European Polymer Journal 45 (2009) 946–952

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Studies on the process variables of the condensation reaction of cardanol and formaldehyde by response surface methodology

Ranjana Yadav, Deepak Srivastava *

Department of Plastic Technology, H. B. Technological Institute, Nawab Ganj, Kanpur 208 002, Uttar Pradesh, India

ARTICLE INFO

Article history:
Received 11 August 2008
Received in revised form 22 October 2008
Accepted 14 November 2008
Available online 24 November 2008

Keywords:
Cardanol-based novolac resin
Response surface methodology
Extent of conversion
Three-dimensional surface plots

ABSTRACT

Different types of cardanol-based novolac-type phenolic resins are produced under a wide range of operating conditions for the application in the resin producing industries. Different operating conditions employed for the production of such resins result in different extent of conversion. In order to understand the system behavior, mathematical relationship between the process variables and the extent of conversion was established by employing the 'Response surface methodology'. Geometrical representation of the mathematical models in three-dimensional surface plots served as a good aid in understanding the behaviour of reaction under different operating conditions. The maximum extent of conversion of the condensation reaction of cardanol and formaldehyde was found to be 93.0 percent at optimum sets of condition of reaction temperature, time, catalyst concentration and pH of the reaction mixture. All the predicted values for optimum process conditions were in good agreement with experimental data.

1. Introduction

The synthesis of polymers from renewable resources represents a very important matter and captures the attention of researchers of the academic and industrial world. In a particular, in the past few years, the synthesis of polymers starting from renewable resources is object of significant research efforts due to the increasing prices of petrol–chemical products associated with growing environmental concerns. Cashew nut shell liquid (CNSL), an agricultural renewable resource and the byproduct of the cashew industry usually *Anacardium Occidental* from cashew tree, holds considerable promise in that direction because it is a source of unsaturated hydrocarbon phenol and behaves as an excellent monomer for thermosetting polymer production [1,2]. CNSL is already in use for the manufacture of special phenolic resins for coating, lamination and as friction materials. These polymers are synthesized from CNSL either by polycondensation with electrophilic compounds, such as formaldehyde, furfuraldehyde or by chain polymerization through the unsaturation presents in the side chain using acid catalysts or by the functionalization at the hydroxyl group and subsequent oligomerization to obtain a functionalized pre-polymer [3–6]. During the extraction process of CNSL, cardanol, also a phenolic compound with a C_{15} aliphatic chain in the meta position having mixture of saturated and unsaturated (mono-, di-, and tri-) compounds, is resulted [7–10].

Response surface methodology (RSM) is reported to be an effective tool for optimizing a process, as highlighted by various workers [11–16]. Such a mathematical model when represented graphically would not only serve as a visual aid to have a clearer understanding of the phenomenon underlying the reaction, but also enable the location of regions of instability in the system [11]. Some good examples of appropriate applications of this technique in dairy products (cheese) [12,13], polyethylene blends [14], grafting of methylmethacrylate (MMA) on nylon-6 fibers [15] etc., are the optimization of process variables.

It is evident from the literature that no work has been reported so far for the optimization of process variables

* Corresponding author.
E-mail address: deepak_sri92@rediffmail.com (D. Srivastava).

0014-3057/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2008.11.019

of the condensation reaction of cardanol and formaldehyde in the presence of dicarboxylic-type oxalic acid. The present investigation was, therefore, undertaken to optimize the process variables viz., mole ratio of cardanol-to-formaldehyde, catalyst concentration, reaction temperature, reaction time, and pH of the reaction mixture, for the production of cardanol-based novolac-type phenolic resin using RSM by adopting a five-level, five-factor central composite rotatable design (CCRD). Second – order model was used to generate three-dimensional response surfaces for the extent of conversion of novolac resin.

2. Materials and methods

2.1. Materials

Cardanol was obtained from M/s Satya Cashew Pvt. Ltd., Chennai, India. Formaldehyde (37% solution) from M/s Qualikem Industries, New Delhi was used for formylation, Oxalic acid from M/s S.D. Fine chemicals, Mumbai, was used as catalyst. Methanol (BDH) was used to dissolve the catalyst.

