CHAPTER 1

INTRODUCTION

Solid polyurethane elastomers are now widely utilized as engineering materials in many industries and are well known for their general toughness, excellent wear and tear resistant properties and good oil resistance.

The name 'polyurethane' is given to a wide range of materials having similar, general characteristics and their different specific properties can be explained by the different chemical structures that constitute the polyurethane backbone. Thirty years ago polyurethanes were so called because the predominant chemical group present in the polymer was the 'urethane' group. Now-a-days the position is quite different. The urethane group is still present but the properties of the final polymer can be greatly modified by the presence of other structurally important groups in the chain. Other more descriptive names are sometimes used such as polyester-urethanes, polyether-urethanes, polyurea-urethanes, although these are technically more correct their general use in rather cumbersome.

Synthetic rubbers and plastics are generally manufactured by a polymerisation process, either addition polymerisation or condensation polymerisation, the former process being the one commonly employed. In addition polymerisation or chain polymerisation as it is some times described, an unsaturated monomer polymerizes by a chain reaction via a free radical or ionic mechanism and the reaction can be controlled only within certain limits. Condensation polymerisation or step polymerisation involves the reaction, between small to medium sized polyfunctional
molecules and the formation of higher molecular weight products by the elimination of simple molecules like HCl, water, sodium chloride or similar low molecular weight compounds. The polyurethane elastomers do not easily fall into either of these two categories. Low to medium molecular weight polyfunctional compounds, one of which is diisocyanate are joined together by an addition type process, but by an intermolecular hydrogen transfer and not by a free radical or ionic mechanism. Crosslinking of the polymer to form a cured elastomer is achieved also by similar addition process. For this reason the term 'diisocyanate polyaddition' (or) even 'polyaddition' alone was coined to describe the reaction process and these terms are still used to describe the process in use today.

One of the most important polymers that find innumerable applications is polyurethane. The basic work leading to the world wide interest in all classes of polyurethane was initiated by I.G. Farbenindustrie in Leverkusen, Germany in 1937. Polyurethanes comprise of a wide class of materials ranging from elastomers to rigid foams. The properties of polyurethanes can be made to vary widely from liquid, soft and rubbery to rigid thermoplastic and thermosetting material depending on the end user needs.

1.1 POLYURETHANES

The polyurethanes are the most important polymers among the commercially important classes of polymers. The term 'polyurethane' is more one of convenience than of accuracy, since these polymers are not derived by polymerizing a monomeric urethane molecule, nor are they usually polymers containing primarily urethane groups. Polyurethanes in one form on another are making a major and growing contribution to our daily lives. The polyurethanes include those polymers which contain a significant number of urethane groups, regardless of what the rest of the molecule may be. Usually the polymers are obtained by the combination of polyisocyanate
with reactants which have at least some hydroxyl groups, eg., polyethers, caster oil and simple glycols. Other reactive groups such as amino and carboxyl groups may also be present. Thus a typical 'polyurethane' may contain, in addition to urethane groups, ester, ether, amide, and urea groups. These polymers are also some times called simply 'urethanes' and sometimes 'isocyanate polymers'. Urethanes can be considered esters of the unstable carbamic acid, or amide esters of carbonic acid and the urethane group has the characteristic configuration.

\[
\begin{align*}
O & \\
- \text{HN} - \text{C} - \text{O} - \\
\end{align*}
\]

Thus polyurethanes have a significant number of these urethane groups, although not necessarily repeating in a regular order.

Polyurethanes can be formed by a variety of methods, although the most widely used production method is the reaction of di- or polyfunctional hydroxyl compounds, eg., hydroxyl-terminated polyesters or polyethers, with di- or polyfunctional isocyanates. The general structure of a linear polyurethane derived from a dihydroxy compound, HOROH, and a diisocyanate, OCN\text{R'}\text{NCO}, can be represented by the following general formula;

\[
\begin{align*}
O & \\
( - R - O - C - NH - R' - NH - C - O - )_n \\
\end{align*}
\]

The functionality of the hydroxyl-containing component as well as the isocyanate can be increased to three or more to form branched or cross-linked polymers. Other structural changes can also be made at will, for example the nature of R may be changed drastically such as in molecular weight and type (polyether, polyester, simple glycol), and mixture of these polyhydroxy compounds can be used. Similarly, the nature of the R' may be
altered, as in the change from napthalene diisocyanate to hexamethylene diisocyanate. For these reasons, the polyureathanes are almost unique in that crosslinking, chain flexibility and intermolecular forces can be varied widely and almost independently. Thus, it is to be expected that the polyurethanes include fibers, soft and hard segmented, flexible and rigid foams, coatings for many purposes, and highly crosslinked plastics.

1.2 HISTORICAL BACKGROUND

The basic work leading to the present world-wide interest in all classes of polyurethanes, foams, surface coatings and solids was initiated by I.G. Farbenindustrie AG in Leverkusen, Germany in 1937. The work by Carothers on the polyamides in the U.S.A. presented I.G. Farbenindustrie with the problem of developing similar materials by processes not covered by the Dupont patents and the polyaddition products from diisocyanates and diamines or glycols emerged as a suitable method suggested by Wright and Cumming (1969). The linear polyureas formed by the reaction between aliphatic diamine and aliphatic diisocyanates were found to be infusible and strongly hydrophilic and consequently not suitable for the production of fibres or plastics. On the other hand, the linear polyurethanes prepared from the aliphatic glycols and aliphatic diisocyanates did exhibit interesting properties and several polymers were eventually marketed under the trade name of 'Igamid U' for plastic moulding use and 'Perlon U' for the production of fibres and bristles. A typical linear polyurethane was prepared by the polymerisation of 1,6-hexamethylene diisocyanate and 1,4-butane diol. The basic principles of this diisocyanate polyaddition process were described in the German Patent 728,981 published in 1942. Concurrent with the investigations at I.G. Farbenindustrie the use of diisocyanate was being studied by Pinten of Dynamit A.G. This work covered the reaction of polyesters with diisocyanates resulting in chain extension with minor network formation (Wright and Cumming 1969).
Although the yearly work by I.G. Farbenindustrie has received the most prominence in the historical literature, both ICI in the United Kingdom and Du-pont in the United States were pursuing similar lines of development in the 1930s. The work of I.G. Farbenindustrie, however, was the first to be exploited commercially. A comprehensive survey of the whole development was covered by Wright and Cumming (1969).

In the U.K. investigation in the possible use of diisocyanates also started in the 1930s, notably by Imperial Chemical Industries Ltd. A patent application was made (Wright and Cumming 1969) in 1941 describing the curing of a polyester amide-diisocyanate adduct with formaldehyde, and this material was sold commercially in the form of a millable gum under the trade name 'vulcaprene'.

1.3 CHEMISTRY OF POLYURETHANES

All polyurethanes are based on the exothermic reaction between diols and diisocyanates. The reaction is a nucleophilic reaction between alcohol and electron deficient carbon of the isocyanate group as shown.

\[
R-N=C=O \rightleftharpoons R-N=C=O \rightleftharpoons R-N=C=O R'-O-H
\]

Polyurethanes are long chain molecules in which the different fragments are linked by -NCOO- groups. The chemical term for the unit is an ester of carbamic acid, but the whole of this polymer is called polyurethane. The urethane linkage can be obtained by an addition type
process, but by an intermolecular hydrogen transfer and not by a free radical or ionic mechanism. Reaction between a diol and di-isocyanate is written as

\[
\text{HO} - R - \text{OH} + \text{OCN} - R' - \text{NCO} \rightarrow \text{C} \cdot \text{N} \cdot R' \cdot \text{N} \cdot \text{C} \cdot \text{O} \cdot R \cdot O
\]

The rate of polymerisation reaction depends upon the structure of both the isocyanate and the polyol. Aliphatic polyols with primary hydroxyl end groups are the most reactive. They react with isocyanates about 10 times faster than similar polyol with secondary hydroxyl groups.

The reaction of dihydroxy functional groups with di-isocyanates produce a linear polyurethanes (Charles et al 1961). If either monomer is trifunctional and the other is difunctional then crosslinked polyurethanes are possible.

