Jurnal Teknologi

Full Paper

CHEMICAL EPOXIDATION OF OLEIC ACID TO PRODUCE AB TYPE MONOMER FOR FATTY-ACID-BASED POLYESTER SYNTHESIS

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Article history
Received
19 April 2021
Received in revised form
17 September 2021
Accepted
23 September 2021
Published Online
20 October 2021

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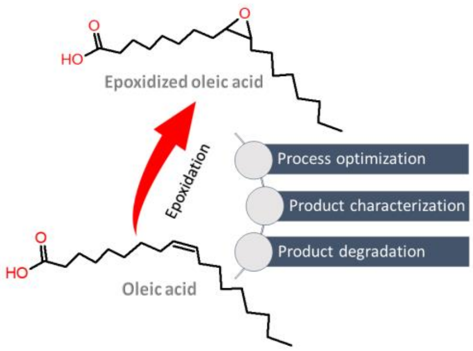
Graphical abstract



Abstract

Epoxides from vegetable oils are currently gaining more attention to replace petroleum-based monomers for polymer synthesis. As one of unsaturated fatty acids derived from vegetable oil, oleic acid can be converted into epoxidized oleic acid by chemical epoxidation. Epoxidized oleic acid is a bifunctional monomer that has the potential to be used as raw material for fatty-acid-based polyester synthesis. This paper proposes the Taguchi-based optimization technique for in-situ epoxidation of oleic acid. The combining factors affecting the maximum yield were also determined to obtain a higher quality of epoxidized oleic acid in a relatively short time. Epoxidized oleic acid was characterized and tested for degradation. The characterization result showed the possibility of the polymerization reaction, and the kinetic study showed that the rate of epoxide degradation at room temperature follows second order with a reaction rate constant of 2.7235 gr.mmol^{-1}.day^{-1}.

Keywords: Oleic acid, fatty-acid-based polyester, chemical epoxidation, optimization, degradation kinetic

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1.0 INTRODUCTION

The utilization of vegetable oils as natural renewable sources to reduce the dependence on petroleum products is advancing significantly. Through several modifications, fatty acids, the primary components in the vegetable oils, are possibly converted into large functional chemicals. These reactions occurred at the carboxyl group or the alkyl chain of the unsaturated fatty acid [1]. One of the potential reactions is described as the epoxidation between the double bond from the alkyl chain and oxidizing agent to produce fatty-acid-based epoxides [2]. Epoxidized vegetable oil is not only a potential substitute for petroleum-based phthalate plasticizer for polymer processing but also a promising starting material for bio-based polymer [3]. Polyurethane, polyester, and polyether are the class of polymer that has been successfully synthesized from epoxidized vegetable oil [4–6].

Oleic acid is a monounsaturated fatty acid derived from various vegetable oil. Epoxidation of oleic acid has been intensively studied as the simplified model for epoxidation reaction [7–10]. Epoxidized oleic acid as the epoxidation product has two reactive functional groups in one molecule: oxirane or epoxide and carboxylic group. Consequently, it can be further applied as a valuable AB-type monomer to synthesize bio-based polyester [11]. The use of AB monomer in step-growth polymerization reaction has been recognized as an alternative strategy to produce polymers with high molecular weight [12]. Self-condensation between phenyl halide and phenoxide owned by AB-type sulfone-based monomers has resulted in poly(ether sulfone) with a molecular weight of more than 110000 [13]. Polymers of intrinsic microporosity for membrane application (PIM-1) has also been successfully synthesized from AB-type monomers, although it still has a reasonably large polydispersity index [14]. Poly(silyl ethers) synthesis from AB monomers with silane and hydroxyl groups has also succeeded in obtaining polymers with thermal stability similar to those synthesized with AA+BB type monomers [15]. On the other hand, AB-type monomers are challenging to be synthesized since the presence of both functional groups in the reaction system can trigger various unwanted side reactions or an early stage of polymerization reaction [16]. Therefore, optimizing the reaction parameters is an important step to achieve high yields of the reaction product.

In this study, epoxidized oleic acid was produced from chemical epoxidation using an in-situ method. This method is the most widely used method for converting unsaturated fatty acid into epoxide chemicals [17–21]. Performic acid was employed as an oxidant without any added catalyst to minimize the reaction system's acidity and suppress the formation of side products. The reaction temperature and the ratio of reactants were optimized using the Taguchi-based design of experiment. This method is well-developed with an orthogonal array to efficiently improve process productivity [22]. Process variables' contribution was quantified using ANOVA, and conversion-selectivity characteristic during the reaction progress was also studied.

