

PREPARATION OF A LOW VISCOSITY AND LIGHT COLOURED FATTY ACID-BASED POLYOL

HOONG, S S*; MOHD NORHISHAM, S*; TUAN NOOR MAZNEE, T I*; KOSHEELA DEVI, P*;
NURUL' AIN, H*; HAZIMAH, A H*; OOI, T L* and SALMIAH, A*

ABSTRACT

Chemical synthesis of a low viscosity and light coloured fatty acid-based polyol was conducted via a three-step reaction. The reaction variables, namely, temperature, pressure, amount of catalyst used, molar ratio of reactants and reaction time were investigated for their effects on the properties of the final polyol produced. Temperature and reduced pressure were found to have a profound impact on the rate of the first reaction step, which was an esterification reaction. In addition, it was observed that the amount of catalyst had a great influence on the colour of the product as well as the rate of the reaction. In the second reaction step, which was an epoxidation reaction, the molar ratio of reactants and reaction time play crucial roles in determining the properties of the final product. At the same time, temperature control was another important factor in this second step. The final reaction step was alcoholysis, in which the amount of catalyst used was one of the important factors that affected the properties of the final product.

Depending on the reaction parameters for this three-step reaction, fatty acid-based polyols with various properties could be prepared. However, polyols with low viscosity and light colour characteristics are preferred because they have the properties that are suitable for the production of 2K polyurethanes for the CASE industry.

Keywords: fatty acid, polyol, low viscosity, low colour.

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INTRODUCTION

Over the last decade, MPOB has embarked on research and development that is aimed at producing polyols from palm oil derivatives in order to increase the usage of palm oil in the non-food related sector. The current MPOB palm-based polyol (POP Pioneer), which can be produced on a pilot plant scale, could be converted into various types of polyurethane (PU) foams. The PU foams can be rigid, semi-rigid or flexible, and are suitable for use in various industrial sectors such as building, furniture, bedding and automotive parts (Ooi *et al.*, 2005). However, there is a sector of the PU industry, which is known as CASE (coating, adhesive, sealant and

elastomer), whose requirements cannot be satisfied by the properties of POP Pioneer.

In view of this shortcoming, MPOB has put in efforts to prepare a suitable palm-based polyol for this sector of the PU industry. The new polyol is based on oleic acid derived from palm kernel oil, which is currently a by-product from the oleochemical industry, *i.e.* after the isolation of lauric and myristic acids for the production of surfactants. The by-product is predominantly oleic acid with a small amount of other fatty acids such as linoleic acid. By converting oleic acid to polyol, we could add value to this by-product and bring about more earnings to the oleochemical industries.

Furthermore, the other component for this polyol is glycerol. Glycerol is produced as a co-product from splitting or transesterification of any vegetable oil or fat to produce oleochemicals, and, therefore, the profitability of the oleochemical industry is very much dependent on the value of this co-product. A recent development in the glycerol market showed

* Malaysian Palm Oil Board,
P. O. Box 10620,
50720 Kuala Lumpur,
Malaysia.
E-mail: sengsoi@mpob.gov.my

that glycerol is coming not only from the oleochemical industry but also from the biodiesel industry. The extra capacity of glycerol in the market has resulted in the price of glycerol nose-diving from USD 956 t⁻¹ in the year 2001 to USD 624 t⁻¹ in 2004, and this price-declining trend will persist as more biodiesel capacity is built (Syamala, 2005). A lot of work has been done to diversify the usage of glycerol by converting it into other useful chemicals, and one of the value-added products is polyol.

This article will describe the preparation of a fatty acid-based polyol from oleic acid and glycerol through several reaction steps and the factors affecting its properties.

PREPARATION OF GLYCERIDES FROM OLEIC ACID AND GLYCEROL

This first step in the preparation of the fatty acid-based polyol is a normal esterification process between acid and alcohol with glycerides and water as the products. Esterification is usually catalysed by an acidic catalyst with the continuous removal of water to force the equilibrium in the desired direction (McMurry, 1995). *Figure 1* illustrates the reaction between oleic acid and glycerol to yield glycerides. Temperature, reduced pressure and catalyst dosage have significant effects on the properties of the product.

Effect of Temperature

Reactions were conducted with 0.5% (w/w) catalyst at 600 mbar reduced pressure for durations from 4 to 10 hr. The molar ratio between oleic acid and glycerol was 1:1. The temperature was varied

from 130°C to 210°C in order to determine its effect on the rate of reaction. Reactions were monitored through acid value determination of the reaction mixture, and reaction was deemed completed when the acid value reached less than 5 mg KOH g⁻¹.

Referring to *Figure 2* (which shows the effect of temperature on the rate of reaction), it may be seen that the higher the reaction temperature, the faster was the reaction rate. However, the product from the reaction conducted at 210°C had a darker colour when compared to products from reactions at lower temperatures. *Table 1* shows the colours of oleic acid and reaction products in Lovibond Tintometer colour units. The reaction temperature of 180°C was subsequently chosen so that a light colour product could be obtained even though the rate of reaction was slower than the reaction at 210°C.

