

Influence of Diethanolamine to Triglyceride Structure for Production of Palm Oil-Based Polyol

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Abstract: Reactions of polyol with a variety of functional groups to produce polymeric materials are well documented in both academic and industrial research environments. Current trends to produce polyols towards green technology have catalyzed the research on renewable resources such as vegetable oils to replace petrochemical-based materials. The introduction of hydroxyl group (OH), via. transamidation of diethanolamine has successfully converted the Refined Bleached Deodorized Palm Oil (RBDPO) into polyol. RBDPO was reacted with diethanolamine and refluxed at 110°C for 5 h without any catalyst and solvent, resulted the establishment of diethanolamide with high hydroxyl number. It was proven by FTIR study where the sample spectrum underwent significant changes, particularly in the gradual appearance of the broad peak O-H band at around 3301 cm⁻¹. Another significant change was the appearance of the peak C = O stretching at around 1619 cm⁻¹ and C-N at around 1049 cm⁻¹. These changes indicated the formation of diethanolamide. The synthesized palm oil-based polyol has hydroxyl number of 254.20 mL NaOH/g with fewer amounts of acid numbers which is 3.60 mL NaOH/g. This study showed that polyols made from RBDPO-diethanolamine reactions can be used as an alternative source of polyols in polymer synthesis.

Key words: Polyol, triglyceride, diethanolamide, palm oil-based polyol, polymer synthesis, RBDPO

INTRODUCTION

Nowadays, most polyols used in plastic industries are petrochemical-based where crude oil and coal are used as starting raw materials (Sharma and Kundu, 2008; Zhou, *et al.*, 2016). However, these materials are expensive (Harrington and Hock, 1997; Szycher, 1999; Woods, 1990). Over the past decade, the price of petroleum escalated, the stability and sustainability of the petroleum market have become growing concerns (Mekewi *et al.*, 2017). Cost of polymeric raw materials has since, risen steadily because of rising feedstock price (Kalam and Masjuki, 2002). Besides, the rate of depletion of petroleum also high and they required high technology processing systems (Guo *et al.*, 2002). In contrast to the less predictable petroleum market, agriculture products such as vegetable oils have not only maintained sturdy prices but also experienced surpluses (Pillai *et al.*, 2016). This necessitates a look at utilizing plants that can serve as alternative feed stocks for monomers in polymer industry (Lumcharoen and Saravari, 2014).

There have been many reports on synthesizing polymeric materials using bio-based polyols from various vegetable oils such as soy (Fan *et al.*, 2012; Zhang *et al.*, 2014), linseed (Calvo-Correas *et al.*, 2015), rapeseed (Kirpluks *et al.*, 2013; Kuranska *et al.*, 2015; Rojek and Prociak, 2012) and castor oil (Gomez-Fernandez *et al.*, 2016). Palm oil is one of the most important vegetable oils due to its price and production efficiency in comparison to any other commercial oils. The production of crude palm oil in Malaysia was approximately 19.22 million tonnes in 2014 (Arniza *et al.*, 2015). The palm oils consist of triglyceride molecules which are esters of glycerol with long chain fatty acids (4-22 carbon chains) with 0-3 unsaturated double bonds per fatty acid (Norhisham *et al.*, 2017). Hence, Palm Oil-based Polyols (POP) can be obtained by an introduction of hydroxyl groups into the active site of double bonds or ester bonds (Malewska *et al.*, 2015).

Palm oil-based polyols can be prepared by using different fractions and derivatives from palm oil

(Arniza *et al.*, 2015). Different synthetic routes are used in the syntheses of POP. One of the method to incorporate hydroxyl group to the palm oil is glycerolysis where triglycerides were converted to monoglycerides which palm oil become POP (Tanaka *et al.*, 2008). Besides that, new technology where Refined Bleached Deodorized Palm Oil (RBDPO) was chemically derivatized using proprietary chemical formulation also a common method to produce an alternative polyol, make it suitable for synthesizing polymeric materials such as polyurethane (Lee *et al.*, 2007). Other methods to add hydroxyl group at the unsaturated sites are hydroformylation followed by hydrogenation (Guo *et al.*, 2002), epoxidation followed by oxirane opening (Saurabh *et al.*, 2011), transesterification (Arniza *et al.*, 2015), microbial conversion (Oertel, 1993) and many more. These different methods of converting vegetable oils into bio-polyols allow obtaining hydroxyl derivatives with different number of hydroxyl group and characterized by various chemical structures (Malewska *et al.*, 2015). The structure of polyols have a significant influence on the final properties of polymeric materials which also depend on the other process conditions (Arbenz *et al.*, 2016; Marcovich *et al.*, 2017).

