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Modeling and simulation of curing kinetics for the cardanol-based vinyl ester resin by means of non-isothermal DSC measurements

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ABSTRACT

The cure kinetics of vinyl ester–styrene system was studied by non-isothermal differential scanning calorimetric (DSC) technique at four different heating rates. The kinetic parameters of the curing process were determined by isoconversional method for the kinetic analysis of the data obtained by the thermal treatment. Activation energy (E_a = 56.63 kJ mol^{-1}) was evaluated for the cure process and a two-parameter (m, n) autocatalytic model was found to be the most adequate to describe the cure kinetics of the studied cardanol-based vinyl ester resin. Non-isothermal DSC curves, as obtained by using the experimental data, show good agreement with the DSC curves obtained by theoretically calculated data.

1. Introduction

Worldwide potential demands for replacing petroleum derived raw materials with renewable plant based products in the production of polymers are quite significant in the social and environmental viewpoint. Due to increasing concern about the tight legislation on the maintenance of greenness in industry processes led us to develop a method using a material that is less hazardous, non-toxic, cheap, and benign to the environment, in the last few years. Cashew nut shell liquid (CNSL) has gained importance in the development of sustainable material which acts as an excellent monomer for thermosetting polymer production [1,2].

Cardanol (*Anacardium occidentale* L.), a phenol derivative having a meta substituent of a C_{15} unsaturated hydrocarbon chain with one to three double bonds, is a major component of CNSL [3,4]. Because of this phenolic nature, cardanol reacts with formaldehyde to form both base-catalysed resoles and acid-catalysed 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 [10–16]. 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 [17–19].

Vinyl ester resins (*VERs*) are free-radical polymerizing thermosets, which are structurally similar to unsaturated polyester resins (*UPE*) with developed to overcome chemical resistance shortcomings of *UPE* resin. As a result of this relationship due to *UPE* resins have been studied in greater depth than *VERs*, numerous characteristics of the *UPE* cure have been attributed to *VER* cure as well. In conventional polyester resins, the ester groups and C–C double bonds are located along the polymer chains and are distributed randomly in the polymer network formed after copolymerization and cross-linking with styrene. In *VERs*, the ester units and methacrylate type double bonds are located only at the end of vinyl ester monomers. Its resistance to degradation by corrosive and hostile environment leads to the use of *VERs* in many applications, such as: in swimming pools, sewer pipes and solvent storage tanks, and thus *VERs* are of considerable interest [20–23]. Vinyl ester systems can be cured at room or elevated temperatures [24].

Curing of *VERs* is a free-radical induced process [25,26] and it starts as the initiator thermally decomposes, releasing free radicals in the system. The role of free-radicals is to link two adjacent vinyl esters to extend the chain by connecting styrene molecules via inter- and intra-molecular reactions. The long chain formed is supposed to have a spherical structure which is due to intramolecular bonding between the C=C bonds of the vinyl ester molecules [25]. In such reactions it is very interesting to follow the progress of the reaction to reach optimal curing. This is due to the fact that any residual unsaturation is considered as a site for degradation or oxidation. Selection of cure conditions is motivated by processing and economic considerations.

Studying the cure behavior begins with studying the cure kinetics of the resins. Vital clues regarding the structure of the network

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can be obtained from the kinetics of cure, which is believed to have significant effect on the development of the network and the resulting material behavior [27]. It is difficult to model the cure kinetics of cross-linking free-radical polymerization [28] because of the competing reactions among the initiators, inhibitors, and comonomers, the heterogeneities during network formation and diffusion limitations. It is of great practical importance to understand the cure kinetics of such systems, to which several reports have been devoted [29–35]. At present, there are primarily two kinds of models used to simulate the reaction rate profiles of *VERs*: autocatalytic models [36–38] and mechanistic models [39–41]. Mechanistic models have many parameters and are not easy to use in process simulations [42]. The autocatalytic models developed by Kamal and Sourour [42] have been used by many researchers to simulate the reaction rate. The literature on cure kinetics and the applications of kinetic models are still untouched for cardanol-based *VERs* inspite of its growing use in various applications.

Differential scanning calorimetry (DSC), which measures the heat flow of the sample as function of temperature and time, has extensively been used to study the cure kinetics of various thermosetting polymers [43–49]. An optimal curing process depends on understanding the curing kinetics, the curing mechanism and accurate modeling of the curing process. This modeling includes determination of the mechanism, or appropriate kinetic equation for an analyzed system, measurement of reaction order and activation energies of the reaction. By assuming that the heat evolved during cure is proportional to the extent of the reaction, the kinetic parameters have been determined by fitting the experimental rate data to the kinetic model using a linear or non-linear regression method. The regression techniques require detailed information relating to the reaction rate as a function of time at any given temperature. In fact, the success and convergence of many regression schemes depends critically on the boundary conditions and the initial assumed values [50,51].

An appropriate method must be used to measure accurately the cure kinetics parameters viz., the degree of conversion (α), conversion rate ($d\alpha/dt$) and the apparent activation energy (E_a). The rate of conversion can, therefore be defined as follows:

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_{Rxn}} \tag{1}$$

where ΔH_{Rxn} is the total heat of reaction.

