CHAPTER 2
SYNTHESSES OF
MONOMERS, EPOXY AND
VINYL ESTER RESINS
CHAPTER 2

Syntheses of Monomers, Epoxy and Vinyl Ester Resins

This chapter is further subdivided into four sections:

Section 2.1: Synthesis of 1,1'-bis(4-hydroxyphenyl) cyclohexane
[Bisphenol-C]

Section 2.2: Synthesis of liquid epoxy resin of bisphenol-C

Section 2.3: Synthesis of vinyl ester resin

Section 2.4: Characterization of vinyl ester resins

Section 2.5: Curing study of styrenated vinyl ester resin

Materials

All solvents and chemicals used in the present work were of laboratory grades and purified or crystallized by appropriate methods or used as such. Physical properties of some of the raw materials used are presented in Table-2.1.

Section 2.1: Synthesis of 1,1'-bis(4-hydroxyphenyl)cyclohexane
[Bisphenol-C]

1, 1'- Bis(4-hydroxyphenyl) cyclohexane (bisphenol-C) here after designated as BC was synthesized according to reported method [1, 2]. Thus, 0.5 mol (49 g) cyclohexanone was treated with 1.0 mol (94 g) phenol in the presence of mixture of HCl :CH₂COOH (2:1 v/v, 100:50 ml) as a Friedel-Craft catalyst at 55 °C for 4 h. The pink colored product was filtered, washed well with boiling water and treated with 2N NaOH solution, and then resinous material was removed by filtration through cotton plug. The yellowish solution so obtained was acidified with dilute sulfuric acid, filtered, washed well with water and dried at 50°C. BC was further crystallized repeatedly from toluene and methanol-water systems to get pure, white, shining crystals of ~81% yield and m.p. 186°C.
Table 2.1: Physical properties of some of the raw materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>B.P., C</th>
<th>M.P., C</th>
<th>M.W., g/mol</th>
<th>Density, g/cm³</th>
<th>Physical state</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexanone</td>
<td>126</td>
<td>16</td>
<td>60.5</td>
<td>1.05</td>
<td>Color less liquid</td>
</tr>
<tr>
<td>Phenol</td>
<td>181.7</td>
<td>40.5</td>
<td>94.11</td>
<td>1.07</td>
<td>Transparent crystalline solid</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>50.5 @ 37%</td>
<td>-114.2</td>
<td>36.46</td>
<td>1.49</td>
<td>liquid</td>
</tr>
<tr>
<td>Bisphenol-C</td>
<td>220</td>
<td>186</td>
<td>268</td>
<td></td>
<td>White shining crystal</td>
</tr>
<tr>
<td>Epichlorohydrin</td>
<td>117.9</td>
<td>25.6</td>
<td>92.52</td>
<td>1.18</td>
<td>color less liquid</td>
</tr>
<tr>
<td>Methacrylic acid</td>
<td>161</td>
<td>-15</td>
<td>86.06</td>
<td>1.02</td>
<td>color less liquid</td>
</tr>
<tr>
<td>Hydroquinone</td>
<td>285</td>
<td>175</td>
<td>101</td>
<td>1.3</td>
<td>White solid</td>
</tr>
<tr>
<td>Methyl ether hydroquinone</td>
<td>243</td>
<td>53</td>
<td>124</td>
<td>1.33</td>
<td>White solid</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>88.8</td>
<td>-115</td>
<td>101.01</td>
<td>0.75</td>
<td>color less liquid</td>
</tr>
<tr>
<td>Styrene</td>
<td>145</td>
<td>-31</td>
<td>104.15</td>
<td>0.909</td>
<td>color less liquid</td>
</tr>
<tr>
<td>Benzoyleperoxide</td>
<td>103</td>
<td>exploded</td>
<td>242.33</td>
<td>1.33</td>
<td>color less liquid</td>
</tr>
<tr>
<td>Methyl ethylketone peroxide</td>
<td>117.9</td>
<td>-25.6</td>
<td>210.22</td>
<td>1.17</td>
<td>color less oily liquid</td>
</tr>
<tr>
<td>Cobalt octoate</td>
<td>148-205</td>
<td>Unknown*</td>
<td>210.22</td>
<td>0.85</td>
<td>clear violet liquid</td>
</tr>
<tr>
<td>N,N Dimethyl aniline (DMA)</td>
<td>193-194</td>
<td>-1.5 – 2.5</td>
<td>121</td>
<td>0.956</td>
<td>color less oily liquid</td>
</tr>
</tbody>
</table>

