Introduction to natural fibers

The word ‘Fiber’ is derived from the Latin word Fibra it means a slender, elongated, threadlike object or structure. In English and French it is called fiber. We are all familiar with fibers of natural origin such as cotton, wool, flax and silk. We are also familiar with man-made or synthetic fibers made of nylon, polyester, polypropylene and acrylics. One general definition of fiber is that its length is at least hundred times its diameter. (Length = 100 diameter) or a morphological term for substances characterized by their flexibility, fineness and high ratio of length to cross sectional area.

Classification of fibers

On the basis of origin fibers can be classified into two main parts.

1. Natural fibers and (2) Synthetic fibers. The class is presented in Fig.1.1.

1. Natural fibers

Any hair like substance or raw material, which is obtainable from a natural element like vegetable, animal and mineral source that can be converted into yarn after spinning and then into fabric.

There are various categories of natural fibers.

(A) Cellulose/Lingo cellulose fibers / Plant fibers

(B) Animal fibers

(C) Minerals fibers

(A) Cellulose/Lingo cellulose fiber

A fiber which can be obtained from the seed pod, stem or skin of a plant is known as vegetable or plant fiber for example cotton, jute, hemp, etc.

Cellulosic fibers can be classified as:

1. Fiber occurring on the seed (raw cotton, java cotton)
2. Phloem fiber from bast (flax, ramie, hemp, jute, kenaf)
3. Tendon fiber from steam and leaves (manila hemp, sisal hemp)
4. Fiber from grass or reeds (bamboo, bagasse, corn, sabai, rape, esparto, canary)
5. Fiber of fruit/nut shells (coconut fiber-coir)
6. Fiber from wood (soft wood, hard wood)
7. Fiber from stalk (rice, wheat, barley, maize, oat, rye)

(B) Animal fibers

Animal fibers are natural fibers that largely of particularly proteins. The animal fibers used most commonly in the manufacturing world as well as hand spinners are wool from domestic sheep and silk. Also very popular are alpaca fiber and mohair from Angora goats. Unusual fibers such as Angora wool from rabbits and Chiengora from dog also exist, but are rarely for mass production.

(C) Mineral fibers

Mineral fibers are fibers made from natural or synthetic minerals. The fiber as such is used as a raw material for its reinforcing purpose in various applications such as friction materials, gaskets, plastic, and coatings. These kinds of fibers can withstand up to 230 to 1200 °C for examples glass wool, stone wool, ceramic fiber wool, asbestos, etc.

2. Synthetic fibers

Synthetic fibers are divided into mainly two types: Organic fibers and (2) Inorganic fibers.

(A) Organic fibers

The compounds, which are used to synthesize organic fibers, come from raw materials such as petroleum based chemicals or petrochemicals. These materials are polymerized into a long, linear chemical that bond two adjacent carbon atoms. These kinds of fibers are known as organic fibers.

Organic fibers are subdivided into two parts:

1. Natural polymers base, examples are rayon, lyocell, acetate, triacetate, rubber (elastodiene), viscose, alginate, cupro, modal, etc.

2. Synthetic polymers base, examples are nylon, fluorocarbon, olefin, acrylic, aramid, chlorofiber, elastane, elastodien, fluorafiber, melamine, methacrylic, polyamide, polyester, polyethylene, polypropylene, polylactide, elastomultiester, etc.
(B) Inorganic fibers

Inorganic fibers, both metals and nonmetals are more resistant, more rigid, have higher melting points and are more heat resistant than traditional fibers. The separation point between organic and inorganic fibers being produced through modification of organic fibers or organic pitch. There are several examples of inorganic fibers namely

1. Carbon fibers: fibers containing at least 90% by mass of carbon obtained by thermal carbonization of organic fiber precursors.
2. Glass fibers: fibers, in textile form, obtained by drawing molten glass.
3. Ceramic fibers: fibers, in textile form, obtained from ceramic materials.
4. Metal fibers: fibers obtained from metals.
Fig. 1.1: Classification of fibers.
Chemical constitution of natural fibers

The fibers are basically a rigid, crystalline cellulose microfibril-reinforced amorphous lignin and/or with hemicellulosic matrix. Most plant fibers, except for cotton, are composed of cellulose, hemicellulose, lignin, waxes, and some water soluble compounds, where cellulose, hemicellulose, and lignin are the major constituents [1].

Biofibers can be considered to be composites of hollow cellulose fibrils held together by a lignin and hemicellulose matrix the cell wall in a fiber is not a homogenous membrane. Each fibril has a complex, layered structure consisting of a thin primary wall that is the first layer deposited during cell growth encircling a secondary wall. The secondary wall is made up of three layers and the thick middle layer determines the mechanical properties of the fiber. The middle layer consists of a series of helically wound cellular microfibrils formed from long chain cellulose molecules: the angle between the fiber axis and the microfibrils is called the microfibrillar angle. The characteristic value for this parameter varies from one fiber to another [2]. Such microfibrils have typically a diameter of about 10–30 nm and are made up of 30–100 cellulose molecules in extended chain conformation and provide mechanical strength to the fiber. The amorphous matrix phase in a cell wall is very complex and consists of hemicellulose, lignin, and in some cases pectin. The hemicellulose molecules are hydrogen bonded to cellulose and act as cementing matrix between the cellulose microfibrils, forming the cellulose-hemicellulose network, which is thought to be the main structural component of the fiber cell. The hydrophobic lignin network affects the properties of other network in a way that it acts as a coupling agent and increases the stiffness of the cellulose/hemicellulose composite. [2] The structure, microfibrillar angle, cell dimensions, defects, and the chemical composition of fibers are the most important variables that determine the overall properties of the fibers.

Generally, tensile strength and Young’s modulus of fibers increase with increasing cellulose content. The microfibrillar angle determines the stiffness of the fibers. Plant fibers are more ductile if the microfibrils have a spiral orientation to the fiber axis. If the microfibrils are oriented parallel to the fiber axis, the fibers will be rigid, inflexible and have high tensile strength. Some of the important biofibers [2] are listed in Table 1.1 and structure of biofiber is shown in Fig.1.2.

**Fig. 1.2:** Structure of biofibers.
Table 1.1: Chemical composition of some natural fibers.

<table>
<thead>
<tr>
<th>Fibers</th>
<th>Botanical name</th>
<th>C</th>
<th>M</th>
<th>A</th>
<th>L</th>
<th>E</th>
<th>P</th>
<th>Ø</th>
<th>H.C</th>
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</table>

Cellulose

The cellulose molecule is the basis for the potentially high values of mechanical stiffness and strength of these fibers. Cellulose gives the strength, stiffness and structural stability of the fiber, and is the major framework components of the fiber. According to the type of fiber, cellulose has its own cell geometry, which is responsible for the determination of mechanical properties of plant fibers. [1,3]. Cellulose is a natural polymer consisting of D-anhydroglucose (C$_6$H$_{11}$O$_5$) repeating units joined by 1,4-D-glycosidic linkages at C1 and C4 position. The degree of polymerization (DP) is around 10,000. Each repeating unit contains three hydroxyl groups. These hydroxyl groups and their ability to hydrogen bond play a major role in directing the crystalline packing and also govern the physical properties of cellulose. Cellulose structure is composed of crystalline and amorphous regions. Solid cellulose forms a microcrystalline structure with regions of high order of its crystalline regions and regions of low order are amorphous regions. Cellulose is also formed of slender rod like crystalline microfibrils. The crystal nature (monoclinic sphenoid) of naturally occurring cellulose is known as cellulose I. Cellulose is resistant to strong alkali (17.5 wt%) but is easily hydrolyzed by acid to water soluble sugars. Cellulose is relatively resistant to oxidizing agents [2].

Fig.1.2 presents the schematic views of secondary layer of fiber cell wall in which crystalline and amorphous regions are indicated. Strong intramolecular hydrogen bonds with large molecules are formed by the crystallite cellulose. Compactness of crystalline region creates cellulose blocks that makes it difficult for chemical penetration to occur. However, dyes and resins are absorbed by amorphous region easily. In addition to this, plant fibers are highly polar and hydrophilic in character as hydroxyl groups are present in their structures. For expansion of crystalline region, elimination of hydrophilic

hydroxyl groups and removal of surface impurities (waxy substances), natural fibers needs to be chemically modified[4].

