



Process modeling, optimization and analysis of esterification reaction of cashew nut shell liquid (CNSL)-derived epoxy resin using response surface methodology

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ABSTRACT

Concept of five-levels–four-factors central composite rotatable design was utilized for the optimization of reaction conditions of cardanol-based vinyl ester resin production, by employing response surfaces methodology, to establish a relationship between the process variables and the extent of conversion under a wide range of operating conditions which resulted in different extent of conversions. The maximum extent of conversion of cardanol-based epoxidised novolac resin (CNE) and methacrylic acid (MA) catalyzed by triphenylphosphine was found to be 95% at optimum set of conditions of molar ratio (1:0.9) between CNE and MA, catalyst concentration (1.49%), reaction temperature (89.96 °C) and reaction time (17,991 s). Geometrical representation of the mathematical models in three-dimensional response surface plots and isoresponse contour plots served as a good aid in understanding the behavior of reaction under different operating conditions by only limited sets of experiments. A statistical model predicted that the highest conversion yield of novolac resin would be greater than 95% at the optimized reaction conditions. The predicted values thus obtained were close to the experimental values indicating suitability of the model.

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1. Introduction

Cashew nut shell liquid (CNSL), an agricultural byproduct abundantly available in the country, is one of the few major and economic sources of naturally occurring phenols and can be regarded as a versatile and valuable raw material for polymer production. Cardanol is a *n*-pentadecadienyl phenol having aliphatic side chain usually a mixture of C₁₅H₂₉, C₁₅H₂₇ and C₁₅H₂₅ i.e., one, two and three double bonds in a linear chain with saturated 8.4%, monoolefin 48.5%, diolefin 16.8% and triolefin 29.33%. The large availability of cardanol could be exploited for the synthesis of thermosetting matrices. Resins derived from CNSL/cardanol are widely employed in the field of surface coatings, adhesives, laminates, rubber compounding and have several miscellaneous applications. Cardanol, like phenol, can be condensed with active hydrogen containing compounds such as formaldehyde to yield a series of phenolic resins, for instance, base-catalyzed resoles and acid-catalyzed novolacs [1–9]. The cardanol-based novolac-type phenolic resins may be modified to develop epoxy resins with epichlorohydrin to enhance the performance of such resins in various fields [10–13]. The introduction of unsaturation at the end of the epoxy resin backbone by the reaction with acid functional

acrylic/methacrylic monomer can produce an eco-friendly vinyl ester resin system.

Vinyl ester resins (VERs) are based on the reaction product of an epoxy resin and an ethylenically unsaturated carboxylic acid, which results in a polymer with chain end unsaturation. Various epoxy resins, such as diglycidyl ether of bisphenol A, or higher homologues, epoxidised phenol-formaldehyde novolac resin and polypropylene oxide diepoxide, etc. are used. The most commonly used acids are acrylic and methacrylic acids. The acid–epoxide reaction is straightforward and is catalyzed by ternary amines, phosphines or alkalis [14–16]. These resins are widely used as thermoset matrix to fabricate a variety of reinforced structures including pipes, tanks, scrubber and ducts. In addition to these applications, vinyl esters are also being used as coating materials, adhesives, molding compounds, structural laminates, electrical insulation products, etc. VERs combine the best properties of epoxies and unsaturated polyesters. VERs based on epoxy novolac are used for chemical storage tanks, pipes and ducting, fume extraction systems and gas cleaning units as these resins showed superior chemical resistance at elevated temperatures [17–20].

Response surface methodology (RSM) is an empirical statistical technique employed for multiple regression analysis by using quantitative data. It solves multivariate data which is obtained from properly designed experiments to solve multivariate equation simultaneously [21]. The graphical representation of this equation is called response surface which is used to describe the individual and cumulative effect of the test variables and their subsequent

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effect on the response. In order to determine quantitative analysis between the response function and the process variables, a central composite rotatable design (CCRD) is adopted in which experiments are randomized in order to minimize the effects of unexplained validity in the observed response due to extraneous factors [22,23]. The function is assumed to be approximated by a second-degree polynomial equation (Eq. (1)).

$$Y_k = b_{k_0} + \sum_{i=1}^4 b_{k_i} X_i + \sum_{i=1}^4 b_{k_{ii}} X_i^2 + \sum_{i \neq j=1}^4 b_{k_{ij}} X_i X_j + \epsilon \quad (1)$$

where Y is the predicted response, X_i the variables in the coded forms of the input variables, b_{k_0} is the value of fitted response at the center point of design, i.e., point (0, 0, 0), and b_{k_i} , $b_{k_{ii}}$ and $b_{k_{ij}}$ are the linear, quadratic and cross-product regression terms, respectively and ϵ is the residual associated with the experiment.

