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Synthesis of Polyurethane from Diphenyl Methane 4,4 Diisocyanate (Mdi) Polymerization with Hydroxilated Avocado Oil Polyol

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Abstract. Polymerization between polyol and isocyanate compounds produces polyurethane in different forms. Polyol used in this study utilized spoiled avocado as the oil source for polyol to produce polyurethane. Avocado oil was epoxidized with formic acid (HCOOH) and H_2SO_4 catalyst at 40-45ºC followed by hydrolysis reaction to produce polyol reaction. Next polyol was purified, and structure confirmation was done using FT-IR spectroscopy analysis. Polyol was then reacted with diphenylmethane 4,4 diisocyanate (MDI) with ratios of (polyol:MDI) 9:1; 8:2; 7:3; 6:4; and 5:5 (v/v) in a total volume of 10 mL with open air stirring at 40-45ºC to produce polyurethane. Characterization for the form was observed visually followed by the determination of gel content, density and structure using FT-IR spectroscopy.The results of polyol from avocado oil reacted with diphenylmethane 4,4 diisocyanate for each of the mixing ratio to produce polyurethane is gel content of 74.63 to 99.80% where the higher MDI ratio is, the higher gel content becomes. Density determination from the polyurethane produced is between 0.1341 g/cm^3 to 0.7220 g/cm^3. FT-IR spectrometer analysis to polyurethane produced is marked with the peaks at 3400-3300 cm^{-1}, 2270-1940 cm^{-1}, 1700-1600 cm^{-1} and 1590-1540 cm^{-1}wavenumbers which are the characteristic of urethane functional groups.

Keyword: Hydroxylation, MDI, Avocado oil, Polyol, Polyurethane

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1 Introduction

Nowadays, the needs of polyurethane in the world, including Indonesia, experiences a dramatical increase. This is because polyurethane is used as the material for elastomer, adhesive, foam, paints and etc. Normally polyurethane is made of polyol from petroleum (Narine et al., 2007). However, petroleum is a non-renewable resource. Consequently, all related party is encouraged to find alternative resource to make polyol (Azmi, 2014).

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Vegetable oil is one of the alternatives that can be used to make polyol for polyurethane. Polyol made of vegetable oil has its own superiority compared to that of petroleum, where it is abundant and a renewable resource. Indonesia has got an abundant source of vegetation resources, palm, soybean, sunflower, olive, corn, canola and nuts are several types of vegetable sources that produce oil. (Azmi, 2014). Those vegetable oils can be utilized to produce polyol for polyurethane. Unfortunately, there may be a competition for those materials to be consumed as food. Therefore, an alternative to other vegetation resources as material to make polyol is necessary, such as avocado (*Persea americana Mill*).

An avocado is a tropical and subtropical fruit with its growth spreads throughout provinces in Indonesia. A better handling of avocadoes is needed along with the increase of production to ensure the fruit is utilized. Avocadoes rot quickly and are not suitable to be kept for a long time (Moehd, 2003).Avocadoes produce oil rich of oleic acid, antioxidant and phytosterol (Requejo et al., 2003). The benefits of avocadoes make the fruits to be high in price. A big supply of avocadoes and the nature to rot easily have enabled processing and utilizing damaged avocadoes.In oleochemical industry, polyol made of vegetable oil that is rich of unsaturated fatty acids like oleic, linoleic and linolenic has been developed through epoxidation of unsaturated fatty acid double bonds as the raw material for polyurethane (Maznee et al., 2001).

Several past studies showed that epoxidation reaction of unsaturated fatty acid followed by hydrolysis can produce polyol derived from fatty acid. Ginting (2010) synthesized polyurethane compound from candlenut oil via epoxidation reaction of unsaturated fatty acid followed by hydrolysis and alkoxylation with glycerol as the source of polyol. Next, the compound is polymerized with TDI that led to the production of various form of polyurethane, from a soft solid like foam to a very firm solid. Azmi (2014) synthesized polyurethane compound though hydroxylation reaction of corn oil as the polyol source and it is then polymerized with TDI to produce rigid polyurethane.

In this study, epoxidation was done followed by hydrolysis of avocado oil with unsaturated fatty acid as its main composition. It contains of double bond to be converted as polyol. Next, polyol compound was reacted with MDI to produce polyurethane. Polyurethane formed was analyzed using FT-IR spectroscopy and gravimetry for density and gel content.

2. Materials and Methods

The equipment used in this research was: laboratory glassware, analytical balance, thermometer, hotplate and magnetic stirrer, aluminium container, desiccator, FT-IR spectrophotometer. The material used in this research was: avocado oil, methylene diphenyl diisocyanate, toluene, bleaching earth, hydrogen peroxide, dichloromethane, n-hexane, benzene, NaOH pellets, anhydrous calcium chloride, anhydrous sodium sulfate, phosphoric acid and diethyl ether.