Cardanol, procured from open market, was distilled under reduced pressure (1 mm Hg) at 206 °C. The purified cardanol was checked for its iodine value, viscosity, specific gravity, etc. These values resembled the values given in our previous publication [17].

2.2. Synthesis of cardanol-based novolac-type phenolic resin

Cardanol-based novolac-type phenolic resin was prepared according to the flow diagram shown in Fig. 1 by a method similar to that adopted by Knop and Schieb [18] for phenol-based novolac resin. The levels of mole ratios of cardanol and formaldehyde, catalyst concentration, reaction temperature, reaction time and pH of reaction mixture were varied according to the experimental design. These values were suggested by previous studies carried out in our laboratory. Free-formaldehyde content and phenol content of the reaction mixture were checked after every 45 min to see the completion of the methylolation reaction [17]. The reaction product was cooled and dried under the vacuum at 60 °C overnight before purification by column chromatography. A resin solution prepared with *n*-hexane, charged to the silica gel column chromatographic purification, was adopted mainly to remove unreacted components, impurities, etc., from the methylolated cardanol. Purification was effected using the elutent mixture of ethyl acetate – benzene (60: 40). The purified resin was analyzed by infra-red (IR) and gel permeation chromatographic (GPC) analysis.

2.3. Experimental design

In order to determine the quantitative relationship between the response function and the process variables, a central composite rotatable second order design [19,20] was employed. This experiment design was considered appropriate since non linear trends in the relationship are likely in the chemical system under study. The process variables identified in the present system are:

(a) mole ratio of cardanol-to-formaldehyde
(b) catalyst concentration

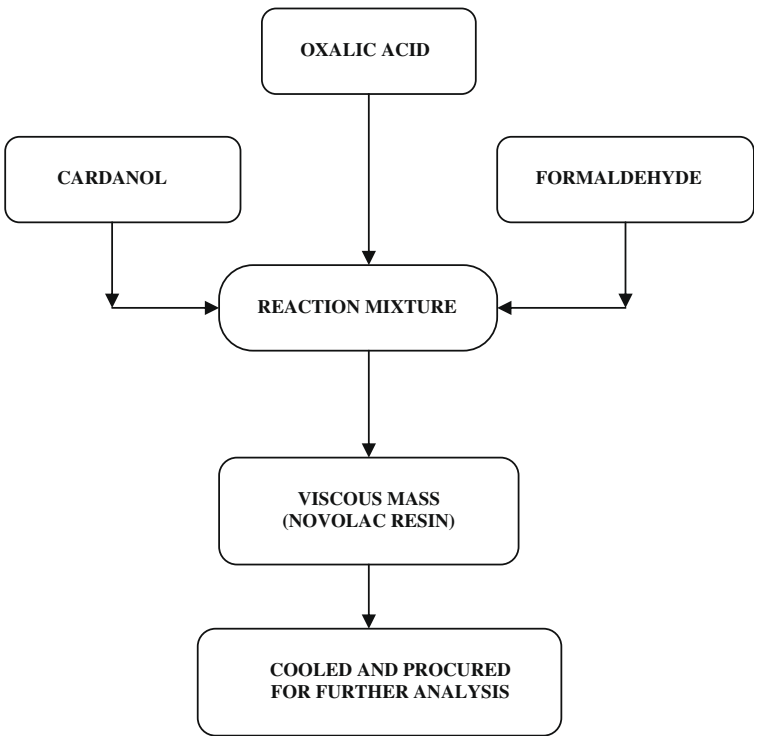

Fig. 1. Flow diagram for the preparation of cardanol-based novolac resin.

