

The Effect of Reaction Temperature on Retaining Oxirane Oxygen Contents in the Synthesis of Epoxidized Diethanolamides

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Abstract: Epoxidized diethanolamides were synthesized by reacting diethanolamine (DEA) with mixture of Epoxidized Palm Olein (EPO₀, 40% w/w) and Refined Bleached Deodorized Palm Kernel Olein (RBDPKO₀, 60% w/w) at 1:3 molar at 80°C for 5 h and continued at 110°C for another 4 h of reaction time. Synthesized diethanolamides with high content of epoxides were reacted with isocyanate in the presence of AlCl₃-THF complex catalyst to produce oxazolidone linkages in polyurethane network. The rigid polyurethane foam produced is of better quality as compared to the commercially available foam.

Key words: Amine value, epoxidized diethanolamides, FTIR, hydroxyl value, oxirane oxygen contents

INTRODUCTION

Alkanolamides is an important non-ionic surfactant using in the household products, personal care and cosmetic industries. Fatty alkanolamides, namely monoalkanolamide and dialkanolamide can be prepared by reacting fatty acids or fatty acid methyl esters with alkanolamine, such as monoalkanolamine or dialkanolamine at elevated temperature^[1]. Lately, secondary fatty amides, such as alkanolamides have been reported to be synthesized by using triacylglycerides from tallow and tripalmitin to react with amine, such as ethanolamine, diethanolamine, ethylenediamine, diethylenediamine and others^[2]. Besides, preparation of the ethanolamides by using laurel oil from black olive-sized fruits of *Laurus nabilis* L. has also been reported^[3]. However, alkanolamides can also be used as one type of natural oil derived from polyols to produce rigid polyurethane foam. They can be prepared from the reaction of diethanolamine (DEA) with natural glycerides, such as soy bean, linseed, peanut and safflower oil^[4]. The synthesis of diethanolamide polyol by using hydroxymethylated oil and carboxylated oil to increase the functionality of the polyol was used to prepare rigid polyurethane foams with the addition of Quadrol (N, N, N', N'- tetrakis [2-hydroxypropyl] ethylenediamine)^[5,6]. Foams are improved in terms of high close cell contents, good

dimensional stability and compression strength. Recently, diethanolamides has been successfully prepared from Refined Bleached Deodorized Palm Kernel Olein (RBDPKO₀) with DEA in the presence of potassium acetate as catalyst^[7]. Sieved empty fruit bunch fibres (EFB) from palm tree were also added as an organic filler to improve the mechanical properties of the rigid polyurethane foam. In other words, polyurethanes prepared from diethanolamides must be modified chemically or blended with other components in order to be sufficiently strong and stable.

Several studies reported that the introduction of heterocyclic groups namely isocyanurate, imide, phosphazene and oxazolidone to polyurethanes, could improve the thermal and mechanical properties of the foams^[8-11]. The addition of oxazolidone groups to polyurethanes was usually performed by reacting isocyanates with epoxy compounds. Yaganeh and co-workers reported that the introduction of oxazolidones to polyurethane backbone from reacting glycidol with isocyanate-terminated polyurethane prepolymers improved the thermal and the stress-strain properties of the elastomers^[12]. Although the epoxy groups in the middle of the fatty acid chain of triacylglycerides have lower reactivity towards isocyanate, Javni and co-workers found that the yield of oxazolidones is actually dependent on the type of catalyst used^[13].

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Therefore, we studied the synthesis of epoxidized diethanolamides from palm oil products. A series of epoxidized diethanolamides had been produced by using varying amount of Epoxidized Palm Olein (EPO_o) and RBDPKO_o to react with DEA^[14]. The synthesized diethanolamides, consisting of reactive epoxy compounds, would provide extra cross-linking sites to allow the epoxides to react with diisocyanates to form oxazolidones during polyurethane foam production^[15]. The formation of oxazolidone linkage would happen at room temperature with the presence of an appropriate catalyst^[16]. In the subsequent study, we proved that epoxides, retained in the diethanolamides, reacted with isocyanate during foam production in the presence of AlCl₃-THF complex catalyst to form oxazolidone linkages in the polyurethane network^[17]. The carbonyl stretch of oxazolidone was identified at 1750 cm⁻¹ through FTIR analysis. Foams produced from higher OOC diethanolamides, reported to be more thermally stable than foams with lesser or without the presence of epoxides. Besides that, the mechanical properties, such as compression strength, thermal conductivity, close cell contents and dimensional stability of foams were improved by the epoxy compounds in the diethanolamides.