TABLE 1. COLOUR* OF PRODUCTS FROM REACTIONS CONDUCTED AT VARIOUS TEMPERATURES AS COMPARED TO COLOUR* OF OLEIC ACID

	Neutral (L)	Red (a)	Yellow (b)	Appearance
Oleic acid	0.2	0.2	0.6	Faint yellowish
P _{120°C}	0.2	0.2	1.2	Slightly yellowish
P _{150°C}	0.2	0.2	1.5	Slightly yellowish
P _{180°C}	0.3	0.2	1.9	Slightly yellowish
P _{210°C}	0.3	0.4	2.7	Yellowish

Notes: P_{120°C} - P_{210°C}: products from reactions using temperatures ranging from 120°C to 210°C.

* Colour measured in Lovibond Tintometer colour units.

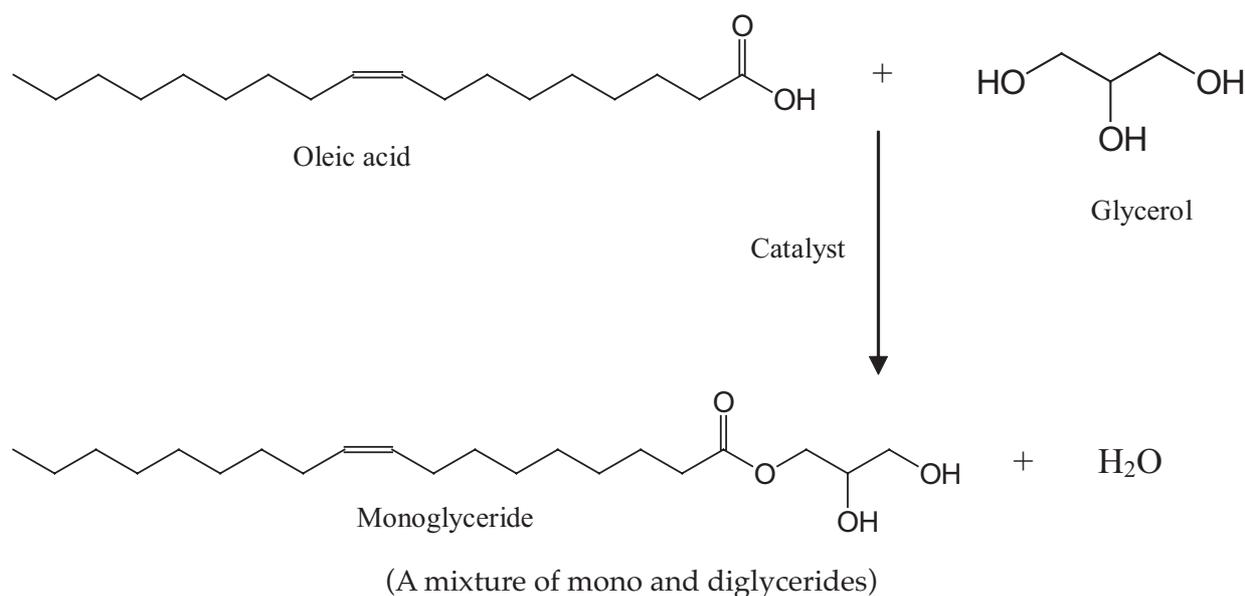


Figure 1. Preparation of glycerides from oleic acid and glycerol.

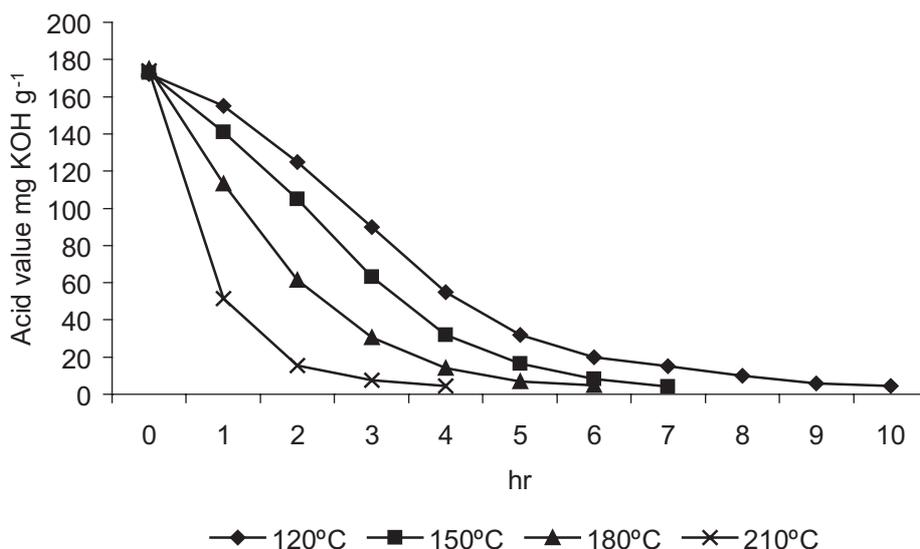


Figure 2. Effect of temperature on the rate of reaction with 0.5% w/w catalyst at 600 mbar reduced pressure.

