3.

INTRODUCTION

Adhesives are used in many types of manufacture and in many cases they have replaced other means of joining. A range of adhesives is used in making cardboard boxes and staple has been rare in use. Apart from expensive handmade shoes adhesive find application in footwear, car-bodies, wooden interiors, metals, glass etc.

History of adhesives [1] shows the first evidence of a substance being used as an adhesive dates back to 4000 B.C. Archaeologists have also uncovered statues from Babylonian temples that have ivory eyeballs glued into eyesockets. About the year 1000 A.D., Genghis Khan overcame all attackers because of the excellent power of the weaponry he had. Bows were made from laminated wood and bullhorn bonded with an adhesive whose formula has been lost and have not been rediscovered. Mud, dung, and clay, along with mixtures of these substances, must also be regarded as adhesives and have been used for centuries.

Adhesive can be defined as a material which when applied to the surfaces of materials can join them together and resist separation. The industrial revolution caused an explosion in technical breakthroughs that resulted in new materials becoming available for use in formulating adhesives.

Glues and other such products have been used as adhesives obtained from natural materials of plant and animal origin. However, due to its less durability, wood bonding has been done using formaldehyde-based resins such as PF (phenol formaldehyde), urea.
formaldehyde and melamine formaldehyde. These synthetically produced resins from non-renewable petroleum resources uses formaldehyde that is considered a priority pollutant itself [2]. To understand different types of adhesive used in past and presently used highly special purpose adhesives one has be clear about some of the basic understandings regarding adhesion, adhesives and other terms used in the adhesion and adhesive technology. This chapter deals with the description of these terminologies, mechanisms of adhesion, classification of adhesives, their uses, review of important literature on adhesion and adhesives, preparation, characterization, application and testing of polyurethane adhesives prepared from the synthesized natural oil-based polyols.

3.1 ADHESION

Adhesion is the attraction of two different substances resulting from intermolecular forces between the substances [3]. Adhesion is a branch of zygology, the science of joining thing together; others include welding, riveting and other forms of mechanical joining. Another relative term is cohesion, which involves only the intermolecular attractive forces within a single substance itself.

3.1.1 Mechanism of adhesion

The mechanism of adhesion has been investigated for years; several theories have been proposed in an attempt to provide an explanation for adhesion phenomena. However, no single theory explains adhesion in a general comprehensive way, as the bonding of an adhesive to an object/surface is the result of a number of mechanical, physical, and chemical forces that overlap and influence one another. As it is difficult to separate this effect on influencing one another, we can distinguish these theories into following categories:

(i) Absorption Theory: The adsorption theory states that adhesion results from intimate intermolecular contact between two
materials, and involves surface forces that develop between the atoms in the two surfaces. The most common surface forces that form at the adhesive-adherend interface are van der Waals forces and hydrogen bonds may contribute to this [4].

(ii) Mechanical Interlocking [5]: Mechanical interlocking is probably the primary mechanism by which adhesives adhere to porous structures, such as wood. This theory of adhesion states that good adhesion occurs only when an adhesive penetrates into the irregularities, holes and crevices of the surface of a substrate, and locks mechanically to the substrate. The adhesive must not only wet the substrate, but also have the right rheological properties to penetrate pores and openings. Deeper penetration into the fine microstructure increases the surface area of contact between adhesive and wood for more effective mechanical interlocking. The most durable structural bonds to wood are believed to develop not only when an adhesive penetrates deeply into cell cavities, but also when an adhesive diffuses into cell walls to make molecular-level contact with the hemicellulosics and cellulosics of wood.
Pretreatments are used to increase the roughness of the surface of the adherend. These pretreatments result in micro-roughness on the adherend surface, which can improve bond strength and durability by providing mechanical interlocking and increases the bond strength of the adhesive.

(iii) Chemical Bondings: This is a variation to the adsorption theory in that stronger chemical bonds (ionic, covalent metallic) form across the joint interface. In this regard, introduction of molecular bonding between the adhesive and the adherent will obviously improve the adhesive bond strength. The chemical bonding mechanism suggests that primary chemical bonds may form across the interface. Chemical bonds are strong and make a significant contribution to the intrinsic adhesion in some cases. Covalent bonds are the strongest of chemical bonds; they are more than 11 times the strength of the hydrogen bond. Even though covalent chemical bonds between adhesive polymer and the molecular structure of wood is a possibility, there is no clear evidence that such bonds constitute an important mechanism in adhesive bonding to wood.

(iv) Electrostatic theory: This theory states that an electrostatically charged double bond develops at the bond interface as a result of the interaction of the adhesive and adherent, which contributes significantly to the bond strength. This is a controversial theory, as many have doubted the actual
significance of the forces involved. While this concept may be useful to explain some specific examples of adhesion, significant doubts have been cast regarding its overall value.

(v) Diffusion theory: When an adhesive contains an adherent solvent, the adhesive can diffuse into the adherent surface (substrate) with an interchange of molecules. The theory is only applicable to polymers where a movement and entanglement of long molecules can occur.

While the diffusion theory applies well for cases of self-adhesion or auto-adhesion, it does not fit well in providing an explanation for polymer-polymer adhesion. High molecular weight thermoplastic polymers often display very high melt viscosity and will not diffuse easily within the time scale of most bonding operations.
3.2 ADHESIVES

An adhesive is a material that binds two material together [3] and it can also be defined as a substance capable of holding at least two surfaces together in strong and permanent manner. Mud, dung, clay, and mixture of these substances are regarded as the first adhesive used by human being [6]. In the initial period, naturally occurring glues and animal glues were used for adhesion. In about 1940, O. Bayer found that polyurethanes made excellent adhesives for bonding elastomers to fibers and metals [7], but, the first synthetic resin to be used as adhesives was phenol formaldehyde and later on epoxy resins were used due to their high bonding strength [8].

The competitive methods for all fastening and joining systems can be generally categorized as follow:

(I) Periodic: the attachment of two things by occasionally placing through hole fasteners or other individual mechanisms. (E.g. rivets, screws etc.)

(II) Linear: a continuous or occasional edge bead attachment, such as welding.

(III) Area: an attachment achieved by full-face contact and union between the two substances (e.g. adhesives and soldering)

At present, there is an increasing demand for adhesives in the market. Paper, footwear and wood are some of the areas finding major applications; however, use of adhesive in the field of construction and structural engineering have been found to be increasing due to the availability of tailor-made and specialty adhesives in the market. Joints can be prepared my physical means or mechanical interlocking but adhesives plays them down in some of the very important field of applications. Some of the advantages of using adhesive-bonded joints [8-10] compared to other joining methods are as follows:
Manufacturing procedures like milling, machining, forming, and riveting can be reduced or eliminated.

Ability to bond variety of material which may be dissimilar and of different shapes and size.

Adhesive bonds provide a high strength-to-weight ratio with three times the shearing force of riveted joints.

It is feasible to fabricate complex shapes where other fastening methods do not suit.

Improved aerodynamic surfaces and visual appearance.

Excellent electrical and thermal insulation properties.

Versatile types, forms and method of applications.

Superior fatigue resistance.

Uniform distribution of stress over wide area.

Allows for variations in coefficients of thermal expansion when joining materials.

Adhesive joints can distribute the load over a larger area and can take advantage of the ductile response of the adhesive to reduce peak stresses.

Ability to join heat sensitive materials which otherwise distort or destroy at high temperature of welding.

Reduction in weight in adhesively bonded material can be achieved as compare to rivet or bolts.

However, adhesive do have some disadvantages,

Optimum bond strength cannot be obtained instantaneously as compare to spot welding or riveting.

Temperature limitations restrict its usage to certain service temperature.

Difficulty in inspection of adhesive joints.

Possible degradation due to light, microorganisms, chemical environment etc.

Environmental hazard due to the use of solvents.
In the wood-based products where adhesives are used as a binder, the performance of the product varies according to the some of the major factors given below:

(i) Compositional factors related to the adhesive (strength, durability, solvents, diluents, fillers, extenders, solids content, etc.) [11-16].

