Synthesis and Application of *Jatropha* Oil based Polyurethane as Paint Coating Material

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Abstract

Recently, the use of renewable sources in the preparation of various industrial materials has been revitalized in response to environmental concerns. Natural oils are considered to be the most important genre of renewable sources. *Jatropha curcas* oil (JPO) based polyol is an alternative material that may possibly replace petrochemical-based polyol for polyurethane coating material. Polyurethane was synthesized by reacting JPO-based polyol with isocyanate. To produce JPO-based polyol, JPO was first epoxidized to form epoxidized *J. curcas* oil (EJP), subsequently it was converted to polyol by the opening ring reaction with acrylic acid (AA) using triethylamine (TEA) as a catalyst. The JPO-based polyurethane film resulting from this study is compared with polyurethane film from commercial polyol for gloss, hardness, and adhesion quality. The result showed that the source of polyol has an influence on gloss, hardness, and adhesion of polyurethane film, but the differences with using isocyanate has less influence. Using visual observation, polyurethane film produced from L.OHV polyol, H.OHV polyol and commercial polyol have similar quality.

Abstrak

Sintesis dan Aplikasi Poliuretan Berbasis Minyak Jarak Pagar sebagai Bahan Pelapis. Baru-baru ini, penggunaan sumber-sumber terbarukan dalam penyusunan bahan berbagai industri telah direvitalisasi karena kekhawatiran dampak terhadap lingkungan. Minyak nabati dianggap sebagai kelompok yang paling penting dari sumber terbarukan. Poliol berbasis minyak jarak pagar (JPO) merupakan bahan alternatif yang mungkin dapat menggantikan poliol berbasis petrokimia untuk bahan pelapis poliuretan. Poliuretan disintesis dengan mereaksikan poliol berbasis JPO dengan isosianat. Untuk menghasilkan poliol berbasis JPO, pertama JPO diubah menjadi jarak pagar terepoksidasi (EJP), kemudian mengkonversi EJP menjadi poliol melalui reaksi pembukaan cincin dengan penambahan asam akrilat (AA) dan adanya katalis trietilamina (TEA). Sifat reologi film polyurethane berbasis JPO dibandingkan dengan film poliuretan berbasis poliol komersial melalui uji daya kilap, kekerasan, dan daya rekat. Hasil penelitian menunjukkan bahwa sumber poliol berpengaruh terhadap sifat reologi poliuretan dibandingkan jenis isosianat. Hasil pengamatan visual film polyurethane dengan poliol L.OHV, H.OHV dan komersial menunjukkan ketiganya memiliki kualitas yang sama baiknya.

Keywords: coating material, JPO-based polyol, polyurethane

1. Introduction

Polyurethane is one of the polymer products made by reacting polyol with an isocyanate. Examples of polyurethane products include elastomers, adhesives, foams, paints, sealants and others. In the paint industry, polyurethane is a type of paint that has many advantages over other types of paint including weather resilience, power high-gloss, hardness and good adhesion on different types of materials such as metal, plastic, and wood [1].

World consumption of polyurethane increases every year with an average increase of 5.1% until 2005. World market for the application of polyurethane coatings, adhesives, sealants, and elastomers is expected to reach 3.1 million tons in 2000 with isocyanate material usage around 900 thousand tonnes and 1.5 million tonnes of polyol. The highest demand from the four types of application is for coating materials (paints) which is 44% [2]. In Indonesia, the needs for polyurethane from 1989 to 1995 also rose approximately 37% from 1160 tons to 6159 tons [3]. Polyurethane usage in Indonesia

reached 17 465 tons/year in 2004 and is predicted to reach 35 thousand tons per year in 2014 [4]. The entire quota of polyurethane in Indonesia is still met through imports from abroad.

Polyol as the raw material for making polyurethane is largely derived from petroleum derivatives [5-6]. The recent trend of oil price increases and the emergence of environmental awareness have prompted the government to seek alternative raw materials for polyol production [7-9]. Vegetable oil is an alternative raw material that can be used to produce polyols. Vegetable oils that can be used as raw material polyols include: soybean oil, *Jatropha* oil, palm oil, sunflower oil, linseed oil and castor oil. Compared with polyols made from petroleum (petrochemicals), polyol made from vegetable oil has the advantage of being biodegradable, abundant and renewable.

