Synthesis and Characterization of Polyurethane Composite Materials Derived from Hydroxy Terminated Polyepichlorohydrin

QUAID-I-AZAM UNIVERSITY

ISLAMABAD

A dissertation submitted to the Department of Chemistry,
Quaid-I-Azam University, Islamabad, Pakistan, in partial fulfilment of
the requirements for the degree of

Doctor of Philosophy

In

Inorganic Chemistry

By

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2017

بسم الله الرحمن الرحيم

Dedicated to Bhai Jan who always remained

a source of inspiration

This is to certify that this dissertation entitled **"Synthesis and Characterization of Polyurethane Composite Materials Derived From Hydroxy Terminated polyepichlorohydrin"** submitted by *Mr. Muhammad Ahmad* is accepted in its present form by the Department of Chemistry, Quaid-I-Azam University, Islamabad, as satisfying the requirements for the award of degree of **Doctor of Philosophy in Inorganic/Analytical Chemistry**.

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Acknowledgements

All praises to Almighty Allah, who created the man with knowledge, intelligence, and wisdom. Peace and blessings of Allah be upon the Holy Prophet Muhammad (PBUH), Who is the best amongst the whole mankind and entreated his followers to delve for knowledge from crib to grave.

It is high time to express my gratitude and sincere thanks to my supervisor, **Dr. Zareen Akhter, Professor of Chemistry, Quaid-I-Azam university, Islamabad, Pakistan,** for her invaluable guidance, constant encouragement and generous co-operation and support at all phases of my work and inspiring me to achieve higher heights. I was exceedingly benefited by her vast knowledge and practical experience on the subject. I can't gauge my feelings with words and something inexpressible which is deep in my heart for my supervisor, whose constant interest and encouragement is unparalleled boon to me.

I am highly indebted to **Prof. Dr. Muhammad Siddiq, Chairman, Department of Chemistry** and **Prof. Dr. Amin Badshah, Head of Inorganic Section,** for providing me research facilities and conducive environment in the department.

I am greatly obliged **Dr. Muhammad Sirajuddin, UST Bannu** for providing facility for electrical properties analysis of samples. I am also thankful to **Dr. Muhammad Riaz, CECOS Peshawar** for providing SEM and mechanical properties studies.

I am also thankful to **National Development Complex (NESCOM), Pakistan** for study leave and lab facilities, required for completing my Ph.D. Special thanks are extended to **Mr. Zafar Iqbal Baig**, Director NESCOM for their valued guidance and admirable co-operation during my Ph.D work.

I extend my deepest gratitude to all my lab fellows **Mr. Ahmad Raza** and **Muhammad Adeel Asghar** for their cooperation and caring attitude, which made my stay in the department more pleasant, enjoyable, memorable and fruitful.

Last but, definitely, not the least, my heartiest gratitude and appreciation goes to my brothers and my wife, without their encouragement, sacrifices and prayers, I would have not been able to accomplish this goal.

(Muhammad Ahmad)

FOREWORD

The entire research work is divided into three chapters. Chapter 1 deals with general introduction of polyurethane elastomers, literature survey with particular emphasis on factors affecting thermo-mechanical properties of polyurethane elastomers, their structure property relationships and brief introduction of polyurethane based polymer matrix composites. Chapter 2 entails the experimental details and methodologies adopted for the synthesis and characterization of polyepichlorohydrins, polyurethane elastomers and their composites. Chapter 3 is segregated into three sections. Section 3.1 describes development of a novel method for the synthesis of bifunctional hydroxyterminated polyepichlorohydrins of different molecular weights and effect of different conditions on quality and yield of the product. Section 3.2 is devoted for the preparation of aromatic and cycloaliphatic diisocyanate based polyurethane elastomers from the synthesized PECH and extended with varying proportions of short-chain diols (1,4-butanediol, 1,6-hexanediol and cyclohexanedimethanol). Furthermore, characterization of the synthesized polyurethane elastomers is elaborated with the help of NMR, FT-IR, DSC, TGA techniques. The structure property relationship of the synthesized elastomers is also discussed in this section. Section 3.3 incorporates the preparation and characterization of polymer matrix composite materials derived from selected novel polyurethane elastomers. The variation in electrical and thermo-mechanical properties of the composites as a function of type and quantity of fillers is also described. The conclusions on the whole research work have been summarized at the end.

Abstract

Hydroxy terminated polyepichlorohydrins (PECH) of different molecular weights were synthesized using a novel catalyst and co-catalyst combinations. Different polymerization conditions like temperature, time and monomer addition rates exhibited pronounced effect on the molecular weight, polydispersity and functionality of the products. After optimization of the conditions, polyepichlorohydrins of three different molecular weights i.e., 1045, 2497 and 3521 daltons were selected for the preparation of their polyurethane elastomers (PUE). The DSC studies of the polyol displayed linear increase in glass transition temperature (T_g) with the increase in its molecular weight (-35.6 to -28.3 ^{o}C).

In second part of the present study two series of polyurethane elastomers were prepared by prepolymer method from polyepichlorohydrins (polyols) of three different molecular weights, aromatic (TDI) and cycloaliphatic (IPDI) diisocyanates and three chain extenders (1,4-butadiol, 1,6-hexanediol and cyclohexanedimethanol). The structural elucidation of PECH and its elastomers was carried out by FT-IR and NMR spectroscopic techniques. The change in molecular weight (polyol), type of diisocyanate, nature of chain extender and amount of chain extenders engendered significant effect on the surface morphology and thermo-mechanical properties of the resulting PUEs. Aromatic diisocyanate based elastomer (P25TDIDM10) exhibited optimum UTS (8.11 MPa) and elongation at break (511.7%) whereas cycloaliphatic diisocyanate elastomer (P10IPDIDM10) showed 8.58 MPa UTS and elongation at break (511.7%). All the polyurethane elastomers were stable up to 200 °C and were degraded without melting to constant mass above 450 °C. T_g of TDI based PUE was increased to -16 ^{o}C while in IPDI series it was further shifted to 7.98 ^{o}C.

In the third part of this research work, selective polyurethane elastomer P10IPDIDM10 was used, due to its superior properties, as a matrix for the synthesis of polymer based composites. Graphite, aluminium flakes and aluminium powder were used in different proportions (5-15%) as fillers in the polymer matrix composites. Incorporation of fillers enhanced the UTS with corresponding decrease in elongation at break, whereas in case of graphite, electrical properties of the composite were also improved. The present study revealed that the synthesized PUEs and composites were found promising candidates for various advanced applications.

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List of abbreviations

AFM	atomic force microscopy
BD	1,4-butanediol
DABCO	1,4-diazabicyclo-[2.2.2]-octane
DMPA	2,2-bis(hydroxymethyl)propionic acid
DP	polydispersity degree
DSC	differential scanning calorimetry
DTA	differential thermal analysis
DTG	differential thermogravimetric analysis
E%	elongation at break
ESI	electrospray ionisation
GPC	gel permeation chromatography
HDI	1,6-diisocyanatohexane
HDI	1,6-hexamethylene diisocyanate
HMDA	1,6-hexamethylenediamine
HMDI	hydrogenated MDI
HMDI	4,4'-dicyclohexyl methane diisocyanate
HS	Hard segment
IPDI	isophorone diisocyanate
PDI	Poly dispersity Index
IPN	interpenetrating polymer networks
MALDI-ToF	matrix-assisted laser desorption spectrometry
MDI	4,4' methylenebis(phenylisocyanate)
M_n	number-average molecular weight of polymer
MWD	molecular weight distribution
PCD	polycaprolactone diol
PDMS	poly(dimethylsiloxanes)
P_n	polymerisation degree
POG	poly(oxyethylene) glycol
PTMO	poly(oxytetramethylene) glycol
PU	polyurethane
PUE	polyurethane elastomer
PUU	poly(urethane urea)
SAXS	small angle X-ray scattering
SEM	scanning electron microscopy
TDI	toluene diisocyanate
TEA	triethanolamine
T_g	thermogravimetric analysis
Tm	melting point
UTS	ultimate tensile strength
WAXS	wide angle X-ray scattering
WAXS	wide angle X-ray scattering

Chapter No. 1
INTRODUCTION AND LITERATURE REVIEW

Polyurethanes are the synthetic organic macromolecules which have urethane group (carbamate ester) in their backbone structure. They are prepared by the step growth poly-addition reaction of a polyol (molecule containing two or greater than two -OH groups) with a diisocyanate and chain extenders in the presence of an appropriate catalyst. Otto Bayer and his co-workers were the first to discover polyurethanes in 1937 at I.G. Farben Germany[1, 2]. Polyurethanes represent a family of polymers rather than a single polymer and ranked 5 after polyolefins, polyvinyl chloride, polystyrene and diene rubber. These polymers are produced with diverse properties, from foams to fibres, and can be used in numerous applications. Scheme 1.1 represents the reaction which leads to the formation of a urethane linkage.

$$R-N{=}C{=}O \quad + \quad R'-\overset{H_2}{C}-OH \quad \xrightarrow{\text{Catalyst}} \quad R-\overset{H}{\underset{}{N}}-\overset{\overset{O}{\|}}{C}-O-\overset{H_2}{C}-R'$$

Isocyanate Alcohol Urethane
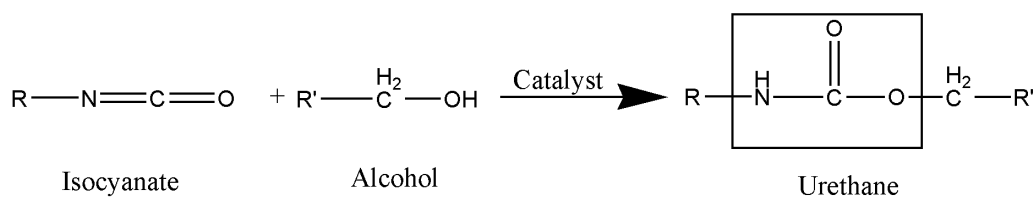
Scheme 1.1: Typical reaction of urethane formation

These materials have engrossed the extensive attention of material researchers due to the ease of processing and indefinite architectural versatility that can be exploited for the optimization of properties using different types and quantities of polyols, diisocyanates and chain extenders. Outstanding flexibility of the chemistry used during the production of polyurethanes accounts for the availability of many commercial products in market. They can be regarded as high-performance polymers having applications in almost every field of life ranging from domestic to industrial fields, from rigid or flexible frivolous foams to tough and inflexible elastomers like adhesives, elastomers, composites, fibres and foams etc.[2, 3, 4]. Some of the applications of polyurethanes are illustrated in Table 1.1.

Table 1.1: Polyurethane applications [3]

Type	Applications
Rigid foam	- Thermal insulation of storage tanks, buildings, equipments, pipelines and refrigerators. - Buoyancy aids (flotation equipments like boats) - Equipment packing - Furniture articles - Housings
Flexible foam	- Household furniture (bedding) - Automotive seating - Cushioning - Textile laminates
Semi-rigid and low density structural foam	- Automotive interior trim components, steering wheels and head rests - Furniture components - Sport goods (skis and surf boards)
Elastomers	- Shoe soles - Body panels of vehicles - Gear wheels and Rollers - Conveyors - Sealants (construction and automotives) - Fibers

1.1   Polyurethane elastomers

Elastomeric materials have long polymeric chains with high degree of mobility along with flexibility within a solid network structure. The response of elastomer to external force is intra-molecular as a whole. When external stress is applied, the long chains alter their configuration resulting in deformation of material due to greater mobility of polymeric chains. The long chains are chemically attached to solid structure which prevents the relative flowing of chains under external stress. When force is applied to elastomers, it shifts on chains and elastomer immediately restores to its original dimension after removal of external force. Generally, the specified elongation for elastomers is greater than 100%.

Polyurethane elastomers (PUEs) are multipurpose polymers which can be extruded, injected, moulded and recycled [5, 6]. These elastomers are lighter and offer high stress recovery and resistance to harsh environmental conditions. They are very flexible, elastic and resistant to impact, abrasion and altering weathers.

Due to the presence of polar hydrogen bonded groups in polyurethanes, strong intermolecular forces restrict the motion of polymeric chains from sliding over each other resulting in a material of higher modulus. Thus, in many cases reinforcing

additives (fillers) are not obligatory to attain the superior properties as in other elastomers. PUEs have been the foremost polymeric materials holding elasticity like rubber along with thermoplastic characteristics [7]. In case of high molecular weight polymers in linear polyurethanes, entanglements of chains take place due to intertwining with the available space giving characteristic molecular structure. A high molecular weight polymer lacking cross-links does not possess permanent intermolecular bonds thus it melts at a particular temperature and shows rubber-like behaviour. When the material is highly cross-linked, it affects the elastic response as well as melting behaviour of the material[8].

PUEs are $(XY)_n$ type block co-polymers with flexible (soft) and hard (rigid) units connected through urethane bonds. The soft segment is incorporated by polyol, which imparts extensibility and flexibility to the elastomer while hard segment is contributed by multi-functional isocyanates and low molecular weight diols/ diamines (chain extender) imparting the pseudo crosslinking which gives mechanical strength to the elastomeric materials. During the manufacturing of thermoplastic elastomers, all components used are bifunctional. Bifunctional raw materials ensure the formation of high-molecular weight linear chains[9, 10]. However, one of the components must have higher functionality for the preparation of thermoset elastomers. The elasticity of PUEs differs from rubber due to the difference in nature of the physico-chemical bonding of polyurethanes. Chains of the polyurethane elastomer have numerous groups of high polarity where hydrogen bonding takes place in entire matrix whereas, in rubber a number of lengthy intertwined chains with peroxide or sulphur links are present throughout the matrix.

The elastomeric properties of polyurethane materials are due to multi-block structure of phase-separated systems[11]. The incompatibility of hard and soft segments at room temperature results in micro-phase separation. The extent of crystallinity, differences in polarity and melting points of both segments are the basic agents for this phase separation. The soft segments form an elastomeric matrix imparting elastic properties while the hard segments having multifunctional tie points are responsible for the rigidity of the matrix. The elastomeric properties of polyurethane materials also depend upon the average functionalities of the starting materials especially polyol, chain extender and diisocyanate. A typical chain of linear PUE is composed of three segments diisocyanate, short-chain diol and long chain polyol segment. Figure 1.1 illustrates the basic structure of PUEs.
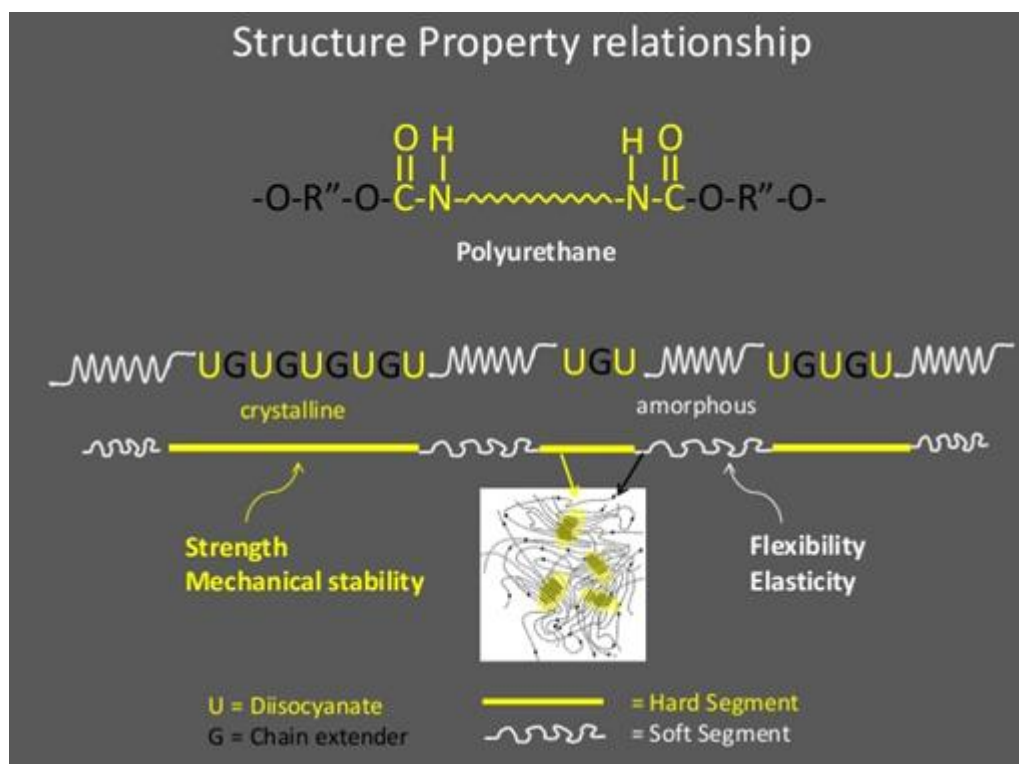
Figure 1.1: **Basic structure of PUE**

1.1.1 Basic ingredients of polyurethane elastomers

PUEs are the reaction product of multifunctional polyols and diisocyanates which are ultimately linked by chain extenders in presence of a suitable catalyst. Polyol is an oligomer having active hydrogen atoms. The backbone of polyol may contain ether, ester or diene functional group terminating with hydroxyl group. Diisocyanate may be an aromatic, aliphatic or cycloaliphatic molecule having two -NCO groups. Chain extender is a short-chain diol. Catalyst used is mostly an organometallic compound of transition elements which enhances the rate of reaction of urethane bond formation. Following are the details of these basic components.

1.1.1.1 Polyol

Polyols are macromolecules having terminal hydroxyl (-OH) groups with molecular weights ranging from 150 to 10000 Daltons[12]. Its structure plays the major role in controlling the properties of PUs. A variety of polyols are employed to manufacture the different polyurethanes; however most widely used PUs mainly belong to two classes i.e. hydroxyl functional polyesters and polyethers. Hydroxyl terminated polybutadiene is one of most widely used polyol in solid rocket propellant applications[13]. Polyether polyols are dominating in the polyurethane market

because of their low cost and acceptable properties. Equivalent weight, hydroxyl functionality, reactivity and compatibility with the ingredients employed in the polyurethane formulations are the key characteristics of the polyols. In some specific applications, blends of polyols with diverse chemical nature are also used[14]. Figure 1.2 shows the polyols with different backbone structures.

The polyether polyols include propylene oxide homo-polymers or random block co-polymers with ethylene oxide. Both ethylene and propylene oxide addition polymerization is possible with either basic (anionic) or acidic (cationic) catalysis. Poly(tetramethyleneglycol), a special class of polyether polyols, is synthesized with cationic ring opening polymerization method[15].

In case of polyester based polyols, aromatic or saturated aliphatic dicarboxylic acids and diols react to form macromolecules[16]. A conventional hydroxyl terminated polyester is synthesized by the reaction of adipic acid and an excess of diols like neopentyl glycol, ethylene glycol, 1,6-hexanediol, 1,4-butanediol, or a combination of these diols. Such polyol is crystalline with 58-60 °C melting range. Furthermore polycaprolactones and aliphatic polycarbonates are two special classes of polyesters of commercial interest[17]. Polycaprolactones are prepared by ε-caprolactone and a bifunctional initiator (1,6-hexanediol).

Polycarbonates show tremendous hydrolytic stability. They are manufactured from diols (1,6-hexanediol) or by transesterification with lower alkyl or aryl carbonates e.g., diphenyl or diethyl carbonate.

Hydroxyterminated polybutadiene (HTPB)   Polyterahydronfuran (PTHF)

Polytetramethylene adipate (PTMA)   Polycarpolactone(PCL)

Polyethylene oxide (PEO)   Polypropylene oxide (PPO)   Polytetramethylene oxide (PTMO)
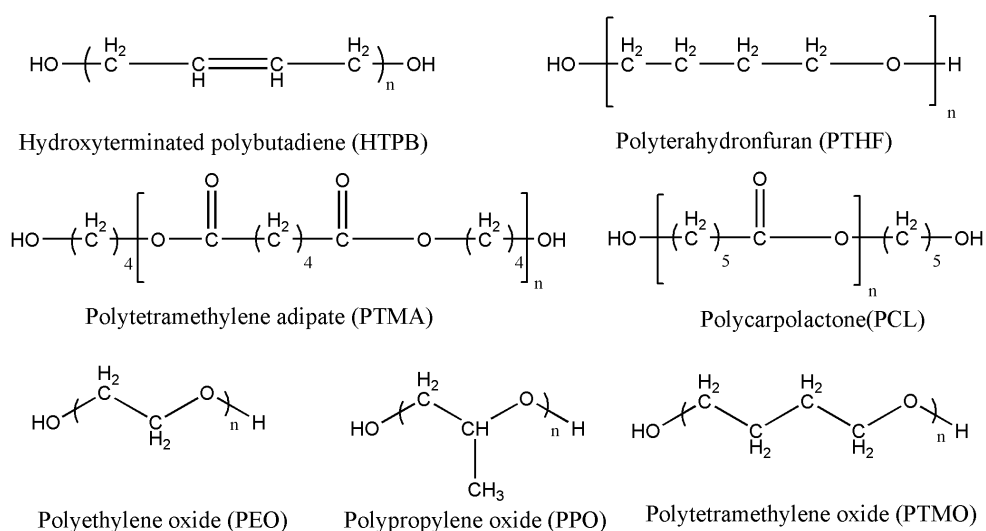
Figure 1.2: Structure of different Polyols

Another type of versatile class of polyols is of vegetable origin like wood flour, starch, castor oil, lignin, cellulose, natural rubber, glucose or fructose and molasses that are also used to produce biodegradable PUEs[18, 19, 20].

1.1.1.2 Isocyanates

Isocyanates are extremely reactive organic molecules which readily react with any other molecule that contain active hydrogen[21]. These reactions build the polyurethane networks which are most important in the formation of elastomers. Several aliphatic and aromatic diisocyanates are commercially available. Diphenylmethane diisocyanate (MDI) and toluene diisocyanate (TDI) are utilized in most of the commercial polyurethanes. TDI used in different applications is a mixture of 2,4- and 2,6- isomers in 80:20 ratio. Based on two diisocyanates purified monomeric MDI and polymeric MDI, several types of products depending upon their functionality are present in international market. The synthesis of polyisocyanate leads to a variety of mixtures having range of isocyanate functionalities. Diisocyanates are mostly used for making elastomers, while higher functionality polyisocyanates e.g. MDI are required for the manufacturing of rigid foams and binding materials.

Some commonly used aliphatic diisocyanates are 1,6-diisocyanato-hexane, 4,4́- diisocyanatodicyclohexylmethane (HMDI) and 1-isocyanato-3- isocyanatomethyl -3,5,5-trimethylcyclohexane (IPDI)[22]. Figure 1.3 lists some commonly used isocyanates for polyurethane synthesis.

Isophorone diisocyanate (IPDI)   Toluene diisocyanate (TDI)   Hexamethylene diisocyanate (HDI)

4,4'-Methylenediphenyl diisocyanate (MDI)   4,4'-Dicyclohexyl methane diisocyanate (HMDI)

1,5-Naphthalene diisocyanate (NDI)   *p*-Phenylene diisocyanate (PPDI)   Cyclohexyl diisocyanate (CHDI)
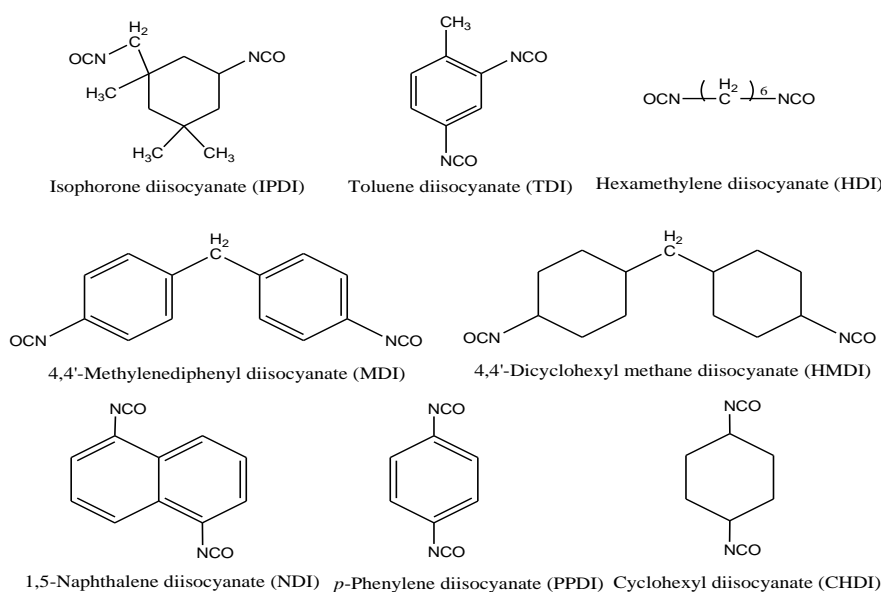
Figure 1.3: Various isocyanates used for making polyurethanes

1.1.1.3 Chain extenders

Short-chain organic molecules with two or more -OH groups (chain extenders) take part in the development of appropriate polyurethane morphology[23]. The choice of chain extender along with diisocyanate dictates particular characteristics to hard segment that governs the physical properties of polyurethane. Linear diols are most widely used class of chain extenders which includes 1,4-butanediol, ethylene glycol, and 1,6-hexanediol. They form well defined crystallined hard segments with isocyanates. Figure 1.4 lists some common chain extenders.
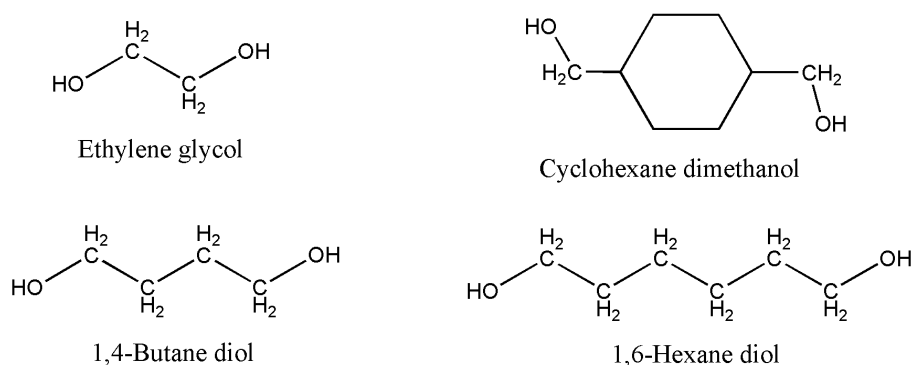
Figure 1.4: Structures of common chain extenders

1.1.1.4 Catalyst

A catalyst changes the rate of a reaction so they are considered as the controlling agent of the polyurethane reactions[24]. Catalysts also allow the reaction to take place at lower temperatures by decreasing the energy of activation of reaction. Tetravalent organo-metallic molecules of tin metal with general formula $R_nSnX_{(4-n)}$ also enhances the rate of urethane linkage formation[25]. R represents the cycloalkyl, alkyl or aryl group and X donates a halogen or a carboxylate functional group. Catalytic activity of such organometallic molecules is due to their ability to form complex with both isocyanate and hydroxyl functional groups[26, 27]. The commonly used catalysts in polyurethane industry comprise tertiary amines[28] e.g. triethyl amine (TEA) and organotin compounds[29], like dibutyltin dilaurate (DBTDL) and stannous octoate (Figure 1.5).
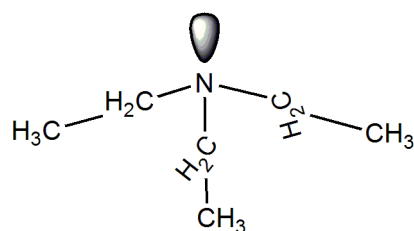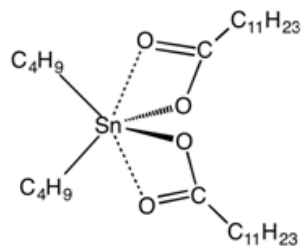
Triethyl amine (TEA)   Dibutyl Tindulurate (DBTDL)

Figure 1.5: Structures of commonly used catalysts used for polyurethanes

1.1.2 Chemistry of polyurethane elastomers

The chemical reactions involved during the synthesis of polyurethanes are principally based upon the reactivity of isocyanates. The higher reactivity of isocyanate towards nucleophilic reagents (electron rich system) is due to the pronounced electrophilic nature of the carbon which is forming double bonds with nitrogen and oxygen atoms[30, 31]. The attachment of -NCO group with aromatic molecules gives rise to the resonating structures which further enhance the reactivity of this functional group. The negative charge shows the delocalization either on the oxygen or nitrogen atom or even on the R group when it is aromatic. This delocalization explains the high reactivity of aromatic isocyanate than an aliphatic isocyanate.

Overall chemical reactions that may occur during polyurethane synthesis are shown schematically in Figure 1.6. Following are the details of these chemical reactions:

(i) The nucleophile having hydroxyl group (-OH), on reaction with the isocyanate group (-NCO), forms **urethane bond** (carbamic acid ester). Following is reactivity order of different hydroxyl groups:

Phenol< secondary hydroxyl< primary hydroxyl

This addition reaction is reversible and the isocyanate group can be recovered at higher temperatures[12, 32, 33].

(ii) The reaction between the amine group ($-NH_2$) of nucleophile reacts with the isocyanate group (-NCO) of electrophile to form the **urea linkage**.

(iii) Water is an additional entrant to react with isocyanate group. It is a specific case of -OH and -NCO reaction that primarily forms less stable **carbamic acid** which rapidly breaks down to corresponding amine and carbon dioxide. This

lately born amine reacts instantaneously with the remaining isocyanates present in the system resulting in the formation of the **urea linkage**. These isocyanates cannot be stored in a humid environment due to high reactivity with water. Moreover, reaction vessel is maintained moisture free to prepare high molecular weight polyurethane elastomer.

(iv) During the reaction of polyurethane, hydrogen of the urea and urethane linkages remain active so they have capability to attack the isocyanate under the particular conditions resulting in the formation of a **biuret** and an **allophanate**. Biurets and allophanates are favourably developed at 120-150 °C and 100-150 °C, respectively. These new linkages are relatively less stable thermally so they dissociate into parent compounds above 150 °C [34, 35, 36, 37, 38]. The formation of biurets and allophanates also result in the cross-linking of polyurethane.

(v) Isocyanates have the capability to react with each other (dimerize and trimerize) in the presence of a basic catalyst to give **uretdione** and **isocyanurate** respectively. There is probability of formation of stable isocyanurates while heating aliphatic or aromatic isocyanate[39, 40]. Only aromatic isocyanates undergo the dimerization depending upon the stereochemistry and the position of the substituted groups at the aromatic ring. For example, TDI does not dimerize at any temperature due to isomerism, while MDI has the tendency to dimerize even at ambient temperature to form uretdione and at temperature greater than 150 °C it readily undergoes a reversible reaction. However, in case of aliphatic and aromatic isocyanates the isocyanurates formed by heating are very stable and the reaction cannot be driven back easily[40, 41, 42, 43].

(vi) **Carbodiimides** formation is another important self-reaction of isocyanate which can further react reversibly with an isocyanate group yielding a **uretoneimine**[41, 44, 45, 46]. Mostly during synthesis of polyurethane, a slight excess of diisocyanate is used which promotes the cross-linking at higher temperatures due to the dissociation of allophanate and biuret bonds (thermally less stable moieties). Formation of **Carbodiimides** in the presence of catalyst at room temperature or at high temperature in absence of catalyst by the condensation reaction is also evident. On further reaction with an isocyanate these carbodiimides also form an **uretoneimine**[43, 44, 47, 48].
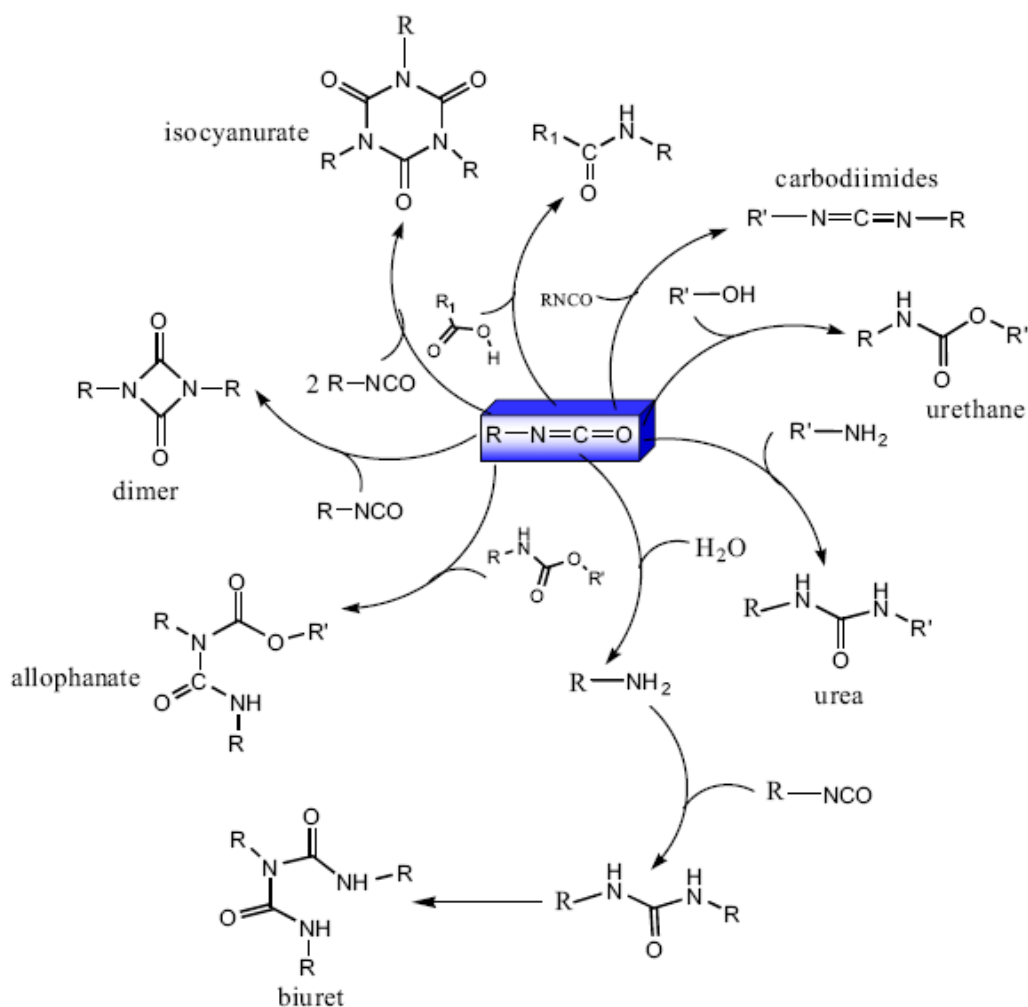
Figure 1.6: Schematic illustration of overall chemical reactions that may occur during polyurethane synthesis

1.1.3 Synthesis of polyurethane elastomers

PUEs are formed by polyaddition reaction of hydroxyl (-OH) and isocyanate (-NCO) groups [37]. A large number of precursors can be used to produce a various final products of tailored properties[47, 49]. The selection of basic ingredients like long-chain polyols, diisocyanates and chain extenders greatly affects the crystallization capability of soft and hard segments. Precision of stoichiometry of the reacting molecules is very important during synthesis of PUEs because its slight change limits the molecular weight of the resulting polymer.

Mostly PUEs are cured at 60-80 °C, phase mixing and major chemical reactions take place at this temperature[50]. In order to obtain the optimum mechanical properties, post-curing is recommended after preliminary curing of the mixture. Post-curing conditions are changed with the chemical nature of PUE raw materials. Mostly storage of the synthesized material at ambient temperature for 2-3

weeks is sufficient to complete the curing process. A post-cure at 110 °C for 8–16 hours in hot air circulating oven is often sufficient to induce specific properties in the synthesized material[51].

Thermoplastic PUEs can be prepared either through the one-shot[35] or prepolymer methodology[36]. Following are two major techniques used for the preparation of polyurethane elastomers.

1.1.3.1 Prepolymer technique

In this technique, a diisocyanate is reacted with a polyol having NCO/OH ratio 1 to produce a structure of free terminal -NCO groups called prepolymer. Then chain extender is added to this prepolymer resulting in high molecular weight polyurethane. Scheme 1.2 illustrates the prepolymer method of polyurethane production.
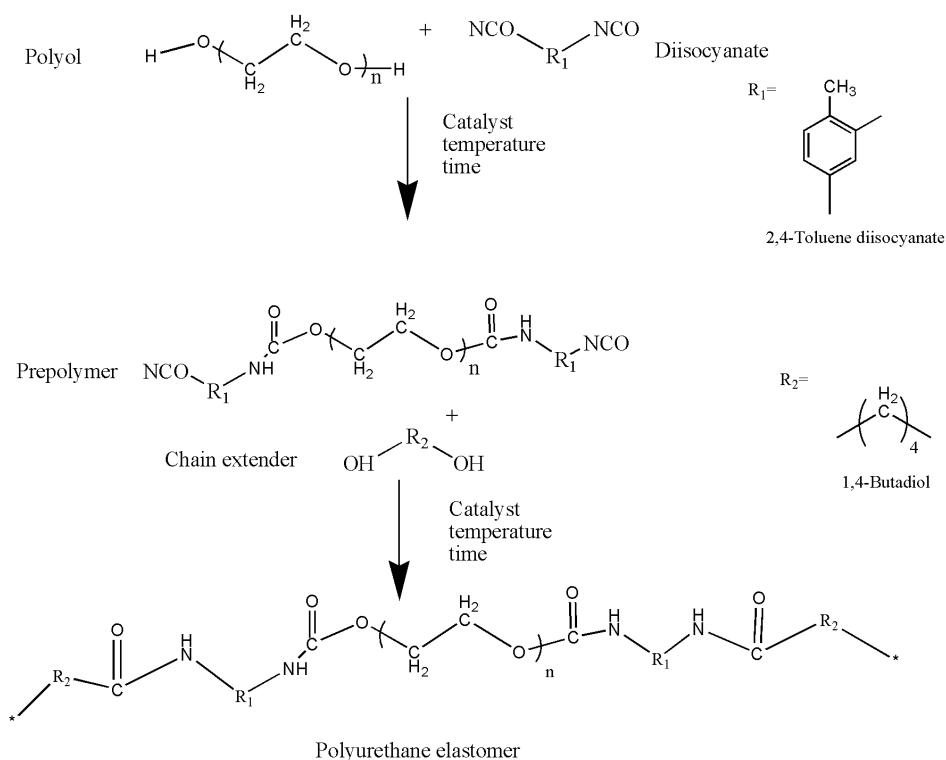
Scheme 1.2 Prepolymer technique

1.1.3.2 One-shot technique

This technique involves the mixing of all the basic constituents of the PUE (polyol, diisocyanate and chain extender) composition at the same time in one step. At the initial stage, the mixture remains in liquid state even after partial reaction between isocyanate and active hydrogen compound. Extremely efficient mixing is essentially

required in this technique to get the elastomer of homogeneous properties. Scheme 1.3 illustrates the one-shot technique.
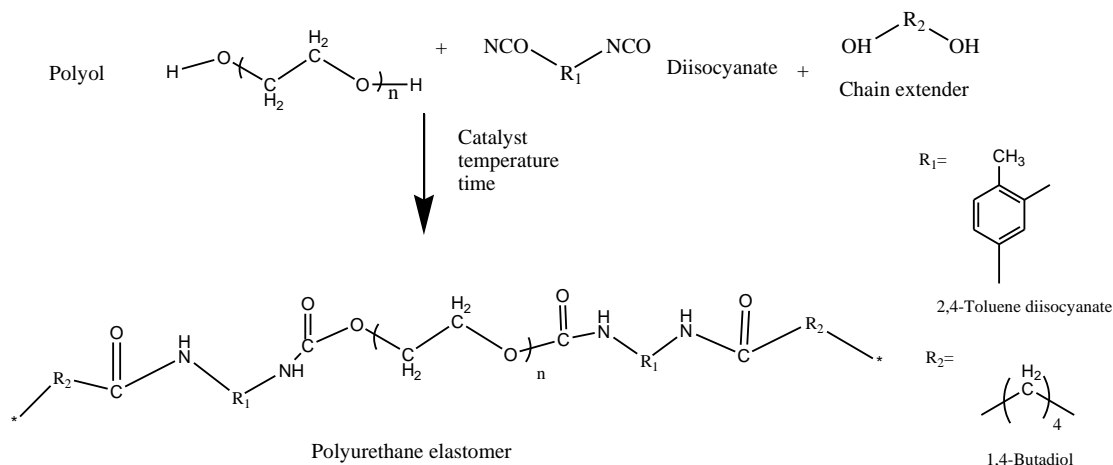
Scheme 1.3: One-shot technique

1.1.4 Structure property relationship in PU elastomers

For the understanding of the structure property relationship of PU elastomers, it is mandatory to study the chemical and physical interactions present in the matrix. PUE is a multiphase system; its matrix morphology directs the final properties of the elastomer which can be tailored by controlled variation of the phase structure. In PU chains, hard and soft segments are arranged alternately and structure of a polyurethane molecule is mainly arrangement of polymeric chains in the condensed phase[37]. When both hard and soft phases become quite immiscible, separate glass transition temperatures (T_g) of both phases are observed in PU elastomers. Hydrogen bonding can introduce hard domains within the soft phase resulting in the dispersion of hard phase in the polymer matrix[52]. In most of the cases, the urethane groups due to high polarity join the soft and hard segments collectively thus forming a cluster at the domain interphase. This interphase is formed by the dispersion of hard segments inside the domains of soft segments. Figure 1.7 illustrates the dispersion of different phases within PU matrix.
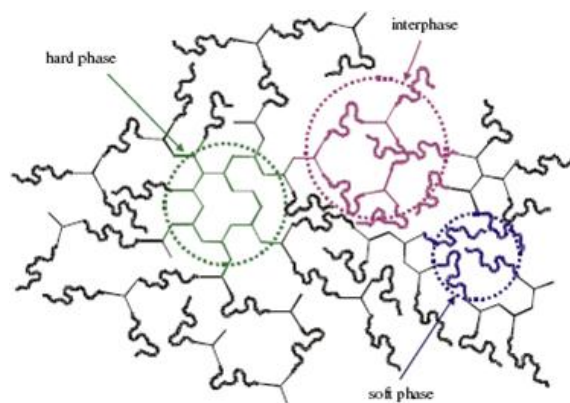
Figure 1.7: Hypothetical structure of PU showing hard and soft segments connected by interphase[42]

The hard domains give strength to PUE in two ways. They function as non-covalent cross-linking moieties as well as reinforcement within the polymer chains to restrain the motion of chains of soft segment. The soft segments provide flexibility and elastomeric property, whereas hard segments provide dimensional stability[45]. Chen-Tsai *et al*., observed a hard domain of about 11 nm with inter-domain distance of 13 nm in HTPB and TDI based polyurethane[46].

In a PUEs, hard segment is solid and the soft segment is liquid at ambient temperature and both chemically bonded phases are dispersed in each other by block polymerization. Above the crystalline melting temperature (T_m), both the segments in PUEs are transformed into liquid form losing the rigidity and strength of polymer[48]. When the molten PUE is cooled, the hard phase becomes solid and the PUE attains its elasticity and strength thus retaining most of its characteristics and each phase regains its specific glass transition temperature (T_g) or crystalline melting temperature (T_m). T_g and T_m determine the working temperature range of the specific elastomer. These polymers show three recognizable regions:

I.   At very low temperature (-70 to -40 °C) PUE is stiff and brittle because at this temperature both phases are in solid form.

