CHAPTER – 1

Introduction
**General Introduction**

Materials have such an influence on our lives that the historical periods of humankind have been dominated and named after materials with the advent of the modern civilization and development of scientific knowledge, there has been an upsurge in demand for developing newer materials for novel applications.

Historians frequently classify the early ages of man according to the materials that he used for making his implements and other basic necessities. The most well-known of these periods are the Stone Age, the Iron Age and the Bronze Age.

From the ancient civilizations of Egypt and Babylonia he was employing a range of materials such as stones, woods, ceramics, glasses, skins and fibers. Until the 19th century man’s inanimate possessions, his home, his tools, his furniture, were made from varieties of these classes of materials.

During last century and a half, two new closely related classes of materials have been introduced, which have not only challenged the older materials for their well established uses, but have also made possible new products, which have helped to extend the range of activities of mankind. Without these two groups of materials, rubber and plastics, it is difficult to conceive how such everyday features of modern life such as the car, telephone, television set could ever been developed.

The most ancient polymeric materials, mentioned in the book of ‘Genesis’ (Chapter-11) described that the builders in the “Babylonia” had a brick of stone and slime they had for mortar”.

In Ancient Egypt mummies were wrapped in a cloth dipped in a solution of bitumen in oil of lavender, which was known variously as Syrian Asphalt. On exposure to light, the product hardened and became insoluble. It would appear that this process involved the action of chemical cross-linking. This in modern times became of great importance in the vulcanization of rubber and production of thermosetting plastics.
[A] LITERATURE SURVEY ON BISPENOLS

Bisphenols are the important constituents or intermediates in dyes, drugs, paints and varnishes, coatings, pesticides, plasticizers, fertilizers, bactericides and in other applications. They are widely applied in manufacturing thermally stable polymers, epoxy resins and polyester resins.

Farbenind [1, 2] has studied the condensation of phenols and ketones in the presence of acetic acid, hydrochloric acid at 50°C and also reported the melting points of 1,1′-bis(4-hydroxy phenyl) cyclohexane (186°C). 1,1′-bis(3-methyl-4- hydroxyl phenyl) cyclohexane (186°C) and 1,1′-bis(4-hydroxy phenyl)-4-methyl cyclohexane (179°C). The products are useful as intermediates for dyes and drugs.

McGreal et al [3] have reported the condensation of ketones (0.5 mol) and phenols (1.0 mol) in acetic acid. The solutions were saturated with dry HCl for 3-4 h and the mixture was kept up to 4 weeks until the mass crystallized. The yields with aliphatic and aromatic ketones were 10-25% and with cyclic ketones 50-80%.

They have also proposed the following mechanism:

1. The addition of phenol to ketone
   \[
   \text{PhOH} + \text{R}_2\text{CO} \rightarrow \text{R}_2\text{C(OH)}\text{C}_6\text{H}_4\text{OH}
   \]

2. \[
   \text{R}_2\text{C(OH)}\text{C}_6\text{H}_4\text{OH} + \text{PhOH} \rightarrow \text{R}_2\text{C(C}_6\text{H}_4\text{OH)}_2 + \text{H}_2\text{O}
   \]

Johnson and Musell [4, 5] have reported synthesis of 1,1'-bis(4-hydroxy phenyl) cyclohexane (I) using 5 mol of phenol, 1 mol of a cyclohexanone, H₂S or BuSH below 40°C with 0.1-0.3 mol dry HCl gave (I) m.p.186-187°C; 4- Me-I 178°C; 1,1'-bis(4-hydroxy-3-methyl phenyl) cyclohexane m.p. 187°C and 1,1'-bis(4-hydroxy-3-isopropyl phenyl) cyclohexane, m.p. 109-111.5°C. Mash containing small quantities of bisphenol (I) protect chickens from coccidiosis better than does a sulfaguanidine.

Bender et al. [6] have reported preparation of various bisphenols by reacting phenol, NaOH and acetone. The mixture was refluxed for 16 h and acidified to pH 2-3 with 6N HCl. The yield was 47.5%. Similarly they have also synthesized 1,1'-bis(4-hydroxy phenyl) cyclohexane (m.p. 187°C), 1,1'-bis(3-methyl-4-hydroxy phenyl) cyclohexane (m.p.186-9°C) and 1,1'-bis(3-chloro-4-hydroxy phenyl) cyclohexane (m.p. 134-41°C).

Bender et al. [7] have reported the preparation of bisphenols by irradiating a mixture of ketone and phenol at 20-100°C with β-rays or ultraviolet in the presence of 37% aq. HCl or 70% H₂SO₄ as condensing agent and stirring at 30-37°C. 1,1'-Bis(4-hydroxy phenyl) cyclohexane (m.p. 186-189°C) was obtained in 93% yield from 1 mol cyclohexanone and 4 mol phenol.

Farbenfabriken [8] has reported the preparation of 4,4'-dihydroxy diphenyl cyclohexane (m.p.186°C) using cyclohexanone (78 kg) and excess phenol (400 kg) in the presence of 38% HCl as a catalyst at room temperature for 6 days.

Alexandru [9] has reported the preparation of bisphenols by reaction of a ketone (cyclohexanone) with phenol, BuSH, ClCH₂CH₂Cl and Me₃SiCl. The mixture was stirred and heated to 50-55°C and finally at 65°C to give bisphenol-Z.

Freudewald et al. [10] have reported the condensation of phenol (94 g) with cyclohexanone (98 g) in the presence of 2 g EtSH and anhydrous HCl (4.7 g) and heating at 70°C in closed system for 3 h to give 97% yield of 1,1′-bis(4-hydroxy phenyl) cyclohexane.

Rao et al. [11] have reported a convenient method for the preparation of bisphenols. Cyclohexanone was treated with PhOH at 40°C and with o-cresol at room temperature in the presence of HCl and AcOH to give 1,1′-bis(4-hydroxy phenyl) cyclohexane and 1,1′-bis(3-methyl-4-hydroxy phenyl) cyclohexane, respectively.

Garchar et al. [12-15] have studied optimization reaction conditions for the synthesis of 1,1′-bis(R, R′-4-hydroxy phenyl) cyclohexane by condensing cyclohexanone (0.05 mol) and phenol, o-cresol, and 2,6-dimethyl phenol (0.1 mol) in the presence of varying mixture of hydrochloric acid and acetic acid (2:1 v/v) at four different temperatures: 40°, 50°, 60°, 70°C.

They have reported optimum catalyst concentration (10-15 ml), time (30-90 min) and temperature (55-70°C) for obtaining yields greater than 80%. They have also synthesized chloro, bromo and nitro derivatives and screened for their potential antimicrobial and antifungal activities against different microbes. Some of these compounds are significantly found active against B. subtilis, S. pyogens and A. niger. The nitro compounds are found to be the most active antifungal agents.

[B] LITERATURE SURVEY ON EPOXY RESINS, EPOXY ESTERS (POLYESTER POLYOLS)

Epoxy resins are the most versatile class of contemporary plastics. Due to tendency of undergoing variety of chemical reactions and became material of choice for researchers for several years. By the help of reactions like co-polymerization, chain extension by reactive diluents, side chain modification, incorporation of variety of fillers and structure modifiers, the resin structure can be modified. The capabilities of undergoing vast chemical reactions of the resins the desire properties can be achieved.

Epoxy resins are widely used as a matrix in composites in different applications where chemical, mechanical, thermal, and dielectric properties are necessary. In addition, epoxy resins are versatile crosslinked thermosetting polymers with an excellent chemical resistance and good adhesion properties to different substrates. Due to these properties, they are used as adhesives and coatings [16]. Epoxy is best for laminates in combination with glass fiber to achieve excellent electrical insulators.

Use of epoxy resins in composite matrix in high technology areas is limited, as these areas require material with inherent low thermal expansion coefficients and high toughness [17,18] and better heat and moisture stability. Recently, a lot of research work has been done to improve the required parameters of epoxy resins through modifications in both the backbone and pendant groups. Urea-formaldehyde and silicon resins have been reported to have excellent properties as modifiers for the epoxy resins. The first commercial attempts to prepare resins from epichlorohydrin were made in 1927 in the United States. Credit for the first synthesis of bisphenol-A-based epoxy resins is shared by Dr. Pierre Castan of Switzerland and Dr. S.O. Greenlee of the United States in 1936. Dr. Castan's work was licensed by Ciba, Ltd. of Switzerland, which went on to become one of the three major epoxy resin producers worldwide. Ciba's epoxy business was spun off and later sold in the late 1990s and is now the advanced materials business unit of Huntsman Corporation of the United States. Dr. Greenlee's work was for the firm of Devoe-Reynolds of the United States. Devoe-Reynolds, which was active in the early days of the epoxy resin industry, was sold to Shell Chemical (now hexion, formerly Resolution Polymers and others).

