

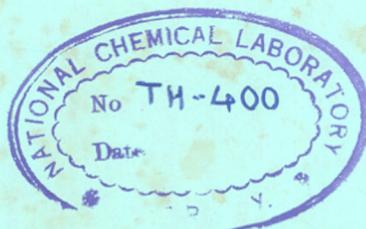
# STUDIES IN POLYURETHANE ELASTOMERS

COMPUTERISED

A THESIS  
SUBMITTED TO THE  
**UNIVERSITY OF POONA**  
FOR THE DEGREE OF  
**MASTER OF SCIENCE**  
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BY  
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1983

## C E R T I F I C A T E

This is to certify that the work incorporated in the thesis entitled "Studies in Polyurethane Elastomers" is an authentic record of the work carried out by Shri M.D. Deshpande, under my supervision in partial fulfilment of the degree of M.Sc. (Chemistry) of the University of Poona and that no part thereof has been presented for any other degree.

  
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May 1983

  
M.D. DESHPANDE

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**CHAPTER - I**

## INTRODUCTION

Synthetic rubbers and plastics are generally manufactured by polymerisation process, either addition polymerisation or condensation polymerisation, the former process being the one more commonly employed.<sup>1</sup> In addition polymerisation or chain polymerisation as it is some times described, an unsaturated monomer polymerises by a chain reaction via a free radical or ionic mechanism and the reaction can be controlled only within certain limits. Condensation polymerisation or step polymerisation involves the reaction, by the use of heat and/or catalysts, between small to medium sized polyfunctional molecules and the formation of higher molecular weight products by elimination of water, sodium chloride or similar low molecular weight compounds. Examples of addition polymers include polychloroprene rubbers produced by the polymerisation of chloroprene and polyvinyl chloride from the polymerisation of vinyl chloride. More than one starting material can be used and materials such as acrylonitrile butadiene styrene copolymers (ABS) are the result. Polyesters are an obvious example of condensation polymers and are prepared by heating together difunctional organic acids and difunctional alcohols, with elimination of water<sup>1</sup>. Other examples include polyamides, phenol-formaldehyde, urea formaldehyde resins and so on.

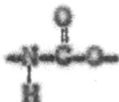
The polyurethane elastomers do not easily fall into either of these two categories. Low to medium molecular weight polyfunctional compounds, one of which is a

di isocyanate are joined together by an addition type process but by an intermolecular hydrogen transfer and not by a free radicle or ionic mechanism. Cross linking of the polymer to form a cured elastomer is achieved also by a similar addition process. For this reason the term diisocyanate poly addition or even polyaddition alone, was coined to describe the reaction process and these terms are still used to describe the process in use today.

In 1937 O. Bayer<sup>14</sup> and co-workers discovered the diisocyanate addition polymerisation for the preparation of polyurethanes and polyureas. He made an elastomer by reacting tolylene diisocyanate (TDI) with various organic polyhydroxy compounds<sup>9</sup>. This lead to the growth of polyurethanes to commercial reality as various products such as elastomers, foams (rigid and flexible) adhesives and surface coatings. Bayer in 1952 developed elastomers and flexible foams. During the period 1952-1954 the German Chemical industry brought about diisocyanate-polyester flexible foam systems as commercial products and further designed and manufactured novel machines for the continuous production of foams<sup>9</sup>. In 1957 American Industries developed polyether based foams<sup>10</sup>. These products offered a wide range of properties than polyester based foams at a significantly lower price.

### 1.1 Chemistry of Polyurethane Elastomers

Polyurethanes can be described as materials containing amongst other chemical groups, a repeating urethane group in the polymerchain as shown below<sup>5</sup>.



#### URETHANE GROUP

Other chemical groups being aliphatic and aromatic hydrocarbon, esters, ethers, amides and urea groups. This urethane can be obtained by either addition polymerisation or condensation polymerisation, but commercially the only important method is the addition polymerisation reaction between a diisocyanate and a diol. The reaction between bischloroformate and diamine is the most interesting of the condensation polymerisation routes but has not reached commercial significance<sup>5</sup>.

#### Reactivity of the Isocyanate group

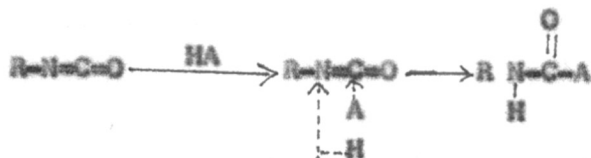
The reactivity of the isocyanate group can be explained by its electronic structure as shown below<sup>5</sup>.



The resonance possibilities indicate the electron density is greatest on the oxygen and least on the carbon resulting in the oxygen having the highest net negative charge the



carbon having the highest net positive charge and the nitrogen being intermediate with a net negative charge. The reactions of isocyanates with active hydrogen compounds, i.e. compounds having hydrogen which is replaceable by sodium, proceed therefore by the attack of a nucleophilic centre upon the electrophilic carbon in the isocyanate group<sup>5</sup>.



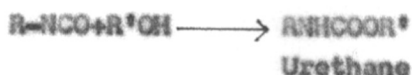
In this reaction the fact that the active hydrogen compound is acting as an electron donor and not a hydrogen donor is confirmed by the effect of electrophilic groups in the active hydrogen compound<sup>3</sup>. In the reaction with compounds containing active hydrogen, the hydrogen atom becomes attached to the nitrogen of the isocyanate and the remainder of the active hydrogen compound (A) becomes attached to the carbonyl carbon as shown in the above equation<sup>15</sup>. In most of the cases, this addition product is stable, but some times the addition product is only moderately stable, it may either dissociate to form the initial reactants again or decompose to other products<sup>15</sup>.

### 1.2 Reactions of the isocyanate group

The reaction of isocyanate groups with OH containing compounds form the basis of all methods for polymer formation.

#### (i) with alcohols

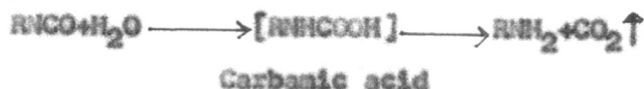
Alcohols react with isocyanate to give urethanes.



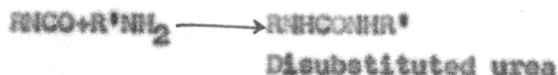
The reaction is strongly catalysed by mild and strong bases, metals, weakly by acids. Stearic hindrance effect can also greatly modify the reaction rates. Thus primary alcohols react readily at 25<sup>o</sup> to 50<sup>o</sup>C, secondary alcohols are less reactive and tertiary alcohols still less reactive<sup>19</sup>. In general the stability of urethane is connected with the rate of formation, slow reaction rates producing more stable urethanes. Polyurethanes from aliphatic isocyanates are more stable than those from aromatic isocyanates<sup>3</sup>.

(ii) with water

The reactivity of water with isocyanate is similar to that of the secondary alcohol<sup>16</sup>. The reaction is not as simple as the formation of urethane, it proceeds through the formation of an unstable carbamic acid which further splits out to yield primary amines and liberate carbon dioxide.



The amines produced are even more reactive towards isocyanates than water and form a disubstituted urea.



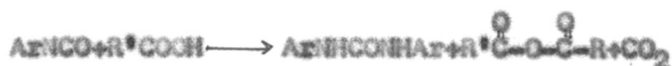
(iii) with carboxylic acids

Carboxylic acids readily react with isocyanates,

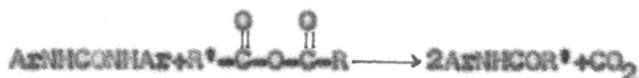
the reaction rate being dependent on the acid strength<sup>4</sup>. They are somewhat less reactive than primary alcohols or water. The reaction proceeds via an unstable intermediate whose decomposition products depend on the type of isocyanate and carboxylic acid. Aliphatic isocyanates and aliphatic acids can give substituted amides<sup>4</sup>.



Aromatic isocyanates and aliphatic acids, however can form the acid anhydrides, a urea and carbon dioxide<sup>4</sup>.



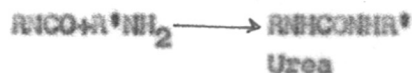
At 160°C the urea and anhydride react to yield the amide.



(iv) with amines

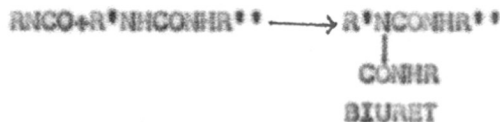
Isocyanates react with amines to form ureas<sup>4</sup>.

Generally speaking, the more basic the amines the faster is the reaction. Primary aliphatic amines are extremely reactive even at 25°C and give high yields of disubstituted ureas<sup>4</sup>. Secondary aliphatic and primary aromatic amines are next in the order of the activity. As with aromatic isocyanates, the presence of substituents in aromatic amines can modify the activity by electronic or stereochemical means<sup>5</sup>.

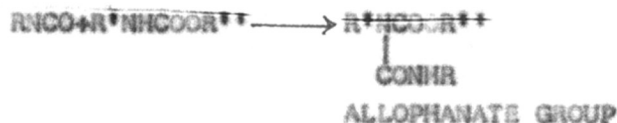


Secondary reactions that are important in the formation of urethane polymers are those with urea and urethanes.

The urea formed by the reaction between amines and isocyanate will react with more isocyanate to give a 'biuret'. Temperatures in excess of 100°C are normally required<sup>5</sup>.



A similar reaction also occurs between the urethane group and the isocyanates giving an 'allophanate'; the urethane group is generally less reactive than the urea group and temperatures of 120°C-140°C are needed for any significant reaction to occur.



Both these reactions are important since they are the means by which branching and cross linking occur in the polyurethane network. Both reactions are relatively slow but do occur at the normal manufacturing temperatures of 100° to 140°C<sup>5</sup>.

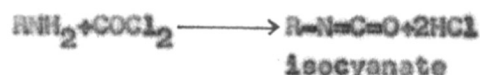
Based on the above reactions a variety of polyurethane commercial products are produced such as foams (flexible, semiflexible and rigid) fibres, adhesives, coatings and elastomers.

### 1.3 Manufacture of raw materials

The raw materials required in the manufacture of polyurethanes are diisocyanates, such as tolylene diisocyanate (TDI), diphenyl methane 4-4' diisocyanate (MDI), naphthalene 1,5 diisocyanate (NDI) and polyols like polyesters and polyethers.

#### (a) Manufacture of isocyanates

Although a number of methods of preparing isocyanates have been reported in the literature (20-22), the only method of commercial importance is the phosgenation of primary amines.



#### (i) Tolylene diisocyanate (TDI)

Toluene is the starting material for the production of tolylene diisocyanate. The process may be varied to give products of differing isomer contents. The nitration of toluene gives a mixture of 2-nitrotoluene (60%) and 4 nitrotoluene (40%). If this mixture is nitrated further without separation, the product is a mixture of 2,4 dinitrotoluene (80%) and 2,6 dinitrotoluene (20%). If on the other hand the mixed mononitrates are separated by distillation, then further nitration of the 2 nitrotoluene yields a mixture of 2,4 dinitrotoluene (65%) and 2,6 dinitrotoluene (35%) while further nitration of the 4 nitrotoluene gives only 2,4 dinitrotoluene. Reduction of dinitrotoluenes (Fe/HCl) leads to the corresponding diamines which on phosgenation give the

corresponding diisocyanates. Thus it is possible to prepare 80:20 TDI (80% 2,4 isomer, 20% 2,6 isomer), 65:35 TDI (65% 2,4 isomer, 35% 2,6 isomer) and 2,4 TDI (100%), all of these materials are commercially available<sup>10</sup>.

Phosgenation is usually carried out continuously as follows.

The diamine feed is injected into a solution of phosgene in an inert solvent (e.g. *o*-dichlorobenzene) at 25<sup>o</sup>-100<sup>o</sup>C (the cold stage) and then the product is passed through a heater at 150<sup>o</sup>-160<sup>o</sup>C (the hot stage). Hydrogen chloride and unreacted phosgene are taken off and the diisocyanate is separated from the solvent by distillation. The flow sheet for the manufacture of TDI is shown in fig.1.

The phosgenation process is generally considered to involve the formation of carbonyl chloride in the cold stage and the decomposition of this product in the hot stage.



Of the various products described above, the 80:20 isomer mixture is the cheapest and is widely used.

