CHAPTER-2
EXPERIMENTAL
2.0 EXPERIMENTAL

2.1 Synthesis of Polyurea

2.1.1 Materials

Toluene diisocyanate -TDI- Fluka Aldrich chemicals
Polyetheramine - Cronell Bros company Pvt Ltd. Mumbai, India.
Curing agent - Aldrich Chemical - AR grade
Methyl ethyl ketone (MEK) - Merck - GR grade
Toluene - Merck - GR grade

All these chemicals were used as such without any further purification

2.1.2 Procedure

Synthesis of polyurea was carried out by sequential monomer addition in a three-necked round bottom flask equipped with a stirrer, pressure equalizing dropping funnel and a condenser as shown in Figure 2.1. The polymerization was continued under inert atmosphere by using toluene diisocyanate and polyether amines at room temperature. The prepolymer formed is further reacted with curing agent to incorporate the urea linkage. The polyurea was processed with an internal mixer and sprayed onto copper sheets and also casted in moulds for curing at room temperature.
Figure 2.1 Typical Polymerization set-up for synthesis of Polyurea and its Copolymers

The polyurea polymers were synthesized via a two step synthesis, (a) Preparation of Prepolymer (b) Reaction of prepolymer with chain extenders which plays a dual function, it act as chain extender and a curing agent as well.

Polyurea polymer was synthesized using three different monomers. The polymers were derived from the reaction product of an isocyanate component, resin component and amine chain extender. Toluene diisocyanate (TDI) as a reactive isocyanate, polyoxypropylene diamine and polyoxypropylene triamine as the resin components were employed. They provide long and soft chain moieties. The polyether amines soft chain moieties provide flexibility to the polymer. The prepolymer resulting from reaction between the amine and the isocyanate give prepolymer. The prepolymer so
formed is reacted with the short chain diamine, chain extender and the curing agent to incorporate hard segments in polyurea polymer.

Homo polyureas of different monomer content were prepared and effect of their content on thermal, electrical and mechanical properties was studied. Polyurea samples were synthesized varying the concentration of polyether amine from 200 g/eq to 750 g/eq coded as PU-1 to PU-4, keeping the concentration of TDI constant. Similarly, the samples were also prepared by varying the concentration of TDI from 104.4 g/eq to 174.0 g/eq keeping the concentration of polyether amine constant coded as PU-5 to PU-8. The reactions were carried out at room temperature in methyl ethyl ketone.

The samples were also synthesized varying the concentration of polyoxypropylene triamine from 334 g/eq to 1250g/eq keeping the concentration of TDI constant to study the effect of higher functionality amine resin on different properties of polymers. During the course of the work the polymerization conditions were optimized. The polyurea samples synthesized were characterized.

The details of the synthesized polymers varying the concentration ratio of monomers are presented in Table 2.1. The schematic representation of the reaction is also mentioned in the Scheme 2.1.
Experimental

Scheme 2.1 Synthesis of Polyurea
Table 2.1 Synthesis of Polyurea

<table>
<thead>
<tr>
<th>Code</th>
<th>TDI (g/eq)</th>
<th>Polyoxypropylene diamine (g/eq)</th>
<th>Polyoxypropylene triamine (g/eq)</th>
<th>Curative amine (g/eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU 1</td>
<td>104.4</td>
<td>200</td>
<td>-</td>
<td>23.2</td>
</tr>
<tr>
<td>PU 2</td>
<td>104.4</td>
<td>400</td>
<td>-</td>
<td>23.2</td>
</tr>
<tr>
<td>PU 3</td>
<td>104.4</td>
<td>600</td>
<td>-</td>
<td>23.2</td>
</tr>
<tr>
<td>PU 4</td>
<td>104.4</td>
<td>750</td>
<td>-</td>
<td>23.2</td>
</tr>
<tr>
<td>PU-5</td>
<td>121.8</td>
<td>750</td>
<td>-</td>
<td>23.2</td>
</tr>
<tr>
<td>PU-6</td>
<td>139.2</td>
<td>750</td>
<td>-</td>
<td>23.2</td>
</tr>
<tr>
<td>PU-7</td>
<td>156.6</td>
<td>750</td>
<td>-</td>
<td>23.2</td>
</tr>
<tr>
<td>PU-8</td>
<td>174.0</td>
<td>750</td>
<td>-</td>
<td>23.2</td>
</tr>
<tr>
<td>PT-1</td>
<td>104.4</td>
<td>-</td>
<td>334</td>
<td>23.2</td>
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<tr>
<td>PT-2</td>
<td>104.4</td>
<td>-</td>
<td>667</td>
<td>23.2</td>
</tr>
<tr>
<td>PT-3</td>
<td>104.4</td>
<td>-</td>
<td>1000</td>
<td>23.2</td>
</tr>
<tr>
<td>PT-4</td>
<td>104.4</td>
<td>-</td>
<td>1250</td>
<td>23.2</td>
</tr>
</tbody>
</table>
2.2 Synthesis of Polyurethane

2.2.1 Materials

Toluene diisocyanate (TDI-Fluka Aldrich chemicals)
Polyols, PPG-2000, PEG-300 and PEG-600 Merck Chemicals – GR Grade
Castor Oil - procured from local market
Short chain diols- Aldrich Chemicals
Dibutyltin dilaurate Catalyst- National chemicals, Vadodara, Gujarat, India.
Toluene-Merck – GR grade
All these chemicals were used without any prior purification

2.2.2 Procedure

Synthesis of polyurethane was carried out by sequential monomer addition in a three-necked round bottom flask equipped with a stirrer, pressure equalizing dropping funnel and a condenser as shown in Figure 2.1. The polymerization was continued under inert atmosphere by using toluene diisocyanate and polyols in presence of catalyst at elevated temperature. The prepolymer formed is further reacted with short chain diols to incorporate the urethane linkage. The polyurethane was processed with an internal mixer and sprayed onto copper sheets and casted in moulds for curing at room temperature.

