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EFFECT OF NCO/OH RATIO AND MOLD SYSTEM ON PHYSICAL AND MECHANICAL PROPERTIES OF RIGID POLYURETHANE FOAM BASED ON PALM OIL

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ABSTRACT

EFFECT OF NCO/OH RATIO AND MOLD SYSTEM ON PHYSICAL AND MECHANICAL PROPERTIES OF RIGID POLYURETHANE FOAM BASED ON PALM OIL. A new kind of rigid polyurethane foam (RPUF) was synthesized from palm oil based polyol. Hydroxy methoxy polyol was prepared from epoxidation and hydroxylation process, and called as hydroxyl methoxy glycerolmonostearate (HMGMS) polyol. Synthesis process of rigid polyurethane foam was conducted by reaction between HMGMS polyol and methylene diphenyldiisocyanate (MDI) via one shoot process in the presence of additive i.e. ethylene glycol (chain extender), silicon glycol (surfactant), dimethylcyclohexylamine (amine catalyst), stannous octoate (organometalic catalyst) and water as blowing agent. In this work, we investigated the effect of NCO/OH ratio (1.8 ; 2.0 ; 2.2 ; 2.4) and mold system (closed mold and open mold) on the physical and mechanical properties of rigid polyurethane foam. The physical and mechanical properties of rigid foam were conducted by determining the bulk density, dimensional stability, degree of water absorption and compressive strength. It was found out that NCO/OH ratio and mold type were important variables in making RPUF.

Key words : Polyurethane, Palm oil, Rigid foam, Mold, NCO/OH ratio

ABSTRAK

PENGARUH RASIO DARI NCO/OH DAN SISTEM *MOLD* TERHADAP SIFAT FISIS DAN MEKANIK DARI BUSA KAKU POLIURETAN YANG BERASAL DARI MINYAK SAWIT. Dalam penelitian ini, busa kaku poliuretan tipe baru telah disintesis dari poliol yang berbasis minyak sawit. Hidroksi metoksi poliol telah dipreparasi dari epoksidasi dan proses hidroksilasi dan disebut poliol *Hydroxyl Methoxy Glycerol Mono Stearate* (*HMGMS*). Proses sintesis dari busa kaku poliuretan ini dilakukan dengan mereaksikan poliol *HMGMS* dan *Methylene Diphenyl diisocyanate* (*MDI*) melalui proses *one shoot* dengan disertai keberadaan aditif berupa *ethylene glycol* (pemanjang rantai), *silicon glycol* (surfaktan), *dimethylcyclohexylamine* (katalis amin), *stannous octoate* (katalis organometalik) dan air sebagai *agent* peniup. Dalam penelitian ini, dipelajari pengaruh dari rasio NCO/OH (1,8 ; 2,0 ; 2,2 ; 2,4) dan pengaruh sistem *mold* (*mold* tertutup dan *mold* terbuka) terhadap sifat fisik dan mekanik dari busa yang dihasilkan. Sifat fisik dan mekanik ini ditentukan dengan mengukur densitas *bulk*, stabilitas dimensi, derajat dari absorpsi air serta kekuatan kompresi. Hasilnya menunjukkan bahwa rasio NCO/OH dan sistem *mold* yang dipakai merupakan variabel yang menentukan dalam pembuatan busa poliuretan.

Kata kunci : Poliuretan, Minyak sawit, Busa kaku, *Mold*, Rasio NCO/OH

INTRODUCTION

Rigid polyurethane foam (RPUF) is one of the most efficient, high performance insulation materials, enabling very effective energy savings with minimal occupation of space [1]. It is usually obtained from reaction between polyol polyether or polyol polyester and polyisocyanate forming urethane linkages [2]. Some applications of rigid polyurethane foams are used as shock and thermal insulators and energy absorption material for sensitive electronic components [3]. Rigid polyurethane foam can be manufactured in various shaped and sizes and can also be produced in situ by a variety of methods. RPUF can be poured in place. This involves mixing the chemicals either manually or by mechanical means and pouring into open molds or spaces where insulation is required. RPUF also can be sprayed directly onto a solid surface using guns that mix and atomize the foam as it is being applied. And also in frothing, the mixture of chemicals is dispensed partially pre expanded, like an aerosol cream [4].

