Chapter 1

Introduction

1.1 INTRODUCTION

Polymer, though introduced in materials field in a meaningful manner only very recently, occupies a major place and position in our life today by penetrating into almost all branches of civilizations like construction, medicine, automobile agriculture, aerospace and transportations in the form of fibers, films, paints, coatings, adhesives, plastics, rubbers etc. This tremendous increase in the importance of the polymer is attributed to some desirable properties like high strength, light weight, good flexibility, excellent dielectric properties, high temperature stability, resistance to chemicals, amenability to quick and mass production and for fabrication into complex shapes in a wide variety of colors. Some of form polymers almost always meet our requirement. Over and above these properties, one of the most important properties is the versatility of this class of materials which allows designing almost any product required that is from strong articles, flexible rubbers, smooth and fine fibers to soft and resilient foams [1].

Further they can also be used to bond objects, seal joints, fill cavities, bear load. In fact, the domain of polymers extends from clothing to powering a space vehicle and to even replacing a human organ.

1.2 POLYMERS: A BRIEF HISTORY

Polymer chemistry plays stupendous role in our daily life and therefore, it is one of the most rapidly growing branches of science. For last 70 years polymers have gained tremendous attentions of researchers in academics and industry in the fields of chemistry, physics, material science etc.

The origin of polymers leads us to the 18th century. Polymeric materials such as woods, skins, fibers, horns and bitumens were used by early men for transportations, tools and shelter. In 1839 Goodyear vulcanized natural rubber with sulfur to form a cross linked rubber and in the same year Simon demonstated conversion of styrene to a gelatinous mass [2]. Cellulose nitrate, produced by Schönbein in 1846 found uses more as an explosive (gun powder) rather than as a plastic materiral, because of the difficulties and hazards associated with the processing of this polymer [3]. In the very early part of the twentieth century the synthesis of Phenol-formaldehyde resin through condensation polymerizations was reported by Backlands. Few advances in polymer technology were recorded prior to pioneering efforts of Staundiger, Carothers, Otto Bayer, Sperling and many other modern polymer scientists who recognized the true structure and nature of macromolecular material. Polymers, in terms of performance characteristics, not only offer unique properties, applications prospects and diversity, but also novelty and versatility which is not found in any other class of materials

As polymers are composed of same or different repeating units, they can have different molecular structure, chemical and physical properties, thermal and mechanical behaviours. By virtue of this functional and structural diversity in polymers, they have been classified in different groups [4-5].

1.3 POLYURETHANE RESINS:

In early days, the most versatile group available was unsaturated polyester resins. However recently, even more versatile polymer group has emerged named polyurethanes. Polyurethanes based polymers, contain two or more urethane groups per molecule along with other groups such as ester, ether and / or urea which imparts a wide spectrum of properties to this class of polymer.

Polyurethanes discovered by Otto Bayer are made by the polyaddition polymerization [6] by reacting two or more functional hydroxyl or amino group containing compounds with di or poly isocyanates.

The basic patents for Polyurethane obtained as early as 1948 quoted that "These highly porous, light weight materials can be used as structural materials. It can also be used for residential construction, for making toys, furniture, wheels, artificial limbs, shoe soles and orthopedic casts" [7-10]. Inventors had realised potential of polyurethane even during those days. The first commercial polyurethane were Igamid U and Pelon U.

Polyurethanes are rapidly developing as products for the coatings and adhesives industries with unique combination of performance and application properties

The major raw materials for polyurethanes are polyols and diisocyanates. The chemical and morphological structure and hence the final properties of polyurethanes depend mainly on the structure, molecular mass and functionality of polyol used and to a lesser extent on the nature of isocyanate. The other factors which signifiactantly affect the properties of polyurethanes are: stoichiometric ratio of isocyanate to hydroxyl groups, the amount of chain extender used and the processing method adopted.

The chemistry and use of polyurethane resins are documented in a wide array of literature, cited in many reference works and monographs [11-15].

For the manufacture of polyurethane, two groups of at least bifunctional substance are needed as reactants.

1. Compounds with isocyanate groups (diisocyanates)
2. Compounds with hydroxyl groups (polyesters, polyethers etc.)

The groups of commercially useful diisocyanates are not as large as the one of the polyesters and polyethers. The chemical character, structure and molecular size of these compounds have a deciding influence on the course of the reaction as well as the workability and properties of the finished product.

1.3.1 Isocyanates for Polyurethane:

Polyurethane resins, of different type, can be produced from monomeric diisocyanates with a relatively low molecular weight and having a high vapour pressure.

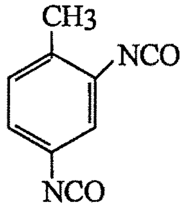
There are a large number of synthesized diisocyanates, which are suitable in principle for the manufacture of polyurethane resins. However, given the requirements of large scale availability and cost efficiency only a few of these products are actually used. These can be divided broadly into (i) aromatic and (ii) aliphatic diisocyanates.

Because of their different structure, the two groups differ widely in their properties, which is of no small significance for their application. Although aromatic diisocyanates and their derivatives are far more reactive than aliphatic diisocyanates, their weather stability is not particularly good and they yellow on exposure to light. Therefore only polyurethanes manufactured from aliphatic diisocyanates are used widely in the formulation of PU systems with high weather stability.

➢ 1.3.1(1) Aromatic Diisocyanate:

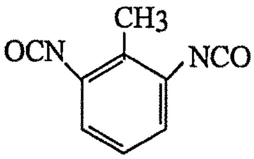
Diisocyanatotoluen or toluene diisocyanate (TDI):

TDI is normally used in the form of an isomer mixture of 80:20 % of 2,4-toluene diisocyanate and 2,6-toluene diisocyanate respectively. The structure of which is shown below.



2,4-TDI

(2,4-toluene diisocyanate)



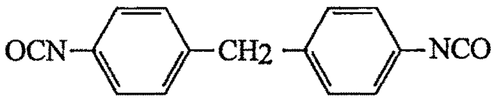
2,6-TDI

(2,6-toluene diisocyanate)

Virtually pure 2,4-TDI or other isomer mixtures (e.g. 65:35) are used for special applications only. Moreover the difference in the reactivity between the ortho and para NCO groups is also exploited specifically for the particular application. At temperatures below 100°C, comapred to the reactivity of the NCO groups in the 2,6 position the NCO group in the 4 position is far more reactive. This important fact is exploited in the variation of reactions by altering the isomer mixture. It also allows to produce derivatives with a narrower molecular weight distribution than that can be achieved with equally reactive NCO groups.

Diisocyanatodiphenylmethane or diphenylmethane diisocyanate (MDI):

The second most important aromatic diisocyanate used in polyurethnes is 4,4'-diphenylmethane diisocyanate. It is also supplied as a standard product by many manufacturers, usually mixed with homologues (approximately 30 to 70% bicyclic, 15 to 40% tricyclic and 15 to 30% polycyclic). These supply forms have the advantage.Unlike pure MDI, they are liquid at ambient temperature and therefore easy to handle and prepare derivatives.



