THE EFFECTS OF CHEMICAL MODIFICATION AND LAYERING ON PROPERTIES OF WOVEN AND NONWOVEN KENAF FIBER REINFORCED EPOXY COMPOSITES

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UNIVERSITI SAINS MALAYSIA

2014

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By

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Thesis submitted in fulfillment of the requirements

for the degree of

Master of Science

August 2014

ACKNOWLEDGEMENTS

Firstly, I would like to express my sincere gratitude and deliver millions of appreciation to my great supervisor, Prof. Datuk Dr. Abdul Khalil bin Shawkataly for his patience guidance, enthusiastic encouragement and constructive comments and suggestions which lead me to learn many valuable information during the planning and development of this research work. Without his supervision and constant help, this dissertation would not have been possible.

I would like to extend my sincere thanks to Universiti Sains Malaysia for giving me Graduate Assistant scheme for two years and other meaningful experiences as the lab assistant. Moreover, my incredible thanks to Ministry of Higher Education Malaysia for providing MyBrain15 funding for the fees.

In particular, my deepest appreciation also goes to all my fellow research colleagues, Nadirah, Ireana, Siti Alwani, Linda, Fizree, Yalda, Rudi, Sri, Dr. Jawaid and others who have directly or indirectly contributed their valuable help, support and comments towards the completion in this venture. Additionally, I am very grateful for the assistance and guidance given by Mr. Azhar, Mr. Shamsul, Mr. Abu, Mrs. Aida, Mrs. Hasni and others technicians of the laboratories.

I would also like to express my sense of gratitude to all my friends Edzuwyn, Iqmal, Hafizah, Darrel, Faadila, Rosnani and others who I have not mentioned, that have made my study enjoyable and meaningful. I am very grateful for everyone’s kindness and our valuable friendship. Last but not least and the most important, I wish special thanks to my father, Mohd Saad Din, my mother, Nurhana Shafii, my sisters, Izzati, Lina, Syafiah, `Amirah and my brother, Afiq for their love, moral support and unceasing encouragement that inspired me to complete this research. May Allah bless everyone.

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
DGEBA	Diglycidyl ether of bisphenol-A
EDX	Energy Dispersion of X-Ray
EFB	Empty Fruit Bunches
FT-IR	Fourier Transform Infrared
GPa	Giga Pascal
MPa	Mega Pascal
SEM	Scanning Electron Microscope
TGA	Thermogravimetric Analysis
WPG	Weight Percentage Gain

LIST OF SYMBOLS

%	Percentage
ºC	Degree Celsius
cm	Centimeter
g	Gram
J	Joule
K	Kelvin
kg	Kilogram
M	Mega
m	Mass
mg	Miligram
mm	Milimeter
T_g	Glass transition temperature
v	Volume
W_f	Fiber weight fraction
W_m	Matrix weight fraction
ρ_f	Fiber density
ρ_m	Matrix density

LIST OF PUBLICATIONS

KESAN MODIFIKASI KIMIA DAN LAPISAN TERHADAP SIFAT-SIFAT ANYAMAN DAN BUKAN ANYAMAN GENTIAN KENAF DIPERKUAT KOMPOSIT EPOKSI

ABSTRAK

Potensi tinggi gentian kenaf digabungkan dengan struktur baru tikar gentian anyaman dan bukan anyaman diperkuatkan dengan resin epoksi melalui proses ‘hand lay-up’. Reka bentuk kombinasi susunan dengan corak lapisan yang berbeza daripada anyaman dan bukan anyaman sebagai komposit tiga lapisan telah dikaji. Walau bagaimanapun, gentian kenaf mempunyai sifat hidrofilik yang menghadkan penggunaannya dalam pembuatan komposit berprestasi tinggi. Oleh sebab itu, modifikasi kimia terhadap gentian ini dengan propionik anhidrida tanpa pemangkin dicadangkan. Berdasarkan hasil yang ditemui, sifat-sifat komposit telah banyak dipengaruhi oleh urutan struktur gentian dan propionik anhidrida telah dikekalkan dalam komposit yang dibuktikan dengan analisis WPG dan FT-IR. Tambahan lagi, komposit modifikasi menunjukkan peningkatan yang ketara dalam sifat fizikal, mekanikal, terma dan morfologi berbanding komposit bukan modifikasi. Selain itu, sifat rintangan air yang tinggi dipamerkan oleh komposit modifikasi. Keputusan SEM mengesahkan ikatan antara muka gentian dan matrik meningkat dan gentian tertanam dengan sempurna. Di samping itu, komposit teranyam menunjukkan sifat mekanikal dan terma yang lebih baik tetapi sedikit penurunan nilai WPG berbeza dengan komposit bukan anyaman. Secara keseluruhannya, keputusan menunjukkan komposit modifikasi dan kombinasi semua lapisan anyaman meningkatkan sifat mekanikal, fizikal dan terma komposit.

THE EFFECTS OF CHEMICAL MODIFICATION AND LAYERING ON PROPERTIES OF WOVEN AND NONWOVEN KENAF FIBER REINFORCED EPOXY COMPOSITES

ABSTRACT

The great potential of kenaf fiber combined with the new structure of woven and nonwoven fiber mat were reinforced in the epoxy resin by hand lay-up process. The design of stacking combination with different layering pattern of woven and nonwoven as a tri-layer composites was studied. However, the hydrophilic nature of kenaf fibers limits its use in high performance composites. Thus, a chemical modification of this fiber with propionic anhydride without catalyst was proposed. The result indicated that the properties of the composites were greatly influenced by fiber structure sequence and the propionic anhydride was retained in the composites which were proved by weight percent gain (WPG) and Fourier Transform Infrared (FT-IR) analysis. Furthermore, the modified composites indicated significant improvement in physical, mechanical, thermal and morphological properties when compared to unmodified composites. Besides, excellent water resistance properties was shown by the modified composites. Scanning Electron Microscopy (SEM) results proved that the interfacial bonding between fiber and matrix increased and the fibers embedded well in the matrix. On the other hand, woven composites showed better mechanical and thermal properties but slightly decreased in WPG value in contrast with nonwoven composites. The overall results showed that modified and combination of all woven layer composites enhanced the mechanical, physical and thermal properties.