A new substitute method to produce POP for polymer synthesis was found. In this study, triglycerides from palm oil were reacted with Diethanolamine (DEA) to form diethanolamide. The produced diethanolamide is the POP that later will react with other reactive groups to produce polymeric materials.

MATERIALS AND METHODS

Conventional Palm Oil-based Polyols (POP) was purchased by Maskimi Polyol Sdn. Bhd., Malaysia. Refined Bleached Deodorized Palm Oil (RBDPO) was obtained from a local company, potassium bromide for IR Spectroscopy, Diethanolamine (DEA) was commercially obtained and silicon oil was supplied by Kras Instrument Sdn. Bhd. Phthalic anhydride, pyridine, sodium hydroxide (NaOH) and phenolphthalein were supplied by Sigma Aldrich.

Synthesis of Palm Oil-based Polyol (POP): Synthesis of diethanolamide was carried out in a pyrex glass reaction flask submerged in a silicone bath. The reaction flask was equipped with a mechanical stirrer, thermometer and condenser. RBDPO (triglycerides) was reacted with DEA at suitable molar ratio (1:3). Glycerol by product of the reaction can act as crosslinker for production of polymers

Table 1: Formulation for synthesis of diethanolamide

Materials	Volume (mL)
RBDPO	100
Diethanolamine (DEA)	300

such as rigid polyurethane foam. Therefore, it was kept in a separate vial instead of removing it. The reaction was carried out at 110°C for 5 h. The hydroxyl values of the synthesized diethanolamide were determined. Formulation of diethanolamide synthesis is shown in Table 1 (Lee *et al.*, 2007).

Determination of hydroxyl number (OH group):

Hydroxyl numbers were determined in accordance with the ASTM D4274-05. Approximately 2 g of synthesized POP was reacted with 25 mL of phthalic anhydride in pyridine. The reaction mixtures were refluxed in oil bath at 115°C for 1 h. Then the mixtures were titrated with 0.5 N sodium hydroxide (NaOH) until pink end point after it was cooling down to room temperature. The procedures were repeated without diethanolamide for the blank titration. These steps were repeated for standard POP as well for comparison with the result of synthesized POP. The hydroxyl number is calculated using the following equation (Anonymous, 2005):

$$\text{Hydroxyl number} = [(B-A)N \times 56.1] / W$$

Where:

A = 0.5N NaOH solution required for titration of the sample (mL)

B = 0.5N NaOH solution required for titration of the blank (mL)

N = Normality of the NaOH solution

W = Sample used (g)

Determination of acid numbers: The results obtained were corrected via, following procedures to correct the significant acidity contains in the samples. Acid numbers were determined using the same standard test method. Approximately 2 g of synthesized POP were weighed in to 500 mL conical flask containing 75 mL of pyridine and 75 mL of distilled water. 0.5 mL of phenolphthalein were added as indicator. Then the mixtures were titrated with 0.1N of NaOH until pink end point. For comparison, the procedures were repeated with standard POP and without the synthesized POP for the blank titration. The acid numbers were calculated using the following equation (Anonymous, 2005):

$$\text{Acidity correction} = [(A-B)N \times 56.1] / W$$

Where:

A = 0.1N NaOH required for titration of the sample (mL)

B = 0.1N NaOH required for titration of the blank (mL)

N = Normality of the NaOH solution

W = Sample used (g)

FTIR spectra analysis: FTIR analysis was carried out using Perkin-Elmer Paragon 500 spectrometer to identify the hydroxyl group in the conventional POP that was bought by Maskimi Polyol Sdn. Bhd. and to monitor the functional groups in the synthesized product. A drop of the sample was sandwiched between two sodium chloride (NaCl) plates and secured using a cell holder. It must be sure that no air trapped between the two cells due to the air trapped will disturb the actual result. The sample was scanned between 4000-370 cm^{-1} of wavenumbers. Hydroxyl groups contained in the POP were determined from the peaks obtained and it was compared with the spectrum of standard POP as well.