The present paper reports the cure kinetics of the cardanol-based vinyl ester/styrene system and determination of the kinetic parameters of the cure reaction from non-isothermal DSC measurements, applying the simple and consistent method [52,53] on kinetic analysis of the data obtained by the thermal treatment. The used method allowed us to select the most convenient model for the curing reaction (Šesták–Berggren equation) of the studied system [54].

2. Experimental

2.1. Materials

Cardanol (M s^{-1} Dheer Gramodyog Ltd., Kanpur), formaldehyde (40% solution from M s^{-1} Qualikem Industries, New Delhi), *p*-toluene sulphonic acid (*PTSA*) obtained from M s^{-1} E. Merck, New Delhi, Methanol (BDH), epichlorohydrin (M s^{-1} Ranbaxy Laboratories Ltd., Punjab), sodium hydroxide, methacrylic acid and triphenylphosphine (from M s^{-1} CDH Pvt. Ltd., New Delhi), styrene, benzoyl peroxide and hydroquinone (from M s^{-1} E. Merck, New Delhi) were used during the investigation.

2.2. Synthesis of cardanol-based vinyl ester resin

Cardanol-based vinyl ester resins (*CNEVERs*) were prepared by using 1:0.9 mol ratio of indigenously synthesized cardanol-based epoxidised novolac resin [3] and methacrylic acid. The reaction was carried out in the presence of triphenylphosphine (TPP) catalyst (1 phr by weight of the resin) and hydroquinone (200 ppm as inhibitor) at 90 °C in nitrogen atmosphere, and the progress of the reaction was monitored by determining the acid value intermittently by the method of Ogg et al. [55]. 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 using a Rotovap^{TM} evaporator under vacuum [56]. The resin was characterized for their structures by FTIR spectroscopy (PerkinElmer FTIR, RX-1 spectrophotometer). This was investigated in our previous publication [57] and the structure of cardanol-based vinyl ester resin was elucidated as given in Scheme 1.

2.3. DSC measurements

Cardanol-based vinyl ester resin, styrene, and benzoyl peroxide were mixed in the ratio of 10:4:0.2, at room temperature and stored at −13 °C. The weighed samples (20–30 mg) was placed in the DSC cell and analyzed at the various heating rates of 2.5, 5.0, 7.5 and 10 °C min^{-1} as per ASTM E-698 method. The data of thermal curing were obtained by means of a TA Instrument, USA; Model DSC 2920 heated from 35 °C to 200 °C with different heating rates in nitrogen atmosphere. Pure indium was used as a standard for calorimetric titration. An identical empty aluminium hermetic pan was taken as reference. The heat flow data, as a function of temperature and time, were obtained using the area under the peak of the exotherm. These were processed further to obtain the fractional conversion (α) and the rate of reaction ($d\alpha/dt$).

The rate of the kinetic process can be described by Eq. (2) [43,53]:

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \tag{2}$$

where $K(T)$ is a temperature-dependent reaction rate constant and $f(\alpha)$ a dependent kinetic model function. There is Arrhenius type dependence between $K(T)$ and temperature according to Eq. (3).

$$K(T) = A\ \exp\left(-\frac{E_a}{RT}\right) \tag{3}$$

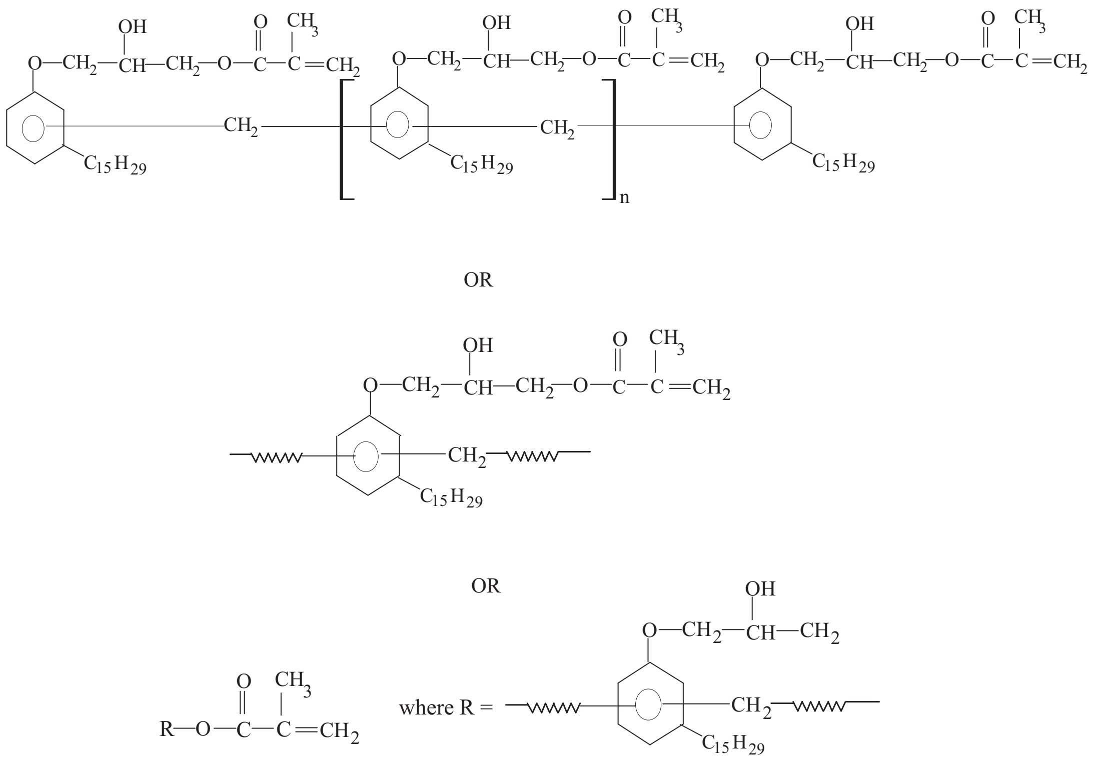
where A is the pre-exponential factor and E_a is the apparent activation energy.

