Control of Biodegradability of Polyurethane Foam Based on Palm Oil by Ratio of Soft Segment on the Polymer Backbone

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Abstract

Polyurethane is polymer synthetic which is formed by reaction between polyols and polyisocyanates. Polyols are compounds which contain two or more hydroxyl groups. Polyurethane can be applied in various forms, such as foam, elastomeric, coating and adhesive. In this work, we developed polyurethane foams by using polyols based on palm oil. Palm oil based polyols as soft segments in the polyurethane backbone accelerate biodegradable process of the polyurethane. Biodegradability is the ability of material to be utilized as a carbon source by microorganisms and converted safely into carbon dioxide, biomass and water. Commercially available polyurethane foams are usually produced from petrochemical based polyols that they are not biodegradable. The biodegradability study was conducted by using *Aspergillus niger* (fungi) and *Pseudomonas aeruginosa* (bacteria), with variation of method and media for biodegradation. Rigid polyurethane foam was synthesized by using one shoot process method, which is reaction between palm-based polyol mixture and methylene diphenyl diisocyanate (MDI) at room temperature. The effect of variation of ratio of polyisocyanates (NCO) as hard segment and polyols (OH) as soft segment to the properties of polyurethane foams were studied in detail. Study of the effect NCO/OH ratio was conducted with variation ratio of 0.8, 1.0 and 1.2. Increasing hard segment (NCO) ratio to the soft segment (OH) affected in the decreasing of hydrophilicity of foam. Thus, the penetration of water into bulk of polymer decreased. The biodegradability of foam was also affected by the soft segment ratio on the polymer backbone.

Keywords: biodegradable, polyurethane, palm oil, polyols, soft segment.

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Introduction

Polyurethane is formed from condensation reaction between polyols and isocyanates (Eaves, 2004; Bastioli, 2005). As one of raw material for producing polyurethane, polyols are compounds which contain two or more hydroxyl groups (Eaves, 2004; Bastioli, 2005). Polyurethane products can be found in various forms, such as foam, elastomeric, coating and adhesive. It is commonly used in building and construction, transportation, furniture and bedding, packaging, textile, fiber and apparel, machinery and foundry, electronic, and also footwear. Among of these applications, polyurethane is mostly used in the form of polyurethane foam (PUF) (Petrovic *et al.*, 2008).

Polyurethane waste will accumulate and arise many problems, because the consumption of polyurethane increases year by year with 12 million tons production world-wide in 2007 (Bastioli, 2005). In addition, polyurethane could not be recycled, due to its thermosetting characteristic (Eaves, 2004). Biodegradation is one alternative to treat polyurethane waste. Biodegradability is the ability of material to be utilized as a carbon source by microorganisms and converted safely into carbon dioxide, biomass and water (Petrovic *et al.*, 2005). Biodegradable matter are generally organic material such as plant and animal matter and other substances originating from living organisms, or artificial materials that are similar enough to plant and animal matter to be put to use by microorganisms (Alfani *et al.*, 1998).

In the market, PUFs are usually produced from petrochemical based polyols that are not biodegradable (Bastioli, 2005). One alternative to produce biodegradable PUF is by using renewable resources which can be degraded by microorganism. Therefore, research on producing polyurethane based on renewable resources has involved actively by many researchers. Vegetable oils such as soybean oil, canola oil, rapeseed oil, corn oil, palm oil, sunflower, castor oil and linseed oil, had been studied as renewable sources of polyol for polyurethane (Nascimento *et al.*, 2007; Ghazali *et al.*, 2005; Kong *et al.*, 2007; Cangemi *et al.*, 2008). Many researches also reported about the development of biodegradable polyurethane. Nascimento *et al* (2007) had reported that biodegradable polyurethane can be synthesized with mixture comprising polymer based on poly(hydroxyl-butyrate), polyols of renewable source, an isocyanate and several optional additives. One important raw material for obtaining polyol is the castor oil, a mixture that contains about 90% of triglyceride of ricinoleic acid (Ge *et al.*, 2003).