FIG. 1. FLOWSHEET FOR THE MANUFACTURE OF TOLYLENE DIISOCYANATE

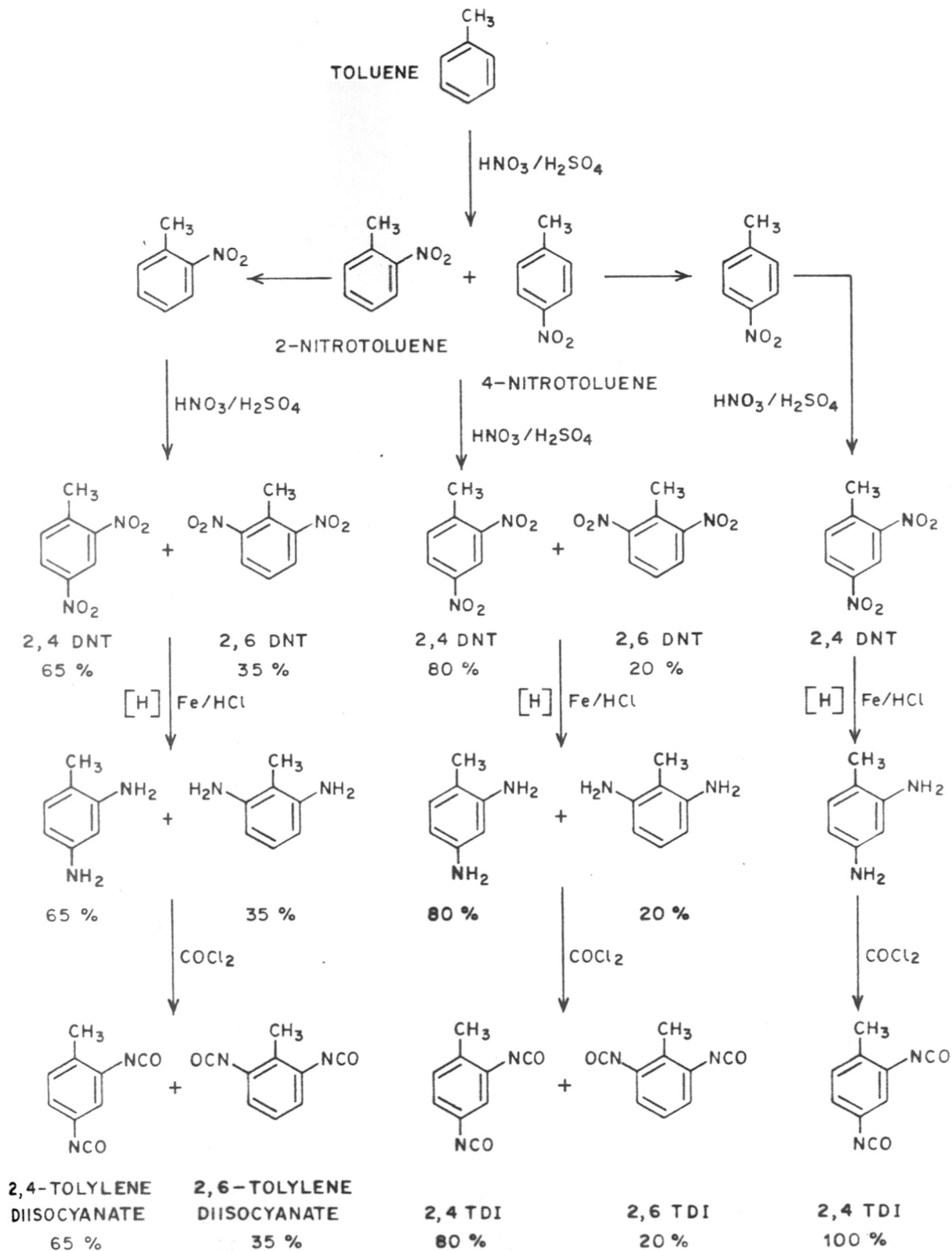


FIG. 2. DIPHENYL METHANE 4-4' DIISOCYANATE MDI

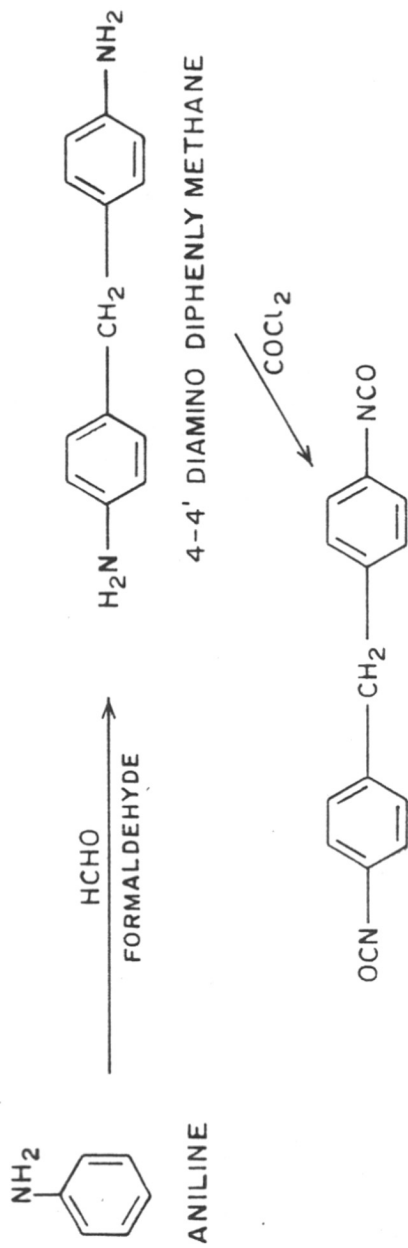
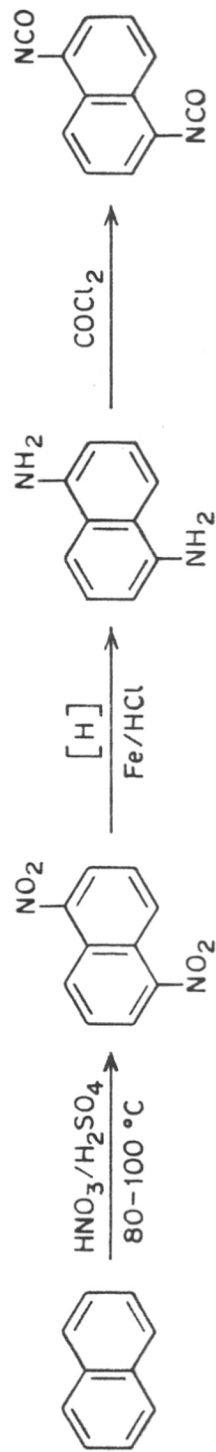


FIG. 3. NAPHATHALENE 1,5 DIISOCYANATE NDI



NAPHATHALENE 1,5 DINITONAPHALENE

1,5 NDI



(ii) Diphenylmethane 4-4' diisocyanate (MDI)

This is derived from aniline, the principal reactions involved are as shown in the figure 2.

Pure MDI is a solid with M.P. 37-38°C while crude MDI is a liquid. Both products have lower vapour pressure than TDI and are therefore less toxic in use. Pure MDI is used in elastomer manufacture and crude MDI is extensively employed in the production of rigid foams.

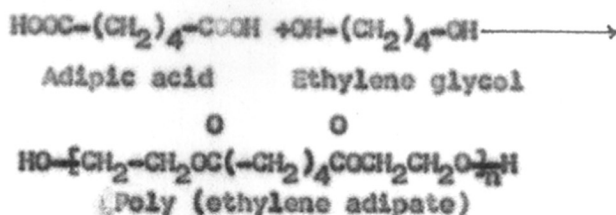
(iii) Naphthalene 1,3 diisocyanate (MDI)

It is prepared from naphthalene as shown in the figure 3. It is solid with M.P. of 128°C. It is mainly used for the manufacture of elastomers.

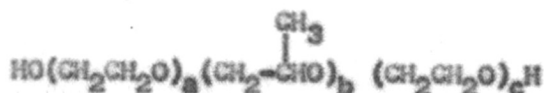
b) Polyols

The earliest polyurethanes were based on aliphatic diols and 1,4 Butanediol was generally preferred for commercial operations. The polymeric hydroxy compounds which have received most attention are polyesters and polyethers.

(1) Polyesters : The polyesters used in the preparation of polyurethanes generally have molecular weight in the range 1000 - 2000 and are liquids or low melting solids, they are usually saturated<sup>21</sup>. All these polyesters are hydroxy terminated which react with the isocyanate groups of diisocyanates resulting urethane groups. They are prepared by the reaction of dibasic acids such as adipic, sebacic etc with glycols like ethylene glycol, diethylene glycol, propylene glycol and polyhydric alcohols like glycerol, trimethylol propane (TMP). In order to have the terminal ends to be hydroxy, excess glycol is used<sup>12</sup>. During the initial development of polyurethane, polyesters were the most commonly used type of polyol. Branched polyesters are prepared by using triols such as 1,2,6 hexane triol, trimethylol ethane<sup>17</sup> etc. For use in elastomers linear polyesters having molecular weights close to 2000 are prepared, whereas slightly branched ones of similar molecular weights are used for flexible foams and elastic coatings and highly branched polyesters are used for rigid foams and chemically resistant coatings<sup>17</sup>. The reaction between adipic acid and ethylene glycol is shown below



(11) Polyethers : Hydroxy terminated polyethers have now assumed a dominant role in the commercial production of polyurethanes<sup>13</sup>. Poly (oxy tetramethylene) glycol (PTMG) derived from tetrahydrofuran (THF) was the first polyether. For the manufacture of flexible polyurethane foam polyethers derived from propylene oxide and or/ethylene oxide. Rigid foams and coatings are based on poly (oxyalkylene). The block co-polymers of ethylene oxide and propylene oxide used in the manufacture of polyurethanes can be represented by the general structure.



In the preparation, propylene oxide is reacted with propylene glycol or water in the presence of a basic catalyst to form a poly (oxypropylene) homopolymer, which is then reacted with ethylene oxide to form the block copolymer<sup>18</sup>. The resulting polyether has a higher percentage of primary hydroxyl groups than does a poly (oxypropylene) glycol of comparable molecular weight. At present the most important class of polyether is poly (oxypropylene) triols. These triols are made by the same general reaction as are poly (oxypropylene) glycols, but with low molecular weight triols such as TMP, glycol and 126 hexane triol, rather than propylene glycol.

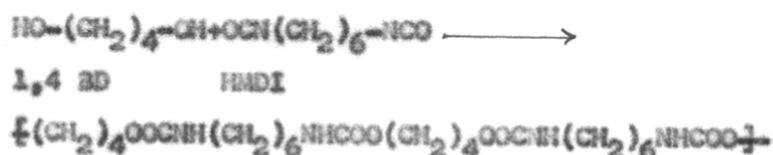
### 1.4 Types of Solid Polyurethane Elastomers

Solid polyurethane elastomers are widely used as engineering materials in many industries and are well known for their general toughness, excellent wear and tear properties and good oil resistance<sup>12</sup>. These elastomers are comparatively new to rigid and flexible polyurethane foams. The last 2-3 decades have witnessed a large increase in the types of different polyurethane available<sup>6</sup>. These can be classified as follows.

- |                         |                           |
|-------------------------|---------------------------|
| 1) Linear polyurethanes | 2) Castable polyurethanes |
| 3) Millable PU          | 4) Thermoplastic PU       |
| 5) Cellular PU          | 6) Sprayable PU           |
| 7) Poromeric PU         | 8) Spandex fibres         |

#### 1) Linear Polyurethanes

These were the first commercially available solid polyurethanes and were prepared by the addition reaction between aliphatic glycols and aliphatic diisocyanates. There was no cross linking between the chains since no trifunctional compounds were added to cause branching<sup>6</sup>. The chains simply consisted of urethane groups joined by short hydrocarbon chains. Herein the polyol used was 1,4 butanediol and the diisocyanate was hexamethylene diisocyanate (HMDI).



In this case the structurally important group is the urethane group and the properties of such materials are very similar to the polyamides and hence these linear polyurethanes are of very limited interest<sup>6</sup>.

## 2) Castable polyurethanes

These were the first to be used to any significant degree and account for the largest proportion of the solid polyurethanes. Different companies gave different trade names such as Vulkollan of Bayer, Adiprene of Dupont and Formmerz of Witcochemical. Castable polyurethanes are subdivided into three main groups<sup>7</sup>.

- a) unstable prepolymers
- b) stable prepolymers and
- c) one shot systems.

Though the technologies of producing these are different the chemical basis is similar. In all these there are three major ingredients (i) a long chain polyol, either a polyester or polyether, (ii) an aromatic diisocyanate such as TDI or MDI and (iii) a chain extender like short chain glycol, water or diamine.

In both stable and unstable prepolymers the polyol is first extended with diisocyanate to yield an isocyanate terminated prepolymer<sup>15</sup>. This prepolymer is further chain extended and cross linked by the use of triols such as glycerine or TMP.

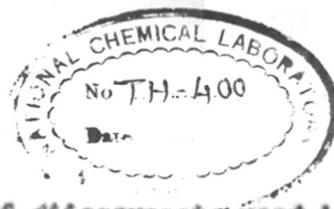
### 3) Millable polyurethanes

Using a deficiency of diisocyanate results in a hydroxy terminated polymer which is relatively stable and non cross linked. Provide the correct molecular weight is chosen this product takes the form of a plastic gum which can be handled on a rubber mill in a similar manner to other elastomers. Cross linking can be effected either by the addition on the mill of more diisocyanate, peroxide or sulphur. Fillers such as carbon black can also be added on the mill, and the whole process, including the high temperature press cure, is analogous to the manufacture of conventional rubber products.

The properties of the final product are similar to those from the castable polyurethanes though the range available is restricted. They are useful materials, however, in cases where the shape or size of the final product is such that casting techniques are unsuitable.

### 4) Thermoplastic Polyurethanes

During the late 50s thermoplastic urethanes were introduced.<sup>31,32</sup> These are linear polyurethanes and possess similar characteristics to other thermoplastics such as nylon. They are elastomeric, but they can nevertheless be processed on modern conventional equipment. Chemically they are very similar to the castable polyurethanes and in most cases an excess of diisocyanate is employed to bring



about cross linking. The choice of diisocyanate used is such that these cross links are thermolabile and at the temperatures encountered during processing through the injection cylinder the cross links are broken around 160°C and the polymer becomes linear. The crosslinks reform upon cooling.