The elementary unit of the cellulose macromolecule is D-anhydro glucose, which contains three hydroxyl groups (-OH). The hydroxyl groups form hydrogen bond inside the molecule itself (intramolecular) and between other cellulose molecules (intermolecular) as well as with hydroxyl group from the air. Therefore, all natural fibers are hydrophilic, that is they absorb water in the range of 8 to 12.6 % [4].

**Hemicellulose**

The hemicellulose is accountable for substantial amount of moisture absorption. Hemicellulose is responsible for the biodegradation, micro absorption and thermal degradation of the fiber as it shows least resistance. Hemicelluloses occur mainly in the primary cell wall and have branched polymers carbon sugars with varied chemical structure.

Hemicellulose is not a form of cellulose and the name is a misnomer. They comprise of a group of polysaccharides composed of a combination of 5- and 6-carbon ring sugars. Hemicellulose differs from cellulose in three aspects. Firstly, they contain several different sugar units, whereas cellulose contains only 1,4–β-D-glucopyranose units. Secondly, they exhibit a considerable degree of chain branching containing pendant side groups giving rise to its noncrystalline nature, whereas cellulose is a linear polymer. Thirdly, the degree of polymerization of native cellulose is 10–100 times higher than that of hemicellulose. The degree of polymerization (DP) of hemicellulose is around 50–300. Hemicelluloses form the supportive matrix for cellulose microfibrils. Hemicellulose is very hydrophilic, soluble in alkali and easily hydrolyzed in acids. Mainly the acid residues attached to hemicelluloses make it highly hydrophilic and increase the fiber water uptake, which increases the risk of microbiological fiber degradation. It has been found that hemicelluloses thermally degrade more at lower temperatures (150-180°C) than cellulose (200-230°C) [1,2,4].
Literature Survey

Lignin

Lignin is often called the cementing agent that binds individual fiber cells together. Lignin is thermally stable but prone to UV degradation. Lignin is amorphous and has an aromatic structure. The lignin content of the fibers influences its structure properties and morphology [1, 3, 5]. Lignin is a complex hydrocarbon polymer with both aliphatic and aromatic constituents. They are totally insoluble in most solvents and cannot be broken down to monomeric units. Lignin is totally amorphous and hydrophobic in nature. It is the compound that gives rigidity to the plants. It is thought to be a complex, three-dimensional copolymer of aliphatic and aromatic constituents with very high molecular weight. Hydroxyl, methoxyl and carbonyl groups have been identified. Lignin has been found to contain five hydroxyl and five methoxyl groups per building unit. It is believed that the structural units of lignin molecule are derivatives of 4-hydroxy-3-methoxy phenyl propane. The main difficulty in lignin chemistry is that no method has been established by which it is possible to isolate lignin in its native state from the fiber. Lignin is considered to be a thermoplastic polymer exhibiting a glass transition temperature of around 90°C and melting temperature of around 170°C. It is not hydrolyzed by acids, but soluble in hot alkali, readily oxidized, and easily condensable with phenol.

Pectin

Pectin structure is complex, side chains of pectin are often cross-linked with the calcium ions and arabinose sugars. The lignin, hemicelluloses and pectin provides the adhesive to hold the cellulose framework structure of the fiber together. Pectins are a collective name for hetero polysaccharides. They give plants flexibility [2,3].


Literature Survey

**Extractive and ash**

Natural fibers also composed of a small amount of organic (extractives) and inorganic (ash) components. Organic extractives are responsible for the color, odour and decay resistance, and inorganic matters enhance abrasive nature of the fiber[3].

**Wax**

Waxes make up the last part of fibers and they consist of different types of alcohols. The waxes are responsible for the wettability and adhesion characteristics of the fiber and they can be removed by extraction with organic solvents [2,4].

Structural representations of cellulose, hemicellulose, pectin and lignin are shown Fig.1.3.

![Structural representations of cellulose (A), hemicellulose (B), pectin (C) and lignin (D)](image)

**Fig. 1.3:** Structural representations of cellulose (A), hemicellulose (B), pectin (C) and lignin (D)
Mechanical properties of natural fibers

The structure, chemical composition, microfibrillar angle, and cell dimension defects are the most important variables that affect the overall properties of the fibers. A fiber is more ductile if the microfibrils have a spiral orientation to the fiber axis. If the microfibrils are oriented parallel to fiber axis then the fibers are inflexible and rigid. The natural fibers exhibit considerable variation in diameter along with the length of individual filaments. Table 1.2 describes the properties of the natural fibers[5].

The tensile strength of plant fiber is higher than other fibers. So for durable yarn, fabric, packaging, and paper these fibers are mainly used. Banana, flax, jute, hemp and soybean are the examples of plant fibers. We can use the natural fibers to reinforce both thermosetting and thermoplastic matrices. And these composites require high performance applications. They provide sufficient mechanical properties with fix stiffness and strength, at acceptably low cost levels. Considering the ecological aspects of material selection, replacing synthetic fibers by natural ones is only a first step. CO₂ gas, which causes the emission of greenhouse effect into the atmosphere can be restricted and an increasing awareness of the completeness of fossil energy resources are leading to developing new materials that are entirely based on renewable resources[6].
### Table 1.2: Properties of some natural fibers.

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Density (g/cm(^3))</th>
<th>Diameter (µm)</th>
<th>Tensile strength (MPa)</th>
<th>Young’s modulus (GPa)</th>
<th>Elongation at break (%)</th>
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<tr>
<td>Jute</td>
<td>1.3–1.45</td>
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<td>393-773</td>
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</table>
Thermal stability of natural fibers

The natural fiber starts degrading at about 240°C. Structural constituents of the fiber (cellulose, hemicelluloses, lignin, etc) are sensitive to the different range of temperatures. It was reported that, lignin starts degrading at a temperature around 200°C and hemicelluloses and cellulosic constituents degrade at higher temperatures. Thermal stability can be enhanced by removing certain proportion of hemicelluloses and lignin constituents from the fiber by different chemical treatment. The degradation of natural fiber is an important issue in the development of natural fiber composites in both composite manufacturing (curing, extrusion or injection molding) and materials in service [3].

Natural fiber treatment

Various treatments have been used in order to improve the compatibility of natural fibers, which are polar and hydrophilic due to the presence of hydroxyl groups with nonpolar and hydrophobic polymeric matrix materials. These treatments can be physical or chemical. Physical methods include stretching, calendaring, thermo treatments, hybrid yarn, cold plasma treatment, electric discharge [7]. Chemical methods involve alkali treatment, silane treatment, acetylation treatment, benzoylation treatment, peroxide treatment.

Alkaline treatment

Among all chemical treatments applied to natural fibers, the most used is alkaline treatment, also called as mercerization. The alkaline treatments promote the removal of partially amorphous constituents such as hemicellulose, lignin, waxes, and oil soluble in alkaline solution, and therefore


reduce the level of fiber aggregation, making a surface rougher. During the alkaline treatment, the OH groups present in the fiber react with sodium hydroxide according to eqn. 1 [7]:

\[
\text{Fibre-OH} + \text{NaOH} \rightarrow \text{Fibre-O}^-\text{Na}^+ + \text{H}_2\text{O}
\]

This treatment changes the orientation of highly packed crystalline cellulose order and forms amorphous region by swelling the fiber cell wall. This provides more access to penetration of chemicals. Alkali sensitive hydrogen bonds existing among the fibers break down and new reactive hydrogen bonds form between the cellulose molecular chains. Due to this, hydrophilic hydroxyl groups are partially removed and moisture resistance property is improved. It also takes out certain portion of hemicelluloses, lignin, pectin, wax and oil covering as a result, the fiber surface becomes cleaner. In other words, fiber surface become more uniform due to the elimination of micro voids and thus stress transfer capacity between the ultimate cells improves. In addition to this it reduces fiber diameter and thereby increase aspect ratio.

These result in better fiber matrix interfacial adhesion. Composite properties such as mechanical and thermal behavior can be improved significantly by this treatment. If the alkali concentration is higher than the optimum condition, excess delignification of fiber take place, which results in weakness or damage to the fiber, treated fibers have lower lignin content, partial removal of wax and oil cover materials and expansion of crystalline cellulose order [3].