II.   Above glass transition temperature, soft segment is converted into liquid phase giving elastomeric properties to the matrix.

III. With the increase in temperature the modulus remains relatively constant until the temperature where the hard phase softens or melts. At this temperature polymer becomes a thick viscous liquid.

Chemical nature (composition and structure) and molecular weight of the polyols used for preparation of PUE have a pronounced impact on the degree of phase

separation[53]. Generally, phase mixing of PUEs derived from polyester polyol is greater than that of a polyether based PUE because of stronger hydrogen bonding in polyesters. In PUEs both hard and soft phases are amorphous or partially crystalline[54, 55]. The phase separation is also directed by the M_n of the basic raw material. Higher the molecular weight, greater will be the phase separation[51].

Polyurethanes are comprised of several moderately polar groups (urethane linkage) which engage in various interactions with one another [56] resulting in matrix phase separation[57, 58]. These phase interactions and phase separations occur at a range of length scales including nanometre dimensions[59]. The chemical composition steers the extent of phase separation, size and properties of the scattered phase (hard segment). The characteristics of the polymer are affected by molecular weight and phase separations e.g., ultimate tensile property is dictated mainly by phase structure. The precise modification of composition provides a means to control structure and ultimately properties of the synthesized polyurethanes.

Thermodynamically phase separation in various materials arises when free energy of mixing (ΔG_m) is positive [60]. The free energy is expressed in the form of entropy (ΔS_m) and enthalpy (ΔH_m) of mixing given in following equation.

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

T donates absolute temperature of the system.

$\Delta H_m > T\Delta S_m$ is the condition for domain formation (i.e., phase separation) with a positive value of the free energy of mixing.

Entropy of mixing and temperature is always positive, therefore $-T\Delta S_m$ will always be negative in PUE systems and this term reaches zero as the molecular weights of both domains become large along with the decrease in temperature. In PUEs, the presence of high molecular weight soft segments and low temperature supports the phase separation.

Superior mechanical properties in polyurethane systems are achieved when both segments are compatible to some extent with each other[61]. Hard and soft segments of PUEs are only compatible to the extent that the interfacial bonding is developed directly on both phases, as a consequence a small degree of mixing takes place[62]. Thermodynamically, phase separation of the polyurethanes originates from the minute entropy gained by mixing various types of polyol chains. Only polyurethanes with zero or negative enthalpy of mixing form single phase. In PU

systems, small scale phase separation occurs because of the covalent bond which links the multiple blocks of polymers inducing re-arrangements in groups of micro-domains[63, 64].

Mutsuhisa Furukawa synthesized PUE by reacting polyoxytetramethylene glycol (PTMG) with MDI and finally chains were extended by 1,4-butanediol and 1,1,1-trimethylolpropane by adopting the pre-polymer methodology. He investigated the micro-phase separation of ultrathin films and bulk polyurethane elastomers. The extent of microphase segregation enhanced with the increase in quantity of chain extender (butanediol) that was evident from atomic force microscopy (AFM). The AFM micrographs clearly showed hard segments enclosed by soft segments throughout the matrix[65]. Piotr Kro experimentally found increase in tensile strength, hardness and abrasion resistance of the synthesized PUs with the use of polyols with lower number average molecular weights[66]. The improvements in the arrangement of both hard and soft domains were achieved because of increased intermolecular interactions within the polymer structures. When these interactions were weakened, the elongation increased and the impact strength was dropped. Aneja and Wilkes found the evidence or even nano scale morphology in a series of PUs containing hard segments(1-4 repeating units) through AFM[67]. Samuels *et al.,* also observed spherulitic morphology through SME and small-angle light scattering[68].

Blackwell *et al*., observed a crisscross chain in PUs obtained from 1,4-butanediol and MDI and found that benzene rings in MDI were present at 90° angle to one another[69]. But in polyurethanes which were synthesized from 2,6-TDI and 2,4-TDI isomers were arranged in the same plane due to the orientation of urethane groups and benzene rings bonded to these rings[70]. This vast structural diversity of polyurethane chains enhances both inter molecular (within individual macro-molecules) and intramolecular interactions (among macro-molecules).

After the phase separation crystallization takes place in polyurethanes. This can be attributed to the organization of different groups in a regular manner in crystalline regions, which affect many properties. There is an increase in hardness, tensile strength and melting point whereas decrease in the solubility, elongation, flexibility and mobility. These variations in physical properties are due to presence of various proportions of amorphous and crystalline domains in the polyurethane structure. The amorphous domains consist of random and intertwined coils, while in the crystalline domains, the polymer is firmly crowded in an ordinary pattern[4, 71].

Hydrogen bonding and Vander Waals forces hold these crystalline and amorphous regions with each other. Diisocyanates and chain extenders mainly contribute for the development of crystallinity in polymer matrix through urethane linkages[39].

The intermolecular interactions (secondary forces) between polymeric chains have a very important role in solid polymer properties and confer the capability to resist mechanical, thermal, chemical, and electrical forces. These secondary forces include Van der Waals forces (0.5-2 kcal/mol), hydrogen bonds (3-7 kcal/mol), london dispersion forces, permanent dipole interaction forces (1.5-3 kcal/mol), and ionic interactions (10-20 kcal/mol)[72]. All these forces give the cumulative cohesive energy. The nature of polyol chains has an intense effect on the physico-mechanical properties of the resulting PU, because the repeating units have various cohesive energies of functional groups. A stronger cohesive energy, leads to higher physico-mechanical properties.

The urethane, ether and ester groups are characterized due to their comparatively high cohesion energy due to their stable dipole moments which influence the overall polymer cohesion energy resulting in development of strong intermolecular forces (hydrogen bonding)[73]. At room temperature, polymer is present in solid state and almost all the hydrogen atoms present in –NH– functional groups in polymer matrix are involved in hydrogen bonding. In the case of polyester-urethanes these groups (–NH–) are proton donors in the urethane structure, whereas the hydrogen acceptors are oxygen atoms in the ester group (–COO–) or ether oxygen (–COC–) in polyether–urethanes within the urethane C=O group[74].

IR spectroscopy confirmed the presence of hydrogen bonding in polyurethanes as absorption peaks of carbonyl groups and –NH groups are appeared at lower frequencies i.e., at 1703–1710 cm^{-1} and 3340–3260 cm^{-1} instead of 1730–1740 cm^{-1} and 3445–3450 cm^{-1}, respectively[75, 76, 77, 78]. The optimum molecular geometry and length of bonds and energies of bonds based on these observed shifts were calculated using molecular orbital methods [70, 79, 80]. The length and energy of the hydrogen bonding in the hydrogen atom of -NH group and the carbonyl group (-CO-) of urethane is dependent on the structure. Figure 1.8 illustrates the schematic arrangement of intermolecular forces in PUE. Interaction between oxygen and hydrogen atoms imparts the conformers cis-cis (structure a) and trans-trans (structure b) the most stable hydrogen bonding. Along with this hydrogen bonding, inter-molecular interactions between the ether oxygen and urethane can be established in

polyether based urethanes (e). These additional hydrogen bonds between the carbonyl of ester group and urethane are also formed in polyester based urethanes (f).
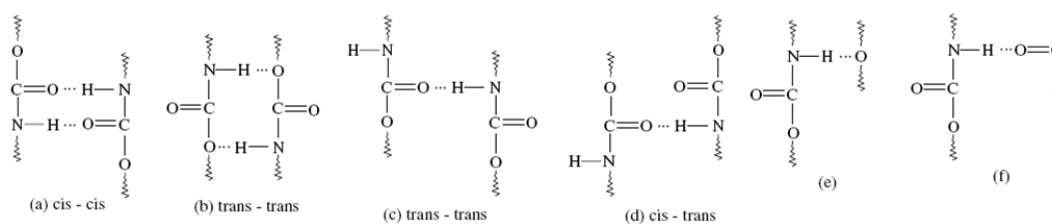
Figure 1.8: Arrangement of intermolecular forces in PUE

Blackwell *et al*., observed that the hydrogen bond between urethane groups was linear and the angle of digression from linearity was found 22.0±6° with the bond length of 2.98±0.05 Å[69]. Above 75 °C temperature, the hydrogen bonds start to lose their strength[53]. Higher hydrogen bonding and increased numbers of polar groups in polyurethanes impose substantial restrictions to chain movement imparting these polymers greater Young's modulus, high strength with low creeping at required operational temperatures[81].

1.1.5 Thermal stability of polyurethane elastomers

The physical properties of PUEs are affected by the change in temperature that are reversible prior to the degradation temperature. With the variation in temperature, major changes occur in modulus, hardness, tensile strength, torsion stiffness and resilience. The temperature tolerance of the PUE for a specific application depends upon the T_g of hard and soft segment of the PU matrix. The service temperature range of the elastomer ranges from the T_g of the soft segment (minimum working temperature) to the T_m or T_g of the hard phase (maximum working temperature). The accurate temperatures are dependent on the nature and structure of the final polymer matrix. As a general rule lower service temperature is above the T_g of the elastomer and the actual maximum working temperature is less than the T_g or T_m of the hard segment[47].

When the PUE is heated from room temperature to 110 °C there is corresponding short-term decrease in its physical properties[82]. In case of polyether-based polyurethane the properties are decreased about 50% of the original at 70-80 °C. Whereas at 110 °C, physical properties drop to about 20% of the original properties so a secure working temperature of 75-80 °C is recommended for this

system. By the use of polyisocyanates this working temperature is increased in the polyurethane.

The secondary thermal effects begins at temperatures above 80 °C and there is a steady decline in physical properties over the time and the rate of change increases at higher temperatures[32]. Polyester based polyurethanes are relatively more stable than polyether based polyurethanes and poly butadiene based materials. The oxygen in the air under the influence of heat reacts with ether group in the soft segment thus adversely deteriorating the properties at higher temperatures.

Thermoplastic polyurethanes can withstand –40 °C to 80 °C in long term use while the tolerance of temperature may increase up to 120 °C or higher in case of short term exposure[83]. Type and amount of chain extender, proportions of hard segments and diisocyanate are the major factors responsible for polyurethanes capability to work at higher temperature[84]. The stability of the urethane groups against temperature depends on the nature of isocyanate and polyol terminal hydroxyl groups. Many investigators studied the thermal transitions like glass transitions, melting and phase segregation. Born L working on PU based on a polyester diol, butanediol and MDI analyzed the thermal response by using differential scanning calorimetry (DSC) with respect to engineering properties[84]. It was found that with the increase of hard segment percentage, the T_g was broad and shifted towards higher temperatures because of higher concentration gradient of hard segments present in proximity of the soft phase interface.

At further higher temperatures chemical degradation of the polymer starts. The structures of the isocyanates and chain extenders which forms hard segment dictates the thermal stability of a PU [33, 85, 86, 87, 88]. The majority of PUs starts to decompose slowly at 150–200 °C whereas at a higher temperature (200-250 °C) rate of decomposition also increases. The general reaction of urethane group decomposition is demonstrated in Scheme 1.4.

Thermal degradation of ether based PUs principally undergoes an oxidative process. Thermo-oxidative stability of ester-based PUs are generally higher as compared to the ether-based counter parts[90, 91].

$$\underset{\underset{O}{\parallel}}{R\text{-}NH\text{-}C\text{-}OR} \xrightarrow{\triangle} \begin{cases} RNCO + HOR \\ RNH_2 + CO_2 \quad + olefin \\ RNH_2 + CO_2 \end{cases}$$
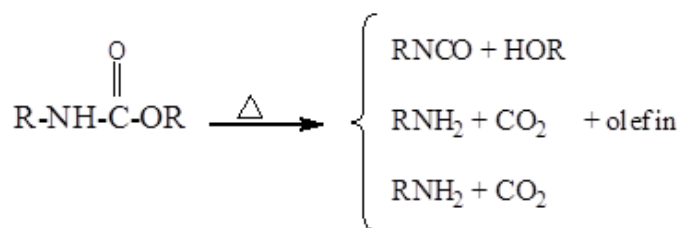
Scheme 1.4: General reaction of urethane groups decomposition[89]

Harris *et al*., performed aging studies of HTPB/IPDI polyurethane rubber by utilizing O^{17} labelling of degradable moieties[91]. It was observed that the major degradation appeared in the unsaturated butadiene segment of the hydroxyl terminated polybutadiene. Nagle *et al*., further concluded in his studies that HTPB/IPDI polyurethanes provided substantial confirmation of the degradation of the polybutadiene segment by an alternative technique i.e., transmission infrared spectroscopy[92]. Based on the values of cohesive energies and dissociation energies of the bonds involved in the polyurethane structure, it may be possible to establish the following relative order regarding the thermal stability of polyurethanes function of the polyol structure:

polybutadiene polyols < polyether polyols < polyester polyols>aliphatic polyols < cycloaliphatic polyols < aromatic polyols

Thermal decomposition of PUs takes place in multi-stages and its degradation pattern depends upon on the nature of hard and segments[93]. Usually primary degradation stage is swift but with the increase of soft segment contents degradation rate decreases. The increase of hard segment contents within the polyurethane matrix makes them more prone to degradation. It indicates that the degradation is kicked off mainly within hard segments. Higher concentration of urethane groups in phenol derivatives is the controlling factor which offers considerably decreased thermal stability. It was due blockage of isocyanate prepolymers by the phenols in the initial phases of development of polyurethane stoving coatings[94]. Enhancement in the rate of decomposition was witnessed at the last phase when the content of hard segments was lowest[82]. The main process involved in the course of degradation is de-polymerization. PUs decompose to produce diisocyanates and polyols i.e., its parent substances.

The presences of aromatic units in hard segments often show stabilizing effect and thus less amount of volatile degradation products are liberated. Unreacted diisocyanate go through secondary reactions and form more stable urea and

isocyanurate moieties[95]. Presence of aromatic units in polyol backbone has pronounced effect on properties of final product. It makes the structure more rigid along with increase in strength of the intermolecular forces , T_g and T_m become higher resulting in decrease of degradation rate and product becomes more stable[96].

1.2   Polyether polyols for polyurethane elastomers

In polyurethanes polyol is the main ingredient that has active hydrogens which readily reacts with the -NCO group of the isocyanate[97]. The first ever polyol was made from tetrahydrofuran and is commercially available since 1957. Today propylene oxides based polyols are most widely used in industry. Its polymerization can be carried out by using basic or acidic catalyst, however mostly the commercial production is achieved with basic catalyst. The epoxide ring opens at less sterically hindered position. Polyether polyols are reaction product of an organic oxide (ethylene oxide or propylene oxide or epichlorohydrin, 1,2-butylene oxide) and an initiator having two or greater number of active hydrogen atoms. Ring opening as well as oxide addition take place in the presence of basic catalyst by the active hydrogen compound. The propagation stage continues until the conditions exist so desired molecular weight is obtained[98]. The polyols used in polyurethane production are predominantly hydroxyl polyethers and they are produced by alkoxylation[12]. The typical reaction for the production of polyether-polyols is shown in Scheme 1.5.
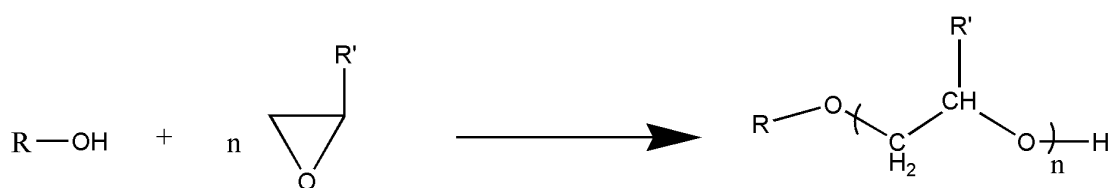
Scheme 1.5: Formation of polyether polyol

polyethylene glycol, polypropylene glycol and Poly(tetramethylene ether) glycol are among the most widely produced polyether polyols. Polyepochlorohydrin (PECH) can be produced through polymerization of epichlorohydrin (1-chloro-2,3-epoxypropane) which contain both epoxide and halide functional groups. Heat of homo-polymerization of ECH is 101.7 kJ/mol, at 25 °C.

Due to the presence of three membered ring, oxiranes (epoxides) have high degree of strain thus they generally undergo polymerization by both cationic and

anionic mechanisms[94, 99]. In case of epichlorohydrin (ECH), presence of chloromethyl group which has greater tendency to react with nucleophile, anionic polymerization of ECH is restricted. Therefore, its polymerization via cationic ring opening mechanism is a preferred choice for the synthesis of polyepichlorohydrin (PECH). At different steps of polymerization, investigation of the propagating polymer end groups disclosed that the ratio of primary to secondary hydroxyl groups does not change during polymerization. The polymerization of epichlorohydrin is highly regio-selective and the carbon atom with least substitution is almost exclusively attacked and propagation of polymerization is carried out by the attack of a secondary hydroxyl[100]. For epichlorohydrin, this ratio is found to be 5/95[101].

Due to strong basic character of the oxygen atom makes the three-membered ring (oxiranes) likely to be opened *via* cationic ring opening mechanism. A number of initiators are utilized to generate the secondary or tertiary oxonium ion propagation centres[102]. The α-carbon of the oxonium ion has adjacent positively charged oxygen which makes it electron deficient. Consequently, oxygen atom of ECH monomer molecule attacks on this carbon. In the presence of lewis acids ($SnCl_4$, BF_3, $SbCl_5$ or $FeCl_3$) epichlorohydrin is deadly polymerized[103]. Many protic compounds like water, alcohols or diols, trichloroacetic acid and trifluoroacetic acid are commonly used co-catalysts[104, 105].

Cationic ring opening polymerization of epichlorohydrin takes place through activated chain end (ACE) or activated monomer (AM) mechanism in the presence of a diol and lewis acid ($SnCl_4$ and BF_3)[106]. The dominance of either mechanism depends upon the relative concentration of diol and catalyst. If less than two moles of diol per mole of BF_3 etherate or $SnCl_4$ are used, only ACE mechanism operates while using greater than two moles of diol per mole of catalyst, both ACE and AM mechanisms will operate[100]. The relative proportions of these mechanisms are also dependent upon polymerization conditions. High temperature and slower addition of monomer (epichlorohydrin) favours the active monomer mechanism resulting in straight chain polymer with relatively higher molecular weight with reduced polydispersity. On other hand, lower temperature and the fast addition of monomer favours active chain end mechanism giving principally lower molecular weight polymer and cyclic products with reduced M_n and increased polydispersity.

1.3 Factors affecting properties of PU elastomers

The properties of the PUEs depend upon the nature and relative ratios of the raw materials. The polyols, diisocyanates and chain extenders have a considerable influence on certain properties of the thermoplastic PUs. Following are the details cited in literature that express the role of nature of raw materials on the attributes of polyurethane elastomers.

1.3.1 Nature of polyols

Nature of the polyols influences the mechanical properties of the PUEs by various means. The important parameters of polyols, which dictate the mechanical properties of the final product, are the chemical nature of polyol chains, chain stiffness, molecular weight and polyol functionality.

1.3.1.1 Effect of the chemical nature of polyol chains

The chemical nature of the polyol defines the performance of the PUEs. Longer polyol chains give a more flexible PUE. The backbone of polyol i.e., ester, butadiene, ether or caprolactone, affects the chemical resistance, oxidation resistance, hydrolytic stability and low temperature flexibility. The polyether-based PUEs are relatively more expensive, however, they show greater resistance towards microbial deterioration, hydrolysis, acids and bases, and are employed where low temperature flexibility is required[107]. The combination of polyether and polyester polyols is also employed for the optimum properties and cost-effective applications like coatings and foams etc. Furthermore, improved mechanical properties of polyether-polyester based PUEs can be achieved by adopting special synthesis procedure[57, 83]. The polyester based PUEs show better heat resistance, good oil/solvent resistance, abrasion resistance, mechanical properties and UV resistance[108]. In case of polyurethane elastomers having polybutadiene soft segments, effective adhesion, greater resistance to basic or acidic hydrolysis and preserving elastomeric behaviour even at lower temperature is witnessed. More importantly, they have better capability to incorporate greater amounts of fillers, thus are used in special applications where extraordinary filler concentration is required[109] [110].

Sonal Desai *et al*., studied the impact of diisocyanates and polyols on thermal, mechanical and morphological characteristic of polyurethanes based on HTPB/ PPG polyols with TDI/MDI diisocyanates[111]. HTPB-TDI system showed maximum

tensile strength and hardness while PPG-MDI system had lowest tensile strength but highest elongation at break. The increase of NCO/OH ratio and decrease in diol and triol ratio resulted in enhancement in the tensile strength but elongation followed the reverse trend. Morphology of the fractured specimens obtained during tensile strength test showed more heterogeneous character in HTPB than polyester based polyurethanes which were susceptible to hydrolysis. Polyether based polyurethanes were less stable under oxidative conditions. PUEs based on aliphatic polycarbonate diols were resistant to both hydrolysis and oxidation [112, 113, 114].

In polyurethane elastomers prepared from polybutadiene, chances of existence of hydrogen bonding in different segments are less due to the presence of hydrocarbon structure in comparison with polyester or polyether polyurethanes. So it favours the phase segregation in Polybutadiene based PUs[115, 116]. Polybutadiene based polyurethanes having greater hydrophobic character and low T_g, exhibited higher flexibility at lower temperatures and better hydrolytic resistance[117]. The mechanical properties of these polyurethane elastomers (tensile strength, abrasion and tear resistance) are high for polyether or polyester containing polyurethanes as compared to polybutadiene based polyurethane elastomers[112, 118]. Polybutadiene has *cis-trans* morphology so it exhibits a zig zag molecular arrangement that renders close-packing of the molecules complicated resulting in a transparent and amorphous polymer. The forces present among the chains are weak because the repeating unit contains only hydrogen and carbon atoms and lack hydrogen bonding due to which the UTS of cured HTPB is very low[119]. Ivan Djordjevic *et al*., synthesized and characterized citric acid based polyester elastomers having enhanced intermolecular bonding which is most probably as a result of greater stuffing of molecules within the crystalline domains[120]. Relative cohesive energy of polyether polyols, polyester polyols and polyhydrocarbon polyols (for example polybutadiene or hydrogenated polybutadiene) are in the following order:

polyester polyols > polyether polyols > polyhydrocarbon polyols

This relative order explains that numerous physico-mechanical properties of the polyurethanes based on polyester polyols are superior to the polyurethanes derived from polyether polyols and from polybutadiene polyols[12]. Table 1.2 shows the magnitude of cohesive energies per mole of functional groups in polyols and PUs.

It is evident from this data that cohesive energy of aromatic units is higher than that of ether or ester units. The presence of aromatic rings (especially in

polyether and in polyester polyols) leads to a strong increase in tensile strength and compression strength with a decrease in elastic properties, such as ultimate elongation[121].

Table 1.2: The molar cohesive energies of functional groups in polyols and PUs

Structure	Name of the group	Cohesive energy (kcal/mol)
—CH$_2$—	Hydrocarbon	0.68
—O—	Ether	1.00
—C(O)—O—	Ester	2.90
—C$_6$H$_4$—	Aromatic	3.80
—C(O)—N(H)—	Amide	8.50
—O—C(O)—N(H)—	Urethane	8.74

The effect of aromatic content which confers rigidity to the resulting rigid PU foams, is very evident in rigid polyols. Thus, an aromatic polyol gives higher physico-mechanical properties and better dimensional stability as compared to a similar rigid PU derived from an aliphatic polyol of the same functionality. The strength of the covalent bonds present in polyols and polyurethanes affects the thermal stability of the material. Thus, polyols having covalent bonds in the main chain with higher dissociation energy (C=O, C=C, C–F) lead to much more thermally stable polyurethanes than oligo-polyols having covalent bonds with lower dissociation energy (C–O, C–N or C–Cl bonds). Dissociation energies are shown in Table 1.3.

As a rule, polyether polyols having C–O bonds lead to polyurethanes with a lower thermal stability than polyester polyols (having C=O bonds). Aminic polyols (–NH–) lead to lower thermally stable polyurethanes due to the low dissociation energy of C–N bond. Polyurethanes based on polyols having double bonds or aromatic moieties (conjugated double bonds) in the backbone exhibit higher thermally stability than saturated aliphatic polyols[73].

Table 1.3: Strength of the covalent bonds existing in oligo-polyols and in PUs

Covalent bond	Dissociation energy (kcal/mol)
C≡N	213
C=O	174
C=C	146
C-F	103-123
O-H	111
C-H	99
N-H	93
C-O	86
C-C	83
C-Cl	81
C-N	73
C-S	62
O-O	35

Aromatic polyols sometimes give polyurethanes with intrinsic fire resistance, due to the very high char yield generated during the burning process[122].

Ge *et al*., prepared PU by using two different polyols, fluorinated polyether glycol and polytetramethylene glycol of same molecular weight and compared their thermal stability under N_2 atmosphere[123]. The study showed that the fluorinated polyurethanes were more thermally stable than their counter parts.

Tao Liu and Lin Ye prepared fluorinated thermoplastic polyurethane (FTPU) by combining polybutylene adipate (PBA) with fluorinated polyether diol (PFGE) as the soft segment of fluorinated PU[124]. As PBA contents were increased, the molecular weight of fluorinated PU was enhanced and elongation at break and UTS of fluorinated PU were improved. With PFGE-PBA (1:1), the elongation at break and UTS of fluorinated PU were found to be 634.3% and 14.33 MPa respectively. Thermal stability of the PU was also improved with the increase in fluorine contents.

1.3.1.2 Polyol chain stiffness

Molecular flexibility or stiffness depends on the extent of rotation around backbone of the polymer molecule and restriction in this free rotation reduces the flexibility. The rigid chemical groups in polymer chains e.g., cycloaliphatic rings,

aromatic rings, heterocyclic rings etc. do not allow molecular flexibility and free rotation thus, causing hardness, high melting points, high T_g and decreased elasticity. In linear saturated aliphatic polyols, free rotation around the carbon-carbon bonds is characteristic but this is restricted by the electropositive repulsion between adjacent hydrogen atoms. When a CH_2 group is replaced by oxygen (as in polyether chains), the rotation of the C-O-C bond (without hydrogen atoms) is easy and the molecule is more bendable, however polarity is enhanced. Presence of the molecules which causes hindrance restricts the rotation around the main chain and the molecule becomes stiffer e.g., cycloaliphatic group. Aromatic rings in the main chain introduce large rigid units and strongly reduce the molecule flexibility. The T_g is related to the flexibility of polymeric chains. A low T_g of the polyol segment in polyurethanes is very important because it conserves the high elasticity at lower temperatures. T_g depends on the stiffness and restriction in rotation of available polymer chains[95].

1.3.1.3 Polyol molecular weight

The molecular weight has an important effect on the PUs properties such as tensile strength, elongation, elasticity, melting point, glass transition temperature and modulus which are enhanced with the increase in the molecular weight of polyol. A lower molecular weight polyol results in rigid PU whereas a high molecular weight polyol gives elastic and flexible PU. Intermediate molecular weight polyol leads to semi-rigid or semi-flexible structures[96]. A short-chain polyol gives rise to a higher concentration of urethane bonds, consequently high cohesive interaction between these bonds (mainly by secondary hydrogen bonds) leads to a rigid structure. In case of long chain polyol, the concentration of urethane bonds is lower thus cohesive interaction between these bonds decreases significantly resulting in elastic structure of PU with high mobility and low T_g. Thus, from reaction of high molecular weight polyols with diisocyanates, higher molecular weight linear polyurethanes are obtained with high elasticity.

It was observed that the hardness and tensile strength reduces when the molecular weight of polyol was increased. The maximum decrease was observed in polypropylene glycol based PU elastomers, but polytetramethylene glycols and poly(ethylene adipate) glycols based PU elastomers also showed a slight decrease. Elastic properties such as rebound resiliency and ultimate elongation increases with

the molecular weight of oligo diol, the best properties being obtained in PU elastomers based on polytetramethylene glycols and poly (ethylene adipate) glycols.

The properties of PUs are also influenced by the molecular weight and molecular weight distribution, because molecular weight affects the kinetics of phase separation which alters the mechanical properties. Increase in molecular weight of the soft segment promotes phase separation in block copolymers during polymerization, which reduces the fractional conversion. Soft segment with average molecular weight between 1000 and 5000 Daltons produce polymer of optimum properties, while under this range, adequate phase separation is not possible. Moreover, low-molecular-weight material does not allow strain crystallization of soft segment that imparts the strengthening process. Block length of the hard segment of polyurethane also affects mechanical properties; lengthy building blocks have greater tendency for phase separation and induce superior properties. Apostolov and Fakirov studied the effect of block length on the deformation behaviour of polyether esters[125]. The overall molecular weight of PUE showed minor effect on the mechanical properties provided these are above the threshold values. Mono-dispersed hard segments give higher modulus and tensile strength presumably because of better packing of hard segments and improved phase separation[126].

1.3.1.4 Effect of polyol functionality

The polyol functionality (number of hydroxyl groups/mol) has a strong influence on the stiffness of the resulting polyurethanes. A high molecular weight polyol with low functionality (f = 2-3 OH groups/mol) leads to the flexible and elastic PUs. In case of low MW polyols with high functionality (f = 3-8 OH groups/mol), rigid polyurethanes with high cross-link density are obtained. When the functionality increases, the cross-link density of the resulting PUE also increases along with an increase in tensile strength[127]. Thus, lower functionalities give high conversion at the gel point while high functionalities impart low conversion at the gel point. The polyether diols are a mixture between a polyether diol and a polyether mono-ol, the real functionality being lower than two[73].

1.3.2 Effect of curing agent

Polyurethanes can be synthesized using both aliphatic and aromatic isocyanates but the manufacturing of commercial polyurethane elastomers is mainly

based on aromatic isocyanates. Use of aromatic isocyanates is particularly due to the fact that aliphatic isocyanates are usually more costly in comparison with aromatic isocyanates[128]. Moreover, deficiency in performance of commercial aliphatic isocyanates based polyurethane elastomers has considerably limited their usage. However, polyurethane elastomers with aliphatic chains have greater hydrolytic resistance, lesser thermal degradation and increased stability to light exposure. Despite these properties, aliphatic elastomers frequently exhibit decreased physico-mechanical properties in comparison with aromatic isocyanate based materials in which stronger cohesion forces are present among the hard chain segments. Generally, higher melting point is observed in case of the polymers having aromatic isocyanates in the hard segments that render stiffness to the polymer chain. MDI and TDI (aromatic diisocyanates) are the most widely used isocyanates in the synthesis of polyurethanes. Selecting a proper polyol backbone and chain extender can produce high performance polyurethane elastomers.

However, aromatic isocyanate based PUEs pose severe drawbacks like change in colour against UV-Visible radiations and thermal shocks, contrary to aliphatic isocyanate based PUEs who never undergo colour change under the same circumstances. It is reported that TDI based PUEs impart excellent properties when amine based curatives are used as chain extenders. When 2,4-isomer of TDI is used, overall 100% enhancement in properties can be achieved. The use of MDI also increases the overall properties of polyurethanes. Isocyanates like *p*-phenylene diisocyanate (PPDI) and cyclohexyldiisocyanate (CHDI) are used to get an increase of 10 to 20 °C in service temperature. Many workers have studied the mechanical properties of HTPB based PUs with various diisocyanates and concluded that change of diisocyanate significantly affected the properties of polyurethanes[129, 130].

When more symmetric diisocyanates and chain extenders are used, they facilitate the crystallization of hard segments[131]. Presence of bulky aromatic or cycloaliphatic groups in hard segments enhances the rigidity which leads to inter-chain steric hindrance. If the inter-chain forces are increased, the hard segments and the potential for macromolecular slippage, rigidity and crystallinity will be decreased. It will increase the modulus of elasticity, tear and tensile strengths, thus enhancing the mechanical properties ultimately.

M. Rogulska *et al*., showed that PU synthesized from hexamethylene diisocyanate had higher tendency to be crystallized than MDI based PU resulting in

improvement in mechanical strength of the elastomer[132]. Ken Kojio *et al.*, studied the characteristic of highly hydrophilic polyurethane based on diisocyanate in which ether groups were present[133]. It was found that the extent of micro-phase separation of 1,2-bis(isocyanate)ethoxyethane (TEGDI) based polyurethane elastomers was lesser in comparison with MDI based polyurethane elastomers. Young's modulus of TEGDI-based PUEs was quite lower and elongation at break was larger than MDI-based PUs due to weak cohesive forces of the hard segments present in TEGDI based PUEs. Due to hydrophilic nature of TEGDI, degree of swelling of TEGDI based PUEs was approximately five times greater than MDI based systems. Ken Kojio *et al.*, investigated the properties of norbornane diisocyanate, aliphatic (HDI) and cycloaliphatic diisocyanate (IPDI, HMDI) based polyurethanes[110]. HDI-based PUE showed the highest young's modulus and tensile strength due to the ability of crystallization of the hard segment component and the increased micro-phase separation. Rui Xie *et al.*, studied mechanical strength and dynamic viscoelastic properties of 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane-polycaprolactone based elastomers and compared with aliphatic diisocyanates (IPDI and H12MDI) based elastomers. 1,3 and 1,4-bis(isocyanatomethyl)cyclohexane based elastomers also showed retention of mechanical and dynamic properties at high temperatures[128].

Elodie Hablot studied polyurethanes based on castor oil and toluene diisocyanate, isophorone diisocyanate and hexamethylene diisocyanate[134]. The polymerization kinetics, degree of swelling and mechanical properties were greatly affected by the diisocyanate nature. The tensile strength and elongation at break were in the following order respectively.

TDI > IPDI > HDI and IPDI > TDI > HDI

TDI based elastomers have the highest tensile strength due to the aromatic character whereas HDI exhibited lowest tensile strength because of aliphatic building units present in it. IPDI offered highest elongation at break due to the higher average molecular weight between the cross-links, higher volume fraction and steric hindrance within the soft segments. HDI (aliphatic diisocyanate), showed lower elongation at break than TDI due to the formation of intra-molecular urethane bonds. This outcome can also be linked with the fast kinetics during the bulk formation of HDI that limited the mobility of the chains and supported the reaction of unreacted NCO groups with the humidity present in air. With the increase in NCO/OH ratio, tensile strength increased but elongation decreased and vice versa[135].

1.3.3 Effect of chain extenders

Chain extenders react with isocyanate terminated polyol (prepolymer) forming the rigid urethane blocks and chain extension to form final polyurethane chains. Chain extenders are typically diols or diamines. Short extenders will give more urethane segments, which make the PUE more crystalline, tougher and with higher strength. B.B Idage *et al*., studied the influence of short-chain aliphatic diols on the PUEs and concluded that modulus, hardness, elongation at break and UTS of polyurethane elastomers were improved by an increase in molar concentration of diols regardless the type of diols utilized[118].

In the work of Minoura *et al*., a number of various cyclo-aliphatic and aromatic diols with melting point greater than 100 °C were used as chain extenders in combination with HTPB[136, 137]. The materials were cured with MDI, yielding materials with a tensile strength in the range of 5 to 6 MPa. K.M. Zia investigated the effect of chain extender length by using α and ω-alkyl diols on the mechanical properties, surface morphology and crystallinity. He found that increase in length of chain extender increases the elongation of the resulting PUE[73] .

R.A. Azzam synthesized poly(ethylene glycol adipate) (PEGA)-MDI based polyurethane elastomers extended with aliphatic diol chain extenders and in another series, used mixture of aromatic diamine and aliphatic diol chain extenders[138]. The chain extender utilized in second series (mixture of aliphatic diol and aromatic diamine) imparted better thermal stability, higher tensile strength and lower elongations at break in comparison with elastomers prepared from aliphatic diol chain extenders. Hence, use of heterocyclic and aromatic diamine chain extenders can produce polyurethane with better thermo- mechanical properties than with mere aliphatic diol chain extenders.

Niklas Wingborg investigated the effect of 1,4-cyclohexanedimethanol and 1,4-butanediol and on the mechanical properties of HTPB, cured with different diisocyanates (IPDI, HDI and H_{12}MDI). Addition of diols enhanced the tensile strength strongly up to two moles of diols per mole of HTPB. It was also observed that diols along with H_{12}MDI increased the tensile strength greater than IPDI. The use of cyclohexanedimethanol in combination with IPDI, increased the tensile strength greater than butanediol whereas butanediol resulted in superior properties than

cyclohexanedimethanol in combination with $H_{12}MDI$ most probably due to the perfect orientation and alignment of resulting molecules[139].

1.3.4 Ratio of reactants

The molar ratio of polyol:chain extender:diisocyanate in polyurethanes dictates the degree of hardness or softness. This ratio range from 1:0.5:1.5 to 1:20:21 for soft and hard grades respectively[140, 141]. These ratios affect the final properties of the polyurethanes both in the pre-polymer production and the final stage curing reactions. At the preliminary prepolymer production stage, the properties vary in accordance with molar ratios of the prepolymer indicating that varying the mixing ratios of the chain extender, influence on mechanical properties is remarkable at the molecular levels. Properties like resilience, abrasion resistance and heat/viscosity build-up are often better at a lower level of curing agent and these properties depend upon unhindered flexibility of the backbone chains. The physical properties (flexibility, tear strength, elongation) require NCO/OH ratio slightly above the theoretical levels. These physical properties require the strongest bonding of PU matrix. When a formulation contains NCO groups in excess over the stoichiometric requirement of hydroxyl groups, the surplus diisocyanates undergo many competing reactions as already mentioned in section 1.3[49].

V. Sekkar *et al*., prepared HTPB based polyurethanes with diverse mechanical properties by varying the NCO/OH ratio[142, 143]. Enhancement in mechanical properties like modulus, tensile strength and stress at 100% elongation with increase in NCO/OH ratio was observed with corresponding decrease in elongation.

1.4 Polyurethane composites

Composite is a material designed from different constituents (two or more) with extensively different chemical or physical properties to produce a material with over all superior aggregate properties like strength, weight, conductance, cost, density, stiffness etc.[144] Composites are composed of a continuous phase called matrix (polymer, metal or ceramic) and a reinforcement phase that is uniformly dispersed throughout the composite. Mostly reinforcement is stronger, harder and stiffer relative to the base matrix that induce significant strength and stiffness. The reinforcement is usually a fiber or a particulate. Particulates might be platelets, spherical, irregular or regular shape and geometry. Particulate composites are

relatively weaker and less stiff in comparison with continuous fiber composites, but on the other hand, they are usually more economical[145]. Use of particulate confronts processing difficulties inducing brittleness; therefore, composites reinforced with particulate usually contain less reinforcement. The matrix performs several critical functions like maintaining the reinforcements in proper orientation and spacing and protecting them from abrasion and environment. In composites, load is transmitted from the matrix to fiber/particulate through shear loading at the interface resulting in increased toughness, strength and stiffness.

Polyurethane binders are used to adhere numerous types of particles and fibers. Use of polyurethanes as matrix material remained a subject of scientific investigation since decades. The introduction of electrically conducting particles into polymeric materials gave interesting and admirable properties to the composites[146]. In general, low content of filler in composite are still an insulator because the conducting particles are well separated. As the percentage of filler is increased, the conductivity is also increased[147].

Development of suitable multifunctional materials having capability to address simultaneously conductivity, flexibility, lightweight, environmental impact and production cost is one of the current and future challenges in electronics. Using polymeric materials in electronics is a high potential technological field which may pave the way to many novel applications and products.

Graphite is used as an electroconductive filler due to its good conductivity and moderate cost. It is also reported that graphite increases the mechanical and thermal properties as well as dimensional stability of the polymeric materials[147, 148]. Polyurethanes are used as potting compounds and as cable insulation, therefore, the frequency dependence of the dielectric properties is important in practical as well as theoretical evaluations[143].
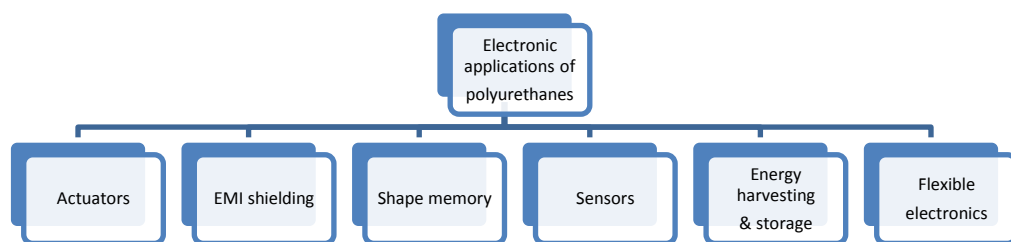
Polyurethane composites and their blends have wide range of applications in electronics including sensors[149, 150], actuators[151], EMI shielding[152, 153],

electrolytes for super-capacitors[154, 155], energy harvesting devices[156], electrostatic dissipative coating and shape memory polymer applications [157]. Use of printed electronic boards is also filling the major gaps in electronics industry. Polyurethanes as well as its composites based adhesives have many applications in printed and flexible electronics[158, 159].

1.5 Scope and objectives of the present work

As explained in the introduction part, the exploitation of structural diversity of polyurethanes is the key research area in modern era where technological and economical aspects need to be addressed on priority basis. Design of new polymeric materials with enhanced thermo-mechanical properties to fulfil the requirements of new challenging applications always remained as a driving force for the advanced research in the field of polyurethane materials.

Molecular weight, chemical structure and functionality of the polyols play the key role in determining the properties of final polyurethane elastomers. One of the objectives of this research was to establish a method for the synthesis of bi-functional polyepichlorohydrins (PECH) of different molecular weights from epichlorohydrin without any solvent.

Another objective was the use of the synthesized PECH in the preparation of multiple novel polyurethane elastomers of diversified structures using aromatic (TDI) and cycloaliphatic (IPDI) diisocyanates extended with three short-chain diols (butanediol, hexanediol and cyclohexanedimethanol) in the presence of DBTDL. The effect of structural diversification on the morphology and thermo-mechanical properties of the synthesized polyurethane elastomers was another object of study.

Finally, use of developed polyurethane elastomer as a matrix in the preparation of polymer based composites of graphite, aluminium flakes and aluminium powder and study of thermo-mechanical along with conductance properties of these composites were planned.

1.6 Plan of work

The present dissertation was an effort to develop and characterize novel polyurethane elastomers and their composites with improved thermo-mechanical properties and study the effects of structural diversification on the properties of PU elastomers. The subsequent part of this section has been devoted to unfold the basic

strategies, and background information employed in the presented thesis. It was planned to divide the research work in three different parts.

1.6.1 Part-I

In the first part, a method for the preparation of bi-functional hydroxyl terminated polyepichlorohydrin PECH) was designed and conditions for preparation of PECH of different molecular weights were optimized. All the synthesized products were subsequently characterized. Scheme 1.6 illustrates the synthesis of PECH.