Epoxidized oleic acid as the reaction product was then purified and characterized for its functionality and thermal behavior to study the possibility of the polymerization reaction. Furthermore, due to its high degree of reactivity, epoxidized oleic acid is susceptible to degradation even during storage at room temperature. Studies on the degradation of epoxides are primarily carried out in a liquid-liquid reaction system with intensive heating to study the behavior of the ring-opening process [23, 24]. Borugadda and Goud investigated the degradation of epoxidized vegetable oils and methyl esters [25]. They concluded that the decrease in oxirane number was strongly affected by storage conditions. However, the kinetic model for degradation reaction has not been studied yet. Therefore, the purpose of this research is to obtain the optimum reaction condition to produce epoxidized oleic acid in high yield to be used as raw material for polymer synthesis and develop the kinetic model for product degradation.

2.0 METHODOLOGY

2.1 Materials

Technical grade oleic acid was purchased from Sigma-Aldrich, Singapore, with 90% purity by weight. Formic acid 98%, hydrogen peroxide 30%, and all reagents used to evaluate iodine and oxirane values were acquired from Merck.

2.2 Epoxidation Reaction

Epoxidation was conducted in a 250 mL reaction flask immersed in a water bath. The flask is flat-bottomed with three necks dedicated to the reflux condenser, thermometer, and feeding/sampling tube. A hot plate magnetic stirrer was used to provide heating and stirring. For each experiment, oleic and formic acids were initially poured into the flask followed by solvent (optional) and heated at a pre-determined reaction temperature. When the desired reaction temperature was achieved, hydrogen peroxide was then introduced dropwise for 20 minutes. For the whole experiment, the volume of hydrogen peroxide for each run was 15 ml to ensure uniformity of the hydrogen peroxide drop rate. The amount of oleic acid, formic acid, and the solvent was calculated based on moles of hydrogen peroxide and adjusted according to the experimental design. Therefore, the total reaction volume varies between 40-130 mL. Subsequent samples were withdrawn from the mixture every 30 minutes, followed by a cold-water wash. The aqueous phase was removed, and the organic material was further purified by centrifugation. However, the optional inclusion of a solvent involves an additional step, where the sample is dried at room temperature to obtain a constant weight. The iodine and oxirane values of the purified sample were evaluated using the standard method based on the previous work [26, 27]. After two hours, the reaction was stopped, and a similar purification procedure was applied for the final reaction mixture.

The reaction performance was ascertained using three parameters, termed double bond conversion (x), selectivity (S), and yield (y). Double bond conversion and selectivity were calculated from oxirane and iodine numbers using the following equations [28]:

$$x = \frac{I_0 - I_t}{I_0} \times 100\% \tag{1}$$

$$S = \frac{O_t/M_o}{(I_0 - I_t)/2M_i} \tag{2}$$

where I, O, Mi, and Mo are iodine number, oxirane number, the molecular weight of iodine, and the molecular weight of oxygen atom, respectively. Subscript 0 indicates the initial value, and subscript t denotes the value at a specific reaction time.

Meanwhile, epoxide yield was calculated from the following equation [29]:

$$y = \frac{O_t}{O_{max}} \times 100\% \quad (3)$$

O_{max} is the maximum attainable oxirane value, where

$$O_{max} = \frac{(I_0/2M_i)M_o}{100 + (I_0/2M_i)M_o} \times 100\% \quad (4)$$

Since the initial value of iodine number for oleic acid was 90 gr I_2/100 gr, O_{max} for epoxidized oleic acid was calculated to be 5.37%.

2.3 Design of Experiment

Taguchi-based design of experiment requires the identification of important parameters influencing the process as factor (F) and level (L), as shown in Table 1. Four parameters were incorporated in the design of the experiment, including reaction temperature, hydrogen peroxide to oleic acid molar ratio (HP:OA), formic acid to oleic acid molar ratio (FA:OA), and solvent (n-hexane) to oleic acid mass ratio (S:OA). There are three levels available for each factor. From the identified factor and level, the orthogonal array is then employed to ascertain the number of experiments.

