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Graphic abstract

Synthesis of lignin-based epoxy resin of a high yield and epoxy content was realized and the synthesis conditions were optimized using Central Composite Design (CCD).

Synthesis of Lignin-based Epoxy Resins: Optimization of Reaction Parameters Using Response Surface Methodology

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Abstract:

Owing to the presence of phenolic groups in the lignin structure, this provides the potential to substitute bisphenol-A in synthesis of epoxy resin. In this work, organosolv lignin (OL) was first depolymerized by reductive depolymerization in supercritical acetone at 350°C in the presence of Ru/C catalyst and 10 MPa H_2. The obtained depolymerized organosolv lignin (DOL), with a low average molecular weight (M_W) and high hydroxyl number, was used to synthesize lignin-based epoxy pre-polymers. A set of experiments was designed by utilizing the central composite design (CCD) to synthesize lignin-based epoxy resin. Three synthesis variables including reaction temperature, reaction time and NaOH /DOL molar ratio were investigated and the synthesized epoxy pre-polymers were characterized by FTIR and potentiometric titrator. The mathematical model derived from the CCD was found to be accurate to predict the optimum conditions. At the optimal synthesis conditions, i.e., 8h at 55 ºC with NaOH/DOL molar ratio of 6.3, a high product yield (99%) and high epoxy content of ~ 8 were achieved.

1. Introduction

Today utilization of renewable biomass resources for biopolymers and bio-chemicals has drawn increasing attention worldwide, due to the serious environmental and resource-depletion issues and concerns related to fossil fuel utilizations [1–3]. Various biomass resources such as lignin [1,4], vegetable oil [5], fatty acid and cellulose [6] were used as a renewable feedstock to synthesize different bio-based polymers including phenolic resin, epoxy resin [2,3,7], polyurethane and polyester [6,8]. Among the renewable resources, lignin may be the best potential candidate for the production of epoxy resin because of its aromatic structure. Lignin is the second most abundant natural renewable polymer after cellulose and accounts for between 15 and 40% of wood stem depending on the type of wood [9]. Lignin is a complex three-dimensional biopolymer of aromatic alcohols. Three monomers, i.e., p-hydroxyl-phenyl propanol (H), guaiacyl-propanol (G) and syringyl-propanol (S) linked together by condensed linkages and ether linkages to generate three-dimensional networks [10,11]. The percentage of these monomers will vary in different kinds of lignin. The dominant monomer in softwood lignins is Guaiacyl (G) monomer, while hardwood lignins consist of both Syringyl (S) and Guaiacyl (G) units [12]. The reactivity of lignin depends on the form and composition of reactive functional groups within monomer units. In particular, lignin mainly contains three functional groups: p-hydroxy-phenyl, aliphatic hydroxyl, and carboxylic acid groups [12]. Owing to the presence of phenolic groups in the structure, lignin has the potential to substitute bisphenol-A in synthesis of epoxy resin.

Several studies have been reported on incorporation of lignin in epoxy resin production [1,13–15]. In some studies, lignin was modified before epoxidation reaction to enhance the reactivity of specific functional groups in lignin. El Mansouri et al.[16] synthesized lignin-based epoxy resin by using a raw kraft lignin recovered directly from pulping liquor and two other modified lignin by methylolation and glyoxalation treatments. The ^{1}H NMR spectra of these lignins showed that the methylated kraft lignin contained more hydroxyl groups than the glyoxalated kraft lignin. Hofmann and Glasser [17] prepared epoxy resins from hydroxylalkyl lignin derivatives with varying degrees of alkoxylation. The modification was performed via two steps: firstly, reacting lignins with propylene oxide to increase their solubility, and secondly, converting secondary hydroxyl groups into primary ones using ethylene oxide. Delmas et al. [18] used wheat straw-derived lignin as a resource starting material to synthesize bio-based epoxy resin. Epoxidation reaction was conducted in alkaline aqueous media and polyethyleneglycol diglycidyl ether (PEGDGE) was used as an epoxide agent. The mechanical and thermal properties of the obtained resin were comparable to a petroleum-based epoxy resin. Zhao et al. [19] succeeded to produce bio-based epoxy resin from calcium lignosulfonate. They reported that the solid and liquid lignin based epoxy resins were formed simultaneously and the chemical structure of both products and polymerization mechanism were evaluated by FTIR and NMR. Sasaki et al. [20] used steam-exploded bamboo lignin as a feedstock for the production of epoxy resin. The synthesized epoxy resin was cured with a commercial curing agent (1-(2-cyanoethyl)-2-ethyl-4-methlimidazol) or the bamboo lignin. The results showed that the bio-epoxy resins cured by bamboo lignin provided favorable properties for being used in the electrical industry, but their thermal and mechanical properties needed to be improved. In some other studies, pretreatment on lignin was performed with acid and phenol derivatives to cleave the lignin intermolecular linkages and hence increase the functionality of phenolic hydroxyl group in the structure of lignin [1,21,22].

Although the epoxidation of various types of lignin have been documented, no report is currently available on the epoxidation of depolymerized-lignin and investigating the process parameters on epoxidation reaction. The objective of this work is to depolymerize organosolv lignin to produce a more reactive feedstock to synthesize epoxy resins, and to screen the important process parameters in order to maximize the yield and the epoxy content of the synthesized epoxy pre-polymers. Three most important factors for expoxidation reaction including reaction temperature, reaction time and NaOH/DOL molar ratio were used in the screening experiments.

Response surface method (RSM)

Response surface methodology, RSM, was introduced in the early 1950s. RMS is a collection of mathematical and statistical techniques which explore the effects of several variables on one or more responses. The aim of the RSM analysis is to optimize the responses [23,24]. The relationships between the response and variables can be a simple polynomial or be a complex system described by nonlinear functions such as exponential function or Lagrange's interpolations [24].

Central Composite Design (CCD) is one of the most commonly used RSM designs using a quadratic fitting model (second-order model) to predict and optimize the responses. The quadratic equation can be presented by following equation [24].

$$Y = \beta_0 + \sum_{i=1}^{K} \beta_i X_i + \sum_{i=1}^{K} \beta_{ii} X_i^2 + \sum_{i=1}^{K} \sum_{j \rangle 1}^{K} \beta_{ij} X_i X_j + \varepsilon \qquad (1)$$

where Y is the response, β_0, β_i, β_ii and β_ij are the regression coefficients for the intercept, linear, quadratic and interaction parameters, respectively, X_i and X_j are the independent variables and ε represents the noise or error component observed in the response [24,25].