RESULTS AND DISCUSSION

Alterations in the POP formulation in terms of varying amount and method will result in different quality of POP. Studies had been conducted to produce POP from reaction of RBDPO with diethanolamine. In this study, hydroxyl group from diethanolamine will attached to the triglyceride structure to form diethanolamide. Schematic diagram for the reactions is shown in Fig. 1 (Lee *et al.*, 2007). The resultant diethanolamide is the POP that contains high number of hydroxyl groups. This can be proved by FTIR characterization.

Diethanolamide (synthesized POP): Starting material of RBDPO was reacted with DEA at molar ratio 1:3 (palm oil triglyceride: DEA). Glycerols were produced as by-product of the reaction. However, it was not being removed from the reaction mixtures as it can be used as

crosslinking agent during the production of polymers. The optimum reaction temperature was 110°C and the reactions were allowed for 5 h. The mixtures were let to settled down and cooled for a few minutes. After a while, two clear separate layers were formed from the mixtures with the upper layer was diethanolamide, product of the synthesis while the glycerol stood at the bottom layer. Upper layer was taken from the reaction mixtures to study the production of diethanolamide and to calculate the amount of hydroxyl groups present in the compound.

FTIR analysis was conducted to monitor the attachment of hydroxyl group to the diethanolamide structure and was compared with the spectrum of standard POP. Figure 2 and 3 showed FTIR spectrum of standard POP and synthesized POP, respectively. Three most important bonds must have in the spectrum to confirmed the formation of the said diethanolamide which are O-H, C = O and C-N bonds. Hydroxyl group presented a broad O-H absorption at around 3301 cm^{-1} . While carbonyl group, C = O was detected at frequency 1619 cm^{-1} . The appearance of carbonyl group at this low frequency suggested an amide functional group. C-N peak for amide was presented a significant change at around 1049 cm^{-1} . In addition, there was visible a very sharp peak at frequency between 2923 and 2853 cm^{-1} that refers to C-H stretching for hydrocarbon in fatty acid structures.

Figure 4 shows the spectrum of glycerol by-product of the reaction. From the spectrum obtained, there was shown an intense peak of C-H stretching frequency forms at around 2929 and 2858 cm^{-1} . Two less intense peaks at around 3473 and 1653 cm^{-1} indicated the formation of O-H functional group in the glycerol and C = O, respectively. The C = O peak may indicated for C = O of triglycerides which means that there were some of the oil that were not reacted with diethanolamine.

