Effect of Different OH Values of HTPB on Thermo Mechanical Properties of HTPB/TDI System Using Inert Filler

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Dedication

This Dissertation is dedicated to my Beloved Parents, siblings

& "Maaro"

Acknowledgments

First of all, I am thankful to ***Almighty Allah*** the worthy of all praises who gave me the knowledge, courage and patience to complete my thesis. The thesis appears in its present form due to guidance and help from many people. I would like to thank all of them.

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Abstract

HTPB is polymer of 1, 3-butadiene terminated at each end with hydroxyl group. It is considered as a workhorse of propellant binder and is used all over the globe. This liquid prepolymer has excellent physical properties such as low glass transition temperature, and good chemical résistance. It is capable of taking solid loading up to 88% without sacrificing the ease of processability. It reacts with isocyanate to form polyurethane polymer. The mechanical properties of elastomer of HTPB vary widely depending on the physical properties of polymer such as molecular weight, molecular weight distribution, functionality, degree of branching and microstructure.

A systematic study has been done on HTPB resin with varying hydroxyl value with a view to achieve the maximum possible strain capability and moderately high tensile strength keeping all other parameters constant. The influence of increasing hydroxyl content (0.7-0.8) (Mn remain same) on mechanical properties of the finished propellant is studied. The filler used is calcium carbonate. The cured elastomer were subjected to be analyzed for the determination of dynamic thermo-mechanical analysis (DTMA), differential scanning calorimetry, uniaxial tensile properties such as tensile strength, percentage elongation, Young's modulus and hardness. It was found that thermal properties of prepared elastomers did not change significantly by varying OH number of polymer. Hardness and tensile strength increases while % elongation decreases by increasing NCO/OH ratio while mechanical properties (tensile strength) decreases by increasing OH value of polymer.

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List of Abbreviations

Abbreviation	Explanation
AFM	Atomic force microscopy
ASTM	American society for testing material
CTPB	Carboxy terminated polybutadiene
Cm^{-1}	Per centimeter
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
DMF	Dimethyl formamide
DMSO	Dimethyl sulfoxide
DMAc	Dimethyl acetacrylate
DTMA	Differential thermo-mechanical analysis
DLS	Dynamic light scattering
Ew	Equivalent weight
FT-IR	Fourier transform infrared
GPC	Gel permeation chromatography
HTPB	Hydroxy terminate polybutadiene
HDI	Hexamethylene diisocyanate
IPDI	Isophorone diisocyanate
ISO	International standard organization
MDI	Methylene diphenyl diisocyanate

Abbreviation	Explanation
Mn	Number average molecular weight
Mw	Weight average molecular weight
NDI	Naphthalene diisocyanate
NCO	Isocyanate
Nt	Normality
NHCOO	Urethane linkage
OH	Hydroxyl number
PBAA	Polybutadiene acrylic acid
PBAN	Polybutadiene acrylonitrile
PDI	Polydispersity index
SEM	Scanning electron microscopy
SAXS	Small angle x ray scattering
TDI	Toluene diisocyanate
Tc	Crystallization temperature
Tg	Glass transition temperature
Tm	Melting temperature
TEM	Transmission electron microscopy
UTM	Universal testing machine
VPO	Vapor pressure osmometry

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Chapter 1

Introduction

In the modern era, technology is improving in the field of rocketry day by day. Different types of rockets, both for space and military purpose, are manufactured all around the globe.

1.1 Rocketry

1.1.1 History

It is believed that rockets were invented by Chinese. Those were shaped same as today's fire work and the people used them on festive and combat occasions. A rod was mounted at rocket rear end which balanced it and thrust was given by burning black powder which comprised of charcoal, sulfur and potassium nitrate.

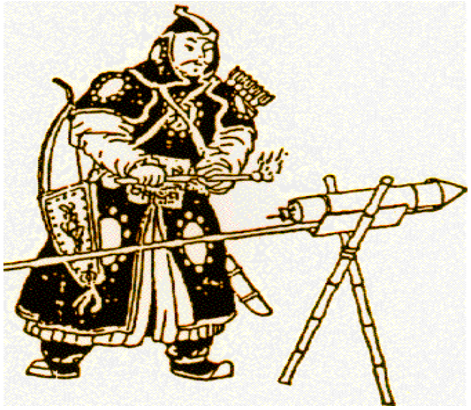


Figure 1.1: Chinese with his <<arrow of flying fire>>

In 1232, rockets were used first time in a war between Chinese and Mongols. During battle of Kai-Keng, Chinese used their "arrow of flying fire" that provided them strategic success [1]. Europe sent an ambassador William for getting knowledge about rockets to Asia. He along with a scholar Roger Bacon and his friend Friar started experimentation with rockets and gunpowder.

Modern age of rockets was introduces by Konstantin E,Tsiolkovsky who proposed jet propulsion theory. In 1897, Tsiolkovsky developed rocket equation [2]. In 1926,a physicist named Robert H.Goddar in America performed experiment with rocketry concept and was succeed to launch a rocket containing liquid propellant [3]. The rocket contained gasoline and liquid oxygen as fuel. Goddar is considered as father of current rocketry. Solid composite propellant was reported first time by John whiteside in 1940s.

Figure 1.2: Picture of Robert H.Goddar with his Rocket (Wikipedia)

1.1.2 Propulsion

According to Newton's 3rd law every action has a reaction that is equal in magnitude but opposite in direction. Rocket propulsion depends on this principle. The ejected gases gives thrust to the rocket in forward direction which is called propulsion .Thrust is basically a force that is measured in unit of kg m/s^2.

1.1.3 Types of Propulsion

There are four types of rocket propulsion.

1. Solid fuel propulsion

It is mostly used for launching vehicles. Solid motors cannot be controlled so these are not used for space missions. These are mostly used for missile purpose .these solid motors have advantages like long shelf life, simplicity and reliability.

2. Liquid fuel propulsion.

Liquid motors are controllable and have many sizes and shapes. These may be mono propellant, bi propellant or cryogenic propellant.

3. Cold gas propulsion

These are lighter and simpler as compared to liquid motors. They work like spray paint and are controllable.

4. Ion propulsion

These are quite different from solid and liquid motors. They provide low thrust as compared to others but run over large period of time (days to months).

1.1.4 Propellant

According to Newton's 3rd law of force, every action has a reaction that is equal in magnitude but opposite in direction. Rocket works on the same principal. When rocket move forward something has to spews out in backward direction and that thing is called propellant. It is a material that is rushing in back direction giving spacecraft thrust. Mostly propellant is fuel which burned in the presence of oxidizer and produced hot gases. In some cases propellant is directly rush out of spacecraft without burning.

1.1.5 Types of Propellant

There are six different types of modern propellant system.

a. Single base propellant
b. Double base propellant
c. Triple based propellant
d. Composite modified caste double base propellant
e. Elastomeric modified caste double base propellant
f. Composite propellant.

Composite solid propellants are used in modern ere and contain binder along with oxidizer, metallic fuel, plasticizer, curatives and other ingredients e.g. cross linking agents and antioxidants.

1.2 Binder

A matrix is provided by binder for the incorporation of metallic fuel, oxidizer and other components. It constitutes 10 to 15 % of composite propellant system. Propellant mechanical properties are determined by binder. Mostly organic polymers are used as binder for solid composite propellant. These polymers can also serve as fuel. Their decomposition produces stable molecule e.g. carbon dioxide, carbon monoxide and water vapors.

1.2.1 Requirements of an Ideal Binder

1. Binder should contain functional groups which are reactive and can undergo in chemical reaction with curing agent producing elastomeric network for compatible system
2. Binder should contain hydrocarbons in its backbone and produce stable products on combustion.
3. Binder viscosity should meet the processing requirement of the system.
4. Glass transition temperature of binder should be low so that it can bear stress up to a large range.
5. Binder should have high heat of formation.
6. Binder should have chemical and physical compatibility with other ingredients of the system.

1.2.2 Propellant Binder Present Status

Following polymeric binder are used for composite propellant.

1. Polysulphide binder
2. Polyester polyols
3. Polyether
4. Polybutadiene binder

Among these, Polybutadiene binders are most commonly used binder in modern age. Polybutadiene acrylic acid (PBAA), Polybutadiene acrylic acid acrylonitrile (PBAN) Carboxyl terminated Polybutadiene (CTPB) and Hydroxyl terminated Polybutadiene (HTPB) are some of polybutadiene binders. Good reproducibility, low viscosity, easy availability, high hydrocarbon content, high solid loading up to 89%, less time for optimum curing, clean stoichiometry and lower glass transition temperature makes HTPB a workhorse binder for various system. HTPB reacts with toluene diisocyanate to form urethane linkage that provides good mechanical properties to the propellant system. The polyurethane network can be altered by various methods which results in changing of mechanical properties so knowledge about polyurethane is necessary for developing a system of required mechanical properties.

1.3 Polyurethane

Polyurethane fits to organic polymer category which has urethane linkage in their structure. Polyurethane belongs to block copolymers which are linear in nature and these are formed by the reaction of polyisocyanate with polyols.

These elastomers consist of following three parts

a) A macro diol which may be polybutadiene, polyester or it may be a polyether.

b) A polyisocyanate which may be aliphatic or aromatic.

c) Chain extender having small molecular weight diamine, water, diol, or amino alcohol.

There are micro domains termed as soft and hard segment which will recognize the properties of polymer blocks.

1. **Hard Segment**

It is synthesized by reacting chain extender with isocyanate. The degree of crystallinity of the elastomer depends upon hard portion and it will decide the final thermal and mechanical properties of the cured elastomer. The temperature at which hard segment has to be used, should be lower than its melting temperature.

2. **Soft Segment**

It is made by macro diol and has amorphous or may be crystalline in nature. The temperature at which the soft segment has to be used, should be far high then its glass transition temperature [4].

Studies show that crystallinity of the hard segment depends upon several factors like chemical structure, molecular volume, chain length and functionality of polyisocyanate, polyols or chain extender. Chain extender structure has noteworthy effect on the morphology and properties of polyurethane [5]. The secondary intermolecular forces and cross link density of the chains effect physical properties of polymers. In the synthesis of polyurethane, there is crosslinking although there may not be addition of crosslinking agent. Allophanates and biurets are formed due to cross linking.

Polyurethanes are under consideration because these can be easily altered and are easily processable. Additives can also be incorporated into these polyurethane for controlling properties. Additives are added during the process of polymerization to change the properties or to regulate the chemical reaction [6]. There are other particles like filler, colorant and emulsifier which can be added in polymerization of polyurethane [7]. There is addition of, catalyst, chain extender or blowing agent for the formation of final product depending on the initial reaction parameters.

1.3.1 History of Polyurethane

Professor Otto Bayer is considered to be the inventor of polyurethane. He was working in I.H Farben laboratory, Germany in 1937 with his coworker when they noticed that liquid diisocyanate reacts with polyester or polyether diol to form polyurethane linkage. They were working to synthesize a polymer which can compete natural rubber. They noticed that when hexamethylene diamine undergoes phosgination reaction, it produces hexamethylene diisocyanate that can serve as intermediate for useful product synthesis.

The intermediate can react with alcohol to form polyurethane polymer. The product formed by this way was used as coating material. When the world war started in 1940's, there was a need to manufacture garments which can resist mustard gas so these coating were utilized to develop such garments. Foams were also synthesized by the reaction of naphthalene diisocyanate with polyester and these foams were used to increase the performance and strength of military aircraft [8, 9].

The research continued at IG Farben industry for the synthesis of raw material which can be used to develop polyurethane products and poly isocyanate were developed which were given name of desmodur and polyols were named desmophen. These were their trademarked name. In the mean while coating, elastomer, adhesive and rigid foams were synthesized. Other companies from different countries like from U.S.A, the DuPont and from United Kingdom, ICI also started to work on urethane linkage and these companies started to produce raw material for polyurethane on industrial scale. After the development of toluene diisocyanate (TDI), the polyurethane industry grew rapidly. By the use of toluene diisocyanate and polyester polyols, there was synthesis of comfortable foams which came into market in 1957. After 3 years, it was noticed that MDI can synthesize elastomer and rigid foams. The foams produced by polyester were more expensive and less stable as compared to polyether polyols [10].

Polyurethane elastomer were developed by reacting naphthalene diisocyanate (NDI) with polyester followed by the addition of chain extender like diamine, diol and alkanolamine having short chains [11]. The DuPont company used polyether polyols to develop milable gum first time and the company sold it by name Adipirine. MDI was developed by ICI in 1960 .

In early 1950s, thermoplastic polyurethanes were synthesized first time. Schollenbergerin in 1958 developed a polymer by the reaction of MDI with polyester polyols and added a chain extender 1, 4-butanediol for the formation of polymer belonging to urethane family. He named the product as trademark name Estane. In these polymers, there was presence of hydrogen bonding which causes cross linking giving them strength and have resistance to reaction. There was also phase separation in these polymers between soft and hard segment. These are in use from films, automotive product to sports equipment application [10].

1.3.2 Types of Polyurethane

Polyurethane has following types

a) Films

There are three methods to synthesize films from polyurethane

1. Two part spray method

This method is used to synthesize coating and paint which are chemically resistant. In this case solvent is sprayed with polyurethane.

2. Single component system

This method is used to synthesize water proof barrier and solid polymer. It happens by the chemical reaction of polymer with moisture in air.

3. Latex

Film is made by the curing of polyurethane followed by the elimination of solvent. This method is adopted to make thin wall films.

b) Fibers

To replace the synthetic fibers, polyurethane fibers were developed. Professor Otto Bayer was forefather of the polymeric fiber to replace natural fiber like nylon. This invention makes breakthrough in polymer field. Spandex and perlon are the common polyurethane fibers [12].

c) Thermoplastics

Thermoplastics are synthesized for handling plastic standard machinery like extruders. These polyurethanes have valuable application in medical field and are used in rubber tubing, prosthesis and sutures. Some applications of thermoplastics are grips, shoe soles, tubing , automobile parts and heels etc.[13].

d) Castables

Castables are in commercial use since 1952. In 1956, after the addition of polyether in polyurethane system by DuPont, this field grew rapidly and there was introduction of different polyisocyanate to optimize the final product properties. Castables are used in many fields ranging from armamentarium to domestic roller [14].

e) Foams

After the introduction of polyether polyols in polyurethane system, foams become popular. These were used in aircraft in world war. Studies have been done to synthesize polyurethane foams. There is cell arrangement having three dimensional systems in foams. End use will decide the openness or closeness of the cell. Polyurethane foams are synthesized by different methods which are described here.

1. For acoustic and thermal insulation, rigid foams are used. These are handled by machine or by hand and are sprayed.

2. Flexible polyurethane includes carpet padding, and cushions. The foam of this type has low density and is mostly treated in large quantity.

3. External non foamed sheets are contained in integral skin foams. Dashboard of motor car is an example of this type foam [12].

f) Millable

These are synthesized by the use of rubber processing machinery. Curing agents are added in this process of synthesis. There are some other chemicals in the Millable having sulfur as curing agent [9].

1.4 Polyurethane Elastomer

1.4.1 Elastomers

Elastomer belongs to polymer material. One of the unique property of elastomer is that these material can bear stress up to a limit and can come back to their original form [14]. Elastomer have their role in developing polymer history even though elastomer has less use then other polymer family member. Elastomer exhibit mechanical properties, have mobility, are flexible and elastic. These elastomers are used in gaskets, in the tires of vehicles, in heart valves and their use as a binder for fuel in space automobile have enriched their importance [15]. As the elastomer can be easily modified by varying monomers, polyurethane elastomer are distinctive type of condensation polymer replacing the metal, cotton, paint, wood and rubber etc.

Now a days, elastomers are being used in aerospace, foams, surface coating varnishes [16]. These are used by injecting, recycling, molding and extruding [17].

1.4.2 Polyurethane Elastomers

Elastomers are important group of urethane family [18]. Polyurethane elastomer have excellent mechanical properties, have chemical resistance and are significant hard. These belong to block polymeric family having hard and soft segment. Macrodiol like polyether, polyester and polybutadiene forms the soft segment and have molecular weight in the range of 200 to 8000 g/mol [6].

Aliphatic or aromatic polyisocyanate form the hard segment of the elastomer. Diol or diamines having less molecular weight are added as chain extender in the synthesis of elastomer. The hard and soft parts are aligned in a fashion to form $(AB)_n$ style block copolymer [19]. The physical properties of elastomer can be altered by changing monomer molecular weight, the structure of monomer and ratio between monomer. Polyurethane elastomers have two phases which are termed as microdomains. Semi crystalline domain consists of hard segment and amorphous latex consists of soft segment having dispersion of hard segment. Hard domain behaves as cross linker providing strength to polymer and soft domain provides elastic properties to elastomer. Microdomain separation will decide the properties (both mechanical and physical) of elastomer. Monomer chemical structure, reaction condition, reaction methodology and hydrogen bonding in urethane linkage will address the phase separation [20, 21]. SEM, DMA, DSC and XRD characterization techniques are used to study the phase separation behavior [22, 23].

1.5 Components of Polyurethane

Carbamate functional group is present as repeating unit in polyurethane polymer. The term polyurethane has been derived from ethyl carbamate which is known as urethane. Chemical reaction of polyols and poly isocyanate give synthesis of polyurethane linkage.

$$\text{R-NCO} + \text{R-OH} \rightarrow \text{R-HNCOO}$$

By selecting the required polyisocyanate and polyols, one can easily adjust the properties of final product because the degree of branching and cross linking is controlled in this way. There may be two or more polyols or polyisocyanate can be used simultaneously. Different type of polyols can be used e.g. polyether, polyester and polybutadiene. Isocyanates can be aliphatic, aromatic or cycloaliphatic which can be used such as or after some chemical modification.

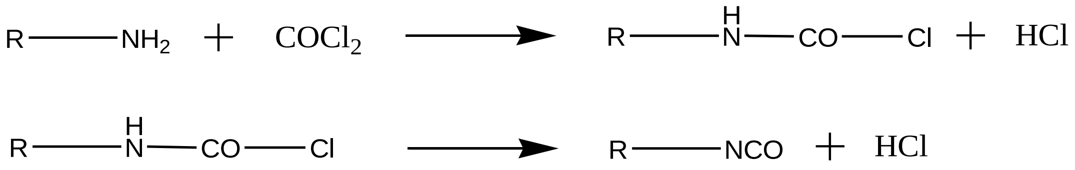
1.5.1 Isocyanates

The isocyanates which are either aliphatic or aromatic are distinctive part of polyurethane elastomer. Aliphatic isocyanates are less reactive then aromatic isocyanate. The aliphatic isocyanates are more stable in light as compared to aromatic isocyanates. Therefore the aliphatic isocyanates are being used to synthesize polyurethane coating. The final product properties depend upon the specific properties of the isocyanates. The steric hinderance, substitution, stereochemistry and structure of isocyanate affect the chemical reactivity e.g. in 2,4-toluene diisocyanate the NCO group present in ortho position in 25 time less reactive then NCO group which is present at para position [6, 14, 24]. After the initial reaction, second NCO group reactivity may be altered.