4,4'-MDI

➤ 1.3.1(2) Aliphatic *Diisocyanates:*

1,6-Diisocyanatohexane or hexamethylene diisocyanate (HDI)

Since its introduction in the synthesis of Polyurethane in the early 1960s, 1,6-HDI has become by far the most important base product for preparations of aliphatic derivatives.

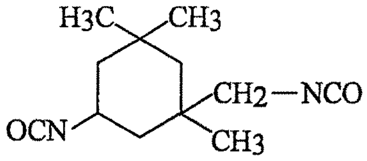
$$OCN-(CH_2)_6-NCO$$

Hexamethylene Diisocyanate (HDI)

PU based on this substance have set a standard of quality which, even today, remains unrivalled.

3,5,5-Trimethyl-1-isocyanato-3-isocyanatomethylcyclohexane or isophorone diisocyanate (IPDI):

This aliphatic diisocyanate is usually supplied as a mixture of approximately 75% cis and 25% trans isomers.



IPDI
(Isophorone diisocyanate)

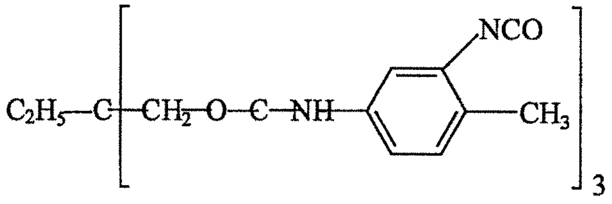
IPDI posseses an unusual characteristic for any industrially available aliphatic diisocyanates, which makes it extremely valuable for custom modification and synthesis. IPDI has two isocyanate groups of differing reactivity, the secondary cycloaliphatic NCO groups being many times more reactive than the primary aliphatic NCO group probably due to steric reasons. Depending upon the type of catalyst used, the reactivity of both the primary and secondary NCO groups could be increased selectively [16] allowing balancing or even a reversal of the reactivity of the two NCO groups

➢ 1.3.1(3) *Polyisocyanates:*

In the PU systems, the term polyisocyanate is used to describe derivatized diisocyanates with at least two and usually three NCO groups, the advantages of which are two fold.

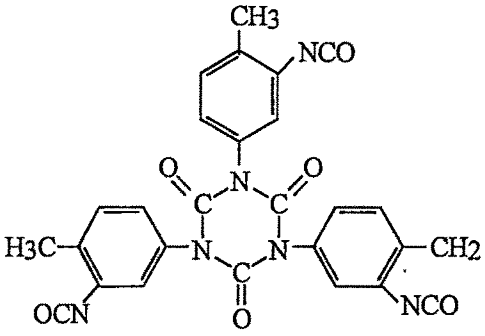
- Increases the functionality so that, when they are subsequently combined with their co reactants, a higher crosslinking density can be achieved in the polymeric film.
- Increases the molecular weight and therefore reduces the volatility of the isocyanate (lower vapour pressure) to ensure safe handling.

The raw materials industry supplies a wide range of polyisocyanates as building blocks for two-pack polyurethane coatings and adhesives. In their 100% supply form, polyisocyanates may be liquids or solids with a hard resin character. To make handling easier, the latter are usually supplied as 50 to 90% solutions. The first polyisocyanate marketed (by Bayer 1955) was based on TDI, where TDI was an adduct with trimethylol propane and smaller amounts of diol of low molecular weight, which is still sold in large volumes. Structure of this adduct is shown below.



Polyisocyanates(approximately 17% NCO)

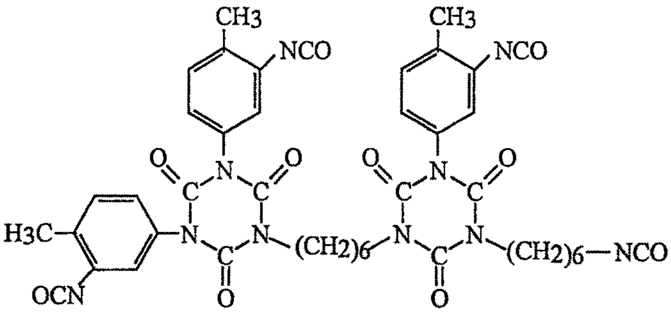
The trimerization of TDI yields polyisocyanates with isocyanurate structures as shown below.



(idealized)

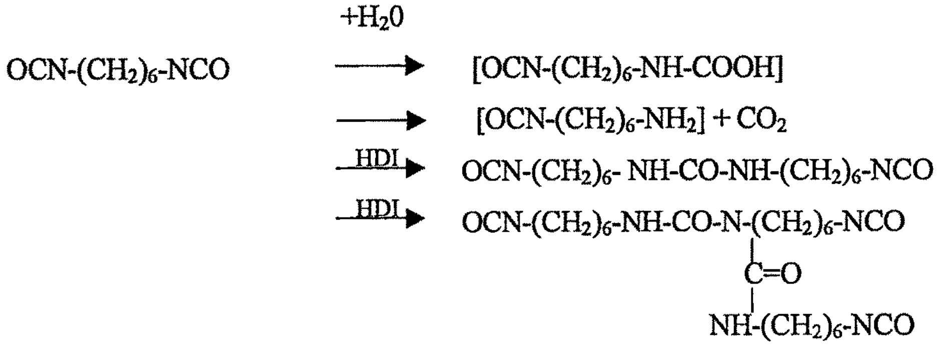
Polyisocyanates (approximately 16% NCO)

Similarly, mixed trimers of TDI and HDI in different ratios could be produced. These substances, which are also solid resins contains approximately 14% NCO and because of their aliphatic isocyanate content, have better lightfastness. Structure of this adduct is as shown below.



Polyisocyanates (approximately 25 to 33 % NCO)

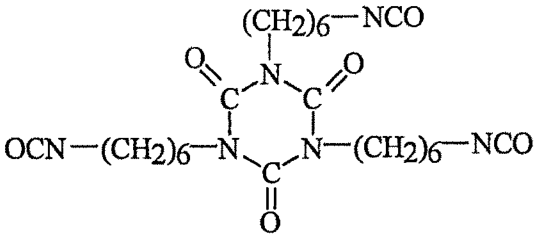
This aliphatic polyisocyanate has since opened many new applications for polyurethane. Two processes can synthesize HDI biuret known, the water process which is widely used, is shown below.



$$\begin{aligned}
OCN\text{-}(CH_2)_6\text{-}NCO &\xrightarrow{+H_20} [OCN\text{-}(CH_2)_6\text{-}NH\text{-}COOH] \\
&\longrightarrow [OCN\text{-}(CH_2)_6\text{-}NH_2] + CO_2 \\
&\xrightarrow{HDI} OCN\text{-}(CH_2)_6\text{-}NH\text{-}CO\text{-}NH\text{-}(CH_2)_6\text{-}NCO \\
&\xrightarrow{HDI} OCN\text{-}(CH_2)_6\text{-}NH\text{-}CO\text{-}\underset{\underset{NH\text{-}(CH_2)_6\text{-}NCO}{|}}{\underset{|}{\overset{}{N}}\!\!\underset{C=O}{}}\text{-}(CH_2)_6\text{-}NCO
\end{aligned}$$

Polyisocyanates (approximately 22% NCO)

HDI trimer is the main component of another important polyisocyanates. Although this type of polyisocyanates was discovered relatively early, the late development of a way to control the trimerization reaction on a large scale [17] meant that the control of the reaction was difficult and hence it attained its current industrial relevance long after the HDI biurets. Polyurethane formulated with the trimer had higher thermal stability and better long-term weather stability than those formulated with the biurets. However, these advantages are tempered by slightly restricted compatibility with certain co-reactants.

