

**CHEMICALLY MODIFIED KENAF BAST FIBRES REINFORCED POLYESTER  
COMPOSITES**

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**UNIVERSITI SAINS MALAYSIA**

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**By**

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## LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
DMF	Dimethyl Formamide
FDT	Final Decomposition Temperature
FT-IR	Fourier Transform Infra-Red
GPa	Giga Pascal
IDT	Initial Decomposition Temperature
kPa	Kilo Pascal
MEKP	Methyl Ethyl Ketone Peroxide
MPa	Mega Pascal
NaOH	Sodium Hydroxide
HCOONa	Sodium Formate
OD	Oven Dry
OH	Hydroxyl
SEM	Scanning Electron Microscopy
TGA	Thermal Gravimetric Analysis
WPG	Weight Percent Gain

## LIST OF SYMBOLS

A	Cross sectional Area
b	Width
cm	Centimetre
C=O	Carbonyl group
-COOH	Carboxyl group
d	Thickness
F	Force
g	Gram
J	Joule
l	Length
<i>m</i>	Mass
m	Metre
mm	Millimetre
N	Newton
v	Volume

## LIST OF PUBLICATIONS & CONFERENCE PROCEEDINGS

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# **KOMPOSIT POLIESTER DIPERKUAT GENTIAN KULIT KENAF TERUBAHSUAI KIMIA**

## **ABSTRAK**

Kenaf merupakan tanaman tempatan dan mempunyai potensi besar sebagai pengukuh dalam polimer komposit. Walaubagaimanapun, penggunaannya terhad disebabkan oleh sifat hidrofilik polimer dinding sel. Tujuan utama kajian ini adalah untuk meneroka potensi pengubahsuaian kimia gentian kulit kenaf dalam komposit berprestasi tinggi. Gentian kulit kenaf bertindak sebagai pengukuh dan poliester tak tepu sebagai matriks polimer. Pengubahsuaian kimia gentian kulit kenaf telah dijalankan dengan menggunakan propionik anhidrida dan suksinik anhidrida. Lima masa rendaman telah ditetapkan iaitu 30, 60, 120, 180 dan 240 minit pada 100 ° C. Pengubahsuaian kimia telah disahkan oleh peningkatan WPG dan juga oleh FT-IR. Keputusan WPG untuk kedua-dua pengubahsuaian gentian menggunakan propionik anhidrida dan suksinik anhidrida menunjukkan bahawa 180 minit adalah masa yang optimum untuk pengubahsuaian dengan memberi keputusan WPG tertinggi. Satu peningkatan yang ketara telah diperhatikan dalam sifat fizikal, mekanikal, haba dan morfologi pada poliester komposit diperkuh gentian kulit kenaf terubahsuai kimia. Komposit dirawat menunjukkan rintangan air yang sangat baik dengan kadar penyerapan air yang sangat rendah. Ketumpatan komposit dirawat juga meningkat berbanding dengan komposit yang tidak dirawat. Sifat-sifat mekanik telah bertambah baik selepas pengubahsuaian kimia. SEM mikrograf menunjukkan interaksi yang baik antara gentian dan matriks dimana gentian melekat dengan kuat dalam matriks yang membuktikan kewujudan rekatan yang baik di antara mereka. TGA menunjukkan bahawa komposit yang dirawat mempunyai kestabilan terma yang baik berbanding dengan komposit yang tidak dirawat.



# **CHEMICALLY MODIFIED KENAF BAST FIBRES REINFORCED POLYESTER COMPOSITES**

## **ABSTRACT**

Kenaf is locally planted and having great potential as reinforcement in polymer composite. However, the limitation occurs due to the hydrophilic nature of cell wall polymers. The main purpose of this research is to explore the potential of the chemical modification of kenaf bast fibre to be use in high performance composites. Kenaf bast fibre was used as reinforcement and unsaturated polyester as polymer matrix. The chemical modification of kenaf bast fibres was carried out by using propionic and succinic anhydride. Five retention times were set which were 30, 60, 120, 180 and 240 minutes at 100 °C. Chemical modification was confirmed by increase in WPG and also FT-IR. The results of WPG for both propionylated and succinylated fibres showed that 180 minutes was an optimum time for modification by giving the highest WPG results. A significant improvement was observed in physical, mechanical, thermal and morphological properties of treated kenaf bast fibre reinforced polyester composites. Treated composites exhibited excellent water resistance which give very low water absorption. The density of treated composites also increased as compared with untreated composite. Mechanical properties were improved after chemical modification. SEM micrograph showed good fibre matrix interaction as the fibres have embedded well in the matrix which proved the existence of good adhesion between them. TGA revealed that treated composites have good thermal stability as compared with untreated composite.

# CHAPTER ONE

## INTRODUCTION

### 1.1 General

The current rapid economic growth and industrialization has caused serious environmental challenges to the world. As globalization continues, the environment also begins to deteriorate at a quicker rate. This critical issue has become a major concern of humanity since the middle of the 20th century. Environmental awareness is also building up in Malaysia and with the 9th Malaysia Plan 2006-2010, the Malaysian government has placed further emphasis on preventive measures to mitigate and minimise negative environmental effects at source, to intensify conservation efforts and to ensure a sustainable development of both the exhaustible and the renewable energy resources.

Utilization of renewable resources is one of the major solutions to overcome the environmental issues. Natural fibres have been increasingly studied in recent times. The worldwide availability of natural fibres and other abundantly accessible agro waste is responsible for this new polymer science and engineering research, and the search for a sustainable technology. Scientist all over the world is seriously looking at natural fibres as alternatives to replace man-made fibres (Akil et al., 2011; Khalil and Ismail, 2001). Natural fibres have a number of techno-economical and ecological advantages over glass fibres. The combination of interesting mechanical and physical properties together with their environmental friendly character has motivated a number of industrial sectors, notably the automotive industry to consider

these fibres as potential candidates to replace glass fibres in environmentally safe products. (Han et al., 2010; George et al., 2001).

