DEVELOPMENT OF VEGETABLE OIL BASED POLYURETHANE ADHESIVES

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DECLARATION

This is to certify that the work presented in this thesis entitled **“Development of Vegetable Oil Based Polyurethane Adhesives”** is original and has been carried out by me for the degree of **Doctor of Philosophy** under the supervision of **Dr. Raminder Kaur**, Assistant Professor, Department of Applied Chemistry. This thesis is contribution of my original research work. Wherever research contributions of others are involved, every effort has been made to clearly indicate the same. To the best of my knowledge, this research work has not been submitted in part or full for the award of any degree or diploma in Delhi Technological University or in any other University/Institution.

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CERTIFICATE

This is to certify that the thesis entitled **"Development of Vegetable Oil Based Polyurethane Adhesives"** has been submitted to the Delhi Technological University, Delhi-110042, in fulfilment of the requirement for the award of the degree of **Doctor of Philosophy** by the candidate **Mr. Manjeet Malik**, (Reg. No.:2K13/Ph.D./AC/09) under the supervision of **Dr. Raminder Kaur, Assistant Professor,** Department of Applied Chemistry. It is further certified that the work embodied in this thesis has neither partially nor fully submitted to any other university or institution for the award of any degree or diploma.

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Dedicated

To

My Parents

Sh. Krishan Malik

And

Smt. Rajia Malik

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ABSTRACT

Polyurethane (PU) adhesives are well known for their properties such as excellent adhesion, flexibility, good performance at low-temperature conditions and cure speeds. These are the most adaptable product known in adhesives market due to vast diversity among the choice of the raw materials, which, gives the liberty to user to adjust the properties of the end product. In the recent years, researchers have focused their attention on the synthesis of polyurethane derived from various bio-based resources due to major hitches like depletion of crude oil stock in world, its inflated price and most importantly the environmental concerns. The present research is conducted with an objective to develop polyurethane adhesive by the use of vegetable oils, owing to their low cost, easy availability and nontoxic nature. The experimental work was primarily focused on exploiting the reactivity of unsaturated vegetable oils to prepare a set of polyols, which are one of the important raw material in the production of PU. These polyols were further utilized for the synthesis of polyurethane adhesives by using different synthetic methodologies. Polyether ester polyols were prepared from epoxidation of transesterified canola oil and polyester polyol was prepared by the transesterification of castor oil. The modified polyols were reacted with different types of isocyanate like Methylenediphenyldiisocyanate (MDI), Toulenediisocyanate (TDI), Isophoronediisocyanate (IPDI), Hexamethylenediisocyanate (HMDI) etc. for synthesis of polyurethane adhesives. As synthesizing vegetable oil based polyols covers only one part for sustainable PU synthesis so to eliminate the toxicity of diisocyanates, non-isocyante route was choosen as a worthy alternatives. For this, 5,10,15-tris(pentaflourophenyl)corrole was utilized as novel catalyst for coupling

reaction between epoxidised canola oil and CO_2 (gaseous) to introduce cyclic carbonate moieties in the oil and the carbonated product was further utilized to obtain Non-isocyanate PU by curing with different diamines like EDA(1,2-ethane diamine),HMDA(1,6-hexanediamine),IPDA(Isophoronediamine),PPDA(p-phenylene diamine). The products obtained in these studies were characterized by nuclear magnetic resonance and FTIR spectroscopy for structural analysis and to determine the extent of reaction. TGA and DSC analysis was done to study the thermal stability of prepared adhesive. Influence of various factors such as the NCO/OH molar ratio, hydroxyl value of polyols and the amount of reinforcing fillers on the properties of adhesive were extensively studied. It has been observed that the addition of TiO_2 in castor oil based PU adhesive led to a remarkable enhancement in its mechanical and chemical resistance, an increase in Tg value and the adhesion. The adhesive with a mole ratio of NCO/OH equaling to 1.2, filled with 3 wt% TiO_2, was found to be much better than the commercial adhesive used for bonding wood, when tested for single lap shear strength in various environmental conditions. Further, the studies conducted to examine the influence of the structurally different diisocyanates on the properties of PU adhesives had shown considerable variations in thermal stability, adhesion strength and environmental resistance. The synthesized adhesive showed much better performance as compared to commercially available adhesive formulation under different conditions of testing. The non-isocyanate PU obtained with the use of 5,10,15-tris(pentaflourophenyl)corrole manganese(III) complex as catalyst had indicated a 1/4th of the reduction in reaction time as compared to the previously reported catalysts in literature studies and the synthesized non-isocyanate PU showed good thermal stability upto 200^0C and a tensile strength of upto 8 MPa.

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LIST OF ABBREVIATIONS

Symbol	Notations
PU	Polyurethane
MDI	4,4'-diphenylmethanediisocyanate
IPDI	Isophorone diisocyanate
HDI	1,6-hexamethylene diisocyanate
TDI	Toluene-2,4-diisocyanate
DBTDL	Dibutyltin dilaurate
NMR	Nuclear magnetic resonance
FTIR	Fourier Transform Infrared
TGA	Thermo Gravimetric Analysis
UTM	Universal Testing Machine
SEM	Scanning Electron Microscope
TEM	Transmission electron microscope
NIPU	Non isocyanate polyurethane
EDA	1,2-ethane diamine
Tg	Glass Transition Temperature
VOC	Volatile organic compound
TPU	Thermoplastic polyurethane
TBAB	Tetra-n-butylammonium bromide
ESBO	Epoxidized soybean oil
HMDA	1,6-hexane diamine
PPDA	para-phenylenediamine
IPDA	Isophorone diamine

CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1.1. Introduction

Polyurethane (PU) adhesives are well known for their properties such as excellent adhesion, flexibility, good performance at low-temperature conditions and cure speeds that can be varied according to need of the manufacturer [1]. Due to a vast diversity among the raw materials, the properties of the PU adhesives can be adjusted to a great extent as per the requirements of the user. The fact is that PU adhesives are the most adaptable product known in adhesives market. Due to the immense disparity among various PU adhesives, it is very difficult to categorize them, as one type of PU adhesive may adhere effectively to a particular kind of substrate whereas other type of PU adhesive even lacks to hold the same substrate. Though, there are more than 40 distinct urethane reactions known till date, the most common reactions that includes the synthesis of more than 90% of the available PU adhesives are addressed here.

1.2. Types of Polyurethane Adhesives

Polyurethane adhesives are broadly classified as one component adhesives and two components adhesives. As clear from the name, one component adhesives are self-curing adhesives which do not require mixing with any other component (curing agent) prior its application on the substrate. One-component PU adhesives are based on isocyanate terminated pre-polymer which usually cures itself due to the moisture present in the air. In some instances, a fine mist of water may be also sprayed on top of the adhesive for faster curing before closing the bonded substrates. Only a simple dispensing equipment is required for application of one component adhesive to the substrate as no mixing of component is required. One component PU adhesives are majorly utilized to gather the sidewalls for recreational vehicles (RV's), mobile homes, and manufactured housing. Moreover, one component PU adhesives are utilized to bond flooring of hardwood, doors of metal, partitions, panels, etc. in construction sector. On the other hand, the two component adhesives are reactive adhesives which are not self-curing but essentially requires a reaction of two components. Both components are homogeneously mixed before application to the substrate. The adhesive then cure itself because of a chemical reaction between two components. The two component adhesive shows limited open time varying from second to hours and a sophisticated meter mixed complicated equipment is required for mixing of two components of adhesive. Two component PU adhesive can effectively wet the surface of a number of substrates like plastics, wood, metal, glass etc. They are extensively utilized as flexible packaging adhesives, in roof coatings and as adhesives for binding metal, wood, glass-reinforced plastic substrates etc. Most of the industrially important adhesives are covered by these two major categories of PU adhesives which are discussed in detail as follows:

1.2.1. PU adhesives- One-component type

PU adhesives, both waterborne and solvent based, are reported to be the high performance adhesives due to their excellence in adhesion properties, heat and chemical resistance, fast curing time, early green strength, high bond strength, and low shrinkage. One component type PU adhesives are broadly categorized as:

i. Moisture-cured (liquid) PU adhesive
ii. Moisture-cured (hot-melt) PU adhesive
iii. Solvent-based PU adhesive
iv. Waterborne PU adhesive

v. Blocked PU adhesive
vi. Thermoplastic PU adhesive
vii. PU adhesives- Two-component type
viii. Structural polyurethane adhesive
ix. Waterborne two component PU adhesives

The working behavior of these different PU adhesives are discussed as below:

1.2.1. PU Adhesives- One-Component Type

1.2.1.1. Moisture-Cured (Liquid) PU Adhesive

In order to act in accordance with volatile organic compound guidelines (VOC), a little or no solvent is present in moisture-curing liquid PU adhesives. At present most of liquid adhesives are MDI based while some adhesive still uses TDI. TDI offers easy formulations of low viscosity liquid adhesive but toxicity concerns due to its volatile nature prohibit its utilization until proper ventilation and respiratory safeguard is provided. On the other hand, as the vapor pressure of MDI is much lower as compare to TDI, which makes it as a preferable choice, being more safer.

The preparation of an isocyanate terminated pre-polymer form the basis for production of most of the one component moisture curing PU adhesives, as shown below:

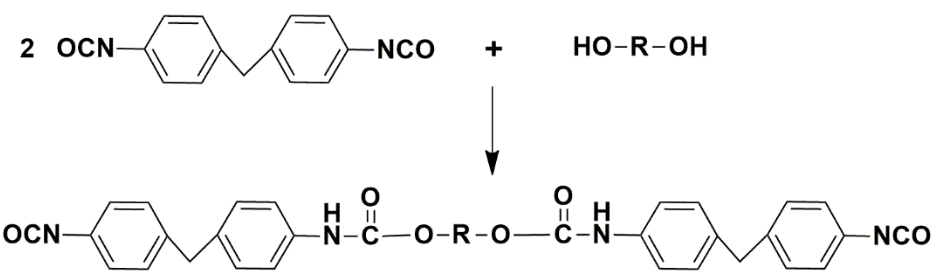

Figure 1.01: Preparation Reaction for Isocyanate Terminated Pre-polymer [1].

Polymeric Methylene Diphenyldiisocyanate with approximate functionality of 2.7 or higher are used for the synthesis of structural wood adhesives. Polymeric Methylene Diphenyldiisocyanate are used for rigid adhesive while pure Methylene Diphenyldiisocyanate is utilized for flexible assemblies. The NCO/OH ratio lies between 1.5 to 3.0 for pre-polymer preparation. Catalysts like dibutyltin dilaurate and dimorpholinodiethyl ether, unveil two major tasks in 1 component moisture cured PU adhesive i.e. one is to catalyze pre-polymer synthesis reaction and the other is to increase the speed of the moisture curing of the polyurethane adhesive. The one component liquid PU adhesives sometime requires a light spray of water droplets after its application on bonding substrate to gain high fixturing strength within 15 minutes even at room temperature.

1.2.1.2. Moisture-Cured (Hot-Melt) PU Adhesive

Majority of moisture cured hot melt polyurethane adhesive makes use of monomeric methylene diphenyldiisocyanate mixed with polyol at NCO/OH ratios ranging from 1.5 to 2.3. Hot melt adhesives are low viscosity liquids at the application temperature but results in fast crystallization as temperature goes down. This crystallizable backbone provides good initial fixturing strength for temporarily holding the substrates. The Moisture-curing hot-melt PU adhesives possess much better structural properties as compared to traditionally used hot melts like EVA. These adhesives holds a small but rapidly growing segment among PU adhesives. Hot melt PU adhesives offers applications in different areas like in bookbinding, footwear, furniture assembly and construction. Due to high sensitivity of these adhesives towards moisture, a care must always be taken for its storage in dry conditions. The green strength of these type of adhesive can be enhanced by incorporating higher melting point polyesters based on dodecanedioic acid or azaleic acid [2, 3]. Alternatively, the initial bonding strength can be increased by the addition of thermoplastics of high melt flow [4]. The heated pot life of hot melt PU adhesives was found to vary between 3 hours to 2 days.

1.2.1.3. Solvent-Based PU Adhesive

Solvent-based PU adhesives are mainly classified as: reactive solvent borne PU adhesive and non-reactive solvent borne PU adhesive. The reactive ones generally involves high molecular weight oligomers possessing isocyanate functionality. Moreover, these adhesives keep on reacting further, even after application on the substrate to improve the physical properties. On the other hand, non-reactive solvent based PU adhesive shows no further reaction after application. Solvents used in these adhesives are: toluene, ethyl acetate, butyl acetate, ketones, etc. The viscosity of solvent borne PU adhesives are much higher in the absence of solvent, which makes its penetration difficult in the substrate surface. The poor ability of adhesive to wet the substrates for bonding lead to poor durability of bond and generally results in adhesive failure. In recent times, the use of solvent based adhesives is somewhat restricted due to increasing regulations in respect of Volatile organic compounds. Solvent-borne PU adhesives are mostly utilized in shoe industries to bond leather components and adhering the sole of athletic shoes. Various kind of additives like tackifiers, plasticizers can also be added to get better adhesion for some particular type of substrates. Penczek and Kujawa-Penczek reviewed the effect of tackifiers and the influence of crystallization speeds on properties of adhesives [5]. The open time of solvent based PU adhesive is regulated by the rate of crystallization of the polyester backbone present in high performance adhesives [5].

1.2.1.4. Waterborne PU Adhesives

High performance waterborne PU adhesives are synthesized by reacting crystalline polyester polyols like hexamethylene adipate with aliphatic diisocyanates like isophorone diisocyanate (lPDI) or methylene bis(cyclohexyl isocyanate). Most of the waterborne prepolymers also comprise an internal emulsifier which may be a cationic or anionic emulsifiers. Rosthauser et al. extensively summarized these stabilizers in his article [6]. Dieterich's review article provides comprehensive details on the preparation and processing of waterborne PU adhesives [7]. A little activation is required in waterborne adhesives in order to form a bond while they do not require much heat energy for activation. The open time of bond is determined by crystallization kinetics. A quick crystallizing backbone like hexamethylene adipate is generally required in automated industrial operations. After cooling of bondline, crystallization can happen in just 2 minutes time period or even lesser. Dormish and Witowski determined the kinetics of crystallization of different waterborne dispersions. They measured an open time of upto 40 minutes [8]. One component waterborne PU adhesives are generally repositionable which allow the correction of poorly aligned bonded substrates by merely heating over bond activation temperature. Then, the realignment of substrate can be done with little or no loss in strength of bond.

1.2.1.5. Blocked PU Adhesives

The term ‘blocked’ signifies that one of the main reactant involved is blocked chemically to inhibit reaction. Figure 1.02 explains the idea of using a blocked polyisocyanate in one component PU adhesives.

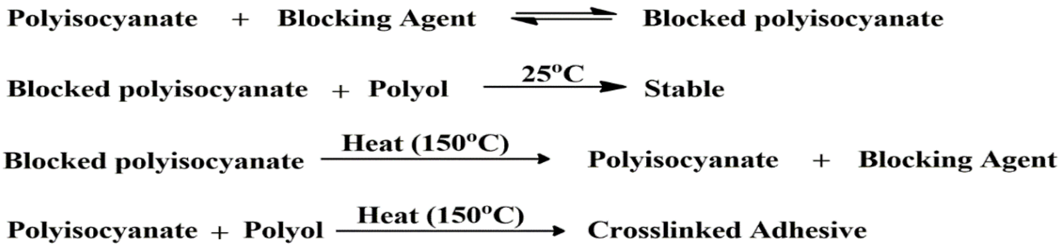

Figure 1.02: Role of Blocking Agent in One Component PU Adhesive System [9].

Commercially available blocked isocyanates are mostly based on Toulene diisocyanate, Isophoronediisocyanate and derivatives of HMDI. No reaction occurs between blocked isocyanate and polyol at room temperature as isocyanate has already combined with the blocking agent. As the temperature of the system rises, the reverse of blocking reaction takes place resulting in unblocking of isocyanate component. Then, the reaction between isocyanate and polyol takes place to yield a tough, crosslinked PU adhesive. The speed of reaction can be increased by addition of catalyst and/or by just providing the higher temperature conditions. Generally, DBTDL is used as a catalyst which is known to lower down the temperature required for unblocking of isocyanates. Blocked isocyanates are extensively reviewed in literature [9]. Most of the blocking agents are considered to be volatile organic compounds which makes the market portion of blocked isocyanate PU adhesive limited due to increase in VOC regulations. Blocked adhesives serves as cross linkers for solvent borne PU adhesives. They may also be utilized as flocking adhesive and as uniting adhesive for belts.

1.2.1.6. Thermoplastic PU Adhesives

Generally, the thermoplastic PU adhesives are linear having a functionality equals to 2. Molecular weights of around 100,000 or higher is desirable to obtain Thermoplastic PU adhesives with good physical properties [10]. Mostly these Thermoplastic PU adhesives possess a high speed crystallizing backbone based on symmetrical polyesters. TPU adhesives are better than hot melt adhesive in terms of having better holding strength just after crystallization. Thermoplastic PU adhesives are utilized in high performance applications where toughness and high flexibility are major requisite as they are found to be costlier as compared to most of hot melt adhesives.

Thermoplastic PU's are being regarded as substitute for solvent based PU adhesive in the shoe market.

1.2.2. PU Adhesives- Two-Component Type

Considering the reactivity factor, the adhesive industry has taken benefit, thus leading to the fast cure two-component adhesives. The two component PU adhesive are broadly categorized as follows:

1.2.2.1. Structural PU Adhesive

The two component PU adhesives shows broad variation in the properties so their characterization is not an easy task. Generally, two component PU adhesives are utilized to get better flexible bond line. Flexible PU adhesive shows excellent impact strength without failure in bond line even in sub-zero temperature conditions. Two component PU adhesives are widely used for bonding two different kind of substrate with a large difference in their thermal expansion coefficients. For example, the bond line between metal and plastic substrates can be stressed but these adhesives possesses higher potential to adjust to these stresses due to very lower Tg values (mostly -20°C or even lower) of continuous phase soft segment. Catalyst like DBTDL, tertiary amines etc. are generally added to alter the reaction times. The level of catalyst employed can greatly affect the open times of two component PU adhesives. Different kind of additives and fillers can be used to enhance the properties of two component PU adhesive systems. The most common fillers used are TiO_2, $CaCO_3$, wollastonite, talc and carbon black. In addition to that, plasticizers and adhesion promoters like silane coupling agents are utilized to control the viscosity and improving the adhesion between certain substrates, respectively [11].

1.2.2.2. Waterborne Two-Component PU Adhesives

The two component PU adhesives comprises of one of the component in PU dispersions, while the second component is generally a crosslinker. The crosslinker usually belong to following material classes i.e. polyisocyanates, epoxies, aziridines and polycarbodiimides. The addition of crosslinkers to the PU dispersions are done with simple stirring. Crosslinkers can vary the pot life of adhesive from 20 minutes to upto 3 hours. Coogan summarizes the analysis of different crosslinkers using a polyurethane and found that water dispersible isocyanates gives the best cure [12]. If only carboxylic acids are present in PU dispersion then aziridines were found to be best for improving mechanical properties and solvent resistance, followed by water dispersible isocyanates and the epoxies [12]. Melamines and water dispersible isocyantes are used for crosslinking in hydroxyl terminated polyurethane dispersions. Melamine shows very good firmness in water but the bond requires some heating for crosslinking as melamine do not start crosslinking at room temperature conditions. Heated curing cycle associated with melamine crosslinker may also liberate formaldehyde or ethanol [13]. Numerous crosslinkers which are not water dispersible needs to be modified using the surface active agents to get emulsified in water.

1.3. Applications of PU Adhesive

The use of adhesive for bonding of different substrate offers various benefits over other affixing methods. Methods like soldering or welding causes permanent changes on surfaces by thermal stresses whereas no local stresses builds up in adhesive bonding as the strains disperse over the entire surface. Further, the weakening of bonding substrate does not happens as occurs with screwing, nailing and riveting methods. Adhesive adds very little weight to substrate as compared to other methods which is also very advantageous. For use in various application, the PU adhesives are prepared in plenty of grades such as one-component or two-component, solvent based, hot melted, etc. Polyurethane adhesives have numerous industrial applications due to their excellent adhesion on different kind of substrates like metals, wood, plastics, glass etc. The applications of polyurethane adhesive in various sectors are described below:

1.3.1. In Construction

Due to high strength and resistance offered by PU adhesives (one or two component), they are extensively used in wood flooring, heavy duty rubber flooring and bonding parquets. Other commercial applications in construction sector include the use of PUR adhesive for fibre board, wallboard, sub flooring, drywall, and plywood. The ability of PU adhesive to adhere wet/frozen timber, their high green strength and shear strength makes them appropriate for ceramic tiles, mirrors, bath surrounds, and concrete. PU adhesive can be customized in various grades for specific applications.

1.3.2. In Packaging

PU adhesive can be used in packaging application as they possess enough elasticity at food freezing conditions [14]. One component PU adhesives are typically used for adhesion in snacks food bags, printed films and shopping bags. In general, solvent free or moisture curable adhesives are suitable for this purpose. Moreover, customized two component PU adhesive are utilized of polyvinyl chloride to aluminum sheets for medical cases [15]. Pertaining to low viscosity and low application temperature, hot melt PU adhesives are found suitable for wrapping applications.

1.3.3. Transportation

Various advanced materials involved in transportation sector i.e. alloys, plastics, carbon fiber, glass, etc. may not properly work if joined with rigid fixing techniques.

Hence bonding with PU adhesive is advantageous as it offers reduction in vibrations, noise dampening, and movement capability. High performance PU adhesives are also used in adhering windscreens in different vehicles due to its watertight and fast installation [16]. PU adhesive are also employed in joining of interior materials that are usually made up of more than two materials such as in dashboards, door trims and headlining. One major application of hot melt PU adhesive is in bonding of vehicle's side walls pertaining to their ability to withstand temperature variation i.e. from -20^{0}C to 70^{0}C.

1.3.4. Marine

Appreciable elasticity with high strength and good resistance to sea water or sewage water which make semi-rigid PU adhesives (one/ two component) flawless for bonding substrates for marine sector [17]. Due to excellent chemical and mechanical resistance of PU adhesives, they are found to be ideal for various marine applications like bonding teak decks, adhering timber components, deck-to-hull bonding, bonding glass windows, bonding internal partitions, adherence of anti-slip plates for engine rooms, etc. PU adhesive with flame retardant properties are extensively used in building divisions panels for ships.

