

The Effect of CTBN Concentrations on the Kinetic Parameters of Decomposition of Blends of Cardanol-Based Epoxidized Novolac Resin Modified with Carboxyl-Terminated Liquid Copolymer

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ABSTRACT: Cardanol-based novolac resins were separately prepared with different mole ratios of cardanol-to-formaldehyde with different acid catalysts. These resins were epoxidized with epichlorohydrin, in basic medium, at 120°C. The resins were, separately, blended with different weight percentages of carboxyl-terminated butadiene acrylonitrile copolymer and cured with polyamine. Structural changes during blending were studied by FTIR spectroscopic analysis. Coats–Redfern equation was utilized to calculate the kinetic parameters, viz., order of decomposition

reaction (n), activation energy (E), pre-exponential factor (Z), and rate decomposition constant (k), for the decomposition of the samples. It was found that the degradation of the epoxies and their blend samples proceeded in two steps. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1694–1701, 2009

Key words: cardanol-based phenolic type novolac resin; carboxyl-terminated butadiene acrylonitrile copolymer (CTBN); thermogravimetric analysis (TGA); activation energy

INTRODUCTION

Cashew nut shell liquid (CNSL), a phenolic compound containing 15-carbon chains with variable unsaturation degrees and meta substituted in the aromatic ring, can be regarded as a versatile and valuable raw material for polymer production. Cardanol, a distillate of CNSL, is a potential natural source for biomonomers and finds various industrial applications. By far the greatest amount of work on polymeric materials, derived from CNSL or cardanol, has been with their use in the manufacture or modification of phenolic resins^{1–4} particularly base catalyzed resoles and acid catalyzed novolacs. The cardanol-based novolac-type phenolic resins may further be modified by epoxidation with epichlorohydrin (ECH) to improve the performance of such phenolic-type novolacs.⁵ Having several outstanding characteristics, epoxy resins show low impact resistance in their cured state^{6–11} which limits the applications of epoxy resins. This deficiency of epoxy resins are overcome by the incorporation of reactive liquid rubber without significant loss in other properties,

particularly mechanical properties.^{12,13} In this way, carboxyl-terminated copolymer of butadiene and acrylonitrile (CTBN) has been used by various workers^{6,7,13} with diglycidyl ether of bisphenol-A (DGEBA) epoxy resin and epoxidized phenolic novolac resins. CTBN is hardly been used with cardanol-based epoxy resins. Therefore, we have tried to produce the modified epoxy matrices, based on cardanol, by physical blending with CTBN and studied the effect of CTBN addition on the overall kinetic parameters for the thermal degradation of blend systems in present investigation.

EXPERIMENTAL

Materials

Cardanol (M/s Satya Cashew Pvt. Ltd., Chennai), formaldehyde (40% solution), oxalic, succinic and citric acid, sodium hydroxide, ECH (all from M/s Thomas Baker Chemicals Ltd., Mumbai), polyamine (M/s Ciba Specialty Chemicals Ltd., Mumbai) with amine value 1240–1400 mg KOH/g, and CTBN (Hycar 1300 × 13) were used during the investigation. CTBN was kindly supplied by M/s Emerald Performance Materials, LLC, Hong Kong having molecular weight M_n of 3500 and acrylonitrile and carboxyl contents 27 and 32%, respectively.

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Synthesis of cardanol-based epoxidized novolac-type phenolic resin

Cardanol, procured from open market, was distilled under reduced pressure 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.¹⁴

Cardanol-based novolac type phenolic resins were prepared as per the method given in our previous work.¹⁴ These cardanol-based novolac-type phenolic resin^{14,15} were epoxidized by a method similar to the method given in literature.¹⁶ Approximately, 1.0 mol of novolac resin was taken in a 500 mL three-necked round-bottomed flask and 10 mol of ECH was added to it while stirring. Then, 40% sodium hydroxide solution was added drop wise to the above mixture for a period of 5 h at 120°C. The reaction mixture was then subjected to distillation under vacuum for the removal of unreacted ECH. The resulting viscous product was stored for further analysis.

Preparation of blends of epoxidized novolac resin and CTBN

The prepared epoxy resin was mixed physically with varying concentration of CTBN ranging between 0 and 20 wt % with an interval of 5 wt %. All the samples were designated according to Table I.

Fourier-transform infra-red (FTIR) spectroscopic analysis

FTIR spectra of the prepared samples, cured or uncured, were recorded on a Perkin-Elmer (Model 843) infra-red spectrophotometer in the wave length

TABLE I
Sample Designation

S. no.	Epoxy (sample code)	Blend (sample code) 15 wt % CTBN
1	ECF ₅₁₀	ECF ₅₁₃
2	ECF ₅₂₀	ECF ₅₂₃
3	ECF ₅₃₀	ECF ₅₃₃
4	ECF ₆₁₀	ECF ₆₁₃
5	ECF ₆₂₀	ECF ₆₂₃
6	ECF ₆₃₀	ECF ₆₃₃
7	ECF ₇₁₀	ECF ₇₁₃
8	ECF ₇₂₀	ECF ₇₂₃
9	ECF ₇₃₀	ECF ₇₃₃
10	ECF ₈₁₀	ECF ₈₁₃
11	ECF ₈₂₀	ECF ₈₂₃
12	ECF ₈₃₀	ECF ₈₃₃

C = Cardanol; F = Formaldehyde; CF = cardanol-based novolac resin; ECF = epoxidized novolac resin; 4,5,6,7,8 = different mole ratios; 1 = oxalic acid; 2 = succinic acid; 3 = citric acid.