Significant research efforts are currently being spent in developing a new class of fully biodegradable green composites by combining natural fibres with biodegradable resins (Shaji et al., 2006). Natural fibres provide with interesting properties of the final composite, especially those related to the protection of the environment such as their capacity to be recyclable, renewable raw material, and less abrasive and harmful behaviour (Akil et al., 2011; Riedel et al., 1999). Thus, some advantages associated to the use of natural fibres as reinforcement in plastics are their non-abrasive nature, biodegradability, low energy consumption and low cost. Additionally, natural fibres have low density and high specific properties. The specific mechanical properties of natural fibres are comparable to those of traditional reinforcements (Hanselka et al., 1995). Thus, the intrinsic properties of natural fibres can satisfy the requests of the global market (Herrmann et al., 1996) especially for those industries concerned in weight reduction. That is why they can be potential substitute for non-renewable synthetic fibres (Gandini et al., 2001).

One of the most widely used natural fibres is kenaf fibre which has been successfully incorporated in variety of applications. Kenaf (*Hibiscus cannabinus L*) is a warm season annual fibre crop closely related to cotton and jute. Historically, kenaf has been used as a cordage crop to produce twine, rope and sackcloth. Nowadays, there are various new applications for kenaf including paper products, building materials, absorbents and animal feeds. Furthermore, there is a growing interest in the use of kenaf fibres especially for composite reinforcement. This is because kenaf has good mechanical properties and can grow quickly, rising to as

height as 4-5 m in within 4-5 month growing season with the kenaf stalk diameter of 25-35 mm. It means that kenaf fibre composite would give the opportunity to produce products similar to that material of wood, but it takes only 150 days to harvest. Thus, it would reduce the demand of timber which now is facing problem of deforestation. Kenaf plant has a single, straight and branchless stalk and made up of an inner woody core and an outer fibrous bark surrounding the core. The kenaf comprises 35-40% bast fibre and 60-65% core fibres by weight of the kenaf stalk (Ishak et al., 2010).

The fibre-matrix interface is the diffusion or reaction zone, in which fibre and matrix phases are chemically and/or mechanically combined. Interfacial adhesion between fibre and matrix plays a predominant part in characterizing the mechanical properties of the composites. If there is a poor adhesion across the phase boundary, then relatively weak dispersion of force occurs and resulting poor mechanical properties of the composite (Wang et al., 2007). For reinforcement of natural fibre in composites, several problems occur along the interface due to the presence of hydrophilic hydroxyl groups on the fibre surface. This hydrophilic nature hinders effective reaction with the matrix. In addition to this, pectin and waxy substance covers the reactive functional groups of the fibre and act as a barrier to interlocking with the matrix. To optimize effective interfacial bonding between fibre and matrix, the fibre surface needs to be modified with different chemical treatment, reactive additives and coupling agents. Chemical treatments expose more reactive groups on the fibre surface and thus facilitate efficient coupling with the matrix. As a result, better mechanical and thermal properties of the composites can be achieved (Dash et al., 2000).

## 1.2 Problem Statement

Natural fibre composites such as kenaf composites offer many environmental advantages and at the same time encourage the development of industrial crops for world generally and for Malaysia specifically. In Malaysia, realizing the diverse possibilities of commercially exploitable derived products from kenaf, the National Kenaf Research and Development Program has been formed in an effort to develop kenaf as a possible new industrial crop for Malaysia. The government has allocated RM12 mil for research and further development of the kenaf-based industry under the 9th Malaysia Plan (2006-2010) in recognition of kenaf as a commercially viable crop (Edeerozey et al., 2007).

Furthermore, Malaysia Agricultural Research and Development Institute (MARDI) have spearheaded the research and development activities of kenaf since year 2000 and continue to progressively developing key technologies to enhancing the competitiveness of the kenaf industry. The multiple uses of kenaf come from its fibre. Kenaf sp.V36 is one of kenaf variety which is widely planted in Malaysia. It was found to be the most suitable for commercial-scale production due to the climate in Malaysia. Kenaf is the fast growing plants and due to this advantage, it become more promising to the industry.

This research tries to explore the potential of kenaf bast fibers as reinforcement in polyester composite. However, the major limitations of using these fibres as reinforcements in such matrices include poor interfacial adhesion between polar, hydrophilic fibres and a non- polar, hydrophobic matrix, as well as difficulties in mixing due to poor wetting of the fibres with the matrix (John and Anandjiwala,

2008). The role of the matrix in a fibre reinforced composite is to transfer the load to the stiff fibres through shear stresses at the interface. This process requires a good bond between the polymeric matrix and the fibres. Poor adhesion at the interface means that the full capabilities of the composite cannot be exploited and leaves it vulnerable to environmental attacks that may weaken it, thus reducing its life span (Wambua et al., 2003).

Thus, in order to overcome this problem, chemical modification of fibres is required. Chemical modification of fibres is well known in polymer composite. In this research, the main purpose is to produce the kenaf bast reinforced polyester composite. This research is differ from others previous work because the aim is to exploring the reactive chemistry of succinic and propionic anhydride towards kenaf bast fibers and to investigate the effect of that modified fibres with unsaturated polyester resin to produce high performance fibre reinforced thermoset composite.

### **1.3 Objectives**

General objective is to investigate the potential of the chemical modification of kenaf bast fibre to be use in high performance composites. Specific objectives are:

- To investigate the effect of chemical modification of kenaf bast fibres by using propionic and succinic anhydride.
- To investigate the effect of chemical modification of kenaf bast fibres towards the physical, mechanical, morphological and thermal properties of composites.

- To investigate the fibre-matrix bonding of succinylated and propionylated kenaf bast fibre with unsaturated polyester using Scanning Electron Microscope (SEM).

