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OPTIMISATION ON SYNTHESIS OF ACRYLATED EPOXIDISED PALM OLEIN USING RESPONSE SURFACE METHODOLOGY

KOSHEELA DEVI, P P*; HAZIMAH, A H*; TUAN NOOR MAZNEE, T I*; YEONG, S K*; HOONG, S S*; KUSHAIRI, A* and CHOO, Y M*

ABSTRACT

Acrylated epoxidised palm olein (AEPO) was synthesised from epoxidised palm olein (EPOo), acrylic acid, hydroquinone and AMC-2® catalyst. Optimisation of the synthesis in terms of the reaction parameters was performed using so-called response surface methodology (RSM). The reaction parameters selected as independent variables were percentage of catalyst; molar ratio between EPOo and acrylic acid; reaction temperature and reaction time. The percentage conversion of epoxy ring to acrylate group was designated as the dependent response. The central composite rotatable design (CCRD) at five coded levels with four factors was used. The quadratic model was used to analyse the experimental data obtained. The quadratic model was significant at a 95% confidence level with Prob>F of less than 0.0001; the regression coefficient value, R^2 was 0.9561 and lack-of-fit of 0.0646 as obtained by using analysis of variance (ANOVA). A percentage of AMC-2® catalyst of 1.0%; molar ratio between EPOo and acrylic acid of 1.0:1.2, reaction temperature of 120°C, and reaction time of 135 min were established as the optimum parameters in order to convert EPOo to AEPO at mild reaction conditions. The reaction temperature and the time for the acrylation reaction were substantially reduced to 75% with the incorporation of AMC-2® catalyst compared to the acrylation reaction in the absence of catalyst. The results also proved that RSM can be employed efficiently for the optimisation of the synthesis of AEPO catalysed by AMC-2®, as the percentage of conversion AEPO obtained with the optimum conditions was 99.26% adequate according to the predicted value by the software. The optimum reaction parameter can be used to scale up the acrylation reaction of EPOo to AEPO.

Keywords: epoxidised palm olein (EPOo), acrylation, optimisation, response surface methodology.

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INTRODUCTION

There has been recent escalating interest, both in academic and industrial laboratories, in innovative radiation-curable oligomers derived from renewable resources, especially those with enhanced mechanical and commercial performances (Cheong, 2009). Numerous plant-oil derivatives have been used for the production of radiation-curable polymerisable monomers due to their abundant supply; comparatively low price and their environmental-friendly character. Typically triglycerides are the major component in all plant oils and contain both saturated and unsaturated

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* Malaysian Palm Oil Board,
6 Persiaran Institusi, Bandar Baru Bangi,
43000 Kajang, Selangor, Malaysia.
E-mail: kosheela @mpob.gov.my

fatty acids. Their reactivity depend on the numbers of double bonds (C=C) or the types of fatty acid. But these double bonds are not highly active for typical radical polymerisation. Therefore, they have to be converted to more reactive functional groups such as epoxy groups, acrylate groups, hydroxyl groups and even some bromoacrylated triglycerides, that can then be used in free radical polymerisation (La Scala and Wool, 2005; Liu and Erhan, 2010; Saithai *et al*., 2013; Petrovic *et al*., 2002). Epoxidised and acrylated triglycerides are usually monomeric liquids, which can be polymerised to form solid gels in the presence of curing agents via free radical polymerisation with or without a co-monomer (Liu and Erhan, 2010).

Acrylation of epoxidised plant oils is one of the most interesting techniques for the preparation of radiation curable materials, and palm oil has favourable characteristics to be one of the resources. Commercially available radiation curable resins are produced from petrochemical-based materials and vegetable oils such as linseed oil, castor oil, tung oil and soyabean oil (Ooi, 2001). Some interesting studies on the utilisation of palm oil to produce such radiation curable resins, their mechanical properties and their potential applications have been reported. For instance ultra violet (UV) curable coatings were prepared from epoxidised palm olein (EPOo) and reacted with acrylic acid by using triethylamine to produce epoxidised palm olein acrylated named EPOLA. It readily undergoes polymerisation in the presence of photoinitiators upon exposure to UV radiation (Nor *et al*., 1992). EPOLA was also evaluated for radiation curable pressure sensitive adhesives (Mahmood *et al*., 2001a, b). Palm oil-based acrylated polyester resin for radiation curable polymers was derived from crude and/or refined, bleached and deodorised palm oil by reacting acrylic acid in the presence of *p*-toluene sulphonic acid with concentrated sulphuric acid as a catalyst. The *p*-toluene sulphonic acid was found to be more efficient as the catalyst compared to concentrated sulphuric acid (Azam *et al*., 2001). Another type of UV-curable pre-polymer was produced via a condensation esterification reaction by reacting palm olein-based polyol with acrylic acid, *p*-toluene sulphonic acid monohydrate and hydroquinone (Cheong, 2009).

The acrylation of epoxidised triglycerides, as illustrated in *Figure 1*, was studied in-depth by Khot (2001), using epoxidised soyabean oil, acrylic acid, hydroquinone, tertiary amine catalyst (DABCO), triphenyl phosphine (TP) and triphenyl antimony (TA) catalyst blends, (TP:TA) and AMC-2®, a commercial chromium-based catalyst. In this study, AMC-2® catalyst was efficient in promoting the acrylation reaction with a 91% yield compared to both tertiary amine catalyst, DABCO and blends catalysts TP:TA. The size exclusion chromatography spectrum of the product indicated a low presence of triglyceride oligomers due to less epoxy homopolymerisation in the product catalysed with AMC-2®, unlike the product using DABCO. If the catalysts were to be ranked according to their ability to promote the acrylation reaction with activity and selectivity, the positioning would be AMC-2®>DABCO>TP:TA>TP. The AMC-2® was found to be extremely effective in accelerating the acrylation reaction as well as in inhibiting any homopolymerisation reaction (La Scala and Wool, 2005).