Nevertheless there were some breakings of epoxy ring in the diethanolamides when prepared at high reaction temperatures. In the previous study, there were 34.5% of epoxy ring breakings when the epoxidized palm olein (EPO_o) reacted with diethanolamine at 110°C for 5 h^[14]. Consequently, in the present work, we report on the preparation method at different temperatures to retain maximum percentage of oxirane oxygen contents in epoxidized diethanolamide products.

MATERIALS AND METHODS

Materials: RBDPKO_o (specifications: iodine value = 26 I₂ mg 100 g⁻¹ sample, free fatty acid = 0.10 mg KOH g⁻¹ sample, saponification value = 250 mg KOH g⁻¹ sample) was obtained from Kempas Oil Sdn Bhd and EPO_o (specifications: oxirane oxygen contents = 3.0%, acidity = 1.1 mg KOH g⁻¹ sample, iodine value = 0.65 I₂ mg 100 g⁻¹ sample) was obtained from the pilot plant of Advanced Oleochemicals Technology Division (AOTD) of Malaysian Palm Oil Board (MPOB). Reagents: DEA (BASF), isopropyl alcohol (J.T. Baker), hydrobromic acid, 33 wt% solution in glacial acetic acid (ACROS ORGANICS), glacial acetic acid (J.T. Baker), were used as purchased. Chemicals: sodium acetate

(MERCK), eosin Y (ACROS ORGANICS), silver nitrate (DU LAB) and gelatin (MERCK) were used as purchased.

Synthesis of diethanolamides: The reaction was carried out in a one liter Pyrex glass reaction flask submerged in a silicone bath. The reaction flask was equipped with a mechanical stirrer, thermometer and condenser. 40% (w/w) of EPO_o was blended with RBDPKO_o to react with DEA at molar ratio of 1: 3 [palm oil triacylglyceride (TAG): DEA]. The reaction was carried out at different temperatures until the sample was homogenous. Samples of the reaction mixture were withdrawn hourly to determine oxirane oxygen contents and total amine value.

Oxirane Oxygen Content (OOC): The OOC was not determined using the standard hydrobromic acid in acetic acid method^[18]. This is because of the presence of DEA traces that will form amine-bromide complexes with HBr and interfere with the results of the determination test. The OOC was instead determined by using the back titration method described by A.J. Durbetaki, 1958^[19]. The formation of amine-bromide complexes will be converted to amine acetate by sodium acetate. The procedure was as followed: 0.5 g sample was dissolved in 10 mL of glacial acetic acid in a 250 mL Erlenmeyer flask. Then, 25 mL of 0.1 M hydrobromic acid in glacial acetic acid, 20 mL of 0.1 M sodium acetate, 6 drops of eosin Y indicator and 0.1 g gelatin were added into the flask. Lastly, 30 mL water was added before the sample was titrated with 0.1 M silver nitrate to an orange-crimson end point. A blank was carried out by adding 25 mL of 0.1 M hydrobromic acid and 35 mL of 0.1 M sodium acetate and titration was done as described above. The OOC was calculated using the following formula:

$$\% \text{OOC} = \frac{(V_1 - V_2) \times M \times 1.6}{W}$$

where, V₁ was the volume (mL) of silver nitrate used in the titration of the blank, V₂ was the volume (mL) of silver nitrate used in the titration of the sample, W was the weight of the sample in gram and M was the molarity of the hydrobromic acid solution.

Indicator method for total amine value determination: The total amine value is defined as the milligrams of potassium hydroxide equivalent to the basicity in one gram of sample. The analysis was based on the AOCS official method [20] but modified by

dissolving 1.0 g of sample in 100 mL of isopropyl alcohol in order to obtain a more significant color change at the end point of the titration.

