# POLYURETHANES FOR EXTREME TEMPERATURE CONDITIONS

A thesis submitted

*by*

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# CERTIFICATE

This is to certify that this thesis is a report of the original work carried out by **Mr. P. Radhakrishnan Nair** under my supervision in the Polymers & Special Chemicals division of Vikram Sarabhai Space Centre, Trivandrum. No part of the work reported in this thesis has been presented for any degree from any other institution.

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# DECLARATION

I hereby declare that the thesis entitled **POLYURETHANES FOR EXTREME TEMPERATURE CONDITIONS** is the original work carried out by me in the Polymers & Special Chemicals Division, VSSC under the supervision of Prof.(Dr.)D.Joseph Francis, Professor, Department of Polymer Science & Rubber Technology, Cochin University of Science & Technology and no part of this work has been presented for any degree from any other institution.

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# Chapter I

## CHAPTER-1

# POLYURETHANE CHEMISTRY, A SURVEY ON GENERALITIES AND CURRENT TRENDS.

Polyurethanes are a class of industrially important polymers which contain significant number of urethane groups regardless of the rest of the molecule. Usually these polymers are obtained by combination of polyisocyanate with reactants which have at least two hydroxyl groups eg. polyethers, castor oil and simple glycols. Other reactive groups such as amine and carboxylic acid may also be present. Thus a typical polyurethane may contain aliphatic and aromatic hydrocarbon, ester, ether, amide and urea groups in addition to urethane moieties.

Polyurethanes can be formed by a variety of methods although the most widely used method is through the reaction of polyfunctional hydroxyl compounds eg. hydroxyl terminated polyesters or polyethers with di - or polyfunctional isocyanates[1]. The general structure of a linear polyurethane derived from a hydroxy compound HO-R-OH and a diisocyanate OCN-R'-NCO can be represented by the following general formula

$$\text{--}[\text{--R-OOC-NH-R'-NH-COO-}]_n\text{--}$$

The nature of R such as its molecular weight and type (polyether, polyester, simple glycol) may be changed. Mixtures of polyhydroxy compounds can also be used. Similarly, the nature of R' may be altered depending on the structure of the diisocyanate. Polyurethanes are unique in that crosslinking, chain flexibility and intermolecular forces can be varied widely and almost independently. One of the earliest commercial applications of isocyanates was in the adhesive field. Urethane coatings based on castor oil-diisocyanate adducts which have found wide commercial applications have been reported by several investigators[2-6] Similary one-or two component polyurethane coatings based on polyethers[7-10] and polyesters[11] have been described.

Another field of application of polyurethanes is foams. The early development in this field took place mainly in rigid foams[12]. The urethane foam industry started with polyester - diisocyanate combinations[13,14] and then with polyether- diisocyanate combination, the latter being used in the largest volume. The polyester employed a one-shot technique. Polyester, diisocyanate, water, catalyst and foam stabilizers were all mixed up in one-stage and then permitted to foam. The first commercial use of polyurethane employed a prepolymer process wherein the polyether and diisocyanate were first reacted to form a prepolymer that was subsequently mixed with catalyst, water and stabilisers to produce the foam.[15] Synthetic elastomers comprise a major application of polyurethanes[16-18].

## 1.1. RAW MATERIALS FOR POLYURETHANE

The principal raw materials for polyurethane preparation are diisocyanates and polyols. Low molecular weight trihydroxy or diamine compounds are used as crosslinking agents.

### 1.1.A. Isocyanates

There are a variety of methods for preparation of isocyanates. The only method used industrially is that of phosgenation of primary amines

$$R\text{-}NH_2 + COCl_2 \longrightarrow R\text{-}NCO + 2\,HCl$$

- Other methods not requiring phosgene, like Curtius rearrangement of acid azides may be more suited for laboratory preparation.

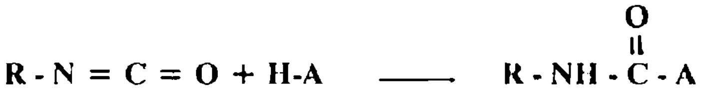
$$RCON_3 \longrightarrow R\text{-}NCO + N_2$$

### 1.1.A1. *Reactions of isocyanates*

The isocyanates are generally highly reactive towards a number of compounds containing active hydrogens and the reaction can occur also with a few other compounds not having labile hydrogens like epoxy, anhydride etc. The electronic structure of the isocyanate group indicates that it should have the following resonance structures.[19]

$$R-\overset{-}{N}-\overset{+}{C}=O \longleftrightarrow R-N=C=O \longleftrightarrow R-N=\overset{+}{C}-\overset{-}{O}$$

The normal reaction ultimately provides addition of the reactent to the carbon-nitrogen double bond as follows[20].



$$R-N=C=O + H\text{-}A \longrightarrow R-NH-\overset{\overset{\displaystyle O}{\|}}{C}-A$$

Aromatic isocyanates are more reactive than aliphatic isocyanates. Substitution of electronegative groups on the aromatic ring enhance the reactivity whereas electropositive groups reduce it.

### 1.1.A.2. *Reaction with compounds containing N-H group*

All compounds containing N-H groups are potentially reactive with isocyanates. The most basic ones are usually the most reactive unless steric hindrance is excessive. Thus primary aliphatic amines are extremely reactive giving a disubstituted urea in high yield [21].

$$\text{R-NCO} + \text{R'-NH}_2 \longrightarrow \text{R-NH-CO-NH-R'}$$

Secondary aliphatic amines as well as aromatic amines react similarly although not quite readily. The secondary aromatic amines are the least reactive [22,24]

$$\text{R-NCO} + \text{R'}_2\text{NH} \longrightarrow \text{R-NH-CO-NR}_2$$

### 1.1.A.3. *Reactions with O-H compounds*

Isocyanates react with compounds containing hydroxyl groups like alcohols in a similar way as with amines giving urethanes.

$$\text{R-NCO} + \text{R'-OH} \longrightarrow \text{R-NH-COO-R'}$$

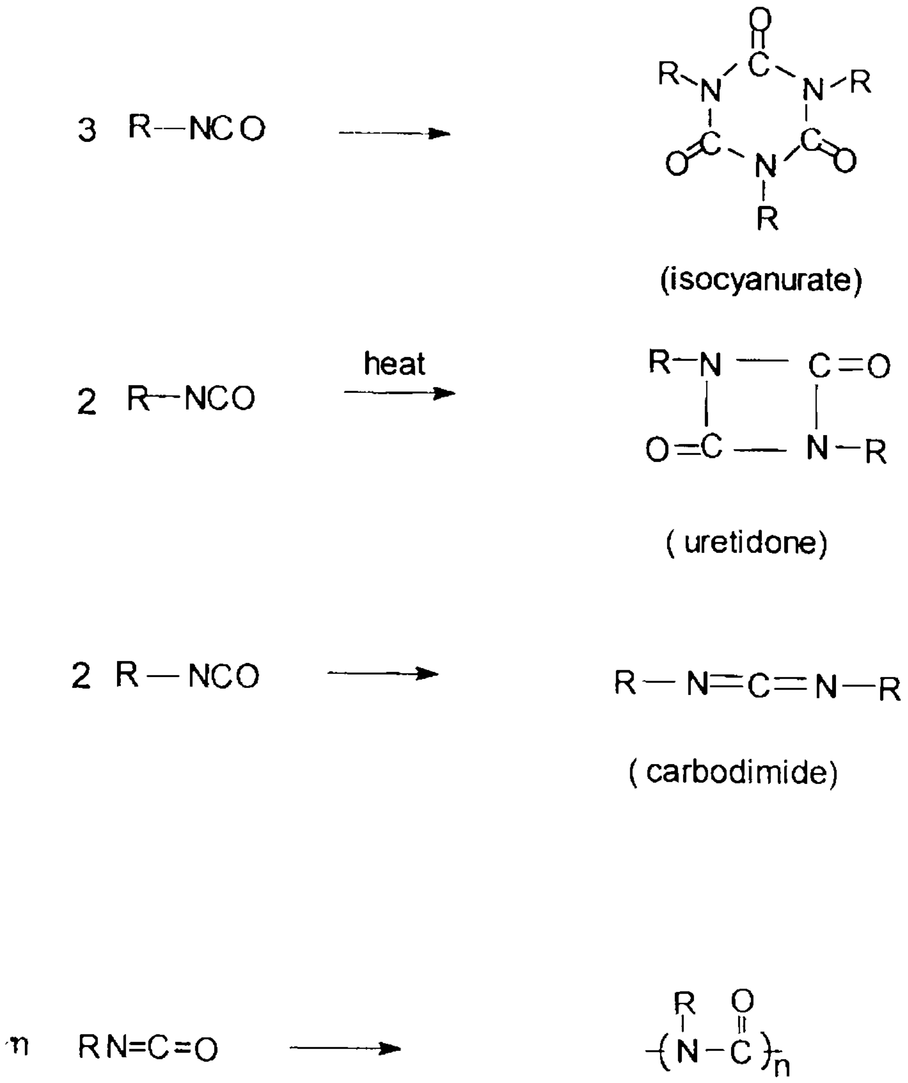
Reaction with carboxylic acids gives amide with evolution of carbon dioxide.

$$\text{R-NCO} + \text{R'-COOH} \longrightarrow [\text{R-NH-COO-OC-R'}] \longrightarrow \text{R-NH-CO-R'} + \text{CO}_2$$

The reactivity of alcohols with isocyanates vary in the order primary > secondary > tertiary[25].

### 1.1.A.4. *Other reactions of isocyanates*

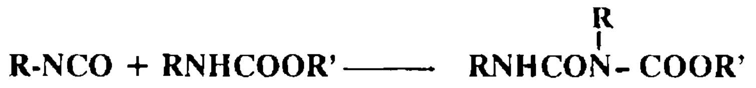
Isocyanates react among themselves by self-addition to give cyclic compounds such as isocyanurates,[26,27] and uretidones[28,29,30]. They can undergo polymerisation by double bound addition[31,32]. The reactions are presented in scheme 1.1.The reaction with water with evolution of carbon dioxide is made use of in urethane foam industry.



Scheme 1.1. The polymerisation and cyclisation reactions of isocyanate

### 1.1.A.5. *Secondary reactions of isocyanates*

In addition to the reactions mentioned above, isocyanates undergo further reactions with the groups containing active hydrogen which are present in the primary reaction products mentioned above at high temperatures and in presence of catalysts to give products like allophanate[33], biuret[14] and acyl urea[35] as



$$\mathrm{R\text{-}NCO + RNHCOOR' \longrightarrow RNHCO\overset{\displaystyle R}{\overset{|}{N}}\text{-}COOR'}$$

All these reactions occur at temperatures above 100°C in presence of amine or stannous catalysts to a lesser extent and these reactions are responsible for spurious crosslinking and branching which have important implications on polyurethane properties.

The polymerisation and cyclisation reactions as given in scheme 1.1 are also of importance in influencing branching and crosslinking during the build-up of polyurethane structures. The third type of polymerisation which results in formation of substituted linear polyamides resembling nylon takes place at low temperatures with special catalysts[36]. It has however no practical importance.

Yet another reaction of isocyanate which is not usually considered as polymerisation reaction but could be classified as condensation polymerisation is that between isocyanate molecules, with elimination of carbon dioxide, giving rise to carbodimide[37].

### 1.1.A.6. *Blocked isocyanates*

Isocyanates react with certain active hydrogen compounds and such addition product has limited thermal stability. A typical example is the urethane from a phenol.

$$\text{R-NCO} + \text{Ar-OH} \longrightarrow \text{R-NHCOOAr}$$

The dissociation of the above urethane takes place at temperatures of the order of 150 - 200° C regenerating the isocyanate and hence they are termed blocked isocyanates [38,39]. The splitting temperatures depend on the nature of the blocking agent used. A lower splitting temperature was observed for aromatic isocyanate. The blocking and deblocking are helpful in protecting the isocyanate group from side reactions.

Isocyanates react with acid anhydrides to give imides and with epoxies to give oxazolidones[40 - 42].

### 1.1.A.7. *Characteristics of Isocyanate reaction*

The primary reaction of isocyanate with active hydrogen compounds occurs easily proceeding at ordinary temperatures with evolution of heat. The rates of reaction differ quite considerably with the type of reactant used. For the reaction with alcohols to form urethane, the different aromatic isocyanates are in one class of reactivity, the aliphatic and cycloaliphatic type of isocyanates, in another.

The aromatic isocyanates are several times more reactive than the aliphatic isocyanates. Different types of isocyanates are available commercially in polyurethane industry[43] . The difference in reactivity of two isocyanate groups in aromatic diisocyanates have been estimated and reported.[44,45] The propensity of isocyanates for the secondary reaction forming biurets and allophanates generally follows the reactivity of these isocyanates in the primary reactions. The secondary reactions without the use of catalysts normally require elevated temperatures and higher concentrations than are necessary for the primary reactions, if a reasonable rate of reaction is to be attained. The reaction between isocyanate and urea to form biurets occurs more readily than the reaction between urethanes to give allophanates.

Isocyanates react with amines faster than with alcohols and the reactivity of the amines is directly dependent on their basicities . The rates of reaction of isocyanate with different types of groups are as follows.

Aliphatic $NH_2$ > Aromatic $NH_2$ > primary OH > water > Secondary OH > Tertiary OH > Phenolic OH > COOH and R-NHCONH-R > R-CONH-R > R-NHCOO-R'

### 1.1.A.8. *Catalysts for urethane reaction*

The most commonly used catalysts for all types of isocyanate reaction are basic compounds either inorganic base such as sodium hydroxide or sodium acetate or more commonly tertiary amines and materials which generate tertiary amines. The more basic the catalyst, the more strongly it promotes urethane formation. Less sterically hindered amines are strong catalysts for isocyanate reaction, the most important one being diazobicyclooctane (DABCO) and hexamethylene tetramine.(HEXA)

Other catalysts which are suitable for reaction of isocyanates with active hydrogen atoms are certain organometallic compounds of tin, iron, copper etc, the most important and widely used ones being dibutyl tin dilaurate and stannous octoate [46,47]. They are highly effective and less volatile over amine catalysts even at higher curing temperatures.

### 1.1.B. Polyols for polyurethanes

Polyurethanes for commercial applications employ telechelic oligomers in conjugation with isocyanates, as reaction with simple organic diols give rise to rigid intractable polyurethanes. The most common polyols used for polyurethane preparation are based on polyester, polyether and polybutadiene.

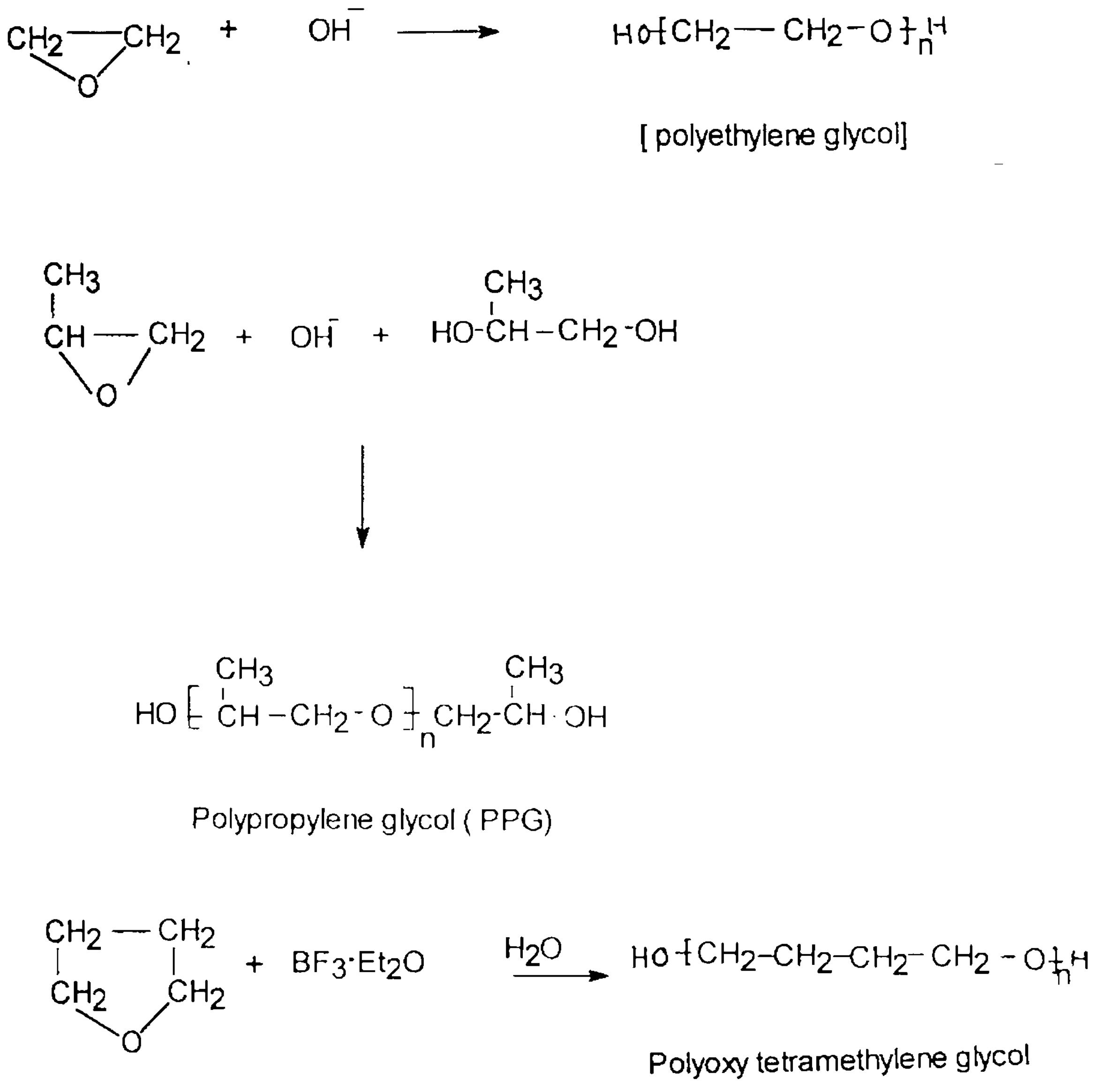
#### 1.1.B.1. *Polyesters*

Polyesters having hydroxyl end-groups are used as polyols mainly in the preparation of elastomers. Polyesters from adipic acid and ethylene glycol (polyethylene glycol adipate) or adipic acid and diethylene glycol are used for manufacture of polyurethane elastomers and films. They are prepared by melt polycondensation of acid and glycol in presence of acidic catalysts, the glycol taken in a stoichiometric excess to get the hydroxyl ends[48-49].

#### 1.1.B.2. *Polyethers*

Polyethers are the important raw material for polyurethane foam manufacture and are widely used in polyurethane industry. Difunctional hydroxy terminated-polyethers like polyoxypropylene glycol and polyoxybutylene glycol are manufactured by the ring opening polymerization of cyclic ethers.[50,51] The reaction sequence is given in scheme 2.2.

Polyethers having trifunctionality are also available commercially for the manufacture of rigid foams. Nitrogen-containing polyols such as



scheme- 1.2. preparation of polyether polyols polyoxyethylene-polyoxypropylene block copolymers with ethylene diamine are used commercially.

### 1.1.B.3. *Polyoxypropylene glycol (PPG)*

The most widely used polyether polyol for urethane foam and elastomers is PPG. It is manufactured by the ring opening anionic polymerization of propylene oxide with base catalysts and propylene glycol or dipropylene glycol as initiator to give hydroxyl ends. The oxirane ring opens up by the initiator anion and terminates by the deactivation of the polymeric anion by a proton.

The base-catalysed polymerisation of propylene oxide yields predominantly secondary hydroxyl groups as shown in scheme 2.2.

### 1.1.B.4. *Polyoxy tetramethylene glycol (POTMG)*

POTMG is manufactured by the anionic ring opening polymerisation of tetrahydrofuran using lewis acid catalysts such as boron trifluoride, antimony chloride etc. A low molecular weight diol or triol is used often as an initiator [52] to get hydroxyl ends. THF has been copolymerised with other cyclic ethers to give co-polyethers.

### 1.1.B.5. *Unsaturated polyols*

Polybutadiene polyol is a comparatively newcomer in the field of polyurethane technology, the applications of which include elastomers, coatings, rocket propellant fuels etc. Hydroxy terminated polybutadiene (HTPB) is widely used polybutadiene polyol as a high energy propellant fuel in solid propellants. It combines high energetic and mechanical properties in solid propellants. HTPB is prepared by the free radical or anionic polymerisation of butadiene. The commercial production of HTPB is based on the free radical polymerisation of butadiene using hydrogen peroxide as initiator[53,54]. The polymerisation reaction is given in scheme 1.3 The radical polymerisation gives polymer of wide molecular weight distribution and non-uniform functionality distribution. The average functionality of the chain is also higher than 2. Anionic polymerisation using alkyl dilithium as initiator in hydrocarbon solvent[55,56] (as given in scheme-3) gives polymer of very narrow molecular weight distribution and uniform functionality distribution. This polymer gives rise to polyurethane elastomers of excellent mechanical properties. The cost of production being very high compared to free radical polymerisation, this method is not industrially preferred.

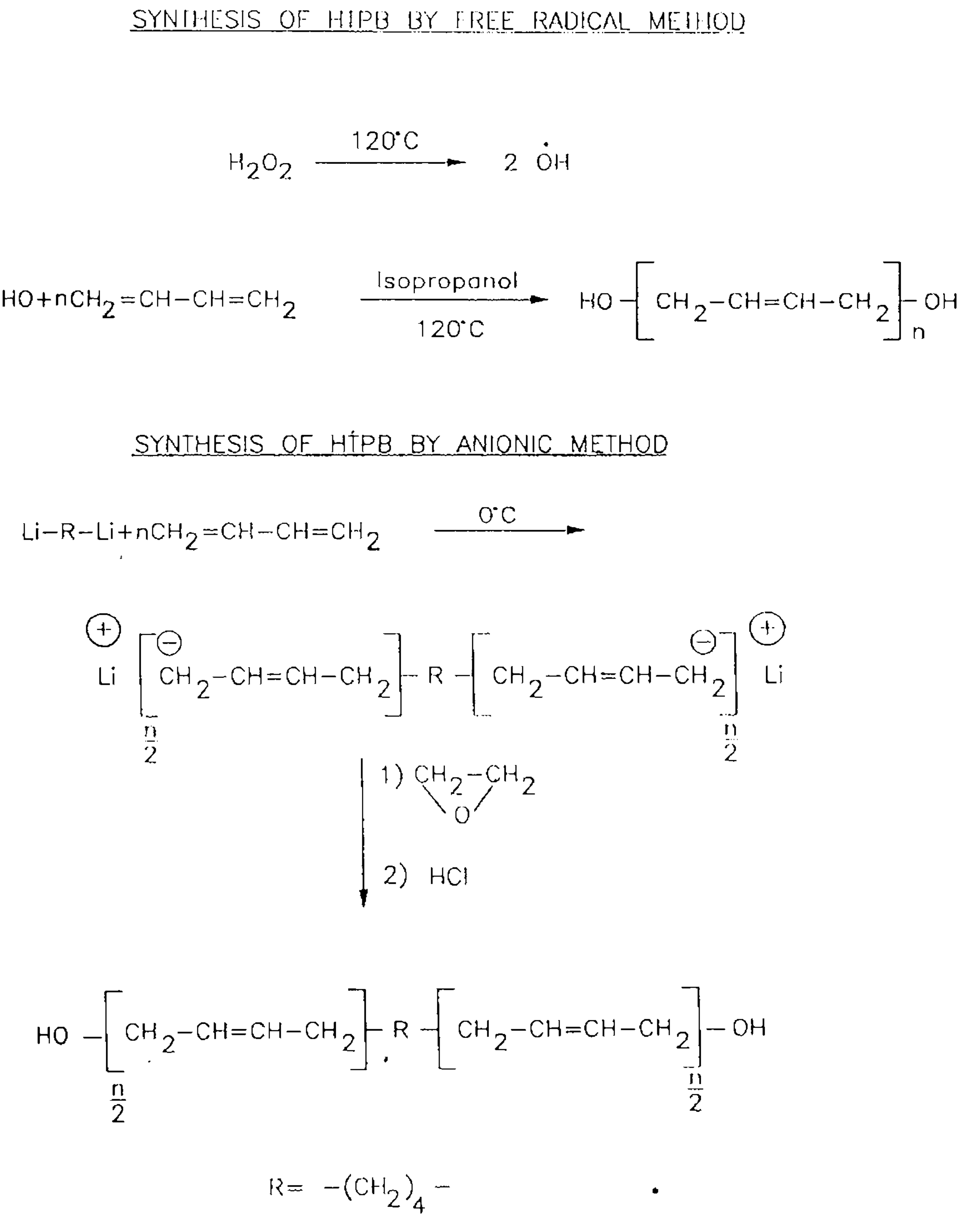
Another class of unsaturated polyols is castor oil based. The fatty acid portion of castor oil, i.e. recinoleic acid is polymerised and end-capped with trimethylol propane to give a recinoleic acid-polyol useful in the preparation of polyurethane foam and elastomers.

### 1.1.B.6. *Basic polyols*

Nitrogen containing basic polyols are also used in the manufacture of polyurethanes.[57]

## 1.1.C. Crosslinking agents

Crosslinking agents are usually used in polyurethane preparation involving a difunctional isocyanate and a difunctional polyol. The mechanical and thermal properties of polyurethane are dependent on the extent of crosslinking in the polymer chain. Hence for optimisation of the properties of polyurethanes, the



$$H_2O_2 \xrightarrow{120^\circ C} 2\ \dot{O}H$$

$$HO + nCH_2{=}CH{-}CH{=}CH_2 \xrightarrow[120^\circ C]{\text{Isopropanol}} HO{-}\left[CH_2{-}CH{=}CH{-}CH_2\right]_n{-}OH$$

$$Li{-}R{-}Li + nCH_2{=}CH{-}CH{=}CH_2 \xrightarrow{0^\circ C}$$

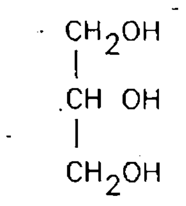
$$\overset{\oplus}{Li}\left[\overset{\ominus}{C}H_2{-}CH{=}CH{-}CH_2\right]_{\frac{n}{2}}{-}R{-}\left[CH_2{-}CH{=}CH{-}\overset{\ominus}{C}H_2\right]_{\frac{n}{2}}\overset{\oplus}{Li}$$

$$\Big\downarrow \text{1) } CH_2{-}CH_2 \text{ (via O)} \quad \text{2) } HCl$$

$$HO{-}\left[CH_2{-}CH{=}CH{-}CH_2\right]_{\frac{n}{2}}{-}R{-}\left[CH_2{-}CH{=}CH{-}CH_2\right]_{\frac{n}{2}}{-}OH$$

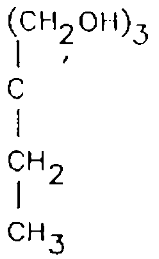
$$R = -(CH_2)_4-$$

Scheme 1.3 : Preparation of hydroxy terminated polybutadiene



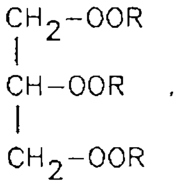
$$\begin{array}{l} CH_2OH \\ | \\ CH\ OH \\ | \\ CH_2OH \end{array}$$

(GLYCEROL)

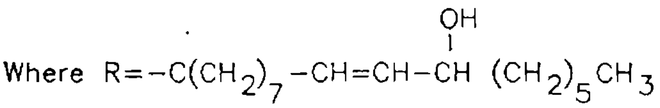


$$\begin{array}{l} (CH_2OH)_3 \\ | \\ C \\ | \\ CH_2 \\ | \\ CH_3 \end{array}$$

(1,1,1 TRIMETHYLOL PROPANE)
(TMP)



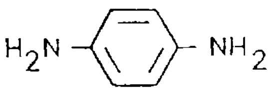
$$\begin{array}{l} CH_2-OOR \\ | \\ CH-OOR \\ | \\ CH_2-OOR \end{array}$$



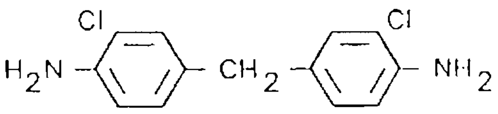
$$\text{Where } R=-C(CH_2)_7-CH=CH-\overset{\overset{OH}{|}}{CH}\ (CH_2)_5CH_3$$

(CASTOR OIL)

AMINES



P-PHENYLENE DIAMINE



METHYLENE BIS ORTHO CHLORO ANILINE

(MOCA)

Fig. 1.1 : Various crosslinking agents for polyurethanes

extent of crosslinking is regulated. The commonly used crosslinking agents are low molecular weight - trifunctional hydroxy compounds and diamines given in figure 1.1. The use of amines as crosslinking agents imparts higher strength for the resultant polyurethane[58].

### 1.1.C.1. *Triols*

Polyoxypropylene triols are mainly used in the manufacture of polyurethane foams.[59] They include the totally hydroxypropylated ethylene diamines, diethylene triamine, various primary aliphatie amines, sucrose, glycerol, trimethylol propane etc[60].

## 1.2. STRUCTURE-PROPERTY RELATIONSHIPS IN POLYURETHANES

The relationship between structure and property of polyurethanes is a well studied subject.[61] The effect of various parameters on the properties of polymer is summarised here

### 1.2.A. Molecular weight.

The mechanical properties of polyurethanes change with molecular weight upto a limiting value and then donot change as the molecular weight increases further. The properties that show a similar relation include melting point, elongation, elasticity and glass transition temperature. Solubility, brittleness etc decrease as the molecular weight approaches a limiting value.

### 1.2.B. Intermolecular forces

Intermolecular forces or secondary chemical bonds are due to hydrogen bonding, dipole moments, polarisability and dispersion effects which tend to hold the polymer chains together in a manner similar to that of primary chemical bonds but are much weaker and are more readily affected by increase in temperature or stress.

The intermolecular forces are reduced by factors which keeps the attractive groups apart eg: plasticizers, bulky groups such as side chains and irregular spacing of attracting groups. The presence of strong intermolecular forces combined with regular geometric arrangement of the groups favour crystallisation of linear polymers. Crosslinked polymers favour high modulus, ultimate tensile strength, tear strength, density, hardness and glass transition temperature and relatively low swelling by solvents.

### 1.2.C. Component group structures in urethanes

The urethane polymers may contain a variety of groups in the polymer chain including hydrocarbon, urethane, urea, ester, ether and aromatic. The ether groups are relatively flexible and the aromatic groups are rigid. The aromatic and ester groups contribute moderate intermolecular forces and the urea and urethane groups contribute very strong intermolecular forces.

## 1.3. POLYURETHANES FOR EXTREME TEMPERATURE CONDITIONS

Polyurethanes are generally not employed for service at higher temperatures. However because of their interesting properties, any modification to improve the thermal stability is of great importance. This necessitates a knowledge of the various mechanisms of thermal degradation of polyurethanes

### 1.3.A. Thermally stable Polyurethanes

The thermal stability of a polymeric material is expressed in terms of a specific temperature or temperature-time limit within which the polymer can be used without excessive loss of properties. There is however the existance of two fundamentally different mechanisms of property loss[62].

a) Physical or reversible change consisting mainly of glass transition, crystallisation or melting and changes in polymer morphology mainly controlling thermoplastics.

b) Chemical or irreversible process which are of importance in the determination of high temperature endurance of the material. The thermal degradation of polymers can be divided roughly into two general categories, random chain scission and depolymerisation. The first type can be considered as reverse of polycondensation. Chain scission occurs at random points along the chain leaving fragments of relatively high molecular weight. No monomer fragments are formed and weight loss to volatile product is nearly negligible. In such a case each scission produces one new polymer molecule. The second type of degradation is essentially a depolymerisation process in which monomer units are released from the chain ends. Such a process is opposite of propagation step. Both reactions can occur simultaneously in a polymer chain or only one of them may occur depending on the polymer, temperature, initiating agent etc.

Oxidative thermal stability is also equally important in the use of polymers as it is a matter of great concern in many of their applications. The actual mechanism is complex but it is believed to be of free radical type. A number of papers have appeared describing thermal stability of specific class of polyurethanes[63-66]. The main factors determining thermal stability of polyurethanes are the nature of starting material and conditions of polymer preparation. Isocyanurate is one of thermally stable structures obtainable from isocyanates. Their degradation usually doesnot start below 270°C [67]. N-N' disubstituted urea starts to dissociate at 160°C to amine and isocyanate. At 390°C diphenyl urea is totally dissociated into aniline. Certain biurets and allophanates dissociate to free isocyanate at temperatures as low as 100°C with biurets generally being slightly more stable than allophanates. [68]. Dissociation in both these classes is ordinarily complete at 160-170°C.

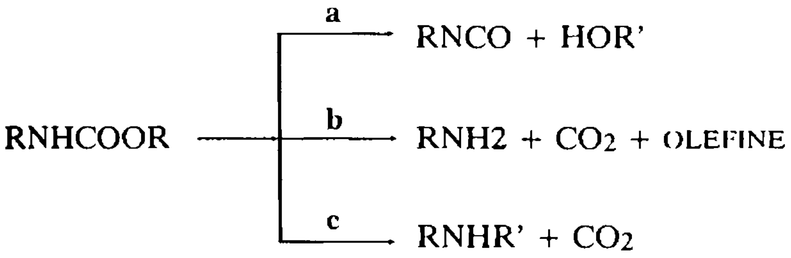
The stability of urethanes, R-NHOCOO--R' depends on the type of hydroxyl compound used in their preparation and generally decrease in the order

R' = Primary alkyl > secondary alkyl > tertiary alkyl

As a general rule the stability of N-substituted carbamates increases with decreasing reactivity of the parent isocyanate. Thus, urethanes in the following series were found to be increasingly thermostable[69]

R = chlorosulfonyl < p-nitrophenyl < phenyl < benzyl < n-alkyl < cyclohexyl < tertiary butyl.

The decomposition of urethanes can take place in a variety of ways. The predominant mechanism depends strongly on the nature of substituents on the N and O atoms. Urethanes of many commercially available isocyanates and primary and secondary alcohols start to decompose at 150-200°C . Their decomposition proceeds at a measurable rate between 200 - 250°C and follows a combination of reactions *a* and *b* given below. The relative ratio of alcohol to carbon dioxide formed depends on the specific substituents and the particular conditions under which the pyrolysis is carried out.



The mechanism by which dissociation takes place is probably a concerted deprotonation and weakening of the C-O bond[70-72]. Any substituent on the isocyanate portion of the urethane which facilitates deprotonation on the nitrogen, should have a similar effect. The dissociation temperature is considered as temperature at which 5% of the urethane group, present in the system dissociates, which is not sufficient to describe the efficiency of the urethane as an isocyanate-donor. The kinetic studies of dissociation are also reported[73,74]. The type of substituent on the phenol ring has also an effect on the dissociation temperature. eg. the strongly electron withdrawing $NO_2$ group exerts a destabilising effect on the urethane by promoting deprotonation.[75]

Aliphatic isocyanates, because of the + I effect of the alkyl group give urethanes with higher thermal stability Electron- withdrawing substituents on N appear to favour decomposition of the urethane group into carbon dioxide and amines or olefins, while electron-donating substituents promote dissociation into isocyanate and alcohol.

### 1.3.A.1. *Dependency of backbone structure on thermal stability.*

Two of the most frequently utilised building blocks in polyurethanes are polyether and polyester. Polyether polyols generally have poly (propylene oxide), poly (ethylene oxide) or poly (1,4-butylene oxide) backbones. Their thermal degradation in vacuum and air[76] has been reported. The stability in nitrogen is generally higher, indicating that the oxidative process play a significant role in the degradation of polyethers[77]. Polyesters exhibit considerably higher thermal stability than polyethers and have generally been found to be quite resistant to oxidation under relatively mild conditions. Traces of metal impurities like copper can catalyse the thermoxidative degradation of polyether urethanes significantly.

### 1.3.A.2 *Thermal stabilisation of Polyurethanes*

The urethanes degrading with greatest difficulty are, as seen those derived from primary alcohols. The decomposition has been found to proceed with a measurable rate at 200-250$^0$C, depending on the N-substitution. This temperature can then be considered as the absolute stability limit which can be reached with urethane bonds. In most practical cases, this limit will be considerably lower unless extreme care is taken during polymer preparation to avoid the formation of weak links like allophanate, biurets, dimers etc resulting from side reactions.

Some of the parameters to be considered in attempting to prepare polyurethanes with optimum thermal resistance are listed below.

1. Choice of isocyanate
2. Choice of hydroxyl component
3. Type and density of crosslinks

4. - Introduction of thermally stable (non urethane) linkages
5. Absence of defective bonds

The selection of the isocyanate has a distinct influence on the thermal stability of polyurethanes. Polyurethanes made from the most commonly used isocyanates can be arranged in the following order of decreasing thermal stability. HMDI > MDI > TDI

Increase in crosslink density of a urethane, as in other polymers results in increased thermal stability because more bonds will have to be broken before total network breakdown occures. Polymers with higher temperature resistance have been obtained by partial replacement of urethane bonds with groups of greater thermostability. The linear chain extension of isocyanate terminated polyurethanes with water or amines leads to the formation of urethane-urea copolymers. The introduction of urea groups imparts higher mechanical and thermal properties to the polymer. There is a marked increase in modulus and tensile and tear strengths.Since the resulting polymers are still essentially isocyanate-derived and contain some urethane bonds, they can be considered to belong to the class of polyurethanes. A variety of thermally stable polymers has been reported which contain characteristic groups like polyimide, polybenzimidazoles, polybenzoxazoles, polyphosphazenes etc.[78]. Most of the thermally stable polymers contain hetrocyclic rings in the backbone which are stable towards thermal scission. Hence introduction of these hetrocyclic groups in polyurethane chain is an accepted strategy for improving the thermal properties of the resulting polyurethanes[79-83]

### 1.3. A.3. *Polyurethanes with heterocyclic groups*

The poor thermal properties of polyurethanes, like low decomposition temperature and loss of mechanical properties at high temperatures is the main reason for limited applications in high temperature environments. The improvement in thermal properties by incorporation of thermally stable hetrocyclic groups like imide, isocynaurate and oxazolidone has been reported[84-94].

Novel heat resistant isocyanate-based polymers, having crosslinked polyurethane-isocyanurate, polyurethane-oxazolidone - isocyanurate copolymers have been reported by Frisch et al.[95] Oxazolidones containing thermally stable epoxy resin laminates were reported by Yomaoka at al.[96] The epoxy laminates prepared from an isocyanate-terminated prepolymer and epoxy compound were highly thermally stable. The use of bis imide compounds gave laminates with much higher thermal stability. The modification of polybutadiene based polyurethanes formed by reaction of Hycar HTBN and TDI with oxazolidone by epoxy reaction has been reported by Sankaran et al[97,97a] A polyurethane elastic copolymer with amide or imide bond in the main chain by reacting a prepolymer with pyromellitic acid is reported[98] The modifcation of polybutadiene with polyepoxide and polyisocyanate in the preparation of heat resistant composition is reported by Toyoda et al.[99] Synthesis of polyurethane imides by one-step reaction of isocyanates with acid anhydrides has also been reported. [100-102] The modification of polyurethane chain with thermally stable groups like triazene with the use of triazene isocyanates has been reported Sarwade et al.[103,104]

- Another thermally stable group used successfully to modify isocyanate polymers is carbodiimide. Siloxane units in the polyurethane chains has led to remarkable increase in thermal and oxidative stability.[105]

In short, there is no generally applicable way to increase the thermal stability of polyurethanes. The possibilities to produce new types of polyurethanes are truly unlimited. The property requirements of the polymer as they are demanded by their end-use has to be taken into account as the modifications conducted on the chain to increase thermal stability invariably affects other properties.

### 1.3.B Polyurethanes for low temperature applications

Polymers which retain their properties at low temperatures are becoming important as a result of requirements in various fields like space and defence engineering.[106] Polymers such as natural and synthetic rubber[107], ethylene-propylene copolymers[108], fluorinated ethylene propylene copolymers,[108] polybutadienes[109,110], substituted polybutadienes[111], polyesters[112] etc have been found to be possessing good low temperature properties. Polyurethanes are an important class of low temperature performance polymers[113-119]. They have been found to be most useful in low temperature applications in the field of foams, coatings, elastomers and adhesives. Properties like low tensile strength[120], high shear strength, moderate thermal conductivity and specific gravity[121] and appreciable elasticity even at liquid hydrogen temperatures[122] make polyurethane better than other types of polymers for low temperature applications.

The low temperature properties of polyurethane elastomers prepared from polyols like polyesters, polyethylene glycols, polyoxytetramethylene glycols etc:

have been studied and reported in literature[123]. It was found that best low temperature properties are obtained with prepolymers based on polyoxytetramethylene glycol. Polyoxypropylene glycol was better than polyoxyethylene and these polyethers were superior to polyesters. The properties such as mix fluidity and better low temperature flexibility allow the polyethers more useful than polyesters in urethane elastomers. Polyurethanes with polybutadiene backbone are also having excellent mechanical properties at low temperatures.

Polyurethanes are the most promising adhesives among the commercially available adhesives for low temperature applications.[124] The polyurethane adhesives are found to be compatible with both liquid oxygen and hydrogen. The superior properties of polyurethane adhesives over epoxy adhesives have been reported.[125,128]

### 1.3.B.1. *Introduction of flexible chains*

The inherent chain flexibility of polyurethanes which is responsible for the low temperature performance of these polymers are mainly due to the rotational freedom present in the polyester or polyether portions of the polymer. The rotational freedom is restricted at low temperatures. It is observed that the polyoxytetramethylene based polymers showed an increase in the peel strength in the temperature range of -270° F to -400° F. This is attributed to the residual segmental rotational freedom due to the entire rotation of the tetramethylene unit below $T_g$125. Thus it is clear that polyurethanes having segmental chain motions which are not restricted below the glass transition temperature display excellent low temperature properties. Thus the introduction of polyoxytetramethylene blocks which has very low $T_g$ improves the low temperature properties of polyurethanes.

### 1.3.-B.2. *Effect of pendant chains*

Another method of improving the low temperature properties of polyurethanes is by way of introducing side chain or pendant groups [129] This causes free volume in the bulk and does not allow the polymer chains to closely pack as the temperature is reduced thereby allowing segmental motion of units at cryogenic temperatures.

## 1.4 CURRENT TRENDS IN POLYURETHANES

The current trends in the field of polyurethanes as understood from literature is focussed on the improvement in mechanical properties and thermal properties by suitable chemical modifications of the backbone structure. The modifications include copolymerisation with compounds having reactive group towards isocyanate, resulting in the formation of highly polar and thermally stable hetrocyclic groups as mentioned earlier. The modification generally improves mechanical strength and thermal stability of the system.

The rapid evolution in modern technology in nearly all areas warrants development of speciality materials that are to pass stringent functional requirements. This poses a technological challenge to material scientists and polymer technologists. Organic polymers are perhaps an important class of materials that have immensely contributed towards the speeding up of technology revolution in material development. They have played crucial role either as active or passive component in shaping the technology related to electronics, telecommunication, automobile and aerospace to their present state. Among organic polymers, polyurethanes constitute an important class of compounds that have found a unique place in material science related to all the above mentioned fields. Other major applications of polyurethanes are in the domain of elastomer, foam, coatings, adhesives etc. The high cohesive force coupled with chain flexibility and consequent mechanical and physical characteristics, adhesive and film-forming properties and possibility of controlling the properties by way of structural and molecular changes makes them an attractive material for polymer technologists. The ease with which the variations in properties could be achieved by way of varying the chemical structure and crosslink density thereby making them suitable for specific end-uses merits special reference. A good amount of research work already published has helped in understanding structure-property correlations. Although polyurethanes have been able to cater to many of the technological requirements in the above said areas, their inherent drawback have prevented them from entering many key industrial areas for critical applications. The inferior thermal and thermoxidative stability, lack of UV and plasma resistance and embrittlement at very low temperatures have been major obstacles towards the versatility of such an easy-to-process system. The rapid growth of modern technology especially in aerospace needing materials of stringent requirements, poses a technological challenge for polyurethane chemist too. The flexibility in the selection of reactants leads to a wide range of physical properties that allows polyurethanes to play an important role in the world market for quality products. There was a rapid improvement in the field of foams, both flexible and rigid, elastomers, coatings, adhesives based on polyurethanes. The recent growth in commercial importance of PU products formed by RIM has provided basic studies of relationship between molecular structure and bulk properties. The improvement in mechanical properties of polyurethanes can be achieved by liquid crystalline moieties in the chain as reported[130-134]. Polyurethane coatings with high impact strength have also been reported by suitable modification.[135] The improvement of the flame retardant characteristics of polyurethane foams is yet another important area. The incorporation of flame retardant elements and thermally stable groups in the chain are known to improve the flame retardant properties[136].

The choice of phosphazene for modification is a consequence of its molecular features. It is fully inorganic and is known for its interesting flame and thermal resistance characteristics[137]. Phosphazene chemistry is well documented. The amenability to design a large number of functionally substituted products makes it an attractive molecule for synthetic chemistry. A large amount of cyclomatrix and linear polyorganophosphazenes have been proposed for use as structural adhesives for high temperature or aerospace applications with serviceability extended to both low and high temperatures[138,139]. Polyphosphazene containing polyesters, polyimides, epoxies and elastomers are also known[140,141]. All of them exclusively claim inherent flame retardancy and enhanced thermal stabilty.Polyurethanes containing polyphosphazenes have also been reported.[142,143]

Triazene -based polymers are relatively new entrants in thermally stable polymers. Among the various hetrocyclic groups capable of imparting thermal stability to polymers, triazene has a prime place. Cyanate esters and phenolic-triazene resins that constitute the new class of thermosetting resins, whose chemistry is based on the cyclotrimerisation of cyanates to the aromatic triazenes by an addition mechanism bear testimony to this. Cyanate ester possesses the processability of epoxies and high temperature performance comparable to polyimide and additional advantage of built in toughness.[144-146] They are poised to replace the epoxies in its application particularly in structural composites.