Finally, three different molecular weights of PECH 1045, 2495 and 3565 Daltons were prepared in appreciable quantity for their onward use in polyurethane synthesis as basic polyol.
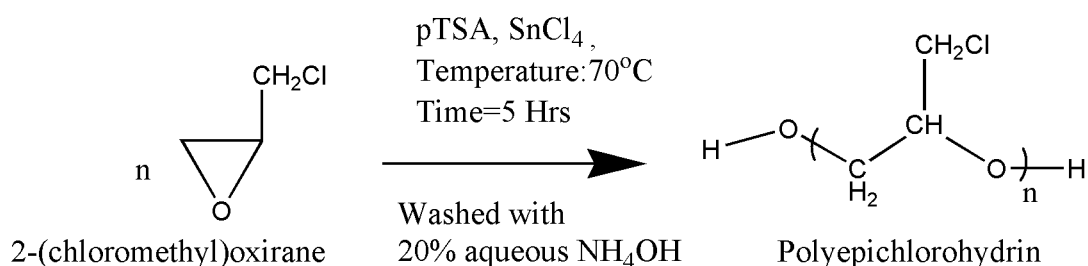
Scheme 1.6: Polymerization of epichlorohydrin

1.6 .2 Part-II

The second part deals with the synthesis and characterization of six different series of novel polyurethane elastomers containing PECHs of different molecular weights as a soft segment, toluene diisocyanate and isophorone diisocyanate in combination with 1,4-butanediol, 1,6-hexanediol and cyclohexanedimethanol as hard segments. All the polyurethanes were prepared by solvent-free prepolymer step-growth polymerization method. Scheme 1.7 represents the general reaction for the preparation of PUEs. Effects of change of architecture in macromolecule on thermal and mechanical properties of PUEs were also investigated. Following effects on properties were studied in this part:

1. Change in molecular weight of polyepichlorohydrin
2. Type and percentage of chain extender

3. Cycloaliphatic and aromatic diisocyanates
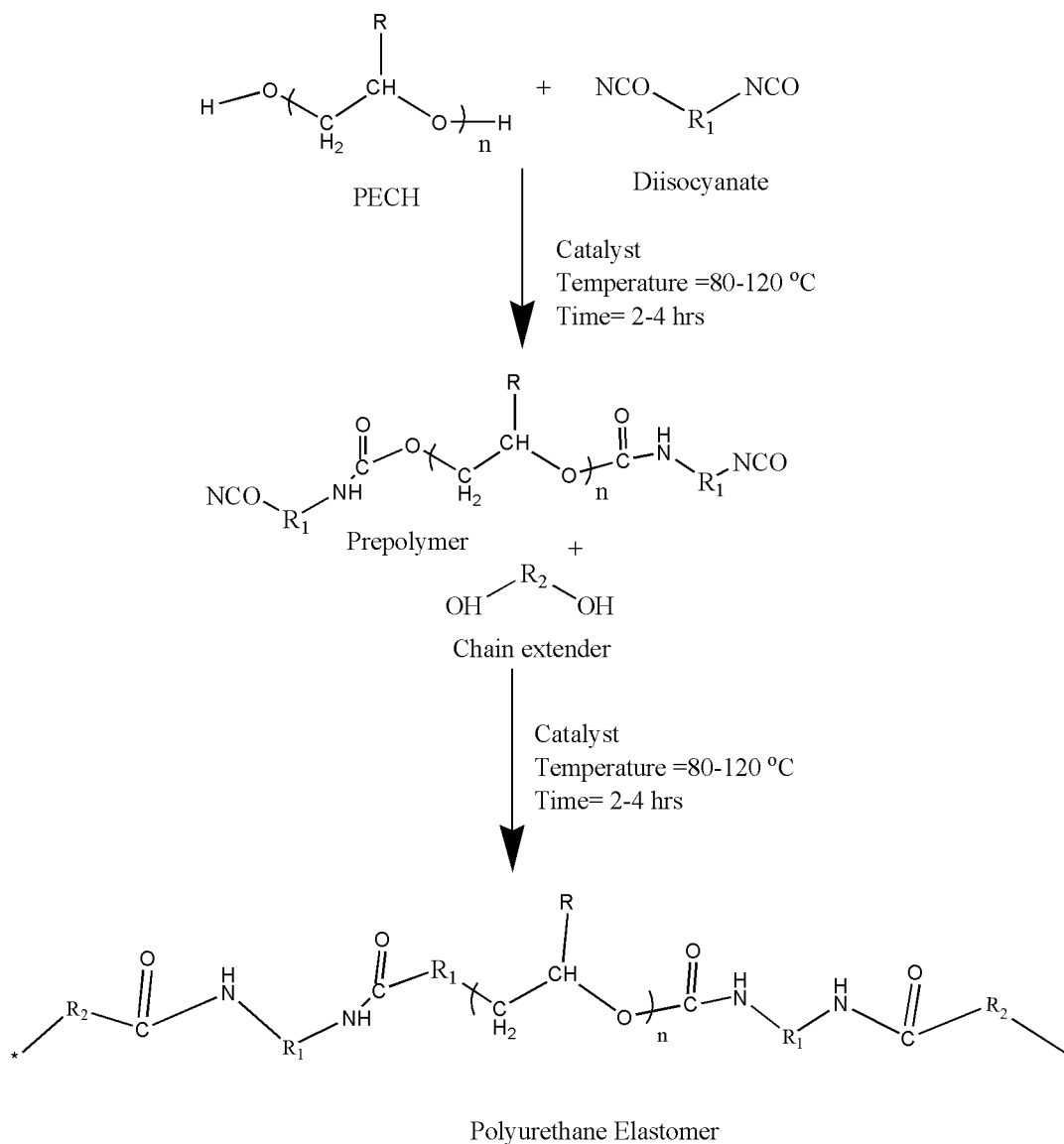
Scheme 1.7: General reaction for preparation of PUEs

1.6 .3 Part-III

In third part of the research, composites of polyurethane elastomer were prepared by using graphite, aluminium flakes and aluminium powder as fillers. Concentration of fillers was changed from 5 to 15 % and impact of this change on thermal and mechanical properties along with direct current resistance of composites was studied.

Chapter No. 2

EXPERIMENTAL

This section provides the details of materials, characterization techniques and methods adopted for the synthesis of polyepichlorohydrin, polyurethane elastomers and their composites.

2.1 Chemicals

For the preparation of polyepichlorohydrin (PECH), epichlorohydrin was purchased from Hainan Huarong Chemical Co., Ltd. China. Before use, it was refluxed with calcium oxide, distilled and fraction collected at 110-115 °C was stored on molecular sieve (0.05% moisture). Commercial ethanol was used after distillation. p-toluenesulphonic acid monohydrate ($CH_3C_6H_4SO_3H.H_2O$) was dried under reduced pressure at 60 °C for 2 and 4 hours to attain 9% and 3% moisture, respectively and stored in a desiccator over silica gel. Anhydrous stannic chloride ($SnCl_4$) and $para$- toluenesulphonic acid ($CH_3C_6H_4SO_3H.H_2O$) from Merck were used.

For the preparation of polyurethane elastomers, PECH of three different molecular weights were prepared in-house and characterized (Table 2.1). Tolylene diisocyanate (TDI) and isophorone diisocyanate (IPDI) were purchased from Sigma Chemical Co. and used as received. The short-chain diols 1,4-butanediol (BD), 1,6-hexanediol (HD) and 1,6-cyclohexanedimethanol (DM) were purchased from Sigma Aldrich and were dried at 100 °C for one hour. One of the synthesized polyurethane elastomer (P10IPDIDM10) with best mechanical properties was selected for the composite preparation. For this purpose, synthetic graphite powder (conducting grade 200 mesh pass) was acquired from Alfa Aesar and nitrogen atomized fine spherical aluminium powder (1-2 µm) was purchased from Frank Lee Hunan Jinhao New Material Technology Co., Ltd China and used as received. Aluminium based metallic flakes were purchased from local automotive paint market and used after washing with petroleum ether and drying in oven at 50 °C for 3 hours.

Table 2.1: PECHs used for the synthesis of polyurethane elastomers

Sample codes	Molecular weight[a]	Molecular weight[b]	OH Value	F_n	PDI (GPC)	Viscosity (Pa.s)	Moisture (ppm)	Volatile matter
P-10	1045	1071	1.914	2.05	1.82	3.1	462	0.12
P-25	2497	2534	0.801	2.03	1.81	12.5	450	0.15
P-35	3521	3685	0.568	2.09	1.85	19.8	430	0.18

a = Molecular weight determined by acetylation method

b = Molecular weight determined by vapour pressure osmometry method

F_n = Number of hydroxyl groups per molecule of polymer

PDI = Polydispersity index

2.2 General Procedure for the synthesis of polyepichlorohydrin

All the reactions were conducted in a reactor equipped with a mechanical stirrer as well as temperature and atmosphere (N_2 or air) controller. Pre-calculated amount of *p*-toluene sulfonic acid was added to equimolar amount of epichlorohydrin with continuous stirring at 60 °C. After 20 mins, the mixture was cooled to room temperature. Predetermined amount of $SnCl_4$ was then added and the mixture was stirred for further 10 mins. Remaining amount of ECH (as calculated from monomer-initiator ratio) was added dropwise with vigorous stirring and the temperature was maintained at 65-70 °C. The stirring was continued for further five hours at 70 °C.

Upon the completion of reaction time, unreacted ECH was stripped off under reduced pressure (100 mm of Hg) at 70 °C. The remaining polymer was reacted with 10% aqueous NH_4OH at 40 °C for one hour. The organic layer was subjected to several washings with distilled water until it was neutral to pH paper. Furthermore, oligomers/cyclic products were removed from polymer with ethanol water mixture. Finally, ethanol and water were removed under reduced pressure (10-15 mm of Hg) at 100 °C. Scheme 2.1 illustrates the preparation of polyepichlorohydrin.

The effects of multiple factors (reaction time, temperature and moisture) on molecular weight, cyclic products formation and oligomers ($M_n < 500$) were investigated by collecting and analysing samples from reaction mixture after time intervals. Table 2.2 shows the sample codes of polyepichlorohydrins with different concentration of catalyst and co- catalyst.

Scheme 2.1: Preparation of polyepichlorohydrin
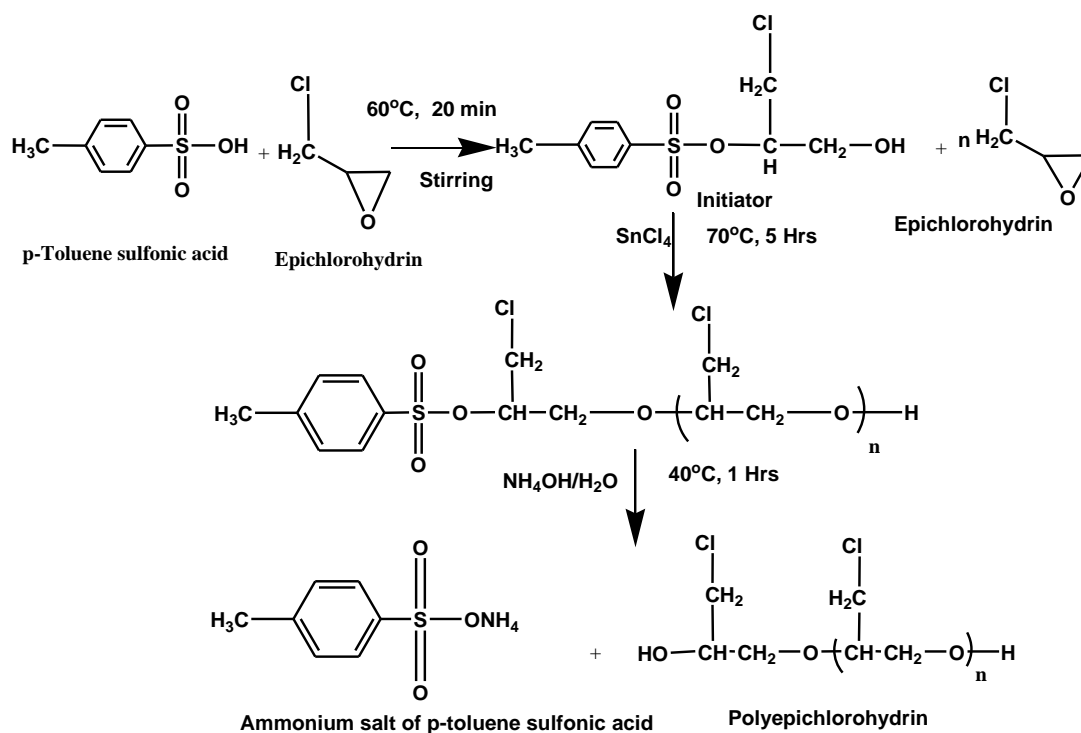
Table 2.2: Sample codes of polyepichlorohydrins with different concentration of catalyst and co-catalyst

S. No.	Sample Code	p-TSA moles(a)	$SnCl_4$ moles	p-TSA/$SnCl_4$
1	P-01 (b)	0.0128	0.0016	8
2	P-02	0.0128	0.0016	8
3	P-03	0.0065	0.0016	4
4	P-04	0.0033	0.0016	2
5	P-05	0.0033	0.0008	4
6	P-06	0.0033	0.0006	6
7	P-07	0.0033	0.0004	8
8	P-08	0.0033	0.0003	11
9	P-09(c)	0.0033	0.0003	11
10	P-10	0.0421	0.0035	12
12	P-11(d)	0.0421	0.0035	12
11	P-12	0.0350	0.0035	10
13	P-13(e)	0.0128	-	-

(a) = para toluene sulfonic acid.

(b) = P-01 was prepared under nitrogen, while all other products were synthesized under air.

(c) = P-09 was synthesized with ECH addition rate of 0.5 mL min-1, while all other products were synthesized by adding 10 mL min-1.

(d) = P-11 was run at ambient temperature.

(e) = P-13 was synthesized with p-TSA and ECH without the addition of SnCl₄

After optimization of reaction conditions, three polyols for the preparation of polyurethane elastomers were prepared. The polymerization conditions are mentioned in Table 2.3.

Table 2.3: Conditions of PECH used for preparation of PUEs

Sample codes	ECH (moles)	p-TSA (moles)	SnCl$_4$ (moles)	p-TSA/SnCl$_4$	p-TSA Moisture (%)	T (°C)	Time (hours)	PECH(g)
PECH10	10.81	0.35	0.015	23.3	3	70	5	950
PECH25	10.81	0.25	0.02	12.5	3	70	5	936
PECH35	10.81	0.15	0.025	6	3	70	5	910

2.3 Synthesis of polyurethane elastomers

Polyurethane elastomers were obtained by the step growth addition polymerization of polyepichlorohydrins (different molecular weight), diisocyanates (TDI and IPDI) and extended with short-chain diols (BD, HD, CHDM) *via* the prepolymer methodology.

The reaction was carried out in a reaction vessel equipped with a mechanical stirrer, reflux condenser, dropping funnel, N$_2$ inlet/outlet and heating bath. 200 g of pre-dried polyol and 1 g of dibutyltin dilaurate (DBTDL) was placed in the reaction vessel and heated at 60 °C. Subsequently, calculated amount of diisocyanate was added and the temperature was raised to 100 °C under a blanket of dry N$_2$ and the reaction mixture was stirred for 4 hours.

Stoichiometric amount of previously dried chain extender was added during vigorous stirring and reaction was further proceeded for 2 hours at 60 °C. It resulted in partial transformation of prepolymer to highly viscous PUE. When the reaction mixture became homogeneous reflecting the complete dispersion of the chain extender, liquid polymer was then cast into a teflon plate to form a uniform sheet. The synthesized polymer samples were first placed under vacuum for 15 minutes to ensure

the removal of air bubbles before casting. PUEs were post-cured for 5 days at 80 °C in a hot air circulating oven. The cured sample sheets were then stored for 24 hours at ambient temperature (25 °C) and 40% relative humidity before testing.

A schematic illustration for the synthesis of polyurethanes is shown in Scheme 2.2 while Table 2.4 and 2.5 show the sample codes and amounts of reactants used for the preparation of PUEs.
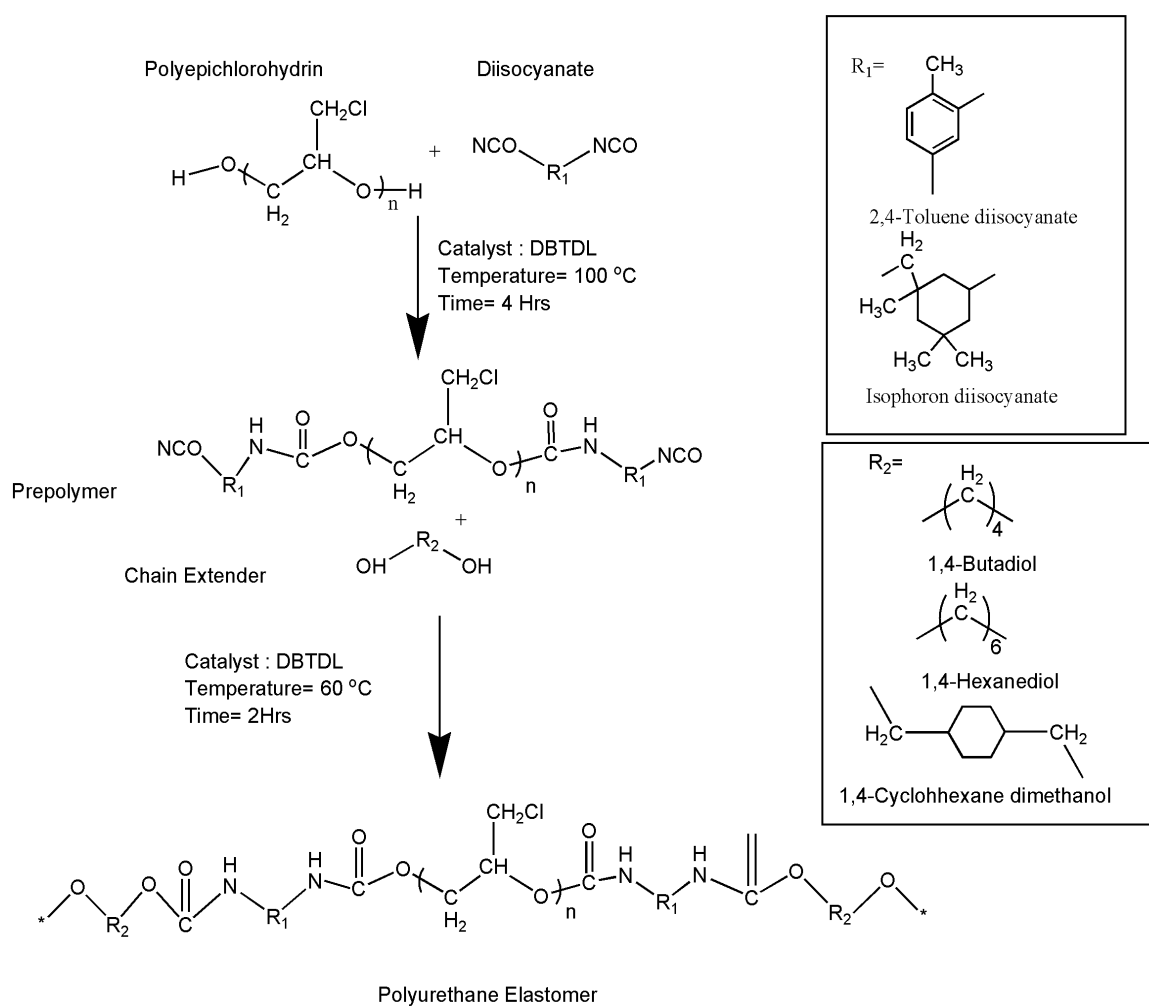
Scheme 2.2: General scheme for the synthesis of polyurethane elastomers

Table 2.4: Sample codes of polyurethane elastomers of toluene diisocyanate

Sample Codes	Moles of PECH	Weight of *CE	Mole of CE	Weight of diisocyanate	Mole of diisocyanate	CE%	% of **HS
P10TDIBD10	0.1914	2.423	0.02689	39.918	0.22920	1.0	17.5
P10TDIBD15	0.1914	3.693	0.04098	42.495	0.24400	1.5	18.8
P10TDIBD20	0.1914	5.004	0.05553	45.155	0.25927	2.0	20.1
P10TDIHD10	0.1914	2.412	0.02041	38.734	0.22240	1.0	17.1
P10TDIHD15	0.1914	3.665	0.03101	40.673	0.23354	1.5	18.1
P10TDIHD20	0.1914	4.953	0.04191	42.666	0.24498	2.0	19.2
P10TDIDM10	0.1914	2.405	0.01668	38.051	0.21848	1.0	16.8
P10TDIDM15	0.1914	3.649	0.02530	39.628	0.22754	1.5	17.8
P10TDIDM20	0.1914	4.924	0.03414	41.245	0.23682	2.0	18.8
P25TDIBD10	0.0801	2.213	0.02456	19.138	0.10989	1.0	9.6
P25TDIBD15	0.0801	3.373	0.03743	21.492	0.12340	1.5	11.1
P25TDIBD20	0.0801	4.571	0.05072	23.923	0.13736	2.0	12.5
P25TDIHD10	0.0801	2.203	0.01864	18.057	0.10368	1.0	9.2
P25TDIHD15	0.0801	3.348	0.02833	19.829	0.11385	1.5	10.4
P25TDIHD20	0.0801	4.524	0.03828	21.649	0.12430	2.0	11.6
P25TDIDM10	0.0801	2.197	0.01523	17.434	0.10010	1.0	8.9
P25TDIDM15	0.0801	3.333	0.02311	18.874	0.10837	1.5	10.0
P25TDIDM20	0.0801	4.498	0.03119	20.351	0.11686	2.0	11.1
P35TDIBD10	0.0568	2.17	0.02408	14.790	0.08492	1.0	7.8
P35TDIBD15	0.0568	3.305	0.03667	17.093	0.09815	1.5	9.3
P35TDIBD20	0.0568	4.479	0.04970	19.476	0.11183	2.0	10.7
P35TDIHD10	0.0568	2.158	0.01826	13.726	0.07881	1.0	7.4
P35TDIHD15	0.0568	3.282	0.02777	15.466	0.08880	1.5	8.6
P35TDIHD20	0.0568	4.434	0.03752	17.249	0.09904	2.0	9.8
P35TDIDM10	0.0568	2.152	0.01492	13.116	0.07531	1.0	7.1
P35TDIDM15	0.0568	3.267	0.02265	14.530	0.08343	1.5	8.2
P35TDIDM20	0.0568	4.407	0.03056	15.975	0.09173	2.0	9.2

%= Percentage   * Chain extender   ** Hard segment

Table 2.5: Sample codes of polyurethane elastomers of isophorone diisocyanate

Sample Codes	Moles of PECH	Weight of *CE	Mole of CE	Weight of diisocyanate	Mole of diisocyanate	% of CE	% of **HS
P10IPDIBD10	0.1914	2.537	0.02815	51.242	0.23053	1.0	21.2
P10IPDIBD15	0.1914	3.879	0.04304	54.717	0.24616	1.5	22.7
P10IPDIBD20	0.1914	5.273	0.05851	58.328	0.26241	2.0	24.1
P10IPDIHD10	0.1914	2.523	0.02135	49.655	0.22339	1.0	20.7
P10IPDIHD15	0.1914	3.841	0.03250	52.258	0.23510	1.5	21.9
P10IPDIHD20	0.1914	5.203	0.04403	54.948	0.24720	2.0	23.1
P10IPDIDM10	0.1914	2.513	0.01743	48.739	0.21927	1.0	20.4
P10IPDIDM15	0.1914	3.82	0.02649	50.854	0.22878	1.5	21.5
P10IPDIDM20	0.1914	5.165	0.03582	53.031	0.23858	2.0	22.5
P25IPDIBD10	0.0801	2.268	0.02517	24.569	0.11053	1.0	11.8
P25IPDIBD15	0.0801	3.468	0.03848	27.676	0.12451	1.5	13.5
P25IPDIBD20	0.0801	4.713	0.05230	30.901	0.13902	2.0	15.1
P25IPDIHD10	0.0801	2.255	0.01908	23.149	0.10414	1.0	11.3
P25IPDIHD15	0.0801	3.434	0.02906	25.477	0.11462	1.5	12.6
P25IPDIHD20	0.0801	4.65	0.03935	27.879	0.12542	2.0	14.0
P25IPDIDM10	0.0801	2.245	0.01557	22.328	0.10045	1.0	10.9
P25IPDIDM15	0.0801	3.415	0.02368	24.222	0.10897	1.5	12.1
P25IPDIDM20	0.0801	4.615	0.03200	26.164	0.11771	2.0	13.3
P35IPDIBD10	0.0568	2.213	0.02456	18.988	0.08542	1.0	9.6
P35IPDIBD15	0.0568	3.381	0.03752	22.013	0.09903	1.5	11.3
P35IPDIBD20	0.0568	4.595	0.05099	25.157	0.11318	2.0	12.9
P35IPDIHD10	0.0568	2.198	0.01860	17.598	0.07917	1.0	9.0
P35IPDIHD15	0.0568	3.348	0.02833	19.869	0.08939	1.5	10.4
P35IPDIHD20	0.0568	4.535	0.03838	22.214	0.09994	2.0	11.8
P35IPDIDM10	0.0568	2.19	0.01519	16.801	0.07559	1.0	8.7
P35IPDIDM15	0.0568	3.329	0.02308	18.645	0.08388	1.5	9.9
P35IPDIDM20	0.0568	4.501	0.03121	20.541	0.09241	2.0	11.1

%= Percentage　　　　　* Chain extender　　　　　** Hard segment

2.4 Preparation of PU composites

The polyurethane (P10IPDIDM10) was prepared following the method outlined in section 2.3. The pre-calculated amounts of filler powders (graphite, aluminium flakes and aluminium powder) were dispersed in PU before (approximately 30 mins) the completion of reaction. The components were mixed vigorously to ensure thorough mixing and the material was fabricated into a film in a petri-dish. For the final curing of polyurethane composites, all steps were followed as mentioned in section 2.3. Sample codes and composition of different composites are mentioned in Table 2.6.

Table 2.6: Sample codes and composition of polyurethane composites

Sample codes	Graphite	Al flakes	Al powder
$PUEG_0Al_0$	0	0	0
$PUEG_5Al_0$	5	0	0
$PUEG_{10}Al_0$	10	0	0
$PUEG_{15}Al_0$	15	0	0
$PUEG_0Al_5$	0	5	0
$PUEG_0Al_{10}$	0	10	0
$PUEG_0Al_{15}$	0	15	0
$PUEG_{2.5}Al_{2.5}$	2.5	2.5	0
$PUEG_5Al_5$	5	5	0
$PUEG_{7.5}Al_{7.5}$	7.5	7.5	0
$PUEG_{2.5}Al_{7.5}$	2.5	7.5	0
$PUEG_{7.5}Al_{2.5}$	7.5	2.5	0
$PUEG_0Al_5PW$	0	0	5
$PUEG_0Al_{10}PW$	0	0	10
$PUEG_0Al_{15}PW$	0	0	15
$PUEG_{2.5}Al_{2.5}PW$	2.5	0	2.5
$PUEG_5Al_5PW$	5	0	5
$PUEG_{7.5}Al_{7.5}PW$	7.5	0	7.5

2.5 Characterization techniques

2.5.1 FT-IR spectroscopy

The functional group characterizations of the products (PECHs and PUEs+) were done by using FT-IR spectrophotometer (IRAffinity-1S) in the range of 4000 cm^{-1} to 600 cm^{-1} with the resolution of 4 cm^{-1}. The equipment was fitted with ATR assembly containing diamond crystal. The spectra were average of over 120 scans.

2.5.2 ^{1}H and ^{13}C NMR spectroscopy

^{1}H and ^{13}C spectra of the samples were recorded by Bruker USA spectrophotometer operating at 300.13 MHz for ^{1}H and at 75.47 MHz for ^{13}C, using deuterated chloroform as solvent and tetramethyl silane (TMS) as internal reference for PECH. For samples of polyurethane elastomers, deuterated dimethyl sulfoxide was used as solvent.

2.5.3 Gel permeation chromatography

A GPC instrument connected with HPLC Pump (515 of Waters Associates), refractive index detector (Shimadzu RID-6A) and three styragel columns (HR1, HR2 and HR3) of WATERS USA were used in descending order. Tetrahydrofuran (THF) was used as a mobile phase with 1 ml/min flow rate. Samples were prepared in THF with a concentration of 0.12% w/v. The molecular weight distribution and polydispersity of the samples were determined by calibrating the instrument with polystyrene standards of 500, 1300, 5000, 10500 and 130000 g mol^{-1}. Empower software was used for data processing.

2.5.4 Vapour pressure osmometry

Absolute molecular weight of polymer was determined by vapour pressure osmometer (VPO, Kneur K 7000 Germany) in chloroform at 43 °C. The instrument constant (K) was determined by benzil (AR grade) and calibration of the instrument was verified by polystyrene standard.

2.5.5 Hydroxyl value/functionality

Hydroxyl value is a measure of free hydroxyl groups present in the polyols and it is expressed as number of milligrams of potassium hydroxide equivalent to the quantity of acetic acid that binds with 1 g of hydroxyl containing substance. It was determined by reacting acetic anhydride with terminal hydroxyl groups of PECH as per ASTM standard D-3446. Hydroxyl functionality of the final product was derived from M_n (by VPO) and hydroxyl value.

2.5.6 Moisture and volatile matter analysis

Moisture in all products was determined by ASTM D 6304 and volatile matter in polymers was determined my ASTM D3030.

2.5.7 Oligomers/cyclic products quantification

Oligomers/cyclic products were extracted from polymer by ethanol and quantified gravimetrically with following formula:

$$\text{Oligomers}(\%) = \frac{\text{Residue after evaporation}}{\text{Total mass of polymer used in extraction}} \times 100$$

2.5.8 Thermogravimetric and differential thermal analysis (TGA)

Thermal stability of the polymers was determined by thermogravimetric analyzer model TGA-7 of Perkin Elmer USA. TGA runs were carried out from 50 °C to 600 °C at 25 °C min^{-1} heating rate in nitrogen atmosphere.

2.5.9   Differential scanning calorimetry (DSC)

In this study, DSC analysis was performed to determine the thermal changes of polyurethane elastomers by using a Perkin Elmer DSC Diamond series, USA. The samples were weighed carefully and thermally examined up to 50-500 °C using liquid nitrogen at a heating rate of 10 °C/min. T_g below room temperature of PECH and PUE samples was determined by DSC1 of Mettler Toledo Switzerland equipped with chiller. The instrument was calibrated by indium standard. The samples (3-5 mg) were sealed in Al pan and analyzed between 50 to 400 °C under nitrogen atmosphere with ramping rate 20 °C min^{-1}.

For T_g samples were analysed on DSC1 Methrom Switzerland from –60 to 50 °C at the heating rate 20 °C min^{-1}.

2.5.10 Wide-angle X-ray diffraction analysis (WAXD)

The amorphous and crystalline nature of elastomers was estimated by Wide-angle X-ray diffraction analysis. The X-rays diffraction patterns were recorded in transmission mode with Ni-filtered Cu K$_\alpha$ radiations. The X-ray diffractometer model Xpert PRO by PANalytical, Netherlanda was used and samples were scanned in the range of diffraction angle 2θ=10-70° and at 0.04 2θ s^{-1} scan rate.

2.5.11 Mechanical properties analysis

Instron uniaxial tensile tester model 10/M instrument was used to determine the mechanical properties, tensile strength and elongation at break. Stress–strain curves were drawn at a strain rate of 50 mm/min. The sample films of 1 mm thickness were stamped out using an ASTM D-638 die and studied at 25 °C.

2.5.12 Scanning electron microscopy (SEM)

A scanning electron microscope model JEOL 30KV was used to observe the surface of the final PU films. To study the surface by SEM, prepared PUE samples were coated with silver paste and placed for 2 mins in sputter coater and vacuum evaporator for gold coating. The images were taken at different magnifications.

2.5.13 Measurement of direct current resistance (DCR) of composite

For electrical properties measurements, square discs with diameter 25 mm and thickness about 0.4-0.8 mm were prepared, while for the measurement of dielectric properties, square discs with length of 10 mm and thickness about 0.4-0.8 mm were prepared.

Direct current resistance measurements were carried by using an Agilent U1730C LCR meter with software package Agilent GUI Data Logger software which was used to maximize the performance and data handling of the system. Analyzer was equipped with a HP 16451B dielectric material test fixture. The measurements were taken in triplicate and average value was reported.

Chapter No. 3
RESULTS AND DISCUSSIONS

The effect of polymerization conditions/amount of co-catalyst on molecular weight of polyol (PECH) as well as structural, thermal and mechanical properties of the synthesized polyurethane elastomers/composites is discussed in following three parts.

The section 3.1 describes a novel method for the preparation of polyepichlorohydrins without using solvent. Polymerization reactions of epichlorohydrins were carried under different conditions. The concentrations of monomer, catalyst and co-catalyst were varied to estimate their effect on the molecular weight, hydroxyl value, functionality and yield of polymers. After the optimization of conditions, three polymers of different molecular weights were prepared for their further use as polyol in the preparation of polyurethane elastomers.

While the section 3.2 presents the preparation of polyurethane elastomers from the synthesized polyols. These polyols were selected due to their optimum viscosities which make them suitable for solvent-free processing for the preparation of PU elastomers. Two series of polyurethane elastomers were prepared from aromatic and cycloaliphatic diisocyanates extended with three short-chain diols. The influence of structural variation of toluene diisocyanate and isophorone diisocyanate on thermo-mechanical properties of PUEs was studied. The impact of type and quantity of chain extenders on the properties of PUEs was also established.

The final section 3.3 has been devoted to the preparation and characterization of polymer matrix composites. Polyurethane elastomer exhibiting optimum ultimate tensile strength, elongation at break and thermal properties was selected for subsequent studies as matrix for polymer based composites. Conducting grade graphite, aluminium flakes and spherical atomized aluminium powder were utilized as reinforcing fillers. Thermo-mechanical properties and direct current resistance of the composite are included in this section.

3.1 Synthesis and characterization of hydroxy terminated polyepichlorohydrin

The main objective of this work is to develop a novel method for the production of bi-functional PECH using a combination of catalyst and co-catalyst. The effect of various molar ratios of p-toluenesulphonic acid and $SnCl_4$ on molecular weight of PECH was investigated. Different polymerization conditions like

temperature, time and monomer addition rates were found to have pronounced effects on the molecular weight, polydispersity and functionality of the products. After optimization of conditions, bulk quantity of PECHs of three different molecular weights were prepared and characterized for their subsequent use in the preparation of polyurethane elastomers.

3.1.1 Synthesis of PECH

The general reaction for the preparation of PECH from epichlorohydrin is illustrated in scheme 2.1 of section 2.2. The details of PECH synthesized under different reaction conditions (temperature, time and inert atmospheric) using different molar ratios of the *para* Toluene sulfonic acid (*p*-TSA) and stannic chloride are given in Table 2.2.

3.1.2 Characterization of PECH

The final viscous liquid products obtained from different experiments were colourless to yellowish in colour. The structural elucidations were carried out by FT-IR and NMR (^{1}H, ^{13}C) spectroscopic techniques. The molecular weight distribution and polydispersity of the synthesized polymers were determined by gel permeation chromatography (GPC). Absolute value of number average molecular weight (M_n) was established with vapor pressure osmometry. Terminal hydroxyl groups were quantified by acetylation method and functionality was derived from hydroxyl value and M_n[160].

3.1.2.1 FT-IR structural elucidation

The FT-IR spectra of all the products exhibited the characteristic peaks of polyepichlorohydrin. The IR spectrum of one of the representative polymer is shown in Figure 3.1b. All the products showed a characteristic peak at 3275-3404 cm^{-1} for O-H stretching vibration, peak at 2950-2850 cm^{-1} for C-H stretching vibration, strong peak at 1065-1128 cm^{-1} for C-O-C and peak at 725-748 cm^{-1} for C-Cl stretching[161]. The disappearance of peak at 750-880 cm^{-1} for a symmetric oxirane ring deformation and appearance of peak at 1065-1128 cm^{-1} for C-O-C indicates the formation of ether linkage. Absorption peak of -OH is broad and weak due to higher molecular weight of the product (Figure 3.1a and 3.1b).
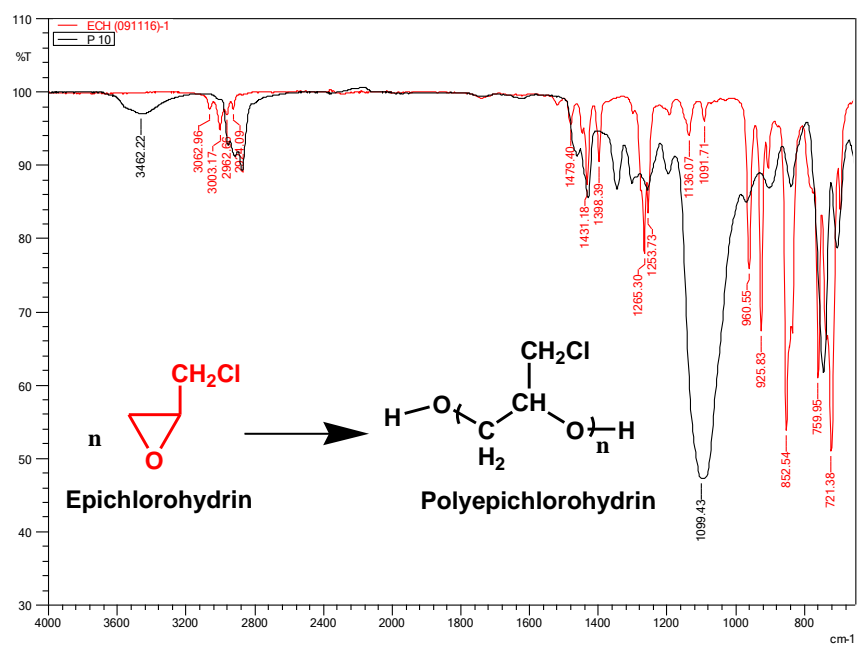
(a)
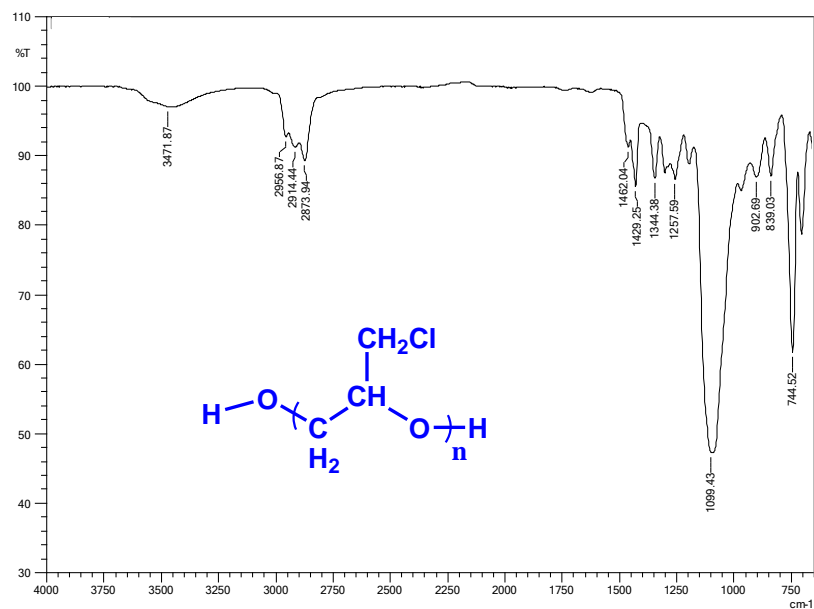
(b)

Figure 3.1: IR spectra of the overlay of ECH and PECH (a) and PECH (b)

The other peaks observed were assigned as: 2957 cm^{-1} (C-H in-skeletal plane asymmetric stretching); 2914 cm^{-1} (C-H out of skeletal plane asymmetric stretching); 2874 cm^{-1} (C-H symmetric stretching). The FT-IR data of all the synthesized PECH samples is given in Table 3.1.