1.3.5. Electronics

PU adhesives are found to be ideal substitute for the other joining methods like welding, brazing, soldering, and thermos-compression bonding. Properties of PU adhesive such as curing at room temperature, durability, high resistance to thermal shocks and vibrations makes them ideal for the bonding of copper foil, electronic coils fabrication, surface fix conductive adhesion and bonding die stamped printed circuit boards. Generally, hot melt PU adhesives which possess good resistance to high temperature and viscoelasticity are used in sound dampener systems, audio speakers and electronic enclosures [18]. PU adhesive are utilized in these application as they exhibit necessary toughness and flexibility upto 130^0C and have ability to bond different kind of substrates.

1.3.6. Footwear

Shoe industry needs PU adhesive to bond waterproof insole materials and in sole attachment because it is highly resistant to water, its appreciable resistant towards heat, flexibility in cold fast setting and good initial strength. Moreover, it is utilized in bonding water resistant footwear as it does not break down even in damp conditions even after considerable flexing.

1.3.7. Tanks and Pipes

Rigid polyurethanes form strong adhesive bonds, which permit them to adhere effectively to a vast variety of building facings. The bonding is so great that the bond strength is generally greater than the shear or tensile strength of the rigid foams. The low thermal conductivity permit it to be utilized as thermal insulators for pipes and its high chemical resistance let it to be used in chemical tanks. These PUR are excellent insulate adhesives because of their efficient retention of heat, high level of compression and shear strength, processability, excellent adhesion, resistance to extreme temperatures, low water permeability, lightness and high chemical resistance.

1.4. Vegetable Oil Based Polyurethane Adhesives

Polyurethane (PU) production with the use of vegetable oils is greatly appreciated by researchers due to their low cost, easy availability, and nontoxic nature. PU is synthesized by reacting isocyanates with compounds containing active hydroxyl groups like polyols [19]. As PU adhesives made from petrochemicals are costly and non-biodegradable, the biomaterial-based PU adhesives have attracted much attention of researchers in the recent past [19-23]. Moreover, various environmental concerns like global warming, limited fossil resources and elimination of toxic intermediates during polymer synthesis are major problems that are need to be addressed for green synthesis of polymers. To produce biodegradable polymers at low cost, the use of easily available and low priced renewable resources are needed to be encouraged. Natural vegetable oils are expected to be a very useful source for the synthesis of biobased polymers and to provide a substitute or augment to traditionally used petrochemical based materials [24,25]. Polyurethane (PU) production with the use of vegetable oils is greatly appreciated by researchers due to their low cost, easy availability, and nontoxic nature.

In the recent years, different research groups had done fruitful efforts towards the synthesis of bio-polyol based polyurethanes, for example, Kiatsimkul et al. showed synthesized polyols with high hydroxyl equivalent weight from epoxidized soyabean oil [26]. Further, Zhang et al. developed polyols by reacting castor oil with epoxidized soyabean oil via ring opening mechanism [27]. The importance of chemical modification of natural oils and its application in Polyurethane (PU) synthesis has been extensively discussed [28]. The studies revealed that that the properties of polyurethanes largely depends on the nature of raw material used in its preparation, i.e., the type of polyol and diisocyanates used (their functionalities and chemical structure). Lu et al. examined the variations in physical and mechanical properties with hydroxyl functionalities in soy based polyols in PU films [29]. Ugarte, et al. [30] studied the effect of nature of diisocyanate on morphology of thermoplastic PU.

Peruzzo et al. in their research showed the variation in different properties of waterborne polyurethane acrylates with different diisocyanates [31].

Among various vegetable oil, Castor oil is unique as it contains ricinoleic acid which is the only mono-saturated fatty acid that bears a hydroxyl functional group and can be employed for the synthesis of PU [32,33]. Further, castor oil is an inedible oil due to presence of toxic protein i.e. ricine in it. Mechanical properties of castor oil–based adhesive shows a high dependency on the NCO/OH molar ratio due to higher or lower cross-linking achieved during a reaction [34]. Somani et al. studied the properties of PU adhesives from three different polyester polyols, obtained by reacting a castor oil derivative and diols (glycols) with diisocyanate adducts in different NCO/OH ratios [35]. They reported that the NCO/OH ratio 1.3 gave excellent lap shear strength. Silva et al. prepared solvent-less castor oil–based PU adhesives to evaluate the influence of the NCO/OH molar ratio and the chemical nature of the substrates (wood/wood and foam/foam) on the adhesive force [34]. They reported that resulted PU adhesive foam joints showed peeling strength values 75% and wood joints showed lap shear strength values 20% higher than that of a commercialized solvent-based adhesive. The physicochemical and mechanical properties of adhesives can also be altered by the incorporation of the fillers [36]. Fillers are reported to impart improved adhesion, improved resistance to ageing, and reduce cost. Commonly used fillers in PU are talc, calcium carbonate, silica, titanium oxide, carbon fiber, clay, etc. In the recent past, research has been focused on the development and incorporation of nanosized fillers, which can uniformly disperse in organic matrix [37]. In one recent study, the influence of nanosized TiO_2 filler on various properties of PU adhesive has been taken into account. The TiO_2 had been reported to improve surface adhesion, solar reflectance, and crack resistance in PU adhesives [38].

1.5. Basic Chemistry of Vegetable Oil Based Polyurethanes

1.5.1 Vegetable Oils

The rationality of picking vegetable oils as renewable stock is due to several advantages like presence of a lot of reactive sites that can be easily transformed by chemical modification to get monomers for PU synthesis with desired functionalities. Moreover, the characteristic inherent biodegradability of oils also makes it an attractive source in the present context of increasing environmental concerns.

1.5.2. Vegetable Oil Composition

Vegetable oils comprises of triglyceride esters of fatty acid chains as shown in Figure 1.03. The composition of fatty acid (in percent) of commonly used vegetable oils and average double bond content per triglyceride are summarized in Table 1.01.

Table 1.01: Composition of Fatty Acid of Commonly Used Vegetable Oils and Average Double Bond Content Per Triglyceride [28-33]

Vegetable oil	***Fatty acid composition (percent)***						
	Avg. double bond/ triglyceride	**Palmitic**	**Stearic**	**Oleic**	**Linoleic**	**Linolenic**	**Ricinoleic**
		C16:0	C18:0	C18:1	C18:2	C18:3	C18:1
Castor	3.04	1	1	3	4.2	-	89
Canola	3.9	4.1	1.2	60.1	21.0	8.8	-
Soybean	4.61	10.6	4	23.3	53.7	7.6	-
Linseed	6.24	5.4	3.5	19	24	47	-
Corn	4.45	10.9	2	25.4	59.6	1.2	-

1.5.3. Available Reactive Sites for Modification in Vegetable Oils

Two strategies are mainly used to obtain polyurethanes from vegetable oil. One of the strategy involves the chemical modifications or the use of triglycerides directly, taking the advantage of the functional groups that occurs naturally. On the other hand, the second strategy uses purified fatty acids to have more control over the chemical structure of monomers which have direct influence on properties of end product.

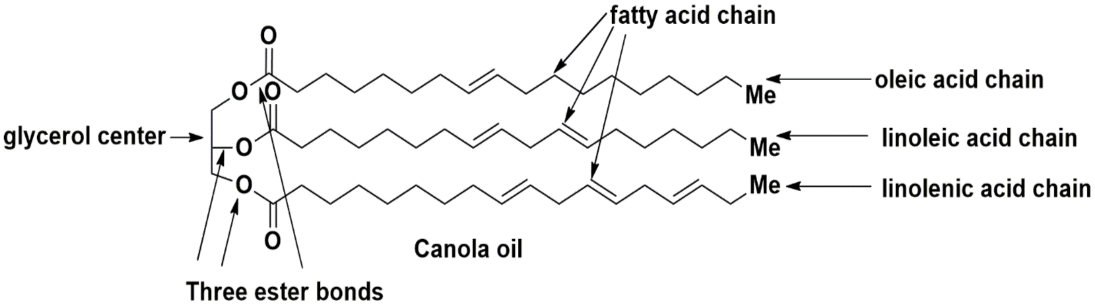

Figure 1.03. Reactive Sites Available for Modification in Vegetable oils [28].

The double bond between carbon atoms, the ester moieties, the carbons at alpha position to the ester group, the allylic carbons and sometimes the hydroxyl groups (e.g. castor oil) are the important reactive sites available for chemical modifications in triglycerides. This property of vegetable oils makes them an interesting renewable precursor for polymer synthesis.

1.5.4. Modification of Vegetable Oils to Obtain Polyol

Different strategies have been followed to insert hydroxyl group into trigycerides to form polyol among which the most common are epoxidation followed by ring opening [39,40], transesterification/ amidation [41], hydroformylation or reduction [42,43], thiol-ene addition [44], ozonolysis[45,46], etc. Various methodologies that have been followed for the modification of vegetable oils to obtain polyols are as summarized in Figure 1.04:

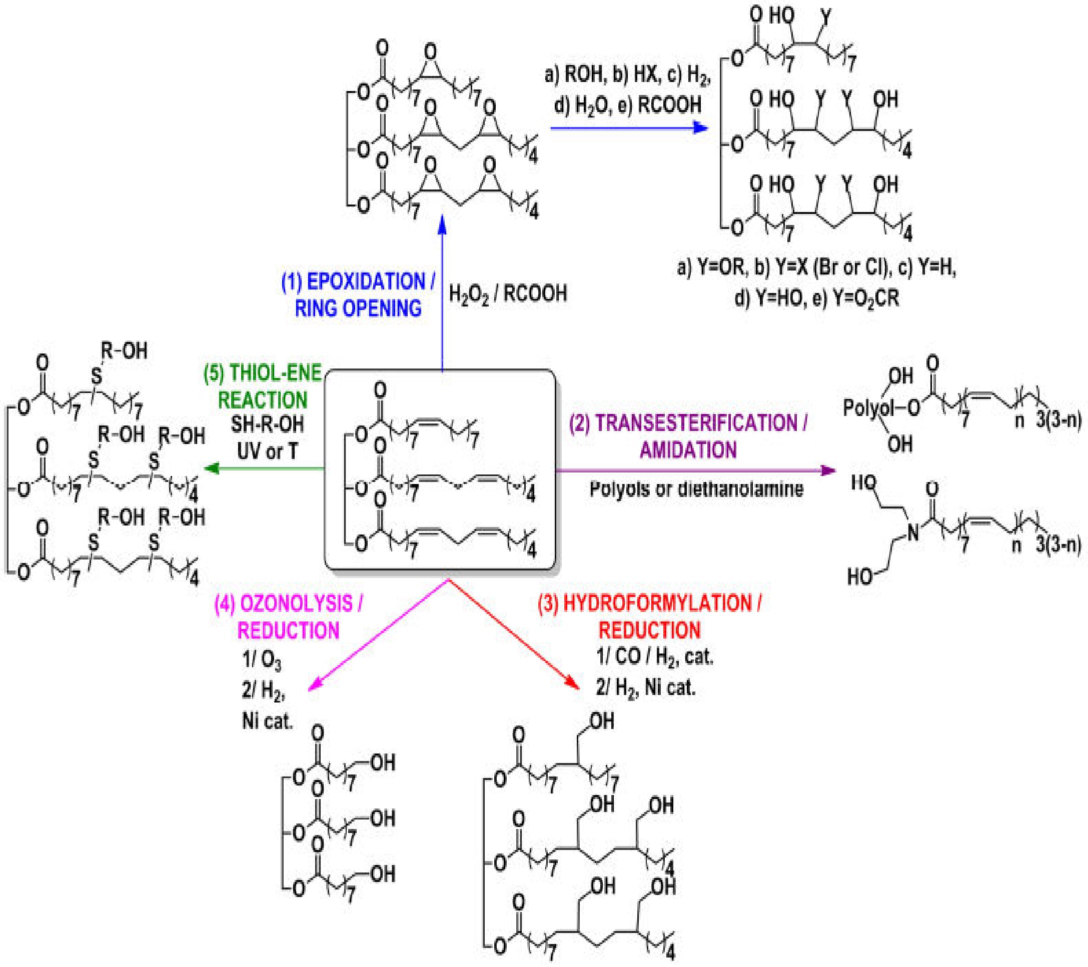

Figure 1.04: Various Methodologies for Modification of Vegetable Oils [39-46].

1.5.5. Reactions with Isocyanates

Due to great extent of area of applications and versatility in properties PU have become one of the most utilized polymer. The basic synthesis reaction of polyurethanes involves a polyol component and a polyisocyanate. By enhancing the functionality of the polyols and isocyanates, branching or cross-linking can be increased in an organized way leading to the materials with improved mechanical properties [1, 20]. After the discovery of polyurethanes by Bayer in 1937, the production of diisocyanates has been tremendously increased as properties of the product can be easily altered by simply varying the isocyanate precursors, e.g., Toulenediisocyanate (TDI) introduce flexibility in the product whereas product made from Methylenediphenyldiisocyanate (MDI) are found to be relatively rigid. Basically, the nature of polyol used and the kind of diisocyanate moiety have maximum contribution in determining the properties of PU formulation. So, products with wide range of mechanical strength (or properties) according to the need of end product can be achieved in PU's mainly by varying the polyols and isocyanate moiety. The high reactivity of diisocyanates even at low temperature conditions and for highly viscous solution makes them much better in tailoring the end product properties by just varying the nature of diisocyanate moiety. So, it is important to study the properties of polyurethanes obtained from different type of isocyanate precursors.

One can obtain linear or crosslinked type of polymers by focusing on the functionality of reactants. As shown in Figure 1.05, urethane linkage is evolved from the reaction of isocyanate with di- or polyfunctional hydroxyl compounds. This reaction can take place even without using catalysts and at ambient temperature condition. Reactivity is higher for primary alcohols, decreasing for secondary, tertiary, and aromatic alcohols. Along with this reaction, isocyanates can show various other kind of reaction like isocyanate lead to formation of amines with liberation of carbon dioxide on reacting with water. Isocyanates possess very high affinity to water, which makes their storage quite challenging. The reaction of isocyanate with water has major role in the process of curing for 1 component PU adhesives. Mostly these one-component PU adhesives are based on isocyanate terminated prepolymer. Generally, the air moisture is sufficient for adhesive curing, whereas other cases sometime requires a light spray of water droplets after its application on bonding substrate to enhance curing, followed by closing of bond. At initial stage, the rate of reaction of water with isocyanate is not high. But it can be increased by catalyzing the reaction with suitable catalysts such as

DBTDL, morpholine tertiary amine, etc. Isocyanate reacts with water forming carbamic acid, an unstable compound which spontaneously decomposes into a primary amine and carbon dioxide. Further amines an also react with isocyanates to yield a urea linkage and polyurea-polyurethane adhesive can be synthesized by making use of this reaction. Primary aliphatic amines react most rapidly followed by secondary aliphatic amines and aromatic amines. Interestingly, excess of isocyanates in the reaction may lead to formation of allophanates by reacting with urethane groups itself. These reactions will occur more readily at higher temperatures and it has been observed that the products, biurets and allophanates, are in equilibrium with the starting materials, active hydrogen compounds and isocyanates. Although the active hydrogen present in the urethane moieties are not highly reactive, however if temperature of reaction exceeds 100°C, or if reaction takes place in the existence of particular catalysts such as allophanate, the reaction can easily predominates over the polyurethane reaction [47]. The allophanate reaction can result into high viscosity, branching and lastly can cause gelation if continued further. Usually, the reaction of allophanate is an unwanted side reaction which can lead to serious processing issues, like shorter shelf lives of certain PU adhesives, higher viscosities of PU prepolymers or decreasing pot lives of curing hot-melt PU adhesives. Moreover, isocyantes can react with other isocyanate molecules to yield isocyanurates. Generally, the isocyanurate reaction happens when a six-membered ring is developed by reacting three equivalents of isocyanates. On proper utilization, the reaction of isocyanurate might become very advantageous in synthesizing two-component structural PU adhesives, as the crosslink density and modulus can be increased by isocyanurate linkages. Isocyanates can also yield amide groups and CO_2 on reacting with carboxylic acids. In reasearches, designing of new polyols has been focused to tune the PU properties and using the commercially available isocyanates because the preparation of isocyanates is more complicated as compared to polyols.

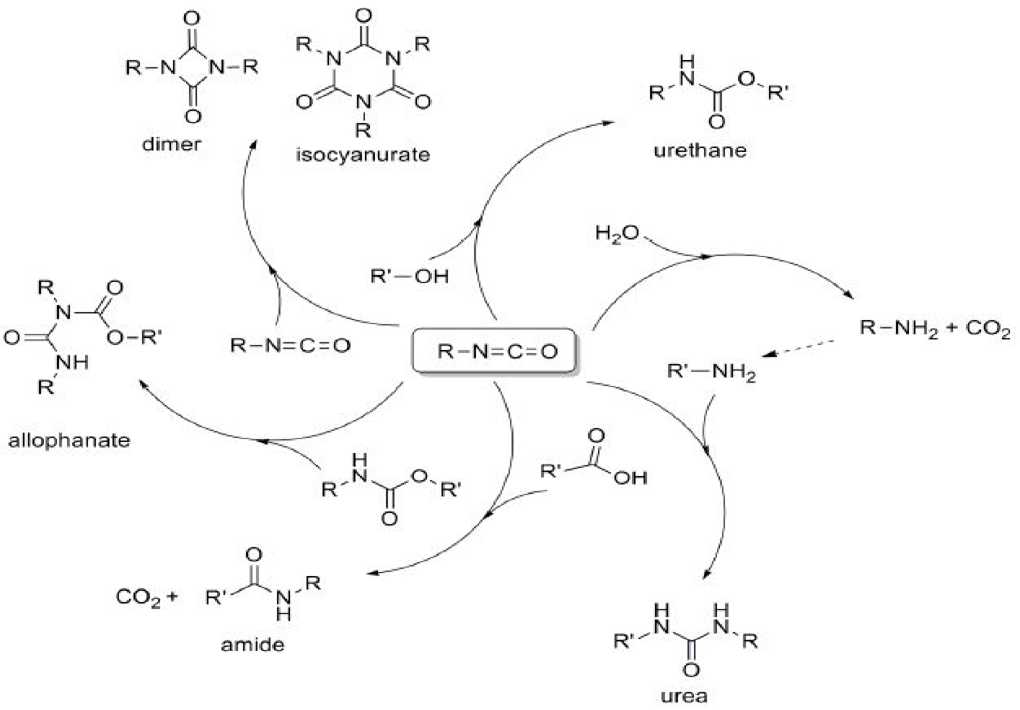

Figure 1.05: Reaction of Isocyanates with Different Molecules [47].

1.6. Synthesis of Non-Isocyanate Polyurethanes

1.6.1. Cyclic Carbonation of Epoxidized Vegetable Oils

To address the issues of limited fossil resources and for the elimination of toxic intermediates and byproducts in polyurethane (PU) synthesis, the latest research is more focused on the use of renewable sources. The prime motivation of the researchers is the modification of bio-based polyurethane systems for the development of performance based end product and to make them more environment friendly [48-50].

The use of toxic isocyanates, a raw material in PU synthesis, produced from phosgene, is still a major issue to be controlled. For the green synthesis of PU, isocyante free routes are good alternatives. The researches mainly involves carbonation of epoxidized soybean oil [52-58] while epoxidized linseed oil is also reported in some works [51,59]. Li et al. [60] had studied the synthesis of soybean oil based non-isocyanate PU using composite of $SnCl_4.5H_2O$ and tetrabutylammonium bromide to catalyze the reaction between epoxidized soybean oil and carbon dioxide. Inoue et al. [61] discovered the use of CO_2 in polymer synthesis back in 1969 to produce an alternating copolymer. After that, the CO_2 is being extensively explored in processing and manufacture of biomaterial based polymers due its abundance, easy availability and most importantly, due to its low toxic nature [62,63]. Inspite of being a renewable source of carbon, the utilization of CO_2 in synthesis is limited due to its quite less reactivity. Therefore, the carbon dioxide fixation in synthesis routes is a prime and demanding task, as it has many important advantages in atom efficient coupling reactions producing no byproduct. Moreover, it can be used as an efficient alternative for various conventional synthetic routes of polymers specially PU production [64-68]. High functionality poses one of the important reason behind the extensive use of these oils i.e. these contain atleast four epoxy moieties per triglyceride, which is highly desirable to get NIPU with high crosslinking density.

All the available literature related to preparation of cyclic carbonation of vegetable oils are categorized in 3 groups on the basis of technology associated with processing methods. The foremost group covers the synthesis conducted in atmospheric CO_2 pressure conditions while the second group include the synthesis conducted at condition of CO_2 pressure. The synthetic procedures involving supercritical CO_2 (ScCD) environment are covered in third group. In this classification the most widely used tetrabutylammonium bromide (TBAB) based catalyst system in synthesis of cyclic carbonates are also considered. Additionally, applications of two component catalytic systems are also been reported, e.g. combinations of tetrabutylammonium bromide with tintetrachloride and tetrabutylammonium bromide in combination with water. e.g.: {TBAB + $SnCl_4$} [56] and {TBAB + H_2O} [55]. The summarized processing conditions on cyclic carbonation of epoxidized vegetable oils are shown in Table 1.02.

Table 1.02: The Summarized Processing Conditions for Cyclic Carbonation of Epoxidized Vegetable Oils.