Phenolic-triazenes (P-T), on the otherhand, possess novolac backbone and have superior thermal and thermo-oxidative characteristics to the conventional phenolics[147,148] . This system is being explored as replacement for phenolics particularly in thermo-structural applications. Both systems (cyanate & P-T resins) owe their excellent physical and thermo-mechanical characteristics to the presence of triazene group, which are polar, symmetric and thermally stable.

Triazene ring has been incorporated in other thermally stable polymers like polyimide, polyamide-imide and polyazomethines for improving their thermal resistance further.[149-153] Triazene has been incorporated into other polymers for improving flame retardant properties.[154]

## 1.5 SCOPE OF THE PRESENT WORK

A scan of literature shows that, in recent years a lot of attention is paid to polyurethane chemistry and technology. Most of them concern research to extend the service temperature of polyurethanes to both high and low temperature sides, in an attempt to meet the present day technological challenges. Several approaches have been reported, many with partial success in achieving the goals of extreme temperature servicability of polyurethanes as presented already. Most of the reports are patented and hence the information available is limited. In other words, polyurethanes for extreme service conditions still remain a potential unattained goal and area of research.

It is generally accepted that the high temperature servicability of any polymer system can be imporved by way of introducing heterocyclic groups in the polymer chain. This concept has been adopted in the case of polyurethanes also. A few recent studies concerns the synthesis of polyurethanes with selected heterocyclic groups like imide and oxazolidone. These groups have been shown to improve the thermal characteristics of the derived PU systems. But the reported methods are laborious affecting the processability of the system as a whole. A few studies have been reported on phosphazene and triazene based PU but they donot furnish details of the impact of these groups on the physico-chemical and thermomechanical profile of the modified PU.

In this work, an attempt has been done to introduce these groups either alone or in combination in PU network by adoption of novel synthesis strategies. The techniques described here permits to retain the processability of the system and make it easily amenable to structural modifications. These groups like imide and a combination of imide-oxazolidone have been incorporated in PU chain through a novel chemical modification method. An alternate method of introducing heterocyclic groups in PU network is through the use of crosslinking agents (CLA) bearing them. The reports on the synthesis strategy is very scanty in literature. Hence network modification through design and use of heterocyclic group borne CLA's has been probed in this work. Phosphazene and triazenes were the groups of choice in view of their reputation for thermal and flame resistant properties. In this context, it was also of interest to examine new CLA bearing combination of heterocyclic groups that cures partly by nonconventional mechanism. In such studies, it becomes imperative to examine the relative efficiency of the various synthesis strategies and nature of the heterocyclic groups in amending the thermal as well as physico-mechanical characteristics of the PU network derived from various polyol backbones. Such comparison also helps in establishing the structure-property correlations.

Polyurethanes are generally characterised by relatively low Tg due to the flexible chain polyols generally chosen for their synthesis. PU for application in extremely low temperature environments can be accomplished by the selection of speciality polyols having good flexibility. However it would be desirable to impart low temperature flexibility to PU systems by way of structural modifications and to investigate the effect of such modification on the properties of the modified system. Tg can be lowered by increasing free volume of polymer chain. The well known methods for this is incorporation of soft polymer segments as either graft or block in the main chain. In this work, these two methods have been resorted to. Grafting has been effected by "grafting from" technique based on macromonomer. Thus, soft polybutyl acrylate grafts of different concentration and chain length was introduced in the PU network through macromonomers based on the former. The consequent changes in the physico-chemical, morphological, mechanical and thermal properties were monitored. In the 'block' copolymer method, inorder to effectively sense the impact of the block on the Tg, a relatively high Tg-polyurethane based on 12-hydroxy stearic acid derived polyester was the choice as the base polymer system. Polytetramethylene oxide blocks of varying concentration and chain length were introduced into the PU network by two techniques and relative merits of the techniques evaluated. The variation in properties by way of block copolymerisation has been evaluated and comparative advantages of two methods assessed.

The work involving synthesis, formulation, physicochemical and thermo-mechanical characterisation is expected to contribute to understanding structure-property correlation of the PU system and thereby accelerate the current trend of research in polyurethanes which is directed towards acheiving the goal of conferring extreme temperature servicability to this wonder polymer.

This thesis describes the attempts to extend the service temperature of polyurethanes by way of structural modifications, Essentially it focusses attention on enhancing the thermal stability of polyurethanes through introduction of thermally stable groups in backbone and improvements in low temperature properties by way of introducing soft, flexible grafted chains and flexible segments in the main chain.

Chapter I presents the generalities of polyurethane chemistry and current trends in the field of polyurethanes.

Chapter II presents the different analytical methods employed at different stages of the research work for characterisation and the instrumental methods employed along with their working principles.

Chapter III is devoted to the research on improving the high temperature properties of polyurethanes by way of structural modifications through introduction of thermally stable groups like imide and imide-oxazolidone combination. Chain extenders and crosslinkers were synthesised. The impact of these groups on the physicochemical and mechanical characteristics of polyurethanes have been examined.

Chapter IV focuses on structural modifications through crosslinking agent bearing thermally stable groups. Essentially, groups such as phosphazene and triazene have been explored. A detailed investigation on the effect of such crosslinking agents on the mechanical properties and thermal properties of the resultant polyurethane have been presented. The triazene moiety was introduced into the main chain by designing triols based on them. A new type of maleimide - triazene crosslinking agent was synthesised, characterised and incorporated into the polyurethane backbone by chain extension of polyether and polybutadiene polyols. The effect on thermal and mechanical properties are studied and data presented.

Chapter V presents the results of the studies conducted on the improvement of the low temperature properties of polyurethanes by way of grafting pendants or making blocks of flexible chains. The influence of the graft and block on the mechanical properties and low temperature properties have been examined. Finally the thesis ends in Chapter VI which presents conclusions drawn from the results of the various modifications done. It evaluates the extent to which these modifications have been fruitful in achieving the objectives.

Most of the results described in this thesis are published in standard journals and presented in national seminars. The potential applications of these systems have also been projected.

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# Chapter II

# CHAPTER II

# CHARACTERISATION METHODS

## 2.1. ANALYTICAL METHODS

### 2.1.A. Isocyanates and NCO terminated prepolymers

The raw materials for polyurethanes like polyols, isocyanates and crosslinking agents are to be analysed for purity. The isocyanates are analysed by isocyanate content usually expressed in percentage which is estimated based on the quantitative reaction of NCO with di-n-butyl amine[1]. The principle of the method is that if an excess of di n-butyl amine is added to the diisocyanate or isocyanate terminated prepolymer, the free NCO groups react readily with the dibutyl amine and the excess amine subsequently determined by an acidimetric titration using standard acid. The number average molecular weight can be calculated from NCO percentage provided the functionality is known. The values must be corrected for the acidic or basic impurities.[2]

### 2.1.B. Polyols and crosslinking agents

The main parameters for characterisation of polyols for polyurethane preparation determined by chemical methods are acid number and hydroxyl number[3].

#### 2.1.B.1. *Acid number*

The method is suitable for the determination of acidic constituents in polyethers, polyesters and polybutadiene polyols and other trihydroxy crosslinkers used in the study soluble in mixtures of benzene, isopropanol and methanol. It is useful as an indication of the extent of reaction of NCO with acids, and the value is taken into account in calculating the true hydroxyl number.

The acid number is determined by titrating a solution of known weight of the compound in benzene-isopropanol mixture against std alkali using phenolphthalein as indicator.

### 2.1.B.2 *Hydroxyl number*

Polyols and hydroxy containing crosslinking agents are characterised by hydroxyl number for fixing the amount of isocyanate for curing of the specimens. The method is applicable to polyether glycols, polyester glycols and polybutadiene glycols.[4] The hydroxyl number of a polyol is defined as the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of one gram of the sample. The hydroxyl group is esterified with a solution of acetic anhydride in pyridine benzene solution at $70^{0}$C as shown in the equation.

$$HO\text{-}R\text{-}OH + (CH_3CO)_2O \text{ --------> } CH_3COO\text{-}R\text{-}OOCCH_3 + CH_3\text{-}COOH$$

The excess acetic anhydride is hydrolysed with water and the acetic acid liberated is titrated with standard potassium hydroxide. A blank is run with the same acetic anhydride- pyridine mixture to determine the amount of anhydride consumed. Excessive amount of water in the sample will interfere in the determination of hydroxyl value by destruction of the acetylating reagent and contributes to a high unreal hydroxyl number. The acid value is to be added to OH value to get the real hydroxyl value.

### 2.1.B.3. *Amine value*

The determination of amine value in polyurethanes and crosslinkers is also carried out by titration against std. acid and expressed in mgm KOH/gm[5]

### 2.1.B.4 *Epoxy Content*

The epoxy content is analysed by a modified ASTM method[6]. The epoxy group is reacted with HCl. The HCl consumed is a measure of the epoxy group concentration.

### 2.1.B.4. *Moisture content in polyols*

Varying amounts of water may be present in polyols which may adversely affect other analytical techniques as well as influence the properties of the polyurethane prepared from the polyols since these systems are sensitive to small amounts of water. In addition, an accurate knowledge of water content of materials of this type will help the accuracy of the formulation since the NCO/OH ratio will be uncertain as NCO groups will be consumed by $H_2O$ molecules. The moisture content is determined by Karl- Fischer (K-F) titration.[7] The K-F reagent reacts quantitatively with water. The excess reagent is added to weighed sample of the polyol or other reagent. The excess reagent is then back-titrated with water-methanol solution.

### 2.1.C. Viscosity

Inherent viscosity of a linear polymer is determined using DMF or DMAc at a concentration of 0.5 dl/g. The viscosity of the solution extrapolated to zero concentration gives the inherent viscosity. Inherent viscocity gives an indication of the chain length. Bulk viscosity of a liquid polymer is determined by Brookfield viscometer.

### 2.1.D. Sol-gel content

Sol and gel content of a cured polymer was determined by swelling the samples in toluene solvent, refluxing and weighing the soluble portion.

## 2.2 INSTRUMENTAL METHODS

### 2.2.A. Spectral analysis

The simplest spectral analysis method is IR spectrum which detects the different functional groups present in a polymer chain based on characteristic group frequencies. The instrument used was Perkin-Elmer model No.283 FT.IR used was Nicolet 510P.

### 2.2.B. Molecular weight and Molecular weight distribution

Molecular weight determination is a very important tool for the characterisation of polymers especially for finding out the chain build-up and for the determination of the average functionality of the polyol and other hydroxyl containing crosslinking agents provided the hydroxyl value is known. The number average molecular weight is measured by the vapour pressure osmometery method using Knauer vapour pressure osmometer[8]. The principle is the Raoult's law ie., the lowering of the vapour pressure of a solvent by a solute is proportional to the mole fraction of the solute.

The average functionality of the hydroxyl component is calculated from the number average molecular weight from VPO. A ratio of number average molecular weight to the equivalent weight gives the average functionality.

Weight average and number average molecular weight and molecular weight distribution of a polymer can also be obtained from gel permeation chromatography (GPC). Waters Associates GPC model Delta prep 3000 $\mu$ styragel colomn was used for analysis.

Other physical property important for characterisation of polymer is the viscosity for liquid polymer and inherent viscosity for solid polymers. The viscosity values are an indirect indication of the molecular weight of the polymer. Bulk viscosity is determined by the Brookfeild viscometer.

### 2.2.C. Thermal properties

Thermal properties like thermal decomposition temperatures, thermomechanical properties, thermal transition temperatures like Tg etc. are also evaluated by instrumental methods given below:

### 2.2.D. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is a dynamic technique in which the weight loss of a sample is measured continuosly while its temperature is increased at a constant rate. Alternatively, weight loss can be measured as a function of time at a constant temperature. The main use of TGA to polymers has been in studies of thermal decomposition and stability. Increasing the heating rate in TGA increases the apparent decomposition temperature. TGA measures the percentage of weight loss against increase in temperature at a fixed heating rate. The initial decomposition temperature as shown by the thermogram is the temperature at which the decomposition of a polymer starts which is indicative of the thermal stability of a polymer. The polymer starts to loose weight as temperature is increased further and the temperature at which maximum decomposition of the polymer occurs as shown by maximum weight loss is the peak decomposition temperature. The temperature above which the compound does not lose weight further is the end temperature. Depending on the structure of the compound under investigation, the residue remaining at the end temperature can vary. The thermogravimetric analysis is a powerful and simple tool for the measurement of thermal stability of a compound. The equipment used for thermogram was Du Pont thermogravimetric analyser model TGA-951 and Mettler TA - 3000 system.

### 2.2.E. Differential Thermal Analysis (DTA)

DTA is a technique for detecting thermal changes which occur on heating or cooling materials. In contrast to TGA, the temperature of a sample and reference are measured and changes in temperature usually accompanying physical changes such as phase transition or alteration in heat capacity or chemical changes such as degradation or loss of adsorbed or entrapped material are detected. Among the changes detected are crystallisation temperature and crystalline melting, the glass transition, thermal degradation etc.

### 2.2.F. Differential scanning calorimetry (DSC)

In DSC, sample and reference are heated seperately by individually controlled elements. The power to these heaters is adjusted continuosly in response to any thermal effects in the sample so as to maintain sample and reference at indentical temperatures. The differential power required to achieve this condition is recorded as the ordinate on the X-Y recorder with the programmed temperature of the system as the absissa.Thermally induced reactions like crosslinking, decomposition, phase changes etc can be found out by the differential scanning calorimetry (DSC). Any endothermic or exothermic transitions such as melting, polymerisation etc are shown as an upward or downward shift from baseline temperature with increase in temperature. The equipment used was Mettler TA 3000, DSC 20 standard cell with TC 10 A processor.

### 2.2.G. Dynamic Mechanical Analysis (DMA)

The changes in mechanical properties of a polymer like modulus as temperature is varied can be found out by the Dynamic Mechanical Analyser (DMA). This also helps to measure thermal stability of a polymer induced by the modification on the polymer backbone and also phase changes with temperature such as glass transition and melting.

### 2.2.H. Thermo Mechanical Analyser (TMA)

Thermo mechanical analysis (TMA) is a technique in which the deformation of a substance is measured under nonoscillatory load as a function of temperature as the substance is subjected to a controlled temperature program. The parameter measured is deformation in volume or length using a dialatometer. The sample is placed on the platform of a quartz sample tube. The appropriate quartz probe is connected to the armature of a linear variable differential transformer (LVDT) and any chagne in the position of the armature results in output voltage from the transformer which is then recorded.

The changes in specific volume of a polymer with temperature is analysed with TMA. This is mainly helpful for the measurement of the temperature transitions like glass transition temperature (Tg) of a polymer. The equipment used in the study was Du Pont model TMA 942.

## 2.3. MECHANICAL PROPERTIES

The analysis of mechanical properties of polyurethanes consequent to structural modification is of importance.

The mechanical properties of polyurethanes are affected by the modifications intended to improve thermal stability as well as low temperature properties. Properties like tensile strength, elongation, modulus, and hardness are dependent on cross link density, type and extent of polar groups present in the backbone etc. The mechanical properties of the polyurethane samples prepared were tested for mechanical properties in Instron Universal Testing Machine UTM 4202. The analysis of the samples were carried out as per ASTM-D 412.

The hardness of the cured polyurethane samples were done using shore A durometer.

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# Chapter III

# CHAPTER III

# IMIDE- AND IMIDE-OXAZOLIDONE-MODIFIED POLYURETHANES

## INTRODUCTION

The polyurethanes exhibit poor resistance to heat as already mentioned in chapter I. At around $100^{0}$C the properties like tensile strength, modulus etc: start to diminish and at temperatures above $200^{0}$C, thermal degradation sets in, depending again on the nature of back-bone. The general approach for improvement of thermal stability of polyurethanes has been by way of chain modification with hetrocyclic groups. The hetrocyclic groups like cyclic imides, oxazolidone, triazene, phosphazene etc generally constitutes the groups of choice for polyurethane modifications. Of these, imide and oxazolidone have evinced some interest in recent years.

In the first section, the possibility of introducing the imide function through a novel synthesis strategy is explored. The effect of the group on the physical, mechanical and thermomechanical properties were examined. In the second part, both imide and oxazolidones groups were incorporated simultaneously in the backbone for a typical polyurethane based on hydroxyl terminated polybutadiene and the effect of such a modification on the properties of the polyurethanes were examined. Polyurethane modified with both imide and oxazolidone together has not been reported before.

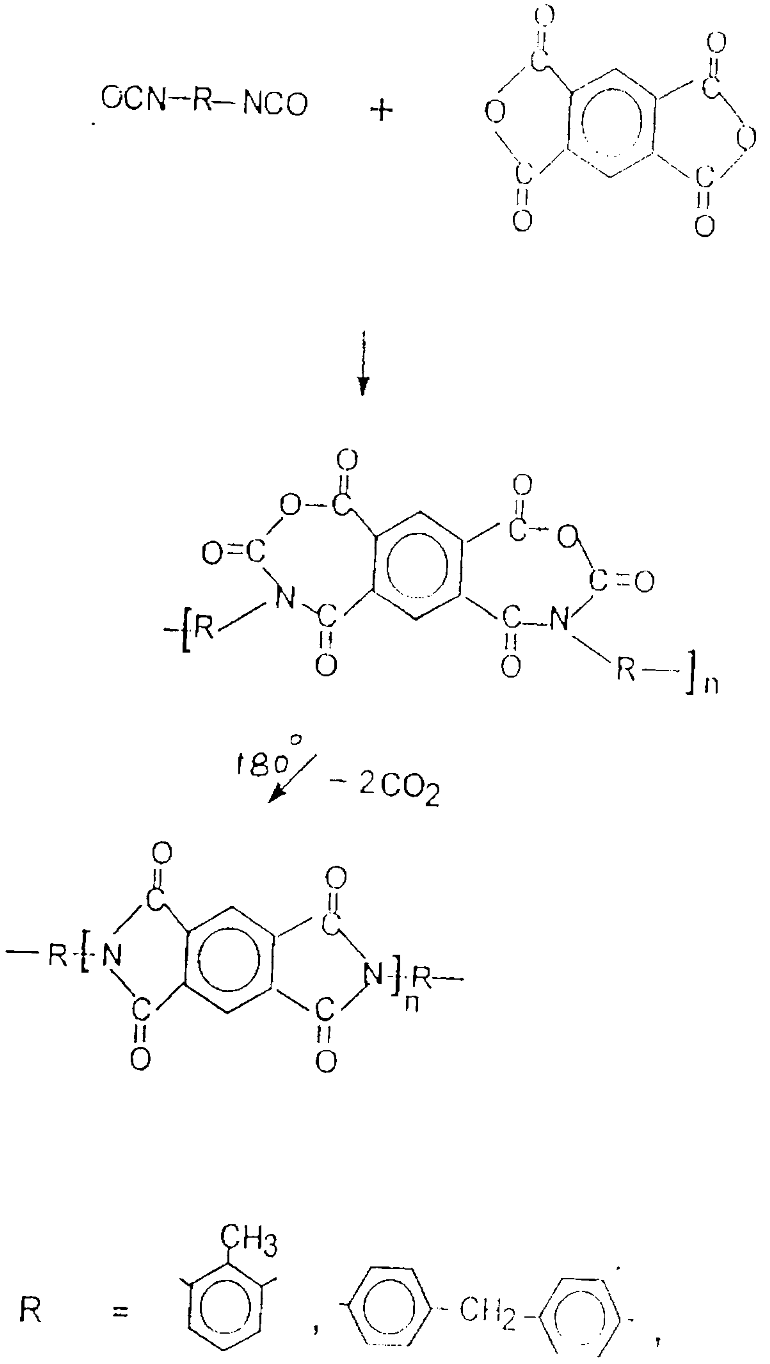
## 3.1 IMIDE-MODIFIED POLYURETHANES

### 3.1.A. Introduction

The synthesis of polyurethane imides by one-shot technique through isocyanate-acid anhydride reaction and the corresponding improvement in mechanical properties and thermal properties have been claimed by several authors,[1-4]. The imide group combined with rigid aromatic rings contributes to increased thermal stability of imide modified urethanes[5].

The synthesis of polyurethane-imide by one shot technique involves the reaction of a polyisocyanate with a polycarboxylic acid in the presence of polyether or polyester. The two-step method reported involves the reaction of a polyimide prepolymer obtained from a dicarboxylic acid anhydride and a polyisocyanate with a diol. The mechanical, thermal and electrical properties of these polyurethane imides have been reported by several authors[6-8].

The one-step method for the preparation of imide polyurethanes gives mainly cellular polyurethane imide due to the evolution of carbon dioxide during the reaction of isocyanate with anhydride as shown in the reaction scheme 3.1. The temperatures required for conversion of the cyclic intermediate to the imide group is high, of the order of 160 to 180°C. The method of direct imidisation as reported[6] has the drawback of the possibility of secondary reactions of isocyanate-urethane reaction, isocyanate trimerisation and the acid impurity present in the anhydride reacting with the isocyanate giving rise to amides. Hence the properties of the resultant polymer are likely to be adversely affected. In the present investigation, the synthesis of polyurethane imides by an alternate method via the amic acid route



**Scheme 3.1:** Synthesis of polyurethane imide by one step reaction (reported)

is conducted. The amic acid of polyurethane is prepared starting from the amine terminated polyurethane synthesized in turn by endcaping of isocyanate terminated prepolymer with diamines as outlined in the reaction scheme 3.2. The reaction of isocyanate with amine gives urea group and hence the amic acid and the resultant imide is actually a polyurethane-urea-imide. The imidisation of the amic acid intermediate can be carried out by thermal and chemical method (using acetic anhydride) as shown in scheme 3.3.

The structure of the polyurethane-urea-imide can be varied by varying the diamine used for endcapping and similarly the isocyanate used for the prepolymer preparation. The properties can be varied over a wide range by variation in diol, anhydride, diamine and isocyanate in various combination and proportion. The present investigation concerns synthesis and characterisation of the polyurethane imide (PUI) using various combination of diamine and plyol and a detailed investigation on the physical, mechanical and thermal and thermo-mechanical properties of the resultant polyurethane.

### 3.1.B. Materials

1. Polyethylene glycol (PEG molecular weights 400, 600 and 1000 of BDH)
2. Polybutadiene diol (HTPB, molecular weight 2800 of M/s NOCIL, Bombay)
3. Isophorone diisocyanate (IPDI) (Rhenus Wtag, Germany)
4. Aromatic diamines like diamino diphenyl methane (MDA), diamino diphenyl sulphone(DDS) and diamino diphenyl ether (DDE) (Aldrich, USA)
5. Pyromellitic dianhydride (PMDA of M/s FLUKA)
6. Dimethyl acetamide (DMAc) (Sisco, Bombay)

## 3.1.C. Experimental

### 3.1.C.1. *Purification of raw materials*

The materials used in the study were purified prior to use. The polyols polyethylene glycol and hydroxy terminated polybutadiene diols were dried throughly before use to avoid isocyanate-moisture reaction. Polyethylene glycol of different molecular weights were taken to vary the extent of imide groups in the chain. The drying of polyethylene glycol is carried out by azeotropic distillation using benzene as the entraining agent as polyethylene glycol is invariably contaminated with moisture. The procedure adopted was as follows:

About 250 ml of polyethylene glycol was mixed with 500 ml of analar benzene taken in a RB flask fitted with a dean and stark coloumn. The mixture was refluxed for about 2 hrs with continuous removal of benzene-water azeotrope. Excess of benzene was removed by distillation and the final traces was removed under vacuum to constant weight.

The isophorone diisocyanate is usually contaminated with polymer impurity and hence it was distilled prior to use. The purity was checked by analysis of the isocyanate content by di-n butyl amine method. The isocyanate part used in the set of studies was fixed as isophorone diisocyanate. The use of toluene diisocyanate was found to give partial chain extension and crosslinking due to the high reactivity of the aromatic isocyanate groups. Isophorone diisocyanate, due to the presence of one primary and other secondary isocyanate groups doesnot cause any chain extension during the amine-modification step.

Pyromellitic dianhydride was purified prior to use to get maximum anhydride content to avoid any side reactions due to the presence of acid impurity. Commercial PMDA contains pyromellitic acid as the impurity due to hydrolysis. The purification of PMDA was effected by refluxing with acetic anhydride for about 2 hours. The mixture was washed several times with dry toluene to remove acetic anhydride and finally washed with dry hexane. It was then dried under vacuum at $60^0$C and stored under controlled humidity conditions. The purity of PMDA was checked by melting point. The melting point obtained was $285^0$ C and the reported value is $285\text{-}287^0$ C. Dimethyl acetamide was purified by distillation under vacuum.

### 3.1.C.2. *Synthesis of isocyanate terminated prepolymer*

The first step in the synthesis of the polyurethane-imide is the preparation of isocyanate terminated prepolymer from the polyols under study and the isophorone diisocyanate. The preparation of isocyanate terminated prepolymer of polyethylene glycol of mol:wt. 600 and IPDI as a typical example is as follows:

10 gms of IPDI was weighted out into a three necked round bottomed flask fitted with a nitrogen gas inlet cum thermometer pocket. A stirrer is attached through a mercury seal and connected to a laboratory motor. 15 gms of polyethylene glycol corresponding to an isocyanate-polyol molar ratio of 2:1 was taken in a constant addition flask. Two drops of benzoyl chloride were added as a retardant for crosslinking reaction during polyurethane formation. The benzoyl chloride neutralises any amine impurity present in the glycol which can catalyse the secondary reactions of the isocyanate leading to crosslinked high viscous products. The reaction flask was kept cooled at about $20^0$C throughout the addition time.

The addition of the glycol to the isocyanate was carried out at a slow rate with nitrogen gas purging and completed within a period of 1 hour keeping the reaction mixture thoroughly stirred. After complete addition of the glycol, the reaction mixture was maintained at 45°C for 2 hours for completion of reaction. The product was kept in controlled humidity conditions.

The same process was repeated for the preparation of isocyanate-terminated prepolymers of polyethylene glycol of molecular weight 1000 and hydroxyl terminated polybutadiene with the quantities of reagents taken in such a way that the molar ratio of isocyanate to polyol is kept as 2:1 in all cases. The isocyanate-terminated prepolymer of polyethylene glycol 600 is a high viscous liquid and that of polyethylene glycol of mol: weight 1000 is of slightly lower viscosity.

### 3.1.C.3. *Isocyanate prepolymer of HTPB*

HTPB, synthesised by free radical polymerisation of butadiene using hydrogen peroxide as initiator available from NOCIL, Bombay has an average functionality of about 2.3. There is distribution of di-, tri-, tetra- and other higher oligomers[9] and hence the prepolymer synthesised using isophorone diisocyanate was having a high viscosity and containing gelled fractions. Therefore the average functionality of HTPB was brought down to about 1.8 by partially blocking the OH group by acetylation. The acetylation reaction was carried out as follows. About 50 gms of HTPB was taken in a round bottomed flask and mixed with 3 ml of pure acetic anhydride. Dry methyl ethyl ketone was used as solvent and heated with stirring for about 2 hours at 60°C. The contents of the reaction flask were poured into 500 ml of methyl alcohol with stirring. The precipitated HTPB was seperated and washed with 500 ml portions of methanol and finally dried at 60 °C in vacuum for 2 hours. The properties of low functional HTPB thus obtained is compared with the high functional one in table 3.1.

**Table . 3.1 : Physical properties of hydroxy terminated PBD polyol**

| Sl. No. | Property | HTPB (NOCIL) | HTPB (low functional) |
|---|---|---|---|
| 1 | Acid value | 0.5 mgm KOH/gm | 0.3 mgm KOH/gm |
| 2 | Hydroxyl value | 45 " | 40 " |
| 3 | Viscosity at 30°C | 6000 cps | 5700 cps |
| 4 | Mol:wt:(VPO) | 2800 | 2720 |
| 5 | OH functionality (av) | 2.3 | 1.8 |

The preparation of isocyanate terminated prepolymer using HTPB was carried out in the same way as detailed for the polyethylene glycol system.

### 3.1.C.4. *Analysis and characterisation*

The isocyanate-terminated prepolymers were characterised by the isocyanate content determined by the n-butyl amine method as mentioned earlier. Spectral characterisation was carried out by I.R technique. A strong absorption peak at 2250 $cm^{-1}$ corresponds to the NCO group and the disappearence of the peak at 3600 $cm^{-1}$ due to OH group and the apperance of a new peak at 1560 $cm^{-1}$ due to the carbonyl of the urethane group shows that the hydroxyl groups in the polyol has been completely converted to the urethane group by reaction with the diisocyanate. A typical I.R spectrum of the isocyanate terminated prepolymer is given in figure 3.1.

Molecular weights of the prepolymers were determined by vapour pressure osmometry method. From the number average molecular weight obtained from the vapour pressure osmometry method and the isocyanate content, the average functionality of the polyurethane was calculated. The viscosity of the liquid polymers were determined by the Brookfield viscometer. The sol content and the gel contents in the prepolymer were determined using toluene as the solvent.

The physical properties of the isocyanate-terminated polyurethane prepared from polyethylene glycol are presented in table 3.2

**Table 3.2: Physical properties of polyethylene glycol- IPDI based polyurethane prepolymers**

| No. | PEG mol.wt | NCO % | Viscosity (cps) at 30$^0$C | Mol.wt of PU | Fn (av:) | Sol% |
|---|---|---|---|---|---|---|
| 1 | 300 | 11 | Solid | 750 | 1.96 | 98.5 |
| 2 | 400 | 9.6 | Solid | 825 | 1.9 | 99.2 |
| 3 | 600 | 7.8 | 12570 | 1120 | 2.08 | 98.9 |
| 4 | 1000 | 5.5 | 11260 | 1460 | 1.91 | 99.5 |

It can be observed from the table that as the molecular weight of the polyol is increased, there is a corresponding decrease in the viscosity due to the reduction in urethane group concentration in the prepolymer.

The determination of sol content shows that there is no crosslinking for the prepolymer. The use of isophorone diisocyanate in the prepolymer preparation was found to be advantageous over other diisocyanates in that it causes minimum side reactions due to the presence of one secondary isocyanate which is less reactive compared to the primary.

### 3.1.C.5. *Comparison of IPDI and TDI based prepolymers*

The diisocyanate used for the studies is IPDI, as TDI based prepolymers are found to be partially crosslinked due to the high reactivity of TDI. The isocyanate-terminated polyurethanes of polyethylene glycol and HTPB were synthesised using tolylene diisocyanate as the endcapping agent and the properties are also presented in table 3.3 for comparison.

**Table 3.3 - Comparison of properties of IPDI and TDI based prepolymers**

| Sl. No. | Polymer | NCO% | Viscosity (cps at $30^0$C) | Mol:wt (VPO) | Fn (av:) | Sol % |
|---|---|---|---|---|---|---|
| 1 | PEG-600-IPDI | 7.8 | 12570 | 1120 | 2.08 | 98.5 |
| 2 | PEG-600/TDI | 4.9 | 18500 | 1525 | 1.77 | 91.5 |
| 3 | PEG-1000/IPDI | 5.5 | 11260 | 1470 | 1.92 | 98.5 |
| 4 | PEG-1000/TDI | 4.5 | 15650 | 1655 | 1.75 | 93.5 |
| 5 | HTPB/IPDI | 2.6 | 15250 | 3850 | 1.92 | 97.5 |
| 6 | HTPB/TDI | 1.75 | 18755 | 4135 | 1.72 | 91.5 |

It may be observed from the table that the TDI based prepolymers are having comparatively higher viscosity, higher molecular weight, lower isocyanate content than the theoretical and a lower sol-content over the isophorone based prepolymers which is due to partial chain extension or crosslinking taking place due to the higher reactivity of primary isocyanate of tolylene diisocyanate.

The polyurethane prepolymer of HTPB was characterised by IR spectrum which showed the following peaks

2250 cm$^{-1}$ -- NCO group
1650 cm$^{-1}$ -- C = C unsaturation due to butadiene
1740 cm$^{-1}$ -- C = 0 in urethane group
3350 cm$^{-1}$ -- NH in urethane group

It was also characterised by the absence of the peak at 3600 cm$^{-1}$ due to OH group.

### 3.1.C.6. *Synthesis of polyurethane diamine*

Polyurethane diamines were prepared starting from the isocyanate-terminated prepolymers of polyethylene glycol and HTPB with isophorone diisocyanate/tolylene diisocyanate by end-capping with a low molecular weight diamine like diamino diphenyl methane and diamino diphenyl sulphone. The experiment was carried out as follows.

About 10 gms of the diamine was accurately weighed out into a round bottomed flask fitted with a nitrogen gas inlet and a thermowell. The diamine was dissolved in about 25 ml of dimethyl acetamide and the reaction medium was kept cooled in a bath of about 10$^{0}$C. Calculated quantity of the isocyanate terminated prepolymer for a molar ratio of the diamine to the isocyanate terminated prepolymer of 2:1 was taken as a solution in dimethyl acetamide in a constant addition flask. The prepolymer solution was added dropwise into the diamine solution with good agitation of the reaction medium keeping the reaction temperature in the range of 10-15$^{0}$C with a continuous flow of dry nitrogen. The addition of the prepolymer solution was completed in a period of 2 hours. After the reaction time, the reaction temperature was slowly increased to about 40°C and the contents kept stirred at this temperature for another 1 hour to ensure the completion of the reaction. The disappearance of the peak at 2250 cm $^{-1}$ in IR for the NCO group shows the completion of reaction. The polyurethane diamine was stored as a solution in dimethyl acetamide for further reaction. The polyurethane diamine, isolated by precipitation in water was characterised by the analysis of amine value and molecular weight by VPO. The amine functionality was calculated knowing the equivalent weight from the amine value and the molecular weight from VPO.

Equivalent weight = 56100 / amine value (mgms KOH/gm)
Amine functionality = Molecular weight (VPO) / Equivalent weight

The synthesis of the amine-terminated polyurethane is as given in scheme 3.4.

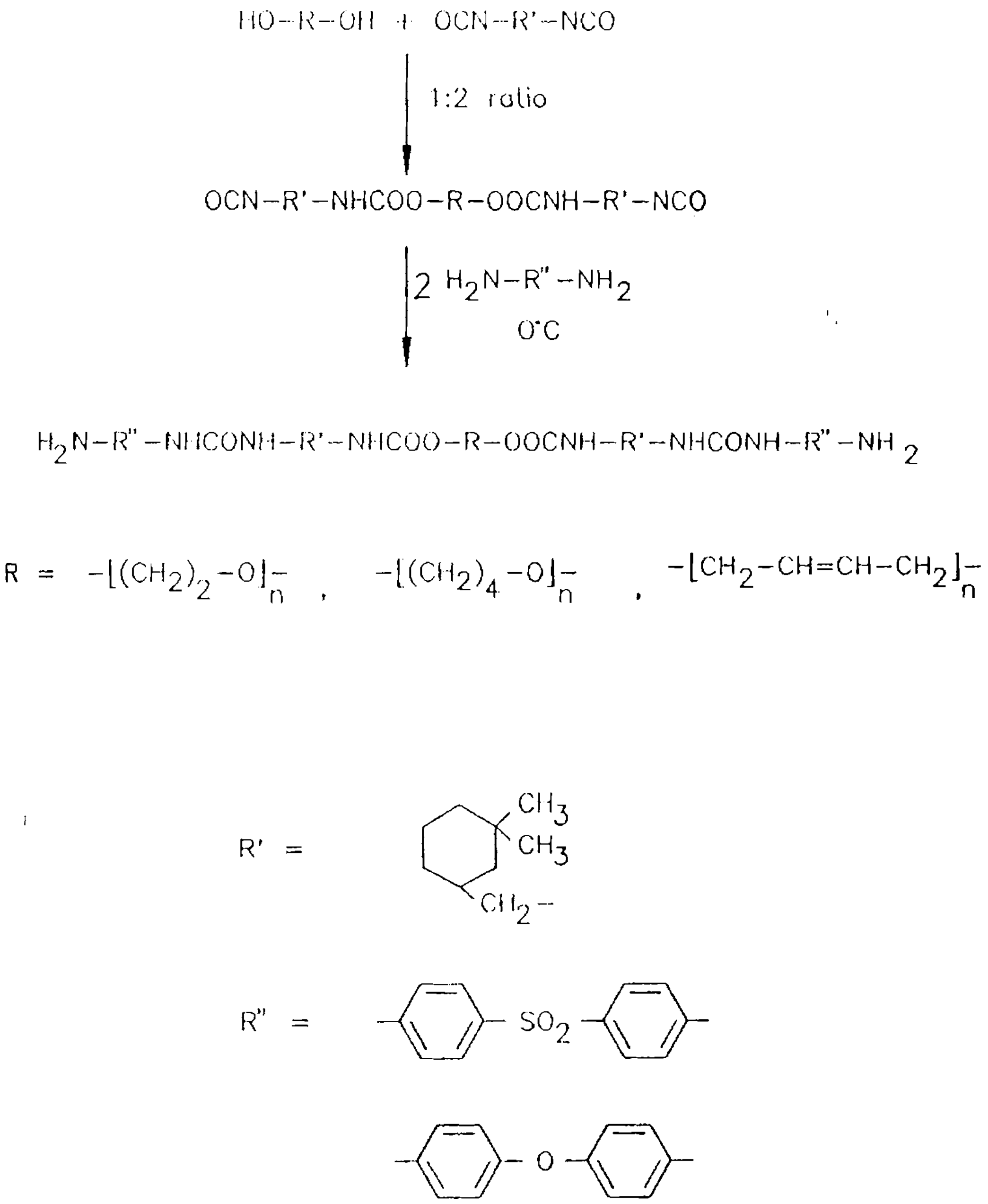
The polyurethane diamine was charcterised by I.R spectrum. The disappearance of the peak at 2250 cm $^{-1}$ characteristic of the isocyanate group clearly indicated that all the isocyanate groups have reacted with the amine. The peak corresponding to urea group was observed at 3310 cm $^{-1}$ and amine group at 3600 cm $^{-1}$. The sol content of the polyurethane diamine was analyzed by toluene as the extracting solvent. The values are given in table 3.4. The high value of the sol content shows that there is practically no crosslinking, which is the case when isophorone diisocyanate is used as the isocyanate. The reactivity of the secondary isocyanate group with amine and urea group is lower than that of primary isocyanate group and hence there will be minimum crosslinking and chain extension.

The molecular weight of the samples were estimated by VPO method, whose values are also given in table 3.4. The molecular weight of the samples showed that there was minimum crosslinking and the average amine functionality calculated is near to the theoretical within experimental eror. The polyurethane diamines were all waxy solids soluble in dimethyl acetamide in which the inherent viscosity values were determined. The schemes of reaction for prepolymer and PU amine are given in scheme 3.2.

### 3.1.C.7. *Synthesis of polyurethane-amic acid*

The polyurethane-amic acid was prepared from the pólyurethane-diamine (synthesised starting from the prepolymer with isophorone diisocyanate) by reaction with pyromellitic dianhydride. The reaction was carried out as follows.

About 20 gms of the polyurethane diamine was dissolved in 20 gms of anhydrous dimethyl acetamide taken in a three necked round bottomed flask. Dry nitrogen was purged into the reaction flask and through the central neck, a stirrer was connected for thorough stirring of the reaction medium. The calculated quantity of finely powdered pyromellitic anhydride was then added slowly into the reaction medium kept at $30^{0}$C over a period of 1 hr with thorough stirring during the addition period. The viscosity of the reaction mixture increases considerably during reaction. The stirring was continued for a further period of 1 hr. The amic acid solution was then preserved in moisture-free condition to avoid hydrolysis.



Scheme 3.2: Synthesis of polyurethane diamine

**Table 3.4 : Characteristics of the PU Amines and PU Amic Acids from polyethylene glycol (P- 600,1000) and HTPB - 2800 mol wt.**

| Sl No. | Polymer type | Amine value (PU amine) | | Mol.wt: of PUA (VPO) | Fn (av:) | Inh: Viscosity of PUA A (0.5 dl/g) | Acid value of PUAA mgm KOH/gm | |
|---|---|---|---|---|---|---|---|---|
| | | Exp. | Theor. | | | | Obs: | Theor: |
| 1 | PP-600/MDA | 76.9 | 78.0 | 1628 | 2.2 | 0.55 | 67.7 | 67.5 |
| 2 | PP-600/DDS | 71.8 | 72.9 | 1550 | 1.98 | 0.57 | 63.9 | 65.0 |
| 3 | PP-600/DDE | 76.9 | 77.8 | 1665 | 2.2 | 0.54 | 67.5 | 67.5 |
| 4 | PP-100/MDA | 60.2 | 61.0 | 1926 | 2.06 | 0.42 | 54.5 | 55.6 |
| 5 | PP-100/DDS | 56.1 | 57.9 | 2115 | 2.1 | 0.47 | 52.1 | 53.2 |
| 6 | PP-1000/DDE | 58.7 | 60.9 | 1950 | 2.04 | 0.42 | 54.4 | 55.0 |
| 7 | HTPB/MDA | 31.9 | 33.6 | 3450 | 1.96 | 0.36 | 31.5 | 32.3 |
| 8 | HTPB/DDS | 30.8 | 32.6 | 3615 | 1.98 | 0.38 | 30.7 | 31.2 |
| 9 | HTPB/DDE | 32.5 | 33.5 | 3210 | 1.95 | 0.37 | 31.5 | 32.0 |

PP-600, PP-1000. = Polyethylene glycol Prepolymer with IPDI.
HTPB/MDA = Prepolymer of HTPB and IPDI endcapped wth MDA

The PU amic acid was isolated from solution by precipitation in anhydrous methanol which dissolves solvent dimethyl acetamide. The precipitated amic acid was washed with methanol and dried under vacuum at 60$^{0}$C for 2 hrs.

### 3.1.C.8. *Cyclodehydration of Polyurethane-amic acids to the imides*

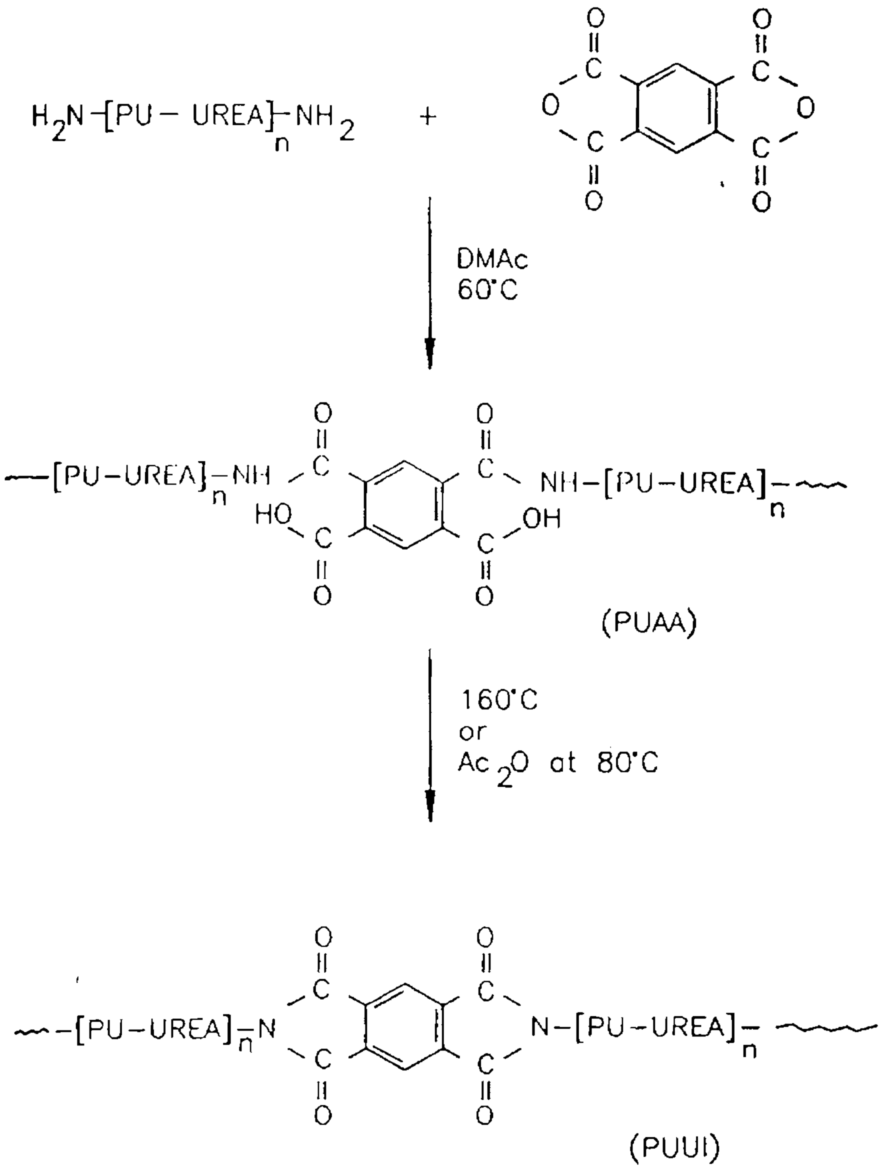
The polyurethane-amic acids synthesised could be converted to their corresponding imides by the conventional chemical as well as thermal imidisation techniques. In the thermal imidisation method, the polyurethane-amic acid solution in dimethyl acetamide was poured into a teflon mould in a thin layer and heated in an oven in a current of nitrogen. The heating was at a controlled rate of about 5°C/min: from room temperature to 180°C. The slow heating rate was maintained to avoid the formation of blow holes during imidisation step. The film so obtained was heated for a further period of 10 hours to complete the imidisation. The polyurethane-imide film so obtained was clear brown and transparent.

