Effect of unsaturated acids on the properties of epoxy resins: Synthesis and characterization

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The effect of unsaturated aliphatic and aromatic acids such as acrylic acid and cinnamic acid on the properties of epoxy resins has been studied by synthesizing related resins in their presence at 110±2°C. These resins have been characterized by IR, 1H NMR, spectroscopy by the thermal analysis. The reactions follows first order kinetics with activation energy 53 and 92 kJ mol⁻¹ for resins containing cinnamic acid and acrylic acid, respectively. The characteristic value, such as epoxide equivalent, specific viscosity increased in the presence of acids due to formation of β-hydroxy ester of diglycidial ether of bisphenol A. However, the hydroxyl content and hydrolyzable chlorine content decreased due to formation of diester of propanol 2 and poly(acryloyl-chloride).

Epoxide resins, having good mechanical thermal and electrical properties, are widely used as engineering materials. It is important to investigate and understand the relationship between structure and properties of epoxy resins for their most appropriate applications. The present paper highlights some aspects of synthesis of epoxy resins in the presence of aliphatic and aromatic unsaturated acid covering structure-properties relationship along with elucidation of mechanism.

Experimental Procedure

Materials
Epichlorohydrin, dioxan, acetone, methanol (Ranbaxy), pyridine (Nice), bisphenol A (Robert Johnson) acrylic acid (Merck), acetyl chloride (Qualigens), cinnamic acid (Loba) were obtained from commercial source and used as received.

Method

Epoxy Resins Synthesis—The epoxy resins were synthesised at 110±2°C according to the method of Lee and Neville using the following amount of reactants.

1. Epichlorohydrin (0.18), bisphenol A (0.018 mol) sodium hydroxide (0.15 mol) and cinnamic acid (3.6×10⁻², 7.2×10⁻², 1.08×10⁻¹, 1.45×10⁻¹ mol). Sodium hydroxide (0.15 mol) bisphenol A (0.018 mol)

2. Epichlorohydrin (0.18 mol), cinnamic acid (3.6×10⁻² mol) sodium hydroxide (0.15 mol) and bisphenol A (0.018 mol).

3. Epichlorohydrin (0.18 mol), acrylic acid (3.6×10⁻² mol) and sodium hydroxide (0.15 mol).

The epoxy resins were characterized as below:

Epoxide equivalent (EE) — EE of various resins was determined by the pyridinium chloride method, which include addition of pyridinium chloride (0.2 N, 2.5 mL) solution of epoxy resins (0.5 g). It was then stirred and refluxed for 25 min followed by addition of 50 mL methanol through condenser and titrated against methanolic NaOH (0.5 M). Blank was used without epoxy resins. The epoxide equivalent was calculated by following formula:

\[
\text{Epoxide equivalent} = \frac{16 \times \text{weight of sample}}{\text{Weight of oxiran oxygen in sample}}
\]

The weight of oxiran oxygen sample=(A-B) (0.16)N

\[
A=\text{mL of methanolic NaOH for blank}
B=\text{mL of methanolic NaOH for sample}
N=\text{Normality of NaOH}
0.016=\text{Miliequivalent of oxygen in g.}
\]

Hydroxyl content — Hydroxyl content was
determined by Acetyl chloride method and using the following formulae:\(^{12}\)

\[
\text{Hydroxyl content} = \frac{\text{weight of sample}}{\text{Normality of NaOH} \times (V_1 - V_2) \times 170}
\]

\(V_1 = \text{the volume of methanolic NaOH used for the blank}\)
\(V_2 = \text{the volume of the methanolic used for the sample}\).

Hydrolyzable chlorine content—Dehydrohalogenation method is used for determination of chlorine content of various resins using the following formula\(^{12}\):

\[
\text{Hydrolyzable chlorine content} (\%) = \frac{355 \times 10^{-4} \times N \times \text{volume of KOH neutralized by epoxy resins}}{\text{weight of sample}}
\]

**Infrared Spectra**—The IR spectrum was recorded on a Perkin Elmer Spectrophotometer (model 377).

**\(^1\)H NMR Spectra**—\(^1\)H NMR spectra were recorded on varian EM 390 spectrophotometer.

**Viscosity**—Ubbelohde viscometer and Abbe Refractometer were used to determine viscosity (in dioxan 40% w/v) and refractive index, respectively.