The characteristic of polyurethane foam is affected by the addition of blowing agent to produce bubble and expansion. There are two type of blowing agent i.e. chemical blowing agent (example: carbon dioxide from reaction result between isocyanate and water) and physical blowing agent (example: trichlorofluoromethane and hydrochlorofluorocarbon) [5]. Because of some physical blowing agent impact on ozone depletion, the environmental legislation forces producers to use more environmental friendly substances. Since carbon dioxide is produced by the reaction of water and isocyanate in the polyurethane reaction, it seems to be one of the best choices as an alternative blowing agent. Carbon dioxide used as a blowing agent is a by product of other manufacturing processes and therefore, it has no impact on the global carbon dioxide concentrations [6].

In the producing of rigid polyurethane foam, the properties obtained depend on their structure, the raw materials used and the manufacturing process. Some researches about synthesis of polyurethane foam to enhance its properties has been conducted by using closed mold and open mold [7,8]. However, comparative study about the effect of closed and open mold to the physical properties of polyurethane foam have not been conducted yet. Closed mold correlated with the closed expansion where the foaming process has been conducted under restricted conditions, while open mold correlated with the free expansion under free-rise no restricted [9].

The preparation of polymers from renewable sources such as vegetable oil-based materials is currently receiving increasing attention because of the economic and environmental concerns [10-11]. Therefore, research on the manufacturing of polyurethane based on renewable resources has becoming an important research activities.

Vegetable oils as renewable resources such as soybean oil, canola oil, rapeseed oil, corn oil, palm oil, sunflower, and linseed oil have been studied as polyol source for polyurethane [12-14]. Vegetable oils are triglycerides of fatty acids. In order to use these compounds as starting materials for polyurethane synthesis, it is necessary to functionalize them to form polyols. Epoxidation and ring opening reaction with haloacids or alcohols, ozonolysis and hydration are some of the common methods for functionalization of unsaturated vegetable oils [10].

In this work, rigid polyurethane foam was produced from polyol based on palm oil by using closed mold and open mold method to investigate the effect of mold system on the physical and mechanical properties of rigid polyurethane foam based on palm oil with the carbon dioxide as chemical blowing agent and in the variation of NCO/OH ratio.

EXPERIMENTAL METHOD

Materials

The palm oil based polyols were prepared through epoxidation and hydroxylation process of glycerol monooleate called as Hydroxy Methoxy Glycerol Mono Stearate (HMGMS) polyol, as previously done in the laboratory of polymer chemistry group, RCChem LIPI. The process for the production of polyol has been patented in Indonesia (P00200700238). The properties of the polyol are showed in Table 1.

Additive such as silicon glycol was used as surfactant. Stannous octoate was used as organometallic catalyst. Dimethylcyclohexylamine was used as amine catalyst. Distilled water was used as blowing agent. Ethylene glycol was used as chain extender and Methylene Diphenyl diisocyanate (MDI) were incorporated in the formulation.

Preparation of Rigid Polyurethane Foam

The rigid polyurethane foam was synthesized by using one shoot processing method. In this method component A which consists of mixture of polyol and additives (silicon glycol, stannous octoate, dimethylcyclohexylamine, ethylene glycol and water) was reacted directly with component B which consist of MDI at room temperature.

The effect of mold system (open and closed mold) and variation of NCO/OH ratio to the properties of Rigid Polyurethane Foam (RPUF) were studied in detail. Closed mold used in this research was glass bottle with dimension 45 mm x 80 mm (diameter x height). Procedure for preparing RPUF with closed mold was employed by stirring component A and component B in the glass bottle by using glass spatula for 1 minute and RPUF was molded directly in the bottle and then bottle was closed. Producing of RPUF by using open mold has been conducted in two methods i.e. open mold molded directly in the place by using polypropylene cup mold and open mold poured by using paper box mold.

