hydroxylation reactions from groups of monohydric alcohol; methanol and butanol with soy epoxide, which yield soy polyol 1 (P1) and soy Polyol 2 (P2).

Soy polyol series 3

Soy polyol series 3 is a dihydric alcohol; ethylene glycol, which hydrolyze soy epoxide to yield polyol 3 (P3).

Preparation of Flexible 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 formulation were three type of polyols; (P1), (P2), and (P3), they respectively blend to petroleum polyol which yield PUF 1, PUF 2, and PUF 3 with the formula seen in table 1.

The foam were prepared by adding TDI (2,4):MDI (4,4') (80:20) to the polyol blend (soy polyol and petro polyol), 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, which were 250 ml and 500 ml of volume. The quantities of all components listed (table 1) are based on the amount of polyol utilized in the formulation.

At the creamy stage (the mixture turning creamy), which was rose freely in an open mould. The foam then was removed from the mould and allowed to postcure for one day at room temperature before cut into the test specimens. Each of the compositions above was done in triplo. The best performed Polyurethane Foam (PUF) was made in five replications, and had been characterized.

TABLE I
FLEXIBLE POLYURETHANE FOAM FORMULATION

Series 1					Series 2					Series 3					
Petro Polyol	Soy (P1)	Distilled water	TDI:MDI (80:20)	Si	Petro Polyol	Soy (P2)	Distilled water	TDI:MDI (80:20)	Si	Petro Polyol	Soy (P3)	Distilled water	TDI:MDI (80:20)	Si	Results[a]
25	5	1	5	0	25	5	1	5	0	25	5	1	5	0	1
30	0	2	10	0	30	0	2	10	0	30	0	2	10	0	2
25	5	2	10	1	25	5	2	10	1	25	5	2	10	1	4
20	10	1	5	1	20	10	1	5	1	20	10	1	5	1	1
25	5	2	10	0	25	5	2	10	0	25	5	2	10	0	2
25	5	2	10	1	25	5	2	10	1	25	5	2	10	1	3
25	2	2	10	0	25	2	2	10	0	25	2	2	10	0	2

[a]1: poor 2: minor 3: moderate 4: good

This work failed on using the 100% soy polyol as a sole polyol in synthesizing foams, which the foaming process did not exist in maximum condition, more over it has many defects and voids. It assumed this related to the OH position on fatty acid chain, as part of tryglicerides which is not in the αC as well as in petro polyol, this result of unreactiveness in making urethane linkage. The best soy polyol is recommended used in this work was 5 in comparing to petro 25.

III. Results and Discussion

Alteration to the foam formulation in terms of varying amount of polyols, surfactant, distilled water will result in different quality of foam products, which range widely in properties. The polyols existed from hydroxylation of epoxide to butanol is more viscous than methanol, and ethylene glycol, which was 569,431 cps (P2); 232,828 cps (P1), and 18,864 cps (P3), this was related to the molecular weight.

The hydroxyl value of polyol were synthesized from monohydric alcohol; methanol and butanol, were more higher than dihydric alcohol; ethylene glycol. The values were 578,923 mgr KOH/gr for (P1), 549,66 mgr KOH/gr for (P2), and 308,55 mgr KOH/ gr for (P3).

The results above has indicated that the inclusion of short chain C_1(metha-) and C_4 (buta-) of monohydric alcohols to the synthesis of polyol has met the optimize condition of reaction. The dihydric alcohol of ethylene glycol which previously expected to contribute more OH's, has voided the theoretical analysis.