The properties of the thermoplastic polyurethanes are close to those of the castable types, their main advantage being in the economic manufacture of small components in large quantities. The standard equipment used by modern plastics manufacturers can be used and the polyurethanes can be injection moulded, extruded, blow moulded and calendered.

### 5) Cellular Polyurethanes

The specific gravity of most solid polyurethane elastomer is in the range of 1.10 to 1.30. The specific gravity of the flexible polyurethane foams used for upholstery and the rigid foams used for insulation is, on the other hand, in the range of 0.02 to 0.20. The solid types, however, can be made in a cellular form with a specific gravity in the range of 0.35 to 0.65. These cellular materials are best regarded as more flexible and softer versions of the solid polyurethane products from which they are derived, and they are not really comparable with the conventional polyurethane foams. Water has often been used as the blowing agent since it produces CO<sub>2</sub> with isocyanates.

The amine produced in this reaction takes part in chain extension. Chemical blowing agents producing nitrogen or suitable low boiling point liquids can be used as alternative for producing the cellular form and are infact sometimes preferred.

6) Sprayable Polyurethanes

These are based on the one shot castable elastomers and are sprayed at elevated temperatures. The use of a catalyst facilitates rapid curing and enables coverings of upto 1/2 inch to be achieved without difficulty. These materials are distinguished from the conventional surface coatings in that no solvent is used. It is also possible to modify thermoplastic or millable grades to be more linear instructure and are then soluble in common solvents such as methyl ethylketone, acetone, ethylacetate etc. and the solutions can be brushed or sprayed on the required surfaces. Only thin coats can be achieved by this method.

7) Poromeric Polyurethanes

These are described as having porous, polymeric structures. A typical example of a poromeric polyurethane is Dupont's Corfam which is leather like material based on polyurethane containing randomly dispersed fibres and possessing a porous structure, enabling it to 'breathe' like leather.

8) Spandex Fibres

Spandex fibres are defined as fibres consisting of



long chain synthetic polymers comprising atleast 85% of a segmented polyurethane. Compared with natural rubber thread spandex rubbers are more resistant to weathering, enabling finer counts to be used. In addition, they can be obtained in excellent white shades and are also easier to dye than rubber thread.

It will be apparent from the above discussion that the technology of polyurethanes is extensive and opens up a range of possibilities for modifying the polyurethane molecular structure to suit the end product application--an aspect in which polyurethanes as elastomers are unique.

### 1.5 Formation of Polyurethane Elastomers

Polyurethane elastomers are prepared from monomeric essentially difunctional starting materials by a stepwise polyaddition mechanism, and consequently present the possibility of building up the polymer net-work along preconceived lines. In a uniform structure a stress applied to the polymer would be evenly distributed over the whole network and each crosslink point would contribute equally to the strength of the polymer. In a more random structure the stress would be concentrated only on a portion of the total number of crosslinks with the consequence that these points would bear a longer share of the applied stress<sup>8</sup>.

The ideally uniform structure is not obtainable in practice for many reasons. For instance, the molecular distribution in the backbone polyol will introduce certain nonuniformity. The complex relationship between rates of chain extension and crosslinking also means that a certain lack of control is inevitable. However, the mechanism of polyurethane polymerization is such that a more uniform structure can be obtained than by the more random crosslinking mechanism obtained from other rubbers. Further it is possible to place rigid grouping at the chain intersections which will help in increasing the overall structural strength. A further improvement can also be effected by making the chains of weakly polar material which would be amorphous in the relaxed state but crystalline when stretched.

The important polyurethane elastomers are three types.

1. Cast polyurethanes
2. Malleable elastomers and
3. Thermoplastic polyurethanes

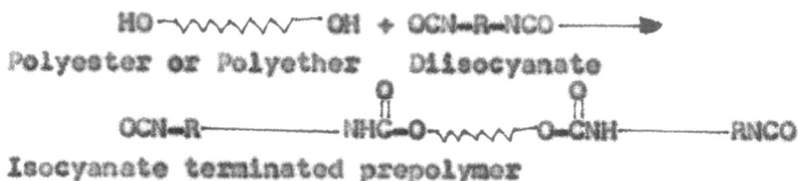
Cast polyurethanes

This class of the elastomers account for the largest proportion of the solid polyurethanes.<sup>6,7</sup> They are sub-divided into three main groups.

- I) Unstable prepolymers
- II) Stable prepolymers
- III) One shot system

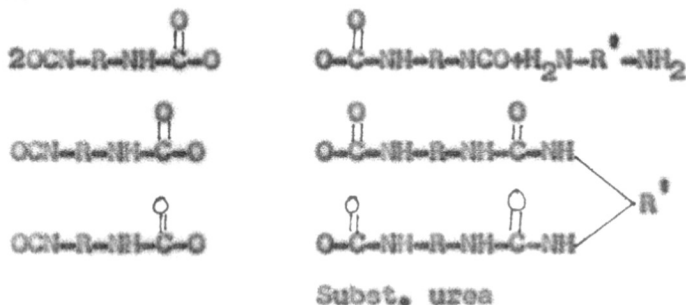
Though the technologies may be different the chemical basis is the same. In all cases there are three major ingredients.

- a) a long chain polyol either a polyester or polyether
- b) an aromatic diisocyanate
- c) a chain extender in the form of either a short chain glycol, water or diamine. In both the prepolymer systems the polyol is first extended with diisocyanate to yield an isocyanate terminated prepolymer.



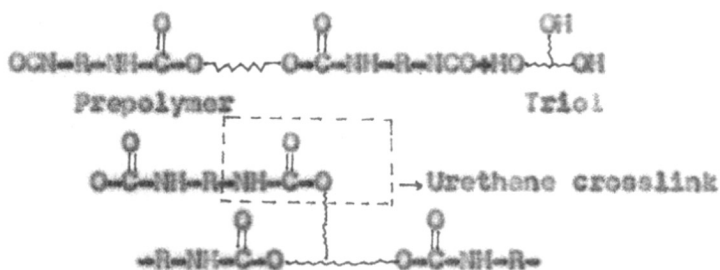


With diamines



Curing or Crosslinking

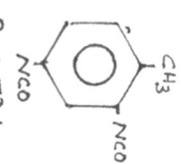
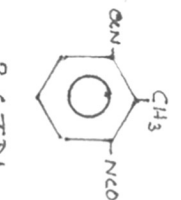
The curing or crosslinking of the elastomer is accomplished by reacting an added curing agent with the intermediate molecular weight elastomer. A convenient means of introducing crosslinking in the urethane polymer chain is the use of triols<sup>33</sup> as mentioned earlier. In this case, crosslinking occurs through the formation of urethane links as shown below.



CHAPTER - II  
EXPERIMENTAL

Description of New Materials and Technical Data

Table 1

MATERIALS	STRUCTURE	TECHNICAL DATA AND NOTES	SOURCE
Polypropylene glycol (PPG) MW = 1090	$\text{HO-CH}_2\text{-CH}_2\text{-fOC(CH}_2\text{)-CH}_2\text{-OH}$ $\text{CH}_3$	Colourless liquid, viscosity at 25°C 85 Cps MW=1090 Functionality = 2	M/s Union Carbide, U.S.A.
PPG MW 1929	--do--	Colourless liquid, viscosity at 25°C 140 cps MW = 1929 Functionality = 2	M/s BASF, West Germany
Tolylenediisocyanate (TDI)	$\text{2,4-TDI}$  $\text{2,6-TDI}$ 	Colourless liquid, 80:20 mixture of 2,4 and 2,6 TDI, B.P. 120°C/10mm Hg Mol. Wt. = 174 Functionality = 2	
Polyethylene glycol (PEG) 200	$\text{HO-CH}_2\text{-CH}_2\text{-fOC(CH}_2\text{)-CH}_2\text{-OH}$		SD's Lab chemical Industry, Bombay.
PEG 400	--do--		IOPL, Hyderabad

MATERIALS	STRUCTURE	TECHNICAL DATA AND NOTES	SOURCE
1,4 Butanediol	HO-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH	Colourless liquid, B.P. 230°C Mol. wt. = 90 Functionality = 2	Kochlight Laboratories Ltd., England.
Glycerine	$  \begin{array}{c}  \text{CH}_2\text{-OH} \\    \\  \text{CH}_2\text{-OH} \\    \\  \text{CH}_2\text{-OH}  \end{array}  $	Colourless thick liquid B.P. 290°C Mol. wt. = 92 Functionality = 3	Smethk Lab, Poona.
Ferric acetyl acetate		Brick red powder M.P. 179-182°C	ENL, Poona-8

● Number average molecular weight  $\bar{M}_n$ , was determined by Vapour Pressure Osmometer Model-Knauer, West Germany.



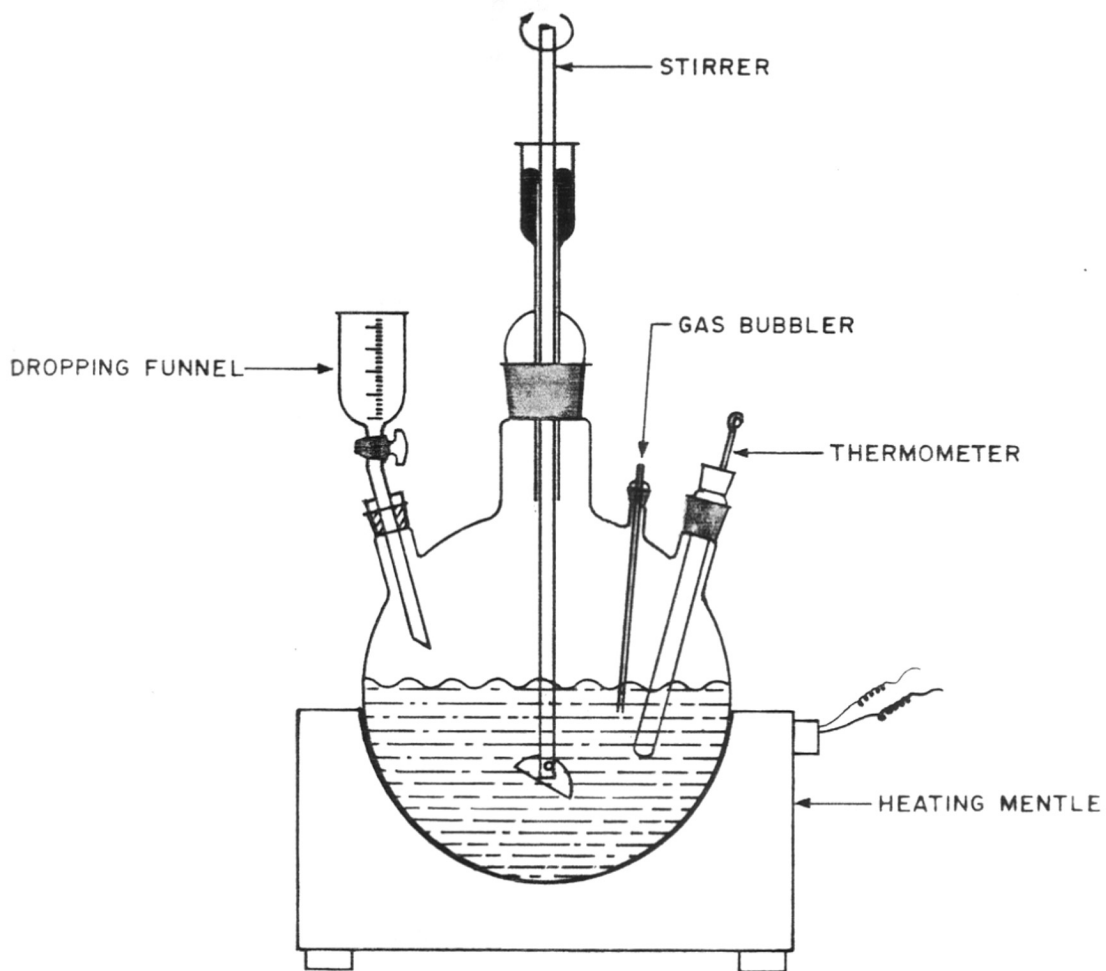


FIG. EXPERIMENTAL SET UP FOR  
PREPOLYMER PREPARATION

## 2.2 PREPOLYMER PREPARATION

The castable polyurethane rubbers were made by first preparing an isocyanate (-NCO-) terminated prepolymer, wherein an excess isocyanate was used, and further chain extension was affected by using various shortchain aliphatic glycols or aromaticdiamines.

### 1) Preparation of prepolymer based on polypropyleneglycol (PPG) of 1090 $\bar{M}_n$ and Toluene diisocyanate (TDI) [Prepolymer I]

Materials taken

- |                         |                |           |      |
|-------------------------|----------------|-----------|------|
| 1) PPG 1090 $\bar{M}_n$ | = 1090 gms     | (1 mole)  | 2OH  |
| 11) TDI (MW 174)        | = 696 gms      | (4 moles) | 8NCO |
|                         | [80/20 mixture |           |      |
|                         | of 2,4 and 2,6 |           |      |
|                         | isomers]       |           |      |

The apparatus for the prepolymer preparation has been shown in the figure. A four neck round bottom flask (5 litre capacity) with a half moon stirrer, a thermowell with a thermometer of  $110^{\circ}\text{C}$ , a gas bubbler for nitrogen atmosphere and a dropping funnel for the addition of toluene diisocyanate was assembled as in the figure. PPG 1090 gms was weighed into the flask, TDI 696 gms was gradually added through the dropping funnel over a period of two hours with constant stirring and nitrogen bubbling. During the addition of TDI, exothermic heat was produced, which was indicated by the increase of temperature to about  $42^{\circ}$  to  $45^{\circ}\text{C}$ . The stirring was continued till there was no more increase in temperature, indicating that the exothermic

heat has subsided. Heating was then started to attain the temperature of about 82-85°C, and this temperature was maintained for three hours. The prepolymer so formed was later cooled to room temperature and was stored in a suitable container with nitrogen blanket.

ii) Preparation of prepolymer from PPG Mn 1929 and TDI  
[Prepolymer II].

