CHAPTER-1

INTRODUCTION
1.0 INTRODUCTION

There are several commercially available polymer and elastomer systems based on polyurethane, modified polyurethanes, polyesters, modified polyesters, epoxies, methacrylates, polysulfides or silicones etc. These systems are commercially used for making commercial products such as coatings, composites and many other industrial applications. The main characteristics required of all these polymer systems are fast reactive, resistant at a wide temperature range, moisture resistance, high chemical and abrasion resistance, high performance mechanical properties, fast curing, solvent free and eco friendly in nature.

1.1 POLYUREA POLYMER

Polyurea and their copolymers have versatile applications for specialty coatings and composites for electrical as well as industrial applications. Polyurea homopolymers are the products with urea groups (-NH-CO-NH-R-)_n occurring repeatedly in aliphatic, cycloaliphatic or aromatic carbon chain. The main interest of the formation of polyurea originates from the potential ability to process by conventional techniques. The polyurea and their copolymers have versatile properties over the other conventional polymers and copolymers used in industrial products for allied industries. The products made of polyurea and its copolymers need minimum solvent and have high solid content, especially in formulating the specialty coatings. They are eco friendly and do not cause pollution while coating.

The synthesis of polymers containing heterocyclic rings in the main chains has been subject of considerable interest because of their relatively good thermal stability and some novel properties [1-4].

Thus on carrying out extensive literature search on polymeric coating materials and elastomeric polymeric materials, polyurea and its copolymers were surveyed as one of the best material compared to other polymers. Polyurea coatings are of very high mechanical strength and lot of work has been carried out on mechanical behavior of polyurea [5-11]. Moreover, it has been observed that polyurea polymeric materials have not been used for electrical applications.
During the course of this work we have focused on synthesis of polyurea homopolymers and its copolymers with varying the monomers concentration mainly for electrical applications.

The polyurea were considered as derivatives of poliamide of carbonic acid from amidation process between diamines and the other reaction monomers of carbon dioxide CO$_2$, carbon oxysulfide COS, carbonic esters –COOR, phosgene, urea, urethane and isocyanates that give rise to (-NH-CO-NH-)$_n$ linkage. As an example, hexamethylene diamine gives polyurea with melting point 300°C, nonamethylenediamine 245°C. The properties observed derived from the preparation of polyurea using diamine and urea seems to offer advantage over the other methods, therefore the process is separated from the poliamides.

The new matrices such as polyurethane-urea and epoxy-silicones have been synthesized and evaluated for thermal, electrical and mechanical properties. These new matrices may find wide applications in formulating products for industrial applications. They overcome brittleness and impact strength of epoxy resins which are having wide consumption in manufacturing the products such as adhesives, sealants and composites.

In order to improve further properties of the existing products, we have synthesized the nanoparticles of alumina, aluminum trihydroxide and calcium carbonate and incorporated in above matrices with a view to develop high performance coatings and composites for different applications. Some applications such as coatings on electrical conductors, metallic sheets and electrical panels were developed.
1.1.1 HISTORIC DEVELOPMENT OF POLYUREA

The main interest of the formation of polyurea originates from the potential ability to process them into fibers. Moreover, they are high melting polymers, having higher melting points than the corresponding polyamides. This is due to the high molecular cohesion present in the N-H hydrogen bonding. Most of the common methods for preparation of polyurea consist of polymerization of diamines with various classes of compounds. They can be synthesized using different starting reagents and monitoring different reaction conditions.

The commonly known method of preparation of polyurea is the reaction of diamines with carbon dioxide developed during early 1913 by Fischer by heating tetramethylene diamine and carbon dioxide under pressure for 36 hr at 220°C as shown in (equation 1) [12-14].

\[
\text{NH}_2-R-NH_2 + CO_2 \rightarrow R-NH-CO-NH- + H_2O
\]

..... (1)

Diamines on reaction with carbon oxysulphide give polyurea with the formation of intermediate thiocarbamate salt. On heating the salt of dry hydrogen sulphide gas is eliminated quantitatively with formation of linear polyurea (equation 2) [15-16].

\[
\text{H}_2\text{N-} \left( \text{CH}_2 \right)_n\text{NH-C-S}^{-} \xrightarrow{\text{heat}} \text{NH}_2(\text{CH}_2)_n[\text{NH-CO-NH-(CH}_2)_m]_m\text{NH}_2
\]

\[
\text{NH}_2(\text{CH}_2)_n\text{NH}_2 + \text{NH}_2(\text{CH}_2)_n[\text{NH-CO-NH-(CH}_2)_m]_m\text{NH}_2 \xrightarrow{\text{heat}} \text{NH}_2(\text{CH}_2)_n\text{NH}_2 + \text{NH}_2(\text{CH}_2)_n[\text{NH-CO-NH-(CH}_2)_m]_m\text{NH}_2
\]

..... (2)
Polyureas can also be prepared using carbonic ester such as dibutyl or diphenyl carbonates and diamines as shown in (equation 3) [17].

\[
\text{n NH}_2\text{R-NH}_2 + \text{n R'-O-CO-OR'} \rightarrow \text{NH-R-NH-CO}_n + 2\text{n R'OH}
\] .... (3)

Another method for the preparation of polyurea is using acid chlorides. A diamine can also be reacted with phosgene in presence of base (equation 4). The main disadvantage of the reaction is presence of residual chloride in the polymer originating from the carbonyl chloride group [18].

\[
\text{NH}_2\text{R-NH}_2 + \text{Cl-CO-Cl} \xrightarrow{\text{NaOH}} \text{NH-R-NH-CO}_n + \text{NaCl}
\] .... (4)

An alternating polyurea (mp 265°C) was obtained from the piperazinedi(carbonyl chloride) and hexamethylene diamine. Polyureas prepared from the five member heterocycle ethylene urea are believed to have the following structure (5) [19].

\[
\text{NHCH}2\text{CH}2\text{NHCO-CNHNCH}2\text{CH}2
\] .... (5)

When molecular-weight regulators N-pelargonyl-nonamethylene diamine or phthalimide are present during the reaction of diamine and urea, the end groups consist of pelargonamide or phthalimide groups as shown in structure (6) [20].

\[
\text{C=C=C=N-R-NH-CO-NH-R-H}
\] .... (6)
Introduction

One of the earliest methods for preparing polyurea is based on the reaction of a diamine with urea [21-23]. Moreover it is also been reported that when diamine is heated with stoichiometric amount of urea in the absence of air, a polyurea is formed with evolution of ammonia as shown in equation (7).

\[ \text{NH}_2-R-\text{NH}_2 + \text{NH}_2-\text{CO-NH}_2 \xrightarrow{\text{Heat}} \{\text{NH-CO-NH-R}\}_n \]  

..... (7)

It is also been reported that the melting point increases with increasing molecular weight of the material. Thus molecular weight increases, viscosity also increases simultaneously. Moreover it is also reported that in aliphatic polyurea the melting point decreases with increase in number of methylene groups. Thus the chain extenders are used for regulating the molecular weight of the polymer from substituted ureas, naphthalene or dodecylbenzenesulphonic acid and aromatic primary or secondary amines.

The polyurea polymers having even number of carbon atoms in the methylene chains have higher melting points than those with an odd numbers of methylene groups. The formation of trialkylureas or aryldialkylureas was reported by reaction of alkyl or arylamines with urea or monosubstituted ureas [24]. Substitution of hydrogen atoms along the carbon chain by alkyl groups lowers the melting point significantly. One methyl substituent per unit causes the decrease of melting temperature by 30°C, similarly two methyl substituent by 60°C, two ethyl substituent by 80°C and isopropyl substituent by 90 °C.

A wide variety of aliphatic and aromatic diamines can be used for the preparation of polyureas by this method [21-23, 25-27]. Unsaturated diamines, diamine containing the heteroatoms e.g. oxygen, or nitrogen (Secondary and Tertiary amines) can be used.

The substitution of methylene by oxygen in methylene chains does not influence the melting temperature of the polymer but on introducing the sulphur, it increases the melting temperature by 25°C. The introduction of nitrogen in the carbon chain causes the melting temperature to decrease significantly. A very large decrease occurs when tertiary amino groups are incorporated in the polymer chain.
The variation in melting point is shown using the below mentioned example.

\[
\text{NH}_2-\text{CH}_2-\text{N}(\text{-CH}_2-\text{NH}_2)
\]

When \( R = \) Aliphatic substituent polycondensation with urea, the melting temperature is in the range of 37-75 °C.

When \( R = \) Aromatic substituent, the melting temperature is higher ranging 110-115°C [28].

It is also been reported that the diurea can be prepared from the diamine and potassium cyanate, thiourea or urea itself, or via interaction of dichlorides with potassium cyanate.