Type of Epoxidized Oil	Catalyst used	Pressure conditions	Reference
Epoxidised Soybean Oil	Tetrabutyl ammonium bromide	Atmosphere pressure	52
Epoxidised Soybean Oil	Tetrabutyl ammonium bromide	Atmosphere pressure Increased pressure	53
Epoxidised Soybean Oil	Potassium iodide + 18-crown-6 ether	Increased pressure	54
Epoxidised Linseed oil	Tetrabutyl ammonium bromide, SiO_2-I	Atmosphere pressure	59
Epoxidised Linseed oil	Tetrabutyl ammonium bromide	Atmosphere pressure	51
Epoxidised Soybean Oil	Tetrabutyl ammonium bromide + water	Atmosphere pressure	55
Epoxidised Soybean Oil	Tetrabutyl ammonium bromide + Tin tetrachloride	Increased pressure	56
Epoxidised Soybean Oil	Tetrabutyl ammonium bromide	Super critical Carbondioxide environment	57
Epoxidised Soybean Oil , Vernonia oil	Tetrabutyl ammonium bromide	Super critical Carbondioxide environment	58
Epoxidised cottonseed oil	Tetrabutyl ammonium bromide	Increased pressure	69

1.6.1.1. Processing at Atmospheric Pressure Condition

The first synthesis approach for cyclic carbonation of vegetable oils took place at atmospheric pressure in 2004 [52]. After that numerous researchers had also attempted to perform carbonation of epoxidized vegetable oils at pressure of 1 atmosphere and found that very long time period i.e. reported in days, is required for conversion of epoxy groups present in vegetable oil [52-55,59]. Tamami reported the complete conversion of epoxy groups in 70 h and obtained 94% yield of carbonated soybean oil with a viscosity of 13,200 cps at 25°C [52]. Javni performed the carbonation of epoxidised soybean oil at the reaction conditions which were already reported by Tamami and obtained much lesser epoxy group conversion when calculated by titrimetric method [53]. This difference in results obtained was because of using different techniques for calculating epoxy group conversion as the data reported by Tamami was based on IR spectroscopic technique. The physico-mechanical testing of obtained non-isocyanate polyurethane (NIPU) indirectly supports the lesser conversion of epoxy group to carbonate moieties [53]. The conclusion drawn from this comparison suggested that more accurate results can be obtained by the chemical method. The spectroscopic techniques can be utilized for qualitative analysis and to keep a check on the occurrence of side reaction, if any, during the conversion. Optimum data for synthesis temperature was not found anywhere in literature as the synthesis has been carried out between 110^{o}C and 150^{o}C and a single valued optimum temperature was not reported. Doll reported that as reaction temperature rises beyond 150^{o}C, the most commonly used catalyst i.e. TBAB begins to decompose [57]. In some other work, the carbonation process at 140^{0}C and atmospheric pressure condition shows 85% conversion of epoxy group in 89 hours [59]. Mazo and his group in their research added water in the reaction mixture in ratio of 1:3 with respect to the epoxy group present. The results of the study revealed that the speed of carbonation reaction was increased upto 30% by addition of water in the mentioned ratio [55]. The advantage of process involved in the cyclic carbonation of vegetable oil is that it does not require the use of any special equipment. On the other hand, the disadvantage of the process is its long reaction time which makes it economically less attractive from industrial point of view. The conclusion is that though, the carbonated oil with functionality over two can be achieved for the preparation of linear polymers by this process, but the complete conversion of epoxy groups in oil is quite difficult at atmospheric pressure of CO_2. The summary of variables involved in processing at atmospheric pressure conditions like temperature, concentration of catalyst and the obtained results are represented in Table 1.03.

Table 1.03: The Summary of Variables Involved in Processing at Atmospheric Pressure Conditions.

Oxirane content of oil (wt. %)	**Catalyst Concentration (mol.%,)**	**Temperature, Degree celsius**	**Obtained Results**			**Reference**
			Time (hours)	**Epoxy Group conversion, %**	**Characteristic of product**	
ELSO (8.5~10)	TBAB (5)	110	72	n/a	Viscosity– 13.2 Pa.s at 25 °C Mw – 2600	51
ESBO (6.8)	TBAB (5)	110	72	94	Viscosity – 13.2 Pa.s at 25 °C	52
ESBO (6.8)	TBAB (2.5)	110	50	63	Viscosity – 13.2 Pa.s at 25 °C	53
			89	78	n/a	
		140	100	62		

ESBO (6.2)	TBAB (5)	120	29	50	n/a	55
	TBAB (5)+H_2O [EG]:[H_2O] = 3:1		70	80	n/a	
			20	50		
			47	80		
			70	90		
ESBO (8.9)	TBAB (2)	140	96	91	90 % selectivity	59
	SiO_2-I [EG]:[I] = 1:0.03		170	53	n/a	

1.6.1.2. Processing at Increased Pressure

Numerous researchers favored the synthesis to be carried out at high pressure in order to reduce the reaction time effectively [53,56,59,69]. Javni submitted the first data on the effect of increased pressure on carbonation of epoxidized vegetable oil. In this study it was claimed that the reaction carried out at 5.65 MPa pressure and 140°C temperature resulted in complete carbonation of epoxy groups in just one day. However in some other studies, it was reported that a rise in pressure more than 1.5 MPa does not have a positive effect on result [56]. Although researchers does not reported a single valued optimum pressure for cyclic carbonation of vegetable oils, however, the results of the various studies revealed that more than 90% conversion can be attained in 12 to 24 hours at increased pressure conditions [53,56,59,69].

During the process of carbonation at any pressure i.e. atmospheric or increased pressure it was a general observation that the rate of conversion was high at the initial stage, which, continuously decreases with progress in epoxy group conversion. For example, as reported by Li in his work, the conversion of epoxy groups upto 86% was achieved in first 10 hours while it took 30 hours for conversion of next 10-12% [56]. These data are particularly important if the obtained cyclic carbonated vegetable oil is considered as raw material for preparation of non-isocyanate polyurethane.

Interestingly, it was found that conversion of just 75 to 85% of epoxy group into carbonate groups is required to achieve the optimum characteristics of soybean oil based non isocyanate polyurethane beyond which the negative effect on the properties was observed due to steric hinderance [56]. The summary of variables involved in processing at increased pressure conditions like temperature, concentration of catalyst and the obtained results are represented in Table 1.04.

Table 1.04: The Summary of Variables Involved in Processing at Increased Pressure Conditions.

Oxirane content of oil (wt. %)	**Catalyst Concentration (mol.%,)**	**Synthesis conditions**		**Obtained Results**			**Reference**
		T ^{0}C	**Pressure Mpa**	**Time (hours)**	**Epoxy Group conversion, %**	**Characteristic of product**	
ESBO (6.8)	TBAB (5)	140	1.03	23	96	Viscosity– 32.0 Pa.s at 25 ^{o}C	53
		160			90	n/a	
		180			40		
		160	0.69	23	91.8		
		180			44.1		
		140	5.65	22	97.8	Viscosity– 33.0 Pa.s at 25 ^{o}C	
ESBO (6.4)	Potassium iodide + 18-crown-6 ether (0.3 mass / 0.2 mass)	130	6.0	12	20.5	Viscosity – 0.87 Pa.s at 20 ^{o}C	54
				48	68.7	Viscosity– 12.4 Pa.s at 20 ^{o}C	
				120	98.3	Viscosity– 30.0 Pa.s at 20 ^{o}C	

ESBO (6.8)	$SnCl_4.5H_2O$ (3)	120	1.0	20	64.4	n/a	56
	TBAB (3)				71.3		
	[TBAB]:[$SnCl_4$] = 1:3 (3)				89.2		
	[TBAB]:[$SnCl_4$] = 1:3 (3)	140	1.5	10	86.9	Viscosity– 11.3 Pa.s at 25 °C	
				20	95.5	Viscosity– 16.4 Pa.s at 25 °C	
				30	98.5	Viscos.– 19.3 Pa.s (25 °C)	
ECSO	TBAB (3.75)	140	3.0	24	99.9	n/a	69
ELSO (8.9)	TBAB (2)	140	1.0	20	Complete	CCG content 26.7 wt. %	59
			3.0	<10	Complete		
	SiO_2-I [EG]:[I] = 1:0.03		3.0	45	Complete		
	SiO_2-I [EG]:[I] = 1:0.03				53	n/a	

1.6.1.3. Carbonation in Supercritical Carbondioxide Environment

Supercritical carbon dioxide environment represent a condition of CO_2 at which no difference lies between its gaseous and liquid phase. This transition of carbon dioxide between different phases i.e. gaseous and liquid phase takes place at a temperature of above 31.1°C and at pressure of more than 7.38 MPa [58]. The advantage of supercritical carbon dioxide is that it is non-toxic and various associated parameters like polarity, density, solubility can be altered by varying the pressure and temperature to get the optimum properties required for particular reaction [58]. The data of carbonation of epoxidised vegetable oil in supercritical carbon dioxide environment using different type of oils is summarized in Table 1.05 [57,58]. A substantial fall in reaction time is observed for obtaining equal amount of epoxy group conversion as compared to the process carried out at atmospheric pressure. It was also observed that better results can be obtained by rising the reaction temperature from 100°C to 140°C [53,56,59,69]. Moreover, it was also observed that this process do not give much time advantage over carbonation carried out at increased pressure and it may complicate the processing along with increase in technology price.

Table 1.05: The Summarized Data of Carbonation Processes of Epoxidized Vegetable Oil in Supercritical Carbondioxide Environment.

Oil (Oxirane Content)	**Catalyst (Concentration mol. %)**	**Synthesis conditions**		**Obtained Results**			**Reference**
		T ^{0}C	Pressure Mpa	Time (hrs)	Epoxy Group conversion, %	Properties of obtained product	
Epoxidised soybean oil (7.0)	Tetrabutyl ammonium bromide (5)	100	10.3	10	82	Viscosity– 70 Pa.s at 25 ^{o}C	57
				20	94	Viscosity– 145 Pa.s at 25 ^{o}C	
				40	100	Viscosity– 170 Pa.s at 25 ^{o}C	
Epoxidised soybean oil (6.9)	Tetrabutyl ammonium bromide (7)	100	13.8	46	90.1	Viscosity– 7.0 Pa.s at 25 ^{o}C Degree of carbonation > 72%	58
Vernonia oil (4.1)					87.5	Viscos.– 0.99 Pa.s (25 ^{o}C) Degree of carbonation 72%	

1.6.1.4. Important Factors Influencing the Carbonation of Epoxidized Vegetable Oils

A very important factor that certainly affect the carbonation process is the way of mixing of components. An illustration of this is available in literature data reported by Javni [53] and Tamami [52] in which Javni reported the 20 hours faster conversion of epoxy group as compared to data reported by Tamami under identical conditions of temperature and pressure. The explanation for this difference in reaction time can be explained by the fact that in Tamami's work simple magnetic stirrer was employed which leads to ineffective mixing of 200 grams of epoxidized soybean oil. Mazo *et* al. [55] claimed that increase in rotation speed upto 400 rpm can accelerate the carbonation reaction and further increase in agitation intensity will not affect the rate of reaction. As researchers have no consensus regarding the optimum concentration of catalyst. The range of concentration from 2 mol % to 7 mol % w.r.t. epoxy group is reported [58,59]. Moreover, the rate of reaction increases with the rise in catalyst concentration [55]. However the reported concentration of catalyst (TBAB) required to obtain high conversion of epoxy groups is 2.5 mol% [53]. Table 1.06 summarizes the characteristics of non-isocyanate polyurethanes synthesized by reacting cyclic carbonates with different type of amines in 1:1. Due to higher functionality offered by linseed oil in terms of content of cyclic carbonate group present, it produces non-isocyanate PU with better strength properties as shown in Table 1.06. It is reported that the complete conversion of epoxy groups in vegetable oil are not required to attain optimal properties in non-isocyanate PU and sometimes it may affect the properties of end product adversely because of the steric factor involved. It can be well understood from data presented in Table 1.06 that among various diamines, ethylene diamine is the best hardener in synthesis of non-isocyanate PU.

Table 1.06: **Properties of Non-Isocyanate PU Obtained from Carbonation of Epoxidized Vegetable Oils.**

Oil	Hardener	NIPU Properties				Reference
		Curing conditions	**Tg, (°C)**	**Elongation at break, (%)**	**Tensile strength, (MPa)**	
ESBO	EDA	10 hours at 70 °C and 3 hours at 100 °C	34	140	0.82	52
	HMDA		18	170	0.33	
	Tris(2-aminoethyl) amine		43	70	1.50	
ESBO	EDA	10 hours at 70 °C and 3 hours at 100 °C	38	90	5.77	53
	HMDA		35.3	190	3.80	
	BDA		40	130	4.71	
ESBO	EDA	10 hours at 70 °C and 3 hours at 100 °C. For IPDA – additionally 12 hours at 70 °C	20	240 ± 30	6 ± 1	59
	BDA		17	310 ± 10	2 ± 0	
	IPDA		40	200 ± 30	5 ± 0	
ELSO	EDA		55	57 ± 20	18 ± 2	
	BDA		45	84 ± 30	17 ± 2	
	IPDA		60	1 ± 0	10 ± 3	
Epoxidised soybean oil Oxirane content(%):	EDA	20-30 hours at 90-100 °C	n/a			56
55.4				232	2.63	
74.3				173	7.0	
85.1				163	6.9	
90.9				207	4.56	

1.6.2. Catalytic Systems for Carbonation of Vegetable Oils

Different catalytic systems have been proposed in past for the synthesis of cyclic carbonates by reacting gaseous CO_2 and epoxides. These catalyst includes metal salts or onium salts, metal halides, metal oxides, organo catalysts, ionic liquids, metal porphyrins [70-75], rhenium, aluminum quinolate, polyoxometalates, heterobimetallic complexes, organometallic compounds, complexes of lanthanoid metals [76-78], main group and transition-metal complexes [79-84]. Jiang et al. [79] have reported the use of $Re(CO)_5Br$ catalyst for preparation of propylene carbonate under 5.5 MPa of CO_2 at 110^oC for a 24 h reaction which give 97% yield; Mann et al. successfully synthesized carbonated veronica oil by using supercritical CO_2 and virgin oil as reactants [85]; Xie et al. [80] proposed the use of ionic liquid/$ZnBr_2$ system to catalyze the reaction under high pressure (3MPa) of carbon dioxide at 140^oC which shows very high initial rate during first hour of reaction; Srivastva and co-authors [82] have used Cu(II)porphyrin/DMAP system to catalyze coupling reaction under the condition of 6.9 MPa CO_2 pressure at 120^0C to give a yield of 78 % in 4 h. It has been observed that catalytic systems have poor solubility in the reactants (epoxidized vegetable oils) such as: NaI, LiBr, KI, benzyltrimethylammonium bromide, ion exchange resins [52] and hence show very little influence on rate of reaction [57]. This limitation was astounded by the activation of potassium iodide by 18-krown-6 ether that led to its successful application for synthesis of cyclic carbonated vegetable oils [54]. Quite interestingly, the silica-supported 4-pyrrolidinopyridinium iodide on SiO_2 (SiO_2-I) [59] which was found successful in carbonation reaction of styrole and propylene oxides [86], whereas it was not so efficient for cyclic carbonation of vegetable oils. In recent past, researches are being focused on enhancing the reactivity of reactants by using homogenous catalysts, generally metal containing porphyrins due to their great efficiency in the conversion of oxirane ring into cyclic carbonates by reacting with gaseous CO_2. Sugimoto et al. [87] reported the use of {(5,10,15,20-tetraphenylporphyrinato)manganese acetate, which catalyse the carbonation reaction of cyclohexene oxide at low CO_2 pressure conditions (under 0.1 MPa) and gives 95% carbonate linkages in 90 h. Metalloporphyrins are efficient because the porphyrin skeleton is quite appropriate for establishing a very functionalized coordination locus, that may give a chance to increase the efficiency of catalyst to a greater extent. These structural features of metalloporphyrins permits the effective conversion of a cheaper, non-toxic, and renewable feedstock such as carbon dioxide into highly competent products [87]. This conversion could be useful in restricting phosgene's use as reagent, as being cent percent atom economical reaction, it is found to be highly desirable conversion [84]. However, in most of cases, some limitation are still not dealt efficiently, as, the long reaction time, high temperature and high CO_2 pressure during the reaction.

1.7. Motivation for this Research

Most PU adhesives are synthesized from petroleum base stocks. The latest advances in PU research have focused on the replacement of petrochemical based polyols with vegetable oil based raw materials. This interest is economically driven because vegetable oils are relatively inexpensive and a renewable resource [23,88,89]. Also, there are significant environmental problems associated with the use of various adhesives that contain urea formaldehyde and/or phenol formaldehyde. To overcome such problems, attempts should be made to develop new polymeric adhesives from renewable resources. The rationality in choosing triglyceride based oil is their easy availability, low cost and high scope of modifications to get desirable results in biopolymer synthesis. Like many other polymers, the present research on the development of vegetable oil based polyurethane adhesives is motivated by the utilization of biobased resources due to major concerns like depletion of crude oil stock in world, its inflated price and to address the environmental concerns [24,25,90]. As the use of toxic isocyanates, a raw material in PU synthesis, produced from phosgene, is still a major issue to be controlled. For the green synthesis of PU, non-isocyante route is choosen to produce isocyanate free PU.

1.8. Objective of the Research Work

During this PhD programme, the main aim of my research is the "**Development of Vegetable Oil based Polyurethane Adhesive**" For more sustainable development of polyurethanes, focus has been on various aspects like synthesis of renewable vegetable oil based polyurethane precursors and development of efficient route for synthesis of PU by using non isocyanate / non phosgene routes. Using renewable feedstocks for PU production is first necessary step for sustainable development. Broadly, this research aims to achieve the following specific objectives as:

a) Synthesis of vegetable oil based polyurethane adhesive.
b) Study of the physico-mechanical properties of the resulted adhesives.
c) Study of the various factors associated with adhesive formulations like curing time, green strength, pot life, viscosity, type of failure, etc.
d) Incorporation of suitable additives to the resulted adhesive formulations with aim to enhance their physico-mechanical properties, improve the resistance against effect of environmental conditions and to reduce the cost.
e) Comparison of prepared adhesive with commercial adhesive, considering cost effectiveness and performance under different environment conditions as major parameters.

1.9. Organization of Thesis

The objective of this thesis is the development of vegetable oil based polyurethane adhesive by developing new synthesis routes. The whole thesis is organized in SIX chapters. The **Chapter 1** of the thesis provides a panoramic overview of bio based PU adhesive as well as non isocyanate polyurethanes. This chapter also contains a comprehensive review on vegetable oil based polyurethane adhesive and a complete description of vegetable oil based non isocyanate polyurethanes. This literature review exposes different synthetic routes along with the properties of end product. Latest trend in the field has also been covered in this chapter. Motivation for this research and its objectives are clearly highlighted. **Chapter 2** elaborates the experimental part which includes the physiochemical studies of raw material used in the synthesis of polyurethane adhesives and non-isocyanate PU. The chapter also includes the methodologies employed at different steps in experimental work such as substrate preparation, bonding of substrate along with overview of various factors associated with adhesive formulation like green strength, lap shear strength, gel time, etc. Characterization techniques that were used for the determination of the structure and properties of reactants, intermediates and products for e.g. Infrared spectroscopy, nuclear magnetic resonance spectroscopy, electron microscopy, TGA, etc. are also briefly discussed. **Chapter 3** elaborates the synthesis of polyurethane adhesives from castor oil based polyester polyols. This chapter also includes the study of various factor associated with adhesive formulation like NCO/OH ratio, hydroxyl value, effect of fillers, etc. The **Chapter 4** elaborates the influence of aliphatic and aromatic isocyanates on the properties of polyether-ester polyol based PU adhesive system. As synthesizing vegetable oil based polyols is covering only one part for sustainable PU synthesis, the toxicity of diisocyanates is another major drawback due to various hazardous health effects associated its use. The **Chapter 5** covers the development of synthesis routes for vegetable oil based non isocyanate polyurethane. The catalyst activity of 5,10,15-Tris-(pentafluorophenyl)corrolato-Manganese (III) complex and effect of structure of various diamines on properties of NIPUs are extensively studied in this part of thesis. Lastly, Conclusion and future prospect of the study are included in the **Chapter 6,** which is followed by the references.

CHAPTER 2

MATERIALS AND METHODS

2.1. Raw Materials/ Chemicals

In the present study, following raw materials/chemicals are employed:

1) Castor oil
2) Canola oil
3) Glycerol (for the transesterification of oils)
4) 4,4'-methylene diphenyl diisocyanate (MDI)
5) Toulene-2,4-diisocyanate (TDI)
6) Isophorone diisocyanate (IPDI)
7) 1,6- hexamethylene diisocyanate (HMDI)
8) Magnesium sulphate anhydrous
9) Sodium chloride
10) Carbon dioxide gas
11) Ethylene diamine (EDA)
12) Hexamethylene diamine (HMDA)
13) Isophorone diamine (IPDA)
14) Para phenylenediamine (PPDA)
15) Manganese acetate tetrahydrate
16) Dimethylformamide (DMF)
17) Dibutyltin dilaurate (DBTDL)
18) Hydrogen peroxide (Oxidising agent)
19) n-Hexane
20) Ethyl acetate

21) Titanium dioxide

22) Methyl ethyl ketone (MEK) (solvent)

23) Calcium carbonate

24) Fevicol^{TM} (Commercial adhesive)

2.1.1. Specification and Sources of Raw Materials/Chemicals

Specification and sources of raw materials/chemicals used in the studies are given in Table 2.01.

Table 2.01: Specifications and Sources of Raw Materials/Chemicals

Sr. No.	Chemicals	Source	Specification
1	Castor oil	Krishna enterprise, Tilak Nagar, Delhi, India	Analytical Reagent Grade
2	Canola oil	Krishna enterprise, Tilak Nagar, Delhi, India	Analytical Reagent Grade
3	Glycerol	Standard Chemicals (ISO 9001:2008 certified), Delhi	Analytical Reagent Grade
4	4,4’-methylene diphenyl diisocyanate (MDI)	Shivathene Linopack Ltd. (Parwanoo, India)	Analytical Reagent Grade
5	Toulene-2,4-diisocyanate (TDI)	Shivathene Linopack Ltd. (Parwanoo, India)	Analytical Reagent Grade
6	Isophorone diisocyanate (IPDI)	Shivathene Linopack Ltd. (Parwanoo, India)	Analytical Reagent Grade
7	1,6- hexamethylene diisocyanate (HMDI)	Shivathene Linopack Ltd. (Parwanoo, India)	Analytical Reagent Grade
8	Magnesium sulphate	Fisher scientific	L R Grade
9	Sodium chloride	Fisher scientific	Analytical Reagent Grade

10	Carbon dioxide gas	Capital gas (ISO 9001:2008 certified) Delhi	Commercial Grade
11	Ethylene diamine (EDA)	Sigma-Aldrich	Analytical Reagent Grade
12	Hexamethylene diamine (HMDA)	Sigma-Aldrich	Analytical Reagent Grade
13	Isophorone diamine (IPDA)	Sigma-Aldrich	Analytical Reagent Grade
14	Para phenylenediamine (PPDA)	Sigma-Aldrich	Analytical Reagent Grade
15	Manganese acetate tetrahydrate	Sisco Industries Pvt. Ltd.	Analytical Reagent Grade
16	Dimethylformamide (DMF)	Standard Chemicals (ISO 9001:2008 certified), Delhi	Analytical Reagent Grade
17	Dibutyltin dilaurate (DBTDL)	HMEDA, India	Analytical Reagent Grade
18	Hydrogen peroxide (Oxidising agent)	Fisher scientific, Delhi	Commercial Grade
19	n-Hexane	Standard Chemicals (ISO 9001:2008 certified), Delhi	Laboratory Reagent Grade
20	Ethyl acetate	Fisher scientific, Delhi	Analytical Reagent Grade
21	Titanium dioxide	Central Drug House (P) Ltd., Delhi	Analytical Reagent Grade
22	Methyl ethyl ketone (MEK)	Central Drug House (P) Ltd., Delhi	Analytical Reagent Grade
23	Calcium carbonate	Central Drug House (P) Ltd., Delhi	Analytical Reagent Grade
24	Fevicol^{TM} adhesive	Local Market	Commercial grade

2.1.2. Purification of Raw materials/Chemicals

The consistency and accuracy in the results highly depends on the quality and purity of reactants employed. The percentage purity of the chemicals used during experimental work is given in Table 2.02. All the chemicals were used as received without doing any further treatment, except the canola oil and the castor oil, that were preheated at 100^0C for 24 h in vacuum oven to get rid of moisture content present, if any.