Desai et. al [19] have synthesized polyester polyols using vegetable oil fatty acids having different characteristics (mainly in terms of hydroxyl functionality) and epoxy resin, using triethyl amine as a catalyst. Polyols were characterized by FTIR spectroscopy. PU adhesives were synthesized from it and used in bonding the rubber. Treatment of sulphuric acid on the non-polar styrene-butadiene rubber (SBR) surface as studied for the bond strength improvement.


via an increase in wettability of the rubber surface. Wettability was found by measuring the contact angle using Goniometer. Bond strength was evaluated by a 1800 T-peel strength test. The surface modification and mode of bond failure were studied by scanning electron microscopy (SEM).

The epoxy resin can be converted into three dimensional infusible networks together by covalent bonds. This conversion from a liquid or a friable brittle solid into tough cross-linked polymer is called curing or hardening in epoxy technology. Mainly amine hardening and acid hardening systems are employed for curing of epoxy resins.

Epoxy resins are widely used for land, marine and space transportation, automobile and electrical components, rehabilitations products and pollution control equipments. The characteristic properties of epoxy resins make them suitable for an increasing number of engineering applications, such as high strength and stiffness, good dielectric behavior, resistance to chemicals, low shrinkage during cure, etc. Despite of excellent properties their brittle behavior with low elongation restricts their use for high performance applications [20]. Many researchers have tried to modify the epoxy resin to improve its mechanical properties by reacting it with dienes [21], acrylates, etc. This modification of epoxy resin is feasible due to highly reactive epoxy ring, which can also undergo ring opening reaction in the presence of acids [22] to yield polyester polyol containing a free hydroxyl group that can be utilized to produce polyurethanes. To make an economic production of polyurethanes, efforts have been made to prepare polyester polyols from the low cost natural oils and their derivatives.

All the vegetable oil fatty acids are used for polyester polyol (epoxy esters) manufacturing but the most commonly used are listed below with their specific properties they confer on the polyester polyol (epoxy esters). Today’s technology of epoxy resins had started only by late 1930’s and early 1940s, when a number of patents were applied simultaneously in U.S.A. and Europe. Special mention may be made of the work carried out by Dr. Castan of Switzerland and Dr. Sylvan Greenlee of the United States simultaneously around the year 1938, who had patented the first epoxy resin out of reaction of epichlorohydrin and bisphenol-A.

Various types of epoxy resins have been produced: glycidyl ethers, glycidylamines, linear aliphatics and cycloaliphatics. However, epoxy resin, which is a reaction product of epichlorohydrin and bisphenol-A, is most commonly used epoxy resin today, known as diglycidyl ether of bisphenol-A (DGEBA) (I).

\[
\begin{align*}
\text{CH}_2\text{CHCH}_2\text{O} & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_2\text{OCHCH}_2\text{O OH} \\
\end{align*}
\]

(I)

The resin can be obtained with different degrees of polymerization ranging from low viscosity liquids to high melting solids [23] as shown in Table 1.1. In order to prepare high molecular weight resin and to avoid contamination the epoxy resin can be prepared by two-stage process. This involves first the preparation of lower molecular weight polymers with a degree of polymerization of about three and then reacted with bisphenol-A in the presence of a suitable polymerization catalyst such that the reaction takes place without evolution of byproduct [24].


Table – 1.1: Effect of reactant ratios on molecular weight

<table>
<thead>
<tr>
<th>Mole ratio of epichlorohydrin/bisphenol-A</th>
<th>Softening point (°C)</th>
<th>Molecular Weight</th>
<th>Epoxide equivalent</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>43</td>
<td>451</td>
<td>314</td>
</tr>
<tr>
<td>1.4</td>
<td>84</td>
<td>791</td>
<td>592</td>
</tr>
<tr>
<td>1.33</td>
<td>90</td>
<td>802</td>
<td>730</td>
</tr>
<tr>
<td>1.25</td>
<td>100</td>
<td>1133</td>
<td>862</td>
</tr>
<tr>
<td>1.2</td>
<td>112</td>
<td>1420</td>
<td>1176</td>
</tr>
</tbody>
</table>
The epoxide resins of the glycidyl ether are usually characterized by six parameters:

- Resin viscosity (of liquid resin)
- Epoxide equivalent
- Hydroxyl equivalent
- Average molecular weight
- Melting point (of solid resin)
- Heat distortion temperature (of cured resin)

The epoxy resin can be converted into three dimensional infusible networks together by covalent bonds. This conversion from a liquid or a friable brittle solid into tough cross-linked polymer is called curing or hardening in epoxy technology. Mainly amine hardening and acid hardening systems are employed for curing of epoxy resins.

Epoxy resins are widely used for land, marine and space transportation, automobile and electrical components, rehabilitations products and pollution control equipments. The characteristic properties of epoxy resins make them suitable for an increasing number of engineering applications, such as high strength and stiffness, good dielectric behavior, resistance to chemicals, low shrinkage during cure, etc. Despite of excellent properties their brittle behavior with low elongation restricts their use for high performance applications [25].

Chemie Produkte [26] has reported the sealing composition for pipe joints and building materials. A typical composition consists of a mixture of an epoxy resin, a hardener and tar, which polymerized rapidly.

Many researchers have tried to modify the epoxy resin to improve its mechanical properties by reacting it with dienes[27], acrylates, etc. This

Modification of epoxy resin is feasible due to highly reactive epoxy ring, which can also undergo ring opening reaction in the presence of acids [28] to yield polyester polyol containing a free hydroxyl group that can be utilized to produce polyurethanes. To make an economic production of polyurethanes, efforts have been made to prepare polyester polyols from the low cost natural oils and their derivatives.

All the vegetable oil fatty acids are used for polyester polyols (epoxy esters) manufacturing but the most commonly used are listed Table-1.2 with their specific properties they confer on the polyester polyols (epoxy esters). Polyester polyol is more effective than polyether polyol in the production of polyurethane.

The commercial interest in epoxide resins was first made apparent by the publication of German patent 6, 76, 117 by I. G. Farben in 1939, which described liquid poly epoxides. In 1943 P. Casten filed US patent 23, 24, 483 covering the curing of the resins with dibasic acids. The Ciba Company subsequently exploited this important process. A later patent of Casten (US patent 24, 44, 333) covered the hardening of epoxide resins with alkaline catalyst used in the range 0.1–5 %. This patent, however, became of somewhat restricted value as the important amine hardeners are usually used in quantities higher than 5%.

In the early stage of their development, epoxy resins were used almost entirely for surface coating. The developments in this field are due to the research work of S. O. Greenlee and described in a number of patents. These include work on the modification of epoxy resins with glycerol, the esterification with drying oil acids and reaction with phenolic and amino resins.

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Epoxy ester properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linseed</td>
<td>Fast air drying system with poor color retention</td>
</tr>
<tr>
<td>DCO</td>
<td>Fast air-drying or stoving system with good flexibility and chemical resistance.</td>
</tr>
<tr>
<td>Soya been</td>
<td>Air-drying systems with good color and soft flexibility films.</td>
</tr>
<tr>
<td>Coconut</td>
<td>Non-air drying system with very good color, chemical resistance and flexibility, good color on oven baking.</td>
</tr>
</tbody>
</table>
Greenlee [29] has prepared the rapid drying composition from diphenols and epichlorohydrin and esterified this product with Tall–oil.

Chemie Produkte [30] has reported the sealing composition for pipe joints and building materials. A typical composition consists of a mixture of an epoxy resin, a hardener and tar, which polymerized rapidly.

Lederman [31] has reported varnish based on bisphenols. A wrinkle varnish or base comprising a blend of tung-oil varnish and fish-oil varnish is described. It gives a fine texture wrinkle finish, good toughness and flexibility.