For non-isothermal conditions, when the temperature varies with time at constant heating rate ($\beta = dT/dt$), Eq. (2) is modified as follows:

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\ \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \tag{4}$$

Usually, E_a values were determined using the integral forms of Eq. (4), the most popular derivative modes being those proposed by Ozawa [58], Flynn and Wall [59], and Doyle [60], which gave E_a from the plot $\ln \beta_i$ against $T_{\alpha,i}^{-1}$ (i is the ordinal number of DSC runs performed at different heating rates, β_i). Generally, the E_a values found by these equations require further corrections [61], which could be avoided using the methods suggested by Coats–Redfern approximation [62], according to which the E_a was evaluated from the plot $\ln(\beta_i/T_{\alpha,i}^2)$ against $T_{\alpha,i}^{-1}$ where $T_{\alpha,i}$ were the temperatures corresponding to different values of α. The experimentally evaluated values of E_a were used to find the appropriate kinetic model which best described the conversion function of the process studied.

The kinetic parameters of the curing process were determined by the isoconversional method given by Málek [52,53]. Once E_a has



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

been determined, the special functions $y(\alpha)$ (Eq. (5)) and $z(\alpha)$ (Eq. (6)) must be evaluated:

$$y(\alpha)=\frac{d\alpha}{dt}e^{x} \tag{5}$$

$$z(\alpha)=\pi(x)\left(\frac{d\alpha}{dt}\right)\frac{T}{\beta} \tag{6}$$

where x, β, T and $\pi(x)$ be the reduced activation energy (E_a/RT), heating rate ($\mathrm{K\,min^{-1}}$), absolute temperature (K), and the expression of the temperature integral, respectively. The expression for $\pi(x)$ was approximated using fourth rational expression of Senum and Yang [63], as in Eq. (7):

$$\pi(x)=\frac{x^3+18x^2+88x+96}{x^4+20x^3+120x^2+240x+120} \tag{7}$$

For practical reasons, the $y(\alpha)$ and $z(\alpha)$ functions were normalized within (for 0,1) range. The maximum α_M of the $y(\alpha)$ function and α_p^{∞} of the $z(\alpha)$ function suggested the choice of the most suitable kinetic model characterizing the curing process studied. Once the kinetic model has been determined, and using the value of E_a, other kinetic parameters could be determined, such as: pre-exponential factor and kinetic exponents. The pre-exponential factor A was calculated according to Eq. (8):

$$A=-\left\{\frac{\beta x_p}{Tf'(\alpha_p)}\right\}\exp x_p \tag{8}$$

where $f'(\alpha_p)$ be the differential form of the kinetic model [$df(\alpha)/d\alpha$], α_p be the conversion corresponding to the maximum on DSC curve and p be the maximum of DSC curve.

3. Results and discussion

On the basis of the appearance and disappearance of various peaks related to uncured *VER* sample [19,57], the following cure mechanism might be proposed. Initially, *VER* with styrene might have proceeded with the decomposition of benzoyl peroxide initiator followed by the formation of monomer free radical (Scheme 2). These radicals might have provided the active sites required to overcome inhibition and to sustain the chain reaction [64,65].

Fig. 1 shows the DSC curve of cardanol-based vinyl ester resin/styrene system at four different heating rates of 2.5, 5.0, 7.5 and 10 °C min^{-1}. As it can be noted from the curves, the cure reaction took place in one stage regardless of the heating rate. According to the figure, the peak exothermic temperature (T_{max}) varied in a predictable manner with the heating rate. Similarly, both initiation temperature (T_i) and final temperature (T_f) also increased with the increase of scan rates [66,67]. A comparison of the values has been summarized in Table 1. It was found that the values of ΔH estimated