Equation (8) represents the synthesis of polyureas by heating alkylene diureas without the diamine. The disadvantage of this method is the presence of biuret, urea or cyanuric acid in the polymer as shown in equation (9).

\[
\begin{align*}
\text{NH}_2-\text{CO-NH}_2 + \text{NH}_2-\text{CO-NH}\_R & \rightarrow \text{R-NH-CO-NH}\_R + \text{NH}_2-\text{CO-NH}_2 \\
\text{NH}_2-\text{CO-NH}_2 & \rightarrow \text{NH-CO-NH-CO-NH}_2 + \text{NH}_3
\end{align*}
\]

When the reaction is carried out in bulk, infusible, insoluble cross linked polymers are obtained instead of the expected linear polyureas. This is due to interaction of highly reactive isocyanate groups with the active hydrogen atoms of amines leads to branching as shown in the Figure 1.1. Thereby, to avoid such cross linking and gel formation, the reactions are favored to be carried out in the presence of a solvent in which polymer is soluble. The preferable solvents are polar solvents such as methyl ethyl ketone (MEK), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), phenols etc.
Cross linking does not take place when reaction occurs between aromatic diisocyanate and aromatic diamine due to the steric hindrance of benzene ring. Large differences in reactivity are observed when aliphatic and aromatic diisocyanate react with amines [29-31]. There are other ways reported for formation of symmetrical polyurea using diisocyanate with equivalent amount of benzoic acid in DMSO. The clear, yellowish and viscous liquid formed is used for casting films [32]. Equation (10) represents the formation of symmetrical polyurea in presence of polar DMSO solvent.

\[
\text{OCN-N} + \text{COOH} + \text{CH}_3\text{S-CH}_3 \rightarrow \text{CO}_2 + \text{COO-CH}_2\text{S-CH}_3
\]

..... (10)

Jewrajka et. al. studied the design, synthesis, characterization, and structure–property behavior of polyureas containing novel soft segments of mixed polyisobutylene (PIB)/poly(tetramethylene oxide) (PTMO) chains and conventional hard segments. This material exhibited the hydrolytic and oxidative stabilities [33].
1.1.2 RECENT DEVELOPMENT/ADVANCES OF POLYUREA

Polyurea forms a state of art, high performance, elastomeric membrane which offers several advantages. It is fast curing even at low temperatures, moisture resistance, has excellent chemical resistance, good mechanical properties, high durability and with negligible volatile organic content. It makes coatings for several applications such as roof repair, containment liners, membrane, car park decks, bridges, offshore etc.

Polyurea system has also been characterized as modified two-component polyurethane system. Polyurea and polyurethane are related on two component system, with one being isocyanate component. Polyetheramine is the second component for the polyurea whereas polyether glycol is second component for the polyurethane. But polyurea is a new technology in itself. The resin blend must be made up of amine terminated polymer resin or an amine chain extenders. These chain extenders should not have any intentional hydroxyl moieties. The presence of hydroxyl moieties results into incomplete conversion of the desired polymer. Moreover, synthesis of polyurea does not require any catalyst whereas, the polyurethane does require a catalyst. The amines have active hydrogen for the reaction and that can speed up the reaction, whereas that active hydrogen is absent in glycols, and therefore, requires catalyst for the reaction. The general reactions leading to Polyurea and Polyurethane are shown in Figure 1.2 (a-b).

\[

c_{\text{OCN}} + \text{H}_2\text{N} \xrightarrow{\text{Polyamine}} \text{NCO} + \text{NH}_2
\]

**Figure 1.2.a General Polyurea Reaction**

\[

c_{\text{OCN}} + \text{HO} \xrightarrow{\text{Polyol}} \text{NCO} + \text{OH}
\]

**Figure 1.2.b General Polyurethane Reaction**
Polyurea and polyurethane are general names for a wide range of polymeric materials that have extensively been used in the coating industry in solid elastomeric or rigid forms. Here, we focus mainly on the synthesis, properties and applications of polyurea in its solid elastomeric form with new combinations of monomers.

The actual reference of polyurea was found in 1948 during evaluation of thermal properties of various polymers [34] and it was found that the polyureas were far better than polyamides, polyurethanes, linear polyethylene, polyesters etc. The two component fast setting polyurea coating was first introduced in 1986 [35-39]. The process evolves the need to develop a more stable, durable and 100% solid polymers system for rigid coating. In 1989, the first coating was introduced which was used in the roofing system. In the 1970s', the modified polyamines and high levels of plasticizers and solvents were used to obtain the sprayable coating system. At the same time the polyurea- epoxy- urethane system was introduced as composite traction system [40].

Several discoveries and advancements in elastomeric polymer chemistry were based on reactive amine terminated resins and high performance isocyanate prepolymers. Polyureas have been formed by direct interaction of a diisocyanate and a diamine, this is a polyaddition reaction. When the reaction components have different backbones, the alternating copolyureas can be prepared provided the factors for random polymerization are completely avoided. The reaction of isocyanate with amine (high molecular weight polyether amine) results in the formation of highly reactive isocyanate terminated prepolymer followed by reaction with a chain extender, an amino group terminated lower molecular weight amine results in to polyurea. The synthesis of polyurea does not require a catalyst, the reaction is autocatalytic and very fast in nature. Whereas, the reaction of isocyanate with diols (high molecular weight glycols) leads to the formation of reactive isocyanate prepolymer in presence of catalyst and solvent followed by the reaction of prepolymer with a chain extender, hydroxyl terminated diols those result into formation of polyurethane. Different probabilities can be carried out using the different functional groups after and before, lead to the formation of different properties. These resulting polymer systems were referred to as polyureas and had certain characteristics suitable for rapid process application. Table 1.1 represents the composition of the polymer with different
polymer backbone as mentioned. Figure 1.3 (a-d) represents the compositional different polymer backbone.

Table 1.1 Resin System for making Polyurea and its Copolymers

<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>Resin part</th>
<th>Chain extender</th>
<th>System type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Polyetheramine</td>
<td>Amine terminated</td>
<td>Polyurea</td>
</tr>
<tr>
<td>2.</td>
<td>Polyether polyol</td>
<td>Amine terminated</td>
<td>Polyurethane-urea</td>
</tr>
<tr>
<td>3.</td>
<td>Polyetheramine</td>
<td>Glycol</td>
<td>Polyurea urethane</td>
</tr>
<tr>
<td>4.</td>
<td>Polyether polyol</td>
<td>Glycol</td>
<td>Polyurethane</td>
</tr>
</tbody>
</table>

Figure 1.3.a Polyurea Polymer Structure

Figure 1.3.b Polyurea/Polyurethane Hybrid Polymer Structure
Thus the polyurea requires the three different components for the synthesis as reactive diisocyanate, high molecular weight amine terminated resin and low molecular weight chain extender.

1.1.3 ISOXYANATE - 1st component for synthesis of Polyurea

Isocyanate are highly reactive liquids or solids capable of undergoing addition reaction across the C=N double bond of the NCO group. The high reactivity can be added due to their resonance structure as shown in Figure 1.4. It is well known that isocyanate readily react with alcohols, carboxylic acids, and amines. The reactions have been widely exploited in developing a variety of commercial products. The basis of high reactivity of the isocyanate is the low electron density on the central carbon, as indicated by the resonance structures. Electron-withdrawing or electron-donating substituent alters the electrophilic nature of the isocyanate. The reactivity of isocyanate is also manifested in their tendency to react with themselves to form dimers, trimers, or higher oligomers and polymers. Analytically, isocyanate is readily identified through derivation (urea formation) or via IR spectroscopy using the strong absorbance between 2300 cm\(^{-1}\) and 2200 cm\(^{-1}\).
The reactivity of aromatic isocyanate depends on the electron releasing or electron withdrawing functional groups present on the ring.

Where $X = \text{electron withdrawing group}$, the reactivity increases

$X = \text{electron releasing group}$, the reactivity decreases.

Generally, during polymerization the diisocyanates are used for the reaction. Isocyanates are classified into aliphatic and aromatic types. Due to their high reactivity apart from their required reactions some side reactions also occurred [41-42]. Different reactions and ultimate products of the reactions are mentioned below.