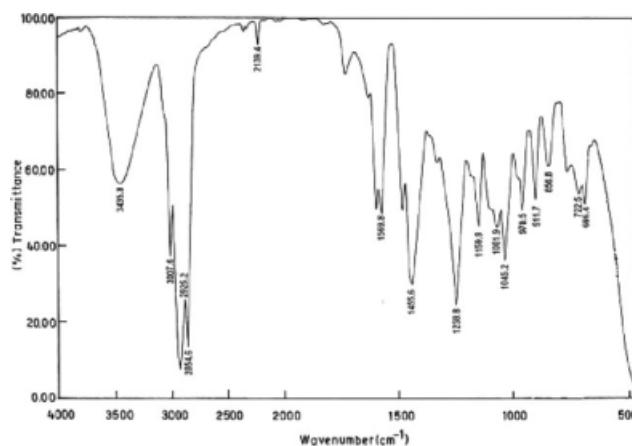


Figure 1 FTIR spectrum of epoxidized novolac resin ECF₇₁₀.

range of 500–4000 cm⁻¹ to study the formation of various functional groups during the reaction.

Thermogravimetric analysis

The thermal stability of the blend samples was determined by a comparison of the onset degradation temperature (up to 5% weight loss) of the cured samples with thermogravimetric analyzer (TGA) of TA Instruments (Model Q50 TGA) at a heating rate of 10°C/min in nitrogen atmosphere from 50° to 650°C.

RESULTS AND DISCUSSION

Epoxidation of novolac prepolymer

The novolac based epoxy resins are synthesized by reaction with ECH. The number of glycidyl groups per molecule in the resin is dependent upon the number of phenolic hydroxyls in the starting novolac, the extent to which they are reacted and the extent to which the lowest molecular species are polymerized during synthesis. Theoretically, all the phenolic hydroxyls may be reacted, but, in practice all of them do not react because of steric hindrance.¹⁷ The reaction between ECH and novolac resin may be thought to proceed in a similar fashion as given by Lee and Neville¹⁷ in their work on phenolic resin and ECH. The epoxide group of ECH reacted with phenolic hydroxyls under the alkaline medium and formed the chlorohydrin ether which underwent dehydrochlorination reaction and resulted in to glycidyl ether.

FTIR analysis of uncured and cured blend sample

Figure 1 shows the IR spectrum of pure epoxy sample, ECF₇₁₀. The peaks related to oxirane

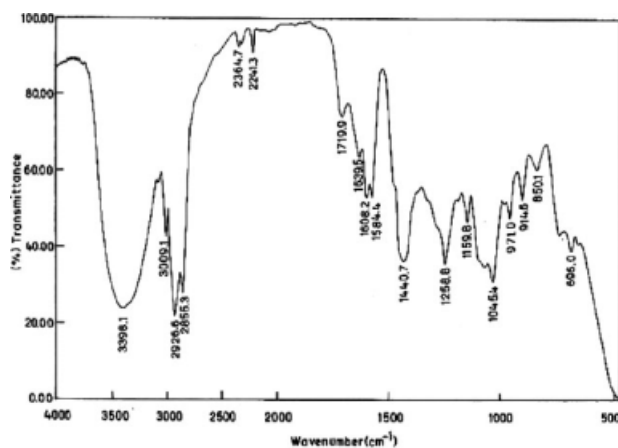


Figure 2 FTIR spectrum of uncured blend sample ECF₇₁₃.

functionality appeared near 911 and 856 cm^{-1} (Fig. 1). When CTBN is added to pure epoxy resin, these peaks disappeared and new peaks appeared near 914 and 850 cm^{-1} (Fig. 2). The peaks appeared near 911 and 856 cm^{-1} (Fig. 1) might overlap these peaks. The peaks near 1719 cm^{-1} owing to carbonyl stretching, 1440 and 972 cm^{-1} owing to C—H bending^{18–20} along with a sharp peak near 2239 cm^{-1} , owing to CN group of the CTBN molecule were also seen in the spectrum of uncured blend system (Fig. 2). These observations clearly indicated that there occurred no chemical interaction between the oxirane group of epoxy and carboxyl group of CTBN. The epoxy resin and CTBN remained as a discrete phase in the uncured stage. However, the addition of CTBN and polyamine into epoxy caused chemical interaction between the oxirane ring and the carboxyl function of the CTBN which resulted in complete diminution of the peaks at 911 and 856 cm^{-1} in cured blend samples ECF₇₁₃ (Fig. 3). The $-\text{C}\equiv\text{N}$ group was also

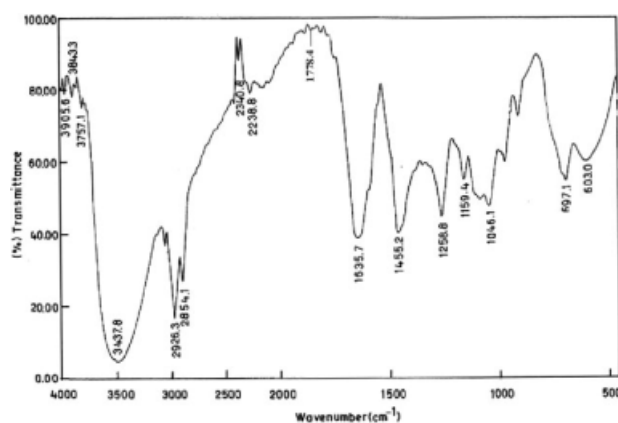


Figure 3 FTIR of cured blend sample ECF₇₁₃.