Previous study by Cangemi *et al* (2008) reported the biodegradable polyurethane from polyol based on castor oil. The biodegradation study was conducted by using *Aspergillus* sp. and *Chryseobacterium meningosepticum* as the microorganism to degrade the polyurethane. It is important to note that the chemical structure of foam derived from castor oil becomes susceptible to microorganism attack and can be considered as a biodegradable polymer. It is presumed, due to its molecular structure that contains polyester segments (soft segments) derived from vegetable oil, the polymeric surface is susceptible to microorganism attack (Han *et al.*, 2009).

Another research by Ghazali *et al* (2005) reported biodegradable PUF from palm oil based polyol. Under a scanning electron microscope (SEM), dense fungal growth was observed covering the samples. Palm-based foams were degraded much faster than the commercial foams in the shake flask test with *Aspergillus terreus*, shown by higher weight losses and deterioration. Complete decomposition of palm-based PUF showed that it could be degraded in the environment in the presence of *A. niger* or *A. terreus*, with sufficient nutrients and maximum contact between the fungi and the foams.

Another study on biodegradable polyurethane with varied ratio of isocyanate and polyol was carried out by Ge *et al* (2003) and Kelly *et al* (2001) as cited by Eceiza *et al* (2008) and Triwulandari *et al* (2008). These researches reported that the biodegradability of polyurethane obviously decreased with increasing isocyanate amount (hard segments) in the formulation of polyurethane. From this report, it can be suggested that it is important to study about the formulation of soft/hard segments on polyurethane preparation to find an optimum formula that can be degraded easily.

The purpose of this research is to study the formulation of biodegradable rigid PUF (RPUF) from palm oil based polyol and its biodegradability properties. Polyurethane materials usually hold a two-phase structure in which "hard" glassy segment-enriched domains are dispersed in a matrix of "soft" rubbery segments. Due to its aliphatic structure and low intermolecular interaction, soft segments can rotate and bend easily that provide compliance, elasticity and low-temperature mechanical properties. Nevertheless, the hard segment acts as filler particles and physical crosslink sites making a significant contribution to the modulus, mechanical strength and elevated temperature properties because of the strong intermolecular interactions such as hydrogen bonding among urethane groups (Troitzsch, 1983). This study also investigates the ratio between "soft" and "hard" segment in the formulation of palm oil-based polyurethane and its effect to the biodegradability property.

Materials and Methods

Preparation of RPUF. Polyurethane used for studying the biodegradability was prepared as follow. Palm-oil-based RPUF was synthesized by reacting palm oil–based polyol with isocyanate. The palm oil based polyol used in this study had previously prepared in the Laboratory of Polymer Chemistry, Research Center for Chemistry, Indonesian Institute of Sciences (LIPI), through epoxydation and hydroxylation process of glycerol monooleate to form polyol HMGMS (Triwulandari *et al.*, 2008). The polyol used had hydroxyl value of 161 mg KOH/g, and iodine value of 28.2 mg I_2/100 g. The RPUF was synthesized through one shoot process method. Component A, which is mixture of palm oil-based-polyol and additives (silicon glycol, stannous octoate, dimethylcyclohexylamine, ethylene glycol, and water). Component A was reacted directly with component B, which is methylene diphenyldiisocyanate (MDI), at room temperature. The formula of additives used for preparation of RPUF was silicon glycol (2.04 pphp), dimethylcyclohexylamine (0.2 pphp), water as the blowing agent (2.67 pphp), and ethylene glycol (1 pphp). RPUF synthesis was performed in closed mold system. Variation in NCO/OH ratio in RPUF synthesis was carried out with the ratio of 0.8; 1.0 and 1.2.