**Results and Discussion**

No reaction occurred between epichlorohydrin and acrylic acid. However, the reaction of epichlorohydrin with bisphenol A in the presence of cinnamic acid/acrylic acid yielded epoxy resin along with a white solid as single component product. The solid was separated from epoxy resins by filtration and identified as poly(acryloyl chloride) on the basis of following data:

It contains chlorine (37.02% in acrylic acid and 20.70% in cinnamic acid) and decolourised Baeyer's reagent. It does not melt up to 250°C. On the basis of IR and \(^1\)H NMR spectral analysis following structure may be assigned to the solid:

\[
\begin{array}{c}
\text{-(R-CH-CH)}_n \quad \text{-(RCH-C)}_n \text{H}_n \\
\text{Cl-C=O} \quad \text{Cl-C-OH} \\
\text{(Keto form)} \quad \text{(enol form)} \\
\end{array}
\]

Fig 1 shows the characteristic band position of white solid by IR spectroscopy:

- 770 cm\(^{-1}\) (C-Cl), 1580 cm\(^{-1}\) (C-C, phenyl group), 1650 cm\(^{-1}\) (C=C), 2900-3000 cm\(^{-1}\) (methylene group), 3020 cm\(^{-1}\) (C-H, phenyl group), 1780 cm\(^{-1}\) (C=C-Cl), 1100-1350 cm\(^{-1}\) (OH, primary alcohol) The following band positions have been observed in \(^1\)H NMR spectrum (Fig 2)

\[
2.0 \delta (\text{m, methylene, protons}), 4.0 \delta (\delta, \text{OH proton}) 7.0-8.5 \delta (\text{m, aromatic protons})
\]

Table 1 shows that the blank epoxy resins as well as those containing acrylic acid/cinnamic acid are amber coloured. The refractive indices of epoxy resins derived from cinnamic acid, and acrylic acid are marginally higher as compared with the blank epoxy resins. Table 1 further reveals that the epoxide equivalent of epoxy resins is in the order ER(i) > ER(ii) > ER(iii) > epoxy resins containing propionic acid\(^{13}\) > epoxy resins containing benzoic acid\(^{13}\) > blank, which may be due to formation of β hydroxyester of diglycidal ether of bisphenol A [B] (Reaction Scheme A)
Mechanism 'A' for epoxy resin formation in the presence of cinnamic acid and acrylic acid.

Step I: Bisphenol A react with epichlorohydrin and acid to give X, Y and Z product.

\[ \text{Bisphenol A} (BA) + \text{Epichlorohydrin} (ECH) + \text{Acid}(R=H \text{ or } C_6H_5) \]
\[ \rightarrow \text{Product [X]} \]


Step III: Product [Y] formed in Step I react with acid and give 1,3 diester of propanol-2 [C]

Step IV: Acryloyl chloride [Z] formed in Step I exist in keto and enol form was polymerized at 150°C to give poly(acryloyl chloride)
However, the higher value of EE for ER (i) in comparison to ER (ii) may be attributed to the greater acidic nature of cinnamic acid than acrylic acid. In both cases ER (i) and ER (ii) the EE decreases on increasing the molar concentration of acid (S) during resinification. It is probably due to the reaction between epichlorohydrin and acid\textsuperscript{14} rather than less acidic bisphenol A. Which results the formation of more 1, 3 diester of propanol 2 in comparison to $\beta$ hydroxydiester of DGEBA and DGEBA. The formation of these products were confirmed by thin layer chromatography.

