

The Effect of Orientation of Various Phenols on the Degradation Kinetics of Blends of Resole and Epoxy

Kavita Srivastava,¹ Manoj Kumar Kaushik,¹ Deepak Srivastava,² Santosh Kumar Tripathi¹

¹Department of Chemistry, VSSD College, Chhatrapati Shahu Ji Maharaj University, Kanpur 208 002, India

²Department of Plastic Technology, Harcourt Butler Technological Institute, Kanpur 208 002, India

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ABSTRACT: Resoles were prepared separately with different phenols, with formaldehyde having phenol-to-formaldehyde mole ratio of 1:2 in basic medium at 70°C. These resoles were physically blended with different weight percentages of diglycidyl ether of bisphenol-A (DGEBA)–epoxy resin. The blends were cured with 40, 50, and 60 wt % polyamide (based on total amount of the blended resin). Decomposition kinetics of blend sample was studied by dynamic thermogravimetric (TG) analysis. It was found that the degradation of most of the blend samples followed two-step second-order degradation kinetics with 50 wt % polyamide and varied reaction orders with 40 and 60 wt % polyamide

and type of phenols used in the resole. The energy of activation (E) was found to be maximum with the blend system containing *p*-cresolic resole and epoxy. The value of pre-exponential factor (Z) decreased when phenolic resole was changed to *p*-cresolic resole in the blend. Also, the plotted values of E and Z were found to be in close resemblance with those obtained from calculated values. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4171–4176, 2006

Key words: orientation; infrared spectroscopic analysis; polyamide; cure time

INTRODUCTION

The blends of epoxy and resole^{1–7} offer a versatile spectrum of superior properties such as outstanding strength and adhesion, good solvent and chemical resistance, high heat and thermal resistance, etc., and are used in electronic industries as molding and sealing compounds for electronic packaging, protective coatings, composites, and many hitech applications such as aerospace, marine, and satellite communications. Such resins can be converted into a void-free highly crosslinked network by the use of proper curing agent, through various chemical reactions, which ultimately affects the thermal stability of the blends.^{8–11}

Decomposition of resole/epoxy blend is based on the formation of various low molecular weight products, and the rate at which these products are formed.^{8,11,12} This is also affected by changing the type of resoles present in the blend systems. Although these resins show excellent resistance to thermal degradation, their kinetics of degradation has been studied by very few workers.^{8,9,11} We have tried to study the effect of changing the type of phenol on the overall kinetic parameters for the thermal degradation of blend systems in the present investigation.

EXPERIMENTAL

Phenol, *o*-, *p*-, and *m*-cresols, formaldehyde (37%, w/v), and sodium hydroxide (all from Thomas Baker Chemicals, Mumbai) were used for preparing different resoles. Diglycidylether bisphenol-A (DGEBA)–epoxy resin (Grade: R-100; EEW: 190 g/eqiv) and polyamide (Grade: PH-851; amine value: 240–400 mg KOH/g) were obtained from Resinova (Nayaganj, Kanpur) for preparation and curing of blends, respectively.

The resoles from various phenols were synthesized by reacting respective phenols and formaldehyde in a molar ration of 1:2 in basic medium at 70°C, by a method adopted by Knop and Schieb.¹³ The DGEBA–epoxy resin was mixed with various resoles at different weight ratios ranging between 0 and 100 wt %, interval of 25 wt %. All the blends were cured with 40, 50, and 60 wt % polyamide (based on the total weight of the blend). The blend samples were designated according to the formulations, given in Table I. For the sake of simplicity, we have considered only the blend samples containing equal weight ratio of resole and epoxy among all the available blend samples. All the blend samples with 40 wt % polyamide were cured in an air oven at 100°C.

Fourier transform infrared (FTIR) spectra of all pure resoles and blend samples were performed on Bruker Victor 22 IR spectrophotometer (USA) in the wave number range 500–4000 cm⁻¹ with standard

Correspondence to: K. Srivastava (vssd_tripathi@rediffmail.com).