With so many extensive studies reported in the literature on the acrylation of triglycerides, the task for process optimisation of acrylation of triglycerides can be embarked on using a method that is capable to evaluate the influence of individual parameter of each reaction condition on overall effectiveness. One such method is by using response surface methodology (RSM), as developed by Box and Wilson (Myers and Montgomery, 2002). RSM has been extensively used in the chemical industry as it has the capability to optimise a process with a minimal

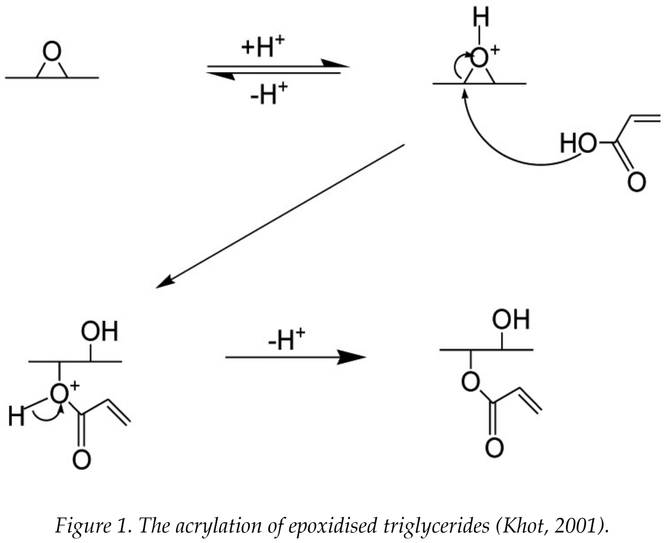

Figure 1. The acrylation of epoxidised triglycerides (Khot, 2001).

amount of experimental data. If there are many factors and interaction in an experiment, RSM is an efficient statistical tool to investigate the parameters that affects the desired response. RSM can predict the impact of various process parameters, either individually or in cumulative interactions between the parameters on the responses studied. Thus, it provides an indication of the optimal operating region of the process (Pilkington *et al*., 2014).

The main objective of this study was to develop RSM models to optimise the percentage of conversion of EPOo to acrylated epoxidised palm olein (AEPO) using AMC-2® catalyst. The AMC-2® catalyst was selected since it has been reported to be more effective in promoting the acrylation reaction (Khot, 2001), and while at the same time reducing the extent of epoxy homopolymerisation (La Scala and Wool, 2005). The parameters investigated were the percentage of catalyst; the molar ratio between EPOo and acrylic acid; reaction temperature and reaction time. The suitability for predicting percentage conversion was then compared with a model generated from experimental data by analysing their coefficient of determination (R^2). The presence of significant lack-of-fit in the experimental data was accessed by using analysis of variance (ANOVA). It is used mainly to compare the variation due to the change in the combination of the variable levels with the variation due to the random errors inherent to the measurement of the generated responses. Through this comparison, it is possible to evaluate the significance of the regression used to foresee responses considering the sources of experimental variance (Myers and Montgomery, 2002; Bezerra *et al*., 2008). To our knowledge, the optimisation of synthesis of AEPO using RSM has not been reported in the literature even though a number of studies have been reported using RSM as a statistical tool for optimisation studies in chemistry, *e.g.* analytical chemistry (Bezerra *et al*., 2008); enzymatic synthesis (Tuan Noor Maznee *et al*., 2012; Ashari *et al*., 2009) and biochemical (Azma *et al*., 2011).

MATERIALS AND METHODS

Materials

EPOo was obtained from the Malaysian Palm Oil Board, Malaysia. Acrylic acid (AA) was obtained from Merck, Germany. Accelerator AMC-2® was supplied by AMPAC™ Fine Chemical, USA and used as the catalyst. Hydroquinone was used as the inhibitor, and triphenyl phosphate was added to the sample before the purification process to prevent post-polymerisation during storage: both these chemicals were obtained from Merck, Germany. For the purification process, diethyl ether was purchased from Fisher Scientific, United Kingdom, disodium phosphate was supplied by Fluka Chemicals, Switzerland and sodium chloride was supplied by J. Kollin Chemicals, United Kingdom.

Synthesis of Acrylated Epoxidised Palm Oil

The EPOo (250 g) having an oxirane oxygen content of 3.21% - was mixed with acrylic acid and 0.1% by weight hydroquinone in a five-necked reactor flask equipped with a thermometer, a magnetic stirrer, a reflux condenser and a dropping funnel. The reaction mixture was heated to the chosen temperature by using an oil bath. The progress of the reaction was monitored by measuring the oxirane oxygen content (OOC) every 30 min until there was no significant change in the OOC. The percentages of catalyst, molar ratios between EPOo and AA reaction temperatures and reaction times were used according to the designed experiment using RSM. Once the reaction was completed, unreacted acrylic acid and catalyst were removed through ether extraction followed by washing with a series of solutions. The synthesised AEPO was first rinsed with a saturated aqueous solution of disodium phosphate to neutralise the acid. This procedure was repeated three times until a pH paper indicated that the mixture was neutral, showing that the only component left in the organic layer was AEPO. Next, the sample was rinsed with saturated sodium chloride solution to remove any residual water from the organic phase. The aqueous layer was removed from the system and discarded. Finally, the ether was evaporated by heating the sample at 40°C under vacuum.