## **CHAPTER TWO**

### **LITERATURE REVIEW**

#### **2.1 Composite Material**

##### **2.1.1 Definition**

Composites have worked their way up among wood and metal due to their outstanding price performance ratio during a lifetime (Rijswik et al., 2001). Composite defined as a combination of two or more materials (reinforcing elements, fillers, and composite matrix binder), differing in form or composition. The individual materials that make up composites are called constituents. Most composites have two constituent materials: a binder or matrix, and reinforcement. The reinforcement is usually much stronger and stiffer than the matrix, and gives the composite its good properties. The matrix holds the reinforcements in an orderly pattern. The reinforcements are usually discontinuous, thus, the matrix also helps to transfer load among the reinforcements.

##### **2.1.2 Classification**

There are two classification systems of composite materials. First system is classified based on the matrix material (metal, ceramic, and polymer). This system categorized in three types which are Metal Matrix Composites (MMC) which composed by a metallic matrix (aluminum, magnesium, iron, cobalt, copper) and a dispersed ceramic (oxides, carbides) or metallic (lead, tungsten, molybdenum) phase. Another type on this first system is Ceramic Matrix Composites (CMC) which is



composed by a ceramic matrix and embedded fibers of other ceramic material (dispersed phase). Thirdly is Polymer Matrix Composites (PMC) which composed of a matrix from thermoset (Unsaturated Polyester (UP), Epoxy (EP)) or thermoplastic (Polycarbonate (PC), Polyvinylchloride, Nylon, Polysterene) and embedded glass, carbon, steel or Kevlar fibers (dispersed phase).

Second system of composite materials is based on reinforcing material structure. It is classified as particulate reinforced composites, fiber reinforced composites and laminar composites. Figure 2.1 illustrate the classification of composite based on reinforcement form.

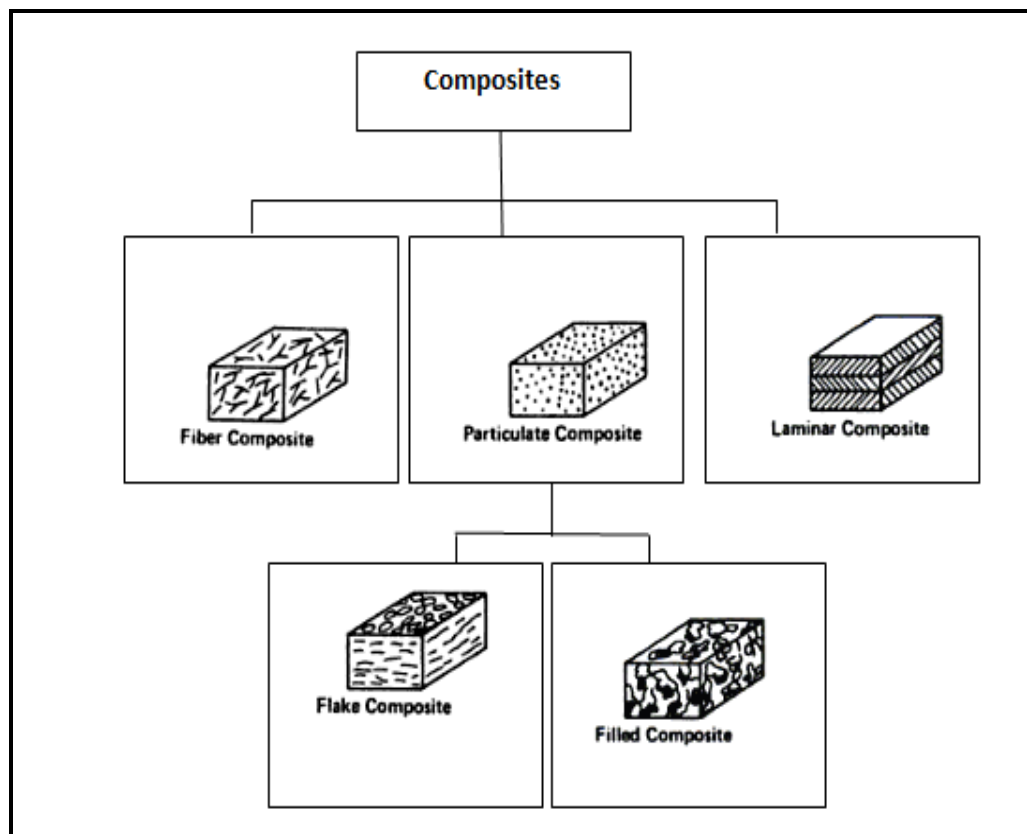


Figure 2.1: Classification of composites based on their reinforcement form (Vinson and Sierakowski, 2002).

Particulate composites consist of a matrix reinforced by a dispersed phase in form of particles. Particle reinforcement can be by ceramics, metallic or other particles of different sizes and shapes (Mishnaevsky, 2007). The particles strengthen the matrices by their hardness, relative to the matrix. The strength of the composite usually depends on the diameter of the particles, the interparticle spacing and the volume fraction of the composite. The particulate reinforcement leads to isotropic properties (Srinivasan, 2010). Examples of well known particulate composites are concrete and particle board. There are two subclasses of particulates which is flake and filled/skeletal. A flake composite is generally composed of flakes with large ratios of platform area to thickness, suspended in a matrix material, e.g. particle board. A filled/skeletal composite is composed of a continuous skeletal matrix filled by a second material, e.g. a honeycomb core filled with an insulating material (Staab, 1999). Particles are generally used to improve certain properties of materials, such as stiffness, behavior with temperature, resistance to abrasion, decrease of shrinkage, etc. The load carrying capacity of particle composites, however, depends on the properties of matrix materials (Ye, 2003).