For the first method of open mold, component A and component B was stirred in the polypropylene cup by using glass spatula for 1 minute and then allowed to rise freely. While, for the second method of open mold, component A and component B was stirred in the polypropylene cup for 1 minute and then at the creamy

Table 1. Properties of the palm oil based polyol (HMGMS polyol)

Hydroxyl value (mg KOH/g)	161
Iod value (mg I_2/100 g)	28,2

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stage (the mixture turning creamy), the mixture was poured into an open mold (paper box mold) and allowed to rise freely. Study of the effect of NCO/OH ratio was conducted with variation ratio 0.8; 1.0; 1.2; 1.8; 2.0; 2.2; 2.4 for closed mold and for open mold start from NCO/OH ratio 1.8. The NCO/OH ratio is given by Equation (1) as follows:

$$[NCO]/[OH]\,ratio = \frac{M_{MDI}\; x W_{MDI}}{M_{HMGSMSpdlyo}\; x W_{HMGMSpdlyo} + M_{ethyleneglycol}\; x W_{ethyleneglycol} + W_{water}\; x \frac{1000}{9}} \quad \text{.......................... (1)}$$

Where :

- M_{MDI} = Content of the isocyanate group in MDI (6.78 mmol/g)
- $M_{HMGMS\ polyol}$ = Content of the hydroxyl group in HMGMS polyol
- $M_{ethylene\ glycol}$ = Content of the hydroxyl group in HMGMS ethylene glycol (hydroxyl number/56.1: 2.87 mmol/g and 4.55 mmol/g)
- W_{MDI} = Weight of MDI
- $W_{HMGMS\ polyol}$ = Weight of HMGMS polyol
- $W_{ethylene\ glycol}$ = Weight of ethylene glycol
- W_{water} = Weight of water

The formula of additive used for preparation of RPUF with variation of mold is presented in Table 2.

Characterization and Property Measurements of RPU Foam

The physical and mechanical properties of RPUF were characterized by determining its dimensional stability, bulk density, degree of water absorption and compressive strength. The chemical structure of palm oil based polyol used was characterized using an FT-IR Spectrophotometer (IRPrestige 21 SHIMADZU).

Dimensional Stability

Dimensional stability was determined by measuring of shrinkage level for five days. For open mold method, shrinkage level was calculated after curing for 24 hours. While for closed mold method shrinkage level was determined after glass bottle was opened and foam was cured (glass bottle was opened after 24 hours and then cured for 24 hours). The shrinkage degree of RPUF was calculated according to the following Equation (2) :

$$\text{Shrinkage degree (\%)} = \frac{V_{initial} - V_{final}}{V_{initial}} \text{ x 100} \quad \text{.... (2)}$$

Where :

- $V_{initial}$ = RPUF volume before curing
- V_{final} = RPUF volume after curing

Bulk Density

For density measurement, the PU foams were cut into specimens with dimension of about (20 x 20 x 10) mm^3 (width x length x thickness) for the open mold method and 45 mm x 10 mm (diameter x height) for closed mold method.

The specimens were accurately weighed to determine their densities using the equation, density = mass/volume. The density for each foam was ascertained using the average value from five specimens.

Degree of Water Absorption

The samples of foam (25 x 25 x 15) mm^3 (width x length x thickness) for the open mold method and 45 mm x 10 mm (diameter x height) for closed mold method) were immersed in 250 mL Beaker glass, containing water and kept for 6 days in room temperature. The samples were removed from water and weight with an analytical balance. The samples mass change resulting from the water uptake (expressed as a gram/volume percentage) was calculated according to the following Equation (3) :

$$\text{Water absorption (g/v \%)} = \frac{m_w - m_d}{v_{foam}} \text{ x 100} \quad \text{.... (3)}$$

Where :

- m_d = Masses of dry sample
- m_w = Masses of wet sample
- v_{foam} = Volume of RPUF foam

