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SYNTHESIS OF PALM-BASED POLYOLS: EFFECT OF K10 MONTMORILLONITE CATALYST

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ABSTRACT

Palm-based polyols were synthesised via an alcoholysis process using K10 montmorillonite catalyst. The alcoholysis process was carried out by using epoxidised palm olein and isobutanol. The catalysing ability of K10 montmorillonite catalyst during alcoholysis process was investigated. The process factors affecting alcoholysis, such as reaction temperature and reaction time, were studied. The optimum reaction conditions discovered of 60°C for 2 hr of reaction time were defined for production of palm-based polyol with optimised hydroxyl value, that is, 124.71 mg KOH g^{-1} of sample. Based on the study, K10 montmorillonite catalyst was able to catalyse the alcoholysis process to produce palm-based polyol with a low acid value, low viscosity, low average molecular weight distribution and low functionality which is suitable to be used as a component in coating applications.

Keywords: epoxidised palm-olein, K10 montmorillonite, alcoholysis, palm-based polyol.

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INTRODUCTION

The production of polyols from petro-chemicals requires a great deal of energy, expensive and could adversely affect the environment. Thus, it is desirable to replace petroleum-based polyols with a more versatile, renewable, less costly and more environmental-friendly natural-based polyol (Tran *et al*., 2005). Vegetable oil-based polyols such as palm-based polyol are natural-based polyols that can be used as raw materials for many applications, such as in the making of polyurethane (PU) foams, adhesives and casting resins.

Many conventional methods for the preparation of polyols from natural oils do not produce polyols that have significant content of hydroxyl groups. Furthermore, many available methods in the preparation of polyols from natural oils do not produce polyols with a desirable viscosity (Chasar and Michael, 2003). Therefore, the alcoholysis process deserves special attention because it opens up a wide range of feasible reactions that take place under moderate reaction conditions, due to the high reactivity of the oxirane ring. Rainer *et al*. (1997) reported work on natural-based polyols by ring-opening reactions of epoxidised natural oils with alcohols, glycols or higher polyols, amines or alkanolamines. The ring-opening reaction was an acid catalysed process and did not require the use of solvents.

On the other hand, Petrovic *et al*. (2000) described a process that converts natural oils into polyols by epoxidising the oil with fluoboric as an acid catalyst, and then hydroxylated the epoxidised oil to a polyol using more fluoboric acid, together with alcohol or mixture of alcohol and water. However, this process is not ideal, since fluoboric acid is expensive; its high reactivity could be hazardous and the reaction is highly exothermic. Nicolas *et al*. (2003) described a process for obtaining oleochemical polyols from natural oils and fats, whereby, a planar Lewis acid was used in the alcoholysis process. The process generally required a large amount of energy as the reaction temperature applied was normally higher than 200°C. However, the yield of the desired products was predicted to be very low, because, most of the substrates were converted to side products. This occurred due to the extreme conditions used such as high temperature and the impure epoxidised oil used.

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In the synthesis of natural products from triglycerides such as palm-based polyols, reactions usually take place at the double bond. The double bond is first converted to an epoxy ring, followed by alcoholysis. Boron trifluoride etherate is the most commonly used Lewis acid for this purpose. The currently used process of producing palm-based polyol utilises homogeneous catalysts systems that always require neutralisation of the product at the end of the reaction (Hazimah *et al*., 2008). On the other hand, uses of solid (heterogeneous) catalysts have increased in importance since they can simplify the process and provide a cleaner process than that using homogeneous catalyst. By using K10 montmorillonite catalyst (heterogeneous catalyst) in this study, the possibility of obtaining a palm-based polyol with a special characteristic was investigated. The K10 montmorillonite catalyst is a type of clay which is sticky and plastic-like when exposed to moisture, but becomes hard and cohesive when dry. It consists of crystalline hydrous aluminosilicates and various other cations. This clay catalyst contains both Bronstëd and Lewis acid sites which makes it very attractive as a catalyst for industrial reactions (Mauricio *et al*., 2001; Gopalpur, 2002).

Clays and clay-based catalysts are among the viable alternatives available for green synthetic methods which have attracted significant attention due to their extremely versatile properties (Sujaya and Béla, 2008). Using K10 montmorillonite as catalyst has many advantages including strong acidity, non-corrosivity, recyclability, low cost, mild reaction conditions, high yields and selectivity towards the desired product.