In the present study, the process variables identified are mole ratio of CNE-to-MA, catalyst concentration, reaction temperature and reaction time. The study is based on the hypothesis that the extent of conversion is functionally related to process variables, and fitting of a multiple regression equation describing the response, i.e., p . The design is dependent on the symmetrical selection of variation increments about the central composition. The levels of variation are chosen to be within the reasonable range, since interpretation of the result is validly within the experimental limits.

It is evident from the literature [24–30] that so far hardly any work has been reported for the optimization of process variables during the synthesis of cardanol-based VER. The present investigation was, therefore, undertaken to optimize the process variables by adopting a five-level, four-factor central composite rotatable design (CCRD). Second-order model was used to generate three-dimensional response surfaces for the extent of conversion of VER.

2. Experimental

2.1. Materials

Cardanol (M/s Dheer Gramodyog Ltd., Kanpur), formaldehyde (40% solution from M/s Qualikem Industries, New Delhi), p -toluene sulphonic (PTSA) obtained from E. Merck, New Delhi, Methanol (BDH), epichlorohydrin (M/s Ranbaxy Laboratories Ltd., Punjab), sodium hydroxide, methacrylic acid and triphenylphosphine (from M/s CDH Pvt. Ltd., New Delhi), were used during the investigation.

2.2. Synthesis of cardanol-based vinyl ester resin

Cardanol-based VER was synthesized as per the method similar to that adopted in our previous publications [31,32]. Cardanol-based epoxidised novolac resin and methacrylic acid were reacted in different levels of mole ratios along with different concentrations of catalyst namely triphenylphosphine (TPP). About 200 ppm of hydroquinone was used as inhibitor during the reaction. The reaction was carried out at different temperatures ranging between 75–95 °C for different time periods (refer Table 1) in nitrogen atmosphere. The progress of the reaction was monitored by determining

the acid value intermittently by the method of Korshak and Vinogradova [33] to get the extent of the reaction, p [34]. In order to remove the free methacrylic acid, the prepared resin was dissolved in benzene and treated with potassium carbonate, stirring for 2 h at 30 °C. The acid, in the form of an acid salt, was extracted by water and benzene was evaporated under vacuum using a rotatory film vacuum evaporator (Buchi Type; model: GSI-BU-6). The purified resin was analyzed by Fourier transform infra-red (Perkin Elmer FTIR spectrophotometer (model: RX-1)), nuclear magnetic resonance (Bruker 400 MHz FT-NMR spectrophotometer) spectroscopic analysis and gel permeation chromatography (E. Merck A.G., Darmstadt, Germany, GPC with column oven injection model L-7350, E. Merck Lachrome-7490 R.I. Detector). These were investigated in our previous publication [31] and the structure of cardanol-based vinyl ester resin was elucidated as given in Scheme 1.

2.3. Analysis of data

The analysis of results was performed with statistical and graphical analysis software, Statgraphics Centurion XVI, Version 16.0.08 (M/s StatPoint Inc., USA). This software was used for regression analysis of the data obtained and to estimate the coefficient of regression equation. ANOVA (analysis of variance) which is statistical testing of the model in the form of linear, squared and interaction terms were also utilized to test the significance of each term in the equation and goodness of fit of the regression model obtained [35]. The mapping of the fitted response was achieved using design expert software (Version 8.0.3). This response surface model was also used to predict the result by isoresponse contour plots and three-dimensional surface plots. Contour plot is the projection of the response surface as a two-dimensional plane where as 3D surface plots is the projection of the response surface in a three dimensional plane [36].

