Novel Palm Oil Based Polyols with Amide functionality

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Abstract

In polymer chemistry, polyol usually used as starting materials for polyurethane (PU) production in which upon reacted with isocyanate will affect the physical and chemical properties of the obtained PU. Polyols that are mostly derived from petrochemical resources are facing the issues such as depletion of petroleum sources as well as the increasing in market price. Ring opening reaction (ROR) of epoxidized palm oil (EPO) had been carried out using isopropanolamine (IPA) to impart polyol with amide functionality. The effect of reaction time on the opening of oxirane ring was investigated. FTIR spectra showed that the oxirane ring of EPO can occurs at 6 hours reaction time, corresponding to the deacreasing intensity of oxirane band at 824-830 cm^{-1}. The OH value of the amide- functionalized-polyol was calculated at around 240-253 mg KOH/g. By prolonging the reaction time the OH value has slightly reduced. Mass spectroscopy analysis revealed that the polyol has a molecular weight in the range of oligo-polyols (400 – 500 Da).

Keywords: Ring opening reaction; epoxidized palm oil; isopropanolamine; bio-based polyols; amide polyol.

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1. Introduction

The awareness to produce eco-friendly materials for environmental sustainability has triggered extensive studies to use renewable resources such as plant oils as raw materials in many polymer syntheses [1]–[3]. Soybean oil, castor oil, sunflower oil, palm oil, rapeseed oil, olive oil, linseed oil and so on, with a worldwide production increasing continuously in 10 years (especially soybean and palm oil), (Figure 1) are used mainly in various of application including food and non-food applications. For instance, polyols derived from soybean oil [4]–[6], canola oil [7] or jatropha oil [8] have been used to react with diisocyanates to produce polyurethane. The abilities of these plant oils to be transformed into polyols are due to the existence of some reactive functionality/unsaturated sites such as ester, double bond or triple bond in their molecular structures [2], [3], [9], [10]. Some oils have natural built-in functional groups such as hydroxyl (castor oil), epoxide (vernonia oil) or ketone (licania oil) [11]. Ester and double bond have been subjected to many chemical reactions to introduce hydroxyl functionality (–OH) including transamidation [12], esterification [13], hydroformylation [14], ozonolysis [15], and epoxidation [3]. Among them, epoxidation gives wide possibilities for chemical transformation due to the high reactivity of oxirane ring to undergo nucleophilic attack by ring opening reagent to produce a variety of products such as alcohols, glycols, alkanolamines, carbonyl compounds and polymers [16].
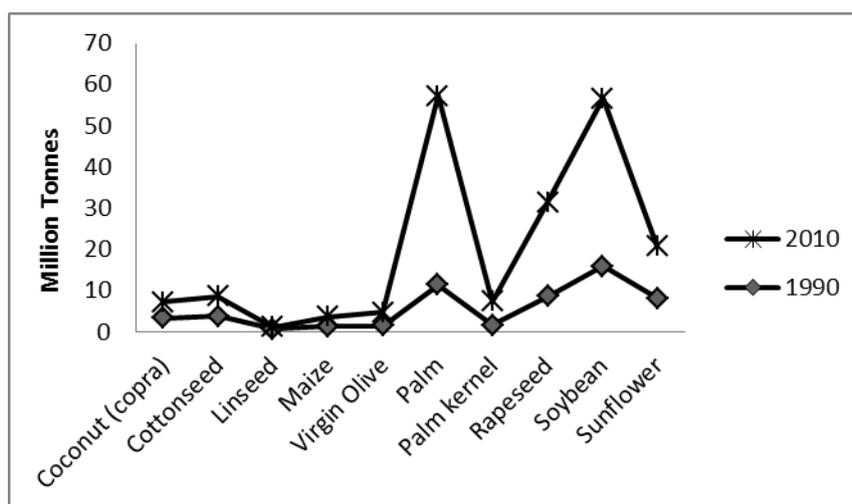
Figure 1: World production of some vegetable oils in 1990 and 2010 [17]