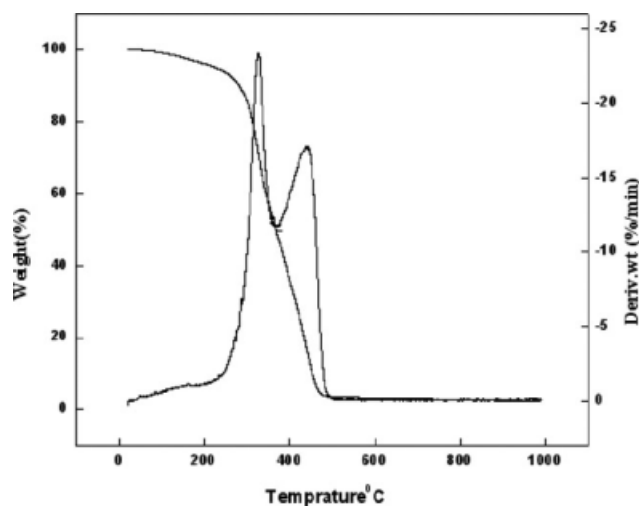


Figure 4 TGA Trace of blend sample ECF₇₁₀.

not observed in the cured blend. This was perhaps due to lower volume fraction of CTBN in the blend system. Another possibility is that it could also be utilized in network modification. The blend also showed the appearance of new stretched peaks between 1258–1635 cm^{-1} and 1046 cm^{-1} and peak broadening at 1608 cm^{-1} owing to C—C multiple stretching.^{21,22}

Thermo gravimetric analysis

Thermal stability

Thermo gravimetric (TG) analysis is one of the most widely used technique to measure the thermal stability of the polymeric samples. In this, the rate of weight loss is measured as a function of programmed rate of increase in temperature (dynamic mode). The thermogram of the sample, therefore, provides the onset temperature (T_o) of reaction corresponding to the first detectable temperature at which the degradation of the material starts, maximum decomposition temperature at which the maximum rate of weight loss (T_{max}) occurs, and the final degradation temperature (T_f) corresponds to the temperature after which no weight loss is observed. Percentage char yield corresponds the ablative performance of the materials. The initial degradation temperature (IDT) is to be considered after 3–5% weight loss as in the initial stages impurities and moisture present in the system decompose first.

The dynamic thermogravimetric (TG) as well as the differential thermo gravimetric (DTG) traces of pure epoxy and its blend sample (i.e. samples ECF₇₁₀ and ECF₇₁₃) containing stoichiometric amounts of polyamine obtained at programmed heating rate of 10°C/min are shown in Figures 4 and 5, respectively. The data on initial (T_o), peak (T_{max}) and final (T_f)

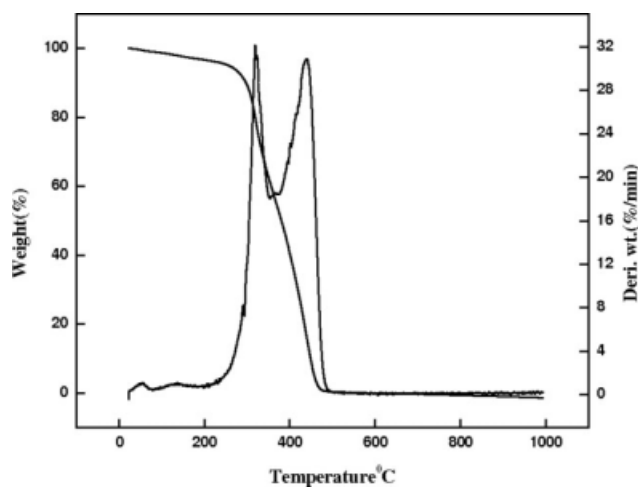


Figure 5 TGA trace of blend sample ECF₇₁₃.

decomposition temperatures as well as char residue at 800°C, derived from these traces are given in Table II for different epoxies and their blend samples. The data clearly indicate that pure epoxies and their blend samples showed two-step mass-loss in TG traces and the shoulders observed in DTG traces also indicated a two-step thermal degradation process. It is clear that the thermal stability of epoxidized novolac resins with dicarboxylic acid

catalysts, viz. oxalic and succinic acids was better than the epoxidized novolac resins based on tricarboxylic acid (i.e. citric acid). Similar behavior was observed in blend samples containing 15 wt % CTBN. This might be because of the structure of novolac resins prepared with these catalysts. Because of the addition of rubber, i.e. 15 wt % proportion of CTBN along with polyamine, the TGA studies showed the enhancement in the thermal stability of the blends and also showed an increase in the final degradation temperatures (refer Table II). The first degradation peaks were marginally shifted to higher temperature scale with 15 wt % CTBN addition in all the blend systems. Further rise in temperature, e.g. in the temperature range of 400–420°C, the rubber might start functioning as thermal stabilizer^{23,24} and, thus, resulted in an increase in the thermal stability of epoxy-CTBN blends for all blend samples (refer Table II).

Percent weight loss at characteristic peak temperatures as enumerated in Table II also justified enhanced thermal stability of the rubber modified blend systems compared to neat epoxies. Plots of derived weight loss versus temperatures for various epoxy-CTBN systems have also been shown in the Figures 4 and 5. Evolution of low boiling volatiles such as water and toluene from the resin alone were

TABLE II
Results of TG/DTG Traces of Unmodified and CTBN-Modified Cardanol-Based Epoxidized Novolac Resins Cured with Polyamine