The NCO/OH ratio is described as follows:

$$[NCO]/[OH]ratio = \frac{M_{MDI} x W_{MDI}}{M_{HMGMSpolyol} x W_{HMGMSpolyol} + M_{ethyleneglycol} x W_{ethyleneglycol} + W_{water} x \frac{1000}{9}}$$

M_{MDI} is the isocyanate group content in MDI (6.78 mmol/g), $M_{HMGMS\ polyol}$ and $M_{ethylene\ glycol}$ is the hydroxyl group content in HMGMS polyol and ethylene glycol (hydroxyl number/56.1: 2.87 and 4.55 mmol/g), W_{MDI}, $W_{HMGMS\ polyol}$, $W_{ethylene\ glycol}$ and W_{water} are the weight of MDI, HMGMS polyol, ethylene glycol and water, respectively. Isocyanate content of MDI was determined according to ASTM D5155, and hydroxyl content of HMGMS polyol and ethylene glycol was determined according to ASTM D4274-88 (Eceiza *et al.*, 2007).

Water absorption property of RPUF. The samples of 45×10 mm (diameter×height) 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 formula:

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

Where m_d and m_w are the masses of dry and wet samples, respectively and v_{foam} is the volume of RPUF foam.

Biodegradability Study. Microorganisms used in this test were fungi (*A. niger*) and bacteria (*Pseudomonas aeruginosa*). *A. niger* used in this study was obtained from culture collection of Research Center for Chemistry, LIPI and *P. aeruginosa* was obtained from Biotechnology Culture Collection (BTCC) of Research Center for Biotechnology, Indonesian Institute of Sciences (LIPI). For tests with bacteria and fungi, mineral salt agar media with the following composition were used (per liter): KH_2PO_4 0.7 g, $MgSO_4.7H_2O$ 0.7 g, NH_4NO_3 1.0 g, NaCl 0.005 g, $FeSO_4.7H_2O$ 0.002 g, $ZnSO_4.7H_2O$ 0.002 g, $MnSO_4.7H_2O$ 0.001 g, K_2HPO_4 0.7 g and agar 15 g. The RPUF based on palm oil with varied NCO/OH ratio of 0.8, 1.0 and 1.2, and commercial RPUF were placed on both mineral salt agar already inoculated with *A. niger* or *P. aeruginosa*. The plates were incubated for twelve (12) weeks at 32°C. Triplicate samples of each foams were taken from agar plates monthly, cleaned with alcohol and conditioned to room temperature for 3 days. For the comparison, this study also uses comercial petroleum-based RPUF as the sample for biodegradability study. Commercial RPUF was obtained from PT. Lancar Jaya Mandiri, Jakarta, Indonesia. Assessment of the weight loss gave a clear indication whether the foams were resistant or susceptible to the microbial attack. The calculation of weight loss of PUF was showed by following equation:

$$\text{Weight loss} = \frac{wt._{initial}(g) - wt._{final}(g)}{wt._{initial}(g)} \times 100\%$$

Results and Discussion

In this work, biodegradable RPUF was produced from palm oil-based-polyol (HMGMS) and methylene diphenyldiisocyanate (MDI) through one-shoot process in a closed mold system. Polyol based on palm oil has the tendency to produce

RPUF, due to its shorter chain than that of petrochemical based polyol (Troitzsch, 1983).

Biodegradability of prepared RPUF could be also associated with the ability of RPUF to absorb water. Water absorption is the amount of water picked up over a specific period of time. Determining compound water absorption is very useful since it assess the hydrophilicity and also its degradability. In hydrolytic polyurethane degradation, soft segment component can determine its degradability in term of hydrophilic property. Higher hydrophilicity from soft segment would increase water uptake of polyurethane that would facilitate degradation process and then increase its mass loss (Lee *et al.,* 2000; Hafeman *et al.,* 2008; Han *et al.,* 2009). The highest water absorption was achieved in the RPUF with NCO/OH ratio of 0.8 with 39.15% (w/v). RPUF with NCO/OH ratio of 0.8 also gave the highest weight loss. Lower NCO/OH ratio of palm oil-based-RPUF gave higher water absorption (Figure 1). Thus, there would be more penetration of water into bulk of polymer to help the degradation process.