Effect of Reduced Pressures

Reactions were conducted with 0.5% (w/w) catalyst at 180°C for durations from 4 to 10 hr. As before, the molar ratio between oleic acid and glycerol was 1:1. The reduced pressure was varied from 300 to 900 mbar in order to determine its effect on the rate of reaction. Reactions were also monitored through acid value determination of the reaction mixture, and the reaction was considered completed when the acid value was less than 5 mg KOH g⁻¹. Figure 3 shows the effect of reduced pressure on the rate of reaction.

The application of reduced pressure is to facilitate continuous removal of water from the reaction system so that the reaction equilibrium will shift forward towards the formation of products. From Figure 3, it may be seen that the reaction rate

conducted at 900 mbar was significantly reduced as compared to the reactions conducted at stronger reduced pressure. This may be due to ineffective removal of water formed by the reaction at a weaker level of reduced pressure. At 300 mbar, we observed that the rate of reaction was similar to the rate of reaction conducted at 600 mbar (lines superimposed on top of one another). However, at 300 mbar, some fatty acid was distilled out from the reaction system and collected in the condenser. This suggests that the 300 mbar reduced pressure was too strong for the system. Therefore, the reduced pressure for a reasonable reaction rate is 600 mbar.

Effect of Amount of Catalyst

Reactions were conducted at 180°C with 600 mbar reduced pressure for durations ranging from 4 to 10

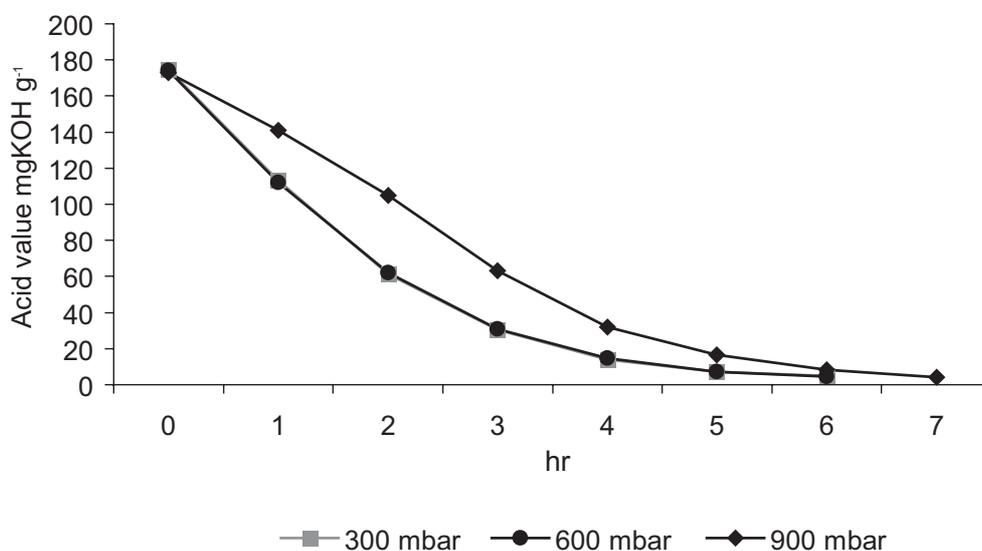


Figure 3. Effect of reduced pressure on the rate of reaction with 0.5% w/w catalyst at 180°C.

hr. The molar ratio between oleic acid and glycerol was 1:1. The amount of catalyst was varied from 0.1% to 1% in order to determine its effect on the rate of reaction. Reactions were monitored through acid value determination of the reaction mixture, and the reaction was considered completed when the acid value was less than 5 mg KOH g⁻¹. Figure 4 shows the effect of catalyst amount on the rate of reaction.

Figure 4 shows that the rates of reaction were almost the same regardless of the amount of catalyst used. In other words, 0.1% of catalyst was sufficient for this particular reaction, and any extra amount of catalyst did not accelerate the reaction. However, the catalyst amount has a profound influence on the colour of the products measured using the Lovibond Tintometer method (Table 2).

The colour of the products became more yellowish as compared to the starting material when 0.1% and 0.25% of catalyst were used in the reactions. The *b* value (yellow) of these products was high, being 15 and 7.8 for 0.1% and 0.25%, respectively. By contrast, the colour of the products from reactions with 0.5% and 1% catalyst was just slightly more yellowish as compared to oleic acid. This indicates that in order to yield light coloured product, the catalyst used should be 0.5% (w/w) or higher.

Properties of the Prepared Glycerides

The typical properties of glycerides prepared with the optimized reaction parameters as discussed are tabulated in Table 3.