RESULTS AND DISCUSSION

In this work rigid polyurethane foam was produced from polyol based on palm oil (called as HMGMS polyol) by using water as chemical blowing

Table 2. The formula of additive used for preparation of RPUF with variation of mold system

Raw Materials	Type	Closed Mold	Open Mold-Molded Directly	Open Mold-Poured
Polyol	Palm oil based polyol (HMGMS)	8.5 g	10 g	20 g
Surfactant	Silicon glycol	2.04 pphp	2.04 pphp	2.04 pphp
Catalyst	dimethylcyclohexylamine	0.2 pphp	0.2 pphp	0.2 pphp
Blowing agent	water	2.67 pphp	2.67 pphp	2.67 pphp
Chain extender	ethylene glycol	1 pphp	1 pphp	1 pphp

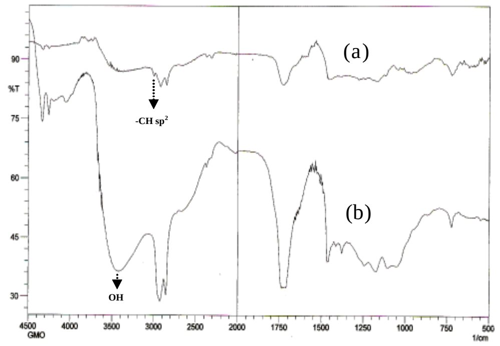

Figure 1. FT-IR spectra of derivative of Palm oil (a) and HMGMS polyol (b).

agent. Polyol based on palm oil has tendency to produce rigid polyurethane foam, due to its shorter chain than that of petrochemical based polyol. The characterization of the effect of mold system and NCO/OH ratio on the physical and mechanical properties has been conducted by determining its dimensional stability, bulk density, degree of water absorption and compressive strength.

Characterization of Palm Oil Based Polyol

Characterization of palm oil-based polyol was employed by using FT-IR technique to analyze the functional groups of palm oil based polyol (HMGMS polyol). Figures 1(a) and 1(b) showed the spectra of derivative of palm oil and HMGMS polyol, respectively. FT-IR spectrum of derivative of palm oil, showed absorption bands at 2924-2852 cm^{-1} assigned to C-H sp^3 vibration and 3005.1 cm^{-1} assigned to C-H sp^2. The characteristic absorption band attributed to carboxylic acid was shown at 1728 cm^{-1} assigned to C=O carbonyl from carboxylic acid and at 1282 -1220 cm^{-1} assigned to C-O group.

The significant distinguish FT-IR spectrum of derivative of palm oil and HMGMS polyol was showed by appearance of absorption at 3427-3332 cm^{-1} in the product which assigned to O-H group. The presence of O-H group in the product suggests that hydroxylation has taken place.

Furthermore, another information which shown that hydroxylation has taken place was disappearance absorption band at 3005.1 cm^{-1}. It was shown that unsaturated bond converted into saturated bond.

Characterization of Rigid Polyurethane Foam

Dimensional Stability

The dimensional stability of an insulation material is a property that is absolutely necessary for the faultless function of an insulation system. Poor dimensional stability can cause shrinkage. Shrinkage is reduction in linear size during cooling from molding to room temperature. Because of polymers have high thermal expansion coefficients, so significant shrinkage occurs during solidification and cooling in mold.