In Malaysia, palm oil has a yield capacity of about 4-6 tons of oil per hectare per year for the best commercial plantation [18]. Due to the increasing awareness of the social community towards environmentally friendly products, it is desirable to study the ability of palm oil to replace for petroleum based polyols. A locally available palm oil has undergone some extensive studies to convert the oil into palm oil-based polyols (PO-p) via few reaction routes such as epoxidation [19], transamidation [20] and transesterification [21]. The second and the third reaction routes usually require high reaction temperature up to $200^{o}C$ [22] and give high yields. Both routes involve the reaction with the ester linkage without disturbing the carbon double bond (–C=C–) of the oil. Therefore, the further reaction is needed to cure the –C=C– site because the presence of π bonds of –C=C– may lower the melting point of the final product, thus affecting its thermal stability [23]. On the other

hand, epoxidation reaction needs lower temperature ranges of 40^oC to 60^oC to give ca. 95% conversion [24] and the reaction occurs directly at the –C=C– reactive site. The epoxidized palm oil (EPO) is an important intermediate for polyurethane industry where EPO undergoes ring opening nucleophilic reaction to form polyol. Ring opening reagents such as alcohol, water, acid and amine [1] have been used to produce various types of polyols. These reagents are crucial in determining the hydroxyl value (OHV) of the respective polyols. For example, if acid and alcohol are used, the OH value is 300 mg KOH/g [25], and if amine was used, the OHV will be higher [26]. In addition, the reagents used will affect the synthesis step in ring opening reaction (ROR). For example, multi preparation step with an excess of solvent and molar ratio are needed for ROR with alcohol and acid reagents [27]. Recently, Miao [28] have used amino alcohol-based reagent, which is isopropanolamine (IPA) to be reacted with epoxidized soybean oil (ESO). The synthesis was conducted at low temperatures of 80 – 100^oC using one-pot synthesis technique with a mild condition, less solvent and produce polyols with OHV around 310 mg/KOH.

This study has adopted the same reagent by reacting IPA with EPO but at different reaction time with Lewis acid to catalyze the reaction due to weak nucleophile character of IPA compared with alcohol or amine alone [29]. Lewis acids such as stearic acid [29], tetrafluoroboric acid [30], and *p*-toluenesulfonic acid [31] were well known to assist the ring opening reaction. However, these acids work well at high temperature i.e. 150^oC [31]. Due to this reason, boron trifluoride-methanol-complex (BF_3-MeOH) was used in this study since it has the ability to catalyze the reaction at moderate temperature, is stable, less toxic and promotes similar manner in reaction pathways like hydrochloric acid (HCl) and sulphuric acid (H_2SO_4) [32], [33]. The main objective of this study was to investigate the availability of the IPA to open the epoxy ring of the EPO. It is important to state here that the palm oil polyols obtained here will be used for polyurethane synthesis that will be reported in another publication.

2. Methodology

Epoxidized Palm Oil (EPO) was supplied by Budi Oil Sdn Bhd (specification : OOC= 2.7 – 2.9%, M_w= 848.75 Da, moisture content = 0.3%), Isopropanolamine (IPA) as ring opening reagent was purchased from Sigma-Aldrich, acid catalyst boron trifluoride-methanol-complex (BF_3-MeOH) was purchased from Merck-Schuchardt and chloroform (AR Grade) as quenching agent was obtained from Friendmann Schmidt. All chemicals were used as received.

2.1 Ring Opening Reaction

The pre-set amount of EPO and isopropanolamine was charged into 250 ml reaction flask. The molar ratio of EPO to the amino group for this study was fixed at 1:3. The reaction mixture was stirred at 70^oC for 30 minutes under nitrogen flow. Then, 1 ml of BF_3-MeOH acid was added dropwise and continuously stirred until finished. Afterward, the reaction temperature was increased to 100^oC and the mixture was continuously stirred for 6 hours. Once completed, the reaction was quenched with 100 ml of chloroform in order to deactivate any unreacted reagent. The unreacted IPA, EPO, as well as the catalyst, were then washed with copious amount of distilled water in a separating funnel. The organic phase which contains the product was collected and further

purified with a rotary evaporator to remove the solvent. The purified polyols existing as a yellowish waxy like semi-solid compound at room temperature was then ready for characterization. This procedure was repeated at different reaction times namely, 6, 12, 18 and 24 hours and the polyols obtained were coded as PRT6, PRT12, PRT18, and PRT24 respectively.