(c) reaction temperature
(d) reaction time
(e) pH of the reaction mixture

The study is based on the hypothesis that the extent of conversion is functionally related to process variables, and attempts to fit a multiple regression equation describing the response, i.e., *p*. Table 1 lists variables in the descending order of assumed importance as process variables. Care was taken to ensure independent operation of the variables, since an error in the choice of variables could lead to an indeterminate solution.

The design dependent up on the symmetrical selection of variation increments about the central composition. These levels of variation were chosen to be within the reasonable range, since interpretation of the result was validously within the experimental limits. The levels selected were also based on the conclusion of previous studies. 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 for solution, process variables were coded for solution of the multiple regression equation. A central composite rotatable design (CCRD) (Table 2) was adopted. In this design, experiments were randomized in order to minimize the effects of unexplained validity in the observed response due to extraneous factors. The function was assumed to be approximated by a second-degree polynomial equation (Eq. 1).

$$Y_k = b_{k_0} + \sum_{i=1}^{5} b_{k_i} X_i + \sum_{i=1}^{5} b_{k_{ii}} X_i^2 + \sum_{i \neq j=1}^{5} b_{k_{ij}} X_i X_j \qquad (1)$$

where b_{k_0} was 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 $b_{k_{ij}}$ were the linear, quadratic and cross-product regression terms, respectively.

2.4. Analysis of data

Multiple regression analysis was conducted for fitting the model represented by the equation to the experimental data. Maximization or minimization of the polynomial thus fitted was performed by numerical technique, using the mathematical optimizer procedure of Quattro Pro12 of Word Perfect Office 12 (M/s Corel Corporation, USA) that deals with constraints. The mapping of the fitted response was achieved using STATGRAPHICS Centurion XV version 15.1.02 (M/s StatPoint Inc., USA). The response surfaces and contour plots for these models were plotted as a function of two variables, while keeping other variables at the optimum level.

Table 2
Central composite design arrangement and response.

Experiment No.	Variable levels					Response *p*
	X_1	X_2	X_3	X_4	X_5	
1	−1	1	−1	1	1	0.78
2	−2	0	0	0	0	0.60
3	0	2	0	0	0	0.70
4	0	0	0	0	−2	0.71
5	0	0	−2	0	0	0.83
6	−1	−1	−1	1	−1	0.78
7	−1	−1	1	−1	−1	0.66
8	−1	1	−1	−1	−1	0.90
9	1	1	1	−1	−1	0.68
10	1	−1	1	1	−1	0.52
11	0	−2	0	0	0	0.70
12	0	0	0	2	0	0.40
13	−1	−1	1	1	1	0.52
14	0	0	2	0	0	0.54
15	1	−1	−1	1	1	0.64
16	1	1	1	1	1	0.52
17	2	0	0	0	0	0.73
18	1	−1	−1	−1	−1	0.91
19	−1	−1	−1	−1	1	0.90
20	0	0	0	−2	0	0.88
21	1	1	−1	−1	1	0.90
22	−1	1	1	−1	1	0.66
23	−1	1	1	1	−1	0.52
24	1	−1	1	−1	1	0.68
25	0	0	0	0	2	0.71
26	1	1	−1	1	−1	0.64
27	0	0	0	0	0	0.69
28	0	0	0	0	0	0.65
29	0	0	0	0	0	0.61
30	0	0	0	0	0	0.69
31	0	0	0	0	0	0.66
32	0	0	0	0	0	0.70

3. Results and discussion

3.1. Diagnostic checking of the fitted model

Regression analyses for different models indicated that the fitted quadratic models accounted for more than 93.0% of the variations in the experimental data, which were found to be highly significant. Multiple regression equations were generated relating extent of conversion to coded levels of the variables.

Model was developed as follows:

Table 1
Variables and their levels for central composite design.