2.1. Avocado Oil Extraction

Modification of the commonly used extraction method was done in order to extract and purify avocado oil (Ketaren, 2008).

2.2. Synthesis of Polyol from Avocado Oil

100 ml of formic acid (HCOOH 90%) was poured into 250 ml three neck flask. 50 ml of H_2O_2 30% was added. While stirring at 40-45ºC for 1 hour, 3 ml of H_2SO_4 was added. Then 60 ml of avocado oil was added and stirred for 2 hours at 40-45ºC. The product was left for one night and it was stirred with 10 ml of NaOH 10% and evaporated. The precipitate was dissolved in 150 ml of diethyl ether. Ether layer was washed with 25 ml NaOH 2M and followed by aquadest for 3 times. The washing result was dried using anhydrous Na_2SO_4 and filtered. The filtrate was evaporated to get polyol avocado oil as precipitate. Iodine value test and FT-IR spectroscopy were conducted.

2.3. Synthesis of Polyurethane

20 ml of dichloromethane was put into a 190 ml aluminium container. Polyol from avocado oil was added and the mixture was heated at 45ºC. MDI was added with stirring with a ratio of polyol : MDI = 9:1, 8;2, 7:3, 6:4 and 5:5 (v/v) with a total volume of 10 ml. Any changes occurred were observed and the gel content and density were analyzed using gravimetry and FT-IR spectroscopy was conducted.

3. Result and Discussion

3.1. Avocado Oil Extraction and Bleaching Result

About 46.51% of oil was obtained from the extraction of avocado oil from avocado fruit. Degumming of extracted avocado oil was done by adding phosphoric acid to precipitate sap or slime like peptide compounds. Bleaching earth was added to produce a clearer oil as the pigment in the oil was absorbed during the bleaching process. In iodine value test, 84.13 shows double bonds existence that can be epoxidized to make polyol. Avocado oil FT-IR spectroscopy gives absorbance spectra peaks at the wavenumbersshown in **Figure 3.1.**

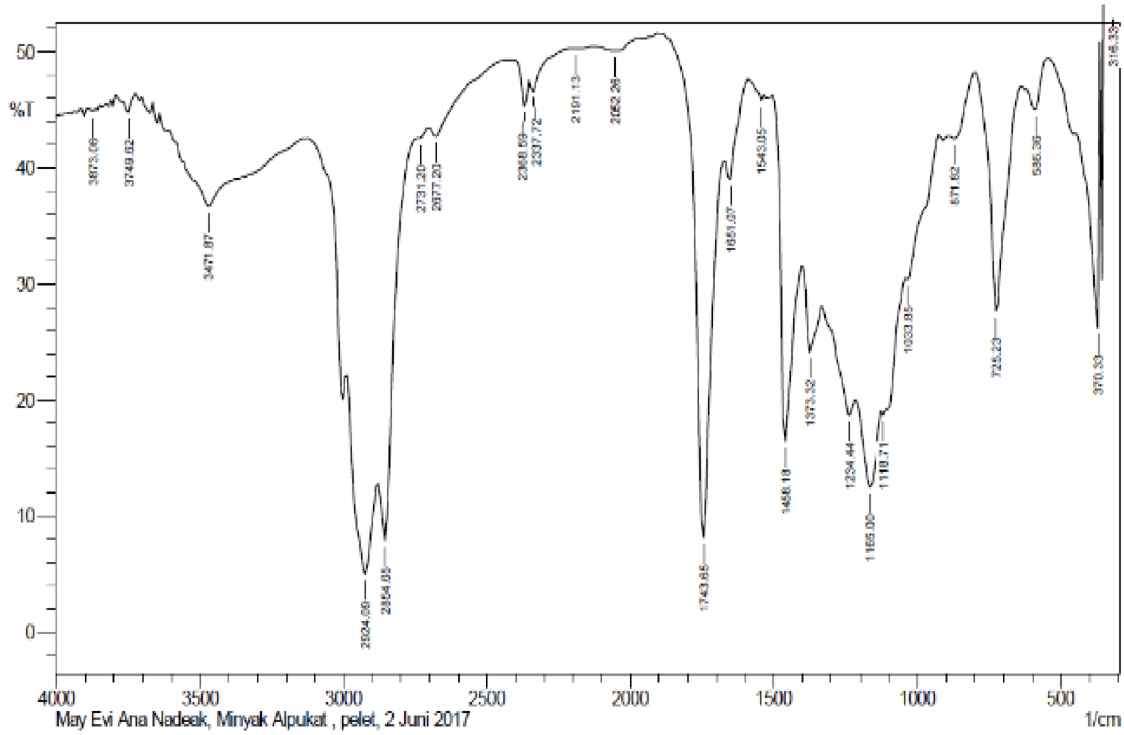

Figure 3.1. Avocado oil FT-IR spectra

3.2. Fatty Acid Composition

The chromatogram of gas chromatography is shown in **Figure 3.2**. Fatty acid composition of fatty acid and the percentage can be seen on **Table 3.1**. The results show that the fatty acid consists of odd total number of carbons. This is due to decarboxylation process in fatty acid biogenesis that causes reduction of carbon atom in fatty acid.