2.2 Fourier Transform Infra- Red (FTIR)

Attenuated Total Reflectance (ATR) FTIR was done to investigate the changes in functional groups of the EPO after ROR was done. Sample measurement was conducted by directly applied the sample on top of the sample detector and was scanned 40 times under wavelength in the range of 4000 cm^{-1} to 400 cm^{-1}. The sample was processed using Shimadzu IRTracer 100

2.3 Nuclear Magnetic Resonance (NMR)

^{1}H NMR (proton NMR) was used to determine the number and type of hydrogen atoms in the molecule. The sample was run using NMR Bruker 400MHz with 5 mm dual probe. For each formulation, 5 mg of sample was dissolved with 3 ml chloroform-D (CDCl$_3$) in the NMR tube before placing it in the sample holder for scanning. The spectra of the sample were processed using TopSpin NMR software.

2.4 MALDI-TOF Mass Spectrocopy

The molecular weight of the PO-p was determined using an MALDI-TOF MS of AB SCIEX 5800. The samples were dissolved in methanol and mixed with the matrix, CHCA (α-cyano-4-hydroxynammic acid) before it was deposited on the plate for measurement.

2.5 Hydroxyl Value (OHV)

The OH value of the polyols was determined using AOCS Official Method Cd 13-60 [34]. The sample preparation was done based on the method described in the standard.

3. Result and Discussion

3.1 Fourier Transform Infra-Red (FTIR) Analysis

The opening of epoxy ring was demonstrated by the intensity reduction of two small peaks at 824-830 cm^{-1} corresponding to ring deformation of epoxide as well as the disappearance of–C–O–C stretching of epoxide at 1160 cm^{-1}, the disappearance of N-H stretching primary amine at 1596 cm^{-1} and the appearance of hydroxyl band (OH) at around 3300 cm^{-1}. During the reaction, the electropositive carbon of the epoxy ring in the fatty acid chain was attacked by an amine (–NH$_2$) from IPA, thus breaking the carbon-oxygen bond of the epoxy. Although IPA contains both –NH$_2$ and –OH nucleophiles, it was found that –NH$_2$ donated the electron to the carbon, owing to its stronger nucleophilicity when compared to –OH [35], [36]. As a consequence, the primary amine of IPA (R–NH$_2$) changed into the secondary amine, (R-NH-R), presented by the changes of two small

peaks of IPA spectrum at 3280 and 3325 cm^{-1} into a single peak as observed in the polyol spectrum. The observations were in agreement with the previous research [37].

It can be seen in figure 2 that the peaks of epoxide rings were still detected at the band around 824-830 cm^{-1} for all reaction times. This indicated that not all the epoxy rings were completely opened at these conditions. However, the peaks' intensities were subtly weakened with increasing reaction times. This may be related to the structure of the palm oil itself. Deffense [38] stated that palm oil consists of 48% monosaturated triglyceride and 44% disaturated triglyceride as shown in figure 3. Hence, the distribution of the unsaturated site of the epoxy groups depends on the location of the unsaturated double bond in the molecule. If the epoxy site is located at the middle of fatty acid, it is difficult for IPA molecule to reach the site due to stearic factor. Furthermore, it was agreed that the $-NH_2$ of IPA favoured the ester linkages than the epoxy ring due to steric hindrance governed by the fatty acid chain. Huge changes were seen on the carboxyl group of ester linkages at 1750 cm^{-1}, where the peak intensities were greatly reduced with the prolonged reaction period. At 6 hours and 12 hours, more amides were produced corresponding to high intensities of amide peaks at 1641 cm^{-1} and 1543 cm^{-1}. Further increase of the reaction times (18 hours and 24 hours) resulted in decrease of amide peaks. This reflected the possibility of the amide being degraded at a longer reaction time. This is in agreement with the previous research where they found that at a longer reaction time, the amide formation decreased [39]. The formation of a sharp peak at 757cm^{-1} at a longer reaction time showed the disintegration of methylene bulky groups into individual fatty acid chains after the breaking of ester linkages by $-NH_2$.