Characterisation of Synthesised AEPO

The OOC of the starting material (EPOo) and the reaction product (AEPO) was determined utilising the American Oil Chemists Society (AOCS) Official Method Cd 9-57 (AOCS, 2007) to calculate the percentage conversion. The percentage conversion of the epoxide group to an acrylate group was determined from equation (Equation (1)] and the OOC of EPOo used in the present study was 3.21%.

$$\text{Percentage of conversion} = \frac{\text{oxirane oxygen content of AEPO}}{\text{oxirane oxygen content of EPOo}} \text{ x } 100 \tag{1}$$

The acid value was analysed according to AOCS Official Method Te 2a-64. It is defined as the amount of potassium hydroxide in milligrams required to neutralise the free acids in 1 g of sample. The AOCS Official Method Cd 1d-92 was used to measure the iodine value based on a cyclohexane-acetic acid titration method. It measures the unsaturation of the fats and oils and is expressed as the number of centigrams of iodine absorbed by per gram of sample (% iodine absorbed). The viscosity of the newly synthesised oligomer samples was measured using a Brookfield Programmable Rheometer DV-III+ Calculating Digital Viscometer with CP51 cylindrical spindle at 25°C. Fourier transform infrared (FTIR) spectroscopy and proton nuclear magnetic resonance were used to characterise the chemical composition of the AEPO. The FTIR was performed using Perkin Elmer Spectrum 100 equipped with Universal ATR. Proton-NMR was conducted on a JEOL-ECA (600 MHz) FT-NMR Cryoprobe spectrometer where the AEPO was dissolved in deuterated chloroform.

The EPOo was characterised prior to the experiments. *Table 1* shows the properties of the analysed EPOo.

TABLE 1. PROPERTIES OF EPOXIDISED PALM OLEIN

Parameters	Value
Acid value (AV)	0.4 mg KOH g^{-1} of sample
Iodine value (IV)	0.8 g I_2 100 g^{-1} of sample
Oxirane oxygen content (OOC)	3.21 %
Viscosity at 25°C	126.2 mPa.s

Experimental Design and Statistical Analysis

A central composite rotatable design (CCRD) was employed in this work to study the effect of the independent variables on the percentage of conversion of epoxy group to acrylate group. It has four variables at five different levels of a high (+2), a moderate high (+1), centre point (0), a moderate low (-1) and a low (-2) CCRD which was applied using the statistical software package, Design-Expert Version 6.0.10 (Stat-Ease, Inc., Minneapolis, MN, USA). The variables and levels to investigate the optimal reaction conditions were based on previous screening experiments conducted using conventional methods. The identified independent variables and their levels selected for acrylation reaction were: a) percentage AMC-2® catalyst (0.5% – 20.0%); b) reaction temperature (90°C-130°C); c) molar ratio between EPOo and AA (1.0:0.9-1.0:1.5), and d) reaction time (90-180 min). A total of 30 experiments were carried out, calculated based on $2^k + 2k + 6$, where k is the number of independent variables. In order to evaluate the pure error in the experiment, 24 experiments were amplified with six replications at centre points. The design of experiments carried out is shown in *Table 2*. For statistical computation, the four variables used were coded according to equation [(Equation (2)].

$$X_i = \frac{U_i - U_i^0}{\Delta U_i} \qquad (2)$$

where X_i is the independent variables coded value, U is the independent variable real value, and U^0 is the independent variables real value at the centre point (Ceylan *et al*., 2008; Elavarasan *et al*., 2009; La Scala and Wool, 2004; Tuan Noor Maznee *et al*., 2012).

In order to determine the adequacy of this model to describe the data obtained from RSM on its interactions between the process variables and response on the synthesis of AEPO, the data obtained were subjected to ANOVA (Myers and Montgomery, 2002). The experimental data were fitted using response surface regression procedure by the second order polynomial equation [Equation (3)].

$$Y = \beta_o + \sum_i \beta_i X_i + \sum_{ii} \beta_{ii} X_i + \sum_{ij} \beta_{ij} X_i X_j \qquad (3)$$

In which Y is the predicted response, X_i and X_j are the independent variables, β_o is a constant, β_i is the i^{th} linear coefficient, β_{ii} is the i^{th} quadratic coefficient, β_{ij} is the ii^{th} interaction coefficient (Bezerra *et al*., 2008; Ceylan *et al*., 2008; Ebrahimi *et al*., 2010; Elavarasan *et al*., 2009; La Scala and Wool, 2004).

The Design-Expert software was used to analyse the regression analysis of the experimental data and to plot the response surface graphs. Three-dimensional surface plots were expressed using the fitted polynomial equation to show the relationship between the responses and the experimental levels of each of the variables studied. Fisher's test (F-test) was used to evaluate the statistical significance of the model equation and the model terms (Myers and Montgomery, 2002). The coefficient of determination (R^2) and adjusted R^2 was used to express the significance of the fit of the second order polynomial model equation (Ebrahimi *et al*., 2010). The point optimisation method was used to optimise the level of each variable to obtain maximum response. Combination of different optimised variables, which gave the maximum response, was determined to verify the validity of the model.

RESULTS AND DISCUSSION

Synthesis and Characterisation of AEPO

The reaction of EPOo with acrylic acid to prepare AEPO is shown in *Figure 2*. Products from the acrylation reaction between EPOo and AA catalysed by AMC-2® were analysed using FT-IR spectroscopy. There are three essential functional groups that indicate the structural information of EPOo and AEPO, these are the epoxide group in the EPOo; the acrylate group and hydroxyl group in the acrylated sample (Bezerra *et al*., 2008). In FT-IR spectra of EPOo in *Figure 1* shows the C-O-C stretching from epoxide vibration appears at 1240 cm^{-1} and twin bands at 824 cm^{-1} and 840 cm^{-1}. FT-IR spectra of AEPO showed

TABLE 2. THE ORDER AND ACRYLATION CONDITIONS FOR CENTRAL COMPOSITE ROTATABLE DESIGN (CCRD) SECOND-ORDER AND EXPERIMENTAL DATA FOR FIVE-LEVEL-FOUR-FACTOR RESPONSE SURFACE ANALYSIS