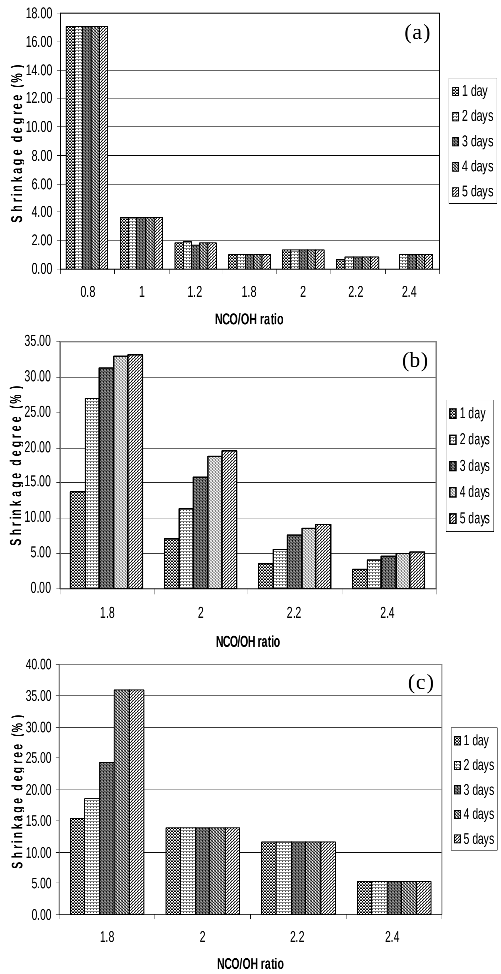

Figure 2. The shrinkage data of RPUF obtained by using (a) closed mold, (b) open mold-poured and (c) open mold-molded directly.

Beside that, shrinkage can be caused by the mix ratio being incorrect. One factor that can reduce the foam shrinkage is by adding higher pressures force, more material into mold cavity and study formulated ratio of RPUF. Foam shrinkage of RPUF was investigated and compared between RPUF which produce by using closed mold (in the presence of pressure) and open mold (allow rise freely).

The foam shrinkage data of RPUF obtained by using closed mold, open mold-poured and open mold molded directly were shown in the Figure 2. RPUF which was produced by using closed mold has smaller shrinkage than open mold poured and open mold molded directly.

The foam shrinkage for closed mold method, start from NCO/OH ratio 1.0 until 2.4, the foam shrinkage was not more than 5 %. In other side, shrinkage data of RPUF which produced by using open mold poured and open mold molded directly showed the smallest shrinkage (under 5 %) when the NCO/OH ratio 2.4. These data showed that the

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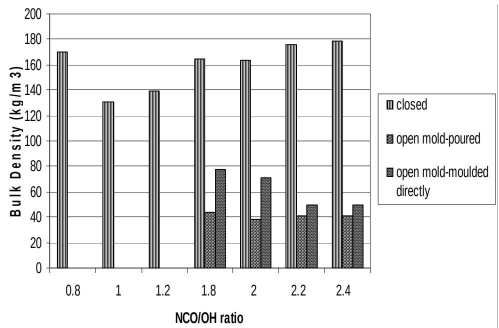

Figure 3. Bulk density of RPUF with variation of mold type and NCO/OH ratio

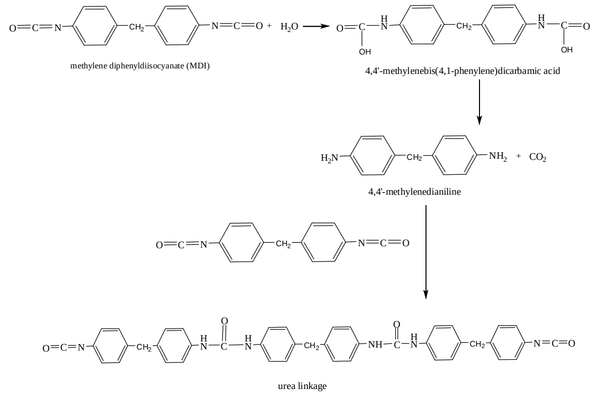

Figure 4. Reaction of methylene diphenyldiisocyanate (MDI) and water

shrinkage degree of RPUF can be reduced in the presence of pressure.

Bulk Density

Density is a most important parameter to control the mechanical and thermal properties of cell foams. Bulk density of RPUF with variation of mold type and NCO/OH ratio were shown in the Figure 3. Bulk density analysis of RPUF obtained by using open mold was started from NCO/OH ratio 1.8 not from 0.8 like in the closed mold. This is due to RPUF using open mold with ratio start from 1.8 has poor dimensional stability so it is supposed that for NCO/OH ratio under 1.8 will have more poor dimensional stability.

