

Synthesis of Acid Polyols As A Feedstock to Produce Flexible Polyurethanes and Their Effect on The Income Level of Furniture Craftsmen

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ABSTRACT

Polyurethanes are widely used as elastomers, coatings, adhesives and binders, interior and exterior cars, furniture, shoe soles, carpets, rigid and flexible foams, membrane materials as well as construction materials. The production of polyurethanes is largely derived from polyols derived from petroleum. However, petroleum is a non-renewable raw material. Thus it is necessary to look alternative feedstock for the manufacture of polyol as a polyurethane raw material. Synthesis polyurethane by polymerization process using polyol volume based on polyol oleic acid polypropylenglycol (PPG) in order to know whether fatty acid can be used as raw materials of polyurethane manufacture. From the result of the study. Based on Fourier Transform Infra Red (FTIR), showed, that the product produced is polyol with obtained hydroxyl group (OH group) with hydroxyl number is 129,81 mg KOH / g and 157,60 mg KOH / g sample of 70°C.

Keyword : Syntesis, Flexible Polyuretan foam, Polyol, Oleic acid.

INTRODUCTION

Polyurethanes are polymers containing urethane group strands formed as a result of the reaction of alcohol (polyol) and isocyanate groups. Polyurethanes are widely used because they have stability during storage, are resistant to chemical reagents, and are durable. World polyurethane consumption continues to increase from year to year with an average increase of 6% in line with the increasing public demand for its products [1], especially the renewable resources for continuity of polyol manufacture (9.10 dihydroxy stearic acid) from oleic acid to become polyurethane foam

Research of making polyol as raw material of polyurethane manufacture is needed in order to master polyurethane manufacturing technology. Polyol or polyalkohol is a compound having more than one hydroxyl group. Polyol is an important compound in the manufacture of polymers such as polyurethane, lubricant and cosmetics. One of the raw materials of polyurethane manufacture such as polyol polyester and polyol polyeter produced from petroleum derivatives such as ethylene oxide and propylene oxide, as one of the main raw material of polyurethane manufacture which is non renewable and limited material, it is necessary to find alternative, cheap, easy material obtained and widely found in Indonesia, and is a renewable natural resource for the continuity of the process and is a resource in the country (local resources). Oleic acid is an unsaturated fatty acid of palm oil can replace ethylene oxide and propylene oxide. The oleic acid by epoxidation reaction using the in situ peroxy acetate acid and the hydroxylation reaction using sulfuric acid catalyst can be made flexible polyurethane foam based oleic acid. Polyurethanes are widely used as elastomers, coatings, adhesives and binders, interior and exterior cars, furniture, shoe soles, carpets, rigid and flexible foams, materials.

METHODS

Oleic acid, ethylene glycol, benzoid peroxide, hydroquinone, sulfuric acid, glacial acetic acid, methanol, sopropanol, hydrogen peroxide, sodium sulfate, aquades and so on A. Polyol Synthesis Procedure.

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At first 100 g of oleic acid was put into a 500 ml three-necked flask equipped with a thermometer, water bath, reflux condenser and stirrer. Peroxy acetate acids consisting of glacial acetic acid, hydrogen peroxide and benzoyl peroxide are added slowly into oleic acid. The mixture is stirred with a magnetic stirrer to obtain a homogeneous solution. Temperature maintained at 100 - 160 ° C The reaction was stopped after 1 - 4 hours After that the mixture was cooled to room temperature, then poured into a separating funnel in order to separate the oil phase in the top layer and the rest of the reactants in the lower phase by about 5 minutes. The epoxidized oleic acid is further reacted with excess alcohol in the three-neck flask. The mixture is stirred with a magnetic stirrer to obtain a homogeneous solution. The temperature is maintained at 60 ° C. After two hours the reaction is stopped. The product is cooled to room temperature, then poured into a separator funnel in order to separate the raw product from the rest of the reactants. Raw products are washed with warm water, shaken and silenced for several hours, resulting in two layers. The raw product is separated from the bottom layer. The crude product is heated slowly to reduce the water content. B. Procedure Synthesis Polyuretan