TABLE I
Sample Designation

S. no.	Type of resole ^a	Resole (wt %)	Epoxy (E) (wt %)	Polyamide			
				0	40	50	60
1.	R ₁	100	0	E ₀ R ₁₁₀	E ₀ R ₁₁₄	E ₀ R ₁₁₅	E ₀ R ₁₁₆
2.		75	25	E ₂ R ₁₇₀	E ₂ R ₁₇₄	E ₂ R ₁₇₅	E ₂ R ₁₇₆
3.		50	50	E ₅ R ₁₅₀	E ₅ R ₁₅₄	E ₅ R ₁₅₅	E ₅ R ₁₅₆
4.		25	75	E ₇ R ₁₂₀	E ₇ R ₁₂₄	E ₇ R ₁₂₅	E ₇ R ₁₂₆
5.		0	100	E ₁ R ₁₀₀	E ₁ R ₁₀₄	E ₁ R ₁₀₅	E ₁ R ₁₀₆
6.	R ₂	100	0	E ₀ R ₂₁₀	E ₀ R ₂₁₄	E ₀ R ₂₁₅	E ₀ R ₂₁₆
7.		75	25	E ₂ R ₂₇₀	E ₂ R ₂₇₄	E ₂ R ₂₇₅	E ₂ R ₂₇₆
8.		50	50	E ₅ R ₂₅₀	E ₅ R ₂₅₄	E ₅ R ₂₅₅	E ₅ R ₂₅₆
9.		25	75	E ₇ R ₂₂₀	E ₇ R ₂₂₄	E ₇ R ₂₂₅	E ₇ R ₂₂₆
10.		0	100	E ₁ R ₂₀₀	E ₁ R ₂₀₄	E ₁ R ₂₀₅	E ₁ R ₂₀₆
11.	R ₃	100	0	E ₀ R ₃₁₀	E ₀ R ₃₁₄	E ₀ R ₃₁₅	E ₀ R ₃₁₆
12.		75	25	E ₂ R ₃₇₀	E ₂ R ₃₇₄	E ₂ R ₃₇₅	E ₂ R ₃₇₆
13.		50	50	E ₅ R ₃₅₀	E ₅ R ₃₅₄	E ₅ R ₃₅₅	E ₅ R ₃₅₆
14.		25	75	E ₇ R ₃₂₀	E ₇ R ₃₂₄	E ₇ R ₃₂₅	E ₇ R ₃₂₆
15.		0	100	E ₁ R ₃₀₀	E ₁ R ₃₀₄	E ₁ R ₃₀₅	E ₁ R ₃₀₆
16.	R ₄	100	0	E ₀ R ₄₁₀	E ₀ R ₄₁₄	E ₀ R ₄₁₅	E ₀ R ₄₁₆
17.		75	25	E ₂ R ₄₇₀	E ₂ R ₄₇₄	E ₂ R ₄₇₅	E ₂ R ₄₇₆
18.		50	50	E ₅ R ₄₅₀	E ₅ R ₄₅₄	E ₅ R ₄₅₅	E ₅ R ₄₅₆
19.		25	75	E ₇ R ₄₂₀	E ₇ R ₄₂₄	E ₇ R ₄₂₅	E ₇ R ₄₂₆
20.		0	100	E ₁ R ₄₀₀	E ₁ R ₄₀₄	E ₁ R ₄₀₅	E ₁ R ₄₀₆

^a Type of resole prepared from different phenol, viz., R₁, resole from phenol; R₂, resole from *o*-cresol; R₃, resole from *p*-cresol; and R₄, resole from *m*-cresol.

KBr pellets. The blend sample having equal weight ratios of resole, prepared from *p*-cresol and DGEBA-epoxy, was considered for IR spectrum, as this blend sample showed least cure time at 100°C. Although, the blend sample containing equal weight ratios of resole, prepared from *m*-cresol and epoxy, showed least cure time, these are not considered as the resole prepared from *m*-cresol took only 30 min for the completion of the reaction and so could not give higher molecular weight resole.¹³