The selection of factors and levels in this study was based on preliminary experiments and literature studies. The reaction temperature was chosen in the range of 55-65 °C, considering that the reaction proceeds considerably fast in that temperature range. The maximum temperature used is close to the boiling temperature of n-hexane. The HP:AO ratio was made to a maximum of 6, referring to preliminary experiments where this ratio gave promising results. While the ratio of AF:AO is made to a maximum of 3 by considering formic acid to have a more dominant effect on side reactions. The solvent is the fourth factor involved in the experimental design because some literature states that the solvent contributes to stabilizing the epoxide product formed during the reaction [18, 30].

Table 1 List of factors and level for the optimization of in-situ epoxidation of oleic acid

Factors	Level 1	Level 2	Level 3
Temperature, °C	55	60	65
HP:OA	2	4	6
FA:OA	1	2	3
S:OA	0	0.5	1

The minimum possible number of experiments (N) from the following correlation was applied to save valuable time and resources:

$$N = (L-1)F + 1 \quad (5)$$

Therefore, the number of experiments for this study is 9 (usually called L9) with the detailed combination as describes in Table 2. In order to ensure repeatability, each experimental number was repeated twice.

Table 2 L9 orthogonal array for the optimization of in-situ epoxidation of oleic acid

Exp no	T, °C	HP:OA	FA:OA	S:OA
1	55	2	1	0
2	55	4	2	0.5
3	55	6	3	1
4	60	2	2	1
5	60	4	3	0
6	60	6	1	0.5
7	65	2	3	0.5
8	65	4	1	1
9	65	6	2	0

Signal to noise ratio (SNR) was then calculated after the data collection. There are three categories to determine SNR: nominal-is-the-best, smaller-the-better, and larger-the-better. The final epoxide yield was selected as a response, and the optimum combination factor with the highest yield value is desired. Therefore, larger-the-better is the most appropriate SNR to be used and was calculated from the equation below [22]:

$$Larger - the - better - SNR_i = -10 log \frac{1}{n}\left(\sum_{j=1}^{n} \frac{1}{y_j^2}\right) \quad (6)$$

Analysis of variance (ANOVA) was performed to quantify the contribution factor on the final yield by the following equation [18]:

$$\%contribution = \frac{SS_f}{SS_T} \times 10\% \quad (7)$$

where,

$$SS_f = \sum_{l=1}^{3} m\left[(SNR)_{fl} - SNR_T\right]^2 \quad (8)$$

$$SS_T = \sum_{i=1}^{9} (SNR_l - SNR_T)^2 \quad (9)$$

SS_f is the sum of the square of the f^{th} factor, SS_T is the total sum of the square, SNR_T is the average signal to noise ratio, i is the number of experiments from 1 to m, j is the number of trials from 1 to n, f is the corresponding factor, and y is the value of the response.

2.3 Product Characterization

The refined epoxidized oleic acid with the highest yield obtained from the optimization process was analyzed quantitatively for oxirane number and acid number [31]. FTIR analysis was performed on Nicolet

Avatar 360 IR (USA) in the range of 4000-400 cm^{-1} and resolution of 2 cm^{-1}. Simultaneous thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) were performed on a single instrument from Mettler Toledo (Switzerland) with a heating rate of 20 °C/min under nitrogen atmosphere from 30-500 °C.

2.4 Product Degradation Study

Epoxidized oleic acid was stored at two different conditions: room temperature (25-30°C) and inside a freezer (-3 to -5°C). The oxirane numbers of samples were analyzed weekly until eight weeks storage period.

3.0 RESULTS AND DISCUSSION

3.1 Optimization Result

The average reaction time to achieve maximum conversion in the epoxidation of vegetable oil and its derivatives is between 6 - 9 hours, depending on the raw material, oxidant, and catalyst. However, a lesser duration can be applied to obtain a notable yield, although usually accompanied by excessive use of reactant [18, 23, 32]. The reaction time was specified at 2 hours to compromise between the duration and the use of reactants. The reaction rate for most epoxidation, particularly using oleic acid, is substantially high at a temperature range of 50 - 70 °C [8]. The primary objective of epoxidation is usually to produce epoxide chemicals, where the most favourable parameter is the product quality represented by the number of epoxide or oxirane groups resulting from the reaction. Since the double bond quality is known, there is also the maximum epoxide value required from the specific raw material. The ratio between the experimental and the maximum value of oxirane number is defined as the yield. In addition, 100% yield denotes all double bonds in the raw material have been converted to oxirane ring, resulting in high product quality. Therefore, the objective function of this study is to maximize the epoxide yield. On the other hand, conversion and selectivity were not incorporated as responses due to the high value of these two parameters not always corresponding to the product quality.