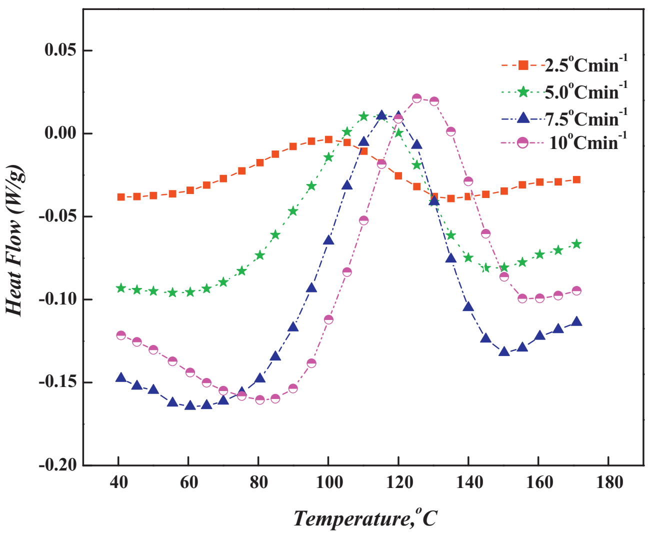
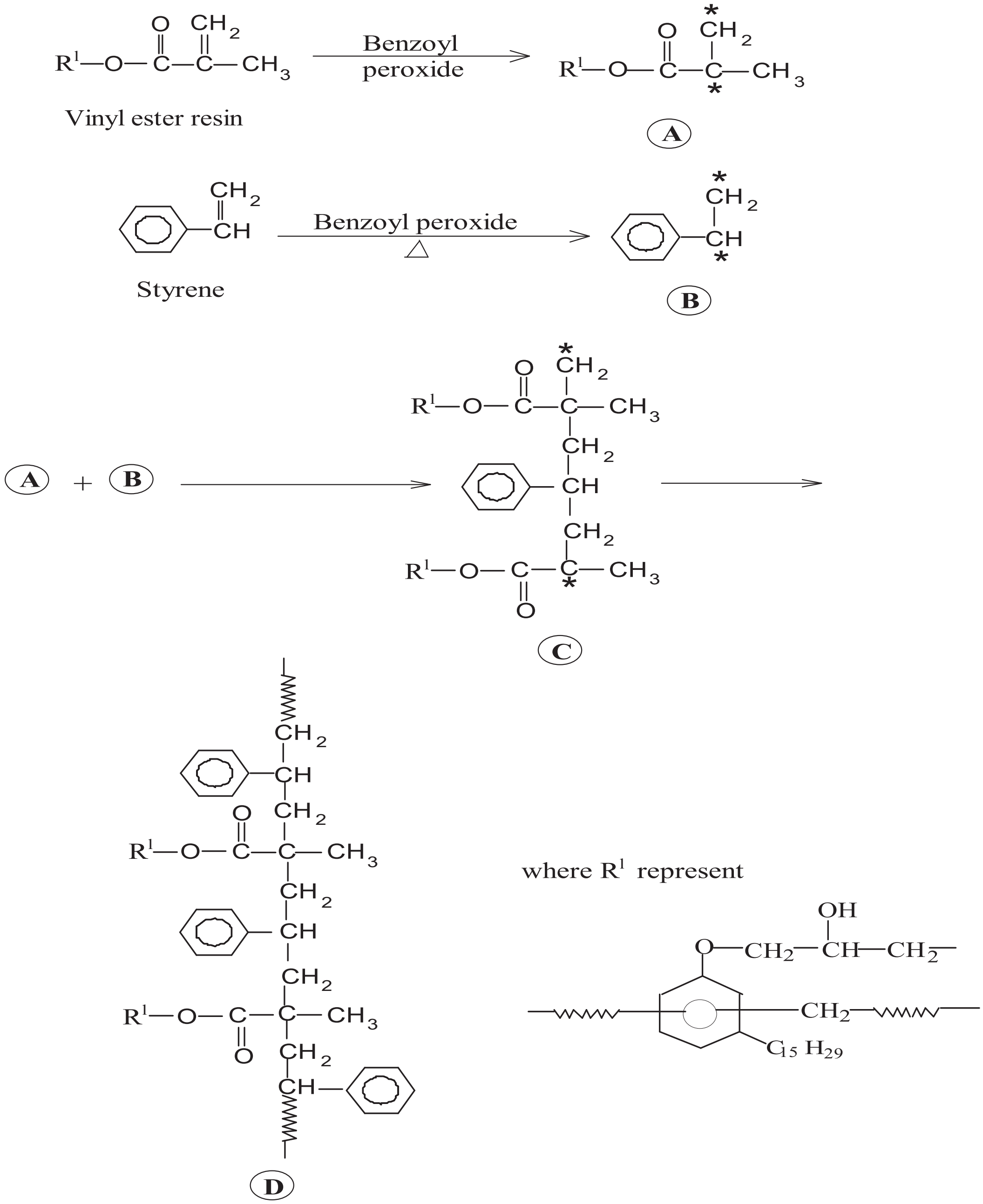


Fig. 1. Typical DSC curves recorded for cardanol-based vinyl ester/styrene system.



Scheme 2. Intermediate stage of reaction (breaking of double bonds by free radicals) and formation of the cross-linked cardanol-based vinyl ester/styrene network.

from the area under the exotherm, was also greater for higher heating rates. This behavior could be related to a more complete curing at a higher heating rate.

Fig. 2 shows the variation of fractional conversion as a function of temperature for the vinyl ester sample at four different heating rates, which could be obtained from integrating the DSC curves of Fig. 2. On the curve of 2.5 °C min^{-1}, the conversion increased very slowly in the initial stage and rose abruptly in the range of 55.5–122.0 °C and it was almost constant in the final stage. The abrupt increment in the short temperature range could be explained by the fact that in this temperature range one of the reactant might act as a catalyst and increase the reaction rate thereby showing an abrupt increase in the reaction [68,69]. Under non-isothermal conditions $K(T)$ and $f(\alpha)$ vary simultaneously giving rise to sigmoidal α versus T curve. So all the curve showed S-shape and shifted to right hand side with increasing heating rate due to the autocatalytic cure mechanism behavior.

Table 1
Curing characteristics of cardanol-based vinyl ester/styrene system at different heating rates.