3.2 Fourier Transform Infra-Red (FTIR) Analysis

^{1}H NMR was used to elucidate the molecular structure of the polyols. Figure 4 shows the ^{1}H NMR spectra of the EPO meanwhile figure 5 shows the 1H NMR spectra of the polyols. The ^{1}H of epoxy ring appeared at 2.89 ppm (signal 6 of figure 4). After 6h reaction, the epoxy ring (signal 8 of figure5) still be detected but with less intensity indicated the unreacted epoxy remaining in the product.

This also indicate that the NMR analysis is more sensitive in detection of a structure compared to FTIR analysis since NMR spectroscopy can detect very fine structural components [40]. The reduction signal of the epoxy proton and the existence of signal 9 (3.11 ppm) and signal 10 (3.99- 3.44 ppm) which represent the (C$\underline{H}$-NH) and (C$\underline{H}$-OH) respectively in the polyol supports that the ring opening of the EPO can be done with IPA. Since the main purpose of this study was to investigate the availability of IPA as ring opening reagent to EPO, the molar ratio was set to 1:3 (EPO: IPA) because it was expected that there are three epoxy group per molecule of EPO. Meanwhile, the disappearance of the signal 7 and signal 8 of EPO which corresponded to the proton of *sn*-1,3 and *sn*-2 respectively showed that the triglyceride molecule has broken into its individual fatty acid chain and this supported the fact that IPA nucleophile breaks all the ester linkages of the triglyceride. In addition, the presence of glycerol proton (signal 12) in the polyols also marks the findings that the breaking of ester linkages is more favourable in this reaction. Signal 1 in figure 5 correspondence to the terminal (-CH$_3$) proton of fatty acid whereas the signal 2 in figure 5 correspondence to the terminal (-CH$_3$) proton of IPA. These two signals together with signal 15(-NH- amide) of figure 5 also support the findings that IPA has the ability to become as ring opening reagent for EPO.
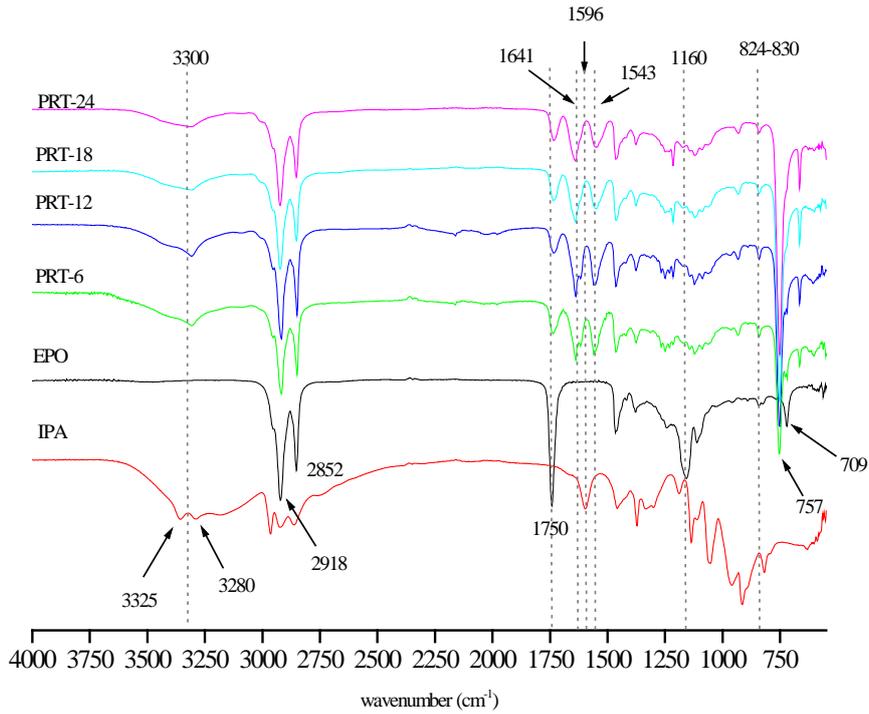
Figure 2: FTIR spectra of polyols at different reaction times from 550-4000 cm^{-1}