Taguchi analysis was employed to obtain the optimum combination factor from the calculated SNR. The experimental value of epoxide yield for each number of experiment and each run, the mean experimental yield, and the calculated SNR can be seen in Table 3.

Table 3 shows the highest value of experimental yield and SNR are attributed to experiment number 3. However, the optimum combination factor required to instigate the highest yield is interpreted from the highest SNR mean value in each factor, as shown in Table 4.

Table 3 Experimental epoxide yield and SNR

Exp no	Yield 1, %	Yield 2, %	Mean Yield, %	SNR
1	73.56	68.97	71.27	37.04
2	85.89	82.46	84.17	38.50
3	88.96	87.77	88.37	38.93
4	82.25	79.83	81.04	38.17
5	40.60	35.31	37.95	31.52
6	68.95	75.83	72.39	37.16
7	14.15	13.36	13.75	22.76
8	55.74	51.24	53.49	34.54
9	65.87	53.97	59.92	35.42
SNR_T				34.89

Table 4 SNR for each level and parameter

Level	T	HP:OA	FA:OA	S:OA
1	38.16	32.66	36.25	34.66
2	35.62	34.85	37.36	32.81
3	30.91	37.17	31.07	37.21
Delta	7.25	4.51	6.3	4.41
Rank	1	3	2	4

Table 4 shows that the highest SNR obtained from the temperature factor is level 1 (55 °C). Thus, the temperature of 55 °C is considered to be the optimum reaction temperature. Analogously, a similar conclusion can be drawn from other parameters. Therefore, the optimum factors and levels to achieve the maximum epoxide yield were at hydrogen peroxide to oleic acid molar ratio (HP:OA) of 6, formic acid to oleic acid molar ratio (FA:OA) of 2, and solvent to oleic acid mass ratio (S:OA) of 1. The contribution rank is determined from the variation between the highest and lowest SNR values. Table 4 highlights this difference as delta. In conclusion, the most influencing factor of the epoxide yield is the temperature, followed by formic acid, hydrogen peroxide, and solvent. However, this rank is qualitative. The ANOVA approach was further applied to express the result quantitatively. The confirmation test was then conducted to obtain the actual yield from the optimized combination factor and level. The mean yield from the confirmation experiment was only 76.37%. This value is not only much lower than expected but also lower than the highest yield obtained from experiment number 3 from the L9 orthogonal array. The difficulty in reaching the high yield for the epoxidation of oleic acid was recognized by several studies [33, 34]. Therefore, the combination factor and level from experiment number 3 were considered the actual optimum condition.

3.2 Analysis of Variance (ANOVA)

The ANOVA was used to calculate the percentage contribution of individual factor from the SS_f value using Equation 7-9, and the results were presented in Table 5. Table 5 shows a similar factor ranking to the Taguchi results, based on the calculated percentage contribution. The reaction temperature is known to produce the most significant impact (38.87%) on the epoxide yield. The second contribution is assigned by the formic to oleic acid molar ratio, and the difference is relatively close to the reaction temperature. Meanwhile, HP:OA and S:OA are attributed to the third and fourth contribution factors, respectively. These latest two factors also indicated similar trends with the first two. Therefore, it can be concluded that the reaction temperature and formic acid observed more significant effects on the epoxide yield compared to hydrogen peroxide and solvent.

Table 5 Sum of square of factor and percent contribution

Factor	SSf	%contribution
Reaction temperature	27.06	38.87
HP:OA	10.19	14.64
FA:OA	22.57	32.43
S:OA	9.79	14.06

This study proves that the reaction temperature produces the highest contribution. This is understandable since the reaction rate appears stronger depending on the temperature. The decreasing trend in SNR ratio for temperature is attributed to side reactions affecting epoxide yield. In-situ epoxidation of oleic acid involves two main reactions and several possibilities of side reactions. The first main reaction produces performic acid from the reaction between hydrogen peroxide and formic acid. Subsequently, the performic acid reacts with the double bond of oleic acid in the second main reaction to produce epoxidized oleic acid. The side reactions consume epoxidized oleic acid. Hence, the rate of side reactions is considered to be more affected by temperature than the rate of main reactions.