Petri et al. [32] have prepared epoxy resin foams from aqueous dispersions. Epoxy resin based on bisphenol-A, benzsulfohydrazide, dipropylene triamine were dispersed in water by 2,3-dibromopropyl phosphate as a dispersing medium. Rigid foam was obtained by this composition, which is suitable for architectural uses.

CIBA Ltd. [33] has reported coating composition for floors, roofs, walkers and walls based on bisphenol–A epoxy resin. The composition was room temperature hardenable having quartz sand, epoxy resin, dibutyl phthalate together with triethylene tetramine. This composition has consistency of mortar and a pot life of 2.0 – 2.5h. It is spread on a concrete floor to a depth of 4mm. hardening required 24-48h. The composition shows excellent adhesion in non-cracking and is highly resistance to chemical.

Union Carbide Co. [34] has reported curing of polyepoxides with liquid glycol diamines \( \left( \mathrm{H}_2\mathrm{N}(\mathrm{CH}_2)_3\mathrm{O}(\mathrm{C}_n\mathrm{H}_{2n}\mathrm{O})_x\ (\mathrm{CH}_2)_3\mathrm{NH}_2 \right) \), where \( n \) is 2-5 and \( x \) is 1-11.

The cured compounds have excellent impact strength and flexibility and are stable as protective coatings. Thus, 100 g of diglycidyl ether of 2,2′-bis(p-hydroxy-phenyl) propane was mixed with 29.4 g stoichiometric amount of H₂N(CH₂)₃O(CH₂CH₂O)₂(CH₂)₃NH₂ for 5 min. The mixture was applied on cold-rolled steel and was cured by storing 7 days at room temperature.

Minnesta Mining and Manufacturing Co. [35] have reported synthesis of flexible adhesive film having honeycomb structure. Thus, an epoxy resin mixture was prepared by heating 100 parts of glycidyl ether of bisphenol–A at 121°C, adding 2-parts fine SiO₂ and stirring at 149°C for 10-20 min. A mixture of 145 parts isophthaloyl dihydrazide, 10 parts MgO and 1 part dimethyl diocta decyl ammonium bentonite was added to epoxy mixture at 104°C and the resulting mixture was milled at 77°C to complete dispersion.

Bremmer [36] has synthesized flame-retardant epoxy resin. In a typical composition tetra bromo bisphenol-A was added to bisphenol-A-diglycidyl ether (epoxide equivalent 186) at 70°C under an N₂ atmosphere with stirring. The composition was cured by triethyl amine.

Taft [37] has reported new polymeric coating agents with improved properties. Such composition consists of a reaction product of hydroxy or epoxy containing compound capped with the bisphenol acid, 4-4′-bis(4-hydroxy phenyl) valeric acid (II) with a poly isocyanate and cross linked with an amine.

Thus (II) reacts with 1,6-hexanediol and the reaction product was treated with Mondur HC (poly isocyanate) to give a composition, which was sprayed to a
10-75 μ thick film on glass, metal or wood and cured for 5-15 sec in triethylamine. On heating 200g (I) and 50 g nonyl phenol for 1h at 66ºC gave the blocked curing agent. A mixture of this compound, bisphenol-A-epichlorohydrin copolymer (epoxy equivalent ~190) and 2,2-bis(o-hydroxy phenyl) propylene oxide copolymer epoxide equivalent ~ 345) were cooked together. The composition has self-life of about 4 h and 70 min at 0ºC.

![Chemical structure](image)

(II)

Castan and Gandillon [38] have reported esterified epoxy resin of phenol formaldehyde with long chain fatty acids, which may be unsaturated, and dehydration is affected with acid catalyst to produce rapid drying films. Co or Pb naphthenate were also used. The resulting films are relatively resistant to alkali. The use of saturated acids in the esterification step gives resins, which can be hardened in the kiln.

Devoe and Raynolds Co. Inc. [39] have reported coatings of polyepoxy resin and dimeric fatty acids. Aliphatic polyepoxides or dihydric phenol react at 150º with dimeric unsaturated fatty acids, especially dilinoleic acid so that all carboxylic groups react only with epoxy groups to give high molecular weight linear polyether-polyester resins with epoxy end group for each carboxylic group > 1 but < 2 epoxy groups are used. Such resins give coatings after baking in the presence of amine catalysts and optically together with phenol or urea HCHO resins.

Kinck and Ditrych [40] had synthesized epoxy resin ester of Bisphenol-C1, epichlorohydrin 1.16, and NaOH 1.25 moles in organic solvents at 80-100º until the softening point was 100ºC. The resin obtained had an ester equivalent of 180 content of epoxy groups 0.11 mole/100 g, and no. of -OH groups 0.33 mole/100 g. Fatty acid (1600 parts) isolated from a soyabean oil was treated with 400 parts dicyclopentadiene at 280ºC during 3h. Volatile and unreacted components were distilled in vacuum. The prepared resin (900 parts) was mixed in a stainless steel vessel with the prepared acids (950 parts) and heated to 140ºC, and stirred under CO2. When the mixture was homogenized, the product was heated to 230ºC during 2 h and kept at the temperature until the acid no was 10 mg KOH /g, then the mixture was cooled to 170ºC and dissolved in a 1:1 mixture of xylene and ligronine to form a varnish containing 30% of dry substances. The hot varnish was filtered and used as an air drying varnish after adding 0.05 % Co-naphthenate.

Nemours & Co. [41] has reported salt spray resistant coating composition of alkyd resin, drying oil (soyabean oil), and liquid epoxy resin (condensation) product of epichlorohydrin and diphenyl isoporpane. These compositions exhibit good adhesion and corrosion resistance under topcoats of acrylic enamel.

Shimizu et al. [42] have esterified epoxy resins with higher fatty acids like dehydrated linseed oil fatty acid in the presence of alkali metal salt catalyst and xylene for 8 h at 230–240ºC under nitrogen atmosphere to give polyester with QGardner viscosity (as a 50 % xylene solution).

Neumann and Hoenel [43] have prepared epoxy resins based on bisphenols useful in adhesive, coating, molded articles, where a part of bisphenols compounds are modified at the aromatic rings with an aryl alkyl

group. For example, bisphenol-F and styrene were reacted in presence of catalyst at 120°C, and equivalent weight 670-690 g/mol and viscosity at 25°C in 40% butyl diglycol solutions 480-510 mPas.

Nakahara et al. [44] have developed new type of epoxy resin containing a 4,4'-biphenylene moiety in the backbone (Bis-EBP) and confirmed its structure by elemental analyses, infrared spectroscopy and $^1$H-nuclear magnetic resonance spectroscopy (NMR). In addition, to evaluate the influence of the 4,4'-biphenylene group in the structure, an epoxy resin having a 1,4-phenylene group in place of the 4,4'-biphenylene moiety (Bis-EP) was synthesized. The cured polymer obtained through the curing reaction between the new biphenyl-containing epoxy resin and phenol novolac was used for making a comparison of its thermal and physical properties with those obtained from Bis-EP and bisphenol-A (4,4'-isopropylidenediphenyl)-type epoxy resin (Bis-EA). The cured polymer obtained from Bis-EBP showed markedly higher fracture toughness of 1.32 MPa, higher than that of glass.

Liu et al. [45] have prepared simultaneous interpenetrating polymer networks (IPNs) based on epoxy (diglycidyl ether of bisphenol-A) and unsaturated polyester resin (UP) using m-xylene diamine and benzoyl peroxide as curing agents. A single glass transition temperature for each IPN was observed with differential scanning calorimetry (DSC), which suggested good compatibility of epoxy and UP. This compatibility was further confirmed by the single damping peak of the rheometric dynamic spectroscopy. Curing behaviors were studied with dynamic differential scanning calorimetry and the curing rates were measured with a Brookfield RTV viscometer. It was noted that an interlock

between the two growing networks did exist and led to a retarded viscosity increase. However, the hydroxyl end groups in UP catalyzed the curing reaction of epoxy; in some IPNs where the hydroxyl concentration was high enough, such catalytic effect predominated the network interlock effect, leading to fast viscosity increase. In addition, the entanglement of the two interlocked networks played an important role in cracking energy absorption and reflected in a toughness improvement.