3. Results and discussion

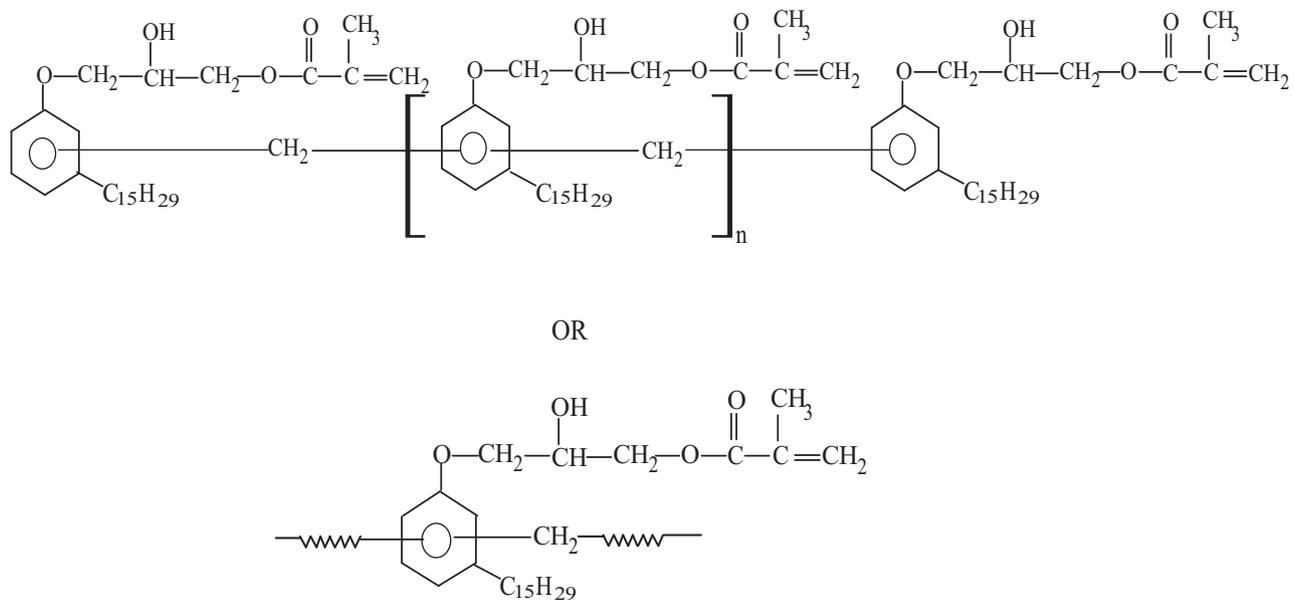
3.1. Design for the optimization of the process variables

The variables that predominantly affected the extent of conversion of cardanol-based vinyl ester resin were (i) mole ratio of CNE-to-MA, (ii) catalyst concentration, (iii) reaction temperature and (iv) reaction time and each parameter was having one lower value and one higher value. The increments of variation for each variable spaced around the center point along with the equation relating the actual and coded ratios are presented in Table 1. By substituting these coded values for the solution of Eq. (1), process variables were coded for solution of the multiple regression equation. Thus, the central composite design was selected for which 30 experimental values were required [26]. Experiments were performed according to the experimental plan (Table 2) where different parameters were changed according to Table 1. The responses, thus, obtained for each combination of the variables are given in Table 2. Significant changes in synthesized vinyl ester were observed for all the combinations implying that these variables significantly affecting the vinyl ester formed.

Table 1
Variables and their levels for central composite design.

Independent variables	Symbols		Levels				
	Coded	Actual	−2	−1	0	+1	+2
Mole ratio	X_1	x_1	0.6	0.7	0.8	0.9	1.0
Catalyst concentration, %	X_2	x_2	0.75	1.0	1.25	1.5	1.75
Reaction temperature, °C	X_3	x_3	75	80	85	90	95
Reaction time, s	X_4	x_4	7200	10,800	14,400	18,000	21,600

$$X_1 = (x_1 - 0.8)/0.1; X_2 = (x_2 - 1.25)/0.25; X_3 = (x_3 - 85)/5; X_4 = (x_4 - 14,400)/3600.$$



Scheme 1. Structure of cardanol-based vinyl ester resin.

3.2. Multiple regression analysis of the fitted model

In order to determine whether given variables should be included or excluded from the model, the hypothesis for the individual regression coefficients was tested. The simple analysis started with a main effects plot. A main effects plot is a plot of the means of the response variable for each level of factor. It allows an experimenter to obtain a general idea of which main effects plot is important. The main effect is calculated by subtracting the overall mean for the factor from the mean for each level. Fig. 1 shows the

main effect plot for the extent of conversion, p , which indicated that the factors mole ratio of CNE-to-MA, catalyst concentration, reaction temperature and reaction time increased when these moved from low level to high level. Each factor at their high level resulted in higher mean responses comparing to that at the low level. The sharp slope of mole ratio was the only factor which showed that the response was sensitive to this factor. A relatively curvature line showed less sensitivity to change in those three factors. If the slope was close to zero, the magnitude of the main effect would be small. The main effect plots are helpful in visualizing which factors affect

Table 2
Central composite design and response.