The polyurethane polymers were synthesized via a two step synthesis, (a) Preparation of Prepolymer (b) Reaction of Prepolymer with chain extenders.

Polyurethane polymer was synthesized using three different monomers. The polymers were derived from the reaction product of an isocyanate component, polyols and short chain diols as chain extender. Toluene diisocyanate (TDI) as a reactive isocyanate, higher molecular weight polyols polypropylene glycol (PPG) and polyethylene glycol (PEG) as long and soft chain moieties were employed. These polyols soft chain moieties provide flexibility to the polymer. The prepolymer resulting from reaction between the glycols and the isocyanate give prepolymer. The prepolymer so formed reacts with the short chain diols, chain extender and thereby provide the hard segments to polymer. The reaction was carried out in the presence of dibutyltin...
dilaurate (DBTL) catalyst at elevated temperature. The castor oil based polyurethane was also synthesized using the TDI and castor oil in presence of DBTL.

Different polyurethane polymers were synthesized using different glycols varying the concentration from 150 g/eq to 800 g/eq and keeping the concentration of the TDI constant. The experimental details are shown in Table 2.2. The schematic representation of the reaction is also mentioned in the Scheme 2.2. The samples synthesized were coded as PUP-1 to PUP-7 and the effect of their concentration on the thermal, electrical and mechanical properties of the polymers was studied. During the course of the work polymerization conditions were optimized. In PUP-5 the PPG-2000 was reacted with TDI followed by propylene glycol as chain extender. The comparative studies on effect of polymer composition on different properties were studied.
Scheme 2.2 Synthesis of Polyurethane
### Table 2.2 Synthesis of Polyurethane

<table>
<thead>
<tr>
<th>Code</th>
<th>TDI (g/eq)</th>
<th>Polyol</th>
<th>Castor Oil (g/eq)</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>PUP-1</td>
<td>104.4</td>
<td>PEG-300 (60 g/eq)</td>
<td>60</td>
<td>Toluene</td>
</tr>
<tr>
<td>PUP-2</td>
<td>104.4</td>
<td>PEG-600 (120 g/eq)</td>
<td>60</td>
<td>Toluene</td>
</tr>
<tr>
<td>PUP-3</td>
<td>104.4</td>
<td>PEG-600 (120 g/eq)</td>
<td>40</td>
<td>Toluene</td>
</tr>
<tr>
<td>PUP-4</td>
<td>104.4</td>
<td>-</td>
<td>100</td>
<td>Toluene</td>
</tr>
<tr>
<td>PUP-5</td>
<td>104.4</td>
<td>PPG-(800 g/eq)</td>
<td>-</td>
<td>Toluene</td>
</tr>
<tr>
<td>PUP-6</td>
<td>104.4</td>
<td>PPG-(400 g/eq)</td>
<td>80</td>
<td>Toluene</td>
</tr>
<tr>
<td>PUP-7</td>
<td>87</td>
<td>PPG-(150 g/eq)</td>
<td>85</td>
<td>Toluene</td>
</tr>
</tbody>
</table>
2.3 Synthesis of Polyurethane-urea Copolymers

2.3.1 Materials

Toluene diisocyanate -TDI- Fluka Aldrich chemicals
Polyols, PPG-2000, PEG-300 and PEG-600 Merck Chemicals – GR Grade
Polyetheramine- Cronell Bros company Pvt Ltd. Mumbai, India.
Methyl ethyl ketone (MEK) - Merck –GR grade
Toluene - Merck –GR grade
All these chemicals were used without any prior purification

2.3.2 Procedure

Synthesis of polyurethane-urea copolymers was carried out by sequential monomer addition in a three-necked round bottom flask equipped with a stirrer, pressure equalizing dropping funnel and a condenser as shown in Figure 2.1. The polymerization was continued under inert atmosphere using toluene diisocyanate and a polyol in the presence of a catalyst at elevated temperature. The prepolymer formed was further reacted with amines to incorporate the urethane and urea linkage. The polyurethane-urea was processed with an internal mixer and sprayed onto copper sheets and also casted in moulds for curing at room temperature.

The polyurethane-urea copolymers were synthesized via a two step synthesis, (a) Preparation of Prepolymer (b) Reaction of prepolymer with amines which plays a dual function. They act as chain extender and curing agent as well.

Polyurethane-urea (PUU) copolymers were synthesized by incorporation of urethane and urea linkages in the polymer chain for the high performance properties. PUU copolymers were synthesized using three different monomers. Toluene diisocyanate (TDI) as a reactive agent reacts with polypropylene glycol(PPG) for urethane linkage as a long and soft chain moieties which provide flexibility in polymer and finally the prepolymer formed from the reaction between two reacts with polyoxypropylene diamine and polyoxypropylene triamine as a chain extender and a curing agent.
Different PUU copolymers were synthesized varying the concentration of the different monomers and the studied the effect of their concentration on the thermal, electrical and mechanical properties of the polymers. The samples were synthesized varying the concentration of PPG from 400 g/eq to 600 g/eq coded as PUU-1 to PUU-4, keeping the concentration of diamine constant. Similarly, the samples were also prepared by varying the concentration of diamine from 400 g/eq to 600 g/eq and keeping the concentration of PPG-2000, constant coded as PUP-5 and PUP-6. The PUU copolymers were also synthesized using the PPG with combination of polyoxypropylene triamine to study the effect of incorporation of higher functionality amines in the polymer matrix and their properties. The reactions were carried out at room temperature and in the presence of a solvent. The effect of different solvents was also studied during the reaction by changing the solvent medium.