Mostly TDI and MDI are commonly used aromatic isocyanate in polyurethane field. When diamine is phosgenated there is production of isocyanate. There are many other ways to synthesize isocyanate [14, 25, 26]. On the other hand the most commonly used aliphatic isocyanates are isophorone diisocyanate IPDI and hexamethylene diisocyanate HDI.H_{12}-MDI,NDI ,TMXDI,CDI,TMDI and TODI are also in use [14, 27].

Urethane structure is formed when NCO group reacts with active hydrogen present in a molecule. There is requirement of bi or polyfunctional isocyanate for the formation of urethane linkage. There is more usage of aromatic isocyanate now a days as compared to aliphatic isocyanates. The reason behind this is that reactivity of aromatic isocyanate is more as compared to aliphatic one and these are more economical.

A German scientist A.Wurtz was the inventor of isocyanate who synthesized first time an isocyanate in 1848 [28]. When calcium cyanate was treated with sulphuric acid ester by alkylation reaction, isocyanate was produced. Hentschel in 1884 synthesized the isocyanate from amine by its phosgination [29]. In this way many types of aromatic and aliphatic isocyanate can be synthesized from respective amine. The nitro compound undergo hydrogenation reaction to produce amine.

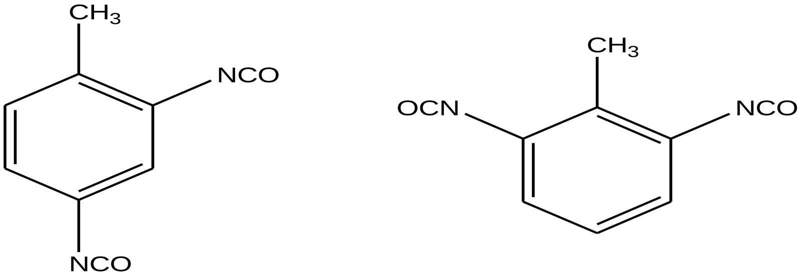


$$R{-}NH_2 + COCl_2 \longrightarrow R{-}NH{-}CO{-}Cl + HCl$$

$$R{-}NH{-}CO{-}Cl \longrightarrow R{-}NCO + HCl$$

Figure 1.3: Synthesis of Isocyanate

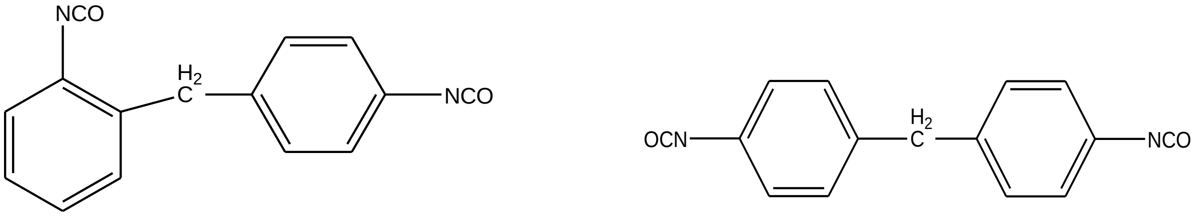
Toluene diisocyanate can be synthesized directly when toluene undergoes nitration. The TDI formed in this way have 80 percent of 2,4 and 20 percent of 2,6-dinitro products which on further hydrogenation can give di amino toluene. TDI obtained by this route have two isomeric form, 2-4 and 2,6 which are 80 and 20 percent, respectively.



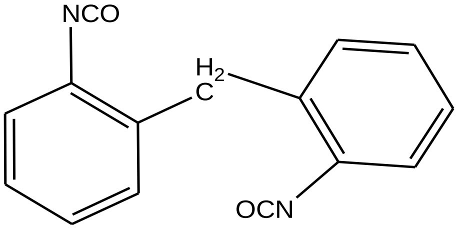
2, 4-Toluene diisocyanate 2, 6-Toluene diisocyanate

Figure 1.4: Structure of Isomers of Toluene Diisocyanate

As the isomers of TDI are highly reactive and are reasonable volatile, TDI effect on skin, respiratory system and on eyes so it is considered to be toxic while diphenyl methane diisocyanate MDI is consider being less toxic because its volatility is low and safer for use. Anyhow its purification is difficult and mostly MDI is used un-distilled.



4, 4' MDI Isomer 2, 4' MDI Isomer

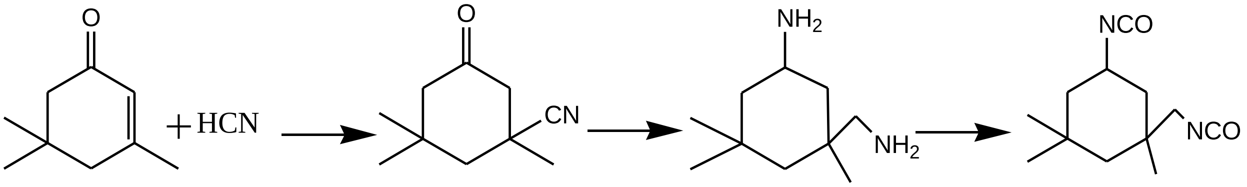


2, 2 MDI

Figure 1.5: Structure of isomers of MDI

When there are external stimuli to the products and the products are bare to radiation, aromatic isocyanates are not appropriate to use because they impart yellow color so aliphatic isocyanate or cycloaliphatic isocyanate are used in this situation when there is requirement of color preservation. IPDI is most commonly used cycloaliphatic isocyanate.

IPDI can be synthesized by following steps [27].



I II III IV

Figure 1.6: Stepwise Synthesis of IPDI

Position of NCO group in molecule will define its reactivity. Aliphatic isocyanate are less reactive then aromatic isocyanate. NCO group attached to toluene are less reactive in comparison to those which are attached to naphthalene and diphenyl methane. In general, the isocyanate group in TDI at 2-position is less reactive due to steric hindrance as compared to 4-position which faces less interferences. In symmetric isocyanate, when 1st isocyanate group reacts, the reactivity of second group decreases. The reactivity of ortho NCO group decreases due to steric hindrance.

Table 1.1: Physical Properties of Isocyanate Compounds

S.No	Common Name	Molecular Weight	MP °C	BP °C	Toxicity
1	Toluene 2-4,diisocyanate	174.2	21.8	121	Toxic
2	Toluene 2,6-diisocyanate	174.2	18.2	120	Toxic
3	TDI 63/35	174.2	5	121	Toxic
4	TDI 80/20	174.2	13.6	121	Toxic
5	4,4 diphenyl methane diisocyanate MDI	250.3	39.5	208	Harmful to health
6	2.4 diphenyl methane diisocyanate MDI	250.3	34.5	154	Harmful to health
7	2,2-diphenyl methane diisocyanate MDI	250.3	46.5	145	Harmful to health
8	Hexamethylene diisocyanate HDI.	168.2	-67	127	Toxic
9	Isophorone diisocyanate	222.3	-60	158	Toxic
10	Dicyclo-hexylmethane 4,4-diisocyanate HMDI	262.3	19-23	179	Toxic
11	Naphthalene 1,5 diisocyanate NDI	210.2	127	183	Harmful to health
12	p-phenylene Diisocyanate PPDI	160.1	96	111	Toxic

1.5.2 Polyols

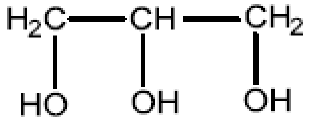
Second major component for polyurethane synthesis is a compound having active hydrogen. The hydrogen may be attached to sulfur, nitrogen or oxygen. Mostly polyols or polyfunctional alcohols are used for manufacturing polyurethane compounds. There is wide range of functionality, reactivity, molecular weight and chain length in polyols.

In polyurethane industry, polyester polyols and polyether polyols are commonly used. Along with these, polybutadiene is used for specific application having more performance. Soft polyurethane elastomeric foams are formed by polyols having functionality in the range of 1.8 to 3 and molecular weight ranging 1600-6000. Rigid foams are formed by polyols having functionality in the range of 3 to 12 having molecular weight 250 to 1000. Additional properties can be incorporated in end product by adding short chain polyols during reaction [30].

A) Polyether

In 1954, first polyether polyol was used for the synthesis of polyurethane. Mostly, ethylene and propylene oxide derivative results in polyether polyols. Polyether polyols are formed by the addition polymerization of propylene or ethylene epoxides. Oxidation of propylene or ethylene results in the formation of their oxide. Initiator functionality will decide the functionality of polyols. Mostly propylene glycol, dipropylene glycol, ethylene glycol and diethylene glycol are used as initiator for difunctional polyether synthesis. Most common initiator used for trifunctional polyether is glycerol. Some common used initiators are given in table [31].

Table 1.2: Common Initiators and their Structures

Initiator	Structure	Functionality
Water	HOH	2
Ethylene glycol	$HO—CH_2—CH_2—OH$	2
1,2-propylene glycol	$HO—CH_2—CH(CH_3)—OH$	2
Glycerin	 $H_2C(OH)—CH(OH)—CH_2(OH)$	3
Triethanol amine	$N—(—CH_2—CH_2—OH)_3$	3
Ethylene diamine	$H_2N—CH_2—CH_2—NH_2$	4
Diethylene triamine	$H_2N—CH_2—CH_2—NH—CH_2—CH_2—NH_2$	5

B) Polyester

These were in the early stage of polyurethane development. No doubt, 80% of the polyurethane industry has been shifted to polyether polyols, polyester are still use because these provide better properties to polyurethane. The superior characteristics originated in polyester based polyurethane are results of better crystalline arrangement of segments [32, 33].

Condensation reaction of di acid results in the formation of polyester polyols. Phthalic acid and adipic acid are commonly used di acid for the manufacturing of polyester polyols. Difunctional reactant gives linear polyester polyols while monomer having functionality above two gives branched polyester like glycerol.

Polyurethane derived from polyester exhibit more resistant to solvents, oils, oxidation and grease. These polyurethanes have good properties like tear strength, flex fatigue, tension, adhesion and dimensional stability.

C) Castor oil

Castor oil has molecular weight in the range of 930 to 1000 and has functionality 2.7. It is naturally existing source for secondary OH group. Plant having botanical name Ricinus Communis gives seeds which contain castor oil.

Castor oil has pale yellow color. Cold pressing or solvent extraction is employed to extract castor oil, however higher iodine value and high acid number is obtained by castor oil extracted by solvent extraction [34].

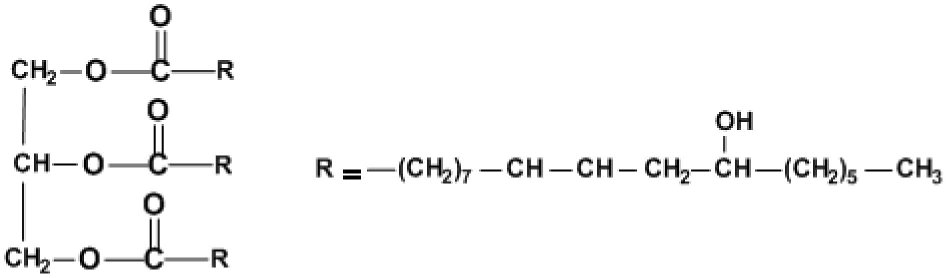


Figure 1.7: Structure of Castor Oil

Table 1. 3: Average Percentage of Acids in Castor oil

Acid name	Percentage
Ricinoleic acid	85-95%
Linoleic acid	1-5%
Oleic acid	2-6%
Linolenic acid	0.5-1%
Palmitic acid	0.5-1%
Stearic acid	0.5-1%

Castor oil serves as raw material for the synthesis of many useful polyurethane products. Low and high functionality compound are obtained by the esterification of castor oil resulting the formation of polyhydroxy compound. Polyurethane coating can be synthesized by derivatives of castor oil which are obtained by oxidation of castor oil.

1.6 Hydroxy Terminated Polybutadiene HTPB

Hydroxyl terminated polybutadiene belongs to telechelic polymeric family with hydrocarbon properties containing carbon carbon double bond. Telechelic polymers are polymeric family polymers which are reactive polymers containing reactive end groups. These reactive group may be same e.g. both OH as in case of HTPB or they may be different. These polymers are pronounced according to number of reactive functional group like mono, di and tri terms are used for one, two and three reactive functional group, respectively.

HTPB polymers have two types which are in use

1. Free radical HTPB

2. Anionic HTPB

Mostly, the HTPB formed by free radical mechanism are used in propellants for fuel binding which binds the energetic particles.

There are two methods for the synthesis of HTPB polymer.

1. Free radical polymerization method
2. Anionic polymerization method

The properties of the polymer and its structure will depend upon the method of synthesis of polymer. Both method give different architecture to the polymer and have unique chemical properties and morphology.

Hydroxyl terminated poly-butadiene was first synthesized in 1960's. These polymer were initially formulated so that they can be used in rocket propellants to hold energetic material together. It was in 1972 ,when a rocket motor having HTPB binder was launched [35].

There are polyurethane elastomer which were made from polyester and polyether containing OH group, used for fuel binder but elastomers which are made from HTPB polyurethane linkage have chemical resistance specially for acid and base even though for strong acid and base. These polyurethane elastomer have more hydrolytic stability as compared to polyether or polyester counterpart. Owing to these properties, HTPB can be used to condense the higher amount of energetic particles in fuel for propellant. These elastomers can also be used to insulate electric goods [36].

But these elastomers have mechanical properties lower than the polyester and polyether polyurethane, mostly the tensile strength and elongation at break is inferior in case of HTPB elastomer. Reason behind the lower mechanical properties is that in case of HTPB based polyurethane, there is absence of hydrogen bonding. In polyurethane polyester and polyether, there is formulation of hydrogen bonding which is intersegment giving the strength to the elastomer [37, 38].

There is mixed phase because of the hydrogen bonding which is within hard and soft segment that results in higher tensile strength and elongation at break. In case of HTPB polyurethane, the hard portion spreads through the soft portion which lowers the mechanical properties. It is concluded that phase separation gives mechanical properties to the polyurethane material [39-41].

1.7 Synthesis

HTPB can be synthesized by free radical or anionic polymerization.

1.7.1 Free radical polymerization

Free radical polymerization is instigated with the help of H_2O_2 having isopropanol, methanol or tricresyl phosphate. The HTPB formed by this way have average molecular weight of 2800-2900 and it contain hydroxyl group at both ends. There is range of functionality between 2.2 to 2.6 OH groups/mol in this method.

In this method butadiene is treated with hydrogen per oxide or azo which serve as free radical initiator and solvent. The reaction is carried out at some particular temperature and pressure. The polymer is collected by the mixing of alcohol like methanol and then it is washed and finally vacuum dried to improve the shelf life of the polymer. There is addition of antioxidant like butylatehydroxyl toluene.

In free radical polymerization, the major step involved is 1, 4-addition having cis or trans 1-4, isomeric structure while there may be addition of 1, 2-form which may result in the formation of vinyl form. The HTPB formed in this way have more percentage of trans form 50-60 percent then cis form which is present 15-25 percent and 15-25 percent of vinyl form.

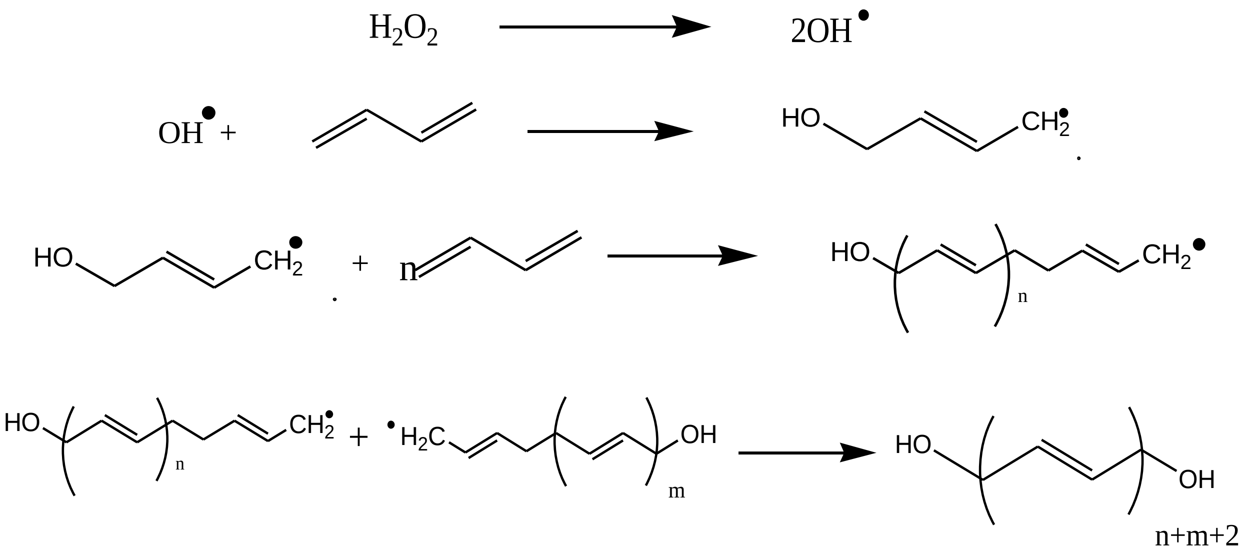


Figure 1.8: Free Radical Polymerization

The reaction is carried out at 120 °C temperature having pressure of 20 bars. There is formation of branched structure if the reaction is carried out at high temperature. There may be synthesis of carbonyl and ether linkage in the fractions having low molecular weight. As a result, HTPB contain nonfunctional low MW polymer and two or more hydroxyl group containing high MW polymer.

The amount of micro structure and molecular weight depend upon following in case of radical polymerization.

A. type of initiator

B. solvent

C. Temperature.

The functionality and polydispersity of resulting polymer is also controlled by the above condition.

Two type of initiator are mostly used.