incorporating a certain amount of mixture comprising 100 ml of polyol both blending and without blending 1 mole water, 1 mole of silicone glycol as surfactant, 0.3 ml stannous. Octonate as a metal catalyst, 0.2 ml tri ethylene was assayed as an alkaline catalyst and 4.5 mole of methylene chloride as blowing agent to be introduced into the reactor, mixed together first and then added 25.30 and 33 ml of toluene diisocyanate (TDI) into the reactor and stirred for 30 seconds with a mixture of polyols. This mixing process takes place in atmospheric conditions. Polyurethane yield is poured in the mold, after that often for 7 days. The result obtained is polyurethane cream-colored foam.

RESULT AND DISCUSSION

Alcohol greatly affects the properties of polyester. The choice of alcohol is important because it affects polyester properties such as flexibility, crystallinity and sensitivity to water and heat. The type of alcohol used is glycol. Monohydric alcohol is used for chain growth, while polyhydric alcohol will lead to the growth of branches in uncontrollable polyester chains. Increasing the length of the glycol chain will lead to increased flexibility, strength and sensitivity to water and heat. The success of the condensation reaction is influenced by: process conditions (temperature, pressure and reactant concentration), the ratio between oleic acid and diglycol used, catalyst / reactant. The esterification reaction between oleic acid and ethylene glycol studied by following Le Chatelier reaction principle will result in polyester. The process conditions were studied at a temperature range of 110 ° C to 160 ° C.

The reaction mechanism at the condensation reaction stage occurs an esterification reaction between the alcohol group and the acid group forming a polyester linear chain and freeing the water molecule.

To maintain the stability of the unsaturated polyester produced, an inhibitor system is required after the condensation reaction takes place to prevent the reaction from attacking the double bond present in a polyester chain by the double bonds present in the other polyester chains during storage. Basically, this inhibitor serves to keep the double bond in the polyester chain is not active before the curing process occurs.

Compounds with two functional groups yield a linear polyester polyol. When added compounds that have more than two functional groups will produce a branched polyol [21]. The most used acids are adipic acid and phthalic. Polyol polyester based adipic acid is used in applications where the desired flexibility, as flexible foam and elastomer.

Influence of Time and Temperature

The influence of temperature and time on the polyol hydroxyl number was studied by reacting oleic acid with glycerol at 50, 60, and 70 °C with a time of 4, 5, 6 and 7 hours with other fixed process conditions (mole ratio of acetic acid: hydrogen peroxide is 2: 1 at epoxidation stage whereas the ratio of methanol is 1 in the hydroxylation stage).

In the epoxidation process oxidizers are needed that are strong enough to break the double bonds of palm oil such as oleic acid and linoleic acid, to form the oxalene group. Generally, epoxidation of glycerides using hydrogen peroxide (H₂O₂). The properties of H₂O₂ as oxidizing agents are not strong enough to be transformed

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into other more active forms such as peroxy acid. Acetic acid reacts with hydrogen peroxide using sulfuric acid catalyst to form peroxy acetic acid. The reaction takes place in a reversible and exothermic manner. Furthermore peroxy acetic acid reacts with oleic acid to form epoxidized oleic acid. The epoxidation process can be seen from the formation of two layers after the epoxidation process and visually can be seen the upper phase layer in the form of yellow epoxidized oleic acid and the undercoat of a clear white side product.

The end result of this epoxidation process is epoxidized oleic acid. Furthermore, after the epoxidation step is the hydroxylation stage, at this step the epoxidized oleic acid is reacted with methanol and water using a sulfuric acid catalyst. At this stage of hydroxylation sulfuric acid catalysts are used because the epoxidized oleic acid is a strong base. Such a reaction does not occur in either the other, but this may occur in the epoxide (this is because of the ring bond) which makes the nucleophile attack a strong base such as an alkoxide ion. In an open ring acid catalyst, the nucleophilic strikes the protonated epoxide ring forming another epoxidation group. The carbon that is being attacked undergoes a reversal. The new C-O bond is always formed from the reverse side of the original epoxide ring.