In the chemical method of imidisation, the amic acid solution is mixed with slight excess of freshly distilled acetic anhydride. Anhydrous sodium acetate was added as the catalyst. The solution was heatd to 70° C for 5 hours with good agitation. It was absorbed that the imide from the polyethylene glycol of 300, 400 and 600 precipitated from solution as yellow solids whereas those derived from polyethylene glycol 1000 and HTPB remained in solution. This is probably due to the lower amount of the rigid urethane and imide groups. The solubility of the polyurethane-imides helps in their applications as a coating over substrates.

The synthesis of amic acid and imidisation are given in scheme 3.3. The polyurethane imide was precipitated from solution in methanol as a pale yellow precipitate. The polymer was washed well with methanol. The solid polyimide was filtered and dried. The inherent viscosity in dimethyl acetamide was determined. The elemental analysis was also carried out.

### 3.1.C.9. *Variation of urethane and imide content for a fixed polyol.*

Inorder to study the effect of imide concentration on the properties, the ratio of imide to urethane content was varied.



Scheme 3.3: Synthesis of polyurethane - urea - imide

Isocyanate-terminated prepolymer of a fixed polyol, eg PEG- 600 with varying chain length and isocyanate contents were prepared by chain extension of the polyol with diisocyanate by varying the molar ratio of polyol to diisocyanate. Typical molar ratio of 1:2 for polyol to diisocyanate gave essentially, a NCO-terminated prepolymer without any chain extension by end- capping. A variation of the molar ratios leads to chain extension with subsequent changes in mol.wt., viscosity and isocyanate content. The formation of the isocyanate terminated prepolymer is as shown.

$$\mathrm{OCN - R{-}NHCOO ---- [CH_2\ CH_2{-}O{-}OCNH{-}R{-}NH\ COO - CH_2\ CH_2O]_n{-}OCNH\ R--- NCO}$$

The isocyanate content, viscosity, molecular weight and sol content of the chain extended polyurethanes were analysed and compiled in the following table 3.6.

**Table 3.6 : Characteristics of the chain extended polyurethanes of PEG-600/IPDI**

| Poly:. Type. | Ratio of OH/NCO | NCO content (%) | Mol.wt. (VPO) | Viscosity (cps) at $30^{0}$C | Sol content (%) |
|---|---|---|---|---|---|
| A | 1:1·4 | 2.35 | 3700 | 25240 | 96.5 |
| B | 1:1·5 | 3.1 | 2725 | 21627 | 98.0 |
| C | 1:1·7 | 3.9 | 2168 | 19450 | 97.5 |
| D | 1:1·8 | 4.4 | 1885 | 16645 | 99 |
| E | 1:2 | 7.8 | 1082 | 12580 | 98.5 |

The diamines and the corresponding polyurethane-amic acids were prepared using DDS and PMDA as the modifying agent in 1:1 ratio. The characteristics of the products are given in the following table 3.7.

**Table 3. 7 : Characteristics of the PU diamine & amic acids (PUAA)**

| Polymer type (of table 6) | Amine value (mgm KOH/g) | | Acid value (mgm KOH/g) (PUAA) | Inh: viscosity (PUAA) (0.5 dl/g) |
|---|---|---|---|---|
| | (exp.) | (Theor) | | |
| A | 25.2 | 26.5 | 24.6 | 0.91 |
| B | 33.1 | 34.3 | 32.5 | 0.90 |
| C | 41.1 | 42.1 | 37.5 | 0.87 |
| D | 46.2 | 47.8 | 42.9 | 0.82 |

### 3.1.C.10. *Characterisation of PU Amic Acids*

The polyurethane-amic-acid of polyethylene glycol and HTPB - based polyurethane-diamines isolated were characterised by chemical analysis of acid value and compared with the theoretical values. The inherent viscosity of the samples are determined in dimethyl acetamide solvent. The values are presented in table 3.4.

It may be observed from table 3.4 that there is good agreement of the experimentally observed acid values with the theoretical values indicating the completion of reaction. A higher value of inherent viscosity of the polyurethane-amic acid from PEG-600 over that from PEG-1000 polyurethane stems from the fact that there is a higher concentration of the amic acid group per molecule in the former. The acid values of the samples when different aromatic diamines are used for modification remains almost constant for a particular polyol under investigation and this shows that there is no change in reactivity of the polyurethane diamines towards the dianhydride when the diamines are varied for end-capping of the isocyanate prepolymer.

The polyurethane amic acids were characterised by IR spectrum.. The strong peaks corresponding to the hydrogen bonded N-H group could be observed at 3310 and 1545 cm$^{-1}$. A sharp peak at 1710 cm$^{-1}$ corresponds to the COOH group and the peak at 1640 cm$^{-1}$ corresponds to the C = O in amide group.

Analytical results support the formation the expected polyamic acid. However their molecular weight data could be generated as they were soluble only in polar solvents like DMAc.

The polyurethane-imides of PEG-PUwere characterised by IR spectrum. The typical IR spectrum of the solid polyurethane-imide polymer obtained by acetic anhydride imidisation is presented in figure 3.2. The following peaks in the IR spectrum were indicative of the polyimide structure.

3310 cm$^{-1}$ & 1545 cm$^{-1}$ - N-H group
1720 cm$^{-1}$ - urethane carbonyl
1640 cm $^{-1}$ - C-O in Urea
1780 cm$^{-1}$ - C-O in imide

The elemental analysis for C,H and N was conducted on three typical samples of PEG-600. PEG-1000 and HTPB based polyurethane-imides and compared with the theoretical values. The sol and gel content of the samples of these typical polymers were carried out by swelling them in toluene at 60$^{0}$C for 5 hours and weighing the dissolved fractions. The gel content values gave an indication of extent of imidisation.

The C,H,N analysis of the PU-imide samples were carried out for a PEG - 600 -

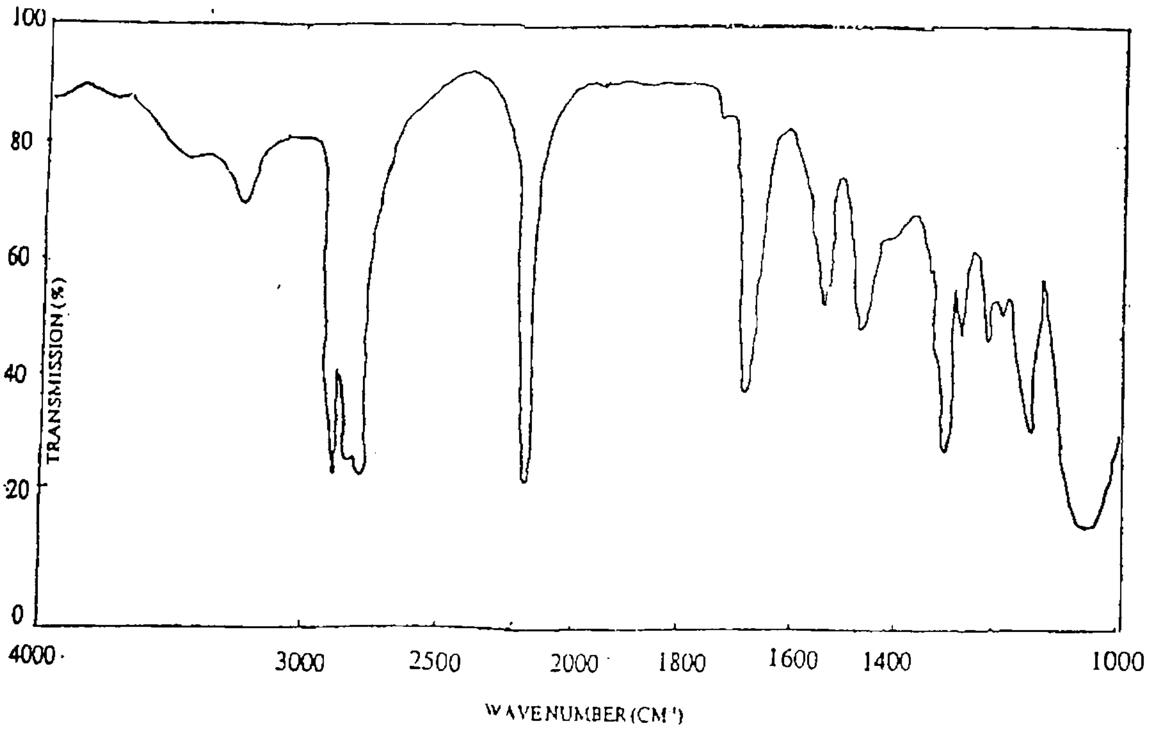


Fig. 3.1 : IR spectrum of NCO terminated polyurethane of PEG

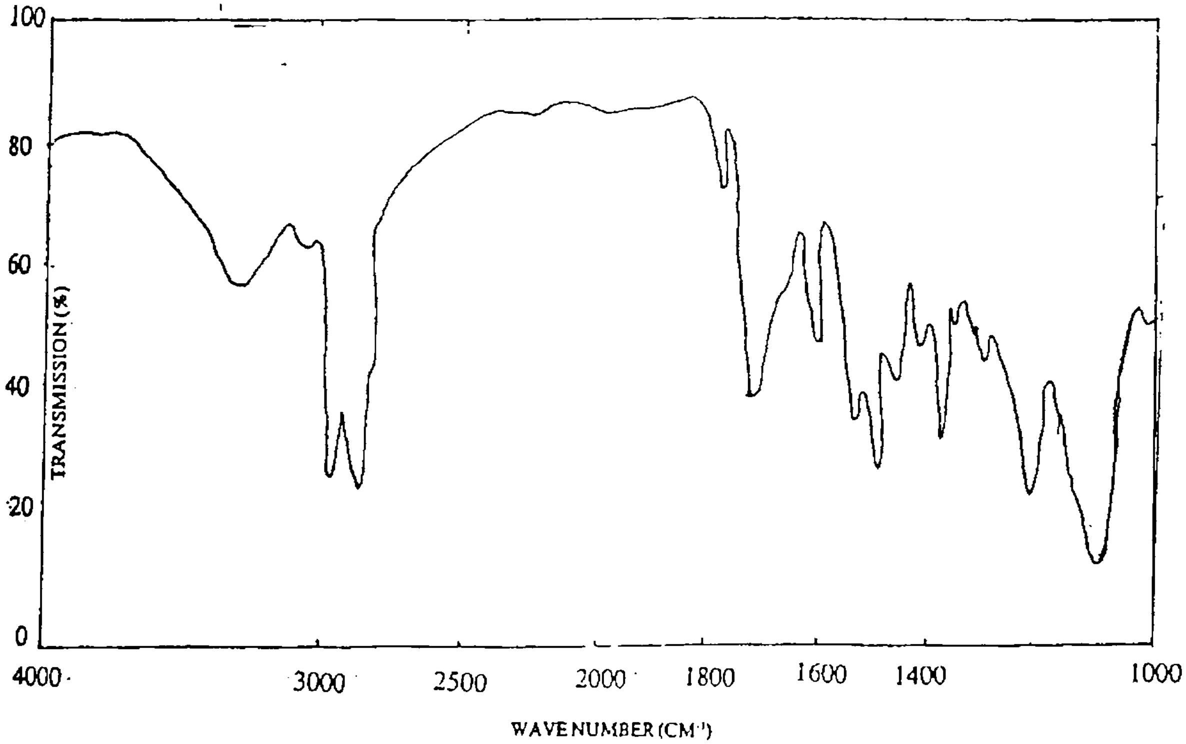


Fig. 3.2 : IR spectrum of polyurethane - urea - imide of PEG

derived and HTPB - derived samples. The values of gel content and elemental analysis are given in the table 3.5.

**Table 3.5 : Elemental analysis results of PU imides**

| Sl No. | Polymer type | gel content (%) | C (%) | H (%) | N (%) |
|---|---|---|---|---|---|
| 1 | PEG-400/ PUI | 95.1 | 55.6<br>(57.2) | 6.1<br>(6.5) | 4.8<br>(5.2) |
| 2 | PEG-600/ PUI | 93.8 | 58.5<br>(60) | 6.9<br>(7.1) | 4.3<br>(4.8) |
| 3 | HTPB/ PUI | 91.7 | 86.4<br>(88.2) | 9.1<br>(8.6) | 1.7<br>(1.5) |

The C,H,N values theoretically calculated are given in the brackets. The values obtained are in good agreement with the theoretical values for the three typical cases proving imidisation. A slightly lower value for C.H & N in all cases, compared to theoretical values may be due to incomplete imidisation which is usually the case when imidesation is attempted for polyamic acids. A higher value for gel content indicate substantial imidisation.

### 3.1.D. Results and Discussion

#### 3.1.D.1. *Evaluation of thermal and mechanical properties*

The preliminary experiment for evaluating the thermal stability of the samples were conducted by thermo gravimetric analysis (TGA) in nitrogen at a heating rate

10°C/min. The weight loss at different temperatures and the initial and peak decomposition temperatures (IDT and PDT) were evaluated from the thermograms. The rate of thermal erosion was correlated to the extent of hard segments in the polyurethane imide chains. The typical thermograms of the samples of polyurethane with IPDI and TMP, the polyurethane-urea-amine using diamino dephenylmethane and diaminodiphenyl sulphone as the modifiers, the corresponding PU-amic acids are presented in figure 3.3. Among the various amine-modified urethane-imides investigated, the sulphone group containing imides are found to have highest thermal stability as seen by the value of IDT and PDT, and the weight fraction remaining at 600°C. The sulphone group is also known to impart high thermal stability. The data are presented in table 9. The films of the samples of polyurethane - urea-imides prepared from PEG - 600 and PEG - 1000 as the basic polyols were analysed for mechanical and thermal properties. The data are presented in table 3.8.

**Table 3.8: Mechanical, physical and low temperature properties of polyurethane - urea - imides.**

| Sl. No. | Polymer Samples | T.S (MPa) | Elongn: (%) | Mod: at 100% eln: | Inh: viscosity | Tg (°C) |
|---|---|---|---|---|---|---|
| 1 | PEG-600/ IPDI/DDS | 8.5 | 275 | 4.1 | 0.58 | -20 |
| 2 | PEG-600/ DDE/PUI | 12.5 | 225 | 5.8 | 0.81 | -- |
| 3 | PEG-600/ DDS/PUI | 18.5 | 200 | 8.7 | 0.85 | -18 |
| 4 | PEG-1000/ IPDI/DDS | 7.5 | 285 | 3.9 | 0.63 | -25 |
| 5 | PEG-1000/ PUI | 10.5 | 210 | 4.9 | 0.91 | -20 |

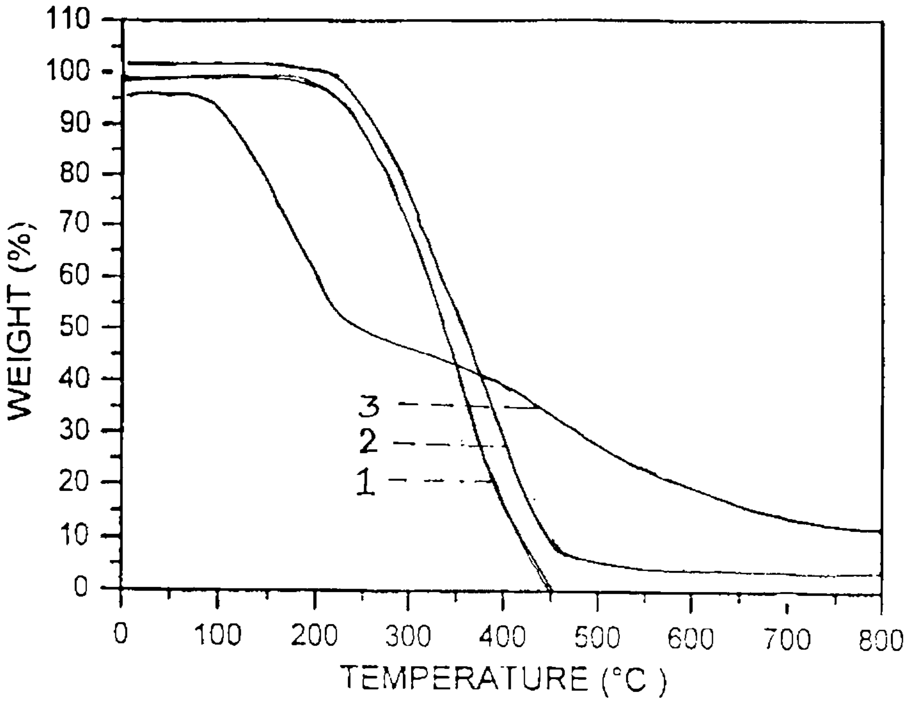


Fig. 3.3 : Thermograms of different polymers in $N_2$ . Heating rate - 10°C.
1 - Polyurethane of PEG/IPDI, 2 - Polyurethane -diamine,
3 - Polyurethane-amic acid

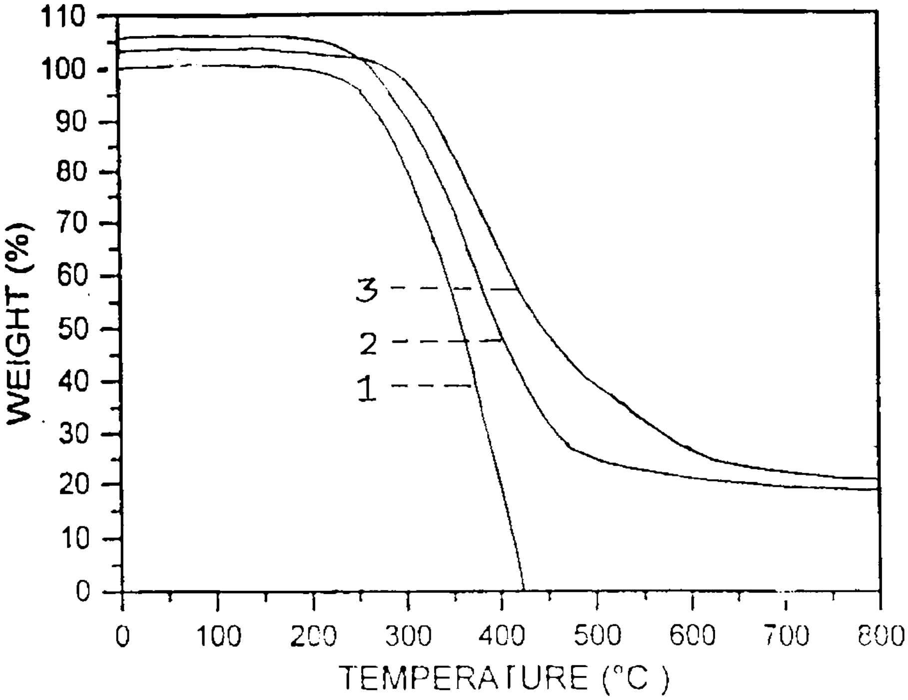


Fig.3.4 Thermograms of polyurethanes and polyurethane-imides in $N_2$ .
Heating rate - 10°C, 1- PU, 2- PUUI ( DDE-modified),
3 - PUUI ( DDS- modified)

The polymer samples 1 and 4 correspond to the diamine cured polyurethanes at 60°C using catalyst.

It was observed that the sulfone diamine (DDS) modified PU Imide has a higher tensile strength, modulus and lower elongation than the corresponding ether diamine (DDE) modified PUI. The thermal properties are also better for the same. This is due to the high polarity of sulfone group which imparts higher strength properties. The higher value of inherent viscosity is an indication of the chain build up and the polar nature of imide group.

The typical thermograms of the samples mentioned above are shown in figure 4. It can be observed from the table and thermograms that the temperature of onset of decomposition has increased from 200°C of the polyurethane to a maximum of 290°C for the polyurethane-imide when diamino diphenyl sulphone is used as the diamine for polyurethane-diamine synthesis. PUAA shows two stage decomposition It may be observed from table that there is an increase of glass transition temperature consequent to the agglomeration of hard urea and imide segments after modification with imide. The behavior is as expected. The glass transition temperatureof PU-U-I is below the room temperature and it is dependent on the basic backbone used.

The effect of imide group modification has been manifested by an increase in the inherent viscosity of the polymer as observed by a steady increase in the value of inherent viscosity when the urethane groups are combined with imide or urea groups. This behavior is also as expected. The introduction of polar groups increases the inter chain attraction. An increase of molecular weight due to chain extension and crosslinking increases the inherent viscosity further. The increase of inherent viscosity determined using DMF is an indirect indication of the imide group formation.

**Table 3.9: Thermal stability of various polyurethane - urea imides (using DDS as the diamine modifer)**

| Polymer Samples | Composition | Initial decomp. temp($^0$C) | Peak decomp. temp($^0$C) | Weight fraction at 400$^0$C | Weight fraction at 600$^0$C |
|---|---|---|---|---|---|
| PU | PEG-600/IPDI | 225 | 380 | 10% | Nil |
| PUA | PEG-600/PUA | 250 | 390 | 15 | 5 |
| PUAA* | PEG-600/PU AA | 1) 150 | 350 | 40 | 22 |
| | | 2) 300 | -- | -- | -- |
| PUI-2 | PEG-400/PUI | 285 | 405 | 62 | 23 |
| PUI-4 | PEG-600/PUI | 290 | 418 | 62 | 28 |
| PUI-5 | PEG-1000/PUI | 290 | 425 | 65 | 25 |

PUI = Polyurethane-imide

PUAA = PU-Amic acid

*It undergoes two-step weight loss. First one (150$^0$C) corresponds to imidisation by loss of water. The second one (300$^0$C) corresponds to the imide decomposition.

As the DDS is found to give higher thermal properties for PUI, the thermal stability of various PUI using varying length of PEG chain has been studied and the results are presented in table 3.9. The IDT and PDT are increased substantially and similarly the wt. fraction at 400$^0$ & 600$^0$C.

### 3.1.D.2. *Isothermal Aging studies*

The results of the isothermal aging studies conducted on the PUI samples in nitrogen and air at different temperatures are given table 3.10.

**Table 3.10: Isothermal aging studies of Sulfone containing PEG - 600/DDS/PU Imide system**

**a) in Argon**

| Sl. No. | Temp (°C) | Time (hrs) | T.S (MPa) | Loss in T.S (%) | Eln: (%) | Loss (%) | Weight loss(%) |
|---|---|---|---|---|---|---|---|
| 1 | R.T | -- | 18.5 | -- | 310 | -- | -- |
| 2 | 170 | 10 | 17.5 | 5.4 | 305 | 1.6 | 4.0 |
| | | 15 | 17.0 | 8.1 | 293 | 5.5 | 4.5 |
| | | 20 | 16.8 | 9.2 | 285 | 8.0 | 5.5 |
| 3 | 190 | 10 | 17.0 | 8.1 | 300 | 3.2 | 5.0 |
| | | 15 | 15.5 | 16.2 | 285 | 8.1 | 6.5 |
| | | 20 | 15.1 | 18.3 | 270 | 13 | 10.5 |
| 4 | 210 | 10 | 15.8 | 14.5 | 275 | 11.3 | 12.6 |
| | | 15 | 15.1 | 18.3 | 245 | 20.1 | 14.5 |
| | | 20 | 14.8 | 20 | 240 | 22.6 | 15.6 |

**Base Polyurethane sample PEG 600 PU (in argon)**

| | | | | | | |
|---|---|---|---|---|---|---|
| RT | -- | 4.2 | -- | 375 | -- | -- |
| 210 | 10 | 3.1 | 26 | 280 | 24 | 21 |
| | 15 | 2.7 | 35 | 240 | 36 | 28.5 |
| | 20 | 2.1 | 50 | 185 | 48 | 31 |

**In air**

(PEG-600/PUI)

| | | | | | | |
|---|---|---|---|---|---|---|
| 210 | 10 | 12.2 | 34 | 215 | 30.6 | 25.0 |
| | 15 | 11.3 | 60 | 165 | 46.0 | 35.5 |
| | 20 | 9.1 | 77.8 | 75 | 75.0 | 48.5 |

The rate of decrease of T.S and elogation and weight of the sample at different temperatures are less for the imide modified PUs. This shows retention of mechanical properties at higher temperatures compared to the original polyurethane. The results are given in table 3.10.

The rate of degradation in air at 210$^{0}$C is highter than in argon as observed from the table. This shows that the mechanical properties are not much affected by heat aging. The improvement in stability over the neat polyurethane can be observed from the table. The variation of strength with time is given in figure 3.5.

The chain extended polyurethanes from PEG-600 discribed in section 3.1.c.6 (table 3.6.) was converted to the corresponding imide as in the usual procedure to study the effect of ratio of urethane to imide group. The results obtained from the evaluation of thermal and mechanical properties can be summarised as below in table 3.11.

**Table 3.11: Mechanical and thermal properties of PUI with chain extended PEG-600/IPDI**

| Sl. No. | NCO% of PU | Mol.wt by VPO | Hard segment (%) | T.S (MPa) | Elongn: (%) | IDT ($^{0}$C) | fraction of residue(%) at 600$^{0}$C |
|---|---|---|---|---|---|---|---|
| 1 | 2.3 | 3700 | 20.1 | 5.5 | 385 | 265 | 15 |
| 2 | 3.1 | 2725 | 25.5 | 8.1 | 365 | 265 | 18 |
| 3 | 4.4 | 1885 | 33.1 | 10.5 | 324 | 275 | 22 |
| 4 | 7.8 | 1082 | 46.3 | 18.5 | 300 | 290 | 30 |

From the table it can be observed that, as the isocyanate content is increased there is a corresponding increase in the urethane, urea and imide content, (hard

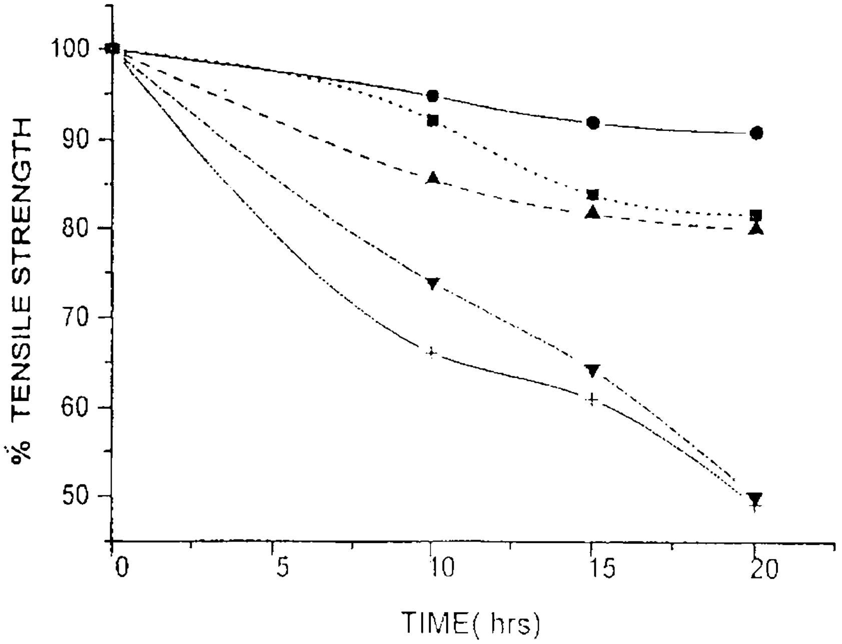


Fig. 3.5 : Retention of T.S during isothermal aging for PUI samples
(● 170°C ■ 190°C ▲ 210°C(all in argon) × 210°C(in air)
▼ Base PU (in argon at 210°C)

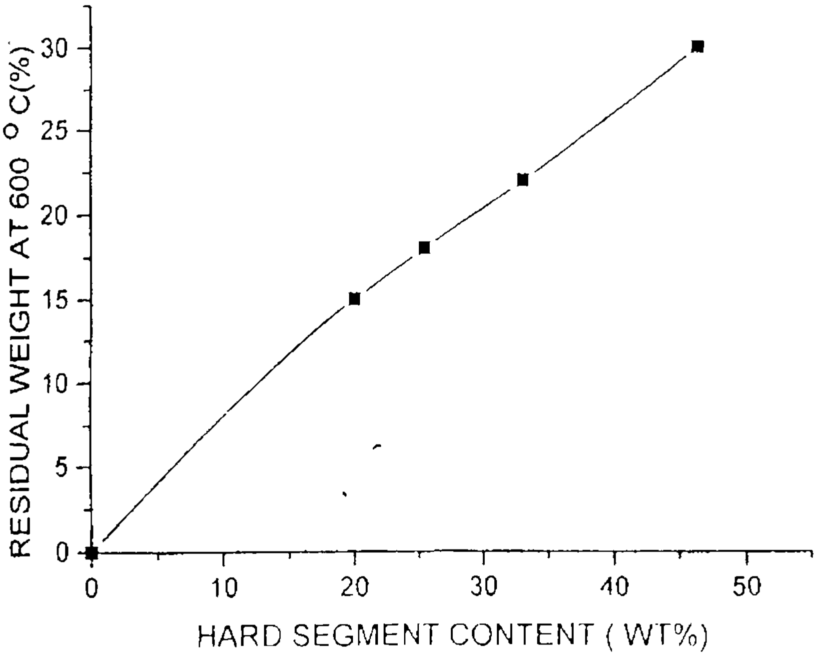


Fig. 3.6 : Variation of residual weight % at 600°C with hard segment content for polyurethane - urea - imide

segment content) subsequently the overall thermal stability is improved. The tensile strength is found to increase followed by decrease in elongation progressively as the hard segment content is increased. The residual weight percent at 600°C is correspondingly increased, as shown in figure 3.6.

This set of studies help in fixing proportion of urethene and imide group in polyurethane-imide for optimum mechanical and thermal properties.

### 3.1.E. Studies on HTPB - based imide-polyurethanes

The prepolymer of HTPB and IPDI was reacted with a diamine as described earlier. Diaminodiphenyl sulfone and diamino diphenyl ether were chosen as the amine modifiers. The properties of amine-modified HTPB - PU and amic acids are given in table 3.4. The amine terminated polybutadiene was reacted with PMDA in DMF medium and stirred for 2 hours at 60°C. The imidisation was done as discribed earlier. The mechanical property and thermal stability were evaluated as in earlier cases. The values for various systems are presented in the following table 3.12.

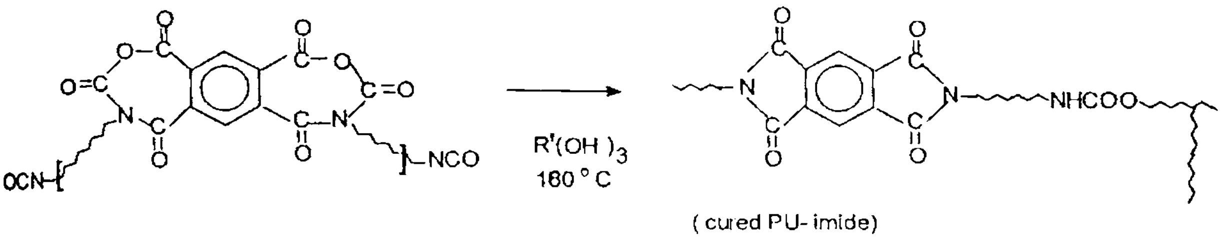
**Table 3.12: Mechanical and thermal properties of HTPB - PU imides**

| Sl. No. | Polymer sample | T.S (MPa) | Eln. (%) | Tg (°C) | IDT (°C) | PDT (°C) | Wt.fraction (at 600°C)% |
|---|---|---|---|---|---|---|---|
| 1 | HTPB-PP/TMP | 1.5 | 450 | --60 | 260 | 475 | nil |
| 2 | HTPB-PP/DDS | 3.5 | 325 | -- | 275 | 482 | 25 |
| 3 | HTPB-PP/DDS/ Imide | 6.0 | 275 | --30 | 300 | 488 | 35 |
| 4 | HTPB -PP/DDE | 3.1 | 345 | -- | 280 | 478 | 25 |
| 5 | HTPB-PP/DDE/ Imide | 5.0 | 315 | --35 | 300 | 485 | 35 |

The sample no. 1 in table 3.12 is HTPB cured with IPDI using TMP as crosslinker with higher equivalent ratio (1:3) for maximum strength. For the same composition the tensile strength and modulus of DDS based PUI is higher than DDE based as observed earlier for PEG. This clearly indicates the contribution of the polar sulfone group towards increasing the cohesive energy of the matrix. We have seen that the amines donot differ in their reactivities to the isocyanate.

### 3.1.F. Comparison of one shot PUI and PUU imide

Polyurethane imides of HTPB were prepared by one shot technique as follows. A weighed quantity of HTPB-IPDI prepolymer having NCO terminals was taken in a RB flask. Anhydrous THF was added and stirred with the help of magnetic stirrer for complete dissolution. The required quantity of finely powdered and pure PMDA was added in small lots into the solution with stirring for a molar ratio of prepolymer: PMDA 2:1. The temperature of reaction is raised to 60°C and maintained for 2 hours. After the reaction, crosslinking agent trimethylol propane is added to maintain an equivalent ratio of 1:1. The PUI films were prepared in the same way as in the previous case. The samples of polyurethane imides of HTPB are analysed for mechanical and thermal properties and compared with the samples made by two shot technique via the polyurethane urea imide. The results are presented in table 3.13. The advantage of the process is that elastomer slabs can be made easily, if the solvent THF is removed before reaction with TMP. The imide-prepolymer is a viscous liquid. The reaction is given in scheme 3.4.



scheme . 3.4

**Table 3.13: Properties of HTPB - PU imides by one shot method**

| Sl. No | Polymer type | T.S (MPa) | Eln: (%) | Mod:at 100%eln: | IDT (°C) | Wt: fraction at 600°C (%) |
|---|---|---|---|---|---|---|
| 1 | HTPB-PU (IPDI-TMP) | 1.8 | 410 | 1.1 | 260 | nil |
| 2 | HTPB/PUI (one shot) | 3.8 | 330 | 2.1 | 285 | 25 |
| 3* | HTPB/PU/DDS | 4.8 | 325 | 1.8 | 275 | 20 |
| 4** | HTPB/IPDI/ Imide | 6.0 | 275 | 2.5 | 300 | 30 |

* HTPB cured with IPDI and DDS.
** PU-U-I of HTPB.

From the above table, it is clear that the mechanical and thermal properties of the polyurethane-urea-imides are higher than the polyurethane imide prepared by the one shot technique which doesnot contain any urea group. Evidently, the presence of urea group adds to the tensile strength and modulus. The properties of the urethane-urea-imides are better than those of the basic polyurethanes from which the imide is derived.

## 3.1.G. Conclusion

Based on the studies conducted it can be concluded that the mechanical and thermal properties of polyurethanes can be improved considerably by the incorporation of urea and imide groups in the backbone. The two- step method of urethane-urea-imide synthesis permits the tailoring of the properties of the imide-polyurethane by proper selection of the aromatic diamine modifiers unlike in the one step method synthesis of polyurethane imides. The enhancement in the mechanical properties by way of incorporation of hard segments is a direct consequence of increasing the cohesive forces of the systems through polar units. The dramatic improvement in mechanical properties when DDE is replaced by DDS in polyurethane urea imide clearly substantiates this. Here as the polar groups chosen are thermally stable moieties, system has the added advantage of enchanced thermal stability as evident from TGA and the thermal aging studies. The properties are found to increase correspondingly for a polyol based system as the hard segment content is increased. The synthesis of urethane imides via the polyurethane amic acid has the advantage that the amic acid is stable in solution and imidisation can be carried out an any surface by applying as a thin film and subsequent heat treatment. This helps in applications such as polyurethane coatings with improved thermal resistance. Alternatively, the properties of polyimides can be tailored by incorporation of flexible polyether or polybutadiene units through the amic acid route. The one step method has advantage in processing as elastomer slabs.

The polyethylene glycol based PUI has shown relatively higher tensile strength properties over HTPB based due to mainly two reasons . The molecular weight of the polyethylene glycols used in the study were lower compared to HTPB and hence the concentration of polar urethane, urea and imide content are higher. This causes a higher interchain attraction causing the tensile strength to increase. The ether group present in the chain causes hydrogen bonding with other polar groups in the chain like imide, urea etc causing more interchain attraction. HTPB having a hydrocarbon backbone doesnot have much effect on hydrogen bonding and hence the tensile strength is relatively lower.

## 3.2. IMIDE-OXAZOLIDONE - POLYURETHANES

### 3.2.A. Introduction

The modification of polyurethanes by introduction of imide was presented in the previous section. The modification of polyurethanes with oxazolidone by reaction of isocyanate with epoxy compounds for improvement of thermal and physical properties of polyurethane has been studied by different authors as presented in chapter 1.

The studies reported on imide-containing polyurethanes and oxazolidone-containing polyurethanes were presented in the chapter 1. The introduction of polyimide, polyamides and amide- imide groups for improvement in properties sof polyurethanes have also been reported.[10-15]

The use of polyols as flexibilisers for Isocyanurate - oxazolidone (ISOX) has been studied and the effect of flexibilisation presented by Roth[16]. using isocyanate terminated prepolymer and simple diepoxy compounds. Uribe and Hodd studied[17] the linear polymers of polyisocyanurate-oxazolidone formed from MDI and diepoxy such as Bisphenol A diglycidyl epoxy compound (BADGE). The reaction between isocyanate and epoxy, resulting is oxazolidone is accompanied by the competing reaction of isocyanate trimerisation giving rise to isocyanurate. The selection of catalysts adjusts the the extent of isocyanurate and oxazolidone groups in the chain. The reaction between BADGE and TDI was also studied by Sandler & Berg[18] with tetramethyl ammonium iodide catalyst and DMF as solvent.

The studies of Kinjo[19] has revealed that excess of isocyanate favours the formation of isocyanurate. The increase of isocyanurate portion in the chain increases the glass transition temperature of the polymer. Hexa methylene tetramine *(HEXA)* catalyses oxazolidone formation more compared to other catalysts like *DABCO* and ethyl methyl imidazole *(EMI)*. Hence it is accepted that the relative proportion of these two structural units are profoundly influenced by the reaction parameters. New thermally stable epoxy resin laminates were developed from the similar isocyanate terminated prepolymer and epoxy compounds by Yamaoka et al[20]. The resulting epoxy resin laminates were highly thermally stable. When bis imide compounds were used, laminates with much higher thermal stability was obtained.

The reaction of isocyanate-terminated polybutadiene prepolymer and aromatic diepoxy compound to yield oxazolidone-urethane copolymer and their properties were reported by Sankaran et al[21,22]. The catalyst used was tetrabutyl ammonium iodide and the DSC studies revealed that oxazolidone was formed and that there was no isocyanurate formation.

Literature, as well as our work described in the previous section shows the advantage of introducing imide groups in polyurethanes. Oxazolidone is also kinown to improve the thermomechanical profile of polyurethanes. Hence, it was of interest to study the influence of both these groups when they are simultaneously present in the backbone. In this perspective, we have designed polyurethane with imide oxazolidone moieties. This section of the chapter describes the synthesis, characterisation and a detailed investigation on the physical, thermal and thermomechanical properties of those polymers in comparison to the sytem with imide alone. The synthesis and characterisation of the related imide-epoxy crosslinkers used have also been described.

In the present work, imide-oxazolidone group is introduced in the polyurethane chain by coupling an isocyanate terminated prepolymer with an imide containing diepoxy chain extender. It is known that aliphatic imide is flexibile compared to aromatic imides but the thermal stability is higher for the latter. The imide-diepoxy crosslinker was synthesised from both aliphatic and aromatic imide diacids.

The copolymer was synthesized by two different methods.

1) Synthesis of isocyanate terminated prepolymer followed by crosslinking using imide containing epoxy chain extenders/crosslinkers with catalyst.
2) By crosslinking of difunctional isocyanate-terminated imide polyurethane prepolymer with aliphatic triepoxy crosslinkers in presence of catalyst *HEXA*. The imide-diepoxy chain extenders were synthesised. The triepoxy curative was synthesised by a reported procedure[23]. The reaction conditions for the epoxy-isocyanate reaction have been established.

Two types of imide oxazolidones have been compared with respect to their properties.

The improvements in thermal and mechanical properties of the resultant oxazolidone - modified polyurethane - imides have been compared with the basic polyurethanes and the polyurethane-imides baised on polyether and polybutadiene polyols. The changes in other physical properties particularly the glass transition temperature have been examined. The adhesive properties of selected systems have been evaluated and the data presented.

The thermal stability of the imide group is higher than isocyanurate group as the latter gets dissociated thermally to isocyanates and hence imide-oxazolidone combination in the chain will be thermally more stable than isocyanurate-oxazolidone in ISOX resins referred earlier.[16]

## 3.2.B. Experimental

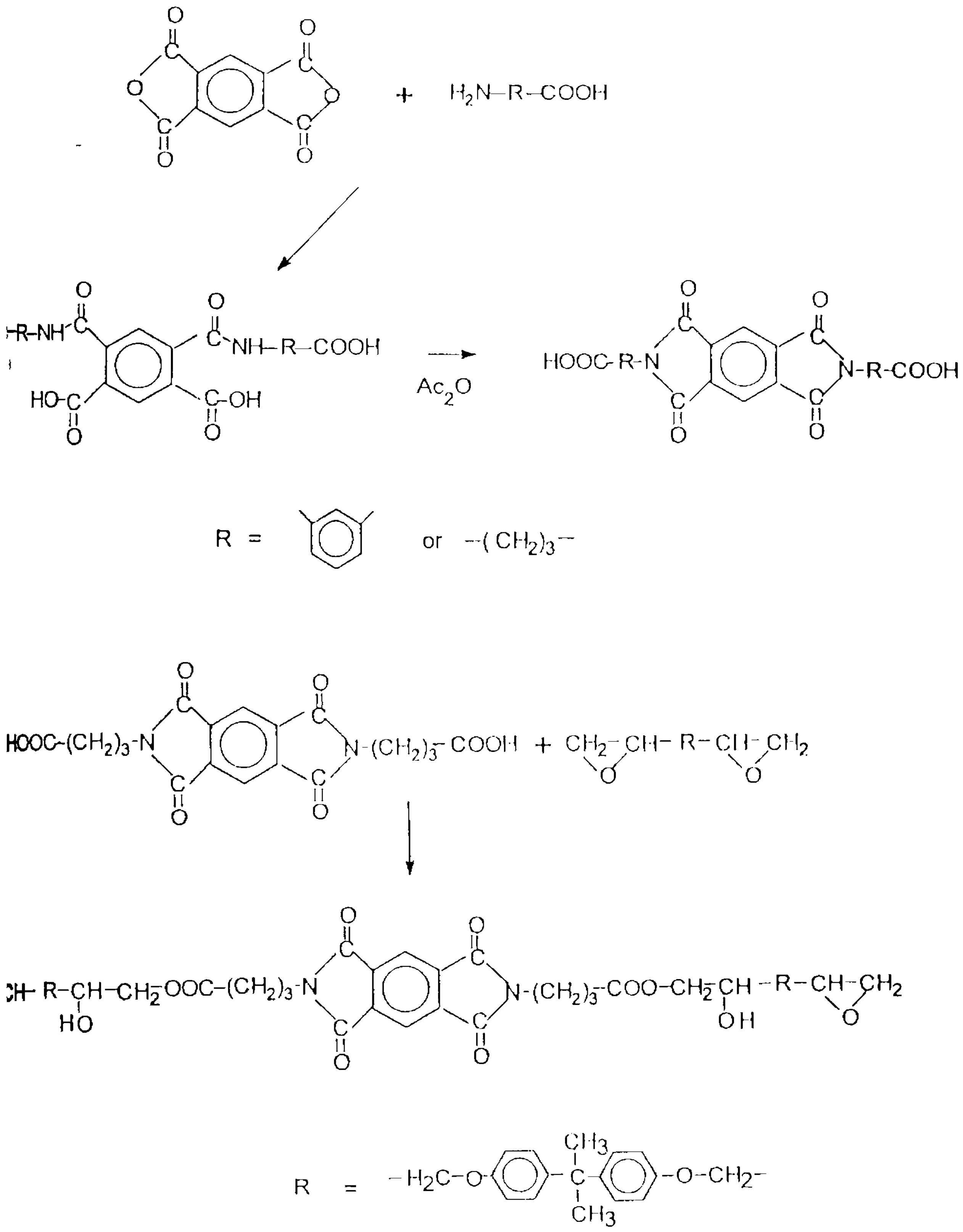
### 3.2.B.1 *Raw materials*

1) Pyromellitic dianhydride (PMDA) (Fluka, Germany)
2) Benzophenone tetracarboxylic dianhydride (BTDA) (Aldrich, USA)
3) Meta amino benzoic acid (MABA) (SISCO, Bombay)
4) 4 - Aminobutyric acid (ABA) (SISCO, Bombay
5) Aromatic diepoxy (GY - 252 of CIBA- GEIGY, Bombay)
6) Aliphatic triepoxy of pentaerythritol and epichlorohydrin) (Synthesised in VSSC by documented procedure)
7) Isophorone diisocyanate (Rhenus Wtag, Germany)
8) Polyethylene glycol (PEG) (BDH, India)
9) Hydroxy terminated polybutadiene (HTPB of NOCIL, Bombay)
10) Hexamethylene tetramine (HEXA) (SD chemicals, Bombay)

The purification of raw materials used in the study are as reported in the imide-polyurethane section.

### 3.2.B.2. *Synthesis of imide -di carboxyllic acids*

The imide-diacid of aminobutyric acid and aminobenzoic acid with pyromellitic dianhydride were realised by the reaction given in scheme 3.5. After



Scheme 3.5 : Synthesis of imide - diepoxy crosslinker

imidisation with acetic anhydride, the imide-diacid was separated by precipitation in water followed by drying at 60°C for about 4 hrs under vacuum to get a pale yellow crystalline solid.