The kinetic parameters for the thermal decomposition of these blends were evaluated by thermogravimetric analyzer (TGA) of DuPont, USA (Model TGA VSIA DuPont 2100) at a heating rate of 10°C/min and in nitrogen atmosphere with flow rate of 10 cm³/min from ambient to 800°C. The percent weight versus temperature curves from TGA were used for this purpose. The data from the TGA curve were utilized in Coats-Redfern equation¹⁴ as given below. This equation was used to determine the values of order of degradation reaction (*n*), activation energy (*E*), and preexponential (*Z*):

$$\log_{10} \left(\frac{g(\alpha)}{T^2} \right) = \log_{10} \left[\left(\frac{ZR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right) \right] - \frac{E}{2.3RT} \quad (1)$$

where

$$g(\alpha) = \left(\frac{1 - (1 - \alpha)^{1-n}}{1 - n} \right) \quad \text{for } n \neq 1$$

and

$$g(\alpha) = -\log_{10}(1 - \alpha) \quad \text{for } n = 1$$

Equation (1) can be reduced to

$$Y = A + \frac{B}{1000} X$$

where

$$Y = \log_{10} \left(\frac{g(\alpha)}{T^2} \right) \quad \text{for different values of } n \text{ lying between 0 and 2}$$

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

$$A = \log_{10} \left[\left(\frac{ZR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right) \right]$$

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

$$\alpha = \frac{w_T - w_f}{w_0 - w_f}$$

where α is the fractional weight loss; $g(\alpha)$, the function of α ; w_T , the weight at temperature T ; w_f , final weight; w_0 , the initial weight; β , the heating rate (°C/min); and R is the gas constant (8.314 J deg⁻¹ mol⁻¹ K).

A graph of X and Y was plotted using the best-fit technique and the value of n was evaluated. This value of n was further confirmed by linear regression

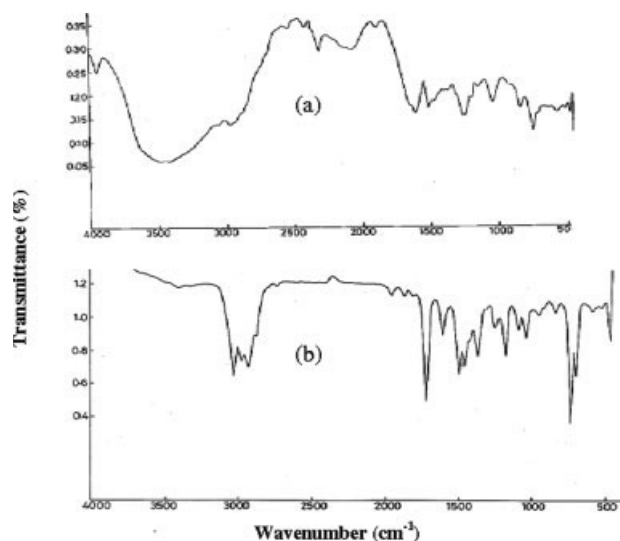


Figure 1 FTIR spectrum of blend samples (a) uncured E_5R_{250} and (b) cured E_5R_{254} .

analysis using computer software and the values of coefficient of determination (R^2) were taken as a measure of validity of data. With this value of n , the activation energy (E) and preexponential factor (Z) were determined from the slope and intercept values of the X - Y plots/regression equations.

RESULTS AND DISCUSSION

Figure 1(a) shows the IR spectrum of uncured blend sample E_5R_{250} . From Figure 1(a), it is clear that a band appeared in the region of $3200\text{--}3500\text{ cm}^{-1}$, which might be due to the presence of *o*-cresolic hydroxyl group in the blend system. Methylol and methylene linkages that were found to be present after blending indicated that there occurred no chemical reaction between hydroxyl of the methylol group

with the oxirane group of the epoxy resin. The peak appearance near 1040 cm^{-1} confirmed the same [Fig. 1(a)]. A similar conclusion has been reported in the literature⁹ for the blend of phenolic resole and general purpose epoxy resin. The shifting of peak related to *o*-cresolic hydroxyl indicated the reaction of oxirane group of the epoxy resin and the hydroxyl group of the *o*-cresol. This was further supported by the peak appearance near 1125 cm^{-1} , which might be due to the presence of aromatic ether group in the blend resin. Also, the characteristic peaks of oxirane group of the epoxy resin appeared as sharp peaks at 970 and 910 cm^{-1} . The disappearance of broad peak near $3200\text{--}3500\text{ cm}^{-1}$ and formation of ether peak near 1700 cm^{-1} in the IR spectrum [Fig. 1(b)] of cured sample (E_5R_{254}) clearly evidenced the progress of curing.