Table 3.1: FT-IR data of synthesized PECH (cm^{-1})

Sample Codes	v_{OH}	v_{CH_2} (asym)	v_{CH_2} (sym)	v_{C-O-C}	v_{C-Cl}
Ref. Values	3400-3200	2955-2922	2880-2835	1130-1057	750-700
P-01	3350	2916	2875	1105	746
P-02	3348	2950	2851	1095	725
P-03	3295	2940	2857	1120	734
P-04	3301	2945	2847	1125	748
P-05	3280	2930	2839	1104	743
P-06	3275	2950	2850	1098	739
P-07	3290	2947	2843	1075	747
P-08	3395	2936	2851	1065	732
P-09	3401	2934	2865	1107	735
P-10	3378	2945	2845	1120	737
P-11	3287	2936	2854	1115	740
P-12	3298	2937	2853	1128	745

3.1.2.2 NMR structural elucidation

The ^{1}H and ^{13}C NMR spectra of the synthesized products showed all the expected peaks. The representative ^{1}H NMR spectrum of PECH (Figure 3.2) showed a multiplet at about 3.6-3.8 ppm corresponding to methyl, methine and chloromethylene i.e., five protons of the epichlorohydrin unit[103, 162, 163]. No peak was observed between 2.687-3.575 ppm, indicating the absence of oxirane ring in the product. ^{13}C NMR spectrum (Figure 3.3) gave peaks at 69.5 ppm for methylene, 79 ppm for methine and 43.6 ppm for chloromethylene carbon[162, 164].
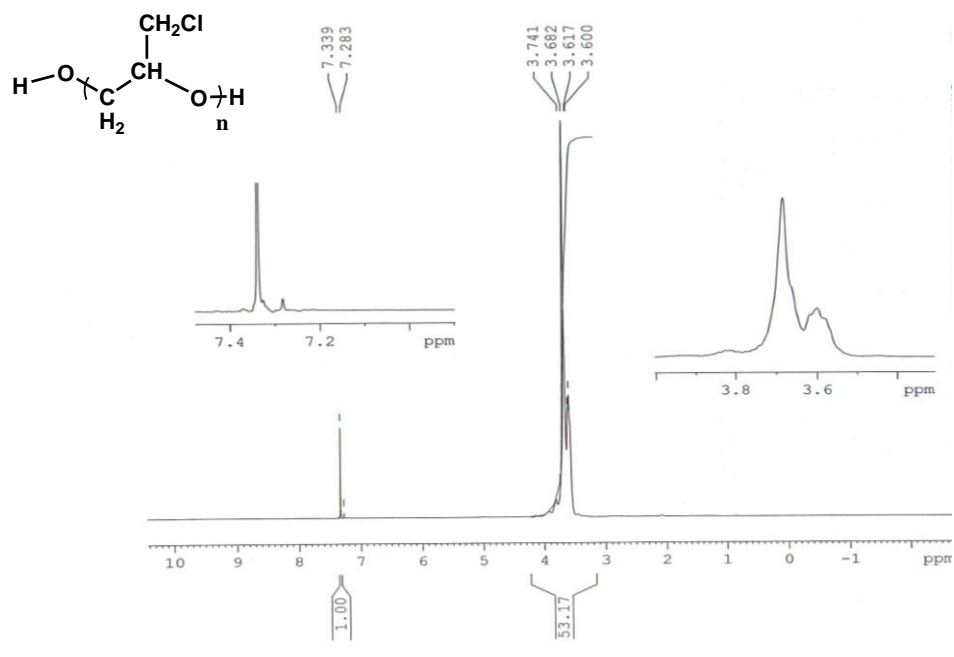
Figure 3.2: ^{1}H NMR spectrum of P-01
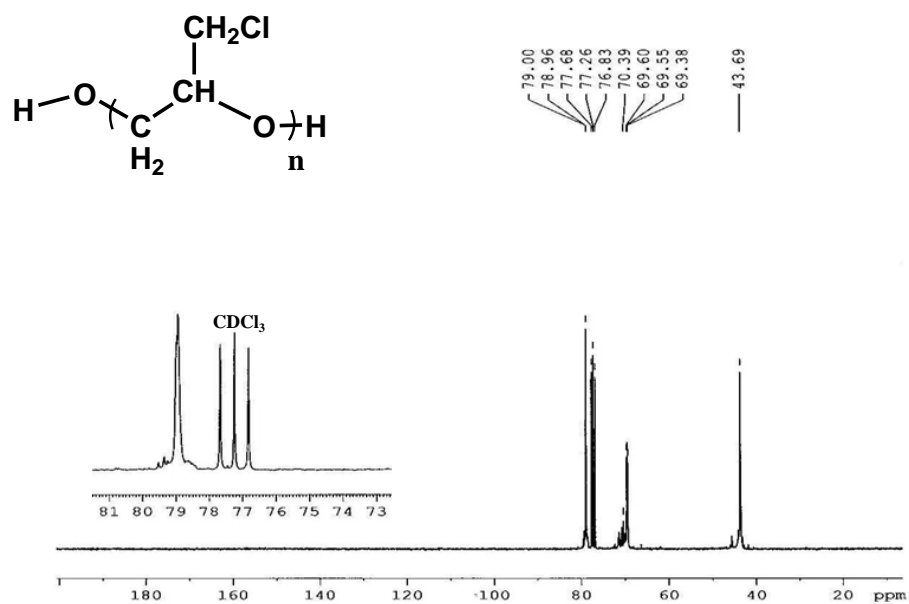
Figure 3.3: ^{13}C NMR spectrum of P-01

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3.1.3 Mechanism of polymerization

It was proposed that *p*-TSA reacted with ECH to form open chain co-initiator which on further reaction with SnCl$_4$ formed an initiator (Scheme 3.1)[165, 166].
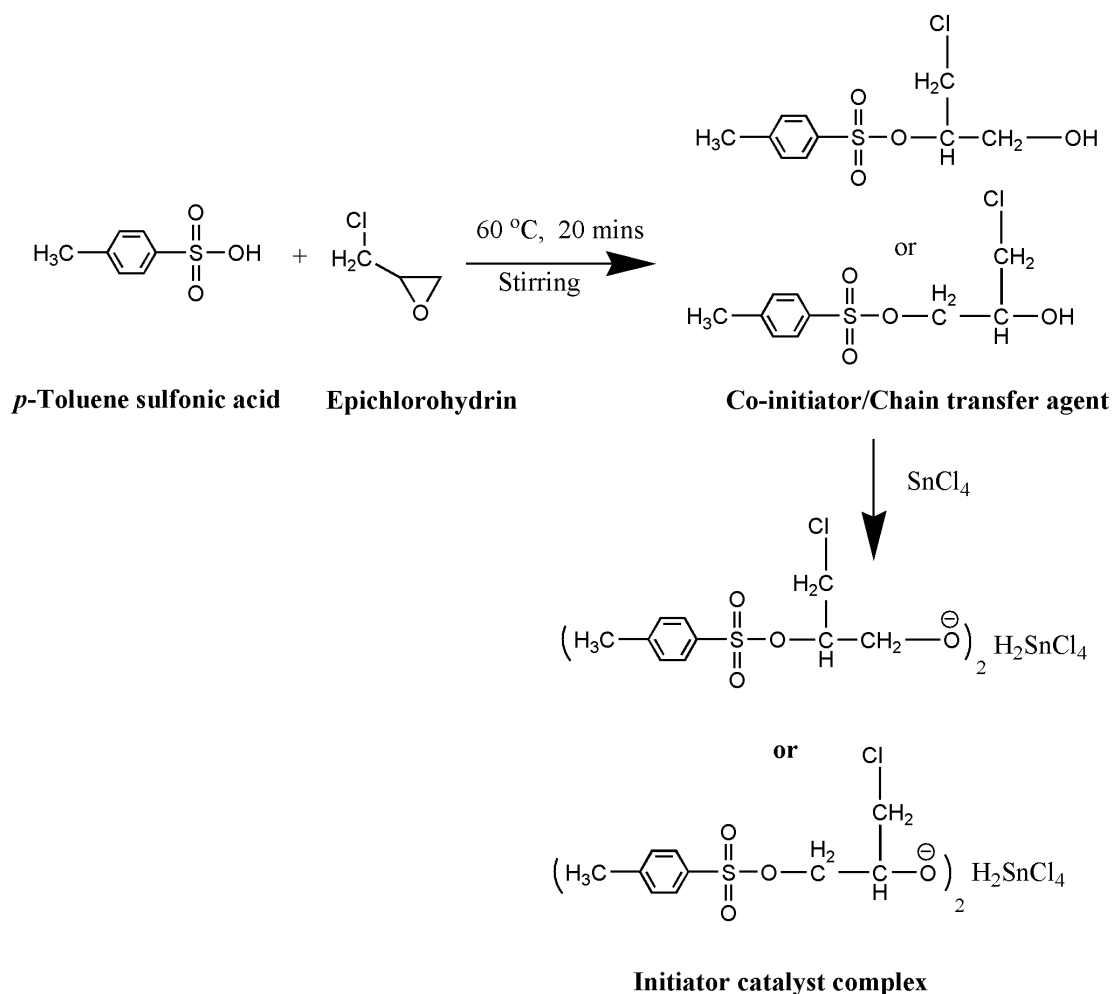
Scheme 3.1: Proposed mechanism for the reaction of ECH and *p*-TSA for co-initiator and initiator formation

This initiator on further reaction with ECH molecules yielded PECH by following either activated monomer (AM) or active chain end (ACE) mechanisms.

In AM mechanism, the initiator (Scheme 3.1) protonates the monomer molecules (ECH) and this protonated molecule then adds up in the growing polymer chain[167, 168]. Several of these protonated monomers incorporate in the growing chain leading to a linear chain PECH (Scheme 3.2).
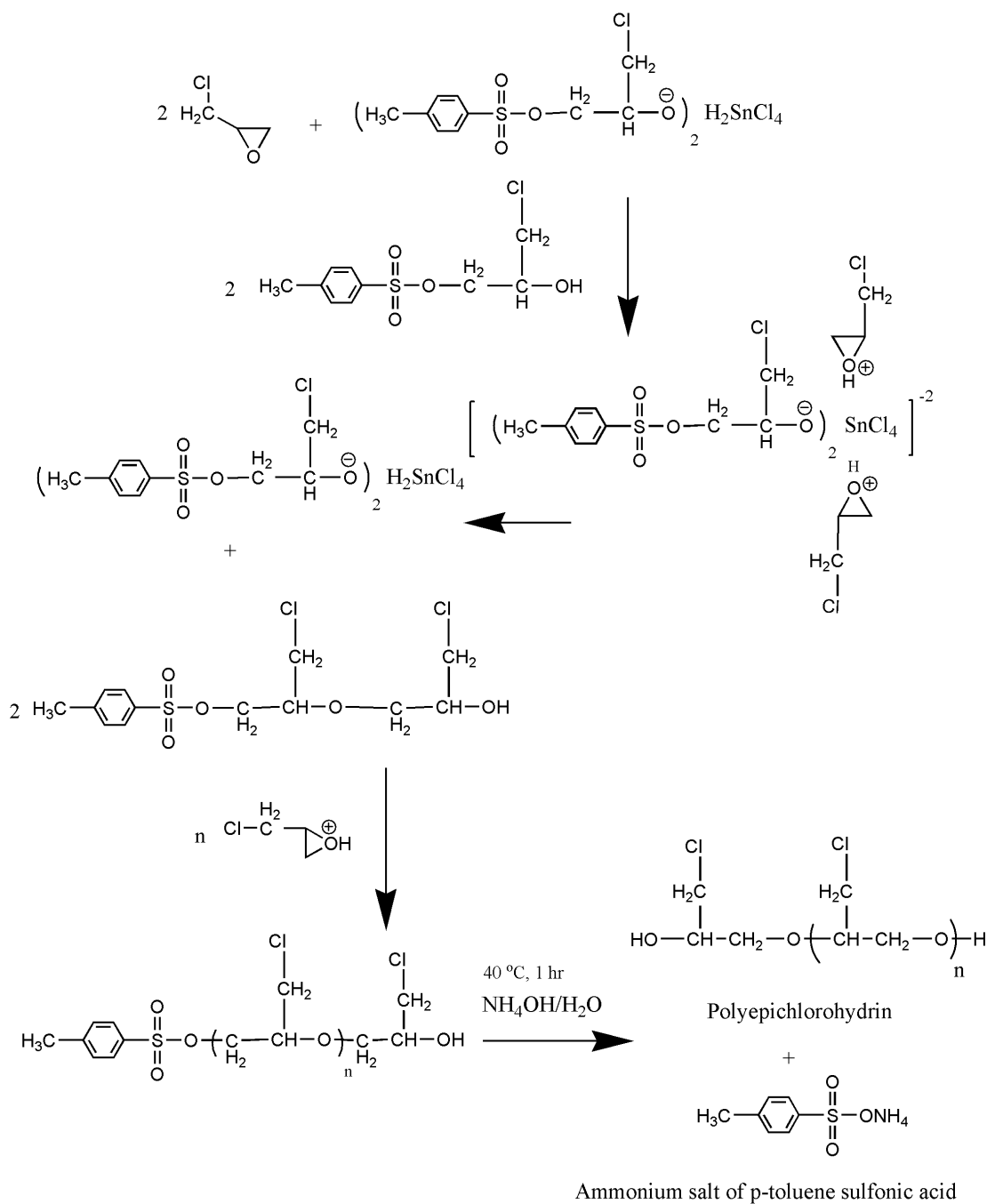
Scheme 3.2: Proposed mechanism for the preparation of PECH by active monomer mechanism

While, in ACE mechanism, the initiator molecules protonate the ECH in the same fashion as in AM mechanism but these protonated ECH molecules are attached to the deprotonated counter ion of initiator *via* electrostatic forces and then ECH attacks as a nucleophile on these positively charged ends extending the chain linearly (Scheme 3.3)[169]. Beside the linear chain polymers, the cyclic products are also

obtained by the intra-molecular back biting attack of the oxygen atom on the growing chain (Scheme 3.4)[106].
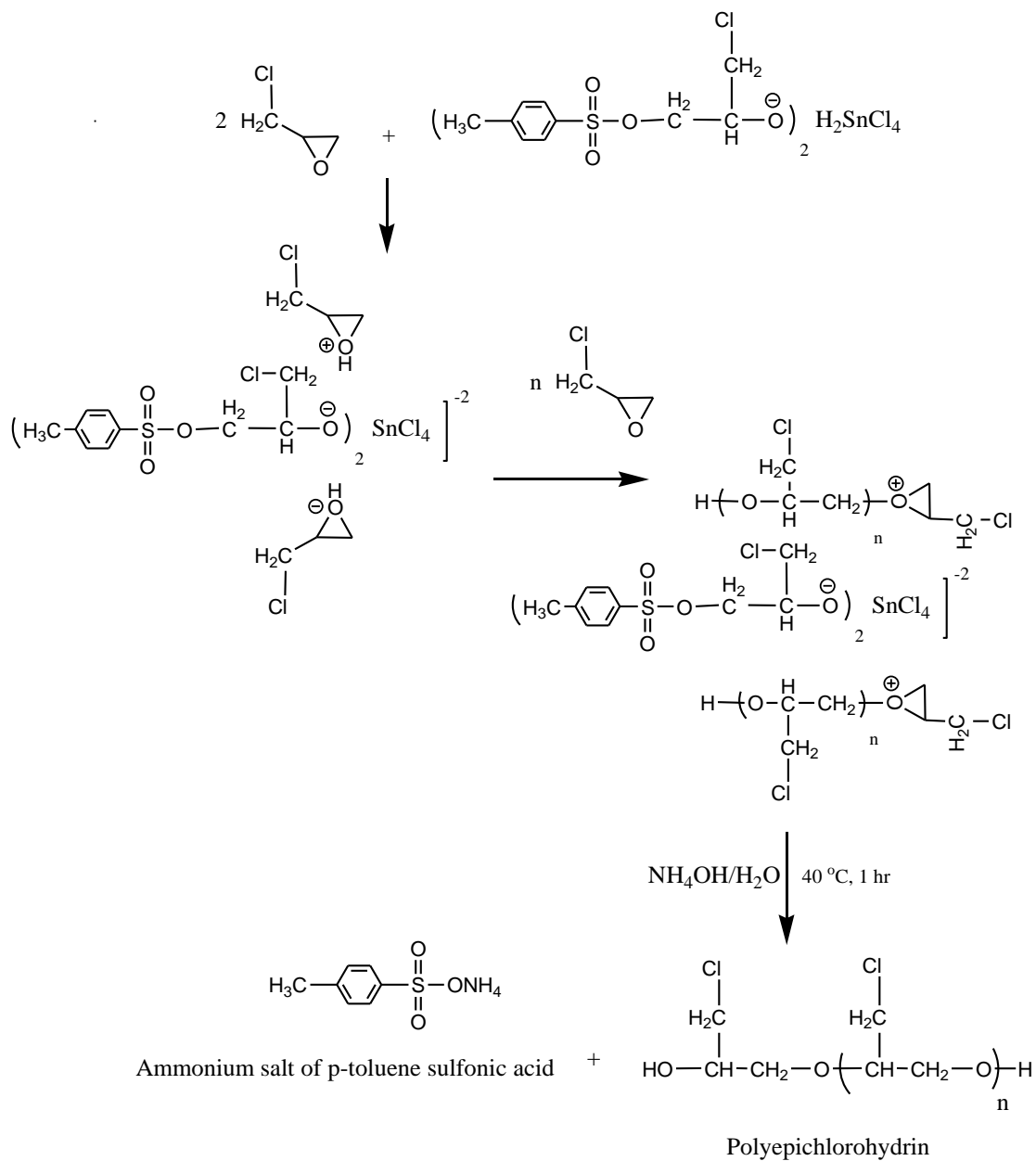
Scheme 3.3: Proposed mechanism for the preparation of PECH by active chain end mechanism
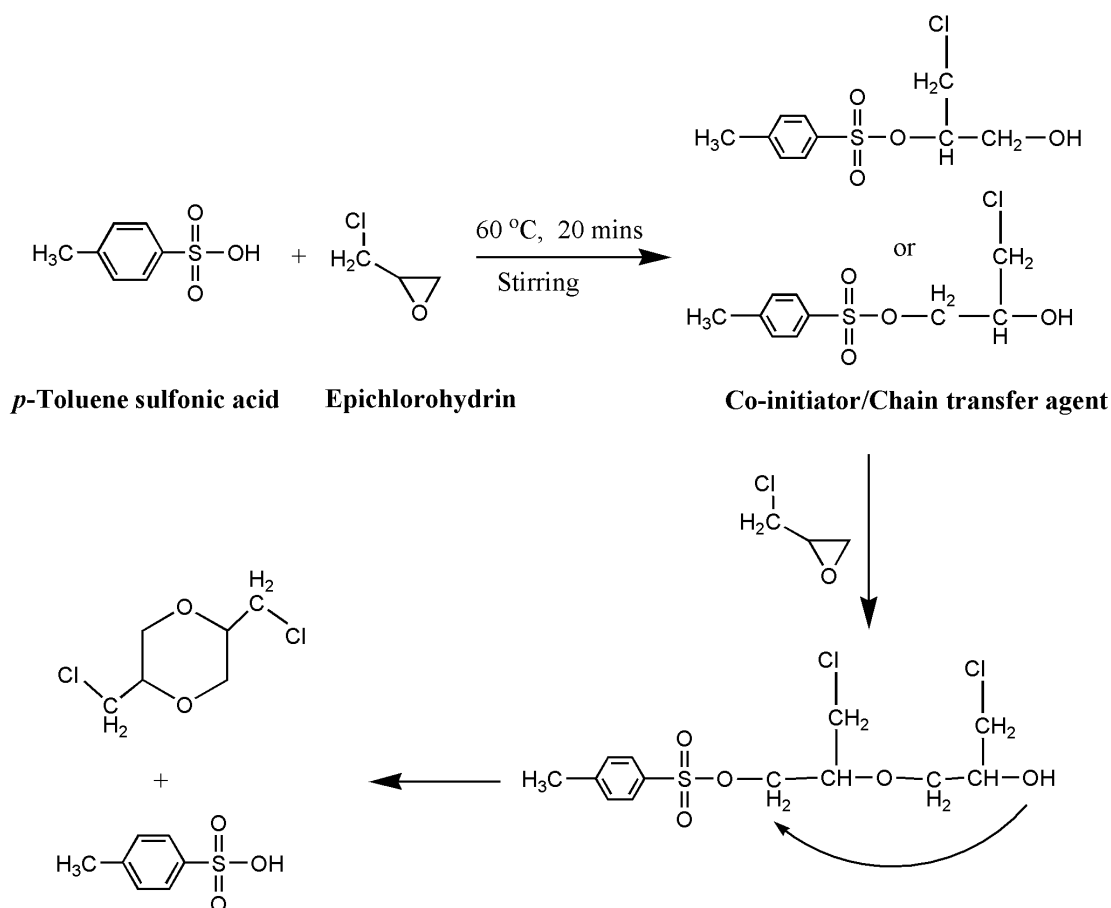
Scheme 3.4: Proposed mechanism for the formation of cyclic products from co-initiator molecules

Another mechanism i.e., pseudo living polymerization is also possible that has was confirmed by synthesizing P-13 using *p*-TSA and ECH without SnCl₄ (Table 2.2). This mechanism was suggested (Scheme 3.5) when excess number of moles of *p*-TSA against SnCl₄ (more than 2 moles per SnCl₄ mole) were used[100] . The contribution of this mechanism is not significant overall; since reaction *via* this mechanism proceeds slowly as P-13 gave less than 10 % yield in 5 hours. However, polydispersity was increased due to the operation of this mechanism as cyclic products were formed frequently.

The relative extent of different mechanisms depends upon the *p*-TSA/SnCl₄ ratio and instantaneous ratio of co-initiator/ECH (addition of ECH). Low concentration of *p*-TSA and slower addition of ECH favour AM mechanism while ACE and pseudo living mechanisms operate to lesser extent[170, 171].
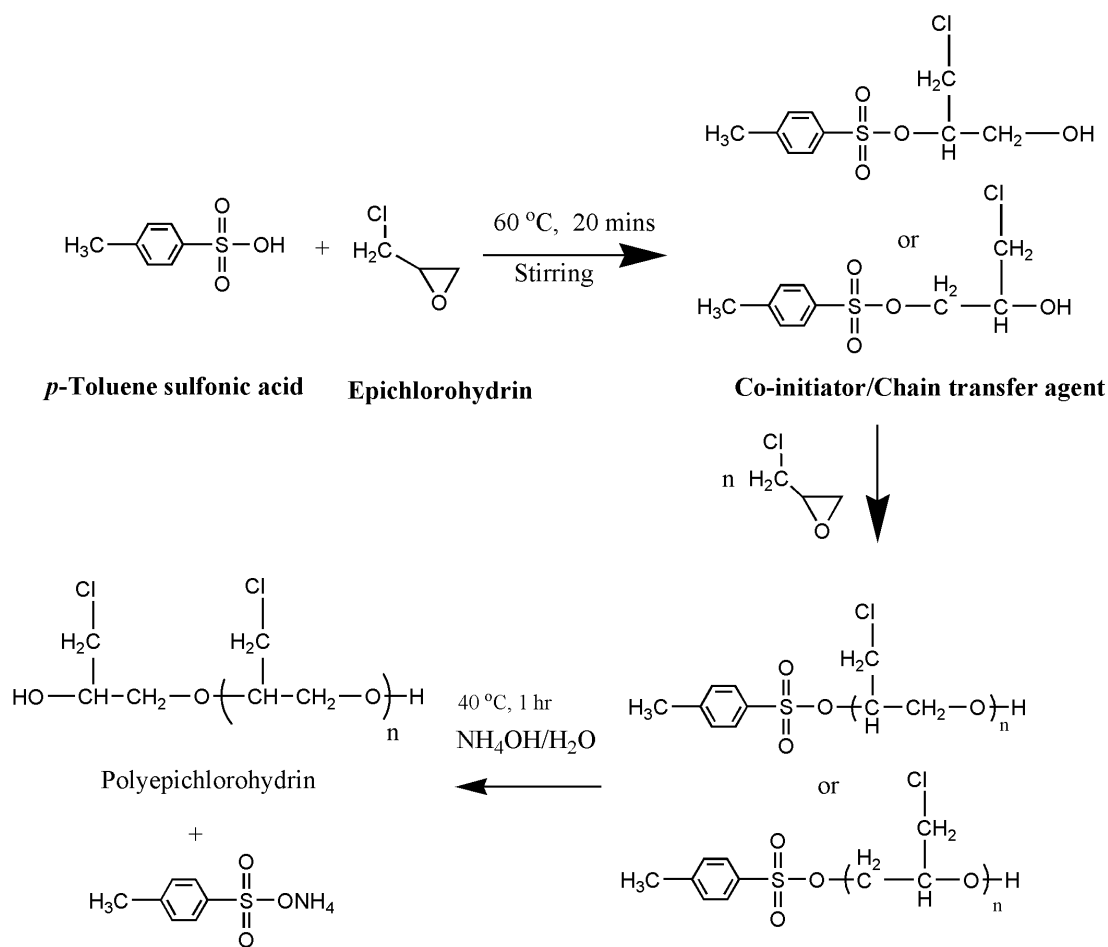
Scheme 3.5: Proposed mechanism for the preparation of PECH by pseudo living polymerization

3.1.4 Impact of processing parameters on the quality of PECH

The impact of processing parameters like quantity of catalyst/co-catalyst, time, temperature, ECH addition rate, moisture in different reagents and inert atmosphere on M_n, PDI and side products formation were studied.

3.1.4.1 Effect of quantity of catalyst/co-catalyst

The amount of *p*-TSA is found to have pronounced effect on M_n, PDI and side product formation. Following are the details of effects of *p*-TSA on the quality of product.

It was observed that M_n decreased with the increase in amount of *p*-TSA (Figure 3.4). As *p*-TSA is a strong acid and it can open the three-membered ring of ECH thus forming open chain molecule containing a good leaving tosylate group at one end and

hydroxyl group on the other end. Now there are two possibilities, either this molecule forms initiator with SnCl$_4$ (Scheme 3.1) or it forms cyclic products *via* pseudo living polymerization (Scheme 3.5). When molar ratio of *p*-TSA/SnCl$_4$ exceeds two, *p*-TSA cannot form initiator with SnCl$_4$, and hence it prefers to form six membered cyclic products (Scheme 3.4) reducing the M$_n$ of the product.

Figure 3.4 shows the effect caused by the number of moles of *p*-TSA on PDI. An increase in PDI was observed with the increase in the *p*-TSA moles. It is again due to the fact that an increase of *p*-TSA amount increases the formation of the side products *via* back biting attack of the OH group on C-atom containing the tosylate group and results in the cyclic products which contribute to the increase in PDI.

In Figure 3.5, the slope shows increasing trend on increasing the amount of *p*-TSA as formation of side products increases with the increase in number of moles of *p*-TSA. Increasing the amount of *p*-TSA, reaction mainly goes *via* pseudo living polymerization that results in cyclic product formation in greater amount rather than giving linear chain polymer. But in present case, although these low molecular weight side products are formed but these are much lower in quantity and not predominantly formed as reported earlier[103]. It is due to the use of *p*-TSA as co-catalyst which favours the chain propagation rather than forming cyclic products particularly when 2 molar ratio of *p*-TSA/SnCl$_4$ (Table 2.3) is used.
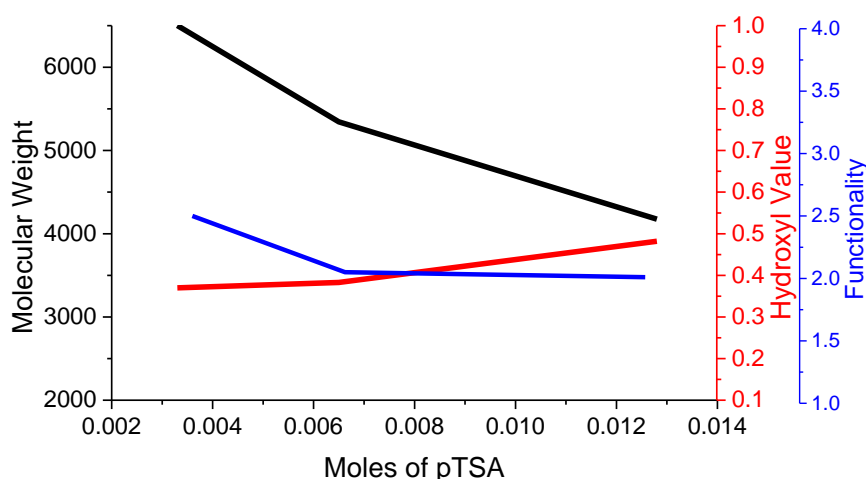
Figure 3.4: Impact of different amounts of *p*-TSA

By increasing the amount of $SnCl_4$ the chances of the operation of pseudo living mechanism decreases due to the unavailability of *p*-TSA, so linear chain polymer forms predominantly *via* ACE mechanism. Formation of cyclic products is also possible *via* ACE mechanism but their rate of formation is less in the present case because of the absence of pseudo living mechanism (solely ACE mechanism operates)[172, 173]. Coordination mechanism also operates when $SnCl_4$ is used as catalyst which also results in the formation of the linear chain products, therefore, M_n increases by increasing $SnCl_4$.

Figure 3.5 also shows an increasing trend in M_n, PDI and percentage of side products with increasing $SnCl_4$. $SnCl_4$ forms hexa-coordinated complexes and two molecules of either co-initiator or ECH can be coordinated as a result of two side-chain growths; the catalyst tend to aggregate and different sides get different rates of chain elongation. Therefore, when the amount of $SnCl_4$ is increased, the relative proportion of this coordination mechanism also increases that leads to an increase in PDI. Figure 3.5 shows that increasing $SnCl_4$ amount, the graph shows a rise in slope owing to the increase in the side products formation. This is due to the fact that the relative proportion of ACE mechanism increases that leads to an increase in side products formation.
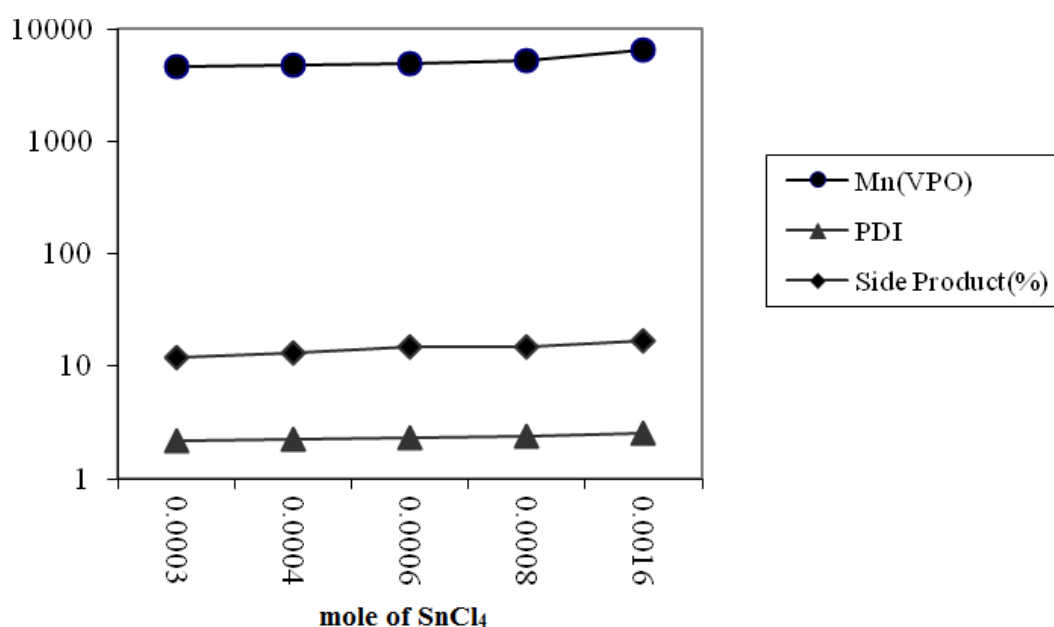
Figure 3.5: Impact of different amounts of $SnCl_4$

3.1.4.2 Reaction time

It was observed that reaction time has no remarkable effect on M_n, PDI and side products formation because the reaction proceeded slowly after two hours. But the reaction time significantly affects the yield of the product. The reaction yield was 40 %, 93 % and 98 % for 2, 5 and 22 hours respectively. Therefore, it was decided that 5 hours reaction time was suitable for PECH polymerization as reaction almost goes to completion. The reason of very slow reaction progress is that after some time (2 hours), the chain length increases slowly due to the decrease in effective collision of growing chain with incoming ECH molecules because the chain has more and more conformations as it elongates, therefore, its M_n does not increase remarkably. Similarly, PDI and side products also remain same over this time period (Figure 3.6).
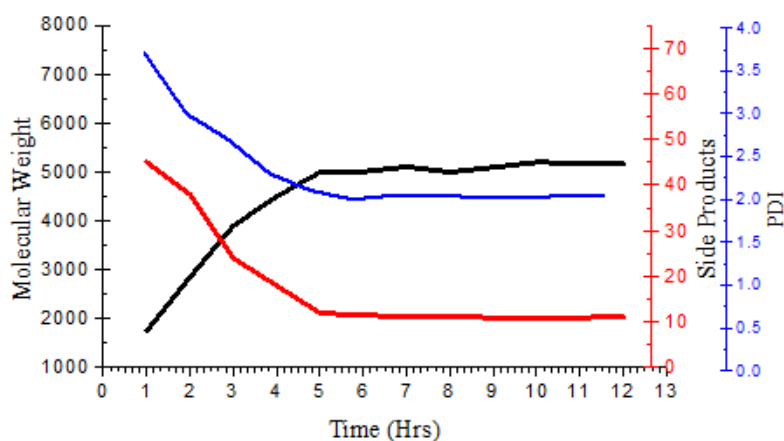
Figure 3.6: Effect of time (h) on reaction

3.1.4.3 Temperature

The effect of reaction temperature on M_n, PDI and side products formation was also studied. At higher temperature, the rate of polymerization (both linear chain as well as side products polymerization) increases, therefore, there should not be remarkable effect of temperature on the M_n[174]. This is evident from the Table 3.1 that P-12 synthesized at 70 °C has M_n 1900, whereas P-11 synthesized at ambient temperature has M_n 1700. Thus, an increase of 45 °C results in an increase of 200 in

M_n at higher temperature range. In fact, slight increase in M_n at higher temperature (70 °C) can be attributed to the relative increase in the rate of linear chain polymerization due to the increase in effective collision of growing long chains with incoming molecules of ECH. As at higher temperature the motion of molecules speeds up increasing the effective collision between molecules, so the rate of reaction increases.

PDI remained unaffected by varying temperatures; P-11 (ambient temperature) has PDI 2.74, whereas, P-12 (70 °C) has 2.72 (Table 3.1). At higher temperature, the rate of reaction increases and the chain grow faster than the cyclic products formation, therefore, side products decrease as is evident from the Table 3.1 that P-11 prepared at ambient temperature has 29 %, whereas P-12 (at 70 °C) has 20 % side products.

Table 3.2: Effect of temperature and ECH addition rates on products quality

S. No.	Runs	M_n (VPO)	M_n (GPC)	PDI	Side products (%)	Temp (°C) of reaction	Addition rate of ECH (mL min^{-1})
1	P-08	4654	1994	2.21	12	70	10
2	P-09	4414	1940	3.07	34	70	0.5
3	P-11	1700	1538	1.74	29	25	10
4	P-12	1900	1870	1.72	20	70	10

3.1.4.4 Addition rate of ECH

In the present study, two rates for ECH addition were employed i.e., 0.5 ml and 10 ml per minutes. From Table 3.2 it is evident that decreasing the rate of addition decreases the M_n. However, the previous studies show that with decreasing ECH addition rates, M_n increases due to the operation of AM mechanism. In present case when the addition rate is decreased (for P-09), the relative proportion of *Pseudo* living mechanism also increases along with AM mechanism, which leads to cyclic products and hence reduces M_n. Whereas higher addition rate favours ACE mechanism leading to increase in M_n.

Similar argument can be given for the increased PDI with decreasing ECH addition rate. It can be seen from Table 3.2 that P-09 has 3.07 PDI at 0.5 mL min^{-1} which is 20 times slower addition than P-08 (10 mL min^{-1}, PDI = 2.21).

There is a tremendous increase in the production of side products with decreasing addition rates. Side products of P-08 prepared with 10 mL min^{-1} rate are 12 %, while P-09 with addition rate of 0.5 mL min^{-1} has 34 % of side products.

3.1.4.5 Moisture

The effect of total moisture in different reagents (Table 3.3) like *p*-TSA, ECH etc., on the products quality was studied. The moisture has very adverse effects on M$_n$ of the products which is in accordance with the observation made by Jairo Sciamareli[175]. The graph in Figure 3.7 shows a dramatic decrease in slope which is due to the fact that when moisture increases, termination of the growing chain takes place, and this immature chain termination results in short-chain oligomers (<500). Thus, frequent formation of the short-chain oligomers results in tremendous decrease in M$_n$. The Figure 3.7 shows a sudden increase in slope due to the formation of increasing number of oligomers as the moisture in reagents increases.
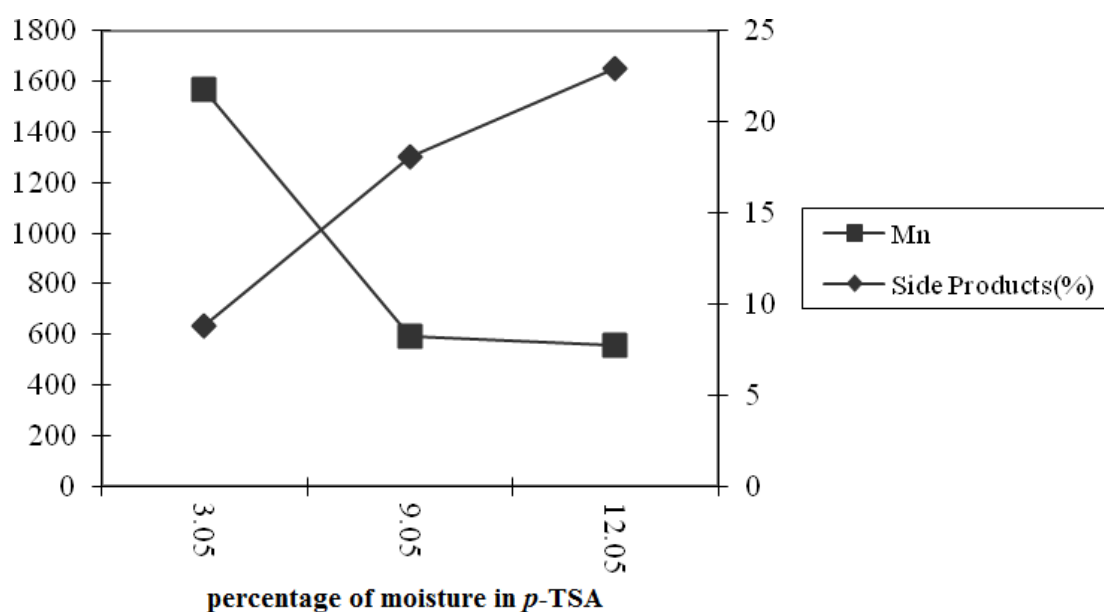
Figure 3.7: Effect of moisture on product quality

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Table 3.3: Effect of moisture on products quality

S. No.	Sample ID	M_n (VPO)	Side products (%)	Total moisture (%)
1	P-14	1567	8.8	3.05
2	P-14 (R1)	594	18.1	9.05
3	P-14 (R2)	560	22.9	0.1205

3.1.4.6 Inert atmosphere

P-01 and P-02 were prepared with and without N_2 provision (Table 3.4) while keeping all the other condition constants. The number average molecular weight, poly dispersity index and functionalities of both the products are comparable.

Table 3.4: Effect of inert condition on the products properties

S. No.	Runs	M_n (VPO)	M_w/M_n	Side products (%)	N_2 Flux
1	P-01	4226	1.92	27	yes
2	P-02	4175	2.09	25	no

3.1.5 Characterization of Polyols used for preparation of PUE:

After optimization of the conditions for polymerization of epichlorohydrin, three polymers of different molecular weights were prepared in bulk. Figure 3.8 shows the overlay of gel permeation chromatogram of P-10 and P-25 samples which confirms the formation of polymers of two different molecular weights.

Further increase of molecular weight results in the reduction of intensity of hydroxyl group in IR region (~ 3450 cm^{-1}) which is illustrated in Figure 3.9. These polyols were completely characterized for M_n, hydroxyl value, functionality, moisture contents and volatile matter. The characteristics of the polyols are shown in Table 2.1.
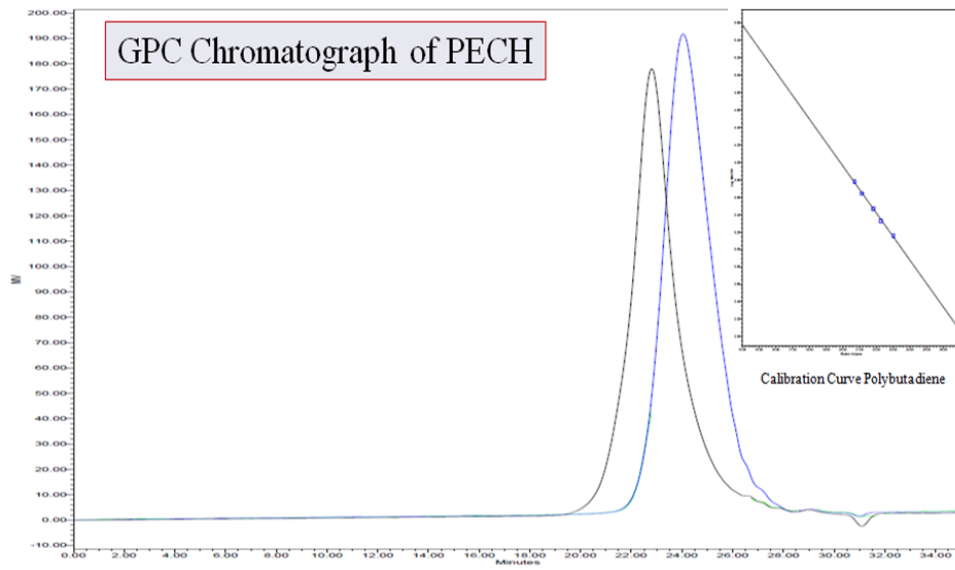
Figure 3.8: GPC of PECH
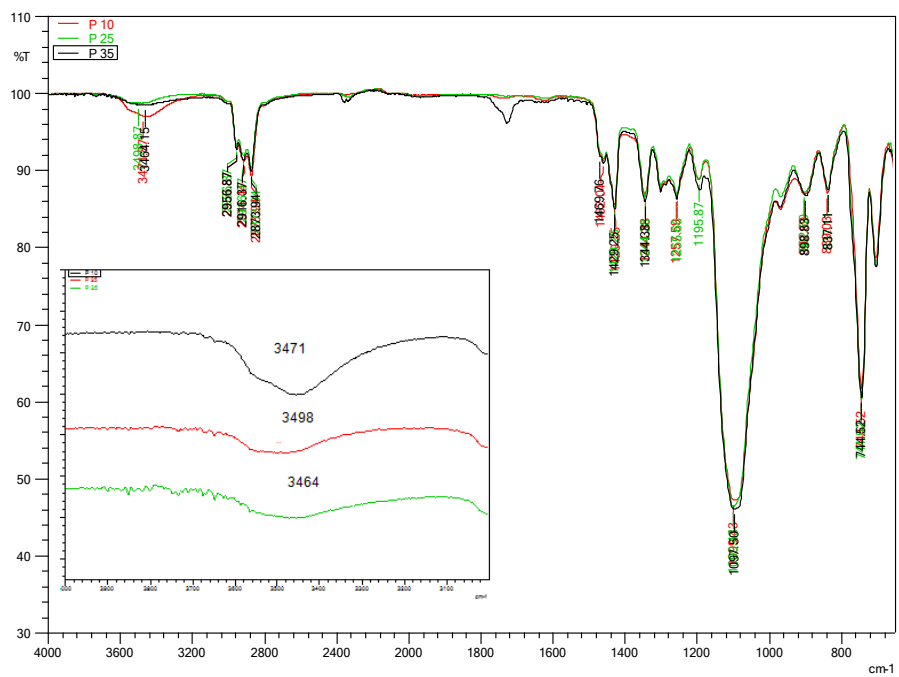
Figure 3.9: Effect of M_n on OH absorption intensity

3.2 Synthesis and characterization of polyurethane elastomers

This section deals with the synthesis, structural, thermal and mechanical characterization of novel polyurethane elastomers prepared from hydroxyl terminated poly(epichlorohydrin) of different molecular weights (1000, 2500 and 3500) cured with aromatic and cycloaliphatic diisocyanates with fixed NCO/OH ratio equal to 1.05 and extended with 1,4-butanediol, 1,6-hexanediol and 1,4-cyclohexane dimethanol. A range of polyurethane samples were synthesized via prepolymer methodology. The reaction of polyepichlorohydrin polyol with excess diisocyanate was performed to get NCO-terminated polyurethane prepolymer, which was subsequently extended with chain extender to prepare final polyurethane. The work was performed to study the effect of molecular weight of PECH, nature of diisocyanates and nature/quantity of chain extenders on the thermo-mechanical properties of PUEs. The raw materials used in this study are shown in Figure 3.10
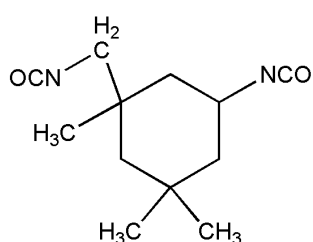
Isophoron diisocyanate (IPDI)   **Toluene diisocyanate (TDI)**
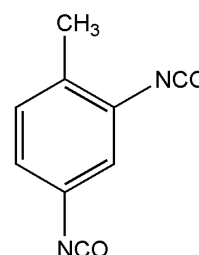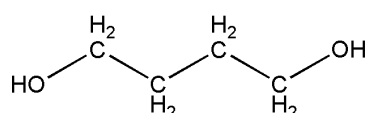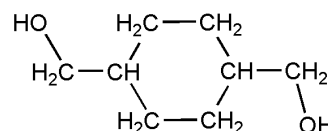
1,4-Butane diol   **Cyclohexane dimethanol**
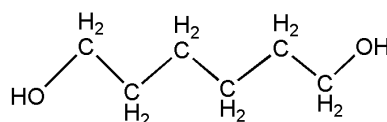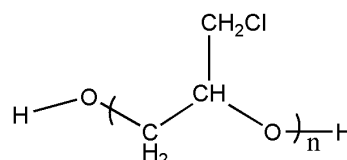
1,6-Hexane diol   **Polyepichlorohydrin**

Figure 3.10: The raw materials used to synthesize the PUEs

3.2.1 Synthesis of polyurethane elastomers

All the polyurethane elastomers were prepared following the pre-polymer method as described in section 2.3. All the reaction conditions were kept constant for comparison purposes. In order to study impact of structural diversification on properties of polyurethane elastomers six series were prepared. In each series, molecular weight of PECH and percentage of chain extenders were varied. Polyepichlorohydrins of 1045, 2497 and 3521 molecular weights were utilized and designated as P-10, P-25 and P-35 while the percentage of the chain extenders was 1.0%, 1.5% and 2.0%.