Sanariya et al. [46] have reported a convenient method for the preparation of epoxy resins based on bisphenols-C. The epoxy resins of bisphenols-C derivatives were synthesized by condensing corresponding derivative (0.5 moles) with epichlorohydrin (1.1 moles) by using isopropanol (500 ml) as a solvent and sodium hydroxide (1.0 mol in 40 ml water) as a catalyst. The reaction mixture was stirred at reflux temperature for 4h. Excess of solvent was distilled off and the viscous resin was isolated from distilled water. The resin was extracted from chloroform and evaporated to dryness to obtain pure resin. The yield was 75-80 %.

Kagathara et al. [47] have reported a convenient method for the preparation of epoxy resins based on halogenated bisphenols-C. The epoxy resins of bisphenols-C derivatives were synthesized by condensing corresponding derivative (0.5 moles) with epichlorohydrin (1.1 moles) by using isopropanol (500 ml) as a solvent and sodium hydroxide (1.0 mole in 40 ml water) as a catalyst. The reaction mixture was stirred at reflux temperature for 4h. Excess of solvent was distilled off and the viscous resin was isolated from distilled water. The resin was extracted from chloroform and evaporated to dryness to obtain pure resin. The yield was 75-80 %.


Liu et al. [48] have reported combination of epoxy and novolac resins. In a typical study, a novel phosphorus-containing Ar-alkyl novolac (Ar-DoPo-N) was prepared. The Ar-DoPo-N blended with novolac and used as a curing agent for o-cresol formaldehyde novolac epoxy, resulting in cured epoxy resins with various phosphorus contents. The epoxy resins exhibited high glass-transition temperatures (159-176°C), good thermal stability (>320°C).

**Polyesters**

Polyester resins are unsaturated resins formed by the reaction of dibasic organic acids and polyhydric alcohols. Among other uses, it is the basic component of sheet moulding compound and bulk moulding compound. Unsaturated polyesters are condensation polymers formed by the reaction of polyols (also known as polyhydric alcohols, organic compounds with multiple alcohol or hydroxy functional groups) and polycarboxylic that contain double bonds. Typical polyols used are glycols such as ethylene glycol. The usual polycarboxylic acids used are phthalic acid and maleic acid. Water, which is a by-product of this esterification reaction, is removed from the reaction mass as soon as it is formed to drive the reaction to completion.

Polyester resins are produced by different reactions such as the esterification of acids or alcoholysis or acidolysis of epoxies, etc. The wide selection of raw materials available allows a very large choice of finished products, with a wide range of properties. Polyester polyols are obtained by using a stoichiometric excess of di- or polyfunctional alcohols over the acid monomers during manufacture, which produces polyester backbones with hydroxyl reactive groups. The selection of raw materials and conditions of polymerization will produce polyesters with primary or secondary hydroxyl groups. The position of these groups will have a strong effect on the final properties of the polyurethane, especially reactivity. Polyester resin is used for casting, auto body repair, wood

filling, and as an adhesive. It has good wear and adhesive properties, and can be used to repair and bond together many different types of materials. Polyester resin has good longevity, fair UV resistance, and good resistance to water. It is important to recognize that all polyester resin products are not created equal; their chemical makeup is complex and can have a wide range of properties. As filler in auto repair, for example, this material is formulated for superior adhesion to paints and metals.

Epoxy resin possessing the secondary hydroxyl groups can be used as polyols. Special silicone resins are especially suitable for the heat stable PU coatings. Vinyl polymers alone or in combination with other polyols can be effectively used as polyols. Also the vegetable or plant oils such as castor oil, linseed oil, tall oil, etc. can be used as polyols. Coal tar contains numerous groups with active hydrogen so it can also be used as polyols.

[c] LITERATURE SURVEY ON POLYURETHANE RESINS

Polyurethanes (PUs) are known to be very attractive materials for various applications such as electrical/electronic potting and encapsulation, constructions, water proofing membranes, asphalt extended membranes, highway sealants, sound and vibration damping, automotive and rubber parts, etc. Due to their unique property, they offer the elasticity of rubber combined with the toughness and durability of plastics. Polyurethanes form an important class of polymers, whose structures and performances can be designed to meet the user’s needs. Polyurethane resins are mainly produced by isocyanation of diisocyanate with polydiols of various molecular weights or other reactants containing hydrogen donors that are reactive with isocyanates.

\[
\begin{align*}
O &= N \equiv R - N \equiv C - O + HO - C_2H_4O - H \\
& \downarrow \\
\left[ C - N - R - N - C - O - C_2H_4O - \right]_n \\
& \left[ \right]_m
\end{align*}
\]

The urethane reaction is catalyzed in a strict technical sense, i.e. the catalysts increase the rate of reaction without themselves being consumed. The most
commonly used catalysts are organo tin compound for example dibutyl tindilaurate (DBTDL) and tertiary amines for example 1,4-diazobicyclo(2,2,2)-octane (DABCO), and tetramethyl butane diamine (TMBDA). Polyurethane resins are characterized by a segmented structure, consisting of flexible segment, the polyol chains, and hard segments, crystallizability of segment, segmental length, intra and inter segment interactions such as H-bonding, overall compositions and molecular weight.

Polyurethanes possess a unique combination of performance and application properties with excellent abrasion resistance, flexibility, hardness, chemical resistance, UV light resistance and anti-microbial characteristics [49]. A great number of factors, which affect or influence the properties of polyurethane resins, are nature of polyl and diisocyanate, crosslinking density, NCO/OH ratio, curing conditions, etc [50, 51]

Over the last few decades polyurethanes are widely used as adhesive materials and have developed a reputation for reliability and high performance in many applications including footwear industry, packaging applications, plastic bonding, furniture assembly and the automotive industry. Polyurethanes are rapidly developing products of coating and paint industry because of unique combinations of performance and application properties such as excellent elasticity, high hardness, high scratch and abrasion resistance, excellent impact resistance, high water, solvents, acids and alkali resistance and resistance to degradation from light and weathering. The polyurethane coated fabrics find applications in inflatable structures, conveyer belts, protective coatings, biomaterials, etc [52, 53].

A urethane is essentially an ester of carbamic acid or substituted carbamic acid. The main advantage of polyurethane is that it can be tailor made to meet

the diversified demands of modern technologies such as coatings, adhesives, foams, rubbers, reaction molding plastics, thermoplastic elastomers and composites. The pioneering work on polyurethane polymers was conducted by Otto Bayer and his coworkers in 1937 at the laboratories of I.G. Farben in Leverkusen, Germany [54]. They recognized that using the polyaddition principle to produce polyurethanes from liquid diisocyanates and liquid polyether or polyester diols seemed to point to special opportunities, especially when compared to already existing plastics that were made by polymerizing olefins, or by polycondensation. The new monomer combination also circumvented existing patents obtained by Wallace Carothers on polyesters [55].

In 1969, Bayer AG exhibited a plastic car in Dusseldorf, Germany. Parts of this car were manufactured using a new process called RIM (Reaction Injection Molding). RIM technology uses high-pressure impingement of liquid components followed by the rapid flow of the reaction mixture into a mold cavity. Large parts, such as automotive fascia and body panels, can be molded in this manner. Polyurethane RIM evolved into a number of different products and processes.

The history of polyurethane can be traced back to the 1930s in the World War II, when Germany was looking for the synthetic material for tyre. Bayer made aromatic diisocyanate in 1930 and he produced the first polyurethane in 1937 by reacting hexamethylene diisocyanate (HMDI) with 1, 4–butane diol (BDO).

During the late 1940s Dupont and Monsanto Company began supplying 2, 4-toluene diisocyanate (TDI) in pilot plant quantities. In 1950-1952 Farben Fabriken Bayer disclosed the development process of polyurethanes elastomers and of flexible foams based on polyesters, and shortly thereafter they came into commercial production.

Full scale commercial isocyanate manufacture began in the United State during 1954-55. The primary use for toluene diisocyanate was in flexible foam based on polyesters; the flexible foam obtained from these products, however had two major drawbacks, high cost and poor hydrolysis resistance, which limited its commercial growth. In 1957, based on ethylene oxide and propylene oxide were introduced commercially into polyurethane industry. These polyols lower the cost and improve the hydrolysis resistance of the products. Initially flexible foam prepared from the poly (alkylene oxide) was prepared through a “prepolymer” technique by which a prepolymer was formed from polyether and diisocyanate, and then catalyst, water and stabilizers were added to produce foam. First in 1958, “One-shot” foaming was developed in which polyether, diisocyanate, water, catalyst and foam stabilizers were mixed in one step.