1.4 RAW MATERIALS

Mainly polyurethanes are obtained from diisocyanates and diols. Polyester polyol and polyether polyol are extensively used as the diols.

1.5 SYNTHESIS OF ISOCYANATES

A large number of references in literature are available for the chemistry and synthesis of isocyanates. Various methods for synthesizing isocyanates are as follows.

1.5.1 Phosgenation

The phosgenation of arylamines to produce the corresponding isocyanates was first reported by Henstchel in 1884, and several years
latter, Gattermann extended this relation to aliphatic amine hydrochlorides. The reaction between primary amines and phosgene lends itself readily to the commercial preparation of isocyanates.

\[
R - \text{NH}_2 + \text{COCl}_2 \rightarrow R - \text{N}:\text{C} = \text{O} \rightarrow R - \text{NCO} + 2\text{HCl}
\]

Two steps are involved for the synthesis of isocyanates. In the first step, an amine solution is mixed with phosgene at a low or moderate temperature. In the second step, the resulting slurry is treated with more phosgene at higher temperature (120-150°C). The product is isolated and purified by distillation.

1.5.2 Rearrangement reactions

Curtius, Lossen and Hoffmann rearrangements are successfully used to prepare isocyanates in the laboratory, especially when the corresponding amines are not readily available or not sensitive to phosgene.

Curtius Rearrangement

\[
\text{RCOCl} \xrightarrow{\text{NaN}_3} \text{RCO} \xrightarrow{\Delta} \text{RNCO}
\]

Hoffmann Rearrangement

\[
\text{RCONH}_2 + \text{Br}_2 + \text{NaOH} \rightarrow \text{RCONH} \text{Br} + \text{NaBr} + \text{H}_2\text{O} \\
\text{RCONHBr} + \text{NaOH} \rightarrow \text{RNCO} + \text{NaBr} + \text{H}_2\text{O}
\]
Lossen Rearrangement

\[ \text{RCONHOH} + \text{COCl}_2 \rightarrow \text{RNCO} + 2\text{HCl} + \text{CO}_2. \]

1.5.3 Reaction of organic halides or sulphates with cyanates

The reactions of organic halides or sulphates with salts of cyanic acid is of historic significance. Wurtz (1848) synthesized the first isocyanate by this procedure.

\[ \text{R}_2\text{SO}_4 + \text{KNCO} \rightarrow \text{RNCO} + \text{K}_2\text{SO}_4. \]

1.5.4 Reactivity of isocyanates

The reactivity of the isocyanate group can be explained by its electronic structure.

\[ \text{R} \equiv \text{N} \equiv \text{C}=\text{O} \]

The resonance possibilities indicate that the electron density is greatest on the oxygen and least on the carbon resulting in the oxygen having the highest net negative charge, the carbon having the highest net positive charge. The reaction of isocyanates with active hydrogen compounds, i.e. compounds having hydrogen which is replaceable by sodium, proceed therefore by the attack of a nucleophilic centre upon the electrophilic carbon of the isocyanate group.

\[ \text{R} \equiv \text{N} \equiv \text{C}=\text{O} \xrightarrow{\text{HA}} \text{R} \equiv \text{N}^{\text{+}} \equiv \text{C}=\text{O} \rightarrow \text{R} \equiv \text{N} \equiv \text{C}=\text{O} \]
In this reaction the fact that the active hydrogen compound is acting as an electron donor and not as a hydrogen donor is confirmed by the effect of electrophilic groups in the active hydrogen compound.

Aryl isocyanates readily polymerise in the presence of catalyst into dimers containing 2 moles of the monomeric isocyanates. The reaction and structure is generally considered to be

\[
\begin{align*}
R &- NCO + OCNR &\rightarrow &\quad R &- N &- C = O \\
& & &\quad | & & \\
& & &\quad O &- C &- N &- R
\end{align*}
\]

These compounds are listed currently in chemical abstracts as uretidine diones, although the term dimer is frequently applied.

Reactions that are important in the formation of polyurethane polymers are those with urea and urethanes.

\[
\begin{align*}
R &- NCO + RNH - C &- NHR &\rightarrow &\quad R &- N &- CO &- NHR \\
& & &\quad | & & \\
& & &\quad CO &- NHR
\end{align*}
\]

biuret

\[
\begin{align*}
R &- NCO + RNHCOOR' &\rightarrow &\quad R &- N &- COO &' \\
& & &\quad | & & \\
& & &\quad CONHR
\end{align*}
\]

tallophanate
Acid catalysed reaction proceeds as follows.

\[
\text{R—NCO} + [\text{R—N=C—\(\overset{+}{\text{O}}\)]} \xrightarrow{HA} [\text{R—N=C—\(\overset{-}{\text{O}}\)H—\(\cdots\cdot\) A}]
\]

\[
\begin{align*}
\text{R—NH—C—OR'} + \text{HA}.
\end{align*}
\]

In both these mechanisms the structure of the isocyanate and the active hydrogen compound play a major role in determining the rate of the reaction.

The effect of substituents on the active hydrogen compound is the opposite to that on the isocyanates, since the primary role of the active hydrogen compound is that of an electron donor. For example, amines containing electronegative groups withdraw electrons thereby reducing the basicity of nitrogen and making it poorer electron donor. Conversely, electron donating groups increase the basicity of the amino nitrogen.

In addition to the electronic effects of substituents, steric factors are also important in aromatic compounds. Bulky groups in the ortho position, or in the aliphatic compound and branching or bulky substituents close to the site of the reaction retard the reaction. These steric factors not only affect the reactivity of both the isocyanate and the active hydrogen compounds but also influence the effectiveness of the catalyst. Since a catalyst must approach the site of the reaction as closely as a reactant itself the ease of approach and the extent to which the approach is possible will be influenced by steric interaction between the catalyst and one or more of the reactants, usually the isocyanate.

Other electron-accepting materials such as many metal compounds could be expected to serve as Lewis acids and hence as catalysts. In general
however it is found that acids are much weaker catalysts than the bases. The following mechanism has been proposed for the metal catalysed reaction.

\[
\begin{align*}
\text{R—N=C=O} & \xrightarrow{\text{MX}_2} \left[ \text{R—N=C=O}^+ \right] \xrightarrow{\text{H—O}} \text{R'} \\
\text{R—N=C=O} & \xrightarrow{\text{MX}_2} \left[ \text{R—N=C=O}^+ \right] \xrightarrow{\text{H—O}} \text{R'}
\end{align*}
\]

This coordination effect which proposes that the hydroxyl group enters on the metal side of the complex and attaches to the metal in close proximity to the isocyanate group nitrogen, can explain the fantastic catalytic activity of the metals. Obviously the order of metal co-ordination complex formation could be the reverse so that the hydroxy compound complex forms first and the isocyanate second. It was suggested that those catalysts which caused the aliphatic isocyanate to react faster than toluene diisocyanate could perform in this manner because the aliphatic diisocyanate is not sterically hindered, whereas 2 and 6 positions in the toluylene diisocyanate are hindered by methyl group in the 1 position.

It was suggested that if the metal does not have the property to complex with the incoming hydroxy compound and the isocyanate group in such a way that the hydroxy group and the isocyanate nitrogen are brought close together, then the only catalytic activity observed will be due to the acid or base reactions of the compound tested (Saunders and Frisch 1961).
1.6 FORMATION OF POLYURETHANES

The polycondensation reactions leading to the formation of polyurethanes are influenced by a number of factors prominent among which are the structure of the isocyanate including its functionality and the type and location of substituents, the structure of polyhydroxy compound, the solvent used and the dilution of the system.