Run	Variables				Response (p)	
	X_1	X_2	X_3	X_4	Experimental	Predicted
1	-1	-1	-1	-1	0.38	0.41
2	-1	-1	-1	1	0.35	0.37
3	-1	-1	1	-1	0.47	0.51
4	-1	-1	1	1	0.55	0.58
5	-1	1	-1	-1	0.54	0.52
6	-1	1	-1	1	0.43	0.47
7	-1	1	1	-1	0.50	0.58
8	-1	1	1	1	0.63	0.64
9	1	-1	-1	1	0.82	0.78
10	1	-1	1	-1	0.61	0.61
11	1	-1	-1	-1	0.62	0.62
12	1	-1	1	1	0.86	0.88
13	1	1	-1	-1	0.72	0.73
14	1	1	-1	1	0.92	0.88
15	1	1	1	-1	0.72	0.70
16	1	1	1	1	0.94	0.95
17	-2	0	0	0	0.42	0.33
18	2	0	0	0	0.81	0.86
19	0	-2	0	0	0.59	0.56
20	0	2	0	0	0.75	0.74
21	0	0	-2	0	0.57	0.59
22	0	0	2	0	0.82	0.76
23	0	0	0	-2	0.57	0.53
24	0	0	0	2	0.76	0.75
25	0	0	0	0	0.75	0.78
26	0	0	0	0	0.76	0.78
27	0	0	0	0	0.79	0.78
28	0	0	0	0	0.78	0.78
29	0	0	0	0	0.75	0.78
30	0	0	0	0	0.82	0.78

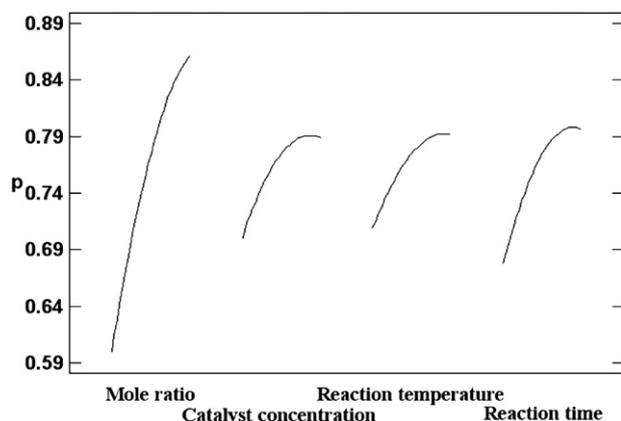


Fig. 1. Main effects plot for extent of conversion, p .

the response the most, but in order to determine the significance of the factors, an appropriate statistical test, t -test, to identify the significance of the main factors is conducted.

Regression analyses for different models indicated that the fitted quadratic models accounted for more than 95% of the variations in the experimental data, which were found to be highly significant. Multiple regression analysis was performed to obtain a quadratic response surface model and equation thus obtained by relating extent of conversion to coded levels of the variables was:

$$p = 0.775 + 0.262X_1 + 0.088X_2 + 0.083X_3 + 0.11X_4 + 0.1X_1X_4 - 0.0908X_1^2 - 0.0633X_2^2 - 0.051X_3^2 - 0.0658X_4^2 \quad (2)$$

The predicted values of extent of conversion obtained using Eq. (2) were close to the experimental values proving that the model was fully applicable. All main effects, linear and quadratic, and interactions were calculated for each model. The estimated effects were used to plot a standardized Pareto chart for the model (Fig. 2); the chart consisted of bars with lengths proportional to the absolute values of the estimated effects divided by their standard values. The chart included a vertical line at theoretical t -value for a 95% confidence level. A bar crossing this vertical line corresponded to a factor or combination of factors that have a significant effect in the response.

