

PHYSICOCHEMICAL PROPERTIES OF PALM OLEIN-BASED POLYOLS PREPARED USING HOMOGENEOUS AND HETEROGENEOUS CATALYSTS

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ABSTRACT

Research and development of palm-based polyols have been intensively carried out to improve their features and characteristics appropriate for their required applications. The physicochemical properties of palm olein-based polyols prepared using homogeneous ($\text{BF}_3 \cdot \text{Et}_2\text{O}$) and heterogeneous (K10 montmorillonite) catalysts in the ring-opening reaction of epoxidised palm olein (EPOo) were compared. Mono alcohols, i.e., methanol and isobutanol were selected as ring opening reagents. The formation of palm olein-based polyols was confirmed by the oxirane oxygen content (OOC), Fourier transformed infrared (FTIR) spectra and hydroxyl value (OHV) determinations. Based on the observation, the molecular weight (MW) of reagent used in the epoxide ring-opening reaction affected the viscosity of the obtained palm olein-based polyols. High oligomerisation was detected in palm olein-based polyol prepared using a homogeneous catalyst. The composition of hydroxyl monomer, dimer, trimer and tetramer in palm olein-based polyols were obtained from Gel Permeation Chromatography (GPC). Palm olein-based polyols prepared using heterogeneous catalyst exhibited the highest mono composition compared to other palm olein-based polyols. Heterogeneous catalyst provided palm olein-based polyols with low viscosity, less oligomerisation and functionality close to theoretical as compared to homogeneous catalyst. This finding can be used as a guideline in the synthesis of polyols with desired properties for targeted applications.

Keywords: homogeneous and heterogeneous catalysts, palm olein-based polyol, ring-opening reaction.

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INTRODUCTION

A growing worldwide research effort is driven by concern about renewable resources and the environment. Malaysia's oleochemical industry is mostly derived from vegetable oil, i.e., palm oil and palm kernel oil, as the major feedstocks (Parveez

et al., 2020). Vegetable oil-based intermediates and products are continuously being developed for valuable polymeric materials as they are known to be cheap in price, abundant supply, environmental-friendly and provide excellent properties (Flora, 2014; Lin *et al.*, 2008; Narine *et al.*, 2007a). The productions of polyols from vegetable oil have been the subject of many studies. Several studies have reported their methods for the preparation of vegetable oil-based polyol such as hydroformylation, transesterification and ozonolysis (Abraham, 2012; Arniza *et al.*, 2015; Narine *et al.*, 2007b). The most widely practiced

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methods are epoxidation followed by a ring-opening reaction which has been identified as the safest route and most economical (Armylisas *et al.*, 2017; Chasar *et al.*, 2005; Hazimah *et al.*, 2011; Silverajah *et al.*, 2012; Siti Munira *et al.*, 2013; Tuan Ismail *et al.*, 2018a).

Alcohols were reported as the best ring-opening reagent for synthesis of polyols where secondary and primary hydroxyl groups were created when using mono alcohols and diols, respectively (Li *et al.*, 2015; Tuan Ismail *et al.*, 2018a; 2018b). In the study by Tuan Ismail *et al.* (2018a), the effect of various nucleophiles (ring-opening reagents) on oligomeric composition and properties of polyols derived from epoxidised palm olein (EPOo) was investigated. The polyols were synthesised using homogeneous catalyst, *i.e.*, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ and the mole ratio of EPOo to nucleophiles was 1:1. Lower degree of oligomerisation was observed in polyols prepared with mono alcohol compared to polyols made with diols. In this study, the oxirane ring of EPOo was opened by mono alcohols such as methanol and isobutanol to form palm olein-based polyols with secondary hydroxyls similar to report by Tuan Ismail *et al.* (2018a). Methanol and isobutanol were selected as ring-opening reagents because of their promising characteristics. Methanol is the cheapest and simplest alcohol, which leads to an easier reaction, while isobutanol contains a branch in β -position, which forms steric hindrance in the reaction and enables the formation of the compound with desired properties.

A catalyst is a substance that increases the rate of a chemical reaction without being consumed and not permanently involved in the reaction process (Clark, 2013; Farnetti *et al.*, 2009; Johannes and David, 2012; Piet, 2004). The catalyst is added into the reaction mixture to reduce the activation energy and thus, increases the reaction rate. Acids or alkalis can be used to catalyse the ring-opening reaction. In the presence of alkaline catalysts, for example sodium methylate and caustic soda, they will react with water and reduction of catalytic activity occurs. The most important factor that influences the success of ring-opening reaction catalysed by alkali is that the oil must contain a total of zero free fatty acids (Seigfried *et al.*, 2002).

