Epoxy/Resole blends—A study of its degradation kinetics

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The degradation kinetics of blends of resole with epoxy resin, having different weight ratios, has been studied by dynamic thermogravimetric analysis in nitrogen atmosphere at a heating rate of 15°C/min. These blends were prepared by physical mixing and were cured with 40% polyamide (based on blend resin and polyamide). The degradation of each sample followed 0.67th order degradation kinetics, which was calculated by Coats and Redfern equation using best-fit analysis. This was further confirmed by linear regression analysis. The validity of data was checked by t-test statistical analysis. From this value of reaction order, activation energy (E) and pre-exponential factor (Z) were calculated. It was found that the activation energy increased while pre-exponential factor decreased as the resole content in the blend decreased from 100 to zero weight percent.

Epoxy resins find applications in wide range of fields such as electrical and electronics, protective coatings, construction industries, composites and others owing to its outstanding properties, encompassing electrical, mechanical and chemical resistance.

In the past years, there have been considerable efforts in the research for techniques to improve the performance of epoxies1,2,11,12. It has become increasingly important to modify an epoxy resin using either thermoplastics or conventional rubbers or elastomers.1-2. Epoxies are also modified with phenolic resole or novolac.13. Resole, because of its poor shelf-life, has very limited applications. The blends of epoxies and resole have a versatile nature and have a great industrial potential. They showed an improvement in their thermo-mechanical and physico-chemical properties.

The degradation behaviour of epoxy and resole has been studied extensively10-13 but the blends of these two need such studies in a much greater details. The mechanism and kinetics of degradation reactions will be helpful for studying the degradation behaviour of such blends. Keeping this in view, various blend compositions of epoxy and resole have been prepared and evaluated their kinetic parameters such as order of degradation reaction, activation energy and pre-exponential factor have been evaluated for developing a reaction kinetics. These parameters were calculated on the basis of best-fit and regression analysis.

**Experimental Procedure**

General purpose epoxy resin (CIBA-GEIGY; GY-250, EEW : 190), phenol (IDPL) and formaldehyde were used during the synthesis of blends. Reactive polyamide (Amine value: 240-400 mg/KOH) was used as curing agent.

Reacting phenol and formaldehyde in the ratio of 1:2.3 (molar ratio) synthesized the resole in basic medium by the method adopted by Lee et al.14. The epoxy resin was mixed with 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 40% polyamide based on total amount i.e. blends and polyamide. The degradation kinetics of blends was studied by thermogravimetric analysis.

The values of activation energy (E) and pre-exponential factor (Z) were determined by Coats and Redfern equation15 (Appendix 1). Best-fit technique was used to calculate the value of order of reaction (n) and confirmed by regression analysis. The synthesized blends have been designated according to the ratio of epoxy and resole (Table 1).

**Results and Discussion**

The infra-red spectrum of pure resole (ER41) (100/0) showed the presence of broad peak in the region of 3200-3500 cm⁻¹ which might be due to the presence of phenolic hydroxyl group and due to the OH group of the opened epoxide. The peak corresponding to terminal epoxy appeared in the region of 840-870 cm⁻¹ in all blend samples (Fig. 1). The appearance of peak in the region of 1030-1240 cm⁻¹ was not observed. The appearance of peak in the region of 1030-1240 cm⁻¹ was not observed.
cm\(^{-1}\) might be due to aliphatic ether group in the blend.

The kinetic parameters viz. order of reaction, activation energy and pre-exponential factor of thermal decomposition of the blends of epoxy and resole cured with polyamide have been evaluated by dynamic thermograms. The fractional decomposition "\(\alpha\)" for the respective temperatures has been calculated from TGA data (Fig. 2) by using the integral equation of Coats and Redfern. If a graph is plotted between X and Y (for \(n\) in the range of 0-2) for all sets, the best-fit value of \(n\) is found to be 0.67 (Fig. 3).
This value of $n$ was further confirmed by linear regression analysis on computer over the TG data in accordance with the values of X and Y obtained from Coats and Redfern equation. The coefficients of correlation $r$ for this order of reaction were found to be 0.96, 0.94, 0.99, 0.95 and .96 for ER41, ER42, ER43, ER44, and ER45, respectively. Other statistical data and related regression equations are given in Table 1. The values of $r$ showed that X and Y are highly correlated.