(ii) Structural characteristics of the wood (species, density, anisotropy etc.) [11, 15-17].

(iii) Surfacing characteristics (cutting mechanism, surface smoothness, grain angle, moisture content, dust, temperature etc.) [15, 18].

One of the most important factors for adhesive to gain its maximum possible adhesion strength is the surface roughness of the substrate or adherent. It affects adhesion in the following ways [3]: (1) it increases the total contact area between the adhesive and substrate, ultimately enhances bond strength, (2) it provides mechanical interlocking effect by trapping the adhesive in the cavities and works as an anchor, which would hold the adhesive and substrate together by mechanical forces and (3) it prevents crack progression by acting as a barrier when a force is applied to the interface because less sharp and smooth interface requires less energy to separate the bonded materials. However, for a rougher interface, the applied force and energy dissipates in the crack.

As also suggested by Nardin and Ward [19], adhesion depends on several factors such as the wettability (affected by surface treatment), the surface roughness and the extent of chemical bonds per unit area between the resin and the substrate. Another important factor for adhesives is its viscosity affecting the penetration behavior of liquids into a wood surface [20].
3.3 CLASSIFICATION OF ADHESIVES

There is no single method to classify adhesives; however, they are classified according to their origin, physical form, different processing techniques, chemical composition and method of application.

*Classification based on origin* [21]: adhesives can be obtained from natural resources like those as animal glue, fish glue, starch based glues, and protein based glues.

*Classification based on bonding temperature* [22]: adhesive can be cold settling (below 20°C), room temperature setting (20-30°C), intermediate temperature setting (30-100°C) or hot setting (above 100°C).

*Classification based on bonding methods* [23]: adhesive can be bonded by pressure setting, chemical bonding, and hot melt or by solvent release.

*Classification based on bond strength* [24]: adhesive can be structural (bond strength more than 1000 N/cm²) or non-structural (bond strength less than 1000 N/cm²).

Following is a brief description of different adhesives followed by delineation of polyurethane adhesives.

### 3.3.1 Animal Glues

These are usually made from the hides and bones of such animals as cattle, horses, and sheep and was usually classified as either hide or bone glue by boiling. The extract is cooked to form a gelatin material, which give setting properties. Good quality animal glue should be able to soak up several times its weight in water and still remain a gelatinous mass. They have low resistance to moisture and damp conditions.

### 3.3.2 Fish Glue

Is a made from the skins and bones of fish. A clear adhesive can be made from fish and was the first adhesive used for
photographic emulsions for photo film and photo resist coatings for photoengraving processes [25].

### 3.3.3 Casein Glue

is made from a protein isolated from milk. The extraction process creates a waterproof adhesive. Most casein glue is sold as a dry powder and must be mixed with water before it can be used. Its first use was in bonding the seam of cigarette paper. Until the introduction of synthetic adhesives, casein glues were important because of their superior moisture resistance.

### 3.3.4 Starch

is a carbohydrate extracted from vegetable plants such as corn, rice, wheat, potatoes. Major use area is in bonding paper and paper products such as bookbinding, corrugated boxes, paper bags, and wallpaper paste; it is also used as a sizing in textiles. The laundry uses starch on your shirt collars to stiffen and give shape to the clothing. They set through loss of water, which may be quite slow, so that glued assemblies must remain untouched overnight.

### 3.3.5 Synthetic resins

are man-made polymers which resemble natural resins in physical characteristics but which can be tailored to meet specific woodworking requirements. These resins impart the highest water resistance.

\(1\) Phenol-formaldehyde (PF) resins are widely used to produce plywood for severe service conditions. These resins are dark reddish in color and are available as liquids and powders or in film form. They may be manufactured to cure at a variety of temperatures. A von Bayer in 1872 was the first to report, that phenol reacted with formaldehyde under both acidic and alkaline conditions. This kind of polycondensation led to the development of the first synthetic resins and plastics in 1909 by Backeland [26]. PF resins are of two types: 1. Novolac (acid catalyzed) and 2. Resol (base catalyzed) [27]. Resol resins are prepared by the interaction if phenol with a molar excess of
formaldehyde under alkaline conditions. Novolac resins are prepared by the reaction between phenol and formaldehyde under acidic conditions. In order to avoid gelation, novolacs are prepared with a molar excess of phenol. Due to high chemical resistance, novolacs can be used as an additive for resols. Phenolic resins are prepared by two-stage reaction.

**Methylolation:** The reaction between phenol and formaldehyde results in electrophilic substitutions of the aromatic ring to form a phenol alcohol. This is termed as methylolation. The phenolic OH group enhances the electron density of the ortho and para positions of the ring and substitution is thus directed toward these positions. As shown below (figure 1), depict the ideal reaction of phenol and formaldehyde.

![Figure 1: Reaction of phenol and formaldehyde](image)

In practice di- and tri-methylol phenol are also produced; however, para substitution can be reduced using a blocked para position in phenol (figure 2).

![Figure 2: p-tertiary butyl phenol](image)
Condensation: Methylol phenols are relatively stable at temperatures below 50°C and alkaline pH. However, at higher temperature, or under acid catalyst, these methylol groups condense to give polymeric product.

Resoles are obtained from these methylol phenols which, when heated, cross-links to form a solid, insoluble, three-dimensional polymer network. Thus, commercially resoles (figure 3) are a mixture of polynuclear molecules joined via methylene or methoxy links and containing residual unreacted methylol groups.

![Figure 3: Resole](image)

Unlike resoles, novolac (figure 4) do not contain residual methylol groups.

![Figure 4: Novolac](image)

(2) Urea-formaldehyde (UF) resins are probably the most widely used thermosetting resin for wood. They are widely used for the manufacture of interior grade plywood and for the manufacture of particleboard. Fillers and extenders are added to the resin to
control flow, viscosity, and resin penetration into the wood. Similarly as in the PF resins, these resins are also formed by two-stage reaction: first is methylolation to produce methylol urea and its condensation and cross linking to form urea-formaldehyde resin (figure 5).

\[
\text{H}_2\text{N} - \text{C} - \text{NH}_2 + 2 \text{HCHO} \rightarrow \text{HN} - \text{C} - \text{NH}_2
\]

\[
\begin{array}{c}
\text{O} \\
\text{HOH}_2\text{C} \\
\text{CH}_2\text{OH}
\end{array}
\]

Dimethylol urea

Figure 5: Cross-linked structure of UF

(3) Melamine formaldehyde (MF) resins are used primarily to improve the moisture resistance of urea-resin adhesives. In this respect, they are substantially more resistant than urea-resins but not as resistant as phenol and resorcinol resins. Due to high cost as compare to UF resins and high cure temperature, its applications have been limited.

MFs are commercially prepared from methylolamine and additives, including hardeners. The additives very depending on the resin products. For example, wheat flour and water are added to make adhesives [28].
3.4 GENERAL REQUIREMENT FOR ADHESIVES

3.4.1 Cleanliness of the substrate surface
Above all other requirements the application must initiate with clean surface. Foreign materials such as dirt, oil, and moisture must be removed before applications.

3.4.2 Wetting the surface
Initially the adhesive must be either liquid or a readily deformed semi-solid so that it can be easily applied on the substrate. Small air pockets caused by roughness of the substrate at the interface must be easily displaced with adhesive. The term “wetting” refers to a liquid spreading over and intimately contacting a solid surface.

3.4.3 Solidification of the adhesive
The liquid adhesive applied must be converted into a solid mass. The solidification may occur in different ways: chemical reaction, by heat, pressure, curing agent, cooling from molten liquid, and drying due to solvent evaporation.