Acidic catalysts in the form of homogeneous and heterogeneous catalysts were used in the study. Both catalysts possess some advantages and disadvantages (Table 1). A homogeneous catalyst is a class of catalysis in which the catalyst occupies the same phase as the reactants that allow a great interaction with the reaction mixture by affecting their bond polarisation. The degree of collisions between catalyst and reactants is high because the catalyst is uniformly dispersed in the reaction mixtures. The difficulty of homogeneous catalyst recovery from the reaction medium becomes

one of their major drawbacks. Meanwhile, heterogeneous catalyst occupies a different phase from the reactants. In order to speed up the reaction, the reactant molecules must collide with proper orientation. A heterogeneous catalyst will align molecules in the right way, so it is easier for them to combine and react. The main advantage of heterogeneous catalyst over the homogeneous catalyst is that it makes the separation and re-utilisation of heterogeneous catalyst cheaper and easier. The availability of surface area of the catalyst is one of the limitations of a heterogeneous catalyst. Once the surface of the catalyst is saturated with reactant molecules, the reaction cannot continue until products leave the surface, and some space opens up again for a new reactant molecule to attach (Anonymous, 2019; Farnetti *et al.*, 2009).

The common homogeneous catalysts that have been used in the ring-opening reaction of epoxidised oils to produce polyols are formic acid, sulphuric acid, phosphoric acid, pentamethyldiethylenetriamine, acid-blocked version of 70% bis(dimethylaminoethyl)ether, 30% dipropylene glycol (DABCO® BL 17), *p*-toluenesulfonic acid monohydrate, heat-activated catalyst based on 1,8-diaza-bicyclo (5,4,0) undecene-7 and boron trifluoride diethyl etherate ($\text{BF}_3 \cdot \text{Et}_2\text{O}$) (Flora, 2014; Hazimah *et al.*, 2011; Lozada *et al.*, 2009; Siti Munira *et al.*, 2013; Tuan Ismail *et al.*, 2018a). Lewis acid in $\text{BF}_3 \cdot \text{Et}_2\text{O}$ also has been reported to play a role in organic synthesis such as in accomplishing esterification of acids, hydroxylation of the double bond, cleavage of epoxides and many other cyclisation reactions (Banerjee *et al.*, 2019). $\text{BF}_3 \cdot \text{Et}_2\text{O}$ was practically used in the ring-opening reaction of EPOo with alcohols to produce palm-based polyols as reported by Hazimah *et al.* (2011) and Tuan Ismail *et al.* (2018a) in their previous studies. Heterogeneous catalysts such as metal salts of carboxylic acids, acid resins copolymer styrene + 20% divinylbenzene (Amberlyst 15), copolymer styrene + 8% divinylbenzene (Amberlite IR-120), copolymer styrene + 2% divinylbenzene (Dowex 50X2) and copolymer of tetrafluoroethene + perfluoro-2-(fluorosulfonylethoxy) propylvinyl ether entrapped on silica (SAC13) and various types of clays (Nafion-H, K10 montmorillonite, Retrol F, Y zeolite, H-Y zeolite and KSF/O) were also being used in the ring-opening reaction of epoxidised oils (Chasar *et al.*, 2005; Fási *et al.*, 2004; Norhayati *et al.*, 2013; 2016; 2018; Rios *et al.*, 2003; 2005).

Based on many literatures that reports on the ring-opening reaction of epoxidised oil in the presence of various types of catalysts, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ and K10 montmorillonite catalysts, which represent homogeneous and heterogeneous catalysts, respectively, were used in the study.

There are limited reports in the literature on the production of palm-based polyols using homogeneous and heterogeneous catalysts and comparison of their properties. This article will highlight the physicochemical properties of palm olein-based polyols obtained using homogeneous and heterogeneous catalysts in the epoxide ring-opening reactions.