**Silane treatment**

Silane is used as coupling agent to modify fiber surface. It undergoes several stages of hydrolysis, condensation and bond formation during the treatment process with the fiber. Silanols form in the presence of moisture and hydrolysable alkoxy groups. It reacts with cellulose hydroxyl group of the fiber and improves fiber matrix adhesion to stabilize composite properties. The chemical composition of silane coupling agent (bifunctional siloxane molecules) allows forming a chemical link between the surface of the cellulose
fiber and the resin through a siloxane bridge. This co-reactivity provides molecular continuity across the interface region of the composite. It also provides the hydrocarbon chain that restrains fiber swelling into the matrix, natural fibers exhibit micropores on their surfaces and silane coupling agent acts as a surface coating, which penetrates into the pores and develop mechanically interlocked coating on their surface. Silane treated fiber reinforced composite provides better tensile strength than the alkaline treated fiber composites[3].

**Acetylation**

Acetylation of natural fibers is generally known as esterification method for plasticizing of cellulose fibers. Fibers are acetylated with and without an acid catalyst to graft acetyl groups onto the cellulose structure. It reacts with the hydrophilic hydroxyl groups and swells the fiber cell wall. As a result, the hydrophilic nature of the fiber decreases leading to improvement in dimensional stability of the composites. In general, acetic acid and acetic anhydride individually do not react sufficiently with cellulosic fibers. For this, to accelerate the reaction, fibers are initially soaked in acetic acid and consequently treated with acetic anhydride between the time periods of 1 to 3 h at higher temperature. Moreover, this treatment provides rough surface topography with less number of void contents that give better mechanical interlocking with the matrix. Young and Rowell investigated acetic anhydride treatment on several types of cellulosic fibers to analyse the effects of equilibrium moisture content and reported that, this treatment improved moisture resistance properties. This was due to the removal of hemicellulose and lignin constituents from the treated fibers [3].

**Benzoylation**

Benzoylation involves benzoyl chloride to decrease the hydrophilicity of the fiber and improves fiber matrix adhesion, thereby increasing the strength of the composite. It also enhances thermal stability of the fiber. During benzoylation alkali pretreatment is used to activate the hydroxyl groups of the fiber. Then the fiber is soaked in benzoyl chloride solution for 15min. Afterwards ethanol solution is used for 1h to remove benzoyl chloride that
adhered to the fiber surface followed by washing with water and oven dried. Joseph implied benzoyl chloride treatment on alkali pre-treated sisal fiber and reported higher thermal stability compared to the untreated fiber composites [3].

**Peroxide treatment**

Interface properties of fiber and matrix can be improved by peroxide treatment. The peroxide induced grafting of polyethylene adheres onto the fiber surface and the peroxide initiated free radicals react with the hydroxyl group of the fiber and matrix. As a result, good fiber matrix adhesion occurs. This treatment also reduces moisture absorption tendency by the fiber and improves thermal stability. It is reported that, treatment with benzoyl peroxide or dicumyl peroxide of the cellulosic fiber led to higher mechanical properties of composites. The mechanism of peroxide treatment involves alkali pre-treatment on the fibers then coated with benzoyl peroxide or dicumyl peroxide (around 6% concentration) in the acetone solution for 30 min. complete decomposition of peroxide can be achieved by heating the solution at higher temperature. It is reported that optimum concentration of benzoyl peroxide (6%) and dicumyl peroxide (4%) treatment on short sisal fiber-reinforced polyethylene composites and led to improved tensile strength [3].

**Conclusion of the treatment of natural fibers**

Natural fibers are gaining interest as reinforcement for polymer composites due to their potential mechanical properties, processing advantages, environmental and economic benefits. The performance of natural fiber-reinforced composites can be affected by many factors. Surface treatment is essential to reduce hydrophilicity of natural fibers, therefore increase their adhesion with hydrophobic matrix. Chemical surface treatments include alkalization, silane, acetylation, benzoylation and peroxide treatment. These treatments modify the structural constituents and surface morphology of the natural fiber. Significant improvements in mechanical properties and thermal stability have resulted from these surface treatments. As a result, introduction of natural fibers from renewable resources for structural
composites can offer acceptable properties and provides benefits to the environment by replacing synthetic fibers according to the applications [3].

**Polymers**

**Monomer:** A monomer word comes from the Greek language, mono means one and meros means “part” is a molecule that forms the basic unit for polymers. Monomers may bind to other monomers to form repeating chain molecules to form a polymer.

**Polymer:** The term “polymer” comes from the Greek, poly meaning “many” and meros meaning “parts” it was first introduced in 1833 by the Swedish chemist, Jöns Jakob Berzelius [8].

**Classification of polymers**

Polymers can be classified on the basis of following:

1. Based on structure
2. Based upon molecular forces
3. Based on source of availability
4. Based on mode of polymerization
5. Based on molecular back bone

**Polymer classification based upon structure**

**Linear polymers**

These are polymers in which monomeric units are linked together to form linear chain. These linear polymers are well packed and have high magnitude of intermolecular forces of attraction and therefore have high densities, high tensile (pulling) strength and high melting points. Some common examples of linear polymers are high density polyethylene, nylon, polyester, PVC, PAN, etc.

Branched chain polymers

These are polymers in which the monomers are joined to form long chains with side chains or branches of different lengths. These branched chain polymers are irregularly packed and therefore, they have low tensile strength, low density, boiling point and melting points than linear polymers. Some common examples are low density polythene, glycogen, starch, etc.

Cross linked polymers

These are polymers in which monomers unit are cross linked together to form three dimensional network polymers. These polymers are hard, rigid and brittle because of network structure e.g., bakelite, melamine formaldehyde resin, etc.

Polymer classification based upon molecular forces

Depending upon the intermolecular forces, the polymers have been classified into four types.

Elastomers

The polymers that have elastic character like rubber (a material that can return to its original shape after stretching is said to be elastic) are called elastomers. In elastomers the polymers chains are held together by weak intermolecular forces. Because of the presence of weak forces, the polymers can be easily stretched by applying small stress and regains their original shape, when the stress is removed. The most important example of elastomers is natural rubber.

Fibers

These are the polymers, which have strong intermolecular forces between the chains. These forces are either hydrogen bonds or dipole-dipole interaction. Because of strong forces, the chains are closely packed giving them high tensile strength and less elasticity. Therefore, these polymers have sharp melting points. These polymers are long, thin and thread like and can be woven in fabric. Therefore, these are used for making fibers. Examples: Nylon 66, dacron, silk, etc.
Thermoplastics

These are the polymers, which can be easily softened repeatedly, when heated and hardened, when cooled with little change in their properties. The intermolecular forces in these polymers are intermediate between those of elastomers and fibers. There is no cross linking between the chain. The softening occurs as the polymer chain move more and more freely because of absence of cross link. When heated, they melt and form a fluid, which can be molded into any desired shapes and then cooled to get the desired product. Examples: Polythene, polystyrene, PVC, Teflon, etc.

Thermosetting polymers

These are the polymers, which undergo permanent change on heating. They become hard and infusible on heating. They are generally prepared from low molecular mass semi fluid substances. When heated they get highly cross linked to form hard infusible and insoluble products. The cross links hold the molecule in place so that heating does not allow them to move freely. Therefore a thermosetting plastic is cross linked and is permanently rigid. Examples: Bakelite, melamine formaldehyde resin, etc.

Polymer classification based upon source of availability.

Natural polymers

The polymers obtained from nature (plants and animals) are called natural polymers (e.g. starch, cellulose, natural rubber, proteins, nucleic acid (DNA, RNA), cotton, silk, wool, etc.).

Synthetic polymers

Polymers synthesized from low molecular weight compounds are called synthetic polymers. (e.g. polyethylene, polyvinylchloride, nylon, teflon, backelite, terylene, etc [9].

Based on polymerization

Carothers, Mark and Flory classified the polymers into two categories based on the mechanism of polymerization.

Addition polymers or chain growth polymerization

Addition polymers are formed by the combination of monomers without the elimination of some byproduct molecules. Addition polymerization can
take place through the formation of either free radicals or ions. Addition polymerization reaction is very rapid and takes place in 3 steps (a) chain initiation (b) chain propagation (c) chain termination [9,10]. In addition polymerization, it is difficult to control polymer molecular weight. Addition polymerization is subdivided into 3 types.

**Ionic polymerization**

The addition polymerization that takes place due to ionic intermediate is called Ionic Addition Polymerization. Based on the nature of ions used for the initiation process Ionic polymerization is classified into 2 types: Cationic polymerization and Anionic polymerization

Cationic polymerization is initiated by an acid (Lewis acids such as BF$_3$, AlCl$_3$, FeCl$_3$, SnCl$_4$, H$_2$SO$_4$, HF) in presence of small amount of H$_2$O, e.g. Isobutylene-butyl rubber, polystyrene, polyvinyl ether. Anionic polymerization is initiated by anion (may be base or nucleophiles such as n-butyl lithium or potassium amide) e.g. polystyrene, poly acrylonitrile.