### Analysis of data

In this section, the significance level of data has been checked. It was done by t-test analysis. In all sets, the calculated value of $t$ was much higher than table value of $t$ at particular degree of freedom (Table 1). It is, therefore, concluded that the experimental data are highly significant (measured at 5% level of significance).

### Activation Energy and pre-exponential factor

From the slope and intercept values obtained from plots (Fig. 3) between X and Y and from the equations obtained from regression analysis (Table 1), the activation energy and pre-exponential factor have been evaluated for $n=0.67$. It is clear from the results that values of the activation energy ($E$) increased while the values of the pre-exponential factor ($Z$) decreased as the resole content in the blend decreased from 100 to 0 wt%. The values of $E$ were found to be 30.4 (calculated) & 28.7 kcal/mol (from plot) for pure resole (ER41) and 76.4 (calculated) & 70.2 kcal/mol (from plot) for pure epoxy (ER45), respectively, whereas the values for $E$ were found to be 36.1, 40.6, and 54.8 (calculated) and 34.2, 38.0, 52.3 (from plot) for ER42, ER43, and ER44, respectively.

The values of $Z$ were found to be 5.083x$10^{12}$ (calculated) and 4.984x$10^{12}$ min$^{-1}$ (from plot) for pure resole and 0.00014x$10^{12}$ and 0.00010x$10^{12}$ min$^{-1}$ for pure epoxy. Other values are indicated in Table 2. It is clear from the results that the calculated values are somewhat deviated from the values obtained from the plots.

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 relative configuration of the reactant molecules that changes during the reaction process. The presence of 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 as evidenced by various workers\textsuperscript{11-13} for different systems. As the crosslinking density increases, the activation energy of decomposition increases due to the lightly packed structures of the cured polymers. Pure resole showed a lower energy of decomposition based on the less crosslinked structure of cured polymer due to steric hindrance during the curing reaction process. Higher values of the preexponential factor give rise to a high rate of curing reaction\textsuperscript{17,18} which might be due to an increased number of collisions which might ultimately lead to a higher interaction of reactive sites.

**Conclusions**

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

The degradation of blends of epoxy and resole proceeds with 0.67th order, which was determined by best-fit and regression analysis.

The obtained data were found to be highly significant i.e. the change in the value of X (temperature) will change the value of Y (activation energy) significantly.

The blends were found to be more thermally stable having high activation energy as the epoxy content in the blend was increased from 0 to 100wt%.

The values of pre-exponential factor have been found to be of the order of $10^{12}$ min$^{-1}$, which indicates a high rate of curing reaction.

**Appendix – I**

The Coats-Redfern equation\textsuperscript{12} was used to determine the value of the activation energy ($E$) and pre-exponential factor ($Z$) as under:

$$\log\left(\frac{g(t)}{T^2}\right) = \log\left[\frac{Z R}{\beta E} \left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{2.3RT} \quad \ldots \quad (1)$$

Where

- $g(\alpha) = \frac{1 - (1-\alpha)^n}{1 - n}$ for $n \neq 1$, and
- $g(\alpha) = \left(-\log_10\left[\log_10(1-\alpha)\right]\right)$ for $n = 1$

Eq. (1) can be reduced to

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

Where,

$$Y = \log_{10}\left[\frac{g(\alpha)}{T^2}\right]$$

for different values of $n$ lying between zero to 2.0

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

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

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

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

$\alpha$ = fractional weight loss, $w_i$ = weight at temperature $T$, $w_f$ = final weight, $w_o$ = initial weight

$R$ = Gas constant (8.314 J deg$^{-1}$ mol$^{-1}$ K$^{-1}$)

A graph of $X$ and $Y$ was plotted on the basis of best fit technique, and the value of $n$ was calculated. This value of $n$ was further confirmed by regression analysis.

The coefficient of correlation ($r$) is given by

$$r = \frac{\sum(x - \bar{x})(y - \bar{y})}{\sqrt{\sum(x - \bar{x})^2 \sum(y - \bar{y})^2}}$$

The values of $r$ can be obtained as,

$$r = \frac{\text{Regression coefficient}}{\text{Standard error of coefficient}}$$

If the calculated value of $r$ be greater than or equal to the table value of $r$, the data are considered to be significant.

**References**