Materials taken

1) PPG Mn 1929	= 964.5 gms	(1/2 mole)	1GH
ii) TDI	= 348 gms	( 2 moles)	4NCO

Procedure : The same procedure which was described earlier for prepolymer I was followed for the preparation of prepolymer II.

The percentage isocyanate content of the two prepolymers<sup>25</sup> was found out as per the following procedure.

Analysis of the prepolymer I for % NCO

Apparatus : 500 ml Erlenmeyer flask, 25 ml b&b pipette  
100 ml measuring cylinder, 50 ml burette etc.

Reagents : Toluene (anhydrous and pure) Di-n-butylamine (AR grade), Isopropyl alcohol (LA grade) 0.6N aqueous HCl (standardized) and Bromophenol blue indicator.

Procedure : In Erlenmeyer flasks, 1.0025 gms, 0.7343 gms and 0.986 gms of prepolymer I was accurately weighed. 10 ml of dry toluene was added to dissolve the resin. After the sample has dissolved, 25 ml of reagent di-n-

butylamine of 0.1 [Prepared by diluting 10 ml di-n-butylamine to 100 ml with dry toluene]. The flasks were stirred intermitently for fifteen minutes after which 100 ml of isopropylalcohol was added and then titrated against standardized 0.6N aqueous HCl using bromophenol blue as the indicator. Blue to green yellow was the end point. Under the similar conditions blank was run induplicate.

Observations

Sample weight	Burette reading in ml
i) 1.0025	18.45 ml
ii) 0.986	18.55 ml
iii) 0.7343	20.0 ml
Blank	24.4 ml and 24.45 ml

Calculations

$$\% \text{NCO} = \frac{(\text{Blank-sample}) \times \text{Normality of HCl} \times 4.202}{\text{Weight of prepolymer taken}}$$

By using this formula, the values for %NCO were as follows

- i) 15.08%
- ii) 15.00%
- iii) 15.00%

The NCO content of prepolymer II was also determined by the same procedure and the values were as given below.

- i) 13.5%
- ii) 13.4%
- iii) 13.35%

**2.3 Storage stability of prepolymers**

For the study of the storage stability and the reactivity of the isocyanate terminated prepolymers, %NCO and viscosity of these resins were determined immediately after they have been prepared and the values were as shown in the table.

**Table 2**

Prepolymers prepared immediately					Values after six months storage		
Prepolymer	%NCO	Eq. Wt.	Viscosity at 30°C *		%NCO	Eq. Wt.	Viscosity at 30°C Cps
I	I	15	280	1175 Cps	14.6	287.6	1290
	II	13.5	311	1400 Cps	13.2	318.8	1650

\* By Brookfield Viscometer.

The two prepolymers from PPG HN 1090 and 1929 were kept in an air tight container, with a blanket of nitrogen, at room temperature 27°-30°C for six months. They were analysed for %NCO and Viscosity. The results of the storage stability of urethane prepolymers have been shown in the table 2.

It is evident from the above table that the two prepolymers maintained nearly the same reactivity as the change in %NCO was negligible, whereas the viscosity slightly increased during the storage.

#### 2.4 Preparation of castable polyurethane elastomers

The preparation of castable polyurethane elastomers consists of the reaction of prepolymers with di- and trifunctional chain extenders in presence of a suitable catalyst. For achieving satisfactory properties of elastomers, the quantities of the reactants such as prepolymer and chain extender are an important and hence the ratio of isocyanate to hydroxyl group (NCO:OH) must be very closely controlled in order to obtain desired properties.

The ratio of NCO to OH can be chosen from the analytical data such as %NCO of the prepolymer, hydroxyl number, molecular weight and functionality of reactants. The NCO:OH in the formulations have been calculated on the equivalent basis. The equivalent weight of prepolymer can be obtained as below.

$$\text{Equivalent of prepolymer} = \frac{4200}{\%NCO \text{ of the prepolymer}}$$

For example if the %NCO of the isocyanate prepolymer based on PPG 1090 and TDI was 13%,

$$\text{Eq. wt. of prepolymer} = \frac{4200}{15} = 280$$

$$\text{Similarly Eq. wt. of prepolymer from PPG 1929 and TDI} = \frac{4200}{13.5} = 311$$

This means that 280 parts by weight of the prepolymer I and 311 parts by weight of the prepolymer II would be used to equate one equivalent of hydroxyl, if the desired ratio  $\text{NCO:OH}$  were to 1:1.

In order to have ratio of 1:2:1 ( $\text{NCO:OH}$ ), the quantity of prepolymer I required would be

$$280 \times 1.2 = 336 \text{ gms}$$

The hydroxyl part contributed by the chain extenders polyethylene glycol (PEG) 200 (difunctional) and the glycerine (trifunctional). The one hydroxyl equivalent can be calculated depending upon the ratio of diol to triol. For example if the required ratio of diol to triol was 3.5:1, then the one hydroxyl equivalent would be shown as follows.

For one hydroxyl equivalent,

$$\text{PEG 200, } 0.35 \text{ moles} = 0.7 \text{ equivalent} = 70 \text{ gms}$$

$$\text{Glycerine, } 0.1 \text{ mole} = 0.3 \text{ equivalent} = 9.2 \text{ gms}$$

Thus for a ratio of  $\text{NCO:OH}$ , 1.2:1, the quantities of prepolymer I, PEG 200 and glycerine required will be as follows.

- i) prepolymer I 336 gms
- ii) PEG 200 = 70 gms
- iii) Glycerine = 9.2 gms

The casting technique<sup>23</sup> (By using the above formulation)  
Quantities taken for moulding

- i) Prepolymer I = 60 gms
- ii) PEG 200 = 12.5 gms
- iii) Glycerine = 1.642 gms
- iv) Catalyst = 15 mgs (about 0.02% of total charge)  
(Ferric acetyl  
acetate)

Here, NCO/OH = 1.2:1

Diol/triol = 3.5:1

Molecular weight per crosslinking = 4154  
( $M_c$ )

Procedure : The above quantities of materials were weighed in a 250 ml beaker and thoroughly mixed with a high speed stirrer. The mixed resin was taken into the 250 ml B.19F joint round bottom flask. The resin was degassed under vacuum at 2-3 mm of Hg, for 20 minutes. During degassing it was observed that the resin temperature raises to about 45°-50°C, having pourable consistency. The material was then poured into the siliconised sheet mould of 5''x6'' size which was preheated to 100°C.



The mould was later kept in the hydraulic press, curing was carried out at 100-105°C at a pressure of 1500 PSI for a period of two and half hours. The mould was then taken out from the press, and cooled. The cured sheet was removed from the mould, washed with water and soap to make it grease free.

The polyurethane sheets thus obtained was aged for 48 hours at room temperature 27-30°C at relative humidity 30-40%. The physical properties of the polyurethane elastomer such as, tensile strength, %elongation at break, tear strength, shore 'A' hardness were determined as per the procedures described in ISI standard No.3400: 1977 (Part I to XII)

Thus, using the prepolymers I (based on PPG 1090) and II (based on PPG 1929), polyurethane elastomers were prepared with the chain extenders, 1,4 Butanediol, PEG 200 and PEG 400, the trifunctional chain extender glycerine was common in all the formulations. The diol to triol ratio was kept at 3.5:1 in all the formulations studied. The castable rubbers were prepared from the above at NCO:OH ratios 1.05:1, 1.2:1 and 1.3:1 and their physical properties were determined and studied. The same moulding conditions (temp.100-105°C, pressure 1500 PSI and two and half hrs curing time) were maintained in all the experiments.

The formulations and the physical properties of the elastomers evaluated have been tabulated in the tables no.3 to 8.

Table 3

(a) Formulations for prepolymer I/1,4 Butanediol/Glycerine

Formulation No.	NCO/OH Ratio	Prepolymer I	1,4 BD	Glycerine	Diol to Triol	Mc
1	1.05:1	60 gms	6.42gms	1.877gms	3.5:1	3360
2.	1.2:1	60 gms	5.625gms	1.642gms	-do-	3769
3.	1.5:1	60 gms	4.5 gms	1.314gms	-do-	3687

(b) Physical properties

Formulation No.	Sp. gravity	Shore 'A' hardness	Tensile strength	% Elongation at break	Tear strength	Taber's Abrasion* loss in mgs/1000 cycles
1.	1.19	65-70	3095PSI (21.34MPa)	350%	338PSI (2.33MPa)	220
2.	1.13	80	3500PSI (24.13MPa)	450%	384PSI (2.64MPa)	165
3.	1.15	95-100	4348PSI (30 MPa)	600%	475PSI (3.3MPa)	48

\* Using H<sub>18</sub> wheels and 1000 g weights

Table 4

(a) Formulations for prepolymer I/PEG 200/Glycerine

Formulation No.	NCO/OH Ratio	Prepolymer I	PEG 200	Glycerine	D <sub>5</sub> T	Mc
4	1.05:1	60 gms	14.28gms	1.877 gms	3.5:1	3723
5	1.2:1	60 gms	12.5gms	1.642 gms	-do-	4154
6	1.5:1	60 gms	40 gms	1.314gms	-do-	3687

(b) Physical properties

Formulation No.	Sp. gravity	Shore 'A' hardness	Tensile strength	%Elongation at break	Tear strength	Tabers Abrasion* loss in mgs/1000 cycles
4	1.17	55-60	1623PSI (11.2 MPa)	300%	213PSI (1.5 MPa)	342
5	1.14	65	2025PSI (14 MPa)	300%	268 PSI (1.84 MPa)	261
6	1.13	80	2630PSI (18.13MPa)	400%	372PSI (2.56MPa)	102

**Table 5**

**(a) Formulation for prepolymer I/PEG 400/Glycerine**

Formulation No.	NCO/OH Ratio	Prepolymer I	PEG 400	Glycerine	D:T	Mc
7	1.05:1	60 gms	23.56gms	1.877gms	3.5:1	4432
8	1.2:1	60 gms	25 gms	1.642gms	-do-	4903
9	1.5:1	60 gms	20 gms	1.314gms	-do-	5692

**(b) Physical properties**

Formulation No.	Sp. gravity	Shore 'A' hardness	Tensile strength	%Elongation at break	Tear strength	Tubers Abrasion* loss in mgs/1000 cycles
7	1.17	45-50	871PSI (6 MPa)	250%	162PSI (1.11MPa)	495
8	1.18	50-55	1120PSI (7.72MPa)	300%	220PSI (1.5 MPa)	370
9	1.12	75	1680PSI (11.58MPa)	350%	325PSI (2.24MPa)	185

Table 6

(a) Formulation for prepolymer II/1,4 BD/Glycerine

Formulation No.	NCO/OH Ratio	Prepolymer II	1,4 BD	Glycerine	D:T	Mc
10	1.05:1	60 gms	5.78gms	1.69gms	3.5:1	3673
11	1.2:1	60 gms	5.06gms	1.479gms	-do-	3728
12	1.5:1	60 gms	4.05gms	1.183gms	-do-	3655

(b) Physical properties

Formulation No.	Sp. Gravity	Shore "A" hardness	Tensile strength	%Elongation at break	Tear strength	Tabers Abrasion* loss in mgs/1000 cycles
10	1.1	55-60	2225PSI (15.4 MPa)	300%	260PSI (1.8 MPa)	153
11	1.19	65	2548PSI (17.57MPa)	420%	300PSI (2.06MPa)	113
12	1.12	80	3120PSI (21.5 MPa)	500%	390PSI (2.7 MPa)	25

Table 7

(a) Formulations for prepolymer II/PEG 200/Glycerine

Formulation No.	NCO/OH Ratio	Prepolymer II	PEG 200	Glycerine	D:T	Ac
13	1.05:1	60gms	12.86gms	1.69gms	3.5:1	4058
14	1.2:1	60gms	11.25gms	1.77gms	-do-	3912
15	1.5:1	60gms	9.00gms	1.183gms	-do-	3472

(b) Physical properties .

