CHAPTER 3
3.1 MATERIALS USED

The present chapter deals with resin used, modification of the resin, monomers used and the catalysts which were used for various reactions.

(I) RESIN: Diglycidal ether of Bisphenol A (DGEBA) was supplied by Dr. Beck & Co. (India) Pune.

\[ \text{CH}_2-\text{CH}-\text{CH}_2-\text{O} \left[ \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{OH} \\ \text{CH}_3 \end{array} \right] \text{O-C-O-CH}_2-\text{CH}_2 \text{O-C}-\text{O-CH}_2-\text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \]

Diglycidal Ether of Bisphenol A

3.1.1

The specifications of the resin is as follows:

(a) Epoxy equivalent : 191 ± 5 (as determined by pyridinium chloride method)
Molecular weight - 380 ± 5

(b) Form - Viscous yellowish liquid. The resin was heated at 100°C for six hours and stored under Nitrogen atmosphere.

(II) Tolylene Diisocyanate (TDI): C₉H₆N₂O₂ was supplied by Ms Aldrich (USA) and used as it is.
52

\[
\begin{align*}
\text{CH}_3 \\
\text{OCN} \quad \text{NCO}
\end{align*}
\]

TDI
3.1.2

(a) NCO equivalent - 48 (as determined by excess DBA method).
Molecular weight - 174.16 g/mol.
Form - Colourless liquid.
Boiling Point - 251°C.

(III) Diphenyl Methane Diisocyanate (MDI) - (Methlene diphenylene diisocyanate). C_{13}H_{10}N_2O_2

\[
\begin{align*}
\text{OCN} - \text{C} - \text{NCO}
\end{align*}
\]

MDI
3.1.3

It was vacuum distilled from commercial sample and the white crystalline compound was stored at 10°C in a blanket of Nitrogen.
Molecular weight - 250.26
Melting Point - 36°C
Isocyanate Equivalent - 33.6 (as determined by excess DBA method)

(IV) N, N Dimethyl Formamide - (DMF) C_3H_7NO
It was distilled under reduced pressure and stored under 4Å molecular sieves.
Boiling Point - 153°C
Molecular weight - 73.10 g/mol

(V) N-methyl Pyrrolidone (NMP). C₅H₉NO
(1-Methyl-2 Pyrrolidone)
(n Methyl - 2 Pyrrolidone)
It was dried overnight using Calcium Hydride and then distilled under reduced pressure and collected over Calcium Hydride. The flask was covered with black paper and stored away from sunlight. A fresh bottle was opened each time.
Boiling Point - 202°C

(VI) Ethyl Methyl Imidazole (EMI) was supplied by Ms Alderich (USA) and used as such.

(VII) Tetrabutyl Ammonium Bromide was vacuum dried at 20°C for 24 hours before use.

(VIII) Benzyl Dimethyl Amine (BDMA) was supplied by Ms Aldrich (USA) and used as such.
(IX) Methanol (A.R.) - Methanol was dried with Calcium Oxide prior to distillation and stored at 20°C using molecular sieves.

(X) Dibutyl Tin Dilaurate - was supplied by Ms Aldrich (USA) and used as such.

\[
\begin{align*}
\text{Dibutyl Tin Dilaurate} \\
3.1.4
\end{align*}
\]

(XI) Triphenyl Phosphine - was supplied by Ms Aldrich and used as such.

\[
\begin{align*}
\text{Triphenyl Phosphine} \\
3.1.5
\end{align*}
\]

(XII) Benzophenone Tetracarboxylic Dianhydride (BTDA) was supplied by Ms Aldrich (USA) and used as such.
3.1.6

(XIII) Pyromellitic Dianhydride (PMDA) - was supplied by Ms Acros Chemicals and used as such.

3.1.7
3.2 EXPERIMENTAL

The experimental work consists of two parts:

[I] (a) Synthesis of oxazolidone by modifying the DGEBA using different isocyanates, catalysts and solvents.
   (b) Characterization of the linear polymer thus formed, using Fourier Transform Infrared spectroscopy (FTIR) and Thermogravimetric Analysis (TGA) methods for thermal evaluation.

