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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Srivastava, Deepak and Mathur, G. N.(1997) 'Degradation Kinetics of Resole-Modified Epoxy. I', Journal of Macromolecular Science, Part A, 34: 1, 59 – 66

To link to this Article: DOI: 10.1080/10601329708014934

URL: <http://dx.doi.org/10.1080/10601329708014934>

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DEGRADATION KINETICS OF RESOLE-MODIFIED EPOXY. I

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Key Words: Resole; Epoxy resin; Degradation; Blends; Regression analysis; Activation energy

ABSTRACT

Blends of resole with epoxy resin (General Purpose) having different weight ratios (0/100, 25/75, 50/50, 75/25, and 100/0) based on physical mixing have been prepared. These blends were cured by adding polyamide in a 60:40 ratio based on blend resins and polyamide. The degradation kinetics of these resins was studied by dynamic thermogravimetric analysis in nitrogen atmosphere at a heating rate of 15°C/min by using the Coats-Redfern equation. It is concluded that the degradation of each sample follows first-order ($n = 1$) degradation kinetics. This is obtained on the basis of best fit analysis, and all the parameters are confirmed by regression analysis. From the reaction order value, activation energy (E) and preexponential factor (Z) were calculated by the slope and intercept of the plot between X and Y , respectively.

INTRODUCTION

Modified epoxy resins [1-3] are an important engineering matrix material for polymeric composites where a high modulus and glass-transition temperature are desirable. Resole-modified epoxy resins as a class offer a versatile spectrum of superior properties. Epoxidized resoles [4-9] have found a wide spectrum of uses because of their outstanding strength [10], toughness [11], and solvent and chemical resistance [12, 13]. In view of their outstanding properties, these resins are used in such hi-tech applications as aerospace [14, 15], marine coating [16], and satellite communication.

The chemistry of these polymers is still not very clear. In the present article an approximate chemistry of these polymers is presented. Although these resins show excellent resistance to thermal degradation, their kinetics of degradation has not been studied much. An approximate kinetics of degradation on the basis of best fit as well as regression analysis is proposed.

EXPERIMENTAL

A general purpose epoxy resin (Ciba-Geigy, GY250; epoxide equivalent weight 190), phenol (IDPL), and formaldehyde (Ranbaxy) were used for the synthesis of blends. A reactive polyamide (amine value = 240-400 mg/KOH) was used as the curing agent.

The resoles were synthesized by reacting phenol and formaldehyde in a 1:2.3 molar ratio in basic medium by a general method of preparation [4]. The epoxy resin was mixed with a resole in different weight ratios, i.e., 0/100, 25/75, 50/50, 75/25, and 100/0, based on physical mixing. These blends were cured by adding a requisite amount of polyamide. The degradation kinetics of the blends was studied by thermogravimetric analysis.

The Coats-Redfern [17] equation was used to determine the value of the activation energy (E) and the preexponential factor (Z).

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

where

$$g(\alpha) = \begin{cases} \left(\frac{1 - (1 - \alpha)^{1-n}}{1 - n} \right) & \text{for } n \neq 1 \\ -\log_{10} \{ -\log_{10}(1 - \alpha) \} & \text{for } n = 1 \end{cases}$$

Equation (1) can be reduced to

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

where $Y = \log \left[\frac{g(\alpha)}{T^2} \right]$ for different values of n lying between 0 and 2.0

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

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

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

$$= \frac{W_T - W_f}{W_0 - W_f}$$

where α = fractional weight loss
 W_T = weight at temperature T
 W_f = final weight
 W_0 = initial weight
 R = gas constant

A graph of X vs Y was plotted on the basis of the best fit technique, and the value of n was calculated. This value of n was further confirmed by regression analysis. The value of r (coefficient of correlation) is given by

$$r = \frac{\Sigma(X - \bar{X})(Y - \bar{Y})}{\sqrt{[\Sigma(X - \bar{X})^2][\Sigma(Y - \bar{Y})^2]}} \quad (3)$$

where \bar{X} and \bar{Y} be the mean values of X and Y , respectively.

The synthesized blends have been designated according to the ratio of epoxy and resole (Table 1).