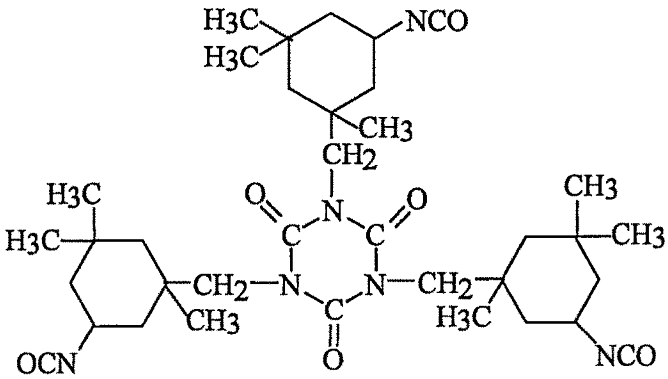


Polyisocyanates (approximately 22% NCO)

Infact, it has already been reported that commercial polyisocyanates are usually mixtures of large analogue chemical compounds.

By shifting the distribution of components towards the low molecular weight range and by specific modification, e.g. the incorporation of allophanates structures in the base molecule, it is possible to reduce the viscosity of the resulting polyurethanes. Such low-viscosity variations of PU based on HDI biurets and HDI trimer have been reported to be particularly suitable for use in the formulation of high-solid coatings, which has only recently become available to the Polyurethane industry.

IPDI trimer was the first technically available cycloaliphatic isocyanurate. Because of its compact and rigid structure, its properties differ remarkably from those of HDI derivatives although it is used in combination with HDI derivatives. This polyisocyanate is a hard resin and cured paint films based on this product range from comparatively hard to brittle. The extent of brittleness could be balanced by the use of a flexible co-reactant. The specific structure of the IPDI trimer gives the paint films better chemical resistance, which may be of key importance in certain applications.



Polyisocyanates (approximately 17% NCO)

Pioneering work by Bayer in the 1980s to transfer polyurethane chemistry to the aqueous phase resulted in completely new formulation concepts for polyurethane [54]. Modified polyisocyanates are becoming increasingly important in this field, where some of the NCO groups are usually saturated with hydrophilic reactants. Substances such as short chain monofunctional polyethers are suitable for this purpose as they are to incorporate in the aqueous phase,however the PU formed has a lower NCO content.

- **1.3.1(4)** ***Prepolymers (Adducts) :***

This umbrella term is used incorrectly to describe products formed by the addition of polyols with an excess of (preferably) diisocyanates or polyisocyanates. The aim is to create reaction products of high molecular weight, which, depending on the functionality and degree of branching of the base components, are themselves, branched to a greater or lesser extent and yet remain soluble. They are characterized by a content of between 3 and 18% of free reactive NCO groups. For this reason, prepolymers are similar in their reaction to the polyisocyanates described in above section.

1.3.2 Polyols for Polyurethanes :

Besides the isocyanates, compounds with several hydroxyl functions(i.e. polyethers, polyesters) in the molecule are the important components for the formations of polyurethanes.

Lower molecular weight compounds such as ethylene glycol, glycerine, butane diol, trimethylol propane etc., act as chain extenders or as cross linkers. Higher molecular weight polyols are major components for the formation of the polyurethanes and their structure essentially contributes to the properties of the final polyurethane product. These higher molecular weight polyols belong mainly to two classes of substance: the polyesters and the polyethers, which themselves are almost exclusively manufactured by the synthetic routes.

The polyols used in polyurethane manufactures have in general an average molecular weight between 200 and 10,000 depending on the applications envisaged. The polyhydroxyl compound could be tailor made for synthesis of a particular PU product by varying the type/ratio of raw materials used along with the manufacturing conditions.

➢ *1.3.2(1) Polyether polyol :*

Polyether polyols are made by the reaction of epoxide (oxarine) with starter compounds containing active hydrogen [18]. There are mainly three groups of materials required for the production of polyether polyols

1. Oxygen containing compounds like epoxides or tetrahydrofuran
2. Starter compounds containing active hydrogen
3. Ionic catalyst.

Among the epoxides, propylene oxide and ethylene oxides [19] are widely used. Limited use of teterahydrofuran and polyethylene glycol has been reported due to its hydrophilic characteristic.

As starter compounds for the polymerizations of epoxides, all organic compounds with active starting alcohols e.g. alcohols such as glycols (ethylene, diethylene and propylene glycols) are used to produce branched, trifunctional polyethers, glycerine and trimethylolpropane.

Almost exclusively strong bases are being used in small amounts as catalyst for the polyaddition reaction as particular potassium hydroxide is used while sodium hydroxide and tertiary amines are being occasionally used. The reaction can also be acid catalyzed by [20] Lewis acids like boron triflouride, stannic chloride or combinations of ferric chloride with thionyl chloride. The acid catalysis is not preferred, because it promotes side reactions [21,22]

- ***1.3.2(2) Polyester polyols:***

In general, organic esters are formed in an equilibrium reaction of alcohols, with organic acids through a condensation reactions where also water is formed as shown below [23].

$$\text{R-OH} + \text{R' COOH} \longrightarrow \text{R' COO R} + H_2O$$

Polyesters contain ester groups as a repeat unit in the main chain backbone, and to obtained by polycondensations of multi functional carboxylic acids and polyhydroxyl compounds. Polyesters with functional hydroxyl group have always been viewed as the classic co reactant in two pack polyurethane systems. Polyesters have a wide range of application, because of their high OH content and the achievable cross linking density, often more suitable for use in formulating systems having high chemical resistance, even though the resistance to hydrolysis is limited by the presence of saponiifable ester group.

Production of polyesters for polyurethane application required essentially two groups of multifunctional components: hydroxyl compounds and carboxylic acid.

For this purpose Ethylene glycol, diethylene glycol, triethylene glycol, 1-4 butanediol, 1,6 hexanediol, neopentyldiol as well as 1,3 butanediol are used as hydroxy compounds. Branched triol components such as trimethylol propane, trimethylol ethane, glycerine as well as few long chain trihydroxyl compounds are also used [24- 27].

Among organic acids used for polyurethane synthesis , the most important are adipic acid [28], phthalic acid, isophthalic acid [29] vegetable oil fatty acid [30] and terephthalic acid. Further, long chain acids such as azaleic acid, sebacic acid, tricarboxylic acid are also useful but their use is limited because of the high cost.