2. Experimental

2.1 Materials

Organosolv lignin (OL) used in this study was supplied by Lignol. It is a dark brown powder with an average molecular weight of ≈ 2600 g/mol (PDI ≈ 3.6) based on our GPC analysis. Other chemicals used in this study included ruthenium 5% wt on carbon (Ru/C) as the catalyst for lignin de-polymerization, acetone, epichlorohydrin (EP), tetrabutylammonium bromide (TBAB), sodium hydroxide, *d*-chloroform, tetrahydrofuran (THF, HPLC grade), pyridine, acetic anhydride and dibromethane. All were purchased from Sigma-Aldrich and used without any further purification.

2.2 Depolymerization of organosolv lignin

Organosolv lignin (OL) was depolymerized according to the methods as described in details in our previous paper [26]. Briefly, 50 g OL, 150g acetone and 2 g Ru/C as a catalyst were loaded into a 500 ml Parr stirred autoclave reactor. The reactor was purged with nitrogen twice to assure the complete removal of oxygen and air from the reactor. Then, the reactor was pressurized with 100 bar H_2. The reactor was heated to 350 °C for 1 h reaction. Then the reactor was quenched to room temperature to stop further reactions. The gaseous phase was collected with a gas bag and analyzed with GC-TCD. The gaseous phase mainly contained H_2, CH_4, CO_2, C_3H_8 and C_2H_6. The liquid phase was filtered to recover the catalyst. Finally, the acetone was removed from the collected filtrate using a rotary evaporator under reduced pressure at 50 °C, and the resulting viscous liquid product was designated de-polymerized organosolv lignin (DOL). The yield of DOL in this reductive depolymerization process was 85 (±2) %.

2.3 Experimental Design

The process optimization for maximizing the yield and epoxy content of the lignin-based epoxy resin was carried out by central composite design (CCD) with 3 variables. Unlike a full factorial design, just 20 experimental runs were performed according to the CCD. This design contains 8 cube points, 6 axial points and 1 center points (Figure 1). For the center point, 6 replicate runs were conducted to check the reproducibility. The three independent variables considered were the NaOH/DOL molar ratio, reaction temperature and reaction time. The range of these three parameters were chosen based on our preliminary experiments and on the literature [27]. The variables and their levels selected for this study are shown in Table 1.

Table 1 Variables and their levels employed in the central composite design

Variables	Unit	Term	Coded level of variables				
			-1.682	-1	0	1	1.682
NaOH/DOL molar ratio	-	X_1	0.364	1	3	5	6.364
Reaction temperature	° C	X_2	36	50	70	90	104
Reaction time	h	X_3	1.7	3	5	7	8.3

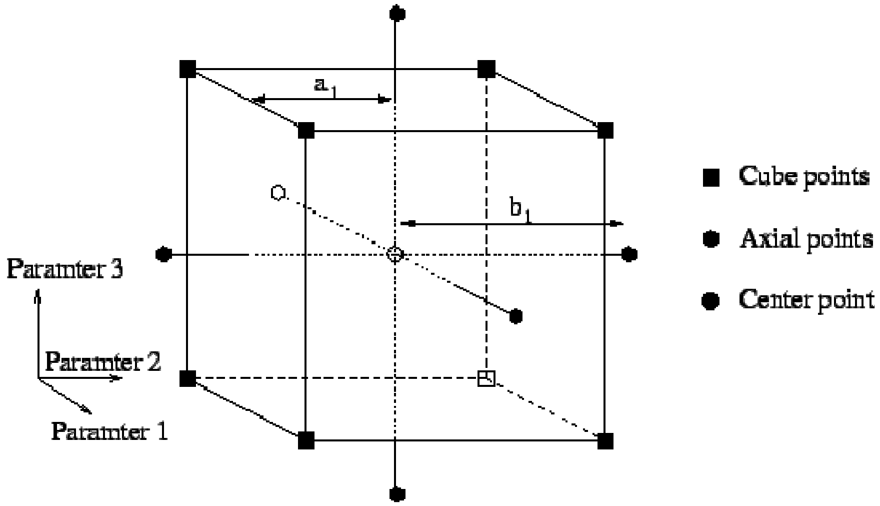

Figure 1 Central composite design for *K*=3

2.4 Epoxidation of the de-polymerized lignin

The synthesis of bio-based epoxy resins were conducted in a three-neck glass reactor (250 ml) based on the conditions that were designed by CCD. Totally 20 tests were performed and 20 samples were obtained by changing three independent parameters including sodium hydroxyl /DOL molar ratio from 0.364 g/mol to 6.364 g/mol, reaction temperature from 36°C to 104°C and reaction time from 102 min to 8h and 18 min. In a typical run, the DOL and epichlorohydrin (EPC, 6 EPC/DOL molar ratio), distillated water and tetrabutylammounium bromide (TBAB, 2% wt TBAB/ wt DOL) as a phase transfer catalyst were charged into the reactor. The reactor was heated in an oil bath while stirring to 80°C for 1 h reaction time. Then, an adequate amount of NaOH solution was added dropwise to the reactor in 15 min and when the temperature reached the required temperature and allowed to react over a pre-specified length of time. Afterwards, the organic phase was separated and weighed to determine the mass balance of reaction. Then, the non-reacted excess EPC was separated from the organic phase by rotary evaporation at 100 °C under reduced pressure. The obtained epoxy resins were dissolved in acetone, and the salts (NaCl and TBAB) were filtered and bio-based epoxy resins were obtained by removal of acetone by rotary evaporation at 50 °C under reduced pressure and then dried in a vacuum oven at 60 °C over night to remove all volatile components. The synthesized epoxy resins were weighed to determine the yield of the epoxidation product.