1. Peroxide initiator e.g. hydrogen peroxide.

2. Azo initiator e.g. azo bis cyanopentanol.

However, the polymer formed by azo initiator has low yield therefore hydrogen peroxide is mostly used in free radical polymerization of HTPB polymer synthesis and its concentration is within range of 48-56 percent. The optimum temperature for this reaction is 100 to 130°C and pressure rang for the reaction is 100-1000 psi.

When temperature is kept 105 °C and initiator concentration is 7 percent, there is formation of polymer having functionality two. The same functionality can be obtained by adjusting temperature of the reaction at 115°C and initiator concentration 5 percent. 65 percent conversion is obtained in 3 hrs. When the temperature of the reaction is increased, there is increase in the OH value along with the increase in viscosity and functionality. In the same way when the amount of hydrogen peroxide is increased, the functionality of the produced polymer is also increased.

Solvents that are commonly used for HTPB synthesis are methanol, 1-butanol, ethanol, 2-butanol, isopropanol and a mixture of solvent can also be used. HTPB having two functional group is synthesized when isopropanol is used as solvent.

The following inferences can be drawn from literature survey.

1. The structure of HTPB which is produced from free radical polymerization is given below.

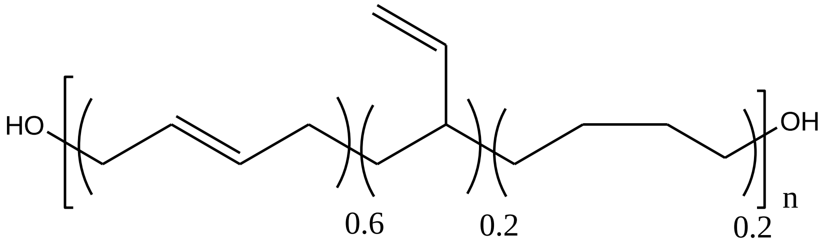


Figure 1.9: Structure of HTPB

2. The HTPB polymer has different molecular weight and it contain non-mono, di etc. polymer and the resulting polymer have functionality and molecular weight distribution.

3. Depending on the synthesis route and condition, HTPB polymer may contain different percentage of cis, trans and vinyl content and functionality.

4. The polymer can have entities of ether and epoxide in polymeric network which is made at higher temperature.

17.1.2 Anionic polymerization

The reaction is instigated with sodium naphthalene which reacts with butadiene form an anion. A dianion is produced when two anion couple together which acts as difunctional initiator. Chain terminate when ethylene oxide or propylene reacts with polybutadiene anion ended by hydrolysis. The polymer formed by this way has average functionality of 2.0 OH group/mol.

This is a living polymerization method. The steps involved in this method are following.

1. Reaction of 1, 3-butadiene with organo-dilithium initiator in the presence of non-polar solvent having temperature range of -80 to -22°C.

2. The mixture of polybutadiene is cooled to -55 °C.

3. There is addition of alkyloxide e.g. addition of ethylene oxide, propylene to produce hydroxyl group at the end of chain.

4. At the end there is hydrolysis of the polymer chain with methanol to produce HTPB polymer.

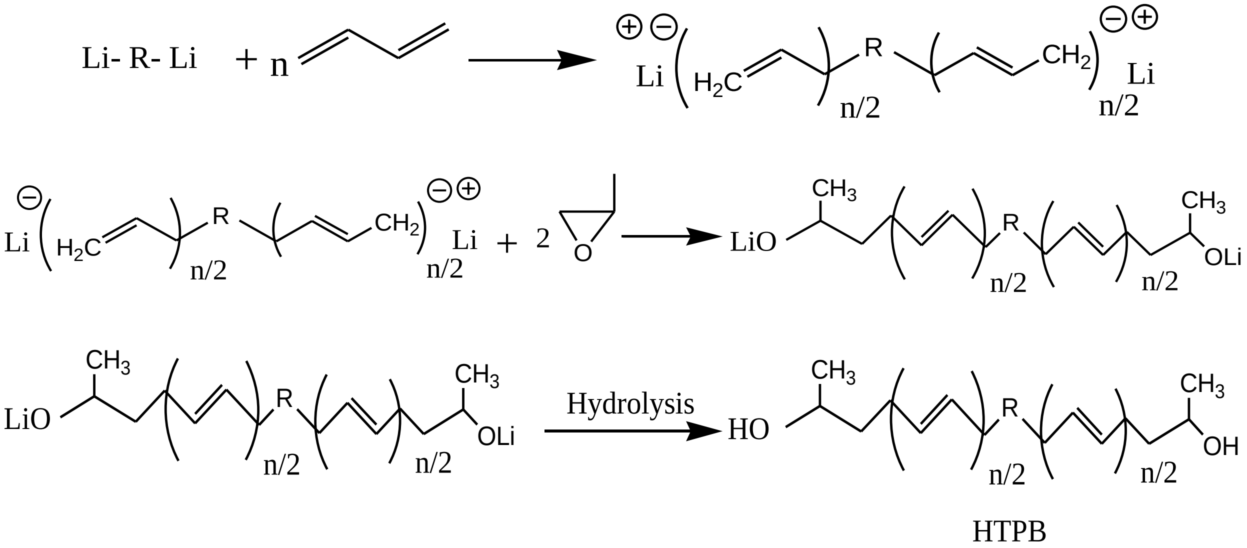


Figure 1.10: Anionic Polymerization

The HTPB formed by anionic polymerization is linear and have definite microstructure.it have 60-80 percent of vinyl content and 20-40 percent of cis and trans content. The functionality distribution is lower in this case and has low molecular weight. The polyurethane formed by anionic HTPB has good mechanical properties. Anionic HTPB is mostly used when excellent mechanical properties are required in elastomer.

The important results can be concluded from literature as below.

1. The structure of HTPB formed by AN-polymerization is.

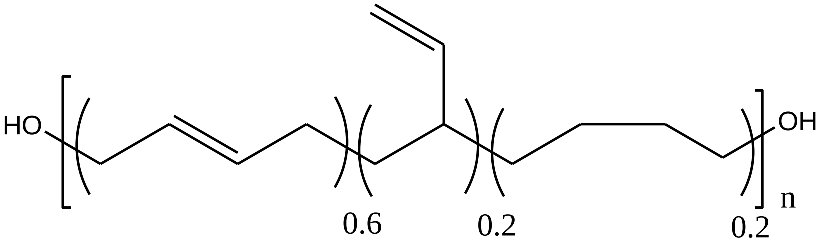


Figure 1.11: General Structure of HTPB

2. There is use of di alkyl initiator.

3. The polymer formed by this way has lower functionality.

4. The polymer formed has high percentage of vinyl followed by trans and cis isomer

Table 1.1: Comparison between Anionic and free Radical Polymerization

Anionic HTPB	Free Radical HTPB
It has more percentage of vinyl content 60-70 percent as compared to trans or cis content.	It have more percentage of trans content then cis and vinyl content
Hydroxyl group can be primary or secondary	The hydroxyl group in this form are mostly primary
Functionality is mostly two	Functionality vary from 2.2 to 2.6
It has narrow band molecular weight distribution	It has broader band molecular weight distribution
Polymer have high glass transition temperature	Polymer have low glass transition temperature
It has low viscosity	It has high viscosity
Polyurethane formed by this polymer lose elasticity at -30 to -40 °C	Polyurethane formed by this polymer lose elasticity at -70 to -80°C
Cost of synthesis is high	Cost of synthesis is low
High dimensional stability and cross link density due to low functionality	Low dimensional stability and cross link density due to high functionality

1.8 Chain Extender and Crosslinker

Cross linker and chain extender are monomers of low molecular weight amine or hydroxyl terminating compound. Any polyfunctional compound can be treated as cross linker and bifunctional compound as chain extender. These chain extender and cross linker contain active hydrogen. There are two types of chain extender for polyurethane

1. Aliphatic or aromatic diamines.

2. Aliphatic or aromatic diols.

A softer material is formed when aliphatic diamine or diol is introduced into polyurethane chain as compared to aromatic diamine or diol because these are added in hard domain which control hydrolytic, mechanical and thermal stability of product [6, 14].

Some common chain extenders are given below.

a. Ethylene diamine.
b. 1, 4-butandiol.
c. 1, 6-hexandiol.

1.9 Catalyst

A catalyst is a compound that can alter the rate of a chemical reaction and can be recovered from the reaction. This process is termed as catalysis. During the synthesis of polyurethane, organometallic salt of Hg, Pb and Sn, carboxylic acid salt and tertiary amines are used as catalyst. Their detail is given below:

A) Organometallic salt of Hg, Pb and Sn can serve as catalyst for polyurethane synthesis. Elastomers are formed in the presence of Pb and Hg salts. As the salts of Pb and Hg have negative effect on health so there is demand for their alternatives organometallic salt catalyst used most widely for polyurethane synthesis is Sn.

B) Carboxylic acid salt of sodium and potassium are used mostly for isocyanurate [6,14].

C) Amines can serve as catalyst for the reaction of NCO with OH group. Tertiary amines are mostly in use because of more reactivity with water. Polyurethane foams synthesis require blowing agent and amine can serve as blowing agent in these reactions.

1.10 Characterization Methods

1.10.1 FT-IR Spectroscopy

Fourier transform infrared spectroscopy is a technique which is used to determine chain orientation, chemical structure and composition of inorganic, organic and polymeric compound [42]. For processing data and its storage, conventional infrared has been modified to Fourier transform IR using computer technology. It has high wavenumber precision, is time saving and have signal to noice ratio better than the conventional IR. IR spectra of all matter states(gases, liquid and solid) can be measured by Fourier transform IR spectrometer. FTIR provide valuable information about polymeric structure. It gives information about functional group present in polymer (carbonyl, hydroxyl, amines and urethanes etc.) and chain structure (cis, trans or vinyl in HTPB) polyurethane elastomer films. FTIR spectra were acquired by using a FTIR spectrometer IR-SHIMADZU Japan. It covers the IR region from 4000-500 cm-^{1} [43, 44].

1.10.2 Differential Scanning Calorimetry (DSC)

In differential scanning calorimetry, thermal changes are analyzed in a polymer sample which are either heated up or cooled down. Transition in crystalline phases, transition temperature and melting temperature can be calculated by DSC. In this analysis, two pans are used which are coupled to furnace. On one pan, sample is placed while the other pan contains reference (standard). Both pans are being heated at specific heating rate for a fix time. Temperature verses heat flow difference between reference and sample is plotted. Heat flow has unit of heat which is supplied in unit time. Plot will be parallel to X-axis in the absence of phase transition [45].

Polymers have glass transition temperature Tg. It is the temperature above which polymer will be elastomeric in nature and becomes soft. Below this temperature, polymer will act similar to hard glass. Transition temperature depends upon degree of branching, side chain length, main chain configuration and degree of crystallinity. Crystallization temperature Tc is highest point, on further heating crystalline phase will melt the polymer at melting temperature Tm. During melting heat is absorbed so in DSC scan endothermic peak will be appeared. Polymer degree of crystallinity can be measured by DSC [45, 46].

1.10.3 Mechanical Testing (UTM)

The response of polyurethane material to stress is measured by mechanical testing ASTM 2004. Tensile test is carried out using universal testing machine (UTM) for determining mechanical properties. In this technique, stress is applies and change in length of elastomer is noted till it breaks. Stress is plotted against strain to obtain stress strain curve. This curve gives information about tensile properties. Young modulus is ratio of stress to strain in the region of elastic limit. It gives information about elongation at break of elastomer [47, 48].

1.10.4 Dynamic Mechanical Analysis (DMA)

This instrument is used to measure relaxation behavior of viscoelastic material by applying external load. The deviation of modulus as function of frequency and temperature is measured. The store and dissipated energy by viscoelastic materials is measured by DMA. An oscillating displacement or force having fixed frequency is subjected to sample and resultant force or displacement is measured. The sample should be displaced within elastic limit of polymeric material. The sample properties are investigated as a function of time and temperature. Which is termed as dynamic thermo mechanical analysis DTMA. Many information like damping factor, loss and storage modulus, dynamic viscosity, loss and storage compliances, transition temperature, creep and stress relaxation can be measured by DTMA [46, 49].

1.11 Motivation

Strategic organizations use HTPB as binder for specific applications. Scientists are working on tuning of HTPB based elastomers for required mechanical properties.

There is no work reported on the mechanical properties of HTPB based elastomer by varying OH number so, I studied the mechanical properties of HTPB having different OH number to find the best composition for required purpose.

1.12 Objectives

My research work is focused on achieving following objectives.

Objective 1

- Determination of OH number in different samples of HTPB
- Determination of NCO percentage in TDI.

Objective 2

- NCO/OH ratio adjustment
- Synthesis of elastomers having different OH number and Rt ratio with calcium carbonate filler.

Objective 3

- Characterization of prepared elastomers
- Identification the elastomer having optimum mechanical proper

Chapter 2

Literature Review

2.1 Chemical Modification of HTPB Polymer

HTPB derivative is synthesized by hydrogenation reaction which gives more resistance to polymer for its oxidation because the double bond is removed in this way resulting the saturation of polymer. Thermoplastic polyurethane elastomers are formed by the bifunctional HTPB and HTPB which is treated with hydrogen. These give good chemical resistance and hydrolytic stability [36].

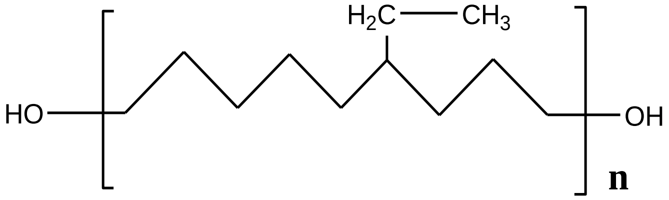


Figure 2.1: Structure of HTPB Polymer

HTPB polymer can adopt multi-functionality. Many types of reaction can happen at hydroxyl group which are present in HTPB polymer chain. HTPB formed by free radical polymerization have primary hydroxyl group which easily undergoes curing reaction when a curing agent like toluene diisocyanate is added to them for the formation of polyurethane elastomer. Double bond which exists in polymer can be browbeaten. More stable compound can be synthesized when HTPB undergo halogenation or hydrogenation reaction. There is more reactivity of double bond in vinyl content then cis or trans form. Unsaturation in polymer can easily react with anhydride, oxygen, halogen, vulcanizing agent, peroxide and dicarboxylic acids.

In the last few eras, there is change in properties both in physical and chemical of the HTPB polymer by its chemical modification by different way with reacting with different reactants enhancing its properties.

The acetylation, hydrogenation and esterification of polymer produce product of valuable application. The hydrogenation of HTPB forms lubricant oil, plasticizer and additives

2.2 Important Characteristics of Raw Material.

2.2.1 Hydroxyl Number

Polyols are distinguished by their OH number.it in number of hydroxyl group that can undergo in reaction with polyisocyanate. Hydroxyl number is determined using acetic anhydride by ASTM E 223-10 method . Another method use Phthalic anhydride to determine OH number and is described in ASTM D4272. Hydroxyl number is determined by reacting acetic anhydride with terminal OH groups followed by the addition of water to convert unreacted acetic anhydride into acetic acid which is titrated against NaOH. Formula to calculate OH number is given below.

$$\text{OH number} = \frac{(A-B) \times Nt \times 56.1}{W}$$

Where

A= volume of NaOH in ml used for the titration of blank.

B = volume of NaOH used for the titration of HTPB sample.

Nt = normality of the NaOH solution which was 0.5 meq/ml in the procure adopted.

W = amount of HTPB sample in grams.

The reaction of p-toluene sulfonyl isocyanate with terminal OH group is described in ASTM E-1899 to calculate OH number and this method reduces the interference of acidic groups [50].

2.2.2 Isocyanate

% NCO content is determined by ASTM D1638-74 and ISO 14896 ;2006 (E) method. ASTM D 1638-74 describes the reaction of isocyanate with di butylamine solution. Excess amount of dibutylamine solution is titrated against HCl. % NCO is calculated from the expression below[51].

$$\% \text{ NCO} = \frac{4.202 \times (V1 - V2) \times C}{mo}$$

Where

V_1 = volume of HCl in ml used for the titration of blank solution.

V_2 = volume of HCl in ml used for the titration of toluene diisocyanate sample

C= concentration of HCl.

M_o = mass of TDI taken.

4.202=equivalent mass of NCO which is 42.02 mg/milliequivalent, converting g to mg.

2.2.3 Number Average Molecular Weight(Mn)

Chain length can be different in polyols. Number average molecular weight. Mn is defined as the mean of individual macromolecule molecular weight which is calculated by adding the moles of polymer molecules multiplied by their molecular weight and dividing by total mole number. Number average molecular weight can be determined by vapor pressure osmometry, dynamic light scattering and gel permeation chromatography. This term have inverse relation with active group number which is hydroxyl group in our case.

Mathematically it is calculated by this formula;

$$\text{Mn} = \frac{\Sigma iniMi}{\Sigma ini}$$

Where *ni* is number of moles of species *i* and *Mi* is corresponding molecular weight.

2.2.4 Weight Average Molecular Weight(Mw)

Mw is calculated by adding weights of polymeric species followed by multiplication of their molecular weight and dividing by total polymeric weight. X-ray scattering, small angle scattering, light scattering and sedimentation velocity are used to calculate weight average molecular weight. When compounds are pure, Mw and Mn will be equivalent.

$$\mathrm{Mw}= \frac{\Sigma iWiMi}{\Sigma Wi}$$

As Wi= niMi

$$\mathrm{Mw}= \frac{\Sigma ini(Mi)2}{\Sigma iniMi}$$

2.2.5 Polydispersity Index

Molecular weight distribution or polydispersity index (PDI) is extent of distribution of mass in a polymer [52]. It is ratio between weight and number average molecular weight. its value is above two. When polymers have uniform chain length, polymers have PDI value unity. Some natural polymers have PDI value unity. It changes by changing polymerization mechanism.

PDI have different values in different type of polymerization e.g. its value is 2.5 to 2.8 in case of poly condensation polymerization, 10 to 20 for step polymerization, 1.05 to 1.3 for cationic or anionic polymerization. Its value should remain in narrow range for desired properties in end product. In case of polyurethane elastomer, good mechanical properties are obtained by narrow PDI range.

2.2.6 Functionality

Functionality is another important characteristic of polyols. It represents the number of hydroxyl groups/molecule of polyols. The usual method of determination of functionality is based on the estimation of the molecular weight of the polyols measured by using vapor pressure osmometry (VPO) or gel permeation chromatography (GPC) along with the determination of the hydroxyl number.