TABLE 1. ADVANTAGES AND DISADVANTAGES OF HOMOGENEOUS AND HETEROGENEOUS CATALYSTS

Item	Homogeneous	Heterogeneous
Active centers	All atoms	Only surface atoms
Selectivity	High	Low
Structure	Defined	Undefined
Applicability	Limited	Wide
Catalyst separation	Expensive/tedious	Cheap/easy
Cost of catalyst losses	High	Low

Source: Ali *et al.* (2010).

MATERIALS AND METHODS

Materials

The EPOo was obtained from Malaysian Palm Oil Board (MPOB) polyol pilot plant with the moisture content of 0.04%-0.05%, iodine value (IV) of 0.8-1.0 g I₂ 100 g⁻¹, oxirane oxygen content (OOC) of 2.9%-3.2%, acid value (AV) of 0.4-0.6 mg KOH g⁻¹ and viscosity of 120-140 mPa.s at 25°C. The EPOo was produced by reacting refined, bleached and deodourised (RBD) palm olein with mixture of formic acid and hydrogen peroxide. Acetone and isobutanol (analytical reagent grade) were purchased from Fisher Scientific, United Kingdom. Methanol (analytical reagent grade) was purchased from System, Malaysia. Boron trifluoride diethyl etherate, BF₃.Et₂O (50% purity) was obtained from Merck, Germany. K10 montmorillonite was obtained from Fluka-Chemica, Germany. Sodium carbonate (Na₂CO₃) and sodium chloride (NaCl) (analytical reagent grade) were purchased from Mallinckrodt Chemicals, USA and System, Malaysia, respectively. Distilled water was used to prepare NaCl and Na₂CO₃ solutions. All materials were used without further modification.

Methods

Syntheses of palm olein-based polyols in the presence of homogeneous catalyst. Reactions were carried out using a 2 L water-jacketed glass reactor equipped with a mechanical stirrer (a flat anchor propeller), thermocouple, dropping funnel and

circulating water bath. A calculated amount of EPOo was placed in the glass reactor and preheated to 60°C under continuous stirring. A freshly prepared mixture of BF₃.Et₂O and isobutanol were added dropwise into the preheated EPOo. The mole ratio of EPOo to isobutanol was 1:10 and 1.0% BF₃.Et₂O catalyst was used in the study. The reaction mixture was withdrawn for OOC analysis in every 30 min interval until the final OOC was less than 0.1%.

The obtained polyol was washed and neutralised at 60°C-65°C with 1% NaCl solution, followed by 0.5% Na₂CO₃ solution. The washing process was repeated a few times until the pH of the polyol was in the range of 6 to 8 (initial pH of polyol was 2). The pH of polyol was measured using pH paper (MColorpHast™). The final washing process was carried out with 1% NaCl solution in order to remove the residual carbonate in the polyol. The pH of the final polyol product was 7. The washed and neutralised polyol was dried under a vacuum of 9 mbar at 90°C-100°C until the moisture content of the obtained polyol was less than 0.05%.

The method described above was applied for the synthesis of EPOo with methanol at 40°C-60°C. The reaction set-up was equipped with a condenser and a chiller to prevent the evaporation of methanol during the reaction. The obtained polyols were designated as PI-HO and PM-HO for polyols prepared with isobutanol and methanol, respectively. The yields of the both polyols were >80 wt% based on the mass of initial EPOo.

Syntheses of palm olein-based polyols in the presence of heterogeneous catalyst. Reactions were carried out using a 500 mL three-necked reaction flask equipped with a mechanical stirrer (a flat anchor propeller) and a thermometer. A calculated amount of K10 montmorillonite catalyst was pre-mixed with isobutanol at 60°C for 10-15 min before the addition of EPOo. The mole ratio of EPOo to isobutanol was 1:10 and 10% of K10 montmorillonite catalyst was used in the reaction following the optimum reaction parameter reported by Norhayati *et al.* (2013). The excess of isobutanol will ease the pre-mixing process between K10 montmorillonite catalyst and isobutanol. It will also avoid the formation of thick slurry of the mixture. Therefore, the activation of the K10 montmorillonite catalyst can occur effectively. The reaction was performed under continuous stirring. The OOC of the reaction mixture was monitored every 30 min and the reaction was stopped when the OOC reached below 0.1%. The obtained reaction mixture was cooled down to room temperature (23°C).