Table 2.02: Percentage Purity of the Chemicals

Sr. No.	Chemicals	Percentage Purity
1	Castor oil	99 %
2	Canola oil	Approx. 99%
3	Glycerol	> 99.5%
4	4,4’-methylene diphenyl diisocyanate (MDI)	99 %
5	Toulene-2,4-diisocyanate (TDI)	99 %
6	Isophorone diisocyanate (IPDI)	99 %
7	1,6- hexamethylene diisocyanate (HMDI)	99.9 %
8	Magnesium sulphate	99.9 %
9	Sodium chloride	>99 %
10	Carbon dioxide gas	> 99.5 %
11	Ethylene diamine (EDA)	99.9 %
12	Hexamethylene diamine (HMDA)	99.9 %
13	Isophorone diamine (IPDA)	99.9 %
14	Para phenylenediamine (PPDA)	99.9 %
15	Manganese acetate tetrahydrate	99.9 %
16	Dimethylformamide (DMF)	>99.5%
17	Dibutyltin dilaurate (DBTDL)	99.9%
18	Hydrogen peroxide	>99.5%
19	n-Hexane	>99.9%

20	Ethyl acetate	99.9%
21	Titanium dioxide	99.9%
22	Methyl ethyl ketone (MEK) (solvent)	99.9%
23	Calcium carbonate	99.9%
24	Fevicol^{TM} adhesive	n/a

2.2. Methodology

The systematic methodology highlighting how the progress of proposed work towards achieving desired objectives, involves the following steps:

- Physicochemical studies of raw materials
- Chemical modification of Vegetable oil.
- Synthesis of vegetable oil based polyurethane adhesive.
- Study of the physico-mechanical properties of the resulted adhesives.
- Study of the various factors associated with adhesive formulations like curing time, green strength, pot life, viscosity, type of failure, etc.
- Incorporation of suitable additives to the resulted adhesive formulations with aim to enhance their physico-mechanical properties, improve the resistance against effect of environmental conditions and to reduce the cost.
- Comparison of prepared adhesive with commercial adhesive, considering cost effectiveness and performance under different environment conditions as major parameters.

2.2.1. Physicochemical Studies of Raw Materials

The properties of raw material greatly affects the properties of the final product. Thus, the study of physiochemical properties of raw materials is an important part in the production of PU adhesives. The following properties of raw material, intermediate compounds and final product were studied during our research.

2.2.1.1. Determination of Hydroxyl Value of Vegetable Oil

The content of free OH groups in a sample can be determined by calculating its hydroxyl value. The hydroxyl values of the different oils used were determined by following the standard process as per ASTM D 1957-86 [91,92]. Briefly, the traditionally used analytical method to find the hydroxyl value involves acetylation of the free OH groups of the sample using acetic anhydride alongwith pyridine as solvent. This step is followed by addition of water to convert the unreacted acetic anhydride into acetic acid. Then, titrating it with KOH using phenolphthalein as end point indicator. The hydroxyl value required for the development of polyurethane adhesive formulation should be in range of 350 to 450.

2.2.1.2. Determination of Viscosity of Oil

It is a property arising from collisions between neighboring particles in fluid that are moving at different velocities. Sample viscosity was determined by using Brookfield viscometer (ASTM D 4878 -98) using spindle 2 at room temperature condition.

2.2.1.3. Determination of Iodine Value

The iodine value of the oils were determined by the Wij's standard procedure as per the ASTM D 974. The experimental determination involved the dissolution of a known weight of sample in non-polar solvent like cyclohexane followed by addition of Wij's solution. When the reaction is complete, a solution of potassium iodide was added to decompose the excess of iodine monochloride to iodine followed by its titration against standardized solution of sodium thiosulfate.

2.2.1.4. Determination of Acid value

The general procedure involves the dissolution of known weight of sample in propan-2-ol which is then titrated against a standardized solution of KOH (potassium hydroxide) using phenolphthalein as end point indicator. At the end of the titration, the color of solution changes from colorless to pink. An increase in the amount of Free Fatty Acid content in a sample of oil or fat refers the hydrolysis of triglycerides which may be due to poor storage and processing conditions such as high relative humidity or temperature. The acid value of the oils were determined by the standard procedure as per ASTM D 5554.

2.3. Substrate Preparation / Bonding

2.3.1. Substrate Preparation

Heat treatment, good design, surface treatment are the important factors during joint preparation for better adhesion [94]. Teak wood without knot, decay, insect, or fungal infection was cut into $300 \times 25 \times 3$ mm^3 strips. Surfaces of wood strips were cleaned with sandpaper grit no. 60 to make them free from loose particles ensuring good quality of adhesion. Strips of wood were retained at 50 ± 5% relative humidity for 7 days at 25^{0}C temperature.

2.3.1. Bonding of Substrates

The prepared adhesive solution was spread over an area of 25×30 mm^2 on both pieces of wood that to be joined with the help of a glass rod. Further the adhered wood pieces were left undisturbed for one day under 2.5 kg load before testing them for the lap shear strength.

2.4. Various Factors Associated with Adhesives

2.4.1. Lap Shear Strength

The strength of bonded substrates are reported to be determined by different testing methods. The results obtained from these testing helps manufacturers in optimizing the processes and formulations of adhesives and trends in results helps the end users in the selection of the adhesive system for desired application. The lap shear strength test is the most widely used testing method for studying the durability of bonded joints. Lap shear testing is a technique for testing adhesion by pulling bonded layers apart along the plane of adhesion. The result obtained can be a clean breakaway of the adhesive layer from the substrate, or a breakdown in the cohesion of either the substrate or the adhesive layer, or both. The easy interpretation of results obtained from this testing and its simplicity makes this test quite popular.

For the testing of lap shear strength, specimens are prepared by applying the adhesives on the wooden substrates (as prepared in section 2.3.1; at 50 ± 5% relative humidity) at room temperature and kept undisturbed for a particular period for curing. The adhesive strength was measured by using a Universal Testing Machine (UTM) Instron 3369 as per the ASTM D 906, with a crosshead speed of 5 mm/min. Five samples for each formulation were tested and visual observation was done for the kind of locus failure at adhesive joints. NIPU samples were tested following the same procedure (i.e. at 5 mm/min crosshead speed, using UTM; Instron 3369 as per the ASTM D882-97 standards. The dimensions of the specimen strips used for testing were 100mm length, 8 mm width and 1 mm thickness. Tensile strength of NIPU samples was also reported as an average of five samples for each formulation.

2.4.2. Curing Time and Green Strength

Green strength is an important property of adhesive that shows the capability of adhesive to grip the substrates together when it is not fully cured i.e. before the attainment of full strength. In general, the adhesives should have immediate bonding strength (green strength) sufficiently high enough to hold the substrates together, but it should not be very high that the bonded substrates cannot be disassembled and refitted in case of wrong alignment. The wood specimens (as prepared in section 2.3.1.) were glued by PU adhesive and were subjected for lap shear strength after 5 h, 10 h, 1 day, 2 days, and 4 days for the determination of its green strength.

2.4.3. Chemical Resistance

As, during its service life the adhesive bond may get exposed to multiple kind of environments. Additionally, the applied stress also enhances the deterioration effect of the environment on the adhesive joint. To determine the suitability of an adhesive for its desired functioning for its end use application, the adhesive joint may be subjected to various kind of environment during its laboratory testing. Prepared adhesives were tested in cold water, hot water, alkali and acid for measuring their surface lives under these extreme conditions. For chemical resistance testing, specimens of wood adhered with PU adhesive were kept in water at 30ºC for 24 h and then tested for its lap shear strength, after drying at room temperature (approximately 30ºC) for 1 day. Similarly, another sets of bonded wood pieces were tested by keeping in hot water at 100ºC for 1 h, in acid solution (0.1 N HCl) at 80ºC for 1 h, and in basic solution (0.1 N NaOH) at 80ºC for 1 h. The results of variation in bonding strength of adhesive after treatment were studied.

2.4.4. Gel Time

The pot life or gel time specifies the maximum time throughout which an adhesive still available in fluid state for use with respect to its application on the substrate. Gel time of various adhesive formulations prepared from polyols of different hydroxyl value were observed.

2.5. Characterization Techniques

Characterization, is a fundamental process in the field of materials science, without which no scientific understanding of engineering materials could be ascertained. Product characterization is the foundation for all formulation and process development. Analysis of material composition and properties is useful in selection of materials, in analyzing failures and other problems, and in validating manufacturing processes. Today, there is a vast array of scientific techniques available to the materials scientist that enables this characterization. Practical description of these techniques will be provided in this section.

Characterizations of the final products formed were done by using FTIR, NMR, TGA, UTM, SEM and TEM.

2.5.1. Infrared Spectroscopy

Infrared spectroscopy is certainly one of the most important analytical techniques available to today's scientists. One of the great advantages of infrared spectroscopy is that virtually any sample in virtually any state may be studied. Liquids, solutions, pastes, powders, films, fibres, gases and surfaces can all be examined with a judicious choice of sampling technique. FT-IR spectrophotometer (Nicolet 380) was used to obtain IR spectra of prepared samples. The spectra of epoxidized vegetable oil and polyol were taken on liquid assembly by applying a thin layer of it on crystal surface.

FTIR spectra of solid PU adhesive were recorded at 25°C by crushing the sample with KBr to form pellets of crushed mixture. Adhesive characterization was done by putting this KBr pellet in solid assembly of spectrophotometer.

2.5.2. NMR Spectroscopy

Nuclear magnetic resonance spectroscopy is a technique used to confirm a molecule's unique structure. It identifies the carbon-hydrogen framework of an organic compound that helps in determining the entire structure of a molecule. The NMR of samples were obtained on 400 MHz FT NMR spectrometer by dissolving about 2 mg of samples in deuterated chloroform. NMR spectroscopy was used to check the reaction progress as well as to check the formation of side products, if any during the course of reaction like epoxidation of canola oil and carbonation reaction of epoxidized canola oil.

2.5.3. Thermal Analysis

Thermogravimetric analysis determines the change in weight of substance either with change in temperature or as a function of time in isothermal condition. The process is carried out in an atmosphere of H_2, He, air, in vacuum, or other gases. Thermogravimetric analysis can be utilized to assess the stability of PU adhesive against heat. In general, polyurethane do not show good thermal stability above 200^0C due to the degradation of urethane linkage [94]. If no weight change is observed in the adhesive sample in desired range of temperature, then adhesive is considered to be thermally stable. Thermogravimetric analysis also provide information about the higher limit of temperature upto which adhesive bond can be subjected after which adhesive begin to decompose. Thermogravimetry analysis (TGA) of PU adhesive was done on a Perkin-Elmer instrument (Diamond SDTA; Shelton, CT, USA) from 25 to

600ºC at a heating rate of 10ºC/min in inert atmosphere by taking 1 mg of sample. TGA of non-isocyanate PU were obtained by analyzing the sample on thermogravimetric analyser by continuous rising the temperature by 10^{o}C per minute between temperatures ranging from 30 to 600 ^{0}C under nitrogen atmosphere. TGA of NIPU were obtained by analyzing the sample on thermogravimetric analyser by continuous rising the temperature by 10^{o}C per minute between temperatures ranging from 30 to 600 ^{0}C under nitrogen atmosphere. Aluminum pans containing 10–12 mg of samples were subjected to a temperature range of 70 to 100ºC at a heating rate of 10ºC/min under inert atmosphere.

2.5.4. Electron Microscopy

2.5.4.1. Scanning Electron Microscopy

Scanning electron microscope uses the electrons to penetrate the gold coated sample only upto a small depth, thus it is only applicable for studying the surface topology of substrate. The technique can also be utilized for determining the chemical composition of the substrates surface as with the increase in atomic number of involved elements will result in increasing brightness of the image formed due to backscattered electrons. Thus the area of substrate possessing lighter elements forms a darker screen image as compared to brighter image of heavier elements. EDX or EDS (Energy Dispersive X Ray Analysis) is utilized to study the chemical composition at substrates surface by collecting the X-rays in scanning electron microscope.

2.5.4.2. Transmission Electron Microscopy

Unlike Scanning electron microscope (SEM), TEM (Transmission Electron Microscope) makes the beam of electron pass through the sample. Transmitted beam consist of elastically scattered electrons displays the formed image after passing through the objective lens. Morphology of TiO_2-doped PU was analyzed using a scanning electron microscope (S-3700N; Hitachi, Japan) and for elemental characterization of TiO_2-doped sample, the sample was examined with the EDXS analyzer unit attached to the scanning electron microscope. TEM images were obtained using a F30S twin 300 HRTEM at 300 kV after preparing a sample on copper grid for HRTEM.

CHAPTER 3

POLYURETHANE ADHESIVES FROM POLYESTER POLYOLS SYNTHESIZED BY TRANSESTERIFICATION OF CASTOR OIL

In the present study, PU adhesive was synthesized by the reaction of glycerol-modified castor oil with diphenylmethane-4,4’-diisocyanate (MDI). The aim is to develop polyurethane adhesive by utilizing renewable resources like castor oil to contribute to a sustainable development in the future. To improve the overall performance of adhesive, nanosized TiO_2 as filler was added.

3.1. Synthesis of Polyol

3.1.1. Transesterification of Castor Oil

Polyols were obtained by the modification of the castor oil with glycerol using an already reported method [95,96]. The polyols with hydroxyl values of approximately 500, 400, 300, and 200 were prepared using the castor oil to glycerol ratios of respectively, 1:1, 2:1, 3:1, and 4:1. The unreacted byproducts were separated from reaction mixture by solvent extraction method using n-hexane as solvent. A representation of polyol synthesis by transesterification is given in Figure 3.01.

3.2. Preparation of Adhesive

The polyol and MDI in stoichiometric ratios of 1:1 to 1:1.3 were added and stirred continuously for 30 min, at room temperature under the atmosphere of nitrogen. The solutions of different NCO/OH ratios were prepared by following the same procedure. Methyl ethyl ketone was added to adjust the adequate flow of the resulted solutions. In another flask, a mixture of polyol along with requisite amount of TiO_2 and DBTDL

(0.05 w/w %) was prepared. The purpose of adding TiO_2 is to improve the performance of the adhesive and DBTDL acts as catalyst for reaction between polyol and diisocyanate. Both the mixtures (as prepared above) were mixed in a separate clean beaker and stirred for 1 min, before applying to the substrate.

The resulted material was characterized by NMR spectroscopy, IR spectroscopy, Thermogravimetric analysis, DSC and electron microscopy i.e. SEM and TEM.

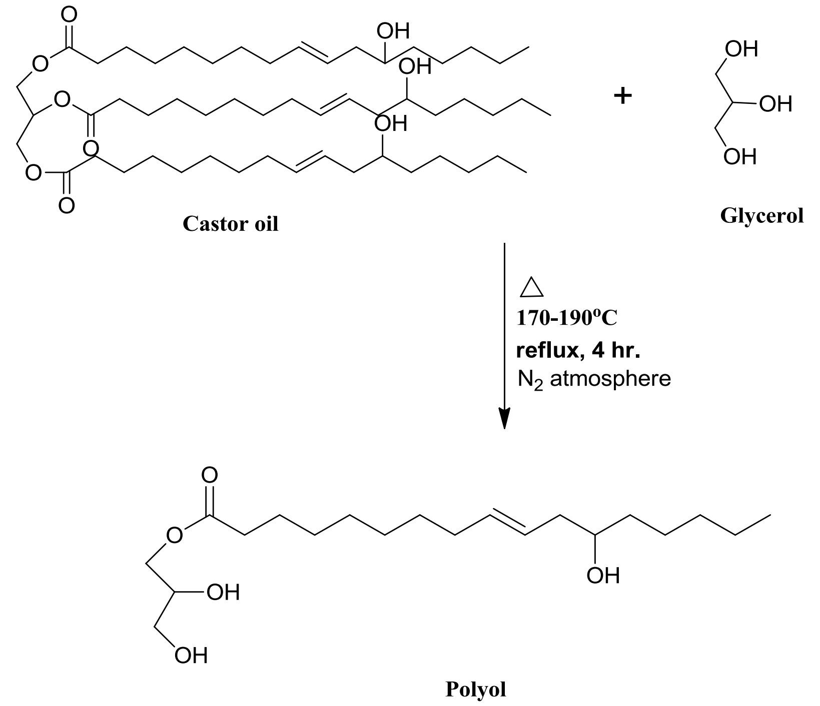

Figure 3.01: Scheme of Polyol Synthesis by Transesterification of Castor Oil

3.3. Significant Findings

3.3.1. IR Spectra

IR spectra of the castor oil–based polyol and synthesized PU adhesive after 5 and 15 min (Figure 3.02) has shown a broad band at 3334 cm−1 due to the OH group. IR bands at 2924 and 2854 cm^{-1} are due to alkyl C-H stretching of aliphatic segment of fatty chain as reported in previous literature studies [97]. It was observed that though the reaction was not taking place spontaneously after the addition of isocyanate and catalyst, but some significant changes were observed. IR spectra taken after 5min indicated the presence of free available NCO by showing stretching frequency at 2270 cm^{-1}. The intensity of this signal decreased with time, but some amount of NCO remained unreacted, even after a reaction with polyol was completed as MDI was taken in excess which is desirable for a reaction with the hydroxyl groups of wood substrates. The IR spectra of solidified PU adhesive, after 15 min, had shown a characteristic peak at 3417 cm^{-1} due to NH stretching, peak at 1530 cm^{-1} due to NH bending of the urethane group and at 1720 cm^{-1} due to the carbonyl stretching. The addition of nano-sized TiO_2 had no effect on IR spectra of PU adhesive.

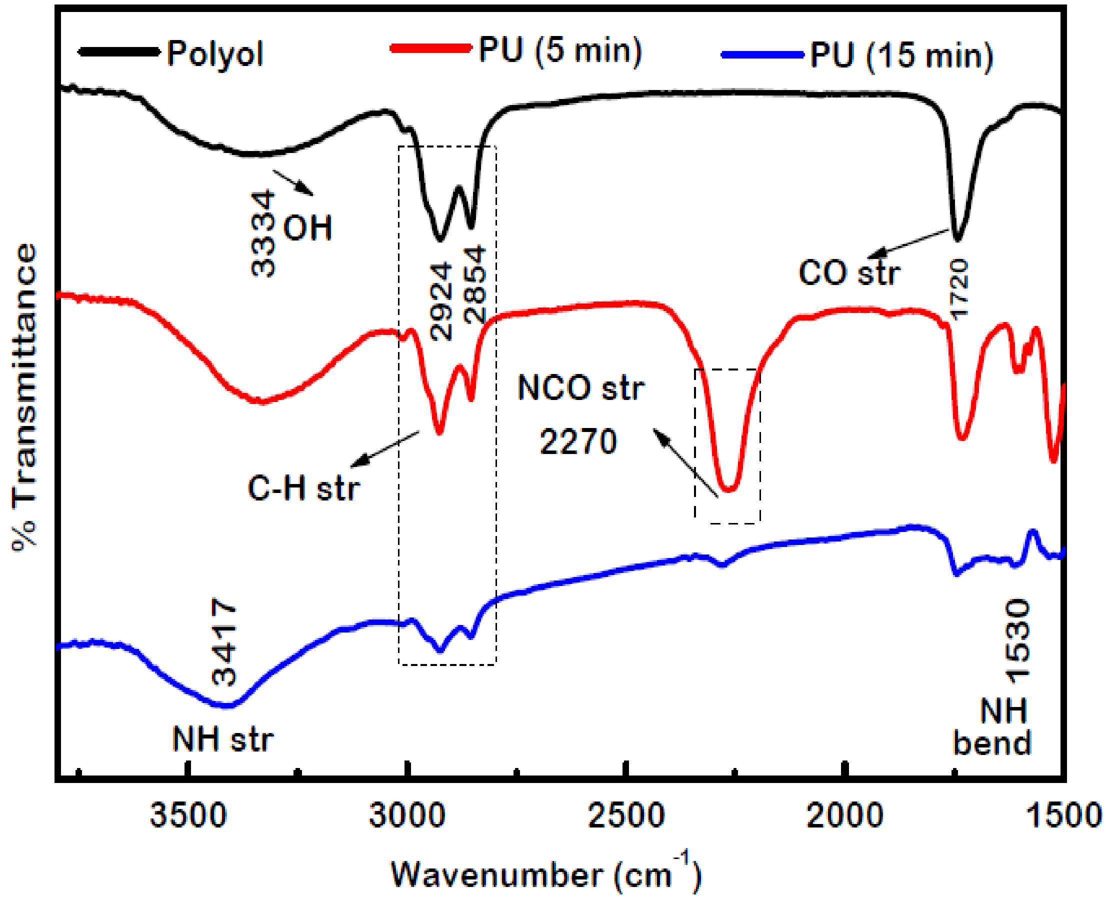

Figure 3.02: FT-IR Spectrum of Polyol and Polyol-isocyanate mixture(after 5 min and 15 minutes of mixing)

3.3.2. Effect of Hydroxyl Value

It is evident from the results shown in Table 3.01 that as the hydroxyl value of polyol increases, the lap shear strength of bonded wood joints also increases. This increase in strength of prepared adhesive might be because of an increase in cross-linking density due to more linkage between the hydroxyl group and isocyanate moiety. As castor oil has low hydroxyl value (160), adhesive containing more amount of castor oil resulted in weak adhesion strength whereas the polyols with higher glycerol content showed a rapid increase in adhesive strength owing to their increased hydroxyl value.

Table 3.01: Effect of Hydroxyl Value on Adhesion

Hydroxyl value (mg of KOH/g)	Avg. Lap shear strength MPa(± 5)	Locus of failure
160	18	Cohesive
200	39	Cohesive
300	43	Cohesive + Adhesive
400	51	Cohesive + Adhesive
500	56	Substrate Failure

3.3.3. Gel Time

The gel time of prepared adhesive was found to be decreased with the increase in the hydroxyl value of polyol. This might be due to the increased ability of polyols for forming cross-links with isocyanate groups,as shown by results in Table 3.02.

