

PALM OIL-BASED POLYOL FOR COATINGS

SITI IRHITH BUSHRAH BINTI NOOR MAHADI

**BACHELOR OF CHEMICAL ENGINEERING
UNIVERSITI MALAYSIA PAHANG**

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PALM OIL - BASED POLYOL FOR COATINGS

SITI IRHITH BUSHRAH BINTI NOOR MAHADI

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

**Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG**

JANUARY 2014

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SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

Signature :
Name of main supervisor : TUAN HAJI MOHD NOOR BIN NAWI
Position : SENIOR LECTURER
Date : JANUARY 2015

STUDENT'S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

Signature :
Name : SITI IRHITH BUSHRAH BINTI NOOR MAHADI
ID Number : KA11086
Date : JANUARY 2015

Dedication

Special dedication for my beloved parent and my family in overall, my supervisor, my friends, all of UMP laboratory staffs, FKKSA staffs and also my seniors for motivation, care, support, cooperation and trust in me for fulfilling this thesis.

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ABSTRACT

Polyols are widely used in the formulations for polyurethanes. Nowadays, the recent thread of oil price increase has lead government to create the new ideas for polyol production instead of using petroleum. Palm oil (PO) based polyol is an alternative material that may possibly replace petrochemical-based polyol for polyurethane coating material. Polyurethane was synthesized by reacting palm oil-based polyol with isocyanate. The parameters that have been focused throughout this experiment were mol ratio of palm difference weight ratio of hydrogen peroxide for crude palm oil (CPO) to Acetic Acid to H_2O_2 during epoxidation process, reaction time in opening ring and the ratio polyol to isocyanate for coating process. The experiment works has been done at UMP's basic engineering laboratory. In this study, PO was first epoxidized to form epoxidation of palm oil (EPO). The process has been carried out with 4 samples at difference weight ratio of hydrogen peroxide (H_2O_2) for CPO to Acetic Acid to H_2O_2 which are 1:5:1, 1:5:2, 1:5:4 and 1:5:6. The presence of oxirane ring of EPO was characterized by Fourier Transform Infrared Spectroscopy (FTIR) and the iodine value of EPO was characterized by Potentiometric Titrator. Then, EPO was converted to palm oil-based polyol by the opening ring reaction with ethyl glycol. The process was carried with difference set of reaction time which is 20 minutes, 40 minutes and 60 minutes respectively. The present of hydroxyl group in polyol was characterized by FTIR and acid value was determined by using Potentiometric Titrator. Palm oil-based polyol was mixed with isocyanate to produce polyurethane coating at different ratio polyol to isocyanate were 1:1, 1:2 and 1:3. Scanning Electron Microscopy (SEM) is used in order to analyze the surface structure of coating that form. The results shown that lower iodine value (0.85 I_2 g/100g) was obtained by using mol ratio of 1:5:4. At 60 minutes reaction of opening ring showed the present of hydroxyl group at peak 3481 cm^{-1} and the acid value of polyol that obtain at this condition was 3.86 mg KOH. Based on SEM image, by using the ratio polyol to isocyanate of 1:3 shows the effect of isocyanate on the bubble size and indicate that the bubble size increase with the increase with isocyanate content. Based on study, palm oil was able to produce palm oil-based polyol with the low iodine value, low acid value and low functional group which is suitable to be used in coating applications.

ABSTRAK

Polyols digunakan secara meluas dalam rumusan untuk poliuretana. Pada masa kini, kenaikan harga minyak telah menyebabkan kerajaan untuk mewujudkan idea baru untuk pengeluaran polyol selain daripada petroleum. Polyol berasaskan minyak sawit merupakan bahan alternatif yang boleh menggantikan polyol berasaskan petrokimia untuk bahan salutan poliuretana. Poliuretana telah disintesis oleh reaksi polyol berasaskan minyak sawit dengan isosianat. Parameter yang diberi tumpuan sepanjang eksperimen ini ialah nisbah mol nisbah berat perbezaan sawit hidrogen peroksida untuk minyak sawit mentah (MSM) kepada Asid asetik untuk H_2O_2 semasa epoxidation proses, masa tindak balas di gelanggang pembukaan dan polyol nisbah untuk isosianat untuk proses salutan. Eksperimen telah dilakukan di makmal kejuruteraan asas UMP. Dalam kajian ini, dimulakan dengan epoxidized proses untuk membentuk epoxidation minyak sawit (EPO). Proses ini telah dijalankan dengan 4 sampel pada nisbah berat perbezaan hidrogen peroksida untuk MSM kepada Asid asetik untuk H_2O_2 yang 1:5:1, 1:5: 2,1:5: 4 dan 1:5:6. Pembentukan cincin oxirane daripada EPO dicirikan oleh Fourier Transform Infrared Spektroskopi(FTIR) dan nilai iodin EPO dicirikan oleh potentiometrik Titrator. Kemudian, EPO telah ditukar polyol berdasarkan minyak sawit oleh cincin reaksi pembukaan dengan etil glikol. Proses ini telah dijalankan dengan perbezaan masa tindak balas iaitu 20, 40 dan 60 minit. Semasa kumpulan hidroksil dalam polyol dicirikan oleh FTIR dan nilai asid telah ditentukan dengan menggunakan potentiometrik Titrator. Polyol berasaskan minyak sawit bercampur dengan isosianat untuk menghasilkan salutan poliuretana pada nisbah polyol berbeza untuk isosianat ialah 1:1,1:2 dan 1:3. Imbasan Elektron Mikroskopi(SEM) digunakan untuk menganalisis struktur permukaan lapisan terbentuk. Keputusan menunjukkan bahawa nilai iodin yang lebih rendah ($0.85 I_2 \text{ g} / 100\text{g}$) telah diperolehi dengan menggunakan nisbah mol 1:5:4. Pada minit ke 60, reaksi pembukaan cincin menunjukkan kumpulan hidroksil terbentuk pada puncak 3481 cm^{-1} dan nilai asid polyol adalah 3.86 mg KOH . Berdasarkan imej SEM, dengan menggunakan polyol nisbah untuk isosianat 1:3 menunjukkan kesan isosianat kepada saiz gelembung. Ia menunjukkan bahawa saiz gelembung bertambah dengan penambahan kandungan isosianat. Berdasarkan kajian, minyak kelapa mampu menghasilkan polyol berasaskan minyak sawit dengan nilai rendah iodin, nilai asid yang rendah dan kumpulan berfungsi yang rendah adalah sesuai digunakan dalam aplikasi salutan.

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LIST OF ABBREVIATIONS

<i>a</i>	isocyanate mass
<i>b</i>	polyol mass
<i>x</i>	% NCO in isocyanate
<i>y</i>	% OH in polyol

CPKO	Crude Palm Kernel Oil
CPO	Crude Palm Oil
EPO	Epoxidation Palm Oil
FTIR	Fourier Transform Infrared Spectroscopy
GPC	Gel permeation chromatography
H ₂ O ₂	Hydrogen Peroxide
IV	Iodine number
MPOB	Malaysia Palm Oil Board
MSM	Minyak Sawit Mentah
PO	Palm oil
SEM	Scanning Electron Microscopy
TGs	Triacylglycerol

CHAPTER 1

INTRODUCTION

Polyol is an alcohol with more than two reactive hydroxyl groups. Moreover, polyol also traditionally produced from petroleum. However, production of polyols from petrochemical are costly, non-biodegradable, required more energy and non-environmental friendly (Noor *et al.*, 2013). Polyol is used commonly in food industry and polymer chemistry. Examples of polymeric polyols are polyethylene glycol, polypropylene glycol and many more. These polyols are widely used in formulations for polyurethanes. Example products of polyurethane are thermal insulation, medical implant and many more.

Vegetable oil is an alternative raw material that can be used as raw material of polyol such as soy oil, palm oil, jatropha oil and so on (Sugita *et al.*, 2012). Production of polyol from vegetable oil has more advantage compared with polyol from petrochemical. According to Kiran K.Y. (2005), petroleum is a non-renewable resource and expensive has encouraged researchers to develop new alternatives to petroleum based products from biomass.

In chapter 1, we will discuss about the background of the research which are included raw materials, process and the product that will be produced in this research. In this chapter, we will include the identification of problems, research objectives, research scopes and rational and significance of the study.

1.1 Research Background

Polyurethane is reaction between polyol and isocyanate. Moreover, polyurethane also one of the polymer products. Example of polyurethane products is coated, adhesives, foam and many more. Based on research by Sugita *et al.* (2012), world consumption of polyurethane increases every year and an average of 5.1% increase until 2005. Polyol is almost important raw material for making polyurethane. Polyol for polyurethane manufacturing are generally derived from petrochemicals (Tanaka *et al.*, 2008).

Nowadays, the recent trend of oil price increase has lead government to find alternative raw material for polyol production. Palm oil is an alternative raw material that may be used to produce polyols. In Malaysia, Malaysian Palm Oil Board (MPOB) collaborates with Klauditz-Wilhelm-Institute (WKI), Germany has been intensively researched for palm oil-based polyol (Sugita *et al.*, 2012). Figure 1 shows the oil palm tree



Figure 1 The oil palm tree

Oil palm tree consists of three main parts which are trunks, fruit bunches and fronds. The oil palm produced two types of oils. Two types of oils are palm oil from the fibrous mesocarp and lauric oil from palm kernel. According to Teoh C.H. (2002), in the conventional process, fresh fruit bunches are sterilized and stripped of the fruitlets. After that, fresh fruit bunches are digested and pressed at certain pressure to extract oil from fruit bunches called crude palm oil (CPO). Figure 2 shows fresh fruit bunches.



Figure 2 Fresh fruit bunches

To produce palm oil-based polyol, palm oil is first epoxidized to get epoxidation of palm oil (EPO), followed by opening ring with alcohol. The synthesis route is outlined in Figure 3.

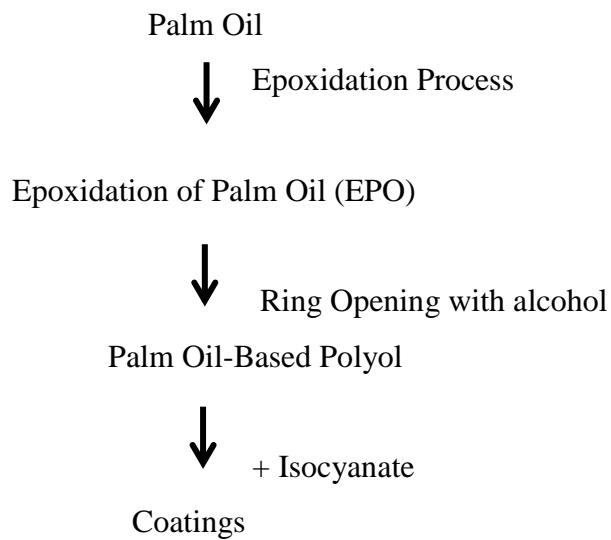


Figure 3 The Synthesis Route of Coating Process from Palm Oil

Epoxidation of palm oil is done by introducing palm oil through an oxidation process. The epoxidation process is a chemical reaction of converting carbon-carbon double bond to epoxide functional group in vegetable oil, which is a cyclic ether with three ring atom. It is a very import process nowadays because epoxides obtained from vegetable oil can be used as high temperature of raw materials for alcohol or glycols. Research by Carson and Chang (1985), epoxides with higher oxirane values and iodine value are considered to be in better quality.

Then, epoxidation of palm oil (EPO) is introduced to the opening ring process. Research by Hazimah *et al.* (2005), epoxidation of palm oil is reacts with alcohol to produce palm oil based polyol. Examples of alcohol that usually use to react with EPO are glycerol and ethylene glycol.

For the coating Polyurethane, research by Yuan-Chan T.,(2008) , polyurethanes are polymers formed by the reaction of alcohol with two or more reactive hydroxyl functional groups per molecule and isocyanates that have more than one reactive isocyanate group per molecule which is a diisocyanate or polyisocyanate.

1.2 Motivation and Problem Statements

Polyol are currently produced from petroleum. Moreover, the production of polyol from petroleum is expensive due to the trend of oil price increase. According to Kiran K. Y.(2005), the uses of polyol in the USA is approximately 3 billion pounds/year, and worldwide uses of polyol is approximately 10.2 billion pounds/year. Petroleum is non-renewable resources. The lack of petroleum resources and the increase the petroleum price which at a point hit USD 150 per barrel in 2008. Petroleum uses based on monomers in the manufacture of polymers is expected to decline in the coming years because of increasing prices and the high rate of depletion of the stock.

Furthermore, polyol from petroleum is non-environmental friendly. Based on research by Kiran K. Y. (2005), producing 0.45 kg of petroleum based on polyol add 1.6 kg of carbon dioxide to the environment. Then, it was found that polyol from petroleum had potential to higher greenhouse gas emission (Richard and David, 2009). Polyol from petroleum not biodegradable compound. This compound does not have fatty acid and will not support any bacteria. So, it cannot be biodegradable.

1.3 Objective of Research

The objectives of this research are:

- 1.3.1 To utilize palm oil as an alternative source to produce polyol
- 1.3.2 To determine the optimum weight ratio for hydrogen peroxide in epoxidation process
- 1.3.3 To study the effect of reaction time of ethylene glycol in epoxidation of Palm Oil
- 1.3.4 To investigate the effect of isocyanate on polyol for coating

1.4 Scope of Research

In order to achieve the objective, the following scopes have been identified and to be applied:

- 1.4.1 The effect of hydrogen peroxide in epoxidation process
- 1.4.2 The effect of ethylene glycol in polyol synthesis
- 1.4.3 The effect of isocyanate in coating process

1.5 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

In Chapter two divide into three parts which is raw material, process production and product. The raw material that used in this research was palm oil. Process production that included in this research ware epoxidation and opening ring process. The product for this research were polyol and polyurethane. Moreover, the related process descibtion , principle and application of the parts were included in this chapter.

Chapter three explains the material and methodology used to achieve the research objectives .It starts with the epoxidation of palm oil (EPO). Then, the synthesis of EPO to polyol by opening ring reaction. The last method was preparation of polyurethane coating. The characterization of the sample was done after finish one process.

In chapter four, results of the present work are presented and discussed. The optimised parameters are compared with the parameters reported in the literature. The experimental results include the wave numbers of EPO and palm oil-based polyol, iodine value of EPO, acid number of palm oil-based polyol and morphology of polyurethane coating were discussed based on the reaction theory and literature.

Conclusions of the present work and relevant recommendations for future work are given in chapter five.

CHAPTER 2

LITERATURE RIVIEW

In this chapter, the finding of related articles from MPOB website and I-portal is needed in order to do a literature review. The literature review is research done in the past by other people and it is needed to support our research objectives.

2.1 History, Habitat, Tree and Industrial Development of Oil Palm

The oil palm or *Elaeis guineensis* Jac is a tropical palm tree. The oil palm tree is a tropical palm tree under the family of palm originally come from Guinea; West Africa (Yusof, 2000) is originally illustrated by Nicholas Jacquin in the year of 1763. Oil palm was introduced to Malaysia in 1910 by Scotsman William Sime. Sime Darby and Boustead who are the first plantations British plantation owner were established and operated in Malaysia.

Furthermore, the most suitable culture for oil palm is soil must be free from draining with low pH, but does not thrive at very high pH, which is greater than 7.5. Oil palm culture is done in low altitude less than 500m above sea level with 15 ° from the equator in the humid tropics. The soil is properly drained with evenly distributed rainfall of 1,800 to 2,000 mm/year, but will tolerate rainfall up to 5,000 mm/year. If there are more than three consecutive months with less than 100 mm rainfall per month, potential yield will be reduced and oil palm is sensitive to poor drainage and drought.

Oil palm tree consists of three main which are trunks, fruit bunches and fronds. The height of oil palm tree usually with an unbranched tree from 20 m to 30 m and its trunk is formed over 3 years old when the apex has reached its full diameter the form of an inverted cone after intermodal elongation take place. The weight of bunches of fruit is about 10 kg to 25 kg and sometime might be up to 50 kg. Moreover, the most suitable time to harvest ripe fruits is 5 to 6 months after flowering. A bunch of fruit can produce 500 until 4000 number of fruit. The fruit is reddish with ovoid type shaped, have 2 cm to 5 cm measurement of length and weight scale from 3 g to 30 g. Each of the fruit

contains a single seed surrounded by a soft oily pulp. The palm oil produces two types of main vegetable oil. The examples of vegetable oil or palm oil extracted from the mesocarp of the fruit and palm kernel oil extracted from the seed.