2.5 Analytical methods

Proton nuclear magnetic resonance (H-NMR) spectra were obtained at 25 °C on a Varian Inova 600 NMR spectrometer equipped with a Varian 5 mm triple-resonance indirect-detection HCX probe. A total of 16–32 scans were accumulated using a 2 s recycle delay, 3.6 s acquisition time, a 45-degree tip angle (pw = 4.8 us), and a spectral width from 2 ppm to 14 ppm (sw = 9000.9 Hz). H-NMR analysis was performed on acetylated OL and acetylated DOL to determine the number of phenolic groups. Acetylation reaction was performed using acetic anhydride in the presence of pyridine as a basic catalyst. In a typical acetylation process, 1 g of dried OL or DOL was dissolved in 10 mL of mixture of acetic anhydride and pyridine (1:1 (v/v)) in a closed vial and mixed in a shaker at 40 °C for 48 h. Then, the mixture was transferred into a beaker containing 100 ml of HCl solution (1wt.%) and the acetylated sample was precipitated in the acidic solution. The precipitated sample was separated and washed with distilled water several times to reach a pH 7. Finally, the sample was dried in a vacuum oven at 80 °C for 24 h to remove the residual water before further analysis. For quantitative H-NMR, 15 mg of acetylated sample was dissolved in *d*-chloroform and 10 mg of dibromomethane (CH_2Br_2) as an internal standard.

The synthesized bio-based epoxy resins were analyzed by Nicolet 6700 Fourier Transform Infrared Spectroscopy (FT-IR) with Smart **iTR**™ ATR accessory in the range of 500- 4000 cm^{-1} to confirm the presence of epoxy groups in the structure of lignin. The average molecular weight and polydispersity index (PDI) of original organosolv lignin and the depolymerized organosolv lignin (DOL) were determined using a Waters Breeze GPC-HPLC instrument (1525 binary pump, UV detector set at 270 nm, Waters Styragel HR1 column at 40 °C) using THF as the eluent at a flow rate of 1 ml/min with linear polystyrene standards for the molecular weight calibration curve. The epoxy content of the synthesized epoxy samples was measured by potentiometric titrator based on ASTM D1652-11. In this method, the resins dissolved in a suitable solvent and the resulting solution is titrated with perchloric acid. As the reaction progresses, the potential of the solution gradually increases until the reaction approaches to completion at which point the potential increases very quickly. This point is the end point of titration and the epoxy content was calculated according to this point.

The yield of the epoxidation product, i.e., the lignin-based epoxy resin, was calculated as follows:

$$Yield(\%) = \frac{S}{L(1+0.301)} \times 100 \qquad (2)$$

Where *S* is the weight of dried epoxidized lignin, *L* is the weight of dried DLO in each epoxidation run, and 0.301 g is the stoichiometric amount of epichlorohydrin for 1g of DOL.

3. Results and discussion

3.1 Characteristic the chemical structure of OL and DOL

Organosolv lignin was chemically modified via the depolymerization process as described previously before being used for the epoxidation reaction. H-NMR and GPC were used to investigate the effects of depolymerization process on lignin structure and molecular weight. Figure 2 shows the H-NMR spectra of acetylated OL and acetylated DOL. The spectra of both samples have two peaks at 4.9 ppm and 7.26 ppm which are attributed to diboromethane (as an internal standard) and d-chloroform (as a solvent), respectively. The peaks associated with the protons of aliphatic acetates and phenolic acetates groups are at 1.6-2.2 ppm and 2.2-2.6 ppm, respectively [16]. The internal standard and solvent were selected in order to prevent any overlapping with the signals of aliphatic and aromatic acetates. In the H NMR spectra, the total integrated peak area of aliphatic and aromatic acetates was normalized with the integrated peak area of diboromethane to calculate the moles of total hydroxyl groups. The total hydroxyl groups of OL and DOL per lignin unit (180 g per unit) were found to be 0.764 and 0.974, respectively. From GPC measurement, the average molecular weight and polydispersity index (PDI) of OL were 2638 g/mol and 3.58, respectively. After the de-polymerization process, the M_w of lignin decreased to 690 g/mol with a narrower PDI of approximately 3.01. These results suggest that the de-polymerization process effectively cleaved the intermolecular bonds, such as ether bonds, which decreased the molecular weight of lignin, increased the content of total hydroxyl groups in DOL, and hence greatly promoted the reactivity of the DOL for epoxidation reaction.

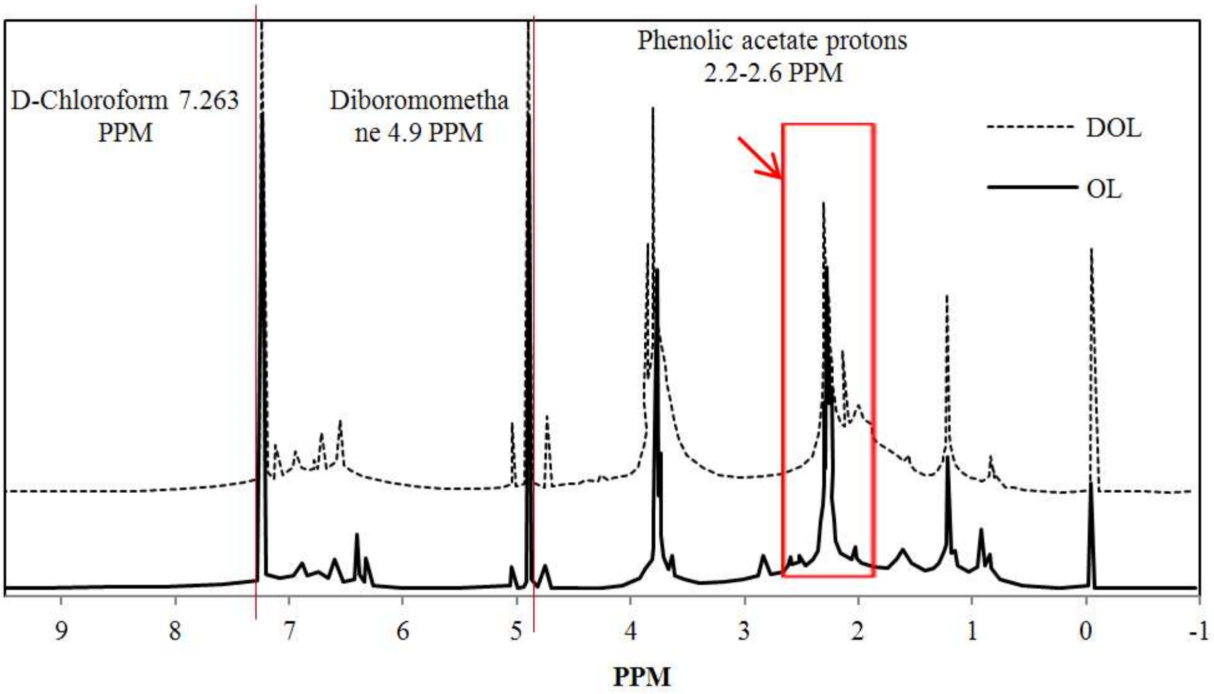

Figure 2 H-NMR spectra and signal assignments of acetylated OL and Acetylated DOL