In Europe and America, the soybean oil-based polyol has been developed and used by industry in large scale replacing petrochemical polyols in producing polyurethane [10]. In Malaysia, palm oil-based polyol has been intensively researched over 10 years by the Malaysian Palm Oil Board (MPOB) in collaboration with Klauditz-Wilhelm-Institut (WKI), Germany. Palm oil-based polyols can be applied as a polyurethane paint resin with two component systems that are suitable for both interior and exterior applications [11].

Harjono *et al.* [12] has successfully synthesized *Jatropha* oil-based polyols (JPO). The technology used is JPO epoxidation reaction to epoxide *Jatropha* (EJP) followed by applying ring opening reaction of a polyol EJP on a wide range of acrylic acid (AA) concentrations, trietilamine (TEA) and reaction time (t). Polyols produced under various conditions of AA (1.4%, 2.9%, and 4.3%), TEA (0%, 1%, 2%, and 3%), at t = 60, 120, 180, and 240 minutes have hydroxyl numbers, numbers and yield oksirana row in the range of 70,234 to 134.915 mg KOH/g, 0.029 to 0.138% and from 58.93 to 91.53%. The average number of hydroxyl, oksirana numbers, and yield of the resulting polyols are respectively 97.418 mg KOH/g, 0.067% and 80.24%.

Under Presidential Decree No.1 of 2006, the MOA with the National Team for Biofuel launched a major biofuel commodity-producing development area of 6.4 million hectares for palm oil, *Jatropha*, sugar cane and cassava in the period 2005-2015. Of this area, 1.5 million hectares is for *Jatropha*. Furthermore, data from the Center for Research and Development of Agricultural Land Resources, land resources available on the exploration scale (1:1,000,000) states that suitable land for *Jatropha* development reached 49.5 million ha, consisting of suitable class (S1) 14.3 million ha, quite suitable (S2) 5.5 million ha, and marginal (S3) 29.7 million ha [13].

Given that *Jatropha* oil-based polyol has potential as a raw material polyurethane and the intense development of *Jatropha* cultivation by the government, the development of JPO as a raw material for making polyurethane that to date is still imported is very important. Therefore, the aim of this study was to synthesize *Jatropha* oil based polyurethane and apply these materials as a coating material. In this study, the preparation of EJP refers to a previous study [12] and the synthesis of polyurethane is prepared by the ring-opening reaction of a EJP polyol with the help of two types of catalysts, acrylic acid and ethylene glycol. Then the resulting polyols are reacted with the isocyanate. This research is expected to support the government's program to increase product added value crops (*Jatropha* in this case) through the implementation of high technology relevant to agribusiness development.

2. Experiment

The materials used in this study are *Jatropha* oil (JPO), amberlite IR-120 (sulfonic strong acid cation resin), acrylic acid (AA) (Sigma), sodium hydrogen carbonate (E.Merck), sodium sulfate anhydrous (E.Merck), toluene (E. Merck), KOH, triethylamine (TEA), NaOH, acetic acid, acetic anhydride, and H_2O_2, commercial polyol type polypropylene oxide (PPO), aromatics isocyanates (NCO-A) and aliphatic isocyanates (NCO-B). The equipment used include a set of reflux tools, rotary evaporator, titration apparatus, Erlenmeyer, beaker glass, heating mantle, magnetic stirrer, hot plate, Glossmeter (BYK Chemie Germany), Mitsubishi Pencil Hardness, Crosscut 3M tape, and infrared spectrophotometer (FTIR) Thermo Nicolet AVATAR 360.

Polyol synthesis. Polyol synthesis of JPO is conducted with 2 stage reactions, the first stage is the epoxidation reaction to produce EJP and the second stage is the EJP ring opening reaction using AA catalyzed with TEA to produce polyols. The first and second reactions use procedures that have been successively reported by Sugita *et al.* [14] and Harjono *et al.* [12] respectively.