**Reactions of Isocyanates**

Isocyanate reacts with all compounds containing hydrogen atoms attached to a hetero atom [43]. There are four basic reactions observed during the study of chemistry of isocyanate. The reaction of isocyanate with hydroxyl groups to produce urethane is the primary reaction. The reaction of isocyanate with amines yields urea and the reactions of isocyanate with urea and urethane produce biurets and allophanates, respectively. The order of reactivity is shown in Table 1.2.
Table 1.2 Reactivity of active hydrogen compounds

<table>
<thead>
<tr>
<th>Hydrogen Compounds</th>
<th>Formula</th>
<th>Reactivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary aliphatic amine</td>
<td>R-NH₂</td>
<td>Highly reactive</td>
</tr>
<tr>
<td>Secondary aliphatic amine</td>
<td>R₂-NH</td>
<td></td>
</tr>
<tr>
<td>Primary aromatic amine</td>
<td>Ar-NH₂</td>
<td></td>
</tr>
<tr>
<td>Primary hydroxyl</td>
<td>R-CH₂-OH</td>
<td>Reactivity decreases</td>
</tr>
<tr>
<td>Secondary hydroxyl</td>
<td>R₂-CH-OH</td>
<td></td>
</tr>
<tr>
<td>Tertiary hydroxyl</td>
<td>R₃-C-OH</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>Ar-OH</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>H-O-H</td>
<td>Less reactive</td>
</tr>
</tbody>
</table>

**Reaction of Isocyanate with Water**

Isocyanate have a strong affinity to water, due to which, there is always difficulty in storing. This reaction is not desirable in applications such as structural adhesives and sealants [44]. Isocyanate reacts with water giving carbamic acid, an unstable compound which spontaneously decomposes into a primary amine and carbon dioxide, together with a subsequent urea formation (Figure 1.5).
Introduction

Reaction of isocyanate with water

\[ i) \quad R_1-N=C=O + H_2O \rightarrow R_1N-C=O + H_2 \rightarrow R_1-NH_2 + CO_2 \]

\[ ii) \quad R_1-N=C=O + R_1-NH_2 \rightarrow R_1-N-C-N-R_1 \]

Overall reaction

\[ 2R_1-N=C=O + H_2O \rightarrow R_1-N-C-N-R_1 + CO_2. \]

Figure 1.5 Reaction of isocyanate with water

Reaction of Isocyanate with Alcohols

Isocyanate groups react with polyfunctional active hydrogen compounds to give high molecular weight polyurethane products. One of the most important reactions of isocyanate compounds is with di- or polyhydroxyl compounds, for example hydroxyl terminated polyesters or polyethers. The nucleophilic reaction occurs between alcohol and the electron deficient carbonyl carbon of isocyanate group [45]. The functionality of the hydroxyl containing compound as well as of the isocyanate can be increased to three or more to form branched or cross-linked polymers. Different degrees of reactivity are expected from different compounds as shown in Table 1.2. This is also affected by the steric hindrance of either the isocyanate or the active hydrogen compounds. The reaction proceeds at ambient temperatures without the use of catalysts. Reactivity is higher for primary alcohols, decreasing for secondary, tertiary alcohols and phenols Figure 1.6.

\[ \text{Isocyanate} + \text{Alcohol} \rightarrow \text{Urethane} \]

Figure 1.6 Reaction of isocyanate with alcohols

Where, \( R_1 \) and \( R_2 \) stand for an aliphatic or aryl group.
Reaction of Isocyanate with Amine

Isocyanate reacts with amines usually at 0-25°C yielding urea. Primary aliphatic amines react quickly followed by secondary aliphatic amines and aromatic amines Figure 1.7.

\[
\text{R}_1\text{—N—C—O} + \text{R}_2\text{—NH}_2 \rightarrow \text{R}_1\text{—N—C—N—R}_2
\]

Isocyanate Amine Urea

\[
\text{R}_1\text{—N=C=O} + \text{R}_2\text{—NH}_2 \rightarrow \text{R}_1\text{—NH—CO—N—R}_2
\]

Isocyanate Secondary amine Substituted urea

Figure 1.7 Reaction of isocyanate with primary and secondary amines

Allophanate and Biuret Formation

Isocyanate can react, in excess conditions, with urea and urethane to produce allophanate and biuret compounds. In polymers containing both urea and urethane groups in roughly same concentrations, branching is introduced principally by biuret formation. These reactions occur more readily at higher temperatures and it can be seen that the products, allophanates and biurets, are in equilibrium with the starting materials, isocyanate and active hydrogen compounds as shown below in Figure 1.8 and Figure 1.9. Figure 1.10 gives the representation of possible products formed during the reaction of isocyanate with different reactants.

\[
\text{R}_3\text{—N=C=O} + \text{R}_1\text{—N—C—O—R}_2 \leftrightarrow \text{R}_1\text{—N—C—O—R}_2
\]

Isocyanate Urethane Allophanate

Figure 1.8 Allophanate Formation
**Introduction**

\[
R_3\text{-N=C=O} + R_1\text{-N=C=O} \rightleftharpoons R_3\text{-N=C=O} + R_1\text{-N=C=O}
\]

Isocyanate

\[
\text{Urea}
\]

\[
\text{Biuret}
\]

Figure 1.9 Biuret Formation

Figure 1.10 Representation of possible products during the reaction of Isocyanate with different reactants
The aromatic and aliphatic diisocyanates used in the synthesis of polyurea along with their structures are listed below.

**Aromatic Diisocyanate**
- Toluene diisocyanate (TDI)
- 4, 4'-methylene bisphenyl isocyanate (MDI)
- Tetramethylxylidene diisocyanate (TMXDI)
- 1,5-Napthalene diisocyanate

**Aliphatic Diisocyanate**
- 1,6 Hexamethylene diisocyanate
- HDI Biuret
- Isophorone diisocyanate (IPDI)
Among the above mentioned diisocyanates the HDI biuret is the cheapest and but the most commonly used are TDI and MDI.

TDI is synthesized from toluene via nitration process followed by reduction and finally, phosgenation. Commercially, phosgenation of primary amine is the most important reaction to prepare an isocyanate [46]. The synthesis of TDI is mentioned in the reaction below in Figure 1.12.

Figure 1.11 Structure of diisocyanate used for the synthesis of polyurea

Figure 1.12 Schematic representation for synthesis of TDI
Similarly, the MDI is synthesized using formaldehyde and aniline followed by phosgenation. Schematic representation of MDI is shown in Figure 1.13.

![Figure 1.13 Schematic representation for synthesis of MDI](image)

Technical products of TDI, HDI and IPDI generally contain isocyanate adducts such as biuret, isocyanurate and allophanate. These isocyanate adducts have lower vapor pressure as compared to the monomeric isocyanate, thereby, reducing the risk of isocyanate exposure due by evaporation [47].

1.1.4 AMINES: - 2nd component for synthesis of Polyurea

A wide variety of amines such aliphatic, aromatic or/cycloaliphatic diamines or triamines are commonly used during synthesis of polyurea. In certain applications, higher molecular weight amine terminated is used in combination with low molecular weight amines.

A polyurea coatings/ elastomer are derived from the reaction product of an isocyanate component and a resin blend component. The isocyanate can be aromatic or aliphatic in nature. It can be monomer, polymer, or any variant reaction of isocyanate, or a prepolymer. The prepolymer or quasi-prepolymer can be made of an amine-terminated polymer resin [35-36, 47-49]. The resin blend must be made up of amine-terminated polymer resins, and/or amine terminated chain extenders. The amine-terminated polymer resins do not have any intentional hydroxyl moieties. Any hydroxyls are the result of incomplete conversion to the amine-terminated polymer resins. The resin blend may also contain additives, or non primary components. It utilizes soft-block and hard-block segments for the reactive constituents. The soft-block segments are the high molecular weight resins, referred to as polyetheramines.
or amine terminated polyethers. These polyetheramines are either di-functional or tri-functional with blends of the two providing for certain elastomer physical properties and performance. The diamine and triamine are used and these resins provide the flexibility in the resulting polyurea polymer system.

Polyetheramine is characterized by repeating oxypropylene units in the backbone. Polyetheramine is a difunctional or trifunctional primary amine with different average molecular weights. The primary amine groups are located on secondary carbon atoms at the end of the aliphatic polyether chain as shown by the representative structure.

The values of ‘x’ differ with different polyetheramine.

\[
\text{H}_2\text{N}-\left(\begin{array}{c}
\text{O} \\
\text{CH}_3 \\
\text{CH}_3
\end{array}\right)^x\text{NH}_2
\]

In the present work the higher molecular weight amines such as polyoxypropylene diamine (D-2000) and polyoxypropylene triamine (T-5000) Jeffamine are used as soft block during the synthesis of polyurea polymers.

The other portion of the resin blend component is the hard-block, or more commonly called the chain extender. A chain extender is the low molecular weight amine terminated resin that completes the polymer chain and extends / controls the overall dry time of the system. The most common chain extender used in two-component polyurea elastomer systems is diethyltoluene diamine (DETDA) [49]. Typical low molecular weight amines such as bis(4-aminocyclohexyl)methane, isophorone diamine (IPDI), diethyl toluene diamine (DETDA), Hexamethylene diamine (HMDA), m-Xylene diamine (m-XDA) etc used as a chain extender for the reaction.
1.1.5 APPLICATIONS OF POLYUREA

Polyurea are being used for specialty coatings in industrial sectors as projected in Figure 1.14 shown below. Their advantageous properties include high abrasion and chemical resistance, excellent mechanical and elastic properties. It has been used for many applications including encapsulation of pharmaceutical, ink, dyes [48], and also widely used for coatings [49] metallic tanks, pipe lines protections etc [50-52].