It gives information about hydroxyl group number in polyols. The method to determine functionality is to calculate molecular weight by GPC or VPO with the calculation of OH number.

$$\mathrm{Mn} = \frac{(f \times 56100)}{OH\ number}$$

And

$$f = \frac{Mn \times OH\ number}{56100}$$

2.2.7 Equivalent Weight

To calculate isocyanate amount required for polyurethane reaction, equivalent weight of polyols is useful measurement. There is reaction between one isocyanate equivalent weight with one polyols equivalent weight and is calculated by following relation.

$$\mathrm{EW} = \frac{M}{f}$$

$$\mathrm{EW} = \frac{f \times 56100}{OH\ number \times f}$$

$$\mathrm{EW} = \frac{56100)}{OH\ number}$$

2.3 Synthesis of Polyurethane

A urethane linkage is formed by the reaction of alcohol with isocyanate. For this reaction, the alcohol should contain two or more OH group and isocyanate should have two or more NCO group. Following are the basic materials required for polyurethane synthesis

1. Diols.
2. Diisocyanate.
3. Chain extender.

Polyurethane can be synthesize by one step or two step process depending upon reactant addition [36, 53].

2.3.1 One Step Process

In one step polymerization, stoichiometrically diisocyanate, polyols and chain extender are added simultaneously. Type of solvent will depend upon methodology of polymerization either solution or bulk is adopted. Mostly in solution polymerization, solvent is used. Commonly used solvents are dimethyl formamide DMF, dimethyl sulfoxide DMSO and dimethylacetamide DMAc. For polyurethane elastomer, reaction is carried out at 80-100 C. When aliphatic isocyanate are used then catalyst may also be recommended [4,6,35].

2.3.2 Two Step Process

Mostly two-step process is used for polyurethane synthesis. This process is also named as prepolymer process. In the first step, there is formation of prepolymer by the reaction of diisocyanate with polyols. This prepolymer is NCO terminated oligomer. In second reaction, there is addition of chain extender in prepolymer to form polyurethane. This step is named as chain extension step [53].

Soft segment mainly effect tear strength, hardness and elasticity. Hard segment influences upper limit of temperature use therefore there is more systematic arrangement in polyurethane elastomer formed by two step process then one step method. Better mechanical properties are obtained by two step process due to structural regularity [54]

2.4 Chemistry of Polyurethane Elastomer

Isocyanate group reactivity will determine the chemistry of polyurethane elastomer. The double bond present between nitrogen, carbon and oxygen give high electrophilicity to carbon atom which make isocyanate group highly reactive to nucleophile reagent. There is resonance in aromatic system which further causes increase in reactivity. Negative charge delocalized on nitrogen atom or oxygen atom or it may move to R group having R group is aromatic.

Due to absence of delocalization, aliphatic isocyanates are less reactive then aromatic one. There may be other groups present on aromatic ring which can affect the electrophilicity of NCO group.

There is increase in reactivity of NCO group if electron withdrawing group are present at ortho or para position and reactivity is decreased in the presence of electron donating group.

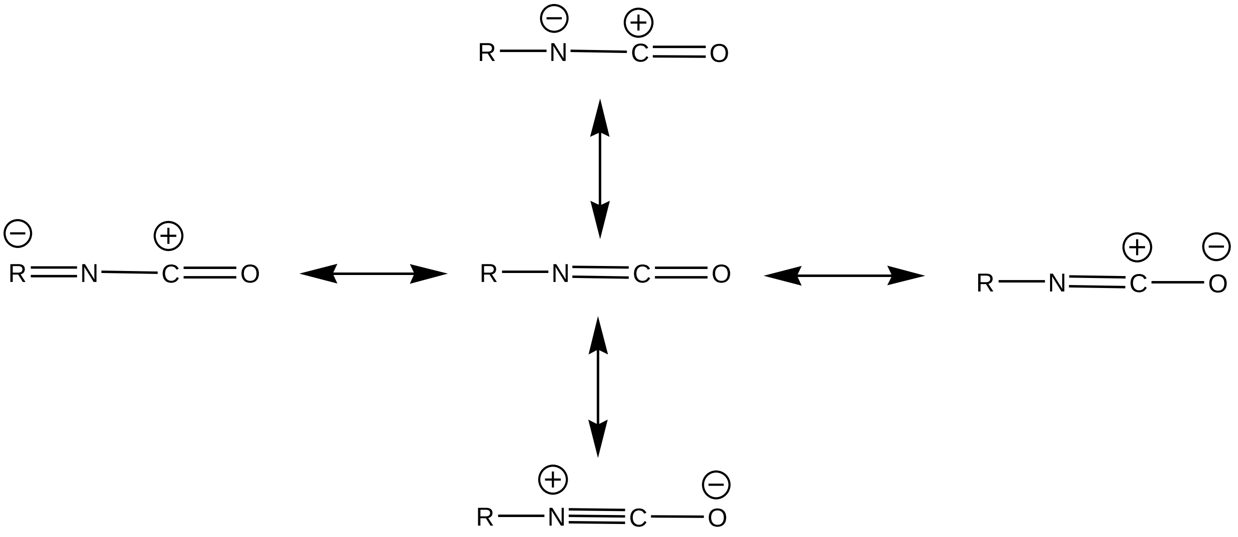


Figure 2.2: Resonance structure of Isocyanate

Reaction involved in the synthesis of polyurethane can be divided in to primary reactions and secondary reactions which are described here.

2.4.1 Primary Reactions

A) Urethane linkage or carbamic acid ester is formed by the reaction of NCO with nucleophiles containing OH group. There is increase in reactivity of OH group from phenol to secondary OH then primary OH.

Phenol < Secondary OH< primary OH.

This reaction is considered as reversible reaction because NCO group is recovered at optimum temperature [6,14,52,53].

B) Urea linkage may be formed by the reaction of NCO group with amino group present in nucleophile.

C) If the reaction environment is humid, water will react with NCO group immediately to form **carbamic acid** which is unstable and will decompose to form carbon dioxide and amine. This amine will cause the formation of urea linkage by reacting with NCO group instantaneously.

2.4.2 Secondary Reaction

The hydrogen atoms of urea and urethane linkage are active and can cause the formation of biuret and allophanates in specific condition. Biuret are formed at 100-150 °C while allophanates are produced at 120-150 °C [36, 55].

Polyurethane cross linking results due to biuret and allophanates formation. If basic catalyst is present, NCO group will react with another NCO group causing dimerization and trimerization to form uredione and isocyanurate. Isocyanate can react with another isocyanate resulting the formation of carbodiimides which react with another NCO group to form uretoneimine [53].

For polyurethane synthesis, isocyanate concentration is kept in excess which enhances crosslinking. Dimerization take place in aromatic isocyanate and it depend on the position of group in ring. For example in TDI there is isomerism so it does not dimerize and dimerization of MDI take place slowly on room temperature. Isocyanurate are stable which are synthesized by heating aromatic and aliphatic isocyanates [56].

Condensation of isocyanate may also result formation of carbodiimides which on further reaction with isocyanate results formation of uretoneimine [6,14,53,54].

2.5 Polymerization in Polyurethane

Polymers are classified on the mode of polymerization as addition polymers and condensation polymers. Polymers can also be classified depending on their kinetics of polymerization. Addition polymerization is now termed as chain addition polymerization and condensation polymerization is termed as step addition polymerization. High weight polymer is formed initially in chain addition polymerization while in step addition polymerization high weight polymers are formed at the end of reaction. Polyurethane polymers follow step addition polymerization kinetics.

In step addition polymerization, propagation reaction causes formation of polymer. Chain termination and chain transfer reaction does not take place in step addition polymerization. There is reaction between monomers forming dimers which on further reaction with another monomer results trimers and so on. Monomers are being used during the early stage of polymerization.

In condensation polymerization, there is change in structure of repeat unit as compared to monomer structure. Step addition polymerization is also termed as functional group polymerization. Polyurethane is also included in condensation polymerization. There is reaction of functional group present on one monomer with the functional group on another monomer e.g. NCO group on isocyanate will react with OH group on HTPB to form polyurethane linkage.

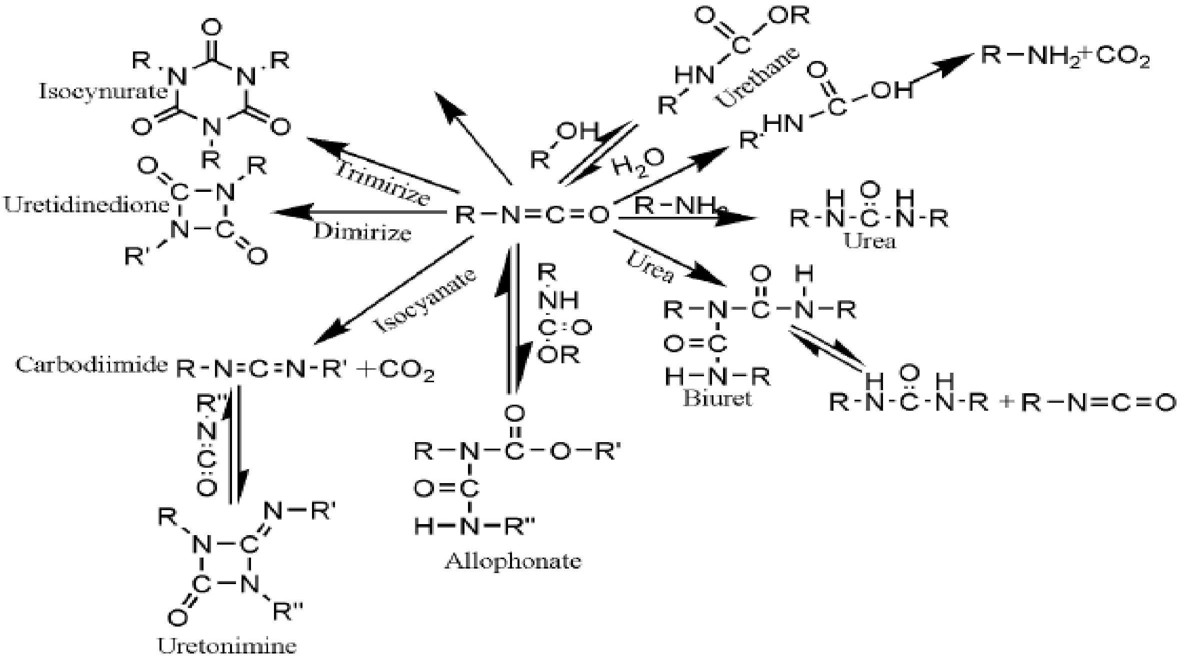


Figure 2.3: Primary and Secondary Reaction Involved in Polyurethane Synthesis.

2.6 Kinetics of Polyurethane Polymerization

Polyurethane reaction extent is given by following expression

$$P = \frac{No-N}{No}$$

where

P= extent of reaction

No = initial number of molecules of monomer

N = number of molecules of monomer at the stage of polymerization.

For 100% conversion

N = 0 and P = 1

And rate equation is given by.

$$\frac{d[NCO]}{dt} = -k\ [\mathrm{NCO}]\ [\mathrm{OH}]$$

Where

[NCO] = concentration of isocyanate group

[OH]= concentration of hydroxyl group

a and b exponents = the order of reaction.

And k = Rate constant

Polyurethane polymerization kinetics can be determine by different analytical techniques like FT-IR,DSC,DMA and Raman spectroscopy [57-59]. Polyurethane polymerization can also be determined by dibutylamine back titration method. These methods are termed direct methods because by following these methods concentration of product or reactant can be measured directly while rheometric and thermal methods are indirect method.

Mostly FTIR spectroscopy is used for observing polyurethane reaction. The absorption band of NCO between 2200-2300 is depleted due to urethane formation. Following equation give information about isocyanate conversion .

$$\text{Isocyanate conversion} = \frac{1-At-Af}{Ao-Af}$$

Where

Ao= absorption peak area for NCO at start of chemical reaction.

At= area of peak during reaction at any time t.

And Af= area of peak at final stage of reaction.

2.7 Structure Property Relationship

Polyurethane contain alternatively polyols segment and urethane and are considered (AB)n type block copolymer [60]. These segments exist as hard and soft segment .There is hydrogen bonding in urethane hard segment. These hard segments are distributed in soft segment. These urethane hard segments behave as filler particles for soft segment. XRD and mechanical properties support the presence of hard domain of nano size (150 nm) in large soft matrix (1000-2000 nm) [60].

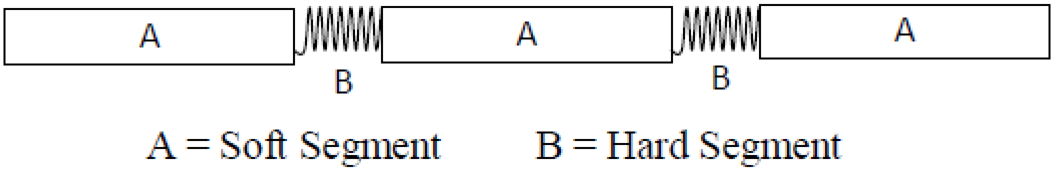


Figure 2.4: Block Structure of Polyurethane.

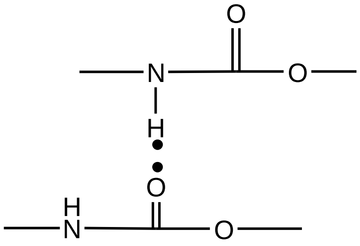


Figure 2.5: Hydrogen Bonding in Urethane Linkage.

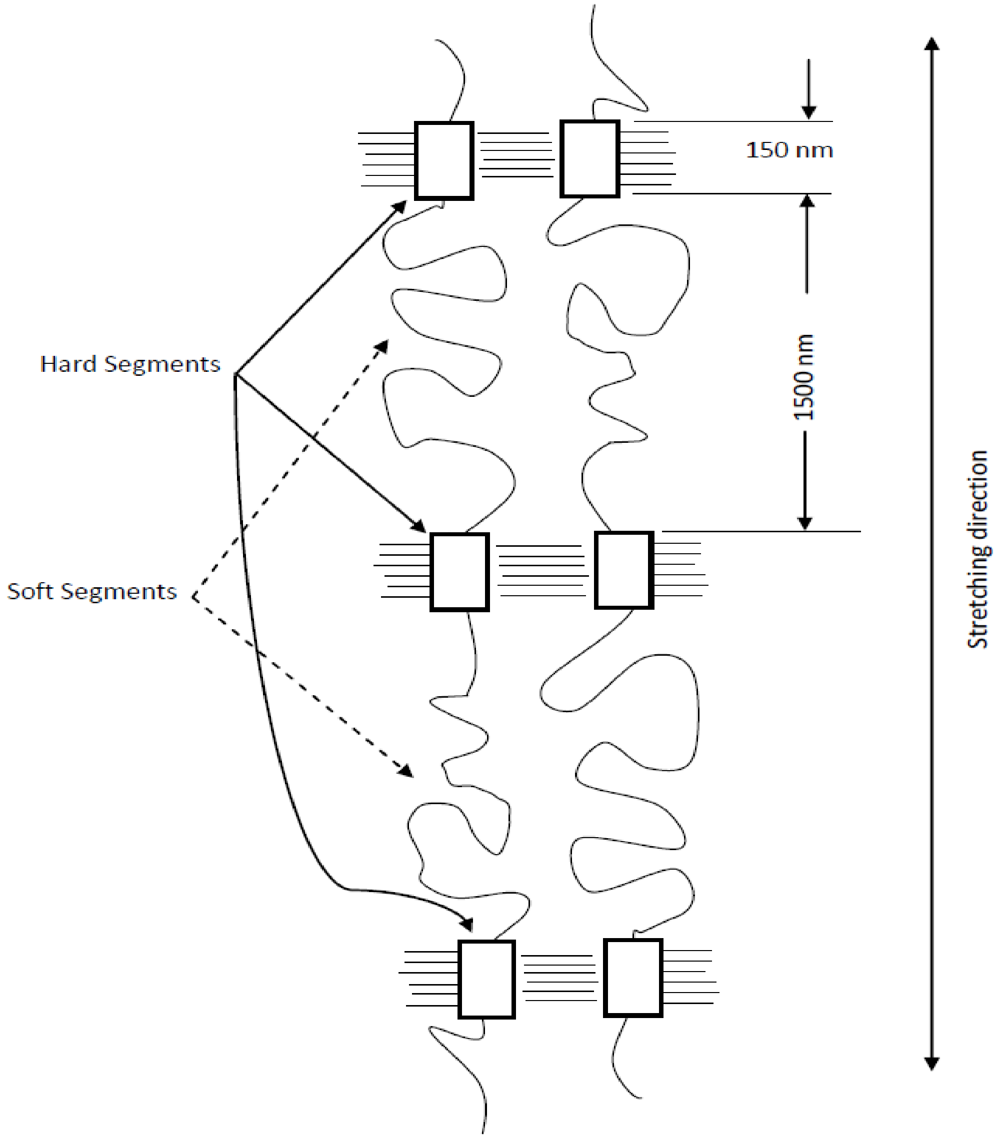


Figure 2. 6: Hard and soft segment in polyurethane elastomer

Polyurethane properties depend upon phase separation of hard and soft segments.

2.7.1 Surface Morphology

The final properties of a polymer depend upon morphology of multiphase system. Processing methodology and monomer chemical nature play role in determining morphology of polymer. For structure property relationship studies, it is necessary to know information about surface morphology. Phase separation complexes the morphology of polyurethane elastomer. Hydrogen bonding and crystallization also play role in determining properties. Many researchers are trying to study the effect of these factors on final properties of polyurethane elastomer [18].

Phase separation depends upon monomer molar mass and interaction of hard and soft segment. Polybutadiene polyurethane has more phase separation then polyester and polyether. Diisocyanate symmetry and chain extender structure also influences phase segregation. Segmental length of hard segment is about 25-100A° [34].

Bonart and clough used SAXS (small angle x-ray scattering) and reported two phase morphology [61, 62]. SAXA itself is not able to describe the two phase polyurethane morphology. Dynamic mechanical analysis and differential scanning calorimetry are used for the accompanying SAXS. Other techniques like polarized light microscopy and electron microscopy are used to study structural phases.

Later on TEM and SAXS was used for the determination of two phase morphology of polyurethane elastomer formed by toluene diisocyanate, polybutadiene and butane diol with different concentration of hard segment. When hard segment reached in rang of 42-67%, hard segment obtained rod like structure. Spheroids or short cylinder forms of hard segment were reported when hard segment was in rang of 31 to 34 % [63, 64]. Hard and soft segment crystallization has also role on polyurethane behavior. Crystallization environment and stereochemistry of hard segment determine its crystalline nature [6] e.g. the length of chain extender varied the properties of hard segment. There is high order of crystallinity of polyurethane formed by the addition of chain extender containing even nmb diols. Physical techniques like SAX,XRD and SEM are used to study surface morphology [65].