The uncatalysed reaction of the isocyanate with a hydroxyl containing compound proceeds as shown below.

\[
\begin{align*}
R\text{-NCO} + R\text{-OH} & \rightarrow R\text{-N} = C\text{-O}^+ \quad \text{ROH} \\
& \quad H \\
& \quad R
\end{align*}
\]

The mechanism for a base catalysed reaction is as follows

\[
\begin{align*}
R\text{-N} = C\text{-O}^- & \rightarrow [R\text{-N} = C\text{-O}^-] + B^- \quad \frac{k_1}{k_2} \\
& \quad R'\text{OH} \\
& \quad B^+ \\
& \quad H \\
& \quad R
\end{align*}
\]

\[
\begin{align*}
R\text{-NCO} & \rightarrow R\text{-NHCOOR} + R\text{-OH} \\
& \quad O^+ \\
& \quad H \\
& \quad R
\end{align*}
\]
The choice of the solvent may affect both the rate of uncatalysed reaction and the effectiveness of a catalyst. In general the solvents that readily complex with the active hydrogen compound or the catalyst by hydrogen bonding or by dipole movement interaction, will provide a slower reaction than will the solvents that cannot do so readily with the reactant or the catalyst.

1.7 EFFECT OF CATALYST

Catalysts are widely used in the manufacture of solid polyurethanes and polyurethane foams. As referred to earlier, one shot solid polyurethane systems are being developed and these could necessitate the use of catalysts particularly when the two active hydrogen compounds differ widely in activity. Acids and particularly bases can influence the isocyanate hydroxyl reaction and also the crosslinking reactions.

The tremendously powerful effect of certain tin compounds compared to other catalysts is shown in Table 1.1.

Table 1.1
Relative Activity of Catalysts for Phenyl Isocyanate-Methanol Reaction in Dibutyl Ether

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Mole Percentage of Catalyst used</th>
<th>Relative activity at 1.0 mole percentage catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dione</td>
<td>1.00</td>
<td>1</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>0.93</td>
<td>11</td>
</tr>
<tr>
<td>Cobalt napthenate</td>
<td>0.47</td>
<td>23</td>
</tr>
<tr>
<td>Stannic Chloride</td>
<td>0.30</td>
<td>99</td>
</tr>
<tr>
<td>n-Butyltin trichloride</td>
<td>0.20</td>
<td>830</td>
</tr>
<tr>
<td>Trimethyl tin hydroxide</td>
<td>0.041</td>
<td>1800</td>
</tr>
<tr>
<td>Di-n-butyltin dilaurate</td>
<td>0.0094</td>
<td>37000</td>
</tr>
</tbody>
</table>
1.8 APPLICATION OF POLYURETHANES AND POLY(URETHANE-UREA)S

Success in the adjustment of the process conditions and the product properties has led to many specialised applications for polyurethanes.

1.8.1 Adhesives, Binders and Sealants

Polyurethane adhesives can be used to join together most of the materials. They make tough, vibration resistant adhesives with wide range of operating temperatures. They are used for bonding metal to metal and metal to rubber and plastics. Polyurethane binders are adhesive systems which are used to bond together particulate materials. Polyurethane sealants include gap filling foam systems provided in convenient aerosol containers.

1.8.2 Foams

Polyurethane structural foams are used to make electrical junction or joint boxes etc. Flexible polyurethane foams have characteristic high strength and elongation at break and fast recovery from deformation. Foams find innumerable applications in vehicle seating, furniture, cushioning, decorative parts, mirror frames, chair shells, instrument-panel trim, safety pads, arm rests, floor mats, underlays, roof insulation, weather stripping, air filters, seating of aircraft, carpet underlay, crash padding, packaging blocks, instrument panel insulation, sound/thermal insulation, oil resistant fillers, shoe soles, artificial limbs etc.

Flexible urethane foams have been introduced for medical application because of their non-binding, non-allergic and soft ventilating characteristics.
Rigid foams are used in trucks such as milk trucks and ice cream trucks, trailers, curtain-wall construction, preformed rigid panels, spray-applied wall construction, roofing insulation and insulation of refrigerators.

1.8.3 Elastomers

The high abrasion resistance and higher load carrying capacity of urethane tyres have resulted in their use for aircraft wheels, heavy industrial trucks, footwear industry, friction drives and belts. They are also used as seals, wiper ring, valve seats and for shock-absorbing and vibration dampening applications which include flexible coupling connectors, shock absorbers for automobiles, pneumatic machinery, farm machinery, cable jackets, conveyor rollers and drive sprockets.

1.8.4 Shoe heal top pieces

The use of thermoplastic poly(urethane-urea) wear cap for shoe heals utilizes the high abrasion resistance of the materials. This was the first major application for thermoplastic poly(urethane-urea)s and remains a sizeable market. The materials are low priced and normally formulated on the basis of polyester macroglycols.

1.8.5 Automobile industry

The properties of thermoplastic poly(urethane-urea)s such as toughness, durability, resistance to oil, grease and fuels, wide service temperature range, good weathering characteristics and heat resistance are of considerable interest to automobile industry. With the world pressure for fuel economy demanding lighter vehicles and because of a tightness of safety legislation governing impact resistance, thermoplastic poly(urethane-urea)s in some cases compounded with glass fiber to increase stiffness is currently under evolution for body work, bumpers and side panels (Horii-Masaaki 1999).
1.8.6 Wire and Cables

Compared with materials currently being used for flexible cable, sheathing thermoplastic poly(urethane-urea)s offer a number of advantages including ease of processability, outstanding toughness, oil resistance and good heat aging characteristics and are currently used in industries including geophysics, electronics, hydrospace and outside broadcasting. Thermoplastic polyurethane is also specified for military applications. In many outdoor uses polyether based poly(urethane-urea)s are preferred to provide the maximum hydrolysis and microbiological resistance.

1.8.7 Biomedical applications

Polyurethanes have been used extensively in biomedical applications. Polyurethanes are widely utilized for development of medical devices for tissue-contact and blood contact applications such as mammary prostheses vascular catheters, artificial skin vascular grafts and artificial heart diaphragms and valves.

Polyether urethanes have proved sufficient biocompatibility and biodurability for short term use in a variety of blood contacting applications such as experimental artificial heart leaf ventricular assist devices and blood pumps. However the long time biostability of polyurethane is a great concern because of failure of polyurethane coated leads to pacemaker during long term implantations. It is essential to develop low elastic modulus polyurethane with reduced bending stress so that fatigue life is increased. Moreover low elastic polyurethane allows membrane to flux more freely without producing adverse changes in blood flow. In addition to the requirement of low elastic modulus, biodurability of the polyurethane is an essential requirement.
Biodegradation induced by hydrolytic and oxidative mechanism leads to catastrophic failure device. Therefore, it is essential to develop polyurethane with minimal or nil chemical groups which are prone to biodegradation. The poly(urethane-urea)s are found to have low elastic modulus, low hydrophobicity and resistance to hydrolytic degradation and environmental stress corrosion cracking (Jayabalan et al 2000).

1.8.8 Films and Coatings

The market for polyurethane and polyurea coated fabrics is very large. The majority of applications take advantage of the outstanding abrasion resistance of poly(urethane-urea)s. In the fashion industry polyurethane coated fabrics are produced to simulate leather for clothing, baggage and footwear. The imitation leather is also used in apholostery applications. Heavier duty coated fabrics are used in protective covers in conveyor belts and also for the manufacture of bulk liquid transport bags. Unsupported film is used for protective sheathing for surgical incision film and also as an emergency skin for the treatment of burns.

1.9 IONIC POLYMERS

Ionic polymers represent a broad classification of polymers with inorganic salt groups attached to the polymer chain. Ion containing polymers are perhaps the most versatile and useful of the new polymeric materials currently being developed. They are generally referred to as 'polyelectrolytes' when they have sufficient ionic charge to be soluble in water and as 'ionomers' when the concentration of ion-containing groups is too low for water solubility. The combination of low ionic content and low polarity backbone results in a class of commercial polymers which continue to be of scientific interest. These ionic polymers are commonly referred to as ionomers.
Unlike homogeneous polymer systems, polymers containing ionic group interact to form ion rich aggregates contained in the non-polar polymer matrix. The resulting interactions strongly influence polymer properties and applications, which have made this a fertile area of research and development.