The onset temperature of degradation (T_0), temperature of maximum rate of mass loss (T_{\max}), and extrapolated final decomposition temperature (T_F) were noted from TG traces and are presented in Table II. The relative thermal stability of the cured blend resins was compared by determining percent char yield at 800°C . All the blend systems containing equal weight ratios of resole and epoxy having 40, 50, and 60 wt % polyamide showed two-step decomposition behavior (Fig. 2), except in few cases where single-step decomposition were observed. A major mass loss of 41–74% was observed in the temperature range of $337\text{--}360^\circ\text{C}$ (Table II). A minor mass loss (16–30%) was also observed above 380°C . These two-stages of mass loss may be attributed to the decomposition of (a) the resole and (b) the epoxy resin. In blend systems containing 50 and 60 wt % polyamide, the values of T_0 and T_{\max} were lower than that of blend systems cured with 40 wt % polyamide. Mass loss in the second step decreased as the phenol in the resole was replaced by *p*-cresol, but increased as the amount of curing agent

TABLE II
Thermal Behaviour of Isothermally Cured Resole(s)/Epoxy Blends with Different Phenolic Resoles in the Blends

Code	I-stage			Mass loss (%)	II-stage			Mass loss (%)	Char yield (%)
	T_0	T_{\max}	T_F		T_0	T_{\max}	T_F		
E_5R_{154}	359	400	426	48.1	484	491	500	27.7	24.2
E_5R_{214}	348	390	405	52.9	448	484	514	27.7	19.4
E_5R_{354}	358	374	397	55.6	429	448	5.3	17.9	26.5
E_5R_{454}	347	381	404	56.4	415	469	513	30.0	13.6
E_5R_{155}	356	396	418	54.0	459	476	513	27.3	18.3
E_5R_{255}	342	376	400	66.4	456	471	589	17.4	16.2
E_5R_{355}	355	426	504	84.0	–	–	–	–	16.0
E_5R_{455}	345	430	498	84.3	–	–	–	–	15.7
E_5R_{156}	350	389	409	61.4	472	479	519	25.8	12.8
E_5R_{256}	338	387	417	73.8	476	485	503	16.1	10.1
E_5R_{356}	351	402	427	40.8	475	491	506	45.8	13.4
E_5R_{456}	337	413	429	51.4	480	486	501	37.8	10.8

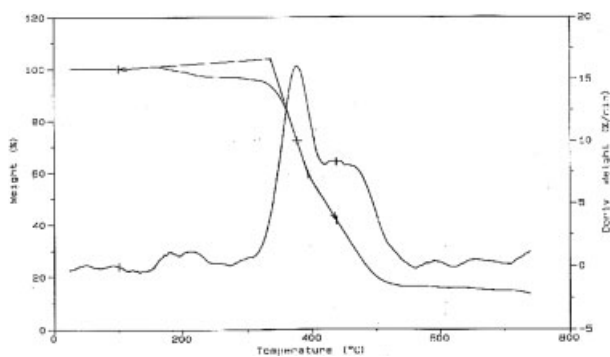


Figure 2 TGA trace of blend sample E₅R₃₅₄.

was increased. Also, the char yield was found to be maximum in the blend sample containing *p*-cresolic resole and epoxy cured with 40 wt % polyamide and its value decreased as the amount of curing agent was increased (see Table II). This could be attributed to the change of aromaticity of phenol present in the blend system.

Kinetic parameters, viz., order-of-reaction (n), energy of activation (E), and preexponential factor (Z) for thermal decomposition of the blends of resole and epoxy cured with polyamide were evaluated by the data obtained from the dynamic thermograms from TGA (Fig. 2). The fractional decomposition α for the respective temperatures has been calculated from the TG curves. The kinetic plots according to equation (1) for different values of n showed a two-step degradation mechanism for all blend samples except for the following blend samples: E₅R₃₅₅, E₅R₄₅₅, E₅R₃₅₆, and E₅R₄₅₆. For these samples the plots showed a single-step degradation mechanism. A typical plot of first-order degradation mechanism for blend sample E₅R₃₅₄ is shown in Figure 3. A similar behavior had been observed for the phenolic resins based on the copolymers of phenol and 3-phenylethynyl phenol.¹⁵