Acetone was added into the reaction mixture to ease the separation of the K10 montmorillonite

catalyst from the reaction mixture. The catalyst can be separated easily from the less viscous reaction mixture by using vacuum filtration (Whatman filter paper No. 5). The used K10 montmorillonite catalyst can be recycled and reused in the alcoholysis of EPOo to produce palm olein-based polyol (Norhayati *et al.*, 2018). The obtained filtrate underwent distillation process to remove the excess alcohol and acetone from the reaction product. The set-up for the distillation process consisted of a 1000 mL three-necked round bottom flask containing the filtrate. The flask was placed in an oil bath, equipped with a condenser and a vacuum pump. A stirring process was carried out by using a magnetic stirrer. Within 5-6 hr at 115°C and 70-80 mbar of vacuum pressure, the excess alcohol and acetone were successfully removed from the reaction product. The reaction product was dried under vacuum (9 mbar) at 115°C until the moisture content of the reaction product was less than 0.05%. The yield of the final polyol was >90 wt% based on the mass of initial EPOo.

The method was also applied for the synthesis of EPOo with methanol at various reaction temperatures, *i.e.*, 40°C, 50°C and 60°C. The reaction set-up was equipped with a condenser to prevent the loss of methanol during the reaction. The ring-opening reaction of EPOo and methanol was only observed at 60°C with a slow reduction of OOC as monitored up to 23 hr of reaction time. No reaction was observed at 40°C and 50°C. The obtained polyols were labeled as PI-HE and PM-HE for polyols prepared with isobutanol and methanol, respectively. Idealised reaction scheme for the ring-opening reaction of EPOo with alcohols in the presence of homogeneous and heterogeneous catalysts is shown in *Figure 1*.

Characterisation of Palm Olein-based Polyols

The Fourier transformed infrared (FTIR) spectra of palm olein-based polyols were recorded using Perkin Elmer FTIR Spectrum 100 equipped with Universal ATR Attachment in the 650-4000 cm^{-1} wavenumber range. The OOC of the reaction mixture and palm olein-based polyol was determined following the AOCS Official Method Cd 9-57 (AOCS, 2007). The hydroxyl value (OHV) and AV were determined according to the AOCS Official Method Cd 13-60 (pyridine-acetic anhydride titration method) and AOCS Official Method TE 2a-64, respectively. The IV was analysed according to AOCS Official Method Cd 1d-92 (cyclohexane-acetic acid titration method). The viscosity of the palm olein-based polyol was measured using a Brookfield Digital Rheometer, Model DV-III+.

The molecular weight (MW) and molecular weight distribution (MWD) of the palm olein-based polyols were measured using a PL-GPC 50 Plus (an integrated Gel Permeation Chromatography (GPC) system by Polymer Laboratories Ltd, United Kingdom). The system was equipped with a differential refractive index (DRI) detector. A set of four Phenogel columns (5 μm particle size and porosities of 50, 100, 1000 and 10 000 \AA) from Phenomenex (Torrance, CA, USA), covering a MW range of $10^2 - 10^6$ Dalton, was used for separation. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1 mL min^{-1} . Palm olein-based polyol was dissolved in THF with a concentration of 2 mg mL^{-1} . The solution was left for 1 hr prior to the GPC analysis. The detectors and columns were thermostated at 30°C. The MWDs were obtained based on a calibration curve generated from polyether polyols standards (Mohd Noor *et al.*, 2016).