Blend sample	First step				Second step				Total % CY
	T_o	T_{max}	T_f	% ML	T_o	T_{max}	T_f	% ML	
ECF ₅₁₀	193	317	337	49.9	337	435	490	47.0	2.9
ECF ₅₁₃	195	305	353	54.4	353	438	491	41.6	4.0
ECF ₅₂₀	199	316	343	49.3	343	438	498	47.2	3.5
ECF ₅₂₃	202	305	355	53.8	355	438	491	42.1	4.1
ECF ₅₃₀	206	316	336	50.0	336	430	480	46.4	3.4
ECF ₅₃₃	220	312	360	52.5	360	433	491	43.2	4.3
ECF ₆₁₀	192	312	328	51.9	328	435	490	46.7	1.3
ECF ₆₁₃	214	305	353	56.3	353	438	486	39.1	4.6
ECF ₆₂₀	191	324	343	50.1	343	434	486	48.5	1.4
ECF ₆₂₃	226	322	345	61.7	345	428	481	35.0	3.3
ECF ₆₃₀	270	329	360	67.4	360	375	485	30.8	1.8
ECF ₆₃₃	272	33	349	53.3	349	430	486	44.0	2.7
ECF ₇₁₀	223	326	359	53.8	354	442	500	42.0	4.2
ECF ₇₁₃	232	318	359	61.4	359	439	508	33.5	5.1
ECF ₇₂₀	228	317	374	60.1	374	386	508	36.0	3.9
ECF ₇₂₃	230	301	349	80.2	349	360	475	13.3	6.5
ECF ₇₃₀	236	322	349	52.4	349	435	491	44.7	2.9
ECF ₇₃₃	239	323	350	53.2	350	428	486	43.0	3.8
ECF ₈₁₀	191	319	350	49.5	350	437	475	47.4	3.1
ECF ₈₁₃	198	318	353	63.0	353	444	485	33.2	3.8
ECF ₈₂₀	194	318	346	50.5	346	438	485	45.3	4.2
ECF ₈₂₃	200	327	361	56.5	361	425	480	38.5	5.0
ECF ₈₃₀	235	325	355	51.4	355	465	496	44.5	4.1
ECF ₈₃₃	239	321	353	63.2	353	434	477	32.0	4.8

T_o , onset temperature of degradation; T_{max} , temperature of maximum rate of mass loss; T_f , extrapolated final decomposition temperature; ML, mass loss; CY, char yield.

by and large not affected by the presence of rubber.²⁰ Therefore, the degradation peaks related to pure epoxies showed no significant changes by the addition of rubber. Subsequent to that, participation of the aromatic groups of cardanol at higher temperatures were delayed due to the presence of rubber indicating higher thermal stability of the blends and the extent of improvement might depend on the concentration of rubber.^{25–27} The higher char yield of the blend systems (refer Table II) could be attributed to the presence of more cross-links present in the blend systems²⁴ as a result of curing which further confirmed the higher thermal stability of the blend systems.

Study of kinetic parameters

The kinetic parameters, viz., order of reaction (n), energy of activation (E) and pre-exponential factor (Z) for thermal decomposition of the blend of epoxidized novolac resin and CTBN cured with polyamine were evaluated by the data obtained from the dynamic thermograms from TGA.^{28–30} The data obtained from TG curves were utilized in solving Coats–Redfern equation³¹ (Scheme 1).

The fractional decomposition α for the respective temperature was calculated from the TG curves. Graphs were plotted between X and Y (Scheme 1),

$$\log \left(\frac{g(\alpha)}{T^2} \right) = \log \left[\left(\frac{ZR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right) \right] - \frac{E}{2.3RT} \quad \dots (1)$$

where,

$$g(\alpha) = \begin{cases} \frac{1 - (1 - \alpha)^{n+1}}{1 - n} & \text{for } n \neq 1 \\ -\log(1 - \alpha) & \text{for } n = 1 \end{cases}$$

Equation (1) may be reduced to:

$$Y = A + \frac{B}{1000} \cdot X \quad \dots (2)$$

where,

$$Y = \log \left(\frac{g(\alpha)}{T^2} \right) \text{ for different values of } n \text{ lying between } 0 - 2$$

$$X = \frac{1000}{T}$$

$$A = \log \left[\left(\frac{ZR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right) \right]$$

$$B = \frac{E}{2.3R}$$

$$\alpha = \frac{w_T - w_f}{w_o - w_f}$$

where,

- α = fractional weight loss
- $g(\alpha)$ = function of α
- w_T = weight at temperature T
- w_f = final weight
- w_o = initial weight
- β = heating rate, °C/min
- R = Gas constant (8.314 J deg⁻¹ mol⁻¹ K)

Scheme 1 Coats–Redfern equation.

as per Coats–Redfern equation, for different values of n ranging between 0 and 2 for both the steps of all prepared samples. The best-fit values of n