CHAPTER 1

INTRODUCTION

1.1 Overview/Background of the Study

Nowadays, the scientists, engineers, students and researchers were attracted to the development of high-performance engineering materials and composites made from natural resources which are expanding worldwide, prior to renewable and environmental issues. Based on Taj et al. (2007), natural fibers have been utilized to reinforce materials for more than 3000 years. For better engineering materials, natural fiber reinforced composites are used today as the option to replace the man-made fibers as they are economical, renewable, easy processing, non-toxic, light weight, low density and abundant (Bogoeva-Gaceva et al., 2007, Graupner et al., 2009, Xue et al., 2009). This fiber reinforced composites were originally developed for the aerospace industry and today, the technologist have found their path in a much broader area of applications including transportation, medical science, sports and more recently in the building and construction industries.

Generally, composites are engineered materials that consists of two different phases and has the characteristics that are not depicted by any of the constituents alone (Sheikh-Ahmad, 2009). Usually, the two reinforce phases are the fibers, sheets, or particles that are embedded in the matrix phase such as thermoset or thermoplastic resin. It is an element that part of the environment itself which the combination typically, the reinforcing materials are strong with low densities while the matrix is commonly a ductile, or tough material. When the composite is fabricated and designed nicely and correctly, it combines the strength of the reinforcement with the toughness of the matrix to achieve a combination of desirable properties with the speciality which is not available in any single conventional material. There are many benefits of fiber reinforced composites over conventional materials, that have been cited by Karnani et al. (1997) on thermoplastic and thermoset based matrices.

While natural resources like nonwood fibers such as kenaf, jute, flax, hemp and sisal are the most commonly utilized natural fiber for reinforcement in biocomposites and have attained commercial success in industries. At the present level of technology, many researchers have done a lot of research on this reinforcing fiber as they show a comparable strength and they are 10-30% lighter than glass fibers and would result in more eco-friendly bio-composites (Abilash and Sivapragash, 2013).

Quality of fiber-reinforced composite products are basically depended on the fiber-matrix interactions and its stress transferability between fiber-matrix. The weak interfaces bonding between natural fibers (hydrophilic) and polymer matrix (hydrophobic) giving reduction of great properties and performances of the composites. However, there have been significant achievements in addressing the concerns that are often raised. Many researchers have put a number of treatment, physical and chemical modification studies on a variety of natural fibers for understanding and enhancing the interfacial strength (Van de Weyenberg et al., 2003, Herrera-Franco and Valadez-González, 2005, Aji et al., 2009, Utsel, 2012). The combination of natural fiber and matrix with some modification or treatment increased the compatibility and the interface adhesion property that giving rise to continuous covalent bonds between the cellulose surface and the macromolecular matrix (Belgacem and Gandini, 2005, Alvarez and Vazquez, 2006, Abdul Khalil et al., 2007b).

The mechanical properties of the composite also can be increased by manipulating the woven and nonwoven fiber mat in fabricating the composites. Extensive studies have been done on natural fibers reinforced composites with some improvement with woven fibers and modification such as jute (Ray and Sarkar, 2001, Ahmed and Vijayarangan, 2008, Jawaid and Khalil, 2011), banana (Joseph et al., 2002, Idicula et al., 2005, Jannah et al., 2009, Thiruchitrambalam et al., 2009), kenaf (Ramaswamy et al., 2003, Aziz and Ansell, 2004, Shibata et al., 2006, Lai et al., 2008, Khalil and Suraya, 2011), EFB (Khalil et al., 2007, Khalil et al., 2011), sisal (Jacob et al., 2004), and have shown that natural fibers and pattern of fiber have the potential to act as effective reinforcement in thermoset and thermoplastic matrix.

Alkaline, silane, acetylation, benzoylation, acrylation and acrylonitrile grafting, maleated coupling agents, permanganate, peroxide, isocyanate and other chemicals (stearic acid, sodium chlorite, triazine) have been used to improve adhesion between polymer matrix and the fiber surface in which they modify the fiber surface and increases its strength. This treatment could also result in decrease of composite's water absorbability and improves their mechanical properties. Different methods and chemicals used in treating natural fibers have different efficiency in causing the fiber-matrix adhesion (Li et al., 2007).

1.2 Problem Statement

Basically, natural fibers are hydrophilic in nature as they are created from lignocellulose, which contain strongly polarized hydroxyl groups. Therefore, these fibers are inherently incompatible with hydrophobic matrices such as epoxy. One of the serious problems of plant fibers is their strong polar character, which creates many problems of incompatibility with most thermosetting and thermoplastic matrices. The major limitations of using fibers as reinforcements in such matrices include poor interfacial adhesion between polar-hydrophilic fiber and nonpolar-hydrophobic matrix, and the inherent high moisture absorption, which could result in dimensional changes of the fibers. This may seriously lead to microcracking and weak interfaces of the composite and degradation of mechanical, physical and thermal properties.

Along with this occurrence, many researchers have been focused on the optimization of interfacial adhesion between natural fibers and polymer matrices (thermoset and thermoplastic) throughout the past two decades. In order to improve high performance of composites, the tremendous improvement in strength and stiffness imparted to the matrix material by the reinforcement fibers, along their fiber direction and transverse the fiber direction is apparent. Furthermore, fabrication of bi-layered and tri-layer hybrid composites indicated high performance and great mechanical properties. In this study, tri-layer of kenaf woven and nonwoven fiber mat with respect to different patterns of layering with propionic anhydride modification were compared and analyzed.

1.3 Objectives of the Study

The objectives of this present research are:

a) To study the effects of chemical modification on the characteristics of woven and nonwoven kenaf fibers.

b) To study the effects of layering between woven and nonwoven kenaf fiber on reinforced epoxy composites.

c) To analyze the physical, mechanical, thermal and morphological properties of modified woven and nonwoven kenaf fiber reinforced epoxy composites.

1.4 Outline of Thesis Structure

This thesis has been organized in five chapters which are:

Chapter 1 - Introduction, which focused on introducing the materials and background, challenges and gaps, scope of study and also the objectives of the research.

Chapter 2 - Focused on literature review of various aspects includes natural fibers, matrix, kenaf fibers and its composites. It also covered detail scientific information about hybrid composites.

Chapter 3 - Described about materials and methodology of the composites making and the characterization of the hybrid composites.