Table 3.02: Effect of Hydroxyl Value on Gel Time

Hydroxyl value of polyol (mg of KOH/g)	Gel time (min)
160	65
200	58
300	45
400	39
500	26

3.3.4. Effect of NCO/OH Ratio on Adhesion Properties

It is evident from Table 3.03 that the value of lap shear strength increased with an increase in the NCO/OH ratio upto 1.2. With further increasing the NCO/OH ratio, a reverse effect on bonding strength of adhesive was observed. This trend showed that a slight excess of isocyanate is favorable, as free NCO can react with hydroxyl groups present on the wood surface, thus leading to higher bond strength. However, the lower value of lap shear strength at low NCO/OH ratio is due to complete consumption of isocyanate by hydroxyl group of polyol, showing cohesive type of failure. Nevertheless, the higher NCO/OH ratio beyond a critical value resulted in an increase in brittleness of adhesive resulting in a mixed mode i.e., cohesive as well as adhesive type of failure.

Table 3.03: Effect of Isocyanate-Hydroxyl (NCO/OH) Ratio on Adhesion

NCO/OH ratio(polyol with hydroxyl value of 400 mg of KOH/g)	Average lap shear strength (MPa)(± 5)	Type of failure
1.0	23	Cohesive
1.1	41	Cohesive
1.2	51	Adhesive + Cohesive
1.3	47	Adhesive + Cohesive
1.4	43	Adhesive

3.3.5. Morphological Study

The particle size of TiO_2 nanoparticles and morphology of TiO_2 filled PU were examined from micrographs obtained from HRTEM and SEM, as shown in Figure 3.03. It is clearly seen that TiO_2 nanoparticles of size ranging from 15 to 18 nm were uniformly distributed in the adhesive sample. From SEM images, no bubble formation or nano-cracks were observed on the adhesive surface. The TiO_2 doping in adhesive was confirmed by chemical composition study using EDXS analysis (Figure 3.04).

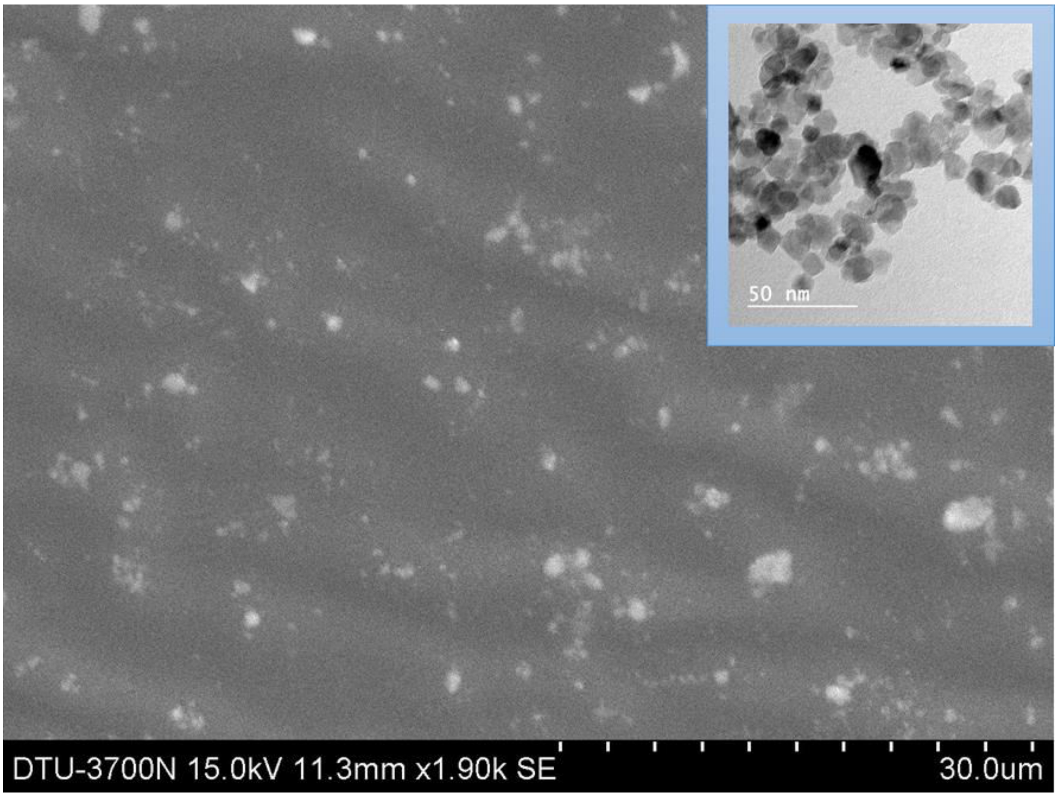

Figure 3.03: SEM and TEM (Inset Image) Micrograph of TiO_2-Filled PU

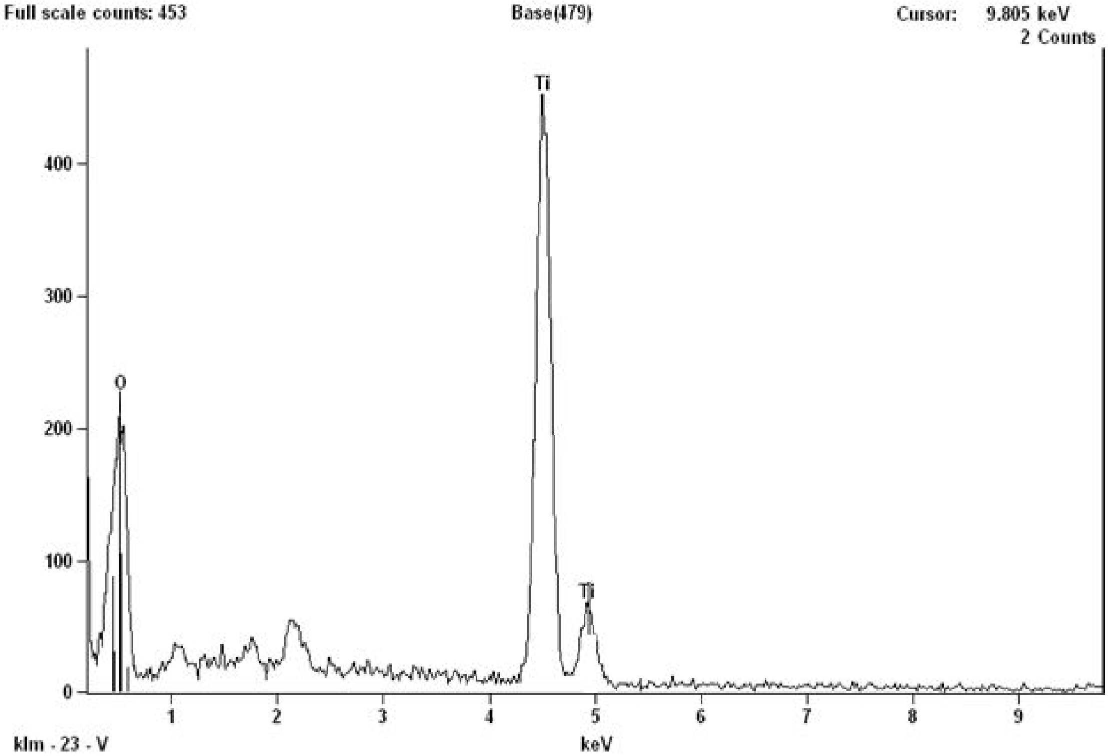

Figure 3.04: EDXS of TiO_2 Filled Polyurethane Adhesive

3.3.6. Effect of Addition of the Filler

The lap shear strength of adhesive filled with nanosized TiO_2 in different amounts ranging from 1 to 5 wt % was measured and the results of the adhesion strength of each composition are shown in Table 3.04. The results reported in Table 3.04 are the average of adhesion strength of five samples tested for each composition. It had been observed that by incorporating TiO_2 upto a concentration of 3%, adhesion strength of bonding wood sample was found to be increased. This might be due to effective transfer of stress between polymer matrix and filler. Furthermore, with increased filler content, i.e. upto 4%, no improvement in lap shear strength was observed. On further addition of filler i.e. upto 5%, the lap shear strength had shown a declining trend that was also evident from increased brittleness of adhesive at joint. It was found nearly impossible to disperse more filler uniformly in the adhesive sample. No significant change was observed in impact strength of adhesive before and after the filling of TiO_2 nanoparticles, when, an average of 10 samples was taken for both. The viscosity of system was found to increase with the addition of TiO_2 as shown in Table 3.06.

Table 3.04: Effect of Amount of Filler on Adhesion

Filler(wt%) in polyol (hydroxyl value-300 mg of KOH/g)	Average lap shear strength (MPa)(+/-5)
1	43
2	44
3	46
4	45
5	39

3.3.7. Curing Time and Green Strength

For determining the green strength of prepared adhesive, polyols of different hydroxyl values were selected with the NCO/OH ratio 1.2. Bonded wood specimens were subjected to the lap shear test at different time intervals, and the results obtained are as reported in Table 3.05. From these results, it is evident that the curing speed of adhesive varies linearly with hydroxyl values of polyol and filled PU adhesive showed a little slow curing rate as compared to corresponding adhesives without any fillers. Prepared adhesive exhibits excellent curing speed and attained 29% of its ultimate strength within just 5 h of bonding and 70% of its final strength in 1 day. Adhesive is found to be fully cured in 4 days; thereafter, no significant change in bonding strength occurred with time.

Table 3.05: Effect of Amount of Filler on Green Strength

Time after adhesive application	**Average lap shear strength (MPa)(± 5) (without TiO_2)**	**Average lap shear strength (MPa)(±5) (3% TiO_2)**
5 h	14	12
10 h	31	35
1 day	38	43
2 day	47	50
4 day	51	51

3.3.8. Chemical Resistance

Prepared adhesive was tested in different conditions such as cold water and hot water, alkali, and acid. The results of variation in bonding strength of adhesive after these treatment are shown in Table 3.07. It has been observed that the prepared adhesive exhibits good resistance to both hot and cold water whereas acid and alkali have some deteriorating effect on adhesive strength. This might be due to penetration of these solutions into the sample. Result of lap shear strength in the filled PU adhesive sample showed lesser loss in adhesion strength under different test conditions. No major changes in dimensions of specimen were observed (i.e., only less than 2%) in all the samples. Visual inspection had shown more dimensional stability in the TiO_2 filled PU sample as compared to unfilled PU. It might be due to the high thermal coefficient of expansion after the addition of nanostructured TiO_2 filler, which was reported in previous studies [100], for the incorporation of nanostructured inorganic fillers in epoxy adhesives. The percent weight change in samples under different chemical environments is presented in Table 3.06. The results showed that hot and cold water has very little effect on prepared PU but in comparison, with acid and alkali environment, it resulted in slightly higher weight loss in specimens. The TiO_2-filled sample showed comparatively higher resistance in all chemical environments.

Table 3.06: Viscosity Change and Weight Loss Data Before and After Doping with TiO_2

Type of adhesive system	**Viscosity (mPa s)(25^0 C)**	**Weight Loss (%) (±1)**			
		In Acid	**In Alkali**	**Cold water**	**Hot water**
PU without TiO_2	190	2.30	2.90	1.20	1.50
PU filled with 3% TiO_2	220	2.20	2.43	1.10	1.40

Table 3.07: Chemical Resistance of Different Adhesive Formulations

Hydroxyl value (mg of KOH/g)	**Average lap shear strength(MPa)(±5) (before exposure)**	**Avg. Lap shear strength (MPa) (± 5) (after exposure)**			
		Cold water	**Hot water**	**Acid, pH 2**	**Alkali, pH10**
200	39	39	36	33	31
300	43	42	40	39	37
400	51	51	47	46	45
400 (TiO_2 -3%)	52	51	49	47	47
Commercial adhesive	34	28	24	22	19

3.3.9. Comparison with Commercial Adhesive

The performance of synthesized PU adhesive was compared with commercially available PU adhesive (Fevicol^{TM}) in India. In accordance with the result shown in Table 3.07, the synthesized PU adhesive had much better performance in terms of adhesion strength as well as against different deteriorating conditions as compared to the commercial adhesive.

3.3.10. Thermal Characterization

Thermogravimetric analysis of castor oil based PU adhesive is shown in Figure 3.05. It can be seen from the curve that synthesized PU adhesive is stable upto 250ºC, as evident from no degradation in weight below this temperature. It was found that adhesive degrades in two stages; the first degradation starts at 270ºC due to breaking of urethane bonds, results in the formation of carbon dioxide, carbon monoxide, amines, and aldehydes, whereas the decomposition at higher temperature i.e. around

470ºC is due to breaking of high energy double bonds and single bonds such as C=O, C=C, C–O, C–H bonds. These results are similar to the results shown by the studies of Somani et al. [35] for stage I and that of Callister [98] for stage II. The TGA curve showed that the onset of decomposition of both unfilled and filled PU adhesive was nearly same, but difference lies in the amount of residue left which is much higher in case of filled adhesive. It was also evident from these curves that unfilled adhesive showed decomposition in three steps but the filled PU had shown the two-step decomposition, thus, indicating a better stability at midrange temperature i.e. around 350ºC. It is apparent from DSC thermograms (Figure 3.06) of unfilled and TiO_2-filled (3 wt%) castor oil based PU adhesive that there are two glass transition temperatures, one is around –55ºC and second is around –20ºC, which correspond to transitions due to soft segment of PU adhesive. It has also been found that addition of TiO_2 filler increased the glass transition temperature slightly, which indicated that the filler has some interaction with polymer chains, thus favoring the phase separation between the hard and soft segments of PU similar to the previously reported studies on other fillers [99].

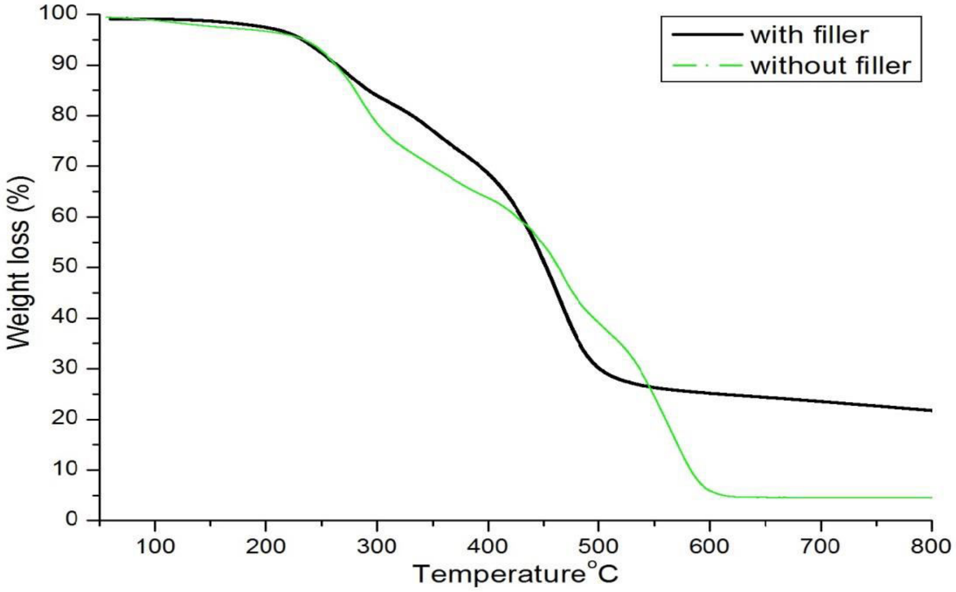

Figure 3.05: TGA of unfilled PU adhesive and TiO_2 filled adhesive.

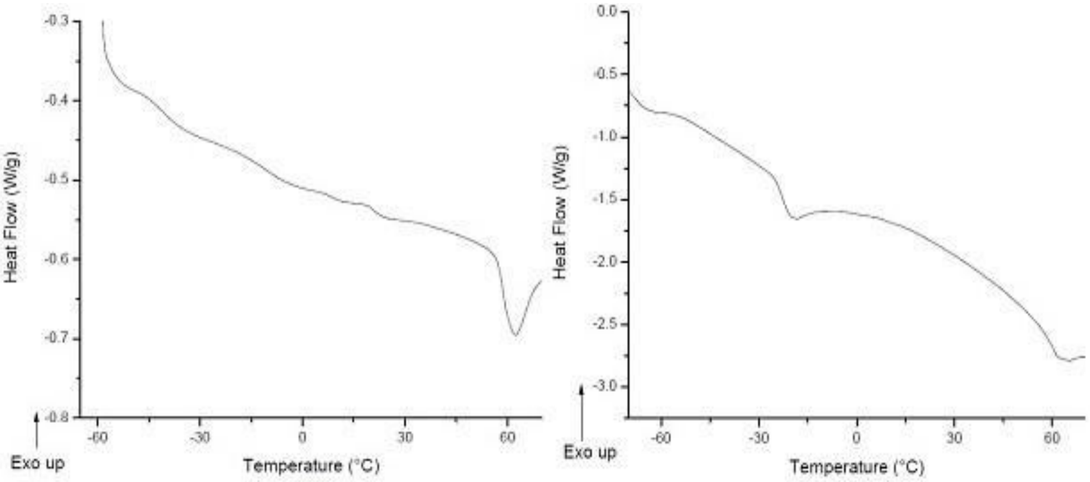

Figure 3.06: DSC Thermograms of the Unfilled (Left Side) and 3 Wt% TiO_2 Filled Polyurethanes (Right Side).

CHAPTER 4

POLYURETHANE ADHESIVE FROM CANOLA OIL BASED POLYETHER-ESTER POLYOLS

This study has been conducted with an emphasis to develop a biobased polyol from canola oil by transesterification reaction followed by epoxidation and ring opening reaction with an intention to insert hydroxyl group at unsaturation sites. The properties of different PU adhesives obtained by the reaction of resulted polyether-ester polyol with different kind of aliphatic or aromatic diisocyanates has been extensively studied.

4.1. Preparation of Canola Oil Based Polyols

Polyol was synthesized in a three step reaction. A schematic representation of the synthesis of polyol from canola oil is as shown in Figure 4.01. The steps involved in the polyol synthesis are discussed below.

4.1.1. Transesterification of Canola Oil (Step I in Scheme shown in Figure 4.01)

Canola oil and glycerol in molar ratio 1:3 along with NaOH (0.5% w/w of canola oil) were mixed in a 500 ml four necked round bottomed flask equipped with N_2 gas inlet, thermometer and a reflux condenser. The reaction contents in the flask were continuously stirred for the next 6 hours at 160^0C in inert atmosphere with the help of a magnetic stirrer. The reaction mixture was then shaken vigorously with 250 ml of n-hexane in a separating funnel to separate the unreacted glycerol that formed the bottom layer in funnel and was discarded. After that the n-hexane present in the reaction mixture was removed from transesterified canola oil on rotary evaporator under vacuum to get the concentrated product.

4.1.2. Epoxidation of Transesterified Canola Oil (Step II in Scheme shown in Figure 4.01)

Transesterified canola oil obtained from aforementioned procedure and formic acid in 1:3 molar ratio were poured in round bottomed flasek and cooled at zero degree Celsius in ice bath followed by dropwise (slow) addition of calculated amount of hydrogen peroxide under continuous stirring. After complete addition of H_2O_2, the reaction was continued at room temperature under vigorous stirring until iodine value indicates maximum consumption of olefinic group. The reaction mixture was then transferred in separating funnel followed by addition of ethyl acetate and lower aqueous layer content is removed. The remaining organic content was further washed with water followed by aqueous sodium bicarbonate and lastly by brine. Lastly the contents were dried with sodium sulphate and concentrated under vacuum in rotary evaporator to get the clear solution of epoxidized oil.

4.1.3. Ring opening with 1, 3-propandiol (Step III in Scheme shown in Figure 4.01)

The dried product obtained after transesterification and followed by epoxidation, was stirred with 1,3-propanediol in 1:10 molar ratio along with 10.0 mol% sulphuric acid at 60^0C for 48 h under low vacuum (10mm Hg) as previously described [101]. After the completion of reaction, ethyl acetate was added in equal volume followed by washing of organic layer with sodium bicarbonate and brine. The remaining aqueous content in the product was then removed with anhydrous sodium sulphate, filtered and separated on a rotary evaporator under vacuum to get the final polyol.

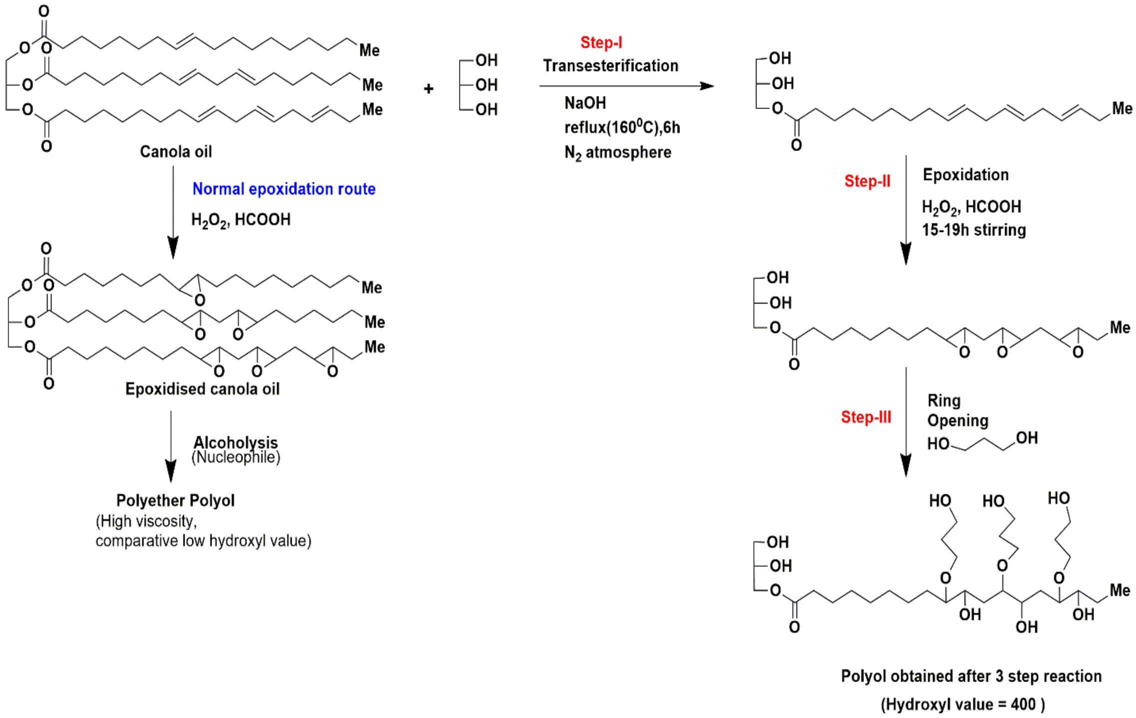

Figure 4.01: Synthetic Route for the Formation of Canola Oil Based Polyol

4.2. Preparation of PU Adhesive

Different adhesive formulations of PU were prepared by following the method already described by the same research group in some other studies [102]. Briefly, the above prepared polyol of hydroxyl value approximately 400, were mixed with 0.05% DBTDL for 30 minutes on a magnetic stirrer under nitrogen atmosphere. This solution was then made to react with MDI (taking NCO/ OH ratio 1.1:1), by mixing them for 1 minute before applying to the wood substrate (preconditioned at 55% relative humidity at 25^{0}C for 7 days). In the similar manner, more PU adhesives were prepared by varying the isocyanate adduct, i.e., TDI, HMDI, and IPDI by the mentioned procedure. Reaction involved is shown in Figure 4.02.