Fourier Transform InfraRed (FTIR) spectral analysis: Nicolet FTIR, Model: Magma-IR 550 spectrometry, series II was used to monitor the functional groups of the synthesized products. The sample was coated on potassium bromide pellets. Averages of 16 scans were recorded for every sample.

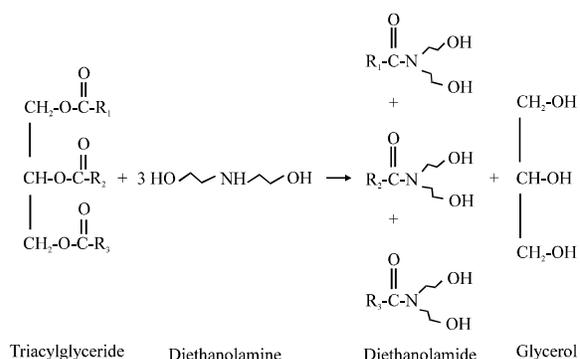
Hydroxyl Value Determination; The hydroxyl value is defined as the milligrams of potassium hydroxide equivalent to the hydroxyl content of one gram of sample. The hydroxyl value was determined by following the AOCS Official Method^[21].

Viscosity Measurement: The viscosity of the diethanolamides was measured by Brookfield DV-III Programmable Rheometer at 25 and 40°C. To determine the viscosity, small amount of test sample (approximately 0.25 g) was filled into the cone plate of the Rheometer. Test data will be gathered automatically by the computer program.

RESULTS AND DISCUSSION

Forty percent (w/w) of EPO₀ was blended with RBDPKO₀ as optimal starting material due to the diethanolamide products appeared as non-viscous liquid at room temperature with low viscosity as reported in another paper^[14]. The starting material was then reacted with DEA at molar ratio of 1:3 (palm oil TAG: DEA) (Scheme 1). Glycerol was being produced as the by-product of the reaction. However, it was not removed from the reaction mixture because it could help in cross-linking during the production of rigid polyurethane foam.

The optimum reaction temperature and reaction duration from the previous study were 110°C for 5 h^[14]. Therefore, in this study, we tried to retain maximum oxirane oxygen contents in diethanolamide products by reacting the reaction mixture at lower temperatures, ranging from 110-80°C. The reaction mixture was initially immiscible and separated into two layers, with the oil on the upper layer while the DEA stood at the bottom layer. When the two immiscible layers became homogenous, the epoxidized diethanolamides were formed and we discontinued the reaction. Sample was taken from the upper layer of the reaction mixture to study the changes of the oxirane oxygen contents. The epoxy functionality was retained more at lower reaction temperature (Fig. 1). The OOC of the diethanolamides,



Scheme 1: Reaction scheme for the synthesis of diethanolamide. R₁, R₂, R₃ are alkyl chains with or without epoxide(s) functionality

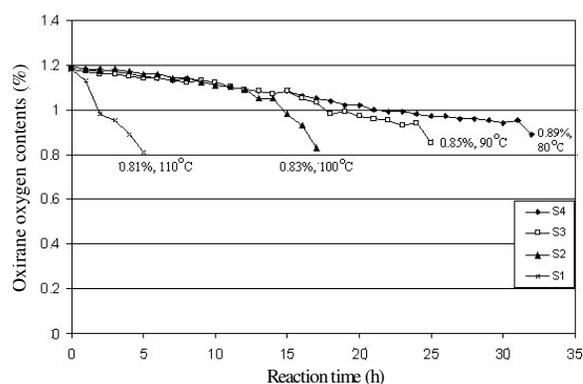


Fig. 1: Effects of reaction temperature on oxirane oxygen contents (S1-4). All samples were blended with 40% (w/w) of EPO₀ and 60% (w/w) of RBDPKO₀ and reacted with DEA at 3:1 (TAG: DEA) molar ratio