3.2 Characterization of the chemical structure of epoxidized DOLs

The FTIR spectra of DOL and epoxidized DOLs are presented in Figure 3. All spectra were normalized based on C=C Aromatic bonds that are expected to be of no changes in all samples to provide better comparison of chemical changes caused by the epoxidation reaction. As the spectra of all epoxidized DOLs were similar, only some of them are shown here. All samples show a strong absorption band between 3200 and 3550 cm^{-1} which is associated with O-H stretch vibration of phenolic and aliphatic hydroxyl groups, with a prominent C-H stretching absorption at around 2900 cm^{-1} [26,28]. The absorption of other functional groups such as C=C aromatic bands and C=O groups are at 1600 cm^{-1} and 1740 cm^{-1}, respectively. The presence of a peak at 915 cm^{-1} for the DOLs is attributed to epoxy groups, which is a proof of grafting epoxy groups to DOL through epoxidation reaction. The intensity of the peaks at 915 cm^{-1} indicates the content of epoxy groups on the synthesized samples. For instance, this peak in some samples such as A2, A6, A10 and A11 is sharper than other samples. These results are in good agreement with the measured epoxy content (EC) that is presented in Table 2.

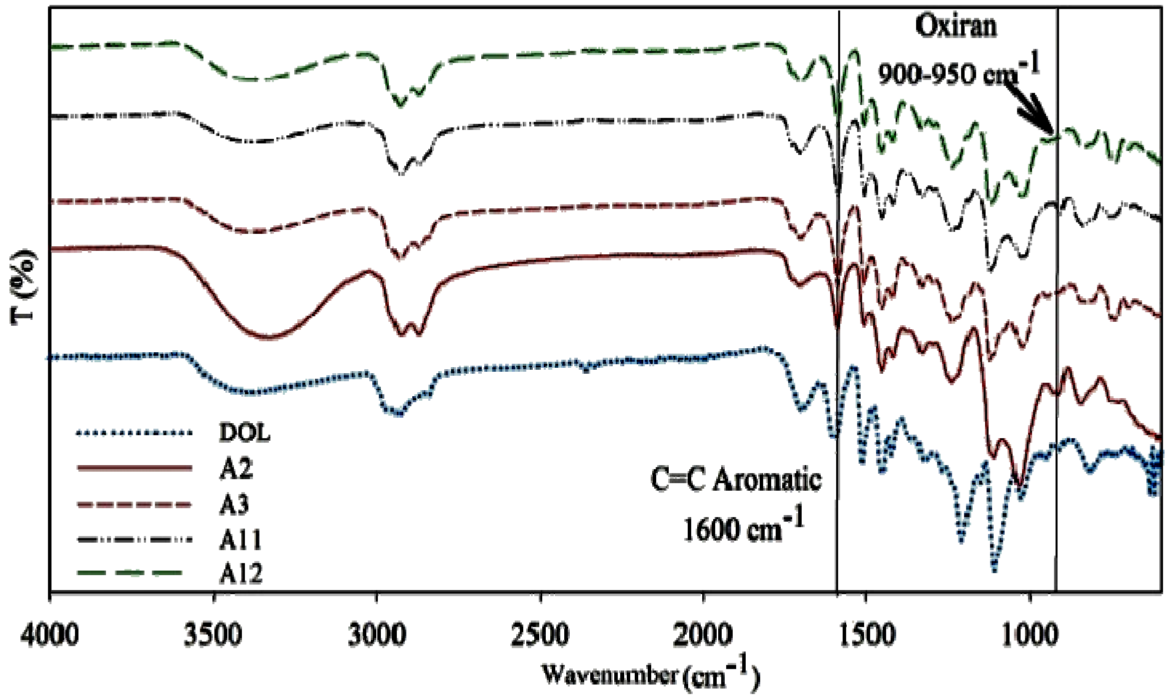

Figure 3 FTIR spectra of the DOL and the epoxidized DOLs.

3.3 Model building and analysis of variance (ANOVA)

The yield and the epoxy content of the epoxy products from all synthesis runs based on the experimental design were measured and the results are provided in Table 2. These results show that the yield of epoxidation and epoxy content of the epoxy products change with the variation of the synthesis conditions.

Table 2 The central composite matrix and output responses

Run #	Level of parameters						Output responses	
	Coded value			Actual value				
	X_1	X_2	X_3	NaOH/DOL	Temp. (°C)	Time (h)	Yield (%)	EC
A1	-1	-1	-1	1	50	3	82.13	2.94
A2	1	-1	-1	5	50	3	89.13	5.25
A3	-1	1	-1	1	90	3	88.52	0.55
A4	1	1	-1	5	90	3	106.7	3.04
A5	-1	-1	1	1	50	7	88.78	3.21
A6	1	-1	1	5	50	7	91.96	6.09
A7	-1	1	1	1	90	7	103.0	0.86
A8	1	1	1	5	90	7	115.5	3.67
A9	-1.682	0	0	0.364	70	5	85.94	0.67
A10	1.682	0	0	6.364	70	5	102.56	6.26
A11	0	-1.682	0	3	36	5	82.60	5.48
A12	0	1.682	0	3	104	5	108.06	0.75
A13	0	0	-1.682	3	70	1.7	89.16	3.08
A14	0	0	1.682	3	70	8.3	104.08	3.45
A15	0	0	0	3	70	5	90.54	3.17
A16	0	0	0	3	70	5	90.69	3.2
A17	0	0	0	3	70	5	90.72	3.18
A18	0	0	0	3	70	5	90.82	3.19
A19	0	0	0	3	70	5	90.80	3.20
A20	0	0	0	3	70	5	90.25	3.21