Heating rate, β (°C min^{-1})	T_i (°C)	T_{max} (°C)	T_f (°C)	Heat of reaction (J g^{-1})
2.5	51.75	101.06	132.27	40.90
5.0	60.96	114.40	142.08	47.20
7.5	67.10	117.31	147.11	48.00
10.0	88.17	127.74	153.56	59.11

The isoconversional temperatures at four different heating rates could be obtained from the cross points of the conversion curves. For vinyl ester, E_a was evaluated from the plot of $\ln(\beta/T^2_{\alpha,i})$ against

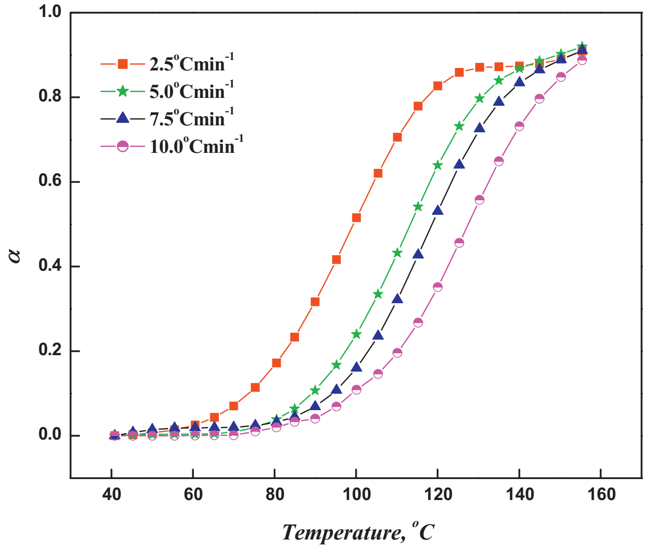


Fig. 2. Fractional conversion as a function of temperature for cardanol-based vinyl ester/styrene system.

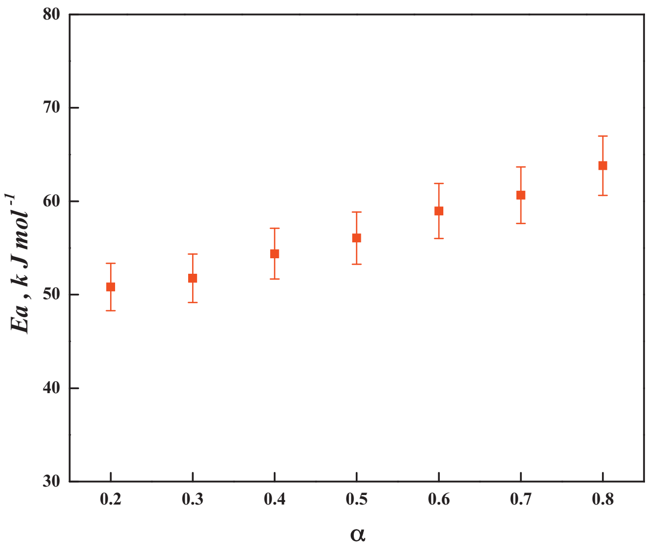


Fig. 4. Variation of E_a versus conversion for cardanol-based vinyl ester/styrene system.

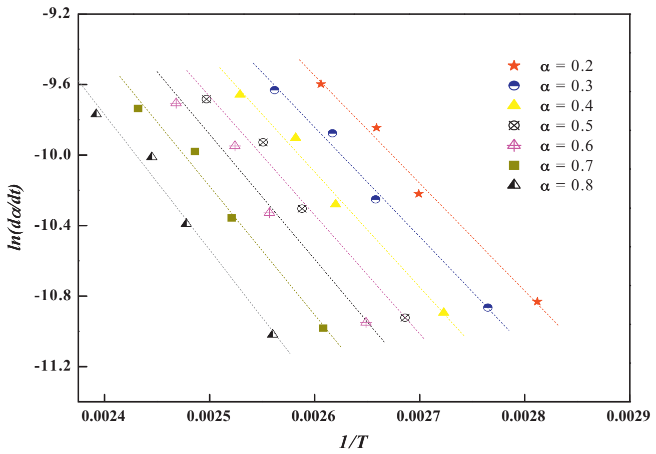
Table 2
The values of α_p, α_M and α_p^∞ evaluated for the curing of cardanol-based vinyl ester/styrene system.

Heating rate, β (°C min^{-1})	α_p	α_M	α_p^∞
2.5	0.53	0.45	0.45
5.0	0.52	0.40	0.45
7.5	0.48	0.40	0.45
10.0	0.50	0.45	0.45

$T_{\alpha,i}^{-1}$ [61]; where T_i be the temperatures corresponding to different values of α ranging between 0.1 and 0.8 (Fig. 3). Further, the variation of E_a with conversion α has been shown in Fig. 4.

The values of E_a changed slightly in the range of 50.82–63.80 kJ mol^{-1} at different degree of conversions ranging in between 0.2 and 0.8. The value of E_a remained unchanged in the initial stage, i.e. upto a value at $\alpha = 0.3$ and showed the value of 54.38 kJ mol^{-1} at $\alpha = 0.4$ (refer Fig. 4), i.e. showed an increasing trend in the later stages. Such variation of activation energy might be due to the free radicals generated in the cure reaction or due to the fact that rate of crosslinking is limited not by the diffusion of small molecules but by the mobility of longer polymer chains present in vinyl ester resin. In the latter case, diffusion encounters a large energy barrier due to the cooperative nature of the motion. Alternatively, an increase in E_a value for the final stage of curing can be associated with the chemical processes that are initiated at higher temperature [69,70].