During the course of the work optimization of reaction time and the reaction parameters were studied and taken into consideration. Thus all the polymers synthesized were characterized. The details of the synthesized polymers varying the concentration ratio are presented in the Table 2.3. The schematic representation of the reaction is also mentioned in the Scheme 2.3. The ratio of hard: soft segment is given in Table 2.4.
Scheme 2.3 Synthesis of polyurethane-urea copolymers
Table 2.3 Synthesis of Polyurethane-urea Copolymers

<table>
<thead>
<tr>
<th>Codes</th>
<th>TDI (g/eq)</th>
<th>PPG-2000 (g/eq)</th>
<th>Polyoxypropylene diamine (g/eq)</th>
<th>Polyoxypropylene triamine (g/eq)</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>PUU-1</td>
<td>104.4</td>
<td>400</td>
<td>400</td>
<td>-</td>
<td>MEK</td>
</tr>
<tr>
<td>PUU-2</td>
<td>104.4</td>
<td>600</td>
<td>400</td>
<td>-</td>
<td>MEK</td>
</tr>
<tr>
<td>PUU-3</td>
<td>104.4</td>
<td>400</td>
<td>400</td>
<td>-</td>
<td>Toluene</td>
</tr>
<tr>
<td>PUU-4</td>
<td>104.4</td>
<td>600</td>
<td>400</td>
<td>-</td>
<td>Toluene</td>
</tr>
<tr>
<td>PUU-5</td>
<td>104.4</td>
<td>400</td>
<td>600</td>
<td>-</td>
<td>Toluene</td>
</tr>
<tr>
<td>PUU-6</td>
<td>174.0</td>
<td>600</td>
<td>400</td>
<td>-</td>
<td>MEK</td>
</tr>
<tr>
<td>PUU-7</td>
<td>104.4</td>
<td>400</td>
<td>-</td>
<td>666.66</td>
<td>Toluene</td>
</tr>
<tr>
<td>PUU-8</td>
<td>174.0</td>
<td>500</td>
<td>-</td>
<td>833.33</td>
<td>Toluene</td>
</tr>
</tbody>
</table>

Table 2.4 Ratio of Hard segments to Soft segments

<table>
<thead>
<tr>
<th>Codes</th>
<th>Hard segments: Soft segments</th>
</tr>
</thead>
<tbody>
<tr>
<td>PUU-1</td>
<td>1.2 : 0.8</td>
</tr>
<tr>
<td>PUU-2</td>
<td>1.2 : 1.0</td>
</tr>
<tr>
<td>PUU-3</td>
<td>1.2 : 0.8</td>
</tr>
<tr>
<td>PUU-4</td>
<td>1.2 : 1.0</td>
</tr>
<tr>
<td>PUU-5</td>
<td>1.2 : 1.0</td>
</tr>
<tr>
<td>PUU-6</td>
<td>2.0 : 1.0</td>
</tr>
<tr>
<td>PUU-7</td>
<td>1.2 : 0.8</td>
</tr>
<tr>
<td>PUU-8</td>
<td>2.0 : 1.0</td>
</tr>
</tbody>
</table>
2.4 Synthesis of Polyamines

2.4.1 Materials

Aniline- Ranbaxy chemicals-GR grade
Formaldehyde- Merck- 37-41% solution W/V GR-Grade
4,4'-Diaminodiphenylmethane- Merck Schuchardt
Dioxane- Merck-GR grade
Cycloaliphatic epoxy resin- Kuver Chemicals, Vadodara
Sodium nitrate-S.d.fine chem. Limited Mumbai, India- AR Grade
Hydrochloric acid- Merck -GR grade
All these chemicals were used without any prior purification

2.4.2 Procedure

Cycloaromatic polyamines were synthesized from aniline, 4,4'-diaminodiphenylmethane and formaldehyde varying the molar ratio of aniline and formaldehyde and keeping the molar ratio of 4,4'-diaminodiphenylmethane constant. The whole reaction was carried out via a single step synthesis in presence of solvent. Three different polyamines were synthesized and coded as PO1, PO2 and PO3. The detailed composition of polyamines is included in Table 2.5. The schematic representation of the synthesis of these polyamines is shown in Scheme 2.4 (a-c).

Scheme 2.4.a Synthesis of PO1
Experimental

Scheme 2.4.b Synthesis of PO2

\[
2 \text{Aniline} + \text{Diaminodiphenylmethane} + \text{Formaldehyde} \rightarrow \text{Polyamine}
\]

Dioxane 100-110° HCl Catalyst

Scheme 2.4.c Synthesis of PO3

\[
3 \text{Aniline} + \text{Diaminodiphenylmethane} + 3 \text{Formaldehyde} \rightarrow \text{Polyamine}
\]

Dioxane 100-110° HCl Catalyst
These polyamines synthesized have different number of amino functional groups which is clearly observed from Scheme 2.4(a-c). The estimation of amino groups was carried out using the diazotization titration.