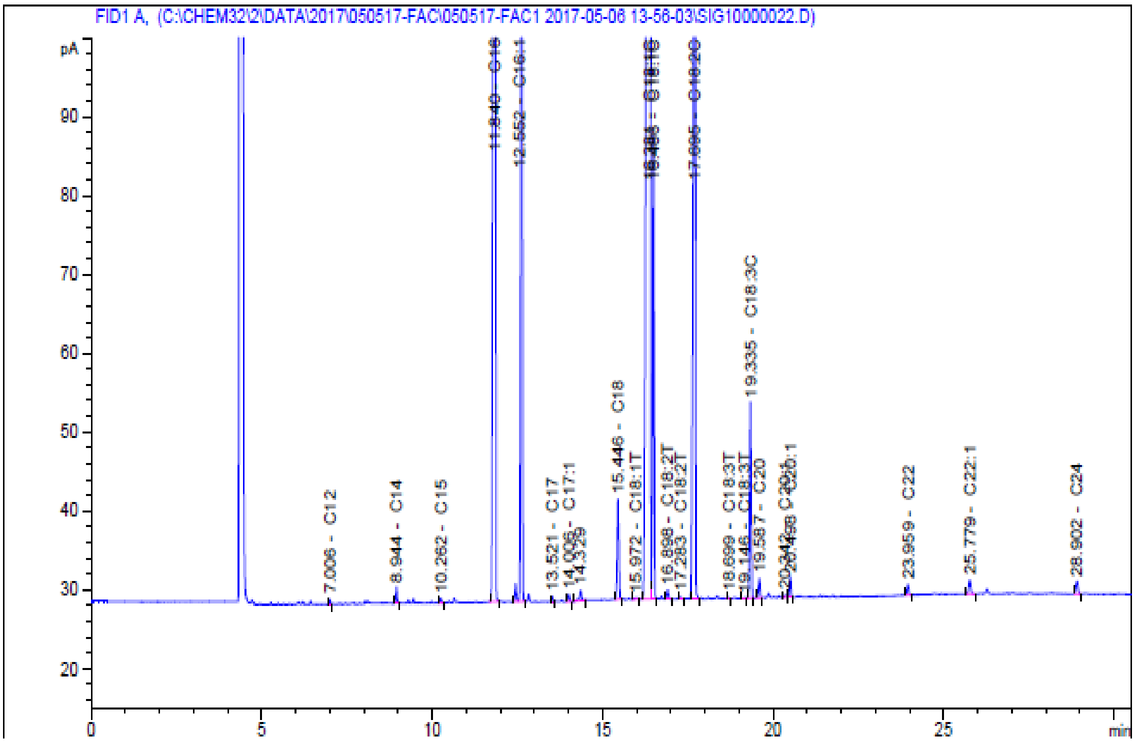

Figure 3.2.Chromatogram of fatty acid composition

Table 3.1. Fatty acid composition of avocado oil and the percentage

Fatty Acid	**Total (%)**
Lauric Acid (C12:0)	0.03
Myristic Acid (C14:0)	0.11
Pentadecanoate Acid (C15:0)	0.03
Palmitic Acid (C16:0)	23.87
Palmitoleic Acid (C16:1)	6.46
Heptadecanoate Acid (C17:0)	0.04
Heptadecanoleate Acid (C17:1)	0.06
Stearic Acid (C18:0)	1.12
Trans Oleic Acid (C18:1T)	0.03
Cis Oleic Acid (C18:1C)	50.62
Trans Linoleic Acid (C18:2T)	0.10
Cis Linoleic Acid (C18:2C)	14.72
Trans Linolenic Acid (C18:3T)	9.56
Cis Linolenic Acid (C18:3C)	1.88
Arachidonic Acid (C20:0)	0.17
Dodecanoleic Acid (C20:1)	0.23
Behenic Acid (C22:0)	0.09
Dodidecanoleic Acid (C22:1)	0.17
Tetradidecanoic Acid (C24:0)	0.16

3.3. Synthesis of Polyol from Avocado Oil

Avocado oil was epoxidized with performic acid with H_2SO_4 catalyst and refluxed at 45^{o}C. Next, it was hydrolyzed to produce polyol compound. The formation of polyol compound, in the condition where epoxidation process and hydrolysis ran perfectly, hypothetically oleic (C18:1) bound as glyceride produces diol. Based on this hypothesis, epoxidation reaction of avocado oil with performic acid and hydrolysis produces polyol compound.