PREPARATION OF EPOXIDIZED GLYCERIDES

The prepared glycerides were further subjected to epoxidation in order to increase the functionality of

TABLE 2. COLOUR* OF PRODUCTS FROM REACTIONS CONDUCTED WITH VARIOUS CATALYST AMOUNTS AS COMPARED TO COLOUR* OF OLEIC ACID

	Neutral (L)	Red (a)	Yellow (b)	Appearance
Oleic acid	0.2	0.2	0.6	Faint yellowish
P _{0.1%}	0.3	2.2	15	Yellowish
P _{0.25%}	0.2	1.1	7.8	Yellowish
P _{0.5%}	0.3	0.2	1.9	Light yellow
P _{1%}	0.2	0.2	1.5	Light yellow

Notes: P_{0.1%} - P_{1%}: products from reactions using amounts of catalyst, ranging from 0.1% to 1%.

* Colour measured in Lovibond Tintometer colour units.

TABLE 3. TYPICAL PROPERTIES OF GLYCERIDES PREPARED WITH 0.5% CATALYST AT 180°C AND 600 mbar REDUCED PRESSURE FOR 6 hr

Property	
Monoglyceride (%)	50.6
Diglycerides (%)	49.4
Lovibond tintometer	0.3 neutral, 0.2 red, 1.9 yellow
Acid value (mg KOH g ⁻¹ sample)	4.3
Iodine value (g I ₂ per 100 g sample)	75.5

the product. The epoxidation process converts the unsaturation of the glycerides to epoxy functionality. This was carried out by reacting glycerides with formic acid and hydrogen peroxide. During epoxidation, performic acid was formed *in situ* from the reaction between formic acid and hydrogen peroxide in the reaction mixture. The performic acid

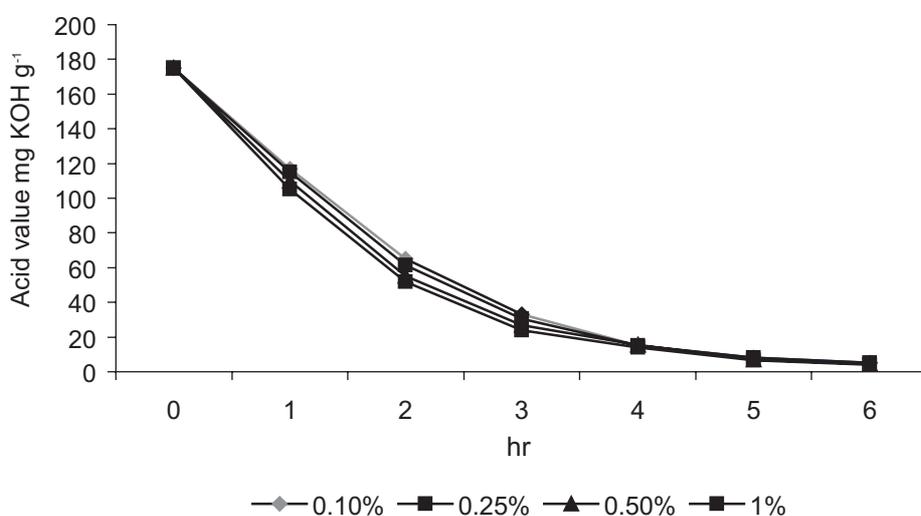


Figure 4. Effect of catalyst amount on the rate of reaction at 180°C and 600 mbar reduced pressure.

then oxidized the unsaturation of the glycerides, converting them to epoxy groups. *Figure 5* illustrates the epoxidation process of glycerides to epoxidized glycerides. There are several reaction parameters in the epoxidation process, namely, the molar ratio between unsaturation of the glycerides and formic acid; the molar ratio between unsaturation of the glycerides and hydrogen peroxide, and the reaction time. The effect of these parameters on the properties of epoxidized glycerides are discussed in the following sections.

Iodine value (IV) analysis was carried out on the products to determine the extent of conversion from unsaturation to epoxy functionality. In addition, oxirane oxygen content (OOC%) analysis was also carried out on the products to determine the amount of epoxy groups in the products in terms of percentages.

Effect of Molar Ratio between Formic Acid and Unsaturation of the Glycerides

The epoxidation process was conducted at a temperature between 50°C and 60°C for 3 hr. The molar ratio between unsaturation of the glycerides and formic acid varied between 0.3 and 1 mol of formic acid per mol of unsaturation of the glycerides, while the molar ratio between the unsaturation of the glycerides and hydrogen peroxide was fixed at 3 mol of hydrogen peroxide per mol of unsaturation of the glycerides. The results of this study are tabulated in *Table 4*, which shows OOC % and IV of the epoxidized products.