Fibrous composites consist of two types which are categorized based on fiber length. The reinforcement of this type of composites is in the form of fibers which are either continuous (long fibers) or discontinuous (chopped fibers, short fibers, etc.) (Berthelot, 1999). Continuous fibre composites can be either single layer or multilayered. The single layer continuous fibre composites can be either unidirectional or woven, and multilayered composites are generally referred to as laminates. Composites in which the reinforcements are discontinuous fibres or whiskers can be produced to have either random or biased orientation. The

discontinuities can produce a material response that is anisotropic, but in many instances the random reinforcements produce nearly isotropic composites (Staab, 1999). Three groups of fibre reinforcement are used: whiskers, fibres and wires. Whiskers are thin single crystals (such as graphite, silicon carbide, silicon nitride and aluminium oxide) are very high strength with almost no defects. Fibres are made usually from either polymers or ceramics, and tend to have much higher strengths than bulk materials, due to their smaller diameters. Fine wires have relatively large diameters, as compared with fibres and whiskers (Mishnaevsky, 2007). The fibres are generally stronger and stiffer than they are in bulk form and therefore serve as the primary load-carrying constituent. The matrix holds the fibres together and serves as an agent to redistribute the loads from a broken fibre to the adjacent fibres in the material when fibres start failing under excessive loads. However, fibres alone cannot support longitudinal compressive loads, and their transverse mechanical properties are generally poorer than the corresponding longitudinal properties (Gürdal et al., 1999, Akbarov et al., 2001).

Laminar composites is a type of composites which consists of several layers with different fiber orientations, it is called multilayer (angle-ply) composite. It consists of at least two different materials that are bonded together. The ability to structure and orient material layers in a prescribed sequence leads to several particularly significant advantages such as strength, stiffness, corrosion resistance, low weight, etc. compared to conventional monolithic materials (Ye, 2003). A lamina is generally assumed to be orthotropic, and its thickness depends on the material from which it is made. The laminate's response depends on the properties of each lamina, as well as the order in which the lamina are stacked. The laminar

composites are classified as laminates, clad metals and sandwich structure (Akbarov et al., 2001, Srinivasan, 2010). Unidirectional laminates are extremely strong and stiff in the 0° direction but very weak in the 90° direction because the load must be carried by the much weaker polymeric matrix (Campbell, 2004).

## **2.2 Matrix Material**

The primary functions of the matrix are to transfer stress between the reinforcing fibres, act as a glue to hold the fibres together, and protect the fibres from mechanical and environmental damage. Matrix is divided into two major groups known as thermoset and thermoplastic. Thermoplastic resins become soft when heated, and may be shaped or molded while in a heated semi-fluid state and become rigid when cooled. Thermoset resins, on the other hand, are usually liquids or low melting point solids in their initial form. When used to produce finished goods, these thermosetting resins are cured by the use of a catalyst, heat or a combination of the two. Once cured, solid thermoset resins cannot be converted back to their original liquid form.

### **2.2.1 Thermoset**

Generally thermoset is defined as a material that hardens when heated and cannot be remoulded. In thermoset polymers, the liquid resins are converted into hard brittle solids by chemical cross-linking which leads to the formation of a tightly bound three-dimensional network of polymer chains. The main characteristic that distinguishes thermoset is the irreversibility of the solidification process that takes place as a result of chemical reaction. This chemical reaction is typically a

polymerization reaction that leads to a macroscopic network molecule. The starting point is a group of small molecules in the liquid state. These small molecules start reacting with each other step by step, forming increasingly larger molecules that branch out like a tree. Eventually the branches of different "trees" start merging with each other, forming a network or "cross linked" structure. Ultimately, all the "trees" end up linked into one giant network. The polymer thus formed will have a permanent shape defined by the shape of the container at the time the network was formed. This polymer is insoluble and infusible as a result of its three-dimensional network structure (Hale, A. 2002). The most common thermoset resins used in the composite industry are unsaturated polyesters, vinyl esters and epoxy. There are differences between these groups that must be understood to choose the proper material for a specific application. Table 2.1 shows a study of the basic characteristics of commonly used thermosets (Polyester, Vinyl Ester and Epoxy).

Unsaturated polyester resin is a thermoset capable of being cured from a liquid to a solid state when subjected to appropriate conditions. A whole range of polyesters is made from different acids, glycols, and monomers, all having varying properties. There are two principal types of polyester resins used as a standard laminating system in the composites industry. Orthophthalic polyester resin is the standard economic resin commonly used, and it yields highly rigid products. Isophthalic polyester resin is now becoming the preferred material in the marine industry, where its superior water resistance is desirable (Ray and Rout, 2005). An idealized chemical structure of unsaturated polyester is shown in Figure 2.2.

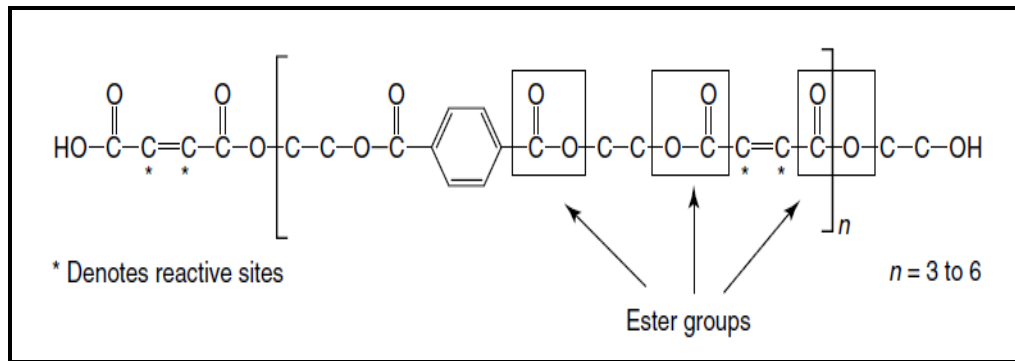


Figure 2.2: Idealized chemical structure of a typical unsaturated polyester resin (Ray and Rout, 2005).