**Condensation polymers or step growth polymerization**

A polymer formed by the condensation of two or more monomers with the elimination of simple molecules like H$_2$O, NH$_3$, HCl, alcohol, etc. are called condensation polymers. It is usually a succession of non catalyzed, chemical condensation reactions associated with the elimination of low molar mass side products like water. In condensation polymerization, polymer molecular weight can closely controlled [9,10].

**Insertion polymerization**

Usually addition polymerizations involve the polymerization of olefinic monomers. Polymerization occurs via an insertion of a monomer at the end of the growing chain, mediated by catalyst. The catalyst stays at the end of the growing chain. Polymers synthesized by insertion polymerization are typically characterized by very high stereoregularity. An example for such a polymerization technique is the Ziegler-Natta polymerization [10].

Based on molecular back bone

**Organic polymers**

A polymer whose backbone chain is essentially made of carbon atoms is termed as an organic polymer. Atoms attached to the side of valences of the backbone carbon atoms, however, usually those of hydrogen, oxygen, nitrogen, etc. The majority of synthetic polymers are organic and they are extensively studied. Leather, cellulose, rayon, etc. are the examples of organic polymers.

**Inorganic polymers**

Polymers, generally containing no carbon atoms in their backbone chains backbone. Glass and silicone rubber are the examples of inorganic polymers.

**Composites**

Composite material is a material composed of two or more distinct phases (matrix phase and dispersed phase) and having bulk properties significantly different from those of any of the constituents.

**Matrix phase**

The primary phase, having a continuous character, is called matrix. Matrix is usually more ductile and less hard phase. It holds the dispersed phase and shares a load with it.

**Reinforced phase or dispersed phase**

The second phase (or phases) is embedded in the matrix in a discontinuous form. This secondary phase is called dispersed phase. Dispersed phase is usually stronger than the matrix, therefore it is sometimes called reinforcing phase.

Many of common materials (metal alloys, doped ceramics, and polymers are mixed with additives) also have a small amount of dispersed phases in their structures, however they are not considered as

composite materials since their properties are similar to those of their base constituents.

There are two classification systems of composite materials. One of them is based on the matrix material (metal, ceramic, and polymer) and the second is based on the material structure:

**Interphase**

*Interphase* has characteristics that are not depicted by any of the component in isolation. The interface is a bounding surface or zone where a discontinuity occurs, whether physical, mechanical, chemical, etc. The matrix material must “wet” the fiber. Coupling agents are frequently used to improve wettability. Well “wetted” fibers increase the interface surfaces area. To obtain desirable properties in a composite, the applied load should be effectively transferred from the matrix to the fibers via the interface. This means that the interface must be large and exhibit strong adhesion between fibers and matrix. Failure at the interface (called deboning) may or may not be desirable [11].

**Classification of composites**

There are two classification systems of composite materials. One of them is based on the matrix material (metal, ceramic, and polymer) and the second is based on the reinforcement material structure:

**Based on matrix material**

Based on matrix material, composites again classified into three parts:

**Metal matrix composites (MMC)**

Metal matrix composites are composed of a metallic matrix (aluminum, magnesium, iron, cobalt, copper) and a dispersed ceramic (oxides, carbides) or metallic (lead, tungsten, molybdenum) phase.

**Ceramic matrix composites (CMC)**

Ceramic matrix composites are composed of a ceramic matrix and embedded fibers of other ceramic material (dispersed phase).

**Polymer matrix composites (PMC)**

Polymer matrix composites are composed of a matrix from thermoset (unsaturated polyester resin, epoxy resin) or thermoplastic
(polycarbonate, polyvinylchloride, nylon, polystyrene and embedded glass, carbon, steel or kevlar fibers dispersed phase).

**Fiber reinforced polymer (FRP)**

Common fiber reinforced composites are composed of fibers and a matrixes. These fibers carry the loads along their longitudinal directions. Common fiber reinforcing agents include carbon graphite fibers, beryllium, beryllium carbide, berylliumoxide, molybdenum, aluminium oxide, glass fibers, natural fibers, etc. Similarly common matrix materials include epoxy, phenolic, polyester, vinylester, etc. Epoxy, which has larger adhesion and lower shrinkage than matrix comes in second for its high cost[12].

**Particle reinforced polymer (PRP)**

They are used for reinforcing ceramics and glasses such as small mineral particles, metal particles such as aluminums and amorphous materials, including polymers and carbon black. Particles are used to increase the modulus of the matrix, and to decrease the ductility of the matrix, Particles are also used to reduce the cost of the composite [13].

**Based on reinforcement material structure**

Based on reinforcing material structure, composites again classified into three parts

**Particulate composites**

Particulate composites consist of a matrix reinforced by a dispersed phase in form of particles.
1. Composites with random orientation of particles.
2. Composites with preferred orientation of particles.

Dispersed phase of these materials consists of two-dimensional flat platelets (flakes), laid parallel to each other.

Fibrous composites

Short-fiber reinforced composites.

Short-fiber reinforced composites consist of a matrix reinforced by a dispersed phase in form of discontinuous fibers.

1. Composites with random orientation of fibers.
2. Composites with preferred orientation of fibers.

Long-fiber reinforced composites.

Long-fiber reinforced composites consist of a matrix reinforced by a dispersed phase in form of continuous fibers. Unidirectional orientation of fibers and bidirectional orientation of fibers (woven)

Laminate composites

When a fiber reinforced composite consists of several layers with different fiber orientations, it is called multilayer (angle-ply) composite.

Hybrid composites

Hybrid composites are more advanced composites as compared to conventional FRP composites. Hybrids can have more than one reinforcing phase and a single matrix phase or single reinforcing phase with multiple matrix phases or multiple reinforcing and multiple matrix phases. They have better flexibility as compared to other fiber reinforced composites. Normally it contains a high modulus fiber with low modulus fiber. The high-modulus fiber provides the stiffness and load bearing qualities, whereas the low-modulus fiber makes the composite more damage tolerant and keeps the material cost low. The mechanical properties of a hybrid composite can be varied by changing volume ratio and stacking sequence of different plies.

The concept of hybrid systems for improved material or structural performance is a well-known concept in engineering design. Nature’s own material and structural designs show how high structural performance can be achieved with non-exotic constituents through hybrid combinations assembled

in optimized hybrid hierarchical configurations. Recent work has shown that the properties of hybrid natural/glass composites with only ~6 wt.% glass fiber loading have been found to be an effective way to improve mechanical properties and dimensional stability (moisture, temperature, etc.) of the composites.

Among nature’s most common and efficient structures are cellular sandwich structures, which consist of a complex network of different-sized cells arranged across the section leading to dense regions (i.e. skins) integrally, connected to regions of lower density, or core. The stiffness of biocomposites can thus be overcome by structural configurations that place material in specific locations for highest structural performance. Cellular materials have the general form of either two-dimensional (honeycombs) or three-dimensional (foams) cell arrangements with unique properties that depend on the solid material composition, the volume fraction of the solid, and the arrangement and geometry of the cells.

Integration of the above concepts of materials hybridization with optimized hierarchical cellular structural forms have been shown to improve the performance of biocomposites materials for load-bearing structures allowing them to effectively compete with glass fiber composites. Cellular biocomposites cores made from industrial hemp or flax fibers with unsaturated polyester and hybridized with woven jute, chopped glass and unidirectional carbon fabrics showed improved stiffness, strength and moisture-absorption stability, while flexural tests on laboratory-scale beams and demonstrated enhanced structural behavior. The mechanical properties are enhanced by efficient material arrangement and contribution of the stiffer and stronger synthetic fibers, whereas the reduction in moisture absorption behavior is due to the barrier provided by the more impermeable synthetic fibers. Micromechanics and sandwich analyses adequately captured material and structural response and the benefit from residual stresses was evaluated. Results from this study indicated that cellular biocomposite beams and plates not only have the potential to serve as primary load bearing components, but
that with additional research they can compete with conventional structural materials.