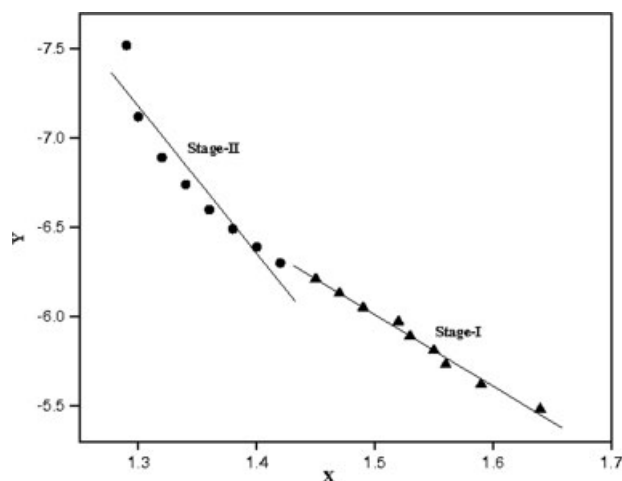


Figure 3 First-order kinetic plot of Coats-Redfern equation for blend sample E₅R₃₅₄.

TABLE III
TGA Data

S. no.	Sample code	Plot of X and Y				Linear regression analysis					
		Slope		Intercept		Equations		R ²			
		1st-step	2nd-step	1st-step	2nd-step	I-step	II-step	I-step	II-step		
1.	E ₅ R ₁₅₄	-5.751	-4.958	-12.957	-13.617	Y = -6.3609X - 15.711	Y = -5.5333X - 14.507	0.9797	0.9787	1.5	2.0
2.	E ₅ R ₂₅₄	-6.325	-5.062	-15.218	-16.256	Y = -6.4394X - 15.392	Y = -5.6544X - 14.613	0.9885	0.9425	1.5	2.0
3.	E ₅ R ₃₅₄	-6.861	-5.531	-14.103	-10.963	Y = -6.8571X - 15.629	Y = -5.8763X - 14.326	0.9762	0.9646	1.0	1.0
4.	E ₅ R ₄₅₄	-6.026	-4.464	-12.464	-12.867	Y = -6.2772X - 14.856	Y = -5.4381X - 13.751	0.9899	0.9821	2.0	1.5
5.	E ₅ R ₁₅₅	-5.317	-4.244	-13.281	-11.840	Y = -6.2973X - 14.968	Y = -5.4328X - 13.644	0.9594	0.9302	2.0	1.5
6.	E ₅ R ₂₅₅	-6.009	-4.777	-14.525	-12.797	Y = -6.3789X - 14.942	Y = -5.9475X - 13.682	0.9900	0.9792	2.0	1.5
7.	E ₅ R ₃₅₅	-5.932	-	-14.037	-	Y = -6.5984X - 15.039	-	0.9799	-	2.0	-
8.	E ₅ R ₄₅₅	-5.262	-	-13.299	-	Y = -6.4099X - 15.074	-	0.9392	-	2.0	-
9.	E ₅ R ₁₅₆	-3.689	-3.618	-11.007	-11.726	Y = -4.6924X - 13.048	Y = -4.7810X - 13.120	0.9300	0.9574	1.0	1.0
10.	E ₅ R ₂₅₆	-4.581	-3.780	-12.419	-11.278	Y = -4.7411X - 12.997	Y = -4.5597X - 12.945	0.9089	0.9583	1.5	0.5
11.	E ₅ R ₃₅₆	-5.091	-	-11.900	-	Y = -4.7351X - 13.213	-	0.8944	-	1.5	-
12.	E ₅ R ₄₅₆	-4.149	-	-11.895	-	Y = -4.7168X - 13.167	-	0.9317	-	1.0	-