Polycarbonates based polyurethanes were synthesized by Zhang et all in 1996 to study surface damage [23]. Polyurethane surface was treated with acidic and alkaline solution. FTIR, DSC, and SEM were used for evaluating surface corrosion. Damage of surface was observed in alkaline solution.

Adsuar in 2000 synthesized thermoplastic polyurethanes and determine their adhesion properties and crystallinity [24]. T-peel test was used for evaluation of adhesion properties while NMR, WAXD and DSC were used for morphological and crystalline studies. It was reported that hard segment content up to 40% causes no crystallinity.

Klose et all in 2002 synthesized carpolactone based polyurethane and analyzed their morphological changes using DMTA, DSC, SEM and WAXS [66]. He reported that there is increase in crystallinity by increasing the soft segment length. SEM images showed that 17-26% by mass was urethane content.

Qin et al in 2007 introduced aromatic diamine containing sulphone to polyurethane as chain extender. DTMA and DSC were used to study morphology. Introduction of aryl sulphone destroyed the crystalline structure of polyurethane. No crystalline evidence was observed by WAXD [67].

Pilcha-pitera et al in 2008 studied qualitatively and quantitatively structure of polyurethanes. Low crystallinity and poor phase order was observed by SEM and WAXD [68].

Larraz et al in 2009 synthesized polyurethane based on HDI and polycarpolactone without catalyst. He characterized the sample by using AFM, DSC, ATR-IR and DMA. He reported crystalline regions were growing [23].

Lai et al in 2009 synthesizes polyurethane based on IPID, HTPB and POSS.XRD, FTIR, AFM and SEM techniques were used to evaluate sample. POSS homogenous dispersion was observed in polyurethane and there was increase in crystalline nature by increasing POSS content [69].

[70]

2.7.2 Hydrogen bonding

Hydrogen bond has bond energy of 20-50 kJ/mol. Hydrogen bonding is present in polyurethane and has the following order. Polybutadiene < polyether <polyester. Sung et al in 1980 explained hydrogen bonding in polyurethane [71].IR spectroscopy is used to detect hydrogen bonding present in polyurethane. Urea carbonyl C=O, free N-H and hydrogen bonded N-H and urethane carbonyl C=O are peaks which are studied [70, 72-74]. Phase separation depends on hydrogen bonding in polyurethanes. Higher degree of phase mixing will be observed in polyurethane having

high extent of hydrogen bonding. Phase separation and crystallinity will be observed if hydrogen bonds are bounded to hard segment.

Polyurethane composition, structure and temperature effect hydrogen bonding extent. A polyester urethane has 40 % less hydrogen bonding then polyether urethane. Hydrogen bonding will increase by increasing hard portion. At room temperature, 90% NH groups are hydrogen bonded in hard segment of polyurethane [75]

It is difficult to distinguish the effect of hydrogen bonding on mechanical properties from structural effect of polyurethane. Literature studies indicate that molecular mobility is not restricted by hydrogen bonding. Hydrogen bonding weaken segmental mobility [76, 77].

Adhikari and Sarkar in 2001 synthesized copolymer based on HTPB and characterized sample by XRD, WAXD and FTIR. They reported that hydrogen bonding decreases crystalline phase [78].

Kloss et al. in 2002 stated that increasing the concentration of polyurethane will decrease soft segment crystallinity and hydrogen bonding will increase [66].

Aneeja and Wilkes in 2003 studied crystalline behavior of polyurethane and reported that diisocyanate group symmetry and structure effect crystallinity [79]. It was reported that kinked diisocyanate structure causes lower in crystalline behavior of hard segment [80]. So hydrogen bonding does not always increases mechanical properties. Sufficient data has been published on effect of hydrogen bonding on mechanical properties of polyurethane.

2.8 Thermal Degradation of Polyurethane

Polyurethanes are vulnerable to photo, thermal, hydrolytic and chemical degradation. Only thermal degradation will be discussed here.

In nineteenth century, polyurethane linkage thermal degradation was study by Nolting. He reported the detection of methylamine, carbon dioxide, aniline and dimethyl aniline when methyl carbanilate was pyrolysis at 260°C [81].

Polyurethane thermal degradation mechanism is complicated. Three independent pathways are possible for thermal degradation of polyurethane.

1. Decomposition to isocyanate and polyols.
2. There may formation of carbon dioxide, primary amine and alkene having cyclic six member transition stage.
3. Four member ring transition stage may be formed resulting the formation of carbon dioxide and secondary amine [82-85].

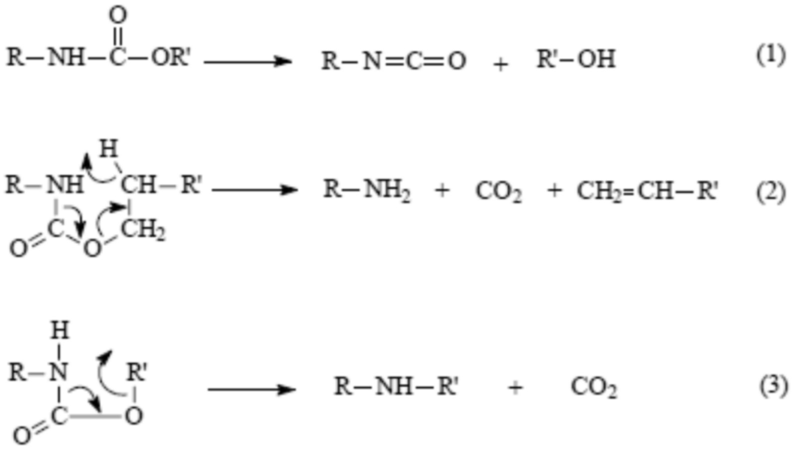


Figure 2.7: Pathway of Thermal Degradation of Polyurethane

Secondary products are obtained by thermal degradation of primary polyurethanes [86].

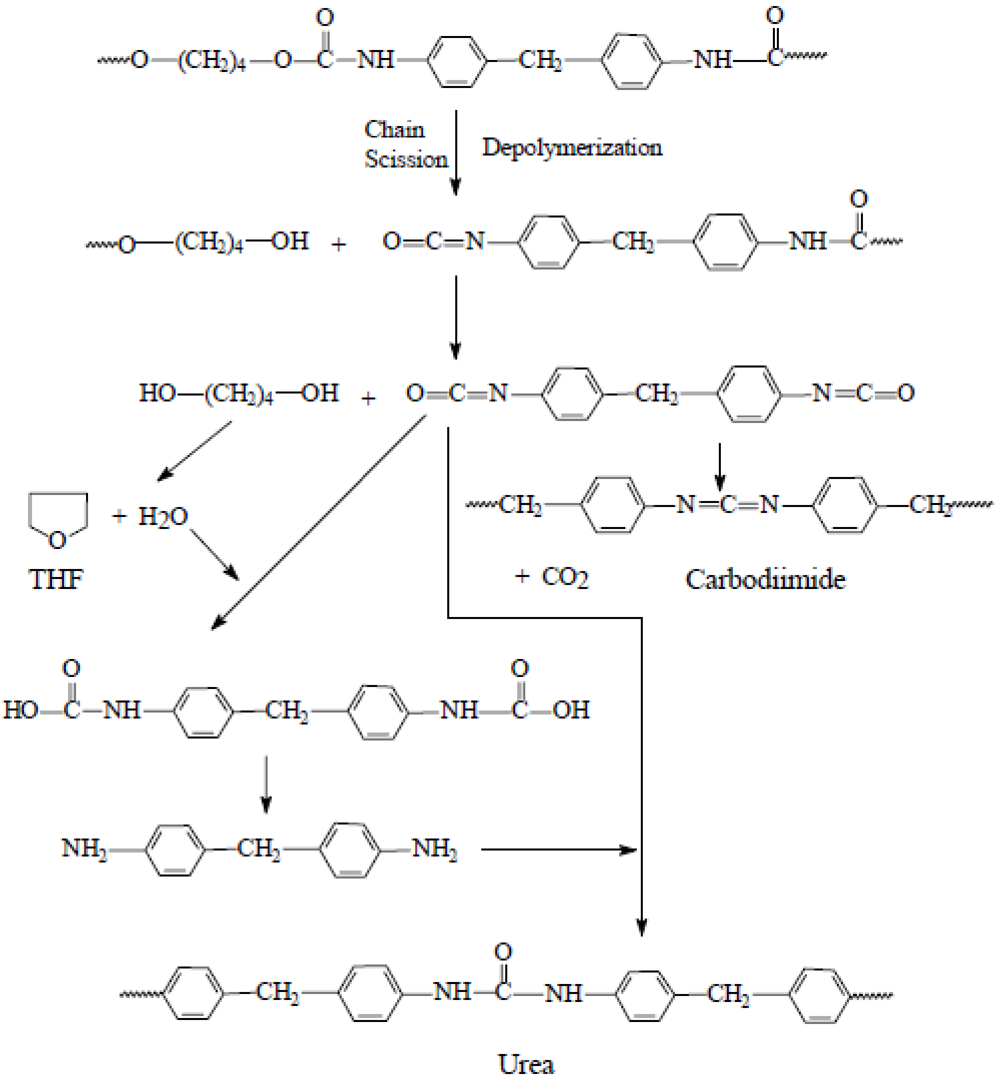


Figure 2.8: Mechanism for Thermal Degradation of Polyurethane

2.9 Process Parameter Effects on HTPB/TDI System

R, Manjari et all studied structure property relationship of propellant based on HTPB cured with TDI. HTPB formed by free radical polymerization having molecular weight 2600, 2900,3300,3500 and 4500 were used. Their OH values were in range of 20 to 45.It was observed that maximum tensile strength is obtained when NCO/OH ratio in between 0.7 to 0.9 and increasing OH value will decrease mechanical properties [87].

S.N.Jawalkar et al. studied effect of plasticizer and toluene diisocyanate addition at different temperature in propellant formulation. Plasticizer used in this study was dioctyl adipate. It was found that viscosity and burn rate of propellant slurry increased when DOA percentage was decreased. TDI was added at different temperature ranging from 35 to 60 °C. It was revealed that addition of TDI at higher temperature decreased viscosity.it was observed more effective in range of 50 to 60 °C. The mechanical properties were not affected by addition of TDI at higher temperature [88].

John Reji, P.Ravindran, N.R.Neelakanthan and N.Subramanian studied the effect of catalyst and filler on viscosity of HTPB/TDI system. HTPB having molecular weight 3000 and OH value 40 was used. Catalyst, tin octanoate and filler calcium carbonate was used. It was found that there was no significant effect on curing reaction by the addition of calcium carbonate filler. It increases initial viscosity so filler calcium carbonate can be added at the start of polymerization reaction

[89].

Chen Chun Yan, Gao Li-Long and wang Xiao-feng studied the effect of molecular weight of HTPB on mechanical properties of HTPB elastomer cured with TDI. HTPB having molecular weight in the range of 1500 to 4000 was used. HTPB was cured with TDI at 60 °C. It was observed that increasing the molecular weight of HTPB will increase the viscosity, curing time and elongation at break while tensile strength, dynamic storage modulus and glass transition temperature will be decreased [47].

Chapter 3

Experimental Work

Experimental part consists of following;

1. Determination of OH number in HTPB polymer.

2. Determination of % NCO in Toluene diisocyanate.

3. Adjustment of NCO/OH ratio.

4. Preparation of elastomer.

5. Characterization.

3.1 Determination of OH Number in HTPB Polymer

OH number in HTPB polymer can be determined by standard method ASTM E222-10. This method is used for the determination of OH groups which are connected to carbon atom (both primary and secondary) in alicyclic and aliphatic compounds. The chemical required for the procedure are given below.

Table 3. 1: List of Chemicals for OH number Determination

Chemicals	Purity	Company
Acetic anhydride	99%	Sigma Aldrich
Hydrochloric acid	35%(Conc)	Sigma Aldrich
Pyridine	99.5%	Xilong chemical
Sodium hydroxide	99%	Merck
Phenolphthalein indicator	98%	Sigma Aldrich

3.1.1 Solution Preparation

A. **Acetylation reagent**

Acetylating reagent was prepared by mixing acetic anhydride(105 ml) with pyridine (1000 ml). This reagent is prepared fresh when is required and it is preserved in a dark bottle .if the color of reagent is much dark then pale yellow then reagent is not used.

B. **NaOH solution (0.5 meq/ml)**

To prepare 0.5 meq/ml NaOH solution, 20 gram of NaOH was dissolved in 1000 ml of water.

C. **Phenolphthalein indicator solution**.

To prepare indicator solution, 1 gram of phenolphthalein was dissolved in 100 ml of pyridine.

3.1.2 Procedure

1. Sample of HTPB was weighed and added to round bottom flask.

2. 25 ml of acetylating reagent was added to flask.

3. Flask was connected to condenser and sealed with 1 to 2 drops of pyridine.

4. Solution was refluxed at reflux temperature for 1.5 hrs.

5. After refluxing the mixture, flask was cooled to room temperature and flask was rinsed with 25 ml of water.

6. 0.5 to 1 ml of phenolphthalein indicator was added to mixture.

7. Mixture was titrated against 0.5 meq/ml NaOH solution.

8. End point appeared when color changed to faint pink color. Solution was magnetically stirred during titration

9. Same procedure was adopted to calculate the volume of NaOH in ml required for the titration of blank (containing all the chemicals other than sample).

3.1.3 Formula to Calculate Hydroxyl Number

$$\text{OH number} = \frac{(A-B)\times Nt\times 56.1}{W}$$

Where

A = volume of NaOH in ml used for the titration of blank.

B = volume of NaOH used for the titration of HTPB sample.

Nt = normality of the NaOH solution which was 0.5 meq/ml in the procedure adopted.

W = amount of HTPB sample in grams.

Six different HTPB samples were used to calculate their OH number and the OH number calculated by above procedure and formula are given below.

Table 3. 2: Samples and their OH number

Sample ID	**OH Number**
HTPB-179	0.710
HTPB-180	0.722
HTPB-173	0.741
HTPB-206	0.741
HTPB-181	0.750
HTPB-300	0.762

3.2 Determination of NCO % in Toluene Diisocyanate

3.2.1 Method A

This is standard method for the determination of NCO % in aromatic compound. I had followed ISO 14896;2006(E method for the NCO content determination. The chemical required for this method are given below.

Table 3. 3: Chemicals used in Method ISO 14896

Chemical	Purity	Company
Acetone	99.9%	Sigma Aldrich
Toluene	99%	Sigma Aldrich
di-n-butylamine	99.3%	Merck
HCl	35 %(Conc)	Sigma Aldrich
Bromophenol blue	98%	Merck

3.2.2 Solution Preparation

A) di-n-butylamine solution 1 mol/L

Mix 129 grams of di-n-butylamine to 1 liter of toluene.

B) Aq HCl solution 1 mol/L.

C) 0.04 % Aq bromophenol blue indicator solution.

3.2.3 Procedure

1. Iodine flask was rinsed with 10 ml toluene.
2. 25 ml of di butylamine solution was added to iodine flask with the help of volumetric pipette.
3. Using syringe, 1.5 grams of toluene diisocyanate was added to the iodine flask and was gently shaken.
4. Solution was left for 15 mints at room temperature for complete reaction which caused some warming. The solution was stand for 5 to 10 minutes to reach room temperature.
5. 150 ml of acetone was added to the solution and precautions were measured to rinse the stopper and wall of the flask.
6. 0.8ml of bromophenol blue solution was added to the solution.
7. Excess di butylamine was titrated against Aq HCl solution (1mol/L).
8. End point appeared when color of solution was changed from blue to yellow. There was bluish green intermediate color.
9. Blank experiment was also run side wise.

3.2.4 Formula to Calculate % NCO

% NCO = $\frac{4.202\times(V1-V2)\times C}{mo}$

Where

V_1 = volume of HCl in ml used for the titration of blank solution.

V_2 = volume of HCl in ml used for the titration of toluene diisocyanate sample

C = concentration of HCl.

M_o = mass of TDI taken.

4.202 equivalent mass of NCO which is 42.02 mg/milliequivalent, converting g to mg.

% NCO = 4.202 x (80-73) x 0.5/30

= 47.9%

3.2.5 Method B

ASTM 1638-74 standard method is also used to calculate % NCO in toluene diisocyanate. The chemicals required for this method are given below.

Table 3. 4: Chemicals used in Method ASTM 1638-74

Chemicals	Purity	Company
Di –n-butylamine	99.3%	Merck
Toluene	99%	Sigma Aldrich
Isopropyl alcohol	99.9%	Sigma Aldrich
Bromocresol	99%	Merck
Hydrochloric acid	35%(Conc)	Sigma Aldrich

3.2.6 Solution Preparation

A. di-n-butylamine solution 1 mol/L

Mix 129 grams of di-n-butylamine to 1 liter of toluene.

B. 0.5 N HCl solution.

C. Bromocresol green indicator was synthesized.

3.2.7 Procedure

1. Iodine flask (quit fit glass) was rinsed with water, alcohol and acetone. Flask was dried at 100 c and then cooled to room temperature.
2. 8 ml of toluene and stirrer was added to flask.
3. 10 ml of di butylamine solution was added to flask and the content was stirred.
4. 1 gram of toluene diisocyanate was added to flask.
5. Flask was allowed to stand for 15 minute for reaction.
6. 45 ml of isopropyl alcohol was added to reaction flask
7. 0.8 to 1 ml of bromocresol indicator was added and reaction mixture was titrated against 0.5 N HCl
8. End point appeared when color changed from green to yellow.
9. Blank experiment was also run side wise.

3.2.8 Formula to Calculate % NCO

$$\% \text{ NCO} = \frac{4.202 \times (V1 - V2) \times C}{mo}$$

Where

V_1 = volume of HCl in ml used for the titration of blank solution.

V_2 = volume of HCl in ml used for the titration of toluene diisocyanate sample

C = concentration of HCl.

M_o = mass of TDI taken.

4.202= equivalent mass of NCO which is 42.02 mg/milliequivalent, converting g to mg.

So

% NCO = 4.202 x (96.2-73.5) x 0.5/1

=47.69 %

3.2.9 Elastomer Formulation

Elastomers of hydroxyl terminated polybutadiene (HTPB) with toluene diisocyanate (TDI) were prepared by following procedure.