The mean values of E_a determined from DSC data were used to calculate both $y(\alpha)$ and $z(\alpha)$ functions using Eqs. (5) and (6), respectively. Figs. 5 and 6 show the variation of $y(\alpha)$ and $z(\alpha)$ values with conversion for vinyl ester sample. The values of both $y(\alpha)$ and $z(\alpha)$ were normalized between (0,1) intervals of vinyl ester/styrene systems for various heating rates. These functions exhibited maxima at α_M and α_p^∞, respectively. Both α_M and α_p^∞ helped to decide the



Linear Fit values
$\alpha = 0.2$: $y = 6.34-6112.39x$, SD $=2.93 \times 10^{-15}$, $R^2 = 1$
$\alpha = 0.3$: $y = 6.34-6224.92x$, SD $=1.96 \times 10^{-15}$, $R^2 = 1$
$\alpha = 0.4$: $y = 6.91-6541.19x$, SD $=5.62 \times 10^{-15}$, $R^2 = 1$
$\alpha = 0.5$: $y = 7.19-6742.09x$, SD $=2.05 \times 10^{-15}$, $R^2 = 1$
$\alpha = 0.6$: $y = 7.84-7091.89x$, SD $=6.59 \times 10^{-15}$, $R^2 = 1$
$\alpha = 0.7$: $y = 8.06-7295.66x$, SD $=1.87 \times 10^{-15}$, $R^2 = 1$
$\alpha = 0.8$: $y = 8.64-7673.39x$, SD $=2.51 \times 10^{-15}$, $R^2 = 1$

Fig. 3. Arrhenius plots for cardanol-based vinyl ester/styrene system in the interval $0.2 < \alpha < 0.8$.

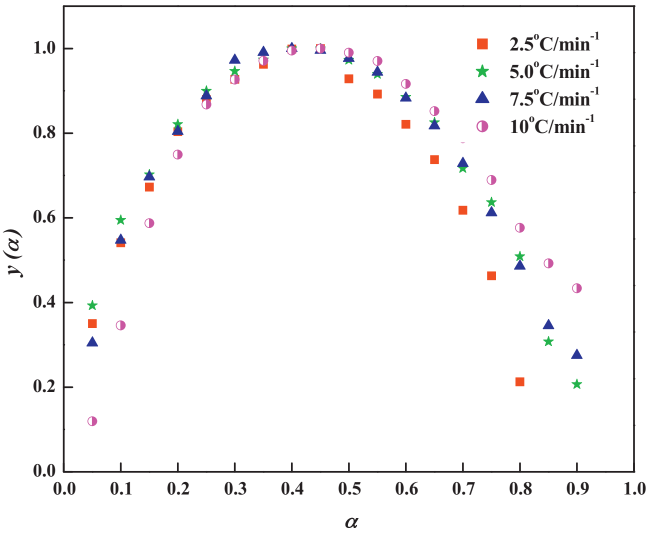


Fig. 5. Variation of $y(\alpha)$ function versus conversion for cardanol-based vinyl ester/styrene system.

Table 3
The kinetic parameters evaluated for curing of cardanol-based vinyl ester/styrene system.

Heating rate, β ($^{\circ}$C min^{-1})	E_a (kJ mol^{-1})	ln A (min^{-1})	Mean	m	Mean	n	Mean
2.5	56.63[a]	11.74		1.33		1.63	
5.0		11. 50	11.97	1.19	1.38	1.78	1.86
7.5		12.07		1.26		1.89	
10.0		12.60		1.76		2.15	

[a] Average activation energy.

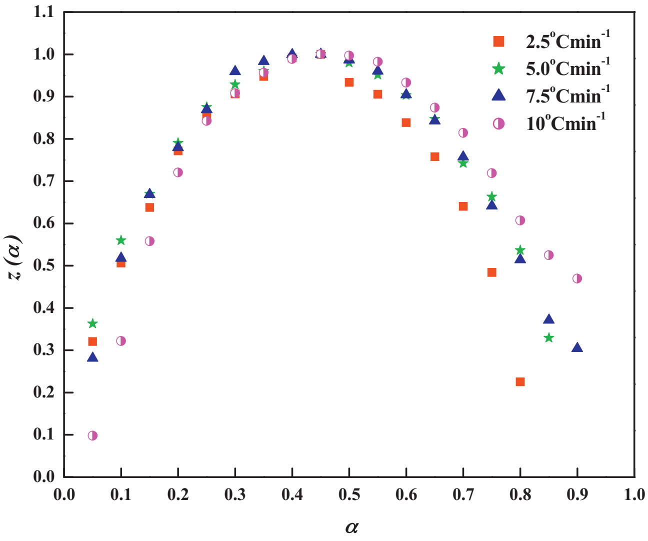


Fig. 6. Variation of $z(\alpha)$ function versus conversion for cardanol-based vinyl ester/styrene system.

choice of the kinetic model [63]. Table 2 listed the values of maxima α_M and α_p^{∞} corresponding to the functions $y(\alpha)$ and $z(\alpha)$ for all the studied samples, together with the α_p taken as the maximum of the DSC peaks. It was found that the values of α_M, α_p^{∞} and α_p values were independent of the heating rate. The values of α_M are lower against the values of α_p, while α_p^{∞} exhibited values lower than 0.632 (a characteristic value for the kinetic model determination) [44]. These results indicated that the studied curing process could be described using a two-parameter autocatalytic kinetic model as given by Šesták–Berggren (Eq. (9)) [54]:

$$f(\alpha) = \alpha^m (1-\alpha)^n \qquad (9)$$

where m and n are the kinetic exponents [44,61]. The kinetic parameters n was obtained by the slope of the linear dependence between $\ln[(d\alpha/dt)e^x]$ and $\ln[\alpha^p\ (1-\alpha)]$ from Eq. (3) and $m = pn$, where $p = \alpha_M(1-\alpha_M)$.