The bulk density of open mold method showed that the bulk density decrease with the increasing of NCO/OH ratio. This is due to the increasing of blowing efficiency and additional blowing as the NCO/OH ratio increases by the CO_2 produced from the reaction between the isocyanate groups and water (Figure 4). The additional of blowing gas caused the increasing of diameter cell wall and affect decreasing of the mass of RPUF.

The bulk density of closed mold method was increased with increasing of NCO/OH ratio. This was in contrary with the bulk density of closed mold method. This is due to the different expansion with the

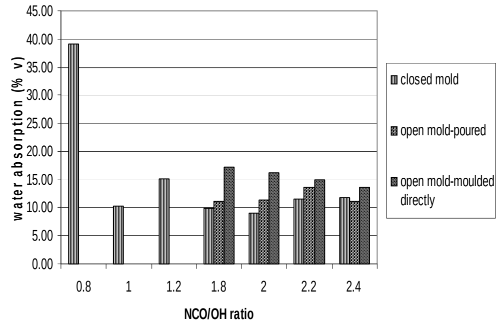

Figure 5. Histogram of water absorption of RPUF with variation of NCO/OH ratio and mold system

open mold method. The expansion in the open mold method is free, while in the closed mold method the expansion is closed. The increasing of additional blowing gas with the increasing of NCO/OH ratio in the closed expansion affected the increasing of pressure. Furthermore the increase of the pressure caused the cell diameter decreased and the mass of RPUF compressed.

Water Absorption

Water absorption is the amount of water picked up over a specific period of time. Water absorption of RPUF with variation of NCO/OH ratio and mold system was shown in the Figure 5. Water absorption of RPUF from open mold and closed mold system has tendency to decrease with increasing of NCO/OH ratio. The increasing of NCO/OH ratio affected the decreasing of hydrophilicity of foam, thus the penetration of water into bulk of polymer decreased. Water absorption of RPUF using closed mold system in the range of NCO/OH ratio from 1.8 until 2.4 showed smaller percentage. This can be explained as RPUF using closed mold system had higher bulk density than RPUF using open mold system. In the higher density, diameter of cell was smaller and this affected on the reducing penetration of water into foam.

Compressive Strength

Mechanical properties of RPUF was determined by analyzing of compressive strength. Compressive strength of RPUF with variation of NCO/OH ratio and mold system was showed in the Figure 6. The data showed that compressive strength of RPUF using closed method was increasing with the increasing of NCO/OH ratio. While the compressive strength of RPUF using open mold method was decreasing with the increasing of NCO/OH ratio. It is generally known that the mechanical properties of a cellular material mainly depend on its density [7]. Therefore, when the RPUF produced using closed mold method, the increasing of the compressive strength may be due to the increase of foam density. And for RPUF produced using open mold

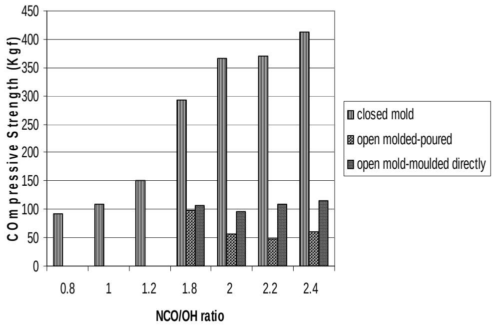

Figure 6. Histogram of compressive strength of RPUF with variation of NCO/OH ratio and mold system

method, the decreasing of the compressive strength may be due to the decreasing of foam density.

CONCLUSION

From the study of the effect of NCO/OH ratio and mold system in the producing rigid polyurethane foam based on palm oil, it was found that NCO/OH ratio and mold system were important variables in making polyurethane foam especially on their physical properties. In order to obtain good properties (good dimensional stability) the appropriate ratio of producing RPUF using open mold system and closed mold was different. In the closed mold system, NCO/OH ratio was started from ratio 1.0 but in the open mold NCO/OH ratio was started from ratio of 2.4.

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