*(not applicable to the solvent free metal soap ASTM D-1078)
Section 2.2: Synthesis of liquid epoxy resin of bisphenol-C

Epoxy resin of bisphenol-C (II), hereafter designated as EBC, was synthesized according to the reported method [3]. Thus, 0.5 mol of bisphenol-C and 4 mol of epichlorohydrin were placed in a round-bottomed flask equipped with a condenser. The mixture was brought to 90 °C with stirring and 2 mol solid NaOH per mole of bisphenol-C was slowly added at such a rate that the reaction mixture remained neutral. The reaction is exothermic and cooling is applied to keep the temperature at 80-90°C. The epoxidation reactions were carried out at different time intervals as shown in Table-2.4. The mass was cooled to room temperature and transferred into a 1 l separating funnel. The liquid resin was washed well with hot water and collected into a wide-mouth bottle and dried in an oven at 70°C for 3 h to remove traces of moisture. The epoxy equivalent weights of the samples were determined according to the procedure described in Section 2.2. Highly transparent yellowish resin is soluble in CHCl₃, acetone, 1, 4-dioxane, DMF, 1, 2-dichloroethane and DMSO, and partially soluble in ethanol and isopropanol.
Section 2.3: Synthesis of vinyl ester resin

Epoxy vinyl ester of EBC (EEW 190-220), here after designated as EBCMA was synthesized according to reported method [4]. The reaction was carried out in a three neck round bottomed flask equipped with a mechanical stirrer and spiral condenser. After taking more than 50 small scale trials at 80°C, the best formulation was established. Esterification reaction was favored by removing water of reaction. The detail procedure is as follows. A 1 mol of EBC and 2 mol of methacrylic acid and 2 ml triethylamine (catalyst) were transferred to the flask and heated to 80°C with stirring in a water bath. The progress of the reaction was monitored by withdrawing sample at different time interval (Table-2.2). The acid value of each sample was determined (IS 6746:1994) according to procedure described in Section-2.4. Similarly bulk vinyl ester resin (acid value < 10) was synthesized at 80°C and keeping reaction time of 2h. A 40% styrene of resin as a reactive diluent and 0.2% hydroquinone as an inhibitor were mixed at room temperature. Here after resin is designated EBCMASt.

Section 2.4: Characterization of vinyl ester resins

Determination of epoxy equivalent weight

Epoxy content is reported in terms of “epoxide equivalent” or “epoxy equivalent weight” and is defined as the weight of resin in grams, which contains one gram equivalent of epoxy. The term “epoxy value” represents the number of epoxy groups contained in 100 grams of resins.

Epoxy equivalent may be determined by infrared analysis. The characteristic absorption band for the epoxy group is 877.2 to 806.45 cm\(^{-1}\) for terminal epoxy groups; 847.45 to 775.2 cm\(^{-1}\) for internal epoxy groups; and 769.2 to 751.8 cm\(^{-1}\) for triply substituted epoxy group [5]. The epoxide equivalent may be determined from changes in intensity as related to change in molecular weight using the absorption band of the epoxy group at 912.4 or 862.1 cm\(^{-1}\) in comparison to aromatic band at 1610.3 cm\(^{-1}\).