It was observed that the imide-diacid of *ABA* is soluble in aprotic solvents like dimethyl acetamide and dimethyl formamide whereas that of *MABA* was only partially soluble in DMAc. The precipitation of the product during imidisation was an indication of completion of reaction.

### 3.2.B.3. *Synthesis of imide - diepoxy crosslinker*

The imide-diepoxy crosslinker was synthesised starting from the imide-diacid by endcapping with a diepoxy compound. The reaction of imide-diacid with GY-252 in 1:2 molar ratio is shown in scheme 3.5. The reaction was carried out in DMAc solvent in presence of *HEXA* as catalyst at a temperature of 60°C. The reaction between the imide diacid of ABA and GY 252 takes place in a homogeneous medium. The imide diacid of MABA although initially insoluble in dimethyl acetamide, the product became soluble as reaction proceeded and the reaction was completed within period of 2 hours, as seen by disappearance of *COOH* peak in IR and acid value by chemical analysis.

The experiment was conducted in a three necked round bottomed flask under thorough agitation. The mixture of imide-diacid and solvent dimethyl acetamide was taken in the reaction flask. Through one neck, a flow of nitrogen was given. A solution of the diepoxy compound in dimethyl acetamide corresponding to a molar ratio of 1:2 for acid and epoxy along with 1% catalyst *HEXA* was added over a period of 1 hour. The system was maintained at 60°C for 2 hours. After reaction, the homogeneous reaction mixture was poured slowly into excess methyl alcohol with stirring. The product, imide-diepoxy was precipitated as a brown solid. It was then washed with methyl alcohol 2 or 3 times to remove any unreacted diepoxy compound. The residue was filtered and dried at 60°C for 2 hours in vacuum oven. The characteristics of imide-diacids based on PMDA and BTDA using aliphatic and aromatic aminoacids are given in the table 3.14.

### 3.2.B.4. *Characterisation*

The imide diacids (IDA) and the diepoxy compounds (IDE) derived from them were characterised by I.R, elemental analysis and melting points and chemical analysis of acid value and epoxy content. Tables 3.14 and 3.15 present the data on characterisation of the product.

**Table 3.14: Physical characteristics of imide diacids (IDA)**

| Ref. No. | IDA Type | Acid value mgm.KOH | Elemental analysis (%) | | | M.Pt (°C) |
|---|---|---|---|---|---|---|
| | | | C | H | N | |
| **IDA-(1)** | (PMDA/ ABA) | 226.5<br>(228) | 55.1<br>(55.6) | 3.9<br>(4.1) | 7.3<br>(7.2) | 210 |
| **IDA-(2)** | (PMDA/ MABA) | 247.2<br>(246.5) | 63.8<br>(63.1) | 2.3<br>(2.6) | 6.5<br>(6.1) | 245 |
| **IDA-(3)** | BTDA/ ABA | 227.2<br>(228) | 61.3<br>(60.97) | 3.8<br>(4.05) | 5.2<br>(5.7) | 190 |
| **IDA-(4)** | BTDA/ MABA | 201.2<br>(200) | 65.1<br>(66) | 2.7<br>(2.85) | 4.8<br>(5) | 225 |

The values given in the brackets correspond to the theoretical values. The experimentally observed values are in good agreement with the theoretical values conforming the formation of the expected imide diacid. The melting points of the imide diacids based on BTDA was less than that of the PMDA based due to lack of symmetry.

**Table 3.15 : Physical characteristics of imide diepoxy (IDE)**

| IDE of | Epoxy content (eq:/kg) | Mol:wt by VPO | Fn (av:) | Elemental analysis(%) | | | M.Pt ($^0$C) |
|---|---|---|---|---|---|---|---|
| | | | | C | H | N | |
| IDA (1) | 1.47 | 1225<br>(1064) | 1.9<br>(2) | 68.5<br>(70) | 5.1<br>(5.8) | 2.8<br>(2.63) | 115 |
| IDA (2) | 1.35 | 1325<br>(1216) | 1.93<br>(2) | 76.1<br>(74.7) | 5.8<br>(5.0) | 2.1<br>(2.56) | 145 |

(The values given in brackets indicate the theoretical ones).

The molecular weight of two imide diepoxy compounds (IDE) synthesised starting from the imide diacids IDA-1 and IDA-2 are slightly higher than the theoretical values and the epoxy functionality is less than 2. This is probably due to the chances of chain extension when the imide diacid is endcapped with the diepoxy. The melting points of the imide diepoxy are lower than the corresponding mide diacid due to the chain extention during endcapping with diepoxy.

The IR spectral characteristics of the imide diacids, imide-diepoxy and the imide-oxazolidones are as given in table 3.16.

**Table 3.16: I.R. Spectral characteristics of Imide-diacids, Imide-diepoxy and the imide-oxazolidones.**

| Compund | Frequency (cm$^{-1}$) | Characteristic group |
|---|---|---|
| Imide diacid of MABA & PMDA (IDA) | 1510 | C = C in aromatic ring |
| | 1728 | C = O in COOH |
| | 1780 | C = O in imide ring |
| Imide-diepoxy of IDA and Gy-252 (IDE) | 1510 | Aromatic ring |
| | 925 & 829 | epoxy group |
| | 1100 | C-O-C in GY 252 |
| | 1780 | C = O in imide |
| | 3600 | OH group |
| Imide Oxazolidone of HTPB (IOX) | 1740 | C = O in Oxazolidone |
| | 1780 | C = O in imide |
| | 1650 | C = C in Polybutadiene |
| | 1510 | Aromatic ring |
| | 3370 | NH in Urethane |
| | Peaks absent in IOX | |
| | 2250 | NCO has reacted |
| | 925 & 829 | epoxy group consumed |
| | 3600 | OH group consumed |
| | 1710 | C = O in isocyanurate (no NCO trimerisation) |

The epoxy content and the elemental analysis values for two samples are included in table 3.15. The typical IR spectra of IDA and IDE are shown in figure 3.7. The absence of the peak at 2250 and 925 cm$^{-1}$ shows that NCO and EPOXY has reacted. The peak at 1740 cm$^{-1}$ shows the presence of oxazolidone absence of peak at 1710 cm$^{-1}$ shows that there is no NCO trimerisation.

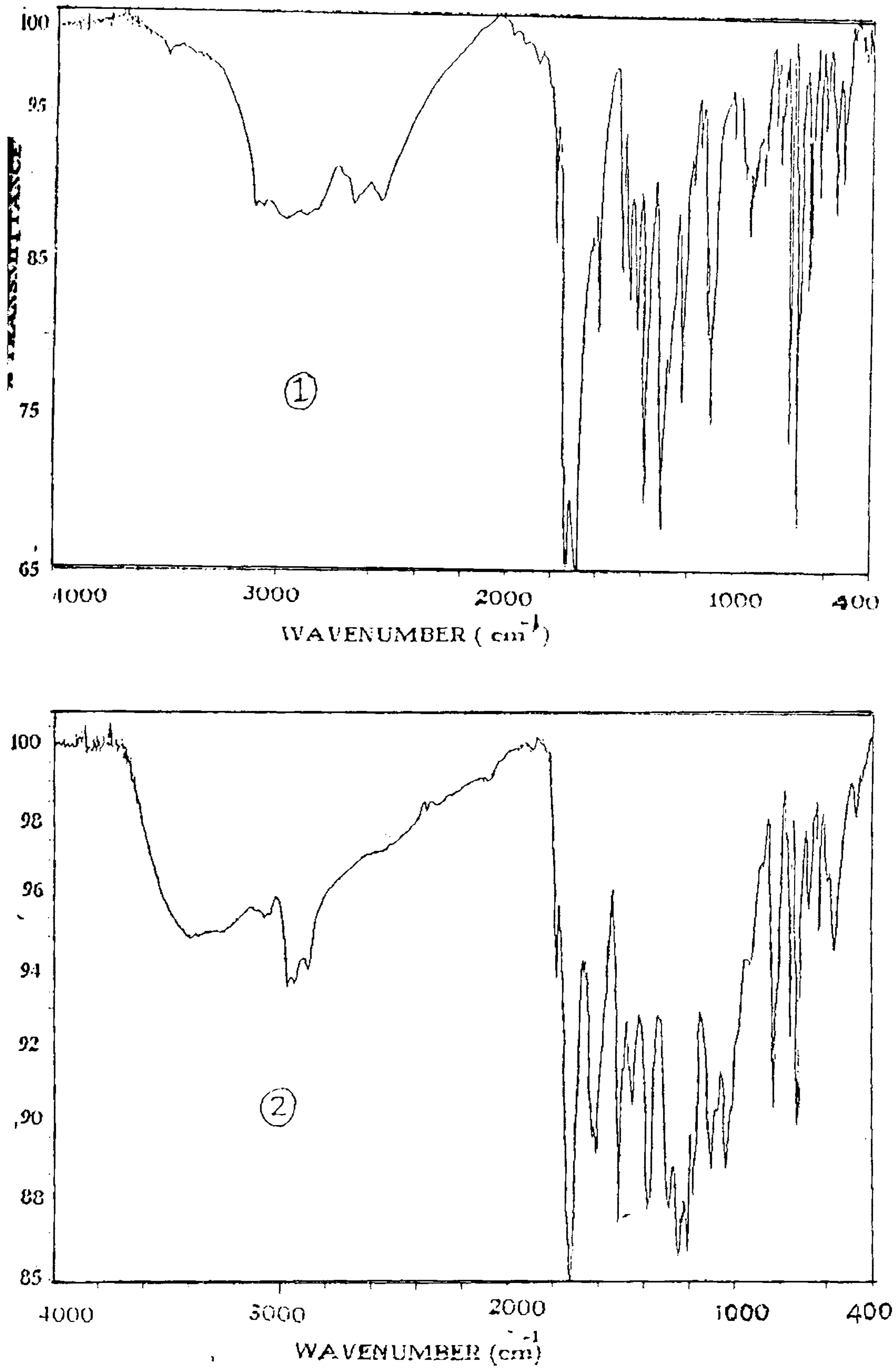
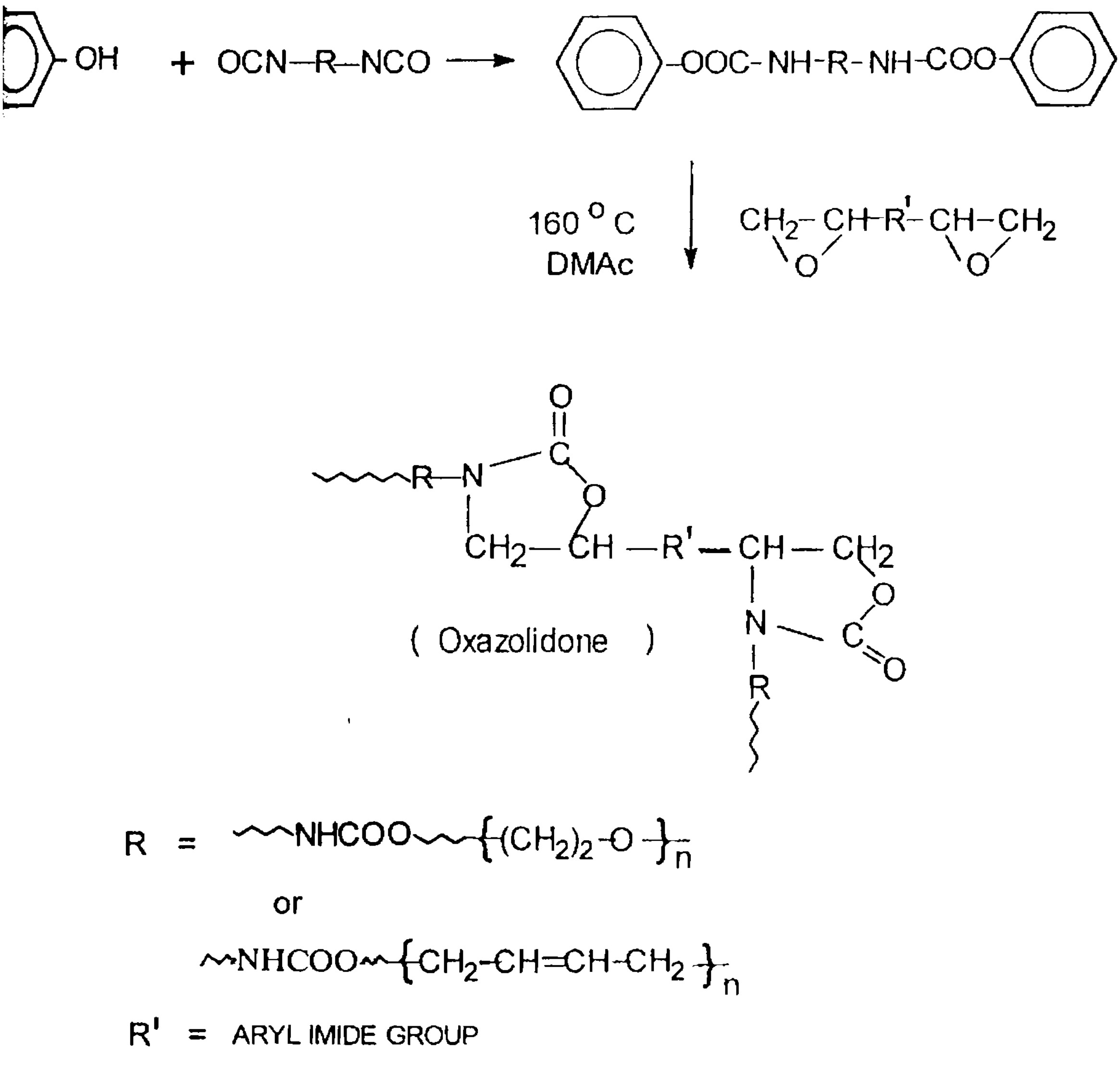


Fig. 3·7 : I.R. Spectra of Imide - diacid (IDA) (1) & Imide - diepoxy (IDE)



Scheme 3.6 : Synthesis of polyurethane - imide - oxazolidone[PUI-OX]

### 3.2.B.5. *Synthesis of imide-oxazolidone-polyurethane*

The first step for the the preparation of the polyurethane-imide-oxazolidone is the preparation of a blocked polyurethane prepolymer. The prepolymer was prepared starting from HTPB as detailed in scheme 3.2. After the reaction, the blocking of NCO group was done using phenol as the blocking agent in 1:1 equivalents ratio and the reaction was conducted in *MEK* solvent at 60°C and *HEXA* catalyst. The completion of reaction was ascertained from the disappearance of peak at 2250 $cm^{-1}$ due to NCO group in IR spectrum. The blocked prepolymer was isolated by evaporation of the solvent. It was then mixed with the imide diepoxy compound in molar ratios 1:1, 1:1.5 and 1:2 (IDE : prepolymer) along with the catalyst 1% *HEXA* in dimethyl acetamide solvent and the reaction mixture was poured into teflon moulds. The solvent was allowed to evaporate slowly and the film so obtained was heated in oven at 160°C in a flow of nitrogen for 15 hours to ensure completion of oxazolidone formation. The optimisation of heating time was studied by keeping the samples for 5, 10, 15 hours and monitoring the epoxy peak by IR . The complete disapperance of epoxy group was seen at 15 hrs and mechanical properties reached maximum value at 15 hrs. The reaction is given in scheme 3.6.

The competing reactions taking place during the oxazolidone formation are trimerisation of isocyanate to yield isocyanurate and allophanate formation. The formation of these units could be avoided by the use of blocked urethanes which decompose to give free isocyanate group at the reaction temperature of oxazolidone formation. Further, the isocyanurate formation is reduced when an isocyanate-terminated prepolymer is employed due to reduced reactivity of isocyanate group at the polymer chain end. The reaction between isocyanate and epoxy was confirmed by DSC which showed an exotherm at $160^0$C. The typical DSC of the reaction mixture of blocked isocyanate and imide-epoxy are given in figure 3.8. The use of catalyst *HEXA* is reported to favour oxazolidone formation only.

### 3.2.B.6. *Polyurethane-imide-oxazolidone via imide - isocyanate prepolymer.*

An alternate method of the preparation of imide-oxazolidone modified-polyurethane is as follows. The isocyanate-terminated imide-prepolymer was synthesized by reacting pyromellitic dianhydride and isocyanate-terminated prepolymer of HTPB (taken in 1:2 molar ratio) in *MEK* solution at $60^0$C for 2 hours. After 2 hrs of reaction, blocking agent phenol was added to block the isocyanate terminated imide intermediate. The blocked prepolymer was then mixed with the aliphatic triepoxy (synthesised as per VSSC document) in 1:1 equivalents ratio along with 1% of *HEXA*. The solvent was evaporated off. The high viscous reaction mixture was poured into mould and heated in oven in a flow of nitrogen at $160^0$C for 10 hrs to effect complete imidisation and oxazolidone formation. The reactions are shown in scheme 3.7. The advantage of the process is that elastomer slabs can be prepared easily. The properties are given in tables 3.18 and 3.19.

### 3.2.B.7. *Characterisation*

The imide-oxazolidones were characterised by IR spectrum, and elemental analysis. The thermal properties were measured by TGA. The mechanical properties of the films and slabs were determined by Instron UTM. A typical IR spectrum of the sample is shown in figure 3.9. The mechanical properties of the films of the set of polyurethane-imide-oxazolidones prepared by the imide-epoxy crosslinkers and

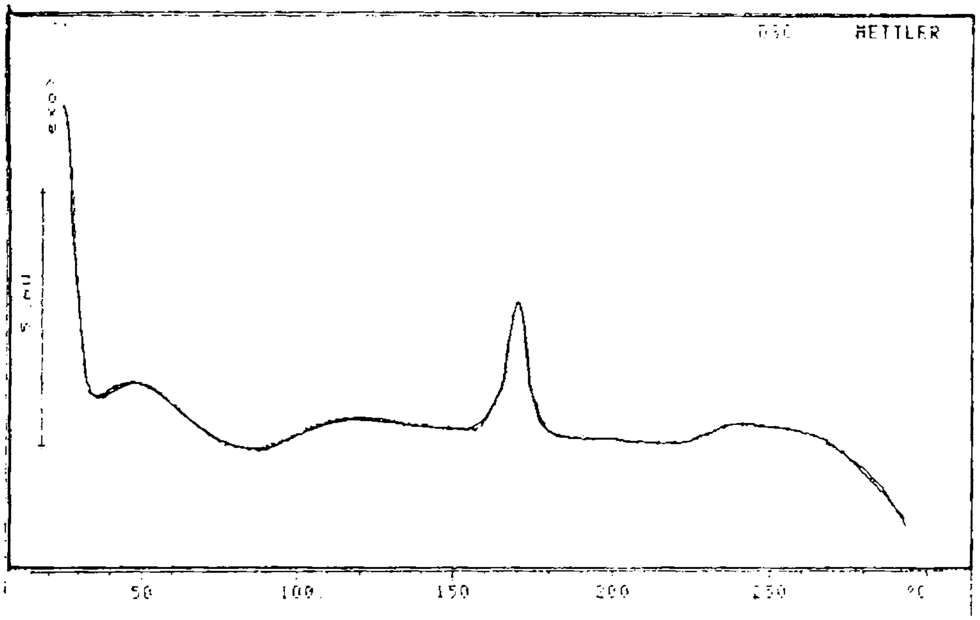


Fig.3.8 DSC thermogram of PU-Oxazolidone formation

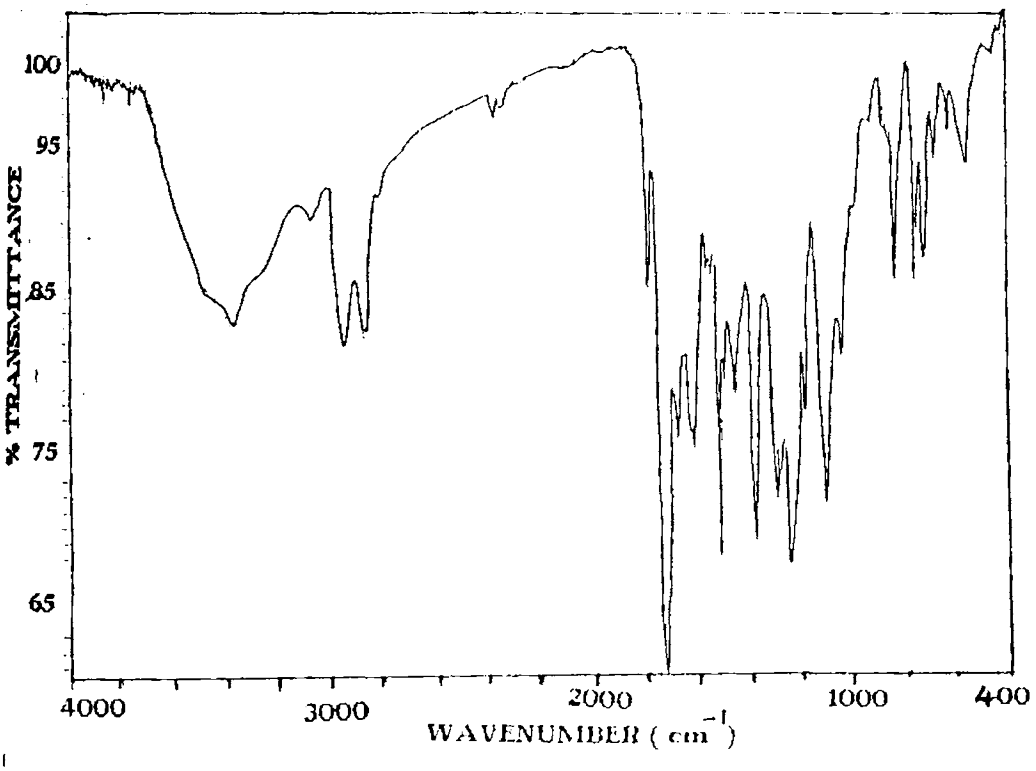
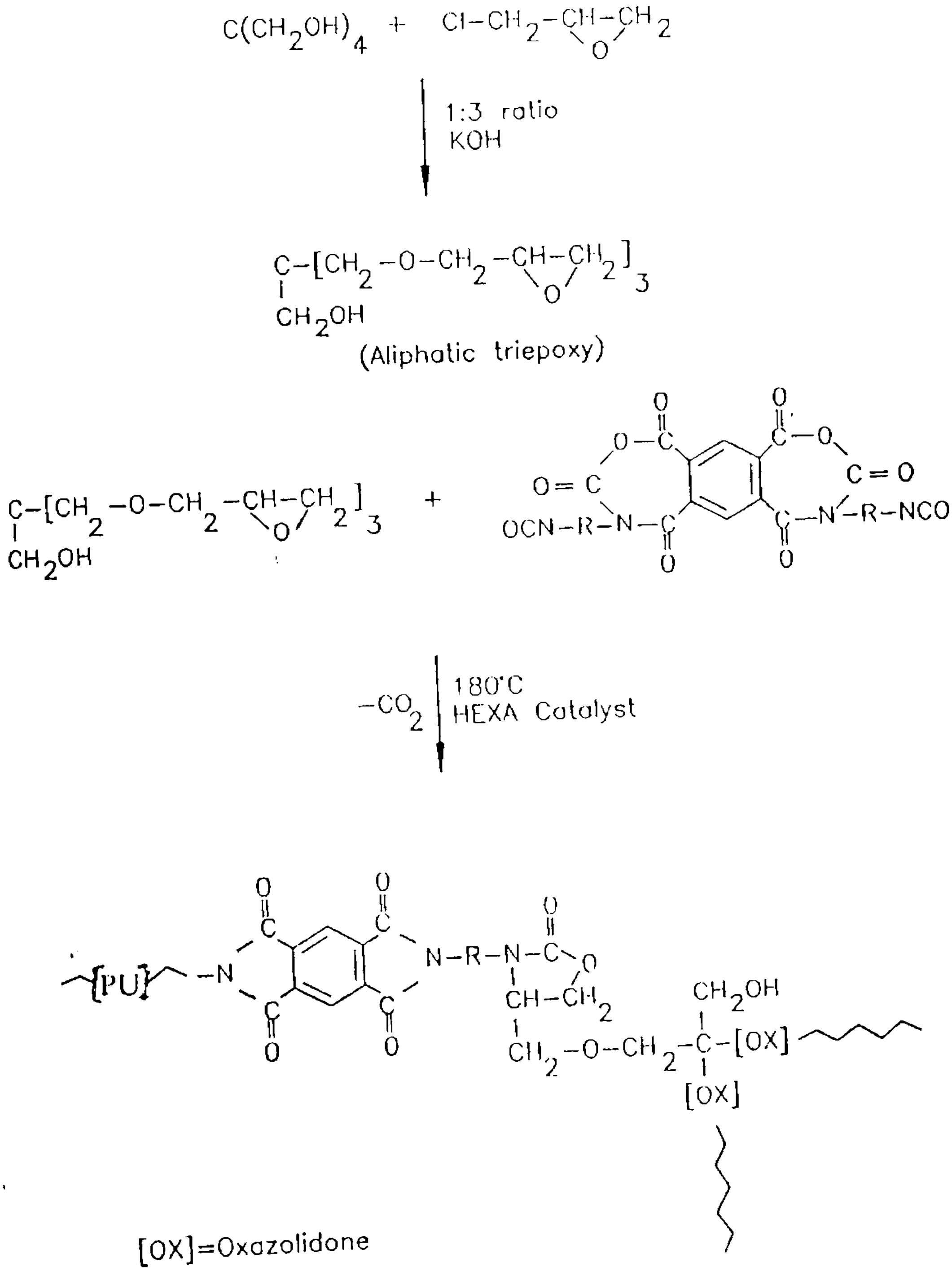


Fig.3.9 I.R Spectrum of PU-I-OX



$R = -[(CH_2)_2-O]_n-$ , $-[(CH_2)_4-O]_n-$ , $-[CH_2-CH=CH-CH_2]_n-$

Scheme.3.7 Crosslinked PUIOX formation from triepoxy-imide isocyanate prepolymer that of the slabs prepared using the imide-isocyanate prepolymer and the epoxy curative were determined separately and the values are presented in table 3.18.

The thermal stability of the oxazolidone copolymer was evaluated by thermogravimetric analysis. The initial decomposition temperature and the peak decomposition temperature were measured and compared with the base polyurethane and the corresponding polyurethane-imides. The improvement in thermal stability caused by the new structures exemplified for a typical system based on HTPB was examined by dynamic TGA and also by isothermal aging studies.

### 3.2.B.8 *Isothermal aging studies of HTPB - imide oxazolidone copolymer*

Inorder to study the thermal stability of HTPB-PU imide- oxazolidone system, the thermal aging studies were carried out. The samples of PUIOX-(3), PUI and PU as shown in table 18 were subjected to accelerated thermal aging by heating at 210°C and 225°C for 20 hrs. The variation in mechanical properties were measured and the weight-loss due to the heating monitered and the data are presented in table-20. The measurement was done using the polymer slabs which was heated in a tubular furnace in a flow of argon. The weight-loss of the samples was taken as a measure of thermal stability of the polymer and it was measured by weighing the samples, before and after heating.

### 3.2.B.9. *Variation of molar ratio of prepolymer : imide diepoxy crosslinker.*

The molar ratio of imide-diepoxy to prepolymer was varied from 1:1, 1:15 to 1:2. The mechanical properties of the resultant polyurethane-oxazolidone were determined. It was found that the tensile strength reached maximum value of 8.0

M.Pa at 1:2 ratio. The values of sol content shows that crosslinking is maximum at the ratio 1:2. The results are given in table 3.17.

**Table 3.17: Effect of imide-diepoxy : prepolymer ratio on properties.**

| Sl.no | molar ratio | T.S.(MPa) | Elongation (%) | Sol content (%) |
|---|---|---|---|---|
| 1 | 1:1 | 3.5 | 360 | 90 |
| 2 | 1:1.5 | 6.8 | 275 | 65 |
| 3 | 1:2 | 8.0 | 200 | 15 |

The studies reported on polyoxazolidones by Uribe and Hodd[17] has employed a molar ratio of 1:1 for polyoxazolidone formation. However due to the difunctionality, the polymer obtained was linear that softened at around 180°C. The use of imide diepoxy crosslinker gives a fully crosslinked polyoxazolidone due to the presence of two hydroxyl groups also in the crosslinker which can react with isocyanate. This has been confirmed also by the increase in strength properties at the molar ratio of 1:2. Hence the imide-diepoxy helps maximum crosslinking leading to a higher tensile strength. The mechanical properties can be controlled by varying the molar ratio of the reactants.

### 3.2.B.10. *Evaluation of adhesive properties*

Adhesive properties of the imide-oxazolidone modified polyurethanes were measured by lap shear strength and compared with the neat polyurethane and polyurethane-imide. The measurement was done as follows. Two aluminium plates of about 1 inch width, 6 inch length and 2 mm thickness were cleaned well. On one end of each plate, about 1 inch portion was etched with chromic acid, washed well and dried. A thin layer of the polyurethane of polyoxytetramethylene glycol (POTMG, a polyether polyol of 2000 molecular weight) with TDI and TMP was applied and joined and allowed to cure at room temperature for 24 hours and at 60°C for 8 hours. The process was repeated with PUI and PUI-OX resins. They are allowed to cure at 160°C for 15 hrs. The lapshear strength (LSS) for all three specimens were determined and the results are presented in table 3.21. The LSS is taken as a meausre of the adhesive property of the resins.

### 3.2.C. Results and discussion

The change in mechanical and thermal properties effected by incorporation of imide and oxazolidone units in the polyurethane chain were studied and the data presented in table 18. As the polyurethane-imide-oxazolidones of polyethylene glycol of lower molecular weights (like 400 & 600) were not elastomeric, the studies were limited to hydroxyl terminated polybutadiene. The incorporation of imide and oxazolidone groups in polyurethane although doesnot improve significantly the temperature of onset of decomposition, the rate of thermal degradation at higher temperatures was significantly reduced. The modification of polyurethanes by imide and oxazolidone affects the mechanical properties of polyurethanes. The hetrocyclic groups being highly polar and rigid the flexibility of the chain is affected causing the elongation to decrease and correspondingly modulus to increase as the polar groups add to the enchanced cohesive force by way of dipole - induced interactions. The mechanical and thermal properties of the films of imide-oxazolidone and that of the polyurethane imide and the polyurethane are presented in the table 3.19. The results of the study indicate that the increase of hard segment in the chain increases the tensile strength and the initial decomposition temperature. Similarly the weight fraction of the residue at 600°C (chosen as the standard) is correspondingly increased as the hard segment content is increased. Incorporation of the oxazolidone group in the polyurethane-imide increases the strength and thermal properties further. The tensile strength of the polyurethane-imide-oxazolidone in all cases studied were higher and elongation lower than the corresponding polyurethane imides. The magnitude of these properties can be arranged in the order, PU - IOX > PUI > PU

The comparative thermal stabilities of three systems evaluated from their thermograms are presented in figure 3.10

The comparative values of the strength properties and the thermal stability for the various samples given in table 3.18 shows that the modification of the polybutadiene based urethane backbone in a typical case with imide and imide oxazolidone has led to sharp improvement in the tensile properties.

**Table 3.18 : Thermal and mechanical properties of HTPB based polyurethane-imide oxazolidones**

| Sl. No | Polymer Type | T.S. (M.Pa) | Eln: (%) | Mod: (M.Pa) | $T_g$ (°C) | IDT (°C) | Weight fraction at 600°C | char (%) |
|---|---|---|---|---|---|---|---|---|
| *1. | PU | 1.8 | 410 | 1.1 | --60 | 275 | Nil | Nil |
| 2. | PUI | 5.3 | 325 | 2.3 | --30 | 290 | 30 | 15 |
| 3. | PUIOX(1) | 6.1 | 265 | 2.9 | -- | 300 | 35 | 15 |
| 4. | PUIOX(2) | 7.6 | 225 | 3.2 | -- | 315 | 38 | 20 |
| 5. | PUIOX(3) | 8.0 | 195 | 4.2 | --35 | 315 | 40 | 25 |

* HTPB polyurethane with IPDI/TMP

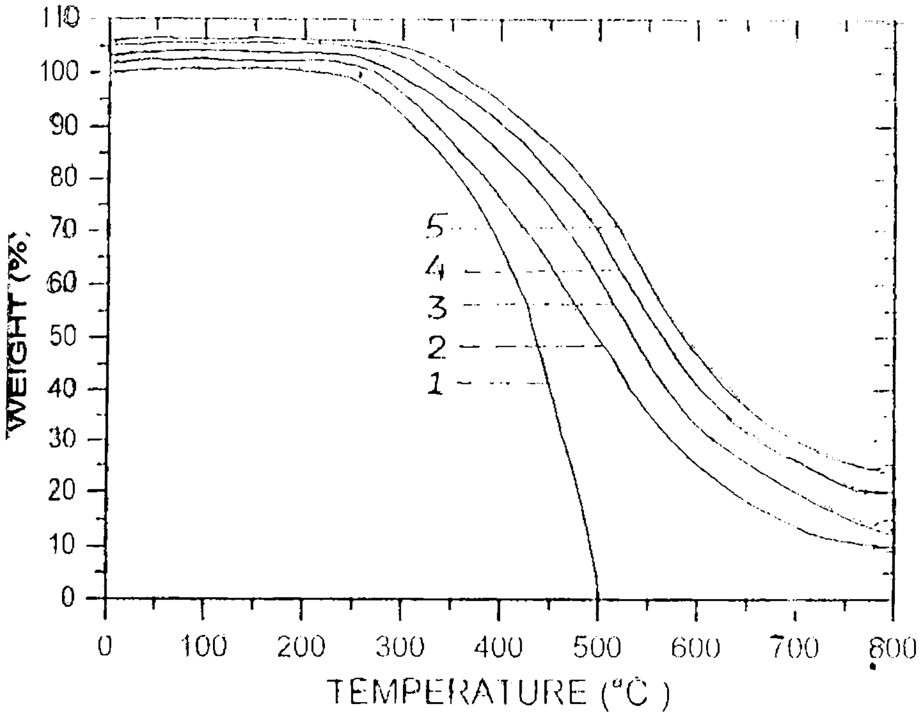


Fig.3·10 Thermograms of PUUI and PUIOX in $N_2$ . Heating rate - 10°C. sample ref. nos. 1 to 5 given in table -18

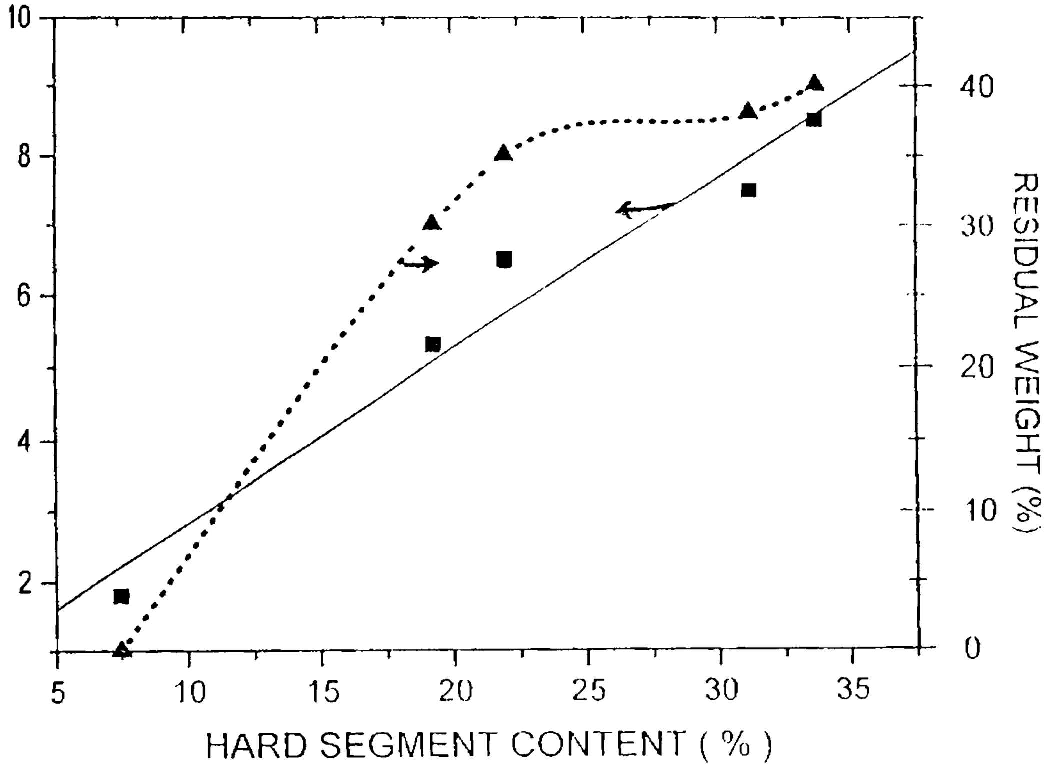


Fig. 3.11 Variation of residual weight % at 600°C and tensile strength with hard segment content

PUI = HTPB based polyurethane urea-imide

PUIOX-(1) = HTPB/ PU - oxazolidone by imide urethane prepolymer - triepoxy crosslinkers

PUIOX-(2) = HTPB/ PU -oxazolidone using *ABA* derived imide diepoxy crosslinkers

PUIOX-(3) = HTPB/PU- oxazolidone using MABA derived imide diepoxy corsslinker.

There is two fold increase in the tensile strength from the PU sample to PUI sample followed by a residual weight fraction of 30% at 600°C. The initial decomposition temperature (temperature at which 5% weight loss occurs) is increased by 15°C. There is a further 50% increase in tensile strength over the PUI as the oxazolidone group is introduced in the PUI chain. The elongation has correspondingly decreased. Among the three different imide-oxazolidones studied, the sample with aromatic acid derived imide diepoxy curative gave the maximum strength and thermal properties. This is due to the chain stiffening rigid aromatic group and thermal stability effects of the aromatic imide units. The glass transition temperature is the lowest for the neat polyurethane and Tg is eleviated by incorporation of imide and oxazolidone units. The char residue is seen after 600°C when TGA is done in nitrogen due to the presence of more aromatic groups.

**Table 3.19: Variation of tensile strength and thermal stability with hard segment content in HTPB based polyurethane - IOX**

| Sl. no. | Polymer type | Hard segment (%) | T.S. (MPa) | Weight fraction (%) at 600°C |
|---|---|---|---|---|
| 1 | PU | 7.5 | 1.8 | Nil |
| 2. | PUI | 19.3 | 5.3 | 30 |
| 3. | PUIOX - (1) | 22.0 | 6.5 | 35 |
| 4. | PUIOX - (2) | 31.3 | 7.0 | 38 |
| 5. | PUIOX - (3) | 33.7 | 8.5 | 40 |

The relative increase in strength and the weight fraction remaining at 600°C against the hard segment content (a combination of urethane, imide and oxazolidone) in figure 3.11 shows the effect of imide and oxazolidone group in improving the thermal and mechanical properties of the modified polyurethanes.

**Table 3.20: Temperature dependency of mechanical properties and weight loss for various HTPB/PU systems.**

| Sl. No. | System | Temp. (°C) | T.S. (MPa) | Loss in T.S (%) | Elongn: (%) | Loss in Eln: (%) | Wt: loss (%) |
|---|---|---|---|---|---|---|---|
| 1. | PU | RT | 1.8 | - - | 410 | -- | -- |
| | | 210 | 1.6 | 25 | 325 | 20 | 25 |
| | | 225 | 1.1 | 39 | 285 | 30 | 30 |
| 2. | PUI | RT | 5.3 | - - | 325 | - - | - - |
| | | 210 | 4.8 | 12 | 305 | 7.1 | 10 |
| | | 225 | 4.2 | 20 | 290 | 16 | 13.5 |
| 3. | PUIOX -(3) | RT | 8.5 | - - | 195 | - - | - - |
| | | 210 | 7.8 | 10.5 | 190 | 2.5 | 5.5 |
| | | 225 | 7.1 | 17.5 | 180 | 7.8 | 8.5 |

The results of the isothermal aging studies (table 3.20) show that the loss in tensile strength and elongation on isothermal aging at 210 and 225°C is correspondingly reduced as the hard segment content is increased from urethane to imide and subsequently to imide-oxzolidone. This result is an indication of the thermal stabilising effects of the imide-oxazolidone combination in polyurethane chain.

Adhesive properties of polyurethanes are important in certain applications. The adhesive property depends mainly on the backbone structure and the specific groups present. Polar groups generally improve this property. With a view to asess the effect of structural modifications on this property, the adhesive property of three types of polyurethanes based on HTPB were measured by LSS and presented in table 3.21.

**Table 3.21:** **Adhesive characteristics of typical modiified polyurethane based on HTPB.**

| Sl No. | Polymer Type | LSS (KSC) |
|---|---|---|
| 1 | PU | 30.5 |
| 2 | PUI | 38.2 |
| 3 | PUI-OX | 42.5 |

Although the absolute values of LSS are not high, a remarkable improvement in LSS can be noted as a consequence of introducing the imide and imide-oxazolidone moieties. The increase in LSS is about 35% over the neat polyurethane which is due to the higher content of polar groups present in the chain on modification.

### 3.2.D. Conclusions

Polyurethanes bearing imide and oxazolidone groups in the backbone could be realised through novel imide diepoxy crosslinkers and imide prepolymer - triepoxy reaction. The mechanical properties of polyurethane-imide-oxazolidones were found to be dependent on the ratio of reactants. The results of the studies conducted on imide-oxazolidone modified polyurethanes indicates that a combination both of imide and oxazolidone in a polyurethane chain is much more conducive in improving the thermal and mechanical properties of the polyurethane system than imide alone. This is due to the polar and thermally stable nature of imide and oxazolidone group. The effect is reflected also in the adhesive strength of the imide oxazolidone modified polyurethane systems. The tensile strength and thermal properties were higher for the oxazolidone system prepared via the imide - epoxy chain extender/crosslinker than with the imide-isocyanate prepolymer cured aliphatic triepoxy. This difference can be attributed to the presence of more number of thermally stable aromatic and imide rings in the former.

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# Chapter IV

## CHAPTER IV

# POLYURETHANES WITH THERMALLY STABLE GROUPS VIA CROSSLINKING AGENTS

### INTRODUCTION

The improvement of thermal stability of polyurethanes by chain modification using thermally stable groups like imide and oxazolidone was presented in the previous chapter. Another method of introduction of thermally stable groups in the chain for improvement of thermal stability is by the use of hetrocyclic crosslinking agents(CLA) in place of conventional crosslinking agents like glycerol and trimethylol propane used for polyurethane preparation. The synthesis of low molecular weight triols having hetrocyclic groups which are miscible with polyols and can be easily used as a CLA in polyurethanes is of great importance. The crosslinker triols or tetraols should easily react with the diisocyanate under normal conditions and should become a part of the crosslinker network. The extent of crosslinking in a polymer which also controls mechanical properties and thermal stability can be varied by adjustment of the type and level of crosslinking agent. Similarly, the extent of thermally stable groups in the polymer can be increased by increasing the level of CLA. The present chapter concerns the introduction of thermally stable groups, phosphazene and triazene into the polyurethane chain through CLA based on these groups and the study of thermal and mechanical properties of the resultant polyurethane networks. The information on the use of heterocyclic crosslinkers in literature are scanty. Triazene containing isocyanates and triols and the crosslinked polyurethanes therefrom have been reported[1,2]. These polymers are crystalline compounds with good flame retardant properties. Polyurethanes with polyether and polybutadiene backbones having triazene and imide-triazene by the use of triazene and imide-triazene crosslinkers have however not been reported. In this study, we have specifically chosen cyclotriphosphazene and triazene as the basic hetrocyclic groups due to their favourable thermal characteristics[3]. The combination of triazene and imide group in the polyurethane chain has also been tried by the use of a novel maleimido-triazene crosslinker synthesised and incorporated in the chain as a chain extender cum crosslinking agent.

## SECTION - 1

## 4.1. PHOSPHAZENE - CONTAINING POLYURETHANES

### 4.1.A. Introduction

In this section of the chapter, the use of phosphazene- containing triols and tetraols as crosslinking agents in various polyurethane system with an aim to introduce phosphazene units in the chain is described. Phosphazene-triols and tetraols designated as PN-3 and PN-4 were synthesised starting from phosphonitrilic chloride trimer (hexachloro triphosphazene) by reaction with 2-ethylaminoethanol. Cyclophosphazene with hydroxyl groups have been reported to be prepared by methylol substitution.[4]. The triol and tetraol differs in number of crosslinking sites and hence tetraol gives a more tightly crosslinked structure. The increase in crosslinking density increases the mechanical and thermal properties.

Cyclotriphosphazene-containing trihydroxy and tetrahydroxy compounds synthesised starting from phosphonitrilic chloride trimer were characterised and were examined as crosslinking agents in polyurethane systems constituted independently with polyether polyols such as polyethylene glycol (PEG) and polyoxytetramethylene glycol (POTMG) and polybutadiene polyol (HTPB) with 2,4-tolylene disocyanate as curing agent. The effect of the nature and concentration of the crosslinking agent on the mechanical and thermal characteristics of the polyurethane network was studied and the results are compared with the system having trimethylol propane (TMP) as crosslinking agent.

## 4.1.B Experimental

### 4.1.B.1 *Materials*

1) Hexachlorocyclotriphosphazene (HCP) - Synthesised in VSSC by reported procedure[5]

2) Polyethylene glycol (PEG), Molecular weight-1000, OH value 110 to 120 mgm KOH/g (BDH).

3) Polyoxytetramethylene glycol (POTMG) (BASF) molecular weight- 2000 (OH value 55 to 58 mgm KOH/g).

