

Chain Extender on Property Relationships of Polyurethane Derived from Soybean Oil

Flora Elvistia Firdaus

Abstract— Polyurethane foams (PUF) has been prepared from vegetable; soybean based polyols. They were characterized into flexible and semi rigid polyurethane foam. This work is directed to production of flexible polyurethane foams by a process involving the reaction of mixture of 2,4- and 2,6-Toluene Di Isocyanate isomers, with portion of to blends of soy polyols with petroleum polyol in the presence of other ingredients such as blowing agents, silicone surfactants and accelerating agents. Addition of chain extender improves the property then further decreases the properties on further addition of the same. The objective of this work was to study the effect of chain extender and role of phosphoric acid catalyst to the final properties and correlate the morphology image with mechanical properties of these foams.

Keywords—polyurethane, soy polyol, chain extender

I. INTRODUCTION

Polyurethanes are an important class of polymers that offer the chance to obtain the designed properties by proper selection of different composition [1]. The combination of polyols, di isocyanates and low molecular chain extender gives rise to a multitude of forms suitable for extremely different practical applications [2].

In the recent years there has been a growing interest in the development of bio-based products that can reduce the widespread dependence on the petroleum feed stocks. Petroleum is a nonrenewable resource, the inevitable depletion of petroleum resources coupled with the high cost has prompted researchers to develop alternatives to petroleum based products from vegetable oil. The use of vegetable oils and their derivatives in polyurethane and specialty chemicals is well known [3]-[8]. Besides their renewable nature, most of these derivatives are biodegradable and environmentally friendly, which make them attractive candidates for development of sustainable technologies [9].

The properties of polyurethane foam (PUF) can be modified within wide limits depending on the raw materials used for its synthesis. The polyols and isocyanates are the major raw materials which largely influence the properties of the foams. These changes are mainly due the differences in chemical structure, equivalent weight and functionality of the polyols or combination of polyols which decides rigidity or flexibility based on the polyol used [10].

The preparation of polyols from vegetable oils for general polyurethane use has been the subject of many studies. For natural oils and derivatives to be used as raw materials for polyol production, multiple hydroxyl functionality is required [11]. Traditionally, plant oil-based polyols have been prepared starting from triglyceride molecules. These polyols have been successfully prepared using different methods; most common is the epoxidation of carbon-carbon double bonds and further oxirane ring-opening with alcohols or other nucleophiles [12–18]. Phosphoric in the present is an appropriate catalyst, the epoxy compounds will react with reactive isocyanate to form oxazolidone during polyurethane foam production [19].

Most of rigid PUFs are prepared from judiciously formulated blends of polyols. The blends may contain several polyols, or so called mixed polyols which can be used for the achievement of specialty properties. Because of the lower tendency to crystallize, PUF synthesized using mixed polyols have better physical properties. The role of difunctional compounds (1,2 ethanediol or ethylene glycol) are essentially chain extenders whereas compounds with higher functionality should be considered as cross link agents [21]. Chain extender are generally low molecular weight reactants which produce hard segments which are believed to result from an increased intermolecular association or bonding induced by the use of chain extenders [22].

The experimental parameters obtained in the study of polyurethanes are influenced by multicomponents system with soft and hard segments. The research was conducted to determine the effects of Phosphoric acid in the soy-epoxide hydroxylation to the property of polyurethane. However, the reports did not explore the optimization amount of ethylene glycol. Moreover studies of the effect of the chain extender and polyol blends on properties of water blown polyurethane. Chemical blowing agents are used in the preparation of PUFs. Distilled water is one of the most widely used, it reacts with isocyanate and generates carbon dioxide and polyurea. The carbon dioxide causes foaming: as a result, a cellular structure is formed.

The application of chain extender and polyol blend to rigid foam PUF is to improve the properties and processing which seldom studies. The aim of the present work is to study the effect of chain extender, different type of polyol and different amount of blowing agents on mechanical and morphological properties of the rigid foam.

II. EXPERIMENTAL PROCEDURES

A. Materials

The samples containing soybean oil of RBD (Refined, Bleached, Deodorized) was supplied by JICO Agung Jinyuone

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Co LTD Korea and Nirwana Lestari from Soine Darby Edible Products LTD Singapore, 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.

A two step process was applied for the preparation of soybean oil based polyol. In the first step unsaturated fatty acids in triglycerides reacted with phosphoric acid to form epoxidized oil. Through epoxidation, the double bonds of triglycerides were transformed into oxirane rings. In the second step the epoxidation, the epoxidized oils were converted into polyols using ethylene glycol. Typically, synthesis of PUF was done by the following procedure as can be seen in table 1.