Unsaturated polyesters are extremely versatile in properties and application and have been a popular thermoset used as the polymer matrix in composites. They are widely produced industrially as they possess many advantages compared to other thermosetting resins including room temperature cure capability, good mechanical properties and transparency. Curing of unsaturated polyester is due to a polymerization reaction that causes cross linking among individual linear polymer chains. In contrast to other thermosetting resins, no by – product is formed during the curing reaction; hence resins can be molded cast and laminated at low pressure and temperature (Aziz et al., 2005).

Vinyl esters are the reaction products of epoxy resins with ethylenically unsaturated carboxylic acids. The terminal unsaturation groups of these products are most commonly methacrylates or acrylates. These groups can react with themselves or with added monomers such as styrene to form cross linked structures. As in the case of unsaturated polyesters, the cross linking reaction involves a free radical mechanism (Hale, 2002). Liquid polyester resins lend themselves very well to casting operations. Some applications include cultured marble and onyx, polymer

concrete, and monolithic flooring (Zaske, 1986). Polymer concretes are used to patch highways and bridges because of their fast cure (Berins, 1991). Unsaturated polyesters and vinyl esters are mostly used in glass-reinforced composites; they are very well suited for processes such as pultrusion, filament winding, injection, compression, and resin transfer molding. Common applications comprise boat hulls, automotive body parts, building panels, housings, bathroom components, pipes and pressure vessels (Berins, 1991). An idealized chemical structure of vinyl ester is shown in Figure 2.3.

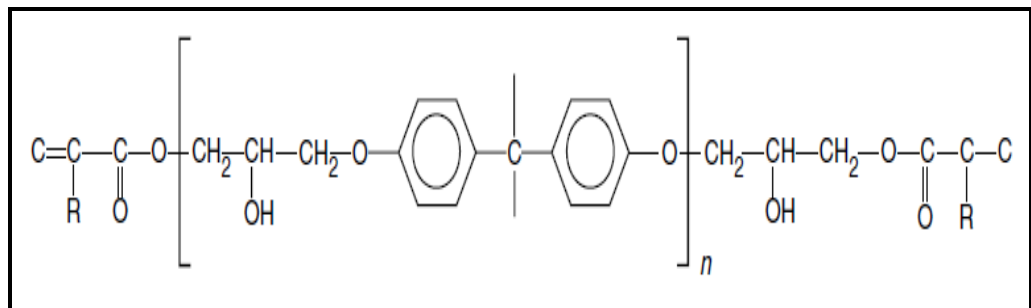


Figure 2.3: Idealized chemical structure of a typical vinyl ester resin (Ray and Rout, 2005).

Epoxy resins are a large family of resins that represent some of the high performance resins available in the market. Epoxies generally outperform most other resin types in terms of mechanical properties and resistance to environmental degradation, which leads to their almost exclusive use in the aircraft industry. As a laminating resin their increased adhesive properties and resistance to water degradation make these resins ideal for use in applications such as boat building. Epoxies are widely used as a primary construction material for high-performance boats or as a secondary application to sheath a hull or replace water-degraded

polyester resins and gel coats (Ray and Rout, 2005). An idealized chemical structure of epoxy is shown in Figure 2.4.

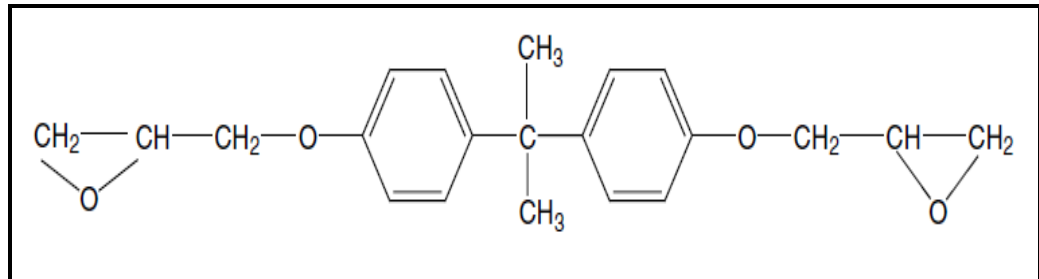


Figure 2.4: Idealized chemical structure of a typical epoxy resin (Ray and Rout, 2005).



Table 2.1: A study of the basic characteristics of commonly used thermosets (polyester, vinyl ester and epoxy) (Ray and Rout, 2005).

Type of Resin	Common Manufacturing Ingredients	Curing Behavior
Unsaturated Polyester	Glycols used are propylene glycol, ethylene glycol, diethylene glycol. Unsaturated acid used are maleic acid or anhydride. Saturated acid used is commonly phtalic anhydride	Catalyst for room temperature curing is Methyl Ethyl Ketone Peroxide (MEKP). For high temperature curing benzoyl peroxide is used as catalyst. Promoter used is cobalt compound like napthenate, octoate, etc. Accelerator : tertiary amines like N,N-dimethyl aniline
Vinyl Ester	Produced by the reaction between epoxy resin and an ethylenically unsaturated carboxylic acid resulting terminal unsaturation. Commonly used acids are acrylic or methacrylic acid	Catalyst for room temperature curing is methyl ethyl ketone peroxide (MEKP). For high temperature curing benzoyl peroxide or t-butyl perbenzoate is used as catalyst. Promoter used is cobalt compound like napthenate,octoate,etc. Accelerator : tertiary amines like N,N-dimethyl aniline
Epoxy	Produced by the reaction between epichlorohydrin and bisphenol-A	Amine hardeners like diethylene triamine and triethylene tetramine are commonly used to cure epoxy by an additional reaction where both the materials take part in the chemical reaction. Anhydride hardeners are sometimes used with the amines to speed up and cure time

### **2.2.2 Thermoplastic**

Thermoplastic is a polymer material that turns to liquid when heated and becomes solid when cooled. While thermosets are crosslinkable polymers, thermoplastics may be characterized as linear polymers which normally need no cure during consolidation into a composite. The consolidated thermoplastic composites are remoldable and reformable (Chang and Lees, 1988). They are often supplied as granules and heated to permit fabrication by methods such as molding or extrusion. Most common thermoplastic include polyethylene, polypropylene, and polystyrene.