Greenlee [6] has described the method for epoxy equivalent. The epoxide content of the complex epoxide resins were determined by heating a 1 g sample of the epoxide composition with an excess of pyridine containing pyridine hydrochloride at the boiling point for 20 min and back titrating the excess pyridine hydrochloride with 0.1 N sodium hydroxide by using phenolphthalein as an indicator and considering that 1 HCl is equal to 1 epoxide group.

\[ \text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O} \]

Jungnickelet al [7] have reported somewhat better results than other hydrohalogenation methods with bisphenol-A epoxy resins and with water containing sample. They recommended the use of a stronger reagent (1 N pyridiniumchloride in pyridine), larger sample sizes and a stronger hydroxide solution (0.5 N) for samples of relatively low molecular weight. They have developed a variation of the pyridiniumchloride method in which pyridinium is replaced by chloroform. The precision and accuracy are somewhat better, due to the reduction of side reactions. The pyridiniumchloride-chloroform method even permits the determination of epoxides sensitive acids such as styrene and isobutylene oxides. However, the preparation of the reagent is cumbersome, and reaction periods of 2 h are required. Especially time consuming is the need for the exact equivalence of hydrogen chloride and pyridine.

Burge and Geyer [8] have also described an extensive procedure for the determination of epoxide equivalent. A weighed sample of an epoxide compound containing 2-4 milliequivalents of epoxy group is placed into a 250 ml round bottomed flask, and 25 ml of 0.2 N pyridiniumchloride in pyridine was added. The solution was swirled and if necessary, heated gently until the sample was dissolved completely and refluxed for 25 minutes, cooled and then added 50 ml of methyl alcohol and 15 drops of phenolphthalein indicator and titrated with 0.5 N methanolic NaOH till pink end point. The epoxide equivalent was calculated according to following relationship:

\[
Epoxide\ equivalent = \frac{16 \times \text{Sample weight in grams}}{\text{grams oxirane oxygen in sample}}
\]  

Where gram oxirane oxygen in sample = (ml NaOH for blank - ml NaOH for sample) x (Normality of NaOH) X 0.016


Synthesis...

The number 0.016 is the miliequivalent weight of oxygen in grams. Epoxy equivalent weight (EEW) of various samples is reported in Table-2.2 from which it is clear that EEW increased with extent of reaction time.

**Molecular weight calculation of vinylester resin**

The molecular weight of vinyl ester resin can be calculated according to Eqn.2.2:

\[
\text{MW of EBCMA resin} = (\text{EEW} \times 2) + (\text{MW of MA} \times \text{mol. of MA}) \tag{2.2}
\]

Where EEW = epoxy equivalent weight and MA = methacrylic acid

Molecular weights of various vinylester samples calculated according to Eqn.2.2 are reported in Table-2.2 from which it is clear that molecular weight is increased with the extent of the reaction time.

**Determination of acid values of vinyl ester resin** *(IS6746:1994)*

Acid value is a measure of the free fatty acids content of oil and is expressed as the number of milligrams of potassium hydroxide required to neutralize the free acid in 1 gram of the sample. Acid value quantifies the reaction, which is in the beginning of the reaction, the acid value is high but as the reaction progresses acid is consumed to form ester and at the end of the reaction the acid value is low which signifies the completion of the esterification reaction.

Acid values of epoxy ester were determined according to reported method [9]. A 1 g of EBCMA was weighed in a dry capsule and transferred to a 150 ml conical flask and 25ml of MEK was added and flask was swirled for few minutes to dissolve the sample completely and few drops of phenolphthalein indicator was added. The solution was titrated by using alcoholic potassium hydroxide. The endpoint was pink to colorless. Similarly blank titration was carried out. Triplicate measurements were carried out and mean values were considered for the calculation of acid values. The acid values were calculated according to Eqn.2.3:

Table 2.2: Epoxy equivalent weights, molecular weights and reaction time of various batches of vinyl ester resins.

<table>
<thead>
<tr>
<th>Samples</th>
<th>EEW</th>
<th>Mol. weight (g/mol)</th>
<th>Reaction time, h</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>EBCMA-1</td>
<td>189</td>
<td>550</td>
<td>2</td>
<td>A</td>
</tr>
<tr>
<td>EBCMA-2</td>
<td>200</td>
<td>572</td>
<td>2.15</td>
<td>A</td>
</tr>
<tr>
<td>EBCMA-3</td>
<td>210</td>
<td>592</td>
<td>2.30</td>
<td>A</td>
</tr>
<tr>
<td>EBCMA-4</td>
<td>220</td>
<td>612</td>
<td>2.45</td>
<td>A</td>
</tr>
<tr>
<td>EBCMA-5</td>
<td>230</td>
<td>632</td>
<td>3.00</td>
<td>A</td>
</tr>
<tr>
<td>EBCMA-6</td>
<td>457</td>
<td>1086</td>
<td>3.15</td>
<td>B</td>
</tr>
<tr>
<td>EBCMA-7</td>
<td>685</td>
<td>1542</td>
<td>3.30</td>
<td>B</td>
</tr>
</tbody>
</table>

Remarks:
A-Easily soluble in styrene monomer and curable at room temperature
B-Soluble in styrene on heating and curable at elevated temperature

Table 2.3: Acid and hydroxyl values of EBCMA samples.