Oil palm tree was first introduced to Malaysia in year 1870. According to Official Palm Oil Information Source, 1.5 million hectares were planted with oil palm tree and the amount of palm oil plant in Malaysia had increased to 4.3 million hectares in year 2007. The total planted area with oil palm tree in Malaysia was 4.917 million hectares until year 2011. Figure 4 shows the planted area of oil palm tree in Malaysia from year 1975 until year 2011. Furthermore, Malaysia now is the second larger producer of palm oil in the world after Indonesia in year 2006.

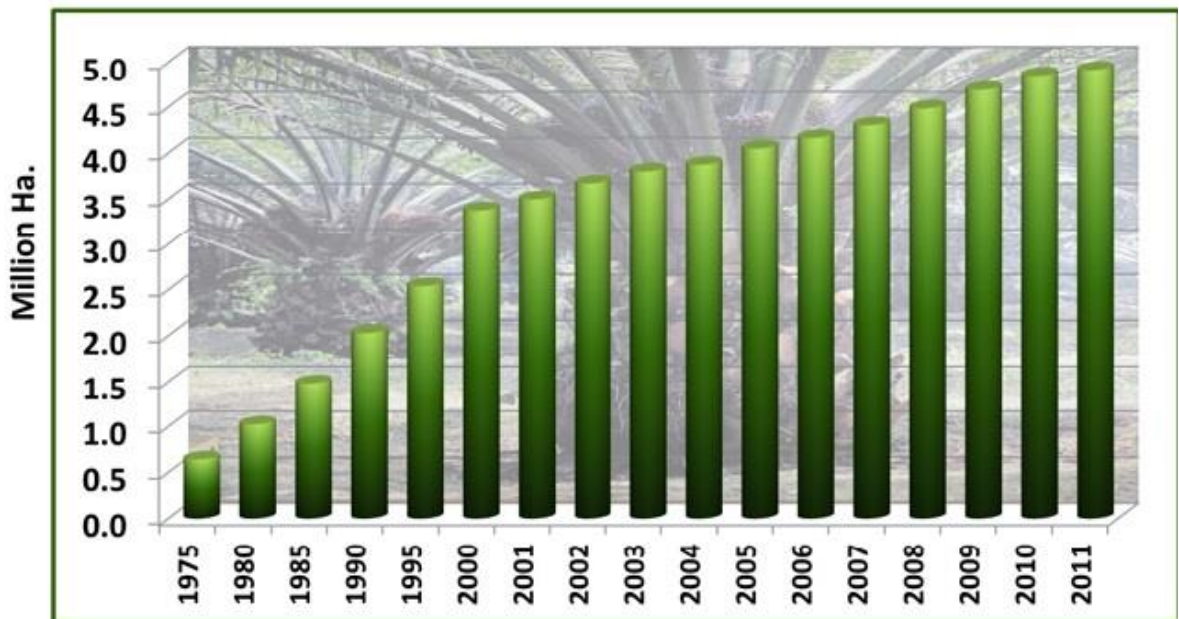


Figure 4 The Planted Area of Oil Palm Tree in Malaysia from year 1975 until year 2011

2.2 Palm Oil

2.2.1 Characteristic of Palm Oil

There are two types of oil, which is palm oil from fibrous mesocarp and lauric oil from palm kernel. Fresh fruit bunches are sterilized and stripped of the fruits. After that, it will digest and pressed to extract the crude palm oil (CPO). The nuts are separated from fibre to obtain crude palm kernel oil (CPKO). Palm kernel cake is the byproduct of fresh fruit bunches.

Then, fractionation of CPO and CPKO in the refinery produces the liquid stearin fraction and solid stearin component. Palm oil has a balanced ratio of saturated and unsaturated fatty acids. Moreover, palm kernel oil has mainly saturated fatty acid, which is similar to the composition of coconut oil. According to Salmiah A. (2000), palm oil has a higher amount of saturated fatty acid, but it is more stable and less prone to oxidation at high temperature compare to soy oil. The composition of fatty acid is compared with coconut oil and soy oil in Table 1. These are shown in Table 1, table of fatty acid compositions of palm oil products, soy oil and coconut oil.

Table 1 Fatty acid compositions of palm oil products, soy oil and coconut oil

Fatty Acids	Weight Percentage						
	Palm Oil	Palm Olein	Palm Stearin	Palm Kernel Oil	Palm Kernel Olein	Coconut Oil	Soy Oil
C6:0				0.3	0.4	0.2	
C8:0				4.4	5.4	8.0	
C10:0				3.7	3.9	7.0	
C12:0	0.2	0.2	0.3	48.3	41.5	48.2	
C14:0	1.1	1.0	1.3	15.6	11.8	18.0	
C16:0	44.0	39.8	55.0	7.8	8.4	8.5	6.5
C18:0	4.5	4.4	5.1	2.0	2.4	2.3	4.2
C18:1	39.2	42.5	29.5	15.1	22.8	5.7	28.0
C18:2	10.1	11.2	7.4	2.y	3.3	2.1	52.6
Others	0.8	0.9	0.7	0.1	0.1		8.0
Iodine Value	53.3	58.4	35.5	17.8	25.5	9.5	133.0

Source :Salmiah Ahmad,2000

2.2.2 Chemical Composition of Palm Oil

The major constituents of palm oil are triacylglycerols (TGs). Over 95% of palm oil consists of TGs which is glycerol molecules and each of it contain esterified with three fatty acid components. Research by Kalyana S.P.(2002), during the oil extraction the hydrophobic of TGS attract to other fat or oil soluble cellular components. Furthermore, there is the minor component in palm oil, which are phosphatides, sterols, pigments and many more. Moreover, in palm oil also have metabolites components that act in biosynthesis of TGs and products from lipolytic activities. Example of metabolites component are monoglycerols (MGs) , diglycerols (DGs) and last but not least free fatty acid (FFAs).

The fatty acids are any class of aliphatic acids that contain in animal, vegetable fats and oil. In palm oil, the major of fatty acid are myristic (14:0), palmitic, stearic, oleic and linoleic (18:2). Table 2 shows the typical fatty acid composition (%) of palm oil in Malaysia.

Table 2 Typical Fatty Acids Composition (%) of Palm Oil in Malaysia

Fatty acid chain length	Mean	Range observed	Standard deviation
12:0	0.3	0-1	0.12
14:0	1.1	0.9-1.5	0.08
16:0	43.5	39.2-45.8	0.95
16:1	0.2	0-0.4	0.05
18:0	4.3	3.7-5.1	0.18
18:1	39.8	37.4-44.1	0.94
18:2	10.2	8.7-12.5	0.56
18:3	0.3	0-0.6	0.07
20:0	0.2	0-0.4	0.16

Source :Kalyana Sundaram PHD,2002

Palm oil is used in edible and non-edible applications. Research by Kalyana S.P.(2002), almost ninety percent of the world palm oil production is used as edible purposes. The remaining ten percent of palm oil is used for non-edible applications such as in soap and oleo chemical industries. For use on edible and non-edible, palm oil is normally refined (Sarmizi *et al.*, 2009). In food industries refined palm oil is used as margarine, deep frying fat and specialty fats.

Moreover, palm oil and palm oil kernel are now used commercially in ice cream production to replace butterfat. This is because palm oil is more economical than other oils and also easily available. Furthermore, palm oil is more stable to oxidation than butterfat. Research by Malaysian Palm Oil Council, palm oil is an attractive ingredient in food industries because it contains a high proportion of higher melting triglycerides. For shortening manufacturing, palm oil combines with palm stearin and blend with liquid oils. In addition, the quantity of palm oil in shortening usually from thirty to forty percent. Palm shortenings are used widely in baking industry. Figure 5 shows the uses in food application of palm oil.



Figure 5 The Uses in Food Application of Palm Oil

The important future application of palm oil in food industry is the use of refined red palm oil in cooking (Sarmizi *et al.*, 2009). Refined red palm oil contains nutritious oil rich in vitamin E and β -carotene. The functions of β -carotene are antioxidant and inhibitor effect in colon cancer cell.

Then, for the non-edible uses of palm oil include the production of soap, polyols epoxidized palm oil, polyurethane, cosmetics, oleochemical and many more. According to Malaysian Palm Oil Council, production of soap is one of the most important applications of oils and fats. Coconut oil and tallow have been traditionally used in soap production. Nowadays, palm oil and palm kernel oil offer good and competitive alternatives respectively as raw material for soap making.

2.3 Epoxidation Process

2.3.1 Principle of Epoxidation Process

Epoxidation is a chemical reaction of converting carbon-carbon double bond to epoxide function group which consists of three member ring with two carbon atoms and one oxygen atom. According to Saurabh *et al.* (2011), double bonds in vegetable oils are used as reactive sites in coating and they also act as epoxidation. Moreover, epoxidation is widely known as a function of double bonds in vegetable oils as it introduces epoxy group or oxirane oxygen at located double bonds (Syafiq *et al.*, 2013). Figure 6 shows the epoxidized with carbon-carbon double bond being converted into oxirane ring.

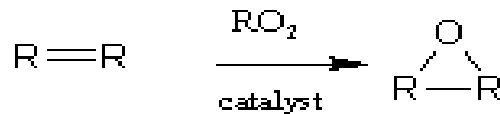


Figure 6 The Epoxidized with Carbon-Carbon Double Bond being converted into Oxirane Ring

Research by Saurabh *et al.* (2011), epoxidized oil contains the epoxide group or oxirane ring which consists of three elements in epoxide ring. There are a few established processes of epoxidation which are

- Epoxidation by conventional method
- Epoxidation using acid ion exchange resin
- Epoxidation using an enzyme

Epoxidation by Conventional method

This method is commonly used in the process of epoxidation. Epoxidation process are usually carried out by reacting a carboxylic acid with concentrated hydrogen peroxide or known as peroxides formed in-situ. Moreover, this process is currently used in large scale by industry.

Kinetics epoxidation of cottonseed oil was done using hydrogen peroxide catalyzed by liquid inorganic acids (Dinda *et al.*, 2008). They used formic acid as an oxygen carrier, but when they further their research they found that acetic acid is more effective oxygen carrier. Hydrogen peroxide act as oxygen donor and acetic acid acts as an oxygen carrier in the presence of catalytic in organic acid (Saurabh *et al.*,2011).Research by Dinda *et al.* (2008), sulphuric acid was found as the most efficient and effective catalyst out of all inorganic acid. Moreover, when the higher temperature and acid concentration it will reduce the reaction time needed to reach the maximum conversion of oxirane value. However, it will simultaneously increase the extent of oxirane ring cleavage to glycols (Patil and Waghmare, 2013).

Similarly, kinetics of in-situ epoxidation of soybean oil, sunflower oil and corn oil by using peroxyacetic acid with sulphuric acid as catalyst. Among all this, soybean has the greatest conversion rate and lower the activation energy for epoxidation by using peroxyacetic acid (Cai *et al.*, 2008).

Epoxidation using organic and inorganic peroxide are suitable for clean and efficient epoxidation for vegetable oil. Research by Campanella *et al.* (2004), epoxidation by using organic and inorganic peroxide can be rendered cleaner by using heterogeneous catalysts instead of using traditional homogeneous catalyst.

Epoxidation using Acid Ion Exchange Resin

Acid Ion Exchange Resin is an insoluble gel type catalyst and in the form of small yellowish organic polymer beads. The conversion of unsaturated fatty acids to oxirane ring using peroxide acid in the presence of ion exchange show the different conversion for difference vegetable oil Research by Petrovic *et al.* (2002), epoxidation of kinetics and side reaction of soybean oil in toluence with peroxyacetic acid and peroxy formic acid in the presence of an acid ion exchange act as catalyst. In addition, peroxyacetic acids are less efficient than peroxy formic acid.

Research by Dinda *et al.* (2008), kinetics epoxidation of cottonseed oil by using peroxyacetic acid generated in-situ from hydrogen peroxide and glacial acetic acid in the presence of Amberlite R-120. The conversion of oxirane is greater than sixty five percent with high selectivity could be obtained if the epoxidation is carried out at optimum conditions.

Epoxidation using an enzyme

Enzymes are biological catalysts which are to function under physiological conditions and catalyze a wide range of reactions. Research by Bhattacharya S.(2012), an enzyme acts by reducing the activation energy of a chemical reaction and it also providing an alternative route converted to product.

Enzyme catalyst is needed to avoid the side reactions and to make the process more environmentally friendly. The epoxidation reaction can be improved by adding lipase, however lipase under reaction condition is the low stability. Based on study by Vlcek and Petronic (2006), they find that the rate of reaction is affected by concentration of lipase biocatalyst on Optimazation of chemoenzymatic epoxidation of soybean oil.

2.4 Principle of Iodine Number

Iodine Value or IV is used to measure of the unsaturation of fats and oil in those particular oils (Haryati *et al.*, 1998). Moreover, it also can determine the amount of iodine that absorb by that oil. Fats and oils are a mixture of triglycerides, which is made up of three fatty acids that linked to glycerol by fatty acyl esters. Moreover, fatty acids contain long chain of hydrocarbon with carboxyl groups. Number of double bonds that contain in fatty acids can be classified into saturated or unsaturated oil. Furthermore, only a single bond between carbon atoms and tend to be solid at room temperature is known as saturated fatty acid while for unsaturated fatty acids, it contains double bonds between the carbon atom and it likely can be exists as a liquid at room temperature.

An unsaturation of fats and oil are mainly referred to amount of double bonds present in oils. Hence, the greater amount of double bonds in that oil will give a higher number of iodine value. There are many different methods to determine the number of iodine. For example, titration is used to determine the number of iodine in the palm oil industry. Another example is by using Wijs solution. Wijs solution or known as iodine monochloride solution is the solutions of iodine monobromide and iodine monochloride in glacial acetic acid will be added to the fatty acid as shown in Figure 7. (AOAC Official Method of Analysis, 1984)

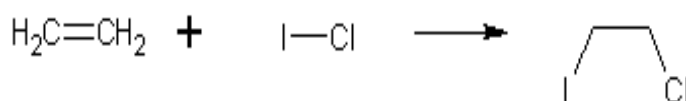


Figure 7 Double bond in fatty acid is reacted with iodine monochloride to produce di-halogenated single bond

2.5 Opening Ring Process

The ring-opening reaction was an acid catalyst process and did not require the use of solvent (Noor *et al.*, 2013). In the synthesis of natural products from triglycerides such as palm- based polyol reaction usually takes place at the double bond. Triglyceride oil is one of the most important sources for biopolymers production (Saremi *et al.*, 2012). Example of triglycerides from the plant is palm oil, soy oil sunflower and many more. Moreover, natural based polyols is done by opening reaction of epoxidised natural oils with alcohol, glycols or higher polyols, amines or alkanamines (Hofer *et al.*, 1997). Moreover, the ring -opening reaction was an acid catalysed process and it did not require solvent.

Research based on Petrović *et al.* (2000), the process converts natural oil into polyols by epoxidising oil with fluoboric as an acid catalyst then hydroxylate the epoxidised oil to polyol using more fluobic acid together with alcohol or mixture of alcohol and water. Hence, this process not ideal since fluobaric acids is expensive. Moreover, fluobaric acids are highly reactivity could be hazardous and reaction is highly exothermic. Furthermore, epoxidation of double bonds can be carried out under moderate reaction condition because the high reactivity of the oxirane rings (Salimon *et al.*, 2014). Acid catalyst also assists epoxide ring opening by providing a good an alcohol at carbon undergoing nucleophilic attack.

2.6 Polyol

The production of polyols is traditionally from petrochemicals which has required the large amount of energy, costly and could affect the environment (Noor *et al.*, 2013). The polyol can be obtained from palm oil. Research by Hazimah *et al.* (2005), the polyol is produced by reacting epoxidized palm oil with alcohols such as glycerol or ethylene glycol. Polyol used for the production of polyurethane foam containing at least two hydroxyl groups. Moreover, polyol may be polyethers, polyesters, polyolefins or vegetable oil based polyol (Lazada-Robríquez Z., 2009).