### **2.3 Lignocellulosic Fibres**

Ecological concerns have resulted in a renewed interest in natural materials, and therefore issues such as recyclability and environmental safety are becoming increasingly important for the introduction of new materials and products. At this moment, designing for recycling or in a somewhat broader perspective, eco-design is becoming a philosophy that is applied to more materials and products. It is for these reasons that natural fibres based on lignocellulose can be considered as an interesting environmentally safe alternative for the use of glass fibres as reinforcement in engineering polymeric materials (George et al., 2001).

Plant-based fibres are already used in a wide range of products. Plant fibres find applications as textiles and geotextiles, twines and ropes, special pulps, insulating and padding materials, fleece, felts and non woven materials, and increasingly as reinforcement for polymers (Bismarck et al., 2005).

Availability of plant fibres and other abundantly accessible agro waste is responsible for this new research interest in the field of polymer science,

engineering, and is responsible for a new interest in research in sustainable technology. Figure 2.5 shows truly green eco-composites in nature's circle of life.

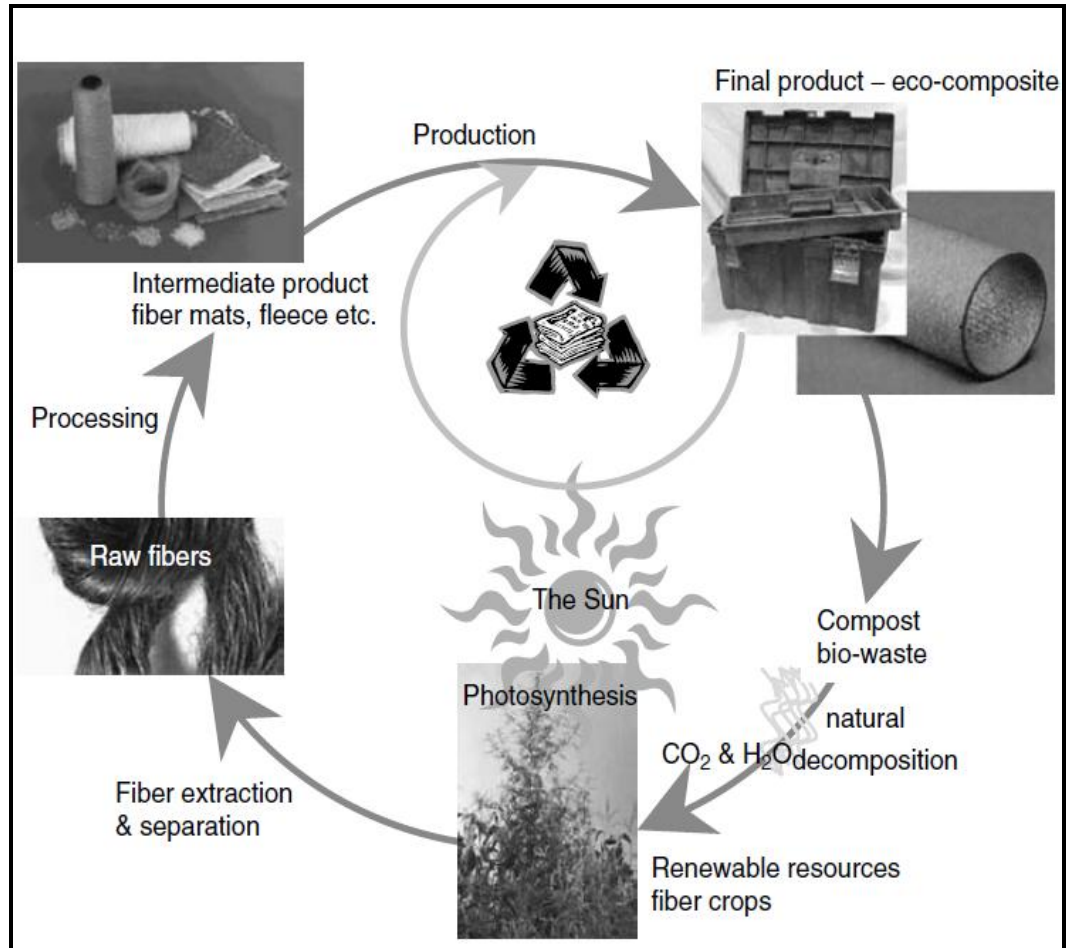


Figure 2.5: Truly green eco-composites in nature's circle of life (Bismarck et al., 2005).

Fibres can be sourced from plants, animals and minerals. A diagram with a classification of the various fibres shows in Figure 2.6. Lignocellulosic fibres have three main categories depending on the part of the plant from which they extracted. First is a bast or stem fibre (jute, flax, hemp, ramie, kenaf, etc). Second are leaf fibres

(sisal, banana, hemp, pineapple, etc). Third are seed fibres (cotton, coir, oil palm etc.). Currently several types of cellulosic fibres reinforced in plastics including flax, hemp, jute, straw, wood fibre, rice husks, wheat, barley, oats, rye, cane (sugar and bamboo), grass, reeds, kenaf, ramie, oil palm empty fruit bunch (EFB) fibres, sisal, hyacinth, pennywort, kapok, paper-mulberry, raphia, banana fibre, pineapple leaf fibre, and papyrus (Jawaid and Khalil, 2011).