Disaturated triglyceride

Monosaturated triglyceride
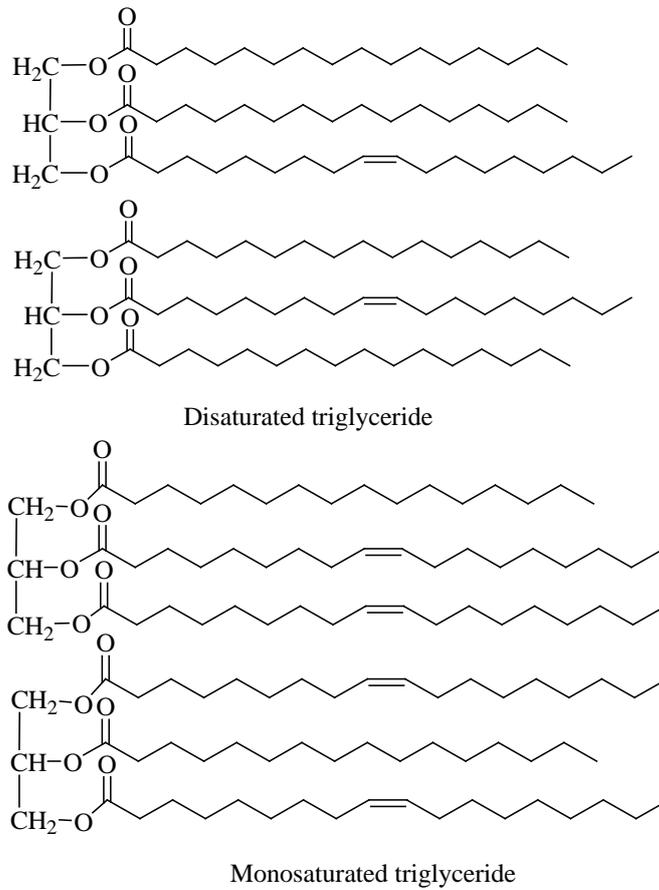
Figure 3: The distribution of unsaturated site in triglyceride of palm oil [38]
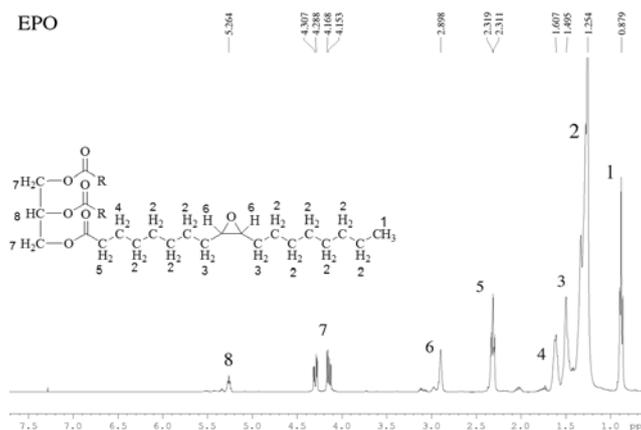
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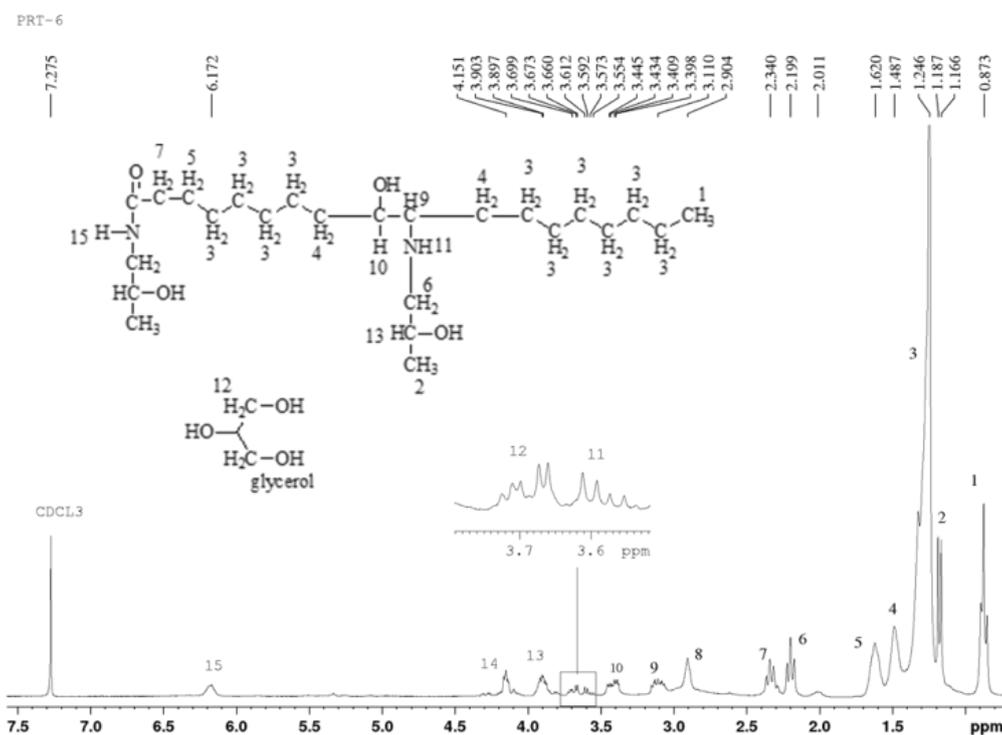**Figure 4:** ^{1}H NMR spectra of epoxidized palm oil (EPO)