1. Calculated amount of hydroxyl terminated polybutadiene (HTPB) was weighed in a beaker.
2. Sample OF HTPB was degassed in vacuum oven at 100 °c temperature and 200 mb.
3. Calculated amount of filler, calcium carbonate $CaCO_3$ was added and mixed by hand followed by stirring the mixture with magnetic stirrer on hot plate.
4. HTPB was allowed to reach at 60 C in heating oven.
5. Toluene diisocyanate was added in stoichiometric amount at 60 °C in $CaCo_3$ filled HTPB and was uniformly mixed by stirring the mixture. TDI reacted with HTPB to form polyurethane linkage. TDI was redistilled before its use.
6. Elastomer was cured in heating oven at 60 C for 72 hours.
7. Curing completed when hardness of elastomer did not change.
8. Prepared elastomers were subjected to characterization.

3.3 Calculations Involved in the Formulation of Elastomer

3.3.1 For OH number Determination

Ew = molecular weight/functionality

Ew = 56100/hydroxyl number

Ew =1000/hydroxyl number

Ew = 1700/%hydroxyl

And Hydroxyl value = milliequivalent

= hydroxyl number/56.1

3.3.2 For NCO % Determination

Ew = Mw of the NCO compound/functionality

Ew = 4200/% NCO in compound.

3.3.3 General Formula for Urethane Formulation

$$\frac{Weight\ of\ NCO\ Compound}{100\ g\ of\ HTPB} = \frac{OH\ Value \times Ew\ of\ NCO\ Compound\ (NCO/OH) ratio}{10}$$

By using above formula 36 different elastomer of HTPB/TDI using inert filler $CaCO_3$ were prepared and were characterized.

Chapter 4

Results & Discussion

4.1 IR Analysis Studies

Polyurethane curing reaction is monitored by detecting change in absorption band of carbonyl stretching (C=O stretching) in range of 1740-1700 cm^{-1} and isocyanate stretching at 2300-2200 cm^{-1} [90-93]. The band growth for C=O and –NCO stretching band disappearance confirms that diisocyanate has been completely consumed and also indicate urethane linkage (NHCOO) in elastomer.

Hydrogen bonding present in polyurethane linkage can also be detected by both these bands. In the presence of hydrogen bonding in polyurethane network, bands for C=O and –NH grow relatively at lower wave number then without hydrogen bonded –NH and C=O band [94-96].

IR spectrum for toluene diisocyanate is shown in fig 4.1. The absorption band at 2239 cm^{-1} is assigned for isocyanate group (-N=C=O). There are sharp bands at 1523, 1573 and 1614 cm^{-1} which are assigned for aromatic ring C=C stretching [96]. The absorption band at 1440 cm^{-1} is assigned for –CH deformation.

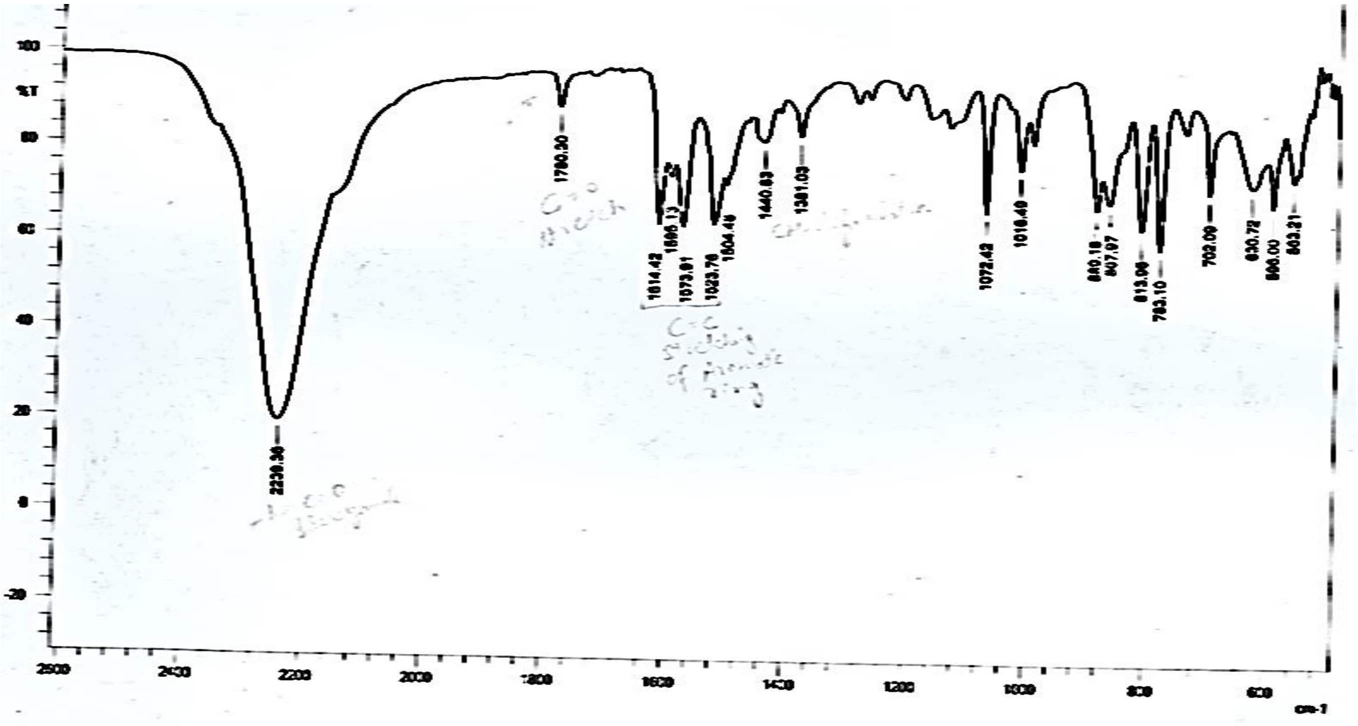


Figure 4.1: IR spectrum of TDI

IR spectrum for hydroxyl terminated polybutadiene (HTPB) is shown in fig 4.2. The band for OH group is suppressed due to low concentration of OH group and OH group present in polymer chains are not freely available so these OH group does not show broad absorption band as observed in alcohol. HTPB contain vinyl (v), cis-1,4 (C) and trans-1,4 (T) microstructure and trans, vinyl and cis structures (T,V,C) are attributed at 964 cm^{-1}, 910 cm^{-1} and 684 cm^{-1} respectively. The other absorption bands in HTPB spectrum are assigned as: 1417 cm^{-1} for CH bending, 1639 cm^{-1} for diene, 2846 cm^{-1} for symmetric CH_2 stretching, and 2913 cm^{-1} asymmetric CH_2 stretching.

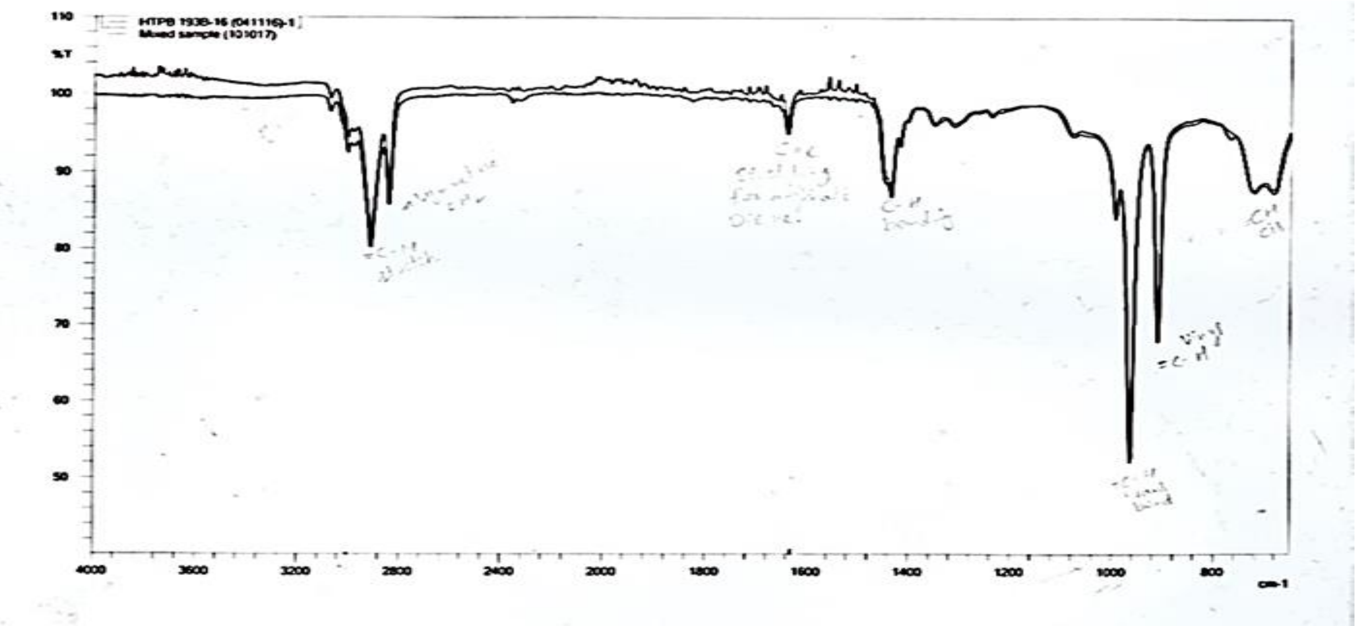


Figure 4.2: IR Spectrum of HTPB

IR spectrum of different polyurethane elastomers formed by curing reaction of HTPB with TDI in the presence of calcium carbonate filler are shown in fig 4.3.

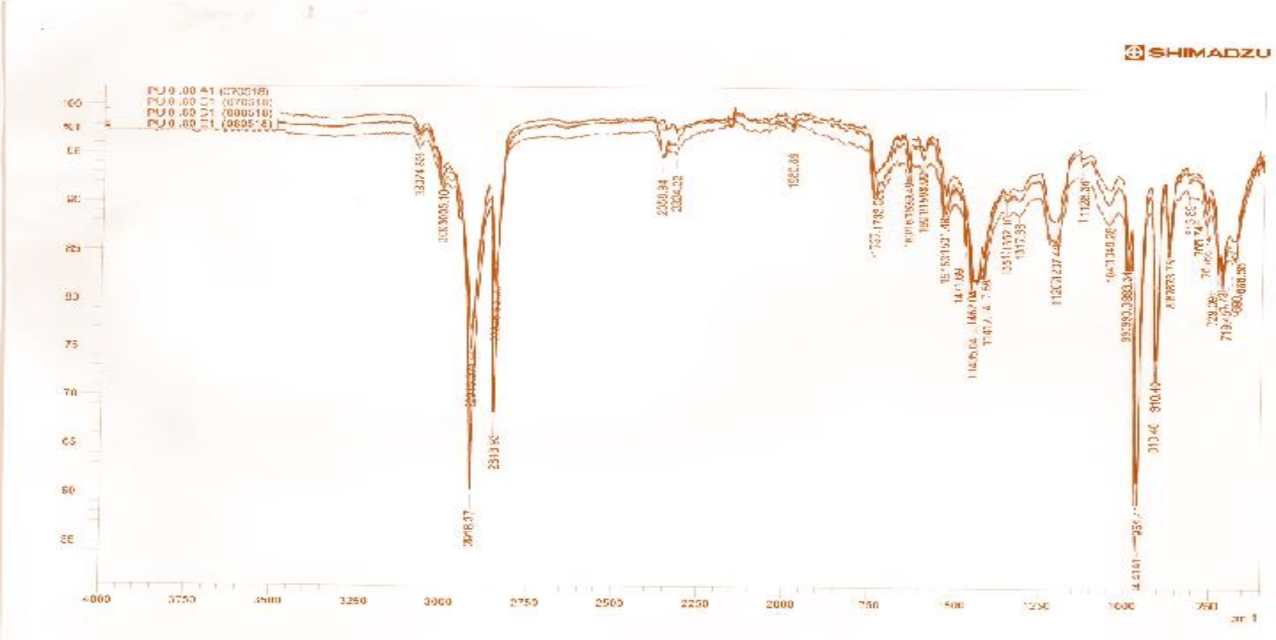


Figure 4.3: IR Spectrum of Polyurethane Elastomer

N=C=O band disappearance at 2239 cm^{-1} and –NH band appearance at 1597 cm^{-1} confirms that all the isocyanate groups have undergone in chemical reaction with hydroxyl group of HTPB and are completely utilized. Furthermore appearance of C=O band at 1737cm^{-}1, NH band at 1597 cm^{-1} , C-N band at 1531 cm^{-1} and C-O-C band at 1051 cm^{-1} confirms formation of urethane linkage (R-NH-COO-R) [97]. IR absorption bands at 710 cm^{-1} (symmetric deformation), 875 cm^{-1} (asymmetric deformation) and 1435 cm^{-1} (asymmetric stretching) confirms presence of CO_3^{-2}. In some spectrum, a band is seen at 2358 cm^{-1}which may attribute to atmospheric CO_2. Major absorption bands in prepared polyurethane elastomers are shown in table 4.1.

Table 4. 1: Polyurethane major Absorption Bands

Frequency(cm^{-1})	Major Assignments
680-690	Cis δ CH
710-720	CO_3^{-2} deformation
910	Vinyl δ CH
964	Trans δ CH
1045-1055	ν C-O-C
1200-1210	C-O
1435-1440	CO_3^{-2} stretching
1531	ν C-N
1597	δ N-H
1639	ν C=C
1737	ν C=O
2845	νs CH_2
2916	νa CH_2
3005	ν CH

ν=Stretching νa=Asymmetric stretching

νs=Symmetric stretching δ=Bending

4.2 Differential Scanning Calorimetery Analysis

Generally, polyurethane decomposition process initiates at temperature in range of 200 to 380 °C. The isocyanates that are emerged during decomposition react themselves forming dimers which later on decomposed to synthesize isocyanurate and urea. The second decomposition stage happens in temperature range between 350 to 500 °C. There is complete decomposition of products at temperature higher than 500 °C to produce volatile material [98].

Different DSC thermograms of prepared elastomers were obtained by heating calculated amount of elastomers at 50 to 550 ° C under N_2. Sample weight was in the range of 4.0 mg to 5.50 mg. Samples were heated at a heating rate of 10 °C /minute. The DSC thermograms give information about degradation, thermal changes and stability.

The decomposition process of polyurethane formed by reacting HTPB with TDI, occurs in two steps.one is exothermic while the other one is endothermic. The initial exothermic peak arises due to cross linking process and exothermic cyclization of HTPB and positive energy balance of endothermic depolymerization. Sample weight is lost during this stage due to volatilization of low molecular weight hydrocarbons. The second endothermic peak arises due to depolymerization of residues which are formed in the cross linking and cyclization process of first decomposition stage [99]. Different DSC thermograms of elastomers are shown in fig4.4.