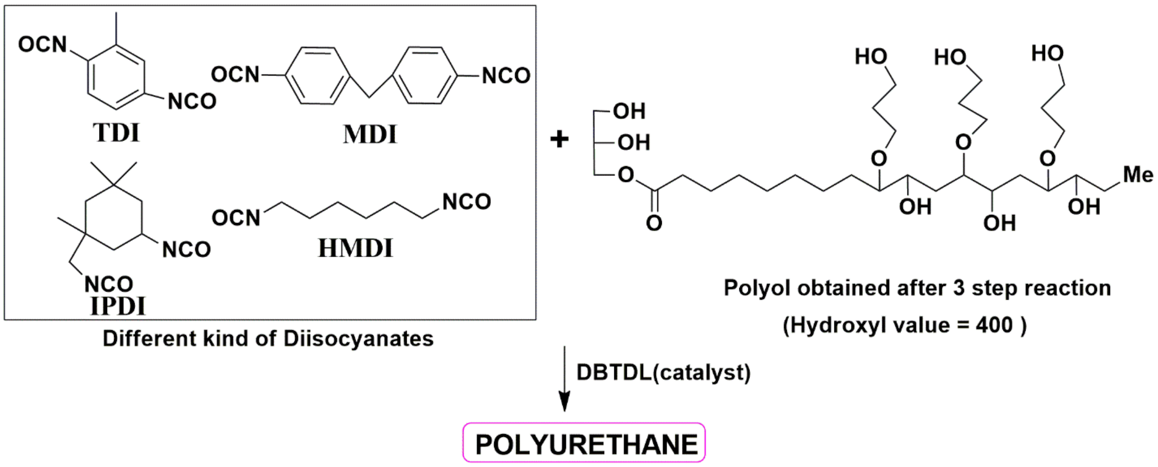

Figure 4.02: Preparation of PU Adhesive

The prepared adhesive was characterized by FTIR spectroscopy, NMR spectroscopy and TGA analysis.

4.3. Significant Findings

4.3.1. FTIR Analysis

FTIR analysis of pure canola oil, fully epoxidised oil, epoxidized -transesterified oil and polyol is as shown in Figure 4.03. As evident from Figure 4.03, FTIR spectroscopy confirms the conversion of double bonds present in vegetable oil into epoxides by the appearance of band at wavenumber 823 cm^{-1} which was not present in spectra of oil initially and complete disappearance of sp^2 hybridized carbon-hydrogen (=C-H) stretching band at 3,010 cm^{-1} which shows that olefinic group has been consumed during the reaction. Further in spectra of polyols, which are formed by ring opening reaction, the above stated bands of epoxide functional group disappeared and new strong bands at 3,440 cm^{-1} due to hydroxyl group (symmetrical stretching), at 1,180 cm^{-1} due to ether linkage (asymmetric stretching) and at 1,740 cm^{-1} due to stretching of carbonyl group appeared. The strong signals at wavenumber ranging from 2,800 cm^{-1} to 3,000 cm^{-1}, that appeared in all the samples are observed because of the characteristic stretching vibrations of sp^3 hybridized C-H bond.

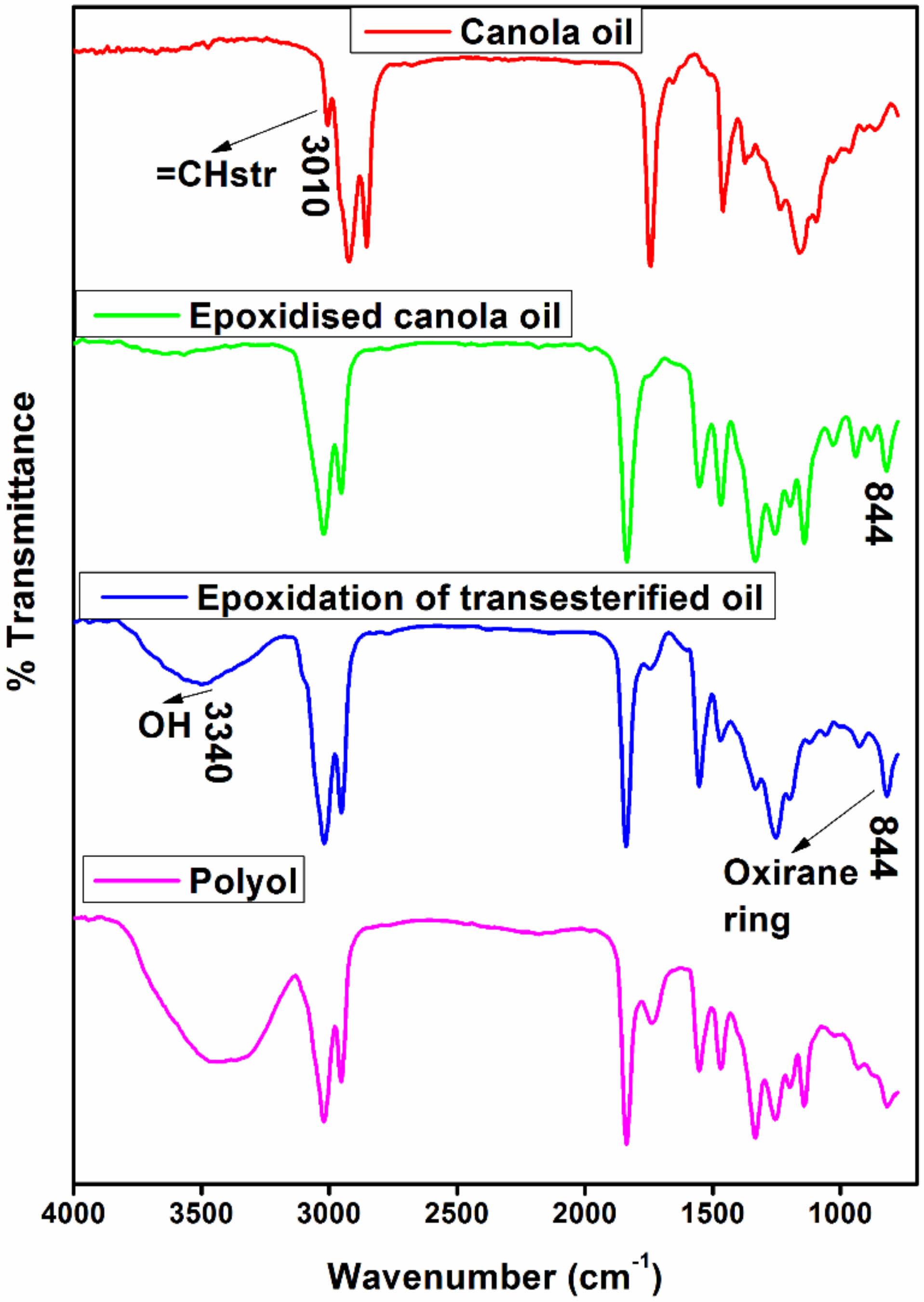

Figure 4.03: FTIR Spectra of Pure Canola Oil, Fully Epoxidised Oil, Epoxidized -Transesterified Oil and Polyol

4.3.2. NMR Spectra

The ^{1}H NMR spectra of canola oil and epoxidized oil after transesterification confirm the successful conversion of double bond to epoxy group, as seen from Figure 4.04. The epoxidised oil sample clearly shows appearance of new peaks at 2.8 to 3.2 ppm (Quatret) due to epoxy protons which were not observed in spectra of canola oil. Also, the spectra of canola oil shows a disappearance of peaks present at 5.2 to 5.4 ppm due to olefinic protons. The common peak shown by both the samples at 0.7– 1.0 ppm (Triplet) is due to terminating methyl group. The glycerol moiety shows peak at 4.1–4.2 ppm due to –CH_2-OH protons. The CH_2- protons in alkyl chain which are common in both canola oil and the epoxidised product shows peak at 1.2– 1.4 ppm. The peaks observed at 2.5–3.0 ppm (Triplet) are due to CH_2 protons adjacent to double bond in case of canola oil sample and are due to CH_2 protons adjacent to epoxy group in epoxidized sample.

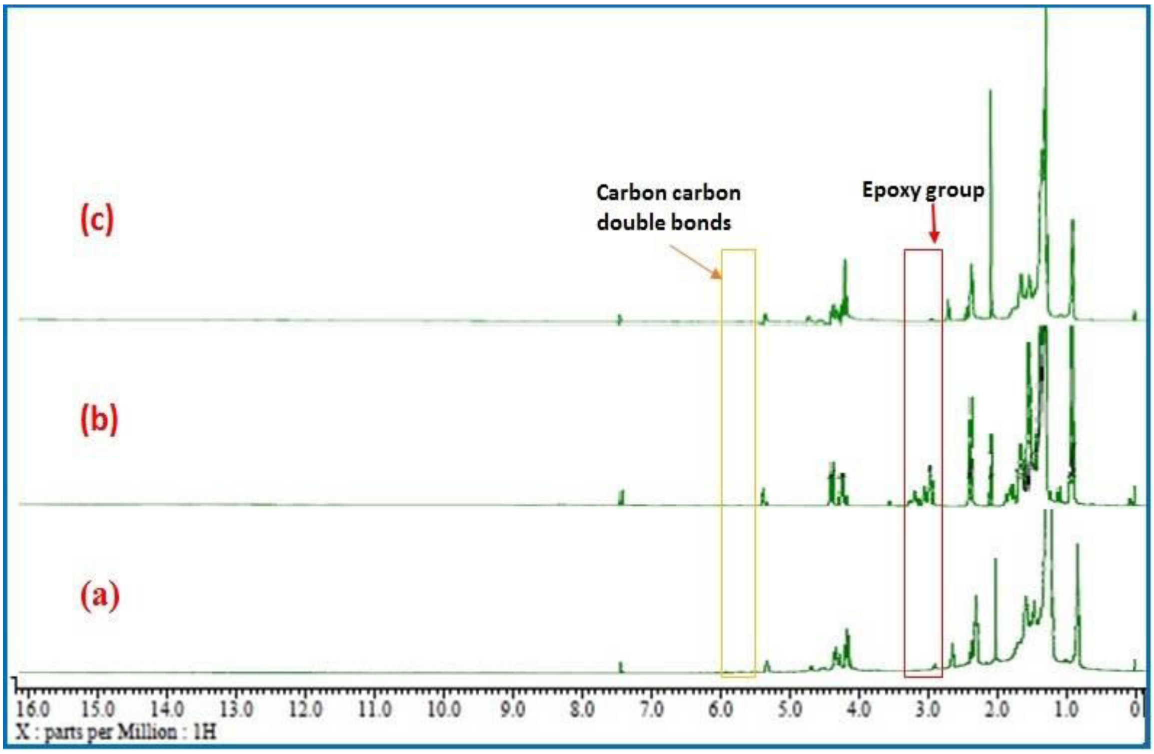

Figure 4.04: Proton NMR Spectra of (a) Canola oil (b) Epoxidized oil (c) Polyol

4.3.3. Thermal Characterization

Thermal analysis of canola oil based adhesive made up of different isocyanates is shown in Figure 4.05 and Figure 4.06. As shown in TGA curve, all of the prepared PU adhesive samples have shown a stability upto 250^0C and no major degradation has been observed below this temperature. Analogous to the previous studies, canola oil based PU had shown degradation in two steps i.e., first degradation is due to decomposition of the urethane bonding into amines or alcohols or isocyanates and the second is due to breaking of olifienic, carbonyl, ether or carbon-hydrogen linkages, similar to that of previous studies [35]. Degradation behavior of PU adhesives made from structurally different diisocyanates are shown in Table 4.01. As it was suggested in literature studies that the ease of urethane bond formation is inversely proportional to their stability [103], accordingly the following is the observed thermal stability order of structurally different diisocyanates PUs: aryl- NCO/aryl-OH<alkyl-NCO/aryl-OH<aryl-NCO/alkyl-OH<alky-NCO/alkyl-OH. The polyurethane obtained from aliphatic isocyanates shows somewhat better (at initial stage) thermal stability as compared to the aromatic ones (shows better mid-range stability towards degradation), but the thermal profiles of all the vegetable oil based samples were found to be similar.

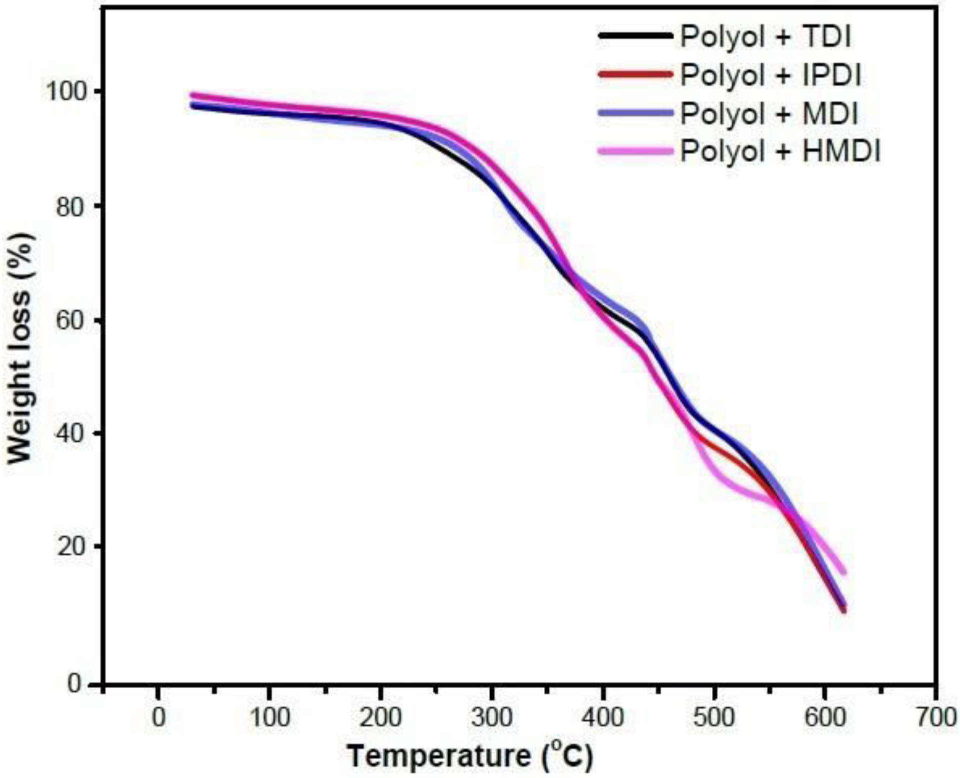

Figure 4.05: Comparative TGA of Different PU Adhesive Systems

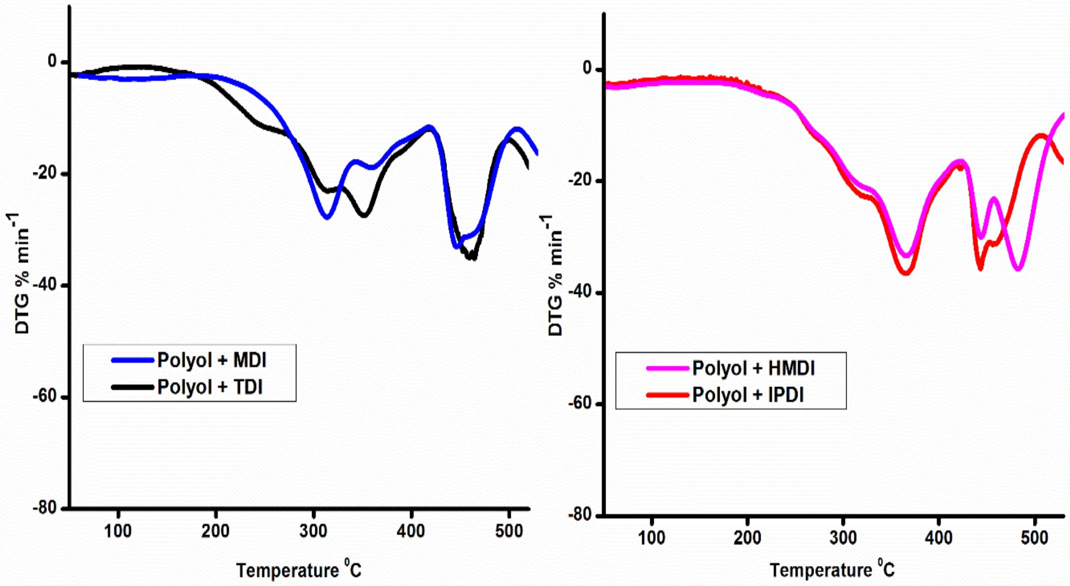

Figure 4.06: Comparative DTG of Different PU Adhesive Systems

Table 4.01: Thermal Stability of PU Adhesive Formulations Obtained From Different Isocyanates.

Components of adhesive sample.	T_{10} (°C)	T_{50} (°C)	T_{90} (°C)	T_{max} (°C)
Polyol+MDI	295	470	616	315, 445
Polyol+TDI	290	465	616	349, 465
Polyol+HMDI	309	452	618	366, 481
Polyol+IPDI	311	455	620	364, 444

4.3.4. Gel Time

The gel time of different PU adhesive formulations are reported in Table 4.02. From the results obtained, it has been observed that the adhesive formulations with aromatic isocyanate adduct shows lesser gel time as compared to formulations with aliphatic or cycloaliphatic isocyanate moiety.

Table 4.02. Gel Time or Pot Life of Different PU Adhesive Formulations

Type of Adhesive Formulation	Gel Time(minutes)
Polyol+MDI	40
Polyol+TDI	35
Polyol+HMDI	50
Polyol+IPDI	55

4.3.5. Green Strength

It is quite clear from the results shown in Table 4.03 that polyurethane adhesives with aromatic isocyanate moiety shows a little faster curing rate with respect to the adhesives samples possessing aliphatic isocyanates moiety. Although a good curing speed had been shown by all the adhesive samples, as they achieved around 70% of their adhesion strength in 24 h and approximately 90% of the fully cured adhesive strength in 48 h. As shown by the experimental results shown in table 4.03, all the samples show no change in the adhesion strength after 4 days, therefore assumed to have been fully cured.

Table 4.03: Green Strength of Different PU Adhesive Formulations

	Average Lap shear strength in MPa (±5)			
Time after adhesive application	**PU1 adhesive (Polyol+MDI)**	**PU2 adhesive (Polyol+TDI)**	**PU3 adhesive (Polyol+HMDI)**	**PU4 adhesive (Polyol+IPDI)**
5h	17	19	14	16
10h	32	33	28	27
24h	39	39	36	34
48h	48	47	44	45
4 day	56	54	53	56

4.3.6. Chemical Resistance of Prepared PU Samples

The adhesion strength of all the samples remain unaffected when treated with water i.e. for both cold and hot water, whereas the treatment with 5% NaCl and 0.1M HCl had shown very little effect. N/10 NaOH had shown the highest deteriorating effect on adhesion strength of prepared PU adhesives. It has been observed that adhesive samples prepared from aliphatic isocyanate and cycloaliphatic moiety show more resistance as compared to isocyanates with aromatic moiety as reported in Table 4.04.

Table 4.04: Chemical Resistance of Different PU Adhesive Formulations

Type of adhesive system	Avg. Lap shear strength (before exposure) MPa ±5	Average Lap shear strength (after exposure) ±5 MPa				
		Cold water	Hot water	5% NaCl	Acid	Base
Polyol+MDI	56	53	52	53	48	44
Polyol+TDI	54	51	51	51	47	42
Polyol+HMDI	53	50	50	50	49	47
Polyol+IPDI	56	53	52	52	50	48
Commercial wood adhesive	36	29	25	26	24	20

CHAPTER 5

DEVELOPMENT OF CANOLA OIL BASED NON-ISOCYANATE PU

5.1. Synthesis of Non-isocyanate PU

In the present work, 5,10,15-Tris-(pentafluorophenyl)corrolato-Manganese (III) complex has been explored as a novel catalyst for coupling reaction between epoxidised canola oil and CO_2 (gaseous) to introduce cyclic carbonate moieties in the oil and further utilized it to obtain non-isocyanate PU , by curing with different diamines. 5,10,15-Tris-(pentafluorophenyl)corrolato-Manganese (III) complex was chosen as catalyst owing to high electronegativity of free base corrole which is desirable for the lewis acid like activation of reactants. As per the available literature, Metalloporphyrins had been proven to be efficient catalyst for carbonation reaction and corroles have similar stable structure like that of porphyrins but are found to be more effective catalyst, as the ligand framework of corroles has 1 carbon less than porphyrins, which increases its catalytic efficiency. Moreover, the catalytic efficiency of reported corrolato complex is further enhanced by presence of 15 fluorine atoms in corrole ligand frame. Manganese metal was selected pertaining to its ability to easily alter its oxidation state during the interaction with reactants. The reactions scheme involved in synthesis of non-isocyanate PU are outlined in Figure 5.01.