The aim of this set of studies was to determine the minimum molar ratio of formic acid per mole unsaturation of the glycerides that is needed to

TABLE 4. EFFECT OF MOLAR RATIO OF FORMIC ACID TO UNSATURATION OF THE GLYCERIDES ON THE PROPERTIES OF EPOXIDIZED GLYCERIDES

Experiment	Molar ratio (Unsat. : FA : H ₂ O ₂)	OOC (%)	IV (g I ₂ per 100 g)
1	1 : 0.3 : 3	2.2	25.0
2	1 : 0.5 : 3	2.3	4.0
3	1 : 0.7 : 3	2.2	3.5
4	1 : 1.0 : 3	2.3	3.5

Note: Unsat. = unsaturated glycerides; FA = formic acid; H₂O₂ = hydrogen peroxide.

effectively convert the unsaturation to an epoxy group. The IV of the epoxidation product is a good indication of the effectiveness of the conversion. In Experiment 1, where the molar ratio of formic acid per mol of unsaturation of the glycerides was 0.3 mol, IV of the epoxidized glycerides was 25 g I₂ per 100 g sample, indicating that the unsaturation of the glycerides was not fully converted into the epoxy group. This suggests that the molar ratio of 0.3 mol of formic acid per mole of unsaturation of the glycerides was not sufficient for the epoxidation process.

In Experiments 2, 3 and 4, IVs for epoxidized glycerides were 4 g I₂ per 100 g sample or lower, indicating that almost all the unsaturation of the glycerides were effectively converted into epoxy groups. These results indicate that for effective conversion of unsaturation group to epoxy groups, the minimum molar ratio of formic acid per mol unsaturation of the glycerides was 0.5 mol formic acid.

Furthermore, in terms of OOC%, the studies showed that values of OOC% for all the prepared

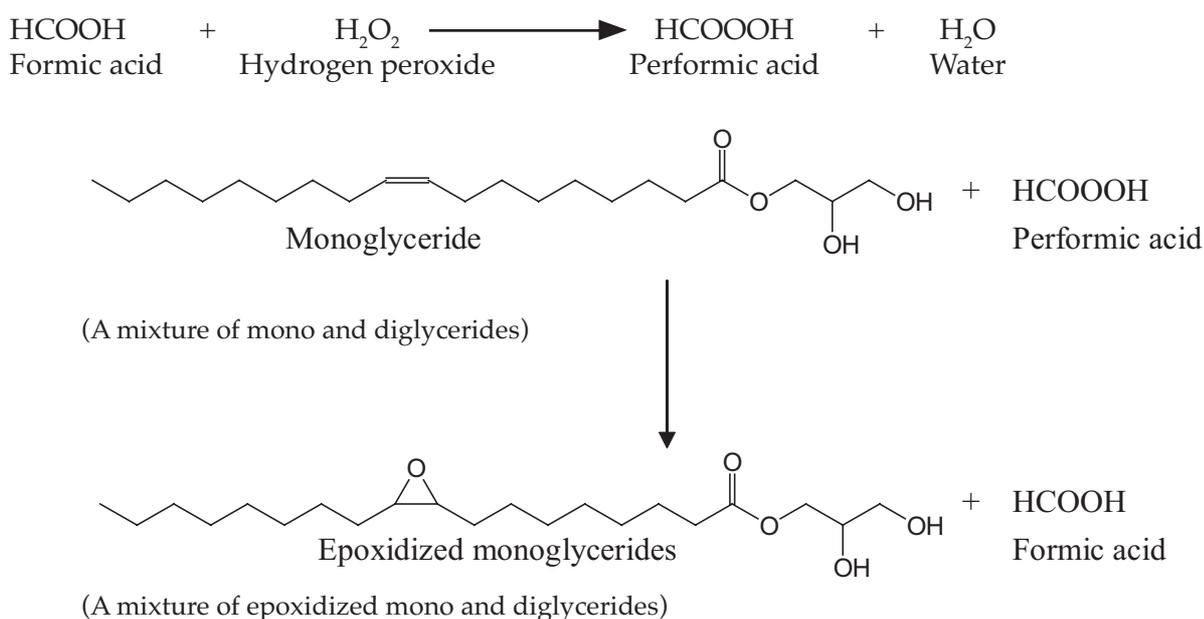


Figure 5. Epoxidation of glycerides with formic acid and hydrogen peroxide.

epoxidized glycerides were similar. This suggests that the molar ratio of formic acid per mole unsaturation of the glycerides had little influence on OOC%. We observed that the OOC% will reach an optimum value that will not rise even though the IV value drops to near zero. We suspected that the oxirane oxygen group was ring-opened to dihydroxy group at the optimum value while at the same time more unsaturation of the glycerides was epoxidized to oxirane oxygen, which eventually replenished those ring-opened to dihydroxy group.

Effect of Molar Ratio between Hydrogen Peroxide and Unsaturation of the Glycerides

As before, the epoxidation process was conducted at a temperature between 50°C and 60°C for 3 hr. The molar ratio between unsaturation of the glycerides and hydrogen peroxide was varied between 1 and 5 mol of hydrogen peroxide per mol of unsaturation of the glycerides, while the molar ratio between unsaturation of the glycerides and formic acid was fixed at 1 mol formic acid per mol of unsaturation of glycerides. The results of this study are tabulated in *Table 5*, which shows OOC% and IV of the epoxidation products.