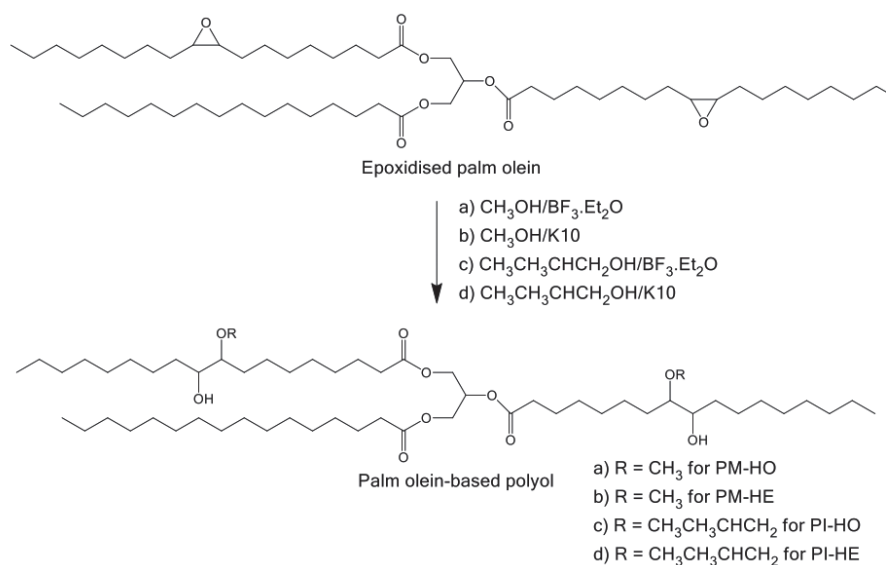


Figure 1. Idealised reaction scheme for the ring-opening reaction of EPOo with a, and b, methanol, c, and d, isobutanol, in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ and K10 montmorillonite catalysts to produce palm olein-based polyols.

RESULTS AND DISCUSSION

Reaction Profile for Syntheses of Palm Olein-based Polyols

Reaction profile such as reaction time, reaction temperature and OOC conversion in syntheses of palm olein-based polyols are shown in *Table 2*. Generally, homogeneous catalyst was more active and selective compared to the heterogeneous catalyst as observed in the ring-opening reaction of EPOo with both alcohols. In the presence of homogeneous catalyst, the reaction was faster and gave high OOC conversion, and it was opposite with the heterogeneous catalyst. This situation occurred when every single catalytic entity in homogeneous catalyst acted as a single active site and accomplished the reaction as required. Interestingly, a different situation occurred when isobutanol was used as a reactant in the reaction involving heterogeneous catalyst. A branch in β -position in isobutanol had created steric hindrance in alcoholysis reaction and this helped heterogeneous catalyst to promote the reaction effectively (Rios *et al.*, 2003; 2005).

All the palm olein-based polyols either prepared using homogeneous or heterogeneous catalysts showed high conversion of OOC, *i.e.*, $\geq 90\%$. Both catalysts had played their roles in the ring-opening reaction of epoxide groups.

Properties of Palm Olein-based Polyols

The structural characteristic and the presence of functional groups in the palm olein-based polyols were identified through FTIR analysis.

The disappearance of the epoxide group stretching band observed at a wavenumber of 824 and 842 cm^{-1} , confirmed the ring-opening of the EPOo as determined via OOC analysis (*Table 2*). Besides, the emergence of broad stretching band at 3450-3500 cm^{-1} for OH group was observed for all the palm olein-based polyols. Ester carbonyl stretching vibration, C-O ester stretching vibrations and ether stretching vibrations were observed at 1743 cm^{-1} , 1125-1250 cm^{-1} and 1092-1098 cm^{-1} , respectively. All these characteristics peaks confirmed the formation of palm olein-based polyol (Norhayati *et al.*, 2018; Tuan Ismail *et al.*, 2018a).

Other properties of the palm olein-based polyols are shown in *Table 3*. The epoxide ring-opening of EPOo via alcoholysis reaction is a slow reaction that requires addition of a catalyst to accelerate the rate of the reaction. Both of the catalysts used showed a high catalytic reactivity that promoted the ring-opening reaction and yielded a maximum OOC reduction for all the polyols except for PM-HE polyol, as shown in *Table 3*. The free fatty acid content in the palm olein-based polyols was low as measured by AV analysis. The AVs of palm olein-based polyols prepared using homogeneous catalyst were lower than AVs of palm olein-based polyols prepared using heterogeneous catalyst. It might be caused by the features of the catalysts themselves, where a single active site in the homogeneous catalyst is more selective towards the desired product as compared to multiple active sites in the heterogeneous catalyst (Farnetti *et al.*, 2009).

The theoretical OHV calculated from idealised structure of palm olein-based polyol prepared from EPOo and isobutanol in the presence of

TABLE 2. REACTION PROFILE FOR SYNTHESIS OF PALM OLEIN-BASED POLYOLS

Types of catalyst		Alcohol	Sample designation	Reaction time	Reaction temperature (°C)	OOC conversion (%)
Homogeneous	BF ₃ .Et ₂ O	Methanol	PM-HO	1 hr	40-60	99
		Isobutanol	PI-HO	1 hr	60-70	98
Heterogeneous	K10 montmorillonite	Methanol	PM-HE	23 hr	60	90
		Isobutanol	PI-HE	2 hr	60	99