Research carried out on polyol manufacture includes the influence of temperature, time at the epoxidation stage, the influence of the amount and mixed moles of alcohol used in the hydroxylation stage.

Table 1. Hydroxyl Polyol Numbers for Comparison of Oleic Acid and 1: 1 Glycerol with Temperatures of 100 ° C, 120 ° C, 140 ° C, 160 ° C and Time 1,2,3, and 4 Hours.

Time	Temperature (°C)			
	100	120	140	160
1	87,55	91,20	92.1	97.8
2	93,46	95,80	96.33	100.15
3	95,80	97,56	99.6	103.5
4	95,95	98,05	100.5	104

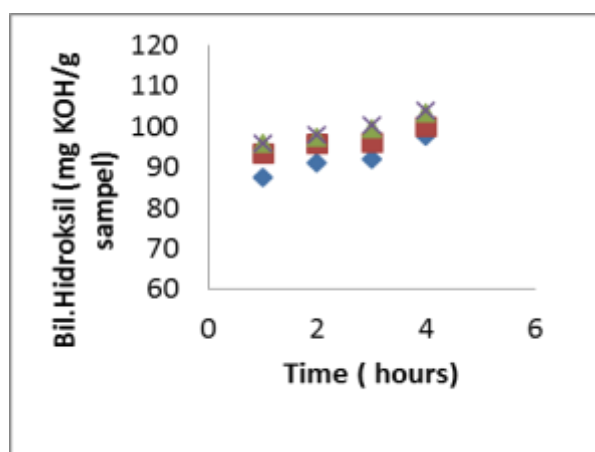


Figure 1. Relationship of Hydroxyl Numbers for Various Epoxidation Times and Temperatures Epoxidation Time (Hours)

Based on the hydroxyl number shown in Table 1 it appears that the resulting polyol has a hydroxyl number of 87.55-104 mg KOH / g of sample for oleic acid ratio with ethylene glycol 1: 1 From Figure 1 shows that with

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the increasing temperature of the epoxidation process polyol which is formed has a higher hydroxyl number. This is because with the higher temperature, the particles will move faster so that the collision frequency will be greater. This speeds up the rate of the reaction. With the length of time the epoxidation process then the chance of the particles to collide the greater. The opening of the oxygen ring bonds of the epoxidized oleic acid will more readily react with the IPA, MeOH and water so that the more hydroxyl groups are formed and the hydroxyl number of the formed product becomes higher.

Table 2. Polyol Viscosity for Raio Mol Oleic Acid and H2O2 1: 1 with Epoxidation Process Temperature 40oC, 50oC, 60oC, 70oC and Epoxidation Time Time 1,2,3, and 4 Hours.

Time (hours)	Temperature (°C)			
	40	50	60	70
1	50.047	38.914	14.486	21.358
2	28.746	27.013	24.936	27.741
3	24.2	29.345	36.126	39.536
4	25.166	29.908	37.667	37.723

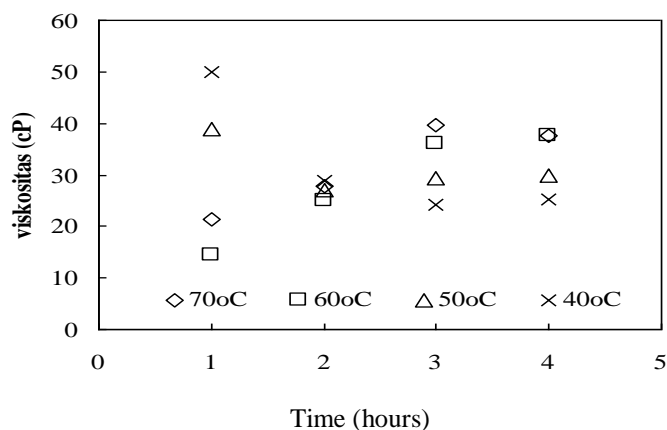


Figure 2. Polyol Viscosity for Raio Mol Oleic Acid and H2O2 1: 1 with Epoxidation Process Temperature 40oC, 50oC, 60oC, 70oC and Epoxidation Time Time 1,2,3, and 4 Hours.