The IV of epoxidized glycerides from Experiment 5 was about 22 g I₂ per 100 g sample, indicating that the unsaturation of the glycerides was not fully converted to epoxy groups. This suggested that the molar ratio of 1 mole hydrogen peroxide per mole unsaturation of the glycerides was not sufficient for the epoxidation process.

In Experiments 6, 7 and 8, IVs for the epoxidized glycerides were less than 5 g I₂ per 100 g sample, indicating that almost all of the unsaturation of the glycerides had effectively been converted to epoxy groups. The results indicate that for effective

TABLE 5. EFFECT OF MOLAR RATIO OF HYDROGEN PEROXIDE TO UNSATURATION OF THE GLYCERIDES ON THE PROPERTIES OF EPOXIDIZED GLYCERIDES

Experiment	Molar ratio (Unsat. : FA : H ₂ O ₂)	OOC (%)	IV (g I ₂ per 100 g sample)
5	1 : 1 : 1	2.3	22.0
6	1 : 1 : 2	2.5	4.5
7	1 : 1 : 3	2.4	3.5
8	1 : 1 : 5	2.5	3.5

Note: Unsat. = unsaturated glycerides; FA = formic acid; H₂O₂ = hydrogen peroxide.

conversion of unsaturation group to epoxy group, the minimum molar ratio of hydrogen peroxide per mole unsaturation of the glycerides was 2 moles of hydrogen peroxide.

Once again, in terms of OOC%, the studies showed that OOC% for all the prepared epoxidized glycerides were similar. This suggests that the molar ratio of hydrogen peroxide per mole unsaturation of the glycerides has little influence on OOC%.

Effect of Epoxidation Reaction Time

The epoxidation process was conducted at a temperature between 50°C and 60°C. The molar ratios were fixed at 3 mol of hydrogen peroxide per mole of unsaturation of the glycerides, and at 0.5 mol of formic acid per mol of unsaturation of the glycerides. The reaction time was varied between 1 hr and 4 hr in order to determine the effect of reaction time on the properties of the epoxidized glycerides.

The duration of the epoxidation process plays a crucial role in determining the final properties of the products. As shown in *Figure 6*, the longer the

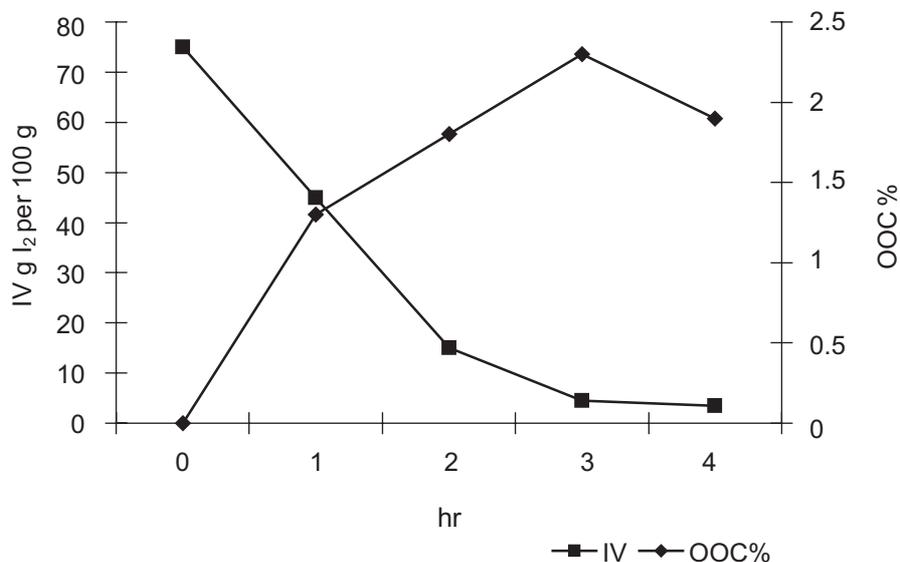


Figure 6. Effect of epoxidation reaction time on the properties of epoxidized glycerides.

duration of the epoxidation process the lower was IV. However, in terms of OOC%, the value of OOC% went up to a maximum at the third hour but decreased drastically at the fourth hour of the reaction. Therefore, it is important to determine the optimum reaction time (hr) which ensures that the highest OOC % and lowest IV possible are obtained.

Properties of the Prepared Epoxidized Glycerides

The best reaction conditions for the preparation of epoxidized glycerides are 3 mol of hydrogen peroxide per mole of unsaturation of the glycerides, and 0.5 mol of formic acid per mol of unsaturation of the glycerides, while the epoxidation process is conducted at a temperature between 50°C and 60°C for 3 hr. The typical epoxidized glycerides prepared with these optimized reaction parameters would have OOC% of about 2.3% and IV of 4 g I₂ per 100 g sample.