In PECH-TDI-BD series, hydroxyl terminated polyepichlorohydrin polyol was reacted with toluene diisocyanate to get -NCO terminated polyurethane prepolymer, which was subsequently extended with 1,4-buatnediol to prepare final polyurethane. The sequence of reactions performed are given in Scheme 3.6 and compositions of each polymer of this series is given in Table 2.4.
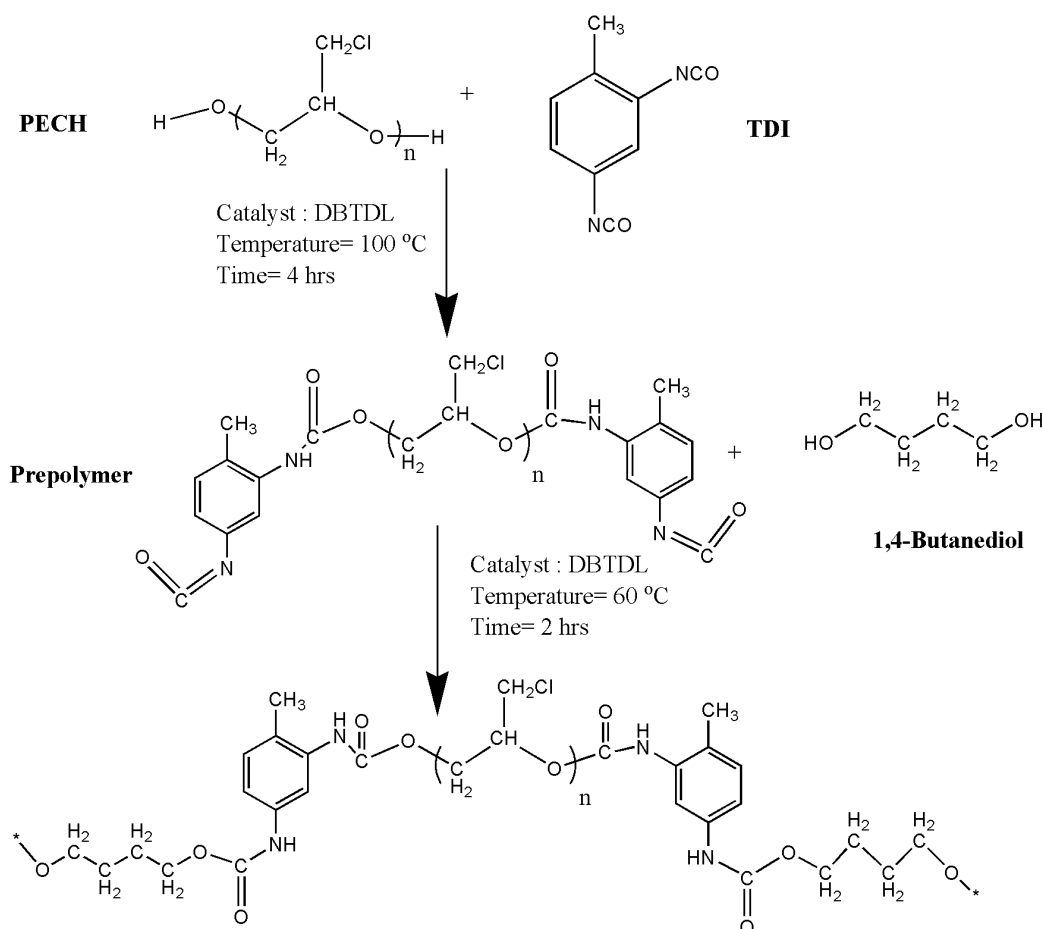
Scheme 3.6: Synthesis of PECH-TDI-BD

In PECH-TDI-HD series, -NCO terminated polyurethane prepolymer was obtained by the reaction of hydroxyl terminated polyepichlorohydrin polyol with toluene diisocyanate. -NCO terminated polyurethane prepolymer was further extended with 1,6-hexanediol to get the product as shown in Scheme 3.7. The composition of each member of the series is presented in Table 2.4.
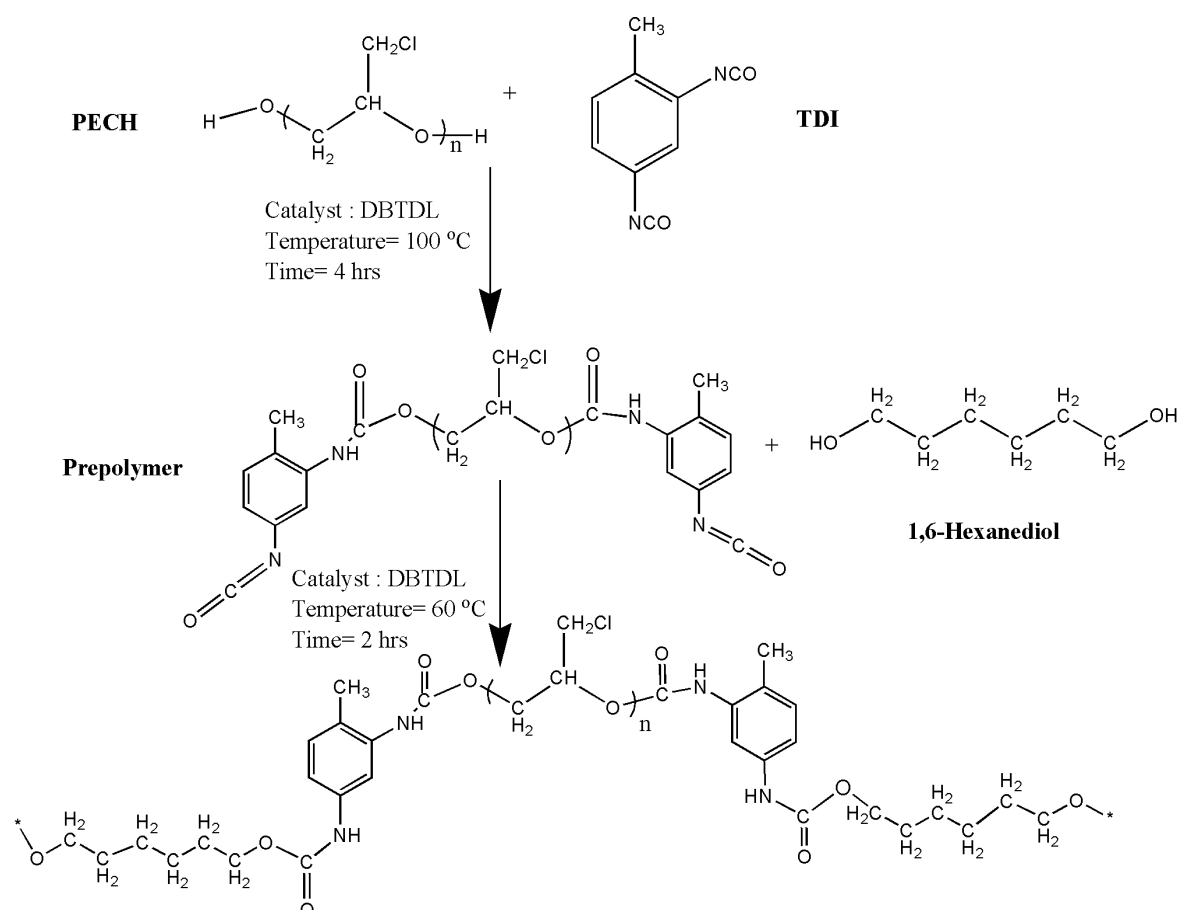
Scheme 3.7: Synthesis of PECH-TDI-HD

In PECH-TDI-DM series, hydroxyl terminated polyepichlorohydrin polyol was reacted with toluene diisocyanate to get -NCO terminated polyurethane prepolymer, which was subsequently extended with cyclohexanedimethanol to prepare final polyurethane. The sequence of reactions performed are given in Scheme 3.8 and composition of each polymer of this series is given in Table 2.4.
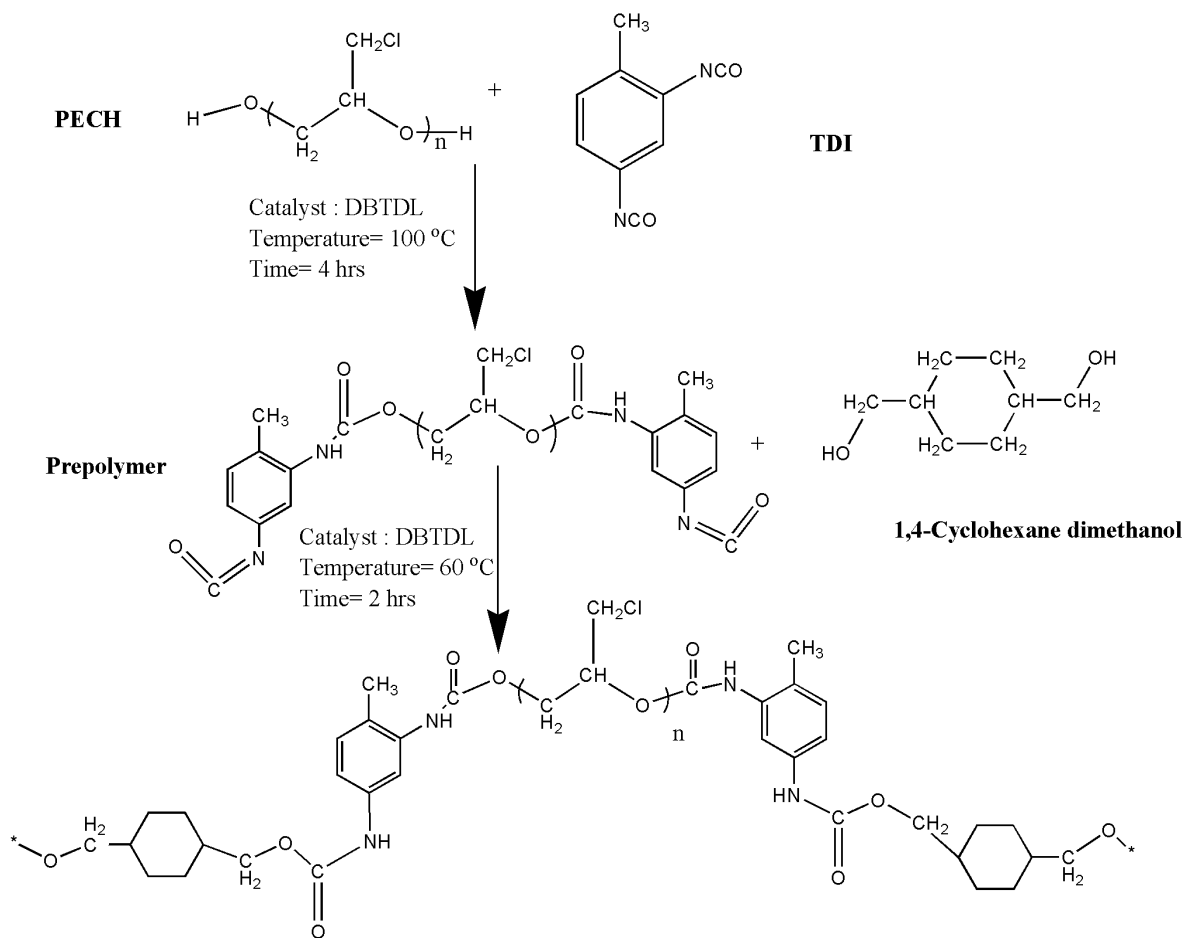
Scheme 3.8: Synthesis of PECH-TDI-DM

In PECH-IPDI-BD series, hydroxyl terminated polyepichlorohydrin polyol was reacted with isophorone diisocyanate to get -NCO terminated polyurethane prepolymer, which was subsequently extended with 1-4-buatnediol to prepare final polyurethane. The sequence of reactions performed are given in Scheme 3.9 and compositions of each polymer of this series is given in Table 2.5.

PECH-IPDI-HD series was prepared by the reaction of isophorone diisocyanate with -OH terminated polyepichlorohydrin polyol to produce -NCO terminated polyurethane prepolymer, which was further extended by 1,6-hexanediol. Scheme 3.10 describes the sequence of reactions and the compositions are described in Table 2.5.
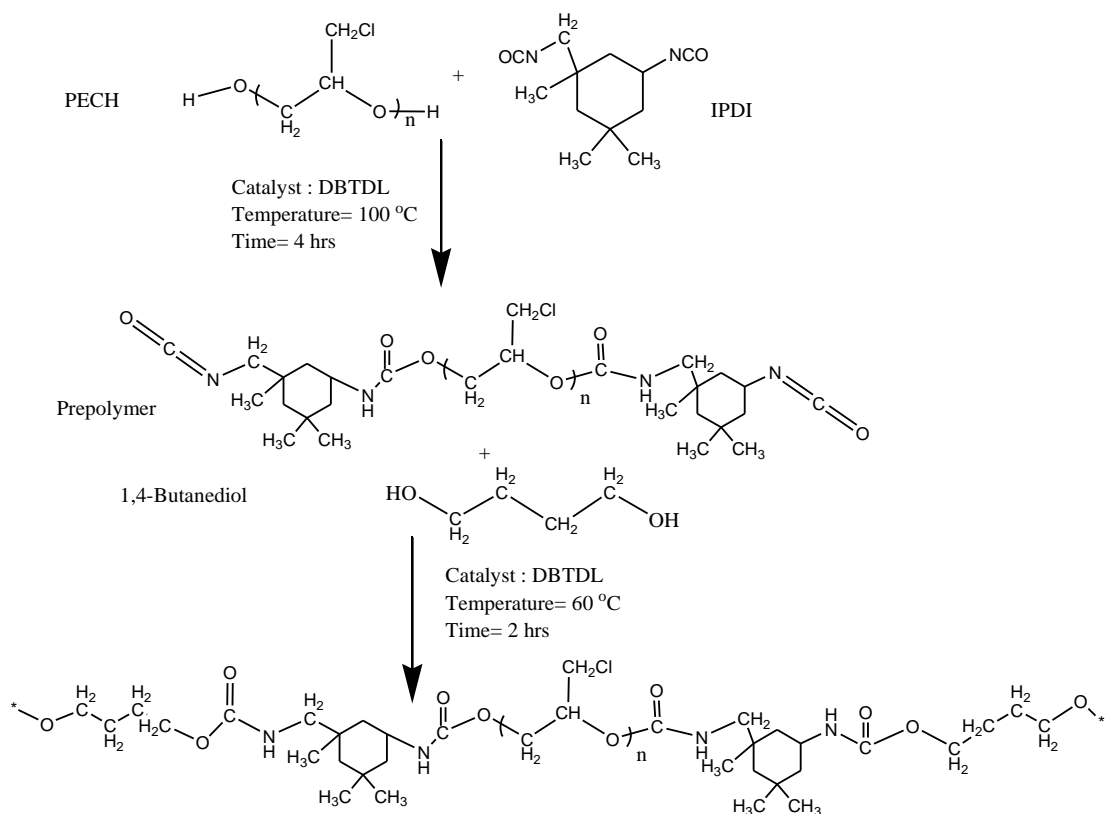
Scheme 3.9: Synthesis of PECH-IPDI-BD
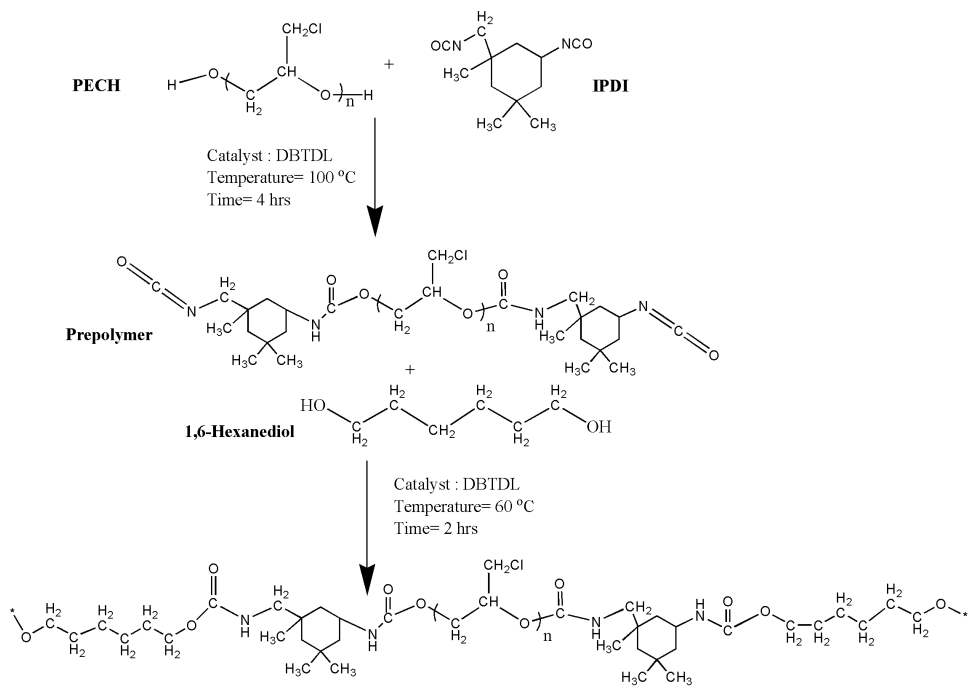
Scheme 3.10: Synthesis of PECH-IPDI-HD

PECH-IPDI-DM series was similarly prepared as described in Scheme 3.8, 3.9 and 3.10 except that -NCO terminated polyurethane was extended with cyclohexanedimethanol to get the final product. Scheme 3.11 describes reaction sequence while Table 2.5 represents composition.
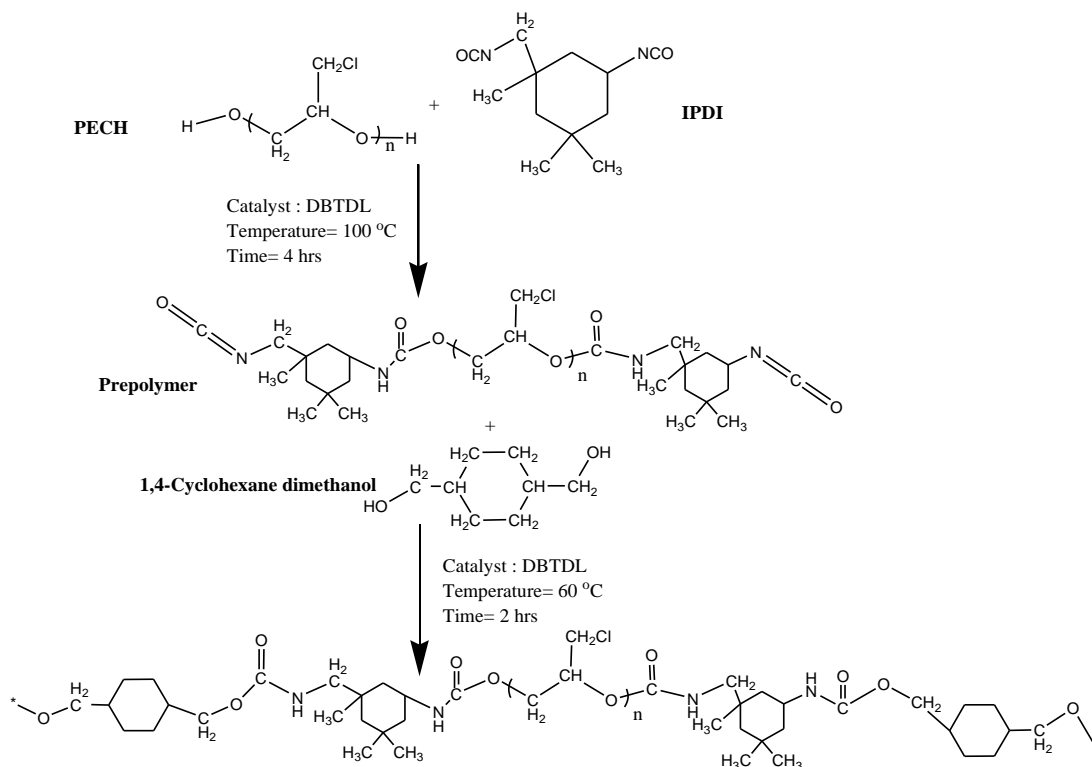
Scheme 3.11: Synthesis of PECH-IPDI-DM

3.2.2 Characterization of polyurethane elastomers

Synthesized polyurethane elastomers were analyzed by using different analytical techniques such as fourier transform infrared (FTIR) spectroscopy, proton nuclear magnetic resonance (^{1}H-NMR), scanning electron microscopy (SEM), X-ray diffraction (XRD), differential scanning calorimetry (DSC) and thermogravimetric and differential thermal analysis (TG/DTA). The mechanical properties of the synthesized elastomers were also investigated .

3.2.2.1 Fourier transform infrared (FTIR) spectroscopy

The FTIR spectrum of TDI have a very strong absorption peak at 2200 cm^{-1} due to the isocyanate (−N=C=O) group attached at 2 and 4 position of toluene[176]. The spectrum shows sharp peaks because of C=C stretching of aromatic ring in three regions 1522, 1578 and 1611 cm^{-1}. Isophorone diisocyanate also have intense

absorption peak of -NCO group at 2200 cm^{-1}. The CH symmetric and asymmetric stretching vibrations of CH$_2$ are observed at 2918 cm^{-1} and 2845 cm^{-1} respectively. The peaks at 1454 cm^{-1} (CH$_2$ bending) and strong absorption peak at 1360 cm^{-1} is for C(CH$_3$)$_2$ present on the carbocyclic ring of IPDI.

The characteristic peaks of PECH have already been discussed in section 3.1.2.1. FTIR spectra of 1,4-butanediol, 1,6-hexanediol and cyclohexanedimethanol have broad OH stretching vibration peak which appeared in the typical region 3400 to 3000 cm^{-1}. The CH symmetric and asymmetric stretching vibrations of CH$_2$ groups are observed in 2936- 2868 cm^{-1} region. After the formation of polyurethane linkage, peaks for the OH and NCO groups vanished and corresponding peaks for NH units appeared at 3307 cm^{-1}, for C=O stretching and CN bending (urethane linkage) at 1715 cm^{-1} and 1531 cm^{-1} respectively. Figure 3.11 shows the typical spectrum showing IR peak shifts during urethane bond formation.
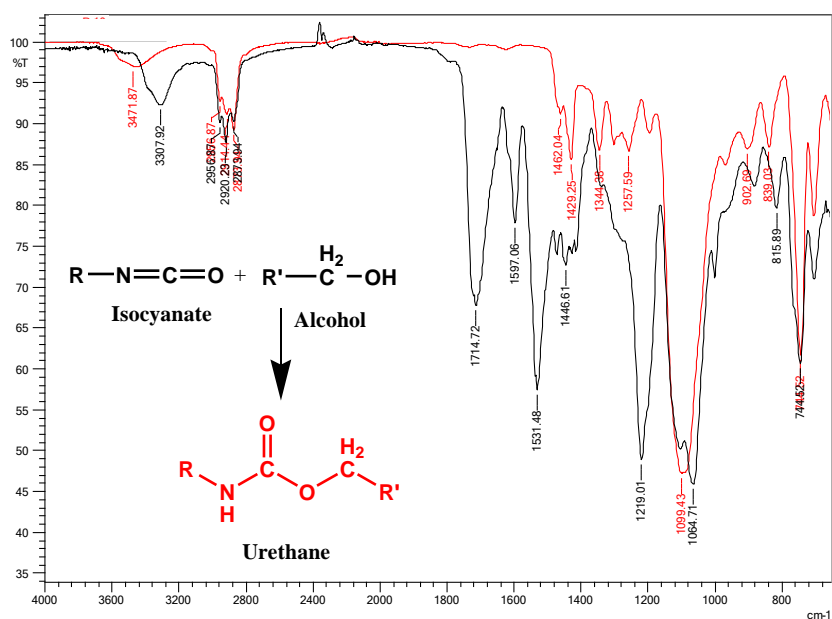
Figure 3.11: IR peak shifts during urethane bond formation

In the FTIR analysis of PECH-TDI-BD series (Figure 3.12), disappearance of the both broad stretching vibration peaks of NCO and OH at 2235 cm^{-1} and 3464-3498 cm^{-1} (PECH) respectively along with corresponding appearance of NH stretching peak at 3308 cm^{-1} and N-H bending vibrations at 1531 cm^{-1} indicates the

formation of urethane linkage. The FTIR spectrum showed strong peaks at 1715 cm^{-1} and 1219 cm^{-1} corresponding to the absorption of C=O (carbonyl) and C-O-C (urethane) respectively which indicated that new synthesized product has urethane group (-NHCOO-). Furthermore, the presence of C-O-C stretching absorption peak of polyether linkage at 1065 cm^{-1}, C-H in-skeletal plane symmetric stretching at 2957 cm^{-1}, C-H out of skeletal plane symmetric stretching at 2914 cm^{-1} and C-H symmetric stretching at 2874 cm^{-1} provided strong evidence for the formation of toluene diisocyanate and butanediol based polyurethane elastomers.

Important absorption peaks by other group members of this series are given in Table 3.5. FTIR spectra of this series showed characteristic peaks of urethane groups in 3308-3335 cm^{-1} region (N–H stretching). In other regions, observed peaks were assigned as: 1697-1717 cm^{-1} (C=O bond); 1587-1597 cm^{-1} (N-H deformations); 1516-1531 cm^{-1} (C-N Bending); 1217-1234 cm^{-1} (urethane C-O-C); 1058-1092 cm^{-1} (C-O-C ether); 743-749 cm^{-1} (C-Cl). These absorption regions implied the synthesis of pre-designed polymer and supported its structure as proposed in Scheme 3.6. The change in molecular weight of polyepichlorohydrin and percentage of 1,4-butanediol showed no significant impact on FT-IR spectra.
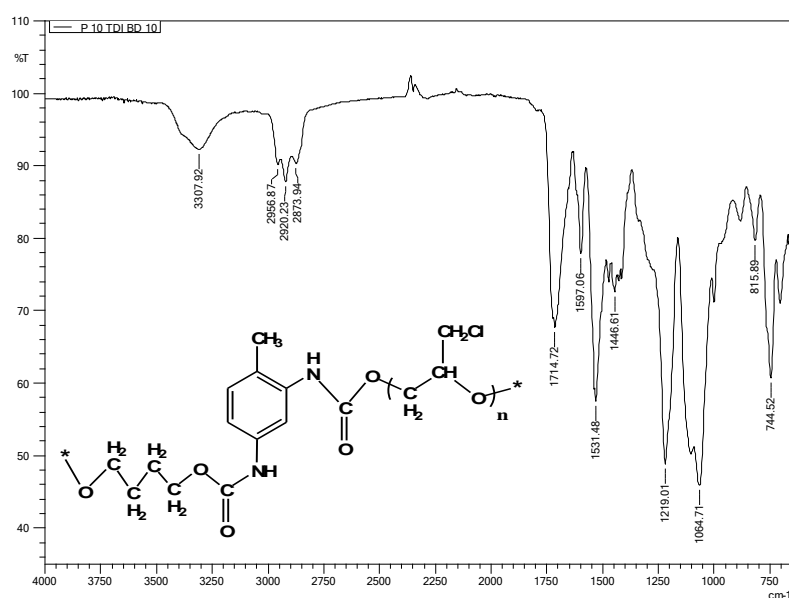
Figure 3.12: FT-IR spectrum of PECH polyurethane based on TDI extended with BD

Compound Codes	ν_{NH}	$\nu_{C=O}$	ν_{NH} (bending)	ν_{CN} (bending)	ν_{C-O-C} (Urethane)	ν_{C-O-C}	ν_{C-Cl}
P10TDIBD10	3307	1714	1597	1531	1219	1064	744
P10TDIBD15	3335	1703	-	1518	1232	1085	746
P10TDIBD20	3327	1697	-	1519	1234	1092	746
P25TDIBD10	3335	1705	1593	1517	1222	1059	749
P25TDIBD15	3329	1699	-	1528	1227	1058	744
P25TDIBD20	3331	1705	1595	1516	1230	1060	746
P35TDIBD10	3330	1717	1589	1521	1233	1063	748
P35TDIBD15	3329	1715	1588	1528	1218	1064	745
P35TDIBD20	3333	1714	1595	1529	1217	1065	743

In the FTIR analysis of PECH-TDI-HD series (Figure 3.13), disappearance of the broad stretching vibration peaks of NCO and OH at 2235 cm^{-1} and 3464-3498 cm^{-1} (PECH) respectively along with the appearance of N-H stretching peak at 3308 cm^{-1} and N-H bending vibration at 1597 cm^{-1} depicts the formation of urethane linkage. The FTIR spectrum contains very strong peak at 1715 cm^{-1} and 1219 cm^{-1} suggesting the presence of C=O (carbonyl) and C-O-C (urethane), which indicates that new synthesized product has urethane group (-NHCOO-). Furthermore, the presence of C-O-C stretching absorption peak of polyether linkage at 1075-1105 cm^{-1}, C-H in-skeletal plane symmetric stretching at 2953 cm^{-1}, C-H out of skeletal plane symmetric stretching at 2924 cm^{-1} and C-H symmetric stretching at 2870 cm^{-1} provides strong evidence for the formation of toluene diisocyanate and hexanediol based polyurethane elastomers.

Table 3.5 shows the summary of the characteristic absorption peaks of rest of group members of PECH-TDI-HD series. FTIR spectra of this series contain characteristic peaks of urethane groups in 3307-3344 cm^{-1} region (N–H stretching). In other regions observed peaks were assigned as: 1698-1718 cm^{-1} (C=O bond); 1518-1531 cm^{-1} (C-N bending); 1219-1234 cm^{-1} (urethane C-O-C); 1058-1072 cm^{-1} (C-O-C ether); 741-749 cm^{-1} (C-Cl). These absorption peaks signify the successful synthesis of pre-designed polymer and support its proposed structure in Scheme 3.7. The

change in molecular weight of polyepichlorohydrin and percentage of 1,6-hexanediol showed no significant impact on FT-IR spectra.
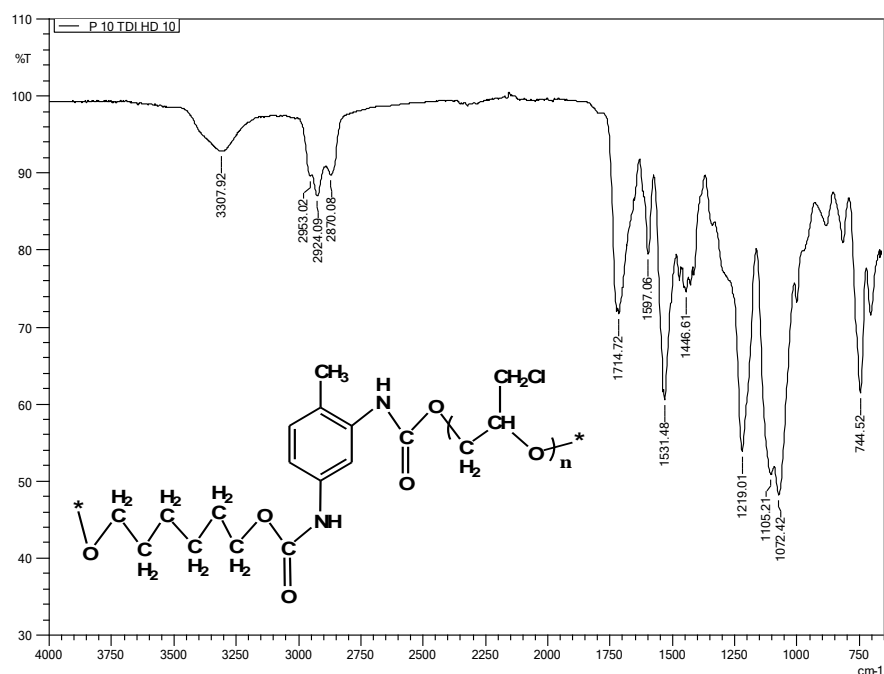
Figure 3.13: FT-IR spectrum of PECH polyurethane based on TDI extended with HD

Table 3.6: FT-IR spectroscopic data of PECH-TDI-HD series (cm^{-1})

Compound Code	ν_{NH}	$\nu_{C=O}$	ν_{NH} (bending)	ν_{CN} (bending)	ν_{C-O-C} (urethane)	ν_{C-O-C}	ν_{C-Cl}
P10TDIHD10	3307	1714	1597	1531	1219	1072	744
P10TDIHD15	3312	1700	-	1525	1231	1065	745
P10TDIHD20	3317	1698	-	1527	1234	1062	747
P25TDIHD10	3344	1718	1593	1518	1224	1059	749
P25TDIHD15	3338	1715	1591	1525	1227	1058	747
P25TDIHD20	3335	1713	1595	1522	1230	1060	744
P35TDIHD10	3340	1718	1589	1519	1221	1063	748
P35TDIHD15	3342	1715	1588	1521	1225	1064	741
P35TDIHD20	3340	1713	1595	1531	1229	1065	745

In the FTIR analysis of PECH-TDI-DM series (Figure 3.14), NCO and OH peaks at 2235 cm^{-1} and 3464-3498 cm^{-1} (PECH) are disappeared while the presence of N-H stretching peak at 3310 cm^{-1} and N-H bending vibration at 1531 cm^{-1} suggested the formation of urethane linkage. The FTIR spectra have very strong peak at 1722 cm^{-1} and 1221 cm^{-1} due to the presence of C=O (carbonyl) and C-O-C (urethane) respectively, which indicated that new synthesized product has urethane group (-NHCOO-). Furthermore, the presence of C-O-C stretching absorption peak of polyether linkage at 1076-1105 cm^{-1}, C-H in-skeletal plane symmetric stretching at 2953 cm^{-1}, C-H out of skeletal plane symmetric stretching at 2922 cm^{-1} and C-H symmetric stretching at 2872 cm^{-1} provided strong evidence for the formation of toluene diisocyanate and hexanedimethanol based polyurethane elastomers.

Figure 3.14 is the representative spectrum of PECH-TDI-DM polyurethanes and significant absorption peaks for the rest of group members of this series are given in Table 3.7. FTIR spectra of this series showed characteristic peaks of urethane groups in 3310-3335 cm^{-1} region (N–H stretching). In other regions, observed peaks were assigned as: 1702-1722 cm^{-1} (C=O bond); 1588-1597 cm^{-1} (N-H deformations); 1527-1531 cm^{-1} (C-N bending); 1219-1230 cm^{-1} (urethane C-O-C); 1058-1085 cm^{-1} (C-O-C ether); 744-749 cm^{-1} (C-Cl). These absorption peaks supported the proposed structure in Scheme 3.8. In case of TDI based polyurethanes absorption band of aromatic C=C (1600-1475 cm^{-1}) is masked with N-H and C-N bending of urethane bond and strong C-H stretching of aromatic ring at 3150–3050 cm^{-1} and out-of-plane bend between 900–690 cm-1 are overlapped by aliphatic C-H and C-Cl.

In the FTIR analysis of PECH-IPDI-BD series (Figure 3.15), absence of NCO and OH peaks at 2235 cm^{-1} and 3464-3498 cm^{-1} (PECH) respectively along with the presence of N-H stretching peak at 3327 cm^{-1} supported the formation of urethane linkage. The FTIR spectra contained very strong peak at 1697 cm^{-1} and 1234 cm^{-1} due to the presence of C=O (carbonyl) and C-O-C (urethane) respectively, which indicated that new synthesized product has urethane group (-NHCOO-). The strong evidence for the formation of toluene diisocyanate and butanediol based polyurethane elastomers is provided by the presence of C-O-C stretching absorption peak of polyether linkage at 1045-1486 cm^{-1}, C-H in-skeletal plane symmetric stretching at 2963 cm^{-1}, C-H out of skeletal plane symmetric stretching at 2920 cm^{-1} and C-H symmetric stretching at 2854 cm^{-1}.
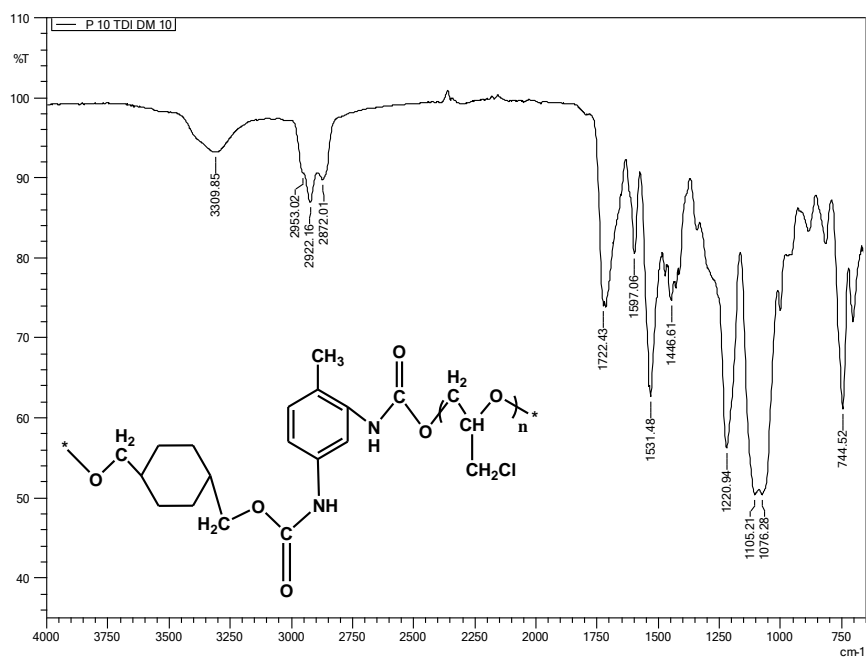
Figure 3.14: FT-IR spectrum of PECH polyurethane based on TDI extended with DM

Table 3.7: FT-IR spectroscopic data of PECH-TDI-DM series(cm^{-1})

Compound Code	ν_{NH}	$\nu_{C=O}$	ν_{NH} (bending)	ν_{CN} (bending)	ν_{C-O-C} (urethane)	ν_{C-O-C}	ν_{C-Cl}
P10TDIDM10	3310	1722	1597	1531	1220	1085	744
P10TDIDM15	3332	1710	1590	1529	1219	1065	748
P10TDIDM20	3330	1711	1594	1528	1227	1062	747
P25TDIDM10	3329	1708	1593	1529	1224	1059	749
P25TDIDM15	3327	1707	1591	1530	1223	1058	745
P25TDIDM20	3334	1704	1595	1525	1225	1060	748
P35TDIDM10	3335	1705	1589	1527	1230	1063	748
P35TDIDM15	3335	1702	1588	1529	1220	1064	749
P35TDIDM20	3331	1709	1595	1530	1222	1065	744

The representative spectrum of PECH-IPDI-BD polyurethanes and important absorption peaks of rest of group members of this series are given in Figure 3.15 and Table 3.8. FTIR spectra of this series showed the characteristic peaks of urethane groups in the region 3327-3355 cm^{-1} (N–H stretching). Other observed peaks were assigned as: 1690-1698 cm^{-1} (C=O bond); 1520-1531 cm^{-1} (C-N bending); 1218-1234 cm^{-1} (urethane C-O-C); 1059-1074 cm^{-1} (C-O-C ether); 746-753 cm^{-1} (C-Cl). The presence of above mentioned additional peaks supported the proposed structure as shown in Scheme 3.9.

Figure 3.15: FT-IR spectrum of PECH polyurethane based on IPDI extended with BD

In the representative spectrum of PECH-IPDI-HD series (Figure 3.16), lack of stretching vibration peaks of NCO and OH at 2235 cm^{-1} and 3464-3498 cm^{-1} (PECH) was observed. The formation of urethane linkage is indicated by N-H stretching peak at 3331 cm^{-1}. The FTIR spectra contained very strong peak at 1697 cm^{-1} and 1234 cm^{-1} due to the absorption of C=O (carbonyl) and C-O-C (urethane) respectively, which is due to the formation of urethane group (-NHCOO-). Furthermore, the presence of C-O-C stretching absorption peak of polyether linkage at 1047 cm^{-1}, C-H in-skeletal plane symmetric stretching at 2951 cm^{-1}, C-H out of skeletal plane

symmetric stretching at 2924 cm^{-1} and C-H symmetric stretching at 2870 cm^{-1} provided strong evidence for the formation of isophorone diisocyanate and hexanediol based polyurethane elastomers.