3.4.4 Strength of adhesive
Once solidified, the adhesive must have strength and toughness to resist failure when exposed to service conditions.
3.5 POLYURETHANES AND POLYURETHANE ADHESIVES

Polyurethanes are versatile and one of the most important classes of polymers. These have been used for variety of applications those includes adhesives, foams, coatings elastomers and medical applications [29, 30]. Comfortable, durable mattresses, automotive and domestic seating are manufactured from flexible polyurethane foams. Rigid polyurethane foam is one of the most effective practical thermal insulation materials, used in applications ranging from domestic refrigerators to large industrial buildings. Polyurethane adhesives are used to make a wide variety of composite wood products from load-bearing roof beams to decorative cladding panels. Items such as shoe soles, sports equipment and car bumpers are produced from different forms of polyurethane elastomers.

From the organic chemistry point of view, the urethane groups (-NH-COO-) are esters of carbamic acid, a hypothetically unstable acid [R-NH-COOH]. The reaction between an isocyanate and an alcohol (Scheme-1) to produce urethane is as below:

\[
\begin{align*}
\text{Isocyanate} & : R-N=C=O + \text{Alcohol} \quad \rightarrow \quad \text{Urethane} \quad R-NHCOO-R' \\
\end{align*}
\]

Scheme-1 Urethane synthesis

The general formula for the production of isocyanate can be given as in figure 6.

\[
\begin{align*}
\text{Primary amine} & : R-N:H + \text{Phosgene} \quad \rightarrow \quad \text{Isocyanate} \quad R-N=C=O + HCl \\
\end{align*}
\]

Figure 6: Isocyanate production

Where, R can be an aliphatic or aromatic group.
The first urethane was synthesized, by this route, as early as 1849 by Wurtz [31, 32]. In 1937, in search of a fiber to compete with nylon, at IG Farbenindustrie, in Germany, Dr. Otto Bayer synthesized the first polyurethane, by the reaction of a diisocyanate with polyester having two terminal hydroxyl groups (Scheme-2) [33, 34]. Sometimes the term polyurethane leads to confusion. Polyurethanes are not obtained from polymerization of urethane monomer, but they contain several urethane groups in the molecular backbone of polymer formed due to the reaction of isocyanate groups and hydroxyl groups. However, it may contain, in addition to the urethane linkage, aliphatic, aromatic, hydrocarbon, ester, ether or amide groups.

\[
\begin{align*}
\text{Diisocyanate} & \quad \text{Polyester diol} \\
O\equiv C\equiv N\quad R\quad N\equiv C\equiv O & + \quad \text{polyester chain} \quad \text{OH} \\
& \downarrow \\
\left[ O\text{CONH} \quad R \quad \text{NHCOO} \quad \text{polyester chain} \right]_n \quad O
\end{align*}
\]

**Scheme-2 Polyurethane synthesis from diol and diisocyanate**

These can also be prepared from bischloroformate and diamines by polycondensation reaction (scheme-3) [35, 36].
Scheme-3 Polyurethane synthesis from diamine and bischloroformate

The high reactivity of the isocyanate group with hydrogen active compound is due to its resonance structures:
The attack of hydrogen and oxygen at nitrogen and carbon atom respectively take place as shown below.

Scheme-4 Urethane formations

Some of the diisocyanate used for polyurethane synthesis are as below (figure 7).
Because a variety of diisocyanates and a wide range of polyols can be used to produce polyurethane, a broad spectrum of materials can be produced to meet the needs of specific applications.
Polyurethane adhesives are one of the most attractive adhesives due to the ability to tailor polyurethanes’ molecular structures to specific property requirements, and due to the same, these can be used to bond numerous substrates such as glass, wood, plastics, and ceramics. Polyurethanes are considered good adhesives as they effectively wet the surface of most substrates; substrates; their low viscosity allows them to permeate porous substrates; and they form covalent bonds with substrates that have active hydrogens [37]. Furthermore, they also have good toughness and a broad range of resistance against water and chemicals [38]. Properties of one component urethane systems (discussed in 3.4.1), normally stored in metallic cans, must remain within acceptable limits. In an industrial environment, isocyanate-based adhesives are frequently stored for a long period before being used. Due to the presence of unreacted isocyanate (NCO) groups, several undesirable by-products may be formed during the storage period and eventually may affect the adhesion properties. da Silva et al. have studied the effect of storage of several isocyanate tipped quasi-prepolymers on their composition and adhesion [39]. Polyurethane adhesives deriving from a natural and renewable source such as oil-based PU adhesives are non-aggressive to the environment and to humans. Plywood, a layer based panel, which is a type of wood-based panels, consists of thin layers of wood superposed orthogonally and glued together, their fibers laid in alternate directions. Dias and Lahr [40] synthesized castor oil based polyurethane adhesive, which was used to produce plywood. They concluded that in the manufacture of the plywood with castor oil-based polyurethane adhesive, the temperature of compression was 60 °C. This represents a significant reduction in energy consumption, considering that the curing of phenol-formaldehyde resin is processed at temperatures of 130 to 160 °C.

As the soft and hard segments of polyurethane adhesive greatly affect the properties of polymer and adhesion of adhesive to the
substrate, the study targeted as the examination of these segments in adhesive could provide useful results. A study towards the structure, composition, and adhesion properties of thermoplastic polyurethane (TPU) adhesives by Adsuar and Martinez [41] reported that the increase in the hard segment content in TPUs favoured the incompatibility between hard and soft domains and TPUs with high hard segment content had a low crystallinity, a low wettability, and a high joint strength.

Water borne PU adhesives have their own advantages such as they are non-toxic and non-flammable and gives excellent range of properties. In addition to the environmental issues, the escalating price of petroleum-based solvents has led to an increased emphasis towards the development of water borne polyurethanes. Aqueous polyurethane dispersions are generally made of linear polyurethane chains having ionic groups and due to uncrosslinked structure, their solvent resistant is poor. However, these drawbacks can be overcome by hydrophobic modification and cross-linking [42, 43]. Sunder et al [44] prepared aqueous polyurethane dispersions using poly (tetramethylene oxide) glycol, TDI and N-methyl diethenolamine. In the process polurethane were prepared using these three chemicals and prepared polymer was converted into cationomers and dispersed in water.

Rehman et al [45] synthesized couple of cross-linkable water borne PU adhesive (figure 8) using 2, 2-bis(hydroxymethyl) propionic acid (DMPA) and hexamethoxymethyl melamine (HMMM) using HMDI and results showed that adhesive strength was significantly increased by cross-linking up to the optimum content of HMMM and then decreased slightly with excess HMMM and also gave increased highest failure temperature.
3.5.1. Types of polyurethane adhesives

(1) One component moisture curing adhesives

These are based on di- or triisocyanates that cure by reacting with active hydrogens on the surface or moisture present in the substrate. The moisture reacts with the isocyanate groups to form urea and biuret linkages, resulting into increase in molecular weight, strength, and adhesion. Prepolymers, which are high molecular weight urethanes, are used as either 100 % solids or solvent-borne one-component adhesives. The prepolymer may contain urethane groups, but the cross-linking bonds are ureas. This group includes nonsolvent-type reactive hot-melt adhesives that are melted at a temperature of around 100°C or higher, applied to the base, and cooled to solid form. They later react with active hydrogens on the base material or moisture in air for curing.

These moisture-curing polyurethane adhesives give a final adhesive layer that is weaker than that of a two-component type adhesive, but are superior in heat resistant. As the adhesion is caused by reaction of moisture, these adhesive has disadvantages in that it is affected by external environmental conditions like low to high temperature and humidity. The invention by Konishi et al [46] disclosed a one-component polyurethane adhesive that uses a polyurethane precursor as a main component having uretdione groups and active hydrogen groups at a preset ratio. One component
Polyurethane adhesives could be divided into sub categories: reactive adhesives and solvent adhesives. In reactive adhesives contains low remaining isocyanate content which react with atmospheric moisture to cross-link; whereas solvent adhesives are carried in solvent, which is eliminated prior or during the cross-linking.