[II] Crosslinking of the linear oxazolidone using aromatic dianhydrides as hardener. Curing process was studied by Differential Scanning Calorimetry and thermal properties were studied using TGA.
   FTIR spectra was recorded on FTIR - NICOLET MAGNA-750-FTIR. The spectra was observed in $\lambda_{\text{max}}$ cms$^{-1}$ throughout these experiments.
   The FTIR peaks can be assigned as follows:
   (a) * Isocyanate peak at 2270 cms$^{-1}$
   (b) * Oxazolidone peak between 1751 - 1754 cms$^{-1}$
   (c) * Isocyanate peak at 1710 cms$^{-1}$
   (d) * Epoxide peak at 910 cms$^{-1}$

The Infra Red spectra of the synthesized oxazolidone modified resin was obtained by using a 1% dispersion samples in KBr and evaluation the resulting disc with a Nicolet Magna FTIR spectrometer.[79 – 82]

The first FTIR scan (Fig. 3.2.1) shows a pure DGEBA sample and isocyanate modified epoxy respectively (Fig 3.2.2). The peak for epoxy at
915 cm$^{-1}$ is clear and sharp, showing free epoxy groups in the resin and the peak for oxazolidone in the modified epoxy is visible at 1754 cm$^{-1}$.

TGA-Thermogravimetric studies were observed on - Hi. Res. TGA-2950- Thermogravimetric Analyzer - TA instruments. The dynamic TGA curves were obtained at heating rate of 10°C/min. All measurements were conducted under a blanket of Nitrogen gas.

The reaction temperature, solvent, catalysts and the isocyanates were the variables studied to determine optimum conditions for the synthesis of the oxazolidone.

3.3 Synthesis of oxazolidone modified epoxy resin

The formation of oxazolidone polymers can be carried out through various synthetic routes.

(i) The most commonly used method is the cycloaddition of isocyanates to epoxies.

\[
\text{OCN-R-NCO} + \text{CH}_2\text{-CH-R'-CH-CH}_2 \rightarrow
\]

\[
\left\{\begin{array}{c}
\text{CH}_2\text{N-R-NCH}_2 \\
\text{O-C-O-C-O}
\end{array}\right\}^n
\]
Fig 3.2.1 FTIR of unmodified epoxy resin

Fig 3.2.2 FTIR of oxazolidone modified epoxy resin
This reaction is carried out in the presence of a suitable catalyst.

(ii) Intermolecular nucleophilic addition between urethane and epoxy group.

\[
\begin{align*}
\text{R-NH} & \text{C-O-R''} + \text{CH}_2\text{-CH-R'} \rightarrow \\
& \text{R-N-CH}_2\text{-CH-R'} + \text{R''-O-H}
\end{align*}
\]

However, the method used in this work was the cycloaddition of isocyanates to epoxies. The reason for use of cycloaddition method is that in this method, there are no byproducts formed which can cause branching and lead to formation of a brittle structure. Also, the byproduct formed may react with unreacted isocyanate leading to completely different products. The cycloaddition reaction has been done in the laboratory both in solution, using suitable solvents and in bulk.

3.3.1. Reaction in bulk phase [Ref. Table I(a)]

A three necked flask, is fitted with a mechanical stirrer, nitrogen inlet and rubber septum. After making sure, it was clean and dry, it was weighed. Then, 4.7 gms. of DGEBA (3.1.1) and 0.025 gms. (0.5% of the weight) of
combined weight of monomers of catalyst (EMI) were added. The I/E ratio in this case being 0.5. The stirrer was started and the flask was flushed with dry Nitrogen gas for one hour. Using an ice-bath, the flask was then cooled to 5°C and TDI (3.1.2) (4.34 gms) was added dropwise with the help of a syringe through the rubber septum over a period of one hour. Mixing was continued under chilled conditions, in the presence of Nitrogen for one hour. This assured, a homogenous mixture of isocyanate and epoxy.

In this reaction, very low temperature conditions (0°C- 5°C) have to be maintained when TDI is used, as the reaction is exothermic and raises the temperature of the reactants, leading to cyclization and hence trimerization of the polymer. As the temperature rises, crosslinking of the polymer takes place, forming a hard mass. At this stage the polymer gels and immobilizes the system if the temperature is not maintained between 0°C to 5°C.