Epoxidation synthesis of *Jatropha* oil (EJP). A total of 100 g of *Jatropha* oil, 8 ml of glacial acetic acid, 29 ml of toluene, and catalyst Amberlite IR-120 3% (w/w) was added into a three-neck flask equipped with a magnetic stirrer, and then the second solution which contained 57.8 g H_2O_2 35% in the separating funnel was added dropwise into the reaction mixture. The mixture was heated in a water bath at a temperature of 70 °C for 12 hours. The reaction product was neutralized with $NaHCO_3$ solution, then separated with a separating funnel. Once the fraction of water discharged, *Jatropha* oil epoxide (EJP) was washed with distilled water and dried with anhydrous Na_2SO_4. The EJP product was then analyzed to determine its iodine number, oxirana number and peroxide number.

Polyol synthesis from the EJP. A total of 100 g EJP was incorporated into the three-neck flask, and a measured amount of toluene and TEA was added as a catalyst. The mixture was heated and stirred in a water bath at a temperature of 50 °C. After the mixture is homogeneous and reached a constant temperature at 50 °C, then some AA was added. Reactions were performed at different times: 60, 120, 180, and 240 minutes. The polyol mixture obtained was further neutralized with NaHCO₃ and the organic phase separated with a separating funnel. The organic phase obtained was washed several times with hot distilled water then added into the reaction mixture in a separating funnel. The mixture was shaken for 3 min, and then allowed to stand for 30 minutes to separate polyol from water and residual reactants. The cloudy and somewhat translucent yellow solution on the top layer is polyol while the white layer on the bottom is a mixture of water and residual reactants. The polyol obtained was further added with anhydrous Na₂SO₄ to reduce the water content remaining after the washing process. Water free polyol was analyzed to obtain hydroxyl numbers, oxirana numbers, yield, and then analyzed with an infrared spectrophotometer. In the synthesis of polyols, to determine the effect of factors or between factors to the research responses used a tool of 3x4x4 factorial experimental design with three factors: the ratio of AA to the EJP (% AA), % TEA and reaction time of each treatment was performed with three replications. Factors % AA being done at three levels, 1.4%, 2.9%, and 4.3%, factor% TEA with four levels ie, 0%, 1%, 2%, and 3%, while the reaction time factor with four-levels, were at 60, 120, 180, and 240 minutes. The resulting polyol is divided into two parts based on the hydroxyl number. Polyol L.OHV group has a hydroxyl number less than 100 mg KOH/g, while polyol H.OHVhas a highest number.

Preparation of polyurethane film and its application on the acrylonitrile butadiene styrene (ABS) Panel. Preparation of polyurethane films in this study is a modified polyurethane manufacturing procedure performed by Kaushiva *et al.* [15] with Kong and Narine [16]. Polyols that are being used in the manufacture of polyurethane film consist of three types: a polyol with a hydroxyl number 81.28 mg KOH/g (polyol L.OHV), a polyol with a hydroxyl number 117.43 mg KOH/g (polyol H.OHV) and a commercial polyol that has a hydroxyl number of 81.22 mg KOH/g as a comparison. A total of 80 g of polyol is poured in to a beaker glass, then added with 20 mL of toluene, and additives as much as 0.1%. The mixture is stirred until it is well blended for 10 minutes. From the mixture of polyols obtained, 4 mL was taken from each batch then put into two separate containers. In container A is added 1 mL NCO-A and into container B is added 1 mL NCO-B. The mixture was stirred at room temperature for 3 minutes, then applied to the prepared panel ABS. The

results of the application are left at room temperature for 15 minutes to evaporate the solvent under a layer of film. Furthermore, the application result was oven-dried for 30 minutes at a temperature of 70 °C. Once it was removed from the oven, it was allowed to cool at room temperature for 24 hours before testing the polyurethane film. Characterization of polyurethane film was analyzed by FTIR analysis and rheological properties include power gloss, hardness and adhesion consecutive Glossmeter 60° angle, Mitsubishi Pencil Hardness, Crosscut 3M tape. The third relationship rheological properties was analyzed using statistical methods of complete random factorial design with three times replication.