4) Hydroxy terminated polybutadiene (HTPB) molecular wt: 2800-3000. (OH value 45 to 50 mgm KOH/g) of M/s NOCIL, Bombay

5) Tolylene diisocyanate (Bayer, Germany)

6) 2-Ethylaminoethanol (Fluka, Germany)

### 4.1.B.2 *Purification of raw materials*

Hexachlorocyclophosphazene or phosphontrilic chloride trimer was synthesised as per the reported procedure by the reaction of phosphorous pentachloride and ammonium chloride in a chlorinated solvent. The reaction is given in scheme41. $(PNCl_2)_3$ obtained which is a mixture of trimer, tetramer and oligomers was separated by sublimation. Fractional sublimation is a suitable method of separation of trimer from higher homologues. The crude product was sublimed to separate the trimer. The purity was checked by I.R spectrum where the peak at $1350 cm^{-1}$ due to the tetramer was absent. Pure HCP is a white crystalline [illegible] melting at 114°C. The melting point of tetramer is 123.5°C. The purity was checked by melting point. The polyols, POTMG and HTPB were dried by stirring under vacuum at 60-70°C for 3 hrs. PEG was dried by azeotropic distillation with benzene to remove the moisture present. Solvents such as chloroform and THF were dried by distillation after adding anhydrous calcium chloride. 2-Ethyl amino ethanol and TDI were used as received.

### 4.1.B.3 *Synthesis of cross linking agent (CLA) PN-3 and PN-4*

To 34.8 gms (0.1 mole) of HCP taken in a three necked flask, 100 ml of dry chloroform was added. Triethyl amine (30.4 gms, 0.3 mole) was added to absorb the liberated HCl during reaction. The system was stirred magnetically and kept cooled at 10°C with an icebath. A solution of 26.4 gms (0.3 mole) of 2-ethyl amino ethanol in 25 ml of chloroform was added dropwise over a period of 2 hrs. The mixture was stirred for a further period of 1 hr. The solution was washed with cold water to remove the triethyl amine hydrochloride and then dried over anhydrous sodium sulphate. Chloroform was removed by a flash evaporator at room temperature to avoid crosslinking of the product. The quantity of PN-3 crosslinker obtained was 35 gms as a white waxy solid melting around 65°C (yield = 70%). The tetrafunctional derivative PN-4 was prepared in a similar way using a 1:4 molar ratio of HCP and amino ethanol. The product PN-4 obtained was 40 gms as a white waxy solid melting at round 75°C (yield = 71.3%). The reaction for the synthesis of PN-3 and PN-4 are as given in scheme 4.1

### 4.1.B.4 *Synthesis of Polyurethanes*

The crosslinking agents TMP, PN-3 or PN-4 was mixed with the polyols in the required ratio using THF as a common solvent. The solvent was removed later under vacuum at room temperature. Polyurethane slabs were prepared by mixing with TDI in presence 0.2 wt% of dibutyltindilaurate as catalyst. After deaeration, it was cured at room temperature for 24 hrs and then at 60°C for 8 hrs. The isocyanate index (NCO/OH ratio) was kept as 0.9 in all cases to avoid secondary crosslinks.

The reaction is as given in scheme 4.2.

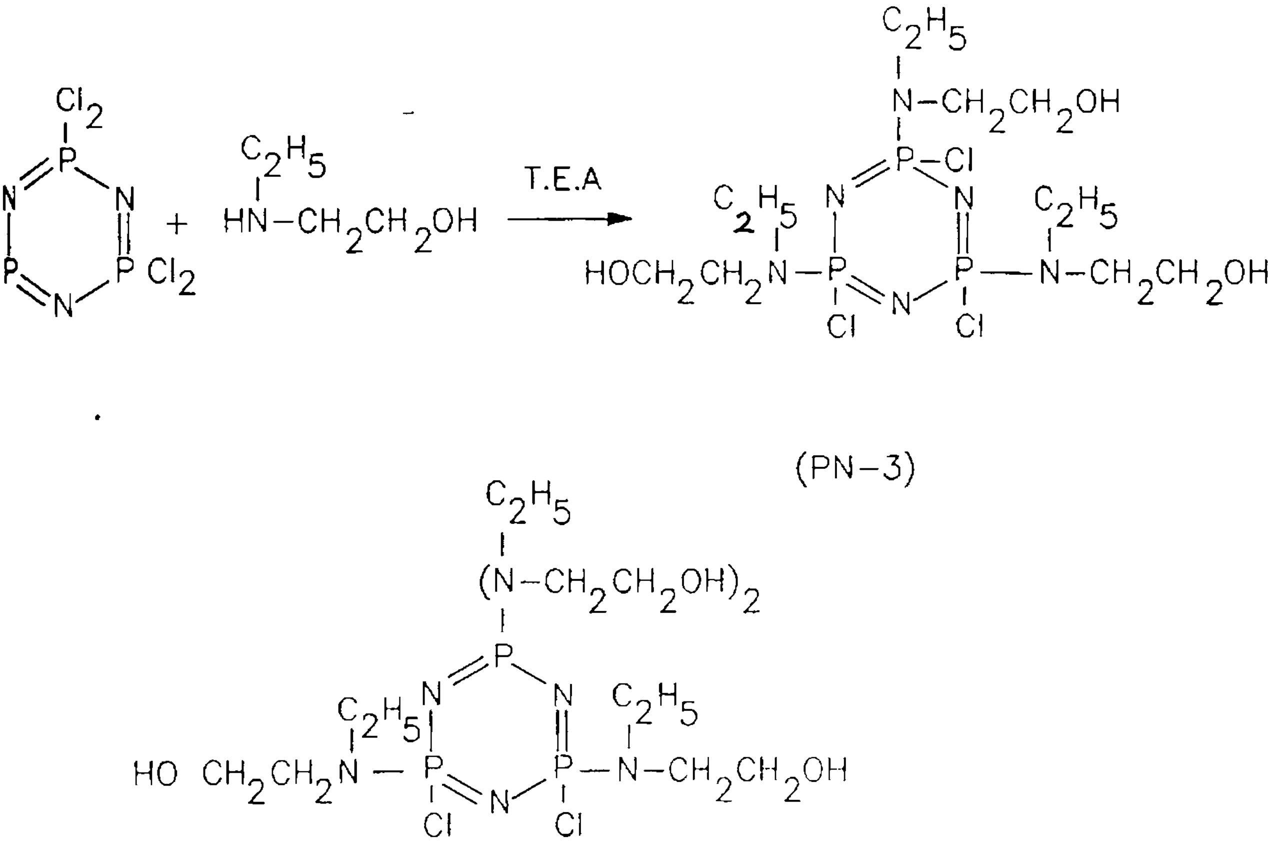
### 4.1.B.5. *Characterisation*

The CLA's were characterised by IR spectrum given in fig.4.1, CHN analysis, molecular weight (Knauer VPO) and chemical analysis of hydroxyl value and acid value. Mechanical properties of polyurethane were determined by instrom UTM. The products were characterised by elemental analysis which gave the direct indication of the degree of substitution which were further confirmed from molecular weight determined by VPO and estimation of hydroxyl value. The results are tabulated in tables 4.1 and 4.2. The degree of substitution was calculated from the elemental analysis data. (ex: C % and N %) as follows:

The empirical formula is $P_3N_3Cl_{(6-x)}(N\text{-}CH_2CH_2OH)_x$, where x is the degree of substitution of chlorine by amine

$$\%C = \frac{48x \ 100}{(348 + 52.5x)}$$

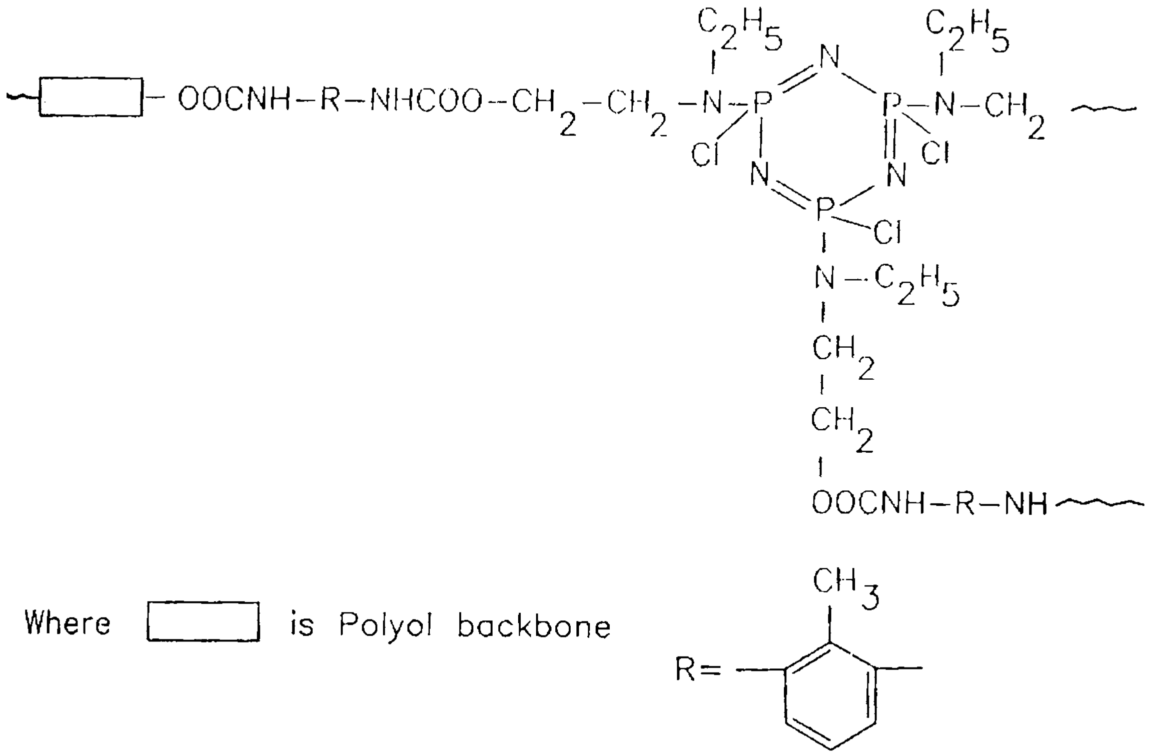
$$PCl_5 + NH_4Cl \longrightarrow (PNCl_2)_3 + HCl$$



(PN-3)

(PN-4)

Scheme 4.1 : Synthesis of phosphazene crosslinkers



Scheme 4.2 : Synthesis of polyurethane with phosphazene crosslinker

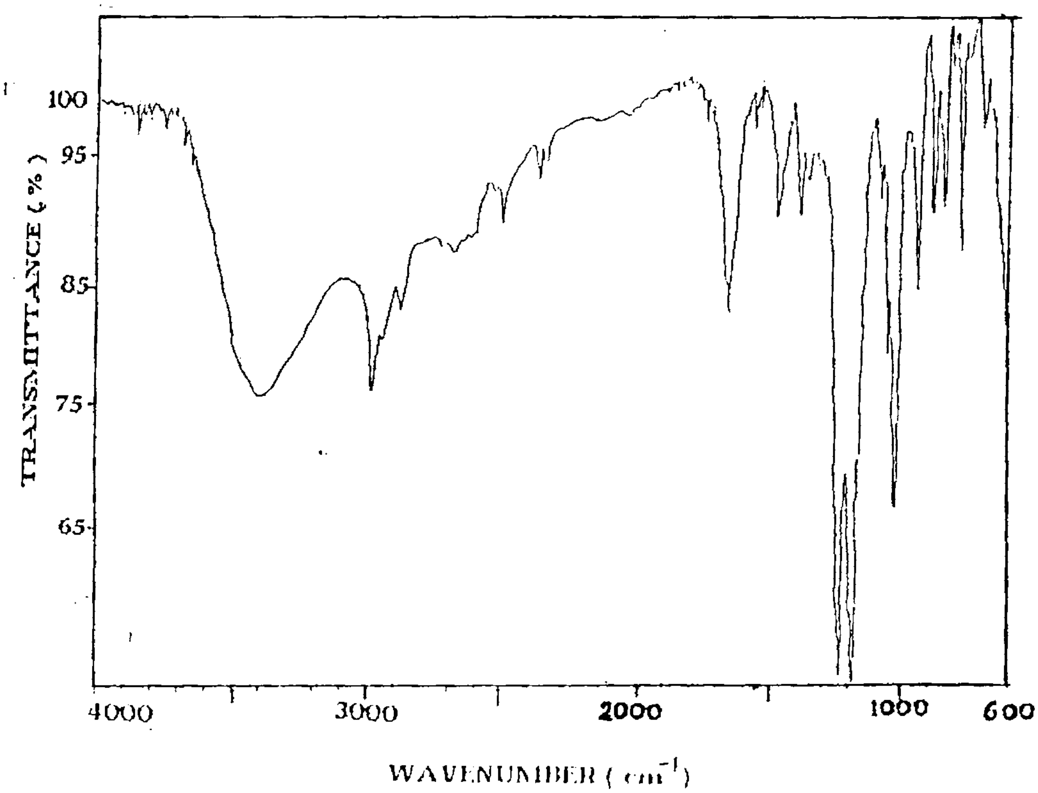


Fig. 4.1 : I.R. Spectrum of phosphazene triol (PN-3)

x could the calculated from the C % and values given in table 4.2.

**Table.4.1 Characterisation of phosphazene triols and tetraols (values in brackets show theoretical ones)**

| Sample | Acid value mgm KOH/gm | Hydroxyl value (mgm KOH/gm) | Mol: weight (by VPO) | OH functionality (average) |
|---|---|---|---|---|
| PN-3 | 0.3<br>(0.00) | 335<br>(350) | 485<br>(504) | 2.90 |
| PN-4 | 0.5<br>(0.0) | 385<br>(400) | 570<br>(558) | 3.95 |

The experimental values are in close agreement with the theoretical values within experimental error.

The hydroxyl functionalities observed are in agreement with the theoretical values of 3 and 4 respectively for PN-3 and PN-4. The acid values are minimum showing negligible hydrolysis of the product. The estimation of functionality through the hydroxyl value and molecular weight and the degree of substitution calculated from C-content all clearly support the expected structure of PN-3 and PN-4. Although aminoethanol is an ambident nucleophile towards $(PNCl_2)_3$, amino group is several times more reactive than OH group. This results in exclusive reaction of P-Cl with NH group leading to the -OH derivative. The elemental analysis results and the functionality calculated from C% are given in table 4.2.

**Table 4.2 : Elemental analyis results and functionality (theoretical values given in brackets)**

| Sl. No. | CLA | C% | H% | N% | $F_{av}$ (from C%) |
|---|---|---|---|---|---|
| 1 | PN-3 | 27.9<br>(28.5) | 5.8<br>(6) | 17.3<br>(17) | 2.87<br>(3) |
| 2 | PN-4 | 32.5<br>(34) | 6.5<br>(7.1) | 17.8<br>(19) | 3.65<br>(4) |

The functionality calculated from the C% is in agreement with that calculated from hydroxyl value and molecular weight by VPO in table 4.1. The IR spectrum of PN-3 is given in figure 4.1. The peak at 1240 $cm^{-1}$ corresponds to P-N-P (asym.stretch) and 740$cm^{-1}$ (sym.stretch) and peak at 1200$cm^{-1}$ corresponds to P-N-C (asym.stretch) and 940 $cm^{-1}$ P-N-C (sym.stretch) The broad peak at 3600-3300 $cm^{-1}$ was indicative of the OH group

**Table 4. 3 : Characteristics of Polyols**

| Sl. No. | Polyol | Chemical structure | Molecular weight | OH value mgm KOH/g | $F_{av}$ |
|---|---|---|---|---|---|
| 1 | PEG | $HO(-CH_2-CH_2-O)_nH$ | 1000 | 112 | 2 |
| 2 | POTMG | $HO(-[CH_2]_4-O)_n-H$ | 2000 | 56 | 2 |
| 3 | HTPB | $HO(CH_2-CH=CH-CH_2)_n-OH$ | 2800 | 45 | 2.2 |

The characteristics of polyols used for synthesising polyurethanes with CLA in this study are given in table 4.3.

### 4.1.C. Results and Discussion

The PN-3 and PN-4 crosslinking agents were prepared as per the reaction given in scheme 4.1. The reaction of $(PNCl_2)_3$ and 2-ethylaminoethanol in 1:3 molar ratio gives preferentially a symetrical trisubstituted product. It is reported that the reaction of HCP with secondary amine gives the non geminal derivative[24]. The average functionality of PN-3 is 3. As it is difficult to isolate the possible by-product such as the difunctional and tetrafunctional derivatives, no attempt was made to isolate the trimer alone and the product was used as such.

#### 4.1.C.1 *Studies using the CLA for various PU Systems*

The above CLA's were co-cured with three typical polyols, the characteristics of which are given in table 4.3. The R value (NCO/OH ratio) of 0.9 and curing temperature 60°C avoids the formation of secondary crosslinks like allophanate, biuret etc.

#### 4.1.C.2 *Polyethylene glycol-based PU*

The CLA was incorporated in different equivalents ratio in PEG and cured with TDI keeping the R value as 0.9. The mechanical properties are compared with that of the network obtained using TMP as the CLA and the values are presented in table 4.4.

**Table 4.4: Physical and mechanical characteristics of PU systems based on PEG**

| Sl. No. | Poyol: CLA eq.ratio | CLA type | Weight % | T.S. (KSC) | Elogn: % | Hard: (Sh: A) | Sol % | Gel % | $T_g$ ($^oC$) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1:0.75 | TMP | 6.2 | 8.0 | 425 | 25 | 10 | 90 | -40 |
| | | PN-3 | 20.0 | 9.1 | 405 | 25 | 9 | 91 | -38 |
| | | PN-4 | 21.5 | 11.0 | 350 | 30 | 8 | 92 | -32 |
| 2 | 1:1 | TMP | 8.1 | 9.2 | 410 | 25 | 8 | 92 | -35 |
| | | PN-3 | 25.0 | 9.8 | 395 | 25 | 7 | 93 | - 30 |
| | | PN-4 | 27.1 | 13.0 | 300 | 40 | 5 | 95 | -28 |
| 3 | 1:1.5 | TMP | 11.8 | 10.0 | 350 | 35 | 7 | 93 | -32 |
| | | PN-3 | 33.5 | 11.5 | 335 | 35 | 6 | 94 | -30 |
| | | PN-4 | 35.8 | 13.0 | 300 | 40 | 5 | 95 | -28 |
| 4 | 1:1.75 | TMP | 13.5 | 11.5 | 340 | 35 | 5 | 95 | -30 |
| | | PN-3 | 37.5 | 12.2 | 328 | 40 | 4 | 96 | -27 |
| | | PN-4 | 39.5 | 15.0 | 285 | 45 | 4 | 96 | -27 |
| 5 | 1:2 | TMP | 15.3 | 12.5 | 310 | 45 | 4 | 96 | -31 |
| | | PN-3 | 40.2 | 13.3 | 300 | 45 | 3 | 97 | -25 |
| | | PN-4 | 42.4 | 18.0 | 245 | 45 | 3 | 97 | -20 |

The sol and gel content were analysed by swelling in toluene, extracting and weighing the extent of non crosslinked fractions. The results are also included in the same table. The glass transition temperatures of the samples measured by TMA are also presented.

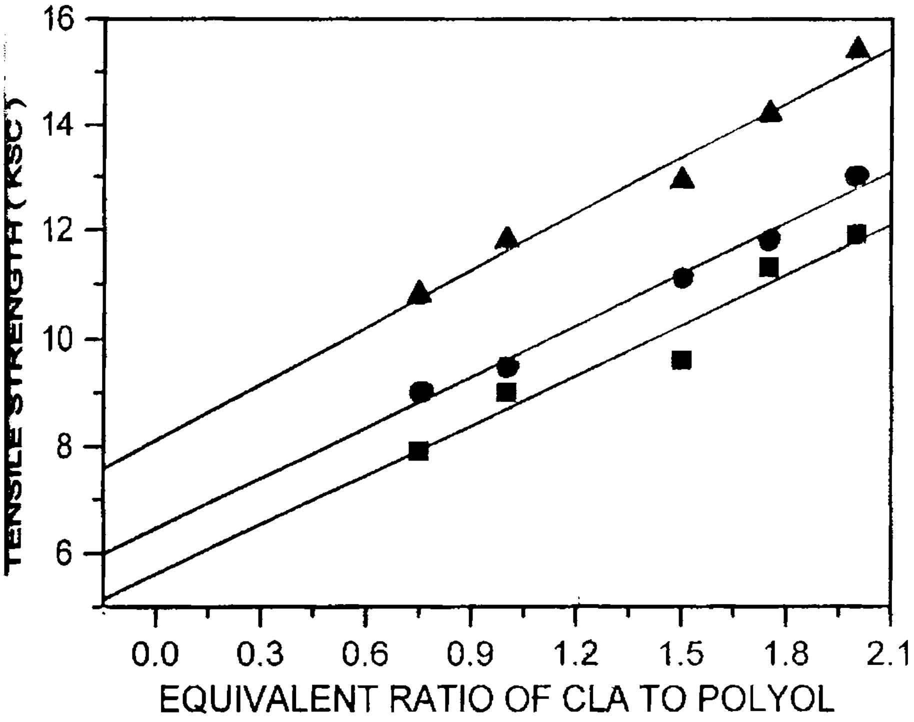


Fig.4.2 Variation of tensile strength with CLA concentration for PEG-PU system
( ■ TMP ● PN-3 ▲ PN-4)

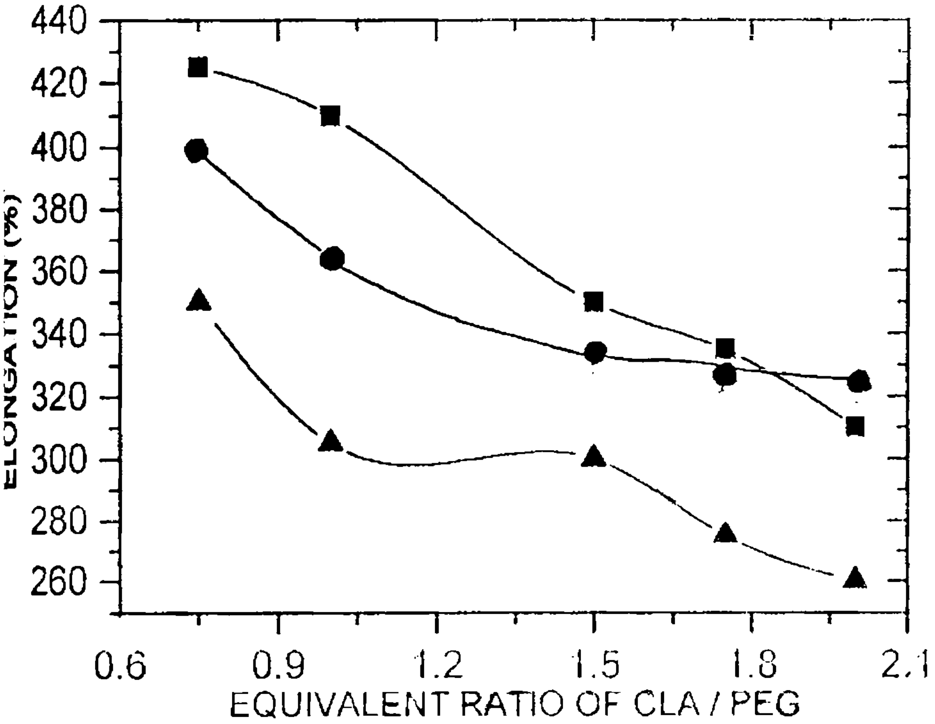


Fig.4.3 Variation of elongation with CLA concentration
(■TMP ●PN-3 ▲PN-4)

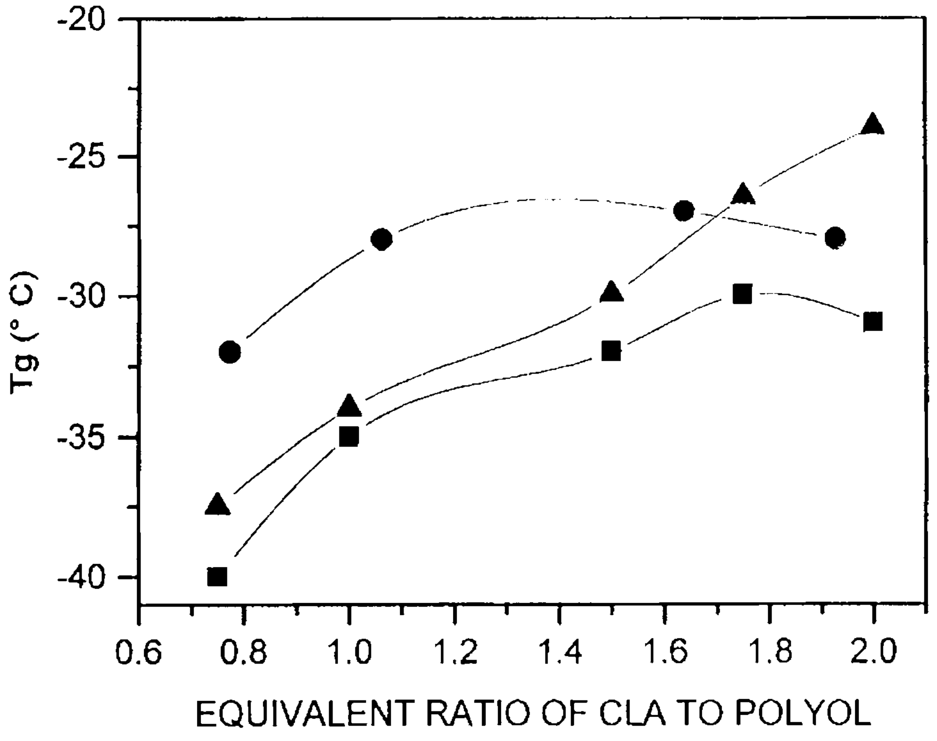


Fig.4.4 Variation of $T_g$ with CLA concentration
( ■ TMP ● PN-3 ▲ PN-4)

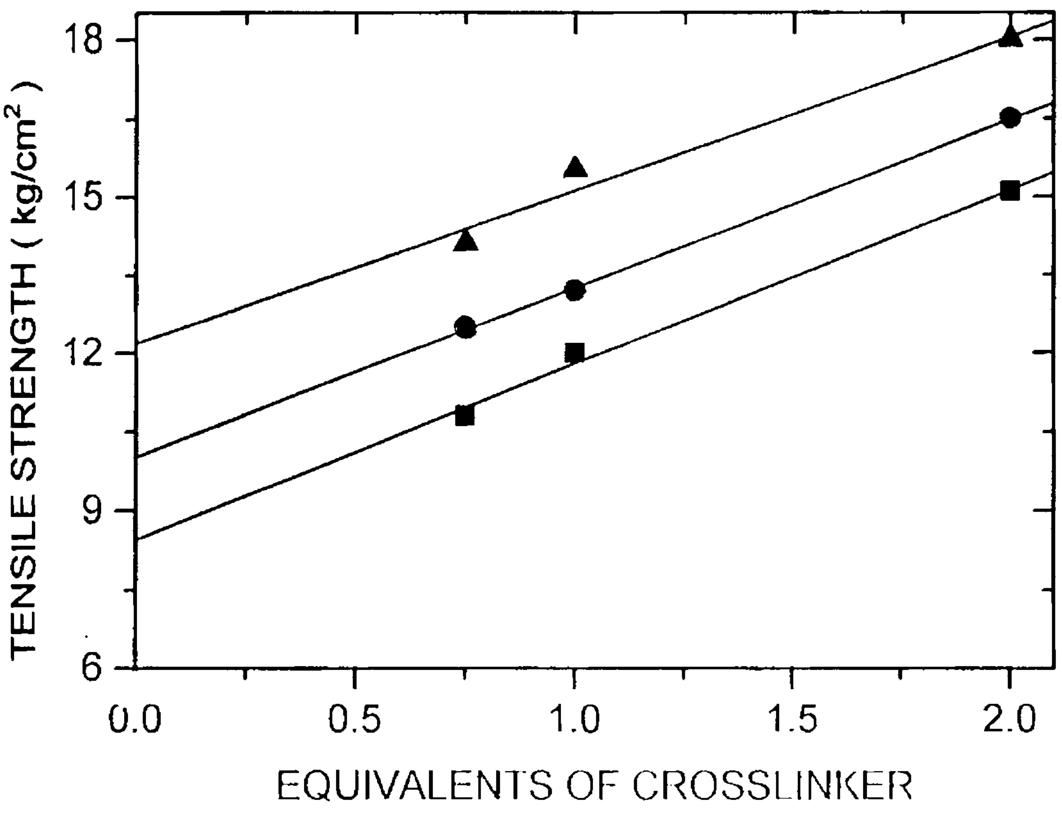


Fig.4.5 Variation of tensile strength with CLA concentration for POTMG-PU system (■TMP ● PN-3 ▲ PN-4)

It can be observed that as the quantity of CLA is increased there is a gradual increase of tensile strength, Tg and decrease of elongation as theoretically expected, due to increase in concentration of urethane groups and enhancement of crosslink dencity. The higher value of sol content and the hardness of the resultant polyurethane samples show that there is a uniform crosslinked net work as the crosslinker is varied from TMP to PN-3 and subsequently to PN-4. The dependency of mechanical properties on the concentration is presented in figs.4.2.and 4.3.

It can be observed from the curve that the effect on tensile strength by increase of concentration of CLA is more pronounced for PN-3 and PN-4 (vis - a - vis TMP) on an equivalent basis. This can be attributed to the structural difference in the crosslinking agents. Phosphazene presents rigid ring structures in contrast to TMP at the crosslinking junction. There could be contribution from the higher functionality present in the former, providing highly crosslinked junction randomly.

Above an equivalents ratio of 2, the polymer and CLA starts to separate and hence studies were limited to the ratio up to 2.

The effect of concentration of CLA on increase of Tg is shown in the fig.4.4. The progressive increase in Tg with concentration of the CLA can be noted. The trend follows the one in mechanical properties. The evolution in hardness value is in strict conformation to that in tensile strength. The system tends to be stiffer on increasing the concentration of CLA. The same set of studies were conducted using HTPB and POTMG as the polyols. The results of the study are presented in tables 4.5 and 4.6.

**Table 4.5 Physical and mechanical characteristics of PU systems based on POTMG**

| Sl. No. | Poyol: CLA eq.ratio | CLA type % | Weight | T.S. (KSC) | Elogn: % | Hard: (Sh:A) | Sol % | Gel % | Tg (° C) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1:0.75 | TMP | 2.7 | 10.8 | 580 | 30 | 5 | 95 | -71 |
| | | PN-3 | 8.5 | 12.5 | 552 | 35 | 5 | 95 | -69 |
| | | PN-4 | 10.5 | 14.1 | 520 | 35 | 5 | 95 | -60 |
| 2 | 1:1 | TMP | 3.8 | 12.0 | 535 | 35 | 4 | 96 | -- |
| | | PN-3 | 12.0 | 13.2 | 510 | 40 | 5 | 95 | -- |
| | | PN-4 | 13.5 | 15.5 | 492 | 45 | 3 | 97 | -55 |
| 3 | 1:2 | TMP | 7.5 | 15.1 | 495 | 40 | 3 | 97 | -65 |
| | | PN-3 | 26.0 | 16.5 | 480 | 45 | 2 | 98 | -57 |
| | | PN-4 | 27.0 | 18.0 | 405 | 45 | 29 | 8 | -51 |

**Table 4. 6: Physical and mechanical characteristics of PU system based on HTPB**

| Sl. No. | Poyol:CLA eq.ratio | CLA type | Weight % | T.S. (KSC) | Elogn: % | Hard: (Sh:A) | Sol % | Gel % | Tg (°c) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1:0.75 | TMP | 1.5 | 6.5 | 550 | 25 | 10 | 90 | -67 |
| | | PN-3 | 10.5 | 7.2 | 535 | 25 | 9 | 91 | -60 |
| | | PN-4 | 12.8 | 8.5 | 510 | 30 | 7 | 93 | -57 |
| 2. | 1:1 | TMP | 2.1 | 8.0 | 495 | 35 | 6 | 94 | -60 |
| | | PN-3 | 15.2 | 9.1 | 480 | 35 | 6 | 94 | -- |
| | | PN-4 | 18.0 | 11.3 | 462 | 40 | 5 | 95 | -48 |
| 3. | 1:2 | TMP | 2.6 | 10.5 | 410 | 40 | 3 | 97 | -55 |
| | | PN-3 | 21.0 | 12.3 | 386 | 45 | 2 | 98 | -47 |
| | | PN-4 | 27.6 | 15.6 | 325 | 45 | 2 | 98 | -40 |

The same trend of increase of tensile strength and glass transition temperature followed by decrease of elongation was observed for the samples of PU prepared from the two polyols POTMG and HTPB.

Results given tables 4.5,4.6 and 4.7 indicate that the improvement in tensile strength is the best for PN-4 followed by PN-3 and TMP. The trend between PN-3 and PN-4 are strictly in conformation to the theoretical expectations ie, PN-4 contains more number of crosslinking sites that can add to the tensile strength, hardness and $T_g$. On a quantitative basis, the efficiency of the crosslinking agent in enhancing the tensile strength of various systems can be obtained by a linear plot of tensile strength against the concentration of the crosslinker. This plot is shown in fig. 4.2, 4.5 and 4.6 for PEG, POTMG and HTPB for the three crosslinkers. The dependency of tensile strength on crosslinker concentration was found to be linear by the relationship $TS = TS_0 + E[X]$ where $TS_0$ is the strength of the material in the absence of the crosslinker and E, the efficiency factor of the crosslinker in enhancing the tensile strength of the network and x is the equivalent ratio of CLA to the polyol. The values of $TS_0$ and E are given in the table 4.7.

Calculations show that except for POTMG, the Efficiency of the CLA is in the order PN-4>PN-3>TMP. The relative increase in tensile strength for the three types of polyurethanes cured using the trifunctional crosslinked PN-3 was calculated over the reference crosslinking agent TMP and the data is presented in fig.4.7. As expected, the PN-3 crosslinker has shown a higher relative increase in tensile strength for the different equivalent ratios of crosslinker. The relative increase was higher for the polyurethane using HTPB as the polyol. The increase in tensile strength in the caseof PN crosslinker can be attributed to the increased cohesive

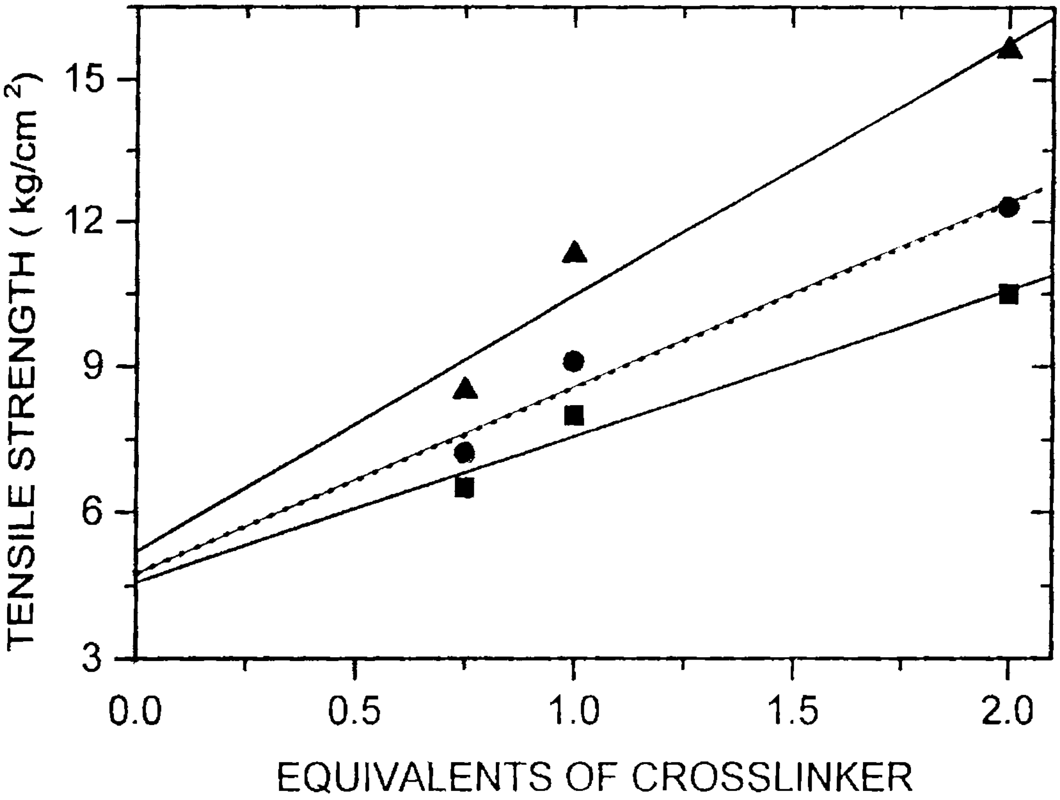


Fig.4.6 Variation of tensile strength with CLA concentration for HTPB-PU
(■-TMP ●-PN-3 ▲-PN-4 )

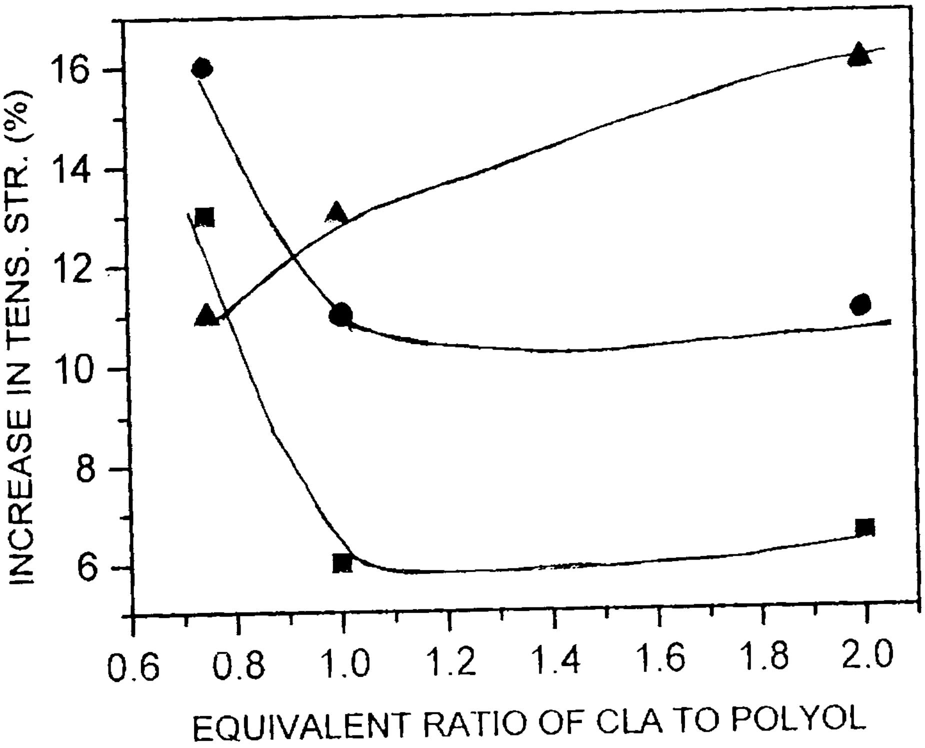


Fig.4.7 Relative improvement in tensile strength with PN-3 over TMP for three types of PU (■-PEG ●POTMG ▲-HTPB)

forces imparted by the presence of phosphorous, nitrogen and chlorine atoms present in the molecule.

**Table 4.7: Efficiency factor for various combinations of CLA and polyol**

| Polyol | Crosslinker | $TS_0$ | E | R* |
|---|---|---|---|---|
| PEG | TMP | 5.5 | 3.4 | 0.980 |
|  | PN-3 | 6.5 | 3.3 | 0.998 |
|  | PN-4 | 7.5 | 4.7 | 0.911 |
| POTMG | TMP | 8.5 | 3.3 | 0.996 |
|  | PN-3 | 10.0 | 3.2 | 0.999 |
|  | PN-4 | 12.2 | 3.0 | 0.985 |
| HTPB | TMP | 4.6 | 3.0 | 0.981 |
|  | PN-3 | 4.7 | 3.8 | 0.982 |
|  | PN-4 | 5.2 | 5.3 | 0.977 |

* correlation coefficient for the linear plot.

The presence of traces of tetrafunctional molecules in trifunctional derivative could also be a contributing factor. In the case of HTPB the better relative increase in tensile strength over the other two polyols, as the ratio of crosslinker is increased, is probably due to the better miscibility of the polyol with PN-crosslinker compared to the polyether polyols studied. Moreover, the poor miscibility of TMP with HTPB due to the hydrocarbon nature of the polyol could be another reason for the observed trend for this pair. The higher miscibility of HTPB with PN crosslinker ensures a uniform crosslinked network.

## 4.1.D. Thermal decomposition studies

Incorporation of phosphazene could be expected to lead to an improvement in thermal decomposition characteristics of the polyurethane network. The various PU systems were subjected to thermal analysis by TGA.

### 4.1.D.1. *PEG-PU system*

PEG has a peak decomposition temperature of about 360°C as reported. The PEG-PU starts decomposing at around 150°C due to the onset of dissociation of urethane groups and the decomposition of the backbone is completed at around 360°C. The initial decomposition temperature (IDT) is arbitrarly fixed as the temperature at which about 2% of the material is lost as the temperature is increased. The IDT values are found to be increased by introduction of phosphazene units in the chain. The introduction of P-N ring in the chain has enhanced the temperature of onset of decomposition. The peak decomposition temperature of back bone is also enhanced as seen from the TGA pattern. The typical TGA patterns for the three types of polyurethanes with TMP, PN-3 and PN-4 crosslinkers for an equivalent ratio of 1:2. are presented in fig.4.8 and fig.4.9. In the case of TMP-cured system, the decomposition is completed at around 360°C, whereas for PN-3 and PN-4 cured PU systems, the decomposition is not complete at this temperature and that the residue remaining above the peak decomposition temperature is about 30-40%. The details are presented in table 4.8.

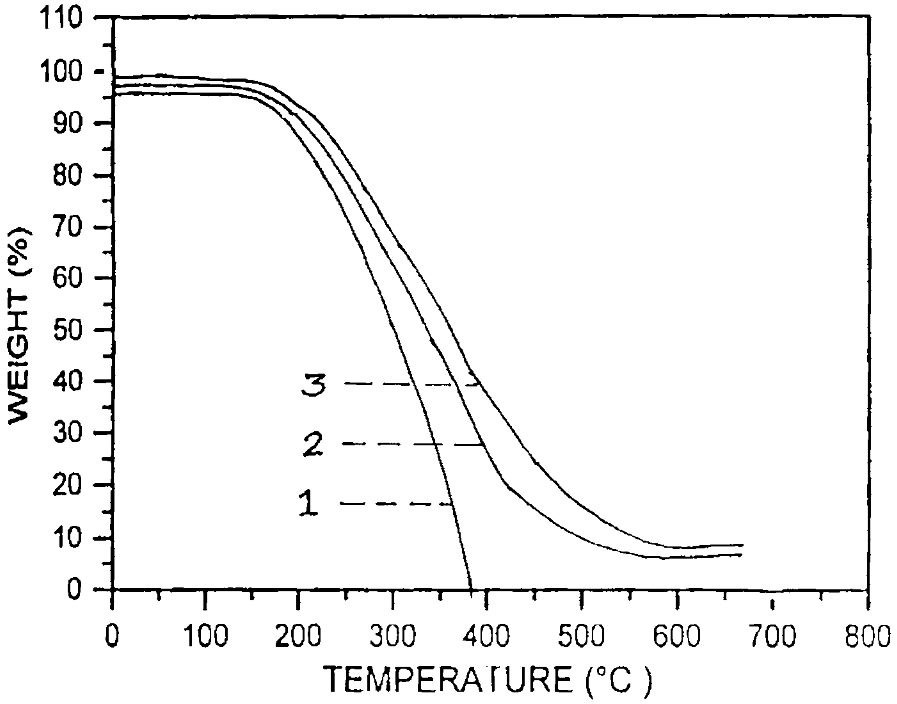


Fig.4.8 : Thermograms of PEG-Polyurethanes (①- TMP based, ②- PN-3 based, ③- PN-4 based)

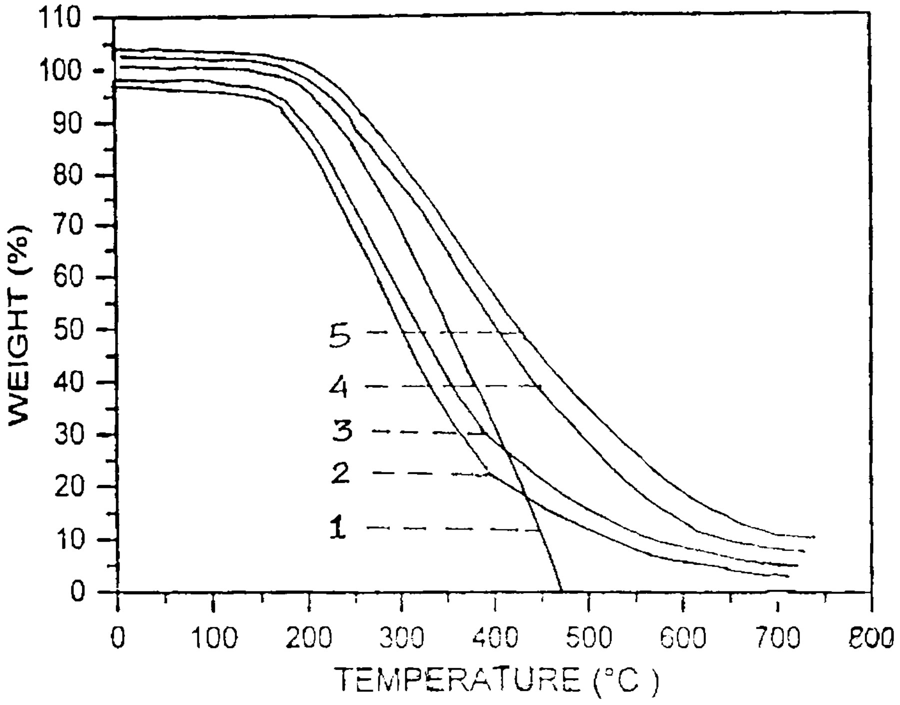


Fig.4.9 : Thermograms of POTMG and HTPB based PU (①-TMP/POTMG, ②-PN- 3/POTMG, ③ PN-4/POTMG, ④ PN-3/HTPB, ⑤ PN-4/HTPB)

**Table 4.8: Thermal decomposition data for PEG-PU system with three CLA's**

| Sl. No. | PEG/CLA equivalents | CLA type | Initial decompn (°C) | Peak decompn: (°C) | End temp: (°C) | Residue above 380°C (%) |
|---|---|---|---|---|---|---|
| 1 | 1:1 | TMP | 150 | 365 | 370 | Nil |
| | | PN-3 | 160 | 380 | 425 | 30 |
| | | PN-4 | 165 | 385 | 430 | 35 |
| 2 | 1:2 | TMP | 150 | 370 | 375 | Nil |
| | | PN-3 | 165 | 385 | 435 | 35 |
| | | PN-4 | 170 | 390 | 445 | 38 |

The TGA pattern for HTPB-based PU was also studied. The thermal decomposition data for HTPB and POTMG polyols are given in the table 4.9.