Table 2 shows a comparative chart of epoxy resins containing unsaturated/saturated acids\textsuperscript{13}. The lower value of hydroxyl content of epoxy resins containing cinnamic acid/acrylic acid/propionic acid\textsuperscript{13}/benzoic acid\textsuperscript{13}, also supported the formation of these products were confirmed by thin layer chromatography.

\[\text{Mechanism 'B': epoxy resins have been formed by the reaction of cinnamic acid and epichlorohydrin.}\]

\[
\begin{align*}
\text{Cinnamic acid} & \quad + \quad \text{Epichlorohydrin (ECH)} \\
& \quad \xrightarrow{\text{NaOH}} \\
& \quad \text{NaCl} \\
& \quad \text{NaOH} \\
& \quad \text{ECH} \\
& \quad \text{NaCl} \\
\end{align*}
\]

\[\text{1,3-Diester (3-phenylpropan-1) propanol 2 (b)}\]

![Fig. 3—IR spectrum of epoxy resins containing 0.07 mol cinnamic acid (ER\textsubscript{A2})](image)

![Fig. 4—\textsuperscript{1}H NMR spectrum of epoxy resins containing 0.07 mol cinnamic acid (ER\textsubscript{A2})](image)

<table>
<thead>
<tr>
<th>Table 1—Characteristic of epoxy resin</th>
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<tr>
<td>Properties</td>
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</tr>
<tr>
<td>Properties</td>
</tr>
<tr>
<td>Molar concentration of acid</td>
</tr>
<tr>
<td>Colour</td>
</tr>
<tr>
<td>Refractive Index</td>
</tr>
<tr>
<td>Epoxide equivalent(eq/100g) (after treatment of NaHCO\textsubscript{3})</td>
</tr>
<tr>
<td>Hydroxyl content(eq/100)</td>
</tr>
<tr>
<td>Chlorine content(wt.%)</td>
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<tr>
<td>Viscosity (30°C)</td>
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<tr>
<td>Specific gravity</td>
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</table>
of [B] and [C] product (Reaction Scheme A) during synthesis. Similarly, the lower value of hydrolyzable chlorine content of epoxy resins containing acrylic acid/cinnamic acid confirms the formation of acryloyl chloride, which undergoes polymerization at 150°C after distillation. However, the hydrolyzable chlorine content of ER (iii) is greater than that of blank which indicates the possibility of side reaction of epichlorohydrin.

Based on the above discussion two specualation mechanism can be proposed for (i), (ii) and (iii) cases.

**Structural evidence for epoxy resins**—IR spectra (Figs 3 and 4) of epoxy resins containing acid (cinnamic acid and acrylic acid) are reported below.

900-950 cm⁻¹ (epoxy group), 1250 cm⁻¹ (ether group), 1650-1670 cm⁻¹ (carboxylic group), 1580-

<table>
<thead>
<tr>
<th>Properties</th>
<th>Blank</th>
<th>Unsaturated acid</th>
<th>Saturated acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar concentration of acid</td>
<td>0.0</td>
<td>Acrylic acid 0.04</td>
<td>Cinnamic acid 0.04</td>
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<tr>
<td>Colour</td>
<td>Amber</td>
<td>Amber</td>
<td>Amber</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.5695</td>
<td>1.512</td>
<td>1.552</td>
</tr>
<tr>
<td>Epoxide equivalent</td>
<td>194</td>
<td>1651</td>
<td>3028</td>
</tr>
<tr>
<td>Hydroxyl content</td>
<td>0.12</td>
<td>0.0006</td>
<td>0.001</td>
</tr>
<tr>
<td>Chlorine content</td>
<td>0.5</td>
<td>0.0775</td>
<td>0.1035</td>
</tr>
<tr>
<td>Viscosity (130°C)</td>
<td>1.58</td>
<td>2.3</td>
<td>2.5</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.173</td>
<td>1.13</td>
<td>1.12</td>
</tr>
</tbody>
</table>

**Table 2—Comparative chart of epoxy resins containing unsaturated/saturated acids.**

**Fig. 5**—IR spectrum of epoxy resins containing 0.041 mol acrylic acid (ER₅₁).

**Fig. 6**—¹H NMR spectrum of epoxy resins containing 0.041 mol acrylic acid (ER₅₁).

**Fig. 7**—IR spectrum of epoxy resins derived from cinnamic acid and epichlorohydrin (ER₅₆).

**Fig. 8**—¹H NMR spectrum of epoxy resins derived from cinnamic acid and epichlorohydrin (ER₅₆).
1600 cm\(^{-1}\) (C-C, phenyl group), 2900-3000 cm\(^{-1}\) (methyl and methylenes group), 3000-3020 cm\(^{-1}\) (C-H, phenyl group), 3500 cm\(^{-1}\) (OH, alcoholic group) IR spectra of epoxy resins containing acid (S) show the virtually additional absorption band due to carboxylic group at 1650-1670 cm\(^{-1}\) showing thereby the formation of \(\beta\)-hydroxy ester of deglycidal ether of besphenol A (B) and 1, 3 diester of propanol -2 (C) (Reaction scheme A).