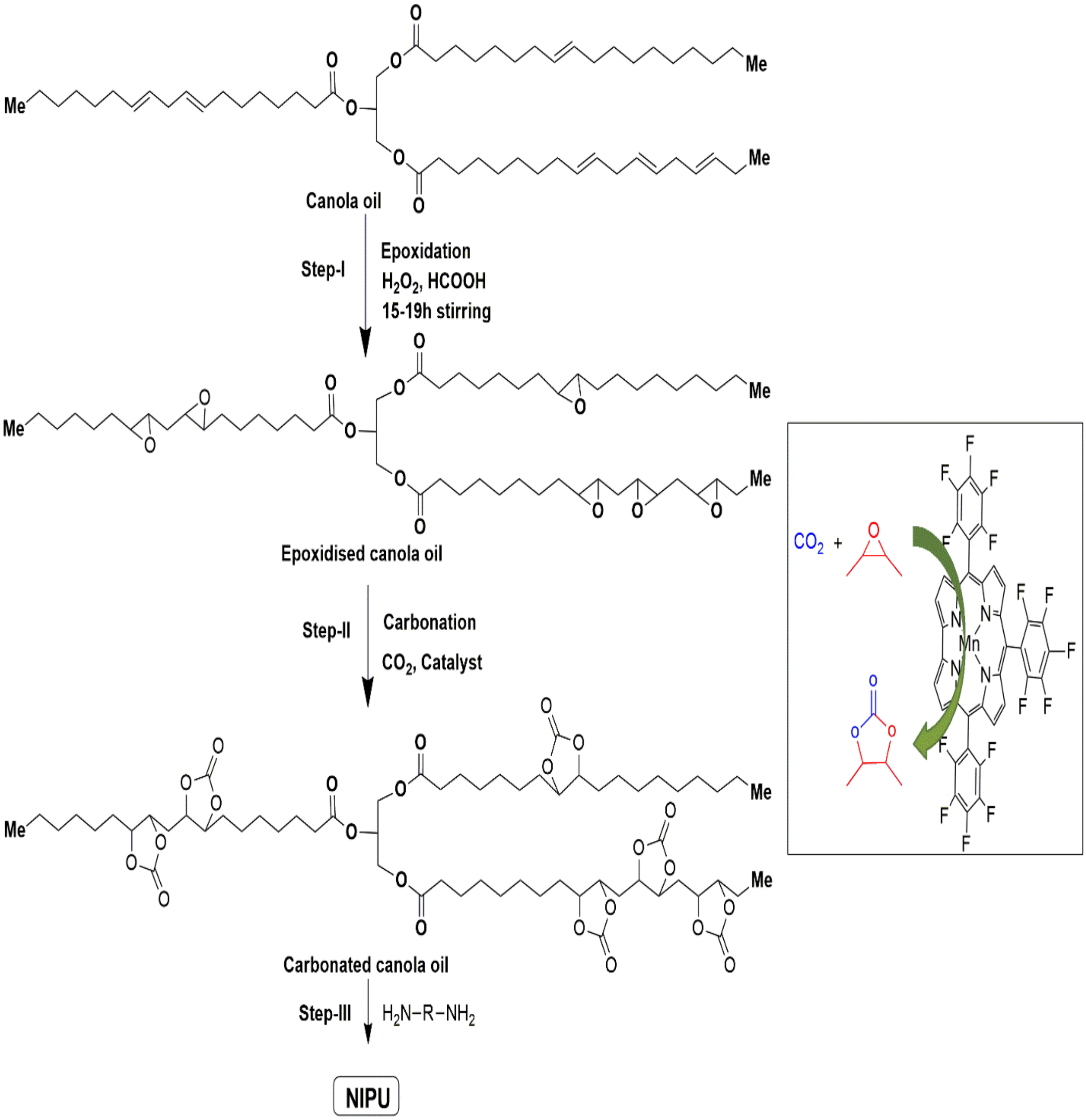

Figure 5.01: Fundamental Reactions Involved in the Synthesis of Non-isocyanate PU (Proposed Catalyst Functioning in Inset)

5.1.1. Synthesis of Catalyst

5,10,15-Tris-(pentafluorophenyl)corrolato-Manganese (III) complex was synthesized by the method already described in prior literature [104]. The reaction scheme for synthesis of catalyst is outlined in Figure 5.02. Briefly, manganese acetate tetrahydrate (308 mg, 1260 µmol) and free base (100 mg, 126 µmol) were dissolved in

Dimethylformamide, followed by refluxing for next 15 minutes. The color of solution changes from purple to green. The progress of the reaction was monitored by Thin Layer Chromatography (TLC). The solution obtained was then dried by evaporation and the green complex was separated by column chromatography. After recrystallization, purple coloured needle-shaped crystals were obtained.

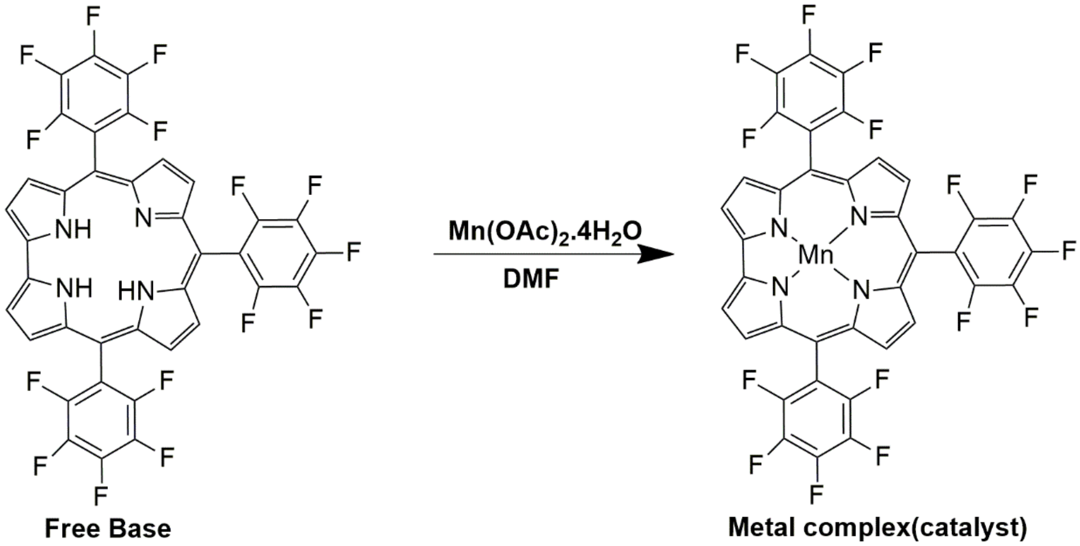

Figure 5.02: Reaction Scheme for Synthesis of 5,10,15-Tris-(pentafluorophenyl)corrolato-Manganese (III) Complex

The synthesis of Non-isocyanate PU from canola oil and CO_2 involves three major steps, the details of process/reaction is as follows:

5.1.2. Epoxidation of Canola Oil

Canola oil and formic acid (1:3 molar ratio) were mixed in a round bottom flask and cooled at 0^0 C in an ice bath. A pre-calculated amount of hydrogen peroxide was then added dropwise to the contents of the round bottom flask with continuous stirring. After complete addition of H_2O_2, the reaction was continued at room temperature under vigorous stirring, until the iodine value of the reaction mixture indicated the complete consumption of olefinic group. The content of the round bottom flask were then poured in a separating funnel followed by addition of ethyl acetate. The lower aqueous layer was removed and discarded. The remaining organic content was further washed with water followed by sodium bicarbonate and brine. Lastly the contents were dried by addition of anhydrous sodium sulphate and concentrated under vacuum in rotary evaporator to get the clear solution of epoxidized oil. The oxirane oxygen content of epoxidized canola oil was determined by method described in literature [105]. The epoxidized canola oil with an oxirane oxygen content of 6.0 wt% was obtained.

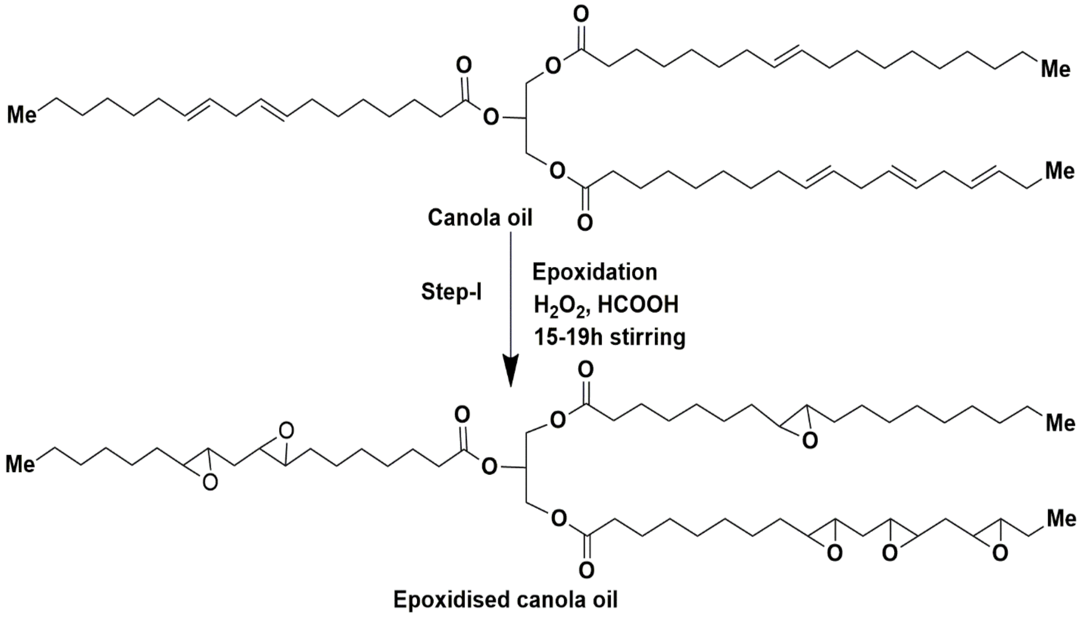

Figure 5.03: Epoxidation of Canola Oil Using Hydrogen Peroxide as Oxidizing Agent

5.1.3. Carbonation of Epoxidised Canola Oil

Epoxidised canola oil obtained as above was mixed with 0.050 mol% of 5,10,15-Tris-(pentafluorophenyl)corrolato-Manganese(III) complex catalyst and stirred in reactor at room temperature and 0.1 MPa CO_2 pressure. The reaction scheme is shown in Figure 5.04. The reaction temperature was then raised to 110^0C and the progress of reaction was monitored continuously by titrating the sample taken after every 2 hr interval for the determination of oxirane content. Infrared spectroscopy and NMR spectroscopy were also used to check the reaction progress by monitoring the disappearance of epoxy group signals i.e. at 845 cm^{-1} and 823 cm^{-1} respectively and the appearance of new peaks due to the carbonyl group of cyclic carbonates at 1805 cm^{-1} as discussed in the subsequent sections. The amount of carbonate groups present per triglyceride were estimated from the difference in oxygen oxirane content using titration method before starting the carbonation and after completion of reaction assuming that no side reactions had taken place which shows a conversion of 95 % [106].

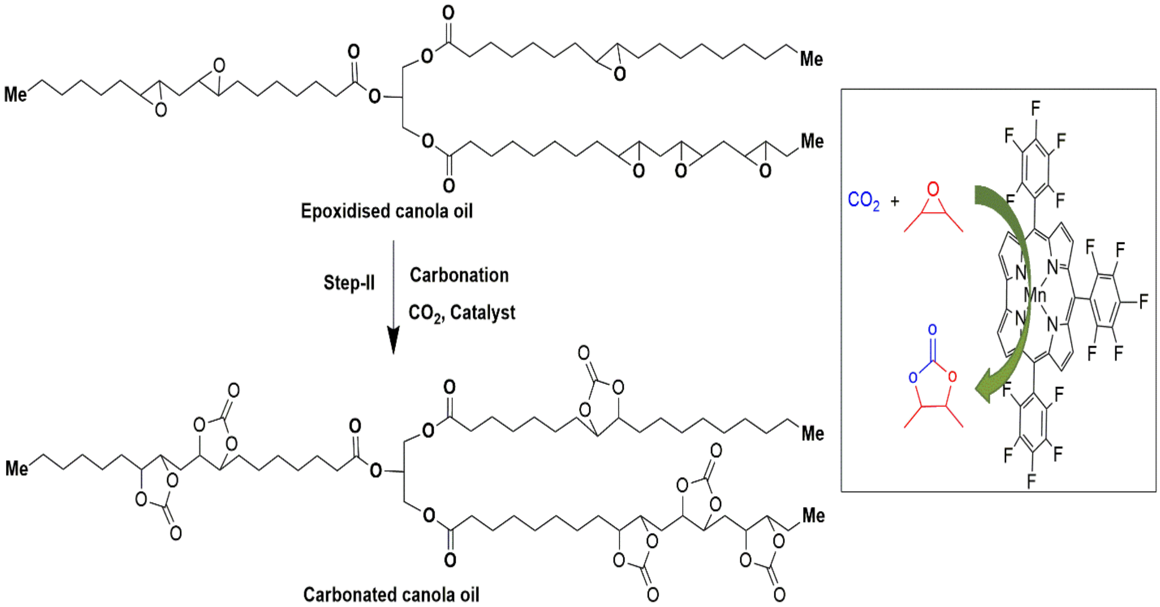

Figure 5.04: Carbonation of Epoxidized Vegetable Oil Using 5,10,15-Tris-(pentafluorophenyl)corrolato-Manganese(III) Complex Catalyst

5.1.4. Preparation of Non-Isocyanate PU from Carbonated Canola Oil

Canola oil based non-isocyanate PUs were synthesized by the reaction of carbonated canola oil obtained as above with various diamines like 1,2-ethane diamine (EDA), 1,6-hexane diamine (HMDA), isophorone diamine (IPDA) and para-phenylenediamine (PPDA). For non-isocyanate PU production, carbonated canola oil was mixed with different diamines (in molar ratio of 1:1) and then cured by heating at 80^{0}C in oven for 8 h. The resulted non-isocyanate PU was further characterized by using UTM, TGA and FTIR for the determination of the correlation between the structures of diamines and the properties of the end product (i.e. mechanical and thermal properties), solvent uptake, etc.

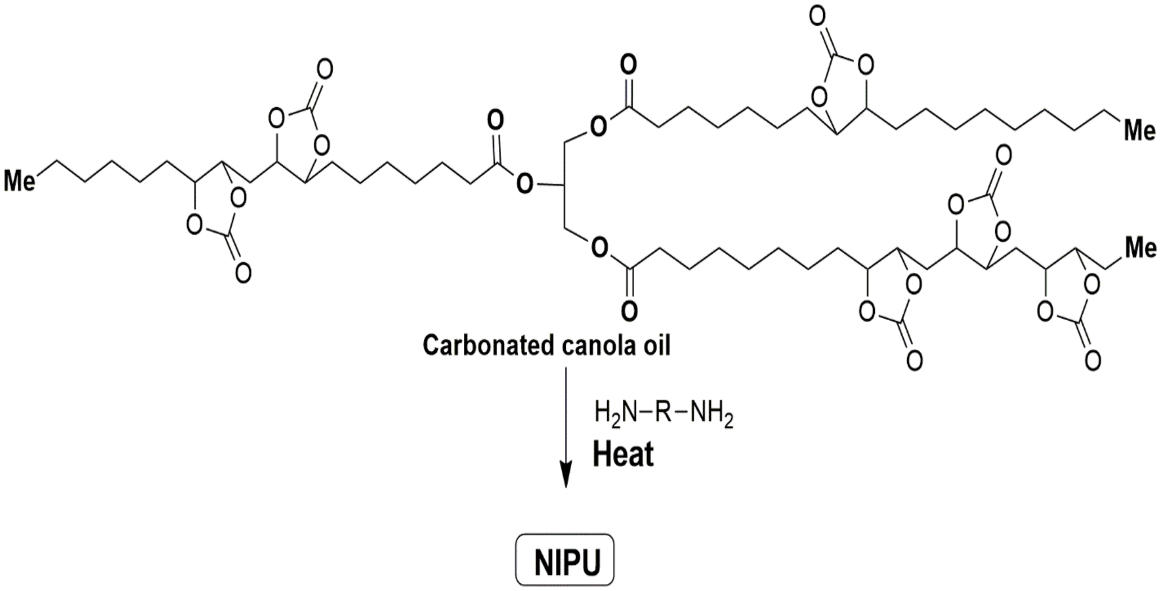

Figure 5.05: Synthesis of Non-Isocyanate Polyurethane from Carbonated Canola Oil

Prepared NIPU samples were tested at 5 mm/min crosshead speed on Universal testing machine (UTM; Instron 3369) in accordance with ASTM D882-97 standard. The ^{1}H NMR spectra of intermediates were obtained on FT NMR spectrometer (400 MHz, Bruker) by dissolving the samples in deuterated chloroform. TGA of non-isocyanate PU were obtained by analyzing the sample on thermogravimetric analyser (EXSTAR 6300) by continuously rising the temperature at the rate of 10^{o}C/min. between temperatures ranging from 30 to 600 ^{0}C under nitrogen atmosphere.

5.2. Significant Findings

5.2.1. IR Spectroscopy

The progress of reaction was determined by monitoring the conversion of epoxy group to carbonate in FT-IR spectra as given in Figure 5.06. Figure 5.06 clearly indicates the disappearance of epoxy peak at 844 cm^{-1} and the formation of new peak due to carbonyl group of cyclic carbonate at 1805 cm^{-1}. An additional peak at 1793 cm^{-1} in spectra of carbonated canola oil is due to carbonyl group present in cyclic carbonate moieties. The complete disappearance of epoxy band in FTIR spectra of sample of carbonated oil also confirms the complete consumption of oxirane ring during the carbonation reaction. Due to weakness of epoxy band, the conversion rate of epoxy group to cyclic carbonates can only be roughly estimated from IR spectra. So the precise estimation of conversion was correlated by NMR spectroscopy, which is discussed in the forthcoming section. The success of reaction between carbonated canola oil and different diamines used was also confirmed by inspecting the disappearance of band at 1800 cm^{-1} due to consumption of cyclic carbonates and emergence of new peaks at 1710 cm^{-1}, 1540 cm^{-1}, 3337 cm^{-1} which are characteristics of carbonyl group of urethane linkage, N-H bending vibrations and stretching vibrations of O-H group respectively and confirms the formation non-isocyanate PU.

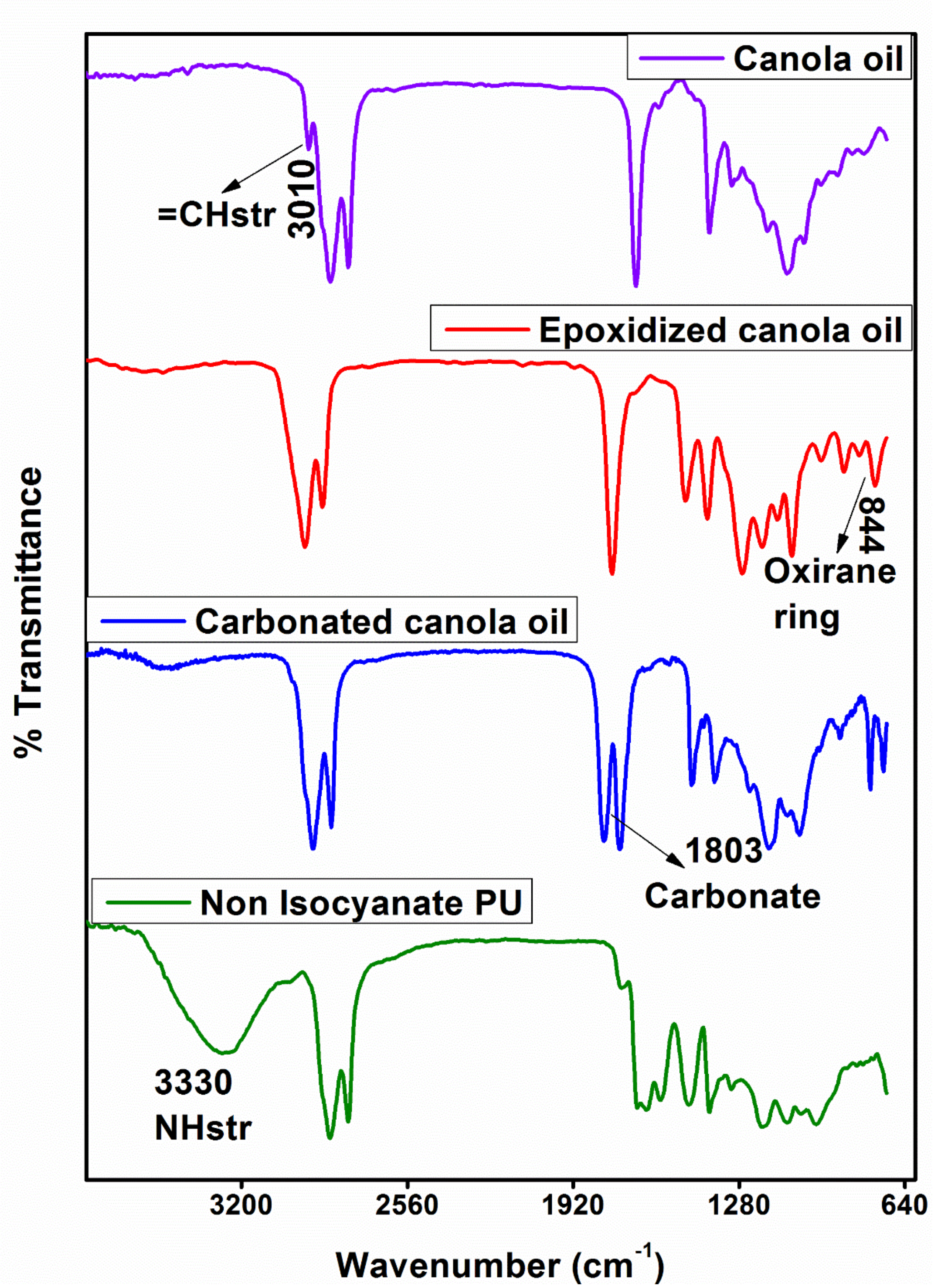

Figure 5.06: FTIR Spectra of Canola Oil, Epoxidized Canola Oil, Carbonated Canola Oil and Non-isocyanate PU

5.2.2. NMR Spectra

The magnetic anisotropy of the corrole ligand with diamagnetic manganese metal center allows the use of Nuclear Magnetic Resonance spectroscopy as a conclusive method to evaluate the character of species interacted with the metal center. ^{1}H NMR spectra also suggest that no side products were formed during the carbonation reaction of epoxidized canola oil. ^{1}H NMR spectra of epoxidised canola oil and carbonated canola oil sample are shown in Figure 5.07. On comparing the curve (a) with curve (b) in Figure 5.07 it is clearly seen that the characteristic peaks of epoxy groups at δ = 2.8 – 3.2 ppm completely disappeared after the reaction of epoxidised canola oil with CO_2 and new bands of cyclic carbonate groups starts emerging at δ = 4.5 – 4.9 ppm which gives an additional evidence of transformation of epoxy moieties to cyclic carbonate groups during the course of reaction. ^{1}H NMR spectroscopy also confirms the proposed mechanism. As previously reported by Heinen et al., there are some common peaks shown by vegetable oil samples i.e. peak at δ = 0.8 ppm shows the presence of terminal methyl group in triglycerides whereas peaks emerging at δ = 1.2 – 1.6 ppm are representing the protons of CH_2 groups present in alkyl chains and slightly downfield signal at δ = 2.4 ppm are due to methylene protons which lies next to the carbonyl moieties [107]. The peaks around δ = 4.1 – 4.4 ppm represents the protons present in glycerol backbone of canola oil.