3. Results and Discussion

Polyol synthesis produced polyols with hydroxyl numbers, oxirana number and polyol yields that ranged from 70.23-134.96 mg KOH/g, 0.03 to 0.14% and from 58.93 to 91.53%, respectively [12]. Based on the hydroxyl value number, polyol synthesis results are grouped into two which are: L.OHV polyols and H.OHV polyol. L.OHV polyol is a polyol with a hydroxyl number value that is less than the average hydroxyl numbers of all treatments. H.OHV polyol is a polyol with a hydroxyl value greater than average. In this study, L.OHV polyol has a hydroxyl number of 81.28 mg KOH/g and H.OHV polyol has a hydroxyl number of 117.43 mg KOH/g. Commercial polyol polypropylene oxide (PPO) was used as a comparison. Vegetable oil-based polyols for coatings applications have been reported by Mannari *et al.* [17]. Vegetable oil-based polyol has several advantages such as: suitable for various types of surfaces, has a reactive functional group that allows it to be modified, inexpensive, renewable, and commercially available. Vegetable oil-based polyols can be applied to water-based coatings (waterborne coating) and coating materials with high solid concentration (high solid coating).

In polyurethane technology, the hydroxyl number is defined as the number of hydroxyl groups which can react with isocyanates [18]. Percent hydroxyl (OH%) can also be used to indicate the number of hydroxyl groups in the polyol. Converting hydroxyl numbers to %OH can be calculated by dividing the number of hydroxyls with the number 33. If the numbers of hydroxyl content of the polyol and isocyanate NCO are known, the stoichiometric amount of polyol and isocyanate equivalent can be calculated using the following Equation (1):

$$b = \alpha \frac{x}{y} \frac{17}{42} = 0.40476\,\alpha x / y \qquad (1)$$

with: a = isocyantae mass, x = % NCO in isocyanate
         b = polyol mass,   y = % OH in polyol

Based on the calculation above, the weight of polyol and isocyanate used in the formulation can be precisely determined. This calculation is necessary to prevent excess of one component to the other components that can affect the quality of the polyurethane film. Excess amounts of polyol component in polyurethane formulations leads to residual unreacted hydroxyl groups with isocyanates. The polyurethane film layer containing residual hydroxyl groups resulted in imperfect formation of polymer chains. In the early stages of polymerization, the remaining hydroxyl groups cause slow dry film coating, and the presence of free hydroxyl groups tend to be hydrophilic. Meanwhile, if the isocyanate component is in excess, it can cause a brittle polyurethane film layer for residual isocyanates in film coating reacts with water vapor from the air.

According to Lonescu [18], the reaction of the formation of polyurethanes included in polyaddition reaction so that the ratio between reactive groups in this case is the ratio of NCO to hydroxyl that to read groups that have a strong influence on the molecular weight of the resulting polyurethane. Optimal molecular weight can be obtained at a molar ratio of [NCO]/[OH] = 1. Slight excess of one component drastically lowers molecular weight of polyurethane produced as shown in Figure 1. The reaction of a polyol with an isocyanate to form urethane bonds can be seen in Eq. 2. The rest of the TEA catalyst remaining in the polyol synthesis can serve as a catalyst in this reaction.