(2) Two component urethane adhesive

It is composed of a diisocyanate terminated prepolymer as one component, a polyhydroxy compound (polyol) and a cross-linking agent (depending on necessity) with a catalyst. From two types of polyols mainly used (polyester polyol and polyether polyol), polyesters are valuable for this type of polyurethane adhesives. Since the two component cure rapidly when mixed, they must be kept separate until just before application. After sufficient and fast mixing of all components and after attaining required viscosity, it is quickly applied on the substrate to be bonded. Polyester polyols obtained from natural oils are particularly useful due to their long fatty acid chain which provides flexibility and good resistance to hydrolysis. Dry solvents like ethyl acetate, acetone, methyl ethyl ketone, toluene etc can be used to ease its application as these type of adhesive while used for application have high viscosity. To reduce the cost and shrinkage during curing, fillers like talc, barites, and asbestos can be used with polyol component [47,48].

(3) Polyurethane dispersions (PUDs)

Due to the use of volatile organic solvents in conventional polyurethane systems, they can cause environmental damage. The increase in usage of water borne PUDs in not only due to some of their important properties, which are discussed below, but also due to environmental laws with a low VOC content.

The advantage for waterborne PUDs are: fast dry, nonflammable, low volatile content and outstanding flexibility and
impact resistance. Commercial PUDs can be classified on the basis of two characteristics. (i) The stabilization method i.e. anionic [49] cationic [50, 51] or nonionic. (ii) Chemical composition of polyisocyante (aliphatic or aromatic) and polyol (polyester, polyether, or polycarbonate etc) used for their preparation. Aqueous dispersions are generally made of linear chain and due to this uncrosslinked structure, solvent resistance properties and not good, however this can be overcome by crosslinking of PU chains [52]. Reischl [53] found that stable ionic dispersions having low viscosity can be obtained by reacting polyisocyanates with compounds having salt groups, in dispersing agents consisting of compounds containing hydroxyl groups.
3.6 WOOD ADHESIVES

Bonding wood has been practiced for many centuries. There is a plethora of wood composite products that rely on adhesives in their manufacturing processes. Wood composite products include beams, plywood, particle board and medium density fiberboard etc. Synthetic polymers are chemically designed and formulated into adhesives to perform a great variety of bonding functions. Thermosetting polymers make excellent structural adhesives because they undergo irreversible chemical change, and on reheating, they do not soften and flow again. They form cross-linked polymers that have high strength, have resistance to moisture and other chemicals, and are rigid enough to support high, long-term static loads without deforming. Phenolic, resorcinolic, melamine, isocyanate, urea, and epoxy are examples of types of wood adhesives that are based on thermosetting polymers.

Bio-based adhesives are alive for many years, and research on their development and application is definitely expanding. Very serious industrial interest exists in these products, always with an eye on their environmental acceptability and on their economical and technical viability. A detailed review by Pizzi [54] on eco-efficient bio-adhesives obtained from renewable resources, which can be used for bonding wood, discussed the improvement and advancement in this direction of environment friendly research.

After using different types of synthetic adhesives for wood, researchers in last decade have targeted eco-friendly wood adhesives, fully or in part synthesized from natural materials. The following points highlight the increasing research on synthesizing eco-friendly wood adhesives.

Weimer et al [55] used the residues from the fermentation of cellulose by the anaerobic bacteria *Ruminococcus albus* containing residual cellulose, bacterial cells and their associated adhesins and
examined their ability to serve as components of adhesives for plywood fabrication. They concluded that this product do not by themselves meet the shear strength and wood failure standards of conventional phenol-formaldehyde (PF) adhesives for plywood when pressed under conditions typical for PF adhesives. However, they can be added to PF adhesives in large amounts (up to 73% by weight) without significant loss of the adhesive properties of the resulting resin.

It is a known fact that lignin is the second most abundant renewable polymer next to cellulose and it is a natural binder for wood. It contains both aliphatic and aromatic hydroxyl groups, which can be used as reactive sites for chemical modification. Khan and Ashraf [56] prepared coffee bean shell lignin-modified phenolic adhesive (PF adhesive) for wood by replacing phenol with lignin at different weight percents. The results shows that phenol can be replaced by alkali-extracted coffee bean shell lignin (Cbsl) up to 50 wt% in PF. The resulting 50% Cbsl containing lignin–PF adhesive has better adhesive and shear strengths. The resulting adhesive gave 3-fold higher viscosity and shorter gel time. Another type formaldehyde-free wood-adhesive system consisting of kraft lignin and polyethylenimine (PEI) was investigated [57] for making two-ply plywood.
3.7 MATERIALS AND METHODS USED

3.7.1 Materials
Magazine paper waste was collected from the local market (Vallabh Vidyanagar). p-toluenesulfonic acid (PTSA), (recrystallised before use) and sulfuric acid (S.D. fine chem. Ltd., Mumbai, India) were used as catalyst. Ethylene glycol (S.D. fine chem. Ltd., Mumbai, India) and acetone (Merck, Mumbai, India) were used for glycolysis and as solvent respectively. Toluene diisocyanate adduct (TDI), containing 13.5 % free NCO, was kindly supplied by Synpol ltd., Gujarat, India. Dibutyltin dilaurate (DBTDL, Merck, Mumbai, India) was used as catalyst.

3.7.2 Methods
(1) FTIR spectroscopy analyses were carried out using Perkin-Elmer Spectrum GX FTIR system, England, using KBr cell.
(2) Lap shear strength of adhesives was measured using single lap shear joints of two wood specimen on Universal Testing Machine (UTM), LR 30 K Plus, Lloyd Instruments Ltd., Hampshire, U K, at pulling rate of 5.0 m m/min.
(3) Thermogravimetry analysis (TGA) was carried out on Pyris-1 TGA, Perkin Elmer, Norwalk, CT, U.S.A., heating rate: 10°C/min. with the 1 mg of the sample.
(4) Differential scanning calorimetry (DSC) was carried out on Pyris-1 DSC, Perkin Elmer, Norwalk, CT, U.S.A. Heating range was – 20°C to 300°C.
3.8 WOOD-WOOD ADHESION STUDY

3.8.1 Surface treatment of substrate (wood)

For an adhesive to make intimate contact with the surface of the substrates, and to hold them with maximum strength, it is necessary that adhesive spread on the surface freely and diffuse over it to make maximum contact. The strength of adhesive bond greatly depends on the ability of the adhesive to wet the substrate. Wetting means the property of adhesive spread on broad area of intimate contact with the surface. The contact angle is the angle at which a liquid/vapor interface meets the solid surface. Consider a liquid drop on a solid surface. If the liquid is very strongly attracted to the solid surface the droplet will completely spread out on the solid surface and the contact angle will be close to 0°.

When the contact angle is nearly zero, the adhesive is said to wet the surface completely, which reduces the distance between molecules and the intermolecular forces increases. A clean solid surface is one of the basic requirements for optimum adhesion between a substrate and an adhesive. Some chemical pre-treatments with chemical reagents are widely applied to wood surfaces in order to improve bonding ability, wettability and reactivate wood surfaces for wood bonds. Mechanical pretreatments such as sanding and planing can be applied to get a fresh surface which eliminates bonding problems and improves bonding of wood. Ismail Aydin studied the activation of wood surface for adhesive bond by sanding process and adhesion properties investigated in the study improved after the sanding process [58].

To increase the wetting of wood substrate, each of the specimens was roughened with sandpaper (no.60).
3.8.2 Adhesive preparation

Adhesives were prepared by using three synthesized polyols. Individual polyols as well as blends of soy oil based polyol and rice bran oil based polyols mixed with castor oil based polyol were used to prepare the adhesives. In a clean dry glass beaker, calculated amount of polyol (based on the hydroxyl equivalent), TDI (based on the NCO equivalent) and catalyst were added to obtain different NCO/OH ratios from 0.9 to 1.5. The content was mixed thoroughly for 1 min and used.