Polyurethane (or polyisocyanate) resins are produced by the reaction of a diisocyanate with a compound containing at least two active hydrogen atoms, such as diol or diamine. Toluene diisocyanate (TDI), diphenylmethane diisocyanate (MDI) and hexamethylene diisocyanate (HMDI) are frequently employed. They are prepared by the reaction of phosgene with the corresponding diamines.
Aliphatic and aromatic isocyanates are the two classes of isocyanates used in the polyurethane coatings. The most commonly used isocyanates or the production of polyurethanes are listed in Table-1.3. The other component in the production of polyurethane is polyol. Polyols are hydroxyl terminated polyesters, polyethers, acrylic polyols and polyols based on natural oils. Applications of polyurethanes in various fields are listed in Table 1.4.

Polyurethanes are very appealing class of polymers for use in the biomedical field. This is because of their relatively good biocompatibility, their physical properties and the ease with which their properties can be tailored to end use. They are widely used in the development of medical devices, for tissue and blood contact such as mammary prosthesis, vascular catheters, artificial skins, vascular grafts, artificial heart diaphragms and valves. They can be biodegradable depending upon their chemical structures [56].

Recent years have shown a growing interest in the development of bio based products that can reduce the widespread dependence of fossil fuels. Indeed, the inevitable depletion of petroleum resources with the attending high cost has prompted the researchers to develop polymers from cheap and renewable resources such as cheap and renewable resources such as natural oils [57]. There are number of natural oils such as castor oil, linseed oil, tung oil, etc. are available in the market but among all of them castor oil and its derivatives are widely used due to its chemical structure [58, 59].
### Table-1.3 The common diisocyanates used for the production of polyurethanes

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Chemical Name</th>
<th>Abbreviation</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Toluene-2,4-diisocyanate</td>
<td>TDI</td>
<td><img src="image" alt="Structure of TDI" /></td>
</tr>
<tr>
<td>2</td>
<td>Hexamethylene diisocyanate</td>
<td>HMDI</td>
<td><img src="image" alt="Structure of HMDI" /></td>
</tr>
<tr>
<td>3</td>
<td>Isophorone diisocyanate</td>
<td>IPDI</td>
<td><img src="image" alt="Structure of IPDI" /></td>
</tr>
<tr>
<td>4</td>
<td>4,4’-Methylene bis phenylene diisocyanates</td>
<td>MDI</td>
<td><img src="image" alt="Structure of MDI" /></td>
</tr>
<tr>
<td>5</td>
<td>Cyclohexane-1,4-diisocyanate</td>
<td>CHDI</td>
<td><img src="image" alt="Structure of CHDI" /></td>
</tr>
<tr>
<td>6</td>
<td>p-Phenylene-1,4-diisocyanate</td>
<td>PPDI</td>
<td><img src="image" alt="Structure of PPDI" /></td>
</tr>
</tbody>
</table>
### Table-1.4 Applications of polyurethanes in various fields

<table>
<thead>
<tr>
<th>Application</th>
<th>Amount of polyurethane used (millions of pounds)</th>
<th>Percentage of total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Building &amp; Construction</td>
<td>1,459</td>
<td>26.8</td>
</tr>
<tr>
<td>Transportation</td>
<td>1,298</td>
<td>23.8</td>
</tr>
<tr>
<td>Furniture &amp; Bedding</td>
<td>1,127</td>
<td>20.7</td>
</tr>
<tr>
<td>Appliances</td>
<td>278</td>
<td>5.1</td>
</tr>
<tr>
<td>Packaging</td>
<td>251</td>
<td>4.6</td>
</tr>
<tr>
<td>Textiles, Fibers &amp; Apparel</td>
<td>181</td>
<td>3.3</td>
</tr>
<tr>
<td>Machinery &amp; Foundry</td>
<td>178</td>
<td>3.3</td>
</tr>
<tr>
<td>Electronics</td>
<td>75</td>
<td>1.4</td>
</tr>
<tr>
<td>Footwear</td>
<td>39</td>
<td>0.7</td>
</tr>
<tr>
<td>Other uses</td>
<td>558</td>
<td>10.2</td>
</tr>
</tbody>
</table>
Lower embedded energy as compared to other structural materials like steel, aluminium

Composites have lower vibration transmission than metal

Long life offers excellent fatigue, impact, environmental resistance and reduced maintenance

Composites enjoy reduced life cycle cost as compared to metals

Improved appearance with smooth surface and wood like finish

Schoener et al. [60] have synthesized moisture curable polyurethane coating compositions with improved pot life. Such enhancement is accomplished by blending with said coating composition a stabilized amount of stabilizing agent from the group of a mercapto compound, a polyphenol characterized by being reactable with an isocyanate group in the presence of a tertiary amine catalyst, and mixtures thereof. The amounts of stabilizing agents ranged from about 1% to 10% by weight. The enhanced pot life is realized even in the presence of significant quantities of water.


Ashraf et al. [61] have synthesized polyurethane from linseed oil epoxy and have developed anticorrosive coatings from it. Trans hydroxylation of linseed oil epoxy was carried out in situ. It is further reacted with TDI to synthesize polyurethane. Physico-chemical characterization of the synthesized resin was carried out as per standard methods. Structural elucidation was carried out using IR and NMR spectral data. Physico-mechanical and weather resistance performance of the coated samples were also studied and found that synthesized resin showed good performance in various corrosion tests.

Mao and Li [62] have studied the damping properties of epoxy resin / PU (EP/PU) semi interpenetrating polymer networks (IPNs) by dynamic mechanical analysis (DMA) method. It showed that the semi IPNs have excellent damping properties at ordinary temperature. The maximum value of tanδ is about 1 when the weight composition of EP/PU is 70/30. Tensile tests also indicate that the system has good tensile strength and elongation at break at this ratio. The effect of structures on the properties of semi-IPNs is discussed. Applied to the cavitation corrosion resistant coating, the semi-IPNs showed good cavitation corrosion resistance.

Opera [63] has synthesized epoxy urethane acrylate from epoxy resins, acrylgic acid and 4,4’-diphenyl methane diisocyanate using two stage polymerization. The oligomer obtained was studied by IR and 1H NMR spectroscopy. The oligomer was cured using thermal treatment. All of these materials formed transparent films used for testing. The low molecular weight oligomers can be used as solvent less coating.

Kolekar and Athawale [64] have synthesized interpenetrating networks composed of glycerol modified castor oil based polyurethane (CG-PU) and


PMMA. The effects of polyol modification, change in NCO/OH ratio and PU/PMMA composition, mechanical, chemical and thermal properties of IPNs were studied. It was found that among the three IPNs synthesized from (1) unmodified castor oil PU (2) glycerol modified castor oil PU (3) glycerol modified mixture of castor and linseed oil PU and PMMA, glycerol modified PU IPNs (CG-IPN) exhibited better tensile strength and chemical resistance. The detailed study of CG-IPNs revealed that tensile strength and hardness increased, while elongation decreased with increase in NCO/OH ratio. However, an exactly reverse trend was observed with increase in PU composition in PU/PMMA IPNs. The chemical resistance and thermal properties of the IPNs were unaffected by the change in NCO/OH ratio and PU/PMMA composition.

Mahesh and Alagar [65] have prepared the inter crosslinked networks of bismaleimide modified polyurethane-epoxy systems and cured in the presence of 4,4’-diaminodiphenyl methane. The grafting of PU onto epoxy skeleton was confirmed by the IR spectral analysis. The prepared matrices were studied by mechanical, thermal and morphological studies. The results revealed that the incorporation of PU into epoxy increased the mechanical strength and decreased the glass transition temperature and thermal stability, while incorporation of chain extended bismaleimide into PU modified epoxy system increased the thermal stability and tensile and flexural properties, while decreased the impact strength and glass transition temperature. The scanning electron microscopy was carried to study the surface morphologies of the matrices.