**Natural fiber reinforced composites**

For making composite of reinforcement polymer, the use of natural fibers; it includes those produced by plants animals, and geological process. Now there is much interest in natural fiber-reinforced polymer composite materials because of their industrial applications and fundamental research. These are renewable, cheap, completely or partially recyclable, and biodegradable. Plants, such as flax, cotton, hemp, jute, sisal, pineapple, ramie, bamboo, banana, etc., are used as a source of lingo cellulosic fibers, and are more and more often applied as the reinforcement of composites. Their availability, renewability, low density, and price as well as satisfactory mechanical properties make them an attractive ecological alternative to glass, carbon and man-made fibers used for the manufacturing of composites. The natural fiber-containing composites are more environmentally friendly, and are used in transportation (automobiles, railway coaches, aerospace), military applications, building and construction industries (ceiling paneling, partition boards), packaging, consumer products, etc.

The matrix has the role to protect the fibers against the environment degradation and mechanical damage, but the main purpose is to hold the fibers together and transfer the loads on it. Generally, this matrix consists of a thermoset or thermoplastic resins, but as a demand for biocomposites, the resin should be made from renewable resources.

**Natural fiber reinforced composite processing**

As in composite product with synthetic fibers, the drivers for the selection of the appropriate process technology are the same with the natural fibers. Issues like the final product shape, performance, cost of the product and low cost of manufacture involves, to the natural fibers. Several factors which must be considered in selecting the process are the distribution of the resin within the fibers; the compatibility between the hydrophobic matrix and hydrophilic fibers; that fiber attrition is minimized due to processing to ensure reinforcement; that the moisture inherent within the fiber is at the desired
Literature Survey

level. These factors were included in the processes presented above as for thermoset process, regarding to the thermoplastic processes extrusion, injection and D-LFT are descript. As a rule, the same process as for synthetic fibers involves the natural fibers, with some changes including the dry process of the natural fiber prior to impregnation.

Biocomposites can compete with glass-polyester composites both on cost and performance basis. Most of the existing results on biocomposites are based on hand-lay-up laboratory-scale fabrication techniques. However the success of a high volume processing technique will be necessary to economically produce biocomposites for housing paneling applications. Recently, M/s TIPCO INDUSTRIES LTD has established a unique process for the fabrication of biocomposites, which is similar to the pultrusion process, but is a new and necessary approach for natural fiber composites.

The many other processing techniques are available for making natural fiber composites. Examples are in thermoset matrix natural fiber composites hand layup technique, pultrusion, sheet molding compound, wet filament winding technique, automated tap placement, resin transfer molding, vacuum bag molding, whereas in the thermoplastic matrix extrusion molding, injection molding, etc. Among all the processes, hand lay-up technique is the cheapest process and all the composites reported in this chapter are fabricated by this technique. Many researchers have reported the fabrication of composites by hand lay-up technique since 1978 onwards.

Applications of natural fiber composites

Natural fibers are becoming increasingly popular for use in industrial applications, providing sustainable solutions to support technical innovation. These versatile, natural based materials have applications in a wide range of industries, from textiles and consumer products to the automotive and construction industries. Industrial applications of natural fibers examine the different steps of processing, from natural generation, fiber separation and fiber processing, to the manufacturing of the final product. Each step is linked to fiber properties and characterization, highlighting how different fibers influence the product properties through a discussion of their chemical and
structural qualities. Industrial applications of natural fibers are valuable resource for scientists in industry and academia interested in the development of natural based materials and products. It is particularly relevant for those working in chemical engineering, sustainable chemistry, agricultural sciences, biology and materials sciences. Some of the pictures of natural fiber applications are shown Fig. 1.5-1.17.
Fig. 1.4: Pultrusion process diagram [7]

Fig. 1.5: Decking
Fig. 1.6: Walkways

Fig. 1.7: Skirtings for pools
Fig. 1.8: Fensing

Fig. 1.9: Fensing-grill
Fig. 1.10: Pallets

Fig. 1.11: Flooring profile
Fig. 1.12: Hollow profile

Fig. 1.13: Hollow profile
Fig. 1.14: Products of natural fiber and glass fiber composites gratings

Fig. 1.15: Louvers
Fig. 1.16: Roof sheet

Fig. 1.17: Door and window frames
Automaker information description

Many components use natural fibers such as flax, wood, coconut, and wheat straw as reinforcement in polypropylene composites, and bio-based foams are also penetrating the market. Some composites use corn or castor oil to produce the polymer matrix. Several components that integrate bio-based materials are displayed in Table 1.3. The components in the table demonstrate the diversity of the materials found in vehicles today, as well as the range of companies from all over the world, which are implementing bio-based materials in their vehicles. Some of the top automakers include Daimler, Ford, and Toyota each with their own unique focuses on various materials and applications.

Most automakers have not publically stated specific targets for use of bio-based materials in their vehicles. The exception is Toyota, which announced in 2008 that it plans to replace 20 percent of the plastics used in its automobiles with bio-based plastics by 2015 has internal goals for renewable materials usage by department, but these goals are not numeric, because it is difficult to predict, when the materials will be available at competitive cost and quality. Ford has, however, modified its specifications requiring suppliers to include a minimum amount of bio-based content in seat foams. Ford’s modification has ensured the automaker will continue to use these materials in its products into the future.

One way automakers initiate the use of new materials is by including them in concept vehicles. Several years ago, Ford unveiled its Model U concept car, which included several bio-based components including soy-based seating foam and body panels and corn-based floor mats, canvas roof material, and tires. Ford is now using soy-based seating foam in all of its North American vehicles. Other concept vehicles integrating bio-based materials include the Honda FCX concept fuel cell vehicle, which uses corn-based interior fabrics; the Toyota ES3 concept car, which uses sweet potatoes and sugar cane in interior components; and the Toyota “i-unit” and “i-foot” concept vehicles, which use kenaf fiber in their body structure. The Hyundai “i-flow” Concept uses ultramid balance, a product from BASF that is
composed of 60 percent renewable materials. These material choices reflect potential consideration of bio-based components for actual production models in the future.

In Europe, the automaker that has been doing the most work on bio-based materials is Daimler, through its Mercedes-Benz brand. Mercedes has integrated a wide variety of natural fibers in its vehicles including flax, hemp, sisal, wool, abaca, cotton, and jute fibers. These fibers have been used in over 50 different parts and components including spare-wheel compartment covers, underbody panels, seat backrests, engine and transmission covers, rear panel shelves, and door trim panels, and have been installed in Mercedes-Benz A-, C-, E-, and S-Class models. Fig. 1.18 shows some of the components for the Mercedes-Benz E-Class that utilizes bio-based materials.

**Advantages of natural fiber composites**

The main advantages of natural fiber composites are:

1. Low specific weight, resulting in a higher specific strength and stiffness than glass fiber.
2. It is a renewable source, the production requires little energy.
3. Producible with low investment at low cost, which makes the material an interesting product for low wage countries.
4. Reduced wear of tooling, healthier working condition, and no skin irritation. Thermal recycling is possible, while glass causes problem in combustion furnaces.
5. Good thermal and acoustic insulating properties.
6. Environmentally friendly product
7. Termite proof
8. Flame retardant
9. Can be painted, coated, polished with polyester, vinyl ester and melamine
10. High fatigue and corrosive resistance
11. Long life offers, excellent fatigue, impact, environmental resistance and reduced maintenance
12. Cost effective
<table>
<thead>
<tr>
<th>Model(s)</th>
<th>Feedstock</th>
<th>Material</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadillac DeVille</td>
<td>Wood</td>
<td>PP</td>
<td>Seatbacks</td>
</tr>
<tr>
<td>Chevrolet Impala</td>
<td>Flax</td>
<td>PP</td>
<td>Trim, rear shelf</td>
</tr>
<tr>
<td>Ford Flex</td>
<td>Wheat straw</td>
<td>PP</td>
<td>Interior storage bins</td>
</tr>
<tr>
<td>Ford Focus BEV</td>
<td>Coconut</td>
<td>PP</td>
<td>Loadfloor</td>
</tr>
<tr>
<td>Ford vehicles (Multiple)</td>
<td>Soy</td>
<td>PU</td>
<td>Foam seating, headrests, headliner</td>
</tr>
<tr>
<td>GMC Terrain</td>
<td>Cotton, kenaf</td>
<td>Polyester</td>
<td>Acoustic insulator, ceiling liner</td>
</tr>
<tr>
<td>Honda pilot</td>
<td>Wood</td>
<td>N/A</td>
<td>Floor area parts</td>
</tr>
<tr>
<td>Lexus CT200h</td>
<td>Bamboo, corn</td>
<td>PET</td>
<td>Luggage-compartment, speakers, floor mats</td>
</tr>
<tr>
<td>Mazda 5 Hydrogen RE Hybrid</td>
<td>Corn</td>
<td>PLA</td>
<td>Console, seat fabric</td>
</tr>
<tr>
<td>Mercedes-Benz A-Class</td>
<td>Abaca/banana, flax, other natural fibers</td>
<td>FRP</td>
<td>Underbody panels, seatbacks, spare tire cover</td>
</tr>
<tr>
<td>Mercedes-Benz C- and A-Class</td>
<td>Flax</td>
<td>PE</td>
<td>Engine and transmission cover, underbody panels</td>
</tr>
<tr>
<td>Toyota Prius</td>
<td>Corn</td>
<td>EPS</td>
<td>Instrument-panel, air-conditioning vent</td>
</tr>
<tr>
<td>Toyota Raum</td>
<td>Kenaf, starch</td>
<td>FRP</td>
<td>Floor mats, spare tire cover</td>
</tr>
</tbody>
</table>