It can be observed from table 9 that the IDT is enhanced by PN crosslinker for both types of polyol-based polyurethanes. The fraction remaining above the peak decomposition temperature (the temperature at which a major portion decomposes), characteristic of the polyol is almost same for the different polyols studied, it is in the range of 35-40%, the decomposition being complete only between 600 to 700°C when the crosslinking agent PN-3 and PN-4 are used. In the case of TMP as CLA, the decomposition is complete almost at the peak decomposition temperature, characteristic of the polyol backbone.

**Table 4.9: Thermal decomposition data for HTPB - and POTMG urethanes**

| Sl. No. | Ratio | Polyol type | CLA type | Initial decompn (°C) | Peak de compn: temp(°C) | Fraction at PDT (%) | End temp (°C) |
|---|---|---|---|---|---|---|---|
| 1 | 1:1 | HTPB | TMP | 185 | 475 | Nil | 480 |
| | | | PN-3 | 200 | 480 | 30 | 650 |
| | | | PN-4 | 200 | 480 | 35 | 700 |
| 2 | 1:1 | POTMG | TMP | 165 | 350 | Nil | 360 |
| | | | PN-3 | 170 | 365 | 35 | 700 |
| | | | PN-4 | 170 | 370 | 40 | 700 |
| 3 | 1:2 | HTPB | TMP | 200 | 475 | Nil | 480 |
| | | | PN-3 | 215 | 485 | 38 | 650 |
| | | | PN-4 | 215 | 485 | 40 | 700 |
| 4. | 1: 2 | POTMG | TMP | 165 | 350 | Nil | 360 |
| | | | PN-3 | 175 | 375 | 35 | 680 |
| | | | PN-4 | 175 | 375 | 40 | 700 |

The results of the studies conducted on improvement of thermal stability by the use of CLA presented in tables 4.8 and 4.9 show that the overall thermal stability of the polyurethane has been augmented by the presence of phosphazene-crosslinking agent.

## 4.1.E. CONCLUSIONS

The use of phosphazene triols and tetraols as crosslinking agents for polyurethanes with toluene diisocyanate as curing agent increases the thermal stability and the overall service temperature range. The tensile strength of the polyurethane samples are increased while the elongation decreased. The glass transition temperature and hardness are also increased. On a relative basis the phosphazene based system is better in inducing the change in properties than the conventional crosslinking agent, TMP. This has been substantiated for all the three polyols investigated. The quantitative estimation of the efficiency factor for enhancing the tensile strength by the crosslinker revealed that it depends on the type of CLA and the polyol. Generally the efficiency increases in the order TMP<PN-3<PN-4 and for the phosphazene based CLA the improvement in properties of polyols based urethanes is in the order PEG<POTMG<HTPB. The phosphazene crosslinking agents are miscible with polyols and the system is easy to process. Phosphazene based crosslinkers can thus be used in place of conventional crosslinkers like TMP for polyurethanes expected to withstand higher temperature environments.

## SECTION - 2

## 4.2 TRIAZENE - AND IMIDE-TRIAZENE- CONTAINING POLYURETHANES

### 4.2.A Introduction

The work given in this section concerns the incorporation of triazene and imide-modified triazene in the polyurethane chain of polyether and polybutadiene backbone using novel crosslinkers synthesised starting from cyanuric chloride. The triol crosslinker of triazene designated as CNT and the diol chain extender cum crosslinker of maleimido-triazene diol designated as MITD were incorporated through reaction with diisocyanate. The CNT was synthesised by reaction of cyanuric chloride and 2-ethyl aminoethanol. MITD was synthesised by reaction of cyanuric chloride with maleimidophenol in 1:1 molar ratio followed by 2-ethylaminoethanol. Further crosslinking was effected by thermal polymerisation of the maleimide double bond. Crosslinking agents (CLA) were incorporated in different polyurethane systems whose backbone were constituted by polyether or polybutadiene units. The mechanical and thermal properties of these modified polyurethanes have been determined at different levels of the two CLA's. The homopolyurethanes and copolyurethanes were synthesised. The variation in physical and mechanical properties of polyurethane with the new crosslinker has been examined. The comparative performance of the triazene based cross linking vis-a- vis the base crosslinker, TMP and the phosphazene based triol (described in preceeding section) for improving propertion of PU has been established.

## 4.2.B Experimental

### 4.2.B.1 *Materials used*

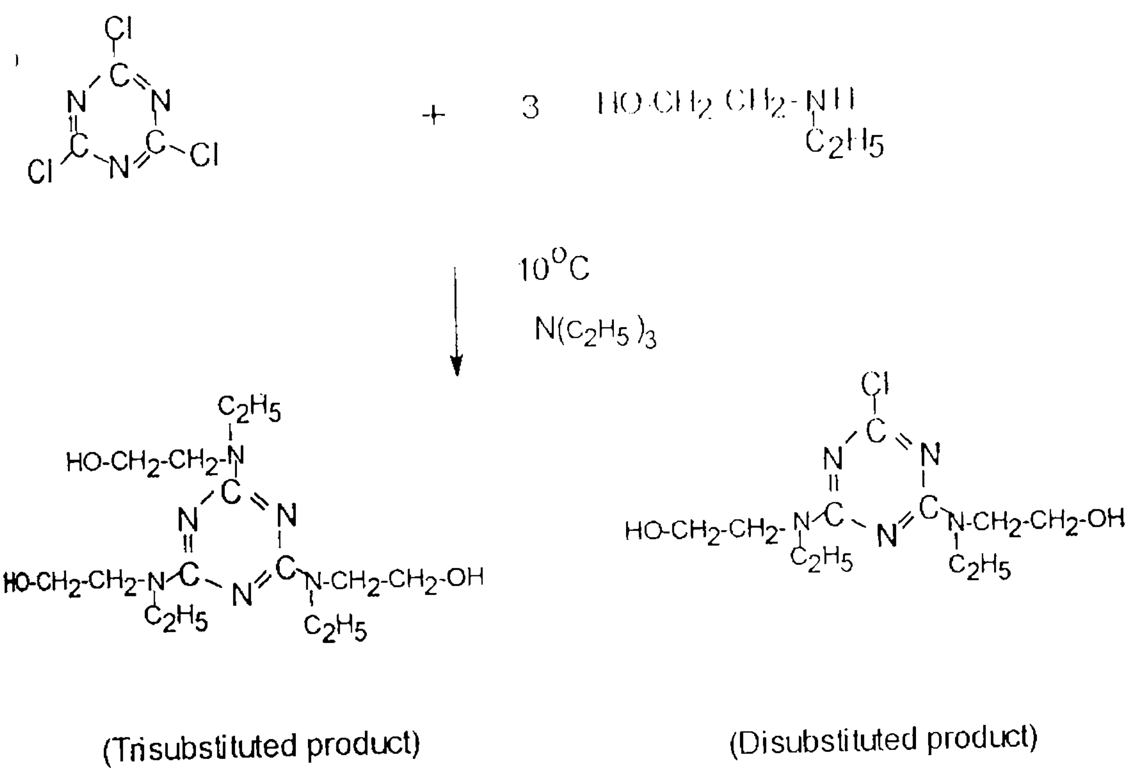
1) Cyanuric Chloride (2,4,6 - trichloro s-triazene, Aldrich Chemicals, USA)
2) 2-Ethyl aminoethanol (Fluka)
3) Triethylamine (SD Chemicals, Bombay)
4) 4-Maleimidophenol (Synthesised by reported procedure[7])
5) Tolylene diisoyanate (mixture of 2.4 and 2.6 isomers in 80:20 ratio of Bayer, Germany)
6) Polyoxytetramethylene glycol of molecular weight 2000(POTMG of BASF, Germany)
7) Hydroxyterminated Polybutadiene of molecular weight 2800 (HTPB of M/s.NOCL, Bombay)

### 4.2.B.2 *Purification of raw materials*

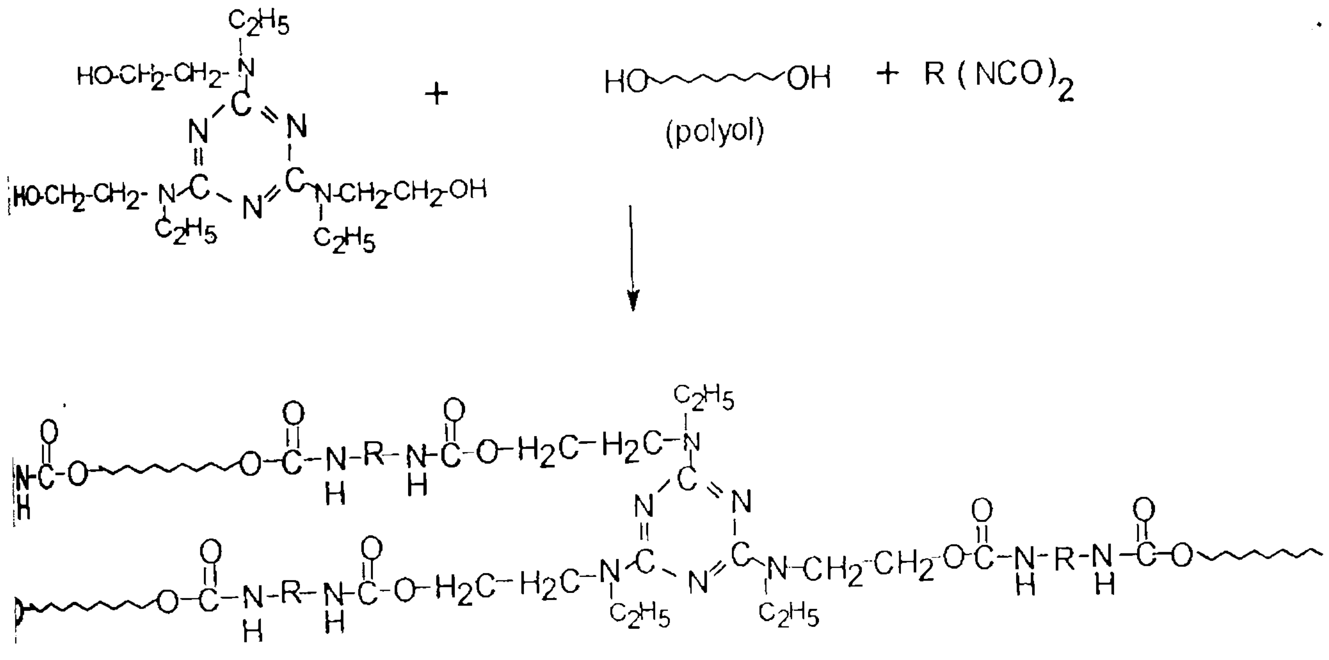
Cyanuric chloride was purified by recrystallisation from benzene. Cyanuric chloride due to the high sensitivity to moisture, contains hydrolysed and crosslinked fractions. The purification was effected as follows. About 10 gms of the compound was mixed and stirred well with 50 ml of anhydrous benzene. Allowed to stand at room temperature for 1 hour. The dissolved fraction was separated and dried to remove traces of benzene. 2-Ethyl aminoethanol was stirred well under vacuum at 80°C for 2 hours to remove traces of moisture. The solvent, dichloromethane was distilled and stored over molecular seive. Triethylamine was purified by distillation and kept over potassium hydroxide pellets. The polyols POTMG and HTPB were dried by stirring under vacuum for 3 hours at 70°C

### 4.2.B.3 *Synthesis of triazene triol -2,4,6 - tris-(N-ethyl, N-hydroxy ethyl) amino-triazene (hereafter referred as CNT).*

In a typical experiment for the synthesis of CNT, 13 gms of 2-ethyl amino ethanol and 15 gms triethyl amine were taken in a three necked round bottomed flask kept on a magnetic stirrer. A solution of 9 gm of purified cyanuric chloride in 25 ml of dichloromethane was taken in a dropping funel. The reaction flask was kept cooled in an ice-bath at 10°C to prevent crosslinking reaction through reaction of the OH groups. The solution of cyanuric chloride in dichloromethane was added slowly dropwise into the solution of 2-ethylamino ethanol taken in the reaction flask with thorough agitation under nitrogen atmosphere. The reaction was done for a period of 2 hours keeping the reaction temperature at 10°C. The liberated HCl during reaction was absorbed by triethylamine forming triethylamine hydrochloride. The reaction is given in scheme 4.3. After keeping the reaction mixture at 10°C for 2 hours, it was stirred at 30°C for 1 hour to complete the reaction. The product was then washed with acidified water three or four times and finally with distilled water three times to remove the by-product, triethylamine hydrochloride and free triethylamine. The solution of CNT in dichloromethane was dried using anydrous sodium sulphate. The solvent was removed by distillation at ordinary pressure at 60°C followed by drying under vacuum at 40°C for 3 hours till constant weight. Yield of the product obtained was 12 gm (about 65%).



Scheme 4.3 : Synthesis of cyanuric triol (CNT)



Scheme 4.4 Synthesis of Triazene incorporated Polyurethane

### 4.2.B.4 *Synthesis of maleimido triazene diol: 2-(p-maleimido) phenoxy, 4,6 - bis (N-ethyl N-hydroxy ethyl) amino s-triazene (hereafter referred as MITD).*

The synthesis of imide-containing triazene crosslinker was carried out as given in scheme 4.5. A solution of 9.2 gm of cyanuric chloride dissolved in dichloromethane was mixed with 15 gm of triethylamine and taken in a three necked RB flask. The solution was kept stirring using a magnetic stirrer at 10°C in an ice bath. Nitrogen gas was purged through the reaction flask. The solution of 11.3 gm of p-maleimido phenol in 20 ml MEK was taken in a dropping funnel and added dropwise into the reaction vessel with stirring. The addition of maleimido phenol was completed over a period of 1 hour and then reaction was carried out for 2 hours by stirring at 40°C. After completion of reaction, the second reactant ie, the solution of 9 gms of 2- ethyl amino ethanol in 20 ml dichloromethane was added over a period of 1 hour keeping the reaction temperature at 10°C. After complete addition of amino ethanol, the reaction mixture was stirred for another 2 hours at 40°C and washed well with water acidified with HCl and then with distilled water three or four times to remove unreacted triethylamine and by-product triethylamine hydrochloride. The solution was dried using anhydrous sodium sulfate. The solvent was removed by distillation and final traces of it removed under vacuum. The product was isolated as a pale yellow solid. Yield of the product obtained was 18 gm (60%).

### 4.2.B.5 *Characterisation*

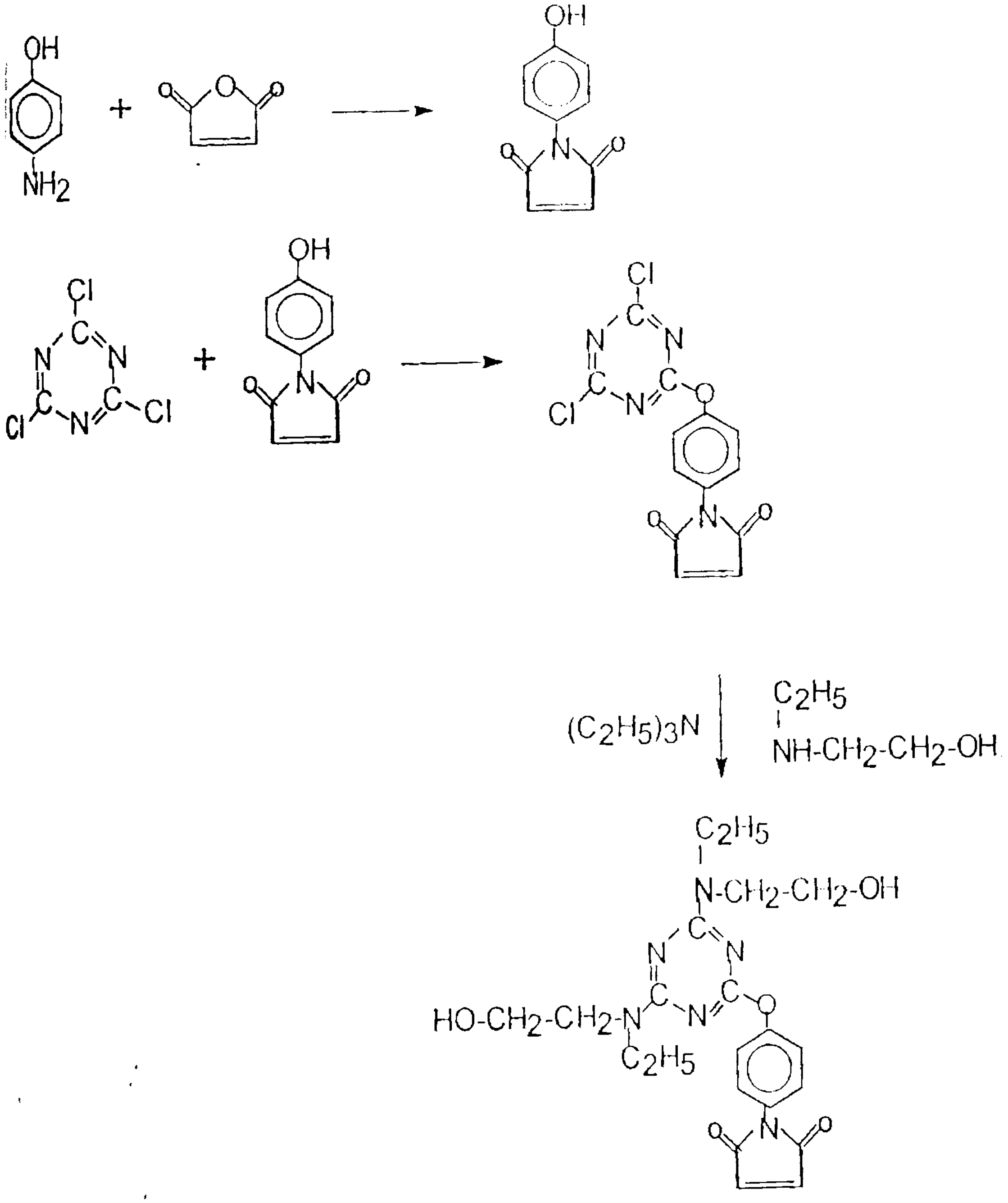
The CNT, separated as white crystalline solid and MITD, as a pale yellow solid were characterised by melting point, I.R spectrum and nitrogen analysis.

### 4.2.B.6 *Preparation of polyurethanes*

The CNT was incorporated in different levels in polyurethane based on polyether and polybutadiene polyols, the typical materials being polyoxytetramethylene glycol and HTPB. The homopolyurethane of CNT with TDI were also made for comparison. The polyurethane from the starting polyols were synthesised using TDI as curative and TMP as crosslinker.

The synthesis procedure for homopolyurethane is as follows. 10 gms of CNT was dissolved in anhydrous methyl ethyl ketone solvent along with 2 drops of dibutyltin dilaurate catalyst. 7.6 gms of TDI corresponding to an equivalent ratio of OH:NCO 1:1 was added slowly with stirring keeping the temperature at $30^oC$ throughout the addition time. The reaction was continued for 2 hours. The reaction product was poured into methyl alcohol with stirring. The homopolyurethane of CNT was precipitated as a white solid. It was washed two to three times with methyl alcohol and dried at $60^oC$ under vacuum.

The CNT was used as a crosslinker in polyurethanes using POTMG and HTPB as the basic polyol as given in scheme 4.4. The crosslinker was dissolved in polyols in different equivalent ratios using dichloromethane as a common solvent. The solvent was evaporated off to obtain a homogeneous mixture of polyol and crosslinker. The preparation of polyurethane slabs are same as detailed in the experimental part of the preceeding section on phosphazene- modified polyurethanes. The mechanical property and thermal stability of these polymers were analysed and the results



Scheme 4.5 : Synthesis of maleimido triazene diol (MITD)

compared with those of the samples prepared using conventional crosslinking agent, trimethylol propane at the same equivalents ratio.

MITD was used as a crosslinker in place of CNT. The procedure for preparation of maleimido-triazene polyurethane was the same as that adopted for CNT crosslinker. The homopolyurethane was synthesised by mixing MITD and TDI in 1:1 (OH:NCO equivalents) ratio in MEK solvent in presence of DBTDL catalyst. The reaction mixture was stirred for about 1 hr and the solvent evaporated off leaving behind a pale yellow residue. The chain - extended linear polyurethane thus obtained having a maleimide unit in each repeat unit could be further crosslinked to a three dimensional network through thermal polymerisation of maleimide group. The double bond of maleimide undergoes addition polymerisation around at 190-200°C.

### 4.2.B.7 *Variation of the quantity of triol crosslinker*

The preparation of polyurethane using CNT and MITD independently as the crosslinkers in different equivalent ratios with POTMG and HTPB as the polyols were carried out as follows. The polyol-CNT mixture at different concentration of CNT were taken and TDI for an NCO/OH ratio of 1 was added and mixed well in presence of traces of catalyst, DBTDL. The slabs were prepared in the same way as detailed for the PN-triol and tetraol crosslinkers. The equivalent ratio of polyol to crosslinker was varied from 1:0.75 to 1:2 keeping the isocyanate index as 1 in all cases to avoid the formation of any secondary crosslinks.

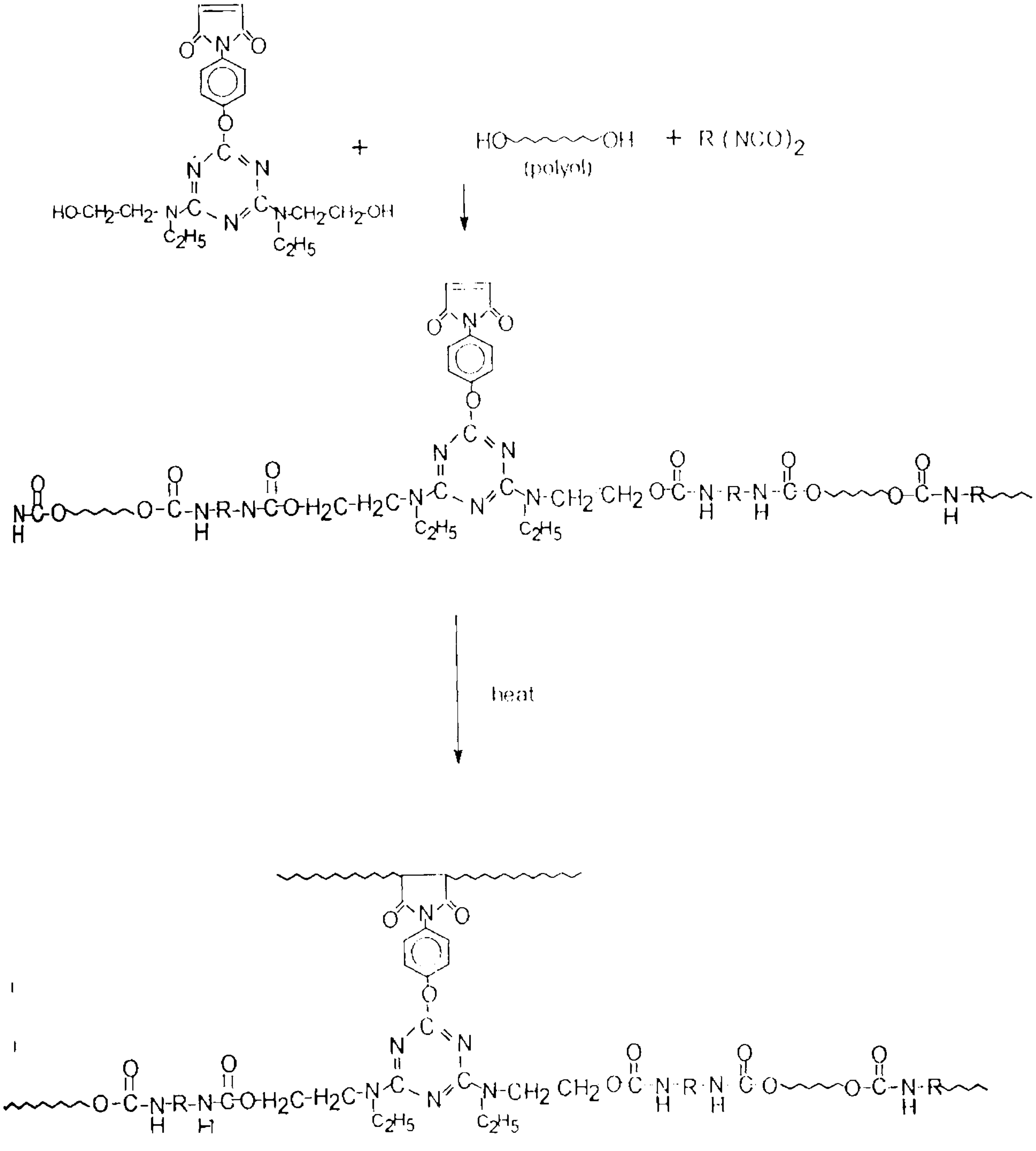
The preparation of polyurethanes with varying concentration of MITD as the crosslinker was also carried out in the same way. The linear, chain-extended polyurethane formed from MITD was poured into a mould and allowed to set at room temperature for 24 hours to complete the OH-NCO reaction. The thermoplastic product so obtained was heated in the mould at 190-200°C in nitrogen atmosphere for 2 hours to complete the crosslinking through polymerisation reaction of the imide. The chain extension and subsequent thermal crosslinking reactions are given in scheme 4.6.

### 4.2.C Characterisation and mechanical property evaluation

After completion of curing, the elastomer was taken out from the mould and analysed for mechanical properties in Instron UTM and for thermal analysis by TGA. The effect of CLA on Tg was monitored by TMA. The sol and gel content of the samples were analysed by swelling in toluene and weighing the undissolved fractions. The analytical results of the polyurethane samples of various compositions are given in tables 4.11 and 4.12.

### 4.2.D Results and discussions

The novel crosslinking agents CNT and MITD were synthesised as per reaction schemes 4.3 and 4.5. The chlorine atom of cyanuric chloride being very reactive, the reaction with aminoethanol and maleimidophenol could be fast and complete giving rise to the expected structures. The CLA's were characterised principally by the nitrogen content and by IR spectrum. Physical properties are given in table 4.10. The chemical method of hydroxyl value could not be adopted due to the intense brown colour developed during acetylation with acetic anhydride/pyridine mixture for the two samples. Hence Nitrogen analysis and IR spectra were used for characterisation The broad peak at 3400 - 3600 $cm^{-1}$ in the IR spectrum



Scheme 4.6 Formation of crosslinked imide-triazene-polyurethane

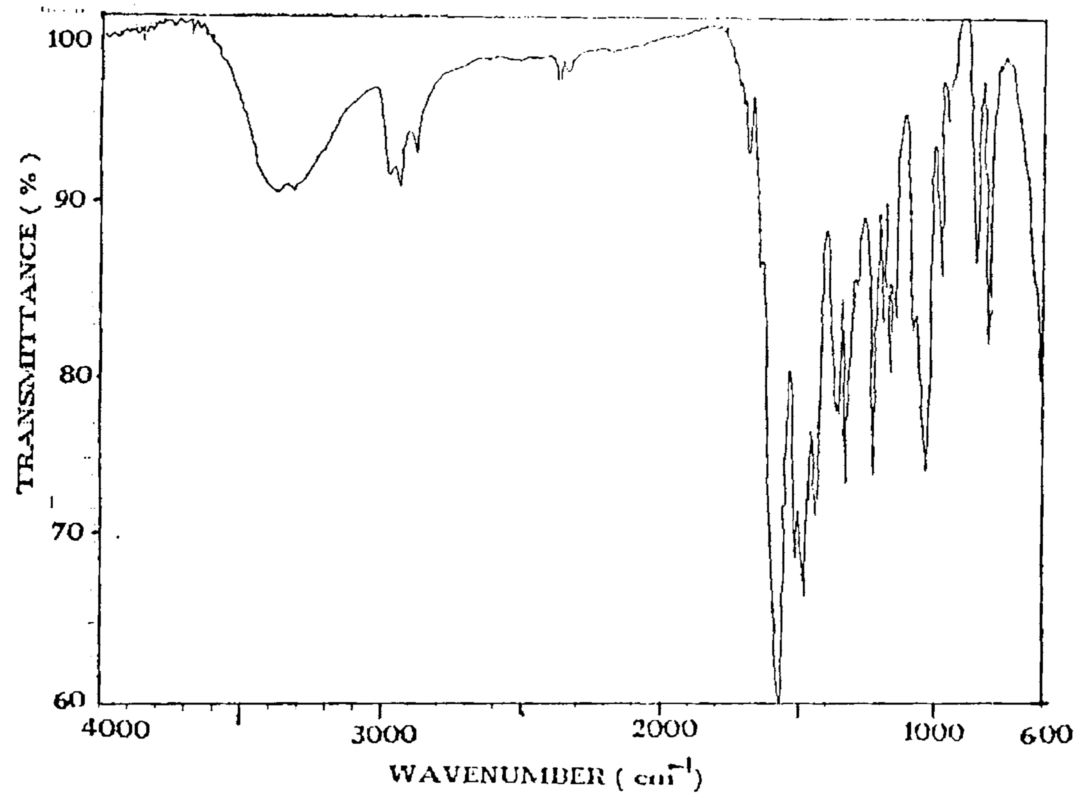


Fig. 4.10 : I.R. Spectrum of traizene triol (Cyanuric triol CNT)

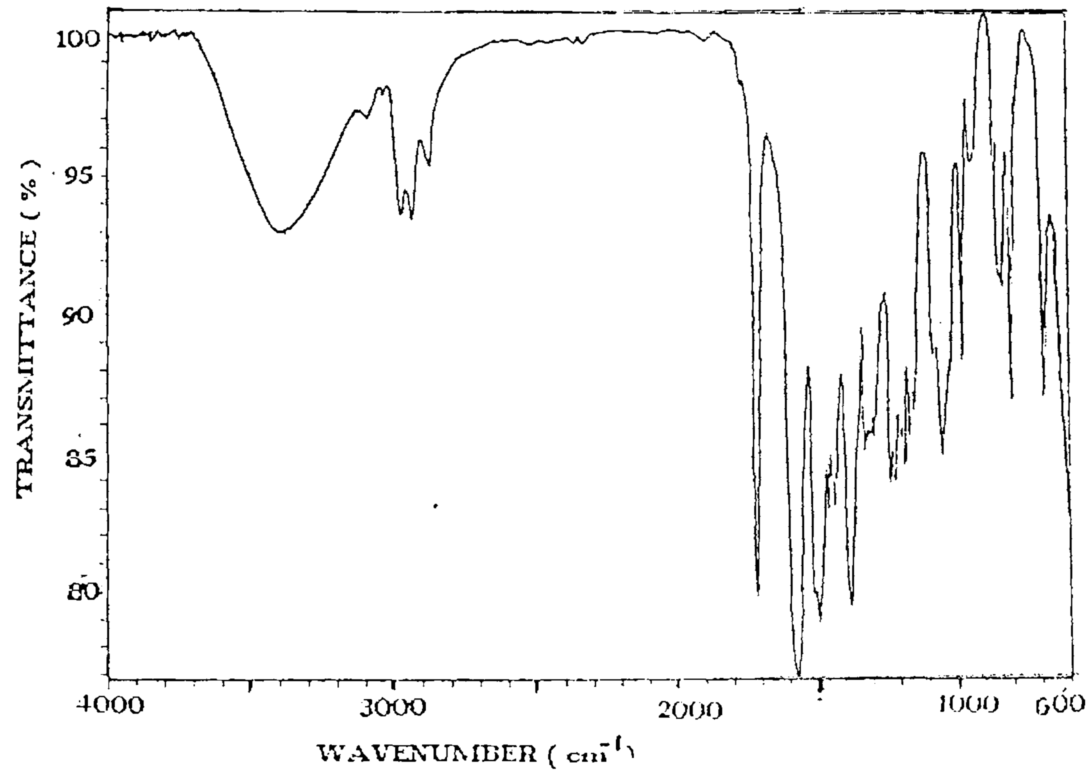


Fig. 4.11 : I.R. Spectrum of Maleimido-traizene diol (MITD).

corresponds to the presence of OH group. The peak at 1740 $cm^{-1}$ in MITD corresponds to C=0 in imide group and that at 1620 $cm^{-1}$ to C=N in triazene ring. IR spectra of CNT and MITD are given in fig.4.10 and 4.11 respectively.

During the synthesis of CNT and MITD, the reaction gives a possible mixture of di-and tri-substituted products. The average functionality of the product could not be determined due to colour formation in acetylation with $Ac_2O$/pyridine mixture. The determination of nitrogen content gave an indication of the extent of reaction.

**Table 4.10 Physical properties and elemental analysis results of CNT and MITD.**

| Sample | Melting point(°C) | Nitrogen content (%) | | Chlorine content(%) |
|---|---|---|---|---|
| | | Theor: | Observed | |
| CNT | 75-80 | 24.5 | 24.5 | Nil |
| MITD | 90-95 | 20.1 | 19.2 | Nil |

The absence of a sharp melting point is probably due to the formation of the mixture of the di and trisubstituted product as shown in scheme 4.3. The formation of gelled products of CNT with TDI proves that its average functionality is near to 3. The chain extended PU of MITD could be cured thermally to gelled products showing the total functionality near to 3. The substituted products do not contain chlorine in both cases showing the completion of the chlorine substitution. The low substituted product therefore could possess C=O group as a result of hydrolysis of the C-Cl bond. Nitrogen content implies the expected extent of reaction in both cases.

Different PU systems incorporating the hetrocyclic units to different extents could be realised by using these compounds as CLA. The formation of the network with CNT is shown in scheme 4.4 . MITD being essentially a diol, its reaction with TDI and polyol was conducive for the formation of a linear solible PU only. However this could be further crosslinked through the polymerisation of the maleimide group. To study the cure characteristics of the imide - PU, a homopolyurethane of MITD and TDI was made by reacting them in 1:1 ratio. The resultant PU was subjected to DSC analysis. The DSC of the sample did not show any appreciable exotherm expected due to the polymerisation reaction of maleimide at 190-200$^0$C. However the curing temperature of the maleimide group were separately ascertained by carrying out the homopolymerisation studies of maleimidophenol. This compound, although doesnot show any polymerisation exotherm in DSC till 300$^0$C, was found to polymerise at around 200$^0$C. The low heat of polymerisation may be reason for the lack of exotherm in its DSC as was the case for the maleimide-containing polyurethanes. Curing of the PU through the unsaturation was confirmed from the insolubility of the cured material. The effect of incorporation of the triazene based CLA's on the mechanical and physical propertion of POTMG based polyurethaness was analysed and the results are given in table 4.11.

It may be observed from the studies conducted on the variation in mechanical properties of the samples of POTMG and HTPB when the three types of CLA's are used (as presented in tables 4.11 and 4.12)that at a particular equivalents ratio, the tensile strength for the MITD crosslinker system was higher than that for the CNT or TMP crosslinker system. The lower value of the sol percent shows that the crosslinking has been completed. Further, the increase in hardness is also caused by the polar, triazene and MITD units.

**Table 4.11 Physical and mechanical properties of polyurethane of POTMG with TMP, CNT and MITD as CLA's**

| Sl. No. | Polyol:CLA eq: ratio | CLA type | Weight (%) | T.S (KSC) | Elong: % | Hard: (Sh:A) | Sol % | Tg ($^{0}$C) |
|---|---|---|---|---|---|---|---|---|
| 1 | 1:0.75 | TMP | 2.7 | 10.8 | 580 | 30 | 5 | -71 |
| | | CNT | 8.5 | 15.5 | 505 | 30 | 12 | -65 |
| | | MITD | 11.0 | 12.5 | 405 | 25 | 15 | -52 |
| 2 | 1:1 | TMP | 3.8 | 12.0 | 535 | 35 | 5 | -65 |
| | | CNT | 11.4 | 16.8 | 480 | 35 | 5 | -- |
| | | MITD | 14.7 | 20.5 | 455 | 35 | 8 | - - |
| 3 | 1:15 | TMP | 5.7 | 13.5 | 515 | 35 | 4 | -- |
| | | CNT | 17.1 | 20.0 | 460 | 40 | 4 | -- |
| | | MITD | 22.0 | 31.0 | 415 | 40 | 5 | -35 |
| 4 | 1:2 | TMP | 7.5 | 15.1 | 485 | 35 | 3 | -55 |
| | | CNT | 22.8 | 21.5 | 420 | 45 | 3 | -- |
| | | MITD | 29.4 | 35.5 | 375 | 45 | 4 | -25 |

The effect of incorporation of CNT and MITD as the CLA for HTPB- based polyurethane was studied and the results are presented in table 4.12.

For the POTMG based polyurethane with MITD crosslinker with an equivalent ratio less than one, the MITD is less efficient than CNT in improving the tensile strength and hardness. The sol content in this case is expectedly higher. At higher ratios the trend was reversed.

**Table 4.12:Physical and mechanical properties and $T_g$ of polyurethane of HTPB with CNT and MITD as CLA's**

| Sl. No. | Polyol:CLA eq: ratio | CLA type | Weight (%) | T.S (KSC) | Elong: % | Hard: (Sh:A) | Sol % | Tg (°C) |
|---|---|---|---|---|---|---|---|---|
| 1 | 1:1 | TMP | 3.5 | 8.0 | 485 | 30 | 5 | -60 |
| | | CNT | 9.1 | 12.5 | 380 | 35 | 4 | -- |
| | | MITD | 11.8 | 14.5 | 355 | 35 | 4 | -40 |
| 2 | 1:1.5 | TMP | 5.4 | 10.5 | 425 | 30 | 5 | -55 |
| | | MITD | 17.7 | 22.0 | 385 | 40 | 4 | -36 |
| 3 | 1:2 | TMP | 7.6 | 12.5 | 410 | 40 | 3 | -55 |
| | | CNT | 18.3 | 22.0 | 365 | 45 | 4 | -- |
| | | MITD | 23.6 | 30.0 | 300 | 50 | 3 | -25 |

Tensile strength and hardness were increased and the sol content decreased more for MITD-based ones than for CNT-based polyurethane. This is probably due to the fact that the crosslinking through maleimide double bond opening doesnot proceed to significant extent at very low concentration of it as fewer numbers of these groups may be scatttered in the matrix and their reaction could be diffusion-controlled in limited cocentration. Hence for HTPB based systems, the equivalent ratios of 1:0.75 was not tried for the CLA.

### 4.2.D.1 *Dependancy on tensile strength and Tg on crosslinker nature and concentration*

The relative increase in the tensile strength for polyurethanes, cured using CNT and MITD as the CLA over the conventional TMP crosslinker was calculated. The data is presented in table 4.13.

**Table 4.13:Relative increase (%) in tensile strength of polyurethane with CNT,MITD and Phosphazene as CLA's over TMP**

| Sl. No. | Polyol | Eq:ratio | Relative increase in T.S over TMP (%) | | |
|---|---|---|---|---|---|
| | | | PN-3 | CNT | MITD |
| 1 | POTMG | 1:1 | 9.0 | 28.5 | 41.5 |
| | | 1:2 | 8.5 | 29.8 | 55.0 |
| 2 | HTPB | 1:1 | 12.0 | 36.0 | 43.0 |
| | | 1:2 | 14.5 | 45.0 | 58.0 |

The data given in table 4.13 shows that the relative increase in tensile strength over TMP taken as the standard is higher for CNT and MITD than for phosphazene, the MITD giving the highest value due to the increase in cohesive forces due to polar imide groups and higher crosslink density. Like in the case of PN-3, the effect of these CLA's is reflected better in HTPB than POTMG. In fact the triazene-based crosslinkers are much more efficient than conventional TMP in enhancing the tensile properties. This is evidently due to the presence of polar and aromatic triazene ring which adds to the cohesion and stiffness of the chain.

It can be observed that the relative increase in tensile strength is higher for the MITD based system in comparison to the other two types of crosslinkers (TMP,CNT). The comparative efficiency of the various crosslinkers, CNT and MITD and the earlier described phosphazene based triols are listed in table 4.14.

**Table 4.14 : Efficiency factor for various combinations of CLA and polyol**

| System | CLA | $TS_0$ | E | R* |
|---|---|---|---|---|
| HTPB | TMP | 3.6 | 4.5 | 0.998 |
| | CNT | 2.75 | 9.5 | 0.995 |
| | MITD | 1.25 | 15.5 | 0.999 |
| POTMG | TMP | 8.5 | 3.5 | 0.996 |
| | CNT | 12.5 | 4.9 | 0.988 |
| | MITD | 2.5 | 18.2 | 0.978 |

*correlation coefficient for the linear plot

Variations in tensile strength caused by the crosslinkers at an equivalent basis have been compared in figures 4.12 and 4.13. In all cases a practically linear relationship existed between the tensile strength and the crosslinker concentration, as $TS = TS_0 + E\,[X]$, where $TS_0$ is the tensile strength of the system in the absence of crosslinker and E the efficiency factor for it. The trend in E values implies that the relative increase in tensile strength is highest for the MITD. It contains an additional polar imido- phenoxy group which effectively transforms the crosslinker to a tetrafunctional one. This effect has added to improve the tensile properties of the imido-triazene crosslinked-PU as seen from the results in tables 4.11 and 4.12.

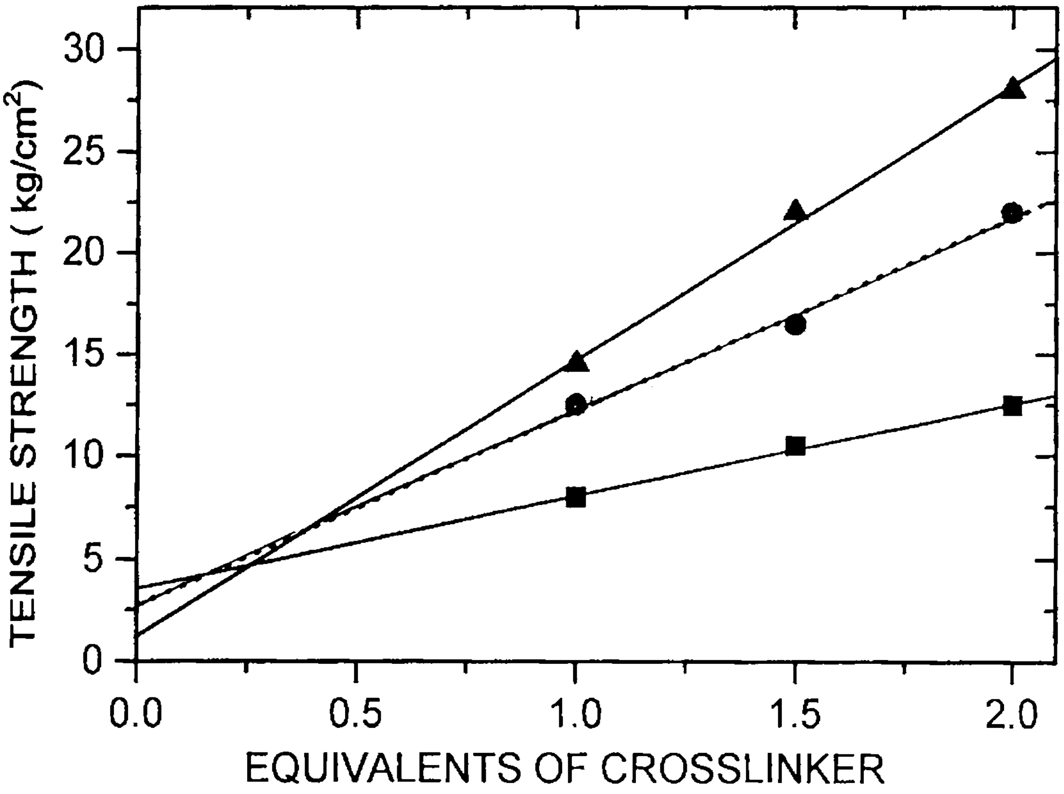


Fig.4.12 Variation of tensile strength with concentration of CLA for HTPB- PU (■TMP●CNT▲MITD)

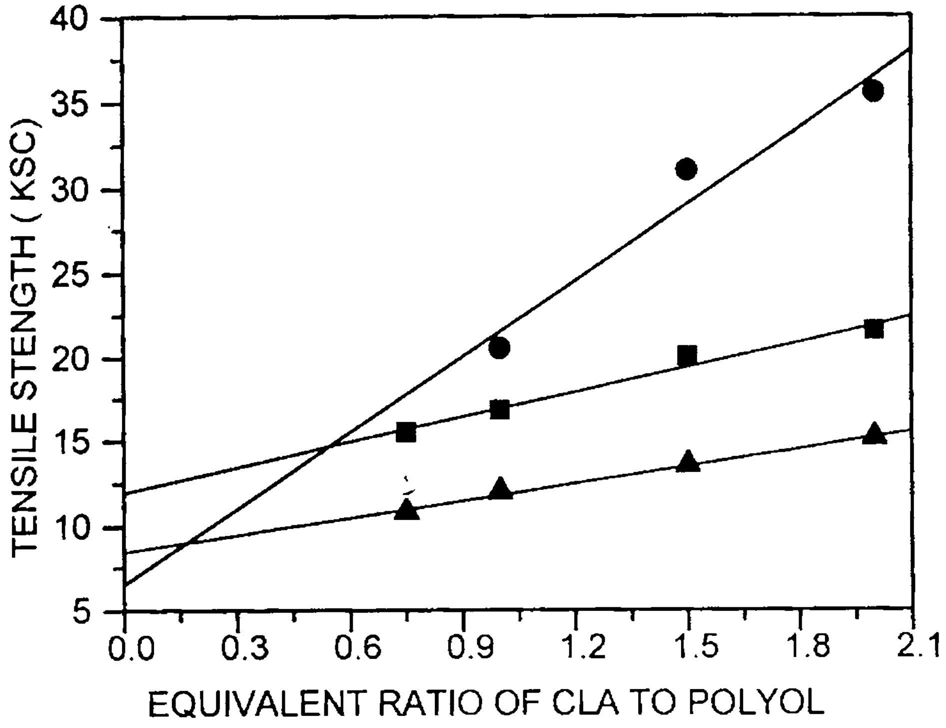


Fig.4.13 Variation of tensile strength with concentration of CLA for POTMG-PU system ( ▲ TMP ■ CNT ● MITD)

Irrespective of the polyol, the efficiency factor of the crosslinker is in the order. TMP < CNT < MITD. The increase in chain stiffness by the presence of these novel crosslinkers is translated as a proportionate increase in both $T_g$ and hardness values as seen from the data in tables 4.11 and 4.12. It can be found that the trend in increase of $T_g$ is the same as that for tensile strength showing that the change in structural and morphological features as a result of the crosslinker contribute identically to both properties. If we consider the phosphazene - based crosslinkers as well, the advantage of the triazene based CLA's becomes still obvious. Globally, the efficiency of the CLA can be classified as TMP < PN-3 < PN-4 < CNT < MITD .