Prabu and Alagar [66] have prepared two different inter crosslinked networks (ICN) of siliconized polyurethane-epoxy / unsaturated polyester (UP) coatings. Epoxy and unsaturated polyester resins were modified with polyurethane prepolymer and hydroxyl terminated polydimethylsiloxane (HTPDMS) using γ-amino propyl triethoxysilane and vinyl triethoxysilane as silane crosslinker and dibutyltindilaurate as a catalyst. The coating materials were obtained in the form of tough films and characterized for their ASTM

methods, while thermal stability of the ICN coatings was studied using differential thermal analysis and thermogravimetric analysis and compared with unmodified epoxy/PU systems. The results revealed that the mechanical properties was increased by the incorporation of the PU (10 wt %) and silicone (10 wt %), while the thermal stability was decreased. Whereas, the incorporation of 10% silicone into the PU modified epoxy/PU system, the thermal stability was increased due to the partial ionic nature, high energy and thermal stability of Si-O-Si linkages have synthesized polyurethane resins from chemoenzymatically modified castor oil and different isocyanates and studied the difference in hardness, flexibility, impact strength and chemical resistance, when the different isocyanate precursors were used. The interesterification of castor oil and linseed oil was carried out near ambient temperature using lipase as a catalyst. The resultant interesterification product (IP) was reacted with isocyanate to form polyurethane resins. Polyurethane synthesized by this method is light in color and compared to conventional ones obtained from chemically catalyzed interested ification reactions at high temperature.

Keun et al. [67] have synthesized the two component polyurethane flame retardant coatings by blending chlorine containing modified polyesters (DCAOs) and polyisocyanates and compared the various properties of these coatings with non flame retardant coatings. The DCAOs used were synthesized by the polycondensation of dichloro acetic acid, a flame retardant carboxylic acid, with 1, 4-butane diol, trimethylol propane and adipic acid. The content of dichloro


Acetic acid was varied in 10, 20 and 30% in polycondensation reaction. The resultant flame retardant coatings were rapid drying and possessed the pot life of 8-10h. Coatings with 30% dichloroacetic acid were not fired by the vertical burning test.

Jimenez et al. [68] have studied the effect of soft segment structure and molecular weight on the microphase separation in segmented polyurethane (SPU) by means of DSC, small-angle X-ray scattering, dielectric constant measurements, pulsed nuclear magnetic resonance and thermoluminesence. Possible changes in the structural properties of SPU after cyclic mechanical fatigue were monitored using the same technique described as above. Samples were divided into two series according to their soft segment structure, i.e. one is linear poly (tetramethylene glycol) (PTMG) and another with methyl group on the PTMG chain. Hard segment consisted of 4, 4'-diphenyl methane diisocyanate (MDI) and 1, 4-butanediol as chain extender in both the sets. It was found that the phase separation increased for both types of SPU as the soft segment molecular weight increased. Samples with methyl group showed little soft segment crystallization. Upon fatigue, samples with methyl group showed a better fatigue resistance.

Chen et al. [69] have synthesized two parts adhesive having superior strength at cryogenic temperatures, which contains a urethane resin composition part and a hardner part. The urethane resin composition part comprises 50-99% by weight of a modified polyurethane prepolymer having an epoxy group at each of its respective end and 1-50% by weight of a modified urethane compound having substantially no ether cyanate (NCO) groups and at least two epoxy groups per molecule and a molecular weight less than 800 daltons. The hardener part is a polyamine containing primary or secondary amine groups. The equivalent ratio of the amine groups of the polyamine to the epoxy groups of the urethane resin composition part is 0.5-2.0.

Somani et al. [70] have synthesized polyurethane adhesives from different polyester polyols. The polyester polyols were synthesized by reacting castor oil derivatives with glycols (diols), while adhesives have been synthesized by reacting different polyester polyols with diisocyanate adducts in different NCO/OH ratios. The polyols and polyurethanes were characterized by FTIR spectroscopy. The effect of NCO/OH ratios, types of isocyanate adducts, and chain length of glycols were studied by determining wood to wood adhesion strength, i.e. by lap shear strength measurements and the change in lap shear strength after being placed in cold water, hot water, acid or alkali solutions was tested. Thermal stability of PU adhesives was determined by TGA.

Papon et al. [71] have synthesized the thermoplastic polyurethane elastomers (TPUs) of constant composition by prepolymer method and studied the influence of synthesis condition (pre polymerization and chain-extension time) on the final properties of TPUs. The TPUs were characterized by gel permeation chromatography, differential scanning calorimeter, stress-strain measurements and contact angle measurements. The adhesion properties of the TPUs were determined by measuring the T-peel strength and found that above the threshold value the pre polymerization time influenced the final properties of the TPUs (viscosity of solutions, molecular weight, mechanical and adhesive behavior), whereas chain extension time does not. Therefore this is possible to prepare TPUs with specific properties by changing the polymerization conditions.

Papon et al. [72] have prepared thermoplastic polyurethane elastomers (TPUs) including different amounts of rosin in their composition, which is used either as an additive or as a reactant in the chain-extension step of the polymer


synthesis. The properties of the materials are studied using solution viscosity measurements, size exclusion chromatography, stress controlled rheometry, differential scanning calorimetry (DSC), wide angle X-ray diffraction and contact angle measurements. Rosin as a chain extender led to increase the viscosity and molecular mass as well as improvements of rheological properties and changes in morphology. The crystalline regions are more affected (variations in the softening temperature and enthalpy) than the amorphous ones (quite constant glass transition temperature). The rosin act as actual chain extender and modified the organizations of both soft and hard segments of the polymers. The adhesive properties of the TPUs were determined by measuring the T-peel strength of the PVC/TPUs adhesive joints.

Kim et al. [73] have prepared polyurethane membranes by an immersion precipitation method. The effect of dope concentration, coagulation bath composition and the chemical structure of the polyurethane on the morphology of the membranes were studied. The degree of concentration was measured by quenching freshly formed polyurethane membranes in liquid nitrogen. A mechanism for the formation of the membrane morphology during immersion precipitation is proposed.

Bessaha et al. [74] have studied the role of prepolymer on the interfacial strength of polyurethane-based assemblies for two hydroxyl-terminated (telechelic) polybutadienes, R45M and R45HT. In this study, they showed that two main effects have to be considered: the length of the free chains, which could diffuse across the interface during the formation of the joint and the relative reactivity of the various hydroxyl groups of the chains and chain extenders with the isocyanate. The R45M chains were more efficient connectors than the R45HT chains.


Migration of chain extenders and isocyanate over large distances created a thick interphase, where physical crosslinks appeared. This interphase was thicker for R45M-based polyurethane showing the role of the chain reactivity.

Pechar et al. [75] have synthesized the polyurethane networks (PUNs) using polyols derived from soybean oil, petroleum, or a blend of the two in the conjunction with diisocyanate. The soybean-based polyols (SBPs) were prepared using air oxidation, or by hydroxylating epoxidized soybean oil. Some of the networks were subjected to several solvents to determine their respective swelling behavior and solubility parameters. Sol-fractions were also determined, and DMA experiments were utilized to monitor the changes in storage modulus and tan δ with temperature for networks with sol and with the sol extracted. A linear relationship was noted between the hydroxyl number of a SBP and the glass transition temperature of its corresponding unextracted PU network within the range of hydroxyl numbers (i.e., 55-237 mg KOH/g) and glass transition temperatures (i.e., -21 to +83°C) encountered in this work. This same linear relationship was realized between the weighted hydroxyl number of soy and petroleum-based polyol blends and the glass transition temperature of the resulting unextracted and extracted network PUs within the ranges utilized in this study (i.e., 44-57 mg KOH/g, -54-19°C).

Kumar et al. [76] have prepared polyethylene glycol-400 (PEG) based polyurethane (PU) and polyacrylonitrile (PAN) semi-interpenetrating polymer networks (SIPNs) (PU/PAN; 90/10, 70/30, 60/40 and 50/50) by sequential polymerization method. The prepared SIPNs have been characterized by physico


mechanical properties. The microcrystalline parameters such as crystal size ($\langle N \rangle$), lattice disorder ($g$), surface ($D_s$) and volume ($D_v$) weighted crystal size of SIPNs were estimated using wide angle X-ray scattering studies, and quantification of the polymer network has been carried out on the basis of these parameters. The microstructural parameters were established using exponential, lognormal, and reinhold asymmetric column length distribution functions and the results are compiled.

**[C] NATURAL FIBER REINFORCED COMPOSITES**

Composite materials are formed by the combination of two or more materials, which retain their respective characteristics when combined together, but their chemical and mechanical properties are improved upon combination. “Two or more dissimilar materials when combined are stronger than that of individual materials.”