Chapter 4 - Proceeds with the results and discussion of mechanical, physical, thermal and morphological properties and the related output from previously published works of modified woven and nonwoven kenaf fiber reinforced epoxy composites.

Chapter 5 - Summarizes the overall conclusions and recommendation for future work proposals of the study.

CHAPTER 2

LITERATURE REVIEW

2.1 Composites

Composite is a substances made up of two or more components with chemically and physically different phases of different substances (matrix phase and dispersed phase) separated by a distinct interface and the combination results in a material that maximizes specific performance properties. The different materials with special properties usually are mixed justly to achieve a better performance with more functional properties and useful structural unachievable by any of the element alone. This wonder composites are becoming an important part in nowadays materials because of many benefits and improvement such as strong in mechanical and physical strength, light weight, corrosion resistance, and faster assembly (Jose et al., 2012).

2.1.1 Introduction

The technology of composite materials is the ability to set strong stiff fibers that usually derived from plants or cellulose in the right place such as matrix, in the right orientation with the right volume fraction (Hull and Clyne, 1996). Every year, society appetite for composites and materials are increasing as growing industrialization and ascending incomes, lead to an increasingly unsustainable rate of raw material extraction.

Furthermore, composites can also be a hard or soft construction in which the fibers consolidated to form a structure instead of form a yarns. This construction's rigidity was contributed by the density, the load-bearing fibers modulus and the fusible fiber’s fraction. The composites strength was depended on the adhesion and shear-yield strength of the matrix.

Besides that, composites were also meant materials that be made up of reinforcement which the strong load carrying materials embedded in weaker material (matrix). Natural fibers which play as the reinforcement helps to bear structural load and also contributes strength and rigidity. While the matrix such as thermoset or thermoplastic, or binder (organic or inorganic) holds the reinforcement in orientation and right position. Significantly, the composites maintain their individual constituents with different physical and chemical properties and the combination of qualities produced together still remain separately and cannot be afford by the individual elements. They are many application of composites that are widely used as materials in making medical equipment to electronic packaging, aircraft structures, space vehicle, home building and much more. The basic difference between blends and composites is that the two main constituents in the composites remain recognizable while these may not be recognizable in blends (Jose et al., 2012).

Some composites also offer the benefit and advantages of being tailorable so that properties, such as strength and stiffness, can easily be changed by changing amount or orientation of the reinforcement material. The mechanical properties and composition of reinforced composites can be tailored for their intended use. In addition, the type and quantity of materials selected to the manufacturing process when fabricating the product, will affect the mechanical properties and performance.

Additionally, composites may also be a structure made by nonwoven fabric lamination with another nonwoven, or woven fabric lamination. It can also be fabricated with other materials, or the woven and nonwoven fabric impregnation with resins such as epoxy.

2.1.2 Types of Composites

The composite is a combination of matrix and reinforcement materials that are mixed in certain proportions. The matrix material may be made from metals, ceramics or polymers. It may be pure, or sometimes mixed with other materials such as additives to enhance it's properties. Besides, the reinforcement may also be treated to enhance the bonding of the matrix.

The most common man-made composites can be classified into three main groups. Firstly, the Polymer Matrix Composites (PMC) which is the main area of discussion for the research. It is also known as Fibre Reinforced Polymers (FRP). These composites use a polymer-based resin as the matrix from thermoset such as epoxy, unsaturated polyester, urea formaldehyde, polyimides or thermoplastic like acrylic, polyvinyl chloride, nylon, polystyrene, polypropylene and a variety of fibers such as natural fibers, glass, steel, carbon, boron and aramid as the reinforcement. These material can be fashioned into many types of shapes and sizes. They provide greater strength and stiffness with simple manufacturing principles, low cost and resistance to corrosion. Secondly, the Metal Matrix Composites (MMC) which are increasingly found in the automotive industry. These materials composed of a metallic matrix (aluminum, magnesium, iron, cobalt, copper) and reinforced it with ceramic (oxides, carbides) or metallic (lead, tungsten, molybdenum) phase. The third group is Ceramic Matrix Composites (CMC) which usually used in very high temperature environments. These materials use the ceramic as the matrix such as alumina, calcium, aluminosilicate and embedded it with short fibres, or whiskers such as those are made from silicon carbide and boron nitride. These composites are naturally resistant to high temperature, hence, it has the tendency to become brittle and fracture resulting the difficulties in composite fabrication.

Besides, there are four types of reinforcing material structure in composites. It is classified as continuous fibers, discontinuous fibers or whiskers, particles and lastly, fabric, braid and others. Figure 2.1 illustrates the types of reinforcement in composites.