TABLE I
CHARACTERISTICS of MATERIALS USED in STUDY

Material designation	Properties	Role
Soybean Oil JICO Co Ltd Korea	53.89 gr Iod/ 100 gr sample viscosity 65.5278 cps Acid value 0.024 mgr KOH/gr sample	Epoxide
Ethylene Glycol	Functionality 2.0	Chain extender Chemical blowing
Water	Functionality 2.0	Agent
Silicone		Surfactant

B. Methods

Polyols have different physicochemical properties that have direct effect on their performances in polyurethane formulations. The properties described below are important criteria for characterizing polyols.

Impact Resilience

Impact resilience is a measure of elasticity, bouncing, or springiness of foam and is expressed as % of return, or % resilience. To obtain % resilience two type of balls: a 46 gram and 2.7 gram is dropped 50 cm onto the foam through with every 5% return calibration marked. Three drops are executed and the averages of the three readings are equal to the % of the return of the ball to its original height.

The Apparent Density

The apparent density of PUF samples were measured as per ASTM D 1622-03. The specimen was 1x1x1 cm³ (length x width x thickness). The apparent density of PUF1, PUF2, PUF3, and PUF4 were measured and average value reported.

The foam morphology

The morphology of the PUF samples was studied with JEOL, Scanning electron microscope, Japan

Foam Preparation and Evaluation

The foam preparation was carried out by free rise method with the chemical composition shown in table 2. In our

investigation the foam elasticity was controlled by polyol series. The isocyanate in the formula was made constant.

TABLE II
FORMULATION of POLYURETHANE

Designation of Polyurethane	Epoxide/alc	Soy polyol (ml)	Water (ml)	TDI Isomers (70:30) (ml)
PUF 1	1:01	5	2	5
PUF 2	1:05	5	2	5
PUF 3	1:07	5	2	5
PUF 4	1:09	5	2	5

This formula were done in three temperature conditions which are: 50, 60, and 70°C

The synthesis of PUF was performed in a 400 mL glass reactor at normal pressure and under vigorous agitation. In the prepolymer procedure, soy polyol or blending soy-petro polyol was reacted to TDI isomers at 70± 5°C for 2 hours, in order to yield a prepolymer that mixed to chain extender ethylene glycol. The resulting material was poured into a glass mold and left at room temperature for 26 hours.

III. RESULTS AND DISCUSSION

A. The Effect of Chain Extender on Density

The effect of chain extender (ethylene glycol) on the density of the water-blown PUF is shown in table 3. It is known that the mechanical properties of a cellular material mainly depend on its density. The characteristics of different materials used in the preparation of PUF are shown in table 1. All the chemicals were used as received.

TABLE III
THE EFFECT of ETHYLENE GLYCOL on
PUF DENSITY

Designation of Polyurethane	Content of EG (ml)	Density (pcf)
PUF 1	4.26	12.27
PUF 2	21.3	12.82
PUF 3	29.8	13.39
PUF 4	38.34	15.86

B. Effect of Polyol and its blends on the properties of PUF

Mechanical properties of water blown PUF depends on functionality, equivalent weight, and hydroxyl value of the polyol and PUF density. There are different types of polyol were used in this work in the preparation of PUF. Use of polyol 4 led to more rigid PUF rather than PUF 1, PUF 2, and PUF 3. This because the value of equivalent weight of the polyol (13.5 mgr KOH/gr) compared to polyol I (208 mgr KOH/gr); PUF 2 (181 mgr KOH/gr), and PUF 3 (122 mgr

KOH/gr). The equivalent weight of the polyol are important parameters in preparation of rigid PUF, this link to density; which declined as the equivalent weight increase.

C. The Effect of Formula to Cellular Morphology

The SEM reveals that foam cells are slightly minor with enhancing temperature conditions to 70°C, (PUF4) compared to 60°C. It is due to the evolution of less blowing gas due to difference in reactivity between polyol and ethylene glycol with TDI isomers.

The cells in PUF with included EG in the polyurethane synthesis was vague. At the initial state most of the cell faces broken. Water acts as a chemical blowing agent by generating CO₂ on reaction with diisocyanate, with the evolution of heat. Because the increase of temperature, the volume of blowing gas in the mixture exceeds its solubility limits and bubble nucleation. The morphology of PUF using petroleum polyol is quite obvious and comparable to soy polyol.