<table>
<thead>
<tr>
<th>Vinylester</th>
<th>Acid value, mg KOH /g resin</th>
<th>Hydroxyl value, mg KOH /g resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>EBCMA-1</td>
<td>10</td>
<td>156</td>
</tr>
<tr>
<td>EBCMA-2</td>
<td>10</td>
<td>153</td>
</tr>
<tr>
<td>EBCMA-3</td>
<td>9</td>
<td>163</td>
</tr>
<tr>
<td>EBCMA-4</td>
<td>8</td>
<td>172</td>
</tr>
<tr>
<td>EBCMA-5</td>
<td>7</td>
<td>176</td>
</tr>
<tr>
<td>EBCMA-6</td>
<td>6</td>
<td>182</td>
</tr>
<tr>
<td>EBCMA-7</td>
<td>6</td>
<td>189</td>
</tr>
</tbody>
</table>
Synthesis...

\[
\text{Acid Value} = \frac{56.1 \times N \times (A - B)}{W}
\]

Where \( N \) = Normality of KOH, \( A \) = Sample burette reading in ml, \( B \) = Blank burette reading in ml and \( W \) = Weight of the sample in grams

The acid values of EBCMA samples are reported in Table-2.3 from which it is observed that acid value decreased \((10^{-6})\) with the extent of reaction and reached constant value after 3h.

**Determination of hydroxyl values of vinyl ester resin (IS 6746:1994)**

Hydroxyl value is a measure of free hydroxyl groups present in the epoxy ester and vinyl ester resin. It is expressed as number of milligrams of potassium hydroxide equivalent to the quantity of acetic acid that binds with 1 g of hydroxyl containing substances. The hydroxyl value gives information about the number of free hydroxyl group present in a material. The determination is carried out by acetylation with acetic anhydride in pyridine. Aldehydes, primary and secondary amines interfere with the determination.

\[
\text{Resin-OH} + \text{CH}_3\text{C} = \text{N} \rightarrow \text{Resin-O-C-CH}_3 + \text{CH}_3\text{COOH} + \text{N}
\]

\[
\text{CH}_3\text{COOH} + \text{KOH} \rightarrow \text{CH}_3\text{COOK} + \text{H}_2\text{O}
\]

Hydroxyl values of EBCMA samples were determined according to reported method [9]. Exactly 1-2 g of EBCMA was weighed in a dry capsule and transferred to a 150 ml conical flask and 20ml of acetylation mixture (1 volume of acetic anhydride and 3 volume of pyridine) was added. The flask was swirled for few minutes with gentle heating to dissolve the sample completely and the content was refluxed on a boiling water bath for 30 min. The solution was cooled to room temperature and 50 ml cold water was added slowly down to the condenser. To this cooled solution few drops of phenolphthalein indicator was added and the free acetic acid was titrated with
Synthesis...

standard 1N NaOH solution. The endpoint was pink to colorless. Similarly blank titration was carried out. Triplicate measurements were carried out and mean values were considered for the calculation of hydroxyl values. The hydroxyl values were calculated according to Eqn.2.4:

\[
\text{Hydroxyl Value} = \frac{(V_2 - V_1) \times N \times 56.1}{W} + AV
\]

Where \(N\) = Normality of KOH, \(V_1\) = Sample burette reading in ml, \(V_2\) = Blank burette reading in ml, and \(W\) = Weight of sample in grams.

The hydroxyl values of EBCMA samples are reported in Table-2.3 from which it is observed that hydroxyl value increased (156-189) with the extent of reaction. Thus, decreased of acid value and increased of hydroxyl value of the vinyl ester resin samples indicated conversion of epoxide groups into ester groups.