2.6.1 Polyol Properties

Polyol have their own characteristic. The important characteristics of polyols are molecular weight and last but not least, functionality to form polyurethane polymer. Polyol is an important raw material to form a coating by the reaction of polyol and isocyanate. Research by Yuan-Chan T. (2008), the functionality of polyols is the average number of functional groups reacting to isocyanate per molecule of polyols and for the equivalent weight of polyols can be defined as follows:

$$\text{Equivalent weight} = \frac{\text{Molecular weight of polyol}}{\text{Functionality of polyols}} = \frac{56100}{\text{Hydroxyl number}}$$

The hydroxyl number (mg KOH/g) is milligrams of potassium hydroxide equivalent to the hydroxyl groups found in one gram of polyols (Herrington and Hock, 1997). The typical properties of polyol and application of polyurethane polymer are shown in Table 3.

Table 3 The typical properties of polyol and application of polyurethane polymer

Applications	Functionality of polyols	Equivalent weight of polyols
Flexible Foams	2.5-3.0	500-3000
Semi-Rigid Foams	3.0-3.5	70-2000
Rigid Foams	3.0-8.0	70-800
Elastomers & Coatings	2.0	70-2000

Source : Yuan-Chan T.,2008

2.6.2 Petroleum-based Polyols

Polyurethane synthesis reaction traditionally uses the petroleum-based polyol as their B-side material. Moreover, there are two major of polyols consumed in global market demand of polyol which are polyether polyols and polyester polyols (Yuan- Chan T., 2008). Based on research Szycher M. (1999), in United State were nearly 90% of four billion pounds of polyurethanes consumed such as 9% on polyesters and 1% on other specialty polyols based on year 1994. Furthermore, in order to form polyether polyols, the initiator such as ethylene glycol, propylene glycol, and glycerin reacts with alkylene oxide to produce polyether polyols with the primary hydroxyl group. Figure 8 shows the chemical structure of common polyester polyol.

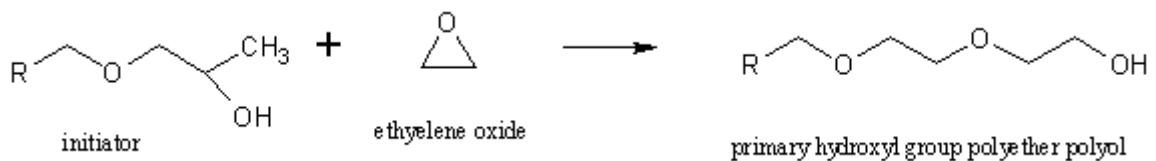


Figure 8 The chemical structure of common polyester polyol

2.6.3 Vegetable-based Polyols

Natural oil polyol also known as biopolyol and polyol derived from vegetable oil by using several different process (Lazada-Robríquez Z., 2009). Moreover, natural oil are water insoluble, hydrophobic substances of vegetable and usually consist predominantly of triglycerides. Research by Colvin B.G. (1995), triglyceride is the reaction product of one molecule of glycerol with three molecules of fatty acids to yield three molecules of water and one molecule of a triglyceride. The main uses of vegetable-based polyol is in production of polyurethane.

In addition, there are a limited number of naturally occurring of triglycerides, which is contained unrest hydroxyl groups that use for reactivity of these polyols. Based on Gua A.(2004), describes a method of making natural oil-based polyols containing of reacting the epoxidized natural oil with a hydroxyl moiety of an alcohol in the presence of ten percent to thirty percent of water.

Based on Nicolas *et al.* (2003), a process for obtaining oleochemical polyols from natural oils and fat by using planar Lewis acid in alcoholysis process. In this process, it required the large amount of energy which is normally higher than 200°C. Then, their predicted that yield production of desired products was to be very low because most of substrates were converted to side products due to extreme conditions used.

2.6.4 Application of Polyol in Industries

There are many polyol in industries such as polyurethane. Polyurethane is one of the polymer products made by reacting polyol with an isocyanate. The polyurethane product can be rigid, flexible and suitable for industrial sectors like building, furniture, automotive parts, foam, paint and many more. According to IAL Consultant Firm (2001), the highest demand from the four types of application is for coating material (paints) with 44 %. In Indonesia, the need for polyurethane from 1989 to 1995 also increases approximately 37% from 1160 tons to 6159 tons and approved by Biro Pusat Statistik (1998). According to MPOB (2006), MPOB has produced products such as sandwiched board for wall panel, dry floral foam, flexible soft for furniture and others. Research on Mannari *et al.* (2003), vegetable oil –based polyol is used for coating application. Furthermore, vegetable oil- based polyol has more benefit such as suitable for various types of surface, cheap, renewable and also can be applied to water-based coating and high solid concentration. Moreover, the application of polyol is commonly used for personal care such as cosmetics and toiletries industries. Example of personal care products are toothpaste, chewing gums, candies, lotion, make-up and other. Some of polyols are acknowledged as an ideal base for toothpaste. Moreover, there are specific properties of certain grades of polyol enable for the production of clear gels.

2.7 Coating

2.7.1 Coating Process

Polyurethane coating is the reaction of polyol with isocyanate. Research by Yuan-Chan T. (2008), polyurethanes are polymers formed by the reaction of alcohol with two or more reactive hydroxyl functional groups per molecule and isocyanates that have more than one reactive isocyanate group per molecule which is a diisocyanate or polyisocyanate. 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 application.

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. According to Ionescu M. (2005), the hydroxyl number is defined as the number of hydroxyl groups which can react with isocyanates. Percentage hydroxyl (OH %) can also be used to indicate the number of hydroxyl groups in the polyol. Converting hydroxyl numbers to percentage 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:

$$b = 0.40476 \frac{ax}{y}$$

With:

a = isocyanate mass, x = % NCO in isocyanate

b = polyol mass, y = % OH in polyol

2.7.2 Application of Coating in Industries

A coating is a covering that is applied to the surface of an object, usually referred to as the substrate. The purpose of applying the coating may be decorative, functional, or both. The coating itself may be an all-over coating, completely covering the substrate, or it may only cover part of the substrate. An example of all of these types of coating is a product label on many drinks bottles- one side has an all-over functional coating and the other side has one or more decorative coatings in an appropriate pattern to form the words and images. Research from IAL Consultant, the highest demand from the four types of application is for coating materials which is 44%. Figure 9 shows the application of polyurethane coating. In Indonesia, the needs for polyurethane from 1989 to 1995 also rose approximately 37% from 1160 tons to 6159 tons. Research by Hoong *et al.* (2005), there are two types of coating have been developed where one was suitable for indoor, while the other suitable for outdoor especially in temperate countries.

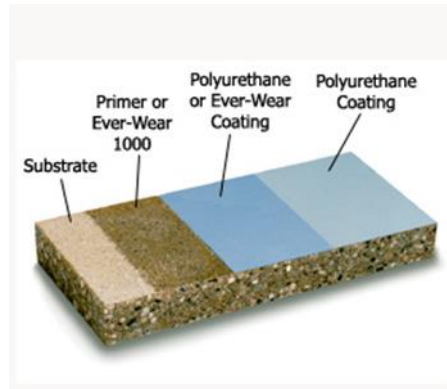


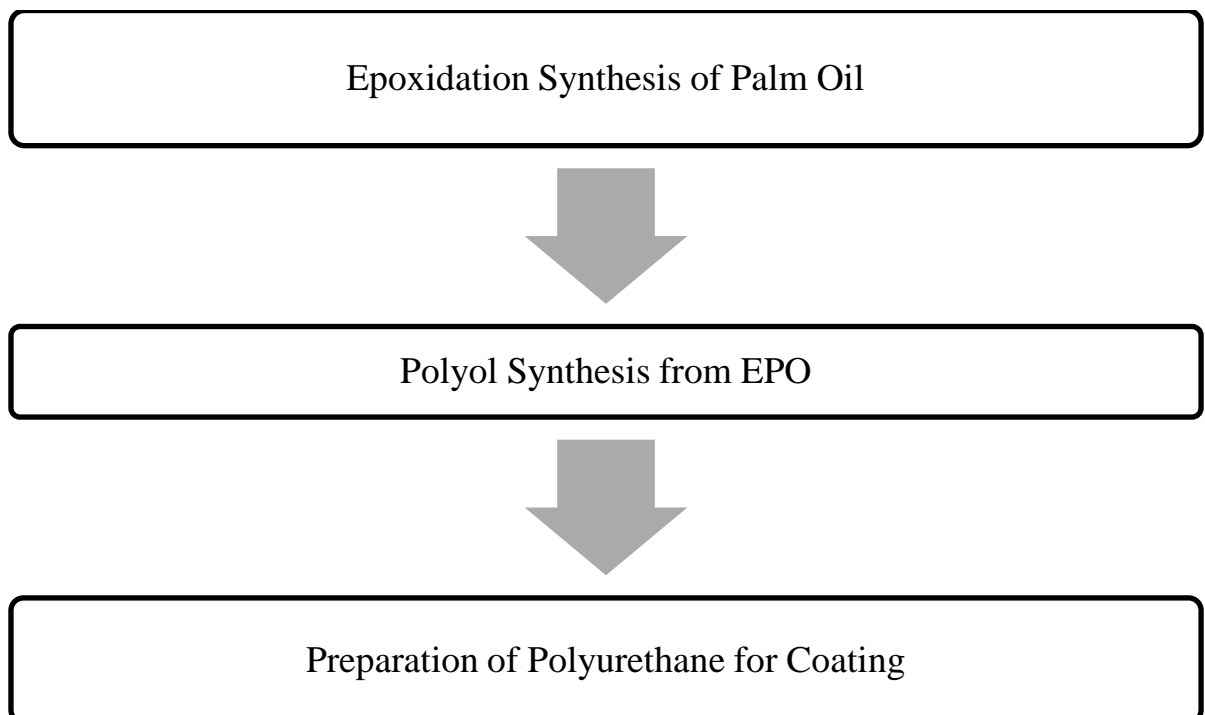
Figure 9 Application of Polyurethane Coating

CHAPTER 3

MATERIALS AND METHODS

In this chapter, we are discussing more detail about the method to conduct this research on production of palm-based polyol from palm oil. The procedures include in this research are the epoxidation synthesis of palm oil (EPO), polyol synthesis from EPO and preparation of polyurethane. There are also including the analytical method in which the method to determine the characteristics of epoxidized palm oil (EPO) that used as a substrate to produce the polyol.

3.1 *Experimental Steps*



Palm oil, which is crude palm oil (CPO), was used as raw material in this experiment. The glacial acetic acid and hydrogen peroxide were purchased from MERCK. The epoxidation processes were carried out in three necked glass (250 ml) flask equipment with mechanical stirrer, thermometer and reflux condenser (Derawi and Salimon, 2010). 20 g of CPO was weighed and pour into three neck flask. After that, CPO was acidified with glacial acetic acid and then, hydrogen peroxide was slowly added drop wise for 3 hours. Research by Wang et al.(1997), a reagent that fast introduced will cause an excessive development of oxygen due to decomposition of hydrogen peroxide at high temperature and this not recommended during the experiment. After 3 hours, which is reaction finish, sample was taken out and thoroughly washed with sodium bicarbonate, distilled water, and sodium chloride to separate the organic layer from the mixture. The sample was then analyzed for and iodine value. Epoxidation was carried out at a certain ratio of hydrogen peroxide. Fourier Transform Infrared Spectroscopy (FTIR) and Wijs solution were used to analyze the sample.

After the palm oil was epoxidized, ethyl glycol between 2 to 30% by weight of EPO can be added to create polyol. 20g of epoxidation of palm oil was measured and pour into the conical flask. Then, 2 g of ethyl glycol was added into the mixture. The reaction temperature was raised to 85°C and maintained for one hour. After the reaction was completed, the wave number and acid number were tested.

A total of 20g of polyol produce from previous process was used to prepare polyurethane for coating. After measuring 20 g of polyol, polyol was poured into the beaker. Then, 5ml of toluene was poured and stirred for 10 min to mix homogeneously. Then, form the mixture obtained, 5mL was taken from each batch. After that, the mixture is put into three separate containers. In container 1 is added 1 ml of isocyanate. Then, for container 2, 2 ml of isocynate is added and last but not least container 3 is added 3 ml of isocyanate. The mixture was stirred at room temperature for 3 minutes (Sugita *et al.*, 2012). Then, the mixture is poured into a plastic container and left at room temperature 24 hour before testing for Scanning Electron Microscopy (SEM).

3.2 *Materials and Methods*

3.2.1 *Raw Material*

Palm oil, which is Crude Palm Oil, will be collected from palm plantation in Lepar, Pahang.

3.2.2 *Chemical*

- 3.2.2.1 Glacial acetic acid
- 3.2.2.2 Hydrogen peroxide 35%
- 3.2.2.3 Sodium hydrogen carbonate
- 3.2.2.4 Distilled water
- 3.2.2.5 Sodium chloride
- 3.2.2.6 Ethyl glycol
- 3.2.2.7 Toluene
- 3.2.2.8 Isocyanate
- 3.2.2.9 Chloroform
- 3.2.2.10 Wijs reagent
- 3.2.2.11 Potassium iodine
- 3.2.2.12 Sodium Thiosulfate

3.2.3 *Equipment*

- 3.2.3.1 Thermometer
- 3.2.3.2 Reflux tools
- 3.2.3.3 Rotary evaporator
- 3.2.3.4 Titration apparatus
- 3.2.3.5 Hot plate,
- 3.2.3.6 pH paper
- 3.2.3.7 Beaker
- 3.2.3.8 Spatula
- 3.2.3.9 FTIR
- 3.2.3.10 SEM
- 3.2.3.11 Heating mantle
- 3.2.3.12 Magnetic stirred

3.2.4 Epoxidation Synthesis of Palm Oil (EPO)

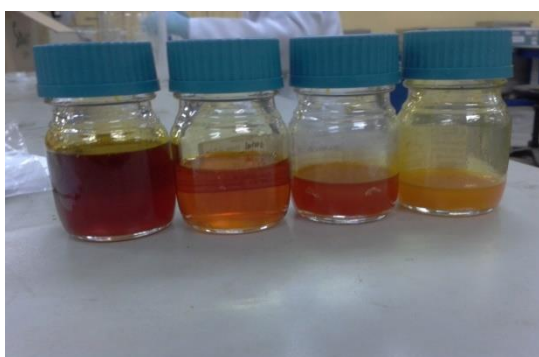
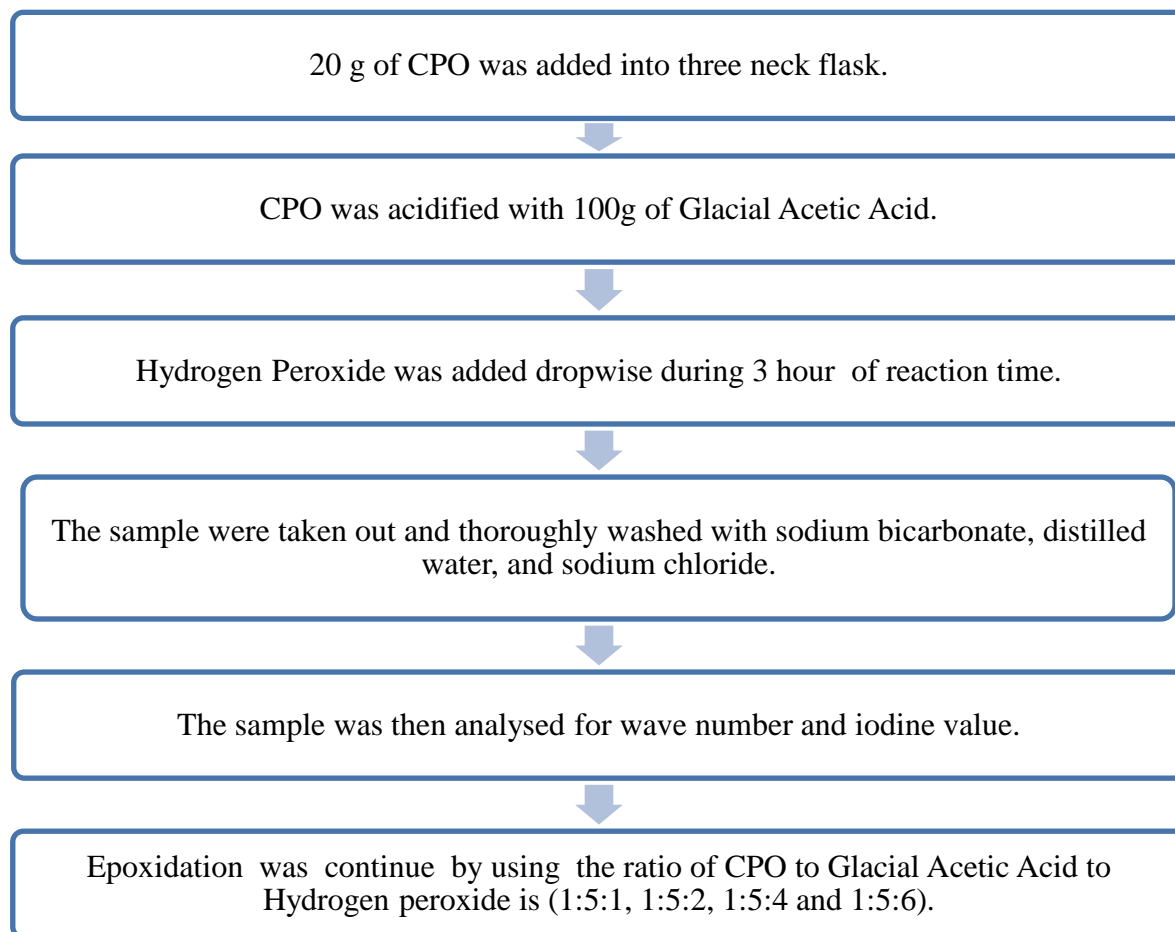


Figure 10 The sample epoxidation that produce by using difference of CPO to Glacial Acetic Acid to Hydrogen peroxide is (1:5:1, 1:5:2, 1:5:4 and 1:5:6).