$$R-N{=}C{=}O + HO-R' \longrightarrow R-NHCOO-R' \qquad (2)$$
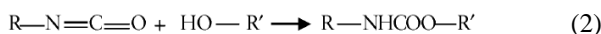
Polyurethane film coating synthesized using either the L.OHV polyol or H.OHV appeared as a slightly yellowish film of polyurethane film compared to
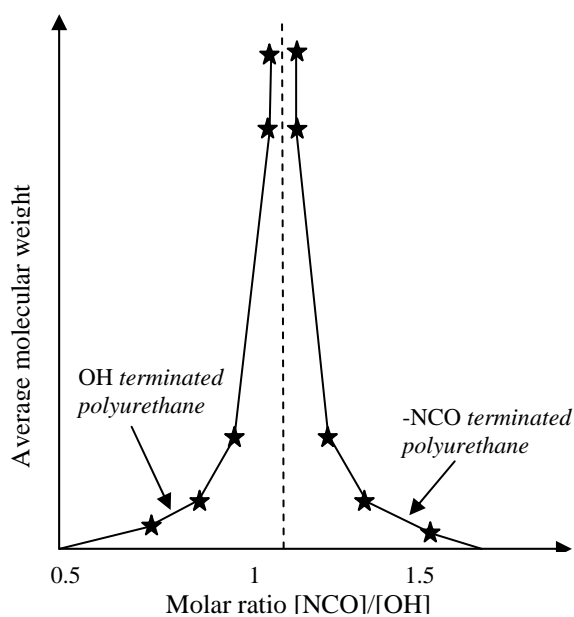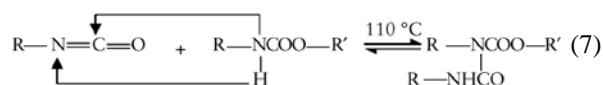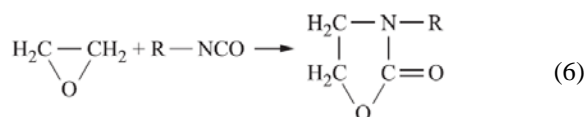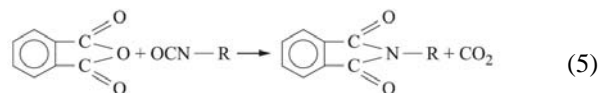

Figure 1. Effect of Molar Ratio [NCO]/[OH] on the Average Molecular Weight of Polyurethane

$$R-NCO + R'-COOH \rightarrow R-NH-CO-R' + CO_2 \qquad (3)$$

$$R-NCO + HCl \rightleftharpoons R-NH-CO-Cl \qquad (4)$$

 (5)

 (6)

 (7)
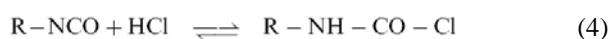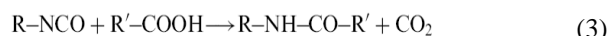
commercial polyols. The yellow color in the polyol synthesis is allegedly caused by impurities present in the raw material, imperfections of the epoxide ring or other materials used. According to Ionescu [18], isocyanates can react successively with organic acids to form an unstable intermediate compound which decomposes into amides and CO_2 (Eq. 3), using HCl to form adduct which decomposes again at high temperature (Eq. 4), with an anhydride to generate imide (Eq. 5), with epoxide produced cyclic compounds-oxazolidon (Eq. 6), and even with the polyurethane product (Eq. 7).

This is supported by the analysis of functional groups of polyurethane film with the IR method. Comparison of infrared spectra between films originating from polyurethane polyols and synthetic polyols demonstrate the suitability of commercial absorption at wave numbers 3521 cm^{-1} (absorption-OH group), 1169 and 1242 cm^{-1} (absorption group CO), 1743 cm^{-1} (absorption group C = O), 1169 and 723 cm^{-1} (absorption epoxy groups), 1376 and 1242 cm^{-1} (absorption which indicates the position of the OH group on the secondary position). Also detected in the absorption spectrum of polyurethane was the isocyanate groups at wave numbers 2271 cm^{-1} (the film of polyurethane polyol synthesis) and 2338 cm^{-1} (polyurethane film from commercial polyols). The isocyanate absorption intensity of the polyol was higher than the commercial polyol because of its slower polymerization reaction rate. In this study, the expected unreacted isocyanates in polyurethane film that is formed will react with residual polyols in the polymer matrix and the surrounding water vapor. There is still a secondary-OH absorption polyurethane film present that shows that the reaction progress of the polymer matrix is not perfect. The loss of isocyanate absorption characteristics can be used to predict the end of the polymerization reaction in the polyurethane matrix. Rheological properties were measured for gloss

polyurethane covering power, hardness and adhesion. The results of the analysis of the resulting polyurethane film layer are presented in Table 1.