The higher percentage contribution of formic acid than hydrogen peroxide is due to its contribution to the reaction system. Formic acid is involved in the second reaction (i.e., epoxidation reaction) as the carrier for oxygen atom by its transformation into performic acid, while only part of the oxygen atom in hydrogen peroxide is involved. In addition, the polarity of oleic acid is closer to formic acid compared to hydrogen peroxide. Consequently, performic and formic acids are possibly present in the organic phase. Based on the SNR mean value, the optimum condition was achieved at the molar ratio FA:OA of 2 and sharply declined at the molar ratio of 3. Not only does formic acid offer a significant contribution to epoxide synthesis, but also simultaneously produces a significant contribution to the ring-opening reaction. Cai *et al.* (2018) concluded that the rate of ring-opening by carboxylic and percarboxylic acid is higher than by water and hydrogen peroxide [24]. The solvent contribution and hydrogen peroxide have almost similar values but are slightly higher for the hydrogen peroxide. From the reaction point of view, the solvent is not an intrinsic part and acting as an inert phase. The role of solvent in the in-situ epoxidation is majorly to stabilize the resulting epoxide by lowering its concentration [21, 29].

3.3 Profile of Conversion and Selectivity

There are two analytical results investigated along with optimization. These include double bond conversion and epoxide selectivity. Conversion is not applied independently due to side reaction interference. In most cases, the decline in iodine number is not always accompanied by the proportional increase in oxirane number [27]. Figure 1 shows the double bond conversion and selectivity for each number of experiments.

Since all experiments possessed completely different combination factors, the trend of conversion and selectivity in Figure 1 cannot be attributed to a specific factor. However, selectivity tends to decrease with consistently high conversion. This is observed in experiments number 5 and 7. In both cases, a high conversion was achieved even in the first 30 minutes of the reaction. When the conversion was high, the epoxide concentration was also high at first until it started to decrease gradually due to ring-opening. The rate of the epoxide ring-opening reaction is directly proportional to the epoxide concentration. Therefore, the epoxide that had been formed at the beginning of the reaction continued to decrease along with the reaction time and resulted in a low yield measured at the end of the reaction, as can be seen in Table 3. From the combination of factors and levels in both experiments and supported by the results of ANOVA analysis, the element that might contribute to the ring-opening reaction is the high concentration of formic acid.

The selectivity remains constant when there is a gradual increase in conversion. The extent of side reaction observed from Figure 1 might contribute significantly to the optimization process. Previous literature barely reported the correlation between selectivity and conversion for in-situ epoxidation. Petrovic *et al*. (2002) plotted selectivity versus time for epoxidation of soybean oil using a different type of percarboxylic acid and concluded the selectivity is high at low temperature and the first hours of the reaction [19]. The incorporation of selectivity in the study of epoxidation reaction was also reported by

Kuranska *et al*. (2019), but only as supporting data [28].

3.4 Product Characterization

The quantitative analysis result of the epoxidized oleic acid showed that the oxirane and acid numbers were 4.8% and 182 mg KOH/gr, respectively. The infrared spectra of epoxidized oleic acid (EOA) and oleic acid (OA) can be seen in Figure 2. The disappearance of the double bond absorption band of oleic acid at 3004.82 cm^{-1} and the appearance of a new epoxide band of epoxidized oleic acid at 844.57 cm^{-1} [35] indicate that the epoxidation reaction was carried out successfully.

Simultaneous thermal analysis was used to study the possibility of self-polymerization of epoxidized oleic acid since it is categorized as an AB-type monomer. Compared to the AABB-type monomer, AB-type monomer offers several advantages in the polymerization, such as the easiness of controlling the stoichiometric molar ratio of the functional group, simpler purification process, and higher yield [36]. With epoxidized oleic acid as an AB-type monomer, the resulting polymer is polyester because the oxirane group reacts with the carboxylic group to form an ester group without side products [11]. Typical polymerization reaction to produce polyester usually uses diacid and diol (AA and BB type monomer, respectively) as raw materials and resulting small molecule as a side product. Therefore, polyester from epoxidized oleic acid polymerization process is simpler in the term of the purification process.