The Central Composite Design (CCD) was applied to optimize the synthesis condition of lignin-based epoxy resin and probe the relative or interactive effects of NaOH/DOL molar ratio, reaction temperature and reaction time on the yield of grafting reaction and epoxy content of the obtained epoxy samples. The responses were developed with various functions such as linear, quadratic and cubic models to find the best fitting model, and a quadratic equation based on the coded value of experimental factors was found to best fit the responses. The significance of the coefficients were evaluated based on a confidence interval of 95% where the corresponding *P*-value > $\alpha = 0.05$. The coefficients with *P*-value lower than 0.05 have a statistically significant effect on the responses, otherwise, the influence of others terms would be insignificant and removed from the regression model. The final reduced model to predict the yield and epoxy content of lignin-based epoxy resin are shown as follows:

$$\begin{aligned} Yield(\%) &= 90.63 + 5.05X_1 + 7.64X_2 + 4.22X_3 + 1.29X_1^2 \\ &+ 1.67X_2^2 + 2.13X_3^2 + 2.54X_1X_2 - 1.21X_1X_3 + 1.75X_2X_3 \end{aligned} \quad (3)$$

$$EC = 3.20 + 1.46X_1 - 1.27X_2 \quad (4)$$

Where X_1 is the coded value of NaOH/DOL molar ratio, X_2 is the coded value of reaction temperature and X_3 is the coded value of reaction time. The positive term indicates a synergistic effect on the responses while the negative coefficient indicates an antagonistic effect on the responses. The built model for the yield of epoxidation product is very complex and all terms including linear, square and interaction factors are significant. It was observed that all coefficients from the model gave positive effect except the interaction term of NaOH/DOL molar ratio and reaction time (X_1X_3) that has a negative effect on the yield. As a result, a higher temperature, longer reaction time and larger NaOH/DOL molar ratio all lead to a higher yield of the epoxidation product. Obviously, harsh reaction conditions promote the grafting of epichlorohydrin into the structure of lignin. In contrast, the epoxy content has a linear relationship with the NaOH/DOL molar ratio (X_1) and the reaction temperature (X_2), while the effects of other factors are not significant on the epoxy content (EC) of the lignin-based epoxy resins. From eq. (4), increasing NaOH/DOL molar ratio increases the epoxy content by 1.46 times and increasing the reaction temperature decreases the epoxy content by 1.27 times.

To evaluate the validity and suitability of the regression models, the analysis of variance (ANOVA) and the *F*-test were applied. The ANOVA results for the yield and epoxy content of the reaction products are presented in Tables 3 and 4, respectively. Statistical analysis for the yield shows that the *P*-value of the model is less than 0.05 which confirms the significance and the desirability of the model for the prediction. The "lack of fit" for the model is not significant as its *F*-value is 4.22 and its *P*-value is greater than the confidence interval (*P*-value > 0.05). The non significant "lack of fit" is desirable because it can be used as a tool to confirm the good fit of the model. The coefficient of determination (R^2) for the epoxy product yield is very high, $R^2 = 0.9992$, indicating that 99.92 % of variations of the yield can be explained by the independent variables. The value of adjusted R^2 is 0.9986 which is a bit lower than R^2 which again demonstrates the significance of model and indicates that the model is not over-fitted. Furthermore, the predicted R^2 is 0.9948, demonstrating a good agreement between the predicted values of the fitted model and the actual experimental values (Figure 4(a)).

As shown in Eq. (4), the reduced model for EC is a linear model depending mainly on the NaOH/DOL molar ratio and the reaction temperature. If these most effective parameters remain unchanged, the effect of changing reaction time on EC is not significant. The ANOVA analysis on the quadratic model for EC is shown in Table 4. A *P*-value less than 0.05 indicates that the model is statistically significant to predict the EC value. Another way to evaluate the applicability of the predicted model is the >0.05 *P*-value of "Lack of fit", meaning less significant. The regression model has a high coefficient of determination 0.9748. According to Table 4, the adjusted R^2 and predicted R^2 are 0.9658 and 0.9199, respectively, which confirm the adequacy of the model to elucidate the real effect of synthesis parameters on EC (Figure 4(b)).

Table 3 ANOVA results of the quadratic model for the yield of reaction

Source	Degree of freedom	Sum of Squares	Mean Squares	F value	P value (prob> *F*)
Model	9	1586.47	176.274	1475.15	0.000
Residual	10	1.19	0.119	-	-
Lack of fit	5	0.97	0.193	4.22	0.070
Pure error	5	0.23	0.046	-	-
Total	19	1587.66	-	-	-

R^2 of the model is 0.9992; adjusted $R^2 = 0.9986$; predicted $R^2 = 0.9948$.

Table 4 ANOVA results of the quadratic model for the EC

Source	Degree of freedom	Sum of Squares	Mean Squares	F value	P value (prob> *F*)
Model	5	51.0804	10.2161	108.34	0.000
Residual	14	1.3202	0.0943	-	-
Lack of fit	3	0.6068	0.1385	3.12	0.070
Pure error	11	0.7134	0.649	-	-
Total	19	52.4006	-	-	-

R^2 of the model is 0.9748; adjusted $R^2 = 0.9658$; predicted $R^2 = 0.9199$.