Formulation No.	Sp. gravity	Shore "A" hardness	Tensile strength	%Elongation at break	Tear strength	Tabers Abrasion* loss in mgs/1000 cycles
13	1.13	95	720PSI (5 MPa)	200%	175PSI (1.2MPa)	175
14	1.14	65	1000PSI (6.9 MPa)	280%	225PSI (1.55MPa)	148
15	1.18	75	1498PSI (10.33MPa)	350%	325PSI (2.24MPa)	76

Table 8

(a) Formulations for prepolymer II/PEG 400/Glycerine

Formulation No.	NCO/OH Ratio	Prepolymer II	PEG 400	Glycerine	D:T	Mc
16	1.05:1	60gms	23.72gms	1.69gms	3.5:1	4758
17	1.2:1	50gms	18.75gms	1.23gms	-do-	4486
18	1.5:1	50gms	15.00gms	0.985gms	-do-	6163

(b) Physical properties

Formulation No.	Sp. gravity	Shore 'A' hardness	Tensile strength	%Elongation at break	Tear strength	Tabers Abrasion* loss in mgs/1000 cycles
16	1.2	40	450PSI (3.1MPa)	150%	132PSI (0.92MPa)	274
17	1.23	45	330PSI (2.63MPa)	200%	132PSI (0.91MPa)	243
18	1.18	55	750PSI (5.17MPa)	250%	213PSI (1.46MPa)	151

### Microcellular polyurethane rubbers

Urethane foams are normally prepared from diisocyanates and hydroxyl terminated polyethers or polyesters. Linear or only slightly branched polymers are used to provide flexible foams, whereas more highly branched polymers produce rigid foams. Cellular structure usually <sup>achieved</sup> achieved by incorporating water in the system, the reaction between water and diisocyanate liberates carbon dioxide for foaming. For rigid foams a low boiling liquid such as trichlorofluoromethane (Freon 11) has been used as blowing agent. Suitable catalyst and stabilizers control the foam formation and cure. The most commonly used catalyst for flexible foam systems are combination of tertiary amines and organometallic compounds. Surfactants in foaming formulations impart stability of the foam system, and regulate the cellsize, thus siliconeoil such as dimethyl siliconeoil was used as a surfactant in PU foam.

Microcellular polyurethane rubber was made from PA-I and the formulation given below.

#### Formulation

i) Prepolymer I	60 gms
ii) 1,4 Butanediol	5.625gms
iii) Glycerine	1.642gms
iv) Dimethyl siliconeoil	0.1 ml



v) Triethylamine	0.25 ml
vi) Cobalt naphthanate	0.6 ml
vii) Lead **	0.4 ml
viii) E Methylene chloride (CH <sub>2</sub> Cl <sub>2</sub> )	5 ml

Procedure

The chemicals (i) to (iii) were weighed, 0.1 ml Dimethylsiliconeoil was then added, mixed first with high speed stirrer at 2000-3000 rpm for about 5 minutes. Later on the chemicals v to viii were added, stirred at high speed for about 30 seconds. The mixed reactants were poured to the mould cavity. The moulding was carried out at 75-80°C for about half an hour at mould pressure of 1500-1800 PSI. The moulded sheet was evaluated for physical properties as per ISI No.3400 : 1977 (Part I to XII) and the values were as follows.

1. Moulded density	0.5 to 0.6 gm/cc
2. Tensile strength PSI	600 ± 30
3. Elongation at break %	400 ± 20
4. Tear strength PSI	200 ± 20
5. Shore 'A' hardness	50-55

Experiments were carried out using PEG 200 and 400, by replacing 1,4 butanediol in the formulations. The same processing conditions were followed with the two chain extenders. The cured cellular rubber were found to be soft and possessed very low shore 'A' hardness about 10<sup>0</sup>-20<sup>0</sup> and did not have sufficient strength. Therefore the evaluation of properties was not carried out.

CHAPTER - III

RESULTS    AND    DISCUSSION

The properties of solid polyurethane elastomers depend mainly on (i) Molecular weight of backbone polyol (ii) Molecular weight per crosslink ( $M_c$ ) (iii) Type of chain extender and (iv) Ratio of isocyanate to hydroxyl group.

The study of the relation between structure and properties of the castable polyurethane elastomer for the above mentioned parameters are discussed in detail.

#### 1) Backbone polyol

There are three different polyols normally employed as the backbone polyol for polyurethanes viz. (a) Polyesters (b) Non branched polyethers (c) Polyethers with pendant chains. The polyols are hydroxy terminated and have molecular weights of 1000 to 3000. The polyester most widely used to date in solid polyurethanes is polyethylene adipate, mixed polyesters such as polyethylene propylene adipate are also of interest. The commonly employed polyethers are polypropylene glycols and poly tetramethylene glycols<sup>26</sup>.

O

Polyester group ( $-C-O-$ ) has a higher value of molar cohesive energy [ $2.9 \text{ K cal mol}^{-1}$ ] than the polyether ( $-O-C-$ ) [ $1.00 \text{ K cal mol}^{-1}$ ], therefore it would be expected that polyester would give stronger polymers than the polyethers of similar molecular weight.<sup>26</sup> This effect can be

overcome to a certain extent by using lower molecular weight polyethers which would have the result of increasing the concentration of urethane groups in the chain.

In the present work, polyethers viz. polypropylene glycol of molecular weight 1090 and 1929 have been employed. It has been observed and found that the physical properties such as, shore 'A' hardness, tensile strength and tear strength were of the higher order for the elastomers based on backbone polyol polyether of  $\overline{M}_n$  1090 than these based on PPG 1929, irrespective of the nature and type of chain extender and the ratio of NCO:OH employed. However, the abrasion properties of the elastomer made from polyether 1929 possessed better abrasion properties than that of the rubber from PP-I<sup>28</sup>.

(ii) Molecular weight per crosslink (Mc)

It is assumed that for most of polymers the properties change with increasing molecular weight. The properties such as tensile and tear strength increase as the molecular weight increases. At the limiting value of molecular weight no major change in properties will occur. At this stage the degree of crosslinking and the resultant molecular weight per crosslink, Mc, becomes important.

In polyurethanes the crosslinking can occur by three main ways (a) by use of a trifunctional chain extender (b) by allophanate formation (c) by biuret formation.

It is difficult to obtain by chemical analysis quantitative data on the degree of allophanate or biuret formation, but the use of trifunctional chain extenders (e.g. Glycerine or trimethylol propane) leading to urethane crosslinks is far more precise, especially when allophanate and biuret formation is kept to a minimum. These conditions are approached when equivalent amounts of active hydrogen compound and di-isocyanates are used and the molar quantity of chain extender is known.

Calculation of Mc

Eg. Table No.4 Formulation No.5 PP I/PEG 200/Glycerine

PP I - 60 gms

PEG 200 - 12.50 gms

Glycerine - 1.642 gms (0.0178 moles)

In the above formulation assuming that the degree of crosslinking is function only of the amount of triol, the molecular weight per crosslink can be calculated by dividing the total molecular weight of the constituents in the formulation (60gms+12.5gms+1.642gms) by the molar amount present (0.0178mole) of the trifunctional reactant glycerine. In this particular formulation the value of Mc was 4154. Pigott<sup>29</sup> prepared a series of compounds of different values of Mc by varying the proportion of diol to triol and studied their physical properties.

Mc as observed from the above can be increased by reducing the molar proportion of the trifunctional chain extender in the formulations. In this study the molar proportion of glycerine (0.1 mole) and the ratio of diol to triol 3.5:1 were kept constant in all the formulations. Hence, the Mc, did vary significantly as seen in the tables from 3 to 8. The change in properties of elastomers may be due to the effect of chain extenders and backbone polyol.

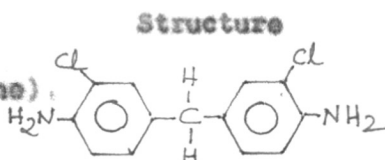
(iii) Type of chain extender

The chain extenders in polyurethane technology play an important role in relation to the various properties of elastomers. The chemicals employed as chain extenders are short chain molecules and are classified into two types.

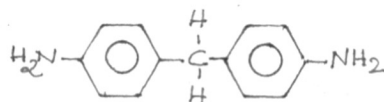
(a) Aromatic and aliphatic diamines<sup>30</sup> (b) Aliphatic and aromatic glycols.

Aromatic diamines

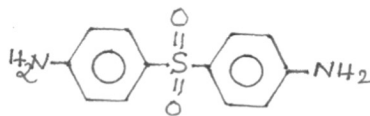
4-4' methylene bis (O-chloroaniline)  
(MOCA)



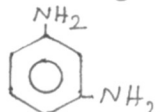
4-4' methylene dianiline  
(MDA)



4-4' Diaminodiphenylsulfone  
(DADPS)



m-Phenylenediamine  
(MPDA)



Aliphatic amines	Mol.wt.	Functionality	Structure
Ethylenediamine	60	4	$\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2$
Diethylene triamine	103	5	$\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH-CH}_2\text{-CH}_2\text{-NH}_2$
Triethylene tetramine	146	6	$\text{H}_2\text{N-(CH}_2\text{)}_2\text{-NH-(CH}_2\text{)}_2\text{-NH-(CH}_2\text{)}_2\text{-NH}_2$

(b) Aliphatic glycols

Glycol	Mol.wt.	Functionality	Structure
Ethylene glycol	62	2	$\text{HO-CH}_2\text{-CH}_2\text{-OH}$
Diethylene glycol	106	2	$\text{HO-(CH}_2\text{)}_2\text{-O-(CH}_2\text{)}_2\text{-OH}$
Propylene glycol	76.	2	$\begin{array}{c} \text{OH-CH-CH}_2\text{-OH} \\   \\ \text{CH}_3 \end{array}$
1,3 Propanediol	76	2	$\text{OH-CH}_2\text{-CH}_2\text{-CH}_2\text{-OH}$
1,4 Butanediol	90	2	$\text{OH-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-OH}$
Glycerine	92	3	$\begin{array}{c} \text{CH}_2\text{-OH} \\   \\ \text{CH-OH} \\   \\ \text{CH}_2\text{-OH} \end{array}$
Trimethylol propane (TMP)	134	3	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{H}_3\text{C-CH}_2\text{-C-CH}_2\text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$

Aromatic glycol	mol.wt.	Functionality	Structure
Hydroquinone-diethylether	198	2	

In the literature, use of low molecular weight short chain polyethers such as polyethylene glycol 200 (PEG 200) and polyethylene glycol 400 (PEG 400) have not been studied in the preparation of polyurethane elastomers. This lead to undertake the study of the influence of PEG 200 and 400 as chain extenders on the physical properties of the cured elastomers.

The elastomers based on PP-I using PEG 200 has higher values of shore 'A' hardness, tensile strength and tear strength as compared to the elastomers from PP-I based on PEG 400, irrespective of the ratio of NCO:OH as seen from the tables 4 and 5. There has been no significant variation in % elongation at break for the two types of elastomers as in the two tables. The Tabers abrasion properties [loss in mgs/1000 cycles/1000 gm.wt.] of the elastomer using PEG 200 were better than that of the one based on PEG 400.

With the backbone polyol PPG 1929, the elastomers were prepared by using PEG 200 and 400. As seen earlier with PPI, the physical properties of polyurethane rubber



from PEG 200 has again showed higher values of shore 'A' hardness, tensile strength and tear strength as compared to that of PEG 400 based rubber as shown in the table 7 and 8. The %elongation at break and abrasion properties were found to be better than that of polymer based on PEG 400 as shown in the tables.

It has been observed from the literature, that 1,4 butanediol has been commonly employed in polyurethane formulations as the standard chain extender. The elastomers were prepared using PP-I and PP-II with 1,4 butanediol, under the same processing conditions. The physical properties of rubber from PEG 1090 and 1929 showed over all better physical properties, as compared to PEG 200 and 400, irrespective of the ratio of NCO:OH as can be seen from the tables 3 and 6.

iv) Ratio of isocyanate to hydroxyl group (NCO/OH)

In the study of polyurethane elastomers based on the two aliphatic short chain polyethers as chain extenders, the mole ratio of diol to triol and the molar quantity of glycerine were kept constant. The ratio of isocyanate to hydroxyl group was varied from 1.05:1, 1.2:1 and 1.3:1, to investigate the effect and influence of PEG 200 and 400 on the final properties.

The increase of isocyanate group in the polymer

further enhances the concentration of urethane groups in the crosslink, leading to the higher values of the properties. This may be due to the high cohesive energy of urethane groups as compared to other groups shown below.

Group	Molar cohesive energy [K cal mol <sup>-1</sup> ]
Hydrocarbon (-CH <sub>2</sub> -)	0.68
Ether (-O-)	1.00
Ester (-COO-)	2.90
Aromatic (C <sub>6</sub> H <sub>4</sub> )	3.90
Amide	8.50
Urethane (-NH-COO-)	8.74

Further the increase in the values of the physical properties in the elastomer may be due to the formation of allophanate groups that is crosslinking, at the normal manufacturing temperature of 100<sup>o</sup>-140<sup>o</sup>C.

The various physical properties of the polyurethane elastomers such as shore 'A' hardness, tensile strength, %elongation at break and tear strength increased with the increase in the ratio of NCO:OH for all the formulations prepared from PP-I and PP-II using 1,4 butanediol, PEG 200 and 400 as can be seen from the figures 4 to 7 and 9 to 12.

The loss in weight of the elastomers decreased with the increase of NCO to OH ratio in the formulations (see fig. 8 and 13) indicating better abrasion properties (wear and tear for the polymers.