TABLE 3. PROPERTIES OF PALM OLEIN-BASED POLYOLS

Sample designations	Properties				
	Oxirane oxygen content (%)	Acid value (mg KOH g ⁻¹)	Hydroxyl value (mg KOH g ⁻¹)	Viscosity at 25°C (mPa.s)	Iodine value (g I ₂ 100 g ⁻¹)
PI-HO	0.04	1.5	102.6	4 533.0	7.1
PI-HE	0.03	1.0	88.6	679.5	16.0
PM-HO	0.03	0.9	95.5	780.0	4.7
PM-HE	0.32	1.4	99.0	447.5	5.8

K10 montmorillonite catalyst is 108.1 mg KOH g⁻¹ (Norhayati *et al.*, 2018). All the palm olein-based polyols prepared showed their OHVs, ranging from 88.6-102.6 mg KOH g⁻¹, and some of them were incomparable to the theoretical OHV, where OHV of the polyols depend to the OOC in the EPOo. All the palm olein-based polyols are expected to have a lower degree of oligomerisation in the alcoholysis process due to an excess amount of alcohol used as reactant. Besides, the OHV of PM-HO polyol, was slightly higher, *i.e.*, 95.5 mg KOH g⁻¹, than palm olein-based polyol prepared using a similar method, *i.e.*, 83.4 mg KOH g⁻¹, in the presence of BF₃.Et₂O but with a different molar ratio of EPOo to methanol of 1:1 as reported by Tuan Ismail *et al.* (2018a).

All palm olein-based polyols prepared with methanol and isobutanol exhibited significantly higher viscosities than EPOo. The viscosity of palm olein-based polyols increased with the increase of MW of reagents used in the epoxide ring-opening reaction. Palm olein-based polyols prepared using heterogeneous catalyst exhibited lower viscosity compared to the palm olein-based polyols prepared using homogeneous catalyst. PM-HE polyol exhibited the lowest viscosity. It can be ascribed to the significantly lower degree of oligomerisation of this polyol in comparison to other palm olein-based polyols. This indicates that substantial side reaction such as polymerisation and crosslinking can be minimised by using heterogeneous catalyst (Chasar *et al.*, 2005).

The presence of the unsaturated fatty chain in the palm olein-based polyol was measured by IV analysis. The IVs of all palm olein-based polyols were observed to be higher than IV of EPOo. The intramolecular elimination reaction of alkane group may occur during the distillation or drying processes of polyol at high temperature thus contributed to the increase of IV (Daley and Daley, 2005). EPOo ring-opened with methanol and isobutanol led to the formation of palm olein-based polyols with secondary hydroxyl groups (2° OH) (*Figure 1*). The sterically hindered 2° OH made it less susceptible for intermolecular epoxide ring-opening reaction.

Molecular Weights and Oligomerisation of Palm Olein-based Polyols

Number average molecular weight (M_n) values determined via GPC analysis were higher in all palm olein-based polyols than the calculated MW based on the ideal structure of palm olein-based polyols. This indicated that some oligomerisations formed during the alcoholysis process except PM-HE polyol (*Table 4*). It was further confirmed with different peaks observed in the GPC chromatogram. In general, the MW of the prepared polyols increased with an increased of MW of reactant used in the preparation of polyols. However, a similar trend

was not observed for palm olein-based polyols prepared using homogeneous catalyst. It could be caused by side reaction, which had affected their MW (Chasar *et al.*, 2005).

Excess amount of alcohol present in the reaction is important to prevent polymerisation and formation of polyols having higher MW due to the reaction between the polyol molecules (Petrovic *et al.*, 2002). Palm olein-based polyols prepared using homogeneous and heterogeneous catalysts had a relatively narrow polydispersity index (PDI), *i.e.*, 1.28-1.45, regardless of the type of reactant used in the ring-opening reaction, demonstrating that the alcoholysis of epoxide ring with an excess amount of reactant led to least formation of oligomerisation. The highest PDI of 1.45 was obtained for PI-HO polyol.

The average equivalent weights and average functionalities of all palm olein-based polyols are tabulated in *Table 5*. The average functionalities were calculated from the average equivalent weights of palm olein-based polyols (from measured OHV) and molecular weight (M_n and M_w) obtained from GPC analysis. Palm olein-based polyols prepared using heterogeneous catalyst exhibited functionalities in the range of 1.67-2.28, which are approximately close to 2. Formation of two hydroxyl groups are expected (*Figure 1*) in one molecule of triglyceride (TAG) with two alkene groups. Functionalities of palm olein-based polyols prepared using homogeneous catalyst were in the range of 2.26-3.42 (*Table 5*) which were related to high degree of oligomerisation during ring-opening reaction (*Table 4*).

