CHAPTER - IV
MODIFICATION OF EPOXY RESIN USING NITROGEN YLIDE:
SYNTHESIS & CHARACTERIZATION*

The modification of epoxy resin which have been widely used as structural adhesives has been subject of interest. A perusal of literature reveals that although, a number of research publications have been documented the effect of various modifiers on the properties of epoxy resins. However, to the best of our knowledge the effects of nitrogen ylide on the synthesis and properties of modified epoxy resin has not been reported so far probably due to the difficulty associated with the synthesis of nitrogen ylide ($\alpha$-PBPy). The present system focuses the comprehensive study of effect of $\alpha$-picolinium-p.bromophenacylide ($\alpha$-PBPy) on the synthesis & properties of epoxy resin.

(1) Effect of $\alpha$-PBPy on the physical properties of epoxy resin:

Physical properties of the resins have been listed in Table IV:4:1 when the epoxidation was carried out, the reaction becomes highly viscous liquid. It has been found that blank epoxy resin (ER$_1$) is pale yellow coloured but as the molar equivalents of nitrogen ylide increases the colour of resin (ER$_2$, ER$_3$, ER$_4$) changes from dark brown in colour. The refractive index of modified epoxy resins range from 1.395 to 1.385, which is less than the observed for blank resin.

* A part of this work has been communicated in "High Performance Polymer" Published by B.P.Chemicals(Hitco) Inc. California (U.S.A.).
(II) **Characterization:**

The effect of [α-PBPy] on the properties of epoxy resin has been studied and expressed in the Table IV:4:2.

The effect of [α-PBPy] on the values of the epoxy equivalent, hydroxyl content, hydrolyzable chloride content and viscosity of epoxy resins decrease as function of molar equivalent of nitrogen ylide (α-PBPy). The decrease in epoxide equivalent in the presence of α-PBPy may be attributed the fact that, the ylide might have reacted with bisphenol-A/epichlorohydrin or both and there by decreases the concentration of reactants epoxidation.

In order to confirm it, the ylide was stirred and refluxed with bisphenol-A for 3½h and then this bisphenol-A was used to prepare epoxy resin (ER₅) with epichlorohydrin. The epoxide equivalent weight of this ER₅ was 168 which is similar to that ER₂ (170). On the other side, when the epichlorohydrin was used to prepare epoxy resin (ER₆) with bisphenol-A, the epoxide equivalent weight was 190 which is near about to ER₁ (196).

Therefore, it can be concluded that the reaction of α-PBPy with bisphenol-A results in decrease of epoxidation hence epoxide equivalent weight decrease.
The values (Table IV:4:2) for viscosity (\( \eta_{sp} \)), decreases with increase in [\( \alpha - \text{PBPy} \)] in the epoxy resin. (Fig.IV:4:1) gives the variation of viscosity (\( \eta_{sp} \)) with temperature for various epoxy resins. No significant difference in viscosity was observed for the epoxy resin (ER\(_2\), ER\(_3\) & ER\(_4\)) with an increase in molar equivalent of \( \alpha - \text{PBPy} \).

(III) Spectral Studies:

IR : KBr, \( \text{cm}^{-1} \) (Fig.IV:4:2)

(Perkin Elmer-1320 Spectrophotometer)

(1) 920 \( \text{cm}^{-1} \) (Epoxy ring)
(2) 1760 \( \text{cm}^{-1} \) (>C=O, group of acrylate)
(3) 3400 \( \text{cm}^{-1} \) (-OH group)
(4) 3030 \( \text{cm}^{-1} \) (-C\(_6\)H\(_5\) aromatic)

\(^1\text{H-NMR: } \text{CdCl}_3, \text{TMS, } \delta \text{ ppm (Fig.IV:4:3)}\)

(Jeol JNM-PMX 60 Spectrophotometer)

(1) 2.7-3.0 (m, epoxy protons)
(2) 7.0-7.3 (m, aromatic protons)
(3) 1.6 (S, CH\(_3\))
(4) 1.0-2.0 (m, methyl protons)

(IV) Curing:

Resins ER\(_2\), ER\(_3\), ER\(_4\) and DGEBA (ER\(_1\)) were cured with polyamide for 24h at 30\(^\circ\)C.
FIG.IV:4:1 PLOT OF $\eta_{sp}$ VS. TEMPERATURE OF EPOXY RESIN ER$_1$ TO ER$_4$
FIG. IV:4:2  IR-SPECTRUM OF EPOXY RESIN IN PRESENCE OF α-PICOLINUM P-BROMOPHENACYLIDE
FIG. IV: 3 \textit{H}-NMR SPECTRUM OF EPOXY RESIN IN PRESENCE OF \textit{O}-PICOLINIMIDE

\textit{P. BROMOPHENACYLIDE}
(V) **Solubility and Chemical resistance:**

Table IV:4:3 shows the solubility and chemical resistance of film (0.1 mm thick) of blank (ER$_1$) and modified epoxy resins (ER$_2$ to ER$_4$), when submerged for 7 days in polar and nonpolar solvents. It is clear that, the modified epoxy resins retain flexibility and appearance, i.e. they have good solvent resistance. However, absorption was observed when they were submerged in dioxane, toluene and hydrochloric acid (1M) which may be due to increased flexibility of the polymer chain.

(VI) **Corrosion, Flexibility and Scratch Hardness:**

The influence of varying concentration of modified epoxy resin on the corrosion test, flexibility and scratch hardness illustrated in the table IV:4:3, shows that all the resin samples pass corrosion test & the flexibility test also passed. The scratch hardness increases as the molar equivalent of ylide ($\alpha$-PBPY) in the epoxy resin increases. The films of modified resins were resistant to scratch hardness as the molar equivalent of ylide in epoxy resin increased.

(VII) **Thermal Properties:**

The effect of $\alpha$-picolinium- p.bromophenacylide on the thermal stability of the epoxy resin is studied by thermogravimetric analysis.
Thermogravimetric curve (Fig.IV:4:5) shows that blank epoxy is stable upto 130°C and it started losing weight above this temperature. However, resin sample containing (ER₂) molar equivalents of α-PBPy was stable upto 125°C and it started decomposition was observed around 350°C to 400°C whereas in modified epoxy resin, ER₄, rapid decomposition was observed around 325°C to 425°C and almost total volatilization of the polymer occurred around 600°C. Initial weight loss (2-5%) was observed around 200°C in modified epoxy resin ER₂ and at 130°C in blank epoxy resin, which confirms that incorporation of α-PCPy increases thermal stability of the polymer.

Thermal stability of the resin was further confirmed by weight loss measurements at 200°C at different time intervals illustrated in Fig.IV:4:4. It increases in the order of epoxy ER₄ > ER₃ > ER₂ > DGEBA. It was noticed that weight loss of DGEBA reaches thrice that of epoxy resin containing zero molar equivalents of α-PBPy in five hours. This further confirms that epoxy resin, modified with varying concentration of α-PBPy is thermally very stable than blank epoxy resin.

(VIII) Glass Transition Temperature (Tg):

The glass transition temperature (Tg) is an important characteristic of polymer. This is the temperature at which amorphous material changes from a
FIG.IV:4.4 PLOT OF WEIGHT LOSS VS. TIME FOR BLANK EPOXY
(◊) AND DIFFERENT [aC-PBPY] AT 200°C
FIG. IV:4:5 T.G.A. THERMOGRAM OF EPOXY RESIN OF
$ER_2$ TO $ER_4$
brittle viterous state to a plastic state. The $T_g$ of blank epoxy resin is 130°C for modified system $T_g$ increases 135°C with the incorporation of $(ER_4)$ 25.68 molar equivalents of $\alpha$-PBPY as depicted in Table IV:4:5. & Fig. IV:4:6.

**Conclusion:**

In the light of above discussion it may be concluded that -

(a) Novel epoxy resin containing nitrogen have been synthesized by reacting ($\alpha$-PBPY) ylide with bisphenol-A and epichlorohydrin.

(b) $\alpha$-PBPY is inversaly proportional to epoxide equivalent weight, molecular weight, hydroxyl content and chlorine content.

(c) The modified epoxy resin have better thermal properties in comparison to blank epoxy resin.