TABLE III
Linear Regression Analysis for Pure Epoxy and its Blend samples

S. no.	Sample code	Plot of X and Y				Linear regression analysis				R^2		n	
		Slope		Intercept		I-step		II-step		I-step	II-step	I-step	II-step
		I-step	II-step	I-step	II-step	I-step	II-step	I-step	II-step				
1	ECF ₅₁₀	-0.99462	-7.5264	-4.198	6.778	$y = -0.9933 \times -4.1531$	$y = -0.1262 \times +0.9404$	0.9879	0.9538	0.5	2		
2	ECF ₅₁₃	-1.55354	-3.31267	-3.484	-0.3486	$y = -0.4837 \times -1.3355$	$y = -0.3348 \times -0.3138$	0.9277	0.9824	0.5	2		
3	ECF ₅₂₀	-1.093	-5.747	-4.086	3.818	$y = -0.8161 \times -3.1811$	$y = -0.1863 \times +0.5868$	0.9703	0.9856	0.5	2		
4	ECF ₅₂₃	-2.21041	-2.27865	-2.627	5.944	$y = -0.8299 \times -3.2494$	$y = -0.179 \times +0.628$	0.8909	0.8639	0.5	2		
5	ECF ₅₃₀	-0.91511	-5.7385	-4.315	3.763	$y = -1.0247 \times -4.3314$	$y = -0.1529 \times +0.7827$	0.9378	0.9504	0.5	2		
6	ECF ₅₃₃	-1.55356	-4.52114	-3.465	1.585	$y = -0.5975 \times -1.9694$	$y = -0.2511 \times +0.1602$	0.99086	0.9717	0.5	2		
7	ECF ₆₁₀	-1.1576	-4.2085	-4.008	1.235	$y = -0.799 \times -3.0932$	$y = -0.2316 \times +0.3298$	0.9249	0.9746	0.5	2		
8	ECF ₆₁₃	-1.68045	-3.78962	-3.308	.3979	$y = -0.5416 \times -1.6657$	$y = -0.2915 \times -0.076$	0.9853	0.9228	0.5	2		
9	ECF ₆₂₀	-1.2524	-5.81298	-3.826	3.733	$y = -0.1208 \times +0.787$	$y = -0.136 \times +0.8632$	0.9340	0.9923	0.5	2		
10	ECF ₆₂₃	-1.54839	-5.27282	-3.445	2.747	$y = -0.584 \times -1.8755$	$y = -0.2009 \times +0.4451$	0.99086	0.9740	0.5	2		
11	ECF ₆₃₀	-0.99861	-0.9748	-2.077	5.577	$y = -0.3823 \times -0.809$	$y = -0.1507 \times +0.7054$	0.9972	0.9504	1.0	2		
12	ECF ₆₃₃	-1.59816	-7.69808	-3.365	6.581	$y = -0.6177 \times -2.0605$	$y = -0.1473 \times +0.7439$	0.9987	0.9809	0.5	2		
13	ECF ₇₁₀	-1.53943	-4.59789	-3.480	1.5881	$y = -0.6192 \times -2.0888$	$y = -0.2267 \times +0.2856$	0.9937	0.9574	0.5	2		
14	ECF ₇₁₃	-2.15632	-5.30723	-2.607	2.6323	$y = -0.4178 \times -0.9489$	$y = -0.2068 \times +0.3772$	0.9998	0.9504	0.5	2		
15	ECF ₇₂₀	-1.98428	-5.8579	-2.912	3.851	$y = -0.0738 \times +1.053$	$y = -0.1606 \times +0.7196$	0.99720	0.9832	1.0	2		
16	ECF ₇₂₃	-0.88907	-3.92507	-4.377	0.7905	$y = -1.0225 \times -4.3465$	$y = -0.2624 \times +0.1527$	0.97729	0.9906	0.5	2		
17	ECF ₇₃₀	-1.16281	-6.88434	-3.975	5.527	$y = -0.8473 \times -3.3465$	$y = -0.1393 \times +0.8387$	0.9853	0.9896	0.5	2		
18	ECF ₇₃₃	-1.34889	-5.06875	-3.723	2.494	$y = -0.7206 \times -2.6434$	$y = -0.2228 \times +0.3265$	0.9988	0.9857	0.5	2		
19	ECF ₈₁₀	-1.11261	-7.08657	-4.048	5.944	$y = -0.9042 \times -3.6687$	$y = -0.1318 \times +0.8974$	0.9821	0.9854	0.5	2		
20	ECF ₈₁₃	-2.24179	-3.55939	-2.544	-0.189	$y = -0.4031 \times -0.891$	$y = -0.3114 \times -0.2499$	0.9925	0.9355	0.5	2		
21	ECF ₈₂₀	-1.11131	-5.14861	-4.062	2.756	$y = -0.8929 \times -3.6149$	$y = -0.1716 \times +0.6777$	0.9972	0.9796	0.5	2		
22	ECF ₈₂₃	-2.49804	-7.0236	-2.313	5.446	$y = -0.3969 \times -0.9056$	$y = -0.1611 \times +0.6544$	0.9937	0.9574	1.0	2		
23	ECF ₈₃₀	-1.22715	-4.697	-3.831	4.996	$y = -0.9315 \times -3.8057$	$y = -0.1498 \times +0.765$	0.9998	0.9900	0.6	2		
24	ECF ₈₃₃	-1.9886	-17.178	-2.873	22.102	$y = -0.0462 \times +1.359$	$y = -0.0462 \times +1.359$	0.9954	0.7449	0.5	2		

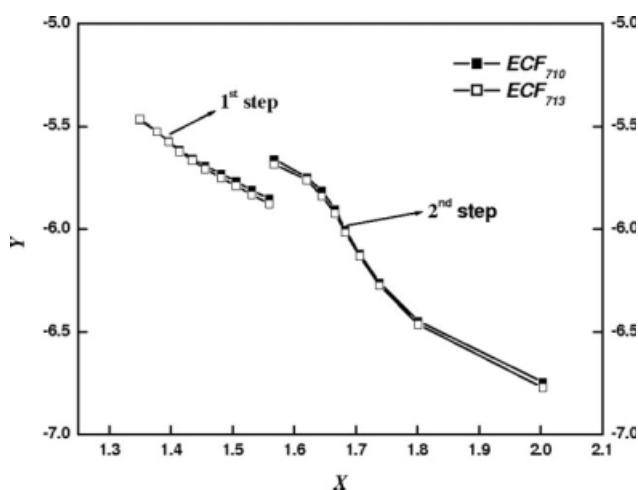


Figure 6 Best-fit plot between X and Y.