From Eq. (2), the correlation coefficient could be obtained for the model. The correlation coefficients for extent of conversion, p ($R^2 = 0.953$) was quite satisfactory for response surfaces. The value of constant was found to be 0.775 which also does not depend on any factor and interaction of the factors. The effect of the linear factors i.e. mole ratio, catalyst concentration, reaction temperature

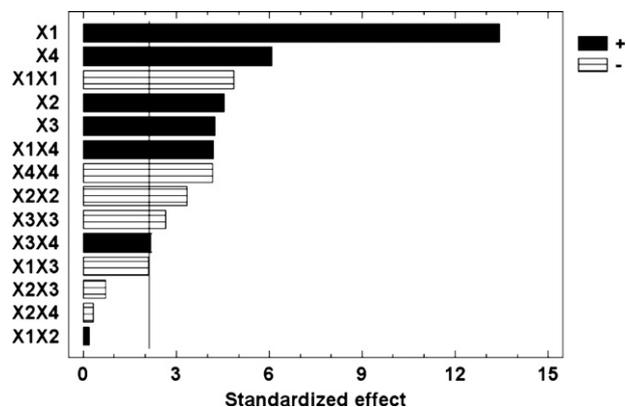


Fig. 2. Standardized Pareto chart for extent of conversion, p .

and reaction time were found to be highly significant ($P < 0.0001$, $P = 0.0006$, $P = 0.0009$ and $P < 0.0001$) on the extent of conversion of cardanol-based vinyl ester resin. All the square terms such as (mole ratio)², (catalyst concentration)², (reaction temperature)² and (reaction time)² were found to be significant ($P = 0.0002$, 0.0044, 0.0169 and 0.0034, respectively). Since the squared terms were significant that means there was a curved line relationship between extent of conversion and square factors. The interaction term i.e. mole ratio \times reaction time ($P = 0.0011$) was found to be significant. A positive sign of the coefficients represented a synergistic effect, while a negative sign indicated an antagonistic effect. The square terms i.e. (mole ratio)², (catalyst concentration)², (reaction temperature)² and (reaction time)² had a negative relationship. So with the increase of these factors there will be a decrease in the extent of conversion. Whereas the linear terms (mole ratio, catalyst concentration, reaction temperature and reaction time) and interaction term (mole ratio \times reaction time) had a positive effect on the extent of conversion which indicated that with an increase of these factors there will be an increase in the response. Furthermore, high value of R^2 (0.9519) and R^2 (adjusted) (0.9070) indicated a high dependence and correlation between the observed and the predicted values of response. This also indicated that about 95% of result of the total variation can be explained by this model.

3.3. Interpretation of variance by ANOVA

When a model has been selected, an analysis of variance is calculated to assess how well the model represented the data. The summary of ANOVA, as shown in Table 3, partitioned the variability in p into separate pieces for each of the effects. It then tested the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, nine effects had P -values less than 0.05, indicating that they were significantly different from zero at the 95.3% confidence level. To evaluate the goodness of the model, F -value test was conducted. The F -value for the extent of conversion was 21.21. The R -squared statistic indicated that the model as fitted explained 95.19% of the variability in p . The adjusted R -squared statistic, which might be more suitable for comparing models with different numbers of independent variables, was 90.70%. The standard error of the estimate showed the standard deviation of the residuals to be 0.0496. The mean absolute error (MAE) of 0.0285 was the average value of the residuals. The Durbin–Watson (D–W) statistic tested the residuals to determine if there was any significant correlation based on the order in which these occurred in the data file. Since the P -value was found to be greater than 5.0%, there was no indication of serial autocorrelation in the residuals at the 5.0% significance level.

3.4. Graphical interpretation of models

The 3D response surface was used to determine the individual and cumulative effect of the variable and the mutual interaction between the variable and the dependent variable. The response surface analyzes the geometric nature of the surface, the maxima and minima of the response and the significance of the coefficients of the canonical equation. The polynomial response surface model obtained may be maximized or minimized to obtain the optimum points whereas a contour plot is a graphical technique for representing a three dimensional surface by plotting constant z -slices called contours, on a two dimensional format. That is, given a value for z , lines are drawn for connecting the (x,y) coordinates where that z value occurs [37]. To investigate the individual and interactive effect of these two factors on the extent of conversion, three dimensional contour plots were drawn and the inferences thus obtained have been discussed below.

Table 3
Analysis of variance for extent of conversion, p .