Study on biodegradability property of palm oil-based polyurethane was conducted using *A. niger* and *P. aeruginosa*. *A. niger* had been used in the biodegradation study of polymer and it was able to penetrate into the foams and cause significant weight losses of polymer (Ghazali *et al.,* 2005; Cangemi *et al.,* 2008). *P. aeruginosa* had also been used as microorganism to determine the biodegradability properties of polyurethane. *P. aeuruginosa* is the kind of microorganism which is recommended by the American Society for Testing and Materials (ASTM-G22) for biodegradability screening.

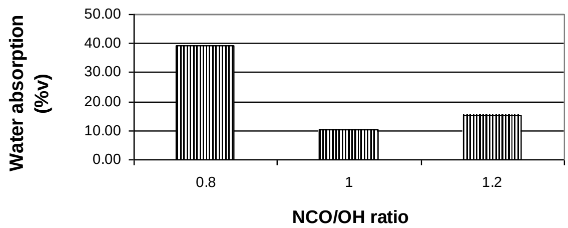

Figure 1. Water absorption of RPUF with varied of NCO/OH ratio

Visual examination on biodegradation result of RPUF based on palm oil and petrochemical using *A. niger* and *P. aeruginosa* was shown in Figure 2. This test was designed so that the PU foam would act as the sole carbon sources for the microorganism as no other carbon source was added into the agar media. We can see that *A. niger* and *P. aeruginosa* can grow on samples of palm oil-based-RPUF, indicating that the fungi and bacteria were able to use foam as its sole carbon source. Meanwhile, no growth of fungi and bacteria was observed on the samples of petrochemical-based-RPUF, indicating that the fungi and bacteria were unable to use this foam as its sole carbon source. The dense growth of microbe on the RPUF based on palm oil with NCO/OH ratio of 0.8 was higher than RPUF with NCO/OH ratio of 1.0 and 1.2.

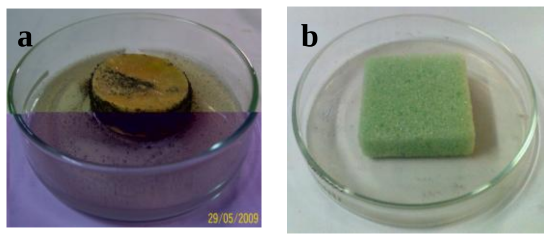

Figure 2. a) Palm oil-based RPUF; and b) petrochemical-based RPUF incubated with *A. niger*.

From weight loss result we could also conclude that both *A. niger* and *P. aeruginosa* were able to degrade palm oil-based RPUF. The weight losses of every RPUF samples from any formulation were increased with increasing incubation test periods. For comparison, biodegradability test was also conducted on petroleum-based-PUF. After 3 weeks, test on petroleum-based-PUF with *A. niger* gave 0.6% weight loss, while test with *P. aeruginosa* gave 0.1% weight loss.

Biodegradable RPUF was prepared by varied NCO/OH ratio as hard/soft segments representatives in the polymer backbone. This formulation was conducted to get optimum formula of RPUF which can be degraded by microorganism. With small NCO/OH ratio, it is expected that the biodegradability of polyurethane would increase. In polyurethane synthesized from natural resource-based-polyol, the polyol would contribute to polyurethane biodegradability. Introduction of polyol biomass in polyurethane formulation would improve the biodegradability, resulting in more easily biodegraded polyurethane (Ge *et al.,* 2002).