Today, where in world market demands for product performance are ever increases, composite materials have proven to be effective in reducing cost and improve in performance. Composites solve problems; raise performance levels by development of many new materials.

**History**

The use of natural composite materials has been a part of man’s technology; the first ancient builder used straw to reinforce mud bricks.

The 12th century Mongols made the advance weapons of their day with bows that were smaller and more powerful than their rivals. These bows were composite structures made by combining cattle tendons, horn, bamboo, which bonded with natural pine resin. The tendons were placed on the tense of the bow, the bamboo was used as a core, and sheets of horn were laminated the compression side of the bow. The entire structure was tightly wrapped using the rosin adhesive. The 12th century weapons designers certainly understood the principles of composite design. In the recent time some of the old museum pieces were strung and tested.
They were about 80% as some modern composite bows [77].

In the late 1800s Canoe builders were experimenting with gluing together 1st graft paper with shellac to form paper laminates. While the concept was such the materials did not perform well.

In the year between 1870 and 1890, revolution was occurring in chemistry, first synthetic (man made) resins were developed, which could be converted liquid to solid polymerization. These polymer resins are transformed from liquid state to solid state by crosslinking the molecules. Early synthetic resin included cellulose, melamine and Bakelite.

In the early 1930s two chemical companies that were working on the development of polymer resins were American Cyanamid and DuPont. In the course of the experimentation, both the companies independently formulated polyester resin first time. In the same time period, Owens-Illinois Glass Company began the glass fiber into a textile fabric on commercial bases.

During the time between 1934 and 1936, experimenter Ray Green, in Ohio combined these two new products and began molding small boats. This was the beginning of modern composites. During World War II the development of required non-metallic housings and the US military advanced fledgling composites technology with many research projects. Immediately following war II composite materials immersed as major engineering material.

First composites industry began in earnest in the late 1940s and developed in 1950s. Most of the composites processing methods used today like molding, filament winding, hand lay-up technique, resin transfer molding, vacuum bagging were all developed and used in production between 1946 and 1950. Some products manufactured from composites during this period included: boats bodies (corvette), truck parts, aircrafts component, underground storage tank, buildings and many familiar products. Composites typically use thermoset resins, which begin as liquid polymers converted to solid during the molding process. This process known as crosslinking is irreversible. Because of this, these

polymers are known as thermosets and can not be melted and reshaped. The benefit of composite materials have fueled growth of new application markets such as transportation, constructions, corrosion resistance, marine infrastructure, consumer products, electrical, aircraft and aerospace application and business equipments.

The benefits of using composites materials include:

- **High strength**: Composite materials can be designed to meet the specific requirements of an application. A distinct advantage of composites over other materials is ability to use many combinations of resins and reinforcement.

- **Light weight**: Composites are materials that can be designed for both light weight and high strength. In fact composites are used to produce the highest strength to weight ratio structures known to man.

- **Corrosion resistance**: Composites products provide long-term resistance from severe chemical and temperature environments. Composites are the materials choice for outdoor exposure, chemical handling application and severe environments service.

- **Design flexibility**: Composites have an advantage over other materials because they can mold into complex shapes at relatively low cost. The flexibility creating complex shapes offers designers a freedom that hallmarks composites achievement.

- **Durability**: Composite structures have an exceedingly long life span with low maintenance requirements, the longevity of composite is a beneficial critical applications. In a half–century of composite development, well-desired composite structures have yet to wear out.

  Compare a ¼ inch diameter steel rod to a ¼ inch diameter glass fiber composites rod. The steel rod will have higher tensile strength and compressive strength, but weight is more. If the fiber glass rod were increased in diameter to the same weight as steel rod, it would be stronger [78].

Automotive industries in Europe show large interest in NFC (Natural Fiber Composite) that can be used in load bearing elements of cars. Some of the

beneficial points for using composites over conventional ones are below [79].

- Tensile strength of composites is four to six times greater than that of steel or aluminium
- Improved torsional stiffness and impact properties
- Composite have higher fatigue endurance limit (up to 60% of ultimate tensile strength)
- Composite materials are 30-45% lighter than aluminium structures designed to the same functional requirements
- Lower embedded energy compared to other structure materials like steel, aluminium, etc.
- Composites are more versatile than metals and can be tailored to meet performance needs and complex design requirements
- Long life offers, excellent fatigue, impact, environmental resistance and reduced maintenance
- Composites enjoy reduced life cycle cost compared to metals
- Composite exhibit excellent corrosion resistance and fire retardancy
- Improved appearance with smooth surfaces and readily incorporable integral decorative melamine are other characteristics of composites
- Composite parts can eliminate joints/ fasteners, providing part by simplification and integrated design compared to conventional metallic parts.

Different types of fibers for reinforcement and study of their properties. Natural cellulose based fibers are gaining attention as their application is diversified into engineering end uses such as building materials and structural parts for motor vehicles [80, 81], where light weight is required. There are at least 1000 types of plant that bear usable fibers [82].


Khan et al. [83] have fabricated jute reinforced polyurethane composites under gamma irradiation. Thick polymer film was prepared under gamma irradiation using urethane acrylate in the presence of N-vinyl pyrrolidone, ethyl hexyl acrylate, and trimethylol propane triacrylate. Both jute dust and hessain cloth (jute fabric) were used to constitute composites based on the prepared resin matrix. Some of their mechanical and physical properties were studied.

Some additives such as acetic acid, acrylamide, urea, talc and titanium oxide were incorporated into the formulation to investigate their effect on the physical and mechanical properties, water absorption and weathering resistance of the resin and composites were also investigated.

Tay et al. [84] have fabricated oil palm empty fruit bunch composites with polyethylene glycol (PEG) molecular weight (MW) of 200 (PEG-200), 400 (PEG-400), polypropylene glycol (PPG) with MW of 400 (PPG-400) used as polyols. The effect of isocyanate (NCO) / hydroxyl (OH) ratio and PPG-400/ PEG-400 ratio on the impact strength, dimensional stability (immersion test), and thermal behavior were investigated. The study revealed that, as NCO/OH ratio was increased from 0.8 to 1.1 the impact strength and enthalpy increased, while swelling of composites either in water or DMF and onset and peak temperatures decreased. While for NCO/OH ratio above 1.1 the onset and peak temperature increased, while enthalpy decreased due to formation of allophanates. Thermal

behavior of the composites made from the glycol mixture was predominantly influenced by the PPG -400.

Tay et al. [85] have fabricated the oil palm EFB-PU composites and investigated the effect of isocyanate (NCO)/ glycol (OH) ratio, glycol type and mixtures [polyethylene glycol PEG-400 (MW- 400) and polypropylene glycol PPG (MW-400)] on the flexural properties. Composites made with PEG-200 exhibited higher flexural properties than with PEG-400 and PPG-400. The flexural properties were also found to be influenced by the PPG-400/ PEG-400 ratio.

Wolcott et al. [86] have fabricated ligno cellulosic fiber reinforced PU composites using difunctional and trifunctional poly(propylene oxide) based polyol. The mechanical properties of the composites were found to depend on the type of fiber and accessibility of hydroxyl functionality on the fiber. Dynamic mechanical analysis, swelling behavior and scanning electron micrographs of failure surfaces all provided the evidence of a substantial interface in the composites that directly impacted the performance properties. Trifunctional polyols generally increased the strength and stiffness, regardless of fiber type. The data suggested that synthetic polyol functionality and relative accessibility of the internal polymer structure of the fiber wall are dominant factors in determining the extent of interphase development. In order to save a crop from extinction and to ensure a reasonable return to the farmers, non-traditional outlets have to be explored for the fiber. One such avenue is in the area of fiber-reinforced composites. Such composites can be used as a substitute for timber as well as in number of less demanding applications [87].

In order to save a crop from extinction and to ensure a reasonable return to the farmers, non-traditional outlets have to be explored for the fiber. One such avenue is in the area of fiber-reinforced composites. Such composites can be


used as a substitute for timber as well as in number of less demanding applications [87].