Figure 1.14: - Application of Polyurea

There is no application found so far in electrical industries. We have synthesized polyurea, its copolymers as a new matrix and fast curing agent.
1.2 POLYURETHANE POLYMER

1.2.1 HISTORIC DEVELOPMENT OF POLYURETHANES

The polyurethanes were prepared as early as in 1937 by Otto Bayer and coworkers at I. G. Farben industries, Germany [53-56]. This discovery was Germany's competitive response to Carothers' work on polyamides, or nylon, at E. I. du Pont. The successful development of high molecular weight polyamides was carried out by Bayer who found the similar materials that were not covered by Du Pont's patents. The initial work was reaction between an aliphatic isocyanate with a diamine to form polyureas that were infusible, but very hydrophilic. Further, research on this subject, demonstrated that when an aliphatic isocyanate reacted with a glycol, a new material with interesting properties for production of plastics and fibers could be made. Du Pont and ICI soon recognized the desirable elastic properties of polyurethanes. The industrial scale production of polyurethane started in 1940 [57-58].

Polyurethane is a versatile class of the polymer, mainly due to their rapid and easy processing and excellent chemical and physical properties which can be tailored to suit a wide range of applications. Polyurethane derived from the natural resources and their possibilities for industrial utilization have gained considerable interest in recent time [59-60]. They are produced by reaction of polyalcohol in presence of a catalyst and other additives. The polyurethane coatings and elastomers developed, consisted of these following components [61-66].

a. Diisocyanate
b. Polyester and polyether based macrodiols (eg. \( M_n \) of 1-2000g/mole)
c. Chain extenders low molecular weight diol or diamine/ or cross linker
d. Catalyst
1.2.2 POLYESTER AND POLYETHER BASED MACRODIOLS

Almost all the dihydroxy compounds react with diisocyanate to form polyurethane. The aliphatic diols with varying number of methylene groups in between hydroxyl groups are commonly used [61-68]. The primary hydroxyl groups are much more reactive compared to secondary and tertiary hydroxyl groups. The difference in reactivity is observed due to steric hindrance of the substitution [27]. Dihydroxy aromatic compounds and biphenylols are another set of compounds which are used to prepare polyurethanes [25, 61-66, 69-71].

Recently, the use of functionalized heterocyclic compounds to prepare the polyurethane, has gained interest due to more versatility and wide applications [72].

Following is the list of the macrodiols used for the synthesis of polyurethanes and the Table 1.3 represents the some of the polyether and polyester polyols with their structure.

- Polypropylene ether diol
- Polyether polyol
- Polycarbonate polyols
- Polybutadiene polyols
- Polycaprolactone polyols
- Polysulfide polyols
- Polytetramethylene glycol (PTMG)
1.2.3 SHORT CHAIN DIOLS/ CHAIN EXTENDER

Short chain diols are used for the chain extension to achieve the desired molecular weight and providing the hard segments to the polymers. When the functionality of monomer exceeds it can lead to the cross linking during polymerization. Thus the short chain diols react with prepolymer and provide the hard segments to the polymer. Following is the list of the short chain diols used during the polymer preparation.

- Diethylene glycol
- Dipropylene glycol
- Trimethylol propane
- Glycerine (1, 2, 3-Trihydroxypropane)
- 1, 3-Propane diol
- Neopentyl glycol

### Table 1.3 Polyether and Polyester Polyol

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Polyol</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG</td>
<td>Polyethylene glycol</td>
<td>HO(\underbrace{\text{C}_n\text{H}<em>2\text{O}}</em>{n})OH</td>
</tr>
<tr>
<td>PPG</td>
<td>Polypropylene glycol</td>
<td>HO(\underbrace{\text{C}_n\text{H}<em>2\text{O}}</em>{n})OH</td>
</tr>
<tr>
<td>PTMO</td>
<td>Polytetramethylene oxide</td>
<td>HO(\underbrace{\text{C}_n\text{H}<em>2\text{O}}</em>{n})H</td>
</tr>
<tr>
<td>PEO</td>
<td>Polyethylene oxide</td>
<td>HO(\underbrace{\text{C}_n\text{H}<em>2\text{O}}</em>{n})H</td>
</tr>
</tbody>
</table>
1.2.4 CATALYST SYSTEM

Polyurethane preparation does require a catalyst for enhancing the speed of reaction. The amines have the active hydrogen for the reaction and that can speed up the reaction, whereas that active hydrogen is absent in glycols, and therefore, requires sufficient amount of catalyst for the reaction to carry forward. Catalysis of the isocyanate-hydroxyl reaction has been studied by many authors who found that the reaction of aliphatic isocyanate with hydroxyl groups is catalyzed by many metal carboxylates and organo-tin compounds. Tertiary amine catalysis of the reaction of aromatic isocyanate with hydroxyl groups has been practiced for some time and is common for the preparation of flexible polyurethane foams [73-74]. The reaction of IPDI with alcohols was studied in absence and in presence of dibutyltin dilaurate (DBTL) and 1,4-diazobicyclo[2,2,2]-octane (DABCO) [61-66, 75-76].

In the presence of DBTL, the reaction of the secondary isocyanate group was favored, while in the presence of DABCO the reaction of the primary isocyanate group was preferred. The relative reactivity of the isocyanate group depends on the mode of catalysis and steric hindrance. Dibutyltin compounds are generally recognized to function as Lewis acid catalysts by complexing with isocyanate [77-78]. The mechanism of catalysis of amines has been related to Lewis base catalysis, the amine complexing with the alcohol. It has been observed that the rate of the reactions between aromatic diisocyanate and primary alcohols was much faster than that of aliphatic diisocyanate and alcohols under the same reaction conditions. Another important observation was the difference in the reactivity of the second NCO group on the same molecule after the first one has reacted.

Yilgör et al [79] studied the effect of various catalysts such as Hg(CH₃COO)₂, Zn(CH₃COO)₂.2H₂O, and SnCl₄.5H₂O on the reaction of HMDI with n-butanol and found that the inorganic salts are effective catalysts for these reactions. It is also possible to have preferential catalysis of primary reaction between NCO and OH over side reactions, depending on the stoichiometric ratio of NCO/ OH and also the concentration of the catalyst used.
Following is the list of the catalyst and Figure 1.15 represents the organometallic catalyst used during preparation of polyurethane:

- Dibutyltindilaurate (DBTL)
- Bismuth octanoate
- 1,4-Diazabicyclo[2.2.2]octane (DABCO)
- Tetraethylene glycol dimethacrylate (TEGDMA)
- Dimethyl cyclohexamine- (Non Organometallic Compound)

![Figure 1.15 Structures of DBTL and TEDA Catalyst](image)

The reaction mechanism followed by the tertiary amines (catalyst) during the synthesis of polyurethane is shown in Figure 1.16. The catalyst used in the reaction does take part in the reaction and is regenerated. Thus catalyst increases the rate of polymerization.
Introduction

Long chain di- or polyhydroxy compounds viz polyols form the backbone for the polyurethane preparation. These technically important compounds made up of polyether, polyester, polycarbonate, hydroxyl terminated polybutadiene and natural rubber. Naturally occurring compounds like castor oil, abietic acid, cardanol and polysaccharides have also been used to prepare polyurethane [61-66, 80-88].

High molecular weight polyurethanes are generally prepared by a two stage process namely a prepolymer stage and a chain extension stage. The prepolymer stage consists of reaction between an excess diisocyanate and a polyol to yield an isocyanate terminated called prepolymer. These two step reactions yield polymer of higher molecular weight distribution [89-92]. The constituent polyols with their long flexible chains form the soft segments. The urethane groups which are obtained by the reaction of short chain diols with the isocyanate groups form hard segments [93-99].
Figure 1.17 represents the general synthesis of polyurethane using the reactive diisocyanate, polyol and short chain diol as chain extender. Figure 1.18 represents the distribution of hard and soft segments of the polymer during synthesis of polymer.

\[
\text{HO} - \overset{\text{polyol}}{\text{O}} - \overset{\text{diisocyanate}}{\text{NCO}} - \overset{\text{chain extender}}{\text{NCO}} - \overset{\text{catalyst}}{\text{OH}} - \overset{\text{OH}}{\text{OH}}
\]

Figure 1.17 Schematic representation of synthesis of Polyurethane
Figure 1.18 Segmental nature of Polyurethane hard segment and soft segments
Introduction

1.2.5 CASTOR OIL BASED POLYURETHANE

Among the polymerized materials polyurethane expresses an important polymer because it has good abrasion resistance and displays the properties of both plastics and elastomers [100-102]. Castor oil is commercially an important product containing the unsaturated and hydroxyl functionality. It could be exploited to prepare new polymeric materials meeting the future demands of polymers. The hydroxyl groups of castor oil are widely used for cross linking polyesters and polyurethanes. Conversion of castor oil into its prepolymer and then sequential or simultaneous interpenetration of vinyl monomers in urethane network to get high strength polymer was studied by many authors [103-106].