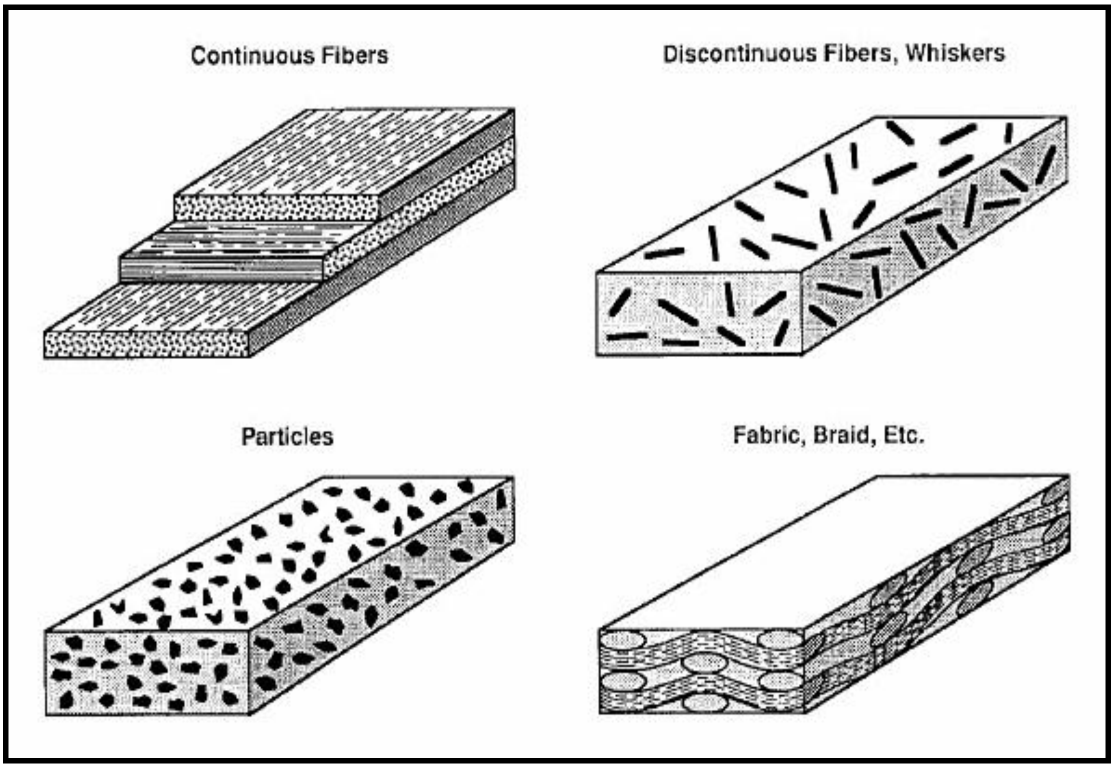


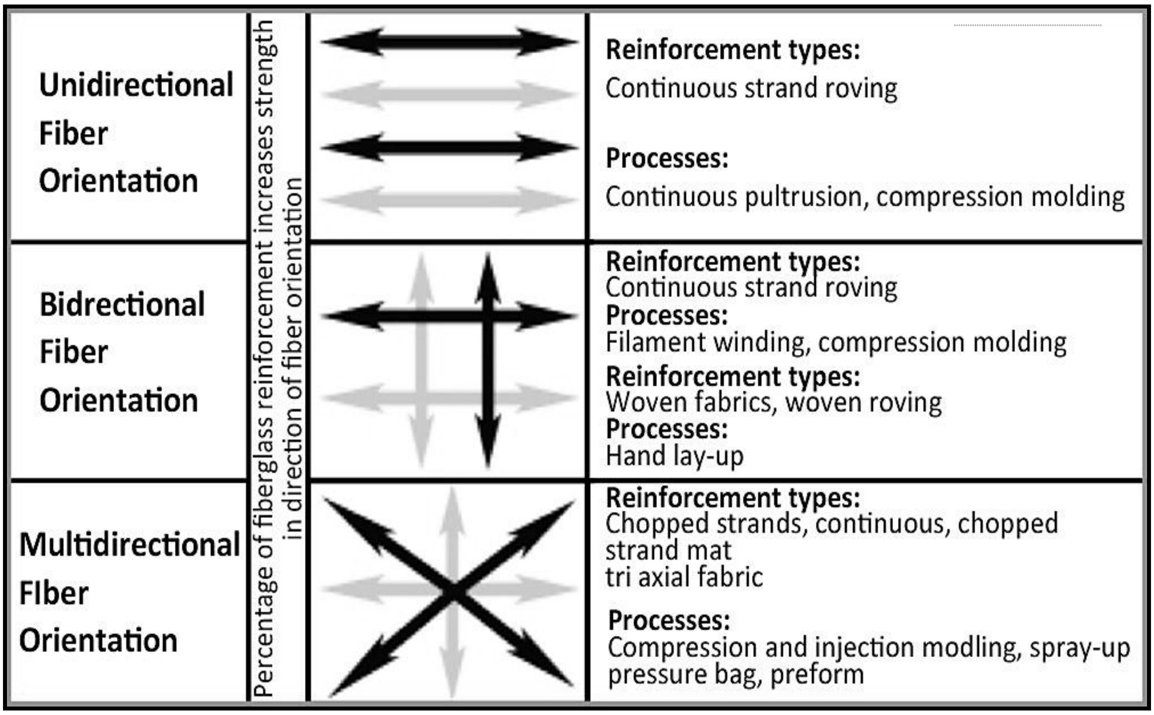
Figure 2.1 Types of reinforcement in composites.

Since Polymer Matrix Composites combine a resin system and reinforcing fibers, the combination properties of the resulting composite material depends on the properties of the resin and the fiber on its own. Fibrous composites reinforcement consist of two types which are categorized based on the fiber length. There are two types of reinforcement for this type of composites which in the form of continuous fibers (long fibers) or discontinuous fibers (chopped fibers, short fibers, etc.). Continuous fibers composites can be in a form of either single layer or multilayered. The single layer continuous fiber composites can be either unidirectional, woven or nonwoven, and multilayered composites that generally called as laminates. While composites in which the reinforcements are discontinuous fibers or whiskers, it can be produced to have either random or biased orientation. The random reinforcements usually produce nearly isotropic composites while the discontinuous one produces as anisotropic composites (Staab, 1999).

A lamina is generally assumed to be orthotropic and the laminar composites are classified as laminates, clad metals or sandwich structure. Laminar composites is a composite consists of several layers with different fiber orientations which is called multilayer or angle-ply composite. The composite consists of at least two different materials that are bonded together with or without resin or adhesive. 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).

Overall, the properties of a composite are determined by four properties. Firstly, it depends on the properties of the fibers used to make the composites. Secondly, the resin's properties which also play an important role. The third one is the ratio of fiber to resin in the composite (fiber volume fraction) and finally, the geometry and the orientation of the fibers in the composites. There are big influenced by the type of resin matrix used in fabricating composites, and the form in which the fibers are incorporated. Generally, the mechanical properties of fibers are much higher than those of resins, thus, the higher the fiber volume fraction of fiber to resin, the higher would be the mechanical properties of the resultant composites. As the good mechanical properties of fibers, the geometry of the fibers give impacts to the properties of the composites along their lengths, rather than across their widths. It is very important and advantageous when considering the application of composites to understand at the design stage, both the magnitude and the direction of the applied loads for high end composites.

Furthermore, unidirectional laminates are extremely strong and stiff in the 0^o direction of fiber but very weak in the 90^o direction because the load must be carried out by the much weaker polymeric matrix. The arrangement of fibers is the position and the way of the individual strands orientation determines both direction and level of achievable strength. The three basic arrangements of fiber orientation are unidirectional, bidirectional and multidirectional which are shown in Figure 2.2.