The OH functional oligomers that existed in EPOo were identified. OH-functional monomer and diglyceride (DAG) were observed at 32.8 min (91.1%) and 33.8 min (8.0%) of retention times and peak areas (in parenthesis), respectively (*Table 6*). Similar observations were reported by Mohd Noor *et al.* (2016), where mono-triglyceride and DAGs in EPOo were observed at 32.8 min (92.6%) and 33.7 min (7.4%) of retention times and peak areas (in parenthesis), respectively. All palm olein-based polyols prepared in this study showed comparable retention times of all peaks.

The overlaid GPC chromatograms of all palm olein-based polyols are shown in *Figure 2*. All the palm olein-based polyols exhibited a multimodal pattern in their GPC chromatograms, which indicated the formation of oligomers (Mohd Noor *et al.*, 2016; Tuan Ismail *et al.*, 2018a). A slightly lower degree of oligomerisation was observed for palm olein-based polyols prepared using heterogeneous catalyst in comparison to the palm olein-based polyols prepared using homogeneous catalyst. The highest mono composition was found in polyols prepared using heterogeneous catalyst, *i.e.*, 77.1% and 71.8% for PM-HE and PI-HE polyols, respectively

TABLE 4. MOLECULAR WEIGHT OF PALM OLEIN-BASED POLYOLS MEASURED BY GPC ANALYSIS

Sample designations	GPC			Theoretical molecular weight ^a (g mol ⁻¹)
	M_w (g mol ⁻¹)	M_n (g mol ⁻¹)	PDI	
PI-HO	1 795	1 237	1.45	1 024
PI-HE	1 443	1 122	1.28	1 024
PM-HO	2 008	1 528	1.31	940
PM-HE	1 219	944	1.29	940

Note: M_w - weight average molecular weight; M_n - number average molecular weight; PDI - polydispersity index; ^aTheoretical molecular weight were calculated based on the molar mass of the ideal structure of palm olein-based polyol (deeming complete conversion of epoxide group to hydroxyls in triglyceride of RBD palm olein without the formation of oligomers).

TABLE 5. CALCULATED EQUIVALENT WEIGHTS AND FUNCTIONALITIES OF PALM OLEIN-BASED POLYOLS

Sample designations	Calculated equivalent weight ^a	Calculated functionality ^b	
		MW = M_n	MW = M_w
PI-HO	546.8	2.26	3.28
PI-HE	633.2	1.77	2.28
PM-HO	587.4	2.60	3.42
PM-HE	566.7	1.67	2.15

Note: ^a Equivalent weight was calculated based on the method reported by Tuan Ismail *et al.* (2018) and Ionescu (2005).

^b Functionality was calculated based on the method reported by Tuan Ismail *et al.* (2018) and Furniss *et al.* (1989).

TABLE 6. THE M_n , PEAK AREA AND RETENTION TIME OF THE DIFFERENT PEAKS IN GPC CHROMATOGRAMS OF EPO₀ AND PALM OLEIN-BASED POLYOLS

Sample designations	Sample designations				
	EPO ₀	PI-HO	PI-HE	PM-HO	PM-HE
Peak 1: (Tetra- and higher TAG)	-	4 596 (7.1) (29.2)	3 401 (3.0) (28.9)	4 839 (9.6) (29.0)	-
Peak 2: (Tri-TAG)	-	3 239 (7.4) (29.6)	-	3 243 (10.0) (29.6)	3 198 (1.2) (29.9)
Peak 3: (Di-TAG)	2 135 (0.9) (30.8)	2 288 (20.7) (30.6)	2 245 (14.6) (30.6)	2 220 (22.1) (30.6)	2 178 (10.4) (30.7)
Peak 4: (Mono-TAG)	1 062 (91.1) (32.8)	1 226 (59.8) (32.5)	1 243 (71.8) (32.4)	1 195 (53.3) (32.5)	1 161 (77.1) (32.6)
Peak 5: (DAG)	757 (8.0) (33.8)	855 (5.0) (33.7)	868 (10.6) (33.5)	834 (5.0) (33.7)	807 (11.3) (33.6)

Note: M_n (g mol⁻¹), peak area (%) (in parenthesis) and retention time (min) (in parentheses) of assigned OH functional palm olein oligomers.