This study investigates the catalysing ability of the heterogeneous catalyst, that is, K10 montmorillonite during the alcoholysis process and the effect of reaction temperatures and reaction times on the characteristics of palm-based polyols. The optimum reaction conditions using K10 montmorillonite catalyst for alcoholysis is also investigated.

MATERIALS AND METHODS

Materials

The epoxidised palm olein (EPO) used in this study was obtained from the Malaysian Palm Oil Board (MPOB) polyol pilot plant. The pH of EPO was 5. The K10 montmorillonite clay catalyst was purchased from Fluka-Chemica (Germany). It was used without further modification. Isobutanol of analytical reagent grade was purchased from Fisher Scientific (United Kingdom).

Methods

Preparation of palm-based polyols. Palm-based polyols were prepared via an alcoholysis process using EPO as the starting material. Reactions were carried out in a 500 ml reaction flask placed in an oil bath held at 40°C, 50°C and 60°C respectively. A polytetrafluoroethylene (PTFE) coated stainless steel shaft, and an anchor flat propeller were used for stirring. The 162.14 g of isobutanol and 10 g of K10 catalyst were mixed for 15 min until the desired mixture temperatures of 40°C, 50°C and 60°C were achieved. The isobutanol was used in excess. Then, 100 g of EPO having an epoxy content of 3.5% were added into the reaction flask.

The reactions were allowed to take place under continuous stirring for between 1 to 6 hr. Samples of the reaction mixture were taken every hour during the reaction in order to monitor the progress of the reactions through oxirane oxygen content (OOC) analysis. The reaction process was considered complete when the OOC of the EPO was less than 0.5%.

Separation and distillation of reaction mixtures. Filtration of the reaction mixture was carried out manually using Watmann filter paper No. 5 that could separate the product (liquid) from the solid catalyst. The remaining isobutanol in the filtered reaction mixture was stripped off via vacuum distillation. A 250 ml one-necked round bottom flask containing the filtered reaction mixture (185.20 g) was placed in an oil bath, equipped with a reflux condenser and a vacuum pump. A magnetic bar was used for stirring. The sample was heated to 115°C, that is, higher than the boiling point of isobutanol and the vacuum pressure was set at 190 to 195 mbar. The isobutanol (95.23 g) was distilled off.

Characterisation of Palm-based Polyols

The OOC was determined for EPO (starting material) and the reaction mixture (reaction product) following the American Oil Chemists Society (AOCS) Official Method Cd 9-57 (AOCS, 2007). The acid value (AV) is defined as the amount of potassium hydroxide in milligrams required to neutralise the free acid in 1 g of sample. It was analysed according to AOCS Official Method Te 2a-64. The hydroxyl values (OHV) and the iodine values (IV) were determined according to the AOCS Official Method Cd 13-60 (pyridine-acetic acid anhydride titration method) and the AOCS Official Method Cd 1d-92 (cyclohexane-acetic acid titration method), respectively. The pH of the products were determined using pH paper (pH 0-14 Universal Indikator by Merck Company). The viscosity was determined using a Brookfield Digital Rheometer, Model DV-III +. The Fourier transform infrared (FTIR) spectra were determined using a Nicolet, Magna-IR 550 Spectrometer, Series II. The infrared spectra were recorded in the range of 400 to 4000 cm^{-1} wavenumber. The molecular weight distribution was measured using a Varian PL-gel permeation chromatography (GPC) 50 Plus equipped with a differential refractive index (DRI)/viscometer which was a combined detector. The molecular weight of the samples were analysed using a PLgel Mixed D column. Tetrahydrofuran (THF) stablised with 250 ppm butylated hydroxytoluene (BHT) was used as the eluent and the flow rate was fixed at 1.00 ml min^{-1}. The molecular weight distributions were obtained based on a calibration curve generated from polystyrene (PS) standards. The PS standards for PLgel Mixed D column used in this study comprised 10 vials with molecular weights ranging from 580 to 275 300 Daltons. For calibration purposes, a concentration of 2 mg ml^{-1} of each of the PS standards was prepared by dissolving it in the THF before analysed it.

The epoxidised palm olein (EPO) was characterised prior to the experiments. *Table 1* shows the properties of the analysed EPO.