### Table 2.5 Molar concentration of Reactants

<table>
<thead>
<tr>
<th>Polyamine</th>
<th>Aniline</th>
<th>Formaldehyde</th>
<th>4,4′Diaminodiphenylmethane</th>
</tr>
</thead>
<tbody>
<tr>
<td>PO1</td>
<td>0.5 moles</td>
<td>0.5 moles</td>
<td>1.0 moles</td>
</tr>
<tr>
<td>PO2</td>
<td>1.0 moles</td>
<td>1.0 moles</td>
<td>1.0 moles</td>
</tr>
<tr>
<td>PO3</td>
<td>1.5 moles</td>
<td>1.5 moles</td>
<td>1.0 moles</td>
</tr>
</tbody>
</table>

### 2.4.3 Estimation of Amino groups

Estimation of amino group is carried out using diazotization titration. It involves reaction between aromatic primary amine (-NH$_2$) with HONO, in presence of excess of mineral acids. The observed values for the aromatic polyamines are shown in Table 2.6.

#### Procedure

Placed 1.0 gm of the sample in a 100 ml measuring flask. Add 50 ml of concentrated mineral acid and make up volume to 100 ml. Pipette out 25 ml of this solution into a conical flask cool the solution so that temperature is maintained between 10 to 15°C. Titrate the solution with N/10 NaNO$_2$ and shake continuously until distinct blue color is produced on a starch iodide paper. The reaction is slow initially but behaves normal as reaction proceeds. The below mentioned are the chemical equations (21) representing the reactions. The values of the experiments are mentioned in Table 2.6.
Functional group determination of the resinous materials was determined using the FT-IR. These resinous materials of polyamines have been employed for curing studies of commercially available epoxy resin. The effect of time, temperature and the concentration of polyamines as curing agent have been studied. The epoxy specimens were further used for testing different dielectric properties.

\[
\begin{align*}
\text{Ar—NH}_2 + \text{NaNO}_2 + \text{HCl} \rightarrow & \quad \text{Ar—N}_2\text{Cl} + \text{NaCl} + 2\text{H}_2\text{O} \\
\text{Kl} + \text{HCl} \rightarrow & \quad \text{KCl} + \text{HI} \\
2\text{HI} + 2\text{HNO}_2 \rightarrow & \quad \text{I}_2 + 2\text{NO} + 2\text{H}_2\text{O}
\end{align*}
\]

\[\ldots (21)\]

<table>
<thead>
<tr>
<th>Codes</th>
<th>Theoretical Value (gm)</th>
<th>Experimental value (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PO1</td>
<td>0.138</td>
<td>0.098 ± 0.035</td>
</tr>
<tr>
<td>PO2</td>
<td>0.137</td>
<td>0.099 ± 0.035</td>
</tr>
<tr>
<td>PO3</td>
<td>0.136</td>
<td>0.170 ± 0.035</td>
</tr>
</tbody>
</table>

These polyamines were then used for curing the cyloaliphatic epoxy resin. The calculated amount of polyamines was mixed efficiently with weighed amount of epoxy resin. The materials were poured in to mould of 100 mm round shaped mould and allowed to cure at 150°C temperatures. The samples were released from the mould after complete curing and used for characterization and evaluation. The time required for curing was also studied. The different samples were prepared varying the concentration of the three different polyamines with respect to epoxy to study its effect in the thermal, electrical and mechanical properties.
2.5 Preparation of Epoxy-PDMS copolymers

2.5.1 Materials

Epoxy resin diglycidyl ether of Bisphenol-A (DEGBA)- Kuver chemicals, Vadodara
Amino terminated polydiedmethylsiloxane (PDMS) having - 0.9 % Nitrogen Kuver
Chemicals- Vadodara.
Polyamide curing agent -Sinpol Industries, Ahmedabad.
Triethylene Tetra amine (TETA) - Sulab reagents, Suvidhinath Laboratories, India -
GR grade
Xylene- Merck-GR grade

2.5.2 Procedure

The copolymers were prepared under controlled reaction conditions and under
constant stirring. The measured quantity of epoxy resin was taken, calculated amount
of PDMS was added (Concentration increases in terms of % of epoxy resin), mixed
efficiently followed by addition of known amount of cross linking agents. The effect
of PDMS was studied on two different systems using commercially available epoxy
resin with polyamide and TETA. The materials were poured in to mould of 100 mm
round shapes and allowed to cure at room temperature for 24 hours. The samples were
released from the mould after complete curing and used for characterization and
evaluation. The time required for curing was also studied. The different samples were
prepared varying the concentration of the PDMS with respect to epoxy to study its
effect in the thermal, electrical and mechanical properties. The test samples were
compared with the sample prepared without blending the amino terminated PDMS.
The details of the different specimens prepared by mixing the varying concentration
are shown in the Table 2.7. Here the effect of PDMS with epoxy system was studied
with two different systems using the polyamides and TETA as the cross linking agent.