Castor oil based polyurethane polymers have been extensively studied as coatings and in network synthesis [107-110]. The domain structure which results from the phase separation of hard and soft segments controls the properties of polyurethane prepolymer. The cross-linking of the castor oil urethane with primary triamine of moderate molecular weight is expected to produce in situ toughening in elastomers due to stiffer urea linkages obtained by reaction between amine and isocyanate. The polyurethane thus modified could be of potential use in aerospace applications. The polyurethane elastomers made from these components were not thermoplastic elastomers, since their melting points were higher than the decomposition temperature of the urethane linkages.

In addition to elastomers, polyurethanes can also be produced as foams (rigid and flexible), adhesives, binders, coatings, and paints. Because of their unique properties, polyurethanes have found a wide variety of applications in the automotive, furniture construction, and foot wear industries, as seating, exterior panels, structural foam, furniture, and housing for electric equipment, shoe and boot soles, and refrigerator insulation. Polyurethanes are in the class of compounds called reactive prepolymer which includes epoxies, unsaturated polyesters and phenolics and are the most widely used polymers [45].
1.2.6 POLYURETHANE CHEMISTRY

The basis of polyurethane chemistry is the high reactivity of isocyanate. They react under mild conditions with all compounds that contain “active” hydrogen atoms. These are mainly alcohols (hydroxyl -OH group) but also amines. When the isocyanate group (NCO) reacts with alcohols, amines, carboxylic acids and water, urethane, urea and amide linkages are formed. The reaction of isocyanate with water is important for the production of foams because during this reaction, gaseous CO₂ is formed and acts as a chemical blowing agent. The reactions involved in the preparation of polyurethane are shown in Figure 1.19. Those reactions proceed, for number of applications, through the reaction of the so-called prepolymer mult with diisocyanate. Prepolymers with terminal NCO groups are obtained by reacting a polyetherol or polyesterol (polyol) with an excess of diisocyanate.

![Figure 1.19 Chemical reactions involved in polyurethane preparation](image-url)
1.2.7 POLYURETHANE ELASTOMERS

Polyurethane elastomers are important members of the thermoplastic elastomers. Their advantageous properties include high abrasion and chemical resistance, excellent mechanical and elastic properties [111]. Polyurethane elastomers usually exhibit a two-phase microstructure, which arises from the chemical incompatibility between the soft and the hard segments. Generally, polyurethane block copolymers are comprised of a low glass transition or low melting "soft" segment and a rigid "hard" segment, which often has a glassy Tg, or crystalline melting point above room temperature. The hard, rigid segment segregates into a glassy or semicrystalline domain and the polyol soft segments form amorphous or rubbery matrices in which the hard segments are dispersed at varying content levels. The hard domain in this two-phase microstructure can act as a physical cross linking point and reinforcing filler, while soft segment behaves as a soft matrix. The degree of phase separation or domain formation not only depends on the weight ratio of the hard to the soft segment, but, also on the type of chain extender, the type and molecular weight of the soft segment, the hydrogen bond formation between the urethane linkages, the manufacturing process, and reaction conditions [45, 111-114].

In general, polyurethane comprises of linear copolymers with soft and hard segment structures. The soft segment is typically a polyester-, or polyether- diol, with a molecular weight between 300 to 5000 (PEG-300, PEG-600 and PPG-2000), though in practice, molecular weights of 1000 and 2000 are primarily used. The hard segment normally includes the connection of a diisocyanate (aromatic or aliphatic) and a low molecular weight diol or diamine, which is the chain extender or is usually polyol (glycol). The hard segments consist of diisocyanate and chain extender using diamine and the diols. The combination of this soft polyol segment and hard segment forms an (AB)n type block copolymer. The hard segment provides physical cross links through hydrogen bonding and filler like reinforcement to the soft segments which plays a key role in imparting elasticity to polyurethane materials [113]. By varying the structure, molecular weight of the segments, and the ratio of the soft to the hard segments, a broad range of physical properties can be obtained. The materials can be hard and brittle, soft and tacky, or anywhere in between. The distribution of NCO/ OH molar
ratio of prepolymer is main factor to affect the structure and organization of polyurethane, thereby its properties [115-117].

1.2.8 APPLICATIONS OF POLYURETHANE

Polyurethanes are used in surprising array of commercial applications. Figure 1.20 represents the universe of polyurethane applications which can be divided into seven major groups: flexible slab, flexible molded foams, rigid foams, solid elastomers, reaction injection mold, carpet backing, and two component formulations. The fabrication and application of slab stock foam is easier and faster than the use of animal hair, bird feathers or other filling materials. Improved molding techniques of flexible foam are responsible for its acceptance in furniture with unusual shapes. Molded rigid foam has made great inroads into the furniture industry. One of the major uses of rigid polyurethane foam is in home refrigerators. Most of the major manufacturers are currently using rigid urethane foam as insulation in their lines, because of the superior insulating characteristics of the fluorocarbon-blown foams. Large ships use rigid polyurethane foam as void fillers and also in lifeboats and refrigerated ships.
The major benefits offered by polyurethane are that it retains its high impact strength at low temperatures, it is readily foamable, and it is resistant to abrasion, tear propagation, ozone, oxidation, fungus, and humidity. Although thermoplastic polyurethane is attacked by steam, fuels, ketones, esters, and strong acids and bases, it is resistant to aliphatic hydrocarbons and dilute acids and bases. The highest recommended use temperature of thermoplastic polyurethane is approximately 104°C. Aromatic thermoplastic polyurethane has poor weatherability stemming from its poor resistance to UV degradation. Since polyurethane can be painted with flexible polyurethane paints without pretreatment, it has found use in many automotive exterior parts.

![Figure 1.20 Applications of Polyurethane](image-url)
1.3 POLYURETHANE-UREA COPOLYMERS

Polyurethane represents an important and versatile class of thermoplastic and thermoset polymers. It is segmented block copolymer composed of alternating soft segments connected by hard segments resulting from the polycondensation of diisocyanate with diol chain extenders [61-66, 118]. By adjusting the chemical nature and respective amounts of reagents of various polyols and polyisocyanate, it is possible to obtain a wide range of materials with tailored mechanical, thermal chemical as well as electrical properties. The polyurethanes include those polymers which contain a significant number of urethane groups (–HN–COO–), regardless of what the rest of the molecule may be. Usually, the polyurethanes are obtained by the combination of polyisocyanate with reactants which have at least two hydroxyl groups, e.g., polyethers, castor oil and simple glycols. The properties of polyurethanes can be varied in numerous ways according to their demand. The functionality of the hydroxyl compound as well as the isocyanate can be increased to three or more in order to form branched or cross linked polymers. The other structural changes can also be made at which, the nature of polyether, polyester, and glycol and (diisocyanate) might be altered by changing its molecular weight and type. For these reasons, the cross linking and chain flexibility properties of polyurethane and its intermolecular forces can be varied widely and independently. Polyurethanes in general, present good adhesive characters due to their elastomer properties, enhanced by soft segments of the polyol and by the polar character of the urethane groups [119-120]. A wide variety of raw materials coupled with adaptable synthetic techniques allows the polyurethane chemist to design useful materials for many applications.

Polyurethanes found a wide range of applications such as coatings, foams, different kinds of plastics, elastomers, adhesives, sealants due to their unique properties. It can be applied on the products to improve their appearance, life span, scratch resistance and corrosion resistance [112, 120-123]. The structural incompatibility between the soft and hard segments results in the phase separation in polyurethane whereas hard blocks act as reinforcing fillers to the soft matrix, which generates a two-phase morphology and confers an elastomeric character to these thermoplastic materials. Their engineering properties are determined, to a large extent, by phase separation.
The use of urea linkages, instead of urethanes, could lead to materials with improved thermomechanical properties [124].

Polyurethane has limitations but, it is also been found that no other class of polymers can match their collective versatility, usefulness, and performance. Urethane polymers are formed by reaction of diisocyanate and diols which create the urethane chemical linkage. The closely related polyureas are synthesized from diisocyanate and diamines, producing urea linkages. Although many types of polyurethane contain both urethane and urea groups and are therefore more properly termed polyurethane-urea (PUU).

The polyol and/or polyamine in these polymers often comprise the majority mass component, so the terms polyurethane, polyurethane/urea, and polyurea refer to the corresponding chemical group linkage and not the whole of the polymer backbone. The urethane and urea functional groups, however, do impart most of the important physical properties.

The synthesis and basic reactions of isocyanate had been explored beginning in the nineteenth century. The addition reactions of the isocyanate group with alcohols and amines to form macromolecules from diisocyanate and either diols or diamines. This led first to the preparation of polyureas from hexamethylene diamine and hexamethylene diisocyanate (HDI) and other diisocyanate, but these polymers were intractable and proved to be unsuited for the preparation of fibers or thermoplastics. However, the reaction of HDI with glycols such as 1,4-butanediol led to polyurethanes which found limited applications under the tradenames Perlon U for fibers and Igamid U for thermoplastics. Throughout the 1940s, a whole new raw material product line was developed at I. G. Farben, including polyisocyanate under the tradename Desmodur and polyester polyols under the Desmophen tradename. Various products such as adhesives, rigid foams, elastomers, and coatings were also designed and tested on a developmental scale.