Source	Sum of squares	Df	Standard error	Mean square	F-ratio	P-value	
Model	0.7292	14		0.0521	21.21	<0.0001	Significant
X_1	0.4108	1	0.2041	0.4108	167.30	0.0000	
X_2	0.0468	1	0.2041	0.0468	19.07	0.0006	
X_3	0.04167	1	0.2041	0.04167	16.97	0.0009	
X_4	0.0726	1	0.2041	0.0726	29.57	0.0001	
$X_1 \times X_1$	0.05657	1	0.1909	0.0566	23.04	0.0002	
$X_1 \times X_2$	0.0001	1	0.2500	0.0001	0.04	0.8428	Non-significant
$X_1 \times X_3$	0.01	1	0.2500	0.0100	4.07	0.0618	Non-significant
$X_1 \times X_4$	0.04	1	0.2500	0.0400	16.29	0.0011	
$X_2 \times X_2$	0.02750	1	0.1909	0.0275	11.20	0.0044	
$X_2 \times X_3$	0.0012	1	0.2500	0.0012	0.50	0.4908	Non-significant
$X_2 \times X_4$	0.0002	1	0.2500	0.0002	0.09	0.7663	Non-significant
$X_3 \times X_3$	0.01772	1	0.1909	0.0177	7.22	0.0169	
$X_3 \times X_4$	0.0110	1	0.2500	0.0110	4.49	0.0512	Non-significant
$X_4 \times X_4$	0.02972	1	0.1909	0.0297	12.10	0.0034	
Residuals	0.03683	15		0.0025			
Lack of fit	0.0331	10		0.0033	4.41	0.0576	Non-significant
Pure error	0.0038	5		0.0008			
Cor. total	0.7661	29					

Table 4
Optimum conditions for maximum extent of conversion, p .

Process variables	Coded values	Uncoded values
Mole ratio	1.005	0.90
Catalyst concentration, %	0.9925	1.49
Reaction temperature, °C	0.9925	89.19
Reaction time, s	0.9975	17,991

Maximum value of extent of conversion, $p=0.956$.

3.4.1. Response 3D surface and contour plots

Table 4 presents the optimum conditions to yield maximum extent of conversion. The optimum value of p was found to be 0.953 which was higher than the highest value amongst the calculated values based on the experimental design. The surface plot of extent of conversion (p) of a cardanol-based vinyl ester resin as a function of mole ratio of CNE-to-MA and catalyst concentration demonstrated maximum extent of conversion ($p=0.89$), as obtained from the respective contour plot (Fig. 3), at maximum value of mole ratio (i.e. 0.95) and catalyst concentration (i.e. 1.44%). The response surface of extent of conversion showed a clear peak, suggesting that the optimum condition for maximum p was well inside the design boundary. It could be observed from 3D plot of Fig. 3 that the conversion increased when molar ratio and catalyst concentration was increased, two other variables viz., reaction temperature and reaction time, held at the middle value. These results

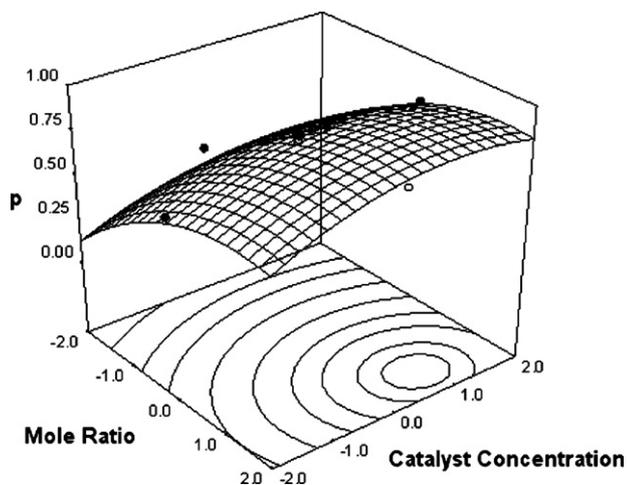


Fig. 3. Surface and contour plot between mole ratio and catalyst concentration.

were somewhat consistent with the earlier observations that at mole ratio of 0.9, maximum extent of conversion of vinyl ester resin was obtained [14,38–40]. This may be due to the fact that complete esterification of epoxy resin is practically difficult as polymerization occurred during the esterification reaction and the product gets gelled before a sufficient low value is attained [41]. However, in our case, it was observed that for higher values of catalyst concentration, p increased with increasing mole ratio up to a certain level whereas for lower values of catalyst concentration the pattern followed a parabolic path. At fixed value of mole ratio the increased catalyst concentration increased the value of p up to a certain level and then remained constant. The increased effect might be due to consumption of more acid and epoxy groups whereas the decrease in value of p might be due to retarding effect of the monomer [34]. Similar pattern was observed for the extent of conversion in the surface plot of mole ratio and reaction temperature (Fig. 4), in which maximum conversion of 0.87 was obtained at maximum value of mole ratio (i.e. 0.94) and reaction temperature (i.e. 85.88 °C).