(Table III) were utilized to calculate the other kinetic parameters of the decomposition reaction. Figure 6 showed the best fit plot for samples ECF₇₁₀ and ECF₇₁₃, for both the steps, with different order of decomposition, as obtained during the best fit analysis. It is clear from Figure 6 that the first step of pure epoxy and its blend preceded with 0.5th order whereas the order of reaction for second step, in both the cases, was found to be of second order. This was further confirmed by the linear regression

analysis using computer software and regression equations (Table III). The values of coefficient of determination, R^2 , for each step, were evaluated (refer Table III). The values of R^2 indicated the suitability of the data and its value was very close to one in both the steps.

The two steps were analyzed separately and the kinetic parameters are presented in Table IV. The activation energy of second step is higher (calculated and plot values of E) than the first step. The variation in E (Figs. 7–10) was found to be random but with an associated proportional variation in Z (Table IV), a phenomenon common in non isothermal kinetic treatments.³² The values of E , in the first step, for pure epoxy samples prepared from novolac resins with dicarboxylic acids, increased slowly, reached its maximum value at $C/F = 0.7$ and decreased thereafter (Fig. 7) whereas for epoxy samples prepared from novolac resins with tricarboxylic acid, the values of E increased sharply and reached its peak value at $C/F = 0.6$ (Fig. 7). In the second step of decomposition, the values of E showed their maximum value at $C/F = 0.7$ for both di- and tri-carboxylic acids (Fig. 8). Similar trends were seen for blend samples for both the steps (Figs. 9 and 10). The rate constant at an arbitrary temperature was calculated for each stage using Arrhenius relation ($K = Ze^{-E/RT}$). It was found that the blend samples

TABLE IV
Variation of E , Z and k Values with CTBN concentration

S. no.	Sample code	E , kJ mol ⁻¹				$Z \times 10^{-4}$, s ⁻¹				$k \times 10^{-7}$, s ⁻¹			
		Calculated		Plot		Calculated		Plot		Calculated		Plot	
		I-step	II- step	I-step	II- step	I-step	II- step	I-step	II-step	I-step	II- step	I-step	II-step
1	ECF ₅₁₀	34.73	88.22	36.89	93.42	3.61	10.2	4.13	12.8	3.59	9.99	3.91	19.9
2	ECF ₆₁₀	40.42	146.95	46.73	151.42	3.84	16.6	4.99	17.3	3.8	16.1	4.08	21.3
3	ECF ₇₁₀	53.75	160.55	59.89	169.37	6.04	12.6	6.32	13.8	5.97	12.2	6.75	15.6
4	ECF ₈₁₀	38.85	142.69	46.77	153.93	8.41	15.6	9.75	19.6	3.78	15.1	4.81	19.7
5	ECF ₅₂₀	38.1	130.84	43.59	140.26	3.7	14.7	4.49	15.1	3.71	14.3	4.36	31.5
6	ECF ₆₂₀	43.73	168.06	49.11	174.31	5.32	13.9	6.69	15.2	5.27	13.4	5.87	18.9
7	ECF ₇₂₀	69.28	204.55	76.44	211.74	6.09	22.1	6.29	26.7	6.00	21.2	6.00	25.4
8	ECF ₈₂₀	38.80	179.78	47.39	183.94	6.11	14.5	6.98	14.9	5.22	13.9	5.98	17.9
9	ECF ₅₃₀	31.95	144.51	37.82	149.63	3.45	16.1	3.87	17.1	3.42	15.6	3.86	18.9
10	ECF ₆₃₀	69.78	173.71	73.99	183.22	7.38	13.8	7.98	15.1	7.28	13.3	8.20	18.4
11	ECF ₇₃₀	40.60	240.39	48.66	249.06	3.94	25.7	4.84	27.8	3.91	24.5	4.63	34.5
12	ECF ₈₃₀	42.85	230.70	50.38	242.93	2.54	18.8	2.63	20.2	5.07	18.0	5.67	27.0
13	ECF ₅₁₃	54.24	115.67	59.66	119.73	4.62	13.0	5.31	14.5	4.57	12.7	5.53	22.7
14	ECF ₆₁₃	58.67	202.16	64.91	208.74	6.68	15.4	7.43	16.0	6.61	14.8	7.11	21.8
15	ECF ₇₁₃	75.29	185.32	79.99	194.94	7.70	14.4	8.37	14.8	7.59	13.9	9.99	18.9
16	ECF ₈₁₃	78.28	194.12	85.01	201.77	5.27	58.1	6.63	63.1	5.25	18.0	6.05	29.1
17	ECF ₅₂₃	42.26	149.4	47.65	153.66	4.03	16.7	4.76	17.8	3.99	16.2	3.99	22.2
18	ECF ₆₂₃	54.06	184.12	61.87	189.87	6.11	14.6	6.99	14.9	6.04	14.0	6.66	23.6
19	ECF ₇₂₃	100.88	276.73	108.43	282.67	1.12	22.1	1.36	26.7	1.10	20.9	1.69	28.9
20	ECF ₈₂₃	87.22	245.25	93.79	256.78	5.12	23.8	5.93	25.6	3.79	62.2	4.31	69.6
21	ECF ₅₃₃	54.24	157.87	59.22	167.59	4.67	17.0	5.62	19.8	4.62	16.4	5.23	24.7
22	ECF ₆₃₃	90.72	268.80	96.27	272.37	9.09	27.5	9.79	29.8	8.94	26.1	9.40	31.2
23	ECF ₇₃₃	47.10	246.83	54.92	256.83	3.81	26.4	4.65	30.1	4.26	25.9	4.98	31.9
24	ECF ₈₃₃	69.43	250.3	76.91	259.3	3.81	59.3	4.71	67.8	5.66	24.3	6.14	31.7