Gloss power is defined as a capability of the film surface layer to reflect back the light. The gloss power film layer derived from commercial polyols statistically looks better than the synthetic polyol. However, visually it is relatively balanced. The effect of the polyol type on the use of Isocyanate A and B to the film gloss power are presented in Figure 2.

Based on the analysis of diversity, the isocyanate type does not affect the gloss power generated polyurethane film significantly, but it appears at Figure 2, that the use of isocyanate A to polyol L.OHV produces film with better gloss power than the polyol H.OHV, but the use of isocyanates B has the opposite effect. The gloss power of film coating depends on the fineness of the dry film coating formed [21]. The fine surface layer of film can generate a high gloss, while rough surface film layers produce a low gloss power.

The effect of polyol type on the use of Isocyanate A and B of the coating film hardness is shown in Figure 3. Hardness is a measure of the indentation resistance of

the film surface, friction, and scratches. The mechanical properties are very important for the film coating to resist wear caused by friction and scratches. According to Marino [19], the property of hardness is necessary both for film layers intended for interior use as well as for exterior use.

Figure 3 shows the hardness level of polyurethane film coatings. Polyurethanes derived from polyols H.OHV tend to have higher levels of hardness. This indicates that a higher number of hydroxyl increases the ability of bond formation with isocyanates. The more networks formed in the polymer matrix, the harder is the resulting film coating, but the analysis shows the diversity, the type of polyol and type of isocyanate did not affect the level of resulting hardness of polyurethane film.

The hardness level of commercial polyol polyurethane film showed higher values than the polyurethane film with synthetic polyols with corresponding hydroxyl numbers though statistically they were not significantly different. The characteristic of polyol chemical structure is believed to be the cause of this fact. Polyurethane film with synthetic polyols has a bulky structure because it originates from a derivative of triglycerides, causing the force between molecules to become weaker

Table 1. Rheological Properties Comparison between L.OHV, H.OHV and Commercial Polyurethane Type

Polyurethane Type	Rheological properties		
	GP[a]	HL[b]	AD[c]
L.OHV-NCO.A	90[1]	3[1]	90[1]
	93[2]	3[2]	95[2]
	91[3]	3[3]	95[3]
L.OHV-NCO.B	91[1]	3[1]	98[1]
	89[2]	3[2]	91[2]
	85[3]	2[3]	86[3]
H.OHV-NCO.A	90[1]	3[1]	94[1]
	90[2]	3[2]	90[2]
	88[3]	4[3]	91[3]
H.OHV-NCO.B	89[1]	3[1]	96[1]
	91[2]	4[2]	92[2]
	94[3]	3[3]	89[3]
Polyol Commercial-NCO-.A	95[1]	3[1]	100[1]
	97[2]	3[2]	98[2]
	94[3]	4[3]	100[3]
Polyol Commercial-NCO-B	96[1]	4[1]	99[1]
	99[2]	4[2]	95[2]
	96[3]	3[3]	97[3]

Note: [1]1st replication; [2]2nd replication; [3]3rd replication; [a] measured using 60° angle; [b] (conversion result data) measured with Mitsubishi pencil hardness; and [c] measured with *crosscut test* method
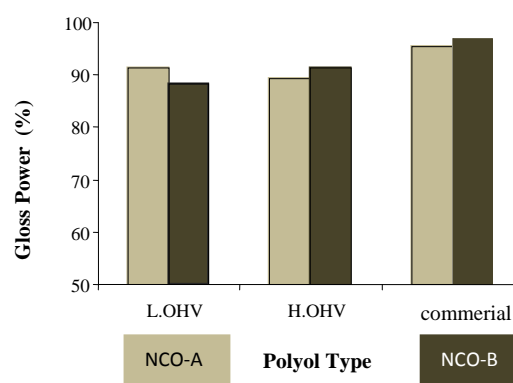

Figure 2. Effect of Polyol Type in NCO-A and NCO-B Application Against Film Gloss Power
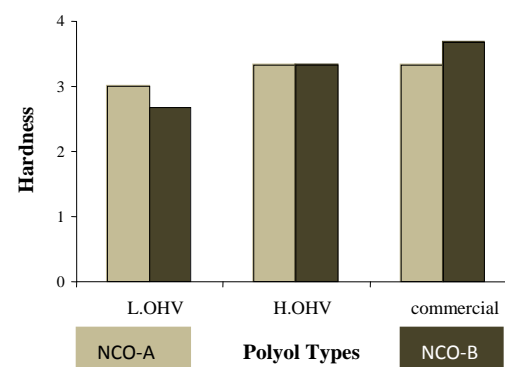