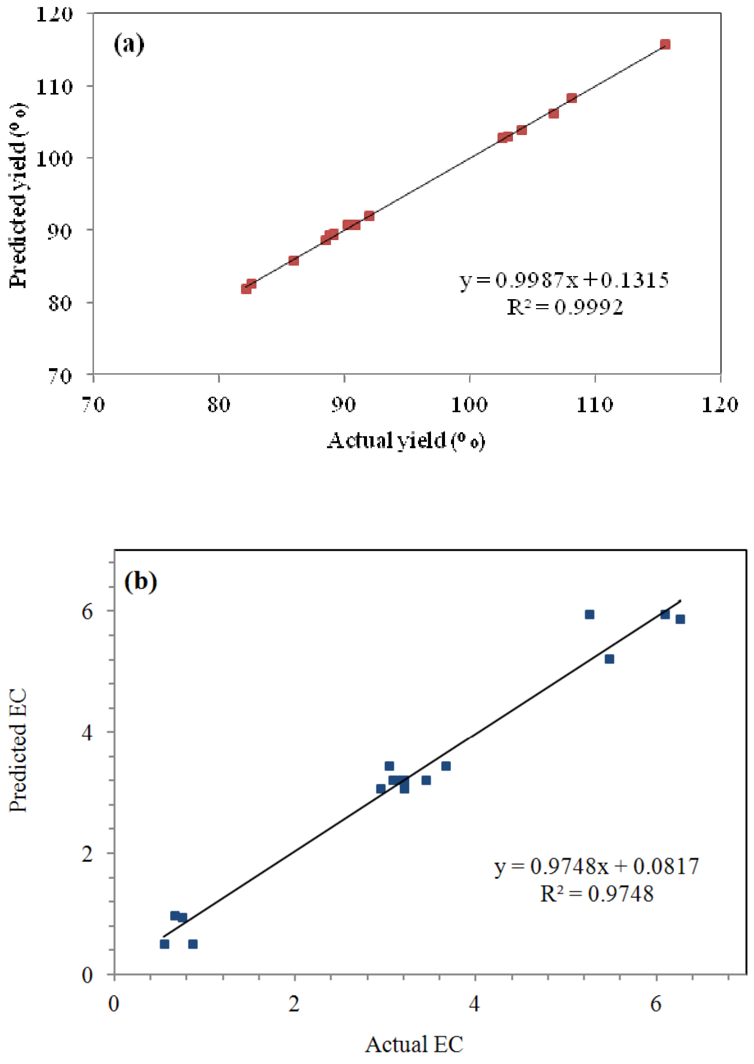

Figure 4 Comparison between the experimental and predicted values of epoxidation product yield (a) and EC (b)

The other evidences to prove the adequacy of models are the normal probability and residual plots, depicted in Figure 5 and 6 for yield and epoxy content, respectively. Figures 5(a) and 6(a) show the data points consistently appear on a straight trend line, i.e., the errors are normally distributed, indicating good prediction by the model. Figures 5(b) and 6(b) show the residual values versus the fitted values for each response. The randomly scattered residuals further prove the adequacy of the models.

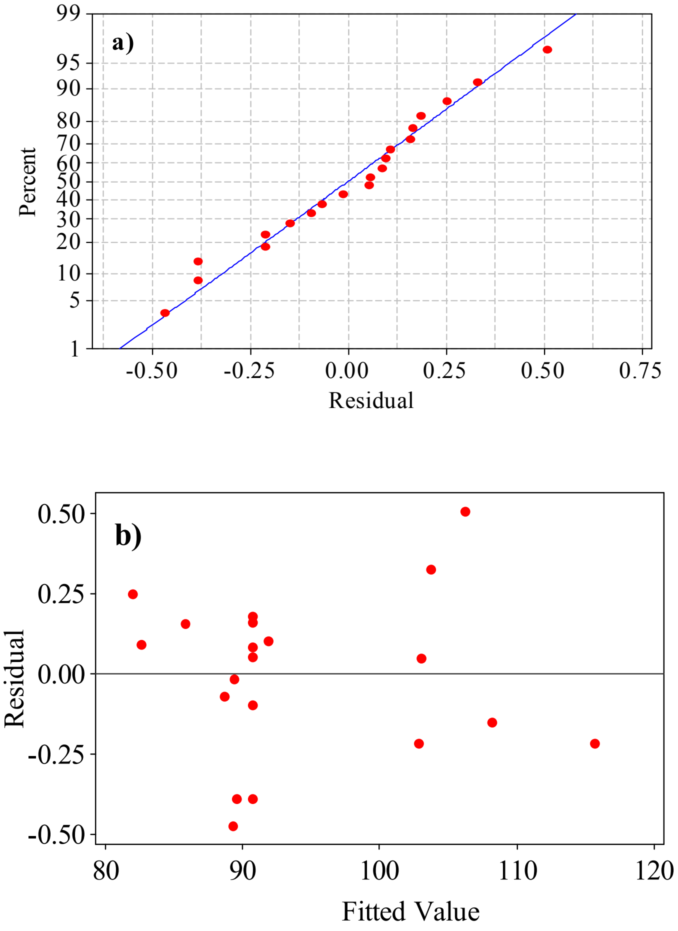

Figure 5 Normal probability plot (a) and residuals vs. fitted values of the regression for product yield (b)