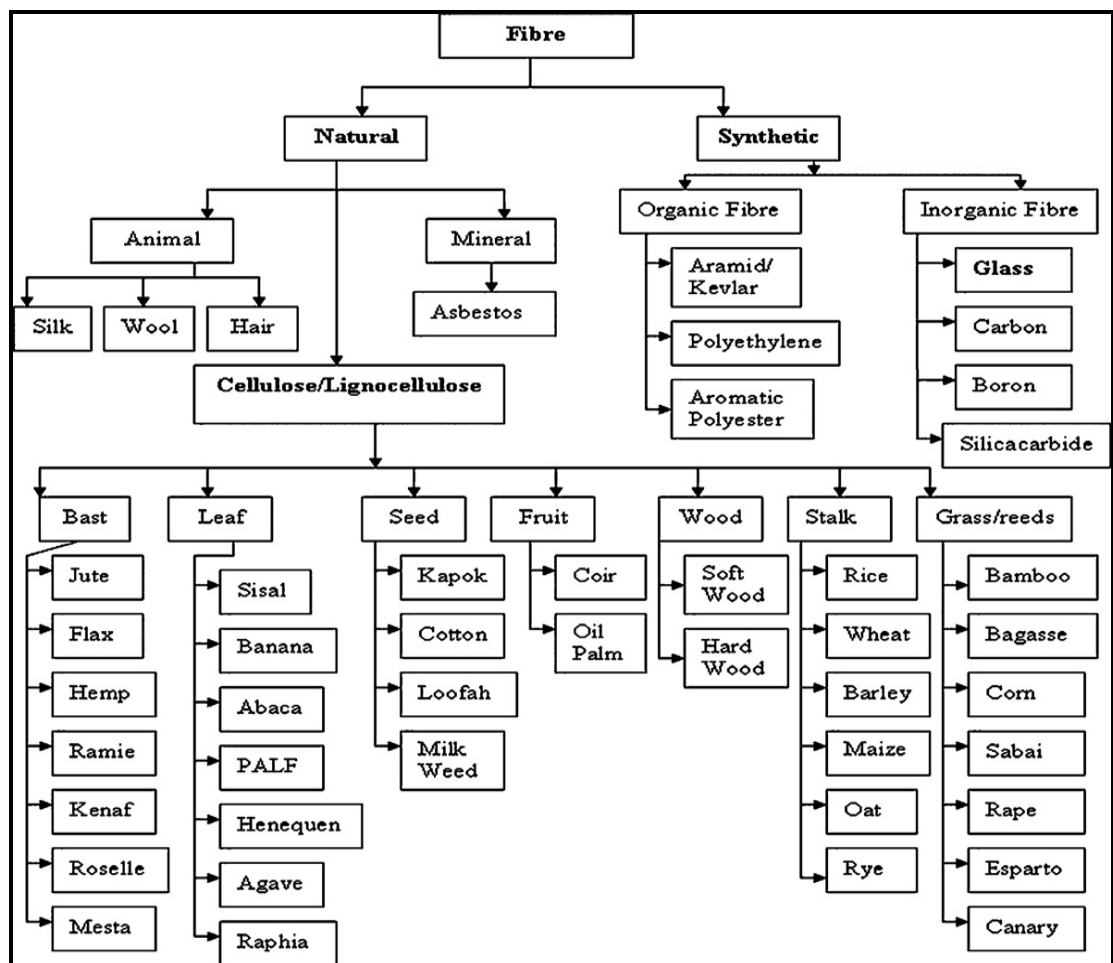


Figure 2.6: Classification of natural and synthetic fibres  
(Bismarck et al., 2005; Lilhot and Lawther, 2003; Rowell, 2008)

### 2.3.1 Cell Wall Structure

Lignocellulose fibres are composite of cellulose microfibrils held together by a lignin and hemicelluloses. The cell wall consists mainly of three layers. Figure 2.7 shows that the fibre consists of four layers, labelled the primary wall, outer layer of the secondary wall (S1), main layer of the secondary wall (S2) and inner layer of the secondary wall (S3).

In all plant fibres, cell wall contains cellulose, hemicellulose and lignin in varying amounts. The individual fibres are bonded together by a lignin-rich region known as the middle lamella (Jayaraman, 2003). Cellulose attains its highest concentration in the S2 layer (about 50%) and lignin is most concentrated in the middle lamella (about 90%). The S2 layer is usually by far the thickest layer and dominates the properties of the fibres. The S2 layer consists of a series of helically wound cellular microfibrils formed from long chain cellulose molecules: the angle between the fibre axis and the microfibrils is called the microfibrillar angle (Jayaraman, 2003; John and Thomas, 2008).

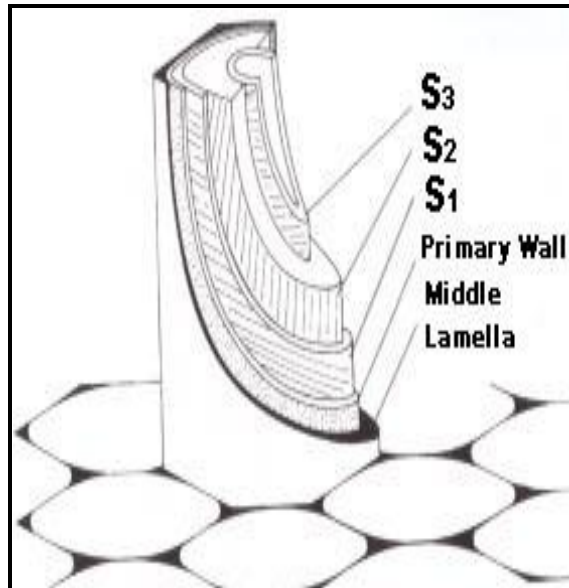


Figure 2.7: Cell wall structure of lignocellulose fibres (Khalil and Rozman, 2004)

## 2.3.2 Chemical Composition of Lignocellulosic Fibres

### 2.3.2.1 Cellulose

Cellulose is a white fibrous material composed of the elements carbon, hydrogen and oxygen. Chemically, cellulose is a carbohydrate of which the elements hydrogen and oxygen are present in the same proportion by weight as they combine to form water (H-O-H). This explains the important properties of cellulose that allows it to swell in water to provide an increased natural bonding affinity for itself and other similar carbohydrates in the plant and collectively referred to as hemicelluloses (Smook, 1992). Cellulose is also a polysaccharide, indicating that it contains many sugar units.