Figure 5: ^{1}H NMR spectra of amide polyols

3.3 MALDI-TOF Mass Spectrometry Analysis

The molecular weight of the polyols was determined by comparing the spectra of the polyols with the spectra of matrix used in the analysis. Based on the analysis, most of the fragmented ions are in the sodiated form $[M+Na]^+$ and the polyols obtained in this study have a molecular weight ranging between 300 - 400 Da which is nearly the molecular weight of the proposed polyols in figure 6.

The reduction of this molecular weight after the reaction (MW of EPO=848.75 Da) showed that the triglyceride molecule has broken into its individual fatty acid chains and as expected from figure 6, the final product mainly of polyol B since it was identical to the molecular weight obtained from this MALDI-TOF analysis.

3.4 OH Value

The OH value of the obtained polyols is shown in Table 1. The OH value is defined as the number of milligrams of potassium hydroxide (KOH) equivalent to the hydroxyl content of 1.0 g of polyol. From this OH value, the quantitative value of the amount of hydroxyl groups available for the reaction with isocyanate can be determined [41]. OH value also gives information on the functionality (f_x) of the synthesized polyol provided that the molecular weight, MW is known.

Table 1: Physical characteristic of polyols

Polyols	Reaction Time (h)	Molecular Weight $[M+Na]^+(Da)$	OH Value (mg KOH/g)	Functionality (f_x)
EPO	-	848.75	-	-
PRT-6	6	445	253.91	2
PRT-12	12	445	253.28	2
PRT-18	18	443	251.04	2
PRT-24	24	431	240.91	2

$$\text{Functionality, } f_x = \frac{molecular\ weight}{equivalent\ weight} \quad ......(1)$$

While-,

$$\text{Equivalent weight} = \frac{[56.1][1000]}{OH\ Value} \quad ...... (2)$$

Even though isopropanolamine itself contains –OH groups, it did not affect the functionality of the polyols obtained.

It was expected that higher functionality of polyols (≥ 4) would be obtained when isopropanolamine reacted with monosaturated triglyceride because when isopropanolamine opened the two epoxy ring, it is possible to produce polyol with functionality equals to four. However, it seemed that the –OH group from the isopropanolamine only contributed to the intermolecular H-bonding instead of active OH that would react with isocyanate functionality in the polyurethane synthesis later. However, the functionality was found to be only 2 and this indicated that there were inactive –OH groups in the polyols. In addition, this low functionality of the palm oil polyols is desirable to formulate flexible polyurethane for coating application [41].