The estimated global tonnage of fibrous raw material from agricultural crops is provided in Table 1.5 [88]. Jute, sisal, banana and coir, the major sources of natural fibers are grown in many parts of the world. Some of them have aspect ratios (ratio of length to diameters) > 1000 and can be woven easily. These fibers are extensively used for cordage, sacks, fishnets, matting and rope and as filling for mattresses and cushions. Cellulosic fibers are obtained from different parts of plants, e. g. Jute are obtained from stem; sisal, banana and pineapple from the leaf; cotton from seeds; coir from fruit, vegetables. The properties of some of the natural fibers are compared in Table-1.6 [89]. The comparison of mechanical properties for jute and glass fibers [90] is given in Table-1.7. Jane L. O’Dell has reported the comparative properties of lingo cellulosic fibers with glass and carbon fibers [91]. The comparisons of properties of different fibers are given in Table-1.8.

### Table-1.5  Estimated global tonnage of fibrous raw materials from agricultural crops

<table>
<thead>
<tr>
<th>Crops</th>
<th>Plant component</th>
<th>Availability in 10^3 tones</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice</td>
<td>Straw</td>
<td>465.2</td>
</tr>
<tr>
<td>Wheat</td>
<td>Straw</td>
<td>739.7</td>
</tr>
<tr>
<td>Oats</td>
<td>Straw</td>
<td>50.8</td>
</tr>
<tr>
<td>Corn</td>
<td>Straw</td>
<td>727.3</td>
</tr>
<tr>
<td>Bast fibrous plant</td>
<td>Straw</td>
<td>25.0</td>
</tr>
<tr>
<td>Sugarcane</td>
<td>Baggasse</td>
<td>100.2</td>
</tr>
</tbody>
</table>

### Table-1.6  Properties of selected natural fibers and glass fiber

<table>
<thead>
<tr>
<th>Property</th>
<th>Jute</th>
<th>Banana</th>
<th>Sisal</th>
<th>Pineapple</th>
<th>Coir</th>
<th>Glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Width or Diameter (mm)</td>
<td>---</td>
<td>80-250</td>
<td>50-200</td>
<td>20-80</td>
<td>100-450</td>
<td>7-8</td>
</tr>
<tr>
<td>Density (g/cc)</td>
<td>1.3</td>
<td>1.35</td>
<td>1.45</td>
<td>1.44</td>
<td>1.15</td>
<td>2.5</td>
</tr>
<tr>
<td>Volume Resistivity at 100 volts</td>
<td>---</td>
<td>6.5-7</td>
<td>0.4-0.5</td>
<td>0.7-0.8</td>
<td>9-14</td>
<td>9-10</td>
</tr>
<tr>
<td>Micro-fibrillar angle (Degree)</td>
<td>8.1</td>
<td>11</td>
<td>10-22</td>
<td>14-18</td>
<td>30-49</td>
<td>---</td>
</tr>
<tr>
<td>Cellulose Content (%)</td>
<td>61</td>
<td>65</td>
<td>67</td>
<td>81</td>
<td>43</td>
<td>---</td>
</tr>
<tr>
<td>Lignin Content (%)</td>
<td>12</td>
<td>5</td>
<td>12</td>
<td>12</td>
<td>45</td>
<td>---</td>
</tr>
<tr>
<td>Elastic Modulus (GN/m^2)</td>
<td>---</td>
<td>8-20</td>
<td>9-16</td>
<td>34-82</td>
<td>4-6</td>
<td>85.5</td>
</tr>
<tr>
<td>Tenacity (MN/m^2)</td>
<td>440-553</td>
<td>529-754</td>
<td>568-640</td>
<td>413-1627</td>
<td>131-175</td>
<td>4585</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>1-1.2</td>
<td>1.0-3.5</td>
<td>3-7</td>
<td>0.8-1.6</td>
<td>15-40</td>
<td>5.7</td>
</tr>
</tbody>
</table>
### Table-1.7 Mechanical properties of glass and jute fibers

<table>
<thead>
<tr>
<th>Property</th>
<th>E-Glass</th>
<th>Jute</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>2.5</td>
<td>1.3</td>
</tr>
<tr>
<td>Tensile strength (MN/m²)</td>
<td>3400</td>
<td>442</td>
</tr>
<tr>
<td>Young’s modulus (MN/m²)</td>
<td>72</td>
<td>55.5</td>
</tr>
<tr>
<td>Specific strength (MN/m²)</td>
<td>1360</td>
<td>340</td>
</tr>
<tr>
<td>Specific modulus</td>
<td>28.8</td>
<td>42.7</td>
</tr>
</tbody>
</table>

### Table-1.8 Comparison of properties of different fibers

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Specific gravity</th>
<th>Specific tensile strength (GPa)</th>
<th>Cost (US $ / ton)</th>
<th>Energy to Produce (GJ / ton)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignocellulosic</td>
<td>0.6-1.2</td>
<td>1.6-2.95</td>
<td>200 - 1000</td>
<td>4</td>
</tr>
<tr>
<td>Glass</td>
<td>2.6</td>
<td>1.35</td>
<td>1,200 – 1,800</td>
<td>30</td>
</tr>
<tr>
<td>Carbon</td>
<td>1.8</td>
<td>1.71</td>
<td>12,500</td>
<td>130</td>
</tr>
</tbody>
</table>
The attractive features of natural fibers like jute [92-93], sisal [94], coir [95, 96], and banana [97] are their low cost, light weight, high specific modulus, renewability and biodegradability. Many plant fibers have lots of applicable part as commercialized materials are concerned. One of the common and very critical environmental solutions is biodegradable nature of all these natural fibers, which increases their demand in world composite manufacture markets. Plant fibers are composed of cellulose, hemicellulose and lignin. Other components, usually regarded as surface impurities, are pectin and wax substances (Table-1.9) [98].

Diversified uses of green fibers

Global trends towards sustainable development have brought to light natural, renewable, biodegradable raw materials. Science and technology continue in extending their use in textile and other industries. Recent achievements and new applications of green fibers and associated products, bast fibrous

**Table-1.9 Important chemical composition (%) of some selected fibers**

<table>
<thead>
<tr>
<th>Fiber type</th>
<th>Cellulose</th>
<th>Hemi cellulose</th>
<th>Lignin</th>
<th>Pectin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton</td>
<td>92</td>
<td>6</td>
<td>---</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Jute</td>
<td>72</td>
<td>13</td>
<td>13</td>
<td>---</td>
</tr>
<tr>
<td>Flax</td>
<td>81</td>
<td>14</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Sisal</td>
<td>73</td>
<td>13</td>
<td>11</td>
<td>2</td>
</tr>
<tr>
<td>Hemp</td>
<td>74</td>
<td>18</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>Coir</td>
<td>43</td>
<td>&lt;1</td>
<td>45</td>
<td>4</td>
</tr>
<tr>
<td>Ramie</td>
<td>76</td>
<td>15</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Straw</td>
<td>40</td>
<td>28</td>
<td>17</td>
<td>8</td>
</tr>
<tr>
<td>Kapok</td>
<td>13</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>
plants can provide from the background for following conclusions:

1. Fast growing population, eco and health awareness creates large space for future expansion of other than cottons, natural cellulosic fibers.

2. Present achievements in breading/production/ processing extended the use of bast fibers in textiles. To make the way for these, difficult in processing fibers, into textile production being beyond their reach for centuries, it was necessary to develop : new, softer, finer 100 percent bast or bast blended yarns, amongst them knitting yarns; new crease- resistant finishing treatments; new products, which could meet the needs of demanding apparel sector.

3. All the textile goods made on the basis of green fibers can boast high comfort / health properties and are ecological items. They can be labeled as “NATURAL”. This is the key to market success.

4. Green fibers / bast fibrous plants will also be used in growing amounts in wide spectrum of biocomposites materials. Being lignocellulosic they can be combined with man-made or natural polymers to provide a wide range of useful composites in textiles.

**AIMS AND OBJECTIVES**

In the field of polymers, these have always been and will continue to be a need for new and novel resins and polymers for the economically viable and environmental beneficial applications. Our efforts are focused on use of the agriculture waste fibers in order to fabricate composites and polyurethane resins for coating and adhesive applications.

I. To collect literature on syntheses and characterization of monomers, resins, and their applications.

II. To synthesize and modify resins and evaluate their thermal, mechanical and electrical properties.

III. To fabricate jute composites and evaluate their mechanical and electrical properties.

IV. To study water absorption behavior of the composites in various environments.