PREPARATION OF THE FATTY ACID-BASED POLYOL FROM EPOXIDIZED GLYCERIDES

The oxirane oxygen ring of epoxidized glycerides is reactive towards nucleophilic addition of alcohol. Therefore, the prepared epoxidized glycerides were further subjected to the ring-opening reaction with a polyhydric alcohol. This reaction is known as alcoholysis during which the polyhydric alcohol will be inserted into the glycerides molecule at the epoxy functionality. This reaction is usually aided by a catalyst and carried out under mild condition. *Figure 7* illustrates the reaction between epoxidized glycerides and polyhydric alcohol. The polyhydric

alcohol used in this study was ethylene glycol because it is the simplest form of diol that is easily available.

Similar to the epoxidation process, alcoholysis was conducted at a temperature between 50°C and 60°C. The molar ratio between oxirane oxygen of epoxidized glycerides and polyhydric alcohol was 1 mol of polyhydric alcohol per mol of oxirane oxygen of epoxidized glycerides. The alcoholysis reaction could be followed by monitoring the reduction of OOC% value of the epoxidized glycerides in the reaction mixture. For this process, the effect of varying the amount of the catalyst (0.1%, 0.25%, 0.5% and 1.0%) on the rate of the alcoholysis reaction was evaluated.

Referring to *Figure 8*, for the reactions with 0.5% and 1% of catalyst (lines superimposed on top of one another), OOC% value dropped from 2.4% to less than 0.1% in the first hour, while for reactions with 0.25% and 0.1% catalyst, the same amount of reduction in OOC % value was seen after 3 hr and 5 hr, respectively. This clearly indicates that the minimum amount of catalyst needed for the alcoholysis reaction is 0.5% w/w.

Properties of the Fatty Acid-based Polyol

The typical properties of the fatty acid-based polyol prepared with the optimized reaction parameters from the three reaction steps discussed earlier are tabulated in *Table 6*. The fatty acid-based polyol prepared using these conditions is light in colour, and therefore is suitable for applications that require transparency or white pigmentation, such as for clear or white coatings and adhesives. In addition, this polyol has a reasonably high hydroxyl value of

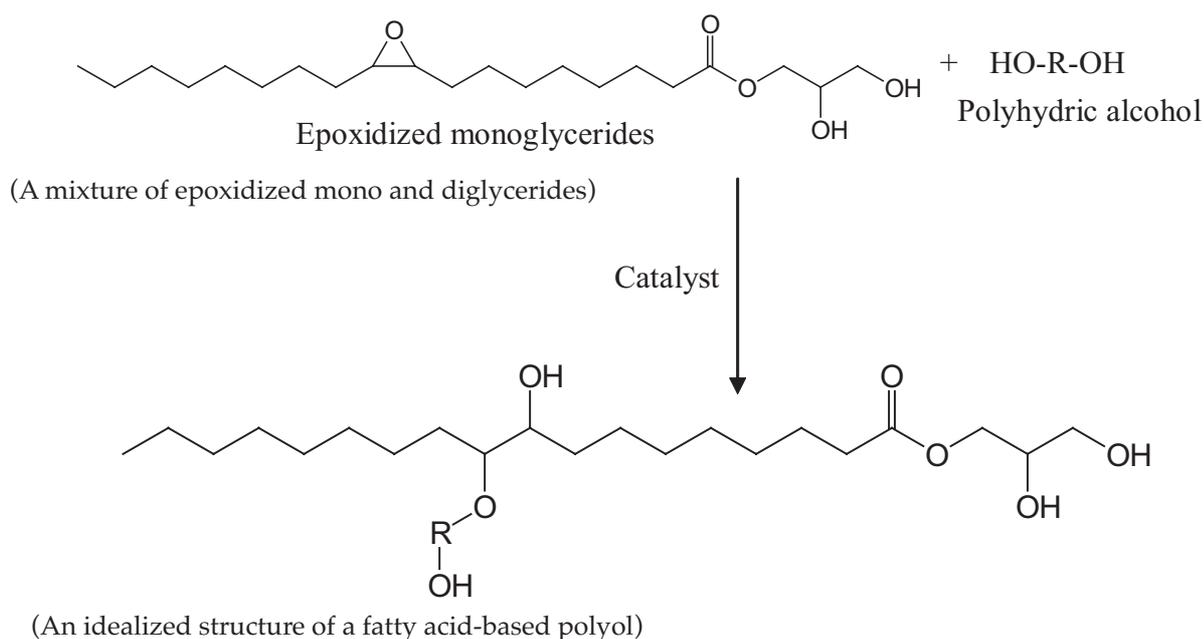


Figure 7. Alcoholysis of epoxidized glycerides with polyhydric alcohol.