Table 3.8: FT-IR spectroscopic data of PECH-IPDI-BD series(cm^{-1})

Sample Code	ν_{NH}	$\nu_{C=O}$	ν_{CN}	ν_{C-O-C}	ν_{C-O-C}	ν_{C-Cl}
P10IPDIBD10	3327	1697	1520	1234	1074	746
P10IPDIBD15	3353	1695	1531	1219	1065	748
P10IPDIBD20	3355	1690	1531	1232	1062	747
P25IPDIBD10	3351	1694	1531	1234	1059	749
P25IPDIBD15	3349	1693	1531	1222	1058	750
P25IPDIBD20	3348	1699	1531	1227	1060	751
P35IPDIBD10	3348	1698	1531	1230	1063	748
P35IPDIBD15	3351	1697	1531	1233	1064	753
P35IPDIBD20	3350	1697	1531	1218	1065	751

The main absorption peaks of rest of group members of this series are described in Table 3.9. FTIR spectra of this series showed characteristic peaks of urethane groups at 3341-3348 cm^{-1} region (N–H stretching). In other regions observed peaks were assigned as: 1695-1704 cm^{-1} (C=O bond); 1520-1531 cm^{-1} (C-N bending); 1221-1234 cm^{-1} (urethane C-O-C); 1058-1068 cm^{-1} (C-O-C ether); 744-751 cm^{-1} (C-Cl). The appearance of new peaks and disappearance of old peaks supported the synthesis of proposed compound and its structure.
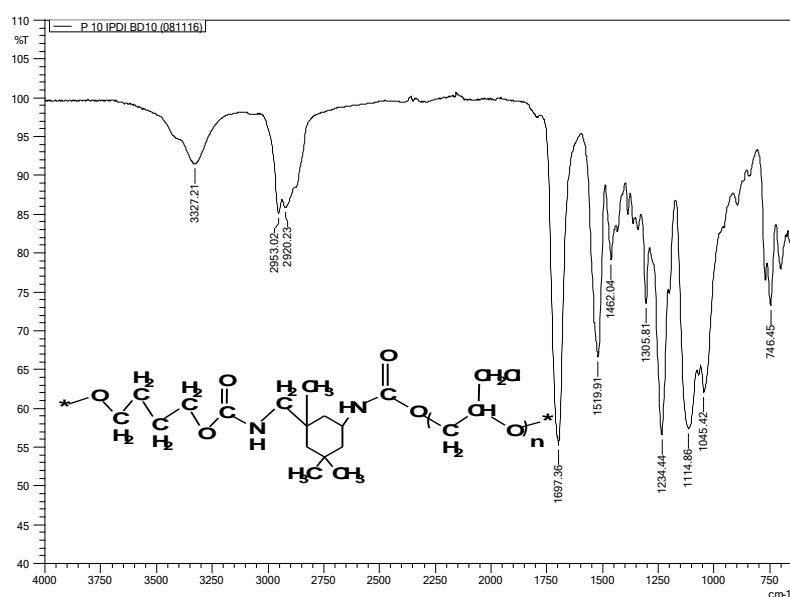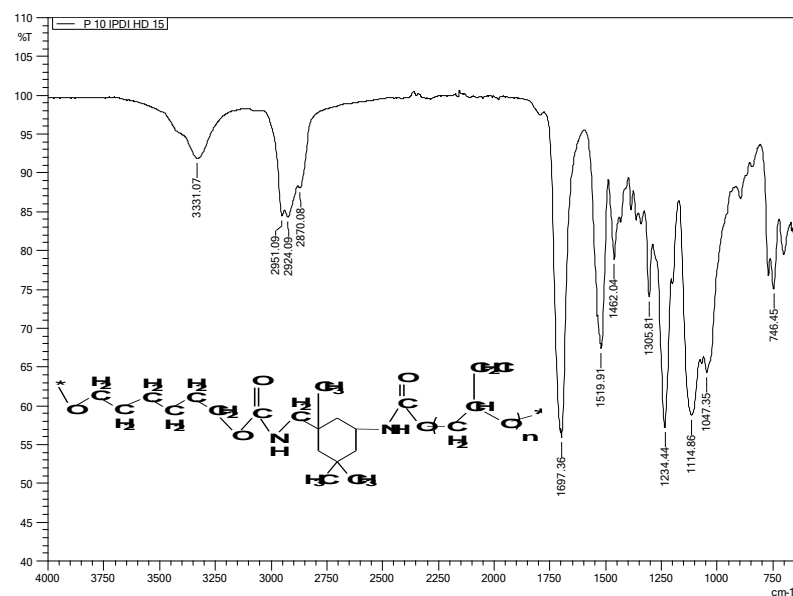
Figure 3.16: FT-IR spectrum of PECH polyurethane based on IPDI extended with HD

Table 3.9: FT-IR spectroscopic data of PECH-IPDI-HD series (cm^{-1})

Sample Code	ν_{NH}	$\nu_{C=O}$	ν_{CN}	ν_{C-O-C}	ν_{C-O-C}	ν_{C-Cl}
P10IPDIHD10	3345	1697	1531	1225	1064	744
P10IPDIHD15	3331	1697	1520	1234	1068	746
P10IPDIHD20	3334	1695	1531	1234	1068	747
P25IPDIHD10	3341	1704	1531	1224	1059	749
P25IPDIHD15	3348	1696	1531	1227	1058	750
P25IPDIHD20	3345	1700	1531	1230	1060	751
P35IPDIHD10	3341	1697	1531	1221	1063	748
P35IPDIHD15	3345	1704	1531	1225	1064	753
P35IPDIHD20	3345	1697	1531	1229	1065	751

The FTIR analysis of PECH-IPDI-DM series (Figure 3.17) showed very strong peaks at 1705 cm^{-1} and 1236 cm^{-1} corresponding to the absorption of C=O (carbonyl) and C-O-C (urethane) respectively, which indicated that new synthesized product has urethane group (-NHCOO-). Furthermore, the presence of C-O-C stretching absorption peak of polyether linkage at 1105 cm^{-1}, C-H in-skeletal plane symmetric stretching at 2951 cm^{-1}, C-H out of skeletal plane symmetric stretching at 2922 cm^{-1} and C-H symmetric stretching at 2873 cm^{-1} provided strong evidence for the formation of isophorone diisocyanate and cyclohexanedimethanol based polyurethane elastomers. While the disappearance of the both broad stretching vibration peaks of NCO and OH at 2235 cm^{-1} and 3464-3498 cm^{-1} (PECH) respectively along with corresponding appearance of N-H stretching peak at 3335 cm^{-1} indicated the formation of urethane linkage.
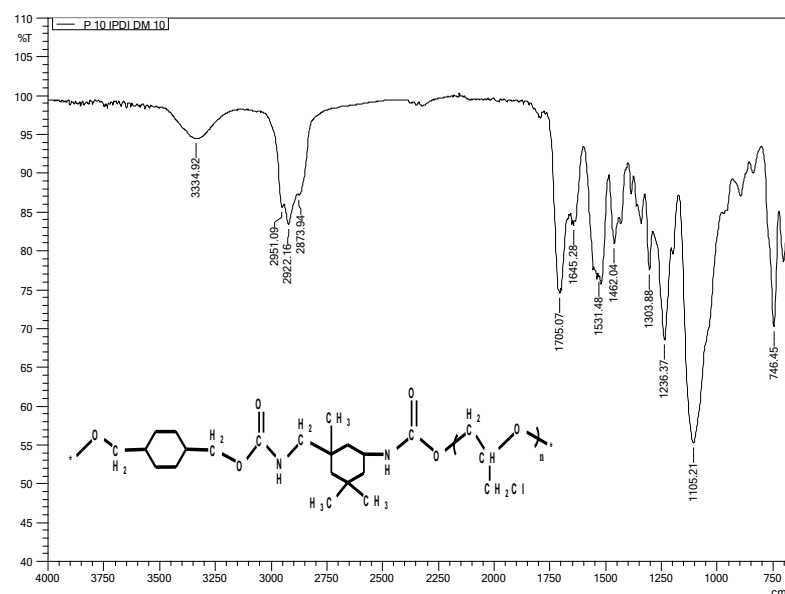
Figure 3.17: FT-IR spectrum of PECH polyurethane based on IPDI extended with DM

The representative spectrum of PECH-IPDI-DM polyurethanes is given in Figure 3.17 while characteristics absorption peaks of remaining members of the series are given in Table 3.10. FTIR spectra of this series showed particular peaks of urethane groups in 3335-3343 cm^{-1} region (N–H stretching). In other regions observed peaks were assigned as: 1690-1705 cm^{-1} (C=O bond); 1531-1531 cm^{-1} (C-N bending);

1225-1236 cm^{-1} (urethane C-O-C); 1025-1065 cm^{-1} (C-O-C ether); 746-753 cm^{-1} (C-Cl). These absorption regions validated the synthesis of pre-designed polymer and confirmed its structure as proposed in Scheme 3.10. The change in molecular weight of polyepichlorohydrin and percentage of cyclohexanedimethanol showed no significant impact on FT-IR spectra.

Table 3.10: FT-IR spectroscopic data of PECH-IPDI-DM series

Sample Code	ν_{NH}	$\nu_{C=O}$	ν_{CN} (bending)	ν_{C-O-C} (urethane)	ν_{C-O-C}	ν_{C-Cl}
P10IPDIDM10	3335	1705	1531	1236	1025	746
P10IPDIDM15	3340	17000	1531	1229	1065	748
P10IPDIDM20	3341	1695	1531	1228	1062	747
P25IPDIDM10	3343	1707	1531	1229	1059	749
P25IPDIDM15	3343	1701	1531	1230	1058	750
P25IPDIDM20	3339	1700	1531	1225	1060	751
P35IPDIDM10	3338	1695	1531	1227	1063	748
P35IPDIDM15	3340	1694	1531	1229	1064	753
P35IPDIDM20	3343	1690	1531	1231	1065	751

3.2.2.2 Nuclear magnetic resonance (NMR) spectroscopy

Formation of polyurethane linkage and proposed structures of synthesized PUEs were further confirmed by proton NMR studies. The samples of polyurethane elastomers were dissolved in dimethyl sulfoxide-D6 which showed its characteristic peak of residual solvent at 2.5 ppm. In the spectra, a weak and broad peak of urethane proton (NH) was observed in the range of 9.2 to 9.4 ppm and characteristic peaks of methylene, chloromethylene and methane contributed by PECH ranging from 3.5-3.8 ppm were also observed. These NMR peaks confirmed the formation of urethane bond and the presence of PECH in the backbone of all synthesized polyurethanes.

Figure 3.18 shows the proton NMR spectrum of PECH polyurethane based on TDI and extended with 1,6-hexanediol. In proton NMR spectrum, along with urethane proton (9.4 ppm), characteristic peaks of PECH (3.5-3.8 ppm) were also observed. The presence of toluene segments in molecular backbone was confirmed by the appearance of aromatic protons at 7.2 ppm and benzylic protons at 3.3 ppm. The protons of 1,6-hexanediol unit after the formation of urethane bond were indicated at 4.1 ppm (methylene protons α to oxygen), 2.2 ppm (methylene protons β to oxygen) and methylene protons α to carbon in the range of 1.2-1.6 ppm. This spectrum is in accordance with polyurethane structure as proposed in scheme 3.7.
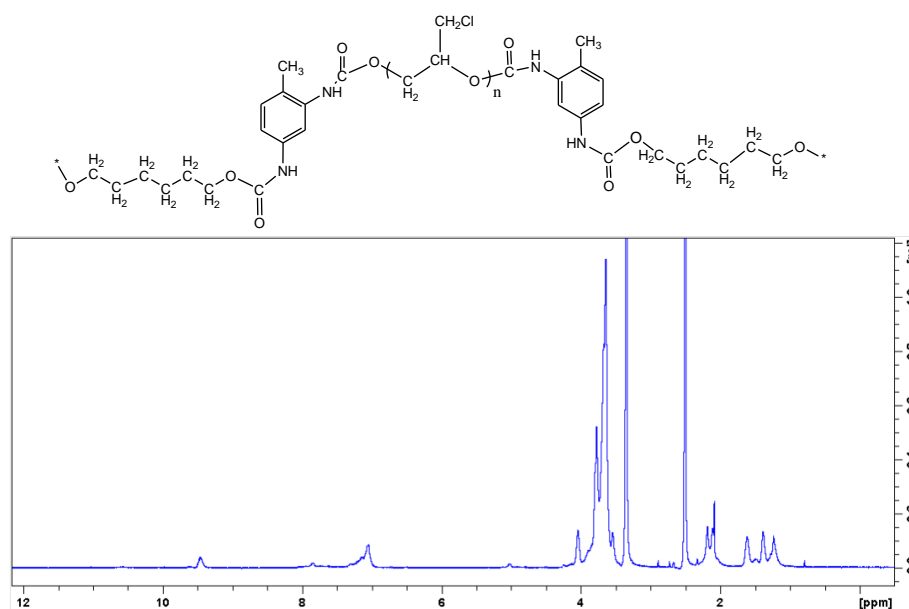
Figure 3.18: ^{1}H NMR spectrum of PECH polyurethane based on TDI extended with 1,6-hexane diol.

The proton NMR spectrum of PECH polyurethane based on TDI extended with cyclohexanedimethanol is shown in Figure 3.19. The presence of urethane proton (9.4 ppm) and characteristic peaks of PECH (3.5-3.8 ppm) was clearly identified. The toluene segments in molecular backbone was clearly observed by presence of aromatic protons at 7.2 ppm and benzylic protons at 3.3 ppm. The protons of cyclohexanedimethanol unit after the formation of urethane bond were unambiguously identified at 4.1 ppm (methylene protons α to oxygen), 4.0 ppm

(methylene protons α to urethane) and 2.2 ppm (cyclohexane protons β to oxygen) while methylene protons of cyclohexane were present in the region 0.7-1.9 ppm. The observed data supported the polyurethane structure as proposed in scheme 3.8.
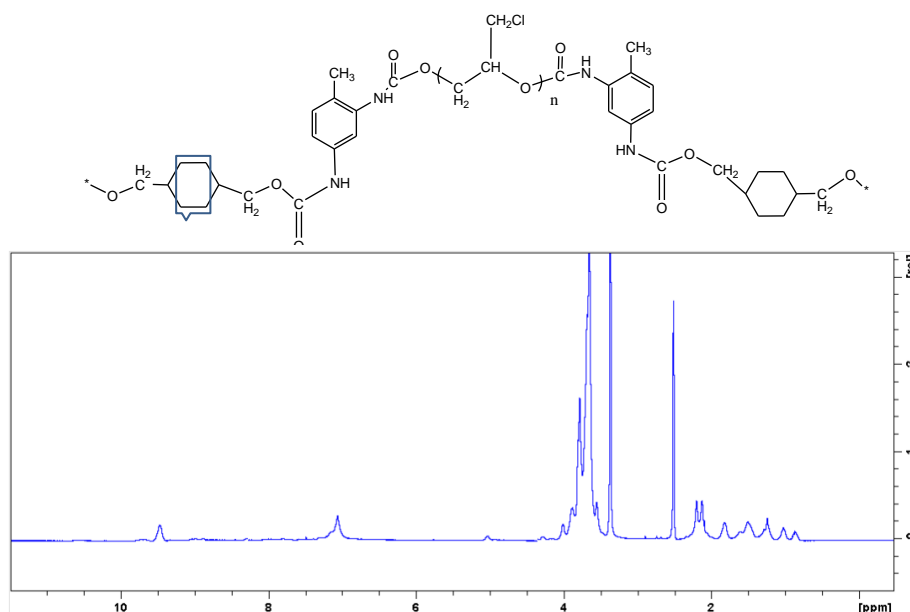
Figure 3.19: ^{1}H NMR spectrum of PECH polyurethane based on TDI extended with cyclohexanedimethanol

In ^{1}H NMR spectrum of PECH polyurethane based on isophorone diisocyanate extended with 1,4-butanediol as shown in Figure 3.20, small broad peak at 9.4 ppm is for urethane proton while multiplet in the range of 3.5-3.8 ppm are characteristic peaks for PECH. However, the incorporation of isophorone segment in molecular backbone was confirmed by the appearance of methine proton α to urethane nitrogen at 2.7 ppm, methylene protons β to urethane nitrogen in cyclohexane at 1.4 ppm, methylene protons of cyclohexane at 1.1 ppm, methylene protons α to urethane nitrogen 3.4 ppm and methyl protons on cyclohexane ring in the range of 0.75-1.0 ppm. The protons of 1,4-butanediol unit, after the formation of urethane bond, were indicated at 3.9 ppm (methylene protons α to oxygen) and 1.6 ppm (methylene protons β to oxygen). The presence of characteristic peaks in the spectrum is supportive to the expected polyurethane structure as sketched in scheme 3.10.
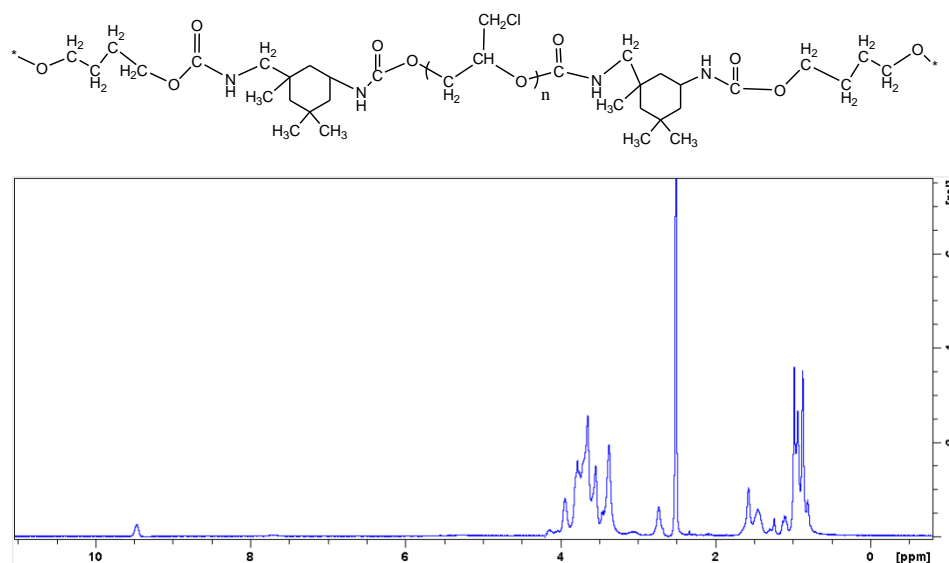
Figure 3.20: ^{1}H NMR spectrum of PECH polyurethane based on IPDI
extended 1,4- butanediol

3.2.2.3 Thermal characterization

Thermal characterization of polyurethane elastomers was carried out by differential scanning calorimetry and thermo-gravimetric analysis.

3.2.2.3.1 Differential scanning calorimetry (DSC)

The influence of molecular weight of polyol, nature of diisocyanate, nature and percentage of chain extender on glass transition and thermal degradation temperature was studied by DSC measurements. Thermal changes were investigated by subjecting the synthesized polyurethane elastomers to the temperature variation ranging from -50 °C to 400 °C.

The thermograms of the PU samples are shown in Figure 3.21 to 3.25 and data is presented in Table 3.11. The DSC results clearly indicated that all the PU samples undergo the thermal changes gradually as the temperature is increased from -50 °C to 400 °C. The polymer degradation started at about 300 °C and TGA thermograms also supported the DSC result (Table 12 and 13).

The DSC behavior of the synthesized compounds is described at different temperature ranges as:

1. -50 °C to 50 °C to study T_g
2. 50 °C to 200 °C to study the T_m
3. 200 °C to 400 °C to study the degradation temperature

As the temperature of a polymer drops below T_g, it behaves in an increasingly brittle manner[177]. As the temperature rises above the T_g, the polymer becomes more rubber-like. Thus, knowledge of T_g is essential in the selection of materials for various applications. In general, values of T_g well below room temperature define the domain of elastomers and values above room temperature define rigid structural polymers.

Before studying thermal behavior of polyurethane elastomers, glass transition temperatures of synthesized polyepichlorohydrins were determined. The DSC curves of polyepichlorohydrins of three different molecular weights are shown in Figure 3.21. It shows only one endotherm between -50 °C to +50 °C probably due to phase change from brittle to rubbery phase. It was observed that with the increase of molecular weight from 1000 to 3500 Daltons, T_g was increased from -35.6 °C to -28.3 °C. This linear increment in T_g with the increase in molecular weight of polymers is in accordance with the reported literature[178].
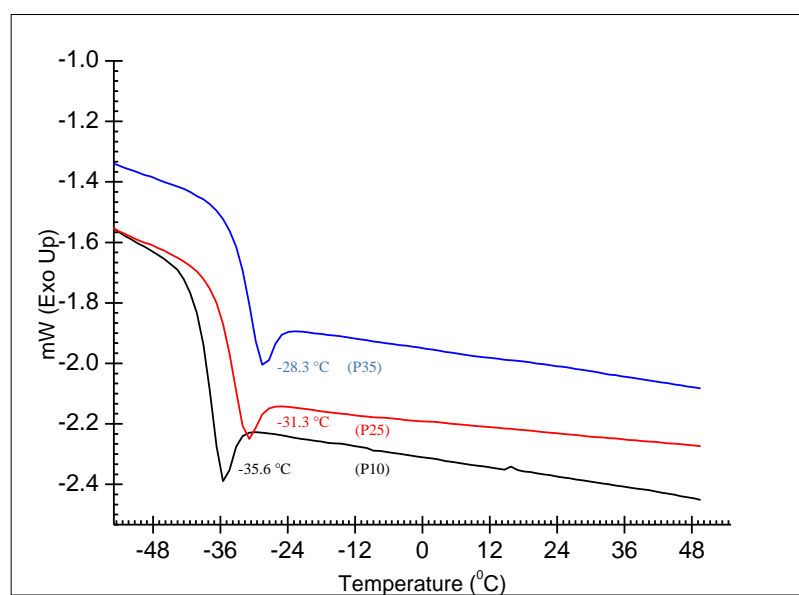
Figure 3.21: Comparative T_g (by DSC) of polyepichlorohydrins of different molecular weights

When these polymers were converted to polyurethane elastomers by reacting with diisocyanates and extended with diols, their T_g were shifted to higher temperatures. In case of toluene diisocyanate based polyurethanes, T_g was shifted from -28.3 °C to -20.8 °C for P-10, -31.3 °C to -18.8 °C for P-25 and -35.6 °C to -16.1 °C for P-35 (Figure 3.21). While, in case of isophorone diisocyanate based polyurethanes, T_g was shifted from -28.3 °C to 7.77 °C for P-10, -31.3 °C to 7.87 °C for P-25 and -35.6 °C to 7.98 °C for P-35 (Figure 3.22). In the toluene diisocyanate series, T_g varied from -20.8 °C to –5.3 °C and their thermal degradation increased from 304.2 °C to 359.1 °C. Whereas, in case of isophorone diisocyanate series, T_g varied from 7.77 °C to 8.05 °C and their thermal degradation shifted from 261.4 °C to 318.6 °C (Table 3.11). The shifting of T_g of toluene diisocyanate based polyurethanes was lesser than Isophorone diisocyanate polyurethanes. It was observed that after the formation polyurethane network, the impact of change in molecular weight of polyol was insignificant. The T_g originated from PECH were not observed which implied that no phase separation of PECH segment took place.
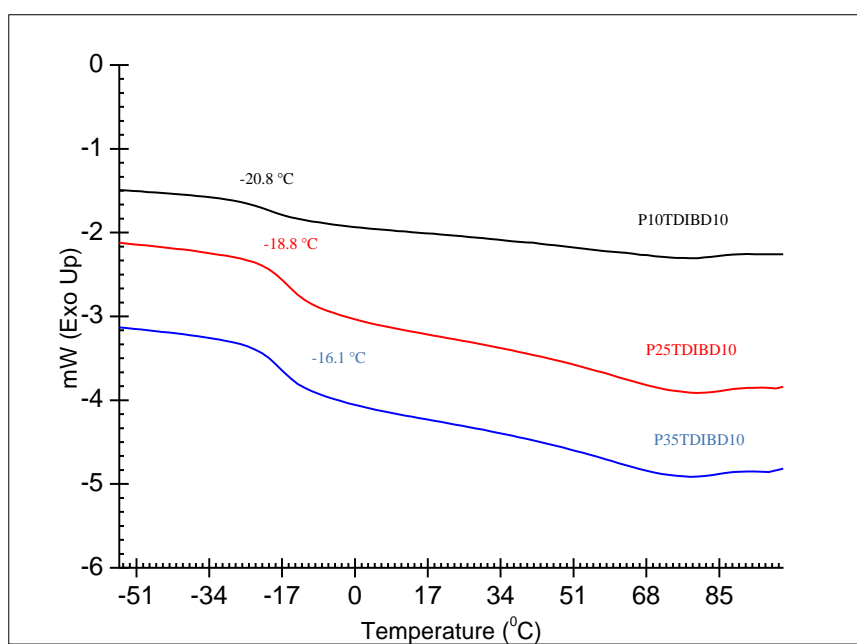
Figure 3.22: Comparative T_g (by DSC) of toluene diisocyanate based PUEs with polyepichlorohydrin of different molecular weights
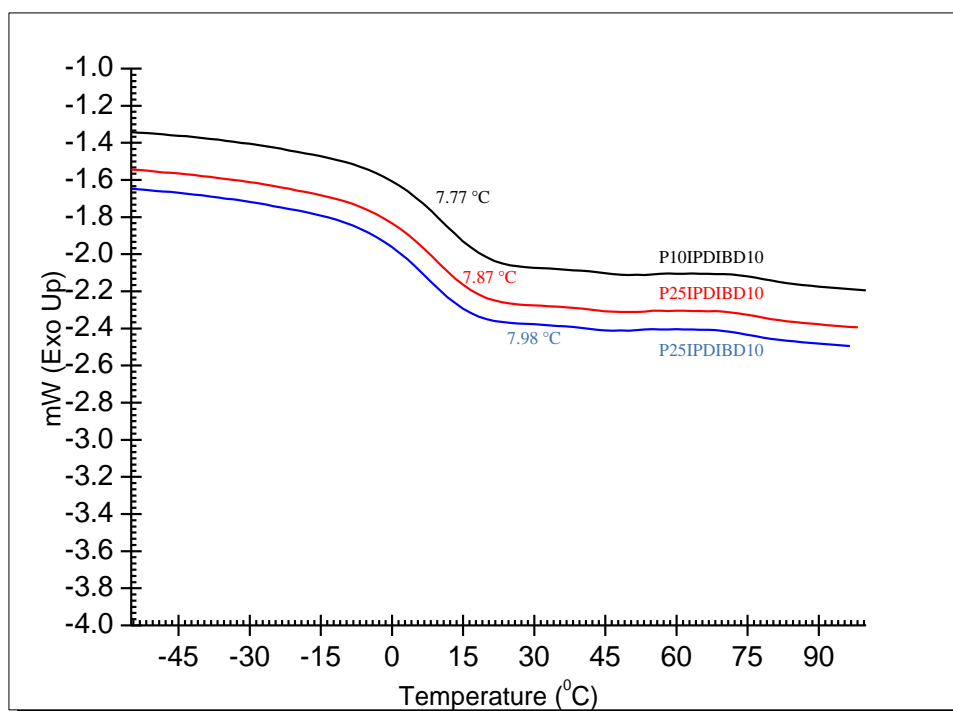
Figure 3.23: Comparative T_g (by DSC) of isophorone diisocyanate based PUEs with polyepichlorohydrin of different molecular weights

In both series, i.e., toluene diisocyanate and isophorone diisocyanate based polyurethanes no melting was observed (Figure 3.24) from 25 °C to 200 °C. After this region, degradation of polyurethane started indicating thermosetting nature of polyurethanes. It might be due to the presence of polar chlorine group and its association with the urethane hydrogen[179].

The polyurethanes derived from TDI were thermally more stable than IPDI based polyurethanes (Figure 3.25). It might be due to the presence of rigid aromatic structure present in TDI which generates strong intermolecular forces than cyclohexane present in IPDI based polyurethanes[180].
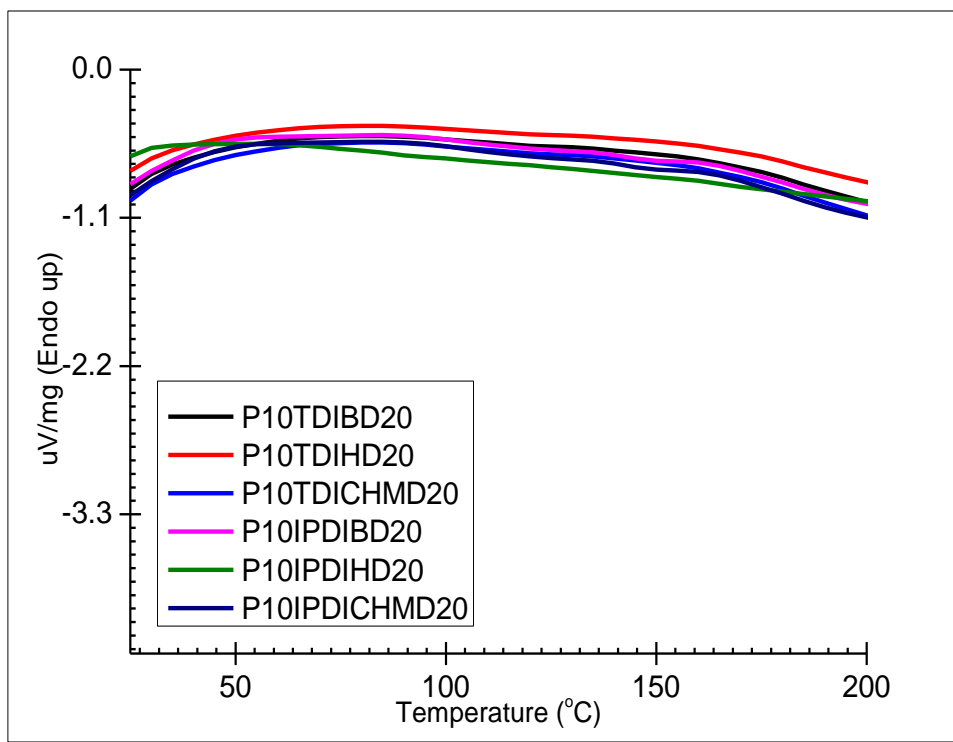
Figure 3.24: Comparative DSC studies of thermal changes in representative samples of synthesized PUEs from 25 °C to 200 °C
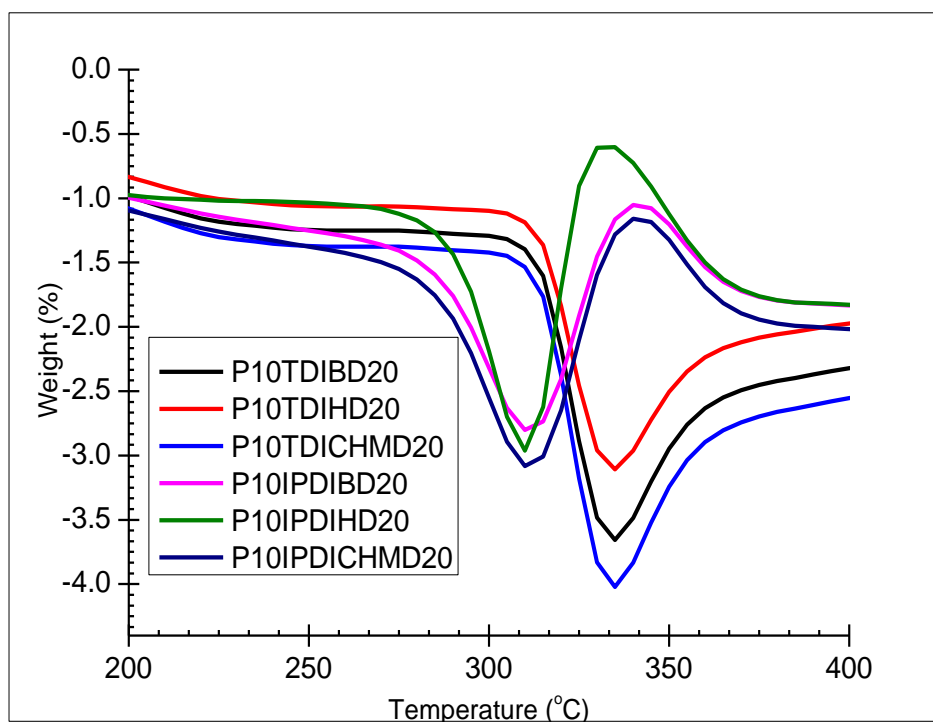
Figure 3.25: Comparative DSC studies of thermal changes in representative samples of synthesized PUEs from 200°C to 400 °C

Table 3.11: Glass transition and thermal degradation temperature of polyurethanes by DSC

PECH-TDI-BD Series

Sample Name	T_g (°C)	T_d (°C)
P10TDIBD10	-20.8	322.5
P10TDIBD15	-19.5	331.8
P10TDIBD20	-19.2	340.0
P25TDIBD10	-18.8	340.8
P25TDIBD15	-18.2	313.2
P25TDIBD20	-17.9	322.3
P35TDIBD10	-16.1	322.0
P35TDIBD15	-15.8	304.2
P35TDIBD20	-15.3	312.2

PECH-IPDI-BD Series

Sample Name	T_g (°C)	T_d (°C)
P10IPDIBD10	7.77	297.9
P10IPDIBD15	7.76	296.8
P10IPDIBD20	7.75	312.0
P25IPDIBD10	7.87	272.0
P25IPDIBD15	7.85	297.2
P25IPDIBD20	7.84	306.6
P35IPDIBD10	7.98	288.4
P35IPDIBD15	7.95	297.2
P35IPDIBD20	7.93	306.6

PECH-TDI-HD Series

Sample Name	T_g (°C)	T_d (°C)
P10TDIHD10	-21.07	341.0
P10TDIHD15	-19.75	348.5
P10TDIHD20	-19.45	359.1
P25TDIHD10	-19.04	329.0
P25TDIHD15	-18.44	338.8
P25TDIHD20	-18.13	339.9
P35TDIHD10	-16.31	319.7
P35TDIHD15	-16.01	329.1
P35TDIHD20	-15.50	329.2

PECH-IPDI-HD Series

Sample Name	T_g (°C)	T_d (°C)
P10IPDIHD10	7.87	294.0
P10IPDIHD15	7.86	310.1
P10IPDIHD20	7.85	318.6
P25IPDIHD10	7.97	268.3
P25IPDIHD15	7.95	294.3
P25IPDIHD20	7.94	302.9
P35IPDIHD10	8.08	285.9
P35IPDIHD15	8.05	294.5
P35IPDIHD20	8.03	303.0

PECH-TDI-CHDM Series

Sample Name	T_g (°C)	T_d (°C)
P10TDIMD10	-21.11	342.0
P10TDIMD15	-19.79	341.6
P10TDIMD20	-19.49	352.7
P25TDIMD10	-19.08	322.3
P25TDIMD15	-18.47	332.8
P25TDIMD20	-18.17	333.2
P35TDIMD10	-16.34	312.3
P35TDIMD15	-16.04	323.2
P35TDIMD20	-15.53	322.7

T_g: Glass transition temperature
T_d: Degradation temperature

PECH-TDI-CHDM Series

Sample Name	T_g (°C)	T_d (°C)
P10IPDIMD10	7.89	287.4
P10IPDIMD15	7.88	304.2
P10IPDIMD20	7.87	312.7
P25IPDIMD10	7.99	261.4
P25IPDIMD15	7.97	286.6
P25IPDIMD20	7.96	296.2
P35IPDIMD10	8.10	278.9
P35IPDIMD15	8.07	286.7
P35IPDIMD20	8.05	296.1

3.2.2.3.1 Thermogravimetric Analysis (TGA)

Thermal characteristics of the synthesized polyurethane elastomers were evaluated by using TGA technique. Thermal degradation temperature of polyepichlorohydrin (P-10) was 379.8 °C and degradation temperature of the synthesized polyurethane was 350.5 °C (Figure 3.26) so polyol (PECH) was found more stable than its analogue polyurethane elastomer.

The results of thermal degradation temperatures for TDI and IPDI based polyurethanes are presented in Table 3.12 and 3.13 respectively. The TGA curves of the PUEs as a function of type of diisocyanate, variation in molecular weight of PECH, nature and amount of chain extenders are shown in Figure 3.28, 3.29 and 3.30. The TGA thermograms showed the thermal stability and thermal degradation behavior of the samples. Thermal analysis data revealed that all of the samples are thermally stable up to 162 °C in an inert atmosphere.
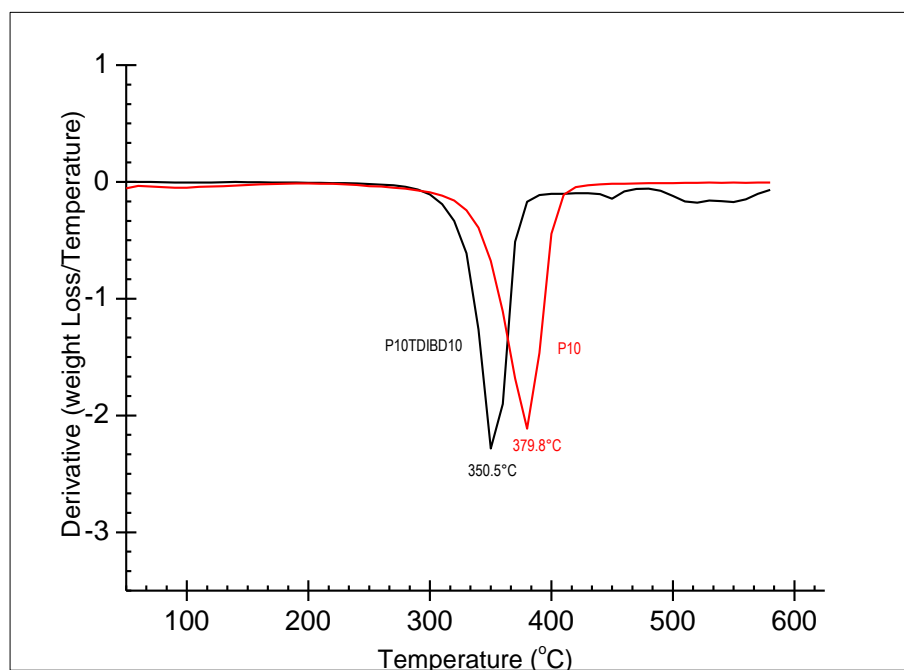
Figure 3.26: Comparative thermal degradation temperature of parent PECH and polyurethane elastomer

In case of aromatic diisocyanate (TDI), variation in molecular weight of polyepichlorohydrin and percentage of chain extenders slightly affected the thermal stability of the polyurethanes (Table 3.12). The series of samples extended with 1,4-

butanediol are stable up to 205.6 °C and faced 10% weight loss in the range of 311.4 °C to 351 °C. Maximum decomposition of the samples was occurred from 330.6 °C to 370.4 °C along with the residual mass in the range of 0.1-1.4%. The series of samples extended with 1,6-hexanediol are stable up to 216 °C and faced 10% weight loss in the range of 312 °C to 349.4 °C. Maximum decomposition of the samples was occurred from 329.6 to 370.2 °C along with the residual mass in the range of 0.1-1.5%. The series of samples extended with cyclohexanedimethanol are stable up to 205.8 °C and undergo 10% weight loss in the range of 301.8 °C to 340.9 °C. Maximum decomposition of the samples was occurred from 314.6 °C to 360.6 °C along with the residual mass in the range of 0.1-1.2%.

Similarly, in case of cycloaliphatic diisocyanate (IPDI), variation in molecular weight of polyepichlorohydrin and percentage of chain extenders slightly affected the thermal stability of the polyurethanes (Table 3.13). The series of samples extended with 1,4-butanediol are stable up to 175.4 °C and faced 10% weight loss in the range of 319.7 °C to 352 °C. Maximum decomposition of the samples was occurred at 320.6-369.4 °C along with the residual mass in the range of 0.2-3%. The series of samples extended with 1,6-hexanediol are stable up to 184.3 °C and faced 10% weight loss in the range of 304.8-356.9 °C. Maximum decomposition of the samples was occurred at 319.4-369.2 °C along with the residual mass in the range of 0.2-2%. The series of samples extended with cyclohexanedimethanol are stable up to 162.4 °C and faced 10% weight loss in the range of 294-346.5 °C. Maximum decomposition of the samples was observed at 309.4-370.1 °C along with the residual mass in the range of 0.1-1.9%.

On the whole, TDI based polyurethanes were found relatively more stable than IPDI based polyurethanes (Figure 3.27). It is most probably due to thermal scission of C-CH$_3$ bonds present in the main chain of the IPDI[181]. Furthermore, the presence of benzene ring in the backbone of aromatic diisocyanate (TDI) might be the cause of increasing thermal stability whereas in cycloaliphatic diisocyanates (IPDI) flexible cyclohexane is present.

Table 3.12: Thermal stability data of Toluene diisocyanate based polyurethanes by TGA

Compound Code	T_{Onset} (°C)	T_{max} (°C)	T_{10} (°C)	T_{20} (°C)	T_{50} (°C)	Residue
P10TDIBD10	217.0	350.5	330.8	343.1	360.8	0.9
P10TDIBD15	224.4	360.7	341.6	354.0	370.0	1.2
P10TDIBD20	239.3	370.4	351.0	363.0	379.0	1.4
P25TDIBD10	210.9	340.4	322.0	337.0	350.6	0.5
P25TDIBD15	215.0	350.3	327.0	339.9	355.5	0.4
P25TDIBD20	229.0	350.0	331.0	343.0	360.3	0.3
P35TDIBD10	205.6	330.6	311.4	323.0	339.4	0.1
P35TDIBD15	206.4	339.4	316.6	330.6	346.4	0.2
P35TDIBD20	218.0	339.9	321.2	333.1	350.1	0.3
P10TDIHD10	256.0	350.3	331.2	343.3	358.9	0.9
P10TDIHD15	268.3	359.3	341.5	352.8	369.1	1.2
P10TDIHD20	257.9	370.2	349.1	363.2	380.7	1.3
P25TDIHD10	228.8	339.2	321.6	332.8	353.6	0.5
P25TDIHD15	225.0	349.3	328.9	340.9	356.2	0.4
P25TDIHD20	220.8	350.4	332.8	334.0	363.2	0.3
P35TDIHD10	216.0	329.6	312.0	323.2	339.2	0.1
P35TDIHD15	244.0	339.3	317.5	329.2	345.9	0.2
P35TDIHD20	233.1	339.4	322.3	332.6	349.7	0.3
P10TDIDM10	222.8	339.4	320.6	332.6	349.7	0.9
P10TDIDM15	235.6	349.3	330.9	342.6	359.3	1.2
P10TDIDM20	282.4	360.6	340.9	354.1	370.5	1.2
P25TDIDM10	215.8	329.6	323.2	324.8	339.2	0.5
P25TDIDM15	218.3	340.3	318.9	330.4	346.8	0.4
P25TDIDM20	226.0	340.7	320.7	334.1	350.7	0.3
P35TDIDM10	207.0	319.3	301.7	314.0	329.8	0.1
P35TDIDM15	217.5	330.5	308.0	319.2	335.3	0.2
P35TDIDM20	224.5	330.0	312.2	323.6	339.8	0.3

Table 3.13: Thermal stability data of isophorone diisocyanate based polyurethanes by TGA

Compound Code	T_{Onset} (°C)	T_{max} (°C)	T_{10} (°C)	T_{20} (°C)	T_{50} (°C)	Residue
P10IPDIBD10	175.4	350.5	329.3	342.4	360.3	3
P10IPDIBD15	229.8	349.2	334.4	344.3	362.3	0.5
P10IPDIBD20	232.3	369.6	352.0	363.4	377.6	0.1
P25IPDIBD10	185.6	320.0	304.0	316.8	331.2	2
P25IPDIBD15	209.1	349.7	327.4	342.8	358.3	0.9
P25IPDIBD20	224.1	360.7	335.4	350.6	365.7	0.8
P35IPDIBD10	218.0	339.3	319.7	332.8	350.8	0.2
P35IPDIBD15	231.9	349.6	329.4	342.8	361.3	1.5
P35IPDIBD20	242.7	360.7	340.4	355.6	370.8	1.8
P10IPDIHD10	218.3	350.0	325.0	341.6	360.0	0.9
P10IPDIHD15	256.9	369.2	348.7	360.7	376.1	0.5
P10IPDIHD20	264.9	379.3	356.9	370.7	386.2	0.1
P25IPDIHD10	184.3	319.4	304.8	316.2	330.8	2.0
P25IPDIHD15	199.4	350.3	329.5	341.6	358.9	0.9
P25IPDIHD20	232.4	360.6	334.1	350.7	365.6	0.8
P35IPDIHD10	234.3	340.4	321.9	333.7	352.2	0.2
P35IPDIHD15	238.9	350.6	329.6	343.6	361.0	1.5
P35IPDIHD20	239.3	360.7	339.6	353.6	371.3	1.8
P10IPDIDM10	198.8	340.1	313.9	331.4	350.6	0.8
P10IPDIDM15	240.0	360.0	337.6	350.4	366.4	0.4
P10IPDIDM20	248.5	370.1	346.5	361.7	376.9	0.0
P25IPDIDM10	162.4	309.4	294.0	305.9	321.4	1.9
P25IPDIDM15	197.2	339.2	321.6	332.8	348.8	0.8
P25IPDIDM20	228.8	350.5	326.9	342.1	353.9	0.7
P35IPDIDM10	209.7	330.1	309.4	323.2	342.1	0.1
P35IPDIDM15	227.8	339.3	319.7	332.7	350.8	1.4
P35IPDIDM20	232.0	350.4	329.6	342.4	361.6	1.7
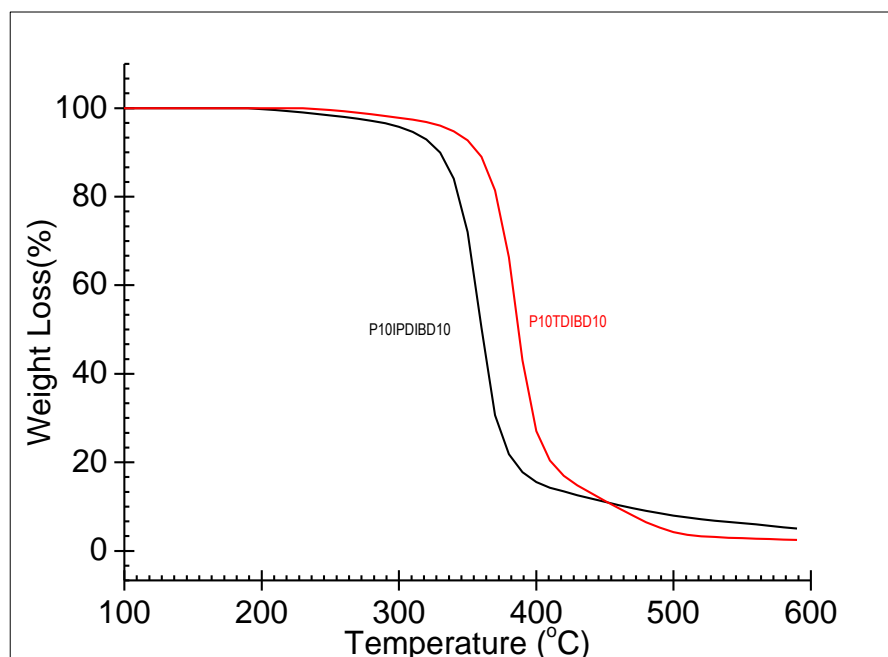
Figure 3.27: Effect of type of diisocyanate on thermal degradation temperature of polyurethane

Thermal stability of both TDI and IPDI based polyurethanes was decreased with the increase in molecular weight of PECH (Figure 3.28). This behavior might be due to the fact that increase in PECH length diluted the NH contents which ultimately mitigated the presence of inter-chain H-bonding. Less H-bonding results in lower thermal stability[182].