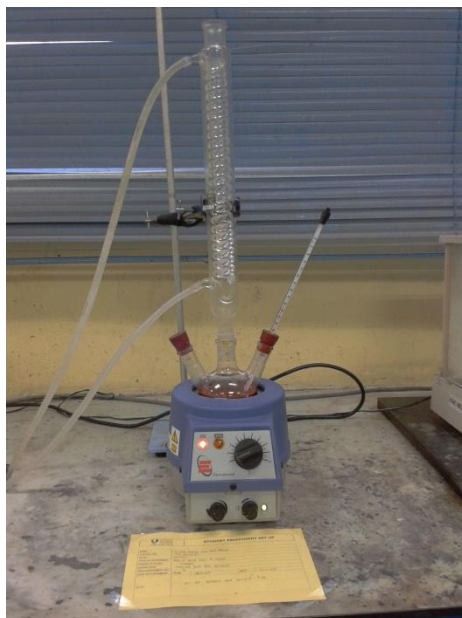


Figure 11 Epoxidation process by using reflux tools

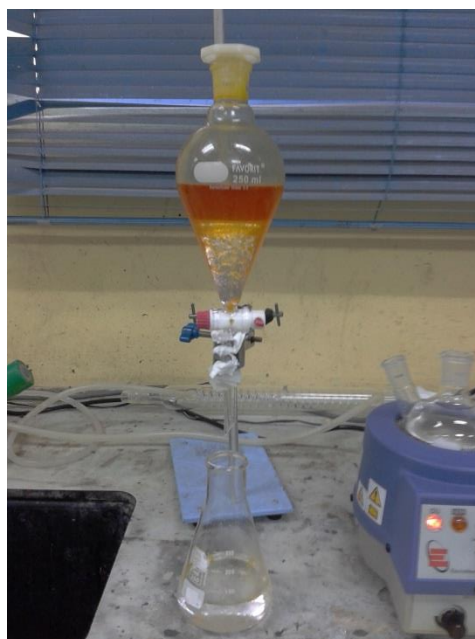


Figure 12 Separating funnel is used to separate the organic form from the mixture

3.2.5 Characterization of Epoxidation of Palm Oil (EPO)

The characterization of the epoxidation of palm oil by using Fourier Transform Infrared Spectroscopy (FTIR) to study the wavelength of epoxidation of palm oil and Wijs solution to determine the number of iodine in the unsaturated oil.

3.2.5.1 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy experiment will be performed by using Nicolet Omnic 3 Fourier Transform Infrared Spectroscopy. The function of FTIR is to identify the presence of certain functional group in a molecule. The test will be run by using SMART collector (Diffuse Reflector). The sample will be used in the liquid form. First, launch OMNIC on the desktop. After the background is completed, place the sample on the Ge plate. Drop of sample on the Ge plate by using a dropper. The reading for sample will be collected once the test is done. The graph will generate as there will be different levels of transmitted between various peaks for different sample. Figure 13 shows the picture of Nicolet Omnic 3 FTIR.



Figure 13 Nicolet Omnic 3 FTIR

3.2.5.2 *Wijs solution*

Several methods were well-established and recognized to be used to test a number of Iodine in the oil. The iodine value will test by using standard testing proposed in AOAC Official Method of Analysis (1984). Figure 14 below show the procedure of Wijs solution.

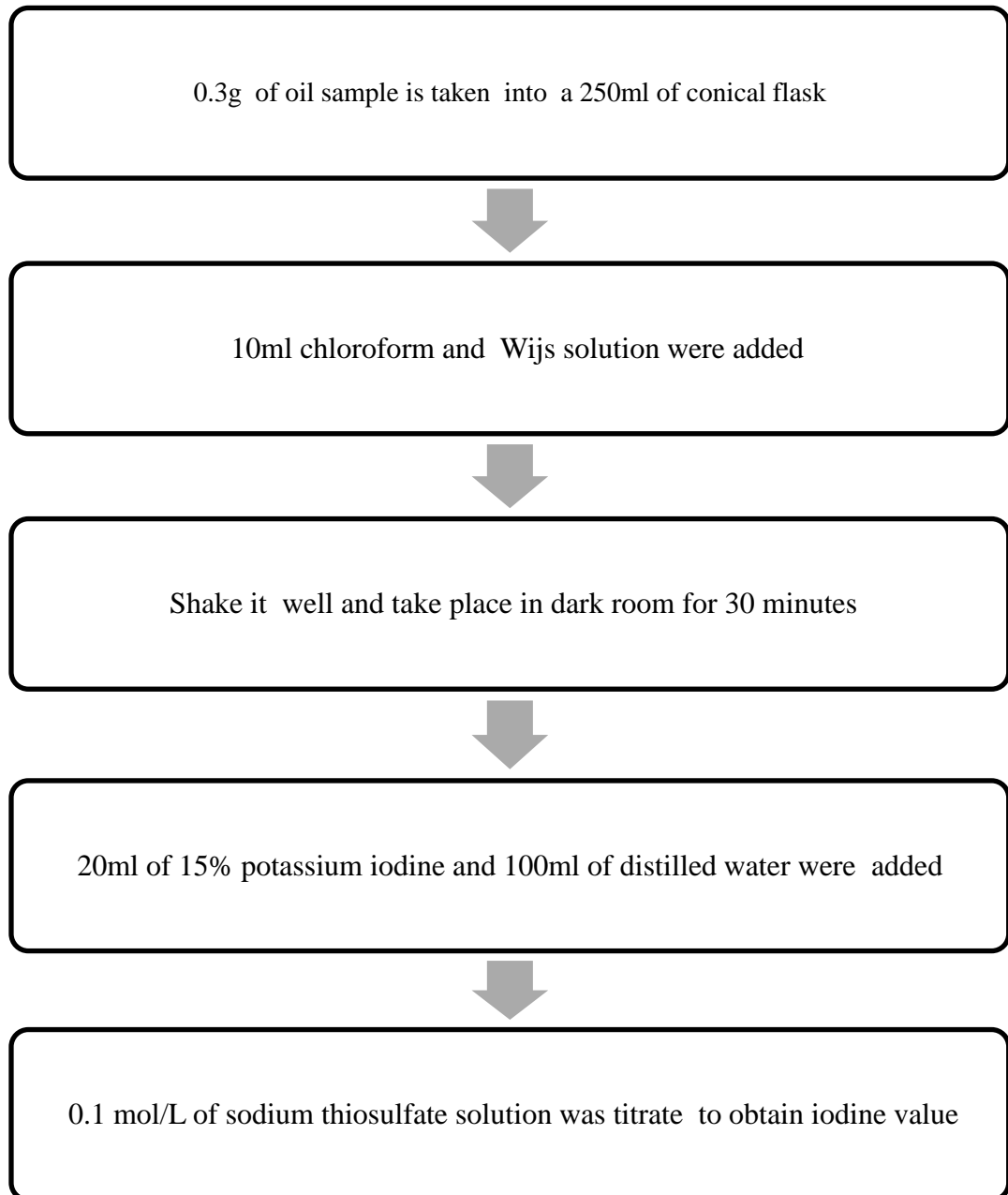


Figure 14 The procedure of Wijs solution

Moreover, number of iodine can be calculated by the following formula:

$$\text{IV} \left(\frac{\text{g}}{100\text{g}} \right) = (\text{Blank sample} - \text{Sample titration}) \times \text{Factor Titration} \\ \times \frac{1.269}{\text{Weight of sampel(g)}}$$

Where:

Blank Titration	= Volume of $\text{Na}_2\text{S}_2\text{O}_3$ titrated for blank
Sample Titration	= Volume of $\text{Na}_2\text{S}_2\text{O}_3$ titrated for sample
Factor Titration	= 1.003

3.2.6 Polyol Synthesis from Epoxidation of Palm Oil (EPO)

20g of epoxidation of palm oil was measured and pour into the conical flask

2 g of ethyl glycol was added into the mixture

The reaction temperature was raised to 85°C and maintained for one hour

After the reaction was completed, wave number and acid number were tseted.

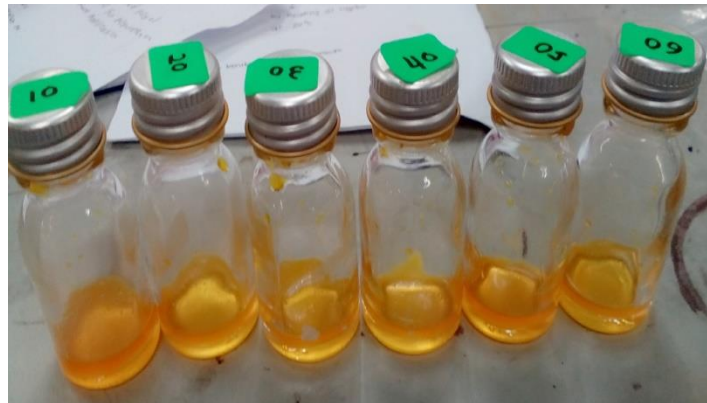


Figure 15 Sample of polyol taken every 10minutes



Figure 16 Process of synthesis EPO to polyol

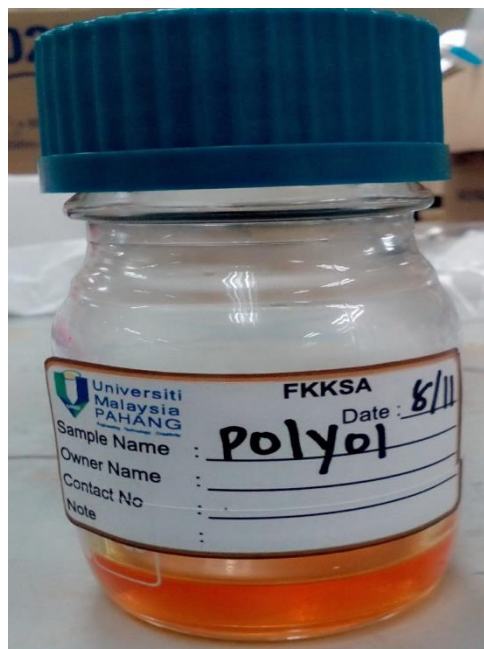


Figure 17 Polyol produce after 1 hour

3.2.7 Characterization of Palm Oil-based Polyol

There are two types of characterization of the palm oil-based polyol by using Fourier Transform Infrared Spectroscopy (FTIR) to study the wavelength of polyol and to determine acid number by using potentiometric titrator.

3.2.7.1 Acid Number

Several methods were well-established and recognized to be used to test an acid number in the oil. Figure 18 below shows the step to determine the acid value by using Potentiometric Titrator.

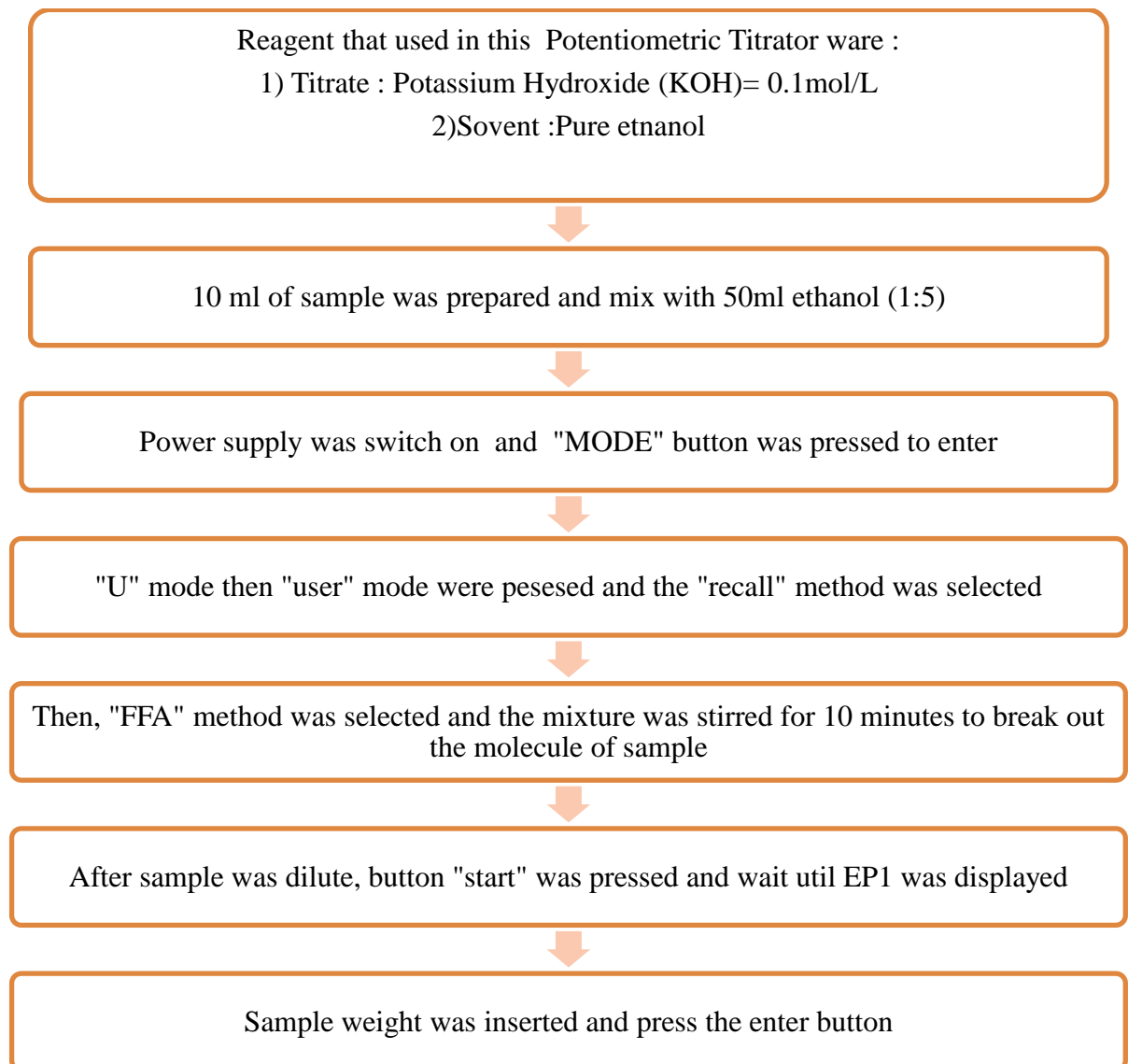


Figure 18 Method of acid value by using Potentiometric Titrator



Figure 19 Potentiometric Titrator machine



Figure 20 The acid value result was appeared on the screen of Potentiometer Titrator after reaction was completed