Independent variables	Symbols		Levels				
	Coded	Actual	−2	−1	0	+1	+2
Mole ratio	$^{a}X_1$	x_1	0.4	0.5	0.6	0.7	0.8
Catalyst concentration (%)	$^{b}X_2$	x_2	0.5	1.0	1.5	2.0	2.5
Reaction temperature (°C)	$^{c}X_3$	x_3	100	110	120	130	140
Reaction time (sec)	$^{d}X_4$	x_4	2700	5400	8100	10,800	13,500
pH	$^{e}X_5$	x_5	1.0	1.5	2.0	2.5	3.0

$X_1 = (x_1 - 0.6)/(0.1)$; $X_2 = (x_2 - 1.5)/(0.5)$; $X_3 = (x_3 - 120)/(10)$; $X_4 = (x_4 - 8100)/(2700)$; $X_5 = (x_5 - 2.0)/(0.5)$.

$$p = 0.6625 - 0.03059X_1 - 0.08107X_3 - 0.10059X_4 + 0.01834X_5 - 0.02286X_1^2 + 0.012143X_2^2 + 0.008393X_3^2 + 0.014643X_5^2 + 0.04089X_1X_3 - 0.0221X_1X_4 + 0.026264X_1X_5 - 0.02339X_2X_4 + 0.020014X_2X_5 + 0.013392X_3X_4 - 0.02751X_3X_5 + \ldots \quad (2)$$

($df = 15$, $R^2 = 0.935$)

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 consists of bars with lengths proportional to the absolute values of the estimated effects divided by their standard values. The chart includes a vertical line at the critical *t*-value for a 95% confidence level. A bar crossing this vertical line corresponds to a factor or combination of factors that have a significant effect in the response.

The regression coefficients are shown in Table 3 as well as the correlation coefficient obtained for the model. The correlation coefficient for extent of conversion, *p*, (R^2 = 0.935) is quite satisfactory for response surfaces. The mole ratios of cardanol and formaldehyde and pH have positive linear and quadratic effect on the extent of conversion whereas the catalyst concentration, reaction temperature and reaction time have negative linear and quadratic effect on the extent of conversion. The interaction effect showed minor effect on the value on *p* at 95% significant level.

3.2. Analysis of a variance

When a model has been selected, an analysis of a variance is calculated to assess how well the model represented the data. An analysis of a variance for the response is presented in Table 4. To evaluate the goodness of the model, an *F*-value test was conducted. The *F*-value for extent of conversion was 24.71. On this basis, it can be concluded that the selected model adequately represented the data for extent of conversion. From analysis of residuals, it is possible to conclude that they were randomly distributed around zero, and there was no evidence of outliers.

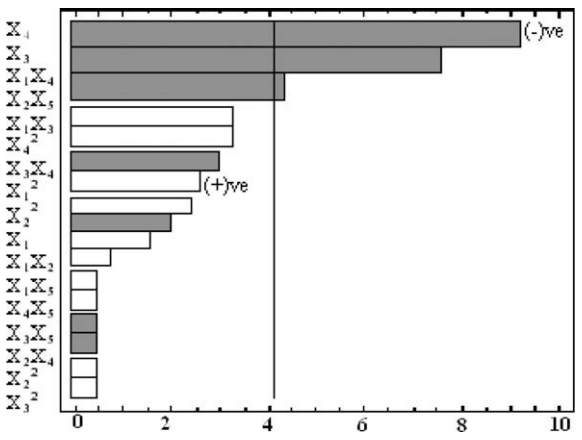

Fig. 2. Standard Pareto chart for the estimated effects of extent of conversion, *p*.

Table 3
Estimated coefficients of fitted quadratic equation for response based on *t*-statistics.

Coefficients	Estimated coefficients
b_{k0}	0.6625
b_{k1}	0.03059
b_{k3}	0.08107
b_{k4}	0.10059
b_{k5}	0.018343
b_{k11}	0.02286
b_{k22}	0.012143
b_{k33}	0.008393
b_{k55}	0.014643
b_{k13}	0.04089
b_{k14}	0.0021
b_{k15}	0.026264
b_{k24}	0.02339
b_{k25}	0.20014
b_{k34}	0.013392
b_{k35}	0.02751

$P < 0.05$ (2.262); $df = 15$.