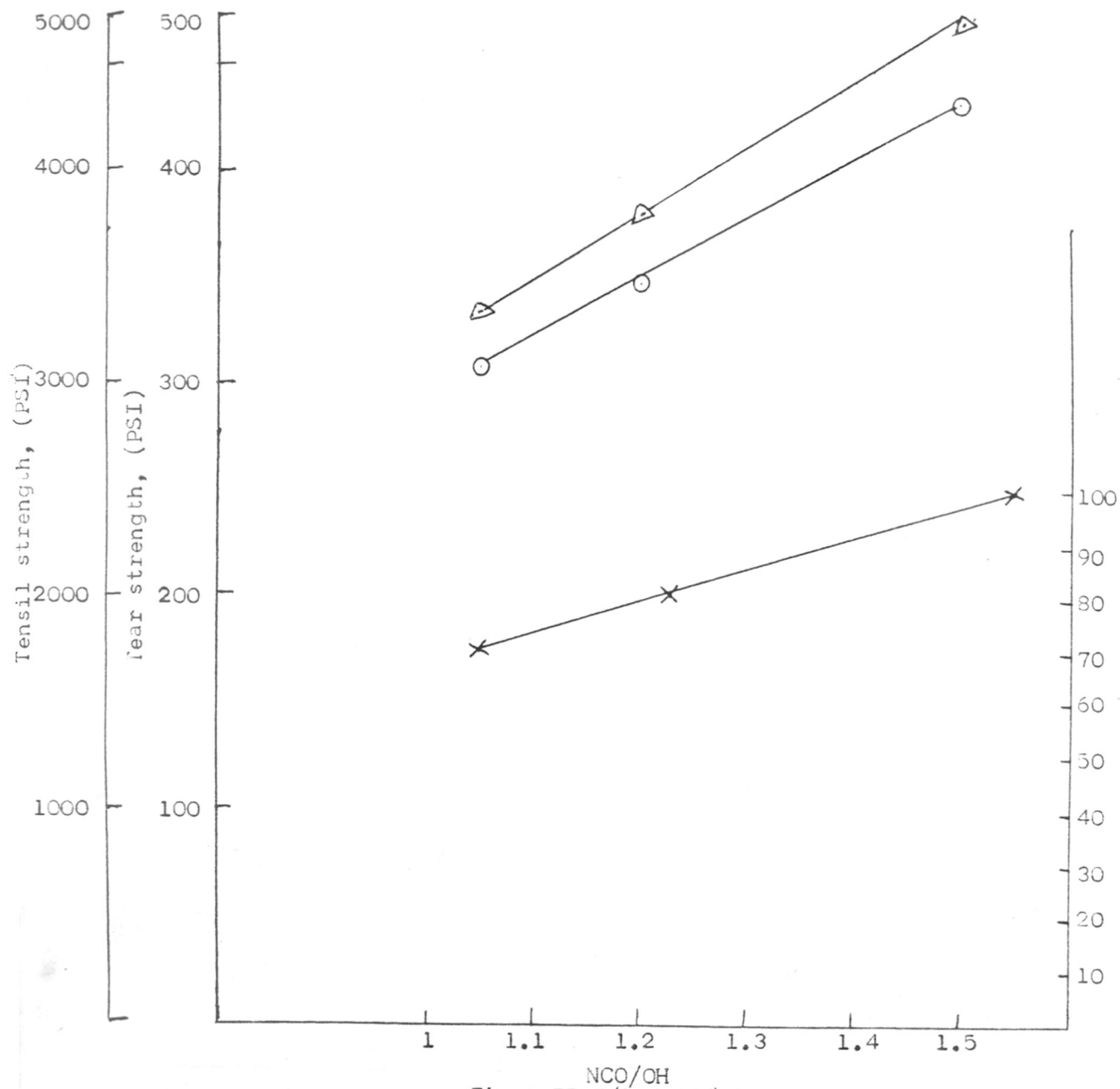
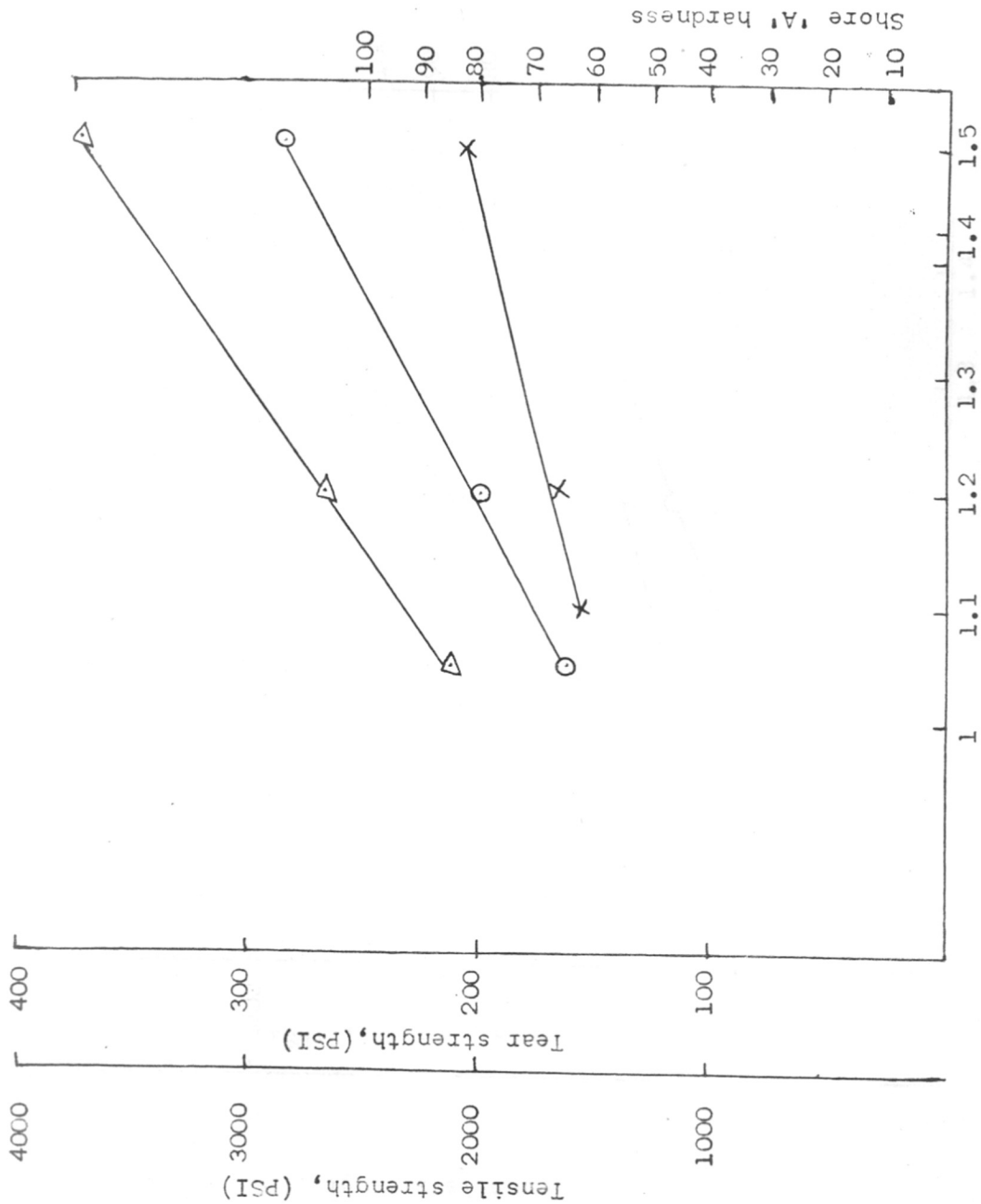
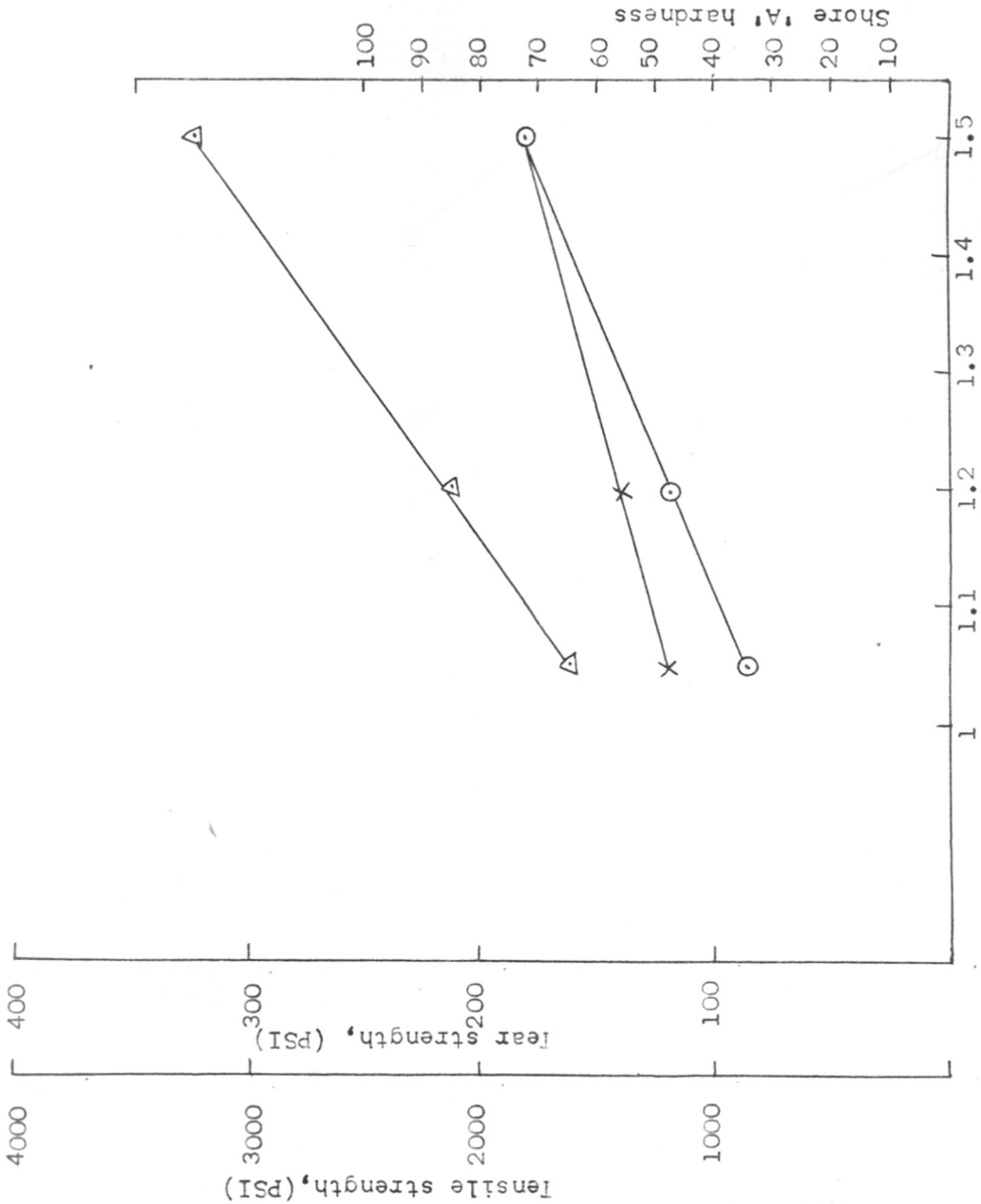


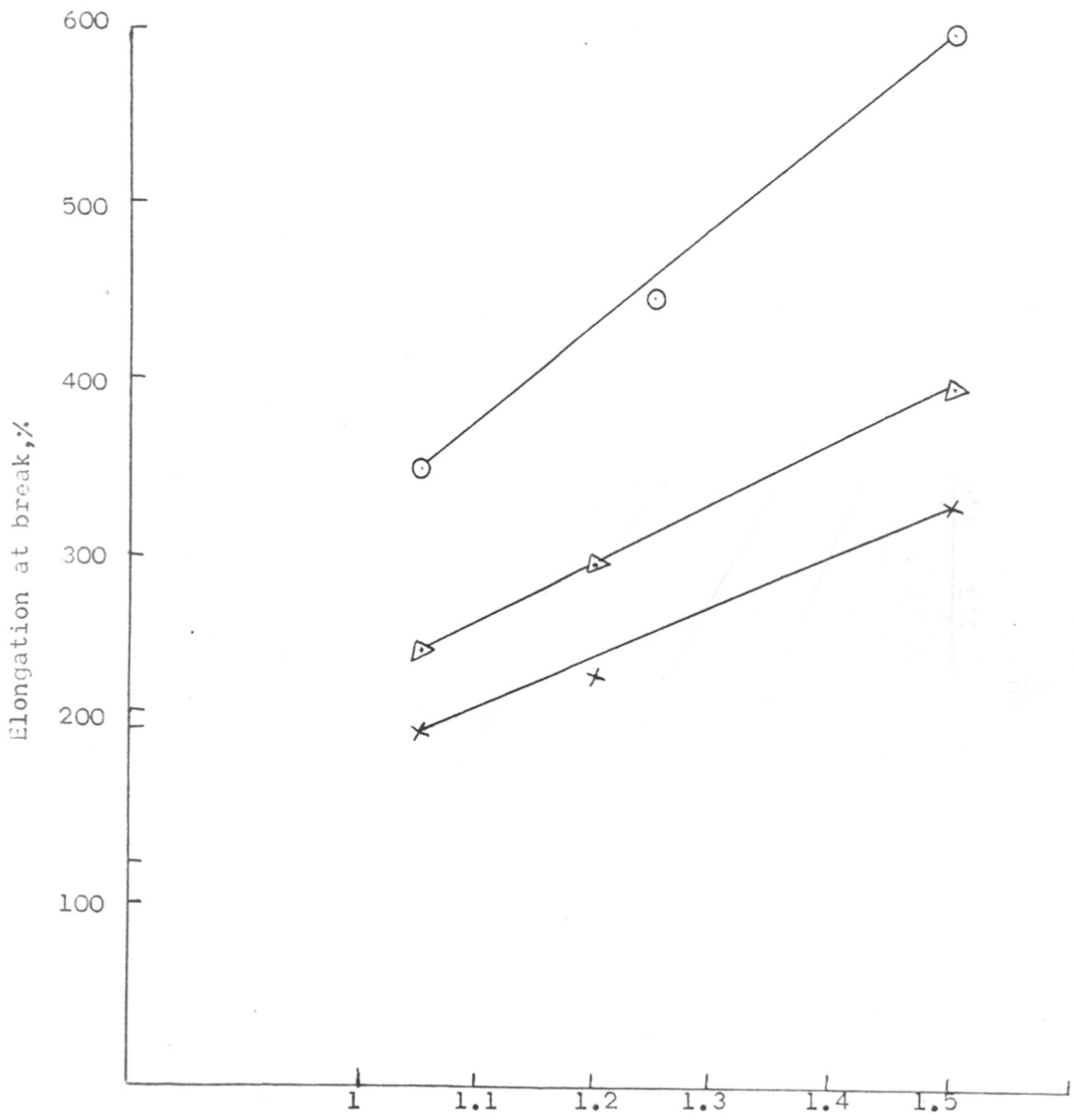
Fig.4 PP-I/1,4 BD/Glycerine  
 ○ Tensile strength    △ Tear strength    x Shore 'A' hardness