Polyurethane-urea elastomers are block copolymers consisting of alternating rubbery soft and crystalline urea hard segments. The hard segment acts as a physical cross linking point and plays a key role in determining the mechanical properties, toughness, elasticity and hardness in the segmented polyurethane copolymers [125-136]. The PUU can be used in different applications such as elastic fibers and
synthetic leather. It can be modified by changing the composition ratio of each component and chemical structure of both segments in order to get desirable performance.

Polyurethane-urea elastomers have excellent elastic properties and they are limited by the melting of hard domains at temperature greater than \( \sim 270^\circ\text{C} \). Synthesis of segmented PUU is one of the perspective trends in high solid coatings as well as reactive hot melt adhesives industries. Formulations can be specially designed for high performance architectural, wood and antistatic coatings. The macrodiol or polyether-diol is soft, flexible and provides elastomeric character to the matrix it is known as a soft micro domains or phase. The soft segment is relatively immiscible with other phase derived from diisocyanate and chain extender and referred as hard microphase which provides cohesive strength to the polymer matrix [25, 130-136].

The chemical structure of a PUU generally consists of long-chain polyols and diisocyanate connected with short-chain diamines, which are used as chain extenders. The long-chain polyols and a diisocyanate form soft segments with urethane linkages, whereas the short chain diamines react with a diisocyanate to form hard segments with urea linkages. Microphase separation resulting from the thermodynamic incompatibility between the hard and soft segments gives rise to a broad range of physical and mechanical properties [137]. The choice of diisocyanate, long chain polyols and chain extenders greatly affects the ability of the soft and hard segments to crystallize, as well as separation of phases and hence is crucial to tailoring the microstructure and the resulting macroscopic properties of these elastomers. A wide range of polyols can be found, hydrophilic or hydrophobic, and sometimes with an excellent thermostability. Their lower reactivity can also facilitate material processing.

The evaluation and characterization of new polyurethane-urea copolymers with structures similar to the previously studied polyureas gives a comparison between urethane and urea linkages was carried out. The influence of the chemical nature of the soft segment on the static and dynamic mechanical properties is also described [138]. Different from diol extender based polyurethane (PU), where there is only one N–H, hydrogen bond (H-bond) donor, the H-bonds in PUU based on diamine as the
Introduction

chain extender, are much more complicated, as there are two N–H in urethane-urea group. It has been shown that the H-bond is closely related to phase separation and properties in PUU [139-142]. The soft segment is relatively immiscible with the other phase derived from diisocyanate and chain extender and is referred as hard microphase, which provides cohesive strength to polymer matrix. At room temperature, the hard segments are aligned together and connected through hydrogen bonds. The presence of hydrogen bond acts as a pseudo cross linker and thermoreversible fillers that reinforces the mechanical properties. In the preparation process of PUU, urethane and urea groups form almost simultaneously, so the information about the effect of urea groups on reaction kinetics of polyurethane formation are necessary for thoroughly understanding the PUU polymerization. Studies have been also carried out on the effect of urea groups on polyurethane formation and confirmed the catalytic effect of urea groups on polyurethane polymerization. The suggested mechanism to explain this effect is based on the hydrogen bonding between the urea carbonyl groups and the hydroxyl groups. There are fewer references, however, studying PUU than that dealing with polyurethane, possibly due to more complicated structure and H-bond properties. Like isocyanate, the type of chain extender also determines the hard segment structure and affects the final polyurethane properties [143-146]. Recently work was carried out to study of polyurethane-urea elastomeric materials and polymeric coatings [135-136, 147-149]. This is because of their unique properties that can be achieved from the 3D network formation by the solid state cure reaction of NCO terminated polyurethane prepolymer with the atmospheric moisture.
Introduction

1.4 EPOXY SYSTEM

Epoxy resin is one of the most versatile materials which has been commercially servable for about 50 years and is now been utilized in many industrial applications [150]. The broad interest in epoxy resins originates from the extremely wide variety of chemical reactions that can be used for curing and different properties that result. It is among the best matrix materials for any composites and widely used polymers for its many good properties. Characteristics like toughness, low shrinkage on curing, high adhesion to many substrates, good mechanical resistance, and versatility in composition make epoxy resins widely used in adhesives, laminates, coatings, for abrasion automotives, electrical components and casting applications [151-152]. It is found to be superior than the phenolic resin, polyurethanes, alkyds, and silicones in their adhesion to the wide variety of substrates. They have excellent moisture and salt-spray resistance, with moisture permeability rates three to four times lower than those of polyurethanes. Epoxies are also superior to alkyds and silicones in solvent and chemical resistance. Electrical properties are good and remain fairly constant under 95 to 100 percent relative humidity and temperature up to 300 °F. Epoxies are generally synthesized by one of two processes from phenols and epichlorohydrin, or from alkenes and peroxy acids [153].

A variety of epoxy resins such as glycidyl ethers, glycidyl esters, glycidyl amines, linear aliphatic, cycloaliphatic etc are commercially available [152, 154-155], and also different polyester modified epoxy resins [156] are used in different areas for variety of applications. Moreover the number of epoxy groups in these resins is also fixed and therefore the based formulations also remain fixed leading to the popularity in market and increase the commercial uses.

The epoxy resin based on diphenylolpropane (DPP), also known as Bisphenol A, and epichlorohydrin (ECH) was first developed and commercialized and still completely dominating worldwide markets. The polyfunctional phenol (DPP) and the epoxide containing compound (ECH) are condensed together in presence of aqueous caustic soda at atmospheric pressure at elevated temperatures. The resins can be represented by the general formula as shown in Figure 1.21.
In the general-purpose area, the diglycidyl ether of bisphenol A (DGEBA) epoxy resin is the preferred resin and has been used for electrical insulations. The dielectric properties of neat DGEBA epoxy resins [157-162] and reacting systems of DGEBA and curing agents have received considerable attention [163-167]. In epoxide resin technology this conversion from liquid or friable brittle solid into a tough cross-linked polymer is called curing or hardening and this can be achieved by two different ways. Epoxy can be polymerized through epoxide groups using a cross linking agents or hardener to form a 3D network [153]. The catalytic curing agent mentioned latter on serves as initiator for resin homopolymerization whereas polyfunctional curing agents are used in near stoichiometric ratios or amounts and lead to the formation of highly cross-linked 3D network e.g. Lewis acid such as BF$_3$ or bases such as tertiary amines. Curing process is exothermic in nature and the reaction proceeds faster as the temperature increases. Klute and Veihmann [168] measured the heat of polymerization of liquid epoxide resins with tertiary amines is 22.0 K.cal/mole and with primary amine is 25.0 K.cal/mole. For some applications, the processing time required is very viscosity dependent, much lower viscosity being more suitable.

Catalytic curing agent usually offers special properties and long pot lives at room temperature. Lewis catalysts used for curing epoxies are base catalyst such as triethylamine, benzyl dimethylamine, $\alpha$-methylbenzylamine, 2-(dimethyaminomethyl)-phenol (DMP-10) etc. Acid catalysts used are boron trifluoride, boron trichloride, aluminium trichloride, zinc chloride, ferric chloride, stannic chloride, boron trifluoride etherate and many more.
The curing agents used for curing epoxy resins are phenols, alcohols, thiols, primary and secondary amines, carboxylic acids etc. Basically there are three main criteria for creating and choosing a curing agent for epoxy formulation are cost, processing requirement and performance requirement. Curing agents can be broadly classified on the basis of their respective curing mechanism and also temperature at which the suitable curing takes place, at room temperature or at an elevated temperature. This curing process can be initiated by using a wide range of curing agents, such as amines (aliphatic and aromatic), anhydrides [169-172], isocyanate [173], cyclohexanone formaldehyde [174] and amino formaldehyde resins [175]. Although the cure of epoxy resins, with primary and secondary amines, occurs by a step-growth process, tertiary amines such as imidazoles initiate chain-growth polymerization, with isocyanate (NCO) groups with oxirane cycle of epoxy resin. Thus curing is of great importance due to high heat resistance and chemical stability to various aggressive agents [176].

A wide variety of commercially available amine compounds are generally used as cross-linking agents for epoxy resins act as a hardener and as they also react easily due to presence of active hydrogen in amines which lead to faster reaction and ultimately faster curing takes place. There are different types of polyamines used for curing such as aliphatic, aromatic, cycloaliphatic polyamine adducts etc. Primary amines are organic materials containing a nitrogen atom linked to two hydrogen atoms (–NH₂). In epoxy formulation, the active hydrogen of amine reacts with epoxide group of resin. The rate of cross linking during the curing process depends on the number of amino functional groups, type of the organic amine functional group containing compounds and nature of cross linking.