Table 3 lists some kinetic parameter evaluated for the proposed Šesták–Berggren kinetic model. Table 2 showed that the variation of the kinetic parameter values with the heating rate was placed in the experimental errors limit (within 10% of the average value).

The correctness of the kinetic model proposed using the Šesták–Berggren equation was verified by plotting $d\alpha/dt$ versus temperature (experimental curves), using the data listed in Table 3, with the curves obtained by computational processing of the thermograms (calculated curves). It was observed that the two parameters Šesták–Berggren model well described the studied curing process.

4. Conclusion

The cure kinetics of cardanol-based vinyl ester resin–styrene system using non-isothermal DSC data has been presented. Several measurements at various heating rates provided a determination of E_a and a simple, reliable method of kinetic analysis which enabled us to select the most convenient model for the curing reaction. The value of E_a was found to be 56.63 kJ mol^{-1}. The values of E_a in the conversion interval between 0.2 and 0.8 were increasing.

It was established that the curing reaction of the cardanol-based vinyl ester resin–styrene cured system could be described by a two-parameter autocatalytic model (Šesták–Berggren equation), which was most suitable for description of the studied curing process. The kinetic parameters, as determined experimentally were used to calculate the theoretical DSC curves. These showed a good agreement with that experimentally determined.

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References

[1] M.L. Santos, G.C. Magalhaes, J. Braz. Chem. Soc. 10 (1999) 13–20.
[2] M.C. Lubi, E.B. Thachill, Des. Monomers Polym. 3 (2000) 123–244.
[3] A. Devi, D. Srivastava, Mater. Sci. Eng. A 458 (2007) 336–347.
[4] M. Jayabalan, S. Rajadurai, Popular Plast. 30 (1985) 30–35.
[5] V. Pansare, A. Kulkarni, J. Ind. Chem. Soc. 41 (1964) 251–255.
[6] M. Sultania, J.S.P. Rai, D. Srivastava, Int. J. Chem. Kinet. 41 (2009) 559–572.
[7] R. Yadav, D. Srivastava, Mater. Chem. Phys. 106 (2007) 74–81.
[8] R. Yadav, A. Devi, G. Tripathi, D. Srivastava, Eur. Polym. J. 43 (2007) 3531–3537.
[9] P. Shukla, S.B. Yadaw, D. Srivastava, Int. J. Chem. Kinet. 42 (2010) 380–389.
[10] A. Devi, D. Srivastava, J. Appl. Polym. Sci. 102 (2006) 2730–2737.
[11] N.B. Patel, V.S. Patel, R.G. Patel, High Perform. Polym. 3 (1991) 243–248.
[12] N.H. Nieu, T.M. Tau, N.L. Huong, J. Appl. Polym. Sci. 61 (1996) 2259–2264.
[13] R.S. Balakrishna, M.N. Sathyanarayana, B.B. Vishwanath, M.M. Shirsalkar, Appl. Polym. Sci. 41 (1989) 1365–1372.
[14] A. Devi, D. Srivastava, Eur. Polym. J. 43 (2007) 2422.
[15] R. Yadav, D. Srivastava, J. Appl. Polym. Sci. 114 (2009) 1670–1681.
[16] R. Yadav, D. Srivastava, Int. J. Chem. Chem. Technol. 2 (2008) 173–184.
[17] M. Sultania, J.S.P. Rai, D. Srivastava, J. Hazard. Mater. 185 (2011) 1198–1204.
[18] M. Sultania, J.S.P. Rai, D. Srivastava, J. Appl. Polym. Sci. 118 (2010) 1979–1989.
[19] M. Sultania, J.S.P. Rai, D. Srivastava, Eur. Polym. J. 46 (2010) 2019–2032.
[20] L.C. Muszynski, in: H.F. Mark, N.M. Bikales, G.C. Overberger, G. Menges (Eds.), Encyclopedia of Polymer Science and Technology, vol. 12, Wiley Publications, New York, 1988, p. 462.
[21] Japanese Patent No. 6356520 (1988).
[22] European Patent No. 286904 (1988).
[23] German Patent No. 2, 621656 (1977).
[24] M.A. Stone, B.K. Fink, T.A. Bogetti, J.W. Gillespi, J. Polym. Eng. Sci. 40 (2000) 2489–2497.
[25] W. Funke, K. Hamann, Mod. Plast. 39 (1962) 147.
[26] K. Horie, I. Mita, H. Kambie, J. Polym. Sci. A1 (1970) 2389.
[27] S. Ziaee, G.R. Palmese, J. Polym. Sci. B: Polym. Phys. 37 (1999) 725–744.
[28] L.E. Nielsen, Mechanical Properties of Polymers, Van Nostrand Reinhold, New York, 1962.
[29] Y.S. Yang, L.J. Lee, J. Appl. Polym. Sci. 36 (1988) 1325–1432.
[30] A. Zheng, T. Ota, T. Sato, T. Tanaka, H. Sasal, R. Zhou, J. Macromol. Sci. Chem. A 25 (1988) 1.
[31] J.F. Stevenson, Polym. Eng. Sci. 26 (1986) 746–759.
[32] H. Ng, I.M. Zloczower, Polym. Eng. Sci. 29 (1989) 1097.
[33] D. Han, D.S. Lee, J. Appl. Polym. Sci. 34 (1987) 793–813.
[34] J.D. Fan, M. Marinelli, L. Lee, J. Polym. Compos. 7 (1986) 239–249.
[35] K. Sakaguchi, J. Macromol. Sci. Chem. A 8 (1974) 477.
[36] A. Crawford, J. Lesser, J. Polym. Sci. B: Polym. Phys. 36 (1988) 1371.
[37] H.L. Bos, J.J.H. Nusselder, Polymer 35 (1944) 2793–2799.
[38] V.B. Gupta, L.T. Drzal, C.Y.C. Lee, M.J. Rich, Polym. Eng. Sci. 25 (1985) 812–823.
[39] B.G. Min, J.H. Hodgkin, Z.H. Stachurski, J. Appl. Polym. Sci. 48 (1993) 1303–1312.