The samples were prepared by varying amount of the PDMS and cured with
polyamide and by TETA. Thus two different sets of samples were prepared. The
Epoxy-PDMS-Polyamide was termed as System-I and Epoxy-PDMS-TETA as
System-II. The detailed composition of the samples is projected in Table 2.7.
### Table 2.7 Synthesis of Epoxy-PDMS Copolymers

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Samples</th>
<th>System</th>
<th>Sample Code</th>
<th>Amount of Epoxy Resin (gms)</th>
<th>Amount of Polyamide (gms)</th>
<th>Amount of TETA (gms)</th>
<th>Amount of PDMS (% of epoxy resin)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Sample 1</td>
<td></td>
<td>S-1</td>
<td>9.0</td>
<td>9.0</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>2.</td>
<td>Sample 2</td>
<td></td>
<td>S-2</td>
<td>9.0</td>
<td>8.55</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>3.</td>
<td>Sample 3</td>
<td>System-1</td>
<td>S-3</td>
<td>9.0</td>
<td>8.10</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>4.</td>
<td>Sample 4</td>
<td>System-1</td>
<td>S-4</td>
<td>9.0</td>
<td>7.20</td>
<td>-</td>
<td>20</td>
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<td>5.</td>
<td>Sample 5</td>
<td></td>
<td>S-5</td>
<td>9.0</td>
<td>6.30</td>
<td>-</td>
<td>30</td>
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<td>6.</td>
<td>Sample 6</td>
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<td>S-6</td>
<td>20.0</td>
<td>-</td>
<td>3.0</td>
<td>0</td>
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<td>7.</td>
<td>Sample 7</td>
<td></td>
<td>S-7</td>
<td>20.0</td>
<td>-</td>
<td>3.0</td>
<td>5</td>
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<td>8.</td>
<td>Sample 8</td>
<td>System-2</td>
<td>S-8</td>
<td>20.0</td>
<td>-</td>
<td>3.0</td>
<td>10</td>
</tr>
<tr>
<td>9.</td>
<td>Sample 9</td>
<td></td>
<td>S-9</td>
<td>20.0</td>
<td>-</td>
<td>3.0</td>
<td>15</td>
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<td>10.</td>
<td>Sample 10</td>
<td></td>
<td>S-10</td>
<td>20.0</td>
<td>-</td>
<td>3.0</td>
<td>20</td>
</tr>
</tbody>
</table>
2.6 Synthesis of Nanoparticles

2.6.1 Synthesis of Alumina Nanoparticles

2.6.1.1 Materials

Aluminum trichloride (AlCl$_3$) anhydrous sublimed for synthesis- Merck Chemicals
Aluminum nitrate- (Al(NO$_3$)$_3$.9H$_2$O) Loba Chemie Pvt. Ltd. Mumbai, India
Sodium hydroxide- Merck chemicals- GR grade
Cetyltrimethylammonium bromide (CTAB)- Loba Chemie Pvt, Mumbai India.
All the reagents were used without any prior purification

2.6.1.2 Procedure

Prepared 0.6 M of aluminum chloride solution in distilled water slowly and cautiously. Secondly 0.05 M of CTAB alcoholic solution was prepared by dissolving the 1.823 g of CTAB in methanol.

Taken four necked R.B. flask containing 0.6 M AlCl$_3$ solution and equipped with mechanical stirrer, water condenser, thermometer pocket and addition funnel. A cold solution of 4M NaOH was added drop wise in the reaction mixture. The pH of the solution was monitored. The NaOH addition was continued till the neutrality was achieved. On addition of NaOH the white precipitates are formed simultaneously. The reaction mixture was stirred at 1000 rpm speed to avoid the agglomeration. After that the 0.05 M CTAB solution was added in two parts to the reaction mixture to achieve the nanoparticles. The temperature of the reaction was raised to refluxing temperature under continuous stirring.

The material separated was filtered and washed to remove excess of surfactant and base. The particles were vacuum filtered and were washed thoroughly and dried at elevated temperature. The dried particles were kept for calcination at 1100°C for 3 hours. These particles were further characterized and evaluated.
Experimental

The alumina nanoparticles were prepared using different alumina precursors as aluminum chloride and aluminum nitrate. Thus, the materials were synthesized and optimization of process was carried out varying the reaction parameters. The details are mentioned in Table 2.8.

Table 2.8 Synthesis of Alumina Nanoparticles

<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>Aluminum Precursor</th>
<th>Concentration of CTAB</th>
<th>Coded</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>AlCl₃</td>
<td>0.10 M</td>
<td>Al₂O₃-1</td>
</tr>
<tr>
<td>2.</td>
<td>AlNO₃</td>
<td>0.05 M</td>
<td>Al₂O₃-2a</td>
</tr>
<tr>
<td>3.</td>
<td></td>
<td>0.1 M</td>
<td>Al₂O₃-2b</td>
</tr>
<tr>
<td>4.</td>
<td></td>
<td>0.15 M</td>
<td>Al₂O₃-2c</td>
</tr>
</tbody>
</table>

2.6.2 Synthesis of Aluminum Trihydroxide

2.6.2.1 Materials

Aluminum trichloride (AlCl₃) anhydrous sublimed for synthesis - Merck Chemicals
Sodium hydroxide - Merck chemicals - GR grade
Cetyltrimethyl ammonium bromide (CTAB) - Loba Chemie Pvt. Ltd, Mumbai, India
All the reagents were used without any prior purification

2.6.2.2 Procedure

Prepared 100.0 ml of 0.6 M of aluminum chloride in distilled water slowly and cautiously. Secondly the 100.0 ml of 0.10 M of CTAB alcoholic solution was prepared by dissolving the 1.823 g of CTAB in methanol.

Taken four necked R.B. flask equipped with mechanical stirrer, water condenser, thermometer pocket and additional funnel. 0.6 M AlCl₃ solution was placed in the flask. A cold solution of 4M NaOH was added drop wise to the reaction mixture. The pH of the solution was monitored. The NaOH addition is continued till the neutrality is achieved. On addition of NaOH the white precipitates were formed. The reaction mixture was stirred at 1000 rpm speed to avoid the agglomeration. After that the 0.05
Experimental

M CTAB solution was added in two parts to the reaction mixture to achieve the nanoparticles. The material was filtered washed to remove excess of surfactant and the base. The particles were vacuum filtrated and were vacuum dried and used for characterization and evaluation of properties.