There are three processes available for the production of polyesters

1. Dry process (Vacuum melt process) [31]
2. Carrer gas melt process [32].
3. Azeotropic process [33]

The common goal of the all the above processes is to remove the resulting water from reaction mixture completely and as mildly and in the shortest reaction time possible in order to push the equilibrium of reaction to the ester side.

The first phase of the esterification is common for all the above three processes. Under the inert atmosphere up to 90% of the reaction water is rapidly distilled out over a temperature range of 125-220 ^{0}C under normal pressure [34]. As acid value reaches significantly low, the reaction rate also decrease immensely. Therefore, subsequently the second phase of the esterification requires vigorous condition to speed up the reaction. The above named three processes attain this goal in the following manner.

In the *Vacuum melt process* as the vacuum is applied to the mixture, oligoesters are formed in the first phase. Between 170 to 230^{0}C temperatures as the pressure is reduced stepwise, along with the remaining water of the reaction, the excess diol as well as the small amount of side products (lower molecular weight ethers, aldehydes and ketones) are also distilled off.

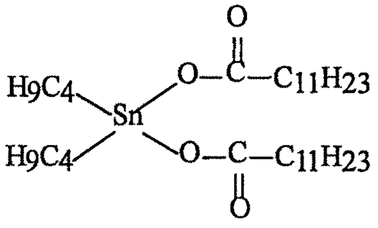
With *carrier gas melt process* the distillable portions are removed through sparging of an inert gas through the reaction mixture. The amount of diol lost in this process is higher than with the vacuum distillation process and must be taken in to account while calculating the stoichiometry of the reaction.

The *azeotropic process* is based on the use of azeoptropic mixture, which is recirculated back to the reactor. For this purpose an inert solvent such as toluene, xylene etc. is used as entraining agent with whose help water of the reaction is removed from the mixtures. The azeotropic process is unsatisfactory when ethylene glycol, 1,2 propylene glycol are used as the diol components, because both can form an azeotropic mixture with the entraining agent, and hence this process is carried out at normal pressure and relatively low temperature (at about boiling point of solvents). Residual amounts of entraining agent are removed by further vacuum distillations.

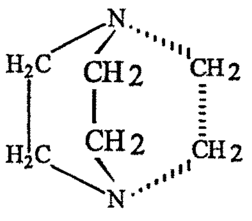
1.3.3 Catalyst for Isocyanate Reactions:

Although the reaction between hydroxyl group and an isocyanate group is relatively fast, reaction rate can still be increased by using a suitable catalyst irrespective of the nature of the isocyanate used i.e. aliphatic or aromatic catalysts also affect the process parameters of the reaction, e.g. the physical properties of the finished products, fluidity of the reaction mixtures etc.

In polyurethane particularly the use of catalyst is more essential. Aliphatic isocyanates in order to compensate for their lower reactivity compared to aromatic isocyanates and this satisfies the requirements for coatings and adhesives applications. Two groups of catalysts are of key interest here. *Metal catalysts* activate the isocyanate group and accelerate the urethane reaction. Dibutyltin dilaurate (DBTL) is often used as in zinc octoate, which is also used as a drier for binders, which cure the raction by oxidation. Also stannous octoate is widely used as catalyst for polyurethane. Amine catalysts; on the other hand, accelerate the urethane reaction primarily by activating the hydroxyl group. 1,4 –diazobicyclo [2.2.2] octane (DABCO) is also widely used as a catalyst



DBTL



DABCO

Combination of both (DBTL and DABCO) types of catalyst produces a synergistic effect which can be utilized beneficially.

1.4 APPLICATIONS OF POLYURETHANES:

There are different applications of polyurethane. Some of the significant and well studied applications are discussed here below.

- *Polyurethane as Foam:*

One of the most widely used common forms of PU is the foam. Innumerable references and patents are available on a variety of PU foams and their modification. The preparations of foams involve the use of blowing agents such as chlorofloro carbon compounds, which bring about ozone depletion. Hence recently, Kanetani et al [35] have reported foams with uniform cell structure by predispersing the heat decomposable blowing agent.

Attempts were also made to obtain foams either without using blowing agents [36,37] or by using blowing agents that do not cause ozone depletion [38]. Quinn et al [39] have reviewed the developments and applications of PU foam. Amayoshi et al [40] have patented the method of preparing heat insulating polyether based PU foams. Mechanical properties of closed cell PU encapsulated foam were measured as function of foam density by Goods et al [41].

- *Polyurethane as Coatings:*

Another important applications of PU are coatings. A huge number of reviews are available on importance of PU coatings on the trends in their developments [42-44]. Important PU coating systems like low temperature curable liquid PU compositions for thick film coatings, Hanabusa et al [45] Takayanagi et al [46] have synthesized acrylic based aqueous PU coating and Chihara et al [47] have developed EPDM based PU coating material useful in automobiles.

- *Polyurethane as Adhesives:*

PU adhesive compositions having good flexibility, alkali resistance and storage stability have been prepared by Yanagusawa et al [48] and Muenzmay et al [49]. Similarly Nagai et al [50] developed a method for the synthesis of one-component moisture curable PU adhesives compositions.

Several reviews are available on urethane adhesives [51-55]. Ratnam et al [56] have developed solvent based PU adhesives for shoe soles by polymerizing Toluene diisocyanate (TDI), polypropylene glycol (PPG) and propylene glycol (PG).The polymerizations were carried out in methyl ethyl ketone at 75 ^{0}C using NCO/OH of 1:1.1. The product with 30 % solid content was tested as adhesives for bonding leather with rubber, PU and PVC soles and the bonding characteristics were also studied.

- *Polyurethane Elastomers:*

The polyurethane elastomer is a very important group of product due to their higher hardness at any given modulus, higher abrasion and chemical resistance, excellent mechanical and elastic properties and also some other specific properties. Elastomers are a class of materials displaying high reversible deformation. During the formation of elastomers two types of cross-linking physical cross-linkings are possible. They are crosslinking through (i) hydrogen bonding or cross linking through interactions between two groups in the tri or multi functional substances. From literature survey, it is apparent that today there are several polyurethane elastomers of different range are available each one having suitable applications [57-59].

With the increasing industrial use of urethane coatings and adhesives, there has been an enormous growth in demand for these groups of raw materials within the space of just a few years. India has been short of urethane in market for a variety of reasons, largely related to the poor availability of raw materials and their high price in the local market. So, research on urethanes has mainly been aimed at improving the performance of the product formed and cost effectiveness.

To cut down the cost of raw materials, the substitution of modified naptha products as primary materials with renewable materials from biological source as primary materials is being pursued. Present day economic policies also favour the use of renewable resources.