Cellulose is a natural polymer consisting of D-anhydroglucose ( $C_6H_{10}O_5$ ) repeating units joined by  $\beta$ -1, 4-glycosidic linkage 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. Solid cellulose forms a microcrystalline structure with regions of high order, i.e. crystalline regions, and regions of low order, i.e. amorphous regions. 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 (John and Thomas, 2008). Figure 2.8 shows the chemical structure of cellulose.

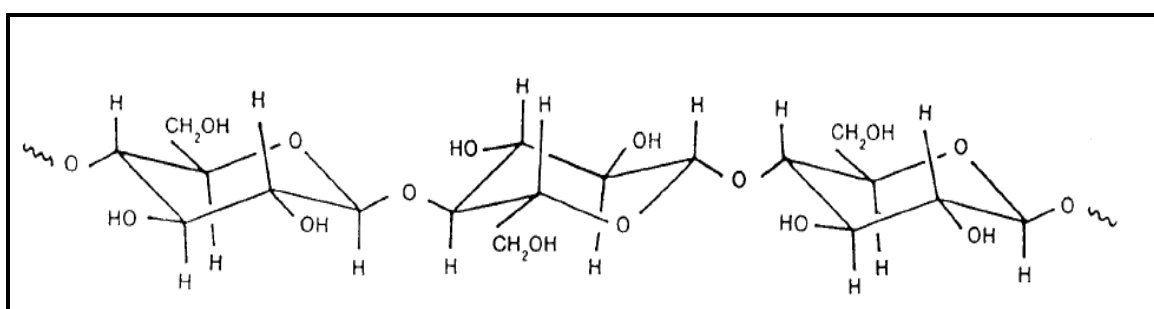


Figure 2.8: Chemical structure of cellulose (Pandey, 1999).

### 2.3.2.2 Hemicellulose

A number of shorter-chain polysaccharides, known collectively as hemicelluloses, also form part of the structure of plants. By contrast to cellulose which is a polymer only of glucose, the hemicelluloses are polymers of five different sugars hexoses; glucose, mannose, galactose and pentose; xylose, arabinose (Smook, 1992). There are different kinds of hemicelluloses. Different species contain hemicelluloses of slightly different composition. The most common hemicelluloses in softwoods are galactoglucomannan. Hemicelluloses accumulate to 20-35% of wood cell material (Kontturi, 2005).

Hemicellulose differs from cellulose in three aspects. Firstly, they contain several different sugar units whereas cellulose contains only 1, 4- $\beta$ -D-glucopyranose units. Secondly, they exhibit a considerable degree of chain branching containing pendant side groups giving rise to its non-crystalline nature, whereas cellulose is a linear polymer. Thirdly, DP of hemicellulose is around 50–300, whereas that of native cellulose is 10–100 times higher than that of hemicellulose. Hemicellulose forms the supportive matrix for cellulose microfibrils. Hemicellulose is very hydrophilic, soluble in alkali, and easily hydrolyzed in acids (John and Thomas, 2008). Figure 2.9 shows the chemical structure of hemicellulose.

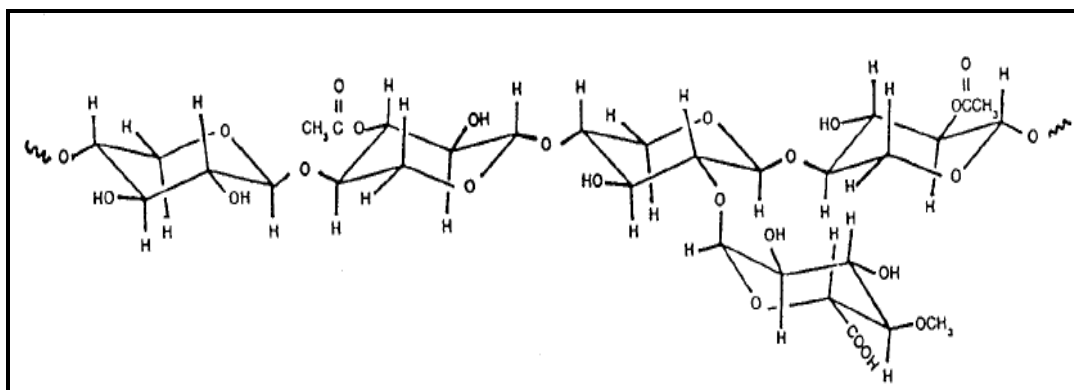


Figure 2.9: Chemical structure of hemicellulose (Pandey, 1999).



### **2.3.2.3 Lignin**

The term “holocellulose” is used to describe the total carbohydrate content of fibres. In addition to holocellulose, plants materials contain an amorphous, highly-polymerized substance called lignin (Figure 2.10). Its principal role is to form the middle lamella, the intercellular material which cements the fibres together. Additional lignin is also contained within the remaining cross-section of the fibre (Smook, 1992).

Lignin is the glue which binds the fibres together and together with hemicelluloses, controls the water content within the cell wall. Lignin is also chiefly responsible for the color in fibres (Kontturi, 2005). 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 in lignin. 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 (John and Thomas, 2008).