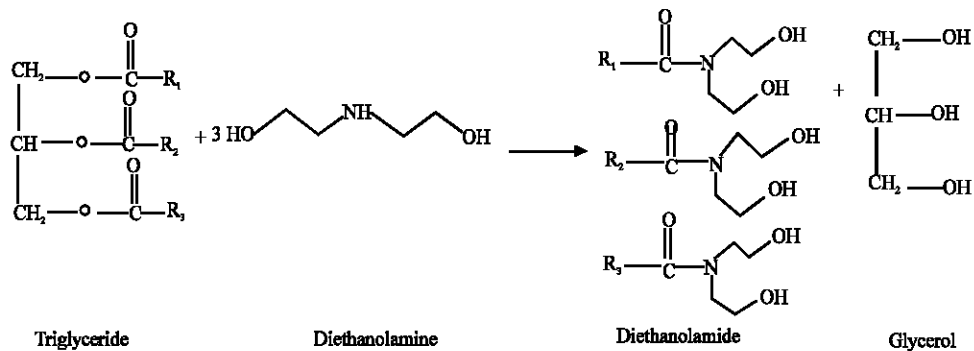


Fig. 1: Schematic diagram for reaction of palm oil-based polyol

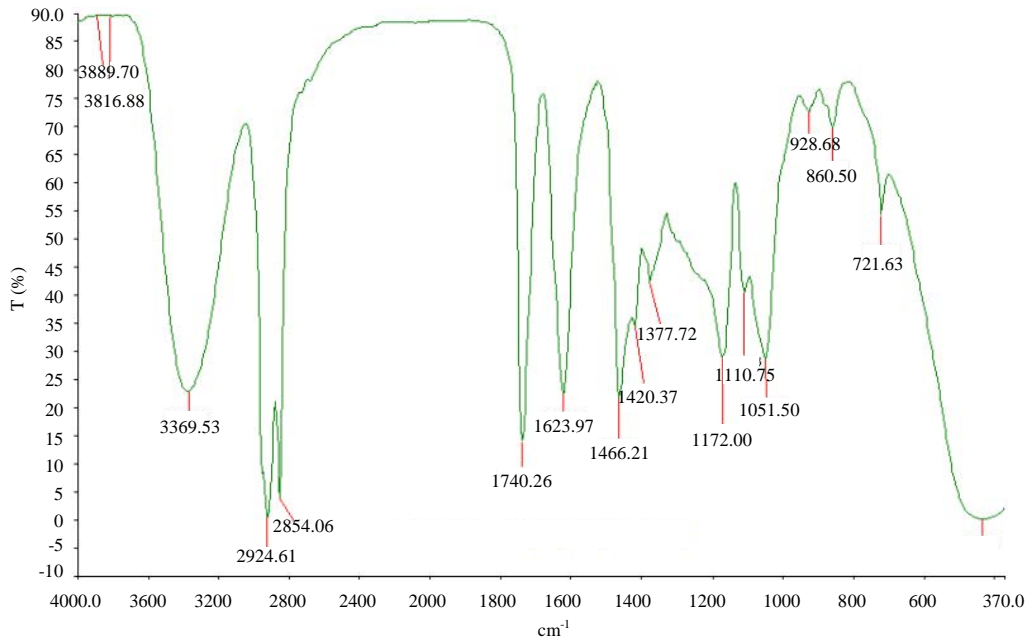


Fig. 2: FTIR spectrum of standard palm oil-based polyol

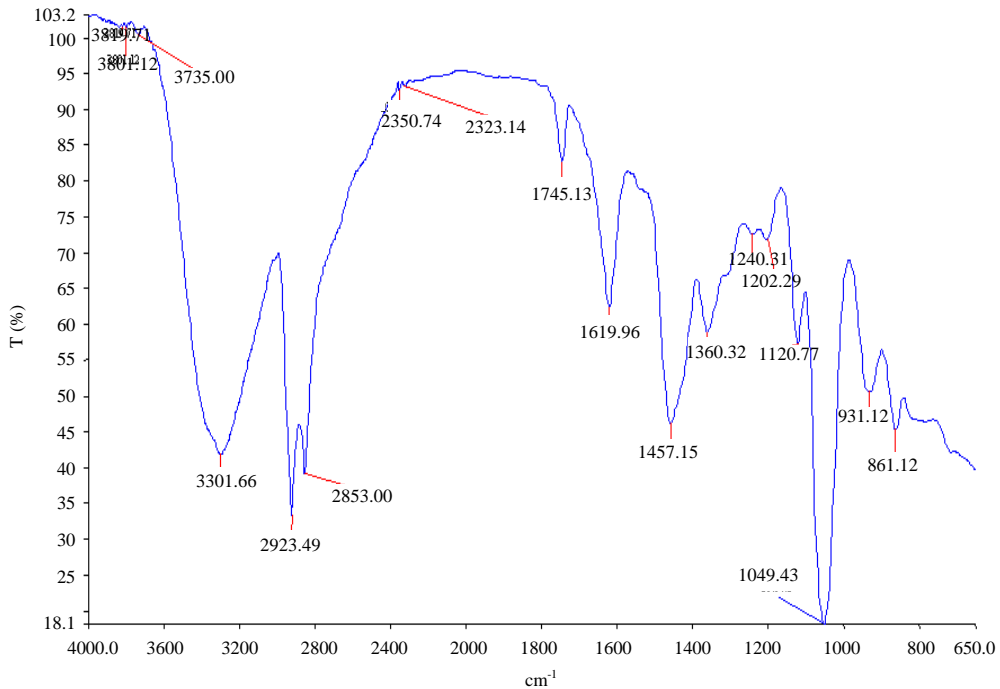


Fig. 3: FTIR spectrum of synthesized diethanolamide

Hydroxyl numbers and acid numbers: Hydroxyl number is no doubt important as it determines the suitability of the diethanolamide in the production of polymers such as rigid or flexible polyurethane foams. Hydroxyl number is also the reflection of yield of

the experiment. The synthesized diethanolamide exhibit high yield where the hydroxyl number is 254.20 mL NaOH/g. The result was found to be nearly similar to the standard POP where it showed 263.83 mL NaOH/g of sample after undergone acidity correction.

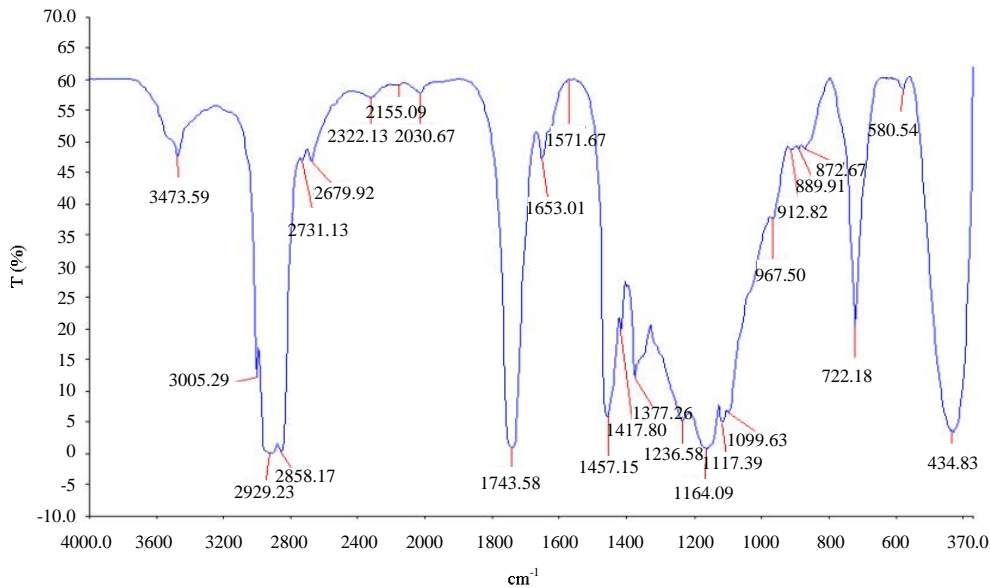


Fig. 4: FTIR spectrum of glycerol as the by product

CONCLUSION

Nowadays, issues on environmental sustainability are well-thought-out and triglyceride oils are expected to play an important role during the 21st century as promising to synthesize polymers from renewable sources. It is marked that RBDPO provides a feasible alternate source to the production of polyols. Reaction of RBDPO with DEA was successfully produced diethanolamide with high amount of hydroxyl number. This can be verified by FTIR study where the sample underwent significant changes, particularly in the gradual appearance of the peak C = O stretching, the appearance of broad peak O-H and C-N bands. The result obtained was compared with the standard POP. It was demonstrated that the hydroxyl group present in the synthesized POP quite similar to the standard after undergone acidity correction with the yield of reaction 254.20 mL NaOH/g of sample compared to the standard POP, 263.83 mL NaOH/g. Thus, the study was showed that polyol was successfully produced from palm oil. Therefore, this will reduce the dependency of petrochemical in producing polyol.

ACKNOWLEDGEMENT

Researchers would like to express their gratitude to the internal research grant from Universiti Teknologi MARA, Lestari grant for financial support to conduct this research.

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