TABLE 1. PROPERTIES OF EXPOXIDISED PALM OLEIN

Parameters	Value
pH	5
Colour	Yellow (visual)
Acid value (AV)	0.4 mg KOH g^{-1} of sample
Iodine value (IV)	0.8 g I_2 100 g^{-1} of sample
Oxirane oxygen content (OOC)	3.5%
Viscosity at 25°C	126.2 mPa.s

RESULTS AND DISCUSSION

In this study, isobutanol was selected as a suitable alcohol, based on a previous report by Luis *et al.* (2005) on the addition of isobutanol to epoxidised methyl oleate. According to their report, isobutanol was categorised as a β-branched alcohol that will give a high yield and good selectivity of hydroxyl-ether and hydroxyl-ester as end products in the reaction. The main difference in this study is that K10 montmorillonite catalyst was used in the alcoholysis of epoxidised palm olein.

During the reaction, the ring-opening of epoxide takes place through the cleavage of one of the carbon-oxygen bonds. Generally, a two-step reaction is involved, with the addition of nucleophilic alcohol to the epoxide. Firstly, the epoxide is activated by a proton supplied by a strong protic nucleophile or by a Bronstëd acid catalyst present in the reaction mixture, then the activated epoxide undergoes nucleophilic attack by the nucleophile in a bimolecular nucleophilic substitution (SN2) mechanism as shown in *Figure 1*.

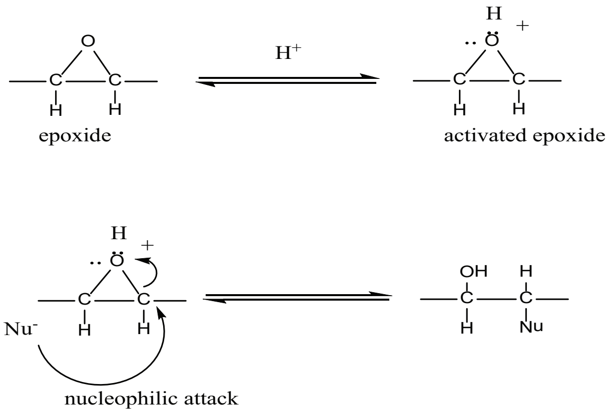

Figure 1. General mechanism for the addition of nucleophilic alcohol to epoxide.

The K10 montmorillonite catalyst provides the Bronstëd acid sites involved in the catalysed reaction. These sites become activated by the dissociation of the intercalated water molecules coordinated to cations such as Al^{3+}, Fe^{3+} and Mg^{2+} in the catalyst structure. The catalyst should also be able to provide enough accessibility of the acidic centres to the bulky epoxidised palm olein molecule in order to promote the reaction.

The EPO in this study contained 0.16% water by weight. A low percentage of water was crucial in the reaction, as it mixed with alcohol in the reaction media. This mixture contributed to defining the polarity of the reaction media and limited the solubility of EPO and polyol in the reaction mixture. Therefore, it could help to promote the main reaction between the epoxy groups and alcohol, and decreased undesirable side reactions. This statement is supported by the FTIR spectra.

The Effect of Reaction Temperature on Prepared Palm-based Polyol Properties

According to Luis *et al.* (2005), the reaction temperature plays a crucial role on affecting the properties of the desired product and by-product formation. Therefore, a suitable reaction temperature is very important to ensure that the possibility of by-product formation is minimised. Three different reaction temperatures were investigated in order to study the effect of temperature to the polyol properties, *i.e.*, 40°C, 50°C and 60°C for 6 hr of reaction time. The palm-based polyols prepared were denoted by P(A)40(6), P(A)50(6) and P(A)60(6), respectively.

Oxirane Oxygen Content

During the alcoholysis reaction, small amounts of reaction mixture were collected hourly for OOC determination. The changes in OOC during the alcoholysis reactions for all the sample mixtures at different reaction temperatures are shown in *Figure 2*. From the beginning to 1 hr of reaction time, the OOC were drastically reduced by up to 90% and then gradually decreased, as the reaction time increased for all the alcoholysis reactions. At a higher temperature, that is, 60°C, the oxirane ring opened up faster than at reaction temperatures of 40°C and 50°C, as shown by the drastic reduction of OOC during the alcoholysis (*Figure* 2). The faster the reaction, the opportunity for cross-linking to occur was less as in case of the reaction of the epoxide with the polyol product. Therefore, the product obtained will have less cross-linking and a minimum by-product formation.

The yield of the obtained products (prepared palm-based polyols) was more than 90% and had a moisture content of less than 0.2%. The pH of all the prepared polyols was between pH 5 to pH 6.