3.3. Conditions for optimum response

Model was useful in indicating the direction in which to change variables in order to maximize extent of conversion. The optimum conditions to yield maximum extent of conversion are presented in Table 5. The optimum value of *p* was found to be 0.93 which was higher than the highest value amongst the calculated values based on the experimental design. The response surfaces in Figs. 3–12 is based on the aforesaid model for *p* (Eq. 2) with three variables kept constant at the optimum level and varying the remaining two within the experimental range. The surface plot along with the contour plot of extent of conversion (*p*) of a cardanol-based novolac resin as a function of a mole ratio of cardanol-to-formaldehyde and catalyst concentration has been shown in Fig. 3. It is clear from the figure that the increase in mole ratio or catalyst concentration beyond the optimum value of extent of conversion increased the value of *p*. Further, at fixed level of a mole ratio, the change of *p* showed almost linearly with catalyst concentration and vice-versa. The change of *p* showed parabolic pattern with mole ratio and reaction time (Fig. 4). Similar effect was observed with mole ratio and reaction time (Fig. 5). The pH of reaction medium changed extent of conversion linearly with a mole ratio (Fig. 6). Also, at fixed level of a mole ratio, the effect of pH on *p* was found to be uniformly increasing. Fig. 7 showed the surface and contour plots of *p* as a function of catalyst concentration and reaction temperature whereas Fig. 8 and 9, demonstrated the effect of catalyst concentration with reaction time or pH, respectively, on the extent of conversion, *p*. The increase of reaction temperature and catalyst concentration decreased the value of *p* up to an optimum value and then increased.

The surface plot of *p* as a function of reaction temperature and reaction time is shown in Fig. 10. The figure

Table 4
Analysis of variance for the proposed model.

Response	Source of variation	*df*	Sum of squares	Mean square	*F*-value
Extent of conversion, *p*	Regression	15	0.481993	0.032133	24.71*
	Residual	16	0.020807	0.0013	
	Total	31	0.5028		

* $P < 0.05$ (3.0) for $df = 15$.

Table 5
Optimum conditions for maximum extent of conversion, *p*.

Process variables	Coded values	Uncoded values
Mole ratio	0.726	0.6726
Catalyst concentration (%)	1.6	2.3
Reaction temperature (°C)	0.4	116
Reaction time (sec)	0.25	11340
pH	1.7	2.8

Maximum value of extent of conversion, $p = 0.93$.

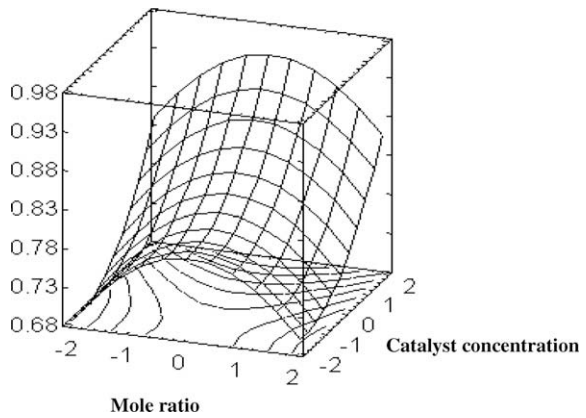

Fig. 3. Surface and contour plot between mole ratio and catalyst concentration.

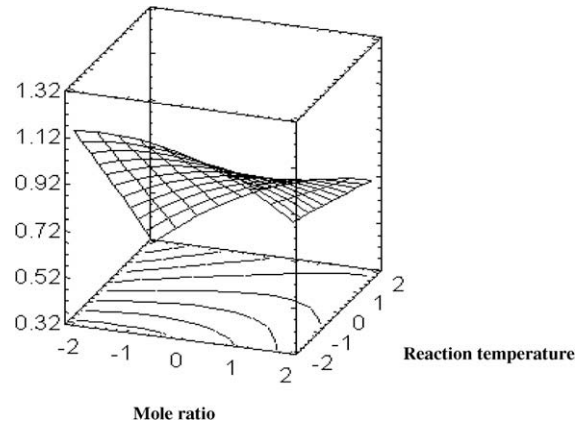

Fig. 4. Surface and contour plot between mole ratio and reaction temperature.