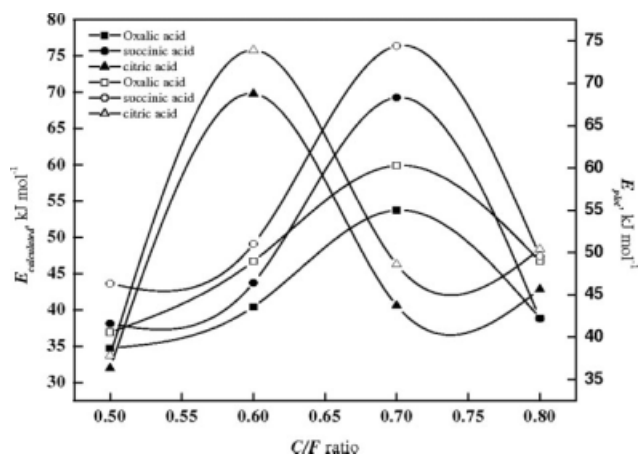


Figure 7 Variation of activation energy of pure epoxy samples with C/F molar ratio for first step. The black and blank bullets are for calculated and plot values, respectively.

containing 15 wt % CTBN showed the lower value of decomposition rate constants, in both the steps, than the respective pure epoxy resins (refer Table IV).

Higher values of activation energy of the blend system, in both the steps, may be attributed to the presence of polynuclearity in the resin backbone chain. Increasing the activation energy indicated the steric hindrance of the molecules of more complex structure of blends and the cured product with polyamine. The curing reaction itself may be a complex function of the energy of reactive molecules as well as the relative configuration of the reactant molecules reaction process may be hindered because of the presence of polynuclear structure in the backbone. Hence, for a system to be perfectly cured, higher energy was required. This is also clear from the higher char yield of blend systems. Higher acti-

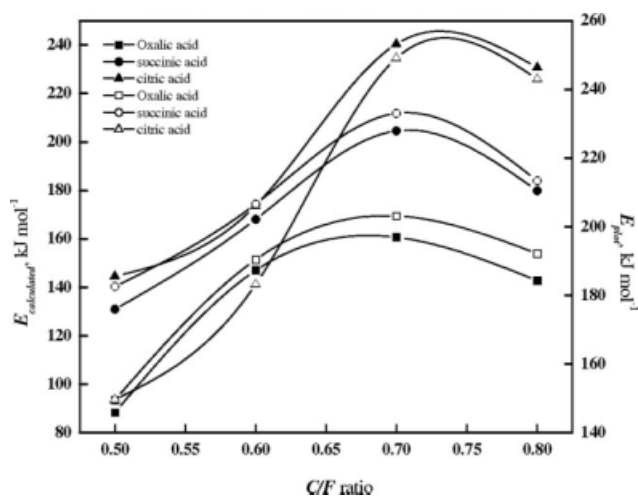


Figure 8 Variation of activation energy of pure epoxy samples with C/F molar ratio for second step. The black and blank bullets are for calculated and plot values, respectively.

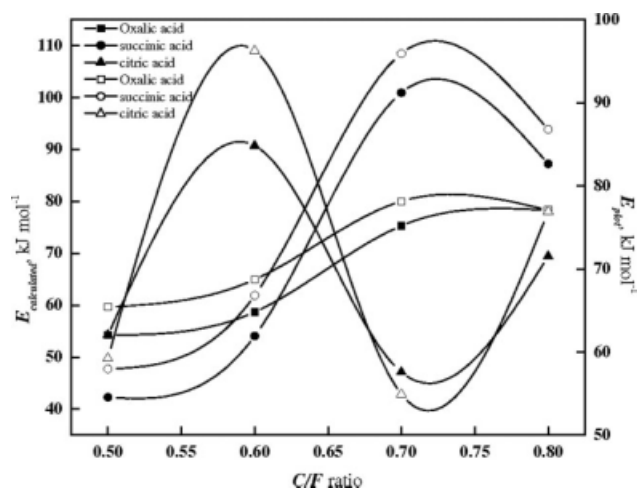


Figure 9 Variation of activation energy of blend samples with C/F molar ratio for first step. The black and blank bullets are for calculated and plot values, respectively.

vation energy for the decomposition of blends led to better thermal stability. This fact has been evidenced by various workers in the past³³⁻³⁷ for different systems.

CONCLUSIONS

The proposed mechanism for curing reaction of the blend of cardanol-based epoxidized novolac resin and CTBN in the presence of polyamine was found to be well suitable for such systems as confirmed by IR analysis. The addition of CTBN liquid rubber improved the thermal stability of the cardanol-based pure epoxy systems. The values of n were found to be second in most of the studied systems whereas, in the first step, the values of n are different for different epoxies and their blend systems. This was based on purely statistical analysis. The values of E ,

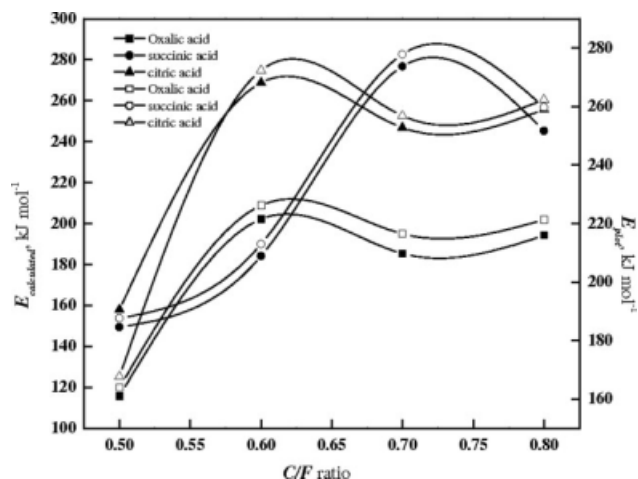


Figure 10 Variation of activation energy of blend samples with C/F molar ratio for second step. The black and blank bullets are for calculated and plot values, respectively.

in the first step, for pure epoxy samples prepared from novolac resins with dicarboxylic acids, increased slowly, reached its maximum value at $C/F = 0.7$ and decreased thereafter whereas for epoxy samples prepared from novolac resins with tri-carboxylic acid, the values of E increased sharply and reached its peak value at $C/F = 0.6$. A similar behavior was observed with the values of pre-exponential factor (Z).