Treatment	Variables			
	Percentage of AMC-2®, (%) A	Temperature (°C) B	Molar ratio EPO: AA, (mol) C	Reaction time (min) D
1	1.50	90.0	0.90	90.0
2	0.00	110.0	1.20	135.0
3	1.00	150.0	1.20	135.0
4	1.00	110.0	1.20	225.0
5	1.00	110.0	0.60	135.0
6	1.00	110.0	1.20	135.0
7	0.50	90.0	0.90	180.0
8	1.50	90.0	1.50	900.0
9	1.50	90.0	1.50	180.0
10	0.50	130.0	0.90	180.0
11	0.50	90.0	1.50	180.0
12	0.50	130.0	1.50	180.0
13	1.50	90.0	0.90	180.0
14	1.00	110.0	1.20	135.0
15	1.00	110.0	1.20	45.0
16	0.50	130.0	1.50	90.0
17	1.00	110.0	1.80	135.0
18	0.50	90.0	0.90	90.0
19	1.50	130.0	0.90	90.0
20	0.50	90.0	1.50	90.0
21	1.50	130.0	0.90	180.0
22	1.00	70.0	1.20	135.0
23	1.00	110.0	1.20	135.0
24	0.50	130.0	0.90	90.0
25	1.00	110.0	1.20	135.0
26	1.00	110.0	1.20	135.0
27	1.50	130.0	1.50	90.0
28	1.50	130.0	1.50	180.0
29	2.00	110.0	1.20	135.0
30	1.00	110.0	1.20	135.0

a broad band at 3200-3550 cm^{-1} which refers to broad absorption band of hydroxyl group (-OH) confirming that epoxide ring was opened. The disappearance of the epoxide (C-O-C) twin bands at 824 cm^{-1} and 846 cm^{-1} for acrylated samples also confirmed the same. The success of acrylation reaction was additionally confirmed by the appearance of FT-IR peaks at 1637, 1465 and 1406 cm^{-1} indicating the occurrence of vinyl functionality (–CH=CH$_2$-) (Behera and Banthia, 2008; Habib and Bajpai, 2011). The occurrence of vinyl functionality of the acrylated polymers was also supported by presence of peaks at 810 cm^{-1} and 985 cm^{-1} as these indicate the presence of vinyl group [CH$_2$=CH(CO)-O] (Habib and Bajpai, 2011) as depicted in *Figure 3*.

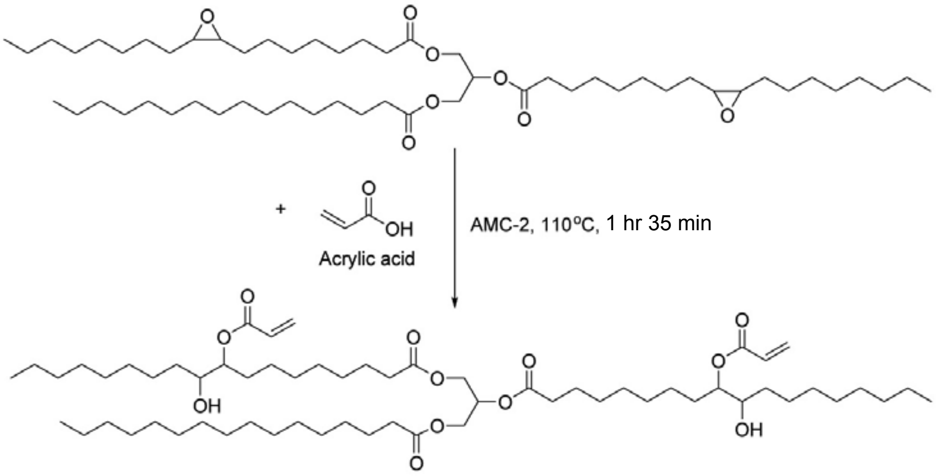

Figure 2. Acrylation of epoxidised palm oilein (EPOo).

The ^{1}H NMR spectrum of AEPO is shown in *Figure 4* and the spectrum presents all the hydrogen signals expected for an acrylated product. The peaks at 5.8-6.4 ppm represent the three protons attached to the -C=C- bond of the acrylate esters. The weak multiplet centred at about 5.25 ppm is due to the resonance of the glycerol methine peak. The peak at 4.9 ppm represents methane proton adjacent to acrylate group. The peaks between 4.1 and 4.3 ppm represents the two glycerol methylene groups. The multiplets at 3.6 ppm represent the hydroxyl group attached to methine protons. The chemical shift range from 2.6 to 2.9 ppm which produces multiplets represents the negligible amount of epoxy rings left after acrylation. The strong multiplets at 2.3 and 0.9 ppm represent the methylene proton adjacent to carbonyl group of the fatty acid and terminal methyl groups resonate, respectively.

Model Fitting and ANOVA

The identified independent variables in the acrylation reaction are the percentage of AMC-2® catalyst, reaction temperature, molar ratio between EPOo, and AA and reaction time. The region of investigation to determine the optimum operating condition were 0.5%-2.0%, 90°C-130°C, 1:0.9-1:1.5 and 90-180 min, respectively. The optimum reaction conditions obtained from previous screening experiments conducted with conventional method were used as the centre points in this study. The centre points were 1.0% of AMC-2® catalyst, 110°C