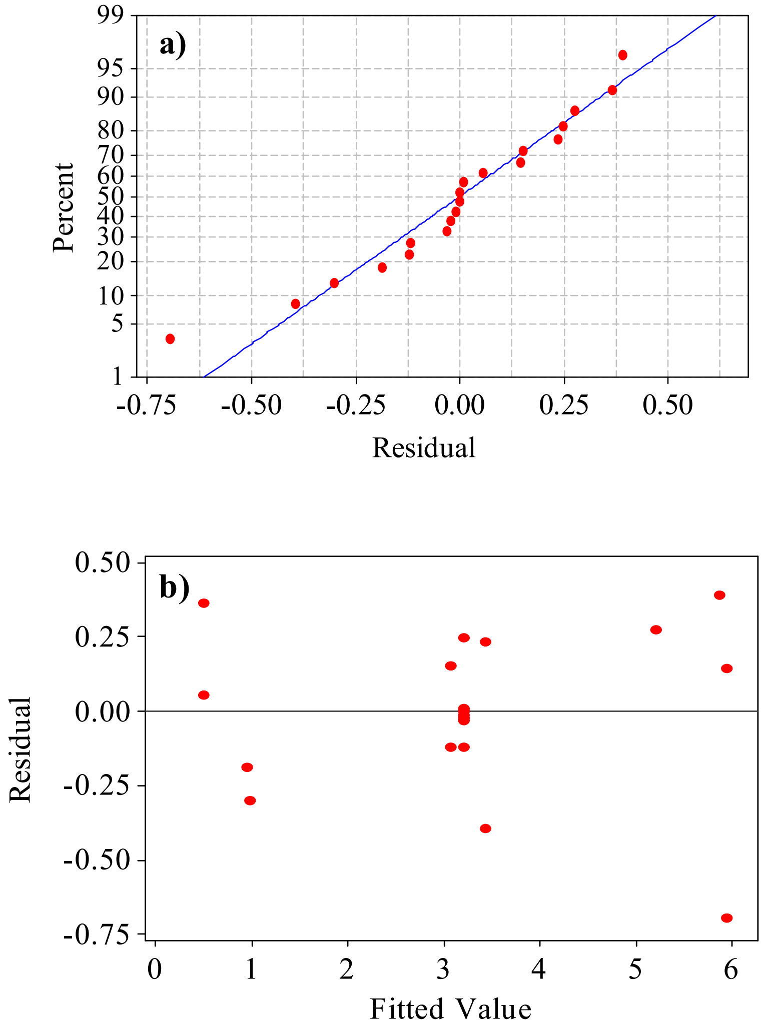

Figure 6 Normal probability plot (a) and residuals vs. fitted values of the regression for epoxy content of lignin-based epoxy resin (b)

3.4 Response surface plot and optimization of variables

The 3-dimenssional plots and contour plots for the product yield and epoxy content are respectively shown in Figures 7 and 8. These plots show the effect of different parameters on the responses and they have a good agreement with the results obtained from the regression equations (3) and (4). These plots were used to optimize the values of different variables to maximize the yield and epoxy content of lignin-based epoxy resins simultaneously.

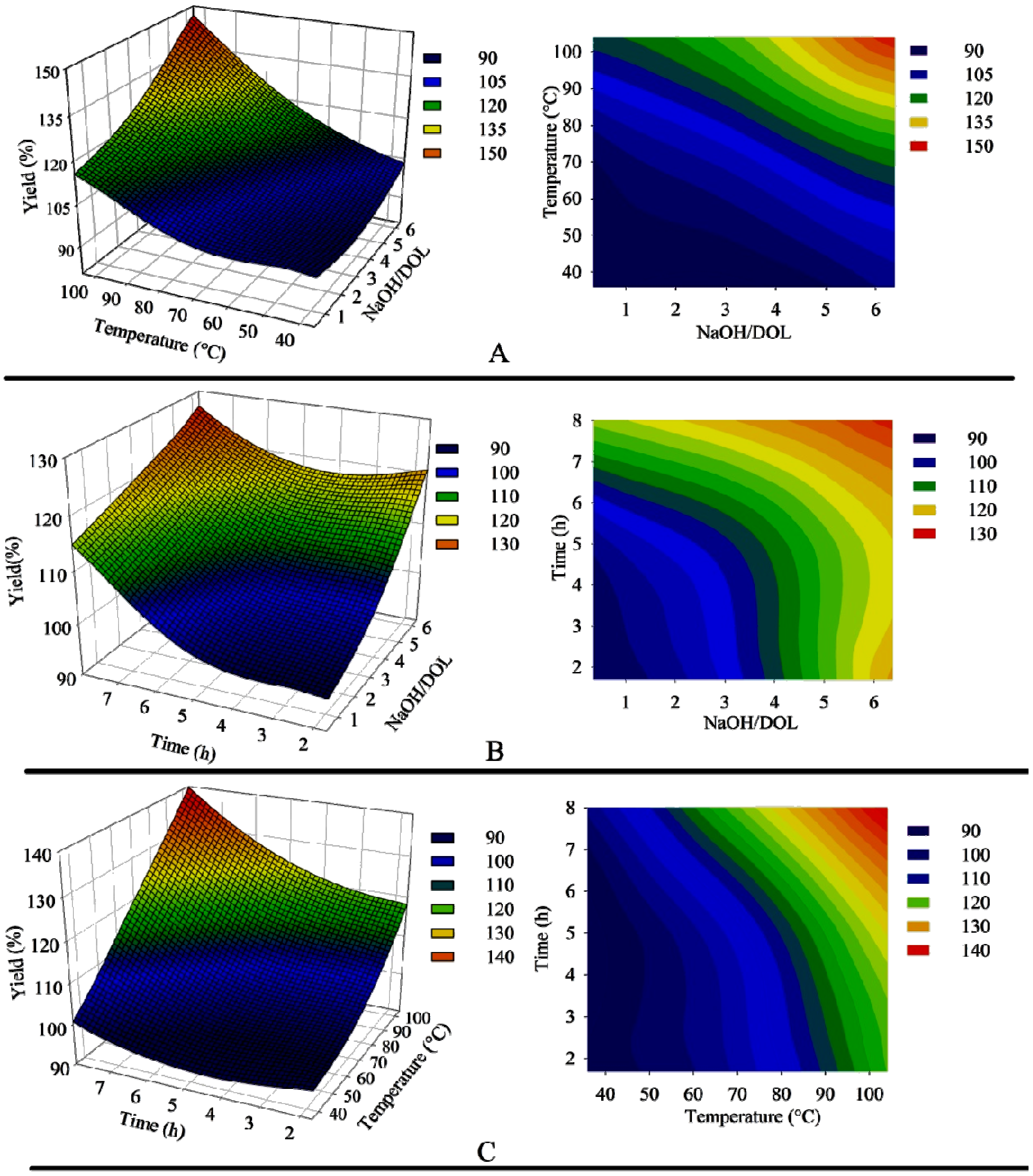

Figure 7 Response surface plots and contour plots of effects of different parameters on the product yield: Effects of NaOH/DOL molar ratio and reaction temperature (A); Effects of NaOH/DOL molar ratio and reaction time (B); Effects of reaction time and temperature (C)

Figure 7A illustrates the interaction of reaction temperature and NaOH/DOL molar ratio on the yield at a constant reaction time. It is clearly shown that at a constant reaction temperature, with the increase of NaOH/DOL molar ratio, the yield of reaction generally increases. At lower temperatures, the yield remains constant while at a high reaction temperature, the yield increases drastically to as high as 150%. The combined effects of reaction time and NaOH/DOL molar ratio on the yield are shown in

Figure 7B. For a given reaction time, the yield increases by increasing NaOH/DOL molar ratio. Figure 7C shows the interactive impact of reaction time and reaction temperature on the yield at a constant NaOH/DOL molar ratio. At constant reaction time, the yield increases with increasing reaction temperature. As a common finding, all these three parameters (reaction time, temperature and NaOH/DOL molar ratio) have a positive effect on the product yield.