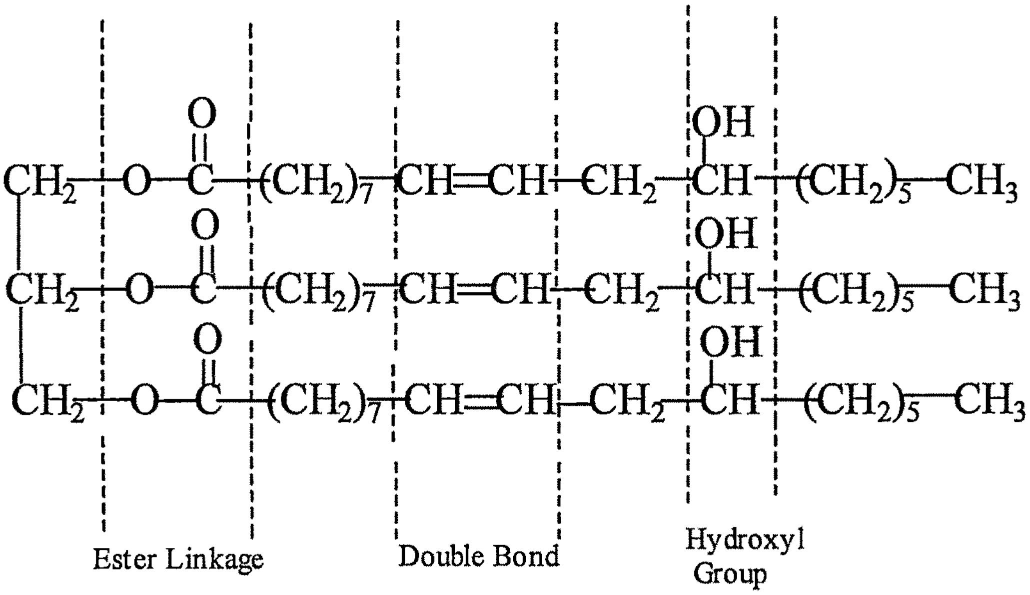
1.5 RENEWABLE RESOURCES

Concern for the stability of future petroleum supply has stimulated much attention in the past few years towards the need to emphasize the use of natural renewable materials as replacements or substitutes for production of materials now derived from petroleum and coal. However, going beyond the set idea of replacements or substitute materials, it shoud be noted that renewable resources have valuable, sometimes different properties of their own.

The term "renewable resource" has come to mean sources of energy or product that can be used, grown or replenished naturally, as opposed to mineral and petroleum products which once used are gone for ever. Among the various renewable resources available, plant product rank very high viz. wood, cellulose, starch, rubber, triglycerides oils etc.

Many plants yield valuable oils, such as corn oil, linseed oil and cottonseed oil, besides food uses, these oils provide the basis for paints, coatings, adhesives and other industrial uses due to the presence of multiple double bonds, which allow the ready polymerization of these oils. Agro based renewable resources like castor oil (CO) is unique among vegetable oils due to the presence of another reactive site like hydroxyl group in addition to points of unsaturations. The number of hydroxyl groups and double bonds are identical in castor oil. Castor oil is unique among all fats and oils in that, it is the only source of an 18 carbon hydroxylated fatty acids with one double bond. The main constituent of castor oil is Ricinoleic acid (12 hydroxy-9 octadecenoic acid) comprises approximately 90% of the fatty acid compositions. Castor oil yields derivative having product uniformity and consistency. Moreover castor oil is non-toxic, biodegradable and obtained from renewable sources. The structure of castor oil represents unique functionality and its unusual versatility.

The hydroxyl groups, double bonds and ester functionalities in castor oil provide reaction sites for the preparations of many useful industrial derivatives. The chemical reactions of these basic functionalities are depicted in Table 1.



CASTOR OIL

The functionality may be modified at the various carbons through a wide range of reactions(Table 1). The unsaturations can be modified by hydrogenation, epoxidations, and addition polymerization reactions. The hydroxyl groups can be readily acetylated and alkoxylated and can also be eliminated by dehydrations to increase the unsaturations, if required.

Table 1: Chemical reaction in castor oil

	Nature of Reaction	**Added Reactant**	**Type of Product**
Ester Linkage	Hydrolysis	Acids, enzymes or Twitchcell reagent catalyst	Fatty acids, glycerol
	Esterification	Monohydrixc Alcohols	Esters
	Alcoholysis	Glycerols,glycols, pentaerythritol etc.	Mono-and diglycerides, monoglycols etc.
	Saponification	Alkalies, alkalies plus metallic salts	Soluble soaps, insoluble soaps
	Reduction	Na reduction	Alcohols
	Amidation	Alkyl amines, alkanoamines, etc.	Amine salts, amides
	Halogenation	$SOCl_2$	Fatty acid halogens
Double Bond	Oxidation, Polymerisation	Heat, oxygen, crosslink agent	Polymerized oils
	Hydrogenation	Hydorgen(moderate pressure)	Hydroxystearates
	Epoxidation	Hydrogen peroxide	Epoxidized oils
	Halogenation	Cl_2,Br_2,I_2	Halogenated oils
	Addition reaction	S, maleic acid	Polymerized oils
	Sulfonation	H_2SO_4	Sulfonated oils
Hydroxyl Group	Dehydration, Hydrolysis, distillation	Catalyst (plus heat)	Dehydrated castor oil, Octadecadienoic acid
	Caustic fusion	NaOH	Sebacic acid, capryl alcohol
	Pyrolysis	High heat	Undecylenic acid, heptaldehyde
	Halogenation	PCl_5, $POCl_3$	Halogenated castor oils
	Alkoxylation	Ethylene and/or propylene oxide	Alkoxylated castor oils
	Esterification	Acetic-, phosphoric- ,maleic-, phthalic anhydrides	Alkyl and alkyl aryl esters, phosphate esters
	Sulfation	H_2SO_4	Sulfated castor oil (Turkey red oil)
	Urethane reactions	Isocyanates	Urethane polymers

Various polyol systems were synthesized with the main aim of producing cheaper raw materials without any compromise in performance properties of the coatings and adhesives. Castor oil, vegetable triglycerides possessing hydroxyl groups, is frequently utilized as polyols in the synthesis of cross-linked polyurethanes [60], in industry because of its excellent required properties.

1.6 SURFACE COATINGS:

Surface Coatings have been a part of man's environment for thousands of years. The caveman was probably the first to use paints for his cave paintings. The ancient applied coatings to their ships, utensils, musical instruments weapons, temples and palaces [61]. For centuries, surface coatings were used only for decorative purpose and their preparations and applications remained more of an art than science. The materials used were derived from the nature. After the industrial revolution the need for protection of metal objects arose. This in turn slowly transformed the art of paint making and its application in to science which gave scientists impetus for making efforts to better understanding of coating compositions, applications and testing. Besides the discoveries of new materials and their various application constantly pose a challenge for surface coatings research in terms of satisfying increasingly stringent requirements of problem coupled with decorations in certain instances under diverse service conditions.

The main constituents of coatings are basically binders, diluents, additives and pigments. Not all coating compositions have every ingredient but much care during formulations are required to produce a coating which will be easy to apply under changing conditions and pleasant to look at when dry.

Binders of resins are polymeric materials and are the needful (principal) ingredient of coatings. Their primary function is to form a film which can withstand normal physical abuses. They also bind other ingredients together in the film. It is therefore, obvious that most of the film properties such as drying properties, mechanical properties, optical properties and the performance properties of the coatings are governed by resin. This effect was especially important in oil based coatings and is the reason for the historical importance of resin [62].