3.2.8 Preparation of Polyurethane for Coating

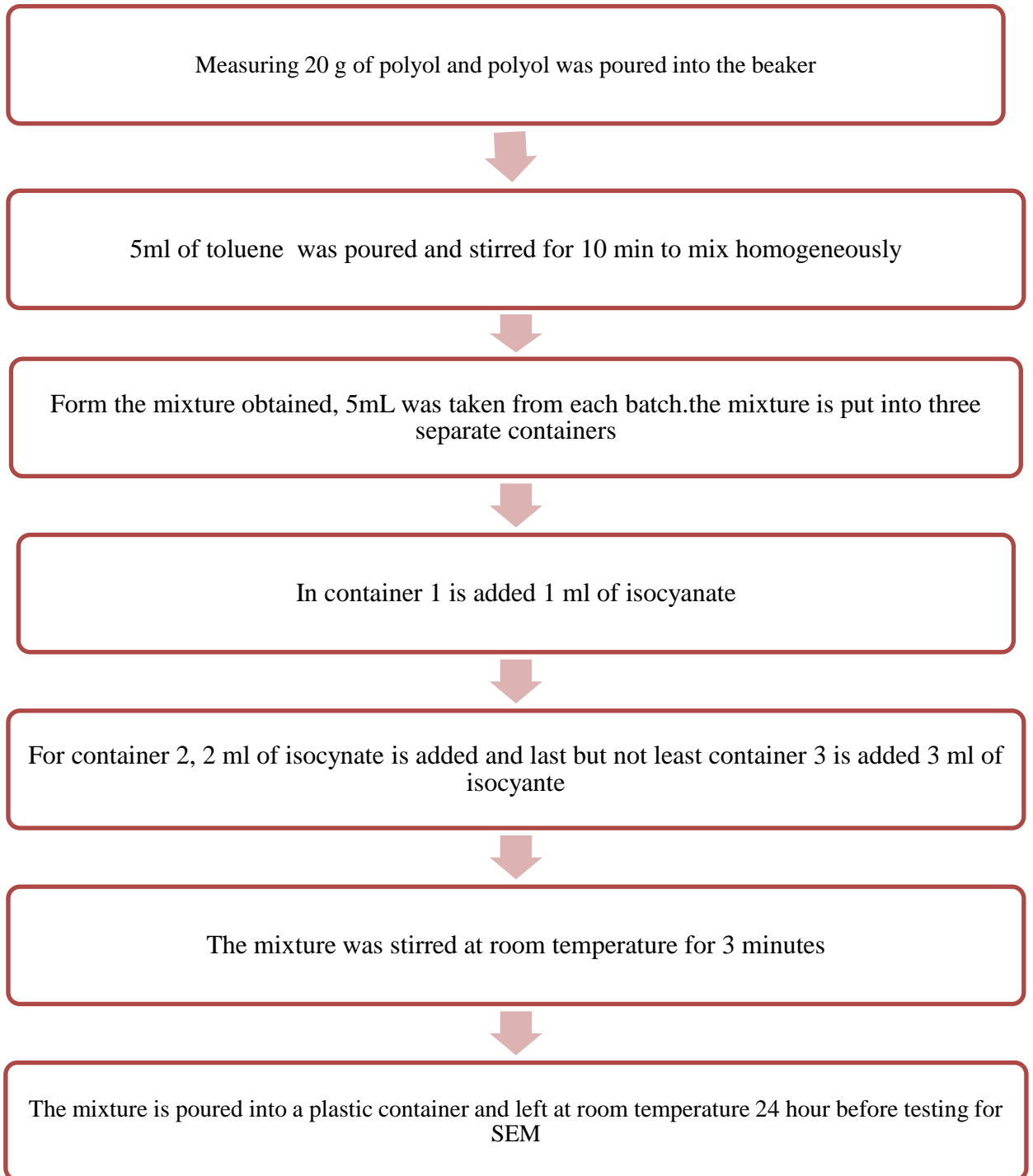




Figure 21 The mixtures of polyurethane before drying process



Figure 22 The polyurethane form after 24 hours

3.2.9 Characterization of Polyurethane for Coating

By running the Scanning Electron Microscopy (SEM) tests, the morphological image of polyurethane for coating of palm oil –based polyol can obtain. Figure 23 shows the scanning electron microscopy .Since the SEM was not provided at laboratory of Chemical Engineering and Natural Resource, the characterization was done in the central laboratory of University Malaysia Pahang. There are four parts to obtain morphological image of PU. The parts are coating the sample, inserting the sample, obtain the image and last but not least, taking out a sample from the chamber. First, the sample was cut into small piece and put into the sample holder. Then, the sample was coated with carbon for three to five minutes.

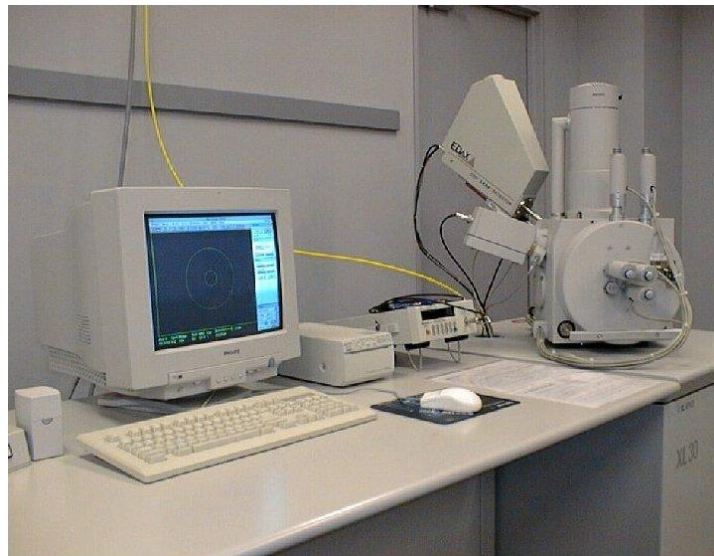


Figure 23 Scanning Electron Microscopy

After that, the sample was inserted into the specimen holder by using line free glove. Make sure the specimen was strewed with appropriate bark unless there have a multi sample holder has been used. The vent button found on work page was clicked. Once the sample was placed properly, the chamber door was closed and vacuum module starts to make sure no air in the chamber. Operating pre-check was done in order to make sure all the testing was set up before vacuuming the chamber.

The next step was scanning images. In order to ramp up the voltage, the HV button in the electron column module was clicked. After a few second, image of morphological of PU appeared in the active Quad. The detector module was clicked in order to adjust the contrast and brightness. Then, the specimen was moved to desired area with X and stage control. The selected area was zooming up or down to the desired magnification and image was focused at 500x to 1500x to get a desired morphological image. The snapshot button tool bar was clicked when image freezing. Then, save as the image in file menu. The sample need to take out from the chamber after obtaining the image of morphology. Lastly, the same procedure was repeated with another sample.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Epoxidation of Palm Oil

4.1.1 Fourier Transmission Infrared Spectroscopy (FTIR) Analysis

FIR was carried out to identify the component and chemical compositions which exist in the crude palm oil and epoxidation of palm oil. FTIR analysis showed the hydroxyl, carbonyl, aliphatic, ether, alcohol, carboxylic and many more groups are present on the surface of raw material. Determination of the main functional group present was based on research by Derawi and Salimon (2010), and Czub and Franek (2013). Table 4 below show details on the spectra group detected by using FTIR.

Table 4 details on the spectra group detected by using FTIR

Wavelength (cm ⁻¹)	Functional Group	Description
~3450	C=O stretch from ester	The vibration occurs mainly from the ester
750-880	C-O-C stretch from epoxide	The vibration occurs from the epoxide
815-950	C-O-C stretch from epoxide	The vibration occurs from the epoxide
1650-1600	HC=CH	Small peak transmittance from alkane
3050-3000	=CH stretch	Vibration of alkane

Source: Derawi and Salimon, 2010

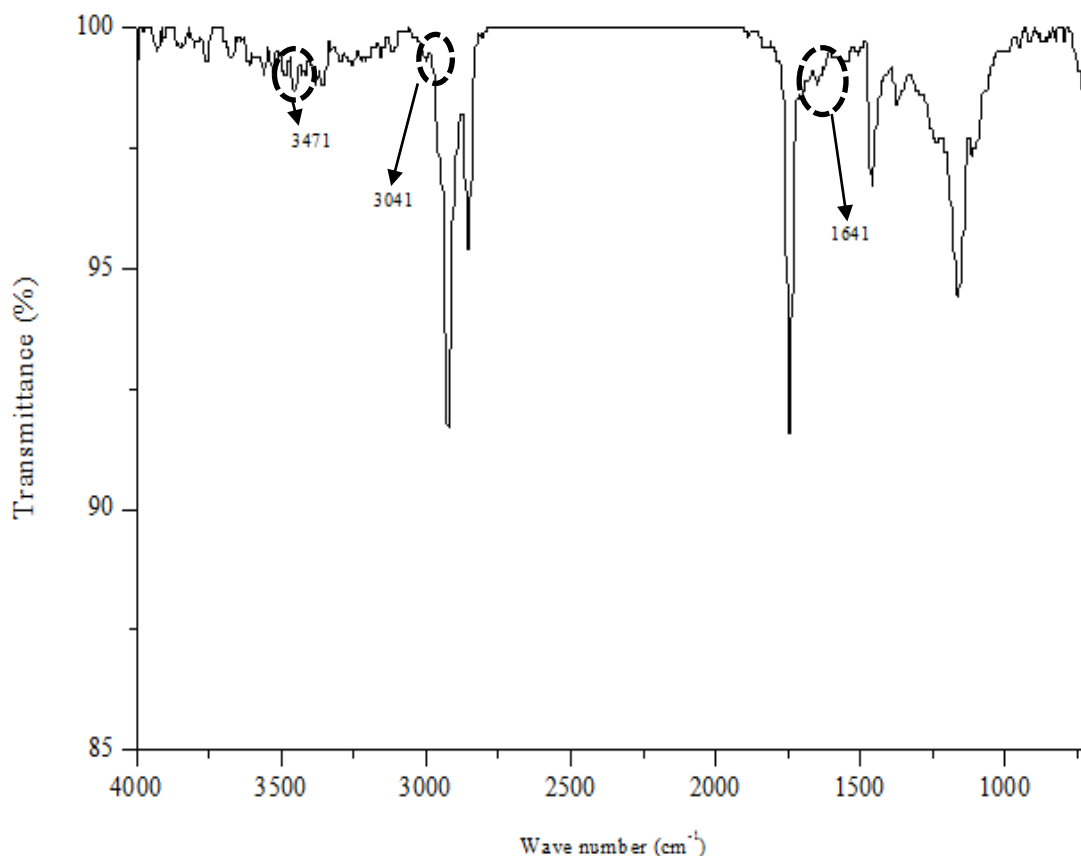


Figure 24 FTIR spectra for raw material (CPO)

The spectra of raw material which is crude palm oil determine by FTIR technique is shown in Figure 24. All spectra were recorded between 700cm^{-1} to 4000cm^{-1} . This spectrum describes the crude palm oil molecules which had absorbed specific frequency that displayed the characteristic of CPO structure. A peak appears at 3471 cm^{-1} which correspond to overtone stretching vibration peak of C=O for ester. This confirms the formation of ester in the CPO. FTIR spectrum of CPO shows the stretching vibration peak of =CH at wavelength 3041 cm^{-1} . This also shows the other one peak at bonding peak of HC=CH (cis) at 1641 cm^{-1} and it confirms the formation of alkane. Table 5 showed the summary of wave number of functional group present in the sample EPO and raw material.

Table 5 The summary of wave number of functional group present in the sample EPO and raw material.

Sample	Wave number (cm ⁻¹)	Functional group
Raw material	3471	C=O for ester
	3041	=CH stretch
	1641	HC=CH (cis) bond
EPO (1:5:1)	3500	C=O for ester
	1643	HC=CH (cis) bond
	780	C-O-C stretch from epoxide
EPO (1:5:2)	3502	C=O for ester
	1643	HC=CH (cis) bond
	778	C-O-C stretch from epoxide
EPO (1:5:4)	3505	C=O for ester
	1644	HC=CH (cis) bond
	779	C-O-C stretch from epoxide
EPO (1:5:6)	3504	C=O for ester
	1648	HC=CH (cis) bond
	781	C-O-C stretch from epoxide

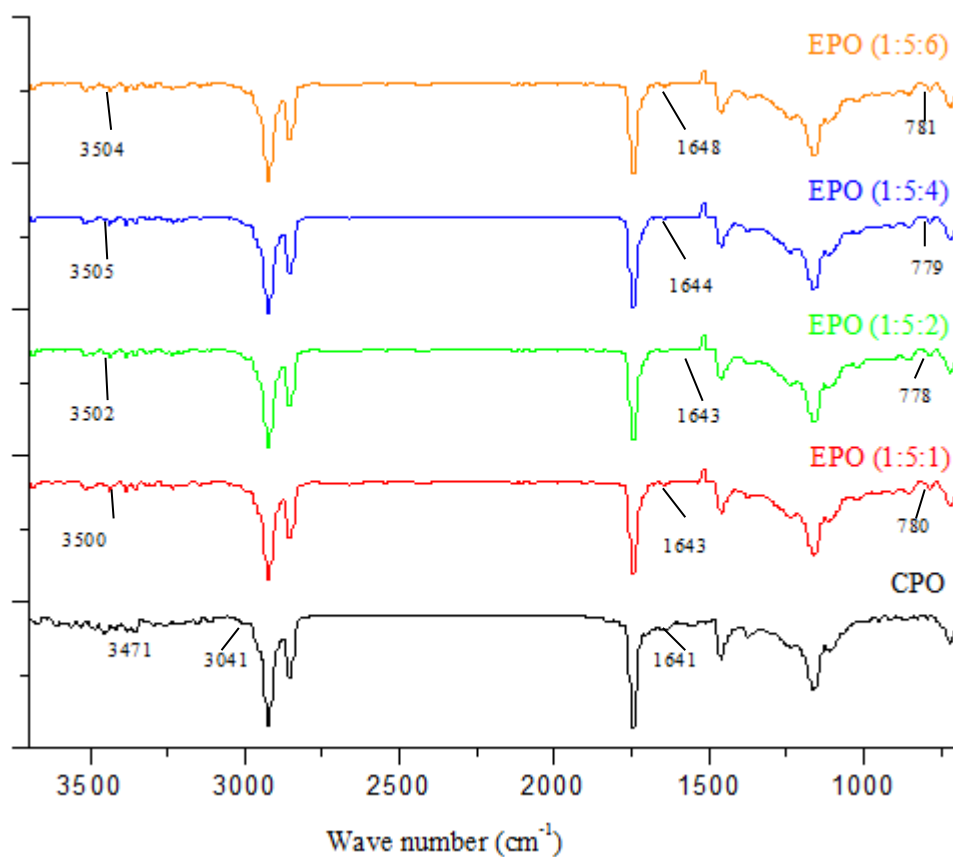


Figure 25 FTIR spectra of (a) CPO (b) EPO(1:5:1) (c) EPO (1:5:2) (d) EPO (1:5:4) (e) EPO (1:5:6)

Figure 25 shows the FTIR spectra of CPO and EPO for difference mol ratio. Moreover, clear difference can be detected in infrared spectra, as taking the CPO sample for comparison in order to prove the presence of an oxirane ring of EPO. The spectrum of EPO (1:5:1) in Figure 25 (b) presents the wave number in the region 3500 cm^{-1} , 1643 cm^{-1} and 780 cm^{-1} , illustrating C=O for ester, HC=CH (cis) bonding peak and epoxide deformation, respectively. Furthermore, this observation was also founded by other research (Derawi and Salimon, 2010). The FTIR spectrum in Figure 25 (c), clearly shown the vibration bonds of the oxirane ring at 778 cm^{-1} which is attributed to an epoxy functional group. When the hydrogen peroxide was added drop wise in the mixture of CPO and acetic acid, as indicate in Figure 25 (d), a major change in FTIR spectra was observed in the 750 cm^{-1} to 880 cm^{-1} region which is the presence of an epoxy functional group. In Figure 25 (e) the unsaturated peak and stretching vibration peak of =CH has been disappeared, but the present of the oxirane ring peak was detected at wavelength 781 cm^{-1} .

4.1.2 Number of Iodine (IV)

From the Table 6 shows the data of iodine value of EPO during experimental work. The titration volume for a mol ratio of EPO 1:5:4 show the highest amount of sodium thiosulfate solution which is 47.8 ml in order to get the iodine value. Based on Czub and Franek (2013), the theoretical value of iodine is approaching zero. When the higher volume of sodium thiosulfate solution was titration, the iodine value that get is nearer to zero.