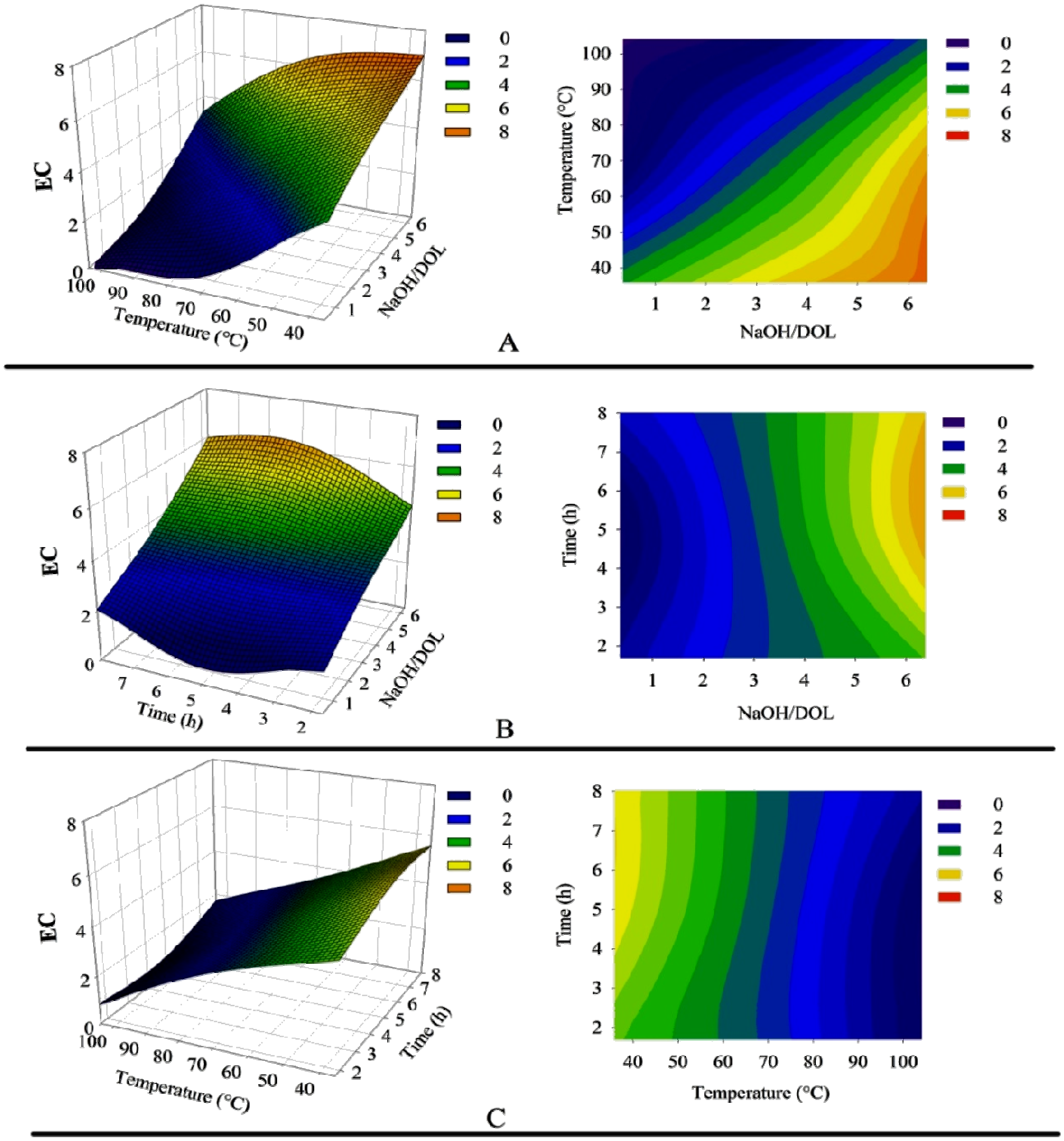

Figure 8 Response surface plots and contour plots of effects of different parameters on the epoxy content of the epoxidation product: Effects of NaOH/DOL molar ratio and reaction temperature (A); Effects of NaOH/DOL molar ratio and reaction time (B); Effects of reaction time and temperature (C)

Figure 8A illustrates the interaction of reaction temperature and NaOH/DOL molar ratio on the epoxy content of the synthesized samples. At a constant NaOH/DOL molar ratio, increasing the reaction temperature leads to a decrease in the epoxy content. The effects of reaction time and reaction temperature on the EC are shown in Figure 8B. When keeping the NaOH/DOL molar ratio constant, an increase of the reaction time does not significantly affect the EC response. This trend is in a good agreement with the regression model (Eq. (4)) indicating the interaction of reaction time and NaOH/DOL molar ratio is insignificant. Figure 8C shows the influences of reaction time and reaction temperature on the EC. Similar to those indicated in Figure 8B, the results shown in Figure 8C demonstrate that the interaction of reaction time and temperature are not significant on the EC response too.

Process optimaization was performed with the response surface methodology to maximize the yield and epoxy content of the lignin-based epoxy products. The recommended optimal conditions were 8h, 55 ºC and a NaOH/DOL molar ratio of 6.3, where the predicted values of the product yield and epoxy content are 100% and 7.8, respectively. A new sample was synthesized at the above optimal conditions, and the resulting reaction yield and epoxy content were 99% and 8, respectively. Thus, the predicted values and experimental resutls are in a very good agreement. As such, the recommended optimal conditions obtained by response surface methodology can be verified and validated.

4. Conclusions

Epoxy resin was synthesized using depolymerized organosolv lignin (DOL) in various conditions. The effects of the variable parameters including reaction time, reaction temperature and NaOH/DOL molar ratio on the reaction yield and epoxy content were investigated using central composite design. The obtained polynomial equations can be used to predict the yield and epoxy content of the products. The optimum conditions were predicted and validated by the experimental data. The optimum conditions determined are 8h at 55 °C with 6.3 NaOH/DOL molar ratio, obtaining an epoxy resin with a high epoxy content of ~8 and 99% reaction yield.

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