NCO/OH  
 Fig. 5 PP-I/PEG 200/Glycerine  
 Tensile strength ◉ Tear strength ◈ Shore 'A' hardness ×

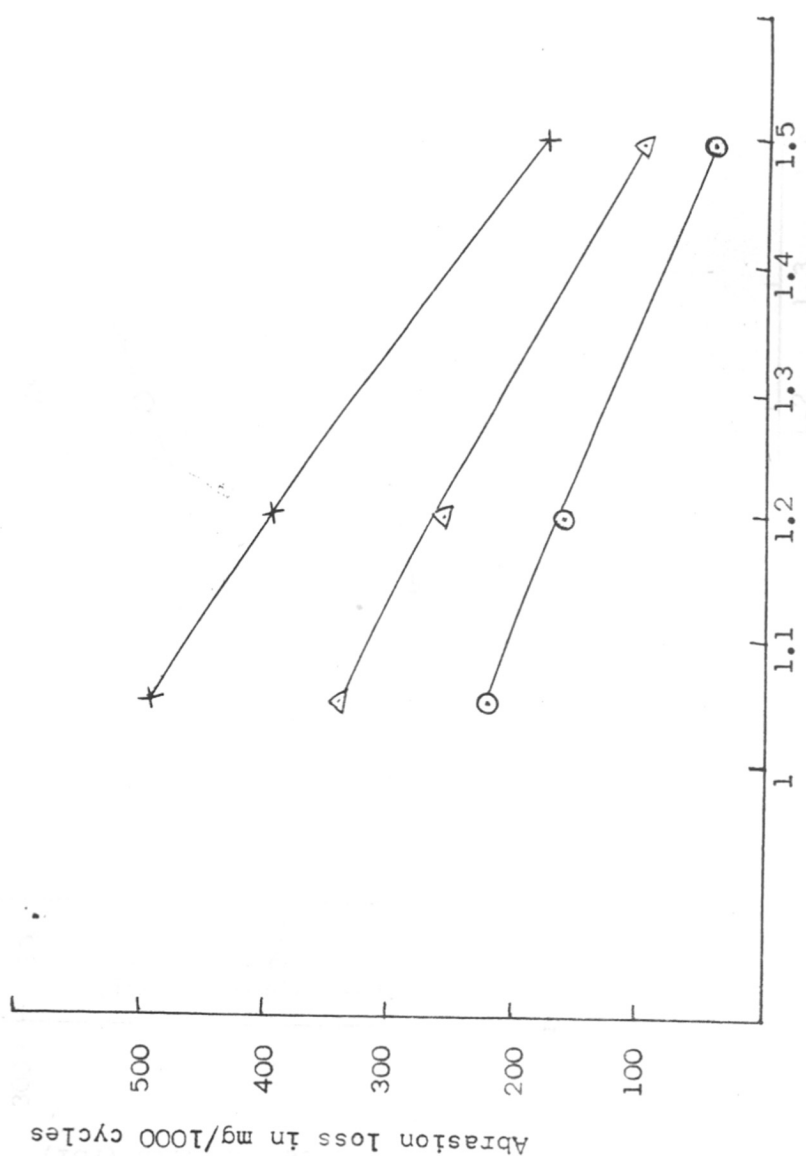


○ Tensile strength    △ Tear strength    x Shore 'A' hardness  
 NCO/OH  
 Fig.6 PP-I/PEG 400/Glycerine



