Role of Silicone on Molded Flexible Polyurethane from Soy Oil

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Abstract

Polyurethane foam (PUF) is formed by a chemical reaction of polyol and isocyanate. The aim of this work is to understand the effect of silicone on molded polyurethane. Silicone perform as surfactant, which influencing the interfacial level as well as within bulk. The method used was one step process, which are simultaneously carried out a blending polyol, TDI (2,4):MDI (4,4') (80:20), distilled water into different volumes of molding. The properties of molded polyurethane were determined by its polymer density, compressive strength, and cellular structures.

Keywords: Soy oil, Silicone, Polyurethane, Density

1. Introduction

Polyurethane foam (PUF) is one the most useful polymeric materials regard to processing methods and mechanical properties. The resulting PUF can be rigid crystalline plastic, flexible elastomer, or viscoelastic gel. This wide range of achievable properties makes PUF an indispensable component in building construction, consumer products, transportation and medical devices (Herrington, 1997). Similar to nearly all polymeric materials PUF relies on petroleum oil as the feedstock for its major components: hydroxyl containing polyols and isocyanates. Using bio-renewable feedstocks for PUF manufacturing becomes highly desirable for both economic and environmental reasons (Schaefer, 2005). Vegetable oils can be potential replacements for polyols. Several methods are currently known to add hydroxyls at the unsaturated sites: hydroformylation followed by hydrogenation (Lsenko et al., 2004), epoxidation followed by oxirane opening (Petrovic et al., 2002), ozonolysis followed by hydrogenation (Petrovic, 2005). 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 (Petrovic, 2005; Javni et al., 2002), John et al., 2002).

Soybean is a preferred feedstock for 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 % (Aneja, 2002). This oil can be hydroxylated to 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 (Casado, 2009). However, the SEM images of entirely soybean polyol provided show large amounts of closed cells (John, 2002). Replacing part of petroleum polyol with soybean oil-derived polyol found improvements in foam load properties without concerning in the number of open cells. (Herrington, 2006; Babb, 2006; Lysenko, 2006).

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. Chain extender plays a very important role in polyurethane. Without a chain extender, polyurethane formed by directly reacting diisocyanate and polyol generally which may exist very poor physical properties and often does not exhibit microcellular separation (Wang, 1998).

As one of reagent, surfactants were 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 (Kanner, 1969). The properties of the PUF depends on the its polyol type such as hydroxyl value, amount of surfactant, and blowing agent (Lim, 2008).

2. Materials and Methods

2.1 Materials

Soybean oil with Iodine value of 53,89 gram Iod/100 gr sample, viscosity was 65,5278 cps, acid value was 0,024 mgr KOH/ sample, were purchased from P.T Variatama Jakarta. Hydrogen peroxide, acetic acid, sulphuric acid, butanol, and ethylene glycol were also used. All materials were used as received without further purification.

2.2 Preparation of flexible PU foam

The ratios of soy epoxide to alcohol used in this study were 1:1; 1:3; 1:5 and 1:6 (mol/mol). Hydroxylation of monohydric alcohols (methanol and butanol) to soy epoxide respectively yields polyol 1 (P1) and polyol 2 (P2), and with dihydric alcohol; ethylene glycol, yield polyol 3 (P3). They respectively blend into petroleum polyol yields PUF 1, PUF 2, and PUF 3.

3. Results and Discussion

3.1 Property measurement of soy based polyol

The optimized conditions found in synthesizing polyol (P1, P2, and P3), were at 2 hour of reaction, with 1:6 (mol/mol) for P1; 1:5 (mol/mol) for P2, and 1:5 (mol/mol) for P3 at 110 $^{\circ}$ C (Figure 1). It assumed by 1 h of reaction the soy epoxide has not met the optimized hydroxylation. The polyols existed from hydroxylation of epoxide to butanol is more viscous than methanol, and ethylene glycol which were 569,431 cps (P2); 232,828 cps (P1), and 18,864 cps (P3), this much related to its 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.

3.2 Characterization and property measurement of PUF

3.2.1 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 have a comparable density (Table 2). The volume of molding can affected to foam density. Moreover, the foam density has relationships to hydroxyl value (Figure 2).

3.2.2 Compressive strength

There compressive strength of three type of foams were not significantly different, eventhough PUF1 seems the lowest amongs others (Table 3).

3.2.3 Cell morphology

The cell size of PUF2 and PUF3 reveals slightly more larger compared to PUF1 this could be effected to the exceeds water content on synthesizing P1. SEM micrograph was used to take images of cured solid polyurethane foams PUF1, PUF2, and PUF3 which used petro in the same composition, it shown in (Figure 3). The cell size of PUF2 and PUF3 reveals slightly more larger compared to PUF1 this could be effected to the exceeds water content in synthesized P1.

4. Conclusion

It is found the used of silicone and volume molding on polyurethane synthesis can be effected to density, mechanical strength, and morphology of the foams. The type of alcohols (monohyric or polyhydric) on producing poyols effected to time of completion. Overall it effected to the properties of polyurethanes.

Acknowledgements

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Polyol Property ^a	P1	P2	Р3
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

Table 1. Characteristics of soy polyols as prepolymer for PUF

^a2 hour reaction and temperature 110 $^{\circ}$ C

Table 2. Density of PUF

Series 1 ^{a,b}			Series 2 ^{a,c}		
Type of	Density	Average	Type of	Density	Average
PUF	(gr/cm3)	Density	PUF	(gr/cm3)	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	

^amolding volume 250 ml

^bSeries 1 PU synthesize without Silicone

^cSeries 2 PU synthesize by used silicone

Table 3. Compressive strength of PUF

Type of	Compressive strenght		
Polyurethane ^a	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 with silicone using molding 500 ml

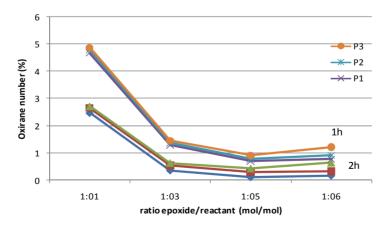


Figure 1. The effect of time to polyol Oxirane number at temperature 110 $^\circ C$

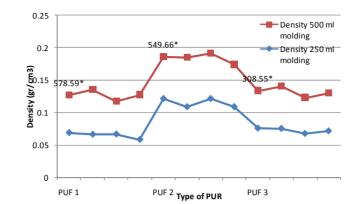
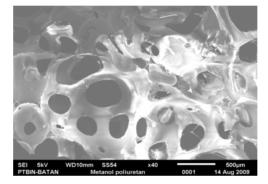


Figure 2. Density of PUF at different volume of molding: 250 ml and 500 ml

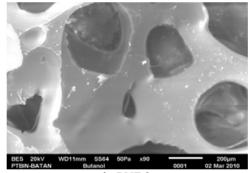
*Hydroxyl value (mgr KOH/gr sample)

PUF was synthesized by silicone

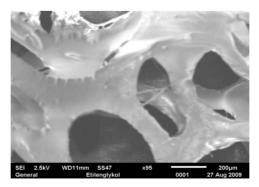
Relationship between hydroxyl value to density



a.PUF1



b. PUF 2



c. PUF3 Figure 3. SEM micrographs of Polyurethane