As per ASTM 906 standard, Tectona grandis (Common Teak) wood pieces were cut into 25 x 300 x 3 mm and were roughened uniformly using sandpaper. Dust was cleaned from the wood samples using a nylon brush and the wood specimens were dried at 110°C for 24 h before use.

3.8.3 Application and Testing of prepared samples

The previously prepared adhesive mixture was used within 2 min of its preparation and was applied on the two pieces of the dried wood samples (having less than 2% moisture content and roughened with sandpaper) using a brush so as to form a film of 0.1 mm (± 0.02 mm) thickness. Both the pieces were overlapped to 25 x 30 mm² areas and after one minute a load of 1 kg was placed on for 24 h. The joints obtained with adhesives of different NCO/OH ratio were cured at ambient temperature for 1 to 10 days (Relative Humidity: 50% ± 4%). The bonded wood joints were tested for lap shear strength using Universal Testing Machine (with pulling rate 5.0 m m/min and error of ± 2.0 MPa) as per ASTM D 906.

3.8.4 Determining the locus of failure

Based on the experience of different types of failure obtained in wood adhesives the locus of failure was determined by manual observation. Five experimental determination of each specimen were repeated and
the results were averaged. Different types of failure are explained below:

i) Adhesive Failure: It is the failure of adhesive bond from the substrate which happens if adhesive material does not or less tends to adhere with the adherend (shown on right side of the figure 9). It shows that the cohesive strength of adhesive is greater than the adhesive strength.

![Figure 9: Locus of failure in wood-wood adhesives](image)

ii) Cohesive Failure: As shown on left side of the figure 9, cohesive failure occurs when bulk of adhesive itself breaks. In this type of failure adhesive layer on the both the side adhere to the substrate/adherend but it fails from inbetween the adhesive material layer.

iii) Substrate Failure: If results when the adhesive strength along with cohesive strength of adherend is more than strength of adherend material (here wood).
3.9 RESULTS AND DISCUSSIONS

3.9.1 Effect of NCO/OH ratio on adhesive properties

A given amount of polyol, calculated from the hydroxyl equivalent, and isocyanate needs to be mixed to avoid free hydroxyl or isocyanate groups. Table 1 contains the lap shear strength of the joints obtained with the adhesive prepared from a castor oil based polyol of hydroxyl value 300 at different NCO/OH ratios. Increasing the ratio up to 1.2 showed an increase in bond strength which decreased thereafter. This may be attributed to the chemical bond between any free NCO in the adhesive and the substrate surface. A lower NCO/OH ratio utilizes all of the isocyanate which does not leave enough free isocyanate to react with wood; on the other hand excess of isocyanates penetrates in wood top layer which results in more strength of adhesive bond as compare to the substrate which in turn results in the substrate failure.

Table 1

Effect of NCO/OH ratio on adhesion

<table>
<thead>
<tr>
<th>NCO/OH Ratio</th>
<th>Avg. lap shear strength (± 2.0 MN/m²)</th>
<th>Locus of Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>20.72</td>
<td>CF</td>
</tr>
<tr>
<td>1.0</td>
<td>26.22</td>
<td>CF</td>
</tr>
<tr>
<td>1.1</td>
<td>33.65</td>
<td>CF</td>
</tr>
<tr>
<td>1.2</td>
<td>36.81</td>
<td>CF + AF</td>
</tr>
<tr>
<td>1.3</td>
<td>36.59</td>
<td>CF + AF</td>
</tr>
<tr>
<td>1.4</td>
<td>32.24</td>
<td>AF</td>
</tr>
<tr>
<td>1.5</td>
<td>25.83</td>
<td>SF</td>
</tr>
</tbody>
</table>

CF: cohesive failure of adhesive
AF: adhesion failure
SF: substrate failure
3.9.2 Effect of hydroxyl value on adhesive

Table 2 (a, b, and c) shows strength of adhesives obtained from three different types of polyols at various ratios. Adhesive produced from castor oil based polyols shows adhesive strength ranging from 15.31 MN/m$^2$ to 42.11 MN/m$^2$. Result for CAS 200 shows that the maximum strength was achieved at NCO/OH ratio of 1.3. The range of strength was 15.31 MN/m$^2$ to 22.52 MN/m$^2$ from ratio 0.9 to 1.3. At ratio 0.9 the locus of failure was adhesion failure which shows that there was less attraction between adhesive and adherend.

Adhesive strength for CAS 300 shows better strength at similar NCO/OH ratio compare to CAS 200. The maximum strength obtained was 36.84 MN/m$^2$ at the ratio of 1.2. The difference in strength of these two adhesive in between ratios 0.9 and 1.0 was less whereas it increased after 1.0 upto 1.5. CAS 400 showed similar trends, but the strength of adhesives in this series was much higher than CAS 200 and CAS 300 at comparative ratios. The maximum strength obtained in CAS 400 was 42.11 MN/m$^2$. Except CAS 200, which shows maximum strength at the NCO/OH ratio 1.3, the other two adhesives of castor oil-based polyols shows maximum strength at the ratio 1.2. Increasing the ratio up to 1.2 showed and increase in bond strength which decreased thereafter. This may be attributed to the chemical bond between any free isocyanate in the adhesive. A lower NCO/OH ratio utilize all of the isocyanate which does not leave enough free isocyanate to react with wood; on the other hand excess of isocyanate penetrate in wood layer which results in more strength of adhesive bond as compare to the substrate which in turn results in substrate failure.

From table 2 b and 2 c, it can be seen that lower adhesive strength of other polyol-based adhesives, was obtained at the comparative NCO/OH ratio with castor oil-based adhesives. This is possible due to the extra pendant hydroxyl group present in the castor
oil backbone, which is more reactive and provide extra cross-linking sites ultimately producing more rapid curing and strength. This gets more pronounced from the obtained results, which shows adhesive failure even at the NCO/OH ratio of 1.3 in the other two polyurethane adhesives.
# Table 2 (a)

Strength of adhesive from castor oil-based polyols

<table>
<thead>
<tr>
<th>Code</th>
<th>NCO/OH ratio</th>
<th>Average lap shear strength (± 0.05 MN/m²)</th>
<th>Locus of failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAS 200</td>
<td>0.9</td>
<td>15.31</td>
<td>AF</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>16.30</td>
<td>CF</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>18.43</td>
<td>CF</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>21.10</td>
<td>CF+AF</td>
</tr>
<tr>
<td></td>
<td>1.3</td>
<td>22.52</td>
<td>CF+AF</td>
</tr>
<tr>
<td></td>
<td>1.4</td>
<td>22.50</td>
<td>CF</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>20.30</td>
<td>CF</td>
</tr>
<tr>
<td>CAS 300</td>
<td>0.9</td>
<td>20.0</td>
<td>CF</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>22.18</td>
<td>CF</td>
</tr>
<tr>
<td></td>
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<td>34.02</td>
<td>CF+AF</td>
</tr>
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<td></td>
<td>1.4</td>
<td>28.15</td>
<td>CF</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>26.46</td>
<td>SF</td>
</tr>
<tr>
<td>CAS 400</td>
<td>0.9</td>
<td>23.34</td>
<td>CF</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>28.19</td>
<td>CF</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>38.40</td>
<td>CF</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>42.11</td>
<td>CF+AF</td>
</tr>
<tr>
<td></td>
<td>1.3</td>
<td>40.30</td>
<td>AF</td>
</tr>
<tr>
<td></td>
<td>1.4</td>
<td>29.57</td>
<td>SF</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>27.08</td>
<td>SF</td>
</tr>
</tbody>
</table>
Table 2 (b)
Strength of adhesive from soy oil-based polyols