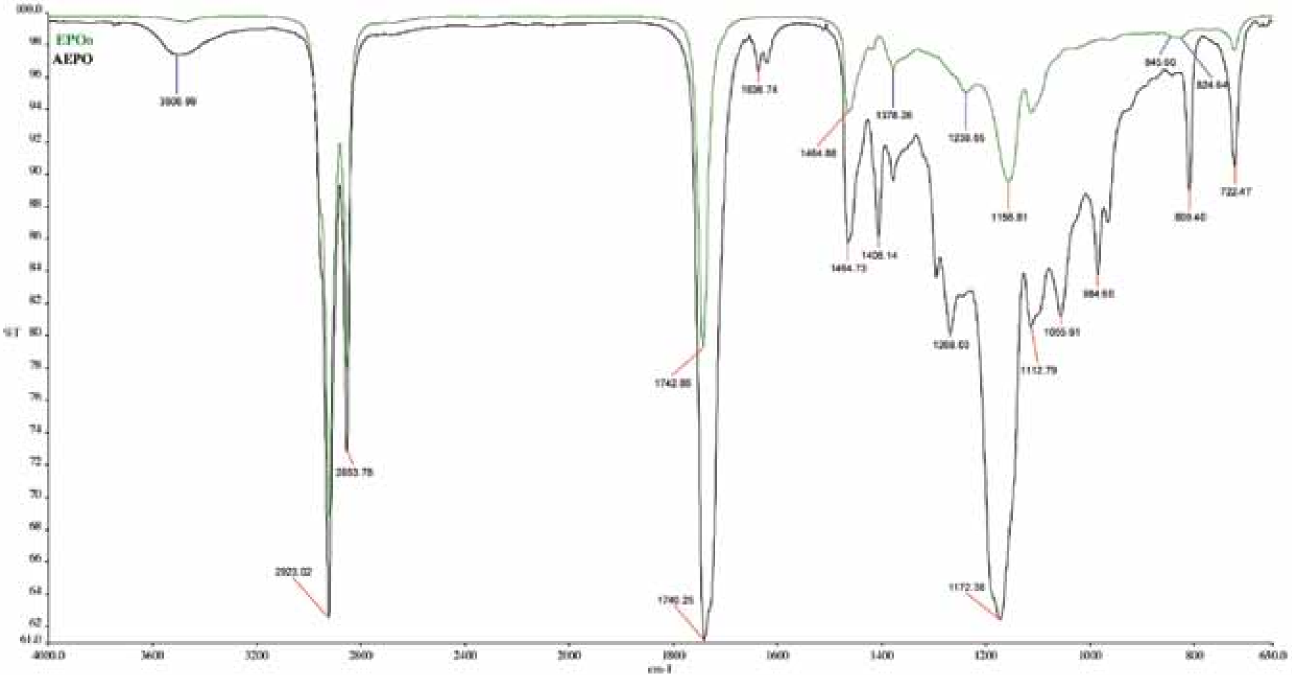

Figure 3. Fourier transformation infrared (FT-IR) spectrum of epoxidised palm olein (EPOo) and acrylated epoxidised palm olein (AEPO).

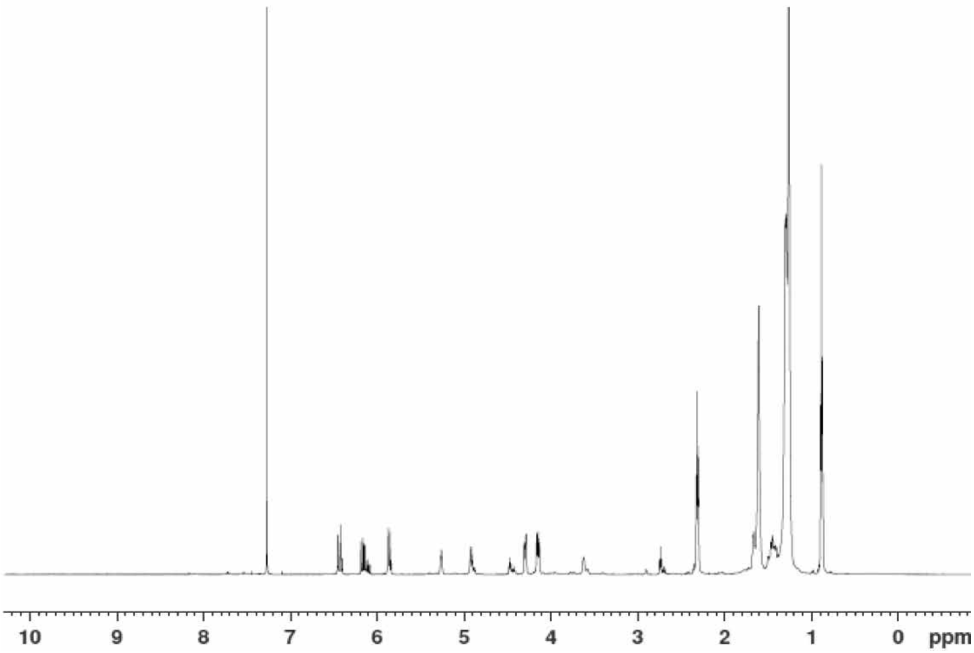

Figure 4. The ^{1}H NMR spectrum of acrylated epoxidised palm olein (AEPO).

reaction temperature, 1.0:1.2 molar ratios between EPOo:AA and 135 min of reaction time. Fitting of the data obtained from the optimisation study to various models (linear, two factorial, quadratic and cubic) and their subsequent ANOVA results showed that the optimisation of AEPO was most suitable to be described with a quadratic model as follows:

$$\text{Percentage of coversion (\%)} = +\ 82.88 + 8.21A + 11.00B + 8.12C + 2.94D - 2.69A^2 - 4.49B^2 - 1.76C^2 - 0.81D^2 - 4.62AB + 0.38AC - 1.00AD + 3.15BC - 2.13BD + 1.06CD$$

where, A is the percentage of AMC-2® catalyst; B is the reaction temperature; C is the molar ratio between EPOo:AA and D is the reaction time.

The ANOVA results from the optimisation study produced the model terms, A, B, C, D, A^2, B^2, AB, BC were significant as the *P*-value (<0.05) was low for the interactive model. The *F*-value for the model was 23.35 and the *F*-value for lack of fit was 4.16 (*Table 3*). The high *F*-value and non-significant lack of fit indicate that the model was a good fit. The *P*-value for the model was <0.0001 and the lack of fit of 0.0646 also suggested that the experimental data obtained were a good fit to the model. The non-significant lack of fit value (more than 0.05) implies the validity of the quadratic model (Sinha *et al*., 2013).