After 12 weeks incubation time, test with *A. niger* gave 13% weight loss from RPUF with NCO/OH ratio of 0.8, 7% from NCO/OH ratio of 1, and 4% from NCO/OH ratio of 1.2. Test with *P. aeruginosa* gave 9% weight loss from RPUF with NCO/OH ratio of 0.8; 5% from NCO/OH ratio of 1; and 2% from NCO/OH ratio of 1.2 after 12 weeks incubation time. This result showed that weight loss was decreases with increasing NCO/OH ratio of RPUF. In both test with *A. niger* and *P. aeruginosa,* highest weight loss was obtained from RPUF with NCO/OH ratio of 0.8. This data showed that when the palm oil-based-polyol content increased, the RPUF would be more easily to degrade. Compared to petrochemical-based-RPUF with highest weight loss of 0.6%, the weight loss of palm oil-based-RPUF was much higher. Lower NCO/OH ratio means more polyol component in polyurethane chain. In this study, more palm oil-based-polyol will gave higher weight loss. In the case of our study, polyurethane soft segment of palm oil-based-polyol affect the biodegradability of palm oil-based-RPUF. More palm oil-based-polyol component in RPUF formulation would improve its biodegradability.

FT-IR analysis was conducted to observe change in ester bond peak of polyester segment in RPUF. Stretching vibration of carbonyl groups was observed at 1730 cm^{-1}. Vibration of C-O-C of ester functional group was observed at 1000-1200 cm^{-1}. Bending vibration of N-H was observed at 1520 cm^{-1}. It is suggested that polyester segment was susceptible to microorganism attack (Cangemi *et al.,* 2008). The change in the intensity of FT-IR ester peak of RPUF before and after degradation could suggest the biodegradability of RPUF. Figure 3 showed the FT-IR spectra of control RPUF, and RPUF degraded with *A. niger* and *P. aeruginosa*. Degraded RPUF gave lower intensity in ester peak (1000-1200 cm^{-1}) compared to RPUF before degradation. This would suggest that in this test, one mechanism of biodegradation was through dissociation of polyester segment in RPUF by microorganism.

The effect of NCO/OH ratio was also shown in the FT-IR spectra of different sample with different NCO/OH ratio. In both biodegradability test with *A. niger* and *P. aeruginosa*, RPUF with lower NCO/OH ratio (0.8) gave lower ester peak intensity (Figure 4 & 5). Peak assigned to carbonyl in 1730 cm^{-1} was also weakened after degradation process by both *A. niger* and *P. aeruginosa*. This means the presence of soft segment in the polymer backbone can accelerate the biodegradable process of RUPF. Ge *et al* (2002) also observed weaken carbonyl and C-O-C peak in biodegraded polyurethane with natural resource-based-polyol component.

The change of RPUF based on palm oil surfaces during microbial treatment were shown in Figure 6. According to the SEM analysis, it is known that there are differences in RPUF surface before and after biodegradation. The RPUF surface before degraded have uniformity microcell, but after biodegraded the RPUF surface become damage and cell had been expanded.

Conclusion

Palm oil based RPUFs were biodegradable in the test with *A. niger* and *P. aeruginosa*. Higher mass loss was obtained from palm oil-based RPUFs with lower NCO/OH ratio that associated with higher palm oil-based polyol component (soft segment) in the polyurethane. Lower NCO/OH ratio would also result in higher water uptake that helps in facilitating polyurethane degradation.

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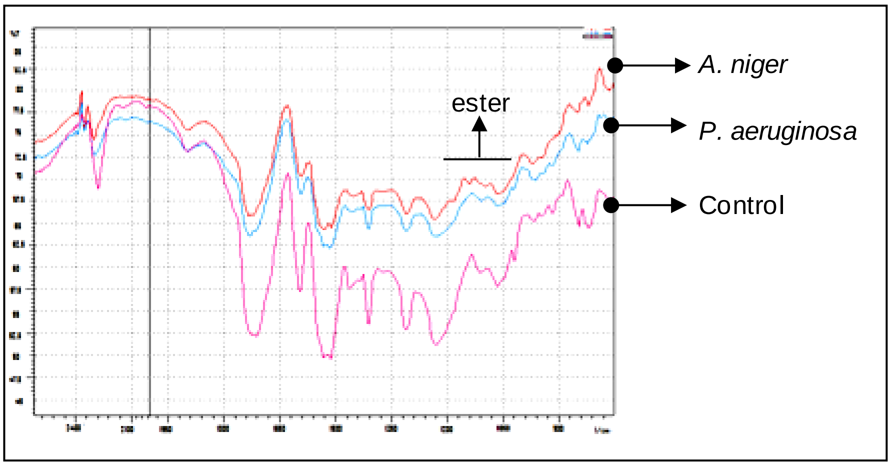