Iodine value test of polyol and avocado oil were 6.26 and 84.13 respectively which show that there is a break of π bond in unsaturated fatty acid of avocado oil. FT-IR spectroscopy analysis with its vibration peak is shown in Figure 3.3. The signal at 3441 cm^{-1}wavenumber shows -OH stretching, while 1172 cm^{-1} shown a secondary -OH vibration. Then the disappearance of 3089 and 1651 cm^{-1} proves that π bond was broken (C-H sp^2 from -CH=CH-) of unsaturated fatty acid. 1743 cm^{-1}wavenumber is a vibration of C=O functional group. 1458-1373 cm^{-1} wavenumbers are bending vibrations of C-H sp^3. The absorbance band of 725 cm^{-1}wavenumber is a hydrocarbon vibration of a long chain alkyl $(CH_2)_n$

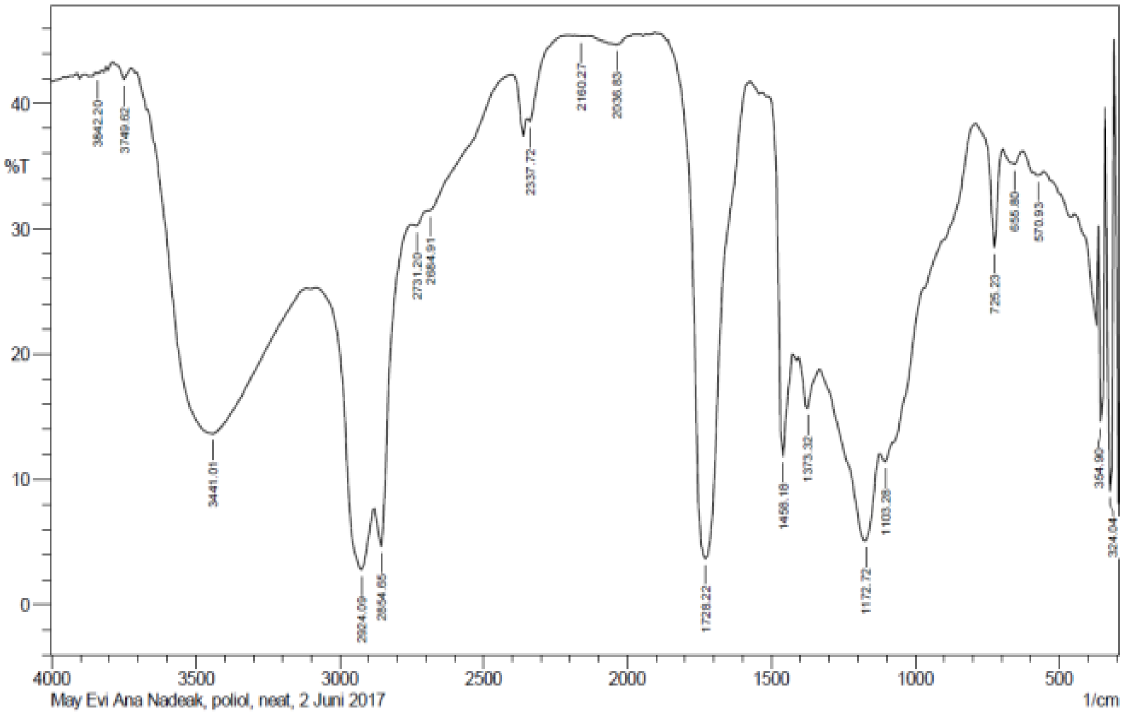

Figure 3.3. FT-IR spectrum of avocado oil polyol

3.4. The Synthesis of Polyurethane

Physical Changes of Polyurethane. Visual analysis shows that polyurethane produced from the polymerization between avocado oil polyol and methylene diphenyl diisocyanate is solid and hard. Polyurethane formed describes that the structure pattern of polyol hydrocarbon used affects the shape of polyurethane. The result of physical properties and gel content analysis are shown in **Table 3.1**.

Table 3.1 The characteristic of polyurethane from avocado oil polymerization with MDI

Polyol	Polyol:MDI ratio (v/v)	Gel Content (%)	Polyurethane Physical Condition
Avocado Oil Polyol	9 : 1	74.63	Soft
	8 : 2	83.86	Hard
	7 : 3	92.13	Hard
	6 : 4	98.12	Hard
	5 : 5	99.80	Hard

Polyurethane Gel Content. The polyurethanes formed from polyol:MDI ratio of 9:1 to 5:5 (v/v) gave various gel contents with an increasing trend (Figure 3.3), which shows that there are different cross-links bonding. This condition happens as polyol with MDI polymerization produces low degree polymer based on the stoichiometry. A lot of -OH functional group from polyol monomers are free and they are not in the reaction. With the increase of MDI ratio used in the polymerization, gel content rises as -OH groups from polyol form a more perfect polyurethane links. The objectives of gel content analysis is to know the degree of cross-links. Gel is a solid that consists of at least two components that have formed cross-link bondage and is insoluble. Therefore, the higher gel content is, the less soluble polyurethane is in organic solvent like benzene, toluene, acetone or other solvents. Furthermore, it has higher durability.