clearly evidenced that the reaction temperature and reaction time affected *p* in a similar fashion as that affected by mole ratio and reaction time (Fig. 5). Change of reaction

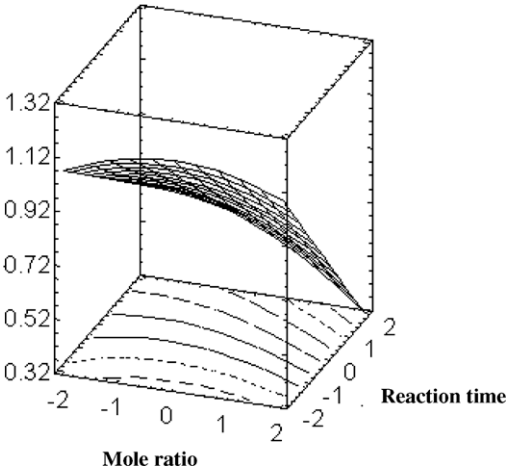

Fig. 5. Surface and contour plot between mole ratio and reaction time.

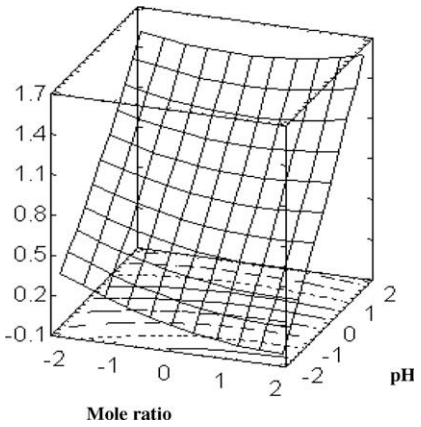

Fig. 6. Surface and contour plot between mole ratio and pH.

temperature with pH (Fig. 11) demonstrated that the extent of conversion increased progressively with reaction temperatures at higher pH while at lower temperatures change due to pH did not produce any significant effect. The value of *p* linearly decreased with pH and increased with reaction time (Fig. 12).

4. Conclusion

It may concluded that using RSM, with a minimum number of experiments, can effectively optimize the condensation reaction of cardanol and formaldehyde to produce novolac-type phenolic resin. The maximum extent

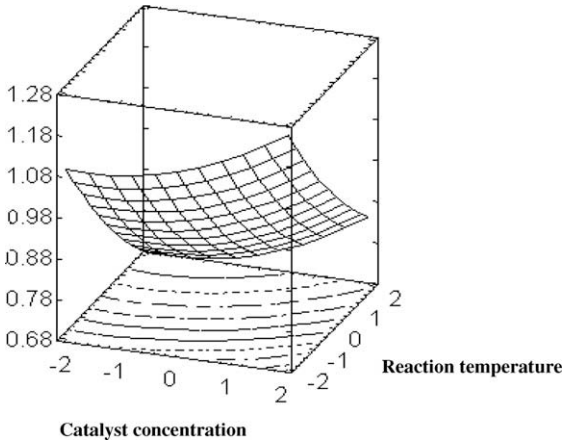

Fig. 7. Surface and contour plot between catalyst concentration and reaction temperature.

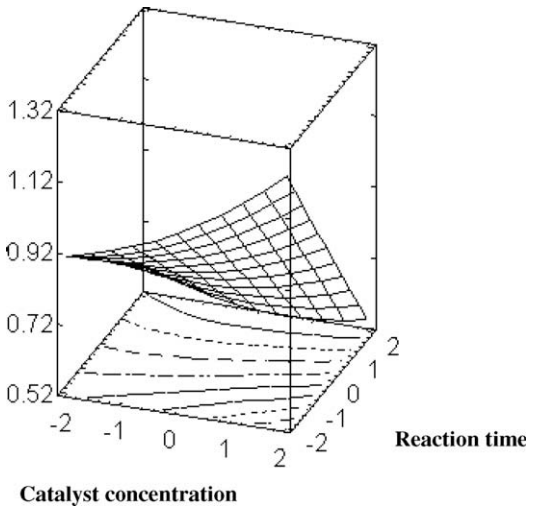

Fig. 8. Surface and contour plot between catalyst concentration and reaction time.