**Determination of viscosity and density of styrenated vinyl ester resin**

Ford viscosity cup is generally used for the determination of viscosity of Newtonian paints, varnish, lacquers, and related liquids. The protocols for the test method are provided in the ASTM D 2196. The Ford viscosity cup is shown in Fig. 2.1. The cup is filled with the liquid under test up to the top level and the time for the liquid to flow through one of the standard orifices is measured. Based on the orifices size, five Ford viscosity cup viscometers are available (Nos. 1, 2, 3, 4, and 5). In present case B-4Ford cup viscometer was used for the determination of the viscosity of the resins. Viscosity measurements were carried at at 25±0.2°C. Triplicate flow time measurements were carried out and the mean values were considered for the calculations of the viscosity. Viscosity of EBCMASt samples were calculated according to Eqn. 2.5:

\[
\text{Viscosity (cp)} = [(t) \times (0.0378) - \left(\frac{\pi}{4}\right) \times \rho \times 100]
\]

Synthesis...

Where \( t \) = average flow time of the resin, \( \rho \) = Density of the liquid resin and 0.0378 = conversion factor

The density of the resin was determined at room temperature according to Eqn. 2.6:

\[
\text{Relative density at } 27 \, ^\circ \text{C} = \frac{A - B}{C - B} \tag{2.6}
\]

Where:

- \( A \) = Mass in g of the relative density bottle with EBCMASt resin at 27°C
- \( B \) = Mass in g of the relative density of Bottle
- \( C \) = Mass in g of the relative density bottle with water at 27°C

A comparative acid value, viscosity and density of EBCMASt and commercial resin are reported in Table-2.4 from which it is clear that EBCMASt possesses comparable acid value, viscosity and density with that of commercial resin.

**Section 2.5: Curing study of styrenated vinylester resin**

Styrenated vinylester resins can be cured either at room temperature or at elevated temperatures. Other monomers such as vinyl toluene, methyl methacrylate, and paramethylstyrene can also be used for the synthesis of vinyl ester resins.

Room Temperature (RT) Curing Systems: Room temperature curing systems are usually based on the use of transition metal soaps as the primary promoters and ketone peroxides as the initiators. Cobalt soaps such as cobalt naphthenate, octoate, or neodecanoate are the most popular metallic promoters are used as room temperature curing systems which give good curing behavior and package life. Other primary metallic promoters that have
Fig 2.1: B-4 Ford cup viscometer

Table 2.4: A Comparative physical properties of EBCMASt, and commercial grade Aeropol-7105 vinyl ester resins.

<table>
<thead>
<tr>
<th>Property</th>
<th>Aeropol-7105</th>
<th>EBCMASt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, g/cm³</td>
<td>1.12</td>
<td>1.12</td>
</tr>
<tr>
<td>Viscosity, cp</td>
<td>270</td>
<td>300</td>
</tr>
<tr>
<td>Acid value, mg KOH / g</td>
<td>9</td>
<td>8</td>
</tr>
<tr>
<td>Gel time, min</td>
<td>22</td>
<td>20</td>
</tr>
<tr>
<td>Peak exothermic temperature, °C</td>
<td>126</td>
<td>135</td>
</tr>
</tbody>
</table>

MMT- Montmorillonite, used 5% as a filler with EBCMASt resin.
been used are compounds of manganese, vanadium, tin, calcium, and barium. Vanadium can give very fast curing at room temperature with ketone peroxide initiators but imparts a pronounced yellow color to the cured resin. The additional drawback is shelf life unless special stabilization methods are used. Manganese is primarily useful with cumene hydrogen peroxide, which is attractive as a lower cost catalyst, calcium and barium have been cited as being able to speed up the cure of promoted systems employing very low cobalt concentrations to minimize cured resin color.

In present study MEKP (1% of resin) was used as a free-radical polymerization initiator, DMA (1.5% of resin) was used as an promoter of epoxy resin and cobalt octoate (1% of resin) was used as an accelerator to promote the decomposition of peroxide at room temperature.