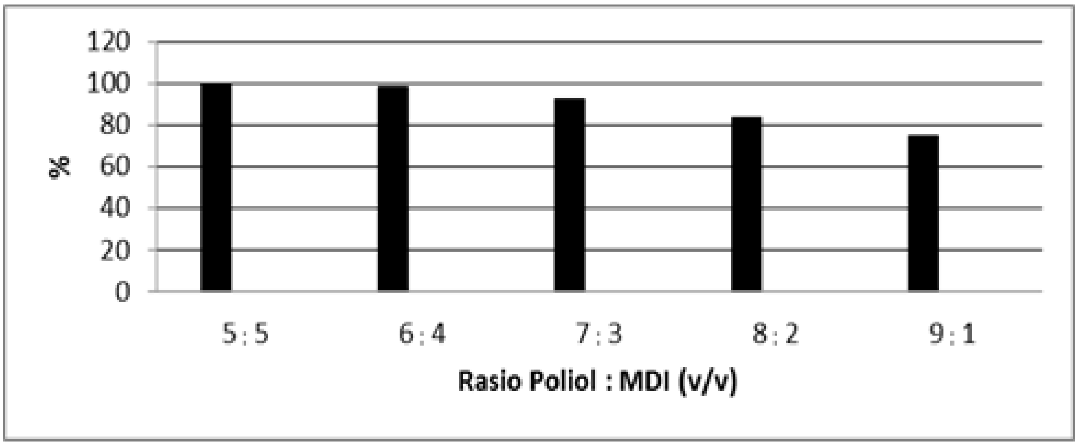

Figure 3.4. Gel content in polyurethane from polyol and MDI polymerization of different ratio

Polyurethane Density. Polyurethane synthesized from avocado oil hydroxylation with isocyanate has different forms. Moreover, it has got different density of every polyol:MDI ratio of 9:1 (v/v) to 5:5 (v/v) as shown in Table 3.2. The density of cross-link is higher with the increasing amount of MDI in the mixture.

Table 3.2 Density of polyurethane from avocado oil polyol with MDI in various ratio

Polyol : MDI Ratio	**Density (gr/cm^3)**
9:1	0.1341
8:2	0.1588
7:3	0.2589
6:4	0.3937
5:5	0.7220

FT-IR Spectroscopy Analysis Spectrum. The characterization of synthesized polyurethane from polyol and MDI with ratios of 9:1, 8:2, 7:3, 6:4 and 5:5 (v/v) using FT-IR spectroscopy produced spectra that can be seen in Figure 3.5 (a), (b), (c), (d) and (e) respectively.