Figs 5 and 6 show the \(^1\)H NMR spectra of epoxy resins containing acrylic acid and cinnamic acid. The following band position has been noticed \(^1\)HNMR spectra:

- 2.0-3.0 \(\delta\) (m, epoxy protons), 3.5-4.0 \(\delta\) (m, methylene and CH=CH\(_2\) conjugated protons), 5.7-6.5 \(\delta\) (m, hydroxy protons) 6.9 - 8.0 \(\delta\) (m, aromatic protons). The peak area ratio about 5.7-6.5 \(\delta\) due to hydroxyl protons in ERA\(_2\) (3.1 cm) and ERB\(_1\) (1.8 cm) is lower than that of blank (6.1 cm) epoxy resins. This observation supported the lower value of hydroxyl content in the presence of acid(s) calculated by acetyl chloride method.

The presence of a bond at 900 cm\(^{-1}\) in the IR spectrum (Fig.7) of epoxy resins synthesised by cinnamic acid and epichloride (ER\(_{iii}\)) confirms the presence of epoxy rings. The band at 1250 cm\(^{-1}\) due to presence of the ether group and an additional band at 1600-1650 cm\(^{-1}\) due to carboxylic group confirm the presence of cinnamic acid in resins. The \(^1\)HNMR spectrum of ER\(_{iii}\) (Fig.8) shows peak in region \(\delta=2.0\) ppm. Which could be attributed to the epoxide protons. The spectra show aromatic signals at \(\delta=1-2\) ppm.

**Thermogravimetric analysis**—The effect of unsaturated aliphatic and aromatic acid on the thermal stability of epoxy resins was studied by TGA (Fig. 9). The epoxy resins containing cinnamic acid (280°C) is more stable in comparison of blank epoxy resins\(^7,8\) (130°C) and resins containing acrylic acid (285°C). The rapid decomposition was observed around 300 to 500°C and almost total volatilization occurred above 500°C temperature in ER\(_{iii}\). However, in the case of ER\(_{iii}\) the rapid decomposition was observed around 385 to 565°C and almost total volatilization occurred above 565°C. These data confirm that the incorporation of the selected acids in the reactants and consequent modification of epoxy resins system by them resulted in increase in thermal stability of the epoxy resins.

**Kinetics**

The activation energy (\(\Delta E\)) and order of reaction
was calculated by Coats and Redfern equation\textsuperscript{15} according to which

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

\[ g = \left(-\log(1-\alpha)^{1/n}\right) \]

The plot of \( \log \left[ \frac{g}{T^2} \right] \) versus \( \frac{1}{T \times 10^3} \) gives a linear curve. Its slope is equal to \( \Delta E / 2.3RT \) and its intercept gives \( \log_{10} \frac{ZR}{\beta\Delta E} \left( 1 - \frac{2RT}{\Delta E} \right) \)

Where \( \Delta E \) = Apparent activation energy
\( \beta \) = linear heating rate
\( Z \) = pre-exponential factor
\( n \) = order of reaction

The activation energy, calculated from the slope of the linear graph plotted between \( \log g(\alpha) \) versus \( 1/T \times 10^3 \) (Fig.10a,b). The activation energy of modified epoxy resins containing 0.36 mol of cinnamic acid and acrylic acid is higher (53, kJ mol\textsuperscript{-1} and 92 kJ mol\textsuperscript{-1} respectively) than that of blank epoxy resins (34 kJ mol\textsuperscript{-1}). The overall reaction for both blank\textsuperscript{7} and modified resins follows first order kinetics.

\textbf{Reference}