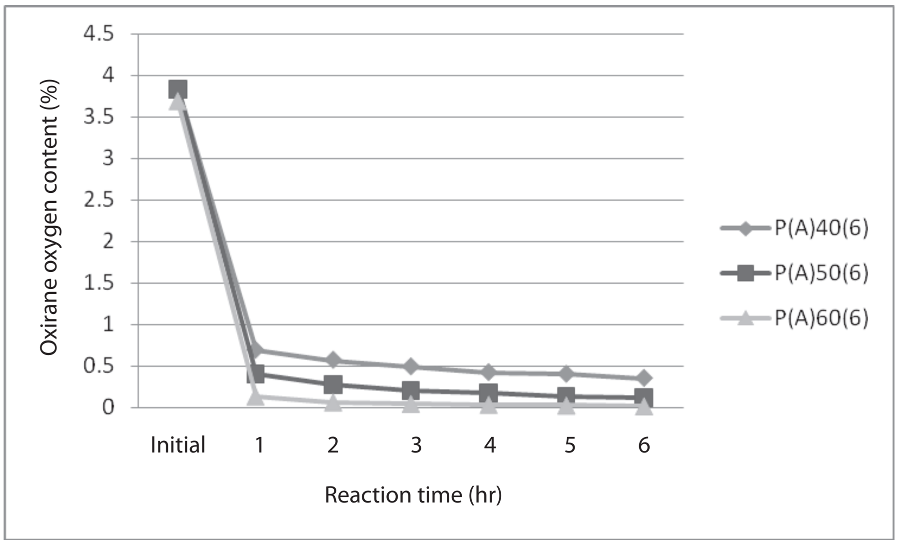

Figure 2. Changes in oxirane oxygen content during the alcoholysis reactions.

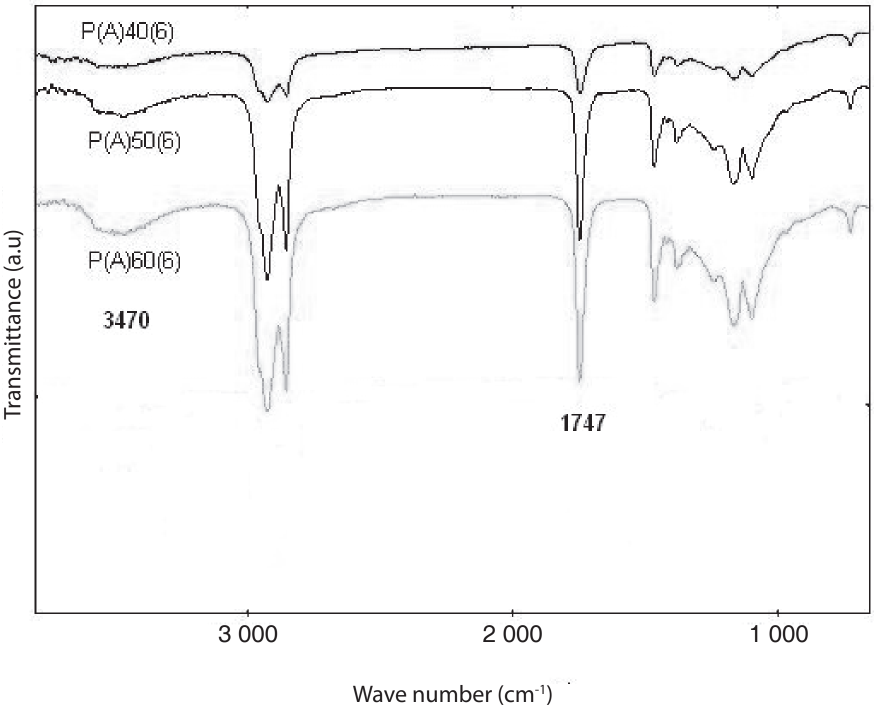

Figure 3. The Fourier transform infrared spectra of prepared palm-based polyols.