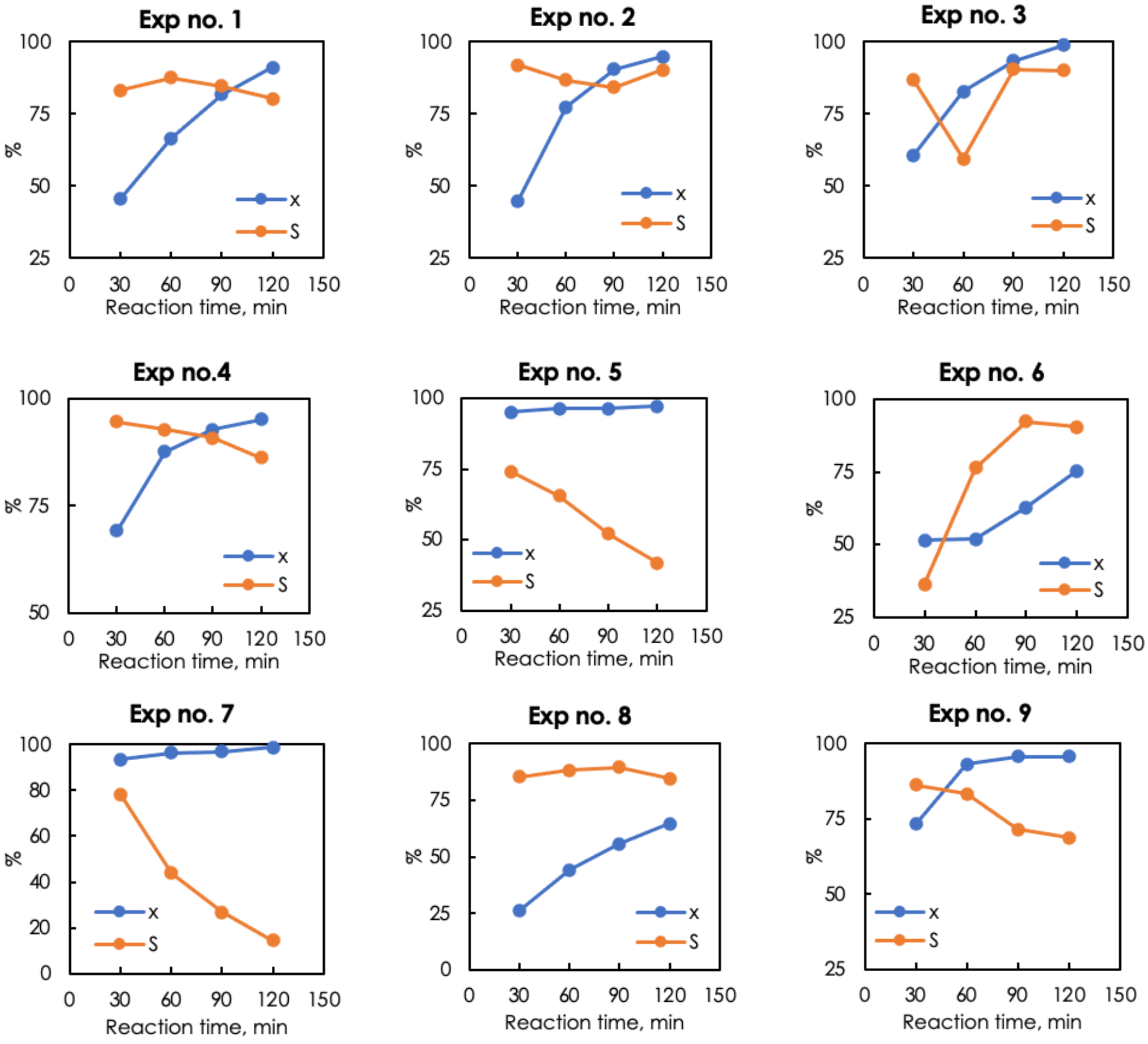

Figure 1 Double bond conversion and epoxide selectivity for chemical epoxidation of oleic acid