Ion containing polymers are perhaps the most important and very useful polymeric materials that are currently being developed. However, among the ionic polymers until relatively recently, mainly the areas of network glasses and polyelectrolytes were receiving extensive scientific interest. New families of ionic polymers have emerged that possess a wide variety of properties leading to different application as aqueous thickeners, impregnants, textile sizers, adhesives, additives (Matsuda 1976; 1983), resins (Matsuda 1974; 1977; 1978), catalysts (Matsuda 1978) and in the biomedical field (Okkeema and Cooper 1991; Silver et al 1992).

1.10 REVIEW OF LITERATURE

Synthesis and studies on polymers containing metals in the main chain are important from the scientific and industrial view points. Generally polyurethanes contain covalent bonds in the polymer chain, and polyurethanes having ionic bonds in the polymer backbone are less common.

Difunctional compounds containing an ionic bond in the molecule, divalent metal salts of mono(hydroxyethyl)phthalate were reported in high purity and high yield by selecting Ca and Hg as divalent metal for the synthesis of metal containing polyurethanes (Matsuda 1974). Durairaj and Venkatarao (1979) reported Mn and Pb salts of mono(hydroxyethyl) phthalate. Based on the above salts, synthesis of metal containing polyurethane has been reported by Durairaj and Venkatarao (1980). Metal containing poly(urethane-urea)s with ionic linkages in the main chain, synthesized by polyaddition reaction of hexamethylene diisocyanate (HMDI)
with mixtures of metal salts of mono(hydroxyethyl)phthalate (M[HEP]₂) and bisureas containing two hydroxyl groups were known (Matsuta 1974a). Metal containing polyurethanes were synthesized from cobalt and copper salts of mono(hydroxyethyl)phthalate with HMDI or TDI (Kothandaraman et al 1985). Polymers based on divalent metal salts of mono(hydroxyethyl)phthalate were reported by Matsuda (1987). The synthesis of metal containing polyurethanes, having ionic links in the main chain, by reacting HMDI with Zn, Cd and Hg salts of mono(hydroxyethyl)phthalate was reported by Rajalingam et al (1990). Rajalingam et al (1992) reported the synthesis of metal containing poly(urethane-urea) having ionic linkage in the main chain from TDI and Mn, Cu, Co and Pb salts of mono(hydroxyethyl)phthalate and bisurea. Matsuda and Takechi (1990) reported the synthesis of polyurea from Ca and Mg salts of p-amino benzoic acid, diamine and diisocyanate, which showed lower decomposition temperature than the polyurea without metal. Halato-telechelic poly(urethane-urea)s were synthesized from divalent metal salts of p-aminobenzoic acid (Ca and Mg), 4-4'-diaminodiphenyl methane, dialkylene glycols and TDI, which shows that the introduction of metal into the urethane-urea backbone resulted in a considerable decrease in decomposition temperature (Matsuda and Takechi 1991).

Matsuda (1975) obtained styrene soluble metal containing polyesters by polycondensation of mono(hydroxyethyl)phthalate, M[HEP]₂ with maleic anhydride(MA), phthalic anhydride(PA) and diethylene glycol(DG) or with mixtures of MA, PA, ethylene glycol (EG) and propylene glycol(PG). Qiu et al (1993) have reported the synthesis of metal containing polyureas having Ba, Zn, Pb and Sr in the main chain, by the polyaddition reaction of TDI with mixture of divalent metal salt of sulfanilic acid and 4-4'-diaminodiphenyl methane. Divalent metal salts (Zn[II] and Cu [II]) exhibit a synergistic effect in the catalysis of the isocyanate water reaction to form polyurea foam (Borsus et al 1981). Matsuda (1977) reported the metal containing cured polyester resins obtained by simultaneous
esterification and polyaddition of compositions which included M[HEP]$_2$, MA, GM and MM. The curing reactions were carried out in the presence of an oxide of 2,5-dimethyl-2,5-di(tertiarybutylperoxy)hexane and under radiation. Generally the peroxide cured resins showed better physical properties, except tensile strength, than radiation-cured resins. Crosslinked metal-containing polyester resin has been prepared by Matsuda (1978) from M[HEP]$_2$-anhydride-diepoxy compound in which Mg salt is found to act as stronger catalyst for the reaction than the corresponding Ca salt.

A number of unsaturated polyesters have been obtained from M[HEP]$_2$, EG, PA, MA and from epoxy compounds such as propylene oxide (PO) and 1,2,-butylene oxide (BO) (Matsuda 1976). Reactions of M[HEP]$_2$, glycol, acid anhydride and epoxy compound yielded unsaturated metal-containing polyesters in which metal carboxylate of M[HEP]$_2$ is found to act as a catalyst for addition reaction (Matsuda 1976a). Metal containing three-dimensional polyesters were obtained by the reaction of M[HEP]$_2$, pyromellitic dianhydride and epoxy compounds such as phenyl glycidyl ether (PGE), propylene oxide, and 1,2-butylene oxide (Matsuda 1977a). These showed a decrease in thermal stability with increase in metal salt content in the feed. In the case of the cured resins based on unisomerized maleic polyesters, their temperature of deflection under load, rockwell hardness and compressive strength increase with increasing metal content. Matsuda (1976b) has reported the unsaturated metal containing polyesters in which the molecules end with methacryl groups and were obtained from M(HEP)$_2$, MA and glycidyl methacrylate (GM).

Crosslinking of partially neutralized liquid rubber containing terminal and pendent carboxyl groups with different number of anhydride and bisepoxide was investigated by the carboxyl-anhydride-epoxide reaction. The partially neutralized liquid rubbers were prepared by the partial neutralization with CaO and MgO (Matsuda 1980; 1980a and 1981). Divalent metal salts (Ba$^{2+}$, Ca$^{2+}$, Mg$^{2+}$, Zn$^{2+}$ and Cd$^{2+}$) of ethylene
glycol-methacrylate maleate were copolymerised with styrene, methyl methacrylate and ethyl acrylate to obtain homogenous curable mixture with good physical properties (Matsuda and Okamato 1978). Matsuda (1979) evaluated the adhesive system based on divalent metal salts of mono(hydroxyethyl) phthalate-anhydride-bisepoxides. Matsuda (1979a) reported the ionic crosslinked carboxy-terminated liquid rubber with metal oxides (CaO and MgO) which showed higher tensile strength than without metal oxide. With increase in the metal oxide content the tensile strength of the rubber also increased.

Water-containing cured resins obtained from inverted emulsion of unsaturated polyester based on divalent metal salt of mono(hydroxyethyl)phthalate, ethylene glycol, maleic anhydride, phthalic anhydride and propylene oxide showed better physical properties than those of commercial unsaturated polyester without metal (Matsuda 1981a). Calcium and magnesium containing partially neutralized carboxy-terminated liquid rubber-anhydride-bisepoxide system showed superior adhesive properties than those systems not containing metal, in which the Mg carboxylate group showed higher catalytic activity than the Ca carboxylate group (Matsuda & Dohi 1981 and Matsuda 1982).

Yanchuk (1984) synthesized flexible phosphorous containing polyurethane semicarbazides by reacting oligo(oxytetramethylene)glycol with a diisocyanate and a phosphorous containing oligoester to form a prepolymer which was then reacted with phenyl phosphoric acid dihydrazide using DMF as the solvent. The polymers having 1.77% to 6% phosphorous and molecular weight 11,000 to 18,000 were obtained. Crosslinked cured rubber was obtained by the reaction of mixture of polypropylene glycol/polyethylene glycol, anhydride, bisepoxide and divalent metal salts of mono(hydroxyethyl)phthalate. The Mg carboxylate group showed higher catalytic activity than the Ca carboxylate group. The rubber containing Mg showed better physical properties than those containing Ca (Matsuda and
Miyoshi 1982; 1983). Matsuda (1983) obtained the copolymer of
methacrylate of partially neutralized carboxyl-terminated liquid rubber
(PNCTLR) with glycidyl methacrylate, in which neutralisation was done
with CaO and MgO. The Mg carboxylate group showed better catalytic
activity than the Ca counter part for the above system. Bis(2-hydroxy-
exthyl)selenide and bis(2-aminoethyl)selenide were condensed with functional
compounds to give polyurethane and polyesters which varied from oils to
brittle materials (Kroll et al 1970).