From Figure 2 above, it shows that the viscosity is irregular at 1 to 2 hours and increases when the time is 2 hours to 4 hours. However, in general from Figure 2 it can be said that the viscosity of the polyol product formed has a tendency to rise for every increase in temperature variables and time of the hydroxylation process. This is because the higher the time and temperature of the epoxidation process the more oleic acid reacts. This affects the occurrence of changes in chemical structure and molecular weight in oleic acid. With the increasing number of hydroxyl numbers, the molecular weight is also higher so that the viscosity also tends to be higher.

Effect of Benzoyl Peroxide Catalyst Concentration

The effect of benzoyl peroxide catalyst concentration on polyol hydroxyl number was studied by reacting oleic acid with glycerol acid each at 1%, 2%, 3%, 4%. The catalyst is another factor that affects the epoxidation-hydroxylation process in addition to the molar ratio. The range of catalyst concentrations studied was 1%, 2%, 3%, 4%. The function of the catalyst is to speed up the chemical reaction by lowering its activation energy)

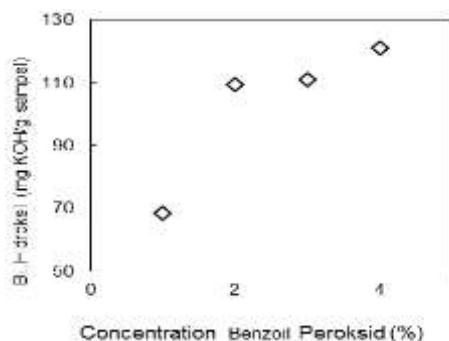


Figure 3. Effect of Benzoyl Peroxide Catalyst Concentration

The addition of the amount of catalyst will further activate the reagents so as to increase the chance of reactants to collide with each other to produce the product. The sulfuric acid catalyst at this epoxidation stage helps speed up the oxidation reaction. The growing catalyst concentration causes a decrease in activation energy. The concentration of the catalyst may affect the reaction speed constant. The greater the hydrogen ion concentration the greater the reaction speed, so the reaction conversion gets bigger. In this study the conversion of the reaction is not measured but the direct conversion of the reaction affects the results achieved, both in terms of quality and quantity. So if the hydroxyl number which is getting bigger then it can be said the conversion reaction will also be greater.

The number of hydroxyl numbers occurred 1% to 2% concentration increase is significant moderate at catalyst concentration 2% - 4% increase is not significant. This is probably due to the above concentration of 2% activation energy is minimal so that the addition of catalyst concentration can not further lower the activation energy.

Effect of Temperature

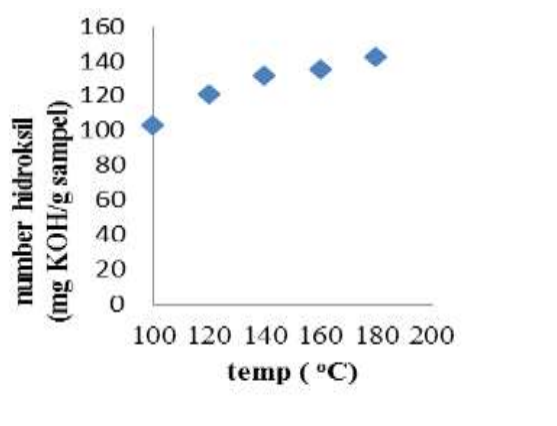


Figure 4. Effect of esterification temperature on hydroxyl number for catalyst 2%