**TABLE-1 (a)**

<table>
<thead>
<tr>
<th>Resin</th>
<th>Isocyanate</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. DGEBA</td>
<td>TDI</td>
<td>Tetra Butyl Ammonium Bromide</td>
</tr>
<tr>
<td>2. DGEBA</td>
<td>TDI</td>
<td>EMI</td>
</tr>
<tr>
<td>3. DGEBA</td>
<td>TDI</td>
<td>BDMA</td>
</tr>
<tr>
<td>4. DGEBA</td>
<td>MDI</td>
<td>Tetra Butyl Ammonium Bromide</td>
</tr>
<tr>
<td>5. DGEBA</td>
<td>MDI</td>
<td>EMI</td>
</tr>
<tr>
<td>6. DGEBA</td>
<td>MDI</td>
<td>BDMA</td>
</tr>
</tbody>
</table>
From the chilled, homogenized mixture, a few drops of the melt were removed and placed on Teflon sheets and pressed between five pound metal plates, and kept in an oven at 150°C for five hours. This method gave thin and transparent films of uniform thickness. These were studied using FTIR and the thermal stability of this oxazolidone-based polymer was evaluated by TGA.

When MDI (3.1.3.) is used as an isocyanate in bulk reactions, the temperature of the system initially is at room temperature. This is because MDI is a solid at room temperature and has a melting point of 36°C. When MDI is used an isocyanate, the temperature of the system is raised to 50-55°C to ensure the melting and hence mixing of epoxy. After stirring the mixture for one hour, a few drops of the melt are again pressed between Teflon sheets, and pressed between metal plates and cured in an oven for 5 hours at 150°C. Thin and transparent films were obtained after 5 hours. Further increase in temperature leads to crosslinking.

In bulk reactions, this procedure is repeated using different catalysts and using both TDI and MDI.

3.3.2 Reaction in solution [Ref. Table I(b)]

The reaction between epoxy and diisocyanate was also carried out in solvent phase. The solvents used were Dimethyl Formamide (DMF) and N-methyl pyrrolidone (NMP). Both are aprotic solvents and both epoxy and isocyanate and the resulting polymer is soluble in them without producing any side reactions. However, it has to be ensured that the solvents are free of moisture and impurities.
TABLE-1 (b)

REACTION IN SOLUTION PHASE

<table>
<thead>
<tr>
<th>Resin</th>
<th>Isocyanate</th>
<th>Catalyst</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. DGEBA</td>
<td>TDI</td>
<td>Tetrabutyl Ammonium Bromide</td>
<td>DMF</td>
</tr>
<tr>
<td>2. DGEBA</td>
<td>TDI</td>
<td>Ethyl Methyl Imidazole</td>
<td>NMP</td>
</tr>
<tr>
<td>3. DGEBA</td>
<td>MDI</td>
<td>EMI</td>
<td>NMP</td>
</tr>
<tr>
<td>4. DGEBA</td>
<td>MDI</td>
<td>DBTL</td>
<td>NMP</td>
</tr>
<tr>
<td>5. DGEBA</td>
<td>MDI</td>
<td>Triphenyl Phosphine</td>
<td>NMP</td>
</tr>
<tr>
<td>6. DGEBA</td>
<td>TDI</td>
<td>BDMA</td>
<td>DMF</td>
</tr>
<tr>
<td>7. DGEBA</td>
<td>MDI</td>
<td>BDMA</td>
<td>NMP</td>
</tr>
<tr>
<td>8. DGEBA</td>
<td>TDI</td>
<td>No catalyst</td>
<td>DMF</td>
</tr>
<tr>
<td>9. DGEBA</td>
<td>MDI</td>
<td>No Catalyst</td>
<td>DMF</td>
</tr>
<tr>
<td>10. DGEBA</td>
<td>Commercial undistilled MDI</td>
<td>EMI</td>
<td>NMP</td>
</tr>
</tbody>
</table>

The procedure involving reactions in solution proved to be more manageable as:-

i) The heat evolved in this exothermic reaction can be controlled and the reaction can proceed at a much slower pace.

ii) It is much easier to study the kinetics of the reaction.