Fig. 5 shows the surface and contour plots of p of a cardanol-based vinyl ester resin as a function of mole ratio of CNE-to-MA and reaction time resulted maximum extent of conversion ($p=1.03$), as obtained from the respective contour plot at maximum value of mole ratio (i.e. 0.998) and reaction time (i.e. 21,579.6 s). It could be observed from surface plot of Fig. 5 that the conversion increased

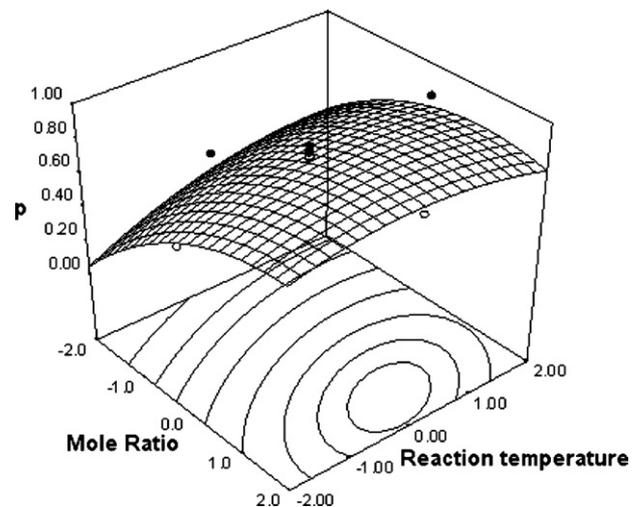


Fig. 4. Surface and contour plot between mole ratio and reaction temperature.

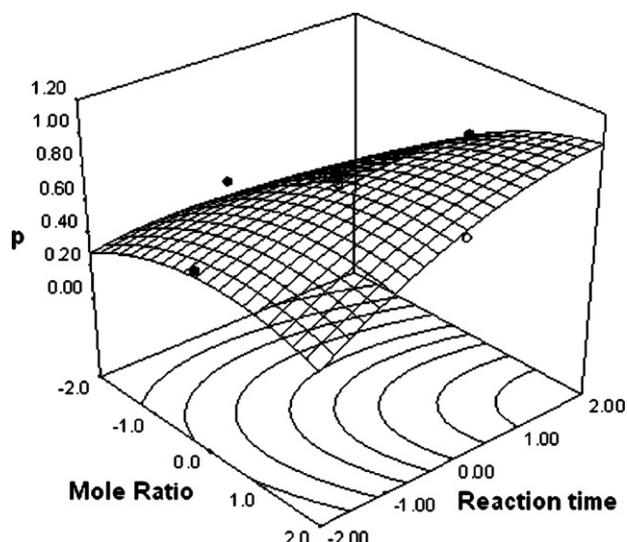


Fig. 5. Surface and contour plot between mole ratio and reaction time.

when molar ratio and reaction time were increased, two other variables viz., reaction temperature and catalyst concentration, held at the middle value. This might be attributed to the fact that with increasing reaction time more and more oxirane groups might combine with the acid functional group resulting to an increased extent of conversion. These results were similar to the results as reported earlier in the literature [39,41]. However, it was observed that increase in the value of mole ratio up to 21,579.6 s of reaction time, increased the value of p almost linearly. The increase of reaction time, at maximum value of mole ratio, increased the value of p exponentially. Almost similar effect was observed with reaction temperature and reaction time (Fig. 6). The maximum extent of conversion of 0.848 was obtained at maximum value of reaction temperature (92.79°C) and reaction time (19,685.5 s). The effect of reaction time and temperature on p at fixed level of mole ratio and catalyst concentration, the increased reaction time and reaction temperature increased the value of p . This might be attributed due to the greater possibility of association of acid and epoxide groups. In terms of p of vinyl ester resin, some of literature studies apparently achieved better results than this work; however, the initial mole ratio, reaction time and temperature used in this study were relatively high in contrast to those in the literature [15,38–40].