<table>
<thead>
<tr>
<th>Code</th>
<th>NCO/OH ratio</th>
<th>Average lap shear strength (± 0.05 MN/m²)</th>
<th>Locus of failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC 200</td>
<td>0.9</td>
<td>5.09</td>
<td>AF</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>6.62</td>
<td>AF</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>9.00</td>
<td>AF</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>14.18</td>
<td>CF</td>
</tr>
<tr>
<td></td>
<td>1.3</td>
<td>16.12</td>
<td>CF</td>
</tr>
<tr>
<td></td>
<td>1.4</td>
<td>17.61</td>
<td>CF</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>17.60</td>
<td>CF</td>
</tr>
<tr>
<td>SC 300</td>
<td>0.9</td>
<td>9.68</td>
<td>AF</td>
</tr>
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<td>1.0</td>
<td>12.12</td>
<td>AF</td>
</tr>
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<td>1.1</td>
<td>15.00</td>
<td>CF</td>
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<td>CF</td>
</tr>
<tr>
<td></td>
<td>1.4</td>
<td>20.52</td>
<td>CF+AF</td>
</tr>
<tr>
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<td>1.5</td>
<td>20.00</td>
<td>CF</td>
</tr>
<tr>
<td>SC 400</td>
<td>0.9</td>
<td>13.32</td>
<td>AF</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>17.18</td>
<td>CF</td>
</tr>
<tr>
<td></td>
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<td>CF</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>18.20</td>
<td>CF</td>
</tr>
</tbody>
</table>
### Table 2 (c)

Strength of adhesive from ricebran oil-based polyols

<table>
<thead>
<tr>
<th>Code</th>
<th>NCO/OH ratio</th>
<th>Average lap shear strength (± 0.05 MN/m²)</th>
<th>Locus of failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>RC 200</td>
<td>0.9</td>
<td>5.35</td>
<td>AF</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>6.29</td>
<td>AF</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>8.16</td>
<td>AF</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>12.22</td>
<td>CF</td>
</tr>
<tr>
<td></td>
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<td>CF</td>
</tr>
<tr>
<td></td>
<td>1.4</td>
<td>15.61</td>
<td>CF</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>16.38</td>
<td>CF</td>
</tr>
<tr>
<td>RC 300</td>
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<td>AF</td>
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<td>9.28</td>
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<td>CF</td>
</tr>
<tr>
<td></td>
<td>1.4</td>
<td>15.09</td>
<td>CF</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>15.01</td>
<td>CF</td>
</tr>
<tr>
<td>RC 400</td>
<td>0.9</td>
<td>8.38</td>
<td>AF</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>10.44</td>
<td>AF</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>15.60</td>
<td>AF</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>18.61</td>
<td>CF</td>
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<td></td>
<td>1.3</td>
<td>20.33</td>
<td>CF+AF</td>
</tr>
<tr>
<td></td>
<td>1.4</td>
<td>21.74</td>
<td>CF+AF</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>21.80</td>
<td>CF+AF</td>
</tr>
</tbody>
</table>
Table 3 shows the adhesion strength of adhesives produced from castor oil based polyols and blend of castor oil polyol with soy oil polyol and rice bran oil polyol. As the hydroxyl content of castor oil increased from 200 to 400, the adhesive strength increased from 22.5 MPa to 42.5 MPa. The results also indicate that the adhesives produced from blends of castor oil polyol and other two polyol, showed the same trend of increase in strength. SC 2 having ratio of 2.33 (castor oil polyol/soy oil polyol) and the sample RC 1 having ratio of 4.0 (castor oil polyol/rice bran oil polyol) gave maximum adhesion strength. Loci of failure of adhesives from hydroxyl value up to 300 was cohesive or mixed (cohesive + adhesion failure). Adhesive obtained from polyol having hydroxyl value 400 resulted in adhesion failure probably due to higher amount of TDI and cured adhesive which increased the attraction between the adhesive material as compare to the attraction between adhesive and wood.
### Table 3

Blends of Castor oil polyol with Soy and Rice bran oil polyols

<table>
<thead>
<tr>
<th>Polyols blends</th>
<th>Castor / other polyol ratio</th>
<th>Average lap shear strength (± 2.0 MN/m²)</th>
<th>Locus of Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Castor and Soy</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SC 1</td>
<td>4.0</td>
<td>39.65</td>
<td>CF + AF</td>
</tr>
<tr>
<td>SC 2</td>
<td>2.33</td>
<td>42.25</td>
<td>CF + AF</td>
</tr>
<tr>
<td>SC 3</td>
<td>1.5</td>
<td>34.13</td>
<td>CF</td>
</tr>
<tr>
<td>SC 4</td>
<td>1.0</td>
<td>25.26</td>
<td>CF</td>
</tr>
<tr>
<td><strong>Castor and Rice bran</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RC 1</td>
<td>4.0</td>
<td>40.44</td>
<td>CF + AF</td>
</tr>
<tr>
<td>RC 2</td>
<td>2.33</td>
<td>38.12</td>
<td>CF</td>
</tr>
<tr>
<td>RC 3</td>
<td>1.5</td>
<td>34.74</td>
<td>CF</td>
</tr>
<tr>
<td>RC 4</td>
<td>1.0</td>
<td>28.31</td>
<td>CF</td>
</tr>
</tbody>
</table>

SC: Blend of soy and castor oil polyols
RC: Blend of rice bran and castor oil polyols
CF: cohesive failure of adhesive
AF: adhesion failure
3.9.3 Gel Time

![Graph showing effect of NCO/OH ratio on gel time of adhesives](image)

Figure 10: Effect of NCO/OH ratio on gel time of adhesives

Where S1 : CAS 300
S2 : SC 2
S3 : RC 2

![Graph showing gel time of adhesives obtained from blends of polyols](image)

Figure 11: Gel time of adhesives obtained from blends of polyols

Gel time or pot life is an important parameter for adhesive system from its application point of view. As NCO/OH ratio of 1.2 gave better...
results, gel time of adhesive obtained from different polyols giving best results from the three oil based polyols were studied at varying hydroxyl values, for which results are shown in the above Figure 10. It can be seen from the results that gel time for castor oil based adhesives was less compare to other two types of adhesives. Gel time was found in decreasing order with the increased hydroxyl value and as gel time is directly related to the reactive sides available in the polyol, higher the –OH functionality in the polyol, it reacts more readily with –NCO groups of TDI ultimately lowering the gel time. As shown in Figure 11 gel time of adhesives, giving best result obtained from blends of polyols having hydroxyl value of 300 was measured at the same NCO/OH ratio to understand the effect of castor oil polyol in the blends. Gel time for SC 1 was least at 9 min and it was highest for SC 4 at 27 min. Same result were found for RC 1 and RC 4 giving least and highest gel time of 13 min and 29 min respectively. This shows that as the content of castor oil-based polyol increases in the blends, it decreased the gel time. SC 1 and RC 1 were of the ratio 4.0 (Castor/other polyol) which is having highest content of castor oil based polyol while SC 4 and RC 4 were of the ratio 1.0. In between these ratios the get time were intermediate.

3.9.4 Curing Time

Curing time, which shows the time required for adhesive to develop ultimate bonding properties, indicated the dependence on hydroxyl value of polyol. It was observed that increase in hydroxyl value required less time to attain a particular value of bond strength. Castor oil polyols having hydroxyl value 200, 300 and 400 were randomly selected for the study. Figure 12 shows the curing time for prepared adhesives. 5 days were required for each adhesive to develop its ultimate strength and no noticeable change was observed thereafter. Adhesive from polyols having hydroxyl value 200, 300 and 400 gained 40.5 %, 53.36 % and 52.25 % of its maximum strength respectively after one day which shows the curing reaction for the adhesives was fast at the initial period and thereafter the increase was less noticeable.
**3.9.5 Chemical resistance**

Table 4 shows the chemical resistance of prepared adhesives before and after treatment with acid, alkali, cold water and hot water. Adhesives were having good resistant against water and moderate resistance to acid. Very less amount of penetration of water and acid solution at the adhesive-wood interface was observed However strength of adhesives decreased after treating the specimen with alkali due to the effect of alkali on lignin present in the wood. During the alkali treatment, alkali penetrated the sample and s a continuous extraction of lignin from the wood by the alkali solution was observed, which caused uneven contact of adhesive surface with substrate and loosening of the chemical interlocking between wood and adhesive ultimately resulting in bond weakening. Alkali penetration in to the wood resulted in a little amount of swelling of the surface in touch with the adhesive as well, which could also have decreased the strength of adhesion.