Table 1: Percentage (%) of oxirane oxygen contents retained (S1-4)

| Sample code | Reaction time (h) | ^b Oxirane oxygen contents (%) | ^c OOC retained (%) |
|-----------------|-------------------|--|-------------------------------|
| ^a S1 | 5 | 0.81 | 68.07 |
| ^a S2 | 17 | 0.83 | 70.75 |
| ^a S3 | 25 | 0.85 | 71.43 |
| ^a S4 | 32 | 0.89 | 74.79 |

^a: S1 to S4: Sample reacted at 110, 100, 90 and 80°C respectively;

^c: OOC retained = $\frac{\text{Oxirane oxygen contents at end of reaction}^b}{\text{Oxirane oxygen contents of starting material} = 1.19} \times 100\%$

synthesized at 80°C for 32 h managed to retain 74.79% of OOC from the starting material, whereas those reacted at 90, 100 and 110°C only managed to retain 68-71% of OOC (Table 1). However, the reaction duration was long when reacted at 80°C. Epoxy ring breakings were rapid at a high reaction temperature and long reaction duration.

Table 2: Reaction conditions to optimize oxirane oxygen contents

| Sample code | Reaction conditions |
|-------------|---------------------------|
| S5 | 80°C (5 h)+110°C (4 h) |
| S6 | 80°C (5 h)+120°C (3 h) |
| S7 | 80°C (5 h)+130°C (2 h) |
| S8 | 80°C (5 h)+140°C (1 h) |
| S9 | 80°C (5 h)+150°C (40 min) |
| S10 | 80°C (5 h)+160°C (30 min) |
| S11 | 80°C (5 h)+170°C (1 min) |

Table 3: Percentage (%) of oxirane oxygen contents retained (S5-11)

| Sample code | ^b Oxirane oxygen contents (%) | ^c OOO retained (%) |
|------------------|--|-------------------------------|
| ^a S5 | 1.06 | 89.08 |
| ^a S6 | 1.04 | 87.39 |
| ^a S7 | 1.02 | 85.71 |
| ^a S8 | 0.98 | 82.35 |
| ^a S9 | 0.96 | 80.67 |
| ^a S10 | 0.95 | 79.83 |
| ^a S11 | 0.94 | 78.99 |

^a: S5-11: Reaction conditions refer to Table 2;

$$^c: \text{OOO retained} = \frac{\text{Oxirane oxygen contents at end of reaction}^b}{\text{Oxirane oxygen contents of starting material} = 1.19} \times 100\%$$

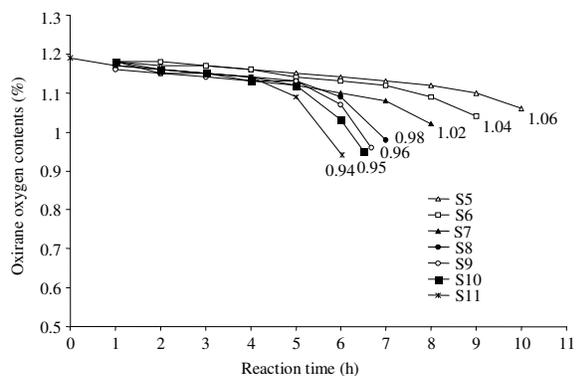


Fig. 2: Effects of reaction temperature on oxirane oxygen contents (S5-11). (i): Reaction conditions for samples S5-S11, refer to Table 2; (ii): All samples were blended with 40% (w/w) of EPO_o and 60% (w/w) of RBDPKO_o and reacted with DEA at 3:1 (TAG: DEA) molar ratio

Therefore, we continued the study by reacting the reaction mixture at 80°C for 5 h and raised the reaction temperature to higher temperatures ranging from 110-170°C until the sample became homogenous (Table 2). Epoxy ring breakings were mild when reacted at 80°C for initial 5 h and raising the temperature for the following hour could help shorten the reaction time (Fig. 2). Diethanolamides from reaction S5 managed to retain 89.08% of OOC from the starting material (Table 3). The retained epoxy ring is expected to provide additional cross-linking sites by forming