The regresssion equation obtained from the ANOVA showed that the R^2 was 0.9561 (a value >0.75 shows fitness of the model). This is a prediction of the fraction of the overall variation in the data accounted by the model. Thus, the model is capable of explaining 95.61% of variation in response. The model was used to navigate the design space based on the adjusted-R^2 obtained, 0.9152 and the adequate precision value of 17.739. The adequate precision value is an index of the signal-to-noise ratio and value greater than 4 are essential prerequisites for a model to be a good fit. The reaction time and reaction temperature of the acrylation reaction were substantially reduced to 75% compared to the acrylation reaction in the absence of catalysts (Nevin, 1964).

Effect of Variable

In order to determine the optimal levels for each variable for higher percentage of conversion, three-dimensional (3D) response surface plots were created by plotting the response (percentage of conversion) on the Z-axis against any two independent variables, while maintaining the other two variables at their optimal levels as shown in *Figures 5a* to *5f*.

Figure 5a shows the 3D response surface graphs as a function of the percentage of AMC-2® catalyst (A) versus reaction temperature (B). The ratio between EPOo and AA (C) and the reaction time (D) were fixed at their centre point (1.0:1.2 and 135 min, respectively). The percentage of conversion of EPOo to AEPO was particularly low at low percentages of catalyst and low reaction temperature. Increase in both variables resulted in an increase on the response surface. The highest percentage of conversion was obtained with 1.25% of catalyst and reaction temperature of 125°C. The conversion remains constant at temperature higher than 125°C and with catalyst more than 1.25%. Similar trend was observed with the 1.5% of catalyst and temperature

TABLE 3. ANALYSIS OF VARIANCE AND MODEL COEFFICIENTS

Source	Sum of squares	DF	Mean square	*F*-value	*P*-value
Model	7 614.18	14	543.87	23.35	< 0.0001
Residual	349.40	15	23.29	-	-
Lack-of-fit	311.89	10	31.19	4.16	0.0646
Pure error	37.51	5	7.50	-	-
Corr. total	7 963.58	29	-	-	-

Note: R^2= 0.9561; CV = 6.43%; Adj-R^2= 0.9152 Pred-R^2 = 0.7676; R^2= coefficient of determination; DF=degree of freedom; Prob>F = level of significant.

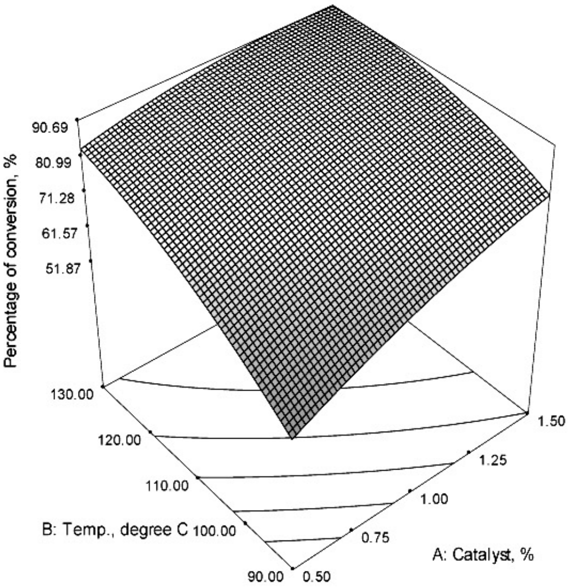

Figure 5a. Percentage conversion as a function of percentage of catalyst (A) and reaction temperature (B) at fixed molar ratio between epoxidised palm olein (EPOo) and AA (C) (1.0:1.2) and reaction time (D) (135 min) in 3D surface view.

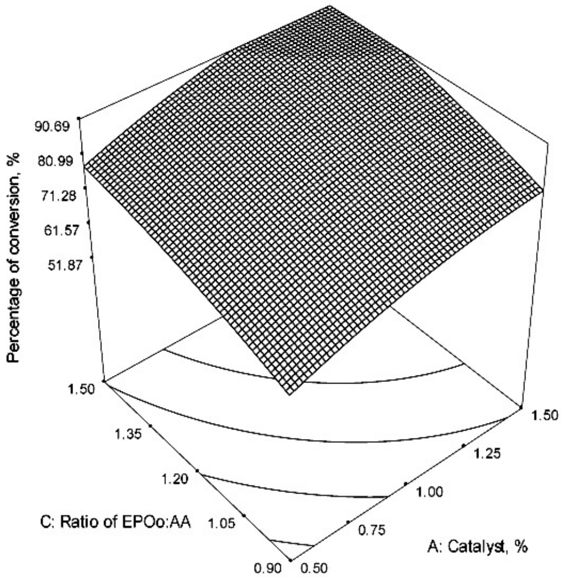

Figure 5b. Percentage conversion as a function of percentage of catalyst (A) and molar ratio between epoxidised palm olein (EPOo) and AA (C) at fixed reaction temperature (B) (110°C) and reaction time (D) (135 min) in 3D surface view.