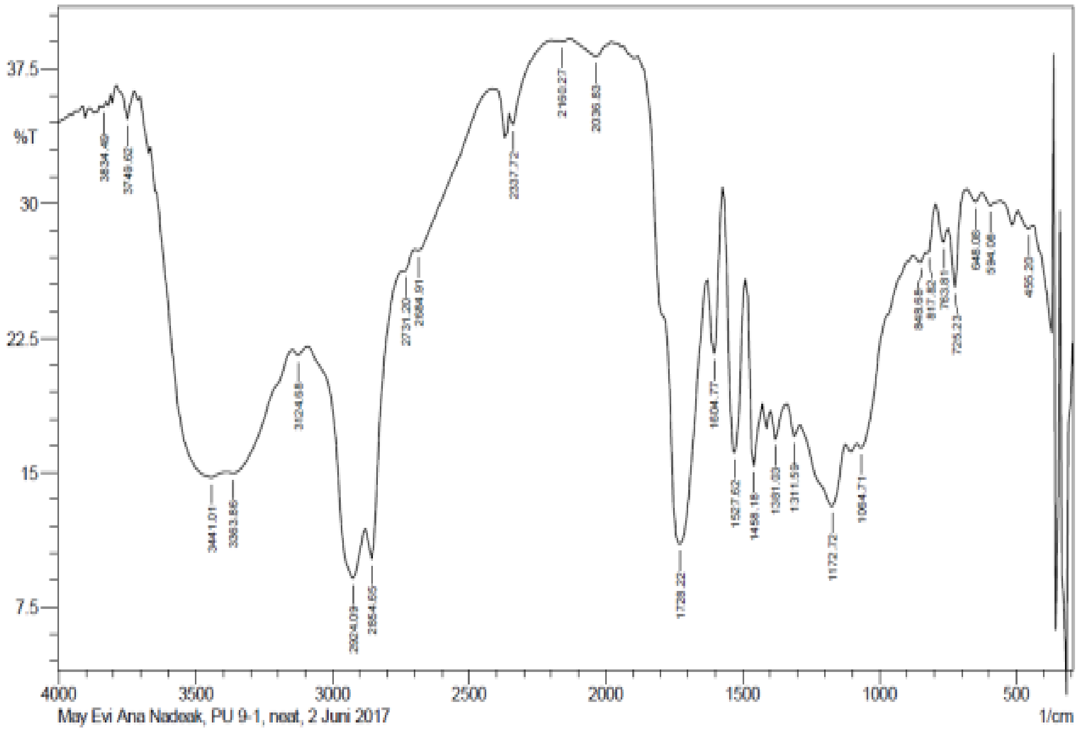

Figure 3.5 (a) FT-IR spectrum of polyol:MDI = 9:1 (v/v) polymerized polyurethane

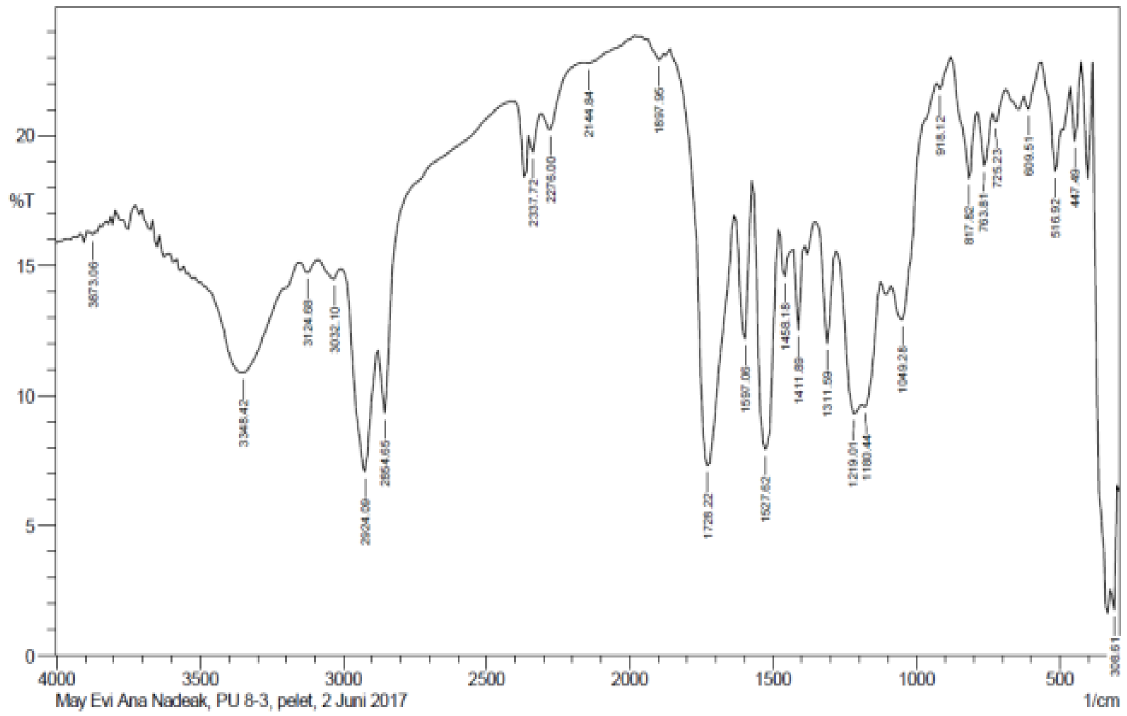

Figure 3.5 (b) FT-IR spectrum of polyol:MDI = 8:2 (v/v) polymerized polyurethane

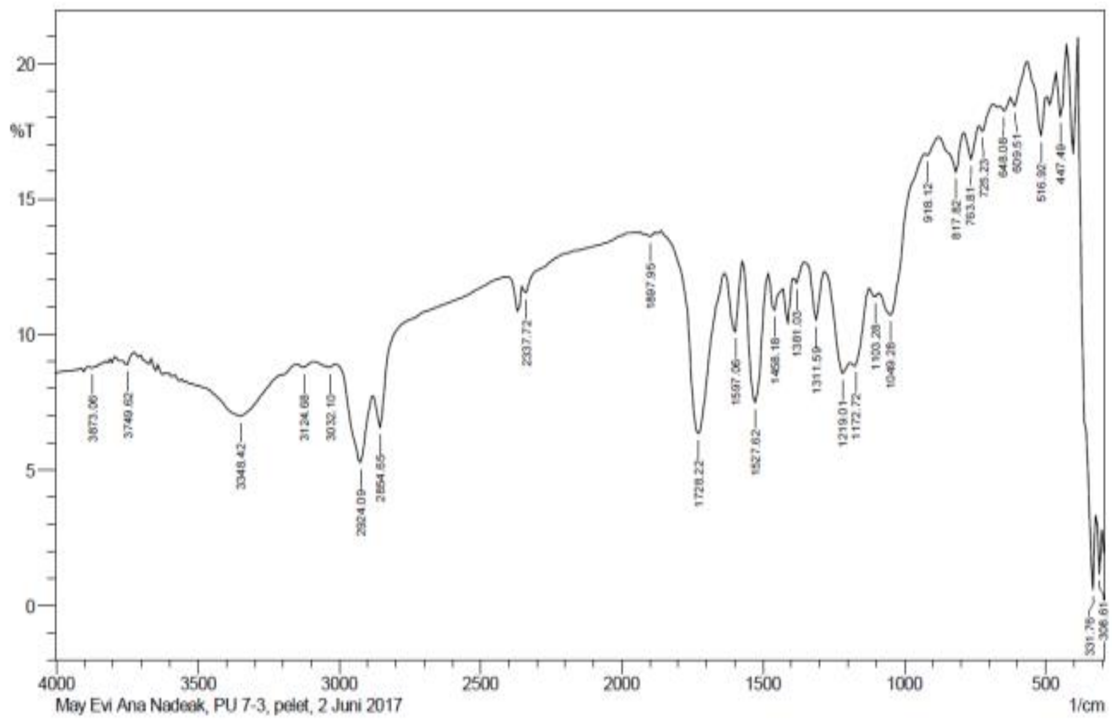

Figure 3.5 (c) FT-IR spectrum of polyol:MDI = 7:3 (v/v) polymerized polyurethane

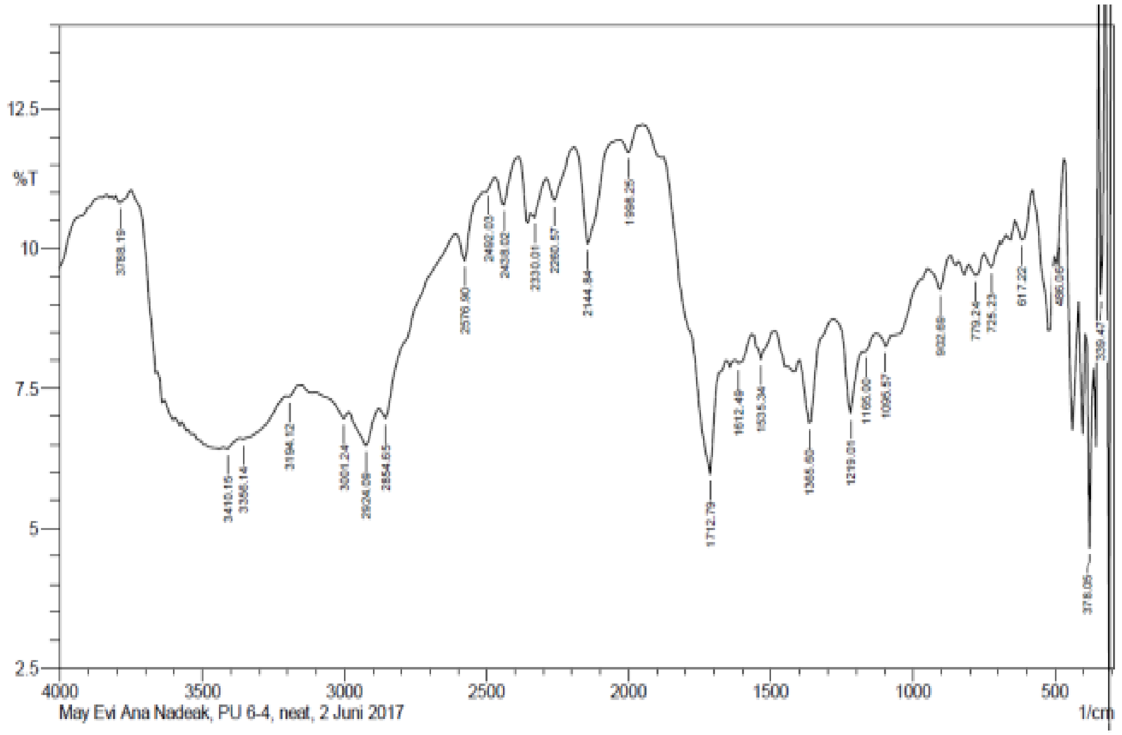

Figure 3.5 (d) FT-IR spectrum of polyol:MDI = 6:4 (v/v) polymerized polyurethane

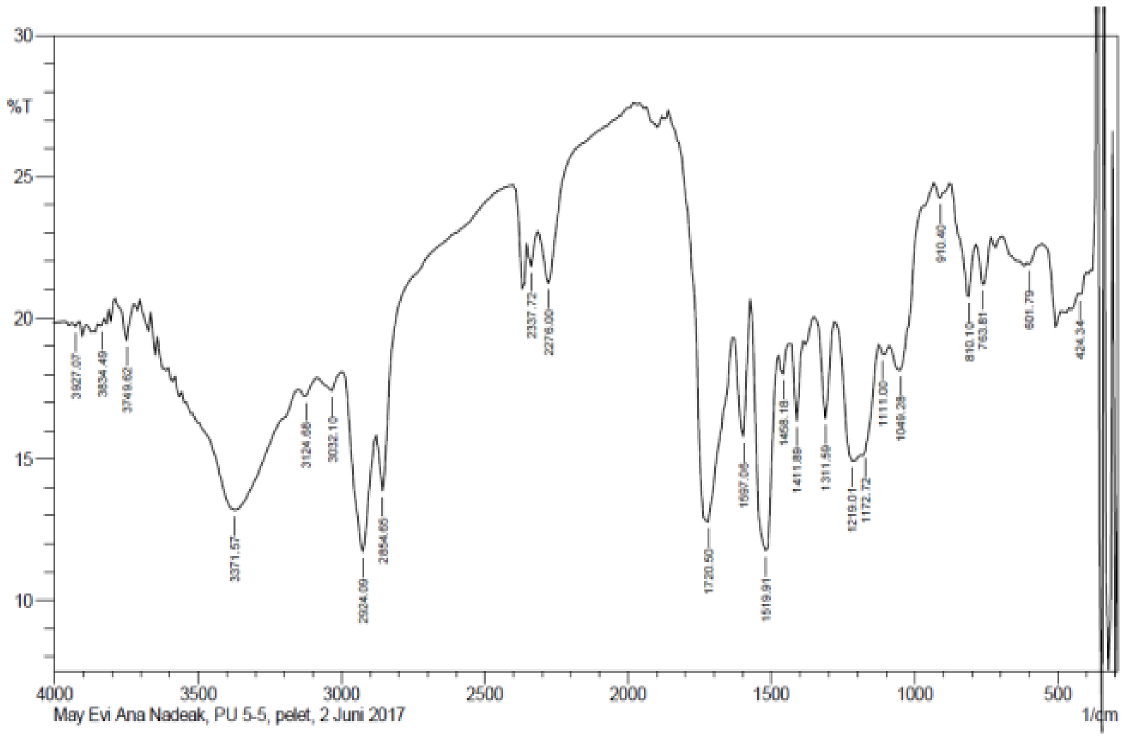

Figure 3.5 (e) FT-IR spectrum of polyol:MDI = 5:5 (v/v) polymerized polyurethane

FT-IR spectrum analysis of every ratio normally shows a similarity, which in this case is the formation of urethane functional groups depicted in 3100-3500 cm^{-1} wavelength (N-H stretching), 1700-1750 cm^{-1} (stretching) and 1000-1300 