Polyurethane thermoplastics were prepared in which the addition
of antifriction additives like graphite, BN, P, MOS₂ and foroplast improved
its wear resistance, thermal conductivity, heat resistance, thermal and
dynamic properties (Gorokh et al 1981). Certain other polyurethane foams
containing calcium stearate were prepared to prevent formation of
independent cells. They were found to have continuous cells and showed no
deformation.

Highly curable and stable one part excellent adhesive was obtained
from divalent metal salts of mono(hydroxyethyl)phthalate-anhydride-
bisphenol-A diglycidylether (BADG) systems by merely mixing these
components at room temperature (Matsuda and Kanaoka 1985). Crosslinking of bisepoxide with divalent metal salts of p-aminobenzoic acid
and diamine was investigated by Takechi and Matsuda (1993), in which
metal carboxylate group have catalytic activity for the amine cure reaction.
The salt containing Ca with the lower electronegativity exhibits higher
catalytic activity than that containing Mg. Crosslinking of curable mixtures
prepared from divalent metal salts of p-aminobenzoic acid-bisepoxide-
anhydride were reported in which Mg salt exhibits higher catalytic activity
than Ca salt (Takechi and Matsuda 1994; 1994a). Crosslinking of bisepoxide
with divalent salts of p-aminobenzoic acid and anhydride has been
investigated to prepare metal containing cured resins (Takechi and Matsuda
1996). It was found that the Mg salt of p-aminobenzoic acid showed higher catalytic activity than Ca containing salt.

Rigid, non elastic, non cellular, amorphous, metal reinforced polyether-polyurethanes were prepared and characterized by Degginner and Edward (1984). Metal containing polyimides with metal (Ba, Sr, Pb and Zn) in the main chain were prepared and investigated by reacting pyromellitic dianhydrate with a mixture of divalent metal salts of sulfanilic acid and 4,4'-diaminodiphenyl methane (Zeng et al 1995). Qiu et al (1996) reported a series of metal containing polyimides with metallic elements (Ca, Mg, Sr, Ba, Pb, Co and Ni) in the main chain which were prepared by reacting pyromellitic anhydride with the mixtures of divalent metal salts of p-aminobenzoic acid and 4,4'-diaminodiphenyl methane.

The variation of glass transition temperature with the weight percentage of urethane linkages for the polyurethanes based on 2,4- and 2,6-toluene diisocyanate were reported by Schenider et al (1975). Eisenberg and Navratil (1972; 1973; 1974 and 1974a) have examined the behaviour of styrene ionomers and the copolymer of ethyl acrylate and acrylic acid ionomers in detail. Paik et al (1980; 1980a) reported polyether poly(urethane-urea)s and polyester poly(urethane-urea)s based on 2,4-toluene diisocyanate, ethylene diamine and poly(tetramethylene oxide)/poly(butylene adipate) and also investigated their thermal properties, phase segregation between soft and hard segments and mechanical properties. Salah et al (1987) investigated the influence of mono and divalent non-transition and transition metal on the glass transition and mechanical properties of polyurethane ionomers. Ray and Bhownick (1991) obtained a series of linear poly(urethane-urea)s by two-step solution polymerization and assigned chemical shift values of the various species of the block copolymer.

A series of sulphonated polyurethane ionomers based on poly(tetramethylene oxide) of molecular weight 1000, neutralized with Ca²⁺,
Ni²⁺, Zn²⁺, Cd²⁺, Cs²⁺ and Ea³⁺ were reported by Ding et al (1989). Toda et al (1987) measured the ion conductivity of poly(ethylene oxide) based polyurethane networks containing alkali metal salts. Yoon and Ratner (1988) synthesized segmented fluorine-containing poly(ether-urethanes) from 4,4'-methylene bis(phenylene isocyanate) and poly(tetramethylene glycol) ($\overline{M}_n = 2000$) and the chain extended with 2,2,3,3-tetrafluoro-1,4-butane diol or 2,2,3,3,4,4-hexafluoro-1,5-pentane diol to investigate the effects of the diol carbon number and the soft-segment chain length on the phase segregation. Lam et al (1989) reported an ionic diol, potassium or sodium 4-(1,2-dihydroxyethyl)benzene sulphonate. Polyurethanes were prepared by step growth solution copolymerization of this ionic diol with diisocyanate in the presence of DBTDL as catalyst.

Yang et al (1991) synthesized polyurethanes based on methylene bis(p-phenyl isocyanate), bis(hydroxymethyl) propanoic acid and poly(tetramethylene)oxide and investigated their morphology and physical properties. Pathiraja et al (1992) synthesized polyurethane elastomers based on 4,4'-diphenylmethane diisocyanate [MDI], 1,4-butane diol and polyether macrodiols which have 6,8 and 10 methylene groups between the ether oxygen. Segmented polyurethane ionomers were prepared from cyclo aliphatic diisocyanate and isophorone diisocyanate and polytetramethylene glycol using as anionic-type chain extender via, dimethylol propionic acid. The effect of ionic content and butane diol on the state of dispersion and physical properties were investigated and reported by Kim and Lee (1992). Visser and Cooper (1992) reported the influence of cation type on the morphology and properties of polyurethane ionomers with different backbone types, pendant anionic type and ionic group concentration. Polyurethane ionomer based on diester ionic diol and HMDI was reported by Ramesh and Radhakrishnan (1993).

Kakati (1994) has reported polyurethane ionomers containing phosphonate group which was prepared by the reaction of
1,2-dihydroxypropyl phosphonic acid and a prepolymer based on 4,4'-diphenylmethane diisocyanate and poly(propylene glycol) with 1,4-butane diol as the chain extender. Poly(urethane-urea) anionomer dispersion containing about 50% hard segments were synthesized by Xiao et al (1995) from poly(oxypropylene) glycols, TDI or mixtures of TDI and polymeric MDI, dimethylol propionic acid, 1,4-butane diol and different diamines as chain extenders. Mix et al (1995) obtained segmented polyurethane composed of 2,4-toluene diisocyanate, poly(butylene adipate) diols (PBA) of different molecular weight and 4,4-bis(6-hydroxyhexoxy)biphenyl. It was observed that by reducing the molecular weight of the PBA unit upto 1000 and further upto 600, the glass transition temperature \( T_g \) of the polyester soft segment phase increased and enhanced the partial miscibility or compatibility of hard and soft segments.


Fengkui et al (1996) prepared a series of segmented polyurethanes based on different composition of polycaprolactone, 4,4-diphenylmethane diisocyanate and 1,4-butane diol. Crystallinity and morphology of the segmented polyurethanes with different soft-segment lengths were investigated. Nabeth et al (1996) synthesized linear polyurethane, linear segmented polyurethane, polyurethane networks and polyurethane acrylate networks of various composition and investigated their variation of \( T_g \) with the type of macrodial, its length and the chemical composition of the polymer in relation with the percentage of soft segments, the molar mass between crosslinks and the concentration of urethane bonds. Samson et al (1998) synthesized segmented poly(urethane-urea)s with rigid domains on
4,4'-dicyclohexylmethane diisocyanate and 4,4'-diamino-3,3'-dimethyl-dicyclohexylmethane using various polar and non polar polyols as soft segments.

Martin et al (1996) obtained a series of thermoplastic polyurethane elastomers from MDI, poly(ethylene oxide) (PEO), polytetramethylene oxide (PTMO), poly(hexamethylene oxide) (PDMO), and poly(1,6-hexylcarbonate) diol (PCDO) and 1,4-butane diol chain extender. They studied the effect of altering the CH₂O ratio in a series of polyether urethanes of fixed soft segment molecular weight and weight percent of soft segment on the morphology and property of the polymers.