**Figure 12: Curing time of adhesive**
Table 4
Chemical Resistance of adhesives

<table>
<thead>
<tr>
<th>Adhesive Code</th>
<th>Original</th>
<th>After acid treatment (1 N HCl)</th>
<th>After alkali treatment (1 N NaOH)</th>
<th>After treatment with cold water (20-25°C)</th>
<th>After treatment with hot water (80-90°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAS 200</td>
<td>22.52</td>
<td>17.01</td>
<td>10.74</td>
<td>21.5</td>
<td>20.45</td>
</tr>
<tr>
<td>CAS 300</td>
<td>36.84</td>
<td>31.12</td>
<td>25.26</td>
<td>36</td>
<td>37.1</td>
</tr>
<tr>
<td>CAS 400</td>
<td>42.11</td>
<td>38.45</td>
<td>30.54</td>
<td>42.18</td>
<td>42.11</td>
</tr>
<tr>
<td>SC1</td>
<td>39.65</td>
<td>32.1</td>
<td>25.22</td>
<td>39.61</td>
<td>37.5</td>
</tr>
<tr>
<td>SC2</td>
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<td>37.25</td>
<td>27.09</td>
<td>42.2</td>
<td>40.05</td>
</tr>
<tr>
<td>SC3</td>
<td>34.13</td>
<td>29.11</td>
<td>24.98</td>
<td>31.33</td>
<td>30.12</td>
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<td>25.26</td>
<td>20.26</td>
<td>17.04</td>
<td>24.33</td>
<td>22.03</td>
</tr>
<tr>
<td>RC1</td>
<td>40.44</td>
<td>33.45</td>
<td>28.1</td>
<td>40</td>
<td>37.13</td>
</tr>
<tr>
<td>RC2</td>
<td>38.12</td>
<td>31.2</td>
<td>26.24</td>
<td>37.55</td>
<td>33.98</td>
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<td>34.74</td>
<td>24.36</td>
<td>20.02</td>
<td>34.22</td>
<td>30.7</td>
</tr>
</tbody>
</table>

3.9.6 Comparison with commercial product

Comparison of one of the prepared adhesives showing the best performance (SC 2) was carried out with two of the widely used commercially available adhesives (trade name: Fevicol™ and Araldite™) in India. The curing conditions for both the adhesives, i.e. synthesized and commercial were identical as discussed in section 3.8. As shown in table 6, the synthesized PU adhesives had better performance than the commercial adhesives, which showed a good possibility to used synthesized adhesive in place of other available adhesives.
3.9.7 Chemical and thermal characterization

(i) Broido’s method for the analysis of TGA data

When a polymeric substance is heated beyond some limit, it undergoes degradation. It is assumed that degradation products are volatile. The fraction (Y) of the number of initial molecules not yet decomposed is defined by the following relation:

\[ Y = \frac{N}{N_0} = \frac{(W_t - W_\alpha)}{(W_0 - W_\alpha)} \quad (1) \]

Where, \( W_0 \) = initial weight of the sample
\( W_t \) = weight of the sample at temperature \( T \) °C
\( W_\alpha \) = weight of the residue at completion of the reaction

If the degradation is carried out isothermally, the rate of reaction is given by

\[ \frac{dY}{dt} = -KY^n \quad (2) \]

Where, \( n \) = order of the reaction

The rate constant is changes with absolute temperature according to the Arrhenius equation

\[ K = A e^{-E/RT} \quad (3) \]

From equation 3 and 4, it follows

\[ \frac{dY}{Y^n} = -K \, dt \quad (4) \]
If, instead of operating the reaction isothermally, the reaction is operated at increasing temperature and if temperature \( T \) is a linear function of a time \( t \) and if the rate of heating is \( \beta \), then

\[
T = T_0 + \beta t \\
\frac{dT}{dt} = \beta \tag{6}
\]

From equation 5 and 7, it follows

\[
\frac{dY}{Y^n} = -\frac{A}{\beta} \int e^{-E/RT} \, dT \\
\int_{Y^n}^{1} \frac{dY}{Y^n} = -\frac{A}{\beta} \int_{T_0}^{T} e^{-E/RT} \, dT \\
\int_{Y^n}^{1} \frac{1}{Y^n} \, dY = -\frac{A}{\beta} \int_{T_0}^{T} e^{-E/RT} \, dT \tag{8}
\]

The thermogravimetric curve of such a relation represents this rate equation integrated from a temperature \( T_0 \) at which \( Y = 1 \). Thus,

\[
\int_{Y^n}^{1} \frac{dY}{Y^n} = -\ln Y = \ln \left(\frac{1}{Y}\right) \tag{10}
\]

Conversely, the integration of the R.H.S. part of the equation 7 is not simple. Vallet [37] has reported the values of integration of the
terms like that involved in equation 9. From these data, the value of integration of the L.H.S. term was obtained by Broido [59].

Krevelen and co-workers [60] revealed that the entire measurable reaction usually occur within 10% of the temperature of maximum reaction velocity ($T_{max}$). They applied a certain approximation and obtained the following relation.

$$\ln \ln \left( \frac{1}{Y} \right) = \left( \frac{E}{R} \cdot T_{m}^{2} + 1 \right) \ln T + \text{Constant} \quad (11)$$

According to equation 11 a plot of $\ln \ln \left( \frac{1}{Y} \right)$ Vs $\ln T$ yields a straight line whose slop is related to the energy of activation. Horowitz and Metzger [61] introduced two alternate approximations and developed relation 12 and 13.

$$\ln \ln \left( \frac{1}{Y} \right) = \left( \frac{E}{R} \cdot T_{m}^{2} \right) T + \text{Constant} \quad (12)$$

$$\ln \ln \left( \frac{1}{Y} \right) = - \left( \frac{E}{R} \right) \left( \frac{1}{T} \right) + \text{Constant} \quad (13)$$

The expression 13, which found to be more accurate than equations 11 and 12, was employed in the present work to calculate the activation energy ($E_A$) of thermal degradation of the polymers from TG thermograms.

(ii) Doyle’s method

Integral procedural decomposition temperature (IPDT) was devised as a means of summing up the whole shape of the normalized data curve. As such, it is consistently available from the cumulative data record of thermogravimetric analysis in an inert atmosphere.

The IPDT values are determined from a weight loss curve as follows. The curve as shown in figure 13 is divided into small squares.
The area under the curve is integrated by weighing a paper cutout of the curve on an analytical balance.

The weight of crosshatched region in figure 13 divided by the weight of the total rectangular plotting area is the total curve area $A^*$, normalized with respect to both residual weight and temperature.

The quantity $A^*$ is converted to a temperature $T_A^*$, by

$$T_A^* = 875 A^* + 25$$

(14)

![Figure 13: Thermogram of polymer](image-url)

It is presumed that all materials volatilize below 900 °C and do so at a single temperature. Thus, $T_A^*$ represents a characteristic end-of volatilization temperature. However, it does serve as a measure of refractoriness, but is not very satisfactory.

To put all materials on an equal basis with respect to experimental temperature range, as in $A^*$, but also with respect to their individual refractory contents, a second curve area $K^*$, was defined, as illustrated by the double crosshatched region given in figure 13. In value, the lesser area, $K^*$, is the ratio between the doubly crosshatched area and the rectangular area bounded by the
characteristic end-of volatilization temperature, $T_{A^*}$ and the residual weight fraction at the fixed end-of-test temperature of 900 $^\circ$C.

Doyle showed that the product $A^*K^*$ represented a comprehensive index of intrinsic thermal stability for 54 polymers of widely different basis types. It was also shown that by substituting $A^*K^*$ for $A^*$ in equation 14 the IPDT obtained had a practical meaning as a half-volatilization temperature.