(d) The modified epoxy resin have dark brown colour, viscous liquid state and refractive index low in comparison to unmodified epoxy resin.
Table IV:4:1

Physical properties of epoxy resin

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Property</th>
<th>ER₁</th>
<th>ER₂</th>
<th>ER₃</th>
<th>ER₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Colour</td>
<td>Pale yellow</td>
<td>Dark brown</td>
<td>Dark brown</td>
<td>Dark brown</td>
</tr>
<tr>
<td>2.</td>
<td>State</td>
<td>Highly viscous liquid</td>
<td>Viscous liquid</td>
<td>Viscous liquid</td>
<td>Viscous liquid</td>
</tr>
<tr>
<td>3.</td>
<td>Refractive index (at 30°C)</td>
<td>1.571</td>
<td>1.395</td>
<td>1.388</td>
<td>1.385</td>
</tr>
</tbody>
</table>
**Table: IV: 4: 2**

Various properties of epoxy resins

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Properties</th>
<th>ER₁</th>
<th>ER₂</th>
<th>ER₃</th>
<th>ER₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Epoxide equivalent weight (eq/100g)</td>
<td>196</td>
<td>170</td>
<td>157</td>
<td>148</td>
</tr>
<tr>
<td>2.</td>
<td>Molecular weight</td>
<td>392</td>
<td>340</td>
<td>314</td>
<td>296</td>
</tr>
<tr>
<td>3.</td>
<td>Hydroxyl content (eq/100g)</td>
<td>0.14</td>
<td>0.10</td>
<td>0.086</td>
<td>0.074</td>
</tr>
<tr>
<td>4.</td>
<td>Chlorine content (%)</td>
<td>0.5</td>
<td>0.8</td>
<td>0.7</td>
<td>0.6</td>
</tr>
<tr>
<td>5.</td>
<td>Specific gravity (25°C)</td>
<td>1.1765</td>
<td>1.1177</td>
<td>1.1017</td>
<td>1.0902</td>
</tr>
<tr>
<td>6.</td>
<td>Viscosity ((\gamma)ₚₑ) (at 50°C)</td>
<td>1.24</td>
<td>1.15</td>
<td>1.08</td>
<td>1.02</td>
</tr>
</tbody>
</table>

\[\alpha-\text{PBPY}) \times 10^{-4}\]:

- \(\text{ER}_1 = \) Zero,
- \(\text{ER}_2 = 8.56\)
- \(\text{ER}_3 = 17.12\),
- \(\text{ER}_4 = 25.68\)
### Table IV: 4: 3

Solubility and chemical resistance of epoxy resin

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Chemicals</th>
<th>ER₁</th>
<th>ER₂</th>
<th>ER₄</th>
<th>ER₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Hydrochloric acid (N)</td>
<td>--</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>2.</td>
<td>Sulfuric acid (N)</td>
<td>++</td>
<td>+--</td>
<td>+--</td>
<td>+--</td>
</tr>
<tr>
<td>3.</td>
<td>Nitric acid (N)</td>
<td>++</td>
<td>+--</td>
<td>+--</td>
<td>+--</td>
</tr>
<tr>
<td>4.</td>
<td>Sodium hydroxide (30%)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>5.</td>
<td>CCl₄</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>6.</td>
<td>Benzene</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

**++** Non soluble

**--** Soluble

**+-** Slightly soluble
### Table IV:4:4

Properties of epoxy resin films caused with polyamide

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Properties</th>
<th>ER₁</th>
<th>ER₂</th>
<th>ER₃</th>
<th>ER₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Corrosion</td>
<td>Passed</td>
<td>Passed</td>
<td>Passed</td>
<td>Passed</td>
</tr>
<tr>
<td>2.</td>
<td>Scratch hardness</td>
<td>1000</td>
<td>1100</td>
<td>1250</td>
<td>1300</td>
</tr>
<tr>
<td></td>
<td>(g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Flexibility**</td>
<td>Passed</td>
<td>Passed</td>
<td>Passed</td>
<td>Passed</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Mechanically operated scratch hardness tester.

** Mandrel (6.35 mm)