Table 6 Iodine Value of Epoxidation of Palm Oil

Sample	Weight of Sample (g)	Titration Volume (ml)	Iodine Value (I ₂ g/100g)
EPO (1:5:1)	0.30	45.8	9.33
EPO (1:5:2)	0.30	47.2	3.39
EPO (1:5:4)	0.30	47.8	0.85
EPO (1:5:6)	0.30	46.7	5.18

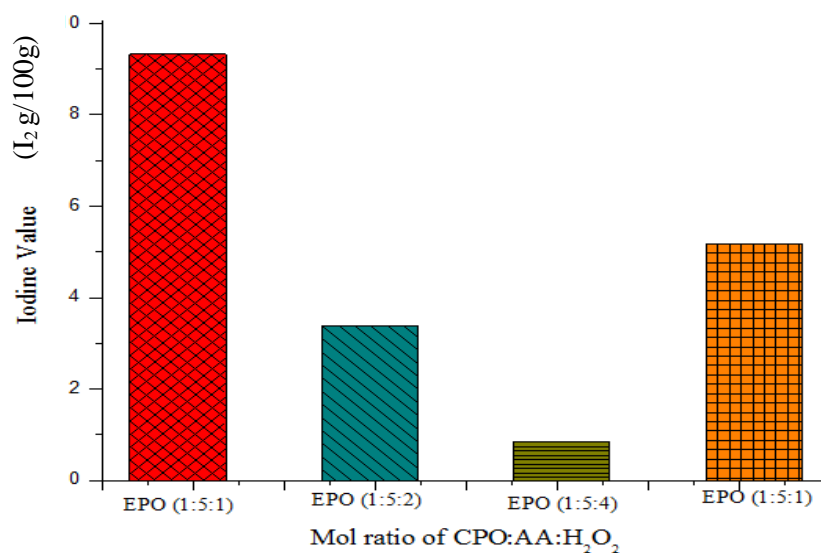


Figure 26 Concentration H₂O₂ effect on Iodine Value of EPO

In fact the palm oil has low IV and considered as natural oil compared to other natural oil such as sunflower oil and soybean oil (Noor *et al.*, 2013). The effect of H₂O₂ concentration on iodine value of EPO has been shown in Figure 26. From the figure the iodine value of a mol ratio of 1:5:4 reach almost zero which is 0.85 I₂ g/100g. The full conversion of double bonds to oxirane ring might be occurring and the rate of reaction was increased as the concentration of hydrogen peroxide in the reaction is an increase, however the stability of oxirane ring was very poor at high concentration of hydrogen peroxide (Derawi and Salimon, 2010). Based on Goud *et al.*(2006), relative conversion of oxirane was decreasing rapidly at same temperature for the higher concentration of hydrogen peroxide. Research by Naidir *et al.* (2012), the lower value of iodine means the opening of double bond allow for the oxirane ring formation in the epoxidation of palm oil to take place.

4.2 Palm Oil-based Polyol

4.2.1 Fourier Transmission Infrared Spectroscopy (FTIR) Analysis

FIR was carried out to identify the component and chemical compositions which exist in the palm oil-based polyol. Determination of the main functional group present in the polyol was based on research by Badri K.H. (2010) and Noor *et al.* (2013). Figure 27 below was shown the spectra of the prepared palm oil-based polyol by using the FTIR technique. All spectra were recorded between 700 cm⁻¹ to 400cm⁻¹. This spectrum described the specific frequency absorbed by polyol's molecules that shown the characteristic of palm oil-based polyol. At 60 minutes, the sample showed the presence of hydroxyl peak at 3481 cm⁻¹. Research by Pawlik and Prociak (2011), a hydroxy group in polyol is needed in order to react with isocyanate and to create a polyurethane. Moreover, at peak 1750 cm⁻¹ show the presence of ester group for all samples. Based on the Figure 27, the epoxide group have been disappearing at peak 820 cm⁻¹ to 860cm⁻¹.

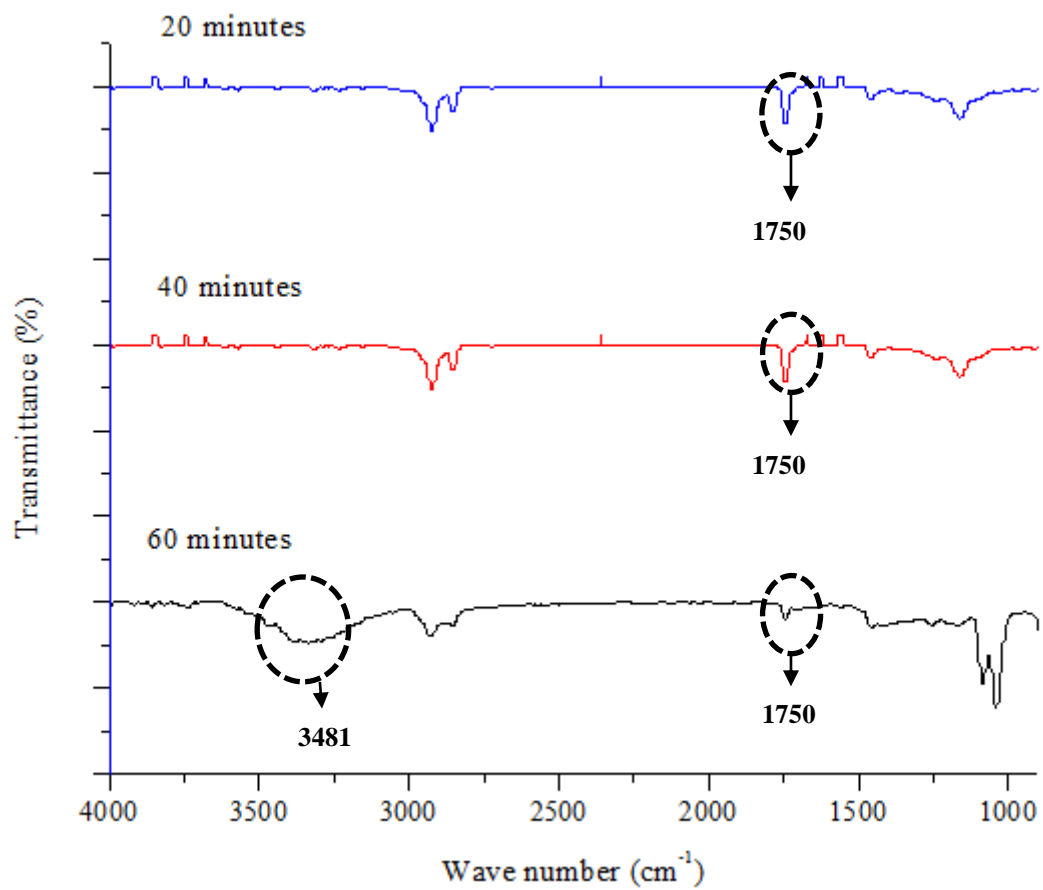


Figure 27 The Fourier Transform Infrared Spectra of the prepared palm oil-based polyol

4.2.2 Acid value

The acid value of polyol is determined by using Potentiometric Titrator. Acid value is the amount of potassium hydroxide in milligrams required to neutralize the free acid in 1 gram of sample (Noor *et al.*, 2013). Table 7 showed the acid value of palm oil-based polyol with reaction time.

Table 7 The acid value of palm oil-based polyol with reaction time

Sample	Time (minute)	Acid value (mg KOH)
Palm Oil –based polyol	20	5.06
	40	4.57
	60	3.86

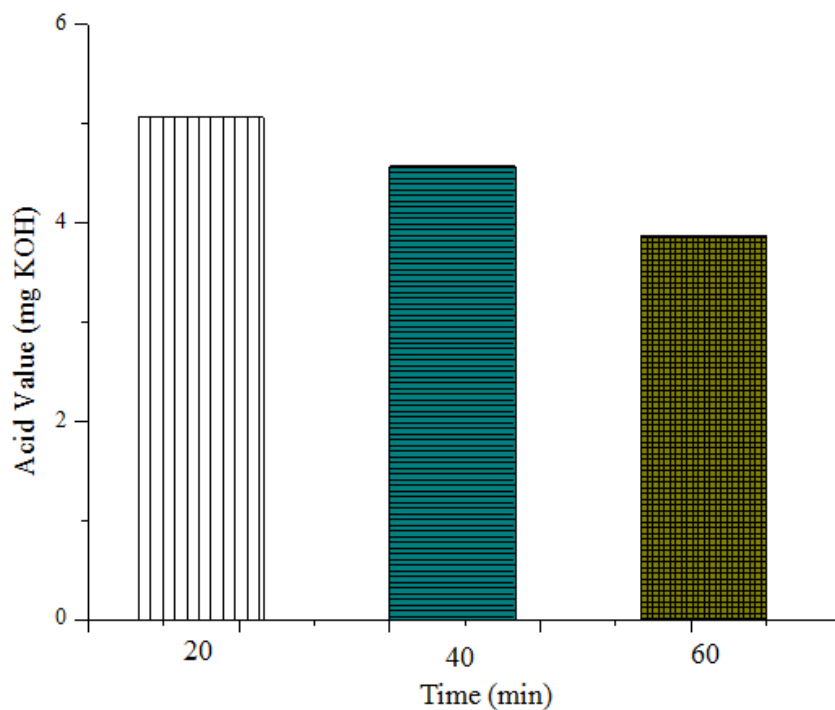


Figure 28 The acid value of palm oil-based polyol with reaction time

Figure 28 represents the acid value of palm oil-based polyol with reaction time. The condition of this reaction was at 89°C and by using the mol ratio 1:5:4 of CPO to acetic acid to hydrogen peroxide. At 20 minutes reaction time, acid value was 5.06 mg KOH. One of the other factors that might contribute to the high acid value was hydrolysis which is basically the process of hydrolysis will increase the free fatty acid content in polyol (Noor *et al.*, 2013). For 40 minutes reaction time, the acid value was 4.57 mg KOH while at 60 minutes reaction, the value of acid was 3.86 mg KOH. The acid value was decreased with time demonstrating opening ring reaction throughout reaction (Ang *et al.*, 2013). Research based on Ooi *et al.* (2006), the maximum acid value is 3.00 mg KOH. Moreover, the acid value of the reaction becomes constant after one hour of the reaction time. Research based on Noor *et al.* (2013) , the neutralisation process was required in production of polyol by using homogeneous catalyst in order to get lower AV in the final product of polyol. Based on the Figure 28 , neutralisation process was not required because the lower value of acid were obtained after one hour reaction of EPO with ethyl glycol reaction to produce palm oil-based polyol.

4.3 Polyurethane Coating

4.3.1 Scanning Electron Microscopy (SEM)

The morphology of coating was analysed by Scanning Electron Microscopy.

Figure 29 and Figure 30 shows the SEM images for the mol ratio of PO to isocyanate (1:2) and (1:3). Moreover, it also provides important information about the morphology of the palm oil-based polyol in the coating.

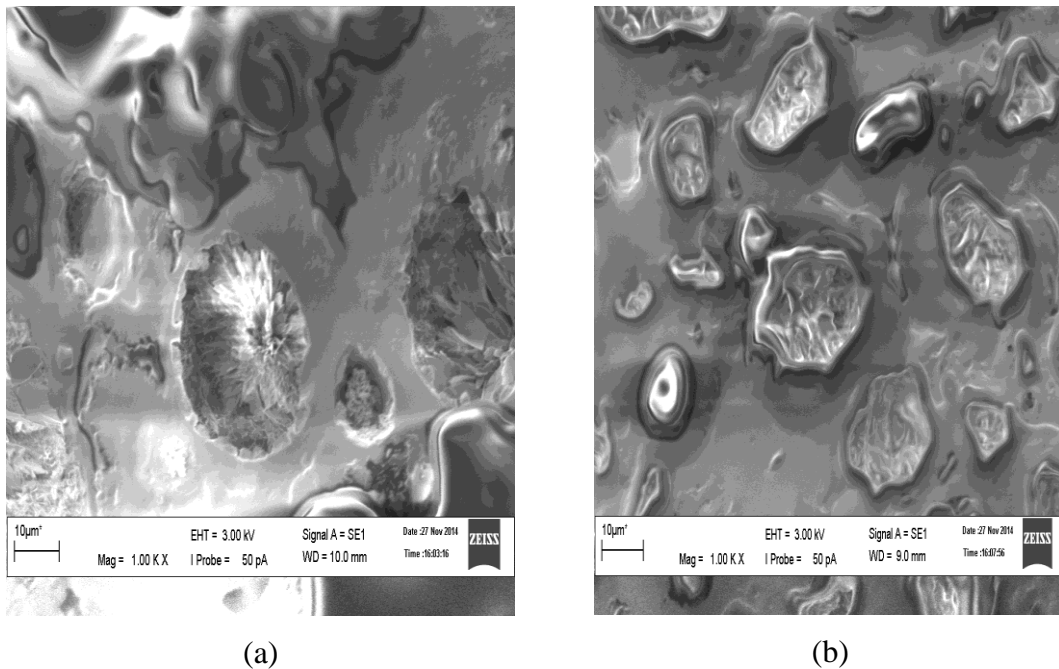
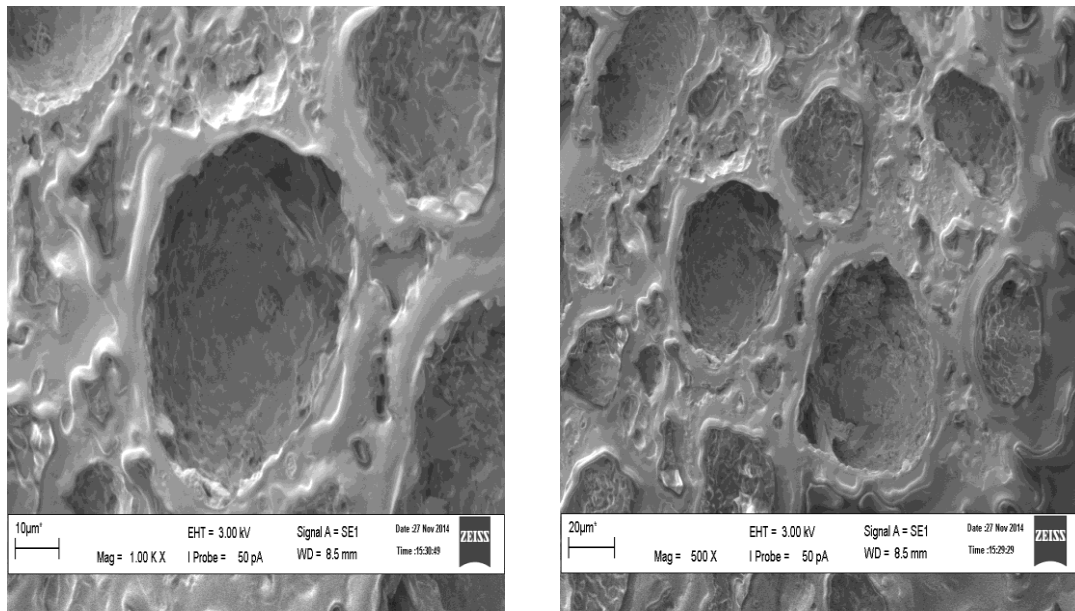


Figure 29 SEM images of the mol ratio of PO to isocyanate (1:2) (a) magnification of X1.00K at 10 nm size (b) magnification of X1.00K at 90 nm size



(a)

(b)

Figure 30 SEM images of the mol ratio of PO to isocyanate (1:3) (a) magnification of X1.00K at 8.5nm size (b) magnification of X500K at 8.5 nm size

Figure 29 show the SEM images of the mol ratio of PO to isocyanate (1:2) (a) magnification of X1.00K at 10 nm size and (b) magnification of X1.00K at 90 nm size. Figure 30 show the SEM images of the mol ratio of PO to isocyanate (1:3) (a) magnification of X1.00K at 8.5nm size (b) magnification of X500K at 8.5 nm size . Based on Figure 30 (a) and (b) shows the effect of isocyanate on the bubble size. This is clear indicate that the bubble size increase with the increase with isocyanate content. The present of bubble in polyurethane coating structure seemed to indicate poor miscibility between isocyanate and palm oil-based polyol. Miscibility means the forming a homogeneous mixture when added together. Research based on Gurke T. (2002), if the isocyanate content is too high, some amount of polyol need to be added and if the isocyanate content is too lower, added the required amount of isocyanate. Furthermore, if water is present in the reaction mixture, the isocyanate will react water to form a urea linkage and carbon dioxide gas. Hence, the polymer that form contained both urethane and urea linkages.