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References

1. Attanasi, O. A.; Bunatti, S. B. *La Chim e l'Industria* 1996, 78, 693.
2. Prabhakaran, K.; Narayan, A.; Pvithram, C. *J Eur Cer Soc* 2001, 21, 2873.
3. Pillai, C. K. S.; Prasad, V. S.; Sudha, J. D.; Bera, S. C.; Menon, A. R. R. *J Appl Polym Sci* 1990, 41, 2487.
4. Bhunia, H. P.; Jana, R. N.; Basak, A.; Lenka, S.; Nando, G. B. *J Appl Polym Sci* 1998, 36, 391.
5. Menon, A. R. R.; Pillai, C. K. S.; Sudha, J. D.; Mathew, A. G. *J Sci Ind Res* 1985, 44, 324.
6. Kinloch, A. J.; Reiw, C. K. *Am Chem Soc* 1983, 22, 67.
7. Kinloch, A. J.; Young, R. J. *Fracture Behavior of Polymers*; Applied Science: London, 1983.
8. Huang, J.; Kinloch, A. J. *Polymer* 1992, 33, 1330.
9. Huang, J.; Kinloch, A. J. *J Mater Sci* 1992, 27, 2763.
10. Riew, C. K.; Rowe, E. H.; Siebert, A. R. In *ACS Meeting: Symposium on Toughness and Brittleness of Plastics*; Division of Organic Coatings and Plastics: Atlantic City, NJ, 1974.
11. Frigone, M. E.; Masica, L.; Aciermo, D. *Eur Polym J* 1995, 31, 1021.
12. Bascom, W. D.; Cottington, R. L.; Jones, R. L.; Peyser, P. *J Appl Polym Sci* 1975, 19, 2545.
13. Tripathi, G.; Srivastava, D. *Mater Sci Eng A* 2007, 443, 262.
14. Yadav, R.; Srivastava, D. *Mater Chem Phys* 2007, 106, 74.
15. Knop, A.; Schieb, W. *Chemistry and Application of Phenolic Resins*; Springer: New York, 1979.
16. Devi, A.; Srivastava, D. *Mater Sci Eng A* 2007, 458, 336.
17. Lee, H.; Neville, K. *Hand Book of Epoxy Resins*, McGraw-Hill: New York, 1982.
18. Evtushenko, Y. M.; Jvanov, V. M.; Zaitsev, B. E. *J Anal Chem* 2004, 58, 347.
19. Smith, A. *Applied Infrared Spectroscopy*; Wiley: New York, 1979; Translated under the title *Prikladnaya Ik-Spektrosopiya*; Moscow: Mir, 1982.
20. Nigam, V.; Setua, D. K.; Mathur, G. N. *Polym Eng Sci* 1999, 39, 1425.
21. Ramos, V. D.; da Costa, H. M.; Soares, V. L. P.; Nascimento, R. S. V. *Polym Test* 2005, 24, 219.
22. Chen, D.; Pascault, J. P.; Bertsch, R. J.; Drake, R. S.; Siebert, A. R. *J Appl Polym Sci* 1994, 51, 1959.
23. Thomas, R.; Durix, S.; Sinturel, C.; Omonov, T.; Goossens, S.; Groeninckx, G.; Moldenaers, P.; Thomas, S. *Polymer* 2007, 48, 1695.
24. Hsu, Y. G.; Liang, C. W. *J Appl Polym Sci* 2007, 106, 1576.
25. Menon, A. R. R.; Aigbodion, A. I.; Pillai, C. K. S.; Mathew, N. M.; Bhagawan, S. S. *Eur Polym J* 2002, 38, 163.
26. Nair, C. P. R.; Bindu, R. L.; Josep, V. C. *J Polym Sci Part A: Polym Chem* 1995, 33, 621.
27. Nam, J. D.; Seferis, J. C. *J Polym Sci Part B: Polym Phys* 1992, 30, 455.
28. Denq, B. L.; Chiu, W. Y.; Lim, K. F. *J Appl Polym Sci* 1997, 66, 1855.
29. Reghunandhan, C. P.; Bindu, R. L.; Ninan, K. N. *J Appl Polym Sci* 2001, 81, 3371.
30. Salin, J. M.; Seferis, J. C. *J Appl Polym Sci* 1993, 47, 847.
31. Coats, A. W.; Redfern, J. P. *Nature* 1964, 201, 68.
32. Seibold, R. W. In *Proceedings of the 20th Sampe National Symposium*; Seattle, WA, 1976; p 327.
33. Conley, R. T.; Bieron, J. F. *J Appl Polym Sci* 1963, 7, 103.
34. Kim, M. G.; Nieh, W. L. S.; Meacham, R. N. *Ind Eng Chem Res* 1991, 30, 798.
35. Monetta, T.; Bellucci, F.; Nicodemo, L.; Nicolais, L. *Prog Org Coat* 1993, 21, 353.
36. Srivastava, K.; Kaushik, M. K.; Srivastava, D.; Tripathi, S. K. *J Appl Polym Sci* 2006, 102, 4171.
37. Srivastava, D.; Mathur, G. N. *J Macromol Sci: Pure Appl Chem A* 1997, 34, 59.