RESULTS AND DISCUSSION

The infrared spectrum of pure resole (ER1) showed the presence of a broad peak in the 3200–3500 cm^{-1} region which might be due to the presence of the phenolic hydroxyl group and the OH group of the opened epoxide group because the epoxy group might undergo homopolymerization in the presence of amine as well as of phenol. As the epoxy is mixed into this, this broad band is still retained due to some unreacted resole in the blend. In all cases the peak corresponding to

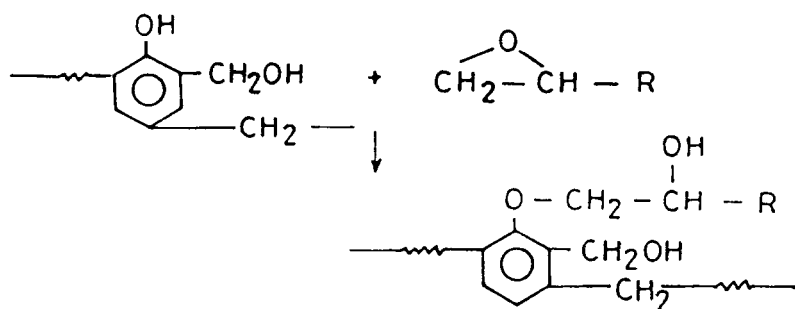
TABLE 1. Synthesized Blends^a

Sample	Blend ratio (E/R)	Sample designation
1	0/100	ER1
2	25/75	ER2
3	50/50	ER3
4	75/25	ER4
5	100/0	ER5

^aE = epoxy; R = resole.

terminal epoxy, i.e., in the 840–970 cm^{-1} region, appeared in the spectra (Fig. 1). The presence of the aliphatic ether group in all blend samples is confirmed by the peak appearing in the 1030–1240 cm^{-1} range. A strong band near 1400 cm^{-1} appeared in all blend samples near 1400 cm^{-1} ; it might be due to hydroxyl methyl phenol in the blends. In the case of pure resole (ER1), the presence of the methylol group in the resin could be confirmed by the peak near 990 cm^{-1} (Fig. 1).

On the basis of above discussion, the following chemical reaction might be expected in the case of blend samples.



The curing process for blends of epoxy and resole is based on reactions between epoxy groups and amide groups in the polyamide. The curing mechanism is supposed to be very similar to that for amines [18]. The cure kinetics of these blends will be presented in our next article.

Kinetic parameters [viz., activation energy (E), preexponential factor (Z), and order of reaction (n)] for the thermal decomposition of the blends of epoxy and resole cured with polyamide have been evaluated by scrutinizing the dynamic thermograms. The fractional decomposition α for the respective temperatures has been calculated from TGA data (Fig. 2). The kinetic parameters of thermal decomposition were deduced by using the integral equation of Coats and Redfern [17]. The order of reaction n was also evaluated from this equation.

The best fit value of n for all sets has been calculated in the 0–2 range by a computational technique. Statistical analysis of the TG data in accordance with the Coats–Redfern equation was done by linear regression analysis and provided the best fit value of n . In all cases the order of reaction was found to be 1 with correlation coefficient r values of -0.987 , -0.990 , -0.989 , -0.989 , and -0.988 for ER1, ER2, ER3, ER4, and ER5, respectively. These results confirm first-order degradation kinetics for all blend samples.

From the slope and intercept values obtained from plots for different blend samples (refer to Fig. 3), the activation energy and preexponential factor have been evaluated for $n = 1$. It is clear from the results that values of the activation energy (E) increase while values of the preexponential factor (Z) decrease as the resole content in the blend decreases from 100 to 0 wt%. The values for E were found to be 23.9 kJ/mol for pure resole and 80.0 kJ/mol for pure epoxy. The activation energy values were found to be 32.0, 38.3, and 57.4 kJ/mol for ER2, ER3, and ER4, respectively. The values for Z were found to be $5.35 \times 10^{11} \text{ min}^{-1}$ for pure resole and $2.0 \times 10^7 \text{ min}^{-1}$ for pure epoxy. The Z values for ER2, ER3, and ER4 were found to be 0.535, 0.204, and $0.015 \times 10^{11} \text{ min}^{-1}$, respectively.