CHAPTER 5

CONCLUSION

5.0 Conclusion

The uses of palm oil as raw material was successfully carried out to produce palm oil-based polyol for coating. In this experimental result, it was shown that the characteristics of the polyol structure which have been detected in FTIR analysis. The absorbed frequency of sample molecules at the condition 85°C of temperature and 60 minutes reaction times showed the present of hydroxyl group at peak 3481 cm^{-1} . Besides that, the acid value of polyol that obtain at this condition was 3.86 mg KOH. The value that obtained was exceed the maximum acid value which is 3.00mg KOH (Ooi *et al.*, 2006).

Moreover, the value of acid number that obtained from opening ring process was also affected from epoxidation of palm oil. The experimental works has been carried out at difference weight ratio of hydrogen peroxide for CPO to Acetic Acid to H_2O_2 of 1:5:1, 1:5:2, 1:5:4 and 1:5:6. All sample of difference weight ratio of hydrogen peroxide show the presence of an epoxy functional group at the 750 cm^{-1} to 880 cm^{-1} region have been detected in FTIR. Moreover, the unsaturated peak and stretching vibration peak of =CH has been disappeared. The results obtained shows that, the titration volume for a mol ratio of 1:5:4 show the highest amount of sodium thiosulfate solution which is 47.8 ml in order to get the lower iodine value, 0.85 I_2 g/100g Based on Czub and Franek (2013), the theoretical value of iodine for EPO is approaching zero.

Based on SEM image, by using the ratio polyol to isocyanate of 1:3 shows the effect of isocyanate on the bubble size. This is clear indicate that the bubble size increase with the increase with isocyanate content. The present of bubble in polyurethane coating structure seemed to indicate poor miscibility between isocyanate and palm oil-based polyol.

5.1 Recommendation

Through the research, it was successfully performed palm oil-based polyol for coating by including the difference weight ratio of hydrogen peroxide for CPO to Acetic Acid to H_2O_2 in epoxidation process, the reaction time of ethylene glycol in opening ring process and the ratio polyol to isocyanate in preparation of polyurethane coating. For further research, a few recommendations to enhance the palm oil-based polyol for coating are

1. More characterization on the inter-stage sampling of epoxidation process and opening ring are needed to obtain the information other than functional group, pH number, acid value and iodine number. Example of other characterization is by using the GPC technique. GPC technique is used to get the characterization molecular weight and related properties of the monomer product. From this information, the quality of palm oil-based polyol can be improved.
2. By including the optimum temperature as a parameter, the further study of palm oil-based polyol for coating application can be done. Example of polyurethane coating testing includes mechanical performance and thermal stability.

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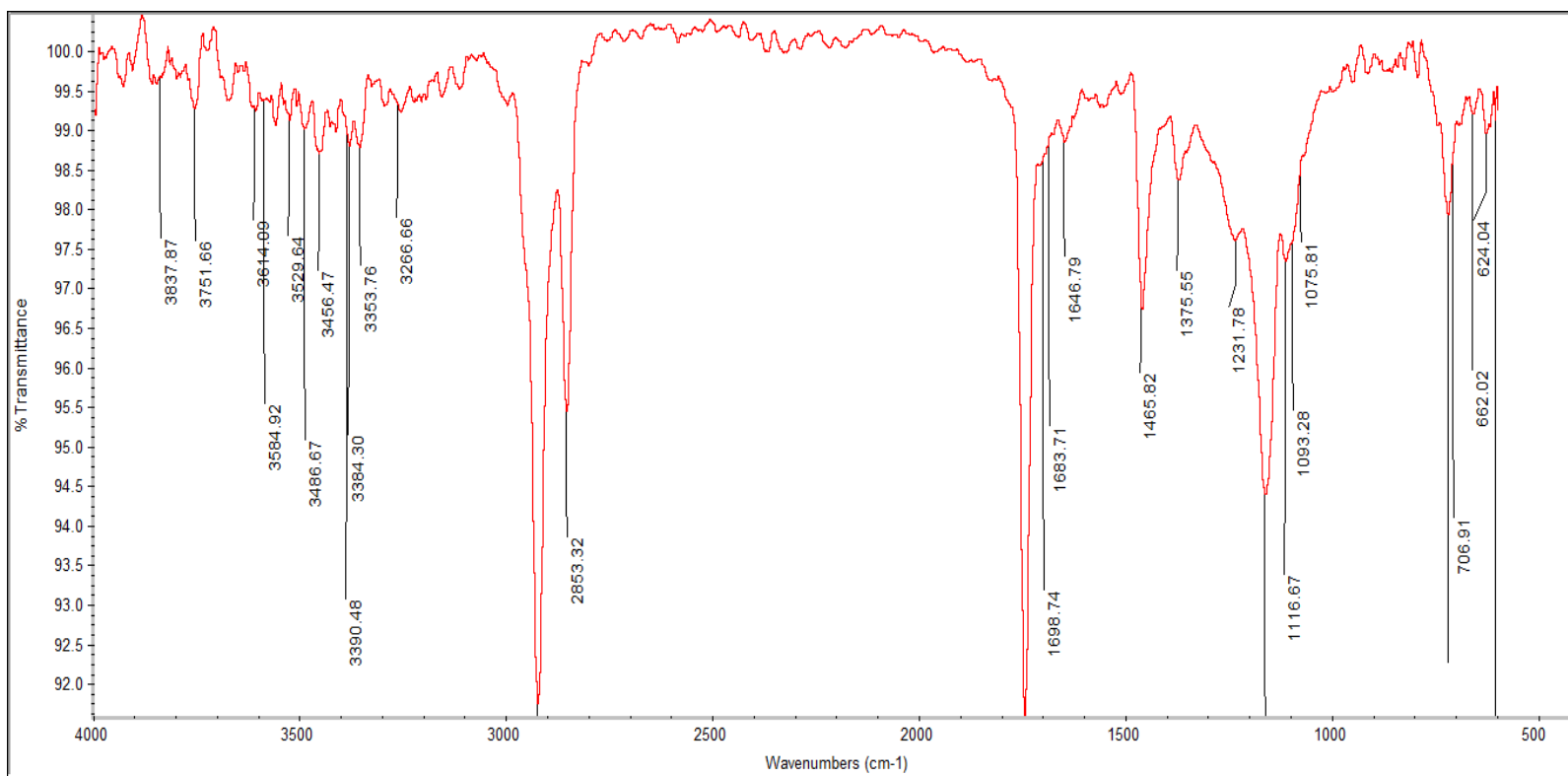
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APPENDICES

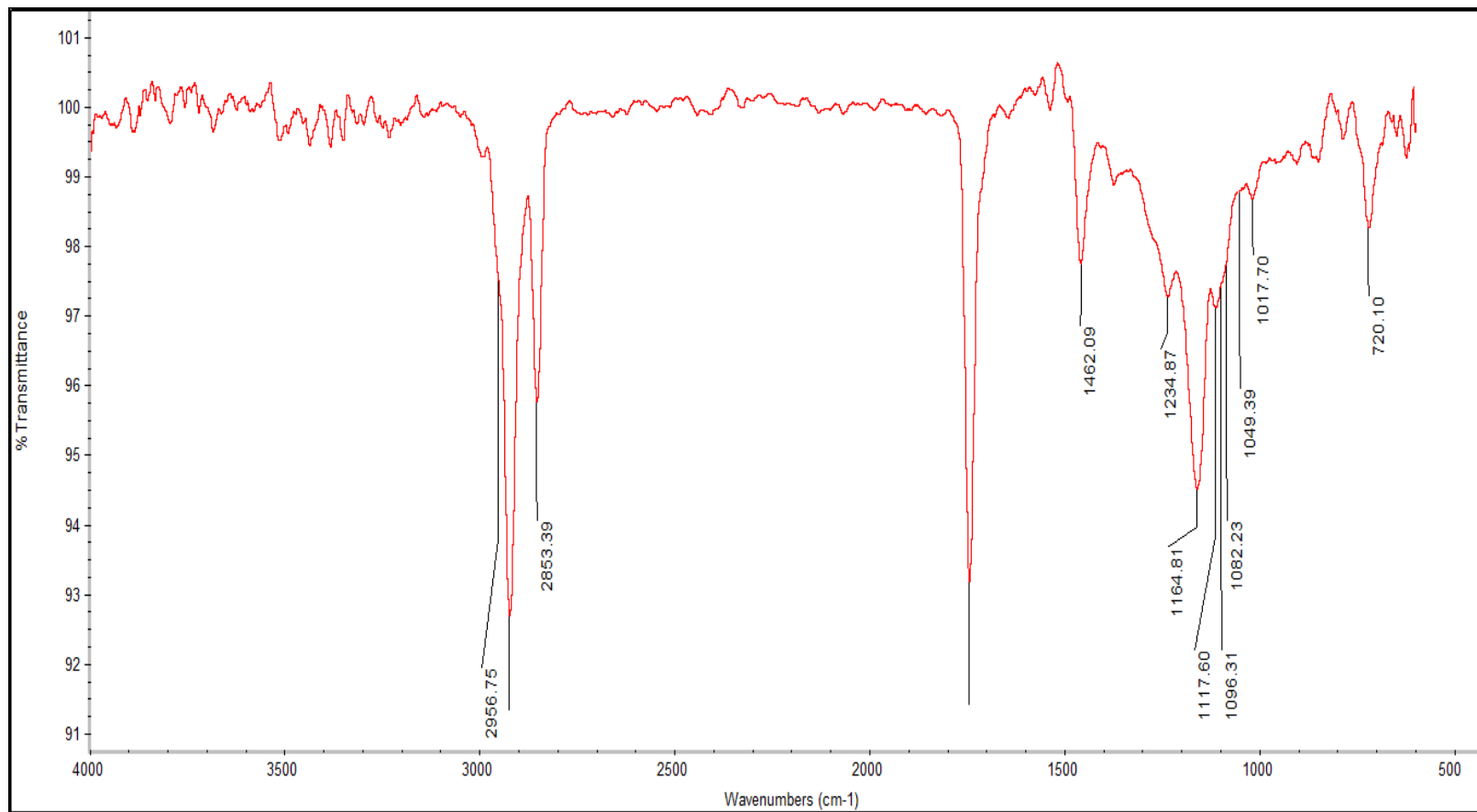
APPENDIX A

FTIR for raw material (CPO)