Figure 3. Effect of Polyol Type In NCO-A and NCO-B Application Against Film Hardness

than the commercial polyol that has relatively linear structure. Intermolecular force of commercial polyol molecules is stronger causing its arrangement within the polymer matrix to become more dense thus physically harder.

According to Mannari & Massingill [20], in vegetable oil-based polyurethane, polyurethane film hardness increased with a larger hydroxyl number. Higher levels of hardness were due to higher crosslinking density formed in the polymer matrix. In this study, polyurethane polyol from H.OHV has higher levels of hardness compared to polyurethane polyols derived from L.OHV. The different types of isocyanates used also affects the level of hardness, especially in the polyurethane film layer from polyurethane polyol with a lower hydroxyl number.

Figure 4 shows the effect of polyol type on any isocyanate A and B against polyurethane film coating adhesion. Film layer derived from commercial polyol has better adhesion than films from synthetic polyol. The difference of the polyol hydroxyl number between L.OHV and H.OHV polyol did not provide a significant difference in the adhesion ability of film. The use of type A isocyanate tends to increase adhesion to the polyol with a smaller L.OHV and hydroxyl number commercial polyol.

According to Baghdachi [21], adhesion between the coating film and media can be caused by primary bonding force (chemical bonds), secondary bonding force (hydrogen bonding, dispersion forces, dipole and induction), and mechanical adhesion (pores) or a combination. Adhesion is highly dependent on the surface properties of the media and the type of resin/polymer used. Good film adhesion can be achieved if there is a bond between media with resin/polymer. According to Backman and Linberg [22], to get a good bond, both media and polymer must be compatible and can build some bonding styles. Based on that statement, a fairly good adhesion of polyurethane
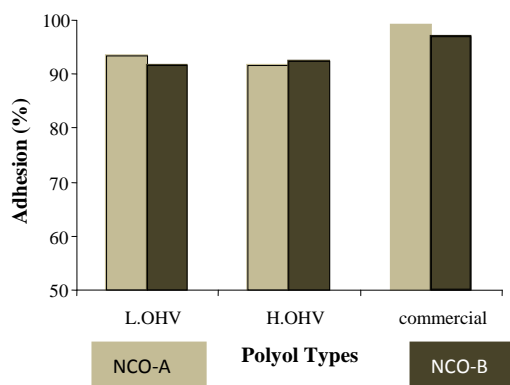
film layer in the ABS media is due to the formation of bonding forces between the ABS sheet with polyurethane film. The general conclusion from this analysis is that the type of polyol effects the quality of the resulting polyurethane film layer. Alternatively, the type of isocyanates has no significantly effect on the quality of the polyurethane film layer.

In polyurethane technology, the position of the hydroxyl group affects its reactivity with isocyanate. Polyols with primary hydroxyl groups are more reactive than polyols with hydroxyl groups in the secondary position. This difference in reactivity determines the type of polyurethane applications. Polyol with a hydroxyl group in the secondary position has the potential to be developed as a polyurethane coating raw material, because its reactivity against isocyanate is lower at room temperature.

4. Conclusions

Polyurethane coating material can be made from isocyanate and *Jatropha* oil polyol that synthesized by epoxidation reaction followed by epoxide ring-opening reaction. Test results indicate the type of polyol affect the gloss power, hardness and adhesion of formed polyurethane film layer, while the types of isocyanates gave less significant effect. Visually, the quality of polyurethane film coating derived from L.OHV and H.OHV polyol are relatively similar to commercial polyol polyurethane. These results demonstrate that *Jatropha* oil is potential to be developed as a polyurethane coating raw materials.

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Figure 4. Effect of Polyol Type in NCO-A and NCO-B Application on Film Adhesion Ability

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