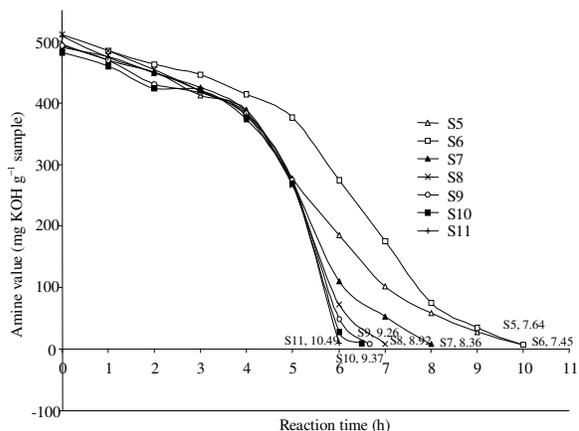


Fig. 3: Total amine value at different reaction temperature. (i) Reaction conditions for samples S5-S11, refer to Table 2; (ii): All samples were blended with 40% (w/w) of EPO_o and 60% (w/w) of RBDPKO_o and reacted with DEA at 3:1 (TAG: DEA) molar ratio

oxazolidone during the preparation of rigid polyurethane foam. In our previous study, diethanolamides with higher percentage of OOC produced improved thermal conductivity, hardness and compressive strength of rigid polyurethane foam^[17].

Sample was taken from the bottom layer of the reaction mixture to study the changes of the amine value (AV) for sample S5-S11. The total amine value of the reaction mixture would decrease throughout the reaction and when the reaction temperature was raised to a higher temperature after 5 h of reaction at 80°C, a sharp decrease in amine content was observed (Fig. 3). The total amine values in samples reacted at lower temperature and longer reaction time (S5, AV = 7.64 mg KOH g⁻¹ sample, S6, AV = 7.45 mg KOH g⁻¹ sample) were lower compared to samples reacted at higher temperature and shorter reaction time (S10, AV = 9.37 mg KOH g⁻¹ sample, S11, AV = 10.49 mg KOH g⁻¹ sample). This indicated that reactions S5 and S6 were more complete as compared to reactions S10 and S11.

FTIR study was subsequently used to monitor the reaction of diethanolamides. Figure 4 and 5 show that the sample underwent significant changes, particularly in the gradual appearance of the peak of C = O stretching for tertiary amide at around 1625 cm⁻¹. Another significant change was the gradual appearance of the broad peak, OH band at around 3396 cm⁻¹. These changes indicated the gradual formation of the diethanolamides. Besides, the peak of C-O stretching

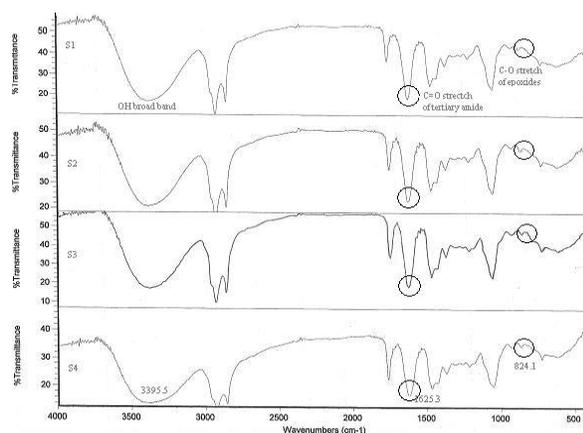


Fig. 4: FTIR analysis on samples S1-S4 to monitor the formation of OH band, C = O stretching of 3° amide and C-O stretching of epoxides. (i): S1: 110°C, S2: 100°C, S3: 90°C and S4: 80°C (Reaction temperature); (ii): All samples were blended with 40% (w/w) of EPO_o and 60% (w/w) of RBDPKO_o and reacted with DEA at 3:1 (TAG: DEA) molar ratio