Fig. 1.18: Mercedes-BENZ E-class with bio-based components [14]
Literature Survey

Literature survey on bisphenols

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 [15,16] 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-hydroxy 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. [17] 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

\[
\text{PhOH} + R_2\text{CO} \rightarrow R_2\text{C(OH)}\text{C}_6\text{H}_4\text{OH}
\]

2. \[
R_2\text{C(OH)}\text{C}_6\text{H}_4\text{OH} + \text{PhOH} \rightarrow R_2\text{C(C}_6\text{H}_4\text{OH)}_2 + \text{H}_2\text{O}
\]

Johnson and Musell [18,19] have reported synthesis of 1,1'-bis(4-hydroxyphenyl)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-I178°C; 1,1'-bis(4-hydroxy-3-methylphenyl)cyclohexane m.p. 187°C and 1,1'-bis(4-hydroxy-3-isopropylphenyl) 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. [20] 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-hydroxyphenyl) cyclohexane (m.p. 186-189°C) and 1,1′-bis(3-chloro-4-hydroxy phenyl)cyclohexane (m.p. 134-141°C).

Bender et al. [21] 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 et al. [22] have 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 et al. [23] have 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. [24] 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. [25] 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-hydroxyphenyl)cyclohexane and 1,1′-bis(3-methyl-4-hydroxyphenyl)cyclohexane, respectively.

Garchar et al. [26-29] 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°C, 50°C, 60°C, 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.

**Literature survey on epoxy resins**

Epoxy resins are widely used as matrices in advanced composites due to their good impregnation and adhesion to fiber reinforcement, resulting in

excellent mechanical performance; chemical and electrical resistance and low shrinkage on cure. Their use is in particular justified in application areas, where their technical advantages balance their relatively higher costs compared to other thermosetting polymers[30].

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 [31]. 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 [32,33] 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. [34] have synthesized polyester polyols using vegetable oil fatty acids having different characteristics (mainly in terms of hydroxyl functionality) and epoxy resin, using triethylamine 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 an 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 equipment. 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 [35]. Many researchers have tried to modify the epoxy resin to improve its mechanical properties by reacting it with dienes [36], 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 [37] to yield polyester polyl containing a free hydroxyl group that can be utilized to produce polyureethanes. To make an economic production of polyurethanes, efforts have been made to prepare polyester polyols from the low cost natural oils and their derivatives.

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).

![DGEBA structure](image)

The resin can be obtained with different degrees of polymerization ranging from low viscosity liquids to high melting solids [38] as shown in Table 1.4. 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 reparation 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 [39].

Table 1.4: 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 (g/mol)</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: (1) Resin viscosity (of liquid resin), (2) epoxide equivalent, (3) hydroxyl equivalent, (4) average molecular weight, (5) melting point (of solid resin), and (6) 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 [35].

Sanariya et al. [40] have reported a convenient method for the preparation of epoxy resins based on bisphenol-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 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. [41] have reported a convenient method for the preparation of epoxy resins based on halogenated bisphenols-C. The epoxy resins of bisphenol-C derivatives were synthesized by condensing corresponding derivative (0.5 mole) with epichlorohydrin (1.1 moles) by using isopropanol (500 ml) as a solvent and sodium hydroxide (1 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. [42] 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).

**Liquid epoxy resins**

In this process ECH and bisphenol A are charged into a reactor in the ratio of 10:1. A solution of 20-40% caustic soda is added slowly to the reaction vessel as the solution is brought to the boiling point. The solution is kept boiling until 2 mol of caustic soda per mole of BPA have been added. The solution breaks up into two layers. Unreacted ECH is removed by vacuum distillation. An inert solvent is then added to the resin and the reaction is completed with excess of caustic soda solution. The resin separates into brine solution, which is thoroughly washed with water to obtain a clear resin. The solvent is removed by vacuum distillation [43].

**Solid epoxy resin**

Here ECH and BPA are added to the reactor in theoretical molar ratio with a little excess of ECH. Aqueous caustic soda is well mixed into the system. After one hour the reaction is completed and taffy like mass is obtained. Phase separation is brought about by adding an inert solvent.


Brine is withdrawn and the resin solution is thoroughly washed with water to remove traces of salts. The solid resin is obtained by removing the solvent by vacuum distillation[43].

**Literature survey on vinyl esters**

**History**

Some of the earliest vinyl ester resins resulted from efforts by the U.S. Commerce Department for better dental adhesive Bowen [44,45] esterified glycidyl methacrylate and acrylate with bisphenol A in these efforts. Unfortunately, these resins were too reactive to afford a practical working life and only further vinyl ester development succeeded in providing commercially useful dental bonding resins. Other workers, such as Fekete and his associates, worked on resins intended for use in electrical insulation and chemically resistant composites. [46,47]

**Introduction**

Vinyl ester resin was introduced commercially in the early 1960s. Today, they are one of the most important thermosetting materials, which have been widely recognized as a material with an excellent resistance to a wide variety of commonly encountered chemical environments. They are used to fabricate a variety of reinforced structures, including pipes, scrubbers and ducts. They are the prime candidates for the use in composites for transportation and/or infrastructure. Such application includes fabrication of parts for automobiles and other surface transportation vehicles, fascia for buildings, reinforcement for bridges, etc. In addition to these applications, vinyl esters are also being used in adhesives, molding compounds, structural laminates, electrical application and military/aerospace application [48-52].


43. M. S. Bhatnagar Epoxy Resins (Overview) the Polymeric Materials Encyclopedia © 1996 CRC Press, Inc.

Vinyl ester resins are step growth polymers of various epoxide resins and unsaturated mono carboxylic acids, most commonly methacrylic acid [53]. They have terminal reactive double bonds derived from the carboxylic acid used.

**Basic vinyl ester resin**

A basic vinyl ester preparation employing simple diglycidyl ether of bisphenol A epoxy resin and methacrylic acid can be represented as shown in Fig.1.19.

![Structure of Methacrylates terminated polyhydroxy ether oligomer.](image)

**Fig.1.19**: Structure of Methacrylates terminated polyhydroxy ether oligomer.

Generally, onium salts, tertiary amines and phosphines are effective catalysts for the acid-epoxide reaction, which proceeds readily at only moderately elevated temperatures. Typical reaction conditions are 120°C for 4-5 h, and hydroquinone is commonly used as an initiator. The conversion of the reaction is 90-95 %. The vinyl ester resins can also be prepared by the reaction of glycidyl methacrylate with a multifunctional phenol [54].

Methacrylic acid is most commonly used for vinyl ester resins intended for composites applications, while acrylic acid is favored for resins intended for application in coatings. The uses of other unsaturated acids such as crotonic and cinnamic acids have been reported [55]. These reactive groups can form across linked network with or without the addition of comonomer. It is common to dilute the vinyl ester oligomers with a low molecular weight comonomer, such as styrene, vinyl toluene or methyl methacrylate, to reduce the room temperature viscosity of a mixture and solution with a typical viscosity in the range of 200 to 2000 Centipoises. In many industrial products, vinyl ester resin contains 40-50 % styrene.

The most common vinyl esters are made by esterifying a diepoxide resin with a mono carboxylic unsaturated acid such as methacrylic acid or acrylic acid. Such epoxy methacrylates or epoxy acrylates can be used in free radical curing reactions alone or can be dissolved in unsaturated monomers such as styrene to give liquid resins, which can be used very much like styrenated unsaturated polyester resins.