TABLE IV
Results from the TGA Traces

S. no.	Sample code	E (kJ/mole)				Z ($\times 10^8$ s $^{-1}$)				k ($\times 10^{13}$ sec $^{-1}$)			
		$E_{\text{calculated}}$		E_{plot}		$Z_{\text{calculated}}$		Z_{plot}		$k_{\text{calculated}}$		k_{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.	E ₅ R ₁₅₄	47.81	41.22	52.88	46.00	0.391	0.078	0.0007	0.010	7.60	4.90	0.0058	0.29
2.	E ₅ R ₂₅₄	52.59	42.09	53.54	47.01	0.0023	0.18	0.0016	0.0085	0.019	9.76	0.011	0.19
3.	E ₅ R ₃₅₄	57.04	45.98	57.01	48.86	0.013	37.54	0.0053	0.017	0.12	1012	0.0036	0.27
4.	E ₅ R ₄₅₄	50.10	37.11	52.19	45.21	1.26	0.41	0.0041	0.060	16.25	53.89	0.047	1.87
5.	E ₅ R ₁₅₅	44.21	35.28	52.36	45.17	0.18	4.23	0.0040	0.077	6.52	773.37	0.035	2.41
6.	E ₅ R ₂₅₅	49.96	39.72	53.03	49.45	0.011	0.50	0.0044	0.075	0.015	41.39	0.033	1.10
7.	E ₅ R ₃₅₅	49.32	–	54.86	–	0.033	–	0.0036	–	0.050	–	0.020	–
8.	E ₅ R ₄₅₅	43.75	–	53.29	–	0.17	–	0.0032	–	6.74	–	0.024	–
9.	E ₅ R ₁₅₆	30.67	30.08	39.01	39.75	26.96	5.11	0.28	0.24	112.24	2363	26.05	19.57
10.	E ₅ R ₂₅₆	38.09	31.43	39.42	37.91	1.17	14.60	0.31	0.35	128.98	5309	27.42	39.54
11.	E ₅ R ₃₅₆	42.33	–	39.37	–	4.11	–	0.19	–	213.06	–	16.81	–
12.	E ₅ R ₄₅₆	34.49	–	39.22	–	3.69	–	0.22	–	775.36	–	19.16	–

This was further confirmed by linear regression analysis using computer software and regression equations (Table III) along with the values of coefficient of determination, R^2 , for each step, were evaluated and the results are presented in Table III. The values of R^2 indicated the suitability of the data and its value was very close to one in the first step.

The two-steps were analyzed separately, and the kinetic parameters are presented in Table IV. The first stage is found to have higher activation energy (both $E_{\text{calculated}}$ and E_{plot}) than had the second stage. The variation in E was found to be random, but with an associated proportional variation in Z , a phenomenon common in nonisothermal kinetic treatment.¹⁵ Hence, for comparison, the rate constant at an arbitrary temperature was calculated for each stage, using Arrhenius relation ($k = Z e^{-E/RT}$). The rate constants at 400°C for the first stage showed that the blend samples containing 40 wt % polyamide had the lowest rate of decomposition than had the blend samples containing 50 and 60 wt % polyamide. The first two blend systems had nearly the same rate constants, confirming to their TGA pattern. This showed that increase in polyamide concentration beyond a certain limit rendered the system thermally more fragile. The second stage of decomposition showed more or less a similar trend as that in the first stage but having higher values of rate constants. In all probability, the second stage of decomposition corresponded to the carbonization process,¹⁶ where the mechanism could be expected to be same for all blend systems, and where the structural variation after the initial volatilization would have a minimum effect. The low Z values for both cases further confirmed the significance of volatilization in the kinetics of the decomposition process. Interestingly,

the values of activation energies for both these steps were found to be very close.

Higher values of activation energies of the blend systems, 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 polyamide. 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 that may change during the reaction process and this reaction process may be hindered due to 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 system containing *p*-cresolic resole and epoxy resins. High activation energy for the decomposition of blends led to better thermal stability of such blend systems (i.e., blend samples E₅R₃₅₄, E₅R₃₅₅, and E₅R₃₅₆). This fact has been evidenced by various workers in the past^{17–19} for different systems.

CONCLUSIONS

The following conclusions were drawn from these studies:

1. The proposed reaction curing mechanism of the blend of resole and epoxy in presence of polyamide was found to be well suitable for such systems as confirmed by IR analysis.
2. The cured blend sample prepared from *p*-cresolic resole and epoxy with 40 wt % polyamide showed the best thermally stable system among all other blend samples.

3. The decomposition reactions proceeded with different orders in two stages in different blend samples. Also, the blend sample based on *p*-cresolic resole and epoxy proceeded with first-order decomposition kinetics as also evidenced by linear regression analysis.
4. The variation in *E* was found to be random, but with an associated proportional variation in *Z*, a phenomenon common in nonisothermal kinetic treatment.
5. The rate constant at 400°C for the first stage showed that the blend samples containing 40 wt % polyamide had the lowest rate of decomposition than the blend samples containing 50 and 60 wt % polyamide. The second stage of decomposition almost showed a similar trend as that in the first stage but having higher values of *k*.

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