According to Kanner & Decker, foam were synthesized from higher hydroxyl value will give a higher density.[16] The hydroxylation leads to the decrease in oxirane number. Lim, Kim and Kim, mentioned that the synthesizing foam by using same formulation, without silicone will significantly result in different on densities, which was more to rigid foam.[17]

TABLE II
CHARACTERISTICS of SOY POLYOLS USED IN FLEXIBLE FOAM FORMULATION

Polyol Property[a]	P1	P2	P3
Hydroxyl value (mgr KOH/gr)	578.923	549.66	308.55
Oxirane Number (%)	0.11	0.09	0.079
Viscosity (cps)	231.828	569.431	18.864
Functionality	1	1	2
Color	Pale Yellow	Pale yellow	Brown

[a]2 hour reaction and temperature 110^0C

Characterization and Property Measurement of Soy based Polyol

The concentration ratio of epoxide to alcohols were 1:1; 1:3; 1:5 and 1:6 (mol/mol) (table 2). This aim is to determine the optimal condition by used the oxirane numbers as the indicator, which is the lowest amongst the formulation. It was considered would formed more active site in other words linkages with urethane.

The optimized conditions found in synthesizing Polyol (P1, P2, and P3), were at 2 hour reaction, the ratio concentration of epoxide to alcohol was 1:6 (mol/mol) for P1; 1:5 (mol/mol) for P2, and 1:5 (mol/mol) for P3 by temperature at 110^0C. (Fig. 1) below shows the comparison of oxirane number in different time of reaction; which were 1h and 2h. It assumed by 1 h of reaction the soy epoxide has not met the optimized hydroxylation.

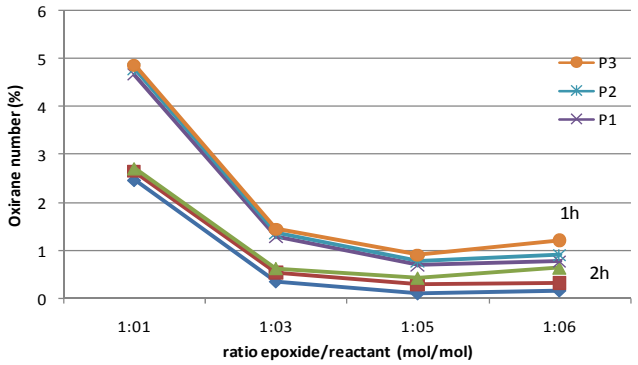

Fig. 1 The effect of length of reaction to Oxirane number of polyol at 110^{0}C.

Characterization and Property Measurement of PU Foam

The obtained PU foams were characterized by using density measurement, the foams were cut into specimens with dimension of 2x2x2.5 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. The data showed that polyurethane butanol, methanol, and ethylene glycol based with Silicone were almost similar.

Many factors and conditions can influence the foaming process of flexible cellular polyurethanes. This work was done to analyzed the relationship between volume of molding to foam density. Generally, foams which were synthesized without using silicone, relatively have higher density to those were synthesized with silicone.

Foams with volume of molding 250 ml and 500 ml has a comparable density, which is volume 500 ml has more higher density than 250 ml. It refers to more space of foam to freely rise.

TABLE III
DENSITY OF FLEXIBLE FOAM

Series 1[a,b]			Series 2[a,c]		
Type of PUF	Density (gr/cm3)	Average Density	Type of PUF	Density (gr/cm3)	Average Density
PUF 1	0.1026	0.1156	PUF 1	0.069	0.06515
	0.1707			0.0664	
	0.1033			0.0667	
	0.0858			0.0585	
PUF 2	0.1791	0.1195	PUF 2	0.1214	0.1151
	0.093			0.1088	
	0.0908			0.1214	
	0.1151			0.1088	
PUF 3	0.1052	0.09928	PUF 3	0.0758	0.07263
	0.0956			0.0754	
	0.0907			0.0676	
	0.1056			0.0717	

[a]molding volume 250 ml
[b]Series 1 PU synthesize without Silicone
[c]Series 2 PU synthesize by used silicone

Table 4 shows the volume of molding can affect the foam density. Moreover, the foam density is higher it is found there is a relationships between hydroxyl value to density.