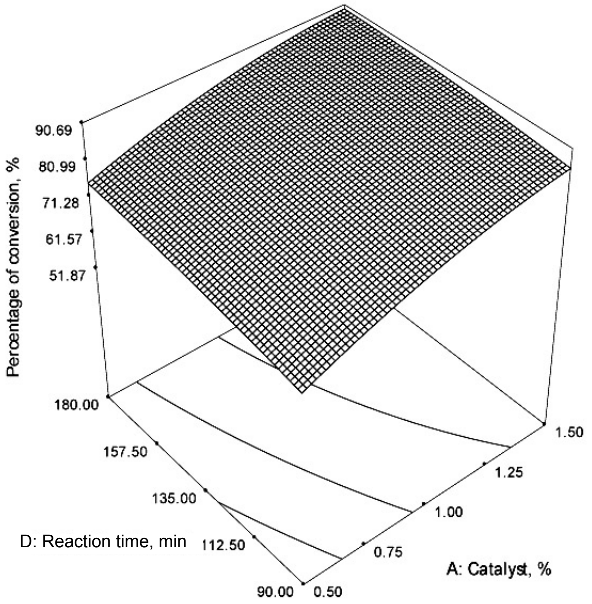

Figure 5c. Percentage conversion as a function of percentage of catalyst (A) and reaction time (D) at fixed molar ratio between epoxidised palm olein (EPOo) and AA (C) (1.0:1.2) and reaction temperature (B) (110°C) in 3D surface view.

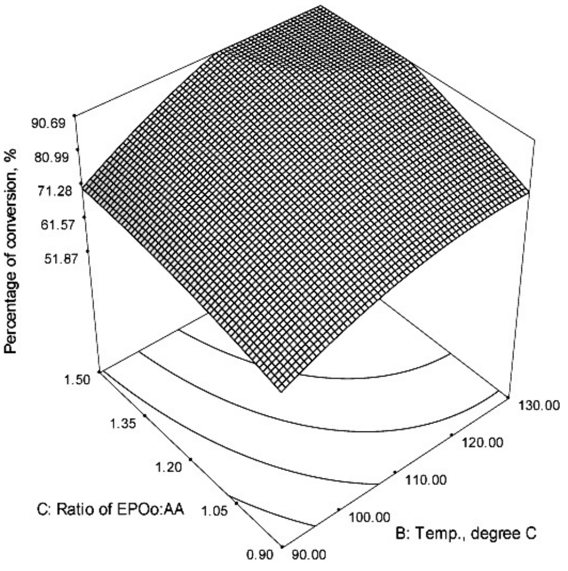

Figure 5d. Percentage conversion as a function of ratio between epoxidised palm olein (EPOo) and AA (C) and reaction temperature (B) at fixed percentage of catalyst (A) (1.0%) and reaction time (D) (135 min) in 3D surface view.

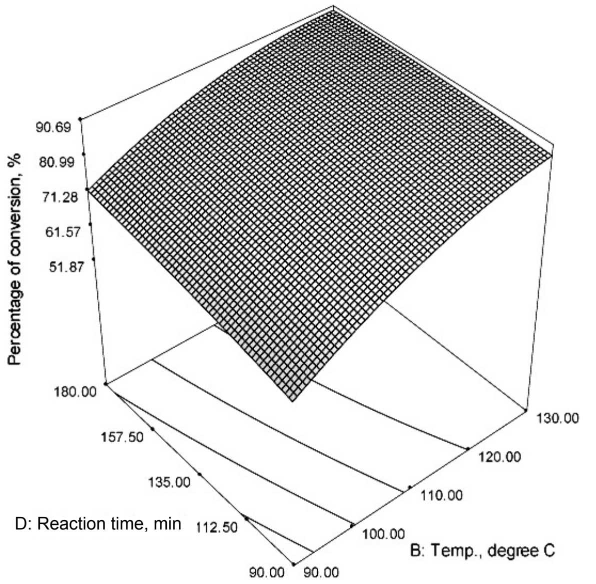

Figure 5e. Percentage conversion as a function of reaction temperature (B) and reaction time (D) at fixed percentage of catalyst (A) (1.0%) and molar ratio between epoxidised palm olein (EPOo) and AA (C) (1.0:1.2) in 3D surface view.

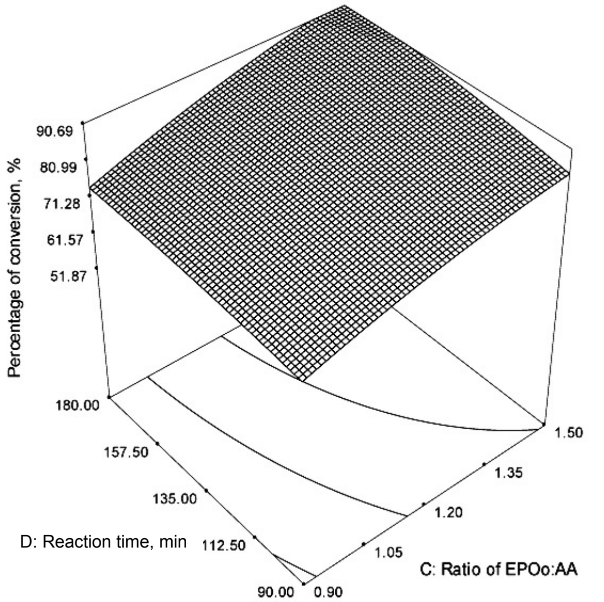

Figure 5f. Percentage conversion as a function of ratio between epoxidised palm olein (EPOo) and AA (C) and reaction time (D) at fixed percentage of catalyst (A) (1.0%) and reaction temperature (B) (110°C) in 3D surface view.

more than 120°C. Thus to simultaneously minimise the catalyst concentration and reaction time, 0.5%-2.0% of catalyst such as AMC-2™ (now known as AMC-2®) may be employed, where one weight percent of AMC-2™ was found to be optimum for the acrylation reaction of glycidyl methacylate and oleic acid (Palmese *et al.*, 2009). Overall, the percentage of conversion of EPOo to AEPO was affected equally by the percentage of catalyst and the reaction temperature (*Figure 5a).*

Figure 5b shows the effect of varying the percentage of AMC-2® catalyst (A) and molar ratio between EPOo and AA (C) on the percentage of conversion in synthesising AEPO. The reaction temperature (B) and reaction time (D) were fixed at 110°C and 135 min respectively. The percentage conversion of EPOo to AEPO was affected equally by the percentage of catalyst and the molar ratio between EPOo and AA. An increase in both variables resulted in an increase in the response surface. The response value achieved its highest level at 1.5% of catalyst and molar ratio between EPOo and AA of 1.0:1.5. The effect on the percentage conversion of EPOo to AEPO was more obviously affected by the percentage of catalyst and the reaction temperature (*Figure 5a)* compared to percentage of catalyst and molar ratio between EPOo (*Figure 5b*) unless the highest percentage of catalyst and molar ratio were used.