Although vinyl ester resins have been used in industries for more than 30 years, they are generally categorized together in the unsaturated polyester family[51]. There is less literature cited in the literature on vinyl esters resins compared to the studies on unsaturated polyesters resins and epoxy resins, especially the study on the synthesis, structure and properties of vinyl ester resins. Most of the information concerning the cure behavior and the morphology of free radical cured resins focused on unsaturated polyester resins. Development and the application of the vinylester resins with the new structural properties in an effort to improve toughness, reduce viscosity, decrease shrinkage, etc. Understanding the mechanism of the cure reaction, and gaining better control of the properties of these materials are also general interest. Vinyl ester resins combine the best properties of epoxides and unsaturated polyester. They can be easily handled at room temperature and have mechanical properties similar to epoxy resins.
They have better chemical resistance than most polyester resins, especially hydrolytic stability, and at the same time offer greater control over the cure rate and the reaction conditions than epoxy resins. The pendanthydroxyl group on the backbone chain can provide adhesion and the reactive site for further modifications. For example, they can be reacted with anhydrides or isocyanates. It was reported that maleic anhydride react with the hydroxyl groups and improved the chemical resistance of the product. The unsaturation bond on the terminal groups of the vinylester oligomers copolymerize with the comonomer to form a crosslinked network similar to the curing reactions of unsaturated polyesters [56,57].

The accelerators most commonly employed are tertiary amines, such as dimethyl or diethylaniline, and metallic soaps, such as cobalt or manganese octoate or napthenate. Many patents for the preparation of this product have been issued within the past 30 years [58].

Vinylester with considerable structural variation can be prepared by the combination of different epoxide resins with various unsaturated acids as shown in Fig. 1.20. It is well known that bisphenol-A epoxy resins have very good mechanical properties and that cycloaliphatic epoxy resins are UV resistant.

Vinylester resins product from novolac epoxy resins have high temperature properties but are very brittle. Methacrylic acid preferred for many applications. Methacrylates based vinyl esters are more resistant to chemical attack than acrylates vinylester, because the methyl group of methacrylic acid can stabilize the polymer. Structural modifications of vinyl esters resin were also studied by many researchers to alter the properties in order to satisfy specific application requirements. For example of viscosities of vinyl esters resins without diluents are typically in the range of about 1000 to 8000 poise and higher, which is too high for many applications. It is necessary to add lower viscosity reactive diluents. Many of these diluents are too volatile or toxic. The added diluents may act as comonomer and can make modified vinyl ester resins having improved toughness. Vinyl ester resins offer toughness and chemical resistance properties, which are generally superior to unsaturated polyesters. The epoxy resin backbone used in making vinyl ester resins confers toughness and greater tensile elongation properties to these resins. The molecular weight of the vinylester resin can be varied by the choice of the epoxy backbone employed. For the most common vinylester resins used for composites two mols of the diglycidyl ether of bisphenol A are chain extended with one mol of bisphenol A to form the epoxy backbone. In this manner, molecular weight and backbone structure dependent properties such as tensile strength and elongation, heat deflection point and reactivity can be varied for different applications.

The commercially toughened vinyl ester oligomers are Derakane 8084 (Dow Chemical ltd.) and Hetron 1642 (Ashland Chemical Inc), both of which contain a carboxyl-terminated butadiene- acrylonitrile copolymer (CTBP). An excess of the selected epoxy resins reacts with a selected difunctional carboxyl terminated reactive liquid polymer and an unsaturated monocarboxylic acid. The reaction is catalyzed by tertiary amine such as pyridine at 175°C [59,60]. The superior chemical resistance (compared to unsaturated polyesters) of vinylester resins is in part due to the absence of ester linkages in the epoxy backbone in those sites, where the polymer units
Fig. 1.20: The structure of various epoxides and acids, which are used for vinyl esters synthesis.
are connected with phenyl ether linkages. These latter moieties are much more resistant than ester linkages to degradation in many chemical environments and especially in high pH alkaline situations. The ester linkages in a vinylester resins are present only at the end of the molecule, which minimizes the number of ester linkages that can be chemically attacked. Further, if the vinyl ester resin molecule is terminated with methacrylate groups the spatially large methyl group pendant on the methacrylate group sterically shields the ester linkage from chemical attack. With the vinyl unsaturation present on the ends of the molecule, vinyl ester resins can be made to be very reactive. They have the ability to cure rapidly with fast green strength development either as homo polymers or as copolymers with monomers such as styrene [55].

Network formation reaction

Thermoset polymers have covalent bonds linking the polymer chains in three dimensions. These links prevents the chain from sliding past one another resulting in a higher modulus and improve creep resistance. Gelation occurs, when a three dimensional network or an infinite molecular weight polymer (insoluble gel) formed. The time to reach the gelation point at a particular temperature can be measured experimentally.

The thermosets are below their glass transition at room temperature. Usually, glassy thermosets are more brittle than thermoplastics [61]. Thermosets are often formed from polymeric chains, which are then covalently bonded to each other in a process known as crosslinking. Crosslinking can be initiated by heat, light, or the addition of other chemical as it is well known. It is generally not a reversible process, and therefore results in materials that cannot be recycled. The vinylester resins are cross linked by free radical chain reaction copolymerization of methacrylate end groups with styrene. Thus, these involve copolymerization between a difunctional monomer with one double bond and tetrafunctional oligomeric components containing a double bond at each end of a linear chain. In this study monomer is styrene and oligomer is vinylester resin. The accelerators most commonly employed are tertiary amines, such as dimethyl-or diethylaniline, and metallic soaps such as cobalt or manganese octoate or napththenate.

**Cross linking reaction**

The free radical polymerization of vinyl ester resins and unsaturated polyester resin systems is commonly initiated by the thermal or the chemical decomposition of various organic peroxides and organic hydroperoxides to produced free radical initiator. The various chemical types of peroxides include diacyl peroxides, ketone peroxides, hydroperoxides, dialkyl and diarylperoxides peroxy esters, and perketals. Some common peroxides for room temperature are methyl ethyl ketone peroxide (MEKP), cyclohexanone peroxide, and acetylacetone peroxides. Peroxides, usually in the form of powders, pastes, or in the liquids, must be thoroughly dispersed throughout the resin for uniform curing. The cure of these systems can be achieved at both ambient and elevated temperature conditions depending on the initiators used. In both cases, the peroxide is cleaved into free radicals, which then react with the unsaturated bonds of the polymers.

Accelerators increase the rate at which peroxide breakdown into free radicals at room temperature. The latter function of the accelerators makes

the cure reactions possible without external heat. The accelerators most commonly employed for room temperature cures are tertiary amines such as dimethyl and diethylaniline, and metal salt such as cobalt (cobalt complexes) and manganese octoate or naphthenate[62,63]. Metal salts are preferred in the industrial application because of their price and good handling properties.

Fig. 1.21 shows a schematic representation of the network formed by free radical crosslinking reaction. Gelation occurs, when a three dimensional network or an infinite molecular weight (gel) is formed. A gel molecule cannot be dissolved in any solvents. Experimentally, gel times (the time to reach the onset of gelation at a particular temperature,) are measured using rheology or solubility experiments. Free radical crosslinking polymerization and copolymerization of multi vinyl system are very complicated and theoretical work in this field has not been well established, although many papers have been published. Due to the overlap and entanglement of polymer chains, free radical polymerization are often diffusion controlled even with the linear chain [64].

Crosslinking certainly confounds the diffusion-controlled reaction. However there is no existing diffusion theory, which is generally applicable to this type of systems. Some special problems during free-radical polymerization with cross linking have been pointed out in a few papers [65,66] such as early onset of the Trommsdorff effect (gel effect) due to both the physical entanglement of polymer chain and the chemical crosslinking, incomplete conversion of pendant double bonds due to vitrification, and reactivity ratio change with the conversion [67,68]. Trapped radicals can also encourage post-copolymerization with oxygen, cyclization, intramolecular crosslinking and microgelation [69].

A vinylester resin usually contains 30-50 wt% styrene and 50-70 wt% vinyl esters oligomers. Early work on the model phenyl glycidyl ether methacrylates showed that it reacts more rapidly than styrene in bulk or in solution because of hydrogen bonding between the polymer radical and the methacrylate monomer [69]. The methacrylate conversion is high relative to styrene, in the early stage of the reaction. Due to the very high concentration of divinyl monomers, gelation begins at very low conversions. For vinyl ester resins the onsets of gelation is usually rapid (depends on reaction conditions)-right after the induction period with little or no appreciable increase in viscosity prior to gelation. The time to the onset of gelation is dependent on the concentration of free radicals.