TABLE IV
DENSITY OF FOAM WITH SILICONE

Type of PU	Hydroxyl Value (mgr KOH/gr)	Density (gr/cm3)[a]	Density (gr/cm3)[b]
PUF 1			
	578.59	0.0574	0.069
		0.069	0.0664
		0.0507	0.0667
PUF 2		0.0686	0.0585
	549.66	0.0648	0.1214
		0.0757	0.1088
		0.0696	0.1214
PUF 3		0.0649	0.1088
	308.55	0.0578	0.0758
		0.0651	0.0754
		0.0553	0.0676
		0.0579	0.0717

[a]Molding volume 500 ml
[b]Molding volume 250 ml
Relationship between hydroxyl value to density

The foams of PUF1, PUF2, and PUF3 which were synthesized by using silicone and molding 500 ml were then the main focus to be analyzed. The compressive strength of the foams was examined, shown at table 5 below.

TABLE V
COMPRESSIVE STRENGHT OF POLYURETHANE FOAMS

Type of Polyurethane[a]	Compressive strenght	
	at 10% (MPa)	Max Load 10% (kN)
PUF1	$3{,}06x10^{-3}$	17
PUF2	$3{,}4x10^{-3}$	18
PUF3	$3{,}3x10^{-3}$	18

[a] PUF was synthesized by silicone and molding 500 ml

There compressive strength of three type of foams were not significantly different, eventhough PUF1 seems the lowest amongs others.

Cell Morphology

It is known that the mechanical properties of a cellular mainly depend on its density.[18] The density and mechanical properties of PUF1 is slightly lower than PUF2, and PUF3, which is beyond affected by P2 and P3. This slightly higher mechanical strength is due to increased crosslink density which results in a higher hard segment content.

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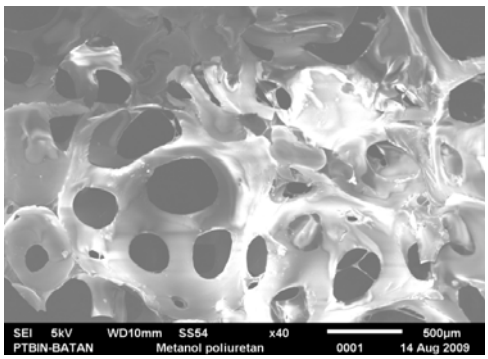
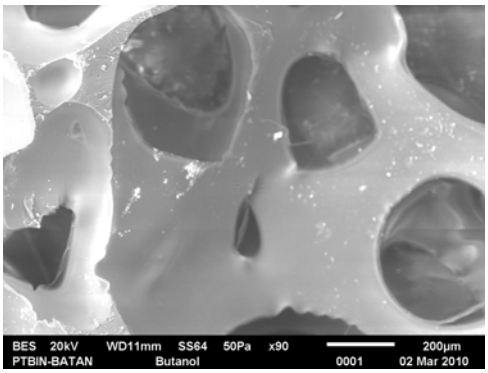
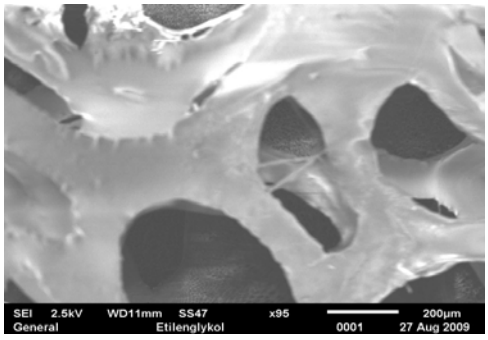
SEM micrograph was used to take images of cured solid polyurethane foams PUF1, PUF2, and PUF3 which used petro in the same composition, it is shown in figure 4. The cell size of PUF2 and PUF3 reveals slightly larger compared to PUF1.



a. Polyurethane PUF1 magnified in 40x, 500µM



b. Polyurethane PUF2 magnified in 90x, 200 µM



c. Polyurethane PUF3 magnified in 95x, 200 µM

Fig. 2 SEM micrographs of Polyurethane

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