**(iii) FTIR and Thermal analysis**

The PU’s are the superspeciality polymer finding applications in the varied field viz. foam, coating, adhesives etc. The product finds uses over a wide temperature range under different chemical environmental conditions. In order to ascertain the reaction of polyol and isocyanate and satisfactory performance of the prepared polymer against elevated temperature conditions, the FTIR and thermal analysis were carried out. Figure 14 shows the IR spectra of adhesives prepared from castor oil based polyols (a), blend of castor and soy oil polyol based polyol (b) and castor and rice bran oil based polyol (c). Broad absorption band around 3420 cm$^{-1}$ is attributed to urethane NH linkage. This band centered at 3420 cm$^{-1}$ in spectra a, was more intense and broad due to the primary hydroxyl group present in the purely castor oil based polyol adhesive, which increases the reactivity whereas in the blends the long fatty acid chain of other oil may interfere with the reaction of hydroxyl with isocyanate. Bands at 2850 cm$^{-1}$ and 2925 cm$^{-1}$ are due to alkyl C – H stretching of soft segment (fatty chain) of the polymer. Splitting of band at 1720 cm$^{-1}$ indicates the H – bonded and non H – bonded carbonyl groups which overlap to give an asymmetrical absorption band. This was less pronounced in the spectra c as compare to a and b showing less interaction of carbonyl group with hydrogen bond in the former. Band at around 1066 cm$^{-1}$ is attributed to C – N and bands at around 1540
and 1604 are due to conjugated double bonds of aromatic ring of the hard segment confirming the reaction of polyol with TDI.

**Figure 14 (a): PU adhesive obtained from castor oil-based polyol**

**Figure 14 (b): PU adhesive from blend of castor and soy oil-based polyols**
Thermogravimetric analysis of prepared adhesives showed almost identical thermal properties after their curing periods. TGA curves of adhesive showing the best performance among the specific type are shown in figure 15 a, b, and c. The obtained curve shows that the decomposition of adhesive started at around 165°C. It can be seen that the average loss for each 50°C rise from 200°C to 450°C was 15.89 %, 16.21 % and 22.9 % for CAS 300, SC 2 and RC 2 respectively. A slight difference in the TGA curves arose between 350°C to 400°C during which there was a difference of almost 5 % weight indicating a better thermal stability of the polymer obtained from the blend. Overall results show the high temperature stability, required for the wood adhesives. The TGA provides various valuable information about stability of polymers, values for which are shown in table-5. The values of Integral Procedural Decomposition Temperature (IPDT) which represents the overall thermal stability of the polymer was calculated by Doyle’s method and were 315°C, 325°C and 337°C for CAS 300 SC 2 and RC 2 respectively.
The results shown that the decomposition started earlier in RC 2 as compare to other PU adhesive but the overall stability shown by IPDT was higher than other because after half volatilization temperature at 315 °C the adhesive obtained from blend of castor and rice bran oil-based polyols showed enhanced thermal stability. However, the maximum weight loss for all of the three types of PU adhesive was in the range of 350 - 400 °C.

Figure 15 (a): TGA graph of PU adhesive on castor oil-based polyol
Figure 15 (b): TGA graph of PU adhesive based on blend of castor and soy oil-based polyol (SC-2)

Figure 15 (c): TGA graph of PU adhesive based on blend of castor and rice bran oil-based polyol (RC-2)
Table 5

<table>
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<tr>
<th>Adhesive</th>
<th>IDT&lt;sup&gt;1&lt;/sup&gt;</th>
<th>IPDT&lt;sup&gt;II&lt;/sup&gt;</th>
<th>T&lt;sub&gt;A&lt;/sub&gt;&lt;sup&gt;III&lt;/sup&gt;</th>
<th>T&lt;sub&gt;H&lt;/sub&gt;&lt;sup&gt;IV&lt;/sup&gt;</th>
<th>T&lt;sub&gt;M&lt;/sub&gt;&lt;sup&gt;V&lt;/sup&gt;</th>
<th>Activation Energy Ea (kJ mole&lt;sup&gt;-1&lt;/sup&gt;)</th>
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<tr>
<td>CAS 300</td>
<td>180 °C</td>
<td>315 °C</td>
<td>430 °C</td>
<td>310 °C</td>
<td>350 - 400 °C</td>
<td>49</td>
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<td>SC-2</td>
<td>178 °C</td>
<td>325 °C</td>
<td>440 °C</td>
<td>330 °C</td>
<td>350 - 400 °C</td>
<td>48</td>
</tr>
<tr>
<td>RC-2</td>
<td>170 °C</td>
<td>337 °C</td>
<td>450 °C</td>
<td>315 °C</td>
<td>350 - 400 °C</td>
<td>52</td>
</tr>
</tbody>
</table>

Where

<sup>1</sup> Initial decomposition temperature

<sup>II</sup> Integral procedural decomposition temperature

<sup>III</sup> End-of-volatilization temperature

<sup>IV</sup> Half volatilization temperature

<sup>V</sup> Temperature range of maximum weight loss

DSC was carried out to find the glass transition and other changes in heat energy of synthesized polurethane adhesives and the DSC graphs are shown in figure16 (a, b and c). DSC defines the glass transition as a change in the heat capacity as the polymer matrix goes from the glass state to the rubber state. This is a second order endothermic transition (requires heat to go through the transition) so in the DSC the transition appears as a step transition and not a peak such as might be seen with a melting transition.

Glass transition temperature of PU adhesive obtained from castor oil-based adhesive (figure 16 (a)) was found at –16.5 °C and no major change in the graph was observed thereafter. Glass transition of PU adhesive obtained from blend of castor and soy oil-based polyol (figure 16 (b)) was at 34.8 °C. As the polyurethane synthesized was from the natural oils and cellulose there is always some possibility of crystallization of melting of one of these fractions in the polyol which could be obtained in DSC. This graph also shows a exotherm at – 10.2
°C which could have been due to crystallization of one of the fraction of polyol in the adhesive. Figure 16 (c) shows the DSC graph for PU adhesive obtained from blend of castor and rice bran oil-based polyol. It does not show any change in enthalpy or glass transition peak in the region above -20 °C which suggest that the $T_g$ could have been much below this temperature, however, there was two exotherms obtained at around 129 °C and 240 °C which could be assigned to $T_c$ of natural oil part of polyol (soft segment) and aromatic part (hard segment) of the PU adhesive.

Figure 16 (a): DSC graph of PU adhesive obtained from castor oil-based polyol (CAS 300)
Figure 16 (b): DSC graph of PU adhesive obtained from blend of castor and soy oil-based polyol

Figure 16 (c): DSC graph of PU adhesive obtained from blend of castor and rice bran oil-based polyol
3.10 CONCLUSION

Polyurethane adhesives suitable for its application in wood bonding were prepared from polyols having comparable adhesive strength with commercially available adhesives. The adhesives were obtained from castor oil polyols, blend of soy oil and castor oil based polyols, and blend of rice bran and castor oil based polyols. For the prepared adhesive, NCO/OH ratio of 1.2 and curing time of 5 days was found to be optimum in terms of adhesive joint strength and a linear increase in adhesive strength was found with increase in hydroxyl value of the polyol. The adhesives showed good resistance to cold and hot water, moderate resistance to acid and less resistance to alkali. The FTIR analysis confirmed the formation of polyurethane. Thermal analysis showed that the PU adhesives obtained from blend of castor and rice bran oil-based polyol was most stable followed by PU adhesive from blend of castor and soy oil-based polyols and castor oil-based polyols. T<sub>g</sub> in negative temperature for CAS 300 suggest its rubbery nature at ambient temperature. The added advantage of the prepared adhesive was its synthesis from renewable resource, utilization of waste and possible economically viable production at industrial level.
REFERENCES


34. O. Bayer (1947). *Mod Plastics*, 24, 149-152.