Unidirectional Fiber Orientation	Percentage of fiberglass reinforcement increases strength in direction of fiber orientation		**Reinforcement types:** Continuous strand roving **Processes:** Continuous pultrusion, compression molding
Bidrectional Fiber Orientation			**Reinforcement types:** Continuous strand roving **Processes:** Filament winding, compression molding **Reinforcement types:** Woven fabrics, woven roving **Processes:** Hand lay-up
Multidirectional FIber Orientation			**Reinforcement types:** Chopped strands, continuous, chopped strand mat tri axial fabric **Processes:** Compression and injection modling, spray-up pressure bag, preform

Figure 2.2 The basic arrangements of fiber orientation

2.2 Matrix

Matrix plays as cementing materials which are used as binder and are maintained the position and orientation of reinforcing materials in its place. It is more ductile and easily phase that holds the dispersed phase and shares load. When composites is carrying load, the matrix deforms and the external load is transferred uniformly to the fibers. Matrix are generally classified into two categories which are thermosets and thermoplastics. The criteria of the matrices for selection are depended on the composite end product requirements. These thermoset and thermoplastic composite products develop new applications, and thus, boosting its market everyday.

2.2.1 Thermoset

Thermoset materials are generally stronger than thermoplastic materials. It is due to the molecules which are chemically joined together by cross-linking bonds and having the property of becoming permanently hard and rigid when heated or cured. Once these crosslinks are formed during polymerization or curing reaction, the thermoset polymer cannot be remelted and reshaped to its original structure (Schwartz, 1992). Thermoset polymers are the most frequently used matrix materials in polymer-based composites production. This is mainly because of the ease of their processing (Akovali, 2001).

Moreover, the thermoset composite is better suited to high-temperature applications and are more brittle. According to Schwartz (1992), it is possible to achieve a good wet-out between the fibers and matrices in thermosets, since the starting materials for the polymerization are low molecular-weight liquid chemicals with very low viscosities and they usually require much longer processing times. The most common thermoset resins used for composite matrices are polyesters, vinyl esters, epoxies, bismaleimides, polyimides and phenolics which are shown in Table 2.1.

Table 2.1 Relative characteristics of composite resin matrices (Campbell Jr, 2003).

Polyesters	Used extensively in commercial applications. Relatively inexpensive with processing flexibility. Used for continuous and discontinuous composites.
Vinyl esters	Similar to polyesters but are tougher and have better moisture resistance.
Epoxies	High performance matrix systems for primarily continuous fiber composites. Can be used at temperature up to 250-275 ºF. Better high temperature performance than polyesters and vinyl esters.
Bismaleimides	High temperature resin matrices for use in the temperature range of 275-350 ºF with epoxy like processing. Requires elevated temperature post cure.
Polyimides	Very high temperature resin systems for use at 550-600 ºF. Very difficult to process.
Phenolics	High temperature resin systems with good smoke and fire resistance. Used extensively for aircraft interiors. Can be difficult to process.

2.2.1 (a) Epoxy Resin

Epoxy resins are a large family of resins that represent some of the high performance resins available in the market. The important class of polymeric materials, epoxy resins are characterized by the presence of more than one three-membered ring known as the epoxy, epoxide, oxirane, or ethoxyline group (Figure 2.3).

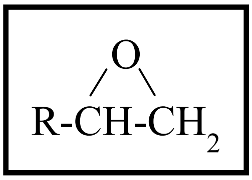


Figure 2.3 Epoxide groups

These thermosetting polymers resins are used in many applications such as adhesives, encapsulating materials and high performance coatings. The most cured epoxy resins provide amorphous thermosets with excellent electrical insulating properties, high mechanical strength and toughness, dimensional stability, good adhesion to many metals, no volatiles emission and low shrinkage upon cure; resistance to moisture, chemical, thermal and mechanical shock. These are the unique combination of properties which are not found in any other plastic material. These superior performance characteristics, mixed with outstanding formulating versatility and reasonable costs, have gained epoxy resins as the choice for a multitude of bonding, structural, and protective coatings applications (Pham and Marks, 2002).

The functional group in epoxy resins (Figure 2.3) is called as the oxirane which is a three-membered strained ring containing oxygen. For the preparation of epoxy resins, a broad range of starting materials can be used thereby providing a variety of resins with controllable high performance characteristics. Generally these resins are prepared by reacting to a poly-functional amine or phenol with epichlorohydrin in the presence of a strong base. Diglycidyl ether of bisphenol-A (DGEBA) is a typical commercial epoxy resin and it is synthesized by reacting bisphenol-A with epichlorohydrin in presence of a basic catalyst as presented in Figure 2.4.

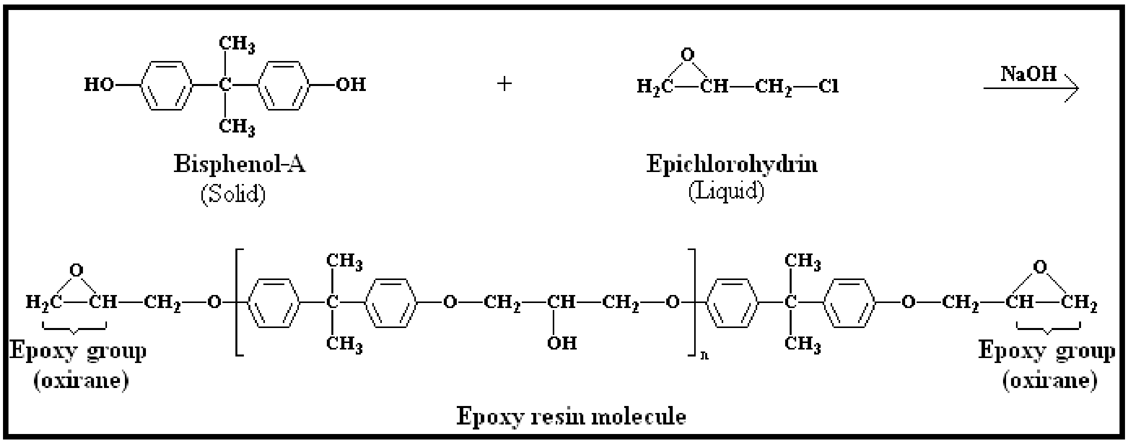


Figure 2.4 Reaction between bisphenol-A and epichlorohydrin to form epoxy resin (Pham and Marks, 2002)

While Figure 2.5 shows the chemical structure of diglycidyl ether of Bisphenol-A (DGEBA). The colour of DGEBA resins are transparent colourless-to-pale-yellow liquids at room temperature. The presence of glycidyl units in these resins improves the processability but reduces thermal resistance.