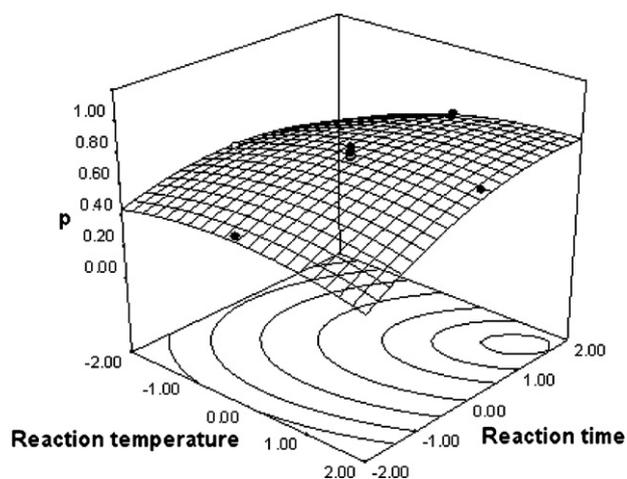


Fig. 6. Surface and contour plot between reaction temperature and reaction time.

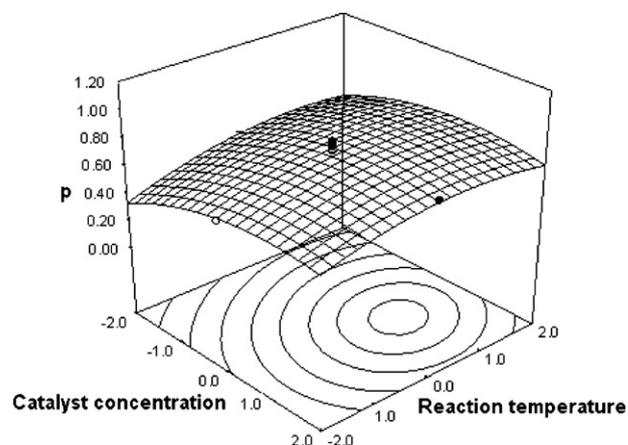


Fig. 7. Surface and contour plot between catalyst concentration and reaction temperature.

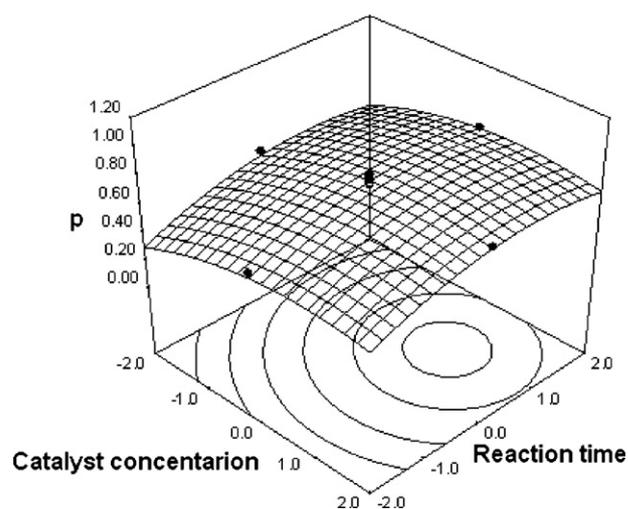


Fig. 8. Surface and contour plot between catalyst concentration and reaction time.

The contour plot of p as a function of catalyst concentration and reaction temperature (Fig. 7) gave maximum value of p i.e. 0.803 at maximum value of catalyst concentration, 1.40% and reaction temperature of 88.75°C . Also, Fig. 7 clearly indicated that with the increase of catalyst concentration, at fixed value of reaction time, p first increased up to a certain value and then decreased and followed a parabolic shape of the plot. However, at fixed value of catalyst concentration, the extent of conversion decreased almost linearly at very slow rate with reaction time which might be due to the antagonistic or the retarding effect of the excess catalyst and consequent formation of the less reactive radical [43,44]. Almost similar behavior could be seen in the surface and contour plots of catalyst concentration and reaction time (Fig. 8) from which the maximum value of p (i.e. 0.811) was obtained at a catalyst concentration of 1.41% and reaction time of 17,241.14 s.

4. Conclusion

It may be concluded that using RSM, with a minimum number of experiments, can effectively optimize the esterification reaction of cardanol-based epoxidised novolac resin and methacrylic acid to produce cardanol-based vinyl ester resin. Computerized computations and model building will go a long way to unrevealing the complexity of the process with different sets of conditions. The maximum extent of conversion (95.3%) was predicted when the cardanol-based epoxidised novolac was reacted with methacrylic

acid (molar ratio 1:0.9) at 89.96 °C for a time period of about 5 h with the catalyst (triphenylphosphine) concentration of 1.49% of total weight of CNE and MA. These predicted values thus obtained for optimum process conditions were found to be in good agreement with experimental data indicating the applicability of the model.

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