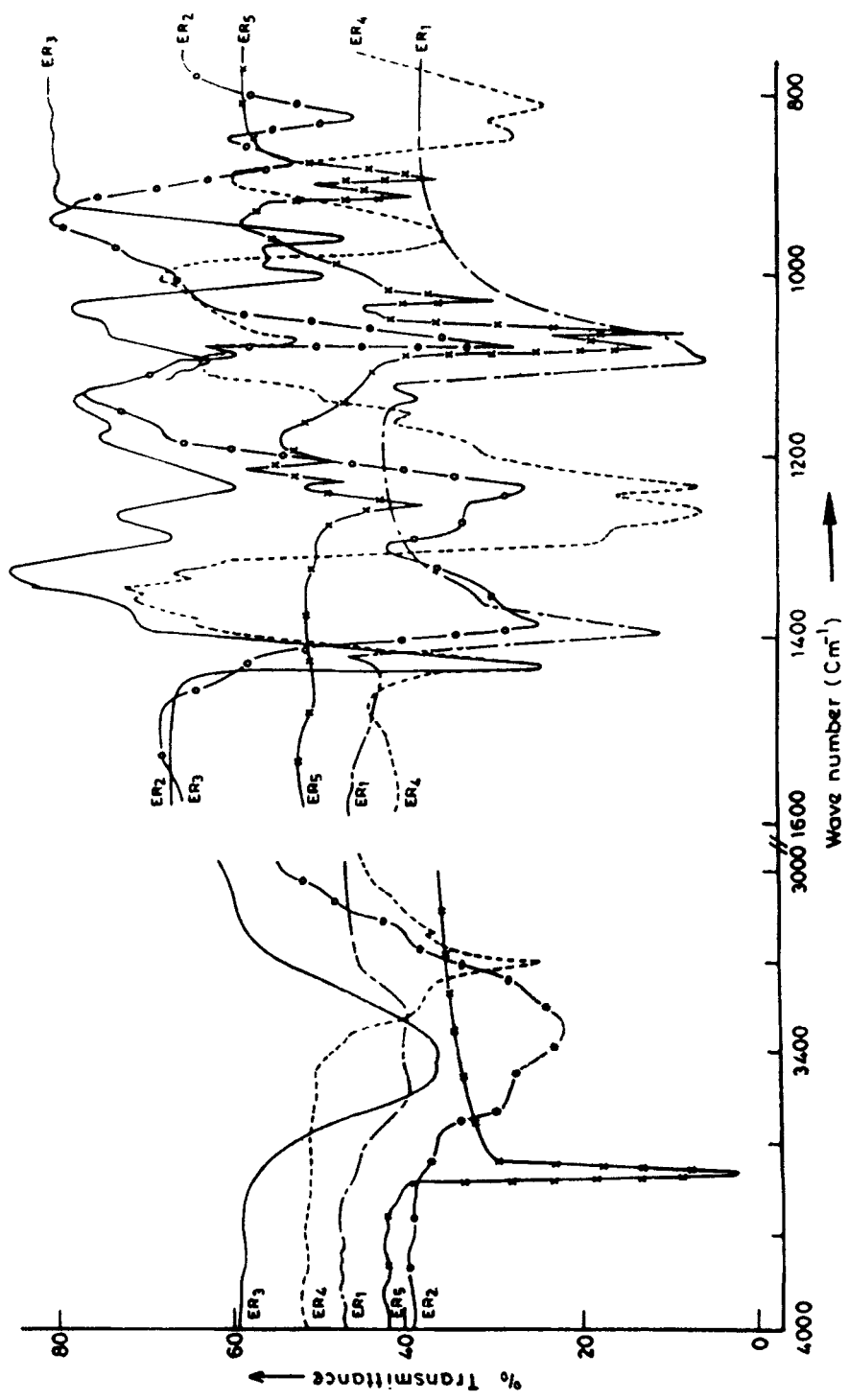


FIG. 1. IR spectrum of blends (ER1 to ER5).

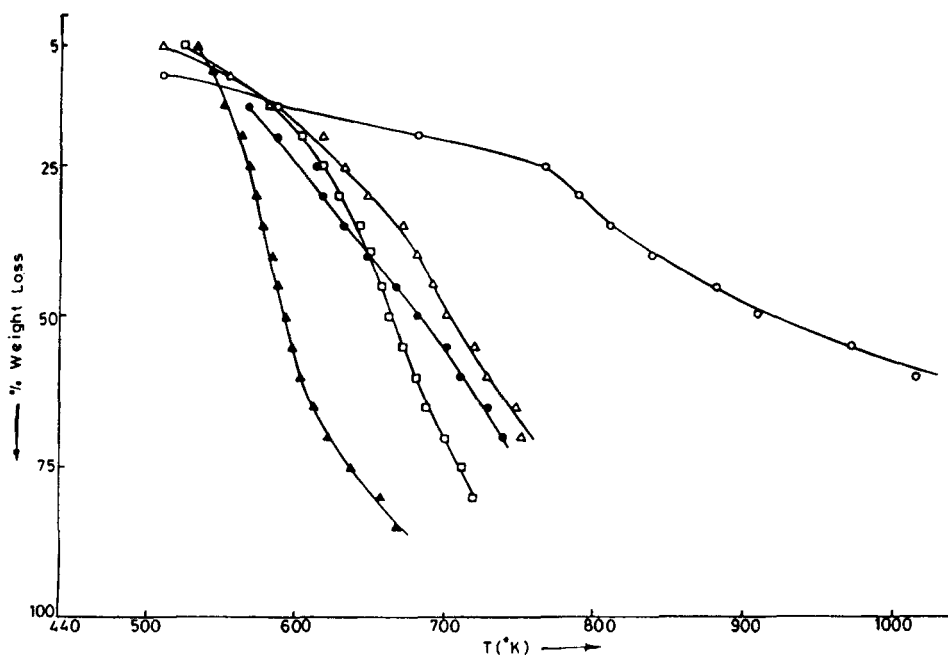


FIG. 2. TGA curves for blend samples: (○) ER1, (△) ER2, (●) ER3, (□) ER4, (▲) ER5.