2.6.3 Synthesis of Calcium Carbonate

2.6.3.1 Materials

Calcium chloride - SRL Chemials, Sisco Research Laboratories Pvt. Ltd, Mumbai, India.
Polyethylene glycol (PEG-6000) – Sulab reagents, Suvidhinath Laboratories, India.
Cetyltrimethyl ammonium bromide (CTAB) - Loba Chemie Pvt. Ltd, Mumbai, India
Sodium carbonate- Sulab reagents, Suvidhinath Laboratories, India
All the reagents were used without any prior purification

2.6.3.2 Procedure

Prepared 1M sodium carbonate and calcium chloride solution. Simultaneously prepared mixture of 0.01 M PEG-6000 and 0.1 M CTAB solutions.
In a three necked round bottom flask equipped with mechanical stirrer, addition funnel and the thermometer pocket was placed the PEG-6000 solution and calcium chloride solution under continuous stirring. The sodium carbonate solution was added drop wise using dropping funnel followed by addition of surfactant to prevent agglomeration. The white precipitates were formed on addition of sodium carbonate solution. The PEG-6000 promotes the medium for the growth of nanoparticles. The solution was allowed to stir for 6-8 hours at 500 rpm at higher temperatures. The resultant solid material was filtered, washed and dried. The particles were then used for further evaluation.
2.7 Synthesis of Quaternary ammonium compounds as Modifiers

2.7.1 Materials

Polyethylene glycol (PEG-300), (PEG-600) and (PEG-6000) Merck Chemicals – GR grade
Thionyl chloride- SDFCL, Sd. Fine. Chem. Limited, Mumbai, India- LR grade
Triethyl amine – Merck GR Grade
Diethyl ether – Merck-GR grade

2.7.2 Procedure

In a four necked round bottom flask equipped with the mechanical stirrer, dropping funnel, water condenser and the thermometer pocket, a calculated amount of PEG-300 was placed and thionyl chloride was added drop wise using dropping funnel. The reaction was refluxed under continuous stirring for 8 hours. Excess of thionyl chloride was distilled off. The reaction mixture was cooled and a calculated amount of the tertiary amine was added. The reddish brown color precipitates were formed immediately on addition of the amine under continuous stirring. The precipitates were collected, washed with diethyl ether and allowed to dry.

Two sets of the quaternary ammonium compounds coded as QS-1 and QS-2 were synthesized varying the glycols, PEG-300 and PEG-600 respectively. The materials prepared were used for modification of inorganic nano sized fillers.
2.8 CHARACTERIZATION

The polyurea, polyurethane, polyurethane-urea copolymers, epoxy polyamine and epoxy – PDMS copolymers were prepared and were characterized by the different techniques like end group analysis, functional groups determination by Fourier transform infrared (FT-IR) analysis, thermal properties by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and molecular weight determination using Gel permeation Chromatography (GPC). The nanoparticles were synthesized for improving the properties of polymers and copolymers. These nanoparticles were also characterized using different analytical techniques. The crystallite size and crystal structure were determined using the X-ray diffraction, the agglomerated particle size and the morphological studies were carried out using the Scanning Electron microscopy (SEM). The purity of samples was confirmed using the Energy Dispersive X-Ray Spectroscopy (EDXs). The polymers and copolymers and the nanoparticles filled polymers were tested for electrical properties such as surface resistivity, volume resistivity, dielectric constant, dissipation factor, dielectric strength and arc resistance. Mechanical Properties such as tensile strength and elongation at break and Izod impact strength of the samples were also tested and evaluated.

2.8.1 End Group Analysis

Weighed amount of isocyanate prepolymer was taken from the reaction vessel was dissolved in 25.0 ml of dibutylamine (DBA) (1N) after 3 minutes, while stirring added a drop of bromophenol blue indicator and was titrated against 0.05 N alcoholic hydrochloric acid.

\[
\% \text{NCO}=4.3 \times \text{Normality of Alc.HCl} \times \frac{(V_1-V_2)}{1000} \times W
\]

Where,

- \( W \) = weight of sample
- \( V_1 \) = Blank reading
- \( V_2 \) = Sample reading (ASTM D-2502 procedure 1981)
2.8.2 IR Analysis
To confirm the presence of functional groups the IR of each test specimen was taken, and studied. The scans were obtained from Perkin Elmer Spectrum BX Fourier transform infrared (FTIR) system (Huenenberg Switzerland). The samples for IR analysis were prepared as potassium bromide pellets.

2.8.3 Thermal Analysis
Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) techniques were used to study the thermal properties of insulating materials [292-294].

2.8.3.1 Thermogravimetric Analysis (TGA)
Thermogravimetric analysis of the elastomers and sheets was carried out on the METTLER TOLEDO TGA SDTA 851 thermo gravimetric analyzer. The samples were placed in aluminum pan in air. The thermograms of samples were recorded from room temperature to 550 °C at heating rate of 10 °C/min. The results were analyzed using the DiCerbo Method [295-296]. Figure 2.2 shows the TGA instrument.

Figure 2.2 TGA Instrument
DiCerbo Method
DiCerbo method involves drawing of tangents to the thermograms, one at a point at which curve start to deviate from its initial straight-line portion and other along the steep portion of the weight loss curve. Based on the temperature corresponding to intersection of the two tangents (A) and temperature at which 50% weight loss observed (B), the temperature index was calculated as given below.