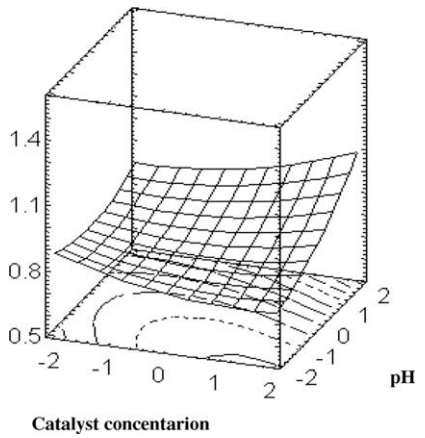

Fig. 9. Surface and contour plot between catalyst concentration and pH.

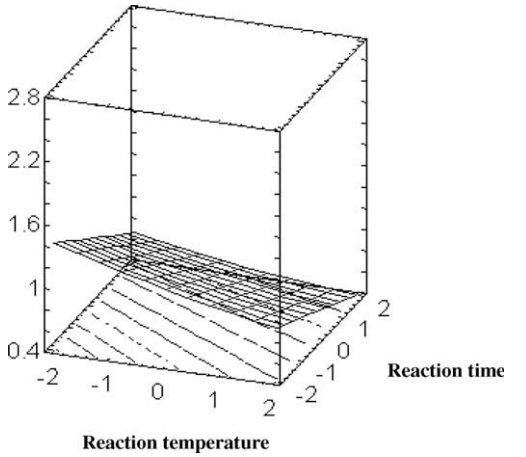

Fig. 10. Surface and contour plot between mole ratio and reaction time.

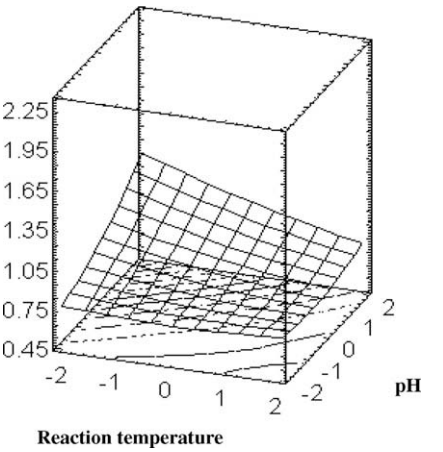

Fig. 11. Surface and contour plot between reaction temperature and pH.

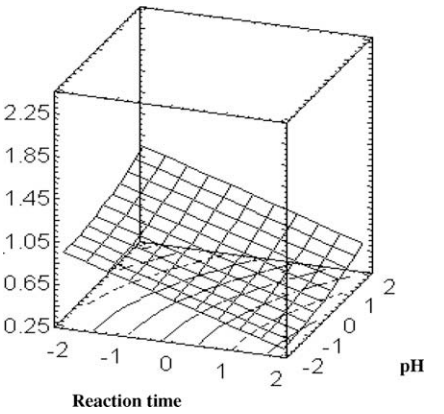

Fig. 12. Surface and contour plot between reaction time and pH.

of conversion (93.0%) was predicted when the cardanol was condensed with formaldehyde (mole ratio 1:0.6726) at 116 °C for a time period of 4 h 15 min with the catalyst (e.g., oxalic acid) concentration of 2.3% of total volume of

cardanol and formaldehyde. The pH of the reaction mixture was maintained at 2.8. These predicted values for optimum process conditions were in good agreement with experimental data.