Higher values of activation energy of the system may be attributed to the presence of polynuclearity in the resin backbone chain. Increasing the activation energy increases the steric hindrance of the molecules of more complex structure of blends as well as of the curing agent. The curing reaction itself is a complex function of the energy of reactive molecules as well as the relative configuration of the reactant molecules that changes during the reaction process. The presence of a polynuclear structure in the backbone may hinder the reaction process. Hence, to obtain a perfectly cured system, high energy is required. High activation energy for the decomposition of blends leads to better thermal stability of the compounds (Table 2). This fact has been evidenced by various workers [6-8] for different

TABLE 2. Data for Blend of Epoxy and Resole (ER1-ER5)

Sample	Composition	IDT, °C	Correlation coefficient r	Activation energy E , J/mol	Preexponential factor $A \times 10^{-11}$ min $^{-1}$
1	ER1	207	-0.987	23.9	5.350
2	ER2	231	-0.990	32.0	0.535
3	ER3	247	-0.989	38.3	0.204
4	ER4	251	-0.989	57.4	0.015
5	ER5	260	-0.988	80.0	0.0002

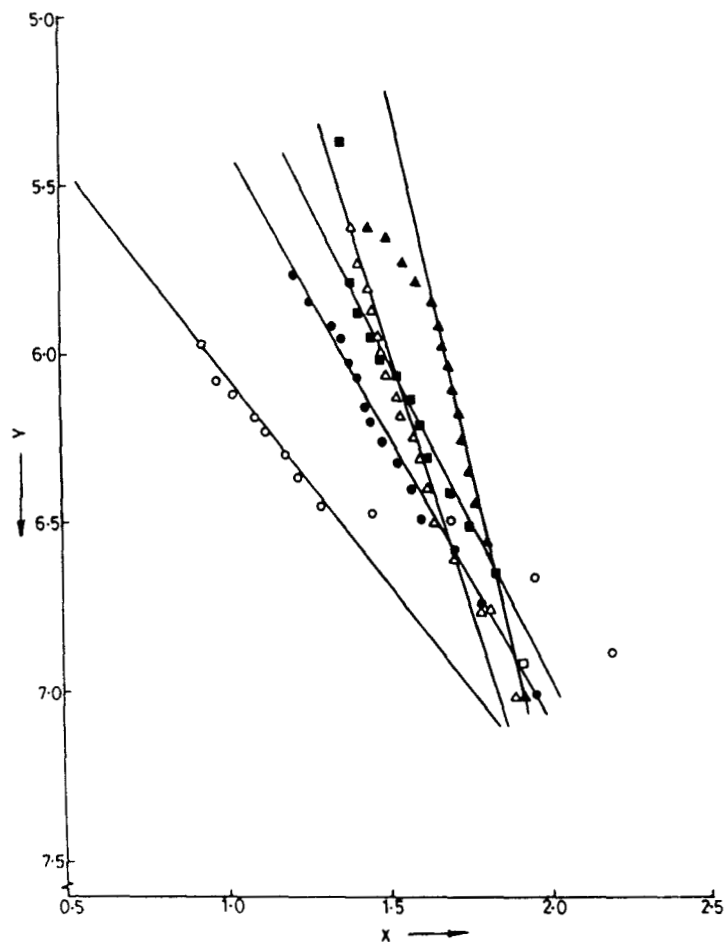


FIG. 3. Plots of X vs Y for $n = 1$: (○) ER1, (●) ER2, (■) ER3, (△) ER4, (▲) ER5.

systems. As the crosslinking density increases, the activation energy of decomposition increases due to the tightly packed structures of the cured polymers. Pure resole showed a lower energy of decomposition based on the less crosslinked structure of the cured polymer due to steric hindrance during the curing reaction process. Higher values of the preexponential factor give rise to a high rate of the curing reaction [9] which might be due to an increased number of collisions which might ultimately to a higher interaction of reactive sites.

CONCLUSIONS

On the basis of preceding results and discussion, the following conclusions may be drawn.

1. Blends of epoxy and resole follow first-order degradation kinetics.
2. The value of n , calculated by best fit analysis, closely resembles that from linear regression analysis.
3. The activation energy shows an increasing trend as the epoxy content in the blend increases, which results in more thermally stable epoxies.
4. Values of the preexponential factor are of the order of 10^{11} min^{-1} , which indicates a high rate of curing reaction.

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Received November 12, 1995

Revision received March 30, 1996