cm^{-1} (stretching C-O-C) as shown in Table 3.3. However, in 9:1 and 8:2 ratios, there is a non-reactive hydroxyl group at 3600-3650 cm^{-1}. This is caused by the number of polyol used has more hydroxyl groups than the available isocyanate group. Mixing ratio between polyol and MDI for 4:6 to 1:9 ratios were not done. With excess MDI, isocyanate that is yet reacted will react with -OH group from H_2O in air. Furthermore, isocyanate is relatively higher in price.

Table 3.3. Table of functional groups wavelength for polyurethane with various ratios

Wavelength (cm^{-1})	Polyol:MDI				
	5:5	6:4	7:3	8:2	9:1
Stretching N-H	3371	3356	3348	33348	3361
Bending N-H	1516	1535	1527	1527	1527
Stretching C-Hsp^3	2854-2924	2854-2924	2854	2854-2924	2854-2924
Bending C-Hsp^3	1411-1458	1365	1381-1458	1411-1458	1411-1458
Vibration N=C=O	2276	2276	2337	2276	2279
Vibration C=O	1720	1712	1728	1728	1728
Vibration C=C	1597	1612	1597	1597	1604
Vibration C=O=C	1172	1165	1172	1180	1172
Vibration $(CH_2)n$	763	725	722	722	725

4. Conclusion

Based on the research done, it can be concluded as follow: avocado oil obtained from rotten avocado fruits can be epoxidized with performic acid and sulfuric acid as catalyst followed by hydrolysis reaction to produce polyol compound. Next, polyol is reacted with MDI to produce polyurethane. Polymerization of avocado oil polyol with diphenylmethane 4,4'-diisocyanate (MDI) produces polyurethane in which with a different ratios of mixture between polyol and MDI = 9:1, 8:2, 7:3, 6:4 and 5:5 gave different gel content. The highest gel content, 99.8%, and density, 0.722 gr/cm^3 is found in the ratio of 5:5 (v/v) polyol : MDI respectively.

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