Primary and secondary aliphatic polyamines and their derivatives, a group of unmodified room temperature curing agent having low viscosity and of low cost are very rare in use. For example diethylene triamine (DTA), triethylene tetramine (TETA) tetra ethylene pentamine (TEPA), amino ethyl piperazine (AEP), and ethylenamine-100(E-100). Almost every amine follows the same mechanism of the curing, due to the presence of active hydrogen, which readily reacts with epoxy group. Good all round properties are obtained from DTA or TETA cures but all values are not maintained above 50°C, for the maintenance of these properties at higher
temperatures, aromatic amines are preferred to aliphatic one as curing agents. AEP is a cycloaliphatic amine possessing primary, secondary and tertiary amino groups, although only the first two groups are involved in curing. DETA and TETA exhibits the same curing properties as aromatic curing agents but, the properties are observed only at low temperature. Therefore the aromatic amines are used for better curing and for the maintenance of all properties even at the high temperatures.

Modified primary and secondary aliphatic amines are also room temperature curing, but as they are fast curing materials and easy to handle, make it more compatible for use. For example amine-ethylene oxide adduct [177-178], amine -acrylonitrile adducts.

Aromatic amines have been used since the early days of epoxide resin technology, because of already mentioned improved thermal and chemical resistance as compared to those obtained from aliphatic amines. In addition, aromatic amines-cured system retains their properties better at elevated temperatures. They also have the advantage of forming dry brittle soluble solids when partially cured. The lower basicity of aromatic amines, the steric factors as the amine groups is separated by rigid benzene rings rather than flexible chains of molecules as in aliphatic amines are some of the important parameters that decide the reactivity of aromatic amines with epoxy resins and lead to the cross linking forming a cured system. Aromatic amines are generally modified for being used as curing agents which although reduce the heat resistance are still good for chemical resistance and even resistance to damp and low temperature. The common aromatic amines curing agent are m-phenylene diamine (MPD), 4,4'-diaminodiphenylmethane [179-180], 4,4'-diaminodiphenylsulphone (DDS) [172, 181-182].

Aliphatic amines DETA and TETA have highest reactivity while DDS has lowest reactivity because of electron withdrawing sulfonyl group. Thermal stability of cured epoxy resin system depends on the structure of the curing agents used. Aromatic amines are ideally suited for electrical insulation, because of their excellent electrical and mechanical properties maintained at even high humidity and high temperature. Aromatic amines are essentially hot curing systems that offer heat and chemical resistance and better strength properties.
The superior mechanical and chemical properties possessed by epoxy polymers are result of the curing process, in which a low molecular weight resin is transformed into an indefinite molecular weight polymer with a three-dimensional network structure. Depending on the chemical structure of curing agent and the curing conditions, it is possible to obtain toughness, chemical resistance, mechanical properties ranging from extreme flexibility to high strength and hardness, high adhesive strength, good heat resistance and high electrical insulation. Acid anhydride has longer pot life, low viscosity and low reactivity in absence of cured system equal in performance to the aromatic amines. e.g. phthalic anhydride (PA), pyromellitic dianhydride (PMDA) [183], hexahydrophthalic anhydride [169]. Figure 1.22 represents the general mechanism followed by each epoxy group during curing with amines.

$$RNH_2 + H_2C\text{O}CHR' \rightarrow \begin{array}{c} H \\ H \\ \end{array} R'N\text{H}_2CH\text{O}CHR'$$

**Figure 1.22 General reaction mechanism for curing of epoxy resin**

The amine first, opens up an epoxy ring, forming a quaternary base and leaving an oxygen atom with a pair of unsatisfied electrons. The negatively charged oxygen atoms than proceed to open up another epoxy ring producing negatively charged oxygen, this still opens up another epoxy ring and so on. In this manner, long chain polyether is formed. This supports $S_N2$ mechanism of attack by amine nucleophile at the methylene group of epoxide ring, accompanied by simultaneous displacement of the ring oxygen.
Amine compounds are very popular curing agents for epoxy coatings, providing rapid cures at room temperature in 1 to 2 hour or in shorter period of time at high temperatures. The resultant coatings have excellent chemical and solvent resistance, electrical properties, and thermal and vacuum stability. However, epoxy resin has poor impact strength and high brittleness.
1.5 EPOXY - PDMS SYSTEM

An insulating material in service is exposed to moisture, oxidation, chemical attack, biological attack, and outdoor weathering, and contamination, electrical, mechanical and thermal stress. Polymers are better insulating materials for high performance applications in contaminated environments [184]. However, these materials also deteriorate due to multiple stresses encountered in service and aging. No single polymer or polymer blend has the necessary properties for an outdoor insulating material to provide the desired mechanical or electrical characteristics.

Polymeric materials with good hydrophobicity and erosion resistance are preferred for better insulation applications. Materials having such properties usually lack good mechanical characteristics. They are not rigid and self-supporting and hence are modified to improve their mechanical characteristics for high performance applications [185-186]. As it is already mentioned that the epoxy resin is the one of the most versatile resin materials has been commercially servable in many different applications [150]. Desired performance and service life over a diverse range of service conditions may be achieved by modifying the epoxy resins.

Epoxy resins are known for their high performance, especially with respect to thermal and dimensional stabilities combined with high stiffness. As a consequence of their highly cross-linked structure, these materials tend to suffer from brittle behavior, poor crack resistance, and low fracture toughness. A well-known procedure to toughen such brittle polymers is to incorporate discrete modifiers into the rigid matrix. Among the modifiers, elastomers, including polycarbonate [187], polyetherimide [188], carboxy, amine-, or hydroxyl-terminated acrylonitrile butadiene rubbers, functionally-terminated acrylates, and polyurethane [189-198], organosiloxane polymers [199-203] have been applied with great success to enhance the toughness of epoxy resins or related matrix resins without sacrificing other useful properties such as dimensional stability, stiffness, and strength.

The silicone polymers are of great importance due to their versatile properties such as resistance to high temperature, high flexibility, dielectric properties, hydrophobicity and chemical inertness. Silicone compounds are well known blocking agents for the hydroxyl groups [204-208]. This combination of excellent features provides the
necessary conditions for the application of polydimethylsiloxane (PDMS) as an elastomeric modifier to make the modified epoxy resin with improved properties [189, 201, 207-215].

PDMS has very little use as a toughening agent because of the poor compatibility between soft segments of PDMS and polar hard segments in epoxy which largely resulted from the lack of hydrogen bonding. These materials, which usually exhibited separate Tg values due to thermodynamic incompatibility, were either macroscopically immiscible or exuded from the cross-linked matrix during curing procedure in the conventional introduction of siloxane into polymers through blending methods [213-216] resulting in poor thermo-mechanical properties and compositional heterogeneity resulting from poor segmental compatibility, this limited the use of larger silicone concentrations [216-218] and hampered their use in surface coatings.

To overcome this limitation and improve the interaction between PDMS and epoxy matrices with improved thermo-mechanical properties and toughness, several techniques are reported in the literature, including using silane coupling agents [219-221] and chemically incorporating PDMS into the main chain of epoxy to form the interpenetrating network [162] but there still existed some drawback in these modified systems, such as the thermo-mechanical properties’ declining swiftly with an increase of the PDMS soft segment.

In the present work attempts were made to modify the epoxy resin by formation of copolymer using amino terminated polydimethylsiloxane (PDMS) cured by polyamide and TETA as cross linking agents. The work has been carried out in order to decrease the brittleness of epoxy resin with improved dielectric properties and mechanical properties.
1.6 NANOPARTICLES

The nanoparticles of alumina, aluminum trihydroxide and calcium carbonate were synthesized using the wet chemical process with the aim of using these nanoparticles with the polymers for high performance properties. Thus the polymers were then filled with these nanoparticles and were used for evaluating the electrical properties of polymers.

1.6.1 ALUMINA NANOPARTICLES

In recent years there has been increasing interest in the synthesis of nanocrystalline metal oxides [222-225]. Because of their special chemical and physical properties that are determined by both shape and size [226-227]. Due to the unique physical and chemical characters of the nanostructure materials, the systematic manipulation of the morphologies of the nanoscale materials has always been a significant challenge in modern materials chemistry [228-229].

A lot of approaches and processes have been developed for synthesis of nanoscale ceramic powder is as follows:

1. Mechanical Milling Process [230-231]
2. Precipitation process/ Coprecipitation [232]
4. Hydrothermal process [233]
5. Vapor Phase reduction [234]
6. Combustion method [235]
7. Heterogeneous azeotropic distillation
8. Thermal spraying
9. Laser induced chemical vapor deposition (LICVD)

Alumina $\text{Al}_2\text{O}_3$ is one of the most important ceramic materials. Nano crystalline $\alpha$-alumina powder has considerable potential for a wide range of applications including high strength materials, heat insulating materials, electronic ceramics, catalyst, catalyst support, fabrication of metal ceramic laminate composites and as a reinforcement phase in polymer and brittle matrix composites. [236-237].
Conventional methods for synthesizing α-Al₂O₃ powder involve solid state thermally driven transformations from the hydrates of aluminum oxide [238]. Recently, efforts have been carried out in synthesis of nanostructured alumina with ordered pore structure [239-243]. Varma et al. prepared a spherical powder with the average diameter of 2μm by sol spray drying technique using Al(NO₃)₃ as raw materials [234].