NCO/OH  
Fig.7

○ PP-I/1,4 BD/Glycerine    △ PP-I/PEG 200/Glycerine  
x PP-I/PEG 400/Glycerine



NCO/OH

Fig. 8

○ PP-I/1,4 BD/Glycerine  
 △ PP-I/PEG 200/Glycerine  
 x PP-I/PEG 400/Glycerine



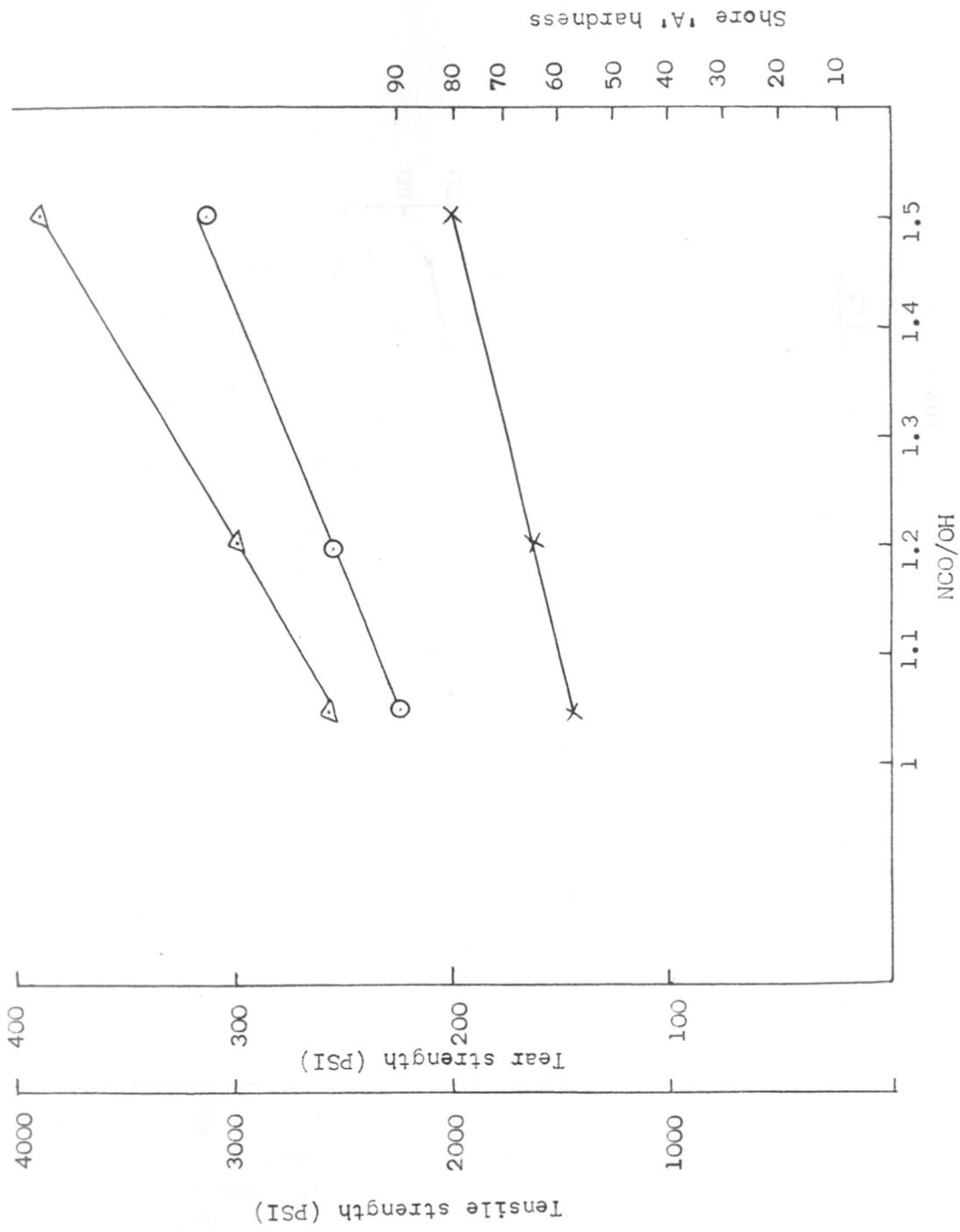


Fig.9 PPII/1,4 BD/Glycerine

⊙ Tensile strength    △ Tear strength    x Shore 'A' hardness

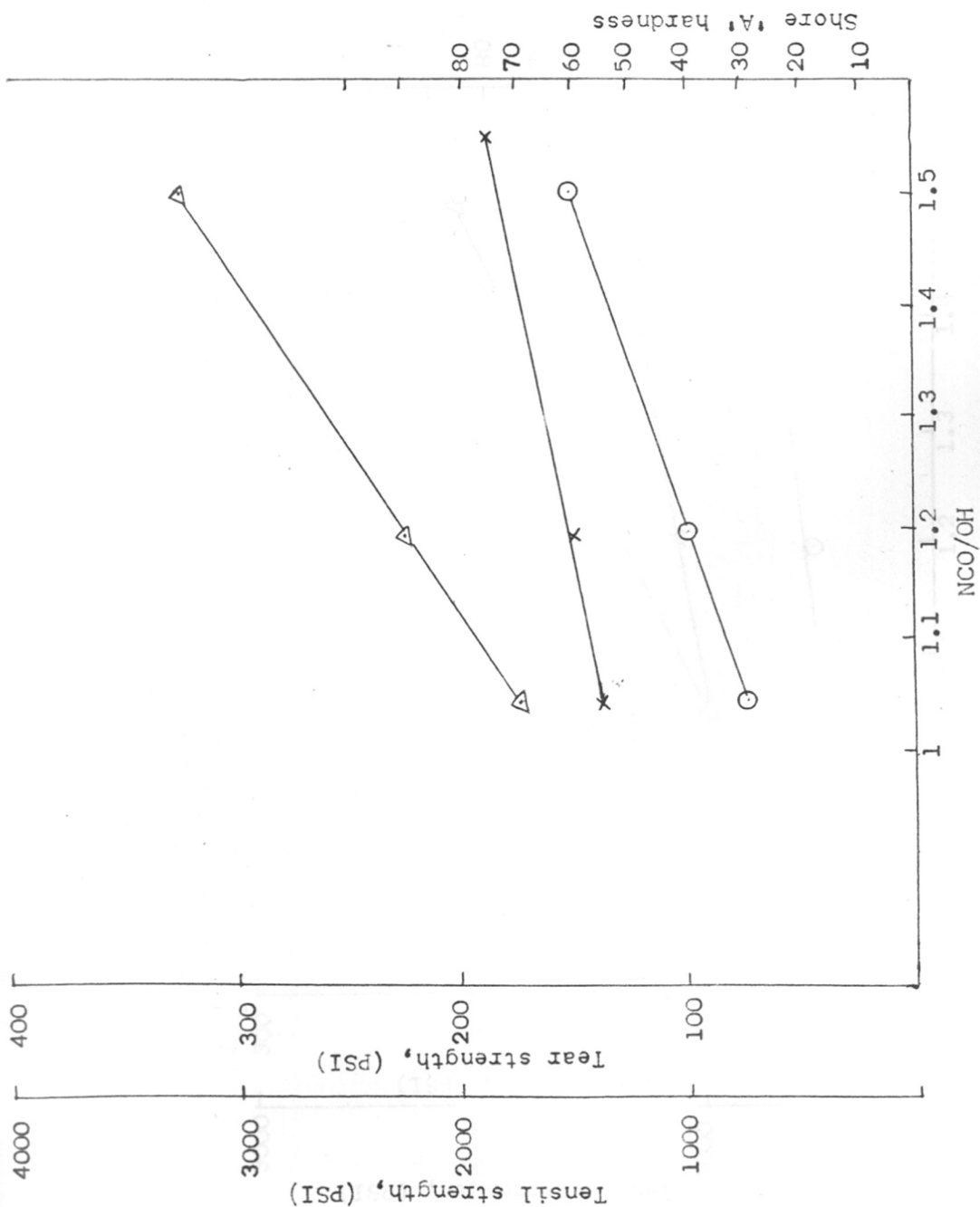


Fig.10 PP-II/PEG 200/Glycerine

○ Tensile strength    △ Tear strength    x Shore 'A' hardness

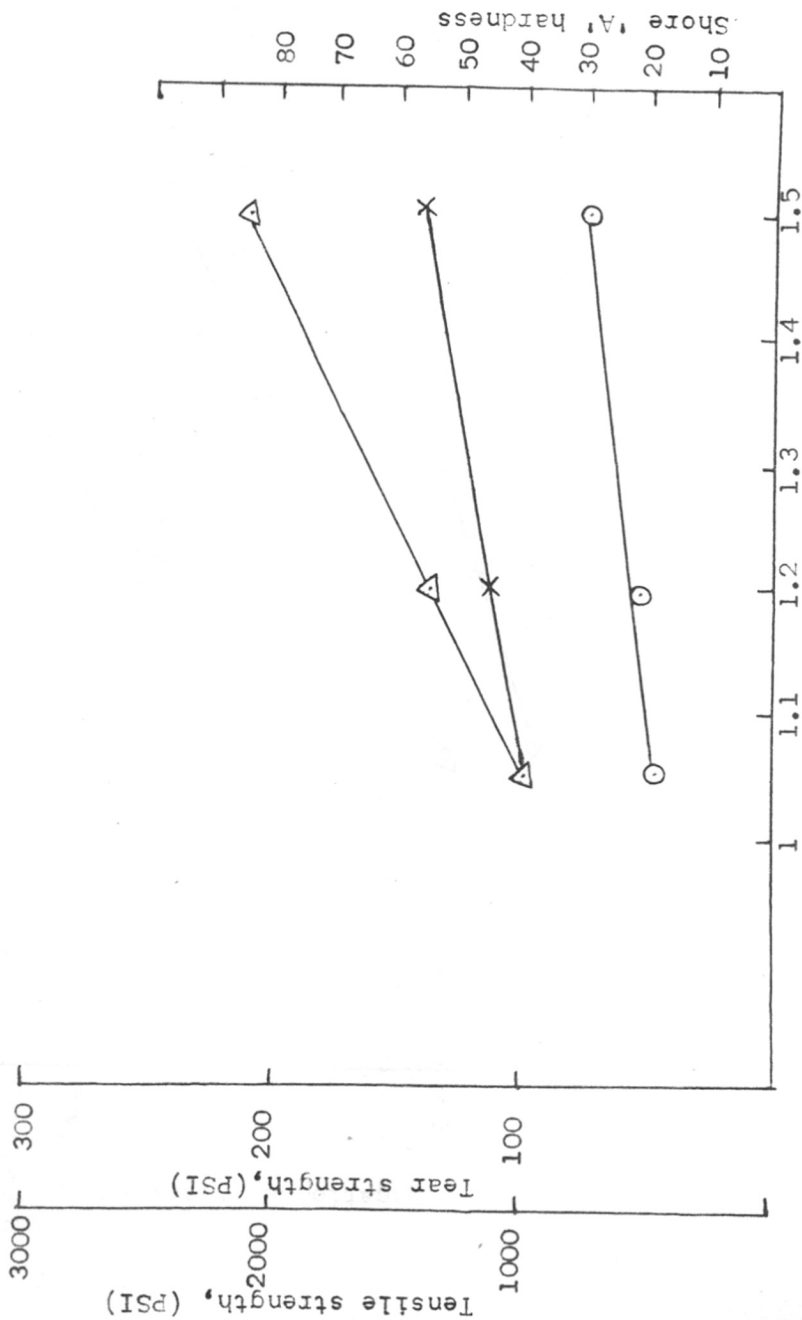


Fig.11 PP-II/PEG 400/Glycerine

○ Tensile strength    △ Tear strength    x Shore 'A' hardness

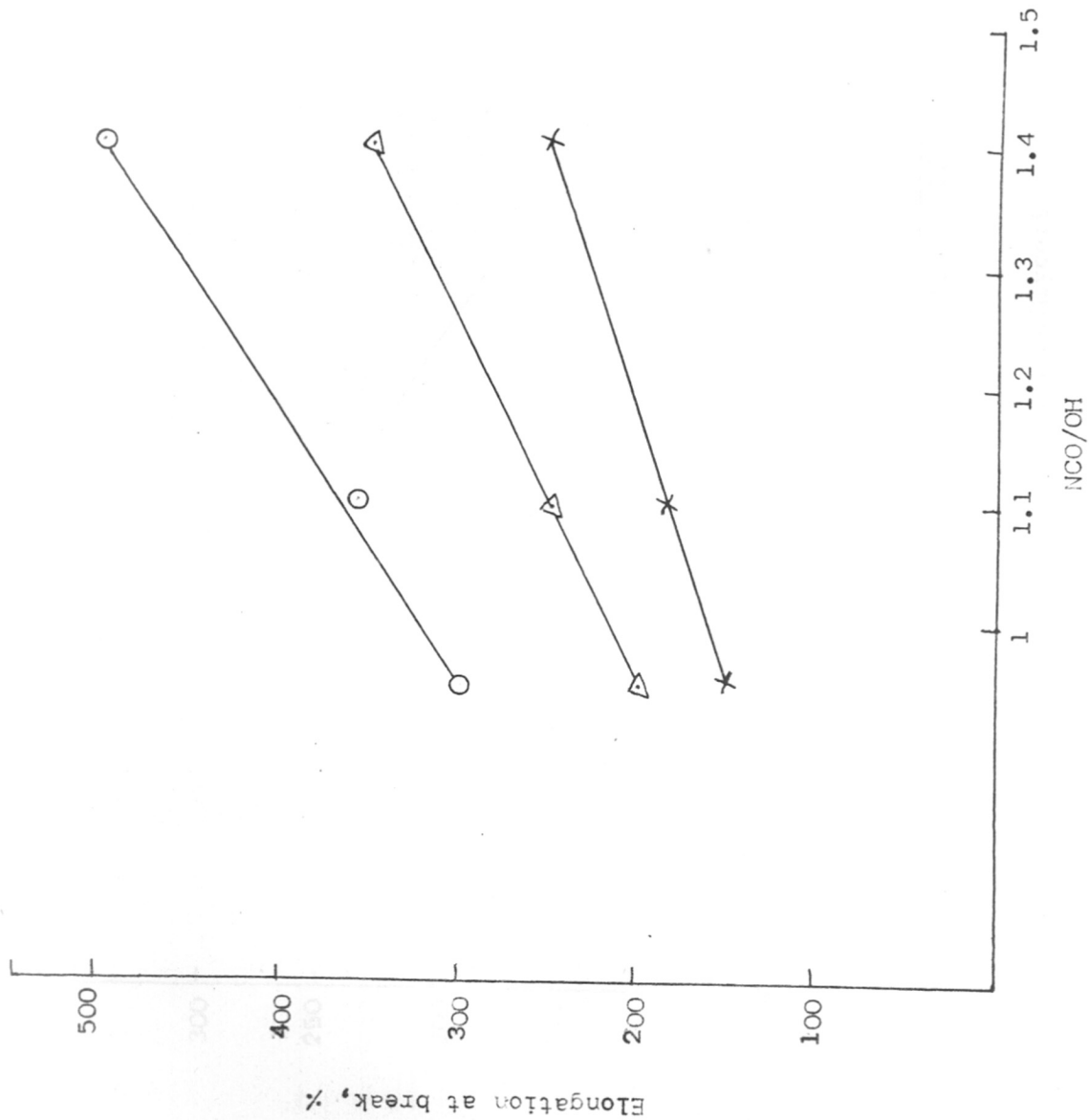
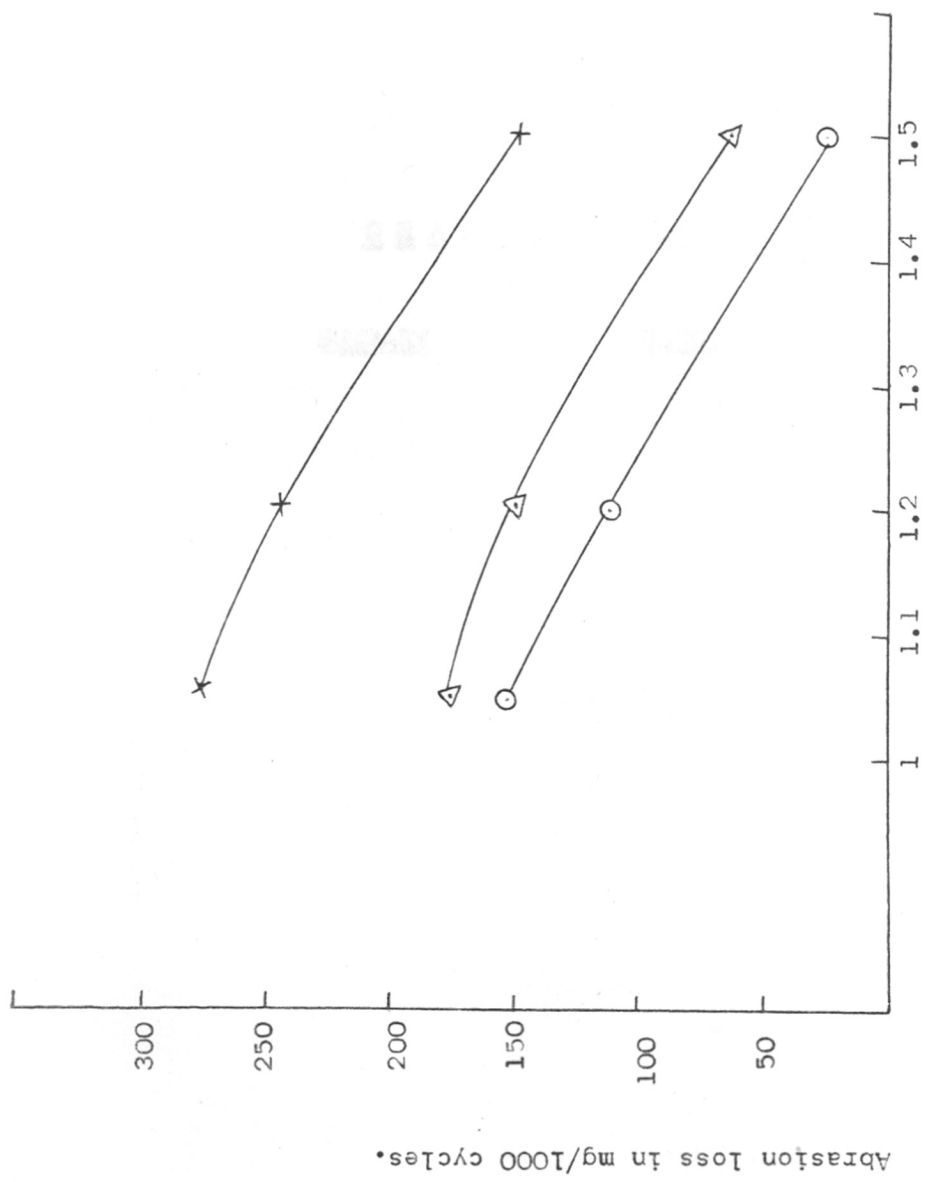


Fig. 12

○ PP-II/1,4 BD/Glycerine    △ PP-II/PEG 200/Glycerine    x PP-II/PEG 400/Glycerine



NCO/OH  
 Fig. 13  
 ○ PP-II/1,4 BD/Glycerine △ PP-II/PEG 200/Glycerine  
 x PP-II/PEG 400/Glycerine

CHAPTER - IV

SUMMARY      AND      CONCLUSION

SUMMARY AND CONCLUSION

The performance of polyurethane elastomers has been governed and influenced mainly by the backbone polyol, the type of diisocyanate, molecular weight per crosslink, ratio of NCO to OH, and the nature and type of chain extenders employed. The elastomers based on PEG 200 and the two prepolymers possessed improved and better properties as compared to the elastomers based on PEG 400. Whereas, the properties of elastomers based on 1,4 butanediol and the two prepolymers have shown superior properties to the one based on PEG 200 and 400.

This leads to the fact that short chain molecules produce close network of crosslinks in the total network of the elastomer, and hence effect more hydrogen bonding leading to overall superior physical properties as observed in the case of 1,4 butanediol. In case of long chain molecules which are employed as chain extenders, the close network of crosslink in the rubber becomes less. Thus the hydrogen bonding effect may be reduced, leading to lower physical properties. In addition, the two polyethylene glycols have ether groups (-C-O-C-) which are flexible, favouring softness, low melting point and low elasticity. Thus, this investigation substantiates the relation between the structure and properties of the polyurethane elastomers studied.

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**SYNOPSIS**

Polyurethanes are defined as polymers which contain urethane groups ( $\text{-NH-CO-O-}$ ) in the main polymer chain. They are prepared by the reaction of di or poly functional hydroxy compounds, such as hydroxy terminated polyesters or polyethers, with di or poly functional isocyanates such as, Toluene di isocyanate (TDI) and diphenylmethane 4-4' di isocyanate (MDI). Polyurethane elastomers are well known for their superior properties like toughness, high mechanical strength, resilience, excellent abrasion resistance with good resistance to oil. Polyurethane elastomers are of three types viz., (1) Castable Polyurethanes (2) Millable elastomers and (3) Thermoplastics.

In the present work, polyethers like poly (oxy propylene) glycol of 1000 and 2000 molecular weights have been employed as glycol backbone. Isocyanate ( $\text{NCO-}$ ) terminated prepolymers were prepared by reacting the polyol with toluene di isocyanate (TDI) at different mole ratios. Prepolymers were then analysed for %NCO content. The high molecular weight urethane rubbers have been obtained by chain extension reaction of prepolymers. The chain extenders employed in the study are (1) polyethylene glycol of molecular weight 200 and 400 (2) 1, 4 Butanediol in presence of a small mole proportion of a triol such as

glycerine. The elastomer sheets of 2mm thickness are moulded in the hydraulic press at 100<sup>o</sup>-150<sup>o</sup>C at a moulding pressure of 1000-1500 Psi. Similarly, microcellular polyurethane rubber was made from the poly (oxy propylene) glycol of 1000 MW with TDI. By varying the different parameters such as (1) backbone polyol (2) ratios of isocyanate to hydroxyl groups (3) type of chain extenders (4) molecular weight per crosslinking, the physical properties of the elastomers were evaluated. Thus the structure and property relationship of polyurethane elastomers has been studied in the thesis.