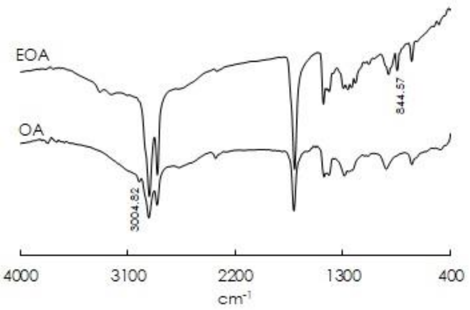

Figure 2 Infrared spectra of oleic acid and epoxidized oleic acid

TGA and differential thermogravimetric (DTG) curves can be seen in Figure 3. TGA curve shows one step thermal decomposition of epoxidized oleic acid as confirmed by one prominent peak in DTG curves. Initial and peak decomposition temperature is 323 and 391 °C, respectively. The decomposition of the ester bond generally occurs at a temperature of 350-395 °C [11]. Thus, it can be assumed that during the heating process, a polymerization reaction occurs, which results in an ester bond. This assumption is also supported by the DSC curve shown in Figure 4. There are two endothermic peaks, and one exothermic peak observed from the curve. The first endothermic peak is large and well-defined, indicating the melting process. The epoxidized oleic acid is in a solid phase at room temperature. From the curves, it can be shown that the melting point of epoxidized oleic acid is 59.9 °C. The second endothermic peak is relatively shallow and broad, as confirmed from TGA and DTG curves. This peak represents the degradation process. Meanwhile, the exothermic peak was observed in the temperature range of 160-250 °C. The presence of this peak leads to the possibility of a polymerization reaction in that temperature range. In order to confirm the self-polymerization reaction, the purified epoxidized oleic was heated until 200 °C, and a yellowish gel-like solid was obtained within several minutes.