Diluents are volatile materials that evaporate from the coatings during the film forming process. They are very important components of liquid coatings formulations. Generally organic solvents are needed in all coatings, including those, which are waterborne, except power coatings and other solvent free coating systems. Solvents give the binders a processable, consistency and provide a means of actually adjusting the viscosity for coating application. Appropriate solvent compositions (methyl ethyl ketone: xylene) improve wetting. The drying of the weight film and stability of condensation products are facilitated. The flow properties and gloss are also increase.

Additives are materials that are included in small quantities to modify some properties of the coatings. They play a decisive role in the formulations and functioning of coatings [63].

1.6.1 Classifications of Surface coatings:

Surface coatings can be classified into two general types, convertible and non convertible. Further classifications are possible – particularly with convertible coatings based on their curing mechanism (air dry, stoving etc.) and also based on their performance characteristics (heat resistance, corrosion resistance etc.). In brief the types are followings [64-65].

1.6.1 (1) Primers:

Primer is the first coat of coatings to be applied to a surface like metal, cement and wood. Its main functions include providing adhesion to the substrates, providing good inner coat adhesion for subsequent coats, regulating moisture movement and providing corrosion resistance.

1.6.1 (2) Sealers

Sealers are used to eliminate the suction of coating when applied on the substrates that are porous and where the coatings medium can upset the pigments/binder ratio of the coating applied.

In some cases the formulations of primers can be modified to enable it to function as a sealer also.

1.6.1 (3) Putty or Fillers:

When substrates contain holes or deep indentation they are treated with putty after applications and drying of the primer. Putties or paste fillers are very highly pigmented so that they dry without shrinkage and can be rubbed down to smooth substrates before applications of further coat of coatings. The putty is an under bound pigmented coating of various components of compositions and thus it is porous when dry and require treatment with sealer before further coatings.

1.6.1 (4) Undercoats:

They are applied over the primers. Undercoats are fairly highly pigmented to give good opacity and adequate dry film thickness of the coated film. They usually dry to an eggshell finish. They serve as a base coat for finishing coat (usually enamel) to be applied on it.

1.6.1 (5) Finishing coatings

Finishing coats are the coatings whose dried films exhibit a high gloss (enamel), semi-gloss, eggshell or matt finish. These are the topcoats and directly exposed to the environments.

1.6.1 (6) High build coatings:

High build coating are meant for protection by giving a high dry film thickness in the minimum numbers of the coats. This is achieved by the incorporations of a gelling agent in the coating compositions, which allows applications of thick coats without the risk of sagging on vertical surface.

1.6.1 (7) High solids coatings

High solids coatings contain non- volatile more than 70% by weight so that the shrinkage of the film on drying is minimum. These coatings are environmentally friendly since the low solvent content leads to less atmospheric pollution that is caused by traditional types of coatings.

1.6.1 (8) Solvent less coating:

Solvent less coating are based on liquid resins of low viscosity and are used where the presence of solvent is undesirable e.g. coatings applied in the interior of tanks. These coatings are applied on submerged parts of steel and concrete structure. These paints of high dry film thickness are formulated to cure either by chemical reaction (two pack types such as epoxides or polyurethanes) or are nonconvertible types (e.g. high build chlorinated rubber), which dry slowly by solvent evaporations

1.6.2 Polyurethane Coating Systems:

The field of polyurethane coatings is one of the most rapidly expanding areas of the coating industry. Polyurethane coatings (or simply urethane coatings) are defined as coatings based on polymers, which contain two or more urethane groups per molecules. Polyurethane coatings can be classified by various criteria such as chemical basis, use of applications and physical composition. There are six different polyurethane coating types in the ASTM D16 Standard [66]. Table 2 summarizes the characteristics and properties of the six ASTM polyurethane coating types. Most high solids and 100% solids polyurethanes coatings for the purpose of high performance are designed using the plural component format of the ASTM D16 Type V.

Table 2: Six ASTM polyurethane coatings types

ASTM description	Type I One–Package Pre reacted	Type II One- package moisture cured	Type III One- package heat cured	Type IV Two-package catalyst	Type V Two-package polyol	Type VI One package reactive lacquer
Characteristics	Unsaturated drying oil modified: no free isocyanates	Contains free isocyanates	Blocked Isocyanates	Isocyanates prepolymer plus catalyst	Part A-Isocyanates rich Part B polyols	Fully polymerized dissolved solvents
Main curing Mechanism	Oxidations of drying oil; Solvent evaporations	Reactions with atmospheric moisture	Thermal release of blocking agents and then reaction	Reactions of Isocyanates with moisture and/or components in catalyst	Reactions between part A and Part B instant curing possible	Solvent evaporations
Polymer	Alcoholyis products of drying oils reacted with isocyanates	Higher Molecular weight diols and triols	Prepolymers forms to an adduct with blocking agents such as phenol	Prepolymer is similar to Type II but catalyst could contain polyols	Relatively lower molecular weight	Thermoplastic copolymer with relatively high molecular weight
Chemical resistance	Fair	Fair to Good	Good to Excellent	Fair to Excellent	Good to Excellent	Fair
Corrosion resistance	Poor	Poor to good	Fair to Good	Fair to Excellent	Fair to Excellent	Poor to Fair
Special considerations	Better Abrasion than most of paints	Properties and Curing affected by humidity	Heat required for cure	Similar to Type II but with speed of curing	Special equipment may be required	VOC limitations

1.7 ADHESIVES:

Adhesion

Adhesion, the phenomenon, is defined as "the state in which two surfaces are held together by interfacial forces which may consist of valance forces or Interlocking action, or both.

Adhesives are the materials which are defined as "substances capable of holding materials together by surface attachment.

These terms are rather general, and it is well known that valence forces are not required in order that excellent adhesion be obtained, but that vander Walls forces are in themselves sufficient to cause excellent adhesion.

The adhesive industry is bolstered by hundreds of years of trial and error. This long history was shared by significant additions to the fundamental supporting sciences and the development of advance materials and processes.

Early man utilized the phenomenon of adhesion without appreciating its significance. The matting of hair with blood, the traping of insects in soft pitch, the sticking of wet leaves to bare skin have been common place, and doubtlessly the early "stoke of genius" in utilizing natural products as adhesives was triggered as result of these simple occurrences.

For thousands of years, natural adhesives were the only materials available and to this day the use of fish glues, blood glues etc. is common practice in certain application, which were generally tacky in their original form

In the early 1900s, synthetic polymeric adhesives began displacing many of these naturally occurring products owing to their stronger adhesion, greater for diverse formulation, and superior resistance to operating environments. The development of modern polymeric adhesives began about the same time as the polymer industry itself early in the 1900s. In fact, the polymeric and elastomeric resin industry is bound very closely to the adhesive industries. Historical developments of various kinds of adhesives has been discussed in a previous report [67].