[40] H. Li, E. Burts, K. Bears, Q. Ji, J.J. Lesko, A.D. Dillard, J.S. Riffle, P.M. Puckett, J. Compos. Mater. 34 (2000) 1512–1528.
[41] H. Li, A.C. Rosario, S.V. davis, T. Glass, T.V. Holland, R.M. Davis, J.J. Lesko, J.S. Riffle, J. Florio, J. Adv. Mater. 28 (1997) 55.
[42] M.R. Kamal, S. Sourour, Polym. Eng. Sci. 13 (1973) 59–64.
[43] S. Montserrat, J. Malek, Thermochim. Acta 228 (1993) 47–60.
[44] S. Montserrat, J. Therm. Anal. 40 (1993) 553–563.
[45] N. Cascaval, D. Rosu, A. Stoleriu, Polym. Degrad. Stab. 55 (1997) 281–285.
[46] R. Thiagarajan, P.V. Reddy, S. Sridhar, M.C. Ratra, J. Therm. Anal. 36 (1990) 277–287.
[47] S.Y. Pusatcioglu, A.L. Fricka, J.C. Hassler, J. Appl. Polym. Sci. 24 (1979) 937–946.
[48] M.E. Ryan, A. Dutta, Polymer 20 (1979) 203–206.
[49] M.R. Keenam, J. Appl. Polym. Sci. 33 (1987) 1725–1734.
[50] D.M. Himmelblau, Applied Nonlinear Programming, McGraw-Hill Book Co., New York, 1972.
[51] W.H. Press, B.P. Flannery, S.A. Peukolsky, W.T. Vetterling, Numerical Recepies, Cambridge Univ. Press, New York, 1986.
[52] J. Málek, Thermochim. Acta 355 (2000) 239–253.
[53] J. Málek, Thermochim. Acta 200 (1992) 257–269.
[54] J. Šesták, G. Berggren, Thermochim. Acta 3 (1971) 1–12.
[55] L. Ogg, W.L. Porter, C.O. Willitis, Ind. Eng. Chem. Anal. Ed. 17 (1945) 394–397.
[56] G. Malucelli, G. Gozzelino, F. Ferrero, R. Bongiovanni, A. Priola, J. Appl. Polym. Sci. 65 (1997) 491–497.
[57] M. Sultania, J.S.P. Rai, D. Srivastava, Paint India LIX (9) (2009) 89–108.
[58] T. Ozawa, Bull. Chem. Soc. Jpn. (1965) 1881–1886.
[59] J.H. Flynn, L.A. Wall, J. Res. Nat. Bur. Stand. 70A (1966) 487–493.
[60] L.D. Doyle, Nature (London) 207 (1965) 290.
[61] J.H. Flynn, J. Therm. Anal. 27 (1983) 95–102.
[62] S. Vyazovkin, N. Sbirrazzuoli, Macromolecules 29 (1996) 1867–1873.
[63] I. Senum, R.T. Yang, Rational approximations of the integral of the Arrhenius function, Therm. Anal. 11 (1977) 445–448.
[64] A. Mousa, J. Karger-Kocsis, Polym. Polym. Compos. 8 (2000) 455–460.
[65] R.P.G. Brill, R. Palmese, J. Appl. Polym. Sci. 76 (2000) 1572–1582.
[66] S.P. Patel, R.G. Patel, V.S. Patel, Brit. Polym. J. 20 (1988) 43.
[67] D.J. Liaw, W.C. Shen, Polym. Eng. Sci. 34 (1994) 1297–1303.
[68] J.Y. Lee, M.J. Shim, S.W. Kim, Mater. Chem. Phys. 52 (1998) 272–276.
[69] K. Kishore, M. Joseph, V. Dharumaraj, M.N. Vijayshree, J. Appl. Polym. Sci. 31 (1986) 2829–2837.
[70] D. Rosu, C.N. Cascaval, F. Mustata, C. Ciobanu, Thermochim. Acta 383 (2002) 119–127.