Song et al (1996) investigated the effect of chemical structure of diisocyanate compounds on the degree of crystallinity and the thermal stability of the polyurethanes prepared from polyester and butane diol with three different diisocyanates like 4,4'-diphenylmethane diisocyanate (MDI), m-xylene diisocyanate (XDI) and 2,4-toluene diisocyanate (TDI). Cheng et al (1996) investigated the direct current and alternating current conductivity of the crosslinked copolymers of poly(ethyleneglycol-co-2,4-toluene diisocyanate-co-alkali-metal-methacrylate).

Wang et al (1997) synthesized a series of segmented polyurethanes based on HMDI and poly(tetramethylene glycol) (PTMG) as soft segments and then with alkylene di(4-hydroxybenzoate), (HB) as hard segments. The effect of number of methylene units in HB on the microphase separation of the segmented polyurethane was evaluated. Lian-Siong et al (1997) investigated the effect of temperature on hydrogen bonding in amine-containing polyurethane and poly(urethane-urea)s.

Rosthauser et al (1997) investigated the physical and thermal behaviour of hard-cast polyurethane and polyurethane polyurea elastomers prepared from prepolymers of 20 and 97% trans 4,4'-diisocyanato dicyclohexyl methane and C₃ and C₄ polyether chain extended with
1,4-butane diol. Sang et al (1997) synthesized polyurethane anionomer dispersions from polyethylene adipate glycol, isophorone diisocyanate, hexamethylene diisocyanate and salt of dimethylol propionic acid as a potential ionic centre. Wei and Yu (1997) prepared a series of polyether polyurethane ionomers having different contents of sodium sulfonate groups in the soft segments. It was reported that increase in the ionization level increased the compatibility of the hard and soft segments and the glass transition region of the soft segment became broader.

Fu-Sen Y and Jin-Long Hong (1997) discussed in detail about the hydrogen bond interactions of urethane-urethane and urethane-ester linkages taking some small urethane model compounds with the help of IR spectroscopy. Ramesh et al (1998) recently reviewed the synthesis, physicochemical characterization and application of polyurethane ionomers. Ismail (1998) investigated a series of water-soluble polyurethane surfactants by polyaddition polymerization of 4:1 ratio of 2,4- and 2,6-toluene diisocyanate with polyethylene glycol (PEG) and/or castor oil and ethylene glycol. He has reported that the water-soluble polyurethane surfactants are found to exhibit excellent surface active properties.

Lin and Chen (1998) investigated on the shape-memory behaviour of polyether based polyurethanes and its influence on the hard-segment and soft-segment molecular weight. Sanchez-Adsuar et al (1998) studied various polyurethane elastomers containing different hard and soft segment ratio and investigated its effect on physical and mechanical properties of the polymers. Yu et al (1998) synthesized polyester based polyurethanes from polyester (M_n = 2000) and MDI with butane diol as a chain extender and glycerol as a crosslinker. The effect of crosslinker content on the degree of H-bond formation in the hard segments and on the physical properties of polyurethanes were discussed.

Velanker and Cooper (1998 and 2000) studied the effect of block length on the microphase separation and rheological properties of polyurethane melts. They also studied the effect of block incompatibility on the microstructure leading to difference in microphase separation and
rheological properties of the polyurethane melts. Tzong-Lin and Fang-Jung (1998) synthesized a class of poly(amide-imide-urethane) thermoplastic elastomers based on two-step synthesis of 4,4'-methylene bis(4-phenylisocyanate) with different polyols (PPG and PTMG), diamine and trimellitic anhydride. It was found that these polymers exhibited better thermal stabilities due to the presence of imide groups than the typical polyurethanes. Soft-segmented ionic polyurethane (linear and crosslinked) based on sodium sulfonate-side chain poly(ethylene oxide) was synthesized and characterized by Wang et al (1999).

A series of polyurethanes were synthesized by Son et al (1999) from poly(oxytetramethylene)glycol (PTMG), 4,4'-diphenylmethane diisocyanate (MDI) and 2,2-bis[4-(2-hydroxyethoxy)phenyl]propane (BHPP) by varying PTMG soft segment length and hard segment content. For these polymers, it was observed that $T_g$ shifted to higher temperature with increasing hard segment content and decreasing soft segment molecular weight, indicating partial phase mixing between hard and soft segment. Chang et al (1999) synthesized polyester-based polyurethane from MDI with butane diol as a chain extender and low molecular weight polyester diol ($\bar{M}_n = 2660$ and 2770) as a soft segment. The effect of even and odd carbon number monomers of polyester soft segments on the phase segregation of soft and hard segments were also reported. Yu et al (1999) synthesized polyester based polyurethanes from polyester ($\bar{M}_n = 2000$) and MDI with butane diol as a chain extender and glycerol as a crosslinker. It was revealed that the degree of phase segregation of soft and hard segments decreased with increasing the triol crosslinker content in the hard segments. Pourjavadi et al (1998) synthesized and characterized the segmented polyurethanes based on poly(cis-2-butyleneadipate)glycol, MDI and 1,4-butane diol as chain extender.

Chang et al (1998) investigated the small angle X-ray scattering and differential scanning calorimetry for the morphological study in the segmented polyester based polyurethane with 4,4'-methylene bis(phenylisocyanate) and 1,4-butane diol a hard segment. The effect of -CH$_3$ side chain content in polyester on the phase segregation of soft and hard
segments of polyurethane at two annealing temperatures were also investigated. A great deal of literature has been devoted to the toughening of epoxy resin via polyurethane incorporation as a second phase in specific matrix to form an interpenetrating polymer network (Hsieh and Han 1990; 1990a and Havani et al 1998). Robila et al (1999) carried out the synthesis of polyurethane anionomers with sodium acetate groups and investigated its film properties and conductivity nature. Lin et al (1999) prepared polyester based polyurethane from a low molecular weight polyester ($M_n = 2000$) and MDI with butane diol as chain extender and glycerol as crosslinker. Its phase segregation effect was studied by using small angle X-ray scattering method. Qun-Dong et al (1999) reported segmented polyurethane with ferrocene units in polyether soft segment, which shows electrochemical properties of redox active polyurethanes. Prochazka et al (1999) obtained linear and crosslinked polyurethane melts by polycondensation reaction of poly(oxypolyol)diol with diisocyanate and studied the dynamic mechanical properties. It was reported that $T_g$ of the polymers was dominated by the urethane links.

A new series of metal containing polyurethanes and poly(urethane-urea)s containing ionic links in the main chain were synthesized by Arun Prasath and Nanjundan (1998) by the polyaddition reaction of hexamethylene diisocyanate (HMDI) or toluylene 2,4-diisocyanate (TDI) with divalent metal salts of mono(hydroxybutyl) phthalate [$M(HBP)_2$] and 1:1 mixtures of toluylene 2,4-bis(o,N-hydroxyethylurea) [TBHEU] and $M(HBP)_2$ and the polymers were also characterized. Wang et al (1999a) synthesized ultraviolet-curable waterborne polyurethane-acrylate ionomer from toluene diisocyanate (TDI), polyethylene glycol (PEG), dimethylol propionic acid (DMPA), triethylamine (TEA) and 2-hydroxyethyl methacrylate (HEMA). It was investigated that the waterborne polyurethane-cured films exhibited excellent adhesion, gloss, flexibility, impact strength and hardness depending upon the hard segment content.

Metal containing polyurethanes having ionic linkages in the main chain were synthesized by Arun Prasath and Nanjundan (1999) from the polyaddition reaction of HMDI or TDI with 1:1 mixtures of divalent metal
salts of mono(hydroxybutyl)phthalate [M(HBP)] and digol [DG]. Similarly poly(urethane-urea)s were synthesized by reacting the diisocyanates with 1:1 mixtures of hexamethylene bis(ω,N-hydroxyethylurea) (HBHEU) and M(HBP)₂. Jiang-Jen and Yong-Chian (1999) prepared segmented polyurethanes from polyethylene glycol, polypropylene glycol and PEG/PPG with isophorone diisocyanate, for which hydrophilicity, crystallinity and electrostatic dissipating properties were investigated.