Zeng et al. has first prepared Boehmite (γ-AlOOH) powder by sol-freeze drying method using cheap AlCl₃·6H₂O as raw materials. The γ-Al₂O₃ nanopowder with the average diameter of 6 nm and α-Al₂O₃ nanopowder with the mean diameter of 30 nm were obtained by the calcination 500°C and 1100 °C respectively [231, 244].

Lee et al. prepared a series of alumina nanotube, nanofiber, and nanorod depending on the nature of the ionic and nonionic surfactants [245]. Wang et al. has present a novel non-surfactant route for the synthesis of the fibrous δ-Al₂O₃ by homogeneous hydrolysis of aluminum nitrate with hexamethylenetetramine (HMTA) followed by supercritical fluid drying (SCFD) process [246]. Chemical solution methods have been widely used to produce nano structured materials, and different strategies have been applied to achieve mono disperse nanoparticles with controlled size and shape.

Research has shown that the addition of surfactant influence the size, shape and stability of particles. Chang et al. has controlled alumina nanoparticles by the solution precipitate using polyamide amine dendrimer as surfactant [247-248]. The effects of amount and size of surfactant on morphological control of powder have also been discussed. Dendrimer possessing spherical structure and active surfaces of carboxylic groups could interact strongly with oppositely charged ions and colloidal particles [249-250]. Isopropoxytitanium(IV) tristearate(TTS) was found to be effective modifier among the titanate coupling reagents [251]. Kim et al. has synthesized mesoporous alumina particles with spherical shape prepared by spray pyrolysis of Al(NO₃)₂·9H₂O precursor. The surface area and the mesopores structure were investigated with varying the concentration of surfactant (cetyltrimethylammonium bromide) CTAB and urea [252], polyacrylic acid as a rheological modifier [253], Benzene disulfonic acid disodium salt (SDBS) and sodium bis-2-ethylhexyl sulfosuccinate (Na(AOT)) were used as surfactant stabilizing...
agents [254]. The chemically synthesized nanoparticles were also used for preparation of nanocomposites [255-258]. Well-dispersed nano particulate mineral particles can enhance properties of polymeric materials such as strength and stiffness, dimensional stability, flame retardancy, gas barrier properties, and UV stability [259-266].

1.6.2 ALUMINUM TRIHYDROXIDE (ATH) NANOPARTICLES

Similarly the nanoparticles of ATH were synthesized for enhancing the properties of polymeric materials. Non-metallurgical aluminum trihydroxide (ATH) is low-cost, non-toxic, environment friendly, recyclable and crystalline powders. It is most widely used flame retardant and smoke suppressant in the plastics and rubber industries [267-268].

ATH/oxides powders are also used in other industry fields such as paper, board, toothpaste, glass, refractories, catalyst, ceramics, medicine, cement, paint [269]. In recent years, many applications of ATH require finer- sized ATH because high loadings of micron-scale ATH powders often lead to processing difficulties and marked deterioration of mechanical, physical, and electrical properties of the polymers [270-271]. As an alternative, nano ATH powders have been successfully applied to EVA polymer without negatively affecting the properties of the matrix and with a loading of 50 wt % of nano ATH powders for a better flame retardancy [272].

Castrovinci et al has studied the effect of aluminum trihydroxide (Al(OH)$_3$—ATH) on the surface protection from fire for a styrene butadiene rubber (SBR) provided by ammonium polyphosphate ([NH$_4$PO$_3$]$_n$—APP) [273]. Here the attempts were made to synthesize ATH using conventional methods and used for preparation of nanocomposites for industrial applications.
1.6.3 CALCIUM CARBONATE NANOPARTICLES

Calcium carbonate (CaCO₃) is extensively used as a pigment, filler in the industries of paper, paint, textile, detergents, adhesives, rubber and plastics, food, cosmetics and biomaterials [274-278]. The main sources of particulate CaCO₃ are ground calcium carbonate (GCC) mined from calcite deposits and precipitated calcium carbonate (PCC) produced by means of a chemical reaction. PCC is more versatile than GCC in terms of its industrial applications, since a large number of particulate CaCO₃ parameters, such as the particle size, the morphology, the polymorphic form or the purity, can be tailored by carefully controlling the reaction conditions [279–280].

Calcium carbonate is traditionally used in plastics as bulking agent to substitute the expensive polymers. All properties of the pure polymer are subject to change as a result of filling, and in fact a new material is created by blending a polymer with inorganic fillers. The properties of the resulting composite material are determined by the properties of the components, namely polymer and filler, filler particle size, shape and modulus, the concentration of filler in the polymer matrix and the kind of interaction between the filler particles as well as filler particles and polymer host [281-284].

Here the attempts were made to synthesize CaCO₃ using conventional methods and used for preparation of nanocomposites for industrial applications.
1.7 MODIFIERS

The nanoparticles filled polymer composites requires the compatibility with the polymer matrix. Thus the quaternary ammonium compounds were synthesized for modifying the synthesized nanoparticles for better compatibility.

QUATERNARY AMMONIUM COMPOUNDS

Quaternary alkyl ammonium salts are cationic surfactants and mostly used as modifiers for inorganic fillers. The organically modified fillers are more compatible for preparation of nanocomposites. Quaternary ammonium salts or amine hydrochlorides, having one or more long alkyl chains, are most commonly used as modifiers [285-286].

Kozak et. al. subjected Sodium montmorillonite SOMASIF ME 100 (M) to modification through ion-exchange reaction by a number of (alkyloxymethyl)dodecyldimethylammonium chlorides with the general formula $[C_{12}H_{25}N^+(CH_3)2CH_2OR]Cl_2$. Different types of the quaternary modifier ammonium compounds listed below were synthesized [287].

- (butoxymethyl)dodecyldimethylammonium chloride (BMDDAC)
- dodecyl(dimethyl(hexyloxymethyl)ammonium chloride (HMDDAC)
- dodecyl(dimethyl(octyloxymethyl)ammonium chloride (OMDDAC)
- (decoyloxymethyl)dodecyl(dimethylammonium chloride (DMDDAC)
- dodecyl(dimethyl(dodecyloxymethyl)ammonium chloride (DDMDDAC)
- (benzyloxymethyl)dodecyl(dimethylammonium chloride (BzMDDAC)

Different researchers had studied montmorillonite modified by octadecylammonium, poly(oxypropylene)diamine, and liquid crystalline diol hydrochlorides and quaternary polyesters [288-291].
Here the attempts were made to synthesize quaternary ammonium compounds via alkyl halide formation. Thus higher molecular weight glycols are converted to the quaternary ammonium compounds and were used for modification of nanofillers. These modified nanofillers were then used for preparation of nanocomposites for industrial applications.
1.8 AIM AND SCOPE OF THE WORK

The main objective of this work was to develop new polyurea and its copolymers, new matrices and fast curing agent for curing these systems. The studies have been focused to develop applications for electrical industries. The scope of the work is given below.

1.8.1 Exhaustive literature search

An exhaustive literature search was carried out on synthesis of polyurea and its copolymers, new matrices to be used for electrical applications and as fast curing agents

1.8.2 Synthesis of Polyurea and its Copolymers

Polyurea and its copolymers coatings were synthesized varying the different monomer content, optimization of polymerization conditions to obtain suitable polymer for Industrial applications

a. Polyurea Homopolymers
b. Polyurethane homopolymers
c. Polyurethane-urea Copolymer
d. Polyamines as cross linking agent for Epoxy resin
e. Epoxy-Polydimethylsiloxane (PDMS) Copolymers
f. Synthesis of Nanoparticles of alumina, aluminium trihydroxide and calcium carbonate

1.8.3 Characterization

The synthesized polymers were characterized for thermal, electrical and mechanical properties.

a. Functional group determination
   ➢ End Group Analysis
   ➢ Fourier Transform Infrared spectroscopy
b. Solubility
c. Thermal Properties
   ➢ Thermo gravimetric Analysis
Introduction

- Differential Scanning Calorimetry

d. Electrical Properties
   - Surface Resistivity
   - Volume Resistivity
   - Dissipation Factor
   - Capacitance
   - Dielectric Constant
   - Dielectric Strength
   - Arc Resistance

e. Mechanical Properties
   - Tensile Strength
   - Elongation at Break
   - Impact Strength

1.8.4 Synthesis of Modifiers

Modifiers to improve the dispensability of the nanoparticles in polymer matrix.

1.8.5 Applications

Coatings
Composite development

1.8.6 Conclusion