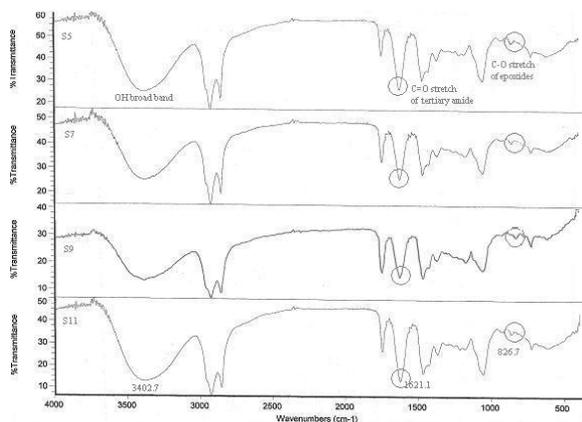


Fig. 5: FTIR analysis on samples S5-S11 to monitor the formation of OH Band, C = O stretching of 3° amide and C-O stretching of epoxides. (i): Reaction conditions of samples S5-S11, refer to Table 2; (ii): All samples were blended with 40% (w/w) of EPO_o and 60% (w/w) of RBDPKO_o and reacted with DEA at 3:1 (TAG: DEA) molar ratio

for epoxy ring at around 824 cm⁻¹ was observed, however the changes of percentage in transmittance were not significant due to the low percentage of epoxy compounds in the samples.

The hydroxyl value is no doubt important as it determines the suitability of the diethanolamides in the production of rigid or flexible polyurethane foam. The

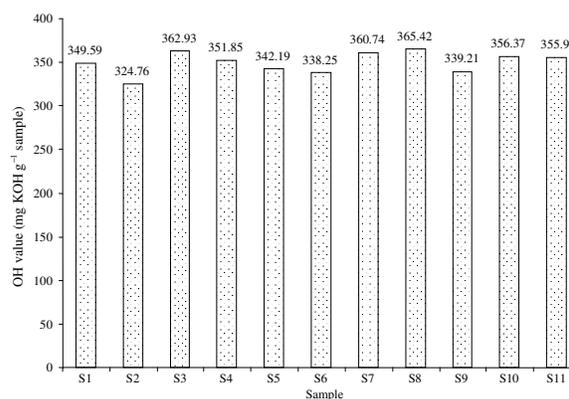


Fig. 6: Hydroxyl value of the diethanolamide products. (i): S1: 110°C, S2: 100°C, S3: 90°C and S4: 80°C (Reaction temperature); (ii): Reaction conditions of samples S5-S11, refer to Table 2; (ii): All samples were blended with 40% (w/w) of EPO_o and 60% (w/w) of RBDPKO_o and reacted with DEA at 3:1 (TAG: DEA) molar ratio

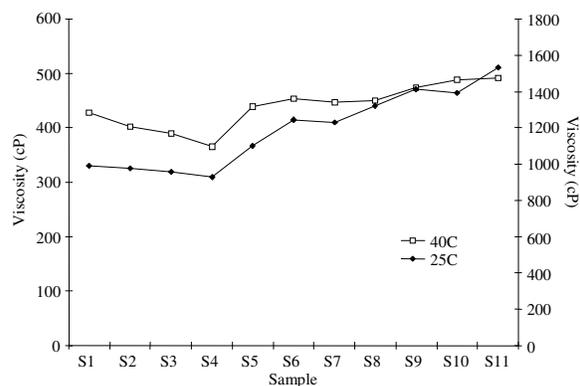


Fig. 7: Viscosity measurement on the synthesized diethanolamides. (i): S1: 110°C, S2: 100°C, S3: 90°C and S4: 80°C (Reaction temperature); (ii): Reaction conditions of samples S5-S11, refer to Table 2; (ii): All samples were blended with 40% (w/w) of EPO_o and 60% (w/w) of RBDPKO_o and reacted with DEA at 3:1 (TAG: DEA) molar ratio

synthesized diethanolamides exhibit high hydroxyl values in the range of 320-370 mg KOH g⁻¹ sample (Fig. 6). The hydroxyl values is found to be quite similar to the hydroxyl values (300-370 mg KOH g⁻¹ sample) of the carboxylated diethanolamides and palm oil-based diethanolamides used in the production of rigid polyurethane foams^[6,7].

At last, viscosity of the final products of each reaction was measured at 25°C and 40°C (Fig. 7). By

reacting the reaction mixture at a lower temperature (S2, S3, S4), a less viscous diethanolamides could be produced. Nonetheless, samples that reacted at a higher reaction temperature (S5-S11) performed as higher viscosity products.

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