Polyurethane anionomers based on isophorone diisocyanate, polytetrahydrofuran and cyclohexane dimethanol were prepared as aqueous dispersions. The ionic moiety used to stabilize the dispersion was dimethylol propanoic acid, dimethylol butanoic acid and an experimental sulphonate diol sodium salt. The influence of the degree of neutralization, the ionic moiety and other conditions on the dispersion of polyurethane in water was studied by Horston et al (1999).

Guan-Nan and Kan-Nan (1999) obtained a hybridized copolymer by reacting blends of the amino-terminated group of aqueous-based polyurethane with the glycidyl methacrylate. They found that the carboxylic acids present in the aqueous-based polyurethane and in the hybridized copolymer could be ion-exchanged with calcium ion. The resulting calcium ion cross-linked polymer systems had improved their mechanical dynamic properties.

Wang et al (2000) carried out the reaction between TDI and 4-hydroxycoumarin, 7-hydroxycoumarin or dicumarol and other additives to form the fluorescent-dye polyurethane ionomer. Ten-chin et al (1999 and 2000) prepared various diisocyanate based waterborne polyurethanes (WPU) from polyaddition of poly(propyleneglycol) (PPG) and dimethylol propionic acid with various diisocyanates [4,4’-methylene bis(phenyl isocyanate), 4,4’-methylene bis(cyclohexyl isocyanate), isophorone diisocyanate and toluene diisocyanate] and doped with lithium perchlorate. It was found out that the soft segment T_g increased with increasing LiClO₄ and the different interactions with lithium cation within the hard segment and between the hard and soft phases occurred.
Quli and Xuchai Yu (2000) synthesized poly-caprolactone containing carboxy group (CPCL) (\(\bar{M}_n = 1200\)) from caprolactone and dimethylol propionic acid. Based on CPCL, MDI and 1,4-butane diol, a novel series of polyurethane ionomers could be synthesized with ions in the soft segment. The tensile modulus and ultimate elongation of the ionomer cast films increased and \(T_g\) of CPCL-rich phase moved to a higher temperature after ionization. Wide angle X-ray diffraction shows an ionic peak at \(2\theta=8.6^\circ\) for the ionomer with carboxylate in the hard segment, which was not present in the ionomer with carboxylate in the soft segment.

Tsonos et al (2000) obtained blends of an anion containing polyurethane and polyaminourethane. They studied the molecular mobility, microphase morphology and their dependence on the composition of the ionomers. Polyurethane ionomers based on poly(tetramethylene oxide) or poly(ethylene oxide) with non ionic hard segments of varying length and flexible segments containing sodium ion (Na\(^+\)) have been prepared and their structure property relationship have been reported by Polizos et al (2000). Polizos et al (2000a) synthesized novel polyurethane ionomers based on poly(ethylene oxide) with non ionic hard segments of varying length and flexible segments containing alkali ions and investigated their structure-property relationship. Wang et al (2000a) synthesized polyurethane ionomers based on sodium sulfonate side-chain poly(ethylene oxide).

Wang and Qi (1985) reported the use of butylated formaldehyde-melamine-urea copolymers as crosslinking agents for acrylic and alkyd resin coatings as energy saving crosslinker. Klugar (1986) reported acrylic polymers as alternative top coating materials for leather finishing because of their better properties and least polluting nature. Traubel et al (1987) have discussed the temperature related behaviour and mechanical properties of crosslinked and uncrosslinked films produced from aqueous dispersions of acrylates, polyurethanes etc. with regard to their stability for use in leather finishing. Delpech and Coutinho (2000) obtained polyurethane and poly(urethane-urea) aqueous dispersions from 4,4'-dicyclocexylmethane diisocyanate, poly(propylene glycol) and dimethylol propionic acid. Its mechanical and adhesive properties were investigated. The relationship
between the rheological properties and various composition of thermoplastic polyurethane elastomers was investigated by Sanchez-Adsuar et al (2000).

Desai et al (2000) synthesized polyurethane elastomers from polypropylene glycol (M_n = 2000) (polyol), starch (multifunctional crosslinker) and varying concentration with TDI. It was observed that the polyurethane containing starch as crosslinker exhibited better mechanical properties and biodegradability than those containing 1,1,1-trimethylol propane as crosslinker. Sanchez-Adsuar and Martin-Martinez (2000) investigated physical and mechanical properties of thermoplastic polyurethane elastomers in which increase in length of hydrocarbon chain of the macroglycol improved rheological and thermal properties of the thermoplastic urethanes.

Georgoussis et al (2000) reported the relationship between structure and morphology on one hand and molecular mobility on the other hand in segmented polyurethane (SPU) based on oligo-oxytetramethylene glycol with metal ions Cu^{2+} and Ni^{2+} incorporated in the chains.

Jayabalan et al (2000) synthesized poly(urethane-urea) without ether linkages and reported the hydrolytic stability of the polymer in vitro conditions for use in biomedical application. Jyn Horng (2000) reported about the biocompatibility of biodegradable polyester urethane membrane with different morphologies for their possible use as orthopedic biomaterials and for the culture of osteoblastes. Jayabalan et al (2001) investigated the effect of virtual crosslinking on the hydrolytic stability of completely aliphatic poly(urethane-urea) with different hard segment content based on 4,4'-methylene bis(cyclohexyl isocyanate), hydroxy-terminated polybutadiene and 1,6-hexamethylene diamine for blood contact application.

Flame retardant polyurethanes resulting from the interaction of an organic polyisocyanate and a polyol material comprising a polymeric halogenated phosphorous diol was reported by Wadim et al (1976). Liu et al (1997) obtained phosphorus containing diisocyanate with various diols. A
series of flame retardant polyurethanes based on 2,4-toluylene diisocyanate with different amount of 3-chloro-1,2-propane diol have been investigated by Pielichowski et al (1998). Park et al (1998) synthesized the two-component flame retardant polyurethane coating by blending the polyester polyols and polyisocyanate. The polyester polyol was prepared by the esterification of trichloroacetic acid with trimethylol propane and the intermediate along with 1,4-butane diol and trimethylol propane undergoes polycondensation with adipic acid. The flame retardant polyurethane coating with 20% by weight of trichloroacetic acid showed a self extinguishing property. Krzysztof et al (1998) synthesized chlorine containing polyurethanes based on 2,4-toluene diisocyanate and different amounts of 3-chloro-1,2-propane diol. Troev et al (1996) synthesized phosphorus containing polyurethanes by reacting phosphoric acid diesters ($RO_2P(0)X$) $X = H, CH_3, Ph$ with hydroxy carbamates. These phosphorus containing polyurethanes were characterized by a combination of molecular weight determination (GPC) and NMR spectroscopy. The thermal stability of the polymers were also evaluated.

Mix et al (1996) synthesized linear segmented polyurethanes based on poly(butylene adipate)s (PBA) of different molecular weight ($\bar{M}_n = 2000, 1000$ and $600$), 4,4'-diphenylmethane diisocyanate (MDI) and mesogenic diol 4,4'-bis-(6-hydroxyhexoxy)biphenyl (BHHBP) as well as the unsegmented polyurethane consisting of MDI/BHHBP units and characterized them. The thermal behaviour and morphology of the polymers were also studied.

Sun and Chang (1996) synthesized four series of thermotropic polyurethane elastomers (TPUEs). The hard segments were formed by using 4,4'-methylene dicyclohexyl diisocyanate ($H_{12}$MDI) reacted with various mesogenic units, such as benzene-1,4-di(iminophenoxy-n-hexanol), benzene-1,4-di(4-iminophenol), and 3,3'-(4,4'-biphenylene)dipropanol, which also acted as chain extender. Poly(oxytetramethylene) glycols (PTMEGs), PTMEG-2000 ($\bar{M}_n = 2000$) and PTMEG-1000 ($\bar{M}_n = 1000$) were used as soft segment. Thermal, liquid crystalline and spectral properties of these polymers were studied.
Liaw (1997) prepared polyurethane elastomers based on polyols such as polycaprolactone diol ($M_n = 2000$) and polytetramethylene glycol ($M_n = 2000$), diisocyanates such as diphenylmethane-4,4'-diisocyanate and dicyclohexyl methane-4,4'-diisocyanate and chain extenders such as bisphenol-A, bisphenol-S, bisphenol-AF, and their brominated derivatives. The effects of polyol, diisocyanate, and chain extender on the physical and thermal properties were also studied.