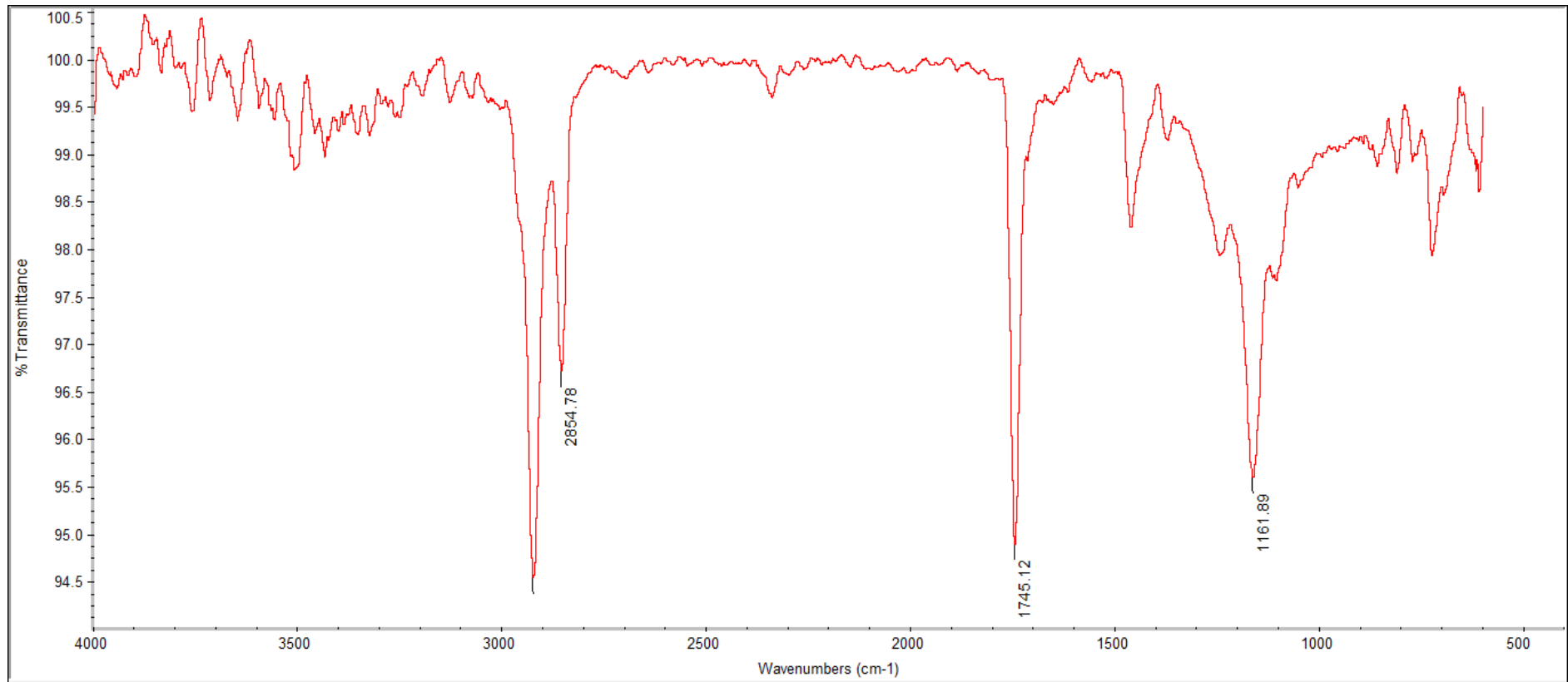
APPENDIX B

FIIR for EPO 1:5:1



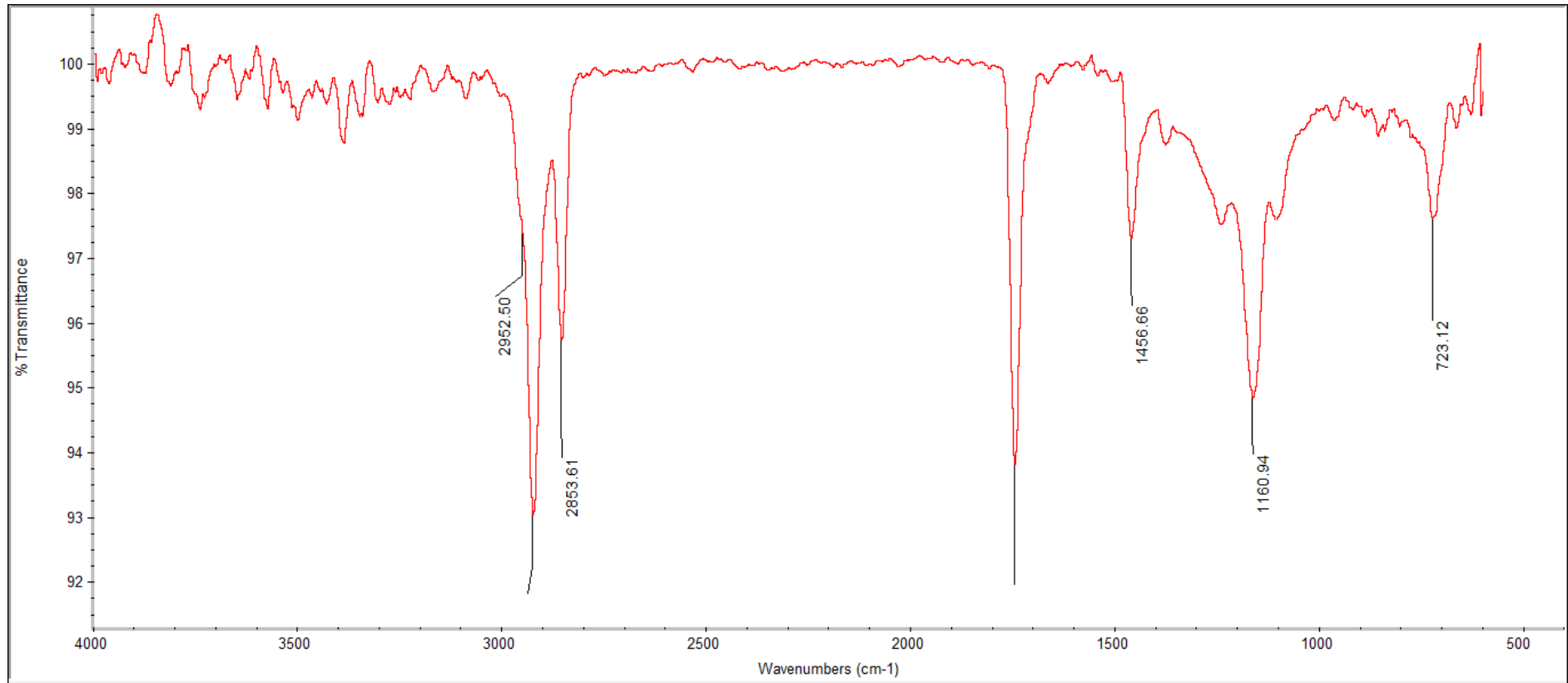
APPENDIX C

FIIR for EPO 1:5:2



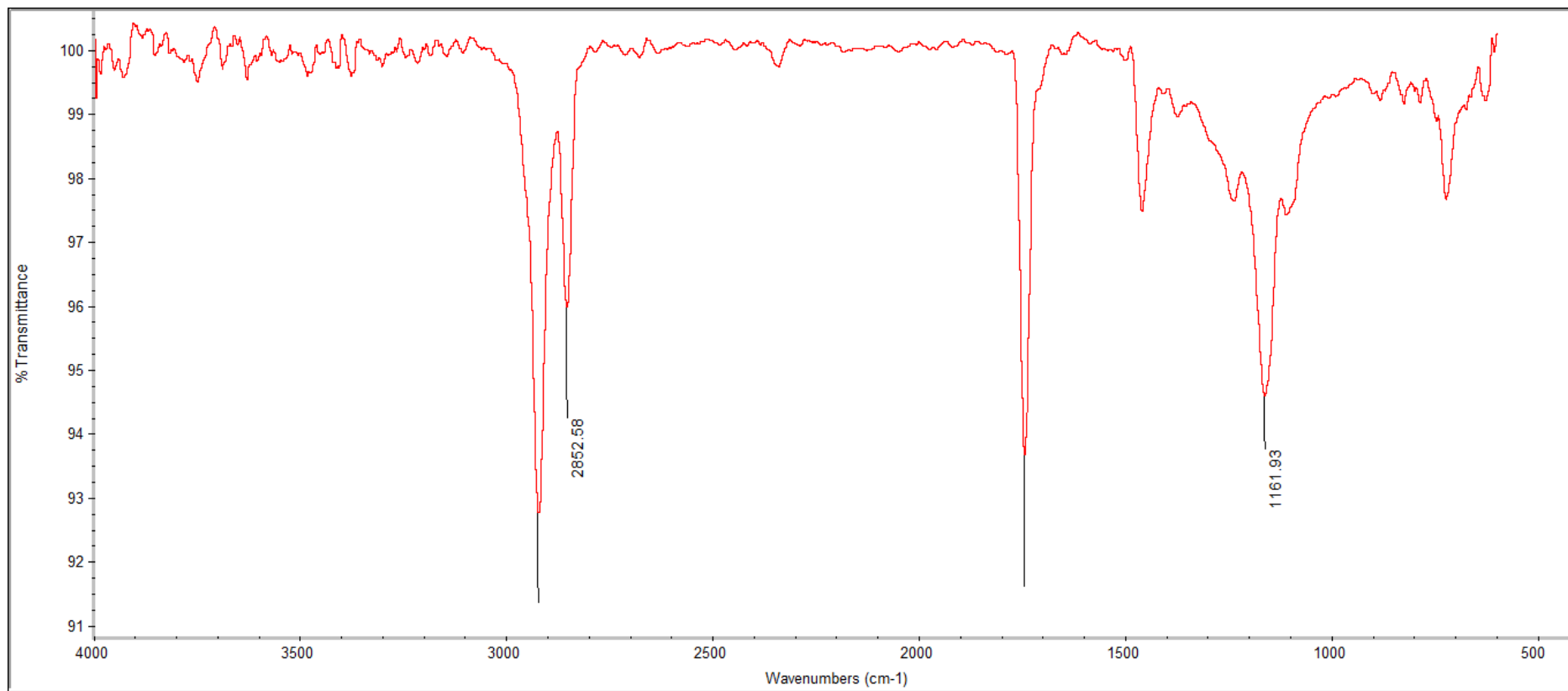
APPENDIX D

FIIR for EPO 1:5:4



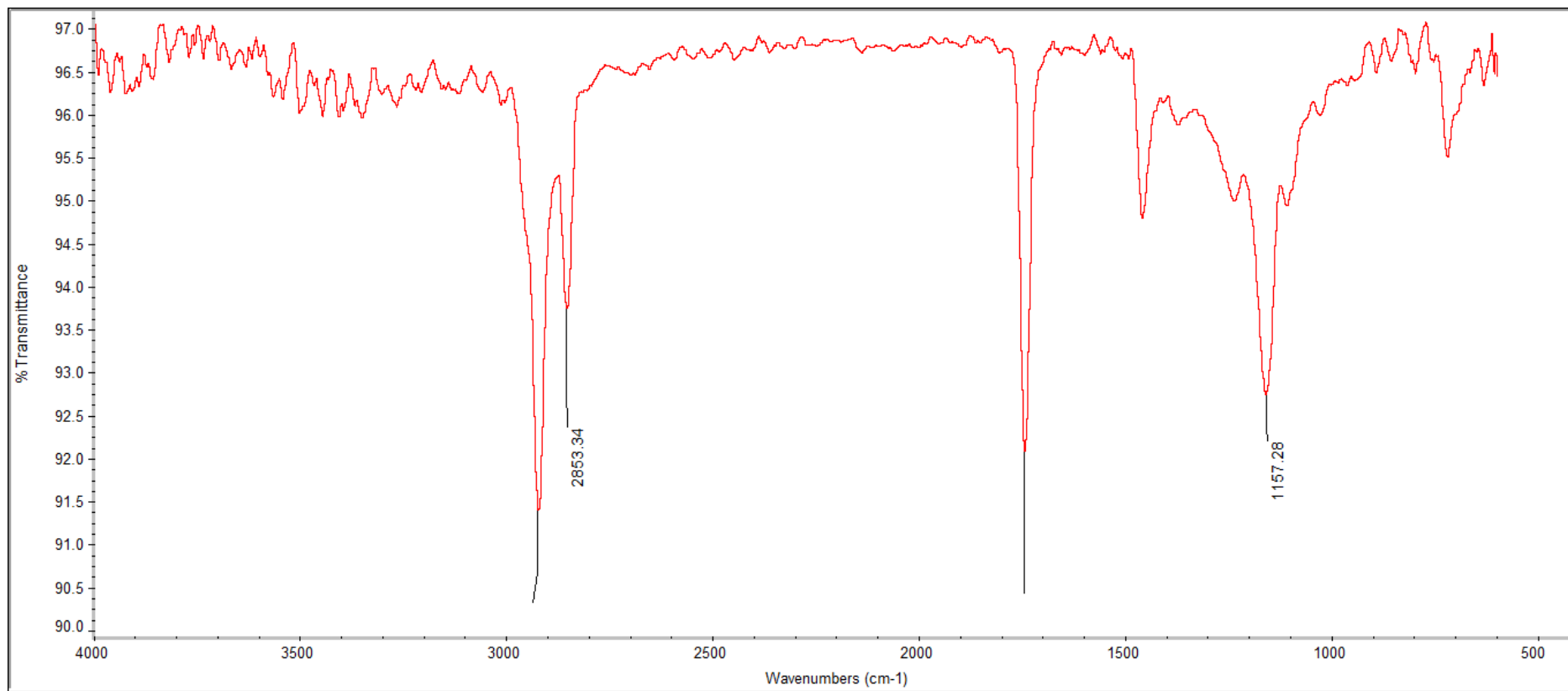
APPENDIX E

FIIR for EPO 1:5:6



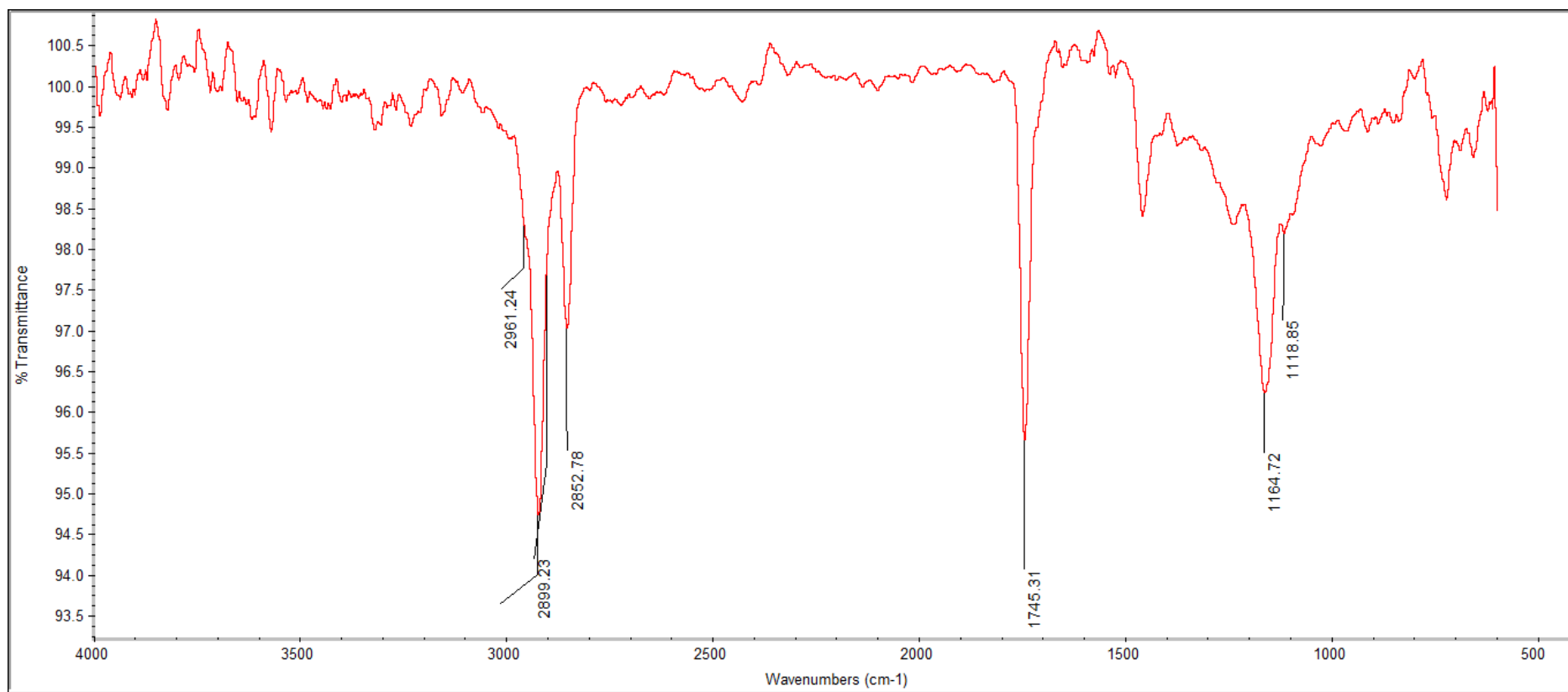
APPENDIX F

FTIR of the prepared palm oil-based polyol at 20 minutes reaction



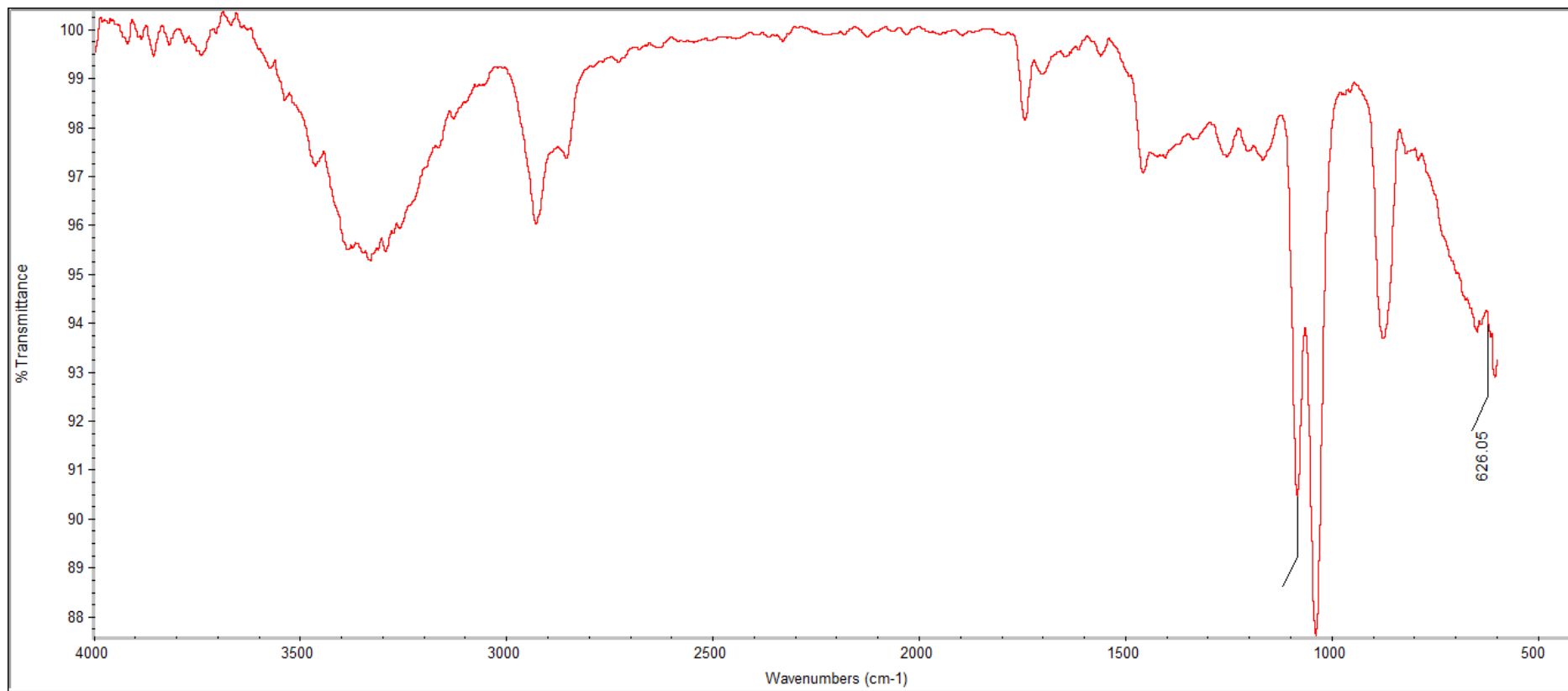
APPENDIX F

FTIR of the prepared palm oil-based polyol at 40 minutes reaction



APPENDIX F

FIIR of the prepared palm oil-based polyol at 60 minutes reaction



APPENDIX G

Title :Research Works Schedule

Week Task	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28
Identifying research title	■																											
Submit title approval form		■																										
Purchasing chemical			■	■	■																							
Finding information	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Start writing research draft			■	■	■	■																						
Completing the proposal			■	■	■	■	■	■	■																			
Proposal presentation									■																			
Prepare partial thesis										■	■	■	■	■														
Submit partial thesis														■														
Conduct experimental work for EPO process																■	■	■	■									
Conduct experimental work for opening process																		■	■	■								
Conduct experiment work for coatingprocess																			■	■	■							
Characterizaion of the sample																			■	■	■	■	■	■				
Writing the thesis																■	■	■	■	■	■	■	■	■	■	■	■	■
Submission of abstract																								■				
Submission of technical paper																											■	
Submission of draft report																										■	■	
Oral presentation																												
Submission final project dissertation																											■	