### 4.2.E Thermal properties

The crosslinked samples using CNT and MITD were analysed for thermal stability by TGA. The initial decomposition temperature (arbitrarly fixed as the temperature at which 2% of the polymer decomposes) and the peak decomposition temperature (fixed as the temperature at which a major fraction of the polymer decomposes) were noted from thermogram. The weight residue remaining at an arbitrarly fixed temperature for comparison of the crosslinkers and the end temperatures of POTMG and HTPB based polyurethanes are given in table 4.14 and 4.15 respectively. Typical thermograms of TMP,PN-3, CNT and MITD-based polyurethanes are given in fig.4.14.

The introduction of triazene and maleimide-triazine combination in the polyurethane chain has been found to increase the initial and peak decomposition temperatures of POTMG and HTPB based polyurethanes. The weight fraction remaining at the peak decomposition temperature has also been proportionately increased.

**Table 4.15: Thermal decomposition data for PU system with CNT and MITD as CLA's for POTMG**

| Sl. No. | POTMG: CLA eq: ratio | CLA type | IDT ($^{o}$C) | PDT ($^{o}$C) | Residue at 450$^{o}$C | End Temp: |
|---|---|---|---|---|---|---|
| 1 | 1:1 | TMP | 185 | 350 | Nil | 380 |
| | | CNT | 200 | 435 | 18 | 460 |
| | | MITD | 215 | 447 | 25 | 500 |
| 2 | 1:2 | TMP | 190 | 350 | Nil | 420 |
| | | CNT | 200 | 435 | 20 | 470 |
| | | MITD | 215 | 455 | 30 | 500 |

(IDT - Initial decomposition temperature, PDT - Peak decomposition temperature)

The residue remaining at an arbitrarly fixed temperature of 450$^{o}$C (as POTMG has a lower PDT than HTPB), is compared for all the three crosslinkers presented in table 4.15 which can be considered as a measure of thermal stability. The PU with TMP gives no residue whereas with CNT and MITD, the residue is between 20 and 30%. The thermal decomposition data of HTPB - based polyurethanes with CNT and MITD crosslinker were compared with that for TMP-based polyurethanes of HTPB. The data presented in table 4.16 show a similar trend as that for the POTMG- based polyurethanes.

**Table 4.16: Thermal decomposition data for HTPB-polyurethanes with CNT and MITD as CLA's**

| Sl. No. | HTPB:CLA eq: ratio | CLA type | IDT (°C) | PDT (°C) | End temp. (°C) | Residue at 500°C (%) |
|---|---|---|---|---|---|---|
| 1 | 1:1 | TMP | 190 | 475 | 480 | Nil |
| | | CNT | 225 | 480 | 500 | 12 |
| | | MITD | 230 | 495 | 510 | 26 |
| | | PN-3 | 210 | 485 | 700 | 30 |
| 2 | 1:2 | TMP | 205 | 480 | 485 | Nil |
| | | CNT | 230 | 490 | 510 | 15 |
| | | MITD | 245 | 500 | 515 | 28 |
| | | PN-3 | 220 | 485 | 700 | 35 |

It may be observed that the thermal stability of HTPB based polyurethane is also improved by the introduction of thermally stable triazene and imide-triazene groups. The residue remaining above the arbitrarly fixed 500°C are 12% and 26% respectively for CNT and MITD. TMP-based polyurethanes goes to complete decomposition at the end temperature. The residue remaining at the peak decomposition temperature given in the table is 25% and 30% for the CNT and MITD-based polyurethanes, whereas TMP - based polyurethane has no residue at the peak decomposition temperature. Increasing the concentration of the crosslinker proportionately increases the thermal stability as seen from IDT, PDT and the char residue. The corresponding values for phosphazene triol-based polyurethane given in table 4.16 for comparison shows the superiority of the latter in augmenting both the end-temperature and the residue above 500°C than for triazene - based system.

The thermograms in fig.4.14 gives a comparison of thermal stability of the three types of hetrocyclic CLA-based polyurethanes using HTPB as the basic backbone.

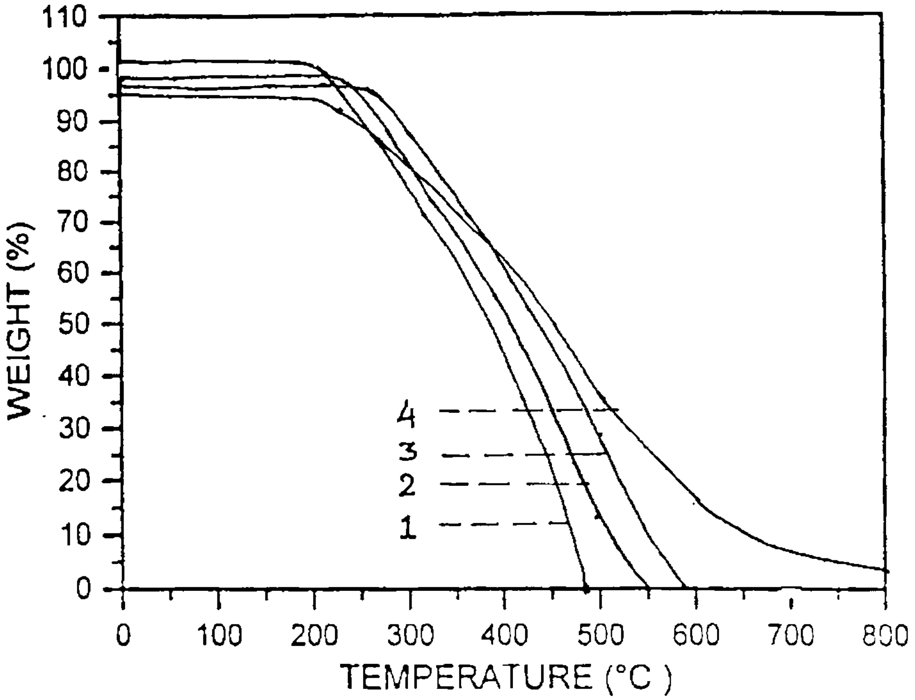


Fig.4.14 Thermograms of HTPB based PU with different CLA's (①TMP ②CNT ③MITD ④PN-3)

The phosphazene units in the phosphazene - modified polyurethanes gives better char residue at higher temperature when thermal decomposition is done in nitrogen. The rate of decomposition is lower for the phosphazene-based polyurethanes as seen from the thermogram. It is seen that the trend in mechanical properties are not in "toto" translated to that in thermal stability. Phosphazene imparts better high temperature performance although it is less efficient in boosting the tensile strength and $T_g$ on an equivalent basis. Although proper selection of the nature and concentration of the crosslinker appears ideal to enhance the mechanical properties and thermal stability, it is to be noted that they are achieved at the cost of the chain flexibility which is reflected as a proportionate increase in $T_g$ of the modified-systems. Since the polyurethane systems possess appreciable built-in toughness,and that the Tg's are still at the subzero temparatures, the partial sacrifice in chain flexibility through the CLA's is not a major obstacle for serving these systems for application demanding comparatively better thermal stability as they are still tough. This has infact been the main objective of this modification study.

## 4.2.F CONCLUSION

Novel triazene crosslinkers starting from cyanuric chloride could be synthesised and used as crosslinking agent for polyurethanes based on polyether and polybutadiene backbone for incorporating triazene rings in polyurethane. The evaluation of mechanical and thermal properties of the resultant polyurethanes has shown that on an equivalent basis, the imide-triazene based crosslinker is more efficient than triazene triol or TMP in improving tensile properties and $T_g$. Presence of imides is fruitful in achieving also better thermal stability. The thermal stability was highest for MITD - based polyurethanes. The effect of the hetrocyclic groups on mechanical properties is not as such translated to the thermal stability of the polyurethane network. Presence of phosphazene although was not so impressive in improving the mechanical properties,as evident from its low efficiency coefficient,it caused a commendable improvement in thermal stability in comparison to the other heterocyclic crosslinking agents.

## 4.3 REFERENCES

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# Chapter V

## CHAPTER - V

# POLYURETHANES WITH FLEXIBLE GRAFTS AND BLOCKS FOR LOW TEMPERATURE APPLICATIONS

## INTRODUCTION

The primary requirement for a polymer to withstand low temperature environment is that it should remain flexible at low temperatures and should be impact resistant at laquid nitrogen temperatures. The principal property that dictates the service temperature of a polymer is its glass transition temperature. For a polymer to be useful for low temperature, it should have the lowest $T_g$ possible and that the polymer chain should exhibit secondary oscillations sufficiently below $T_g$. Secondary glass transition ($\beta$,$\gamma$ relaxations) are exhibited by pendant substituents and certain group in the main chain. The presence of flexibilising groups like ether which can facilitate rotation of the bonds of the polymer chain making coiled structures impart better low temperature properties to a polymer.

The introduction of polyurethane in epoxy polymers is known to improve the low temeprature properties by the toughening of the latter. Among the polyols polyoxy tetramethylene and hydroxy terminated polybutadiene respectively are best recommended for polyurethane meant for low temperature performance(1,2). A generally accepted convention in improving the low temperature performance is by introducing free volume in the polymer chain thus avoiding their close packing at low temperatures thereby facilitating bond rotation and chain coiling. This reduces the brittleness of the system. Free volume can be introduced by incorporation of bulky side groups and long pendant chains which have also low Tg values. These concepts have been well explored and exploited in designing low $T_g$ polymer systems[3]. This chapter focusses on the introduction of grafts and blocks into polyurethane systems with a view to bring down their $T_g$. Polyurethane with flexible pendant grafts were designed by the macrodiol technique. The influence of the grafts on the mechanical properties and $T_g$ has been investigated. The second part of the chapter examines the effect of introduction of flexible polymer blocks in the main chain of a polyurethane system on its physico-chemical and mechanical properties. Here a relatively rigid polyurethane system was chosen for a better understanding of the effect of the softer blocks on improvement of the low temperature properties of a commercially important polyster of 12-hydroxy stearic acid.

The mechanical properties at low temperatures were not determined in all samples, but an indirect assessment of the low temperature performance was made from the trend in glass transition temperature.

## SECTION 1

## 5.1 POLYURETHANES WITH POLYBUTYL ACRYLATE GRAFTS VIA MACROMONOMER TECHNIQUE

### 5.1. A Introduction

This section of the chapter discusses the synthesis of polyurethane networks based on polyethylene glycol, polyoxytetramethylene glycol and polybutadiene polyol possessing polybutyl acrylate grafts through the macromonomer method. The dependency of the grafts on the mechanical and thermal characteristics with a focus particularly on the glass transition temperature of the crosslinked system (which is indicative of the low temperature performance) has been investigated and the results presented.

Grafting is a convenient method of introducing pendant chain in the main backbone. Introduction of uniform size graft chains can be achieved by the well known grafting technique using macromonomers.(4) This method permits designing of well defined graft copolymers as the nature, chain length and the spacing of the grafts are predeterminable. Several methods exist for the synthesis of macromonomers.(5) Condensation type macromonomers like macrodiols, macrodicarboxylic acids, diamines etc. can be conveniently prepared by free radical chain transfer reaction using functional chain transfer agents.(6) The functionality and molecular weight of the macromonomers thus prepared can be predicted if the reaction parameters like concentration of initiator and chain transfer agent, temperature, chain transfer constant etc are known, Synthesis of grafted polyurethanes, polysiloxane, polyamide etc using the macromonomer technique have been reported.(7-9) The effect of the concentration of the grafts on the glass transition temperatures of different polymers have also reported.(10,11)

## 5.1.B. Experimental

### 5.1.B.1. *Materials*

(1) Polyethylene glycol (PEG of M/s BDH, India, molecular weight 10000)

(2) Polyoxytetramethylene glycol ( POTMG of BASF, molecular weight 2000)

(3) Hydroxy terminated polybutadiene (HTPB of NOCIL, India, molecular weight 2800)

(4) Tolylene diisocyanate (TDI of BAYER, 80:20 mixture of 2,4 and 2,6 isomers)

(5) 1-Mercapto, 2-3 propane diol (SRL, India)

(6) Butyl acrylate (Aldrich, USA)

(7) Azobisisobutyronitrile (SD Chemicals)

The purification of item 1 to 4 has been described in preceeding chapter. Butyl acrylate monomer, free of polymer was purified by passing through basic alumina coloumn to remove inhibitor present. AIBN was freshly recrystallized from methanol. Mercapto propane diol was distilled prior to use.

### 5.1.B.2. *Synthesis of macrodiol*

In a typical synthesis of macrodiol, butyl acrylate (12.8gm, 0.1 mole) mixed with 1.08 gm of AIBN initiator in a round bottomed flask was sealed under vacuum and heated at 70$^{o}$C for 2 hours. After reaction, the mixture was poured into methanol -water mixture of 1:1 by volume. The separated polymer was dissolved in THF and reprecipitated in the methanol-water mixture. The polymer was dissolved in chloroform and dried using anhydrous sodium sulphate. The polymer was separated as a viscous liquid on evaporating the solvent in vacuum. The reaction sequence is given in scheme 5.1. For determination of chain transfer constant, the reaction was done in glass tubes sealed under vacuum and polymer conversion was limited to about 10%.

### 5.1.B.3. *Preparation of polyurethane specimens*

The polyurethane samples were prepared by mixing the polyol and macrodiol in appropriate ratios. Trimethylol propane was used as the crosslinking agent. Calculated quantity of tolylene diisocyanate was added to the system for a R value (NCO/OH eq: ratio) of one and dibutyl tin dilaurate (0.5 wt%) served as catalyst. The mixture was deareated and poured into mould. It was allowed to cure at room temperature for one day followed by curing at 60$^{o}$C for eight hours. The reaction is illustrated in scheme 5.2.

### 5.1.B.4. *Characterisation*

Macrodiols were characterised by IR spectrum and chemical estimation of hydroxyl value. Molecular weights were determined by GPC using THF as elutant and also by knauer VPO using toluene as solvent.

### 5.1.B.5. *Evaluation of mechanical properties*

The mechanical properties of the polyurethanes like tensile strength and elongation were analysed as per ASTM method in INSTRON UTM.

## 5.1.C. Results and Discussion

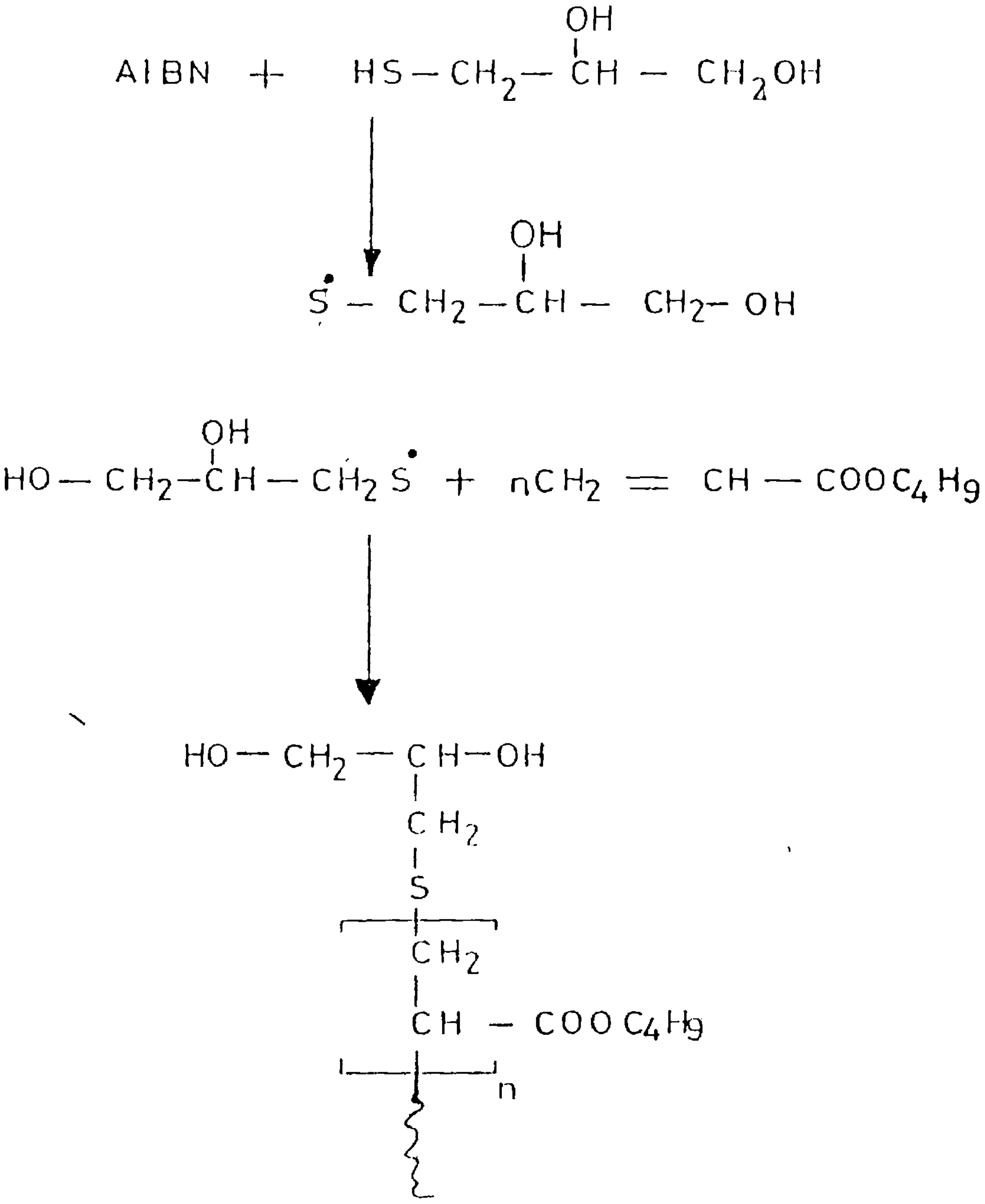
### 5.1.C.1. *Synthesis and characterisation of macrodiols*

Macrodiols of butyl acrylate were realised by the free radical polymerisation using 1-mercapto 2,3 propane diol as the chain transfer agent (CTA) as per the reaction given in scheme 1. Similar method for synthesis of macrodicarboxylic acid has been reported.(12)

The functionality of the resultant macrodiol depends on the chain transfer constant of the mercaptan. This was determined by the Mayo's method by monitoring the molecular weight of the polymers as the function of the concentration of the chain transfer agent at fixed initiator concentration and temperature and doing a linear plot using the equation.

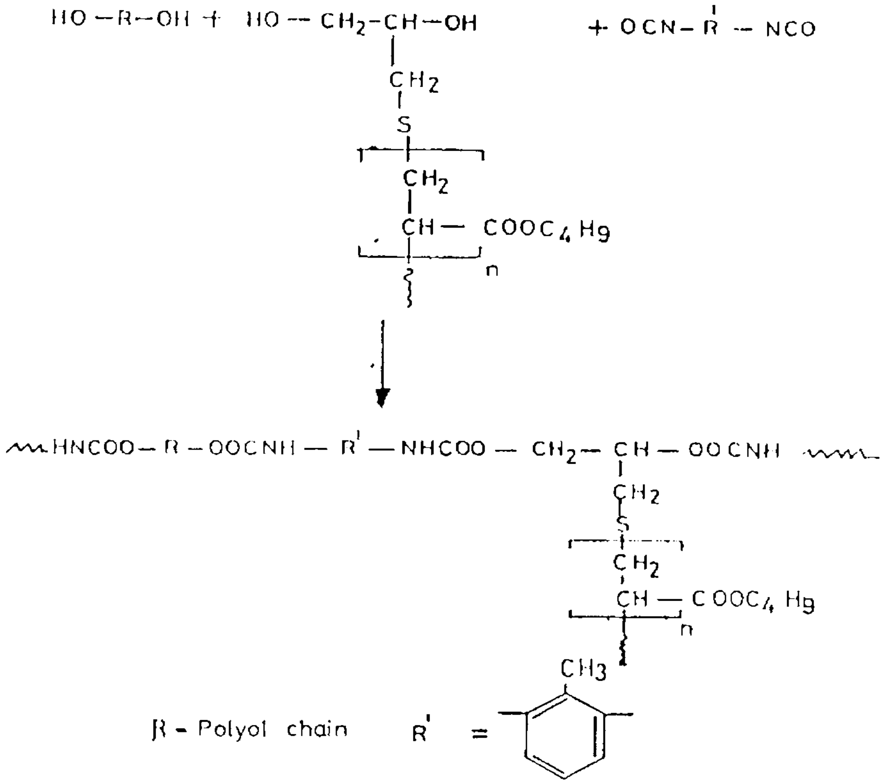
$$\frac{1}{DP} = \frac{1}{DP_0} + Cs\frac{[S]}{[M]}$$

[S] and [M] are the concentration of the chain transfer agent and of the monomer respectively. DP is the degree of polymerisation. The experimental conditions for the determination of the chain transfer constant (Cs) are cited in table 5.1. The Cs was determined as 0.55 at 70°C from a plot of 1/DP against [S]/[M]. The high Cs value indicates that the mercaptan is an excellent functionalising agent.



( MACRODIOL )

Scheme 5.1 : Synthesis of Macrodiol of butyl acrylate



Scheme 5.2 : Synthesis of polyurethane with graft PBA

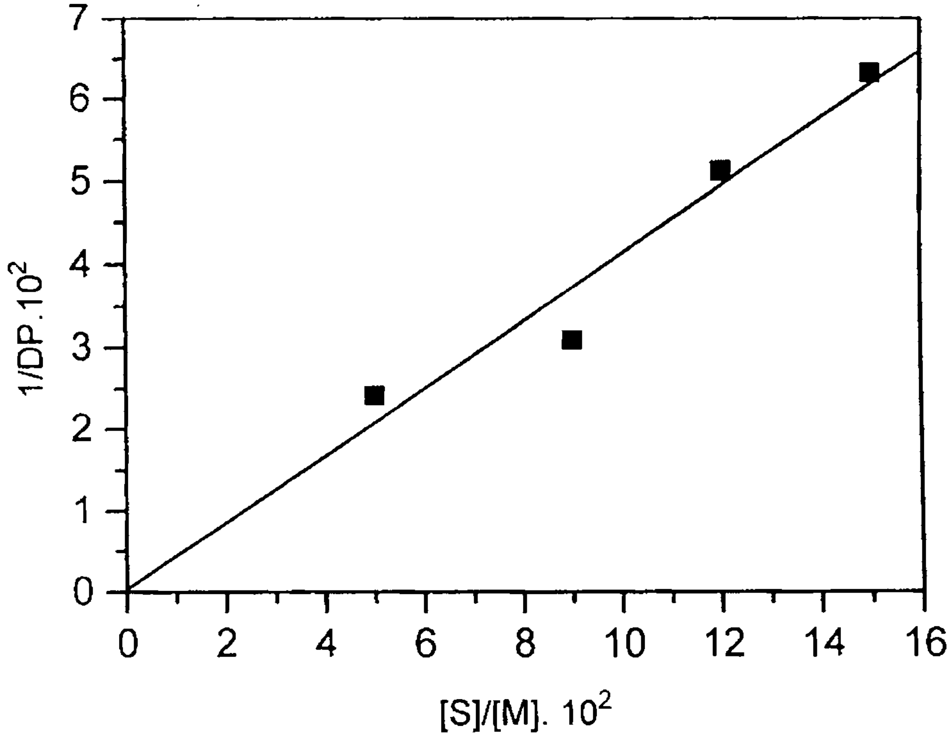


Fig. 5.1 : Plot of [S]/[M] vs 1/DP for determination of Cs'

The Cs for butyl acrylate monomer for similar chain transfer agent is in the vicinity of 0.6.

**Table 5.1: Variation of DP with CTA concentration for determination of Cs.**
**[AIBN] = 0.05 mol %, Temp : 70°C**

| No: | [S]/[M] | Mn by GPC | Dispersity | DP |
|---|---|---|---|---|
| 1 | 0.0053 | 29030 | 2.56 | 226 |
| 2 | 0.0086 | 22630 | 1.97 | 176 |
| 3 | 0.0151 | 13250 | 2.14 | 103 |
| 4 | 0.0180 | 4760 | 2.90 | 37 |
| 5 | 0.0226 | 6340 | 2.74 | 49 |

Macrodiols of desired molecular weight were obtained by adjusting the ratio of butyl acrylate to mercaptopropane diol. For getting low molecular weight macrodiols, appreciable concentration of the CTA was employed. From the molecular weight, determined by VPO and estimation of hydroxyl group content, the avarage functionalities were calculated. The results obtained are given in table 5.2.

**Table 5.2: Variation of hydroxyl value and functionality of macrodiols with concentration of chain transfer agent**

| Sl. No. | [S]/[M] | OH Value (mgm KOH) | Eq:wt (calc:) | Mol:wt (by VPO) | Molwt: (from Cs) | Fn (Theor:) | Fn (Exptl) |
|---|---|---|---|---|---|---|---|
| 1 | 0.15 | 54.5 | 1028 | 2025 | 1550 | 1.94 | 1.97 |
| 2 | 0.12 | 46.2 | 1214 | 2500 | 2500 | 1.92 | 2.06 |
| 3 | 0.09 | 25.8 | 2170 | 4150 | 4150 | 2.39 | 1.92 |
| 4 | 0.05 | 20.7 | 2650 | 5300 | 5300 | 1.69 | 1.96 |

### 5.1.C.2. *Theoretical prediction of macrodiol functionality*

Although knowledge of Cs helps in predicting the molecular weight and functionality of the formed polymers under a given set of reaction conditions, the $C_s$ value determined by Mayo's method is applicable only to ideal system using very low concentration of chain transfer agent. When high concentration of CTA is used, secondary reactions leading to retardation is an inevitable consequence. Retardation is caused by the reduced reactivity of the thiyl radical (RS.) to reinitiate the monomer and also by the chain termination by combination with these radicals. In this case the Cs from Mayo's equation can no longer be used to predict precisely the molecular weight under the macromonomer synthesis conditions. This is evident from the disparity in values of theoretically expected molecular weights and the observed molecular weights for the experimental conditions employed as given in table 5.2. Hence for a reliable prediction it was imperative to determine the apparent chain transfer constant (Cs') from the molecular weight data pertaining to macromonomer synthesis conditions. A plot for determining Cs' using the data in table 5.2 is shown in figure. 5.1. The Cs' was calculated as 0.41. Fig. 5.1 also depicts the macromonomer molecular weight as a function of concentration of chain transfer agent under the given condition of temperature and initiator concentration. Cs' is inferior to Cs as the former doesn't account for the correction for retardation. Similar observation has been reported earlier.(13) The avarage functionality of the macrodiol comes to approximately 2. The functionality can be theoretically calculated from the chain transfer constant as,

$$Fn = DP_n . Cs' \frac{[S]}{[M]}$$

-The values are included in table 5.2. The experimental values are in close proximity with the theoretical values.

The I.R spectrum of the product shows a peak at 3600 cm-$^1$ corresponding to OH group and peak at 1740 cm$^{-1}$ for the ester carbonyl peak. The macrodiol of butyl acrylate is a colourless viscous liquid soluble in all polar solvents. It is miscible with HTPB below a concentration of 30% only.

### 5.1.C.3. *Synthesis and characterization of grafted PU*

**PEG - PU system: Effect of variation of graft concentration.**

The macrodiol was mixed with dried PEG in different ratios inorder to vary the extent of grafting and was cured using TMP as crosslinker and TDI as curative keeping R value (NCO/OH ratio) as 1. Curing was done at 60$^o$C to avoid secondary crosslinks like allophanate and biuret. The mechanical properties and glass transition temperature were measured and thermal stability was measured by TGA. The molecular weight of the macrodiol and hence that of the graft was fixed as 2025 in this set of study. The results are presented in table 5.3.

**Table 5.3 : Variation of mechanical properties and Tg with concentration of macro-monomer(MD) for PEG-PU system for fixed graft molecular weight (2025)**

| Sl. No | Wt. ratio of PEG :MD | T.Strength (KSC) | Elongation at break (%) | Hardness (Shore A) | Tg ($^o$C) |
|---|---|---|---|---|---|
| 1 | 100:0 | 8.5 | 385 | 25 | -36 |
| 2 | 80:20 | 9.8 | 326 | 30 | -38 |
| 3 | 70:30 | 12.5 | 302 | 35 | -45 |
| 4 | 60:40 | 14.2 | 285 | 40 | -47 |
| 5 | 50:50 | 15.3 | 256 | 40 | -35 |
| 6 | 40:60 | 16.5 | 235 | 45 | -22 |
| 7 | 30:70 | 17.8 | 215 | 45 | -23 |

Interestingly, as the quantity of the graft increases (for the fixed graft chain length), the tensile strength increases with a proportionate decrease in elongation. Grafting would be expected to lead to an enhanced free volume and hence to a lower strength due to easier deformation and a higher elongation. In this case the proportionate increase in tensile strength can be attributed to the increased intermolecular cohesive interaction through polar urethane linkages whose concentration increases in the main chain as the concentration of the macrodiol is increased. The increase in hardness values of the samples can be attributed to the same reason and the increase is proportional to the increase of cohesive forces by the polar groups . The trend cannot be attributed to the enhanced degree of entanglement of the grafts since they are shorter in size.

The analysis of glass transition temperature by TMA showed a single value indicating miscibility of the two polymer segments for this graft chain length. The Tg value shows an initial dip and then an increase as concentration of the graft increases. The Tg value has come down from -36°C to -47°C for the same case and thereafter the value starts to increase due to the increase in concentration of polar groups from the macromonomer and urethane links from the macromonomer. The initial decrease is caused by the enhanced mobility of the chains as aided by the grafts which prevent close packing of the chains thereby increasing the free volume. However, beyond about 50% concentration of the graft the cohesive interaction of the closely spaced urethane linkages takes over the free volume effect causing Tg to increase. Hence, for low temperature performance a 60:40 weight percentage of PEG to macrodiol combination appears optimal.

### 5.1.C.4. *Effect of molecular weight of the graft on the mechanical and low temperature properties*

Increase of molecular weight of the macrodiol increases the length of the pendant groups in the polyurethane graft which prevents close packing of the chains at low temperatures. This is expected to bring down the Tg. The effect of molecular weight of the macrodiol used in the preparation of the grafted polyurethane on the mechanical and low temperature properties of the resultant polyurethane was studied and the results are presented in table 5.4 for a constant weight ratio of 60:40 of polyol to macrodiol.

**Table 5.4: Variation of mechanical properties and Tg with molecular weight of the graft for a fixed weight ratio of graft for PEG-PU system (60:40)**

| Sl. No. | Molecular wt: of PBA | T. Strength (KSC) | Elongn: at break (%) | Hardness (Shore A) | Tg(°C) |
|---|---|---|---|---|---|
| 1 | 2025 | 14.2 | 285 | 40 | -47 |
| 2 | 2300 | 13.8 | 295 | 40 | -48 |
| 3 | 4150 | 12.5 | 310 | 35 | -50 |
| 4 | 5300 | 11.8 | 335 | 35 | -51 |

On increasing the graft length for a fixed graft concentration, the tensile strength decreases and elongation increases. The hardness value decreases. Tg was found undergo a systematic dimunition although the decrease is not substantial.

The decrease of the tensile strength and increase of elongation can be attributed to the lesser number of urethane linkages formed as the molecular weight of the macrodiol is increased. The cohesive forces through the urethane groups decreases systematicaly. Further the longer graft permits easier deformation causing poorer mechanical performance. Although longer grafts permits lowering Tg, this is achieved at the cost of the mechanical properties.

### 5.1.D Studies with HTPB and POTMG polyols

HTPB and POTMG being polyols with better low temperature performance than polyether PEG, same series of studies were conducted with these polyols as well. The graft polyurethane samples were prepared in same way as in the case of PEG-PU system. The graft length was fixed as 2025 and its concentration was varied. The R value was kept as 1 in all cases and curing was done at 60°C for 8 hours. It was observed that as the quantity of macrodiol was increased above 30%, phase separation occured and the PU samples have shown two glass transition temperatures for HTPB and POTMG based polyurethanes as seen in the TMA thermograms shown in figure 5.2. The variation of mechanical properties and Tg with varying percentages of macrodiol is given in table 5.5.

Data given in table 5.5 indicate that the PU system based on POTMG and HTPB show similar trend in mechanical performance. The tensile strength and hardness increased progressively with the concentration of the graft. Tg value decreases systematically till about 30-40% of the graft. Beyond this concentration, phase separation occurs. The trend in mechanical properties and Tg and morphological features makes a difference from the PEG based system. In the case of graft-POTMG, the Tg remains more or less intact since the constituents of the graft PU homogeneous phase ie POTMG and PBA (low molecular weight) form a hemogeneous phase.

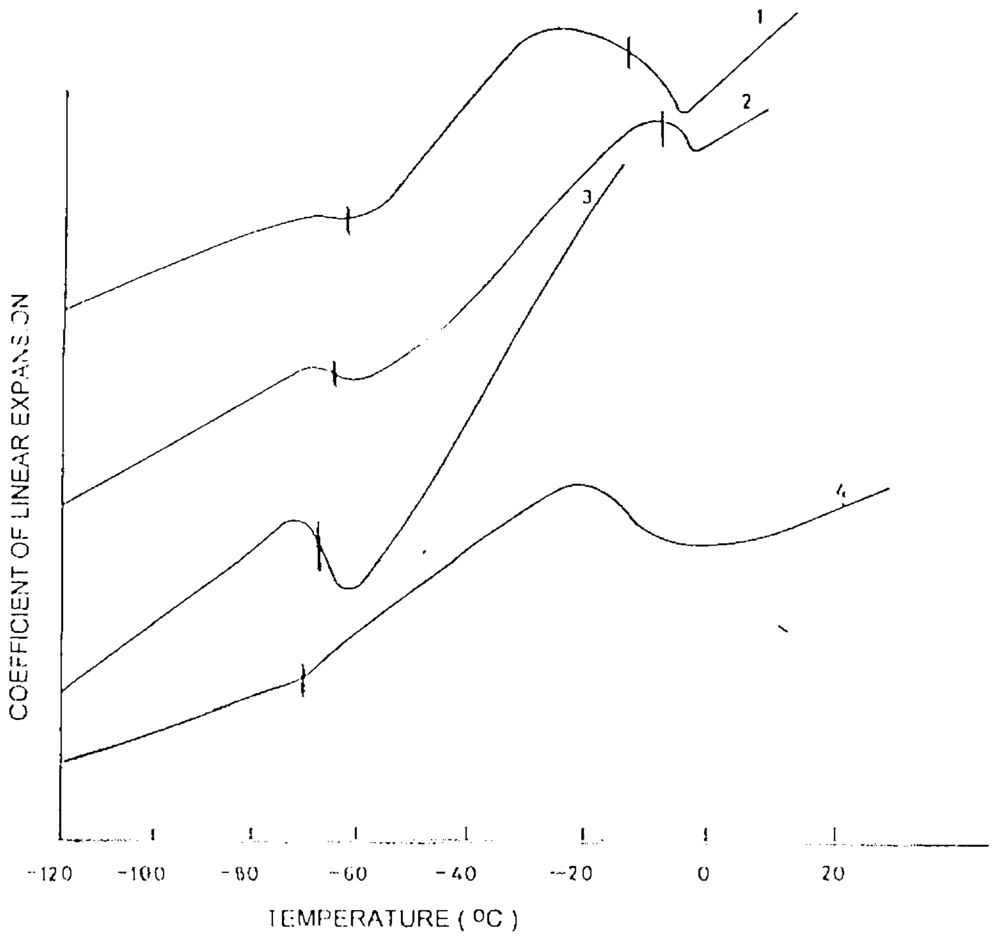


Fig. 5.2 : TMA thermograms of PBA - grafted POMTG - and HTPB - Polyurethanes.
1. POMTG/PBA - 60:40, 2. HTPB/PBA - 60:40, 3. HTPB/PBA - 70:30,
4. POMTG/PBA - 70:30

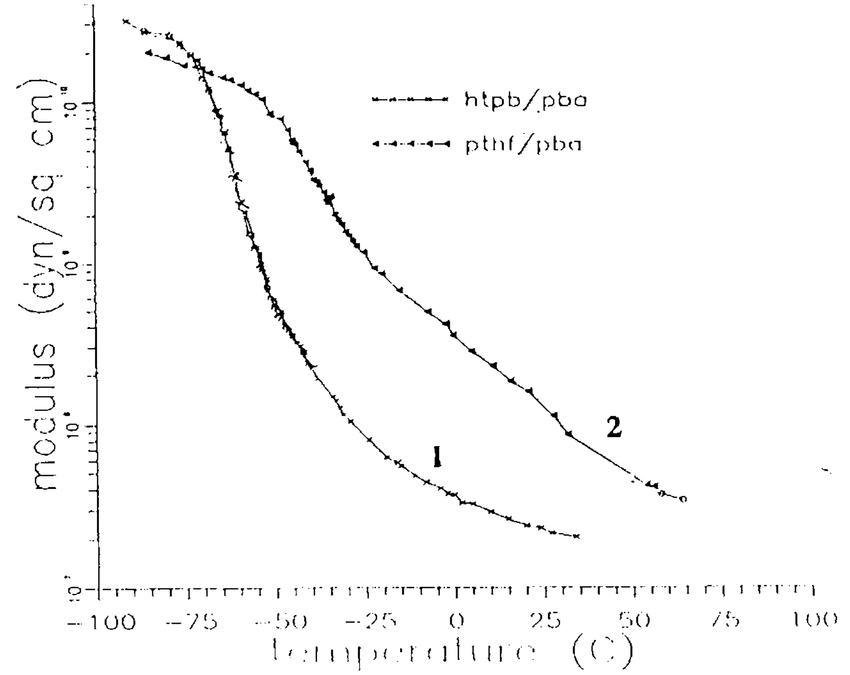


Fig. 5.5. DMA thermograms PBA - grafted PU's, 1 - HTPB/PBA - 60:40,
2 - POMTG/PBA - 60:40

**Table 5.5 : Mechanical properties and Tg for graft-PU based on HTPB and POTMG with varying concentration of the graft of fixed molecular weight. (2025).**

| Sl. No. | MD weight fraction | Polyol used | T.S. (KSC) | Elongn: (%) | Hardness (shore A) | $T_{g1}$ | $T_{g2}$ |
|---|---|---|---|---|---|---|---|
| 1 | 0 | POTMG | 16.0 | 425 | 35 | -65 | -- |
| | | HTPB | 7.5 | 410 | 30 | -62 | -- |
| 2 | 10% | POTMG | 18.5 | 400 | 35 | -68 | -- |
| | | HTPB | 9.0 | 375 | 30 | -64 | -- |
| 3 | 20% | POTMG | 20.0 | 382 | 35 | -69 | -- |
| | | HTPB | 10.5 | 355 | 35 | -66 | -- |
| 4 | 30% | POTMG | 25.0 | 325 | 40 | -71 | -- |
| | | HTPB | 15.0 | 332 | 40 | -68 | -- |
| 5 | 40% | POTMG | 28.0 | 305 | 40 | -69 | -10 |
| | | HTPB | 12.0 | 295 | 45 | -65 | -7 |
| 6 | 50% | POTMG | 35.0 | 285 | 50 | -68 | -7 |
| | | HTPB | 19.5 | 290 | 45 | -62 | -5 |

In the case of HTPB, Tg decreases slightly. Since the phase gets staturated at about 30% the Tg stagnates at this concentration beyond which a second phase probably the homopolyurethane of the macrodiol is generated whose Tg appears separately at -5 to -10°C as shown in figure 5.2.

The morphology of graft polyurethanes of POTMG and HTPB were examined by SEM analysis. The phases are homogeneous at low concentration of grafts. The phase separation in HTPB based samples at 40 and 50% concentration of PBA are clearly visible in SEM patterns given in fig.5.3 and that of POTMG/PBA grafts are given in fig. 5.4

The temparture dependency of the mechanical properties was monitored by DMA. DMA for two typical graft-PU of HTPB and POTMG are shown in figure 5.5. Only a single Tg was observed showing the miscibility of the segments. No perceptible secondary transition could be seen below $T_g$. The thermograms above Tg reflects the temperature dependency of the mechanical properties. It can be observed that for two typical samples having the same percentage of graft, POTMG based PU shows a better temperature retention of properties.

### 5.1.D.1. *Effect of molecular weight of the graft on HTPB and POTMG based* PU

Keeping the weight ratio of macrodiol as 25%, the effect of the molecular weight of the macrodiol on the mechanical and glass transition temperature was studied. The results are tabulated in table 5.6. Only one glass transition was observed for all the molecular weight ranges as the system is homogeneous at this concentration (of 25% of the graft). It was observed that there was a gradual decrease of Tg when the molecular weight of the macrodiol was increased and that there was also an increase of elongation and decrease of tensile strength. The behaviour is similar to the case of PEG - PU.

The impact of the grafts on the mechanical characteristics of the three systems has been depicted in fig. 5.6 on a comparative basis where the relative increase in tensile strength by way of introducing shorter grafts of fixed chain length has been plotted as a function of its concentration.