Figure 3. FT-IR spectra of palm oil-based-RPUF

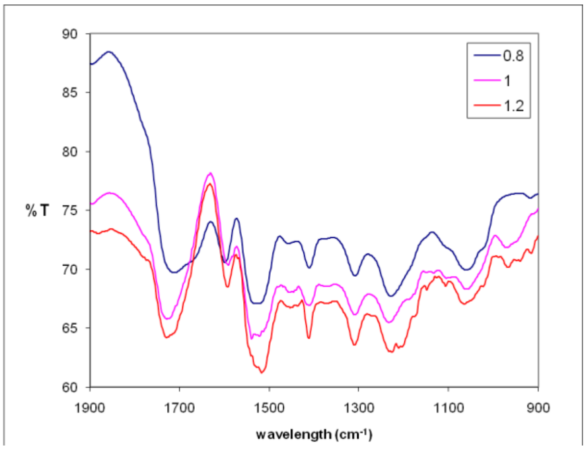

Figure 4. FT-IR spectra of palm oil-based-RPUF with varied NCO/OH ratio inoculated by *A. niger*

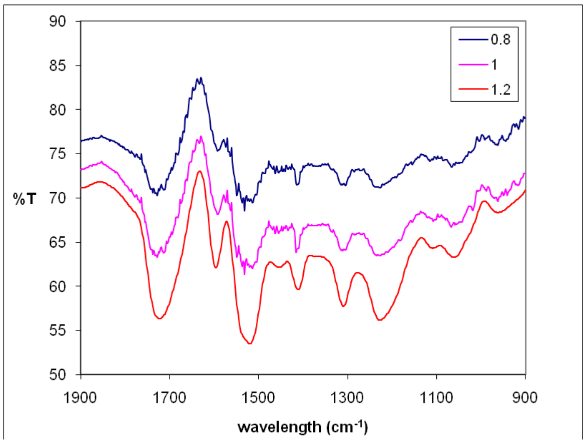

Figure 5. FT-IR spectra of palm oil-based-RPUF with varied NCO/OH ratio inoculated by *P. aeruginosa*

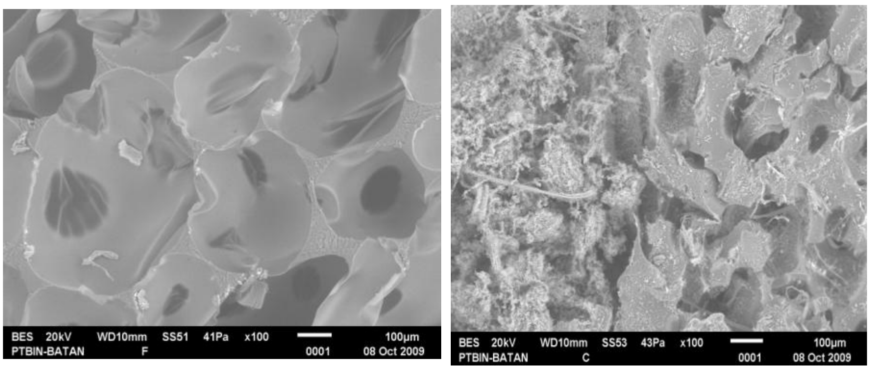

Figure 6. The change surface of RPUF based on palm oil after degraded by *A. niger*

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