Polyester-based polyurethanes were synthesized from 4,4'-methylene bis(phenyl isocyanate) (MDI) with butane diol as a chain extender and low molecular weight polyester-diol as a soft segment. Two polyesters were used in the synthesis of polyurethanes. One of the polyesters was synthesized from adipic acid and 1,6-hexane diol, which had an even number of carbon atoms. The other polyester was synthesized from pimelic acid and 1,5-pentane diol, which have an odd number of carbon atoms. The effect of even carbon number monomers and odd carbon number monomers of polyester soft segments on the phase segregation of soft and hard segments were studied by DSC and FTIR (Chen et al 1999).

Jung et al (2000) synthesized polyurethanes using the high functional 4,4'-diphenylmethane diisocyanate, polyester polyol, and 1,4-butane diol. Spectral, thermal and swelling properties of the polyurethanes were studied. Kultys and Pikuš (2001) obtained three series of new thermoplastic, high molecular weight, segmented thiopolyurethanes by a one-step melt polymerization from newly obtained thiodiols, including bis[4-(2-hydroxyethyl)thiomethylphenyl]methane, bis[4-(3-hydroxypropyl)thiomethylphenyl] methane, and bis[4-(6-hydroxyhexyl)thiomethylphenyl] methane (BHMM) as chain extenders, hexamethylene diisocyanate and 20-80 mol% poly(oxytetramethylene) glycol (PTMG; $M_n = 1000$) as the soft segment. Solution polymerization with the chain extender BHMM gave considerably lower molecular weight polymers. The structure and thermal properties of all the polyurethane were studied. Shore A/D hardness and tensile properties were also determined. Arun Prasath et al (1998) studied the effect of divalent metal ($\text{Mg}^{2+}$, $\text{Ca}^{2+}$, $\text{Mn}^{2+}$, $\text{Zn}^{2+}$, $\text{Cd}^{2+}$, $\text{Hg}^{2+}$ and $\text{Pb}^{2+}$) salts
Jayakumar et al (1999) synthesized divalent metal salts of mono(hydroxybutyl)phthalate from 1,5-pentane diol, phthalic anhydride and divalent metal (Mg$^{2+}$, Ca$^{2+}$, Mn$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, Hg$^{2+}$ and Pb$^{2+}$) acetates. These ionic diols were characterized by elemental analysis, solubility, spectral studies, thermogravimetric analysis (TGA) and their antimicrobial activities were tested in vitro against Pseudomonas fluorescence, E. coli, Streptococcus sp. and Salmonella sp.

Jayakumar et al (2000) reported divalent metal salts of mono(hydroxyethoxyethyl)phthalate M[HEEP]$_2$ containing ionic bonds in the molecule in high purity and high yield. Divalent metal salts of mono(hydroxyethoxyethyl)phthalate were synthesized by the addition of diethylene glycol, phthalic anhydride and divalent metal (Ca$^{2+}$, Cd$^{2+}$, Mn$^{2+}$, Zn$^{2+}$, Hg$^{2+}$ and Pb$^{2+}$) acetate. These ionic diols were characterized by spectral studies, elemental analysis, solubility and thermogravimetric analysis (TGA). The effect of the metal containing ionic diols on the growth of various micro-organisms were investigated by disc plate agar technique.

Jayakumar et al (2001) synthesized polyurethanes containing metal ions in the main chain by reacting hexamethylene diisocyanate (HMDI) or toluylene 2,4-diisocyanate (TDI) with Cu$^{2+}$, Mn$^{2+}$ and Zn$^{2+}$ salt of mono(hydroxyethoxyethyl)phthalate using di-n-butyltin dilaurate (DBTDL) as catalyst. The spectral and thermal properties of the polyurethanes were studied. The antibacterial activity of these polyurethanes have also been investigated using agar diffusion method.
1.11 SCOPE

The literature review reveals that a considerable amount of work has been done on metal containing polymers in which the metal ions are co-ordinated to groups attached to the pendant groups and less work has been done on polymers containing metal ions in the main backbone of the polymers. Literature review shows that there is no report about studies on metal-containing polymers based on metal salts of mono(hydroxyethoxyethyl)phthalate and mono(hydroxypentyl)phthalate. The scope of the present work is presented as below.

1. To prepare calcium salt of mono(hydroxyethoxyethyl)phthalate [Ca(HEEP)$_2$] by reacting phthalic anhydride with diethylene glycol and calcium acetate.

2. To prepare calcium salt of mono(hydroxypentyl)phthalate [Ca(HPP)$_2$] by reacting phthalic anhydride with 1,5-pentane diol and calcium acetate.

3. To prepare toluylene bis(o,N-hydroxyethylurea) (TBHEU) and hexamethylene bis(o,N-hydroxyethylurea) (HBHEU) by reacting ethanolamine with toluylene 2,4-diisocyanate (TDI) and hexamethylene diisocyanate (HMDI) respectively.

4. To prepare toluylene bis(o,N-hydroxypropylurea) (TBHPU) and hexamethylene bis(o,N-hydroxypropy lurea) (HBHPU) by reacting propanolamine with TDI and HMDI respectively.

5. To prepare four different polyurethanes from Ca(HEEP)$_2$, Ca(HPP)$_2$ and the diisocyanate, HMDI or TDI.
6. To prepare sixteen different poly(urethane-urea)s by reacting a mixture containing Ca(HEEP)$_2$ or Ca(HPP)$_2$ and any of the four bisureas TBHEU, HBHEU, TBHPU and HBHPU with diisocyanates (HMDI or TDI). Eight different blank poly(urethane-urea)s are to be prepared by reacting each of the bisureas with diisocyanate (HMDI or TDI).

7. To prepare two copolyurethanes by reacting a mixture of Ca(HEEP)$_2$ and 1,5-pentane diol (PD) with diisocyanate (HMDI or TDI). Two blank polyurethanes are to be prepared by reacting PD with diisocyanate (HMDI or TDI).

8. To prepare two copolyurethanes by reacting Ca(HPP)$_2$ and diethylene glycol (DG) with diisocyanate (HMDI or TDI). Two blank polyurethanes are to be prepared by reacting DG with diisocyanate (HMDI or TDI).

9. To prepare twelve different poly(urethane-ether)s by reacting a mixture of Ca(HEEP)$_2$ and PEG$_{300}$ (polyethylene glycol) or PEG$_{400}$ with diisocyanate (HMDI or TDI). A series of poly(urethane-ether)s are to be synthesized by varying the mole ratio of Ca[HEEP]$_2$ : PEG$_{300}$ or PEG$_{400}$ : HMDI or TDI as 3:1:4, 2:2:4 or 1:3:4 to study the relative properties of the copolymers. Four different blank poly(urethane-ether)s are to be prepared by reacting PEG$_{300}$ or PEG$_{400}$ with diisocyanate (HMDI or TDI).

10. To prepare twelve different poly(urethane-ether)s by reacting a mixture of Ca(HPP)$_2$ and PEG$_{300}$ or PEG$_{400}$ with diisocyanate (HMDI or TDI). A series of poly(urethane-ether)s are to be synthesized by varying the mole ratio of Ca(HPP)$_2$ : PEG$_{300}$ or PEG$_{400}$ : HMDI or TDI as 3:1:4, 2:2:4 or 1:3:4 to study the relative properties of the copolymers.
11. To characterize the monomers by elemental analysis, FT-IR, $^1$H-NMR, $^{13}$C-NMR, TGA and solubility.

12. To characterize the polymers by FT-IR, $^1$H-NMR, $^{13}$C-NMR, solid-state $^{13}$C-CP-MAS NMR, elemental analysis, TGA, DSC, XRD, solubility and viscosity.

13. To apply solutions of poly(urethane-ether)s based on Ca(HEEP)$_2$ and Ca(HPP)$_2$ as top coat on acrylic coated leather and to study the mechanical and physical properties of the finished leather.