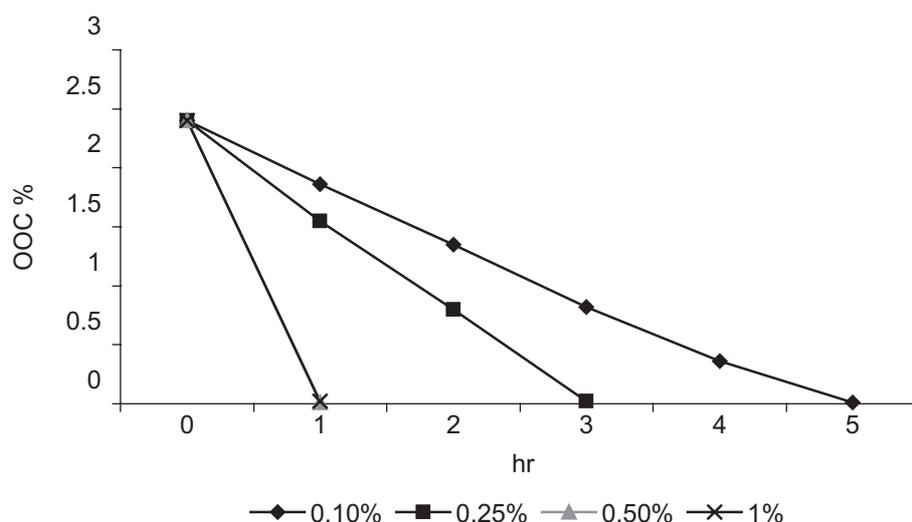


Figure 8. Effect of catalyst amount on the rate of alcoholysis reaction at a temperature of 50°C to 60°C.

TABLE 6. TYPICAL PROPERTIES OF A FATTY ACID-BASED POLYOL PREPARED FROM OPTIMIZED REACTION PARAMETRES FROM THE THREE REACTION STEPS

Property	
Hydroxyl value (mg KOH g ⁻¹ sample)	240
Acid value (mg KOH g ⁻¹ sample)	3
Iodine value (g I ₂ per 100 g sample)	5
Moisture content (%)	0.5
Lovibond tintometer	0.3 neutral, 0.2 red, 1.5 yellow
Viscosity at 25°C (cP)	6 600

240 mg KOH g⁻¹, which makes it suitable for 2K PU adhesive and coatings formulations. However, for 2K PU coating applications, it is recommended that the molecular weight of the polyol be further increased by esterification with dibasic acid while maintaining the light colour property. Further development is being carried out to lower the acid value and moisture content of the prepared polyol to values acceptable by the industry.

Effect of Epoxidation Reaction Time on Polyol Viscosity

Another attribute that required our attention was the viscosity of the polyol. The viscosity of the current polyol is considered high for some applications. We noticed that by varying the reaction time of the epoxidation process, we could vary the viscosity of the polyol. An example is given in Table 7, where the epoxidation reaction time had been varied between 1 hr and 3 hr with the same optimized reaction parameters for epoxidation as discussed earlier. The epoxidized glycerides from this study were subjected to the same optimised alcoholysis process as well.

Table 7 shows that the viscosity of the polyol increased with a longer epoxidation time, with the polyol prepared from a 3 hr epoxidation process having the highest viscosity. It also had the lowest IV and the highest hydroxyl value among the polyols prepared from the three reaction conditions. It was considered as a full epoxidation process, where almost all of the unsaturation of the glycerides had been converted into epoxy groups.

By contrast, the 1 hr epoxidation produced a polyol that had the lowest viscosity, highest IV and slightly lower hydroxyl value. Therefore, in order

TABLE 7. PROPERTIES OF POLYOLS PREPARED FROM VARIED EPOXIDATION REACTION TIMES

Epoxidation time (hr)	Molar ratio (unsat. : FA:H ₂ O ₂)	Viscosity at 25°C (cP)	IV (g I ₂ per 100 g)	Hydroxyl value (mg KOH g ⁻¹)
1	1 : 0.5 : 3	1 200	45	220
2	1 : 0.5 : 3	2 300	20	230
3	1 : 0.5 : 3	6 600	4.5	240

Note: Unsat. = unsaturated glycerides; FA = formic acid; H₂O₂ = hydrogen peroxide.

to prepare a low viscosity fatty acid-based polyol, partial epoxidation is the method by which we could vary the epoxidation time to yield a low viscosity polyol. In our studies, the low viscosity polyol was prepared from the 1 hr epoxidation process. The properties of the low viscosity fatty acid-based polyol were generally similar to the properties of the typical fatty acid-based polyol listed in *Table 6* except that its viscosity, IV and hydroxyl values were 1200 cP, 45 g I₂ per 100 g sample and 220 mg KOH g⁻¹, respectively.

CONCLUSION

Fatty acid-based polyols that have suitable properties for the PU CASE industry may be prepared from oleochemical co-products, namely oleic acid and glycerol, through a three-step synthesis pathway. At each stage of the synthesis pathway, there are parameters that determine the properties of the final product, and we have been able to optimize these parameters. Fatty acid-based polyols with low viscosity and light colour characteristics can also be prepared using the same method by controlling the extent of epoxidation of the glycerides.

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