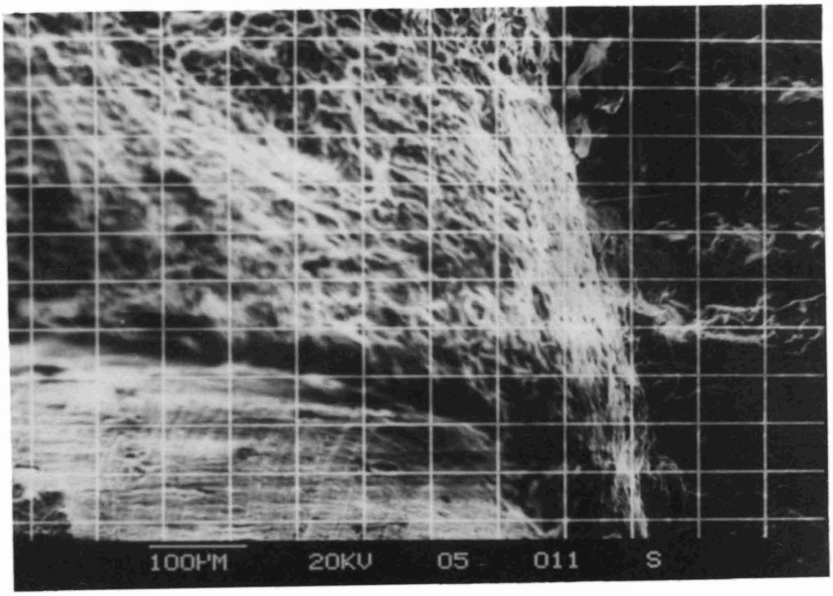


Fig.5.3: SEM photographs of PBA grafted HTPB polyurethanes (50:50 ratio)

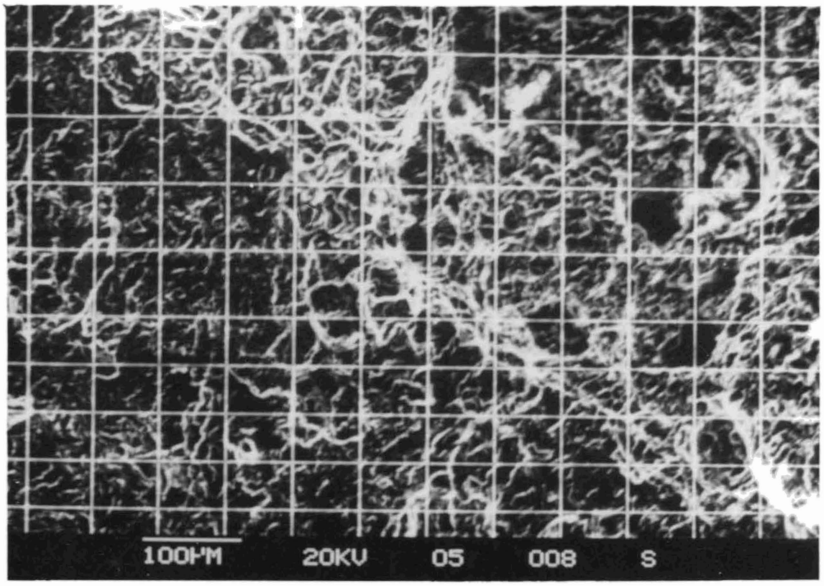


Fig.5.4: SEM photographs of PBA grafted POTMG polyurethanes (50:50 ratio)

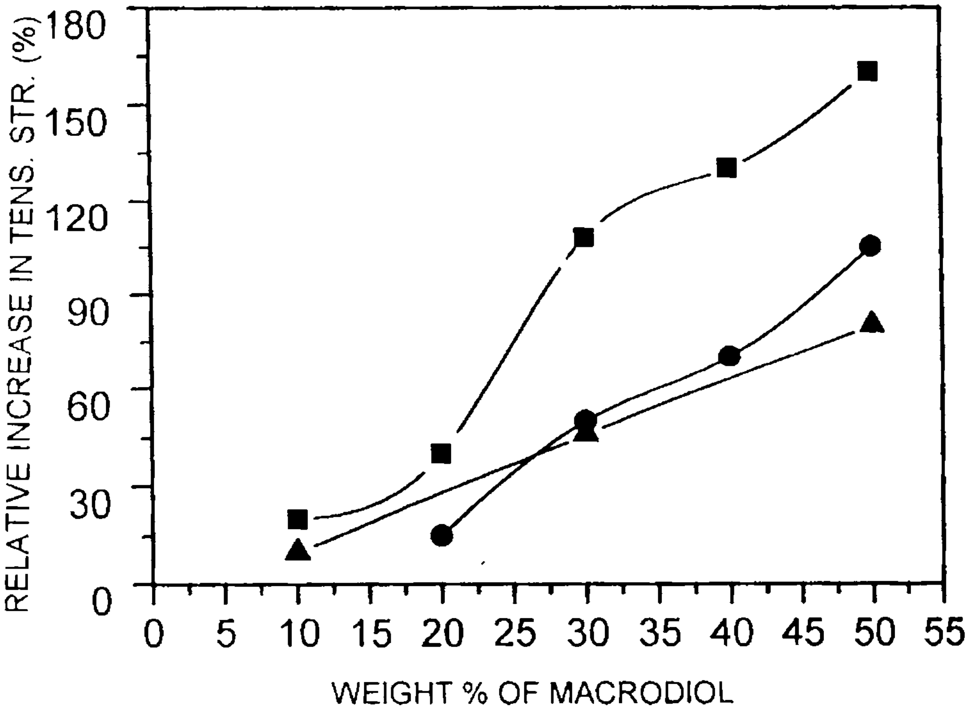


Fig.5.6 : Relative increase in tensile strength for PBA grafted polyurethanes with respect to concentration of PBA (▲ PEG ● POTMG ■ HTPB)

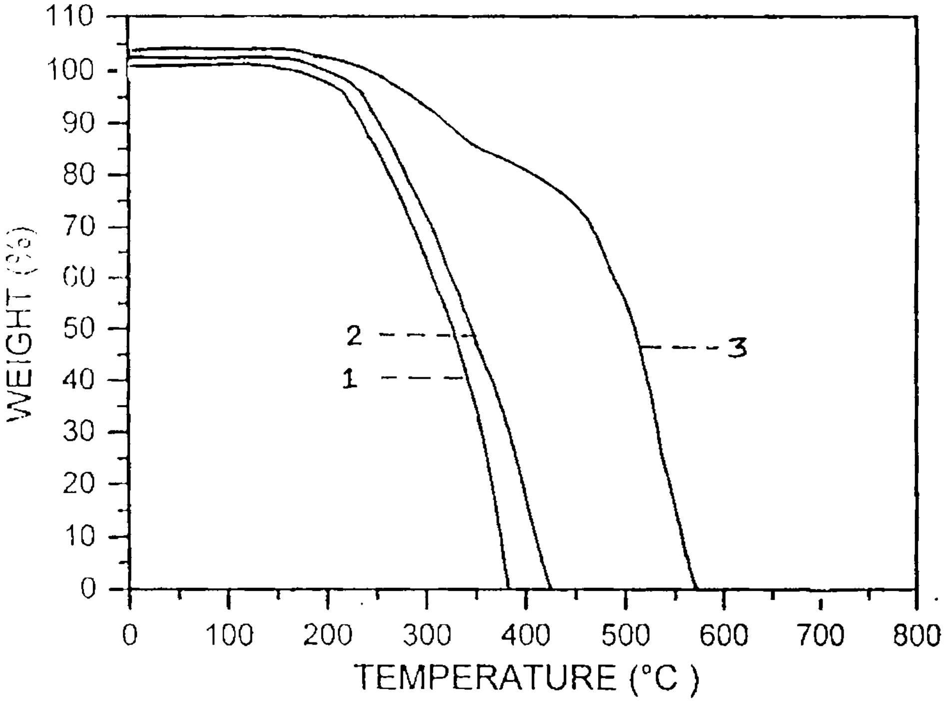


Fig.5.7 : Thermograms of PBA graft polyurethanes (①- PEG ,②- POTMG, ③- HTPB)

**Table 5.6: Mechanical properties and $T_g$ for graft-HTPB and POTMG polyurethanes with varying molecular weight of graft for a fixed weight fraction of the graft, 25%.**

| Sl. No. | Mol:weight of grafts | Polyol used | T.S. (KSC) | Elongn: (%) | $T_g$ ($^{o}$C) |
|---|---|---|---|---|---|
| 1 | 2025 | POTMG | 21.0 | 378 | -69 |
| | | HTPB | 11.8 | 351 | -61 |
| 2 | 2500 | POTMG | 20.0 | 381 | -71 |
| | | HTPB | 10.5 | 360 | -63 |
| 3 | 4950 | POTMG | 18.5 | 391 | -71 |
| | | HTPB | 9.0 | 365 | -65 |
| 4 | 5300 | POTMG | 17.5 | 395 | -74 |
| | | HTPB | 9.0 | 374 | -67 |

As seen, the improvement is better for HTPB and is more or less identical for POTMG and PEG at a fixed concentration of the graft. HTPB has been found to possess higher functional oligomers(14). Addition of more amount of macrodiol can cause hyperbranched junctions and urethane linkages that contribute to the enhanced strength properties and related hardness values in this case.

### 5.1.E. Evaluation of thermal properties

Although the main objective of the modification was to effect a decrease in $T_g$, it was of interest to see if the grafts could affect the thermal behaviour of the resultant networks. The thermal decomposition patterns of the cured polyurethanes were determined by TGA. Typical thermograms taken in nitrogen atmosphere for the three different polyols under study are presented in fig.5.7. The decomposition patterns for polyethylene glycol-based and polyoxytetramethylene-based samples are almost same as the starting polyol -based polyurethane without the graft. There is no appreciable change in thermal stability. The polybutyl acrylate doesnot contribute to the thermal stability and it has the same decomposition maxima as polyethyleneglycol and polyoxytetramethylene glycol. In the case of HTPB-based polyurethane with polybutyl acrylate grafts, the thermograms manifest two- step decomposition which is due to the difference in decomposition patterns of the individual polymers. The overall thermal stability of the polyurethane system is found to be unaffected by the incorporation of polybutyl acrylate grafts.

## 5.1.F. Conclusions

The mechanical properties and the low temperature performance of the polyurethane systems can be tamed by the incorporation of polybutyl acrylate grafts through the macrodiol technique. The macrodiol-method permits design of tailor made graft polyurethane system. Incorporation of longer grafts although decreases glass transition temperature, results also in a concomitant decrease in mechanical properties. The $T_g$ decrease is limited by miscibility of the grafts in the main chain and the profile depends on the choice of graft-backbone pair. The incorporation of shorter chains in a limited concentration appears ideal as it decreases the glass transition temperature along with an improvement in mechanical properties. But Tg-concentration profile is offset at high concentration of shorter grafts. The results of the study reveal that the cohesive force by the polar groups is determinant in predicting the properties of the graft polymer rather than the free volume or entanglement effect of the graft.

## SECTION 2

## 5.2 POLYURETHANES WITH FLEXIBLE BLOCKS FOR LOW TEMPERATURE PERFORMANCE : POLYESTER - POLYURETHANE WITH PTMO BLOCKS

### 5.2.A. Introduction

The present investigation focusses on the introduction of Poly tetra methylene oxide (PTMO) segments in the backbone of polyurethane based on polyester. The system selected for this set of studies was a typical polyester derived from 12 -hydroxy stearic acid, obtained from castor oil. Generally, aliphatic polyesters also display excellant low temperature properties. The polyester selected here is having a reduced concentration of ester groups and having a higher glass transition temperature than polyesters like diethylene glycol adipate. The effect of incorporation of PTMO on the properties can be clearly observed if the glass transition temperatures of the two individual system are widely different. This has been the reason for selecting this polyester -PU as the base polymer in this study. Polyester-polyether block copolymers have been reported by Lilaonitkul[15,16] wherein the polyester part is crystalline tetramethylene terephthalate. The polyether part is PTMO. The properties like $T_g$ has been reported to vary considerably with the concentration of ether segment. The impact of concentration of PTMO on the properties has also been reported. The present investigation is in similar lines but incorporating polyurethane segments in the chain.

Polybutadiene-based polyurethanes, like HTPB also exhibit good low temperature properties[17]. In the present study' HTPB was not considered as the basic backbone due to two reasons.

HTPB also shows glass transition temperature in almost the same region as that of PTMO and hence the effect of incorporation of PTMO block cannot be clearly understood.

Due to the difference in polarity of the two systems, the two individual polymers are not miscible and hence it pauses heterogeneity problem for the resultant polyurethanes. The immiscibility of the polymers could be partially reduced on reaction with diisocyanate. However the resultant polyurethane was found to be not perfectly homogeneous. Hence, studies were focussed on the polyester-polyether system which gives a uniform matrix.

The studies on incorporation of PTMO in the polyester based urethane system was carried out by two approaches.

1. Incorporating PTMO at the polyurethane synthesis stage
2. Incorporating PTMO in the polyester polyol by chemical modification prior to conversion to PU.

## 5.2.B Experimental

### 5.2.B.1 *Materials used*

a. ISRO polyol. (a polyester based on 12-hydroxy stearic acid, proprietory item of VSSC whose synthesis details cannot hence be given)

b. 12-hydroxy stearic acid, (THSA, M/s Bombay oil Co. Bombay)

c. Polyoxytetramethylene glycol (PTMO polyol, mol.wt. 2000 BASF, Germany)

d. Tetrahydrofuran (BDH, India)

e. Trimethylol propane (Aldrich, USA)

f. Dibutyl tin dilaurate (DBTDL, SD chemicals, Bombay)

g. $BF_3$. etherate (SISCO, Bombay).

### 5.2.B.2. *Purification of raw materials*

THF was purified by distillation after removing traces of peroxides. It was finally dried using sodium wire. Acetic anhydride was purified by distillation. $BF_3$ etherate was used as received. TMP was dried throughly under vacuum at $80^0$C.

### 5.2.B.3. *Preparation of polyester-polyether co-polyurethane*

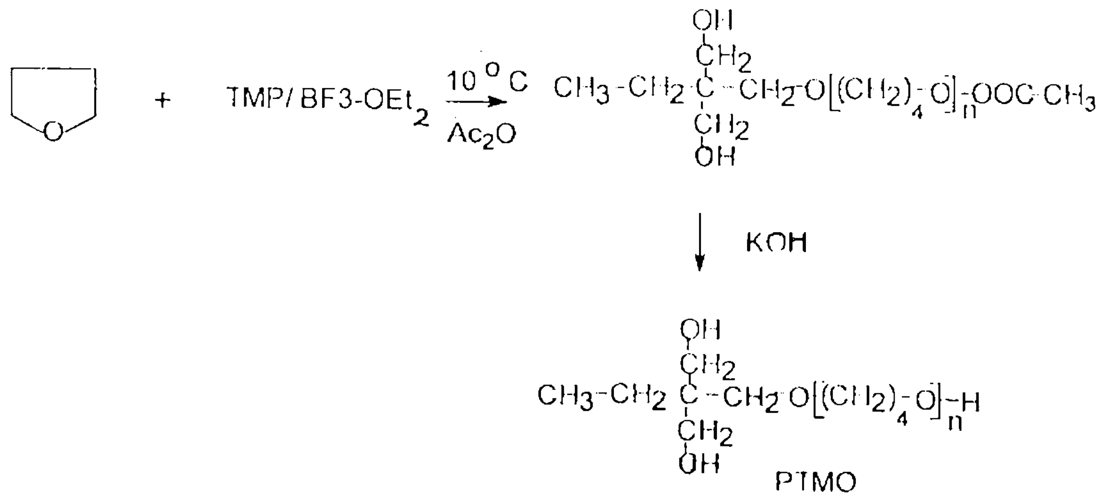
The polyester of 12-hydroxy stearic acid, designated as ISRO polyol (synthesised as per an internal document) was dried by heating under vacuum at $60^0$C for 2 hours. The polyester polyol and PTMO polyols were blended at different weight ratios. The catalyst, 0.5 weight% of DBTDL was added. TMP as a crosslinking agent was added at 5% by weight of the mixture of polyols. TDI for an equivalent ratio of 1:1 was added and the system was mixed well. Polyurethane slabs were made as described in the previous section. The mechanical and low temperature properties of the cured slabs were determined. This set of studies were conducted to study the effect of PTMO segment on the properties of co-polyurethane. The PTMO polyol used in the set of studies was having a molecular weight of 2000 and average functionality of about 2. The table 5.7 shows the variation of mechanical properties and Tg of the various compositions.

### 5.2.B.4. *Synthesis of PTMO polyol*

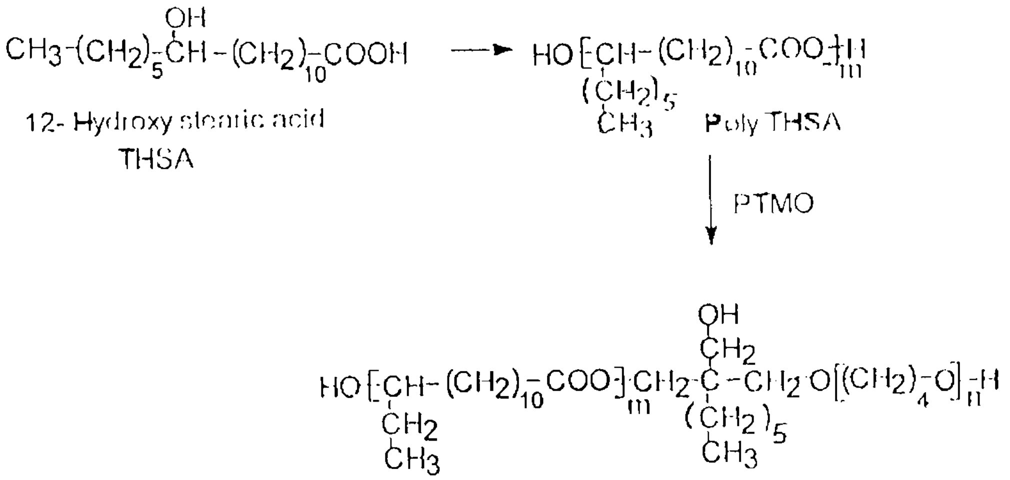
The synthesis of trifunctional PTMO with different molecular weight ranges was carried at by ring opening polymerisation of THF with $BF_3$ etherate/TMP as catalyst and acetic anhydride as the chain transfer reagent. The reaction is shown in scheme 5.3. THF, acetic anhydride and TMP in required quantities were taken in a round bottomed flask, stirred at -10°C in nitrogen atmosphere. $BF_3$ etherate was added through dropping funnel slowly. It was stirred for two hours during which time, the viscosity of the system increased. After the reaction, the contents were poured into methanol with stirring. The precipitated polymer was washed well to remove $BF_3$ and acetic anhydride . It was then mixed with excess of ethanolic KOH and heated at 70°C for 2 hours to hydrolyse the terminal acetyl groups. It was then washed well with methanol and dried at 60°C. The product was characterised by IR spectrum and determination of hydroxyl value and molecular weight (by VPO). The molecular weight could be varied by varying the quantity of acetic anhydride. The average functionality was calculated from molecular weight and OH value.

### 5.2.B.5 *Synthesis of polyestor -b-PTMO polyol (block copolyol)*

The synthesis of the block copolymers was done by co- polyesterification. The reaction is given in scheme 5.4. 12-hydroxy stearic acid (THSA) was self polymerised in toluene at 110°C in presence of acid catalyst. The poly THSA (PTHSA) of molecular weight 1550 thus obtained was reacted with PTMO of different molecular weight under the same conditions to yield polyester-PTMO copolymer of varying molecular weights. The terminal COOH group of the poly THSA was esterified with the OH group of the PTMO polyol using the same catalyst.



Scheme 5.3 : Synthesis of trifunctional PTMO



Scheme 5.4 : Synthesis of polyester of THSA - PTMO block copolyol

The product was purified by washing with water followed by drying at 60°C under vacuum.

### 5.2.B.6 *Synthesis of block copolyurethane using block copolyol.*

The block copolyurethane of the copolyol was prepared as described in chapter 5 section 1. The copolyol was mixed with TMP as the crosslinker and reacted with TDI in presence of DBTDL as the catalyst at room temperature, and poured into mould for preparation of PU specimens.

### 5.2.C. Analysis and characterisation

The polyether of THF was analysed by IR spectrum and hydroxyl value. A peak at 3600 $cm^{-1}$ corresponds to OH group. Peak at 1100 $cm^{-1}$ corresponds to the ether group. The absence of a peak at 1710 $cm^{-1}$ shows that acid groups are not present. Molecular weight was determined by VPO method.

### 5.2.D. Results and discussion

The synthesis of co-polyurethane of polyester and polyether was attempted by a one shot reaction by blending the individual polyols and curing the mixture with TDI in presence of TMP as crosslinker. The effect of PTMO segment quantity on the mechanical and low temperature properties of the resultant copolyurethane was studied by varying the weight percentage of PTMO in the co-polyurethane. The mechanical properties and $T_g$ were measured for various compositions. The sol content was also measured as an index of the extent of crosslinking. It can be observed from table 5.7 that as the amount of PTMO increases, initially there is an increase in tensile strength and elongation and decrease of Tg which is clearly due to the effect of PTMO.

**Table 5.7: Mechanical properties and Tg of one-shot copolyurethane (molecular weight of PTMO 2000)**

| Sl. no. | Polyster wt: % | PTMO wt: % | T.S (KSC) | Elon: % | Tg (°C) | Sol % | Remarks |
|---|---|---|---|---|---|---|---|
| 1 | 100 | 0 | 4.5 | 295 | -25 | 10 | contains mono and - difunctional polyester |
| 2 | 90 | 10 | 6.0 | 350 | -25 | 10 | |
| 3 | 80 | 20 | 7.5 | 365 | -- | -- | Slightly opaque due to improper miscibility |
| 4 | 70 | 30 | 5.0 | 385 | -45 | -- | |
| 5 | 60 | 40 | -- | -- | -- | 80 | sample not cured properly |
| 6 | 50 | 50 | -- | -- | -- | 80 | |

As the quantity of PTMO increases further, the samples were found not to undergo proper curing as seen from the sol percentage. This could be due to the avarage functionality of the polyol mixture being low. The polyester from THSA designated as ISRO polyol is having a lower average functionality of about 1.8 which is due to a low OH functionality of the starting material THSA obtained from castor oil. The low avarage OH functionality of the polyester-polyether mixture results in polyurethanes with inferior properties compared to other polyesters. The addition of more quantity of TMP to compensate for the loss in average functionality ($F_{av}$) causes hetrogenity. At the weight ratio 70:30, of polyester : PTMO the sample became slightly opaque and displayed two $T_g$'s characteristic of hetrogenity of the polymer blends.

The type of hydroxyl group in the polyester studied is both secondary whereas that in PTMO polyol is primary. This can cause a difference in reactivity for the individual polymers towards TDI. This difference in reactivity could lead to a block copolyurethane whose structure is different from the statistically expected random block copolyurethane. The possible structure contains mixture of sequences of PTMO-PU and PTHSA-PU formed by the reaction of diisocyanate with PTMO polyol first followed by reaction with PTHSA polyol during the formation of the polyurethanes. Therfore, the effective molecular weight of each segment in copolyurethane is several times more than the starting polyols. The crosslinker is also having primary OH groups. Due to the low molecular weight of TMP, it is more reactive towards TDI than the polyols. Possibility exists for formation of homopolymer of PTMO followed by homopolymer of polyester which makes the system hetrogeneous. At lower levels of PTMO concentration, this effect is not felt every much. The reactivity of the ingredients towards TDI is in the order TMP > Polyether > Polyester.At ratios 60:40 and 50:50 studied, the samples did not cure properly and addition of more TMP to overcome the loss in $F_{av}$ gave more opaque products probably due to the preferred consumption of TMP by TDI preventing interblock reaction and this resulted in the higher value of the sol content. Inorder to overcome the problem of heterogenity and reactivity difference, polyether and polyester blocks were preformed by copolyesterification in a way to endcap with OH grups. This block copolymer was synthesised using PTMO of different molecular weights the latter being synthesised as per reaction scheme 5.4. The reaction condition for the synthesis of PTMO are given in 5.2.B.5. The molecular weight of PTMO could be controlled by variation of the quantity of chain transfer reagent, acetic anhydride. The use of TMP as the cocatalyst gave polyol with average functionality near to 3. Synthesis conditions and characteristics of the polyol are given in table 5.8

**Table 5.8 : Variation of molecular weight and functionality of PTMO polyols with chain transfer agent**

| Sl. no. | THF:Ac2O mole ratio | Mol. wt. by VPO | OH Value mgm KOH | Eq.wt (calc:) | $F_{av}$ | Viscosity (cps at 30°C) |
|---|---|---|---|---|---|---|
| 1 | 0.14 | 550 | 280 | 196 | 2.8 | 600 |
| 2 | 0.072 | 1160 | 131 | 429 | 2.7 | 875 |
| 3 | 0.043 | 1415 | 112 | 505 | 2.8 | 1125 |
| 4 | 0.036 | 2120 | 77.5 | 724 | 2.9 | 1550 |

### 5.2.D.1 *Hydroxy terminated PTHSA-b-PTMO copolyol*

The PTHSA was coesterified with PTMO polyols of varrying molecular weight mentioned in table 5.8. Experimental conditions are given in 5.2.B.5.The effect of variation of the chain length of PTMO on the properties of the polyether - polyester copolyol could be studied using the different grades of PTMO polyols. The avarage functionality of the resultant polyols were seen to be near to 2.5, as calculated from hydroxyl value and molecular weight by VPO. The functionality of the polyols remains almost same for all samples (2.4 to 2.6) as the mol% of the PTMO is in the same range (49-50%). The results are given in table 5.9.

**Table 5.9: Synthesis and characterisation of Polyester-PTMO block copolyol**

| Mol.wt of PTMO | Wt.% of PTMO | Mol% of PTMO | Mol.wt : of copolyol | OH value | Eq.wt (calc:) | $F_{av}$ | Viscosity (cps) |
|---|---|---|---|---|---|---|---|
| 550 | 26.2 | 50.0 | 2150 | 66.7 | 840 | 2.5 | 1200 |
| 1160 | 43.7 | 50.8 | 2685 | 55.0 | 1020 | 2.6 | 1850 |
| 1415 | 47.0 | 49.5 | 3015 | 46.5 | 1205 | 2.5 | 2100 |
| 2120 | 56.9 | 49.1 | 3725 | 36.2 | 1549 | 2.4 | 3100 |

(Viscosity in cps at 30°C and OH value in mgmKOH/gm. Mol.wt. of PTMO given in the table is that of the block in the copolymer).

The viscosity of the samples increases uniformly as the weight percentage of PTMO and the final molecular weight increases. The completion of the reaction was seen by the disappearence of COOH group and minimum acid value of the product.

### 5.2.D.2. *Polyurethanes of block co-polyol*

The polyurethane of the polyester-PTMO block copolyols discribed in table 5.9 were synthesised with TDI as the curative and TMP as the crosslinker with isocynate index 1 as detailed in section 1 of this chapter. The samples were analysed for mechanical properties and Tg. The results are given in table 5.10.

**Table 5.10: Characteristics of PTHSA-b-PTMO copolyurethane (2-step synthesis)**

| Sl No. | Mol.wt.of PTMO in copolymer | Mol.wt. of copolyol (VPO) | Wt.% of PTMO | T.S (KSC) | Elongn: % | Sol % | Tg (°C) |
|---|---|---|---|---|---|---|---|
| 1 | (TMP) | 1550 | -- | 6.5 | 350 | 10 | -25 |
| 2 | 550 | 2150 | 26.2 | 8.5 | 375 | 8 | -35 |
| 3 | 1160 | 2680 | 43.7 | 10.5 | 410 | 8 | -41 |
| 4 | 1415 | 3015 | 47.0 | 12.5 | 425 | 5 | -50 |
| 5 | 2120 | 3725 | 56.9 | 13.2 | 430 | 5 | -50 |

It may be observed from the table that there is a gradual increase in tensile strength and reduction in Tg as the PTMO content is increased. As the weight fraction of PTHSA decreases in the co-polyol, the tensile strength increased due to the decreasing content of the pendant and nonfunctional hydrocarbon units present in poly THSA. The efficiency of PTMO in altering the mechanical properties and Tg of PTHSA is illustrated in fig 5.8. The avarage polarity of the polyol is also increased when the PTMO content increases. This could add to the cohesive forces. Irrespective of the composition, the different copolyurethanes have shown signs of homogenity visually and this was also manifested in the appearence of a single Tg. The decrease in $T_g$ was found to be proportionate to the PTMO content. The variation in $T_g$ was found to be almost in conformation with the FOX's equation which predicts Tg for homogeneous copolymer systems.

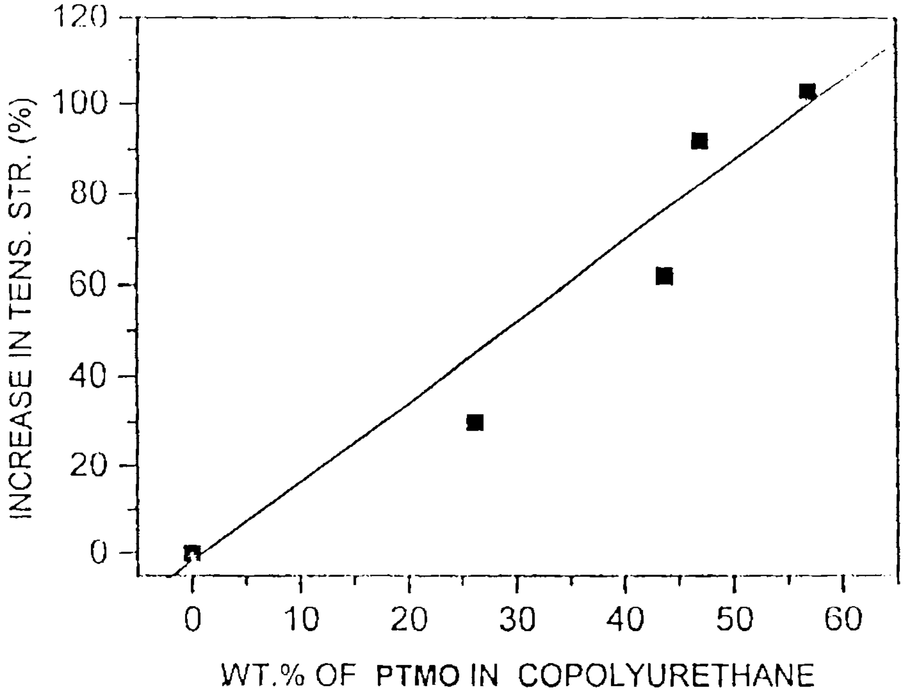


Fig. 5.8 : Variation of tensile strength of polyester PU with PTMO content

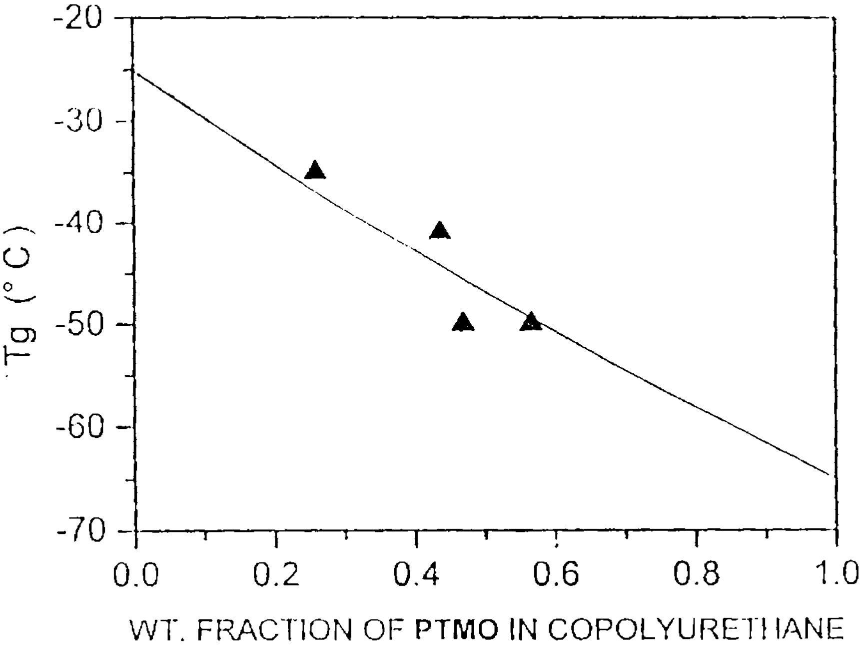


Fig. 5.9 : Variation of $T_g$ of polyester PU with PTMO content

$$\frac{1}{T_g} = \frac{W_A}{T_{gA}} + \frac{W_B}{T_{gB}}$$

Where $W_A$ & $W_B$ are the weight fractions of the individual sequences whose $T_g$'s are $T_{gA}$ and $T_{gB}$ respectively. The $T_g$ variation as predicted by FOX's equation is shown in figure 5.9. The experimental $T_g$ values fit close to the theoretical curve within experimental error.

The pre-copolymerisation of the two polyols, polyester and polyether has therefore helped in the homogenisation of the phases in the polyurethane unlike the one shot method described in table 5.7.

### 5.2E Conclusions

Polyester polyurethanes with flexible polyether block were synthesised. The studies on the synthesis of co- polyurethanes of polyester and polyether through isocyanate reaction has shown that the difference in reactivity of the individual polyols to isocyanate leads to a block copolyurethane structure containing sequences of PTMO-PU blocks and PTHSA-PU blocks and hence gives heterogeneous system. This can be conveniently avoided and controlled structure accomplished by preforming the block copolymer of polyester and polyether and subsequently converting to PU. The mechanical properties could be improved and glass transition temperature decreased with increasing chain length and concentration of the polyether block on the polyester system studied.

- The synthesis of a block copolymer appered an ideal route than the graft technique towards achieving the goals of enhanced mechanical performance and lower $T_g$. This gives a uniform distribution of the urethane groups than thegraft method which gives an agglomoration of polar urethane groups at higher weight percentage of macrodiol due to proximity of the hydroxy functionality in the latter. The non uniform distribution of the urethane groups can affect the property prediction. In block copolyurethanes,the properties are dictated principally by the blocks and their interactions. The urethane groups, as they are sufficiently spaced do not contribute to the cohesion unlike in the case of the graft PU.

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# Chapter VI

# CHAPTER VI

# SUMMARY AND CONCLUSIONS

Polyurethane is a versatile polymer indispensable in various fields of applications ranging from footwear to space technology. The lack of high temperature resistance, has however been a major concern for application of this otherwise wonderful material in certain areas demanding tolerance to thermal strain. This problem has drawn considerable interest of researchers and the current trend of research in polyurethane is directed towards addressing this problem. This is evidenced in bibliographic survey compiled in chapter I. Polyurethanes (PU) are generally acknowledged as low temperature performance polymers, the service temperature being dictated mainly by the polyol constituting the backbone. However it has always been an intriguing problem if the low temperature serviceability of a PU can be extended further without significant alteration in the backbone structure and its mechanical properties.

In this thesis, a humble attempt has been made to illustrate the feasibility of extending the service temperature of PU to both low and high temperature by way of structural modifications. The strategy in enhancing the high temperature resistance was to incorporate hetrocyclic groups in the backbone either through modification of the reaction of isocyanate or by usage of hetrocyclic group - based crosslinking agents. Towards decreasing the glass transition temperature the network was modified with soft pendant grafts and with flexible polymer blocks. In all cases, the effect of structural modifications on the physico-chemical, mechanical, thermal and thermo-mechanical characteristics of the resultant network was examined and correlation established. The studies have been extrapolated to various polyol backbone using tolylene diisocyanate as the curative.

The accepted method for improving high temperature properties of PU is by modification using thermally stable monomers. In this work, mainly two approaches were made. 1) By chain modification through introduction of imide and imide - oxazolidone groups using isocynate terminated prepolymer and 2) By using hetrocyclic group -containing crosslinkers like phosphazene triols, triazene triol and imide-triazene diol

The imide- PU was synthesised by amic acid route unlike the conventional isocyanate-acid anhydride reaction. This method involved the reaction of NCO terminated prepolymer with a diamine which was subsequently transformed to PU amic acid by reaction with pyromellitic dianhydride . The amic acid was imidised thermally or chemically. The technique led to a polyurethane imide (PUI) whose structure incorporated urea groups in addition to the imide, unlike the one-step reaction. As a consequence, the mechanical and thermal properties of the resultant PUI were higher than those of PUI by the one-step reaction. The thermal stability could be improved by variation of the aromatic diamine used for PU diamine synthesis. Diamino diphenyl sulphone was better than diaminodiphenyl ether and diaminodiphenyl methane in imparting thermal stability for given backbone in PUI. The studies conducted on the variation of imide content with respect to urethane content has shown that presence of imide is conducive in causing a proportionate increase in tensile strength and the anaerobic char yield at higher temperatures. The same trend was observed for the different polyols investigated for PU synthesis.The improvement of thermal stability due to imide units in the chain was also confirmed by isothermal aging studies. The decrease in properties caused by heating at different periods and temperatures was lower for the imide - PU than for the base polyurethane. In another series, oxazolidone group was introduced in PU chain in conjunction with imide group for improving further the thermal stability of polyurethanes. The imide-oxazolidone polyurethanes were synthesised by reaction of NCO group of prepolymer with a novel, imide - diepoxy compound which inturn was obtained by reaction of imide-dicarboxylic acid and a diepoxy compound. The imide - oxazolidone combination gave a still higher mechanical and thermal properties in comparision to imide-polyurethanes. The superiority in thermo - mechanical profile of this system was further proven by isothermal aging studies. The increase in tensile strength and the char residue at high temperatures was found to be a direct function of hard segment content for the two types of modified polyurethanes. An increase of hard segment content through imide or imide-oxazolidones was fruitful in increasing the magnitude of these properties. The hetrocyclic groups, apart from conferring thermal stability, imparted improved intermolecular cohesive interactions that was reflected in higher mechanical properties. This effect was pronounced also in raising $T_g$ of the modified polymers. The increase in $T_g$ was proportional to the hard segment content although the magnitude of the increase was not substantial.

Alternatively, polyurethanes with hetrocyclic groups could be realised by way of designing crosslinking agents (CLA's) containing hetrocyclic groups. In this study, typically phosphazene and triazene were chosen. They were selected for introducing in PU chain, as both these units are known for higher thermal stability and flame retardant properties and are currently explored for application in high temperature resistant composites. A combination of imide and triazene was also explored for their effect in increasing thermal stability. This strategy employed novel maleimide-triazene diol (MITD) that was synthesised and used as chain extender for polyurethanes which could be further crosslinked through polymerisation of the maleimide double bond. The phosphazene - triols and tetraols were synthesised from hexachloro cyclotriphosphazene and 2-ethyl aminoethanol whereas the triazene-triol (CNT) from cyanuric chloride and 2-ethyl aminoethanol. The variation in physical, mechanical and thermal properties caused by the crosslinking agents was monitored and compared to that of PU based on TMP as the CLA. A comparison has been made between phosphazene, triazene and imide triazene - based CLA's in bringing about the improvement in properties and in most of the cases, the relative performance of indivitual CLA in various polyol backbones has been examined.

The effect of concentration of phosphazene - CLA on mechanical properties was studied using three types of polyols. The effect on mechanical and thermal properties was more pronounced for these systems compared to TMP on an equivalent basis. This could be the result of the structural difference in the crosslinking agents. Phosphazene presents rigid ring structures at the crosslinking junction. There could be contribution from the higher functionality present in the phosphazene based CLA's providing highly crosslinked junction randomly. The presence of phosphazene was found to increase tensile strength and raise Tg for all the three types of polyols investigated viz: PEG, POTMG and HTPB . The efficiency for increasing the mechanical strength and thermal properties was found to be in the order PN-4 > PN-3 >TMP. Evaluation of the relative increase in tensile strength for PN-3 based polyurethanes over TMP based polyurethanes at different equivalents ratios for the three polyols revealed the superiority of HTPB based polyurethanes over the polyether based ones. This has been ascribed to the better miscibility of PN-3 (than TMP)with HTPB which helps in making a uniform crosslinked network and presence of higher functional molecules in the latter. The polyurethanes using phosphazene-derived crosslinking agents provided an increase of about 10-15°C in the initial decomposition temperature and a slower rate of thermal erosion as seen by the higher amount of residue remaining at higher temperatures compared to the TMP -based polyurethanes. The char residue after complete decomposition of the polymer was about 10-15% for the phosphazene based system, whereas the non-phosphazene ones left no char residue.

Similarly two types of CLA's based on a triazene triol and an imide -triazene diol were synthesised and characterised. They were incorporated in various polyol backbones by the usual method of polyurethane preparation. Examination of the dependancy of mechanical properties on the type of crosslinking agents revealed the superiority of imide-triazene based CLA to other systems investigated. In general, presence of triazene was found to be better than phosphazene in enhancing mechanical properties although the trend in thermal properties was reversed. The simultaneous presence of imide and triazene was the best in improving the mechanical properties. Critical analysis of the properties for both phosphazene and imide-triazene crosslinkers has shown that the improvement in mechanical properties of polyurethanes with CLA's is in the order MITD > CNT > PN-4 > PN-3 > TMP on an equivalent basis. On the other hand, the improvement in thermal stability was found to be in the order PN-4 > PN-3 > MITD > CNT > TMP. This implies that when thermal stability is the major property of concern, phosphazene is the preferred system for crosslinking agent. Imide -triazene, on the other hand, gave superior mechanical properties eventhough thermal properties were not upto that of the phosphazene based system on an equivalent basis. for a give CLA, the thermal stability was found to be in the order HTPB > PEG > POTMG .

Although increase of equivalent quantities of the CLA's proportinately increased the properties, it could be achieved only at the cost of chain flexibility which was reflected as a proportinate increase in $T_g$ of the modified systems. The $T_g$ values were however below room temperature after modification. Extension of high temperature serviceability and the consequent improvement in mechanical performance was found to impair the low temperature serviceability for all the modified polyurethanes studied. As polyurethanes possess inherent low temperature flexibility and built-in toughness due to secondary relaxation and that the Tg of the modified systems studied are well below room temperature, this increase in Tg is not a major concern. A critical analysis of the results show that the chemical modification of the backbone for incorporation of the hetrocyclic groups possess an edge over similar modification through CLA's in terms of the mechanical and thermo-mechanical profile of the resultant PU network. Although a one to one comparision looks meaningless as the nature of the hetrocyclic groups introduced by the two techniques are different, an apparent comparison in terms of the hard segment content substantiates this conclusion. Although the CLA method is inferior in property amelioration, it is more acceptable from the point of view of ease of processability, design flexibility etc.

Polyurethanes are generally characterised by excellent low temperature properties. The $T_g$ which is an index of the low temperature property and flexibility of a polymer is dependant principally on the nature of the backbone polyol keeping other factors such as type and level of isocyanate, extent of crosslinking etc constant. Thus, PU with very low temperature flexibility as required for cryogenic conditions warrants choice of speciality polyols. But it would be interesting if the chain flexibility could be improved and thereby the $T_g$ decreased for a given PU through appropriate structural modification without causing substantial alterations in its physico-mechanical characteristics. The later part of the thesis concerns studies in this perspective. Two approaches were done to lower $T_g$, namely introduction of soft polymer grafts and soft polymer blocks in the chain. The grafts were constituted by the polybutyl acrylate (PBA) which was introduced in three different backbones by the macromonomer technique. Detailed investigations were performed to study the effect of concentration and length of the graft on the polymer, properties notably the $T_g$. The graft method was expected to introduce free volume in polymer due to pendant group from polybutyl acrylate. The same type of polyols studied for high temperature modifications as employed for this study. This "graft from" method through macromonomer permitted synthesis of well defined polyurethanes with PBA grafts. PBA macromonomer of different molecular weights were synthesised by radical polymerisation of butyl acrylate using mercapto propane diol as the functional chain transfer agent. Determination of the chain transfer-constants under the ideal condition and the actual experimental condition helped predict the experimental conditions for synthesis of macromonomer of defined characteristics including functionality. Grafting was done by copolymerisation of the polyol and macrodiol (macromonomer) in required proportions with a diisocyanate. Graft length was prefixed by choice of the macromonomer. Incorporation of longer grafts was found to decrease the $T_g$ but this resulted in a concomitant decrease in mechanical properties. Short length PBA chains initially decreased $T_g$ and then increased it as the concentration was enhanced. Thus incorporation of shorter chains in a limited concentration appeared ideal for decreasing $T_g$ accompanied by an improvement in mechanical properties. This concentration should be a function of graft although such a correlation was not established in this study. The results of the study on graft PU revealed that the cohesive forces by the polar urethane groups is determinant in predicting the properties of the grafted polymer rather than the free volume or the entanglement effect of the grafts.

The synthesis of PU with flexible blocks was carried out on a polyester from 12-hydroxy stearic acid (THSA) using Polytetramethylene oxide (PTMO) blocks. For forming the blocks,polytetramethylene oxide (PTMO) unit was selected because of its known low temperature retention of properties. In order to effectively study the influence of the blocks, a typical polyester polyol, poly THSA - based PU with relatively higher $T_g$ was chosen. The one-shot synthesis of block copolyurethanes did not meet with success due to the difference in reactivities of the polyols with diisocyanates resulting in a hetrogeneous system. This problem could be successfully overcome by synthesising a polyol containing blocks of the polyester and polyether. The'block' polyol of varying compositions were pre-designed by an esterification reaction. The mechanical properties of the resulting copolyurethane were found to be improved and $T_g$ reduced by increasing chain length of PTMO block. The increase in hardness values was indicative of chain stiffness. The prepolymerisation technique led to homogeneous polyurethane network as evidenced also from a single Tg value whose variation with composition of the block was in conformation to the prediction by Fox equation for homogeneous system. The available data led to the conclusion that the block copolymer technique was better suited one than the grafting technique in inducing the low temperature flexibility. However, as the nature of the blocks and grafts and the backbone studied were different in both cases, a general conclusion cannot be drawn.

The modification studies on polyurethane carried out and presented in different chapters will be helpful in tailoring the available systems suitable for applications in high and low temperature environments.

## PUBLICATIONS

1. **Polyurethane - Imides : Synthesis and characterisation**

   P.Radhakrishnan Nair & D.Joseph Francis, presented in National seminar on Advances in Polymer Technology (**APT '91**)
   Conducted at Cochin University of Science Technology on February 5-6,1991 [Part of the work contained in Chapter 3]

2. **Phosphazene modified polyurethanes : synthesis, Mechanical and Thermal characteristics** (in press)

   P. Radhakrishnan Nair, C.P.Reghunadhan Nair & D. Joseph Francis accepted for publication in **European Polymer Journal** in October 1995 (No. 160/95) (Part of the work contained in Chapter 4)

3. **Polyurethanes with Polybutyl acrylate grafts via Macromonomer Technique : Thermal and Mechanical Properties.** (in press)

   P. Radhakrishanan Nair, C.P.Reghunadhan Nair & D.Joseph Francis Accepted for publication in **European Polymer Journal** in November 1995 (No. 207/95) (Part of the work contained in Chapter 5, Section 1).

4. **HTPB based Polyurethanes with Polybutyl acrylate grafts via Macrodiol technique,**

   P.Radhakrishnan Nair, C.P. Reghunadhan Nair & D.Joseph Francis.
   Presented in National seminar on Advances in Polymer Technology (**APT '96**) conducted at Cochin University of Science & /Technology on Feb 8-9,1996 (Part of the work contained in Chapter 5)