Temperature Index = A + \frac{1}{2} (B-A) / 2.16

Where;
A = Temperature (°C) at which decomposition starts
B = Temperature (°C) at which 50% weight loss occurs

2.8.3.2 Differential Scanning Calorimetry (DSC)
DSC was conducted with METTLER TOLEDO DSC 822 shown in Figure 2.3. Ten milligram of sample was subjected to DSC analysis at 10°C per min heating rate and 20 cc per min air flow rate. The temperature was varied from ambient to 300°C. The objective of studying DSC was to find out the glass transition temperature and melting temperature of the polymer. The effect of molar concentration of different monomers on curing mechanism can also be studied using DSC.

Figure 2.3 DSC Instrument
2.8. 4 Gel Permeation Chromatography (GPC)

Gel Permeation Chromatography (GPC) is the most common used technique to find out the molecular weight distribution of polymers, resins, oils, oligomer, and organic compounds. It is a technique for measuring the molecular weight of polymers ranging from very low to very high molecular weights. Gel Permeation Chromatography was performed on GPC Perkin Elmer Series 200 Model to determine molecular weight of synthesized polymers at SICART Vidyanagar. The typical GPC system consists of injector, column and refractive index detector shown in Figure 2.4. GPC system has software for characterization techniques to find number average molecular weight, weight average molecular weight, Z average molecular weight Mz, Z+1 average, n-1 average molecular weight, Viscosity average molecular weight and polydispersity.

![Figure 2.4 Gel Permeation Chromatography](image)
2.8.5 X-Ray Diffraction (XRD)

X-Ray diffraction was performed on a Bruker AXS D8 shown in Figure 2.5. Advance X-Ray diffractometer uses Ni filtered Cu-Kα radiation. Normal XRD scans with step resolution of 0.02° with time step of 0.5 sec was used. To ensure stability of the measurements with respect to change in resolution in angular co-ordinates and time, measurements were repeated with angular step size (in 2θ) of 0.05° with time step of 2s. The Cu-Kα2 diffraction signal was removed by a standard stripping procedure to obtain the correct lattice parameters and grain size.

Figure 2.5 Powder XRD
2.8.6 Scanning Electron Microscope (SEM)

The morphology and the agglomerated particle size of the samples were analyzed using Scanning Electron Microscope. SEM analysis was carried out on cryogenically broken samples using field emission SEM on JEOL JSM-6380LV, Japan at accelerating voltage of 20 KV. The samples were coated by Platinum Sputter Coater vacuum coater (JEOL, JFC 1600, Auto fine Coater) to minimize electrostatic charging. Figure 2.6 represents the SEM instrument.

![Figure 2.6 Scanning Electron Microscope](image)

2.8.7 Energy Dispersive X-Ray Spectroscopy (EDXs)

Energy Dispersive X-Ray Spectroscopy was used for the elemental analysis of the materials. Energy Dispersive X-Ray Spectroscopy JEOL JSM-6380 LV INCA X-Sight, Model 7583 manufactured by Oxford instruments was used to detect the elements present in the inorganic fillers thus confirm the purity of samples. It was also used to determine the distribution of inorganic filler in the polymer matrix using Mapping technique. Energy Dispersive X-Ray Spectroscopy analysis with an accelerating voltage of 20 kV and a energy resolution of 85 eV, was employed to identify the elements on and under the nanocomposite surface. The samples were kept at 10-15 mm from the detector at a takeoff angle of 35°. Special care was taken to
attach the sample to the sample holder on the SEM machine in such a way that it actually stand outside the sample holder. This prevents false element identification by making sure that the sample holder is relatively far away from the electron beam. SEMs are equipped with a cathode and magnetic lenses to create and focus a beam of electrons, and since the 1960s they have been equipped with elemental analysis capabilities. A detector is used to convert X-ray energy into voltage signals; this information is sent to a pulse processor, which measures the signals and passes them on to analyzer for data display and analysis. EDAX-SEM elemental mapping analysis was carried out on cryogenically broken samples and samples were coated platinum Sputter Coater (JEOL, JFC 1600, Auto fine Coater) to minimize electrostatic charging before analysis.

2.9 Dielectric Properties
Since the materials developed were intended to be used for insulation purpose, the testing of their electrical properties was essential. Thus, the surface resistivity, volume resistivity, dielectric constant, dissipation factor and dielectric strength of the materials were evaluated.

2.9.1 Surface Resistivity
Surface resistivity measures the resistance of the material to moving or distributing a charge over its surface. Samples were prepared five measurement of the thickness each specimen was taken, and their average values were recorded. Surface Resistivity was measured as per ASTM specification using High Resistance Meter Model 4329A. The sheet prepared having diameter 100 mm was inserted into sample holder (cell) and charged for 1 minute at 500 V (direct current). The surface resistance measurements were carried out at 27 ± 2 °C.

Surface Resistivity (Ω) = 18.8*Rs

Where, Rs - the surface resistance (Ω)

2.9.2 Volume Resistivity
Volume resistivity measures the ability of the material to resist moving charge through its volume. The samples were prepared and five measurements of thickness on each specimen were taken, and their average values were recorded. High Resistance Meter of Hewlett-Packard (Model-4329 A) make was used for the
measurements. One sample was inserted at a time into the sample holder (cell) with the surface in contact with the graded electrode and charged for 1 min at 500 V, DC. The volume resistivity measurements were carried out at 27±2 °C and were measured in Ohm-cm. Figure 2.7 shows the High resistance meter.