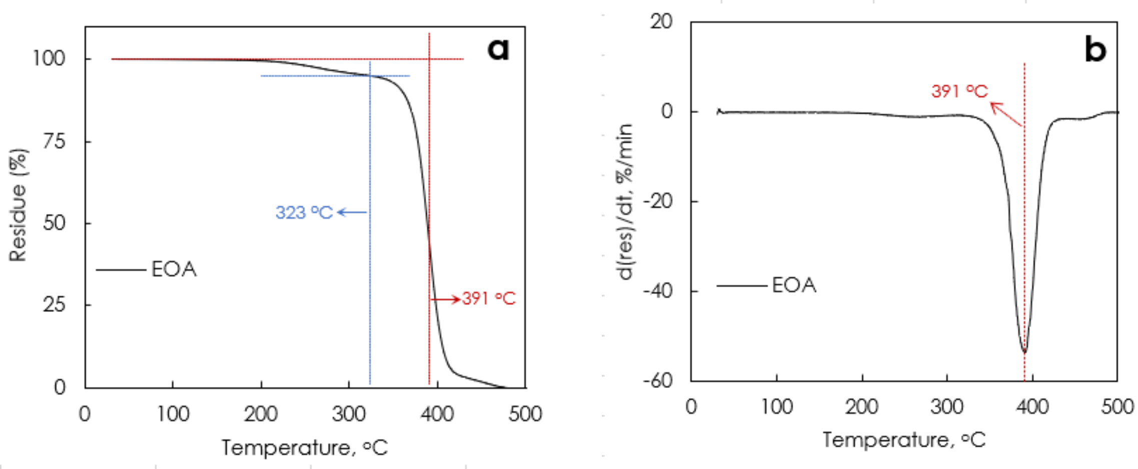

Figure 3 (a) TGA and (b) DTG curves of epoxidized oleic acid

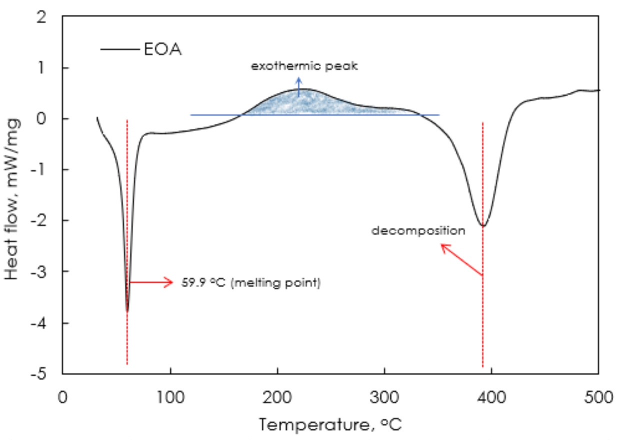

Figure 4 DSC curve of epoxidized oleic acid

3.5 Degradation Kinetic

A preliminary experiment on the utilization of epoxidized oleic acid revealed that there was a significant decrease of oxirane number as a function of storage time, especially when the product was stored at room temperature. Only one published work in the epoxidation of vegetable oil and its derivatives was concerned about this phenomenon [25]. However, it covered only the epoxidized vegetable oil and methyl ester without the involvement of the epoxidized fatty acid. Moreover, the kinetic study of epoxides degradation has not been found in the literature. In this study, degradation study, as well as degradation kinetic of epoxidized oleic acid, have been developed. Epoxidized oleic acid was stored in two different storage conditions (room and low temperature), and the oxirane number was analyzed weekly. The trend of oxirane number of epoxidized oleic acid can be seen in Figure 5.

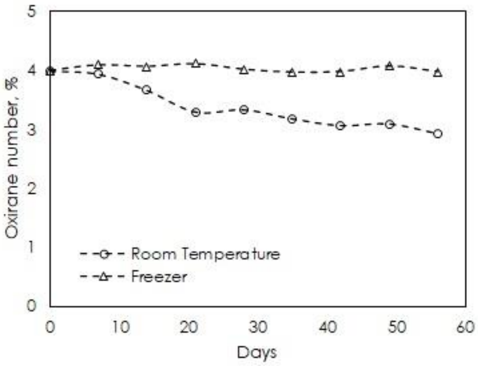

Figure 5 Oxirane number profile at different storage condition for two months

Figure 5 shows that low-temperature storage is favorable because the oxirane number can be maintained without significant change. However, after eight weeks at room temperature, the oxirane number decrease was measured to be 27%. The degradation kinetic was developed based on the power-law model. Interpretation of kinetic parameters was made, and second-order reaction kinetic was found to give the best linearity. Figure 6 shows the plot between epoxides concentration (represented by $1/C_{EOA}$) versus time. The degradation rate constant was calculated from the slope of the line with the value of 2.723 $gr.mmol^{-1}.day^{-1}$.

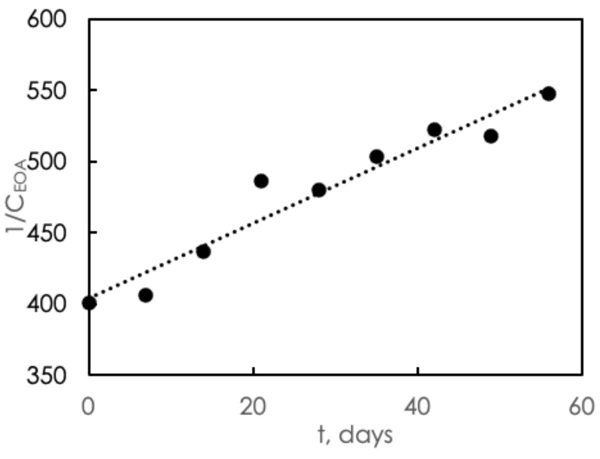

Figure 6 $1/C_{EOA}$ vs storage time

Since the second-order reaction kinetic gave the best fit, it is possible that the cause of the degradation was ascribed to the early stage of the oligomerization reaction. Epoxidized oleic acid contains two functional groups on the same molecule, i.e., oxirane ring and carboxylic acid. The dual functionality of the molecule usually led to instability during synthesis and storage [16].

4.0 CONCLUSION

Chemical epoxidation of oleic was optimized to produce a high yield of epoxidized oleic acid. Taguchi-based design of experiment was applied to optimize the reaction conditions, and the highest yield was obtained at the reaction temperature of 55 °C, hydrogen peroxide to oleic acid molar ratio of 6, formic to oleic acid molar ratio of 3, and solvent to oleic acid mass ratio of 1. In conclusion, the reaction temperature and formic acid delivered the highest contribution to epoxide yield compared to hydrogen peroxide and solvent. From the conversion and selectivity profile, the side reactions were known to interfere with the overall process. The characterization of epoxidized oleic acid showed the possibility of a self-polymerization reaction in the temperature range of 160-250 °C. Additional study of product degradation denoted that the degradation reaction of epoxidized oleic acid at room temperature follows second-order reaction kinetic.

Acknowledgement

The authors are grateful to LPDP (Indonesia Endowment Fund for Education, Ministry of Finance, Republic of Indonesia) for the financial support.

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