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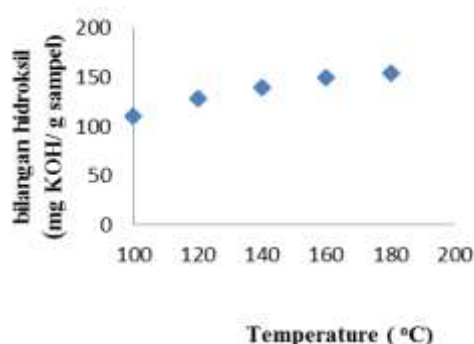


Figure 5. Effect of ion Temperature on Hydroxyl Numbers for Catalysts 4%

From Figure 4. and 5 it can be seen that the polyols produced for the 2% catalyst have hydroxyl numbers of 103.2-242.25 mg KOH / g sample, while for the 4% catalyst the hydroxyl number is 110.73-154.15 mg KOH / g samples. In Figs 4.4 and 4.5 show that with the increasing temperature of the esterification process, the polyol product formed has a higher hydroxyl number, this is because with the higher temperature, the particles will move faster so that the impact frequency will be greater. This speeds up the rate of the reaction. As for the length of time of the hydroxylation process, the chance of the particles to collide is greater so that the opening of the oxygen ring bonds contained in the epoxidized oleic acid will more easily ultimately allow the bonding of an epoxidized oleic acid oxirene ring to more readily react with methanol and water so that the hydroxyl group which is also formed more and more hydroxyl number of products formed even higher. As a comparison, the amount and number of hydroxyl obtained by the scientists ranged from 110-250 mg KOH / g sample while the polyol obtained from oleic acid obtained hydroxyl number from the range 103.2-154.15 mg KOH / g sample. This is a sign that the polyol produced by oleic acid has met requirement as raw material of polyurethane manufacture.

Qualitative analysis with FTIR Spectroscopy

For comparison, the amount and number of hydroxyl obtained by the scientists is about 110-250 mg KOH / g sample while the polyol obtained from oleic acid obtained hydroxyl number from the range 103.2-154.15 mg KOH / g sample. This is a sign that polyols produced by oleic acid are qualified as raw materials for polyurethane manufacture.

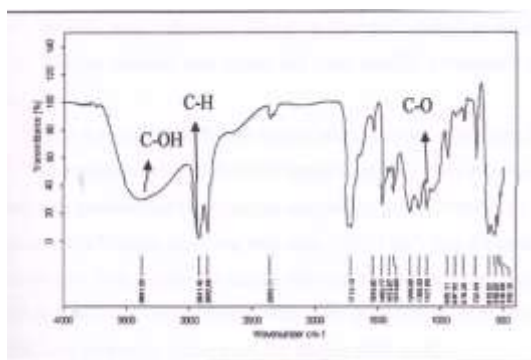


Figure 6. FTIR of the oleic acid spectrum

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In Figure 6 for the Oleic Acid raw material it appears that the spectrum of unsaturated carbon groups (double bond) with the wave number 1583.70 cm⁻¹ also shows the wave number 1743,48 cm⁻¹ indicating the presence of ester groups in the sample.

A polyol sample can be seen that the sample contains an alcohol group (hydroxyl) with a wavelength of 3361.21 cm⁻¹. It also appears that the absorption of an unsaturated carbon group is lost. This means that there has been a reaction to the double bond present on the raw material to a single carbon strand, so it can be ascertained that all epoxide (ether) contained in the sample is converted to polyol via an epoxide reaction and followed by a hydroxylation reaction. This is highly desirable as more epoxides are converted to polyhydroxy alcohol, the more hydroxyl or OH groups the polyhydroxyl alcohol possesses can also be observed in the presence of the wave number 2921,42 cm⁻¹, which is an aliphatic C-H group (methyl group CH₃). And another absorption area proves that the sample contains an alcohol group, that is, by the presence of a wave number value in the range of 1107.53 cm⁻¹, which is a C-O stretch (for alcohols).