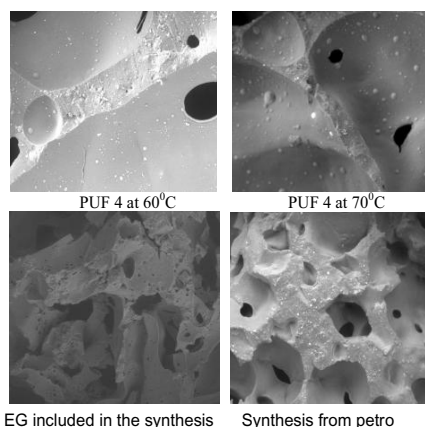


Fig. 1 SEM photograph of PUF samples with different content of Ethylene Glycol

D. The Effect of Chain extender on PUF Impact Resilience

Water reacts with isocyanates forming carbondioxide as chemical blowing agent, which in most cases chemical blowing agents such water are used in lower quantities compared to physical blowing agents.

TABLE IV
THE IMPACT RESILIENCE on PUF

Designated Polyol	Chain extender (ml)	Initial Foam Height (cm)	PUF is with 1.0% (v/v) H3PO4		Ball is with 1.5% (v/v) H3PO4	
			Ball 1 (cm)	Ball 2 (cm)	Ball 1 (cm)	Ball 2 (cm)
Polyol1	4.26	3.5	nb	nb	3	nb
Polyol2	21.3	2	1.5	2	3	1
Polyol3	29.8	2	1	nb	2.5	1
Polyol4	38.34	2.5	0.5	1.5	3	1.5

Nb* is indicated that the ball is not bouncing
Ball I is weight of 46 gram
Ball II is weight of 2.7 gram

As in general, the bouncing response on PUF has been made, the table above viewed the relationships of chain extender concentration to the bouncing response of polyurethane. It is clearly seen the formula of chain extender to PUF 1 has made the foam become very flexible. The chain extender simultaneously chemical blowing agent, and catalyst formed PUF which in this work; the PUF 2 and PUF 4 are comply as semi flexible foam.

E. Polyurethane Water absorption behavior

The water absorption behavior of PUF prepared from blended polyol containing soy polyol and petro polyol. The hydrophobic nature of the long carbon chain as well as of the ester linkage in the PUF. It is quite of comparable to PUF which synthesize using sulfuric acid as catalyst. The ingredient used for PUF 2 and PUF 4 seems to be more water absorbance rather to PUF 1 and PUF 3.

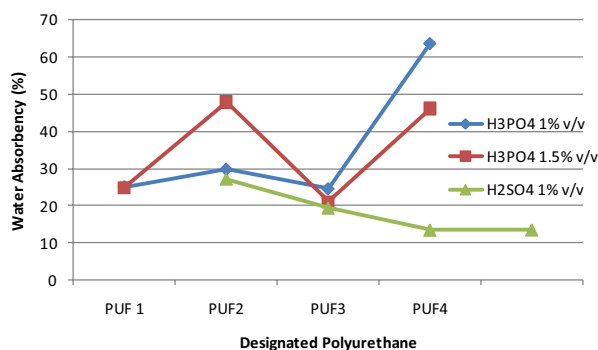


Fig. 2 Polyurethane Water Absorbency

The percentage of compression set test justified the flexibility of foam by value recovered after compressed between two metal plates at controlled time period and room temperature. The formula of polyurethane on PUF 2 at 70°C is the better amongst, because it has the lowest value to recover to its original thickness.

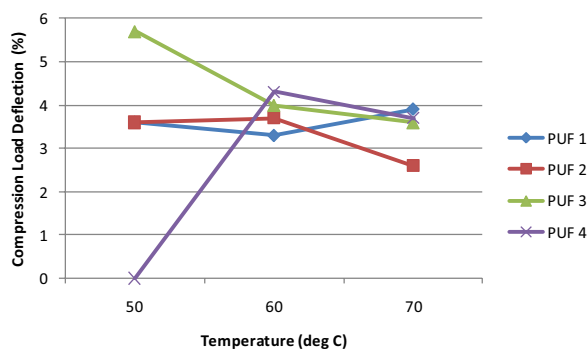


Fig. 3 The Compression set of Polyurethane

IV. CONCLUSION

This study has investigated the various properties of polyurethane with the use of ethylene glycol as chain extender in the synthesis. The inclusion of ethylene glycol has made the foam responded as flexible and semi flexible. The formula has made the polyurethane responses to density, impact resilience, compression set, water absorbency behavior and cellular morphology a great deal to compare. Results show that these properties are dependent on the chain extender content in the polyurethane synthesis. For the 4.26 ml of ethylene glycol with either 1.0% and 1.5% (v/v) H₃PO₄ shows had no bouncing effect to during the test. The compression set test as an advanced test has proven the formula apply for PUF 2 is the best amongst.

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