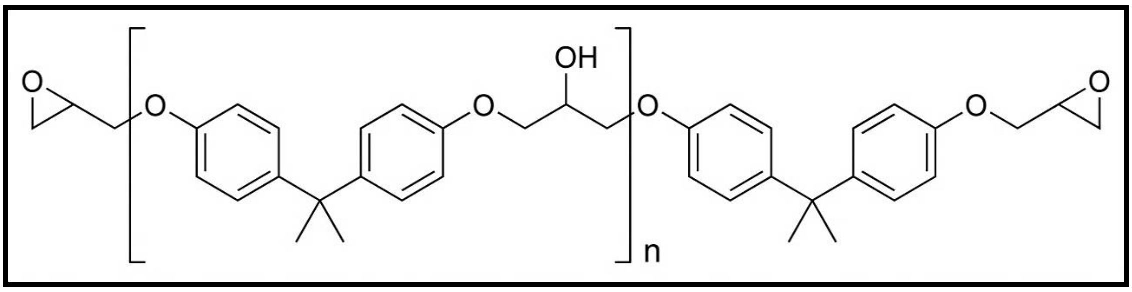


Figure 2.5 Diglycidyl ether of bisphenol-A (Pham and Marks, 2002)

Epoxy resins are converted into solid, rigid, infusible, and insoluble three-dimensional thermoset networks by curing with cross-linkers for their high performance applications. Their optimum performance properties are obtained by cross-linking the right epoxy resins with hardeners or curing agents which are the cross-linkers. To select the proper curing agent, it depends on the application process, pot life, curing conditions, and ultimate physical properties. The viscosity and reactivity of the formulation affects by the curing agents used as it determines both the types of chemical bonds formed and the degree of crosslinking that will occur. After all, the cured thermosets affect the chemical resistance, electrical properties, mechanical properties, and heat resistance (Pham and Marks, 2002).

There are various curing agents used for epoxy resins such as primary and secondary amines, anhydride, dicyandiamide, polysulfide, and polyamide. While curing, three basic reactions are happened in epoxy resin. Firstly, epoxy groups are rearranged and form direct linkages between themselves. Secondly, the aromatic and aliphatic hydroxyl groups link up to the epoxy groups. Then, the cross-linking takes place with the curing agent through various radical groups.

Epoxies generally outperform the most than other resin types in terms of mechanical properties and resistance to water and environmental degradation. Their properties lead to exclusive used in the aircraft industry, boat building and other high performance applications. Table 2.2 describes the advantages and disadvantages of different types of curing agents for epoxy resin.

Table 2.2 The comparison of the properties of different types of curing agents for epoxy (Ratna, 2009)

Types	**Advantages**	**Disadvantages**
Aliphatic amine	Low cost, low viscosity, easy to mix, room temperature curing, fast reacting	High volatility, toxicity, short pot life, cured network can work up to 80 ^oC but not above
Cycloaliphatic amine	Room temperature curing, convenient handling, long pot life, better toughness, and thermal properties of the resulting network compared with aliphatic amine-cured network	High cost, can work at a service temperature < 100 ^oC, poor chemical and solvent resistance
Aromatic amine	High T_g, better chemical resistance and thermal properties of the resulting network compared with aliphatic- and cycloaliphatic amine-cured network	Mostly solid, difficult to mix, curing requires elevated temperature
Anhydride	High network T_g compared with amine curing agent, very good chemical and heat resistance of the resulting network	High temperature curing, long post-curing, necessity of accelerator, sensitive to moisture
Dicyandiamide	Low volatility, improved adhesion, good flexibility and toughness	Difficult to mix, high temperature curing and long post-curing
Polysulfide	Flexibility of the resulting network, fast curing	Poor aging and thermal properties, odour
Polyamides	Low volatility, low toxicity, room temperature-curing, good adhesion, long pot life, better flexibility and toughness of the resulting network compared with aliphatic amine-cured networks	Low T_g of the resulting network, high cost and high viscosity

2.2.2 Thermoplastic

Thermoplastic is a polymer material that becomes pliable or moldable when heated above specific temperature and returns to a solid state when cooled. Thermoplastics may be characterized as linear polymers which do not normally need curing during consolidation into a composite and no chemical bond between long chain molecules. They are held by weak intermolecular bonds such as van der Waals or hydrogen bonds (Muccio, 1994). The consolidated thermoplastic composites are reversible, reformable and reprocessable. The most important advantages of thermoplastics are their high impact strength and fracture resistance which give excellent damage tolerance characteristics to the composite material (Schwartz, 1992). They are often supplied as granules and heated by some methods such as molding or extrusion to permit fabrication. The most common type of thermoplastic used for manufacturing composite materials include polyethylene, polypropylene, polyvinylchloride and polystyrene.

As a consequence, many researchers have done studies using various kinds of lignocellulosic materials to produce thermoplastic-lignocellulosic composites (Rozman et al., 1999, Ishak et al., 2001, Stark and Rowlands, 2003).

2.3 Fiber Reinforcements

2.3.1 Natural Fiber

In recent years, natural fibers, as reinforcement, are giving major attention to the scientist, engineers and technologist as substitute candidate for synthetic fibers in biocomposites making. The advantages of natural fibers are cheap, low weight, less damage to processing equipment, environmental friendly, good relative mechanical properties, abundantly available, high specific properties, biodegradable, nonabrasive and renewable resource, and can replace the man-made fiber in fiber reinforced composites as reported by many researchers (Li et al., 2007, Satyanarayana et al., 2009, Ismail et al., 2010, Jawaid and Abdul Khalil, 2011, Jose et al., 2012). Presently, people are aware of the need to utilize resources on a sustainable manner for better productions than wasted through combustion and should contribute to a healthy ecosystem. Fibers can be classified into two main groups which are man-made and natural fibers. The classification of natural fibers and synthetic fibers is summarized in Figure 2.6.