As time passed, other naturally occurring materials were converted to useful adhesives. The discovery of phenolic resin by Backlands, literally opened the door for the multiplicity of adhesives. Different types of adhesives are available like phenolic resin, urea-melamine, cellulosics, poly (vinyl chloride), poly(vinyl acetate) caused a rapid acceleration in the use of synthetic polymer as adhesives. Among the recent successful additions to the above catagory of adhesives are the epoxides and urethanes, with significant volume of both of these resins widely appearing in adhesive fromulations

One of the important areas of the present day research is to explore potential use of renewable and non convertible raw materials for adhesive production [68]. Now a day's about 40 % of the total adhesive production is plant derived [69]. Also, the chemistry of natural materials or renewable resources has been explored in the adhesive industry and it opened a new route of synthesizing novel resin which can be used as adhesives having good adhesion property.

The most common among these materials are oils. Incorporations of oils- both vegetable and animal are used in manufacturing and modifications of various resin, are frequently practiced in laboratory as well as at commercial level. Often such attempts have been made to imporve the cost effectiveness of the synthesis of the resin. Synthesis of adhesives from renewable resource like ligin, tannins, carbohydrates and fatty acids have been reported [70].

1.7.1 General requirements of all adhesives:

If one look at the adhesives bonding "process" as a complete procedure, encompassing all aspects of material selection, joint design, productions, etc., then the basic requirements irrespective of the application intented are same and the prerequisites for successful application of adhesives described as below [71].

1) Cleanness of the substrate surfaces
2) Wetting of the substrate surface (intimate contact of the adhesives on the substrates)
3) Solidification of the adhesive
4) Forming a "Joint" structure (adhesive, interface regions and adherends) that is resistant to the operating stress and environment.
5) Design of the joints
6) Selections and control of materials and manufacturing process.

The testing of adhesives is a complex process owing to the involvement of various parameters that can affect the test results. Interactions of the adhesives and adherends are often obscure.

A standard test report usually documents the result measurements such as tensile shear strength, peel strength, lap shear strength, cleave strength., fatigue strength, impact strength etc. It also indicates all of the pertinent conditions that are required to assure reproducibility in subsequent testing.

As science has progressed over the centuries, the science that supports adhesives has developed a jargon and language of its own.

1.7.1(1) Types of Adhesives :

Adhesives are chosen for their holding and bonding power. They are generally materials having high shear and tensile strength. Generally there are two types

Structural adhesives and ii) Non structural adhesives

Structural Adhesives are adhesives whose strength is critical to the success of the assembly

e.g. epoxy based adhesives
Thermosetting acrylic based adhesives
Thermosetting urethane based adhesives

Structural adhesives provide long lasting adhesion strength to the materials on which they are applied.

Non-structural adhesives are adhesives with much lower strength and permanence

e.g. pressure sensitive films, wood glues, elastomers, sealants

1.7.2 Polyurethane Adhesives:

Polyurethane chemistry has added valuable contributions to the improvements of adhesive bonding by developing many raw materials for the productions of polyurethane adhesives.

Polyurethane adhesives are normally defined as those adhesives that contain a number of urethane groups in the molecular backbone or are formed during use, regardless of the chemical compositions of the rest of the chain. Thus typical urethane adhesives may contain, in addition to urethane linkages, aliphatic and aromatic hydrocarbons, esters, ethers, amides, urea and allophanate groups.

The demand of PU adhesives has increased tremendously from shoe sole manufacturing to aerospace programme sectors.

As already described, polyurethanes are made by the polyaddition. Polymerization where two or more functional hydroxyl groups containing compounds are allowed to react with di-or polyisocyanates.

An isocyanate group reacts with hydroxyl groups of a polyol to form the repeating urethane linkage. Isocyanates will react with water to form urea linkages and carbon dioxide as a by product. Linear PUs may be obtained by using compounds with two reactive groups such as diisocyanate and diols. When polyols with three or more hydroxyl group are reacted with an isocyanates, or when isocyanate with three or more isocyanate groups react with a polyol the resulting polymer is cross linked. The amounts of cross linking affect the stiffness of the polymer.

Urethane adhesives make good adhesives for a number of reason:

They effectively wet the surface of most substrates.

They can interact with the substrate through polar interactions

Their relatively low molecular weight / small molecular size allows them to permeate porous substrates

They can form covalent bonds with substrates that have active hydrogen atoms

Through molecular compositions the adhesives stiffness, elasticity and cross linking can be tailored to suit specific needs.

The most commonly used isocyanates in polyurethane adhesives are MDI (methylene di phenyl diisocyanates and TDI (toluene diisocyanates), both aromatic isocyanates.

Aliphatic isocyanates are also used but in smaller volumes of the different polyols of widely different types are used for the production of adhesives, the most commonly used polyols are polyethers and polyester polyols.

Polyurethane adhesives can be classified in the following product segments:

1.7.2 (1) Non reactive Polyurethane adhesives:

Solvent borne adhesives: Polyurethane solvent adhesives consist of a high molecular weight hydroxyl terminated polyurethanes dissolved in a solvent. The polyurethane are obtained by reacting a high molecular weight polyester polyols and diisocyanate solvent systems were mixed and applied on to the surfaces to be bonded, after evaporations of solvents, up on pressing and curing was allowed to take place, bonding occcures.

Hot melt adhesives: These adhesives also consist of high molecular weight hydroxyl terminated polyurethane. Hot melt adhesives are most commonly applied as adhesives film in lamination type of application. These adhesives from the adhesive bond by cooling from the molten state.

Water based adhesives: These adhesives are high molecular weight polyurethanes dispersed in water. The water carrier is eliminated during use, leaving the precipitated and coalesced polymer to form the adhesive bond.

1.7.2(2) Reactive Polyurethane adhesives:

One component adhesives: This is a liquid isocyanate terminated polyurethane with a relatively high molecular weight and rather low remaining isocyanate content. The prepolymers are prepared by reacting an excess of isocyanates with high molecular weight polyester or polyether polyols. The free isocyanate groups react with moisture from the environment to form urea linkages. If the functionality of the prepolymer is larger than two (i.e. contains more than two isocyanate groups per molecule) the cured film will be chemically crosslinked.

Two component adhesives: Such adhesives consist of two relatively low molecular weight components: the polyol and isocyanate. When the two components are mixed they from urethane groups in the adhesive films. The polyols are usually of the ether or ester type. The isocyanates and polyols employed may have a functionality of two or higher and in the latter case a crosslinked film is formed.

Reactive Hot melt adhesives: Reactive hot melt adhesives are highly viscous or solid prepolymer with a low melting point. The prepolymer are produced from solid polyester polyols and isocyanate and have a low number of free isocyanate groups. The adhesives is applied above its melting point and bond through the physical process of cooling as well as through reaction with ambient moisture (as a one component adhesive).

Wood binders: Aromatic isocyanates are used as binders to manufactures oriented strand board (OSB), medium density fiberboard (MDF) and particleboard. For these boards, the isocyanate is blended with wood strands, fibers and chips, respectively. The cure takes place in a press at about 200^0C. The curing reaction is predominating via the reaction with water and thus the formation of urea groups. Additionally, a wide range of reactions with wood components will also occur depending on the temperature, moisture content and the specific location within the wood matrix.