Fourier Transform Infrared Spectroscopy

The spectra of the prepared palm-based polyols determined by the FTIR technique is shown in *Figure 3*. All spectra were recorded between 500 to 4000 cm^{-1}, where the same patterns of spectra were obtained for all prepared palm-based polyols. These spectra described the polyol's molecules which had adsorbed specific frequencies that displayed the characteristics of the palm-based polyol structure. All the samples showed the presence of hydroxyl absorption at about 3470 cm^{-1} and the absence of an epoxide group at 820 to 860 cm^{-1}. The characteristics of all prepared palm-based polyols also indicated the presence of the ester group by the appearance of sharp peak at 1730 to 1750 cm^{-1}. Based on these spectra, the reactions can be considered successful without undesirable side-reactions, where the absorption peak of the ketone group between 1705 to 1725 cm^{-1} was not observed.

Acid Value

Figure 4 shows the AV of the prepared palm-based polyols. One of the main factors that might contribute to the high AV in these polyols was hydrolysis. Basically, the hydrolysis process will increase the free fatty acid content in the polyol. Among all the prepared palm-based polyols, P(A)60(6) gave the lowest AV, indicating that at high temperature, the tendency of hydrolysis process to occur was limited. The neutralisation process is one of the processes required in the production of polyol using a homogeneous catalyst. Hydrolysis occurred rapidly during the neutralisation process and hence contributed to a high AV in the final product. Meanwhile, in this study, the neutralisation process was not required because a low AV polyol was obtained.

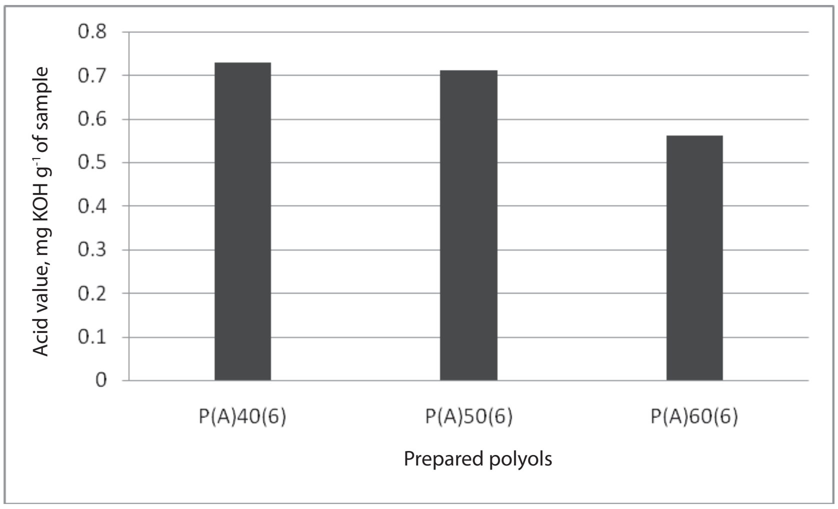

Figure 4. Acid value of prepared palm-based polyols.

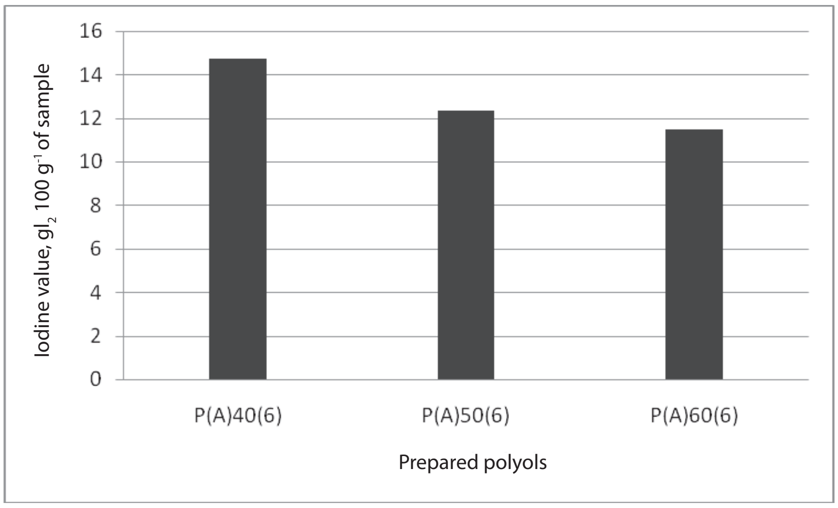

Figure 5. Iodine value of prepared palm-based polyols.