Polymers extended with 1,4-butanediol were found to be the most stable and polymers containing cyclohexanedimethanol chain extender were the least stable. Stability of polymers having 1,6-hexanediol have intermediate stability in TDI based systems (Figure 3.29 a). It is most probably due to thermal scission of cycloaliphatic C-C bonds present in the main chain of the cyclohexanedimethanol. In case IPDI system extended with both 1,4-butanediol and 1,6-hexanediol, comparable stability was observed and polymers containing cyclohexanedimethanol chain extender were found relatively less stable (Figure 3.29 b). In all the polymers, increase in percentage of chain extender enhanced the thermal degradation temperature (Figure 3.30) which might be due to the increase in percentage of hard segments.
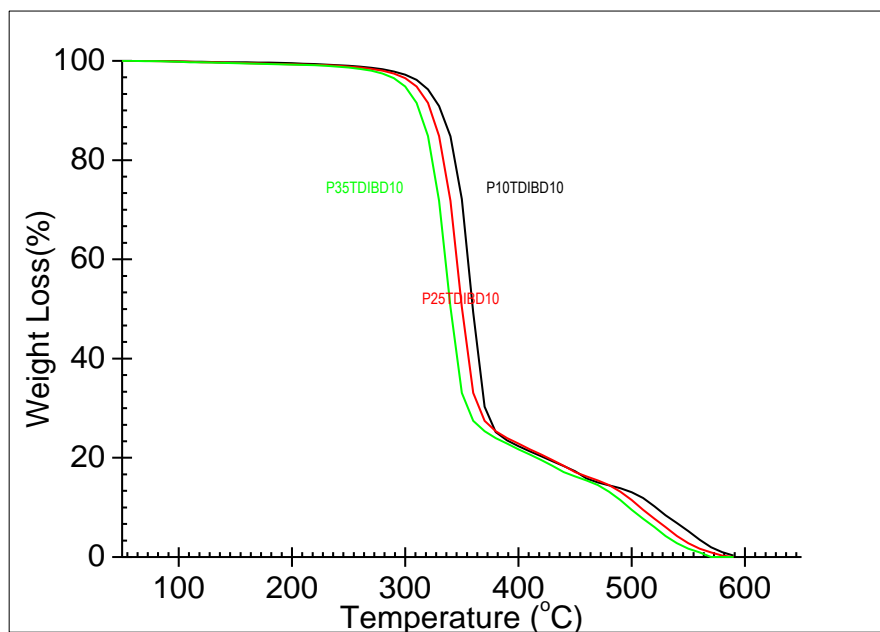
(a)
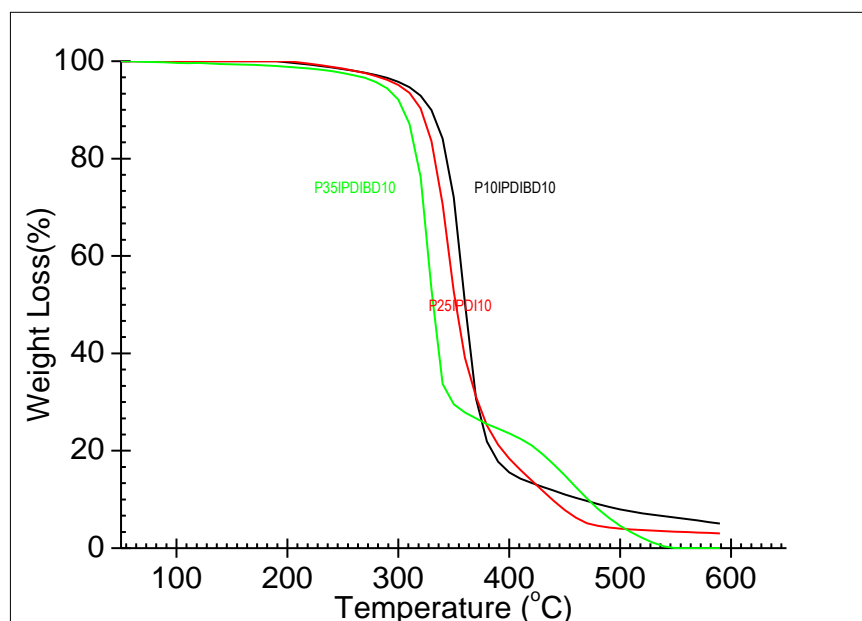
(b)

Figure 3.28: Effect of molecular weight of PECH on thermal degradation temperature of polyurethane (a) TDI based and (b) IPDI based
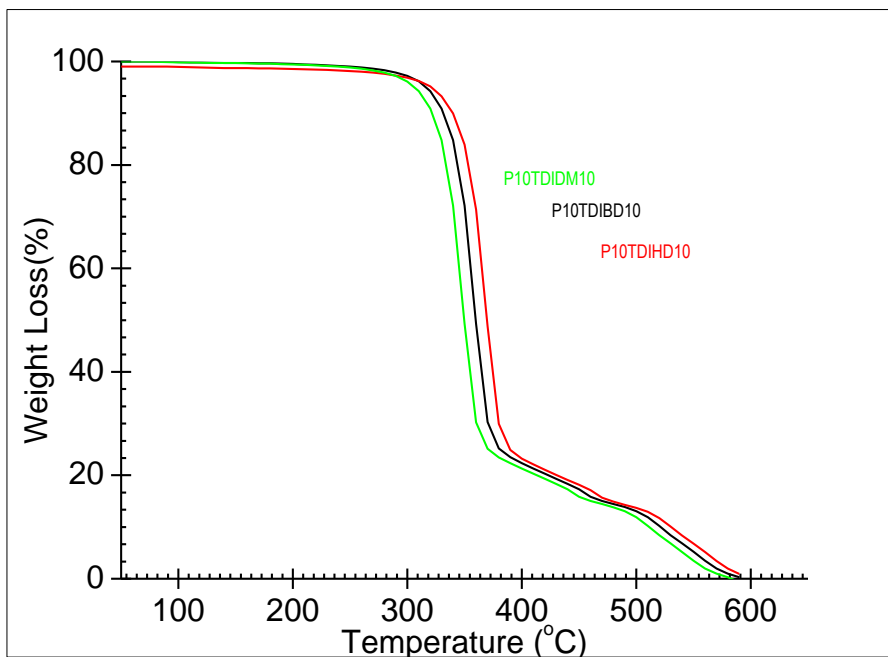
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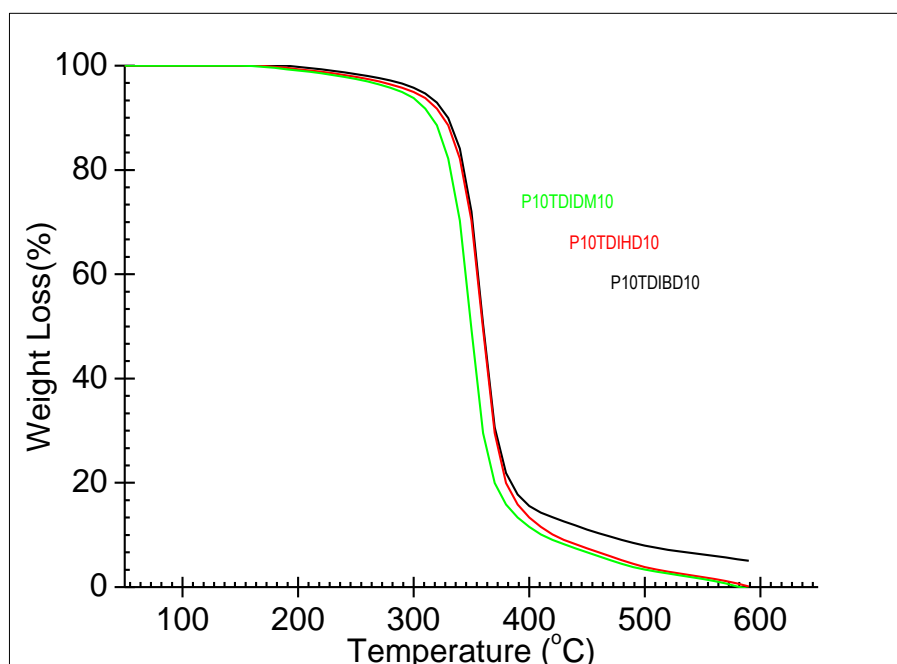
(b)

Figure 3.29: Effect of type of chain extender on thermal degradation temperature of polyurethane (a) TDI based and (b) IPDI based

95
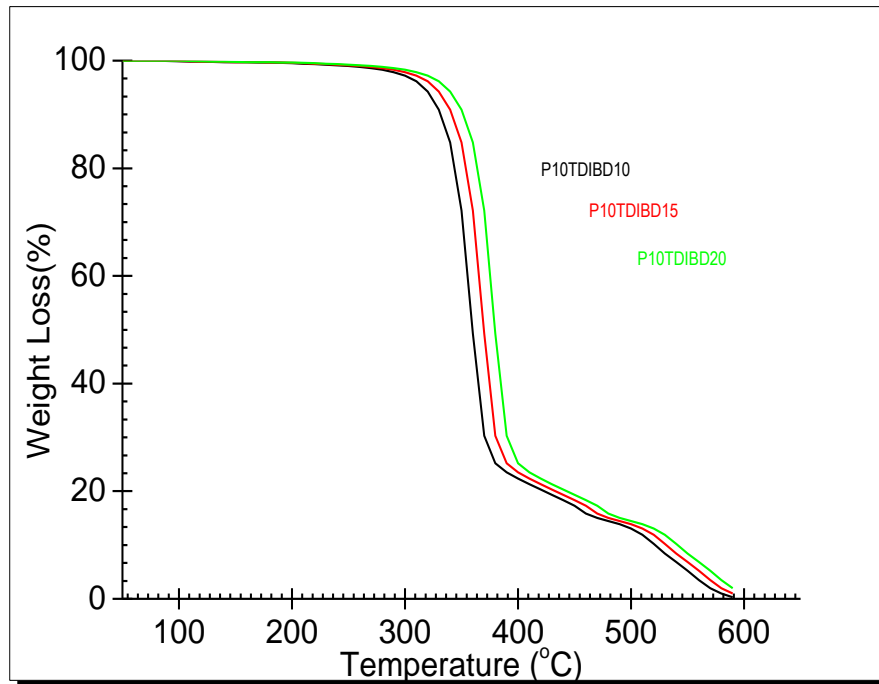
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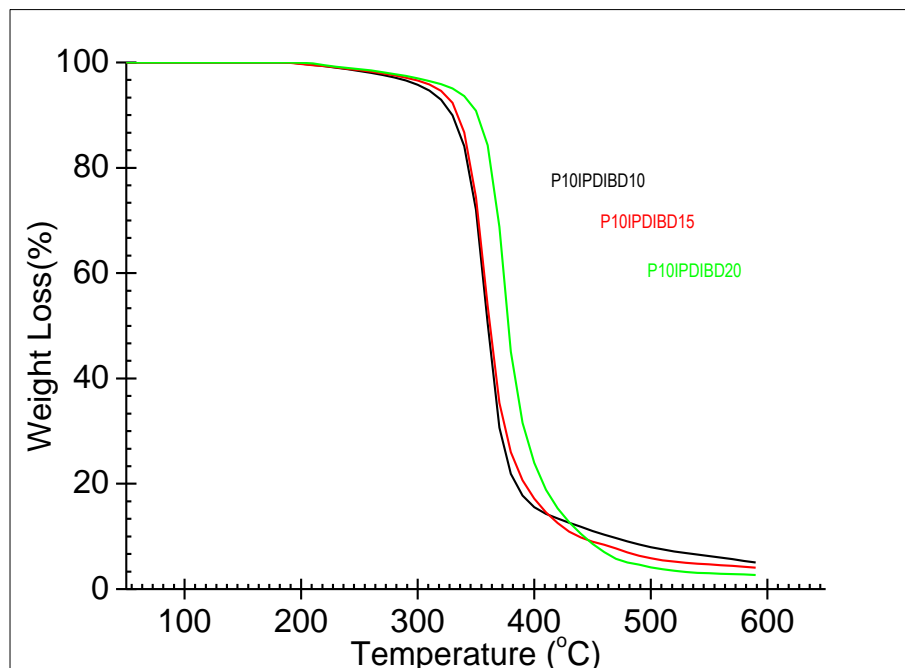
(b)

Figure 3.30: Effect of quantity of chain extender on thermal degradation temperature of polyurethane (a) TDI based and (b) IPDI based

3.2.2.4 X-ray diffraction (XRD)

Polyurethanes phase separation depend upon the relative amount of soft segments (SS) and hard segment (HS) domains resulting from their structural regularity and thermodynamic incompatibility. Hard segments tend to form crystalline domains and soft segment form amorphous phase. The crystallinity of the PU samples was estimated by using the intensity of the crystalline peaks of the respective samples by XRD studies. In these studies, diffused broad scattering peaks with maximum intensity at about $2\theta = 19-27°$ were observed (Figure 3.31 and 3.32) indicating the presence of less crystalline domains. The reported literature showed that the well oriented crystallinity is observed at about $2\theta = 20°$ but when the hard segments are annealed or present at higher concentration, diffraction peak is observed at about $2\theta = 11-12°$[183] so in synthesized polymers overall lower concentration of hard segments are present.

The broad crystalline peaks indicated low crystalline character in both TDI and IPDI based polyurethane systems. The crystallinity is mainly due to the ordered packing of the hard and soft segments. So, the overall behavior of the polyurethane based on PECH is amorphous and glassy. The shifting of peaks in diffractograms can be attributed to lesser hydrogen bonding and lower contents of hard segment.

Figure 3.31 shows the diffraction patterns of polyurethanes prepared from PECH of different molecular weights. It indicates that increase in molecular weight of PECH results in the decrease in signal intensity due to the reduced crystallinity which may be as a result of the dilution of soft segment because of increasing molecular weight of parent polyol.

The X-ray diffraction studies represented that crystallinity is highly depended on the structure of diisocyanates in the polyurethane backbone (Figure 3.32). It is obvious that the crystallinity decreased from aromatic to aliphatic nature of the diisocyanates used in the final PU. In the comparison of TDI and IPDI based polyurethanes, it can be concluded that the PU having aromatic diisocyanate have the greater peaks intensities due to the better degree of chain orientation. The other factors like hydrogen bonding in the hard segments, chemical cross linking at soft segments and annealing during the curing of samples might also be the cause of such crystallinity.

In both aromatic and cycloaliphatic diisocyanate based systems, increase in the percentage of chain extenders resulted in greater phase separation and increase in signal intensity. It was most probably due to the linear increase in hard segment contents [184]. Polyurethanes prepared from 1,4-butanediol and 1,6-hexanediols showed comparable crystallinity but in case of cyclohexanedimethanol, peak intensities observed in WAXD were remarkably less than aliphatic chain extenders. It may be attributed to the greater phase mixing of cycloaliphatic diol within polymer matrix. It revealed that there is no significant effect of chain extenders having different number of methylene units (1,4-butanediol and 1,6-hexanediol) on the crystallinity of PECH based PUEs.

FTIR spectroscopy is another tool to estimate the extent of hydrogen bonding in the region of 1610- 1760 cm^{-1} which is the absorbing region for C=O group[185]. FT-IR studies of the synthesized polyurethanes as described in section 3.2.2.1 also supported the absence of hydrogen bonding thus resulting in decreased crystallinity in the synthesized polymers.
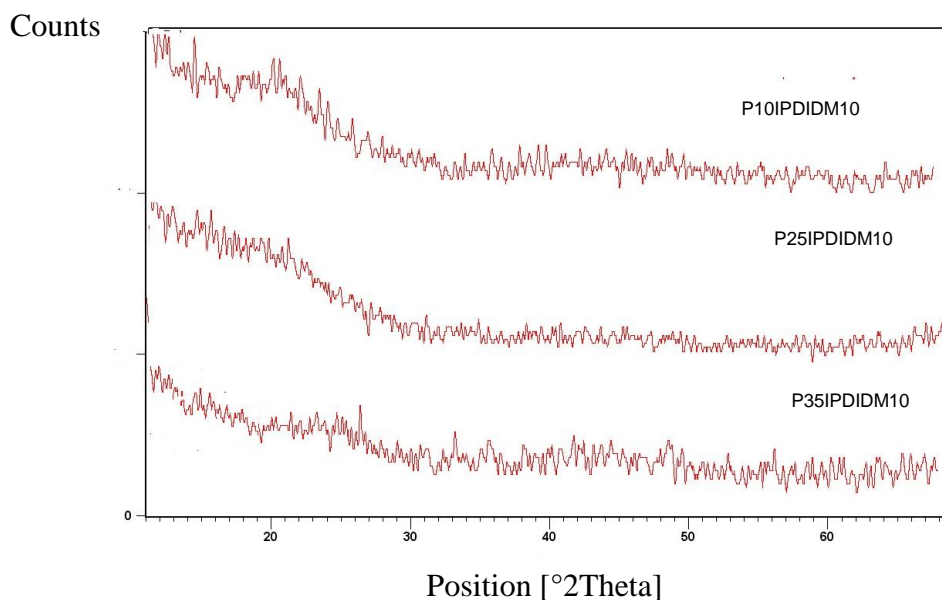
Figure 3.31: Effect of molecular weight of PECH on XRD patterns of polyurethanes
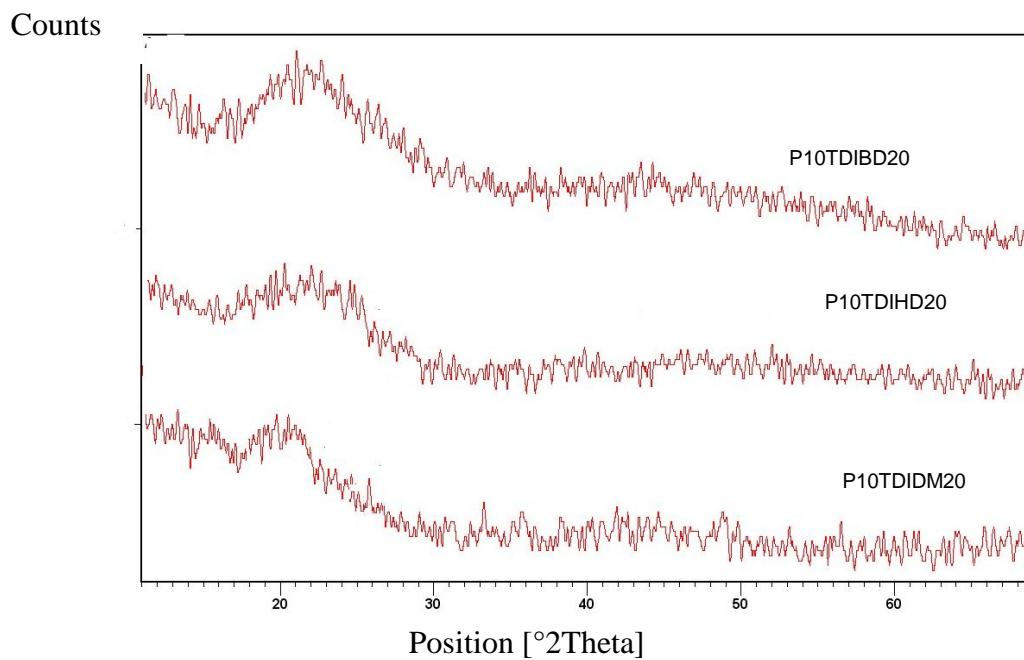
(a)
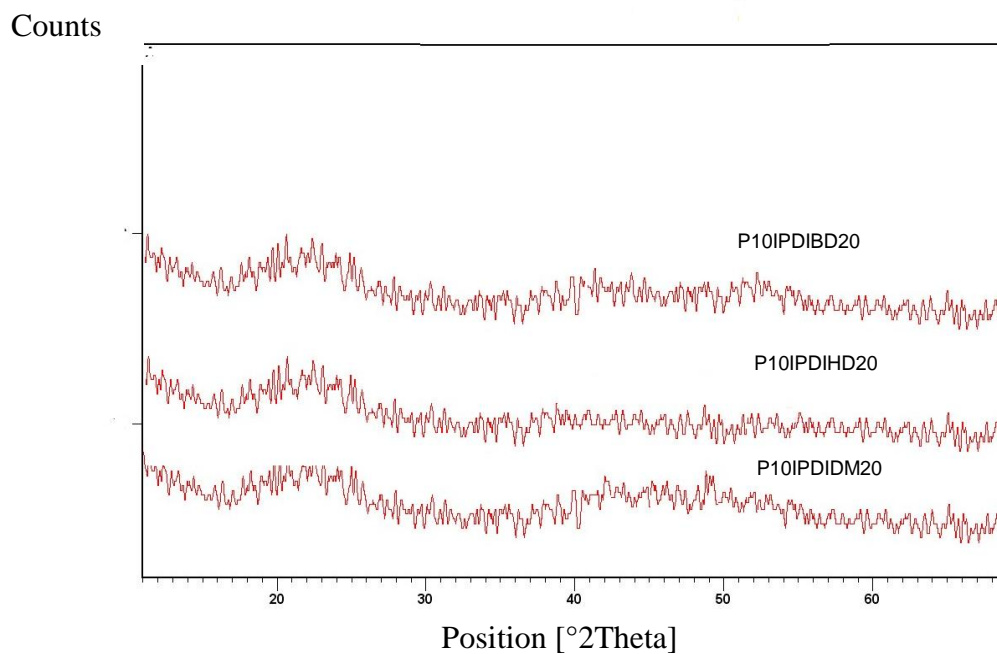
(b)

Figure 3.32: X-Ray diffractograms of polyurethanes (a) TDI and (b) IPDI

3.2.2.5 Scanning electron microscopy (SEM)

The SEM was employed to explore the surface morphology of these PUEs. Figure 3.33 shows the scanning electron micrographs of the synthesized PUEs. A continuous phase is visible in SEM micrographs which are developed by the amorphous part of the soft phase and the intermediate phase, i.e., matrix. Particles of the hard phase are dispersed, and are encapsulated in that matrix. The soft phase amorphicity is varied with isocyanate type which is represented by the SEM images[186]. Such variation is due to different geometries of the isocyanates as well as the percentage (%) of hard segments in the polymers. The XRD studies also represented this irregular behavior.

SEM images of aromatic diisocyanate based PU samples clearly revealed the presence of two phases and granular structures forming aggregates. Cycloaliphatic diisocyanate based polyurethanes showed better mixing of the soft and hard segments with respect to the aromatic diisocyanate based PUs.

A continuous phase is visible in SEM micrographs which are developed by the amorphous part of the soft phase and the intermediate phase. Particles of the hard phase are dispersed, and are encapsulated in the matrix. They are formed by the crystalline element of the hard phase. Such biphasic structure is formed due to three vital thermodynamic factors that is mobility of hard segments, viscosity of the system, and interactions between hard segments[187].

The domains of rigid segments are partially crystalline. The crystallites can be observed in the images which are not regular in shape and their sizes are of the order of a few micrometers. The soft phase is amorphous in most cases as represented by the SEM images of all the samples. This was also determined by the WAXD studies which showed the semi-crystalline behaviour due to the hard segments.

The SEM images confirmed the presence of greater phase segregation of hard segments in TDI based systems as compared to IPDI based systems. These observations are in accordance with FT-IR and WAXD studies.
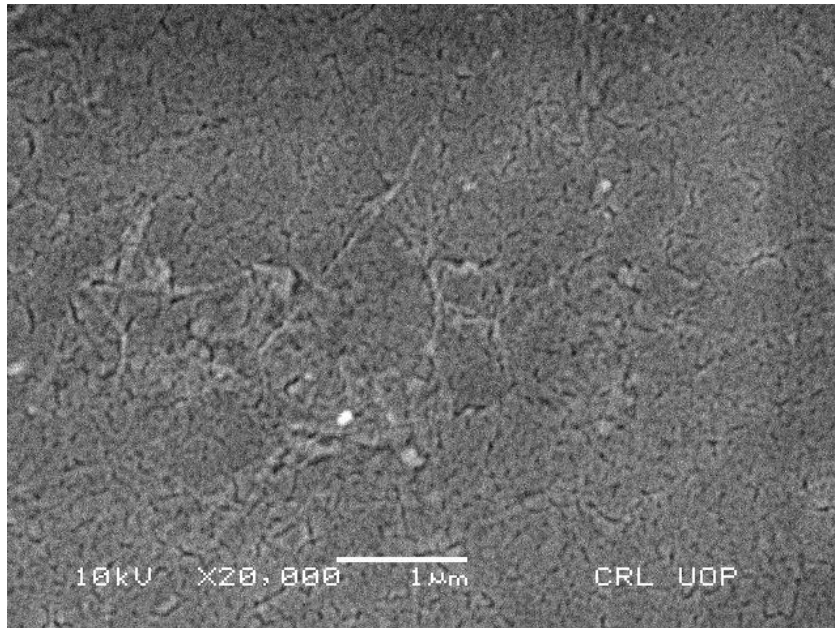
(a) P10TDIBD20
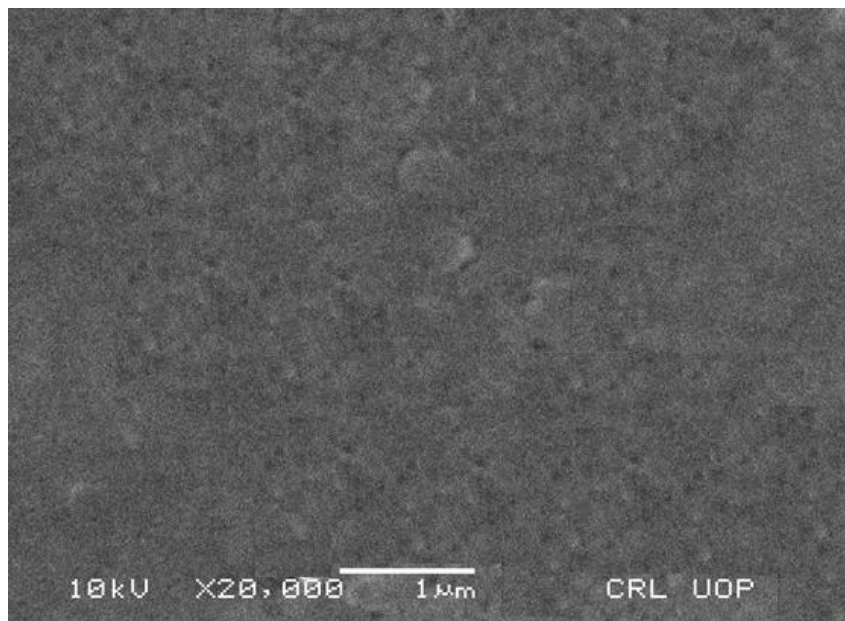
(b) P10IPDIBD20

Figure 3.33: SEM images (20,000X) of polyurethanes (a) TDI and (b) IPDI

3.2.2.6 Mechanical properties

The mechanical behavior of polymeric materials is examined by using tensile testing and is commonly expressed by stress (force) and strain (extension) curves. These curves indicate whether the material is hard, brittle, ductile or soft. The thermo-mechanical properties of the elastomers play key role for their selection in a particular practical application. In polyurethane chemistry of elastomers, matrix morphology, micro-phase separation, phase structure and polyol chain stiffness decide the mechanical properties of the whole matrix. Relative proportions of hard and soft segments also affect the tensile strength and upper use temperature of PUEs. The hard segments are derived from urethane linkage obtained from the reaction of di-isocyanates and low-molecular weight diols or diamines used as chain extenders. The soft segments, on the other hand, are composed of major polymer backbone structures (polyester or polyether polyol or polybutadiene). The certain properties of these PUEs are directly related to the two-phase microstructure where the hard segment domains not only act as multifunctional crosslinks but also reinforce the flexible soft segments, thus forming materials of high modulus and elastomeric properties[111]. Morphologically, PUEs have interlocked hard segment domains embedded in the soft segment domains. The stress-strain curve of PUE is generally affected by the hard segment to soft segment ratio, soft segment length, hard segment crystallinity and susceptibility of the hard segment to adopt optimum orientation and alignment. The chemistry of polyol regarding chemical nature of polyol chains, polyol functionality and polyol molecular weight affects the mechanical properties of final polyurethanes.

In the present study, six series of polyurethanes (aromatic and cycloaliphatic diisocyanate extended with BD, HD and DM) were prepared to investigate the impact of molecular weight of PECH, type of diisocyanate and type and quantity of chain extender on mechanical properties as well. The mechanical parameters such as tensile strength and elongation at break of synthesized polyols are summarized in Table 3.14 and Figure 3.34. Overall results showed that increase in ultimate tensile strength of each polymer was accompanied by the decrease in elongation.

It is observed that the TDI based PUEs have shown high tensile strength and low elongation in comparison to IPDI (Figure 3.34). This variation in mechanical properties is due to the aromatic nature of TDI while IPDI is aliphatic in nature. This aromatic structure of TDI leads to high rigidity due to the presence of two isocyanate

groups on the same phenyl ring. In addition, the higher reactivity of TDI resulting from the delocalization of negative charge on the isocyanate groups and the aromatic nature are responsible for the greater tensile strength. The polyurethanes based on cycloaliphatic diisocyanates do not show such delocalization and are less reactive and catalyst is involved to proceed the polymerization. TDI also provides the degree of freedom to the hard segment for orientation and crystallinity has been increased which is also shown by the WAXD and SEM studies as described earlier.

The molecular weight of PECH has an important effect on the polyurethane properties. When PECH has a low molecular weight, hard polyurethane will result but if the polyol has high molecular weight, it creates flexible polyurethanes. Intermediate M_n lead to semi-rigid or semi-flexible structures. It is clear that a low molecular weight chain gives rise to higher concentrations of urethane bonds[188]. The high cohesive interaction between these bonds (mainly through secondary hydrogen bonds) leads to a rigid structure, i.e., hard polyurethanes. Same effect was observed in all polyurethane series. With the increase in molecular weight of PECH, elongation was increased with corresponding decrease in tensile strength (Figure 3.35) regardless of type of diisocyanate.

The structure of chain extender is one of the major factors which dictate the mechanical properties of polyurethanes. The rigid chemical groups like cycloaliphatic rings, aromatic rings and heterocyclic rings do not permit molecular flexibility and free rotation thus causing hardness along with decrease in elasticity. The chemical composition of the chain extender has a major effect on the extent of phase separation of the PUs. In linear aliphatic chains having -C-C-C- bonds, free rotation around the carbon-carbon bonds is characteristic but this is restricted by the electropositive repulsion between adjacent hydrogen atoms. When a CH_2 group is replaced by oxygen (as in polyether chains), the rotation around the C-O-C bond (without hydrogen atoms) is easier and the molecule is more flexible but polarity is enhanced. The steric hindrance restricts the rotation around the main chain and the molecule becomes stiffer e.g., cycloaliphatic group. In the present study, three different chain extenders (1,4-butanediol, 1,6-hexanediol and cylohexanedimethanol) were utilized to access the impact of type of chain extender on the mechanical properties of polyurethanes. The comparison of mechanical properties (Figure 3.36) of different chain extenders revealed that in both TDI and IPDI based polyurethanes, cylohexanedimethanol has greatest elongation with minor compromise on UTS as

compared to aliphatic diols (BD and HD). It may be due to the greater flexibility of cyclohexanedimethanol chair structure. Chain extension with 1,4-butanediol resulted in polyurethane with maximum UTS and lowest elongation in both aromatic and aliphatic diisocyanate systems.

The percentage of chain extender alters the proportions of the hard and soft segments in PUE and play an important role in the determination of the properties of final product. The proportion of hard segments controls the mechanical properties whereas proportion of soft segments determines the elastic and low-temperature properties. It can be observed that the elongation at break increased along with gradual increase in tensile strength when the length of chain extender was increased. This behavior can be attributed to the increased intermolecular forces and also due to the higher cohesive forces between soft and hard segment contents. The data of mechanical properties of PU samples can be related to the number of carbon atoms in the chain extender molecules. These results are in accordance with the literature [189, 190]. The mechanical properties depend on the phase separation as well as on the hydrogen bonding. A reduction in hydrogen bonding resulted in a decline in the mechanical properties. As CE length increases, the NH content per unit volume decreases, which ultimately reduces the hydrogen bonding and consequently, the mechanical properties of the PU will decrease[191]. In all the synthesized polyurethane systems, regardless of the type of diisocyanates and molecular weight of PECH, increase in amount of chain extender resulted in an increase in UTS with corresponding decrease in elongation (Figure 3.37). It is probably due to the increase in percentage of hard segment which is in accordance with the previously discussed results of XRD in section 3.2.2.4 and SEM in section 3.2.2.5.

With the increase in molecular weight of PECH (1000, 2500 and 3500) in aromatic diisocyanate (TDI) based polymers extended with 1,4-butanediol, UTS was decreased from 6.4 to 5 MPa along with an increase in elongation from 431.9 to 546.6 %. In case of 1,6-hexanediol, UTS was declined from 5.88 to 4.78 MPa with corresponding increase in elongation from 471.7 to 575.5 %. Whereas, incorporation of cyclohexanedimethanol resulted in a decrease in UTS from 8.65 to 7.19 MPa with equivalent increase in elongation from 465.3 to 563.3%. In case of cycloaliphatic diisocyanate (IPDI) based polymers extended with 1,4-butanediol, UTS was decreased from 6.07 to 4.94 MPa with corresponding increase in elongation from 495 to 598.9 %. Incorporation of 1,6-hexanediol as chain extender resulted in decrease in

UTS from 5.76 to 4.69 MPa with corresponding increase in elongation from 520 to 628 % whereas use of cyclohexanedimethanol caused a decrease in UTS from 8.58 to 6.86 MPa with respective increase in elongation from 511.7 to 620.3%.

Table 3.14: Mechanical properties of polyurethanes

PECH-TDI-BD Series			PECH-IPDI-BD Series		
Sample Codes	UTS (MPa)	Elongation%	Sample Codes	UTS (MPa)	Elongation%
P10TDIBD10	6.16	449.2	P10IPDIBD10	6.07	495.0
P10TDIBD15	6.24	438.9	P10IPDIBD15	6.19	485.0
P10TDIBD20	6.40	431.9	P10IPDIBD20	6.38	475.0
P25TDIBD10	5.62	495.0	P25IPDIBD10	5.45	545.0
P25TDIBD15	5.71	485.0	P25IPDIBD15	5.55	533.3
P25TDIBD20	5.76	475.0	P25IPDIBD20	5.69	523.3
P35TDIBD10	5.00	546.6	P35IPDIBD10	4.94	598.9
P35TDIBD15	5.24	533.3	P35IPDIBD15	5.16	587.2
P35TDIBD20	5.33	523.3	P35IPDIBD20	5.29	575.5

PECH-TDI-HD Series			PECH-IPDI-HD Series		
Sample Codes	UTS (MPa)	Elongation%	Sample Codes	UTS (MPa)	Elongation %
P10TDIHD10	5.88	471.7	P10IPDIHD10	5.76	520.0
P10TDIHD15	5.95	463.9	P10IPDIHD15	5.88	503.3
P10TDIHD20	6.07	454.2	P10IPDIHD20	6.00	498.3
P25TDIHD10	5.31	520.0	P25IPDIHD10	5.19	571.7
P25TDIHD15	5.41	510.2	P25IPDIHD15	5.29	560.0
P25TDIHD20	5.50	498.3	P25IPDIHD20	5.41	548.3
P35TDIHD10	4.78	575.5	P35IPDIHD10	4.69	628.0
P35TDIHD15	5.02	563.3	P35IPDIHD15	4.92	616.3
P35TDIHD20	5.09	550.0	P35IPDIHD20	5.00	604.7

PECH-TDI-CHDM Series			PECH-IPDI-CHDM Series		
Sample Codes	UTS (MPa)	Elongation%	Sample Codes	UTS (MPa)	Elongation%
P10TDIMD10	8.65	465.3	P10IPDIMD10	8.58	511.7
P10TDIMD15	9.14	456.9	P10IPDIMD15	8.70	501.7
P10TDIMD20	9.39	447.2	P10IPDIMD20	8.90	491.7
P25TDIMD10	8.10	511.7	P25IPDIMD10	7.63	563.3
P25TDIMD15	8.24	501.3	P25IPDIMD15	7.83	551.7
P25TDIMD20	8.45	491.7	P25IPDIMD20	7.93	541.7
P35TDIMD10	7.19	563.3	P35IPDIMD10	6.86	620.3
P35TDIMD15	7.63	551.7	P35IPDIMD15	7.27	606.7
P35TDIMD20	7.76	541.7	P35IPDIMD20	7.42	595.0
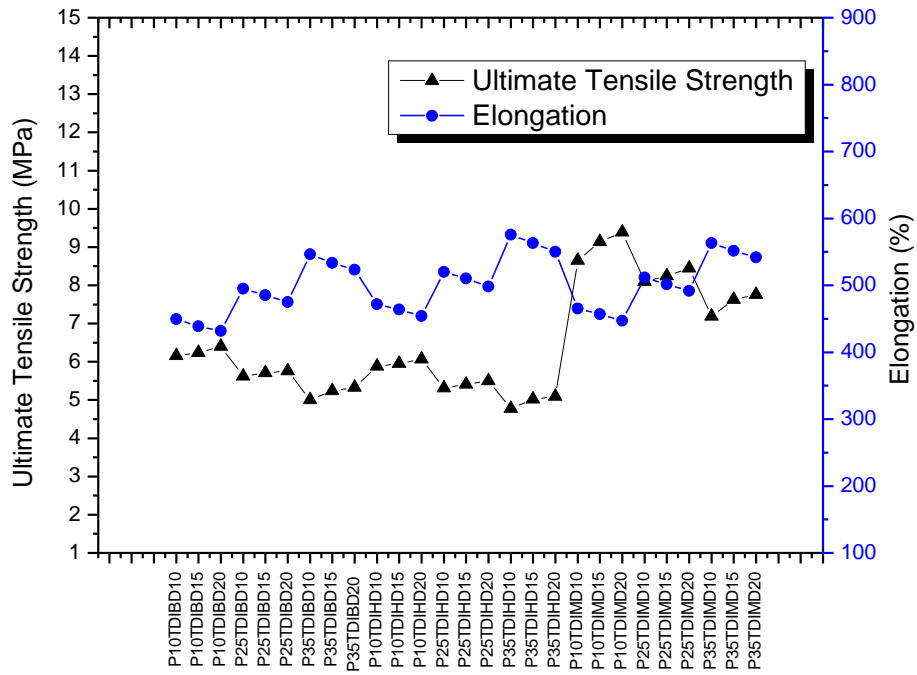
(a)
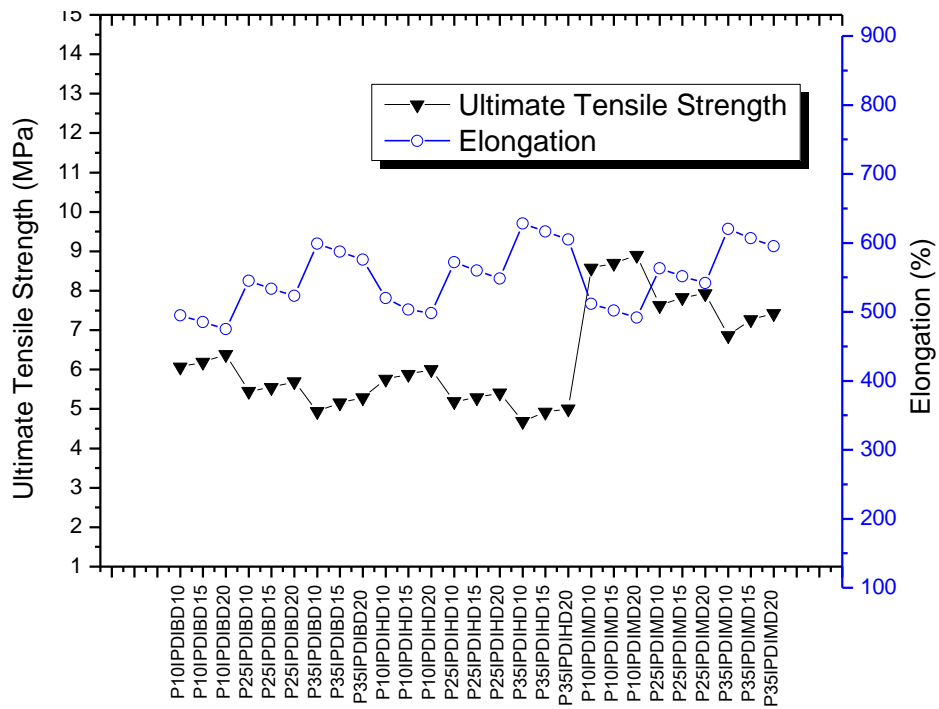
(b)