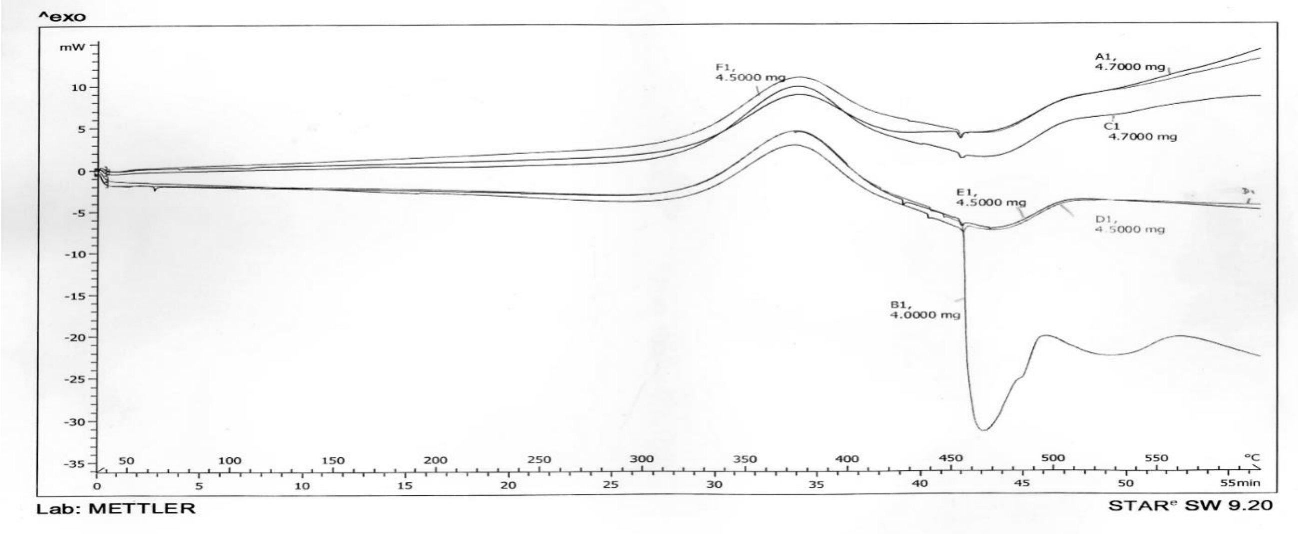


Figure 4.4: DSC Thermogram of Prepared Elastomer at 0.80 Rt

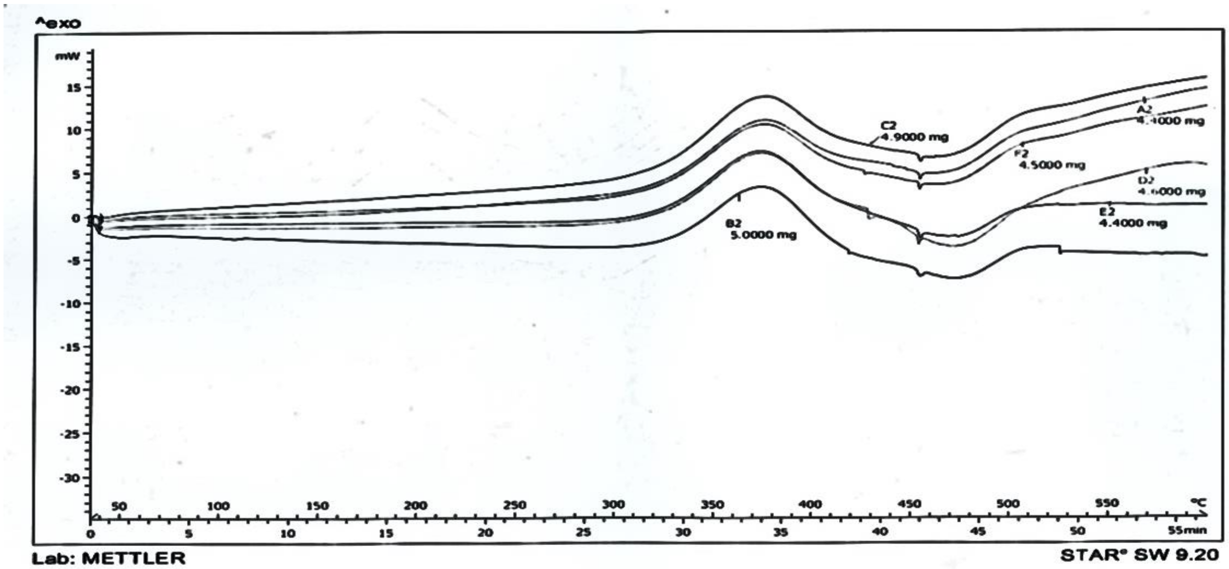


Figure 4.4: DSC Thermogram of Prepared Elastomer at 0.82 Rt

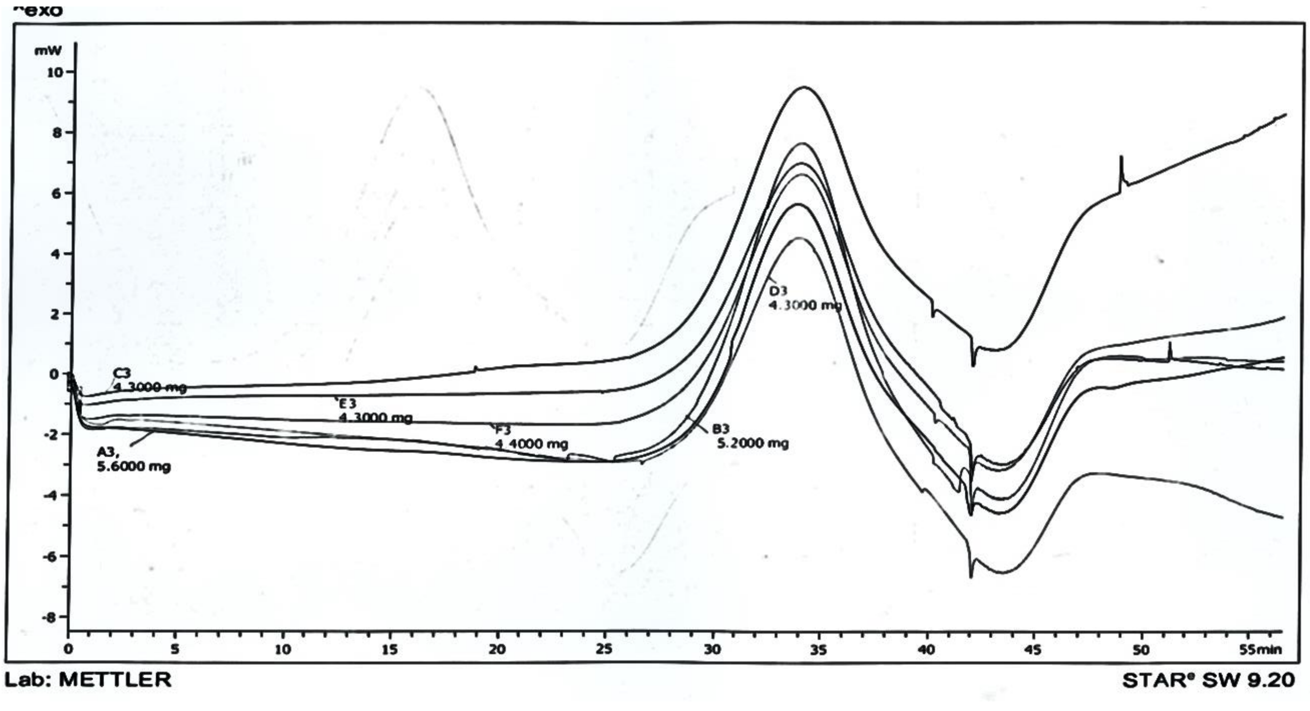


Figure 4.5: DSC Thermogram of Prepared Elastomer at 0.84 Rt.

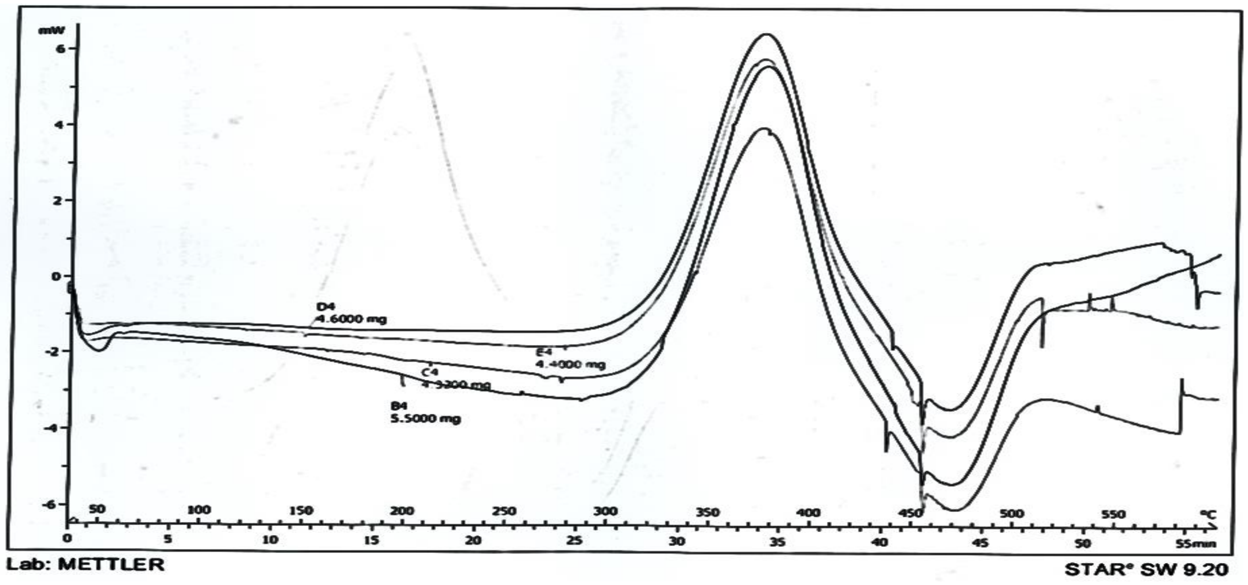


Figure 4.6: DSC Thermogram of Prepared Elastomer at 0.86 Rt.

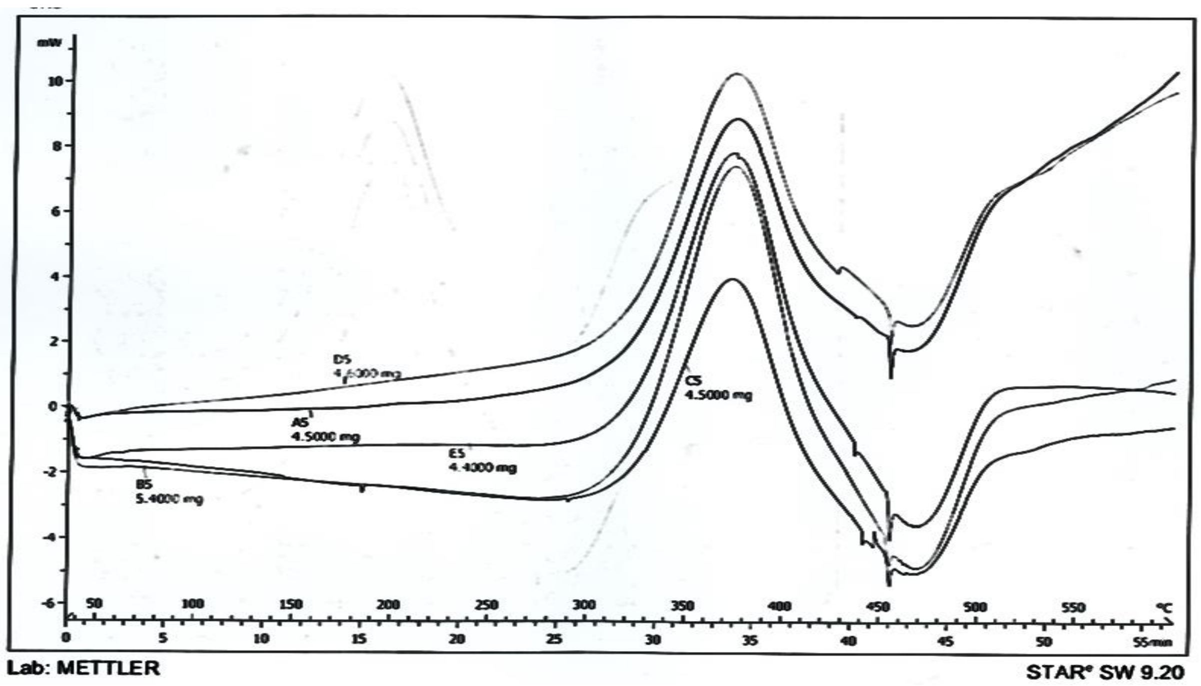


Figure 4. 7: DSC Thermogram of Prepared Elastomer at 0.88 Rt

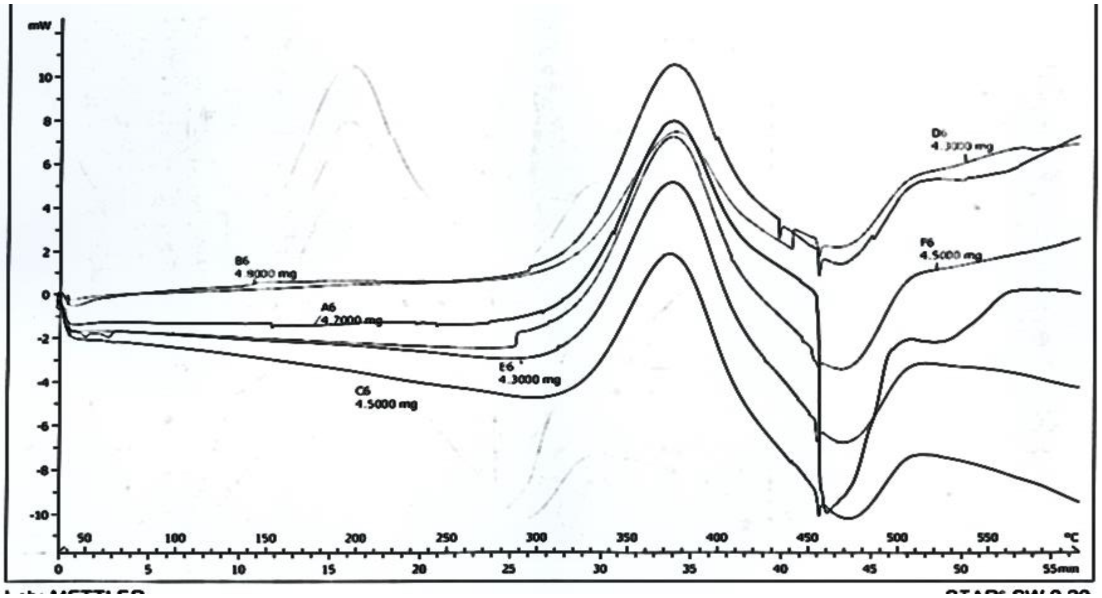


Figure 4. 8: DSC Thermogram of Prepared Elastomer at 0.90 Rt.

Fig 4.4 represents the DSC thermogram of elastomer at 0.80 NCO/OH (rt). The exotherms are arising at 373°C to 374 °C while endotherms are arising at 454 °C. In case of B_1 elastomer, third peak is emerging at 524 °C which shows complete decomposition of products. There is not significant change in exothermic and endothermic temperature (only 1 to 2 °C) when OH nmb of HTPB is increased from 0.71 to 0.75 which indicates that the prepared elastomers have almost same thermal degradation and stability.

4.3 Dynamic Mechanical Analysis

Dynamic mechanical analysis was performed to find out glass transition temperature. As filler ($CaCO_3$) content of prepared elastomers is very low (10%) while it can take solid loading up to 88 %, storage modulus and loss modulus cannot be calculated in this case. The sample used for DMA has 20 mm length, 9.50 mm width and 3.0 mm thickness (20mm x 9.50mm x 3.0mm). DMA analysis was performed at a characteristic frequency of 1 H.Z for elastomer having OH values ranging from 0.71 to 0.76 at 0.84 NCO/OH ratio (Rt. value) as shown in fig 4.10.

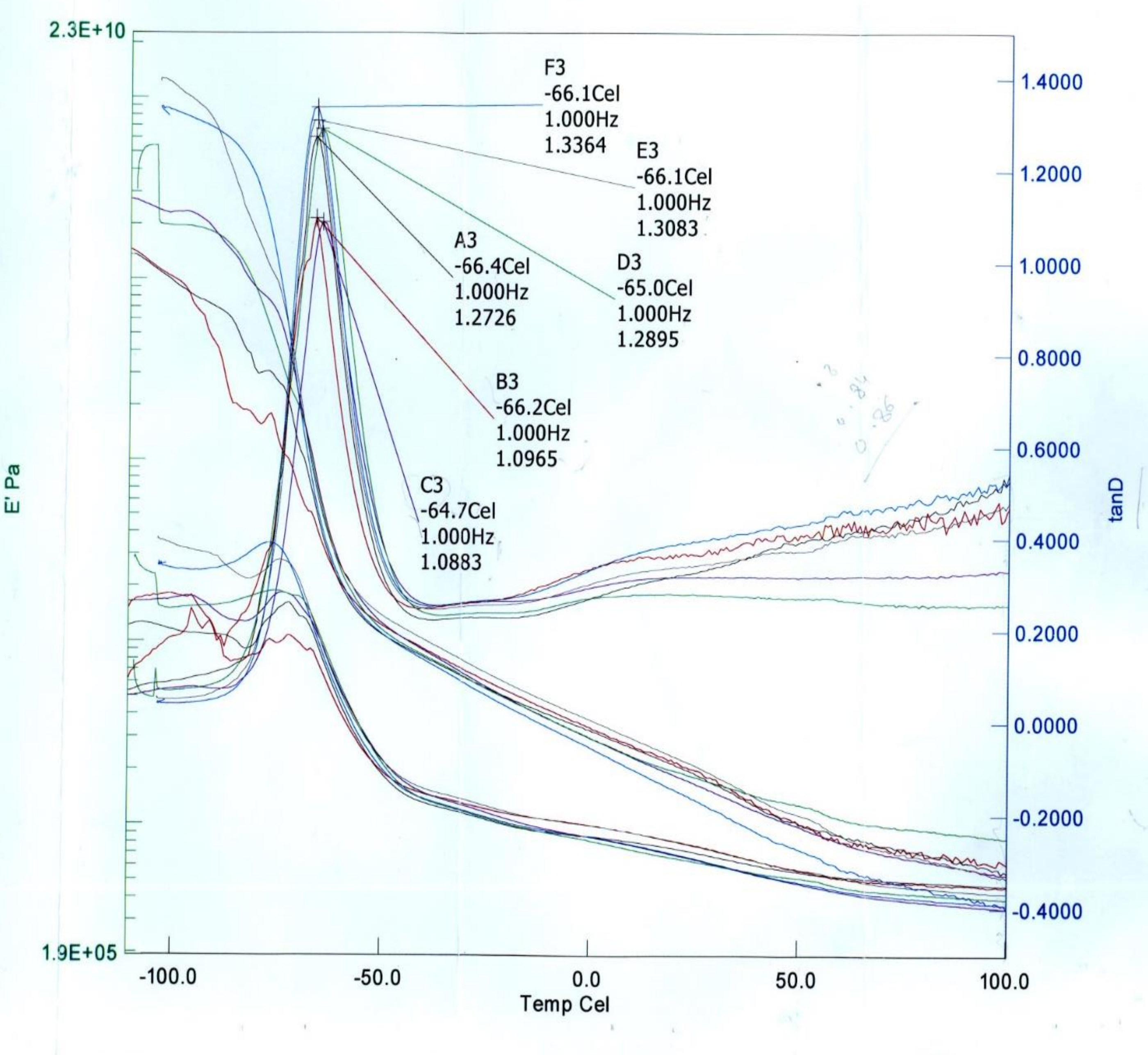


Figure 4. 9: **DMA Thermogram of Elastomer at 0.84 Rt.**

Table 4. 2: Comparison of Tg at Different OH values

Sample	**OH value**	**Glass transition temperature**
A3	0.71	-66°C
B3	0.72	-66°C
C3	0.73	-64°C
D3	0.73	-65°C
E3	0.75	-66°C
F3	0.76	-66°C

The glass transition temperature of polymer depends on translational and rotational motion of chain segments in polymer.it also depends upon nature of side groups in polymer [90].

The elastomers have very close glass transition temperature (-66°C to -64°C) and are comparable to each other. As all elastomer were prepared from OH terminated HTPB, and have same polymer back bone so it is suggested that polymer backbone defines viscoelastic properties of polyurethane elastomers. OH range used in the study is very narrow (from 0.71 to 0.76) so it is deduced that polymers having different OH nmb at fixed molecular weight does not significantly affect glass transition temperature.

4.4 Hardness Analysis

Hardness test was performed with durometer and shore A scale was used for calculating hardness. Fig 4.11 represents variation of hardness with Rt value at different OH values.