Figure 4. it appears that there is still a C = O (carbonyl) group spectra, indicating that the oxidation reaction does not occur in the carbonyl group but in the alkane group (double bond unsaturated).

Polyol viscosity analysis

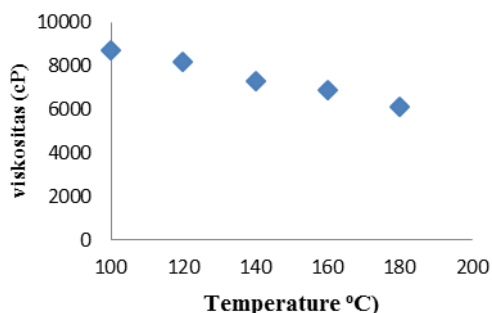


Figure 7. Temperature effect on polyol viscosity for catalyst 2%

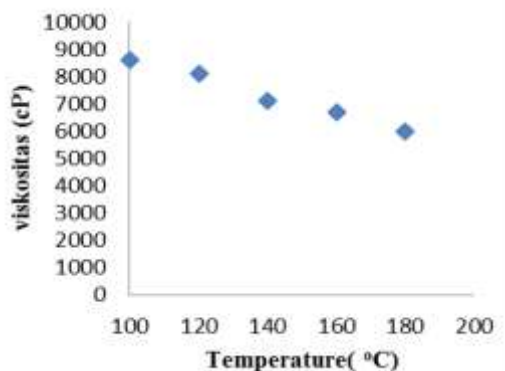


Figure 8. Effect of temperature on viscosity for catalyst 4%

From Figure 7 and 8 it can be said that the viscosity of the polyol product formed has decreased tendency for every increase of temperature variable in the esterification process. This is because the higher the temperature of the esterification process, the more oleic acids that react.

The limitation of polyurethane formulation formulation is based on visually visible elastomeric physical properties, ie, polyurethane formation which may become solid after curing process. The preliminary experiments using polyb-based RBD palm olein, resulting in a brittle polyurethane foam, were attempted by

mixing polyol with polyol polypropylen glycol. The effect of blending between polyol-based RBD palm olein and polypropylene glycol (PPG) on polyurethane manufacturing was studied by reacting polyol blending between RBD palm olein-based polyols with polypropylene glycol (PPG) in comparison (50/50, 75/25, 80/20) and 100: 0 (100% polyol based RBD palm olein) with TDI at various volumes, as shown in Table 3.

Table 3. Effect of Polyol Volume Ratios (Polyol oleic acid: PPG) on Various Volume of TDI

Rasio Polyol (ml)		TDI (ml)	Keterangan Hasil
Polyol asam oleat	PPG		
100	0	25	<i>Shrinking, collapse, getas</i>
80	20	25	<i>Shrinking, collapse, getas</i>
75	25	25	<i>Shrinking, agak rigid, mudah dipatah</i>
50	50	25	<i>Shrinking, agak kenyal, mudah dipatah</i>
100	0	30	<i>Shrinking, collapse, rigid</i>
80	20	30	<i>Shrinking, collapse, rigid</i>
75	25	30	<i>Agak flexible, mudah diputus</i>
50	50	30	<i>Flexible, agak mudah putus</i>
100	0	33	<i>Shrinking, rigid, mudah dipatah</i>
80	20	33	<i>Shrinking, collapse agak rigid,</i>
75	25	33	<i>Flexible, sukar diputus</i>
50	50	33	<i>Flexible polyurethane foam (berhasil), sebanding dengan flexible polyurethane foam</i>

Sumber : (La Ifa & Sumarno, 2007)[3]

Table 3 shows that the use of polyol oleic acid polyol ratio with polypropylene glycol (PPG) (80/20) and the use of polyol based Polyol oleic acid (100%) result in polyurethane which tend to occur shrinking, brittle, collapse and easily broken. Polyol-based Polyol oleic acid has more secondary OH groups whereas polypropylen glycol has a primary OH group. The reactivity of the primary OH group is greater than that of the secondary OH group. In addition the primary monovalent alcohol has one OH group and does not form polymerization, so the molecular size and viscosity of the solution during the reaction does not change and the

functional group reactivity remains unchanged. Polyol-based polyol structure of complex oleic acid will provide lower reactivity compared to hydrocarbon alcohols.