Natural fibers may be classified in two other different categories which are wood fibers and nonwood fibers. In the other word, it is the principal source of cellulosic materials in natural fiber based industries and can get from plants, animals and minerals. This element which part of the environment itself and have the capability to be recycled back to its chemical content, components and properties. There are many types of different fibers which can be applied as reinforcement of fillers. While synthetic fibers are divided to organic and inorganic fiber and usually used in aircraft industries.

The fiber reinforcement can also be done in many forms including woven roving and chopped strand mat. Nowadays, manufacturer and technologies have applied the natural fibers and synthetic materials in a wide range of textile and structural applications. However, it is now preferred to use natural resources for composite materials with increasing awareness of sustainability.

The cell wall polymers of natural fibers contain major lignocellulosic materials which are cellulose, hemicellulose, lignin and extractives. This component will be affected if it has been modified and has been experimented. Usually, the performance of wood (natural fibers) will be changed once the properties of the components are modified.

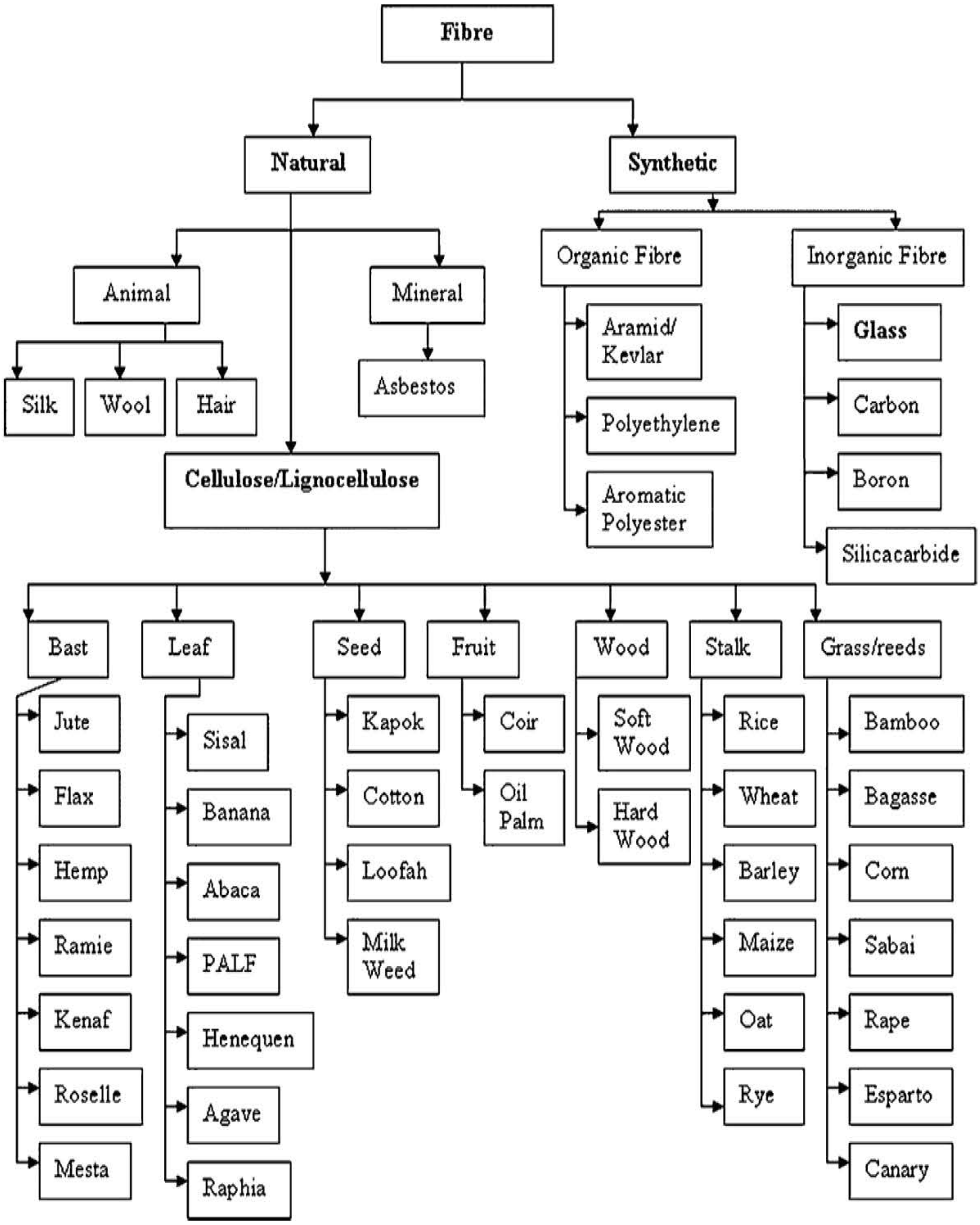


Figure 2.6 Classification of natural and synthetic fibers (Rowell, 2008, Jawaid and Abdul Khalil, 2011)

The use of natural fibers such as jute, kenaf, sisal, banana, hemp, ramie, coir etc. as reinforcements in composites and other application is increasing tremendously. Fine and delicate fibers and other wood flour are primarily used as fillers in thermoplastic and thermoset decking, building materials, furniture, automotive components and much more applications. Long agricultural fibers such as kenaf, jute, flax, hemp and bast are used as structural reinforcements in fabricating thermoset or thermoplastic composites as a replacement of synthetic and man-made fiber. Natural fiber composites can easily be recycled compared to glass composites and it is environmental friendly as well as abundant in nature. World production levels of commercially important types of fiber are presented in Table 2.3.

Table 2.3 Commercially important natural fibers (Suddell, 2008).

Fiber	Main Countries	Origin	World Production 2004 (tonnes)
Wood	Various (>10,000 species)	Stem	1,750,000,000
Bamboo	China (>1250 species)	Stem	10,000,000
Jute	India, Bangladesh	Stem	2,861,000
Kenaf	India, China	Stem	970,000
Coir	India, Vietnam, Sri Lanka	Fruit	931,000
Flax	China, Europe	Stem	830,000
Sisal	Brazil, Tanzania, Kenya	Leaf	378,000
Ramie	China	Stem	249,000
Hemp	China, Europe	Stem	214,000
Abaca	Philippines, Ecuador	Leaf	98,000
Agave	Columbia, Cuba, Mexico	Leaf	56,000

The variety of chemical composition of natural fibers depending on the type of fiber in which primarily, fibers contain cellulose, hemicelluloses, pectin, lignin and extractives. Each constituent of the properties contribute to the overall properties of the fiber. Hemicelluloses are responsible for the moisture absorption, biodegradation, and thermal degradation of the fiber as it shows the least resistance while lignin is thermally stable but is responsible for the UV degradation. The percentage composition of each one component varies for different fibers. Commonly, the fibers contain 60–80% cellulose, 5–20% lignin, and up to 20% moisture (Saheb and Jog, 1999).