The obtained OH value in this study was found to be higher than palm oil polyols obtained using transesterification reaction by [22] and ring opening reaction with phthalic acid by [42]. It was also observed in this study that by prolonging the reaction time, the OH value was found to be decreased.
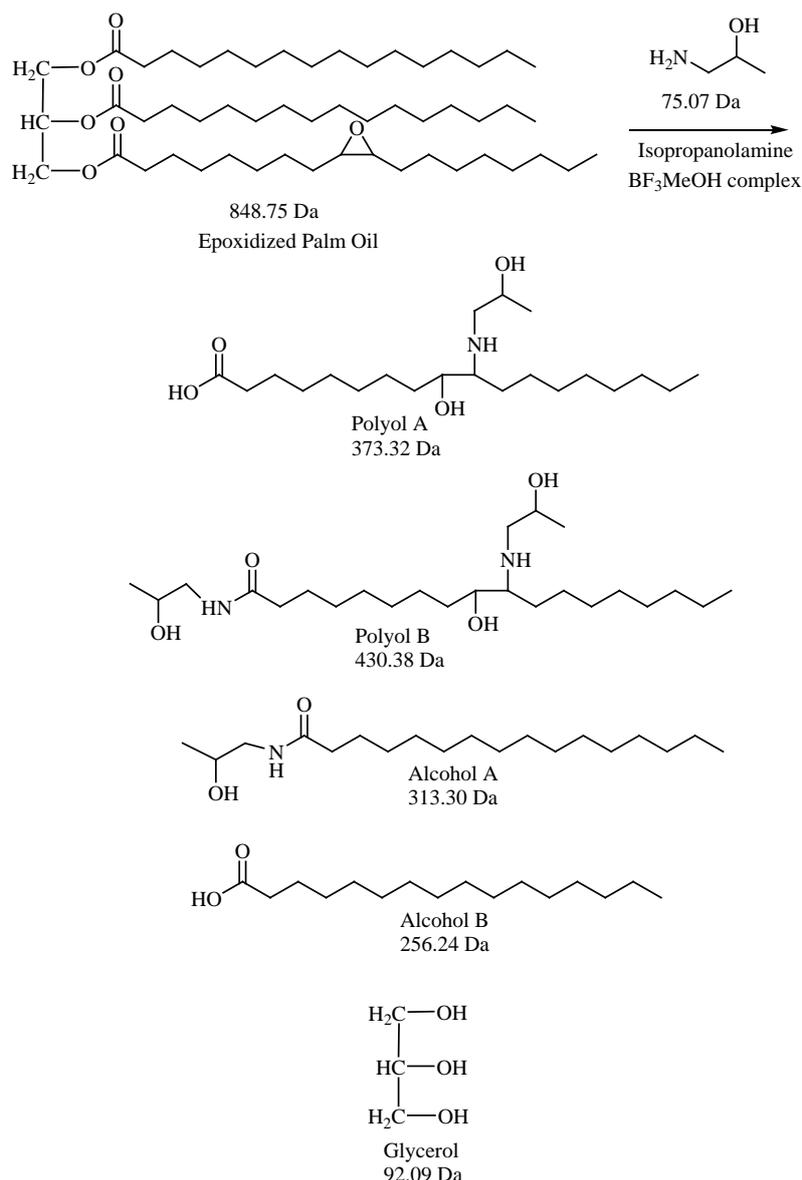
Figure 6: Possible amide polyols obtained from ring opening of epoxidized palm oil with isopropanolamine

4. Conclusion

This study has proven that a bio-based polyol with amide functionality have been successfully synthesized. The reaction time was found to have no significant effect on the characteristic of the polyols. In addition, the presence of hydrogen bonding will influence the hard and soft segment of the corresponding polyurethane synthesized from these polyols. However, the effect of this polyols in polyurethane counterparts has not been study in this paper. It was expected that the presence of amide functionality in the polyols will improve certain properties like antioxidant characteristic of the corresponding polyurethane.

5. Recommendations

Since IPA is not a stereoselective ring opening reagent, a suitable ring opening reagent such as aniline should be

used. This is based on the study that showed aniline was able to open the ring of the epoxide without side reaction and disruption of the triglyceride linkage [40] so that high molecular weight polyols can be obtained.

Acknowledgment

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