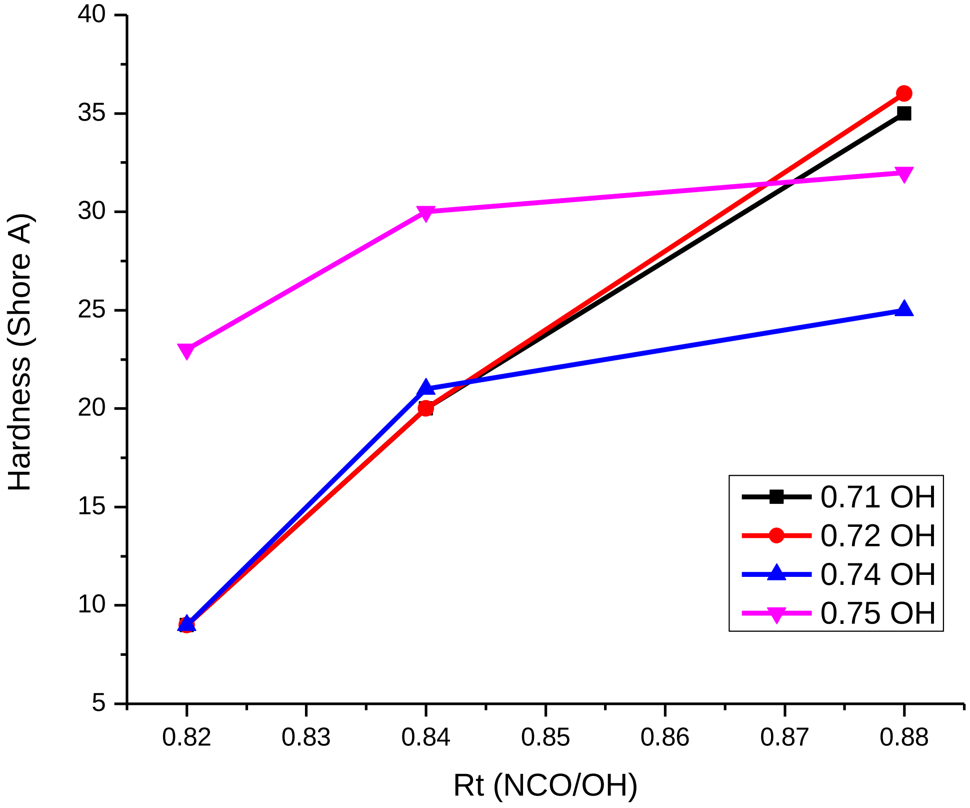


Figure 4.10:Hardness verses Rt Graph at Different OH values

It is seen in above figures that hardness increases with increasing Rt value which is attributed to increase in cross link density. Increasing NCO/OH ratio increases the chances of side reaction which results in formation of cross linking within polyurethane network and hardness of the elastomer increases. Maximum hardness is obtained at 0.88 Rt value.

4.5 Mechanical Properties Determination

Mechanical properties of prepared elastomer were determined on uniaxial testing machine. Elastomers were cut at a size of 50mmx10mmx5mm and the test was performed at 50 mm/min cross head speed. Tensile strength and percentage elongation at break were measured. Fig 4.12 shows variation of tensile strength at different Rt values and OH number.

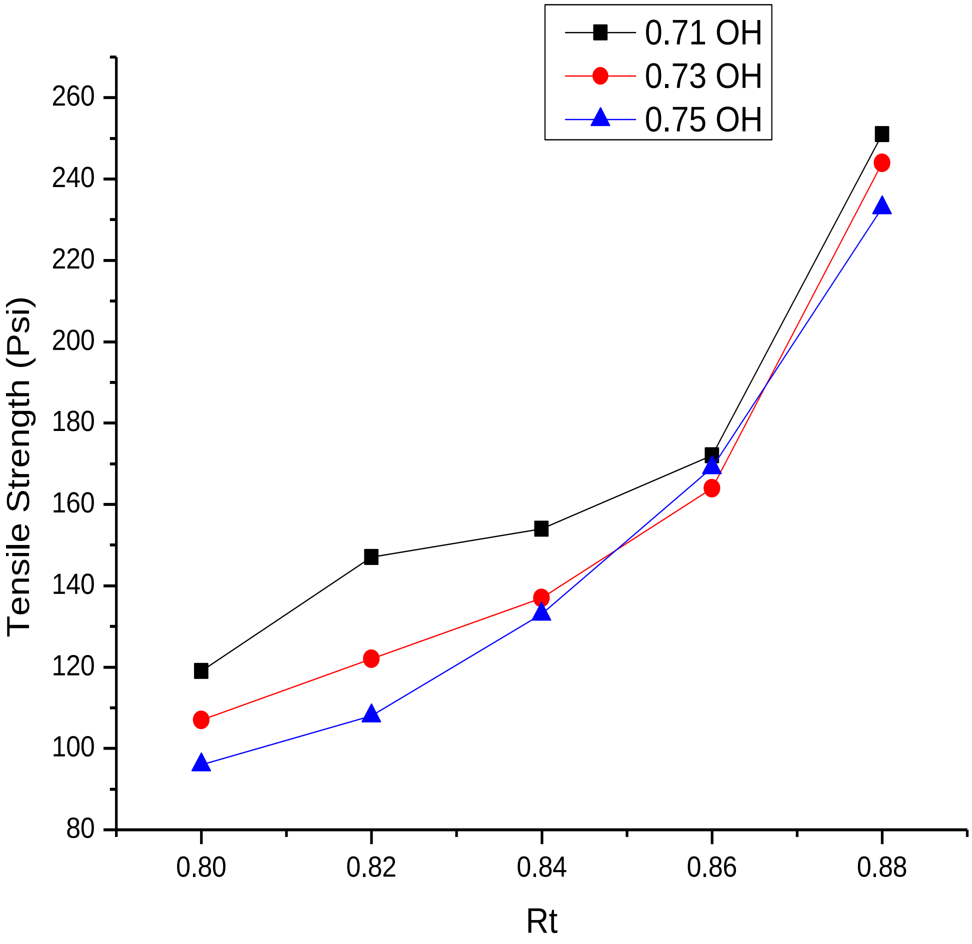


Figure 4. 11: Graph between Tensile Strength and Rt at Different OH value

It is seen from the above fig that increasing Rt value increases tensile strength. Tensile strength increases due to increase in cross link density. When Rt ratio is increased, there is more chances of networking due to which tensile strength of elastomers showed increasing trend. At a specific Rt, if OH number is increased then tensile strength shows decreasing trend (tensile strength decreases with increase in OH number) because the elastomers starts to become brittle causing decrease in tensile strength.

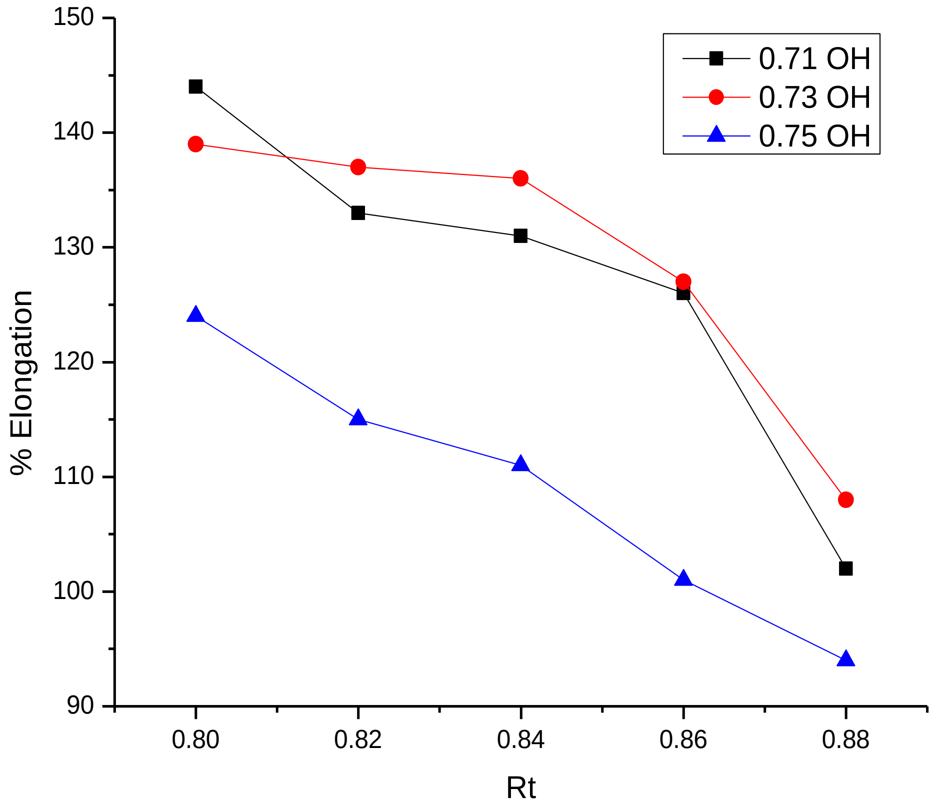


Figure 4. 12: Graph between % Elongation and Rt at Different OH value

When Rt ratio is increased,% elongation is decreased.

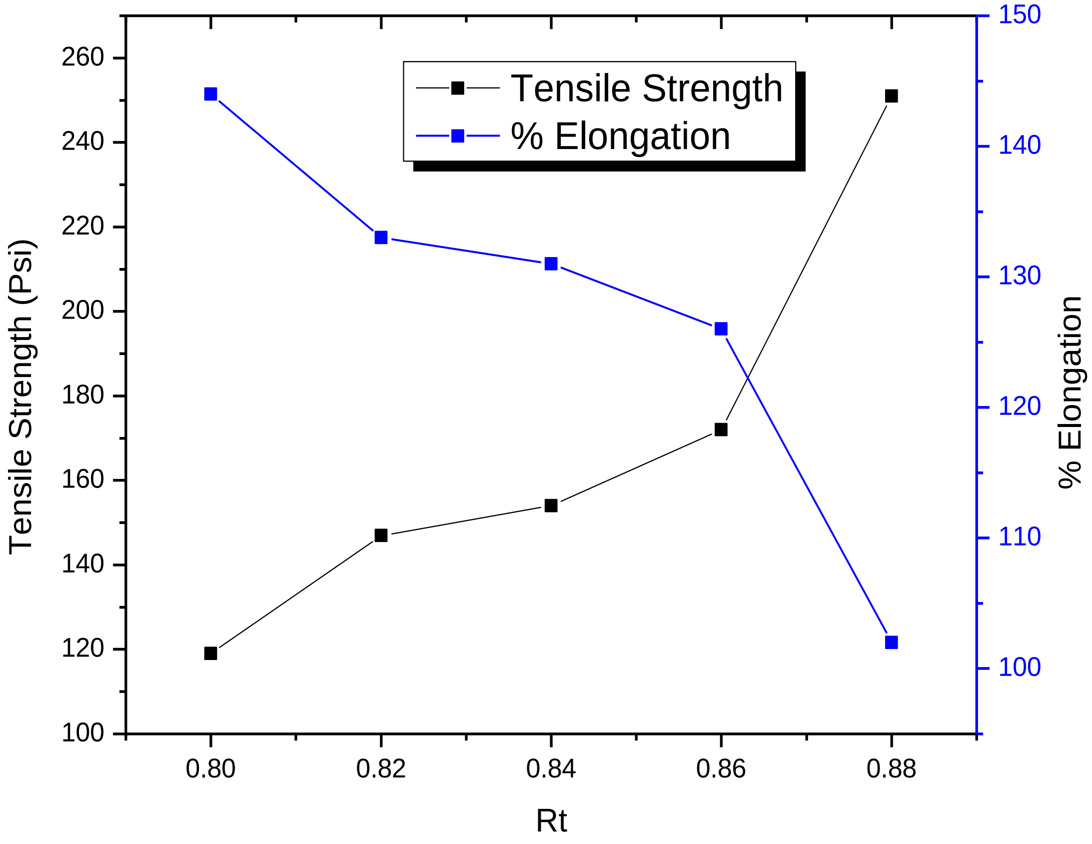


Figure 4. 13: Combine Graph of Tensile Strength and % Elongation verses Rt at 0.71 OH.

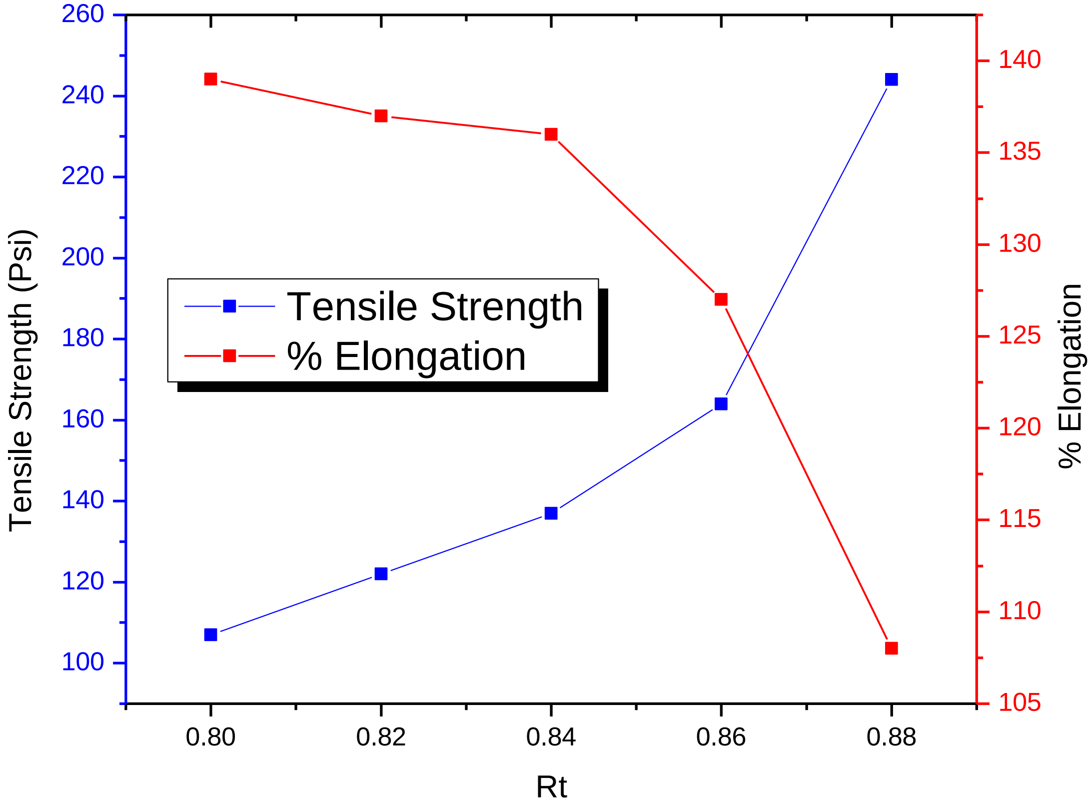


Figure 4. 14: Combine Graph of Tensile Strength and % Elongation verses Rt at 0.73 OH.

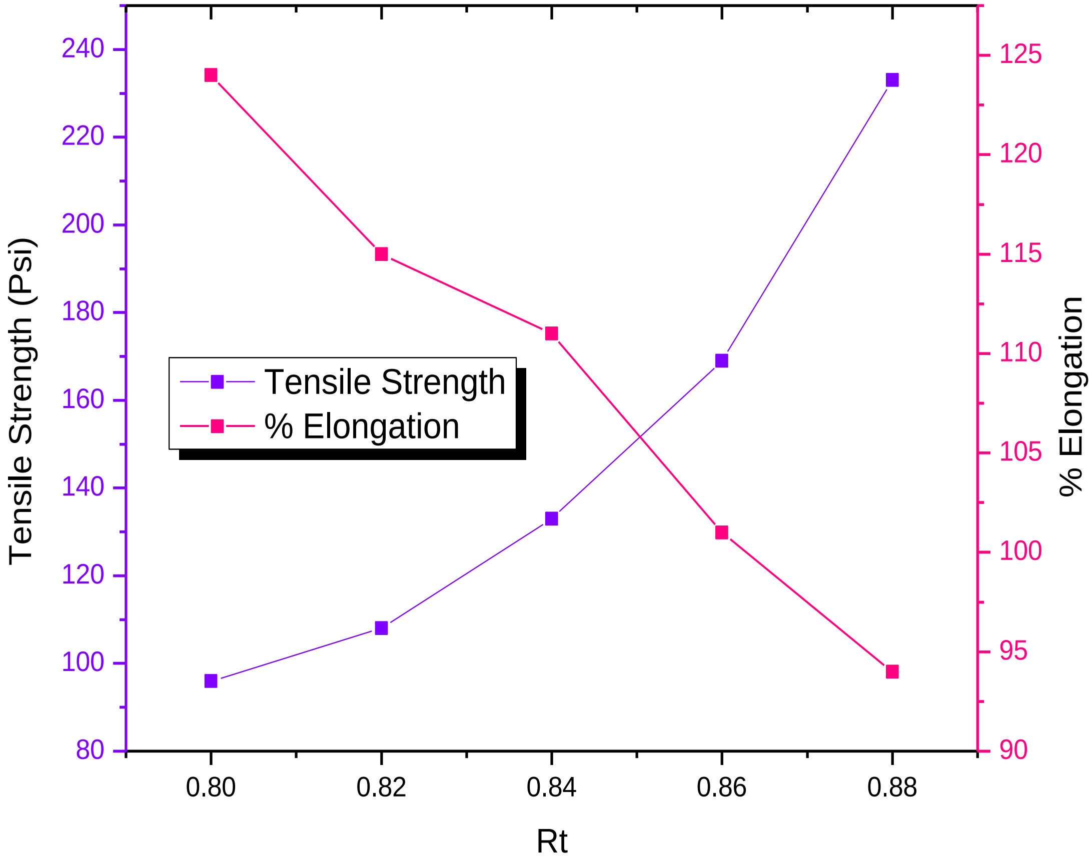


Figure 4. 15: Combine graph of Tensile Strength and % Elongation verses Rt at 0.75 OH.

It can be seen in above figures that increasing NCO/OH ratio increases tensile strength and decreases percentage elongation. This trend can be explained on the basis that increasing Rt value will increase hard segment content and cross linking will also be increased . This causes increase in intermolecular bonding of hard to hard segment and the cross linking also causes resistance in polymer chain flow which ultimately results in increased tensile strength and decreased percentage elongation. The most suitable mechanical properties are obtained at 0.88 Rt by elastomers which are formed by HTPB having 0.71 OH number.

Chapter 5

Conclusions

1st Objective was achieved by determination of OH number of different HTPB samples by following ASTM E222-10 standard method. Percentage of NCO in TDI was determined by ASTM D5155-01 standard method.

2nd Objective was achieved by NCO/OH ratio adjusted by stoichiometric calculations. 36 elastomers with inert $CaCO_3$ filler were prepared at different OH number and NCO/OH ratio.

3rd objective was achieved by characterization of prepared samples by IR, DSC, UTS, hardness test and DTMA. It was observed that by increasing Rt ratio, tensile strength increases and percentage elongation decreases. It was concluded that hardness of elastomer increases with increasing OH number of polymer. By Increasing OH number of HTPB from 0.71 to 0.75 caused no significant change in phase transition temperature. Glass transition temperature does not change by varying OH number. Increasing OH number of HTPB from 0.71 to 0.75 caused decrease in tensile strength. Elastomer with optimum mechanical properties was prepared at 0.71 OH number.

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