Figure 3.34: Mechanical properties of polyurethanes (a) TDI and (b) IPDI
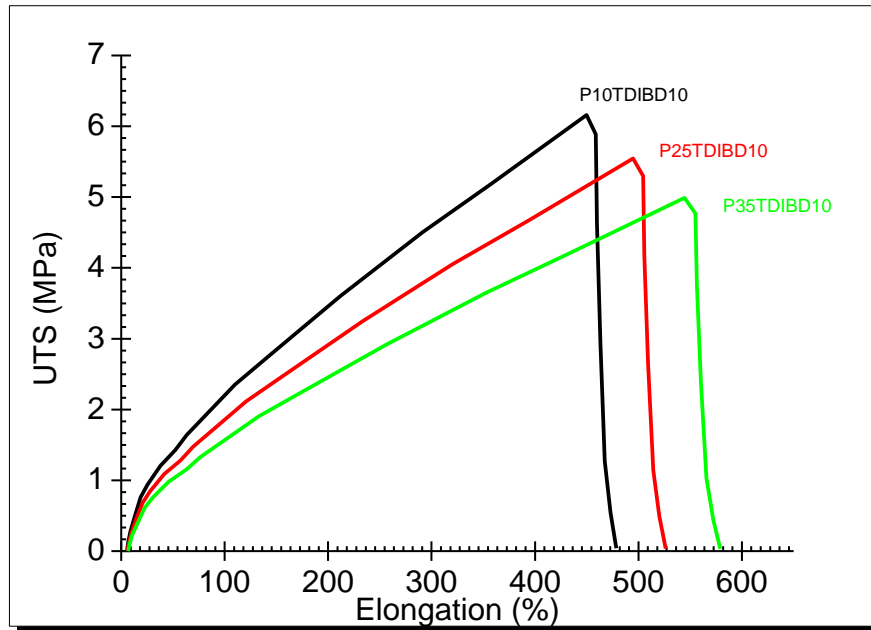
(a)
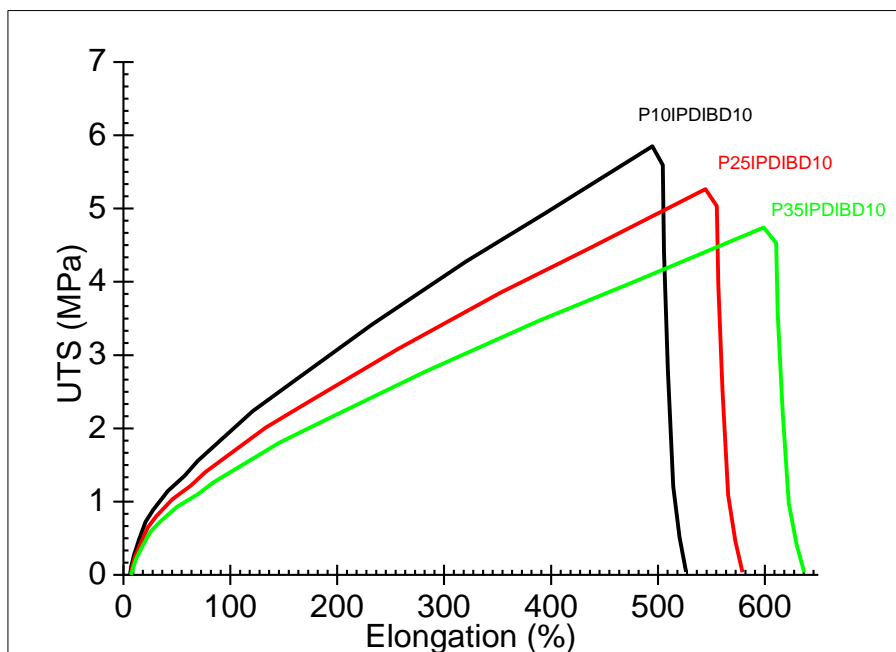
(b)

Figure 3.35: Impact of molecular weight of PECH on mechanical properties of polyurethanes (a) TDI and (b) IPDI
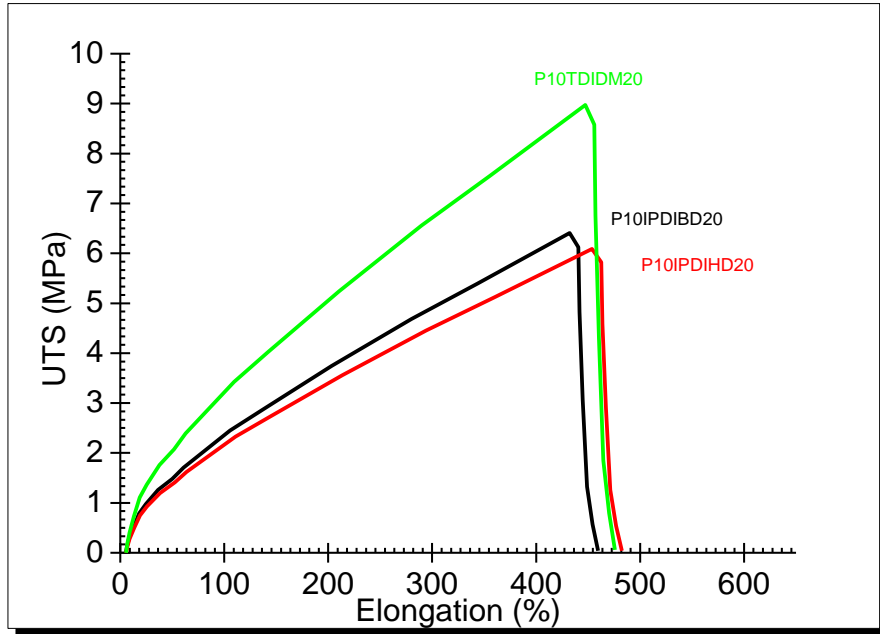
(a)
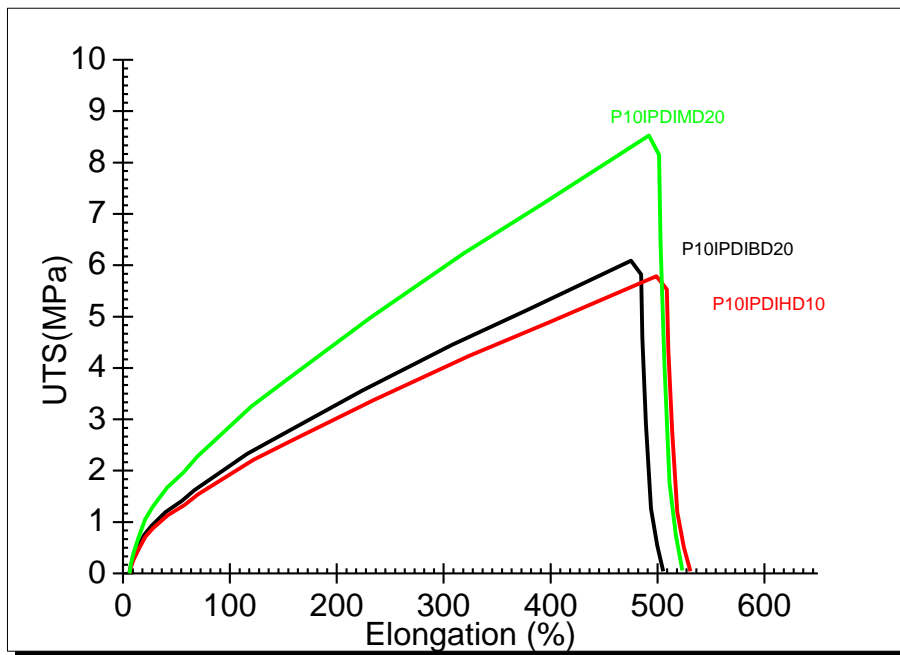
(b)

Figure 3.36: Effect of Type of chain extender on mechanical properties of polyurethanes (a) TDI and (b) IPDI
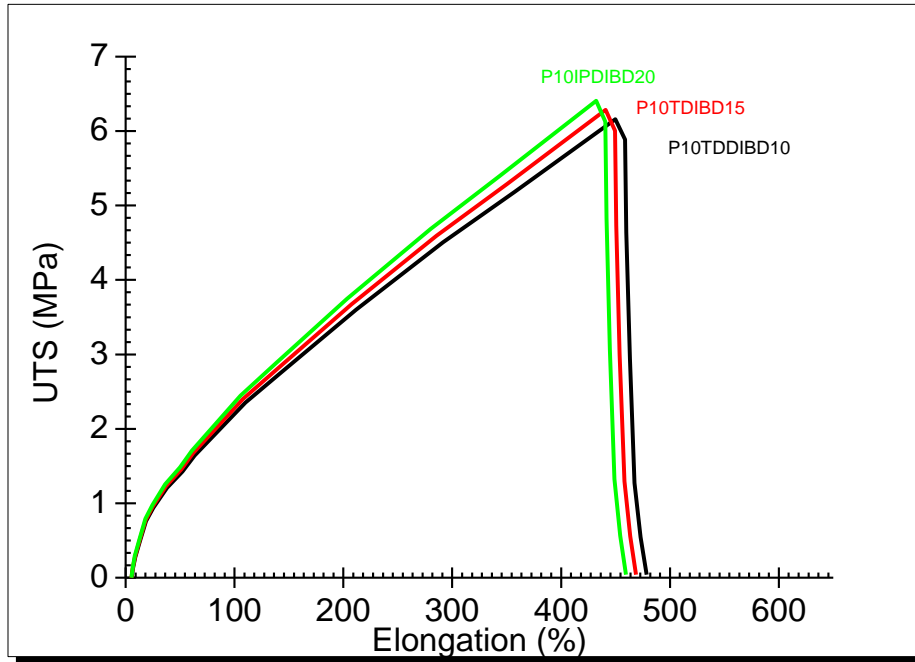
(a)
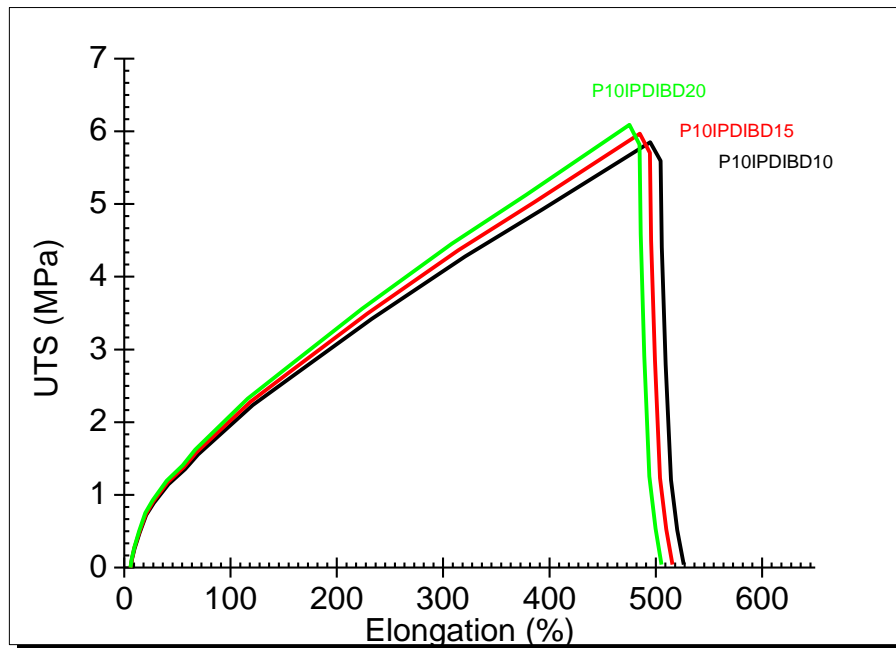
(b)

Figure 3.37: Effect of percentage of chain extender on mechanical properties of polyurethanes (a) TDI and (b) IPDI

3.3 Preparation and characterization of polymer matrix composites

This section deals with the preparation and characterization of composites of polyurethane elastomer prepared by using graphite, aluminium flakes and aluminium powder as fillers. Commercially available fillers were selected to determine the capability of synthesized polyurethanes as matrix materials for composite applications. The work was performed to study the thermal behaviour, mechanical properties and direct current resistance of the composites prepared by using 5 to 15 % fillers of different types. The combinations of these fillers were also used in the composite synthesis.

The polyurethane matrix was selected from six series of polyurethane elastomers prepared and characterized. From the Figure 3.34, two polymer samples were found having optimum mechanical properties. In aromatic diisocyanate based polyurethanes, P25TDIDM10 has 8.11 MPa UTS and its elongation was 511.7%, whereas in cycloaliphatic diisocyanate, P10IPDIDM10 has 8.58 MPa UTS and elongation similar to P25TDIDM10. The P10IPDIDM10 was found more stable (T_{max} = 340.1°C) than P25TDIDM10 (T_{max}= 329.1°C). Due to superior UTS and thermal stability, P10IPDIDM10 was selected as matrix for composite materials. In our forthcoming discussion, code SPUE (selective polyurethane elastomer) will be used instead of P10IPDIDM10.

3.3.1 Preparation of polymer matrix composites

The polymer matrix composites were prepared following the method given in section 2.4 and concentrations of different fillers used are given in Table 2.26. The polyurethane matrix was synthesized via prepolymer methodology. The reaction of polyepichlorohydrin polyol with excess diisocyanate was performed to get -NCO terminated polyurethane prepolymer, which was subsequently extended with chain extender to prepare final polyurethane. After the chain extension, calculated amount of filler already presented in Table 2.26 was slowly added with vagarious stirring for homogenous dispersion of filler in matrix. Finally, composites were post-cured as per optimized protocols for the synthesis of polyurethane elastomers.

3.3.2 Characterization of polymer matrix composites

Synthesized polymer matrix composites were analyzed using different analytical techniques such as scanning electron microscopy (SEM), thermogravimetric analysis (TGA), mechanical properties and direct current resistance. The structural elucidation of matrix by fourier transform infrared (FTIR)

spectroscopy and proton nuclear magnetic resonance (^{1}H-NMR) has already been discussed in section 3.2.2.1 and 3.2.2.2 respectively.

3.3.2.1 Scanning electron microscopy (SEM)

The dispersion of the filler in polymer matrix was visualized by Scanning electron microscopy. Figures 3.38 to 3.41 show the SEM images of polymer matrix and its composites with aluminium powder, aluminium flakes and graphite. All the images show the homogeneous dispersion of all the fillers in polymer matrix.

SEM image of PUE (Figure 3.38) shows continuous phase derived from intermixing of soft and hard segment of polyurethane. It was found that both the phases have better mixing of soft and hard segments.
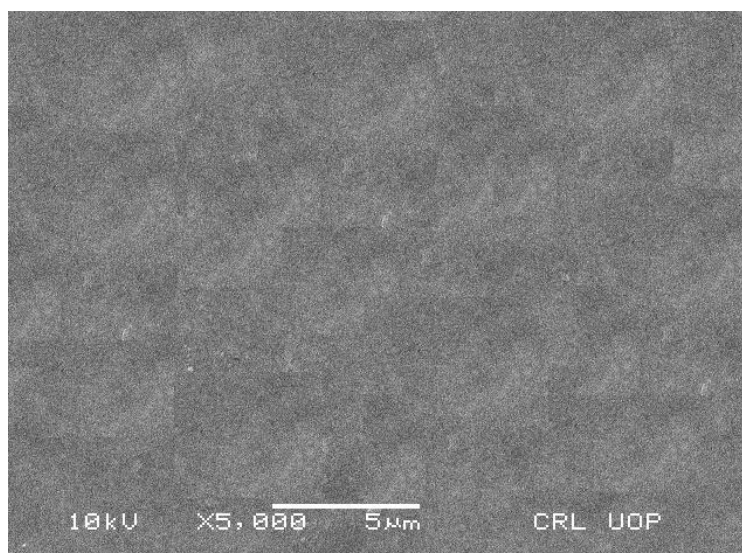
Figure 3.38: SEM image (5,000X) of PUE (PUEG0Al0)

Figure 3.39 shows the SEM image of aluminium powder composite. The small spherical particles of aluminium of the order of 0.1 to 0.5 μm were dispersed within the polymer matrix. The outer surface of the particles was dull due to the presence of fine layer of aluminum oxide formed during pneumatic atomization of the molten aluminum as a result of reaction of aluminium with oxygen present in air. This fine layer of oxide further prevents the oxidation of core aluminium. It is clear that pure aluminium is not in contact with the polymer matrix.

Aluminium flakes are flat particles produced after prolonged milling of spherical aluminium particles. In order to prepare aluminium flakes, atomized powders are charged together with mineral turpentine and fatty acid into a ball mill where the powders are milled to minute flat flake-like particles. SEM images of

aluminium flakes based polymer composite (Figure 3.40) shows homogenously dispersed shiny particles embedded in PUE matrix. During the milling action, dull aluminium oxide layer is disintegrated, therefore, aluminium is in contact with the polymer matrix. The particle size of the aluminium flakes is of the order of 1 to 2 μm.
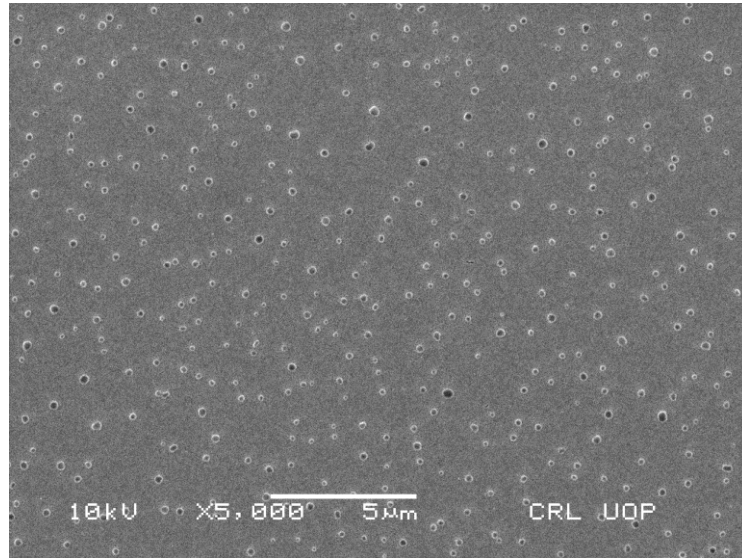
Figure 3.39: SEM image (5000X) of PUE-Al powder composite (PUEG0Al10PW)
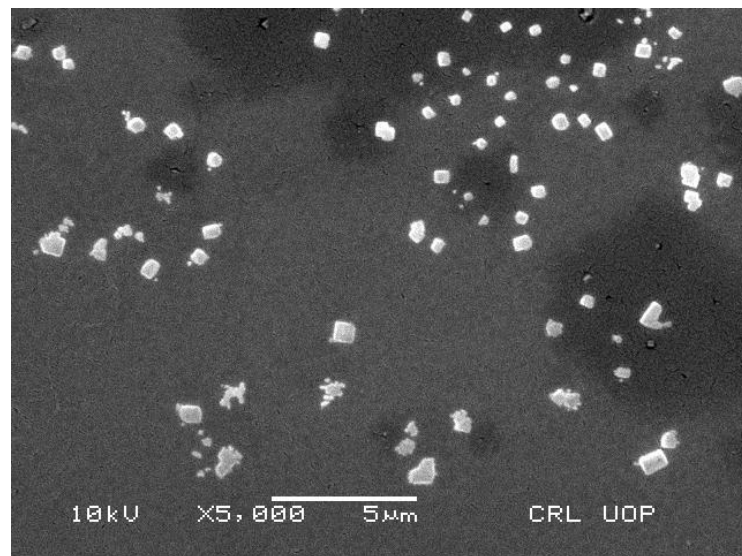
Figure 3.40: SEM image (5000X) of PUE-Al paste composite (PUEG0Al5)

Graphite powder contains many unique physical properties including superior electrical and thermal conductivity, highly crystalline structure, high purity,

temperature stability and inertness. SEM image of PUE-graphite composite is shown in Figure 3.41. The particles of less than 0.3 μm are well dispersed in polymer matrix.
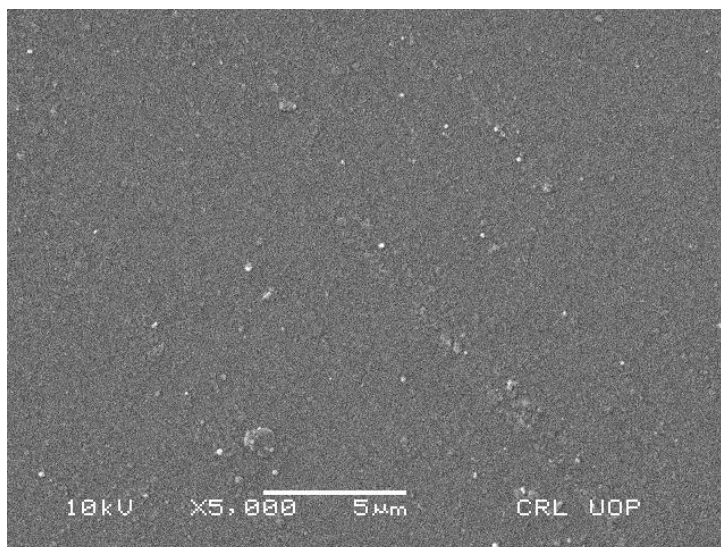
Figure 3.41: SEM image (5,000X) of PUE- graphite composite (PUEG15Al0)

3.3.2.2 Mechanical properties

The mechanical properties of the composite materials were investigated in terms of filler and their percentages. Table 3.15 shows the data of mechanical properties of all the composite materials. The addition of graphite, aluminium powder and aluminium flakes increased the UTS and decreased the elongation thus giving more strength to composite materials (Figure 3.42). The stress-strain behavior of graphite is elaborated in Figure 3.43. The aluminium powder and aluminium flakes composites followed the same trend. This enhancement in strength may be due to shifting of the forces from matrix to solid fillers[192].

The addition of 5% fillers (graphite, aluminium flakes and aluminium powder) enhanced the UTS of composite from 8.58 MPa (PUE) to 9.81, 9.3 and 10.3 MPa respectively with subsequent decrease of elongation at break from 511.7% (PUE) to 500, 475 and 416.6% respectively. Thus, maximum strength (16.7% enhancement) was achieved by the incorporation of 5% aluminium powder whereas addition of 5% graphite and 5% aluminium flakes enhanced the UTS to 12.5% and 7.7% respectively. Addition of 5% graphite marginally reduced the elongation at break (2.3%). Loss of elongation at break was found 7.2% for aluminium flakes and 4.9% for aluminium powder. 35.5% enhancement was achieved by the incorporation of 10% aluminium powder whereas addition of 10% graphite and 10% aluminium flakes

enhanced UTS by 33% and 29.9% respectively. Addition of 10% graphite reduced 12.3% elongation at break. Loss of elongation at break was found 16.7% for aluminium flakes and 14.5% for aluminium powder. By the addition of 15% filler, UTS was improved up to 54.1% with aluminium powder, 51.8% with graphite and 49,5% with aluminium flakes along with reduction in elongation at break up to 18.6%, 16.4% and 20.8% respectively.

In all the composites, incorporation of aluminium powder resulted in an increase in maximum UTS (54.1%). It may be attributed to the spherical shape of the particles and their uniform size distribution. Being smaller in size, graphite was reasonable for 51.8% enhancement in composite strength whereas aluminium flakes elevated the UTS up to 49.5%. However, among all composites, relatively less change in mechanical properties was observed in case of aluminium flakes which may be due to their flat shape and larger particle size. The impact of different combinations of these fillers on mechanical properties of the composites was almost weighted average.

Table 3.15: Mechanical properties of polymer matrix composites

Sr. No	Sample Code	UTS (MPa)	Elongation (%)
1	$PUEG_0Al_0$	8.58	511.7
2	$PUEG_5Al_0$	9.81	500
3	$PUEG_{10}Al_0$	12.8	448.6
4	$PUEG_{15}Al_0$	17.8	427.8
5	$PUEG_0Al_5$	9.3	475
6	$PUEG_0Al_{10}$	12.1	426.4
7	$PUEG_0Al_{15}$	17	405.5
8	$PUEG_{2.5}Al_{2.5}$	9.3	475
9	$PUEG_5Al_5$	12.1	426.4
10	$PUEG_{7.5}Al_{7.5}$	17	404
11	$PUEG_{2.5}Al_{7.5}$	11.2	406.9
12	$PUEG_{7.5}Al_{2.5}$	12.3	426.4
13	$PUEG_0Al_5PW$	10.3	486.6
14	$PUEG_0Al_{10}PW$	13.3	437.5
15	$PUEG_0Al_{15}PW$	18.7	416.6
16	$PUEG_{2.5}A_{l2.5}PW$	9.5	485
17	$PUEG_5Al_5PW$	12.4	436.1
18	$PUEG_{7.5}Al_{7.5}PW$	17.2	413.9
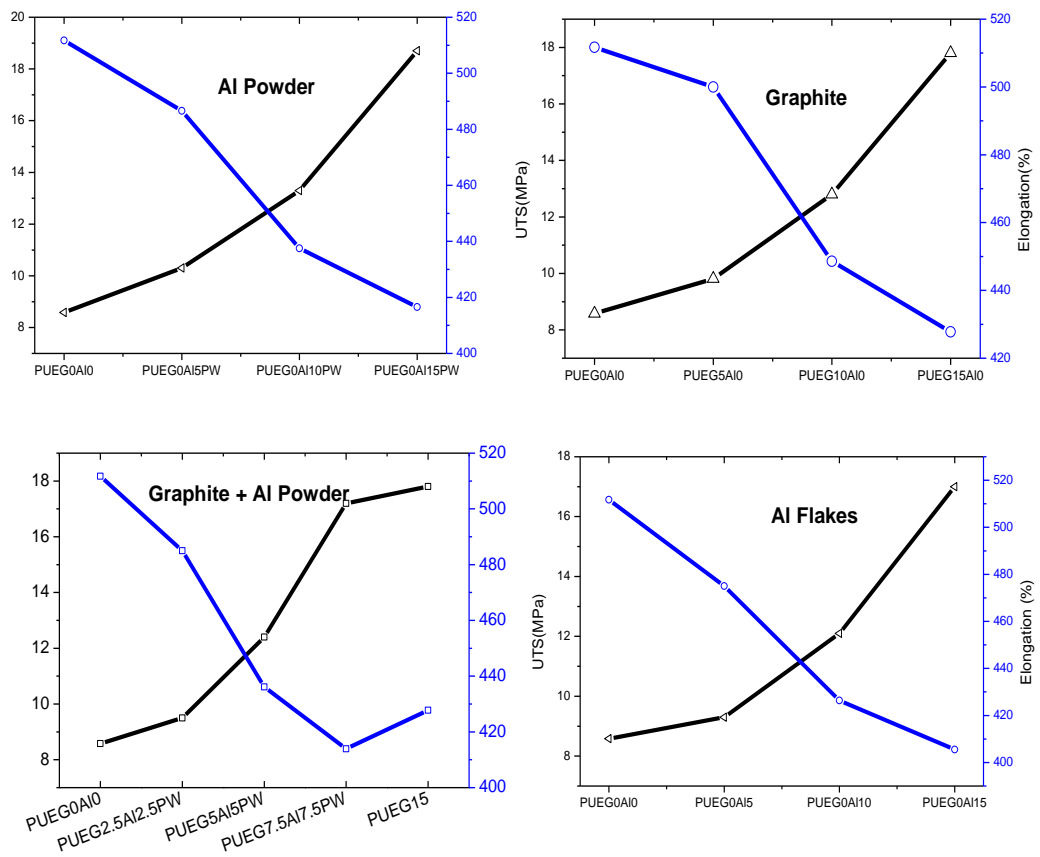
Figure 3.42: Variation of mechanical properties polymer matrix composites
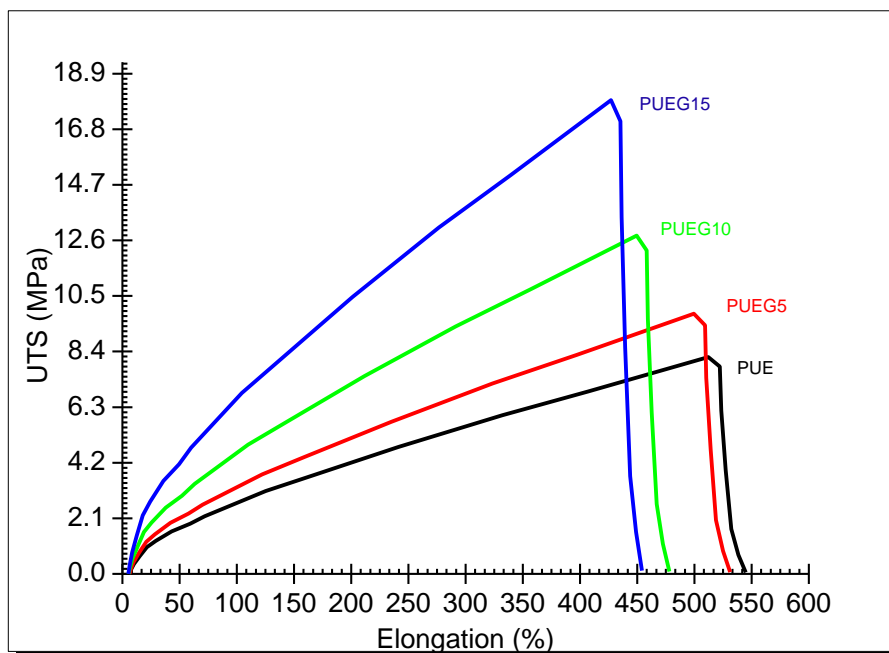
Figure 3.43: Stress-strain curve for PUE and PUE-graphite composites

3.3.2.3 Thermal characterization by TGA

Effect of temperature on thermal degradation behavior of polymer matrix composite materials was evaluated by TGA. The weight loss of the synthesized composite materials is illustrated in Figures 3.44-3.46. The percentage of filler was confirmed by the residue obtained after thermal analysis which was found almost comparable to the amount of fillers in all the composites.

The addition of graphite stabilized the composites as compared to matrix PUE. The stability of graphite based composites was slightly increased with the increase of percentage of graphite from 5% to 15% (Figure 3.44) that can be attributed to the stronger interaction of filler with matrix because of larger surface area.
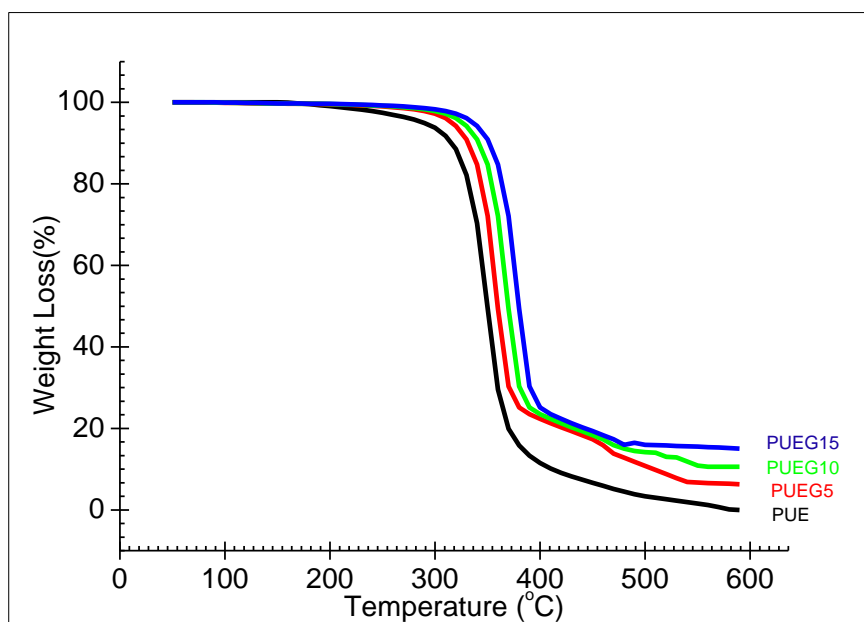
Figure 3.44: Thermal degradation behaviour of PUE-graphite composites

Composites based on aluminium flakes showed the reduced thermal stability and increase in percentage of filler substantially decreased the stability (Figure 3.45)[193]. It might be due to direct contact of aluminium metal with polymer matrix.

On contrary to above mentioned fillers, aluminium powder did not affect the thermal degradation pattern of the composite material (Figure 3.46) and was found inert. Even the increase in amount of aluminium powder did not show any impact on the stability. It may be due to the presence of fine layer of alumina (Al_2O_3) present at the polymer-filler interface which prevented the direct contact of aluminum metal

with polymer. Alumina was inert when composites were subjected to thermal shocks [194].
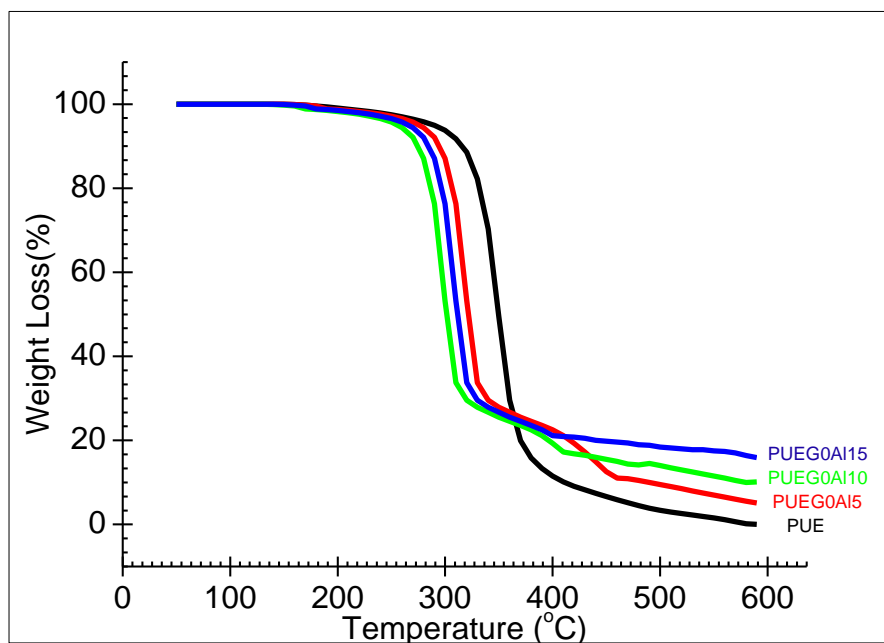
Figure 3.45: Thermal degradation behaviour of PUE-Al paste composites
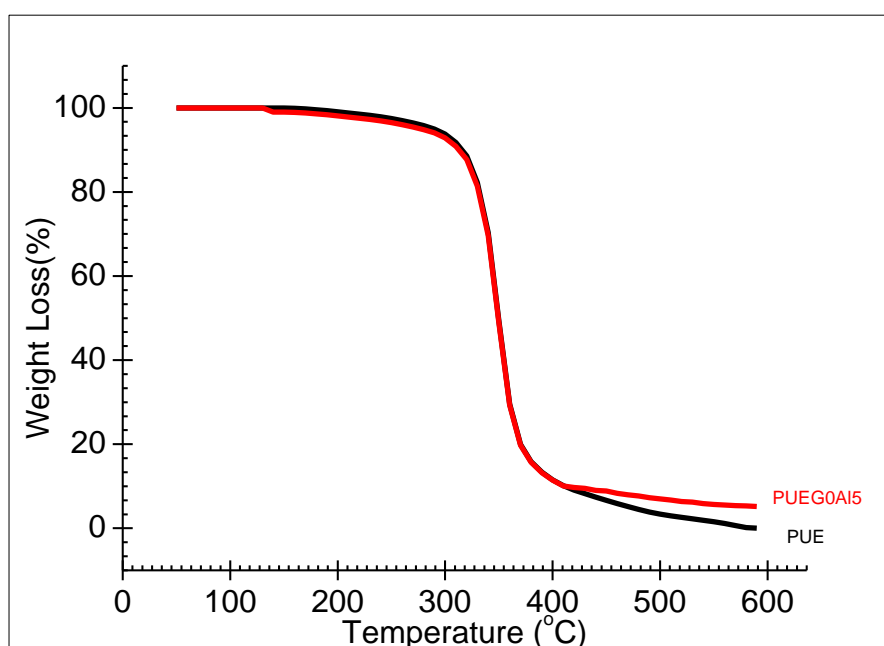
Figure 3.46: Thermal degradation behaviour of PUE-Al powder composites

3.3.2.4 Direct current resistance (DCR)

The polyurethanes are not conductor of electricity as they are intrinsically electrically insulating materials like plastics. In some applications, imparting

electrical conductivity has significant value and utility. For example, electrically conductive plastic compounds are used as jacket coverings for high power transmission cables thus reducing induced currents from nearby cables and used for shielding sensitive electronic components.

Several additives are used to achieve antistatic performance levels e.g., carbon black, graphite, metal powders, wires or combination of two or more than two additives. A number of factors influence the conductivity of plastic compounds like the inherent conductivity of the plastic, the level of dispersion achieved for the conductive additive and the intrinsic conductivity of the additives.

The fillers used to impart electrical conductivity to plastics exhibit a phenomenon known as percolation which is the concentration of the filler when internal conductive network of particles is formed within the polymer matrix and the material becomes electro-conductive. As the concentration of filler in the matrix increases, the conductivity passes through a sharp and abrupt rise over a very narrow concentration (loading) range of carbon black[195]. Further increase in loading past this threshold causes little increase in the conductivity. This narrow range is known as the percolation threshold. There are many contributing factors involved in the formation of conductive networks in filled polymers. Among the parameters influencing the percolation concentration, filler distribution, filler shape, filler/matrix interactions and the processing techniques are the most important ones.

Ideal conductive filler for the industrial users should be of low percolation threshold (high efficiency), improved mechanical properties, thermally stable and cost effective. Keeping in view commercial availability, graphite, aluminium powder and aluminium flakes were utilized as additive. Graphite is used as electro-conductive filler due to its good conductivity and moderate cost. It is also reported that graphite increases the mechanical and thermal properties as well as the dimensional stability of the polymeric material.

In order to study the direct current resistance, 5%, 10% and 15% of above mentioned fillers were used to prepare composites. The concentration versus Log DCR relationship of composite is shown in Figure 3.47. It is evident from the figure that addition of aluminum powder and flakes could not create the conducting network resulting in no signal in DCR measurements. It might be due to the presence of insulating oxide layer on the surface of aluminium.

Incorporation of graphite particles enhanced the conductivity and hence reduced the direct current resistance. The DCR decreased significantly up to 7.5% of graphite concentration after which graph became parallel to x-axis which indicated the entrance of percolation threshold in polymer matrix. It signifies that the developed polymer was capable to sustain the conducting network of graphite. The mechanical properties and thermal stability along with electro-conductive nature of composite proposes it as a promising candidate in a conducting polymer matrix composite for various applications.
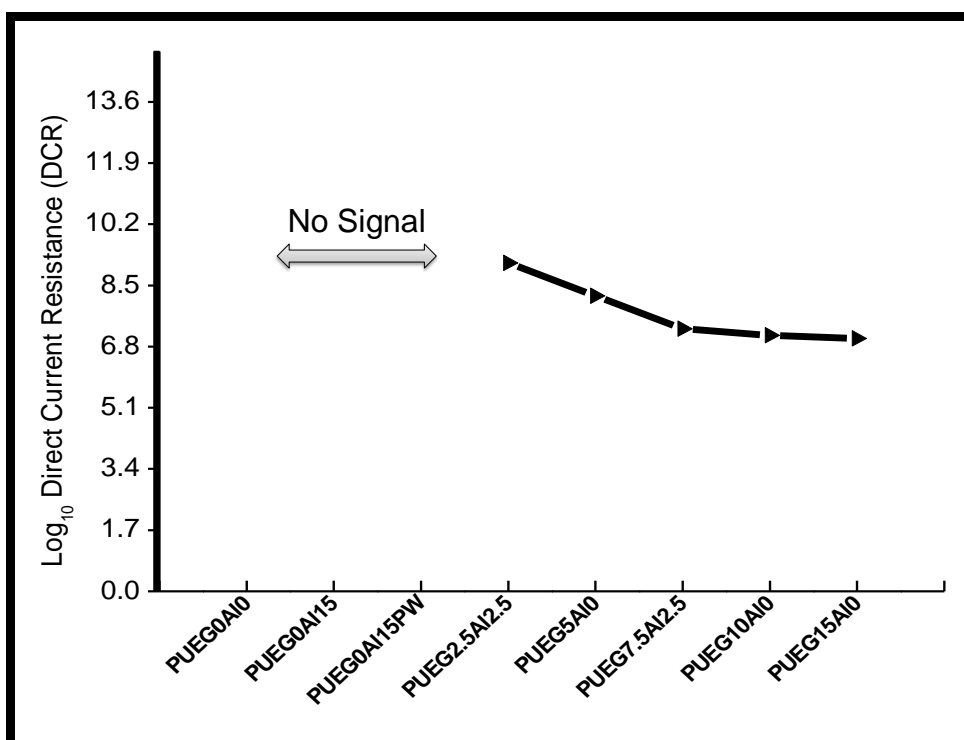
Figure 3.47: Direct current resistance of polymer matrix composites

CONCLUSIONS

A method for the synthesis of bi-functional polyepichlorohydrins (PECH) of different molecular weights (1000-6500) from epichlorohydrin in the presence of *para*-toluenesulphonic acid (*p*-TSA) and $SnCl_4$ without any solvent was successfully established. Increasing the number of moles of *p*-TSA resulted in product of lower molecular weight. The structure of PECH was elucidated by FT-IR and ^{1}H-NMR techniques and functional parameters were determined by VPO, GPC and chemical analysis. The molecular weight distribution and polydispersity of the synthesized polymers were determined by gel permeation chromatography (GPC). Absolute value of number average molecular weight (M_n) was established with vapour pressure osmometry, terminal hydroxyl groups were quantified by acetylation method and functionality was derived from hydroxyl value and M_n. Presence of two hydroxyl groups per molecule demonstrates the capability of synthesized PECH to be used as a polyol in the preparation of polyurethanes. This procedure furnished products of improved functionality (2.01-2.53) with good yield (85-88%).

Fifty-four polymers with diversified structures were synthesized from PECH of different molecular weights (1000-3500), TDI and IPDI extended with three short-chain diols (BD, HD and DM) in the presence of DBTDL as a catalyst. Formation of elastomers was confirmed by FTIR and NMR spectroscopy. XRD studies indicated low crystallinity in all synthesized polyurethanes. However, increase in the amount of chain extender and use of aromatic diisocyanate relatively enhanced the crystalline state. SEM images of PUEs have shown that hard segments are completely dispersed in the soft segment matrix. Glass transition temperature (T_g) of PECH rises linearly (-35.6 to -28.3 °C) with the increase in its molecular weight. T_g of TDI based PUEs were increased to -16 °C while in IPDI series it was further boosted to 7.98 °C. It reflects relatively greater homogeneity of IPDI based polymers than TDI based counterparts. SEM and XRD analysis further supported this observation. TGA and DSC data revealed that synthesized polyurethanes were stable up to 200 °C and they were decomposed without melting. Variation of molecular weight of PECH, type of diisocyanate and chain extender affected the thermal behavior of PUEs. Mechanical properties of PUEs were significantly improved by the variation of molecular weight of PECH, type of diisocyanate and chain extender. TDI based polyurethanes had

greater UTS but lesser elongation than IPDI based PUEs. In TDI based polyurethane elastomers, maximum UTS observed was 9.39 MPa with 447.2% elongation at break while in IPDI based polyurethanes highest UTS achieved was 8.9 MPa UTS with 491.7% elongation. Use of cyclohexanedimethanol as chain extender enhanced mechanical properties of PUEs in comparison with butanediol and hexanediol.

Polymer based composites were prepared by using graphite, aluminium flakes and aluminium powder as fillers in synthesized PUEs. The composites based on aluminium flakes were thermally less stable than PUEs while highest stability was observed for PU/graphite composites. Aluminium powder showed no significant effect on thermal stability of PUEs. Addition of solid fillers substantially enhanced the mechanical properties. Graphite resulted in greater increase in UTS without any significant loss of elongation which is attributed to its stronger interactions with the PU matrix. The composites based on aluminium flakes were thermally less stable than PUEs however PU/Graphite composites showed superior stability relative to its parent elastomer. Addition of solid fillers substantially enhanced the mechanical properties of the composites. By the addition of 15% fillers, UTS was enhanced up to 54.1% with aluminium powder, 51.8% with graphite and 49.5% with aluminium flakes along with 18.6%, 16.4% and 20.8% reduction in elongation at break respectively. Incorporation of graphite boosted the conductance of composite; however, aluminium powder was found more efficient in improving mechanical strength of composite. Incorporation of graphite enhanced the conductance of composite however aluminium powder was found more efficient in improving composite strength. PU-composite with 7.5% graphite has DCR 1.976×10^7 Ohm which is suitable for charge dissipative and antistatic applications. The synthesized elastomers have enormous potential to be used as matrix material in polymer matrix composites.

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List of Publications

1. Muhammad Ahmad, Muhammad Sirajuddin, Zareen Akther, Waqar Ahmad
   Spectrochimica Acta Part A: Molecular and Biomolecular
   Spectroscopy, Volume 151, 5 December 2015, Pages 164-1