Shrinking can be caused by an overlapping crosslink on the polymer chain. As a result the diffusing gases enter the cell are unable to resist the bonding force in the polymer matrix so that cell size can not develop. This is probably due to the polyol obtained from Polyol oleic acid having a relatively different molecular structure with molecular structure of polypropylene glycol (PPG), the polyurethane product is also relatively different, so to make flexible polyurethane foam must be blended with polypropylene glycol (PPG) which is better (Kircher, 1987).

From Table 3, it appears that for various Polyol oleic and PPG acids on the use of TDI 25 and 30 ml, polyurethane results in collapse, brittle, shrinking due to insufficient crosslinking (the amount of isocyanate groups $N = C = O$ is insufficient for crosslinking with urethane group formed). If the foam does not have enough gel when the cell is broken, it will collapse. The reaction of polyurethane formation in 33 ml TDI for various (PPG) on polyol ratio of oleic acid polyol with polypropylene glycol (PPG) was (50/50, 75/25) obtained by flexible polyurethane foam.

The rise in TDI will form a fast polyurethane because the straight bonding and crosslinking reactions occur very quickly. Isocyanates are highly reactive to a nucleophile, this is due to the position of the C atom in the isocyanate is between two elements of electronegative, namely oxygen and nitrogen. In this condition, the carbon atom becomes electron-deficient (electrophilic) so that when it encounters an electron-rich atom (nucleophile), it quickly forms a bond.

The isocyanate reaction with polyol based Polyol oleic acid is a nucleophilic substitution reaction, in which isocyanate reacts with hydroxyl form an activated complex, which subsequently reacts with isocyanate to form urethane. Thus, the more isocyanates available the more rapid the reaction. As the TDI is increased, the more isocyanate concentrations available to react form a straight or crosslinked bond so that the reaction rate will increase.

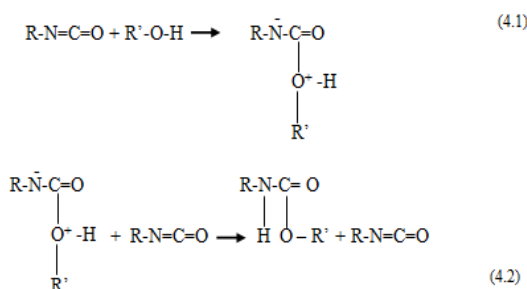


Figure 9. Polyol oleic acid with polypropylene glycol (PPG) carbonyl bonding

From the above results, taken the ratio of polyol volume based Polyol oleic acid with polypropylene glycol (PPG) 50:50 is a successful polyurethane, just like polyurethane obtained from PPG. The structures in the resulting polyurethane material were analyzed by using Scanning Electron Microscope to determine cell diameter and density. To identify the presence of urethane in the carbonyl group and the hydrogen bonding, the Fourier Transform Infra Red (FTIR) Spectroscopy method was used.

CONCLUSION

Increased temperature in the esterification stage obtained greater hydroxyl number of 142.29 mg KOH / g and 154.15 mg KOH / g samples at a temperature of 180oC. The greater the catalyst concentration in the esterification process obtained by the greater number of hydroxyl catalyst concentration 4% with hydroxyl

number 154.15 mg KOH / g sample. Based on the Fourier transform Infra Red (FTIR) test Spectroscopy can be concluded that the resulting product is a polyol obtained by hydroxyl group (OH group).

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