Crosslinkers: Although crosslinks are not seen as "adhesives" perse, they do improve the adhesives properties of solvent and water borne adhesives, solvent borne crosslinkes are added to solvent borne polyurethane or chloroprene adhesives, water borne emulsifiable isocyanates are added to latex to PUD adhesives, in the bond crosslinking reactions occur and the resulting cross linked adhesives has improved mechanical properties as compared to the non-crosslinked adhesives.

Based on their outstanding properties, their simple and economical processing, as well as high strength and plasticizer resistance of their bonds, polyurethane adhesives found broad use in many application areas. The segments in which polyurethane adhesives are used most are: footwear industry, constructions, woodworking, transportations, medicine, packaging and assembly operations [72-78]. However, in certain area of applications, such as indirect food contact, approvals for use need to be taken from appropriate regulator authorities. Polyurethane adhesives are widely used in different industries. Due to the versatility of polyurethane chemistry, there are many different types of PU adhesives reported [79].

Possibility for industrial utilizations of polyurethanes derived from natural sources has gained considerable attentions in recent times [80-83].

Use of castor oil for Polyurethane synthesis is known since long because it is the only well known oil which is abundantly available in asian region which have free hydroxyl groups, a very essential requirements in polyurethane synthesis.

Use of castor oil directly in unmodified form yields urethane resin with limited hardness. Many modifications of castor oil have been proposed by researchers to utilize double bonds of unsaturated fatty acids and carboxyl group to yield polyols which can be utilized for polyurethane formulations [84].

Castor oil based PU has been extensively studied for coatings and IPN's [85]. Currently avialable castor oil based polyurethanes are widely used in telecommunications, electrical industries, coatings, foams and adhesives [86].

Compared to other area of application like coatings, foam and IPN's etc only a very few studies have been carried out to synthesized castor oil based adhesives. Also, very limited information is available regarding the influence of molecular structure (different moieties or chain length) of polyols,use of different isocyanates and effect of different NCO/OH ratio on adhesion.

Martin Martinez et al synthesized various polyurethanes and for use as solvent based adhesives and also studied various properties of the above PU with different hard and soft segment ratios [87,88].

Polyurethane ionomers contain a relatively small number of ionic sides in the polymer backbone and these materials are dispersible in aqueous medium and hence widely used in adhesive formulations [89-95].

Also hydroxyl terminated polybutadiene based polyurethane have been studied extensively as they could be efficiently used as adhesives [96,97]

Xie et al. synthesized castor oil based IPN's for bonding of rusted iron. They studied the effect of NCO/OH ratio, types of PU type monomer on the adhesive properties of IPN's between two rusted iron plates [98].

Extensive reports are available on use of inter penetrating network (IPN's) and semi inter penetrating network (semi IPN's) as adhesives. Takemura and Mizumachi [99] prepared PU/ poly(alkyl methacrylate) IPN's and studied their use as a vibration damping adhesives. Jia et al [100] reported the synthesis and properties of three component IPN's and their application in adhesion of polymers. In other study Sperling and coworkers

[101,102] first reported IPN's from castor oil based polyurethanes. They prepared sequential and simultaneous IPN's by the formation of a polyurethane network from castor oil and toluene diisocyanates (TDI) and through the polymerization of styrene and crosslinking agent at elevated temperatures to form another network, which is used as an adhesive.

1.8 SCOPE OF THE PRESENT WORK:

Polymers have become the most versatile commodity in today's life style of the mankind. During last 50 years, polymer chemists and chemical engineers have greatly improved their ability to make broad range of polymer structure. Polymer physicists and mechanical engineers have learned to measure the significant and critical properties of these polymers. Production engineers and industrial designers have learned to use these materials in thousand of applications.

Polyurethane is the rapidly developing product of the coatings and adhesive industry with unique combination of performance and application properties.

Urethane is in short supply in the Indian market for a variety of reasons, largely related to the poor availability of raw materials and their high price. So, research in urethane has mainly been aimed at improving the performance and cost effectiveness of urethane based formulations/ products.

Hence polyol systems were synthesized with the main objective of producing cheaper raw materials without compromising the performance properties of the coatings and adhesives obtained. For this purpose a comparative study of end use application properties of renewable resource base resin with most standard commercially available product is also made in the present study.

The increasing legislative restrictions on the emissions of volatile organic contents (VOC's) emission and awareness among the surface coating users forced the technologists to develop eco-friendly coatings, which are safer during productions, storage and applications. The eco-friendly methods of surface coatings viz. high solid coatings, powder coatings, radiation cured coatings and water borne coatings and the findings are well documented.

Also the better ease of processing the surface coating materials and the developments of newer high performance coatings are in demand. This includes the development of alternative raw materials, curing agents, pigments, additives and several types of newer additives and several types of newer resins. Looking to the above demands and the awareness regarding ecological , economical factors influencing the surface coatings and adhesives industry, the present work includes the study and development of newer castor oil based polyols by using the conventional raw materials having better ease of processing in place of common polyols in various thermosetting coatings, sacrificing the end performance of the surface coatings.

The evaluation of relavant performance properties depending on the intended applications, concering the coating and adhesives has been discussed in the various chapters. The work under taken on synthesis and characterisations of polyurethane from castor oil based polyols has been elaborately described. The whole work has been divided into six chapters, the brief account of which is given below

The first chapter includes the general introduction on polyurethane, history and development of surface coatings and adhesives. It also includes the general introduction to polyurethane: raw materials, catalysis, processing, types, components and formulation of various urethane systems. Further it also informations about the testing and evaluation by various methods has been presented, including the scope of the present work.

The methods and materials for synthesizing of polyols, which is important materials for synthesis of polyurethanes with experimental techniques as well the characterizations of these polyols by various methods has been described in second chapter.

In the third chapter, which has been divided in two part, in part A includes the synthesis of polyurethane coating system from polyester polyols having various chain length with aromatic as well as aliphatic isocyanates under different NCO/OH ratios. These coatings were characterized by various methods. In part B we have synthesized polyurethane coating systems using castor oil and epoxy resin based polyol and three different isocyanates with varying NCO/OH ratios have been reported. These coatings systems were characterized by various methods. Also thermal stability and activation energy of polyurethanes was studied by TGA.

In the fourth chapter synthesis of polyurethane from different polyols and different isocyanates having various NCO/OH ratio has been given. The performance of these polyurethane adhesives were evaluated as a wood bonding adheisves in terms of lap shear strength and over all adhesion strength as compared to commercially available wood to wood bonding. Also, acrylated polyol was reacted with R60 isocyanates and aromatic isocyanates to form polyurethanes and the resultant PU was evaluated as metal-to-metal bonding adhesives interms of lap shear strength.

In the fifth chapter of the present thesis, the studies on swelling behaviour of the varouos PUs have been described to measure the sorption and diffusion coeffcient and an attempt has also been made to correlate the effect of chain length and crosslink density on above parameters of polyurethanes has been made.

In the last and final chapter of the thesis, summaries of our studies are reported.

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