The yield of oxazolidone is higher and FTIR studies do not indicate the presence of isocyanate and urethane. For solution phase reaction, a three necked flask which was previously fitted with a condenser, magnetic stirrer and pressure equalizing dropping funnel was weighed and 5.73 gms (0.002 moles)
of DGEBA was added. Then 0.037 gms of EMI (0.1% by weight of the combined monomers) was added into the flask. 10ml of the solvent. NMP was added with the help of syringe and stirred while being flushed with dry Nitrogen gas for one hour. The temperature of the DGEBA/EMI stirred solution was raised to 180° - 185°C using on oil bath, 2.50 gms. (0.002 moles) of MDI dissolved in 10ml of NMP was added dropwise over a period of one hour the mixture was allowed to remain at 180°C to 185°C for an additional 4 hr. and then cooled gradually.

The viscous mixture from the flask was poured into 400ml of dry and distilled methanol and vigorously stirred for 10 minutes. A colloidal suspension appeared and a few drops of saturated NH₄Cl in methanol were added while stirring was continued. A precipitate was observed which was filtered and dried. This was re-dissolved in DMF and re-precipitated in methanol as described earlier for purification. This process was repeated three to four times and the polymer, which was whitish to tan in color (depending on the isocyanate used), was dried in a vacuum oven at 40°C for six hours. The polymer is soluble in DMF, THF and DMSO.

The reaction in solution was studied at various temperatures.

1. Room Temperature
2. 90°C
3. 130°C
4. 160°C
5. 180°C

Also this reaction was carried out under similar conditions for varying time periods as given below:

1. 2 hrs.
2. 4 hrs.
3. 6 hrs. 
4. 8 hrs. 
5. 10 hrs.

In each case the product was evaluated by FTIR. The same procedure was adopted for preparing oxazolidones using various catalysts.

The polymer obtained was characterized using Hi.Res. TGA 2950-Thermogravimetric Analyzer.

It was assured that all the glassware was completely clean and dry and kept in an oven for six hours at 150° C before use.

3.4 Preparation of blends

The oxazolidone blends were prepared using dianhydrides (BTDA-3.1.6) and (PMDA-3.1.7) and BDMA was used as a catalyst.

Method of preparation: The synthesized oxazolidone was dissolved in epoxy resin. This mixture was warmed to 50°C and stirred till a uniform solution was obtained. Weighed quantities of the anhydride were then gradually added till it was evenly dispersed in the epoxy. Benzyl dimethyl amine (BDMA) was then added, (5 phr in all cases) while stirring the above solution. Samples were drawn for DSC analysis. The same procedure was used to prepare all the combinations. The schemes used were: -

SCHEME-A
The amount of anhydride was kept constant (at 0.5 mole w.r.t. epoxy resin) and the amount of oxazolidone was varied i.e. 1%, 5%, 10%, 15%, 25% and 50%.

SCHEME-B

Keeping the oxazolidone constant at 10%, the amount of anhydride was varied i.e. 0.1, 0.2, 0.3, 0.4, 0.5 mole.

After taking the sample for DSC analysis, the rest was kept in preheated metal plates in an oven at 160°C for 5 hours and post cured at 180°C for 2 hours.

The cured samples were then evaluated for thermal stability using TGA in these studies of various compositions.

3.4.1 Stoichiometric Ratios (A/E)

No satisfactory general ratios have been developed for the curing and DSC characterization. A/E ratios for all anhydride curing agents have to be adjusted, taking into account the specific cure temperature employed and the extent to which the reaction takes place at elevated temperatures.

In these cure processes, if anhydride is present in excess the reversible monoester reaction will result in splitting of the anhydride and this will lead to high weight loss.

On the other hand, when insufficient amount of anhydride is present, the excess resin fragments in the material will be driven off at aging temperatures at around 240°C.
Stoichiometric ratio of the anhydride to resin ratios have been developed as follows:

380 gms of epoxy is equivalent 332 gms of BTDA

(molecular weight of DGEBA is 380 as determined by pyridinium chloride method)

190 gms. of epoxy = 161 gms. BTDA (because 1 epoxy is equivalent to 1 anhydride

So, 100 gms of epoxy need 0.85 gms of anhydride,

This is the theoretical 1:1 A/E ratio of epoxy resin to anhydride.