Since natural fibers are light in weight, abundant, strong, non-abrasive, inexpensive and non-hazardous to nature, they can act to be an excellent reinforcing agent for polymeric materials. As natural fibers posses moderately high specific strength and stiffness, it can be used to substitute synthetic fiber in reinforcing composites material. More about the advantages and disadvantages of natural fibers is displayed in Table 2.4.

Table 2.4 Advantages and disadvantages of natural fibers (Pickering, 2008).

Advantages	**Disadvantages**
Low specific weight results in a higher specific strength and stiffness than glass	Lower strength especially impact strength
Renewable resources, production require little energy and low carbon dioxide emission	Poor moisture resistance which causes swelling of the fibers
Production with low investment at low cost	Variable quality, influence by weather
Friendly processing, no wear of tools and no skin irritation	Restricted maximum processing temperature
High electrical resistance	Lower durability
Good thermal and acoustic insulating properties	Price fluctuation by harvest results or agricultural politics
Biodegradable	Poor fiber/matrix adhesion
Thermal recycling is possible	Poor fire resistance

The reinforcement phase in the most cases made of a stronger, harder and stiffer material than the matrix. It is the primary load bearing constituent and its shape, volume and arrangement of the materials adversely affect the properties of the composites. Reinforcements can be in many types such as in the form of long fibers, short fibers, particles or whiskers. This fibers reinforcement can also be arranged into continuous, discontinuous, aligned or random. Commonly, the composite materials show remarkable anisotropy which are the properties of the composite materials depend on direction because of the distinctive properties of the constituents and the inhomogeneous or textured distribution of the reinforcement. While the composite materials approach isotropic state as the reinforcement phase becomes smaller in size and randomly oriented as reported by Sheikh-Ahmad (2009).

2.3.1 (a) Kenaf

Natural fiber like kenaf, a bast fiber, used in this research is a strong fiber, owned desirably properties for instance, high toughness, acceptable specific strength properties, recyclable and enhanced energy recovery. As they are suitable for reinforcement or fillers in polymer composite, kenaf attracts the attention of scientists and researchers in the composites industry.

Kenaf or scientifically named *Hibiscus cannabinus L.* is a type of fiber crop normally grown during the warm season annually and it looks similar to bamboo and is known to be closely associated with cotton and jute. Some of kenaf varieties could be found in Malaysia and their varieties are differentiates based on its stem color, leaf shape, flower and seeds color and also its adaptability in different environmental conditions. Kenaf sp. V36 is one of kenaf variety that is normally planted in Malaysia as it is suitable to grow in the country's climate (Khalil and Suraya, 2011). Kenaf stalk consists of inner woody core and an outer fibrous bark that surrounds the core. The outer fibrous bark can be used to produce bast fiber, which have a superior flexural strength and tensile strength. These properties have made bast fiber as the perfect choices to build wide range of extruded, molded, woven and non-woven products.

Nowadays, there are many new applications for kenaf including paper products, building materials, absorbents, animal feeds and automotive parts. Many applications has been successfully incorporated with kenaf fiber as the growing rate is faster and have good mechanical properties in composite reinforcement. Within 4-5 month growing season, it can rise to a height of 5-6 m with the diameter of stalk is 25-35 mm. In the other word, it takes about 150 days to harvest and thus, reduce the demand of timber. In year 1995, kenaf was priced at $400 per tonne while in year 2000, the price decreased between $278 to $302 per tonne. From the viewpoint of energy consumption, it takes 15 MJ of energy to produce 1 kg of kenaf; while it takes 54 MJ to produce 1 kg of glass fibre (Akil et al., 2011).

Performing the high possibilities of commercially exploitable derived products from kenaf, the National Kenaf Research and Development Program in Malaysia has been formed in an effort to develop kenaf as a possible new industrial crop. The government has allocated RM12 million under the 9th Malaysia Plan (2006-2010) for research and further development of the kenaf-based industry as a commercially viable crop (Edeerozey et al., 2007). The chemical composition of kenaf fiber are illustrated in Table 2.5.

Table 2.5 Chemical composition of kenaf core and bast fibers (Tsoumis, 1991)

Chemical composition	Kenaf Core (%)	Kenaf Bast (%)
Holocellulose	87.2	86.8
α-Cellulose	49.0	55.0
Lignin	19.2	14.7

2.4 Chemical Modification of Fibers

2.4.1 Introduction

Chemical modification of lignocellulosic materials can be defined as chemical reaction between some reactive part in a cell wall structure of natural fibers and a chemical reagent resulting in the formation of covalent bond between the two components, with or without the presence of catalyst (Rowell, 2004). Modification of fibers usually enhance and improve the wood performance and abilities, hence suitable for high performance end-products (Abdul Khalil and Ismail, 2000, Mohanty et al., 2001, Edeerozey et al., 2007). Based on previous studies, the effectiveness of chemical modification with various anhydrides show improvement in surface bonding, the mechanical properties and water absorption.

Modification can be classified in two types which are active modifications or passive modifications. Active modifications give alteration to the chemical nature of the material while passive modification give a change in properties without affecting the chemistry of the material. Most of the chemical modification methods investigated that the chemical reaction resulting in the formation of a single chemical bond or cross linking between the cell wall polymer hydroxyl groups and the reagent. The chemical modification has been reported that it has improved mechanical properties, hardness, strength, chemical resistant and improved fiber/matrix adhesion (Trejo-O'reilly et al., 1997, Rowell, 2006b). Furthermore, to improve the properties, layering pattern is experimented with woven and nonwoven kenaf fiber mat. The different fiber alignment give strength in various direction to the composites.

Many advantages associated with the renewable material have gained the interest in using cellulose fibers as reinforcing elements in composite materials based on polymeric matrices. However, the major drawbacks of natural fibers with the