**Volume Resistivity (Ω-cm) = 19.6 \( R_v/t \)**

Where, \( R_v \) = indicated volume resistance (Ω)

\( t \) = Thickness (cm)

![Figure 2.7 High Resistance Meter](image)

**2.9.3 Dielectric Strength**

The dielectric strength of an insulating material is defined as the maximum voltage required to produce a dielectric breakdown. The brass electrodes consisting of opposing cylindrical metal rods of 1mm in diameter with edges rounded to a radius of 0.8 mm were taken in a wooden set-up and polished prior to testing. The electrode faces were kept parallel and held exactly opposite to one another. The sample was kept between the two electrodes and applied voltage method was used to measure the voltage at 27±2°C. According to this method, the voltage raised from zero at a uniform rate at 500 V/sec (as per Test Method ASTM D 149) such that break down occurs on an average between 10-20 sec. Five measurements of breakdown voltage were taken and the electric strength was calculated in kV/mm. The set up for the
Experimental measurement is shown in Figure 2.8. The different sources supply for measurement on different kind of samples. Figure 2.9 represents the 0-5 kV source is required for the measurement of dielectric strength of coated sample, or thin film. The samples of more than equal to one mm thickness sheets were tested on 0-50 kV source panel shown in Figure 2.10 using the same arrangement as show in Figure 2.8. Similarly the 0-100 kV source panel is shown in Figure 2.11. The dielectric strength of the materials were calculated using the below mentioned equation.

\[
\text{Electric strength (kV/mm) = Breakdown Voltage (kV)/ Average thickness (mm)}
\]
Figure 2.8 Measurement Set-Up for Dielectric strength
Figure 2.9 0-5 kV Source Panel Instrument

Figure 2.10 0-50 kV Source Panel Instrument
2.9.4 Capacitance and Dielectric Constant

The dielectric constant is defined as the ratio of the capacitance of the material placed between two plates and the capacitance of the same plate with a vacuum between them. In many applications, insulating materials are required to perform as capacitor. Such applications are served by plastic materials having high dielectric constant and when insulating materials are used to isolate the current carrying conductor, it is desirable to have the low value of capacitance.

Samples were prepared and five measurements of thickness on each specimen were taken, and their average value was recorded. The samples were cut in circular shape with diameter of 80 mm. These cut samples were placed between the two electrodes of Schering Bridge of Tettex A G Instrument. The measurements were carried out at 250 V, 50 Hz frequency at 23 °C, applying a little pressure of 2 N/cm² to ensure the absence of any air gap between the samples as per ASTM D-150. The capacitance value was measured in pF was directly used for calculating the dielectric constant of the material using the below mentioned equation.

\[
\text{Dielectric Constant} = 0.5647 \times C_p \text{ (pF) } \times \text{thickness (cm)}
\]
The dielectric constant values were calculated and presented in the respective tables. The schematic representation of the set-up of Instrument for measurement of capacitance and dissipation loss is shown in Figure 2.12. The whole measurement was carried out through controlled computer programme.

2.9.5 Dissipation Factor (Tan $\delta$)

In all electrical applications it is desirable to have minimum electrical losses. The dissipation factor measures electrical inefficiency of the materials. Lower the dissipation factor, greater is the electrical efficiency of the material. Samples were prepared and five measurements of thickness on each specimen were taken, and their average value was recorded. The samples were cut in circular shape with diameter of 80 mm. These cut samples were placed between the two electrodes of Schering Bridge of Tettex A G Instrument. The values of resistance, capacitance and frequency were entered into the formula mentioned below to calculate tan $\delta$. The measurements were carried out at 250 V, 50 Hz frequency at 23°C applying a little pressure of 2 N/cm$^2$ to ensure the removal of the any air gap between the samples as per ASTM D-150.

Dissipation factor (tan $\delta$) = $R_4 \omega C_4$

Where, $\omega = 2 \pi f$

$\omega = 2 \pi f$

$f = \text{Frequency (Hz)}$

$R_4 = \text{Resistance (}\Omega\text{)}$

$C_4 = \text{Capacitance (F)}$
2.9.6 Arc Resistance

Arc resistance is the ability of plastic material to resist the action of the high voltage electrical arc, and usually stated in terms of time required to form material electrically conductive. The arc resistance is tested on Arc Resistance Tester-Beckman instrument according to ASTM D 495-99. The 12.5 kV voltage was applied to the sample in the step up form. The values were measured in the seconds.
2.10 Mechanical Properties

Since the materials developed were used for insulation purpose, along with the electrical properties mechanical properties too have an important role during applications.

2.10.1 Tensile Strength and Elongation at Break

Tensile strength and elongation at break of polymer were measured according to ASTM D638 (Type 4) using universal testing machine, Hounsfield, U.K. at a cross head speed 100 mm/min with 5kN load cell keeping gauge length 25 mm. The average value of five samples is reported. The instrument for measurement is shown in Figure 2.14.

\[
\text{Tensile Strength (N/mm}^2\text{)} = \frac{\text{Load (N)}}{\text{Width (mm)} \times \text{thickness (mm)}}
\]

\[
\% \text{ Elongation} = \frac{E \times 100}{20}
\]

2.10.2 Impact Strength

Impact Strength was measured on Impact Tester make CIPET as per ASTM D256. The two Joules energy hammer was used and striking velocity was 3.46 m/sec. The Izod impact strength of the unnotched samples was tested and average of three readings is reported.

\[
\text{Izod Impact Strength (J/cm}^2\text{)} = \frac{\text{Load (joules)}}{\text{Width (cm)}} \times \text{Thickness (cm)}
\]
Figure 2.14 Tensile strength Meter

Figure 2.15 Impact Strength Tester