Iodine Value

Palm oil is in fact considered as a natural oil that has a low IV compared to other natural oils such as soyabean oil and sunflower oil. The IV content describes the unsaturation content in the polyol. Logically, low IV will lead to the formation of polyols that contain low OHV, and thus, lower viscosities of polyols are created. *Figure 5* shows the IV of the prepared palm-based polyols. In this study, the unsaturation decreased as the reaction temperature increased. As discussed earlier, at the 60°C reaction temperature, the possibility for the side reaction occurring was low compared to the reactions carried out at 40°C and 50°C. The side reaction may contribute to the formation of unsaturated carbon chains. Generally, the unsaturation in the polyol products is higher than the unsaturation in the EPO. As reported by Petrovic *et al*. (2002), the excess of alcohol present in the reaction was important to prevent polymerisation, which can cause the formation of branching polymer in the product. In this study, excess alcohol was used.

Hydroxyl Value

The reactive group for polyol is the hydroxyl group (OH) and the concentration of OH is measured by the hydroxyl value (OHV). The OHV of the prepared palm-based polyols is shown in *Figure 6*. As the temperature of the reaction increased, the OHV also increased. The OHV of the prepared palm-based polyols varied with the IV as described earlier, where the OHV increased as the IV decreased.

Viscosity

Figure 7 shows the viscosity of prepared palm-based polyols at 25°C. All prepared palm-based polyols exhibited low viscosity, that is, below 1000 mPa.s. The viscosity of these polyols was low because the applied experimental method in this

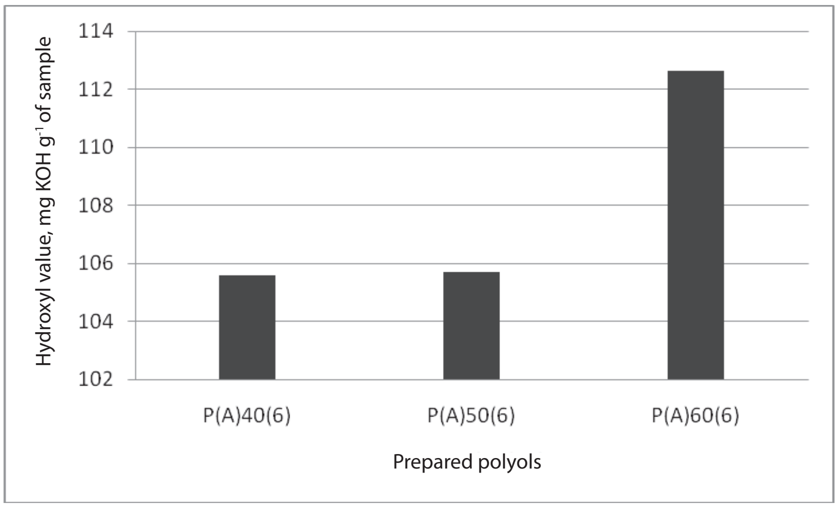

Figure 6. Hydroxyl value of prepared palm-based polyols.

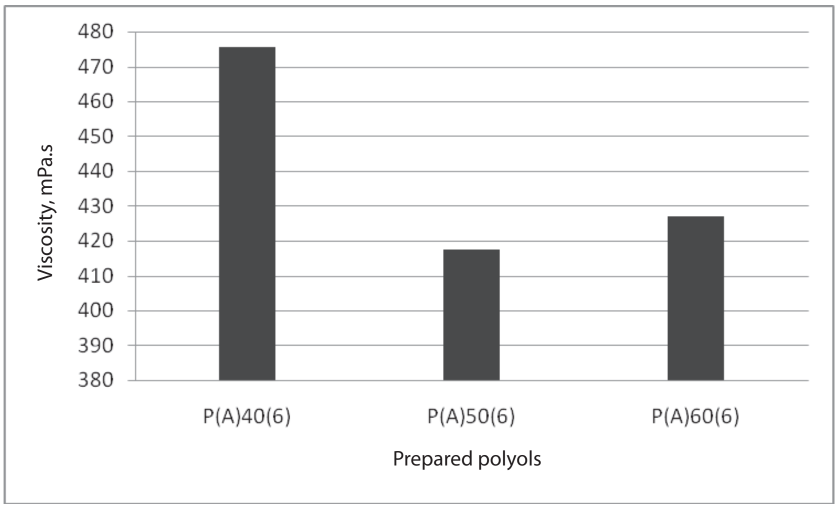

Figure 7. Viscosity of prepared palm-based polyols.

study had produced less side reactions such as polymerisation or cross-linking that contributed to a high viscosity.