The effects of percentage of AMC-2® catalyst (A) and reaction time (D) on the percentage conversion at a fixed molar ratio between EPOo and AA (C) of 1.0:1.2 and reaction temperature (B) of 110°C is shown in *Figure 5c.* The percentage conversion was small at low percentage of AMC-2® catalyst and with shorter reaction time. The response surface increased when both variables were increased. The response surface was at the highest level at 1.5% of AMC-2® catalyst and at 180 min of reaction time, respectively. The percentage catalyst had more effect on the percentage conversion compared to the reaction time as illustrated in *Figure 5c.* The percentage conversion did not increase significantly after carrying out the reaction for more than 135 min even when the higher percentage of AMC-2® catalyst (1.5%) was used. The effect of percentage catalyst was more obvious than the effect of reaction time on the response. Accordingly the use of catalysts that promote opening of epoxy ring with carboxyl had the advantage of shortening the time and/or lowering the temperature of acrylation reaction to obtain same degree of acrylation (Nevin, 1964).

The effects of reaction temperature (B) and molar ratio between EPOo and AA (C) on the response at a fixed percentage of AMC-2® catalyst (A) of 1.0% and reaction time (D) of 135 min are as shown in *Figure 5d.* The highest percentage of conversion was achieved with a reaction temperature of 130°C and with a molar ratio between EPOo and acrylic acid of 1.0:1.5. The percentage conversion was more affected by reaction temperature compared to molar ratio between EPOo and AA especially when the molar ratio between EPOo and AA was increased to more than 1.0:1.2.

The acrylation reaction time would be expected to be 4-8 hr at 120°C-160°C in the absence of catalysts. Temperatures above and below this is operative, however, provided the reaction time is adjusted to the temperature (Palmese *et al.*, 2009). *Figure 5e,* illustrates the effects of reaction temperature (B) and reaction time (D) at a fixed percentage of AMC-2® catalyst (A) and molar ratio between EPOo and AA (C) of 3.0% and 1.0:1.2, respectively. The percentage conversion was found to be optimum (~90%) with a reaction temperature of 130°C and a reaction time of 135 min. Above this temperature, the advantage of a decreased reaction time must be balanced against the disadvantages of greater product discoloration and a tendency of premature vinyl polymerisation. Besides this, the boiling point of acrylic acid is 141°C. It was found that any further increase in reaction time did not give any significant effect on the percentage of conversion. The reaction temperature significantly affected the percentage of conversion compared to the reaction time.

The effects of the molar ratio of EPOo and acrylic acid and the reaction time at a fixed percentage of catalyst of 1.0% and reaction temperature of 110°C (*Figure 5f*). The highest percentage conversion was achieved with the highest of molar ratio between EPOo and AA 1.0:1.5 and the longer reaction time (180 min). The percentage conversion was greatly affected by the molar ratio between EPOo and AA compared to the reaction time where the similar effect is illustrated in *Figure 5e.* Therefore, based on this study, the reaction could be conducted up to a maximum of 135 min as any further increase in the reaction time seems to have a less significant effect.

The residuals from the least squares fit play an important role in checking the model adequacy. A plot of the studentised residuals versus predicted values was used to check the model adequacy using the software (the plot not shown). Mainly the residuals were randomly scattered around ±1.5 and not exceeding ±3.0, showing that the experimental data fitted well with the predicted ones obtained from the model. In a plot of studentised residuals versus the run order tested, the residuals scattered randomly on the display, suggesting that the variance of the original observation was constant for all values of responses (Myers and Montgomery, 2002; Tuan Noor Maznee *et al.*, 2012).

Hence, the optimum conditions for the synthesis of AEPO with AMC-2® were determined as - percentage of AMC-2® catalyst of 1.0%, reaction temperature of 120°C and molar ratio between EPOo and AA of 1.0:1.2 and reaction time of 135 min with predicted percentage of conversion of 87.26%. The solution was obtained with some constraints applied on the reaction conditions in order to achieve maximum percentage conversion such as targeted of percentage of AMC-2® catalyst 1.0%, targeted reaction time at 135 min, molar ratio between EPOo and AA in range of 1.0:1.0 to 1.0:1.2 and reaction temperature in the range of 100°C to 120°C. The optimum prediction using the software was verified by conducting experiments with the given solution. Through the experiment, it was found that the observed percentage of conversion AEPO with the optimum condition was 86.60%, which was 99.26% according to the predicted value. Thus, the response (percentage conversion) evaluated using a quadratic model has sufficient agreement with the observed percentage conversion and it could be used for future scale-up process.

CONCLUSION

The determination of the optimum conditions for the synthesis of AEPO catalysed by AMC-2® was successfully carried out with RSM using CCRD with four variables at five levels (-2, -1, 0, +1, +2). The reaction time and reaction temperature of the acrylation reaction were substantially reduced to 75% compared to an acrylation reaction in the absence of catalysts. Significant agreement between the values generated by the model and the experimental data was confirmed using ANOVA. The results also demonstrated that RSM can be used efficiently to optimise the synthesis of AEPO catalysed by AMC-2® catalyst as the model provided satisfactory predictions on the percentage of conversion to be obtained with the solution given by the software. The optimum conditions could be used to scale up the process

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