**Specialty vinylester resins**

Specialty vinylester resins can be made based on the use of epoxy novolacs (epoxy resins based on phenol formaldehyde novolacs) for the epoxy resin backbone. Heat deflection points of 132 to 149°C can be achieved, while still maintaining excellent chemical resistance. Flame retardant vinylester resins can be made by using diepoxide resins based on the use of tetrabromobisphenol-A.

**Vinylester resin thickening for SMC**

Conventional vinylester resins do not respond well to the divalent Group II metal oxides and hydroxides used for thickening sheet molding compounds (SMC). Good thickening response can be obtained by introducing carboxyl group functionality on the vinylester molecule. R.J. Jackson described acid modification of a vinylester resin by replacing part of the mono carboxylicmethacrylic acid with a dicarboxylic acid, maleic acid [65]. An example from Jackson’s patent illustrates such a formula change and the improvement in thickening response. This is shown in Table 1.5[70]
Fig. 1.21: Free radical crosslinking mechanism [49]

One step vinylester resin thickening for SMC

An early novel “one step” approach to the preparation of vinyl step type resins was described by C. A. May, who using a kettle charge of bisphenol- A, epichlorohydrin and methacrylic acid, first reacted the epichlorohydrin with the methacrylic acid and then adding sodium hydroxide, reacted the bisphenol-A with the methacrylated epichlorohydrin residue. Other variants were explored by May. Among these was the modification of a vinylester resin by reacting the secondary hydroxyls of the resin with isocyanate to give a urethane modified vinyl ester resin [71,72].

Rubber modified vinylester

An early novel “one step” approach to the preparation of vinylester type resins was described by C.A. May. More impact resistant vinylester resins were made by D.J. Najvar by replacing up to 20% of the unsaturated monocarboxylic acid, such as methacrylic acid with a functionally equivalent amount of a liquid carboxy terminated polydiene rubber [73]. As an example the following were reacted to an exotherm of 190°C as shown in Table 1.6.

Vinylester overview

The epoxy backbone and methacrylic/acrylic acid used to make vinylesters make them significantly more costly than conventional unsaturated polyester resins. Vinylesters, however, do offer advantages over unsaturated polyester resins, which have been very well summarized by Anderson and Messick [74].

1. Excellent reactivity due to terminal vinyl unsaturation in either homo polymerization or copolymerization reactions.
2. With methacrylate termination, increased hydrolysis resistance due to ester linkage shielding by the methacrylate methyl group.
3. 35 to 50% fewer hydrolysis prone ester linkages than conventional unsaturated polyester resin.
4. Better wetting and bonding to glass reinforcements due to secondary hydroxyls on the vinyl ester resin molecule.
5. Improved elongation and toughness conferred by the epoxy resin backbone, whose ether linkages give superior acid resistance.
Applications of vinylester resins

Vinyl ester resins combine the best properties of epoxies and polyesters. Although they are higher in cost than polyesters, vinylester resins have excellent chemical resistance and low water absorption compared with polyester resins. At the same time vinylesters offer greater control over cure rate and reaction conditions than epoxy resins. They can be easily handled at room temperature and have properties close to epoxy resins. Therefore, they are used in applications in many of the same areas that typically use polyesters and epoxies as materials. Typical applications for vinylesters include structural materials, coatings, adhesives, molding compounds, electrical applications, dental materials, and military/aerospace applications.

Because of their excellent thermal performance and mechanical properties, they are the prime candidates for composites in transportation or infrastructure with applications in construction of parts for automobiles and other surface transportation vehicles, fascia for buildings, reinforcements for bridges, etc. For example, as the materials for sheet molding compounds (SMC), vinylester resins provide greater toughness, heat distortion temperature, and corrosion resistance compared to conventional unsaturated polyesters [75]. Novolac epoxy-based vinyl ester resins with their higher glass

**Table 1.5:** Maleic acid modified vinyl ester SMC resin

<table>
<thead>
<tr>
<th>Stage 01 Raw material</th>
<th>Standard vinylester resin</th>
<th>Acidmodified vinylesterrer resin.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy resin(DGEBA)</td>
<td>795</td>
<td>795</td>
</tr>
<tr>
<td>Bisphenol-A</td>
<td>237</td>
<td>237</td>
</tr>
<tr>
<td>Trimethyl ammonium chloride</td>
<td>0.825</td>
<td>0.825</td>
</tr>
<tr>
<td>Stage 02 Glacial methacrylic acid</td>
<td>195.2</td>
<td>171.3</td>
</tr>
<tr>
<td>Hydroquinone</td>
<td>0.45</td>
<td>-</td>
</tr>
<tr>
<td>Trimethylammonium chloride</td>
<td>6.6</td>
<td>6.6</td>
</tr>
<tr>
<td>Maleic acid</td>
<td>-</td>
<td>32.25</td>
</tr>
<tr>
<td>Styrene</td>
<td>970</td>
<td>970</td>
</tr>
</tbody>
</table>

Note:

Stage 01 was processed for 1 h at 171°C, Stage 02 was processed for 3 h at 116°C in N₂ atmosphere.

DGEBA: Average MW 350, equiv. wt. about 170-190

**Table 1.6:** Formulation of rubber modified vinylester

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy resin(DGEBA)</td>
<td>455</td>
</tr>
<tr>
<td>BisPhenol-A</td>
<td>155</td>
</tr>
<tr>
<td>Tert.butylphosfonium acetate</td>
<td>0.5</td>
</tr>
<tr>
<td>Methacrylic acid</td>
<td>76</td>
</tr>
<tr>
<td>DMP-30 catalyst</td>
<td>1.2</td>
</tr>
<tr>
<td>B.F. Goodrich Hycar CTBN (COOH)terminated butadiene acylonitrile rubber with 2.5% COOH</td>
<td>228</td>
</tr>
<tr>
<td>Hydroquinone</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Note:

This gave polyeoxide resin with EEW 600 was then reacted further at 120 C° to 130°C with methacrylic acid.

DGEBA: EEW 189 (Dow 331)
Table 1.7: Styrenated vinylester resin liquid properties

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene content (%)</td>
<td>45-50</td>
</tr>
<tr>
<td>Nonvolatile matter (%)</td>
<td>50-55</td>
</tr>
<tr>
<td>Viscosity (cps)</td>
<td>80-600</td>
</tr>
<tr>
<td>Color gardener</td>
<td>2-3</td>
</tr>
<tr>
<td>Flash point (°C)</td>
<td>35</td>
</tr>
<tr>
<td>Gel time (min)</td>
<td>20-25</td>
</tr>
<tr>
<td>SPI gel time (min)</td>
<td>10-19</td>
</tr>
<tr>
<td>Peak exotherm temperature (°C)</td>
<td>130 max</td>
</tr>
</tbody>
</table>

Table 1.8: Mechanical properties of typical styrenated vinyl ester cast resin.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength, MPa, 25°C</td>
<td>69-76</td>
</tr>
<tr>
<td>Tensile elongation, %</td>
<td>5.3 – 5.8</td>
</tr>
<tr>
<td>Flexural modulus, MPa, 25°C</td>
<td>2482-3033</td>
</tr>
<tr>
<td>Notched Izod impact, kJ / m</td>
<td>27-29</td>
</tr>
<tr>
<td>Tensile modulus, Mpa</td>
<td>3102-3172</td>
</tr>
<tr>
<td>Flexural strength, MPa( 25°C)</td>
<td>124-131</td>
</tr>
<tr>
<td>Heat deflection temperature, (°C)</td>
<td>88-99</td>
</tr>
<tr>
<td>Barcol hardness</td>
<td>40-50</td>
</tr>
</tbody>
</table>
transition temperatures are used for high temperature formulations such as chemical storage vessels and chemical reactors. Another application for novolac epoxy-based vinylester resins is in the construction of waste incineration gas cleaning units [76]. Modified DGEBA resins are used where improved adhesion, wear resistance, and fracture toughness are required. Vinylesters can also be used in applications ranging from electro-refining tanks to swimming pools.

Vinylesters also find a variety of applications in optical fiber coatings, topcoats for metal containers, UV curing inks, as well as in printed circuit boards because of their ability to constitute photo crosslinkable systems [77]. For example, Actocryl-400, an aromatic epoxydiacrylateresin based on DGEBA from ancomer, Manchester, UK, can be photo-crosslinked with photo initiator dimethoxy phenyl acetophenone (Irgacure 651 from Ciba Geigy), and used as a photo-crosslinkable coating materials.

76. D. H. Kelley and J. F. Perey, Polymer Composites, 18,34, 1997
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.