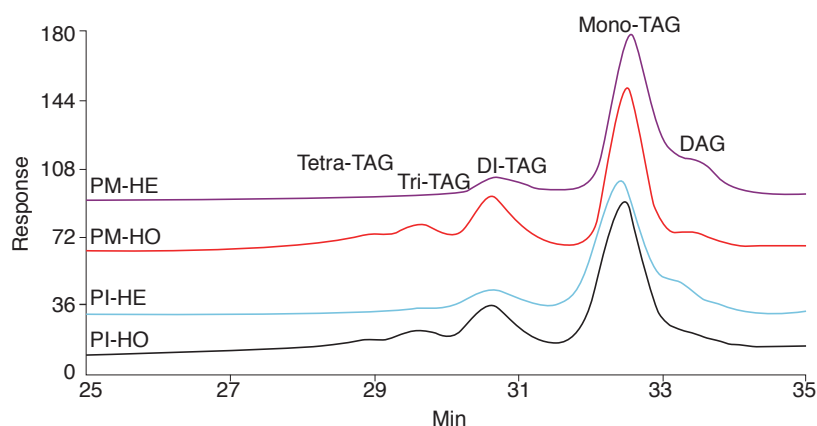


Figure 2. Overlaid of GPC chromatograms of palm olein-based polyols.

(Table 6). Based on GPC chromatogram, PM-HE polyol had the lowest degree of oligomerisation, where 77.1% of the total area was assigned to the OH-functional monomer, 10.4% to the dimer and 1.2% to the trimer of TAG.

The reduction of peak area of DAG was observed in palm olein-based polyols prepared using homogeneous catalyst compared to the DAG peak area measured in EPOo, *i.e.*, 8.0%. This phenomenon might be caused by oligomerisation of EPOo with DAG present in EPOo itself (Mohd Noor *et al.*, 2016). However, the increase of DAG composition in PM-HE and PI-HE polyols were detected. Limitation of heterogeneous catalyst in reactivity and selectivity possibly led to the formation of DAG, where glycerolysis of TAG might occur during the epoxide ring-opening reaction. During the glycerolysis process, an acyl moiety from TAG molecule was removed and DAG was formed. This process happened in the presence of homogeneous or heterogeneous catalysts at high temperature (Satriana *et al.*, 2016).

CONCLUSION

The physicochemical properties of palm olein-based polyols prepared using homogeneous ($\text{BF}_3 \cdot \text{Et}_2\text{O}$) and heterogeneous (K10 montmorillonite) catalysts were evaluated. Both catalysts were selected to be used in ring-opening reactions of EPOo based on their performance as reported in previous literatures. The ring-opening reaction of EPOo with methanol and isobutanol had led to faster reaction time in the presence of homogeneous catalyst with high reduction of OOC. The special feature in isobutanol has established steric hindrance in the reaction, which allowed the heterogeneous catalyst to play a role in the reaction efficiently. All the palm olein-based polyols exhibited low OHV than their theoretical OHV. The OHV of the palm olein-based polyols were dependent on their OOC in the EPOo itself. The viscosities of palm olein-based polyols prepared using heterogeneous catalyst were low as compared to palm olein-based polyols prepared using homogeneous catalyst. Increase in the MW of the reagent used in the epoxide ring-opening reaction had also increased the viscosity of palm olein-based polyol.

The obtained M_n of palm olein-based polyols prepared using homogeneous catalyst was much higher than the calculated MW based on ideal structure of palm olein-based polyol. While, palm olein-based polyols prepared using heterogeneous catalyst contain M_n values close to the theoretical MW. It clearly indicated that the degree of oligomerisation was higher in palm olein-based polyols prepared using homogeneous catalyst than heterogeneous catalyst as evidenced in GPC chromatograms that

exhibited a prominent multimodal pattern. The excess of alcohols used in the reaction had minimised the polymerisation reaction and oligomerisation of the product, as shown in palm olein-based polyols prepared using both catalysts. The results from our study can serve as a reference in the production of the polyol with desired properties. The relationship between different degree of oligomerisation in polyol and polyurethane's mechanical properties could be useful for exploring target application of polyols in polyurethanes.

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