Acknowledgements

This work was sponsored by Council of Science and Technology, UP, Lucknow. Also, we thankfully acknowledge the contributions rendered by M/s Satya Cashew Pvt. Ltd., Chennai for providing cardanol as gift samples.

References

[1] Menon ARR, Pillai CKS, Sudha JD, Mathew AG. Cashew nut shell liquid – its polymeric and other industrial products. J Sci Ind Res 1985;44:324–38.
[2] Tyman JHP. Synthetic and natural phenols studies in organic chemistry, vol. 52. Amsterdam: Elsiever; 1975. p. 518.
[3] Attanasi OA, Bunatti SB. Cardanol – a versatile natural fine chemical largely available today. La Chimica e l'Industria 1996;78:693–6.
[4] Prabhakaran K, Narayan A, Pvithram C. Cardanol as a dispersant plasticizer for an alumina/toluene tape casting slip. J Eur Cer Soc 2001;21:2873–8.
[5] Pillai CKS, Prasad VS, Sudha JD, Bera SC, Menon ARR. Polymeric resins from renewable resources II synthesis and characterization of flame retardant prepolymer from cardanol. J Appl Polym Sci 1990;41: 2487–501.
[6] Nimuru N, Miyakoshi T. Structural characterization of cashew resin film using two-stage pyrolysis-gas chromatography/mass spectrometry. Int J Polym Anal Char 2003;8:47–66.
[7] Lee YK, Kim DJ, Kim HJ, Hwang TS, Rafailovich M, Sokolar J. Activation energy and curing behavior of resol- and novolac-type phenolic resins by differential scanning calorimetry and thermogravimetric analysis. J Appl Polym Sci 2003;89:2589–96.
[8] Bender HL, Farnham AG, Guyer JW. Crystalline dehydroxy phenols. U.S. Pat. 2464207; 1949.
[9] Jayabalan M, Rajadurai S. A study on the utilization of CNSL for the development of fast curing resins and glass fabric laminates. Popular Plast 1985;30:30–5.
[10] Panasare V, Kulkarni A. Azo dyes from cashew nut shell liquid derivatives. J Ind Chem Soc 1964;41:251–5.
[11] Kumar RN, Nagarajan R, Fun FC, Seng PL. Effect of process variables on the exothermicity drying the production of phenol-formaldehyde resins- modeling by response surface methodology. Euro Poly J 2000;36:2491–7.
[12] Pintado ME, Malcata FX. Optimization of modified atmosphere packaging with respect to physicochemical characteristics of Requeijao. Food Res Inter 2000;33:821–32.
[13] Thakur S, Saxena DC. Formulation of extruded snack food (gum based cereal- pulse blend): optimization of ingredients levels using response surface methodology. Lebensm Wiss Technol 2000;33: 354–61.
[14] Srivastava D, Garg R, Saxena DC, Mathur GN. Optimization studies of blend composition and ageing parameters for making LDPE/HDPE/ LLDPE films by response surface methodology. Macromol Mater Eng 2000;283:81–7.
[15] Srivastava D. Optimization studies on the development of methylmethacrylate (MMA)-grafted nylon-6 fibers with high percentage grafting. J Polym Eng 2002;22:457–71.
[16] Nanda V, Singh S, Raina CS, Jindal N, Singh K, Saxena DC. Optimization of the process variables for the preparation of processed paneer using response surface methodology. Eur Food Res Tech 2004;218:529–34.
[17] Yadav R, Srivastava D. Kinetics of the acid – catalyzed cardanol – formaldehyde reactions. Mater Chem Phys 2007;106:74–81.
[18] Knop A, Pilato L. Chemistry and application of phenolic resins. Berlin: Springer-Verlag; 1979.
[19] Montgomery DC. Design and analysis of experiments. 3rd ed. New York: Wiley; 1991.
[20] Yadav R, Devi A, Tripathi G, Srivastava D. Optimization of the process variables for the synthesis of cardanol based novolac type phenolic rein using response surface methodology. Eur Polym J 2007;43(8): 3531–7.