The average molecular weights of the prepared palm-based polyols were in the range 1000 to 2200 Daltons, while polydispersities were less than 2, which indicated that the polyols system were homogeneous. Lower polydispersity will lead to lower viscosity polyols. Polyol functionality is the number of reactive hydroxyl groups per molecule of polyol. The functionality can be calculated from the average molecular weight distribution and OHV of the polyol. The functionalities of the prepared palm-based polyols were 2 and this were considered low.

The Effect of Reaction Time on Prepared Palm-based Polyol Properties

The reaction time is one of the reaction parameters which plays an important role to establish an ideal reaction system, that leads to the selective addition of alcohols to epoxidised oils, under as mild as possible working out conditions. In order to study the effect of reaction time on the polyol properties, six experiments with different reaction times were carried out, *i.e.,* 1, 2, 3, 4, 5 and 6 hr respectively. The selected reaction temperature was 60°C. Based on the previous results, the palm-based polyol prepared at 60°C gave the best properties in terms of AV, IV and OHV among others. The prepared palm-based polyols were coded P(A)60(1), P(A)60(2), P(A)60(3), P(A)60(4), P(A)60(5) and P(A)60(6) for 1, 2, 3, 4, 5 and 6 hr of reaction, respectively.

The OOC of the reaction mixtures determined hourly reduced as the time of reaction increased. The OOC decreased drastically from the beginning to 1 hr of reaction time. It was observed that more than 90% of the oxirane ring opened within 1 hr of reaction time. As the reactions progressed beyond 1 hr, a slower reduction of OOC was observed. The yield of the obtained products (prepared palm-based polyols) was more than 90%.

The FTIR spectra of all prepared palm-based polyols were similar to the previously described spectra (*Figure 3*). Their moisture contents were in the range of 0.04% to 0.10%, with pHs between 5 and 6. It is very important to ensure that the pH of the polyol product is neutral, otherwise, it will affect its stability and also its shelf-life. No significant changes in AV, IV, OHV and viscosity (at 25°C) of the prepared palm-based polyols were observed as the time of reaction increased, as tabulated in *Table* 2. The highest (optimum) OHV was obtained at 2 hr of reaction time.

The average molecular weight distributions of the prepared palm-based polyols were in the range of 1000 to 2200 Daltons with polydispersities less than 2 and functionalities in the range of 2 to 3.

The colour of all the prepared palm-based polyols was brown. As reported by Gibson (1990), the brownish colour of the product was caused by atmospheric oxidation. In this study, the atmospheric oxidation possibly occurred during the filtration process. In order to avoid this atmospheric oxidation, the reaction mixtures needed to be filtered as quickly as possible. It could be done by Buchner filtration.

CONCLUSION

The alcoholysis of epoxidised palm olein using K10 montmorillonite as a catalyst was succesfully carried out to produce palm-based polyol. The products obtained were confirmed as palm-based polyol when the absorbed frequencies of the sample's molecules showed the characteristics of the palm-based polyol structure which have been detected in FTIR analysis. It also has been identified by OHV analysis which showed the formation of OH (reactive) groups in the samples. The yield of final products (palm-based polyols) was more than 90%. The prepared palm-based polyol with optimised OHV was produced using a 60°C 2 hr reaction time. Based on this study, it is confirmed that heterogeneous catalyst (K10 montmorillonite)

TABLE 2. THE PROPERTIES OF PREPARED PALM-BASED POLYOLS AT DIFFERENT REACTION TIMES

Samples	Acid value (mg KOH g^{-1} of sample)	Iodine value ($g\ I_2$ 100 g^{-1} of sample)	Hydroxyl value (mg KOH g^{-1} of sample)	Viscosity (at 25°C, mPa.s)	Mw (Daltons)
P(A)60(1)	0.59	11.79	109.85	470.77	1 419
P(A)60(2)	0.60	11.88	124.71	417.39	1 454
P(A)60(3)	0.61	13.07	124.15	475.63	1 747
P(A)60(4)	0.59	12.30	115.78	456.21	2 207
P(A)60(5)	0.57	11.46	121.64	359.15	1 815
P(A)60(6)	0.55	11.48	112.63	427.09	1 898

Note: Mw = molar mass averages of the weight.

is able to convert epoxidised palm oil to palm-based polyol having low acid value, low viscosity, low molecular weight distribution and low polydispersity index with a functionality in the range of 2 to 3. Palm-based polyol with a low molecular weight distribution and a functionality of 2 can be used in coating applications.

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