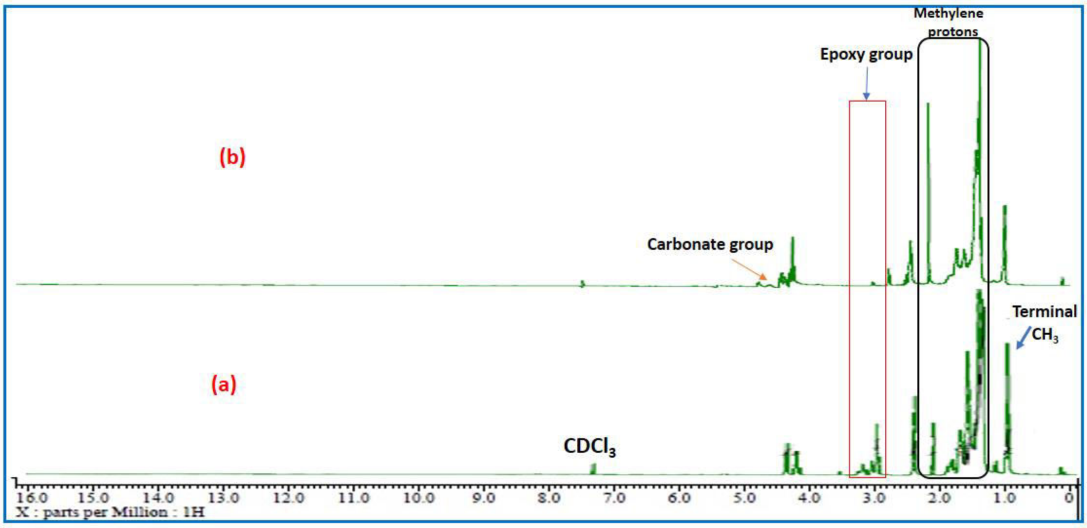

Figure 5.07: ^{1}H NMR Spectra of (a) Epoxidised Canola Oil (b) Carbonated Canola Oil

5.2.3. Thermal Stability of Resulted Non-Isocyanate PU

Decomposition of canola oil based non-isocyanate PU with increase in temperature was monitored using TGA. The TGA curve of non-isocyanate PU obtained by reaction of carbonated canola oil and different diamines is shown in Figure 5.08. The products obtained shows good stability below 200^{0}C temperature followed by slow weight loss between 200 and 300^{0}C. A sudden weight loss was observed at temperature values ranging 320^{0}C to 430^{0}C. As per the DTG curves shown in Figure 5.09, the decomposition of canola oil based non-isocyanate PU was observed in two stages [108]. TGA analysis reveals that non-isocyanate PU obtained from EDA shows better thermal stability at temperature rise of upto 290^{0}C as compared to its linear aliphatic counterpart i.e. HMDA and other diamines. The non-isocyanate PU obtained from IPDA shows higher rate of decomposition at initial temperature rise i.e. above 230^{0}C as compared to non-isocyanate PU obtained from other diamines whereas at higher temperature value i.e. above 410^{0}C the rate of decomposition was similar to the decomposition rate of non-isocyanate PU obtained from PPDA. A comparative weight loss percent data has been shown in Table 5.01 to assess the thermal stability of different formulations.

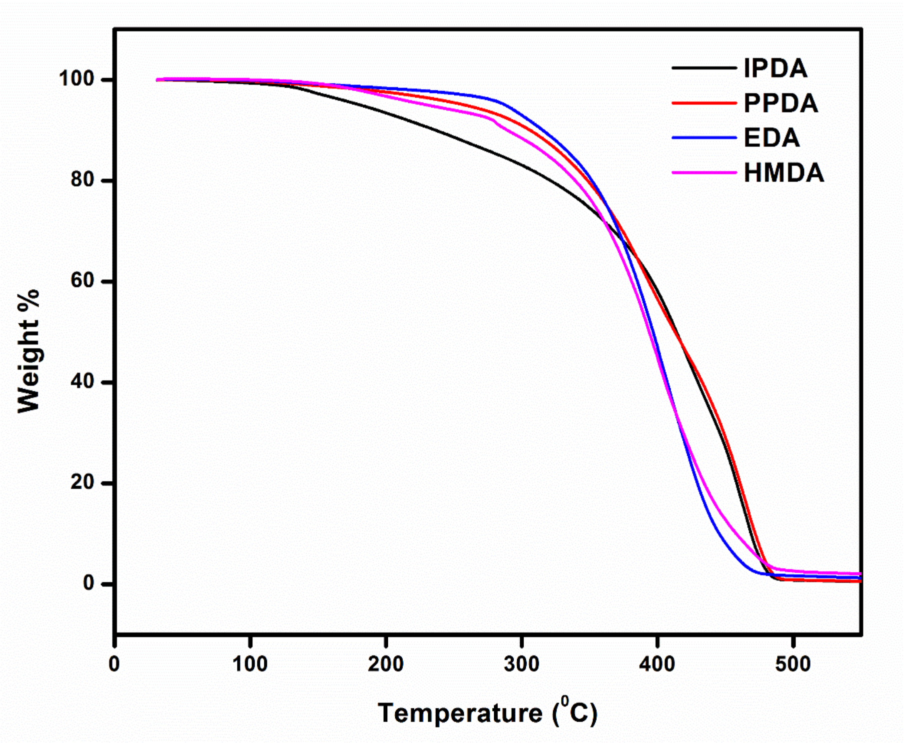

Figure 5.08: TGA Curve of Non-isocyanate PU formulations obtained from different diamines

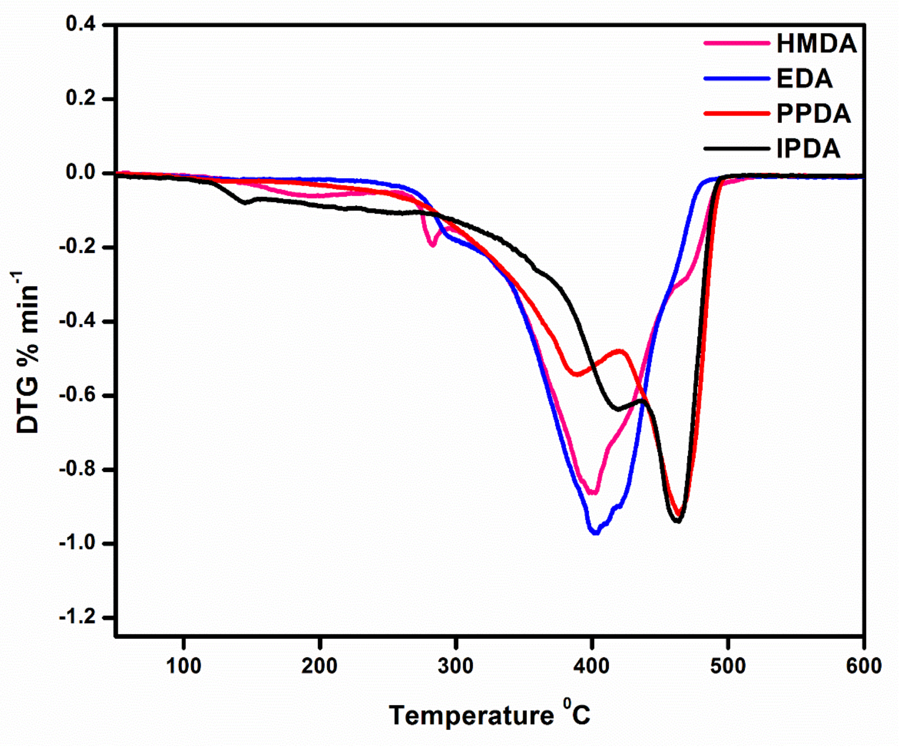

Figure 5.09: DTG Curve of Non-isocyante PU Formulations Obtained from Different Diamines

Table 5.01: Thermal Stability of Non-isocyanate PU Formulations Obtained from Different Diamines

TEMPERATURE* (OCCURANCE OF 10%, 50%,90% DEGRADATION) → **FORMULATION** ↓	**$T_{10\%}$**	**$T_{50\%}$**	**$T_{90\%}$**
Carbonate + EDA	**315**	**397**	**445**
Carbonate + HMDA	**288**	**393**	**457**
Carbonate + IPDA	**236**	**413**	**468**
Carbonate + PPDA	**305**	**412**	**471**

***Temperature in ^{0}C.**

5.2.4. Mechanical Strength

The results of tensile testing of non-isocyanate PU samples are shown in Figure 5.10. It can be clearly seen from the results that the tensile strength varies greatly with change in structure of diamines. It was found that aliphatic diamines with shorter carbon chain length i.e. EDA shows higher strength as compared to diamines having cyclic ring moieties i.e. IPDA. It has been observed that mechanical properties of the conventional polyurethanes obtained by reacting polyols and isocyanates are better as compared to the tensile strengths of non-isocyanate PU synthesized via carbonate route from epoxidized canola oil and different diamines. Lower crosslinking density in non-isocyanate PU as compared to conventional polyurethane can be the reason for this relatively lower tensile strength.

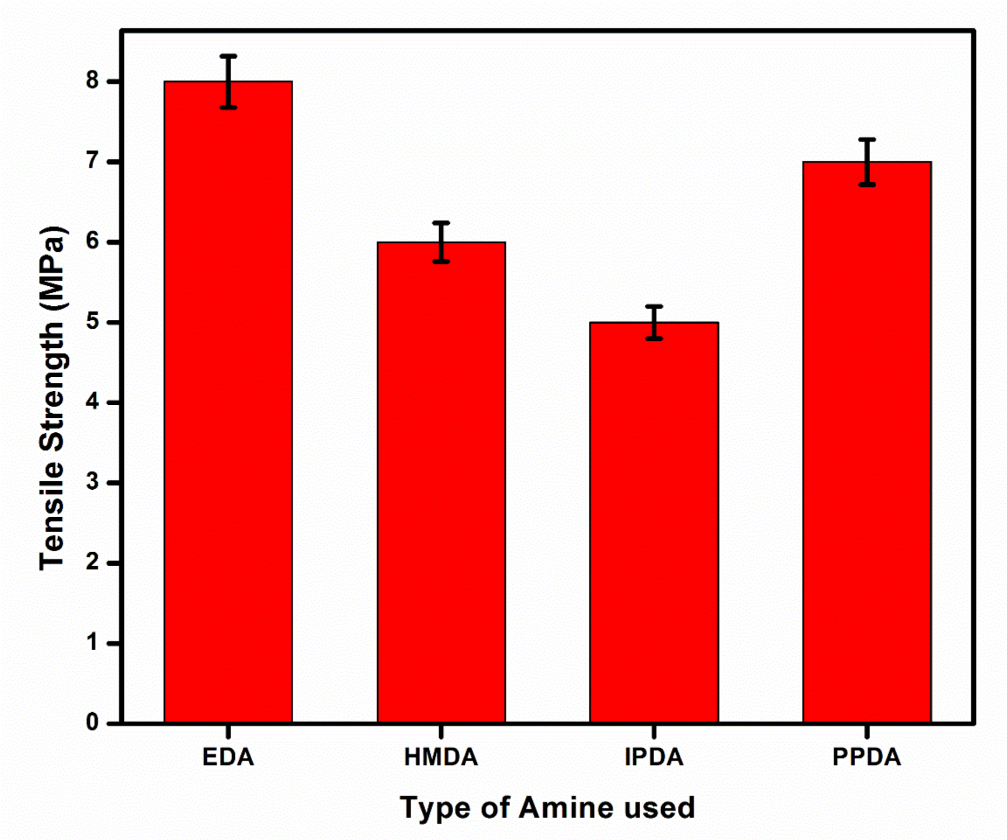

Figure 5.10: Tensile Strength of Non-isocyanate PU Samples of Different Formulations

5.2.5. Chemical Resistance of Non-isocyanate PU

Chemical resistance of the resulted non-isocyanate PU in organic phase and water was studied by observing its swelling behavior in toluene and water. The swelling in toluene is directly influenced by structure of amines i.e. Ethylene diamine showed lowest degree of swelling whereas swelling was found to be highest in case of Hexamethylene diamine. The degree of swelling in different formulations of non-isocyanate PU are shown in Figure 5.11. From the obtained results, it was concluded that the longer chain length in amines i.e. HMDA causes higher swelling (35%) due to low concentration of urethane functional group as compare to amines having shorter alkyl chains i.e. EDA (25%). Also, the aromatic diamines (PPDA) shows lesser extent of swelling as compare to cyclic diamines (IPDA). Water absorption in case of non-isocyanate PU was found to be much higher as compare to organic solvent even at room temperature. The accurate measurement of weights of samples after swelling in water was also not possible due to increase in stickiness of samples before reaching the equilibrium. This high degree of swelling in aqueous medium can be explained due to high polarity of non-isocyanate PU caused by presence of polar hydroxyl and amine groups.

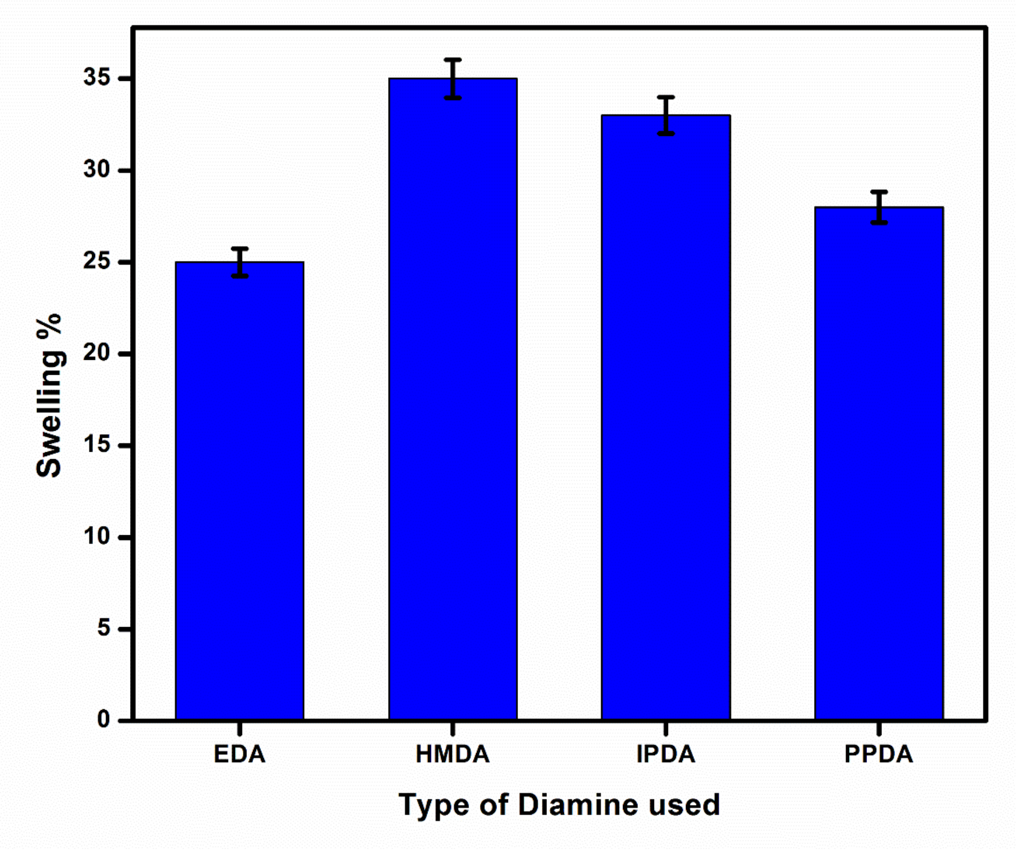

Figure 5.11: Degree of Swelling in Different Formulations of Non-isocyanate PU

CHAPTER 6

CONCLUSION & FUTURE PROSPECTS

6.1. Conclusions

PU Adhesives are one of the important class of polyurethane products. Analogous to other polymeric products, the latest research in PU adhesives is inspired by the utilization of renewable resources as raw materials. The present research is focused on the development of PU adhesives from renewable vegetable oils. Vegetable oils are found to be most useful renewable feedstock for PU synthesis due to the presence of various active site which can be chemically modified into new tailored polyurethane precursors. As polyols are one of the important raw material for PU production, a polyether ester polyols was developed by the epoxidation of transesterified canola oil and polyester polyol from the transesterification of castor oil. The modified polyols were reacted with different types of isocyanate like Methylenediphenyldiisocyanate (MDI), Toulenediisocyanate (TDI), Isophoronediisocyanate (IPDI), Hexamethylenediisocyanate (HMDI) etc. for synthesis of polyurethane adhesives. Further, the isocyanate free route for the PU production was also explored to make the product more ecofriendly. For this, 5,10,15-tris(pentaflourophenyl)corrole was utilized as novel catalyst for coupling reaction between epoxidised canola oil and CO_2 (gaseous) to introduce cyclic carbonate moieties in the oil and further utilized it to obtain non-isocyanate PU by curing with different diamines like EDA,HMDA,IPDA,PPDA. Influence of various factors such as the NCO/OH molar ratio, hydroxyl value of polyols and the amount of reinforcing fillers on the properties of adhesive were studied in detail. The resulted PU adhesives were subjected to NMR,FTIR, DSC, TGA and Universal Testing Machine for characterization and other testing for its properties. Significant findings of this research work are concluded as below:

- The lap shear strength of the resulted adhesive is less at low NCO/OH ratio, which is due to complete consumption of isocyanate by hydroxyl group of polyol, thus shows cohesive type of failure.
- The isocyanate-hydroxyl ratio (NCO/OH) of 1.2 is required to develop the best performing adhesive. As the value of lap shear strength increased with an increase in the NCO/OH ratio upto 1.2. But, with further increase in the NCO/OH ratio, a reverse effect on bonding strength of adhesive was observed.
- It had been observed that, by incorporating nanosized TiO_2 upto a concentration of 3%, adhesion strength of bonding wood sample was found to be increased.
- The introduction of TiO_2 upto 3 wt% to PU adhesive led to a remarkable increase in the lap shear strength and chemical resistance.
- The lap shear strength of synthesized PU adhesive was found to be better than commercially available adhesive i.e. Fevicol^{TM}.
- In case of non-isocyanate PU, it was found that aliphatic diamines with shorter carbon chain length i.e. EDA shows higher strength as compared to diamines having cyclic ring moieties i.e. IPDA.
- TGA analysis of all the prepared PU adhesive samples had shown a stability upto 250ºC and no major degradation has been observed below this temperature.

- It was found that formulations possessing aliphatic diisocyanate moiety shows more stability initially whereas the aromatic ones shows better mid-range thermal degradation resistance.
- Prepared adhesive exhibits excellent curing speed, attained 29% of its ultimate strength within just 5 h of bonding and 70% of its final strength in 1 day.
- Adhesive is found to be fully cured in 4 days; thereafter, no significant change in bonding strength occurred with time.
- The curing speed of adhesive varies linearly with hydroxyl values of polyol.
- Polyurethane adhesives with aromatic isocyanate moiety shows a little faster curing rate with respect to the adhesives samples possessing aliphatic isocyanates moiety.
- The gel time of prepared adhesive was found to be decreased with the increase in the hydroxyl value of polyol.
- It has been observed that adhesive samples prepared from aliphatic isocyanate show more environmental resistance as compared to isocyanates with aromatic moiety.
- Adhesive exhibit good resistance to both hot and cold water, whereas acid and alkali have some deteriorating effect on adhesive strength.
- The addition of nanosized fillers in vegetable oil based PU adhesive led to a remarkable enhancement in its mechanical and chemical resistance, an increase in Tg value, and the adhesion.
- Result of lap shear strength in the filled PU adhesive sample had shown lesser loss in adhesion strength under different test conditions. The TiO_2-filled sample showed comparatively higher resistance in all chemical environments.

- The synthesized adhesive showed much better performance as compared to commercially available adhesive formulation under different conditions of testing.

6.2. Future Prospects

Use of phosgene based isocyanates is the major concern of PU production units. Different catalysts have been reported in past, for synthesis of non-isocyanate PU, such as metal oxides, alkali metal salts, transition metal complexes, ion-exchange resins, Schiff bases, functional polymers, quaternary ammonium and phosphonium salts, ionic liquids, lanthanide oxychloride etc. But, as evident from extensive literature studies the major drawback for non-isocyanate PU production is much long reaction time, which makes the production of non-isocyanate PU almost impossible at commercial scale. This drawback can be overcome by the development of new catalytic systems which actively work on the reduction of time of synthesis of non-isocyanate PU. The proposed catalysts, also related to the present research are the different corrole metal complexes with improved activity, that can be utilized for this type of reactions to reduce the reaction time for quantitative conversion. The future research in the field of non-isocyante PU may include: synthesis of polyfunctional cyclocarbonates, optimization of technologies and experimental procedures for carbonation of vegetable oils, improving the non-isocyante PU formulations for adhesives and sealents and development of non-amine room temperature curing agents for non-isocyante PU synthesis.

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PUBLICATIONS (FROM THESIS WORK)

1. Malik, M. and Kaur, R., “Mechanical and Thermal Properties of Castor Oil–Based Polyurethane Adhesive: Effect of TiO_2 Filler”, Advances in Polymer Technology, 2016, DOI 10.1002/adv.21637.
2. Malik, M. and Kaur, R., “Influence of aliphatic and aromatic isocyanates on the properties of polyether-ester polyol based PU adhesive system”, Polymer Engineering & Science, 2017, DOI: 10.1002/pen.24537.
3. Malik, M. and Kaur, R., “Synthesis of Soyabean Oil based Non-Isocyanate Polyurethane Using Carbon dioxide” published in National Conference on Organic Synthesis and Catalysis, February 17-18, 2016. (held at Guru Jambheshwar University of Science & Technology, Hisar)
4. Malik, M. and Kaur, R., “Study of Different Analytical Techniques Used in Determining the Reaction Extent and End Use Properties of Biobased NIPU Adhesive” published in National Conference on Analytical Techniques and their Applications, March 16-17, 2017.(held at Guru Jambheshwar University of Science & Technology, Hisar)
5. Malik, M. and Kaur, R., “Effect of Adding Nanosized Calcium carbonate as Filler in Soybean Oil Based PU Adhesive”, published in National Conference named NANO INDIA 2017, March 15-16, 2017.(held at Indian Institute of Technology, Delhi)
6. Malik, M. and Kaur, R., “Synthesis of canola oil based NIPU using highly efficient 5,10,15-Tris-(pentafluorophenyl)corrolato-Manganese (III) complex as novel catalyst”, Polymers for advanced Technologies. **(Accepted for publication)**
7. Malik, M. and Kaur, R., “Novel Green synthetic route for development of canola oil based non- isocyanate polyurethane adhesive”, Journal of Adhesion **(under review)**

8. Malik, M. and Kaur, R., “Synthesis, properties and application of bio based non-isocyanate PU adhesives: A review” (manuscript under preparation)

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