BONDING
with Natural Fibres

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with **Natural**
Fibres

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Contents

ABSTRACT

The earliest evidence of humans using fibres is the discovery of wool and dyed flax fibres found in a cave in the Republic of Georgia more than 30,000 years ago. It all started with the use of natural fibres in composite materials. Clay was reinforced by straw to build walls in ancient Egypt about 3,000 years ago. The famous Great Wall of China was made using a combination of clay and rice flour reinforced with straw. Now composites dominate our lives in many ways – automotives, buildings, sports, defence, aerospace, and the list continues. With its apparent endless uses, natural fibres are indeed phenomenal and eternal.

Natural fibres are bio-based fibres, *i.e.,* fibres of vegetable or animal origin. Between the two, the former which is the focus of this book, has received tremendous attention for decades and the interest are still growing strongly. Natural fibres are sometimes referred to as plant fibres. These field crops are grown for their fibres, which are traditionally used to make paper, cloth, or rope, products that are responsible for its continued existence. While wood comes from forest trees that requires many years (>15 years) to mature, the non-woods mature between 3-10 years, and fibre crops are generally harvestable after a single growing season (5-6 months). In specific circumstances, fibre crops can be superior to single wood fibre in terms of technical performance, environmental impact and cost. Biomass is another source of fibres that can be derived from plants, either from forest trees or field crops, normally in the form of residues. It is usually associated with energy production and bio-refinery. In this book, the term "natural fibres" is used to describe fibres that are obtained from wood, non-wood, plant fibres and biomass.

All natural fibres are chemically made up of cellulose, hemicellulose and lignin which are aligned in crystalline and

amorphous regions in the form of microfibrils. Aggregates of microfibrils make up a fibre. These fibres are arranged in different manner depending on the type of plant. Some examples of wood are pines, spruce, oak, beech, hemlock (temperate woods), meranti, keruing, chengal, rubberwood, (tropical woods). Examples of non-woods are bamboo, rattan and all types of palms. Plant fibres are represented by many types depending on where the fibres are taken, *e.g.,* bast fibres - the fibres that come from the phloem tissue of the plant, as exemplified by jute, kenaf, ramie, flax, and hemp. Other fibre crop fibres are from seed padding, such as coir, leaf fibre, such as those of pineapple, abaca, sisal, henequen, or from other parts of the plant.   All plant fibre residues from the forests, plantations/estates and processing mills are regarded as plant biomass.

In recent years, materials scientists and engineers have begun exploring further uses of natural fibres through composite materials. This book reviews the basic properties of some natural fibres particularly those found in Malaysia, and highlights issues in bonding with polymer, surface wettability, buffering capacity and their influence on composite performance.

INTRODUCTION

Sustainability has become a hot topic in the 21ˢᵗ century, where extensive efforts and programmes have been initiated and inaugurated globally with mix results. In the past few years, various industries have attempted to decrease the dependency on petroleum-based fuels and products due to increased environmental consciousness. Business as usual is no longer an option. To succeed in the long-term, companies must safeguard their reputations, maintain a safe, healthy and productive workforce and ensure that the materials they need have been sustainably sourced. This is leading to the need to investigate environmentally friendly, sustainable materials to replace existing ones. One of the most highlighted initiatives is the use of natural fibres in various sectors in particular, automotive and construction. Global natural fibre composites market reached USD$2.1B in 2010, with a compounded annual growth rate of 15% in last five years (Lucintel, 2011).

In the 1990's, automakers made significant advancements in the development of natural fibre composites. This was mainly due to increasing environmental awareness. These products are used primarily in automotive interiors. A number of vehicle models, first in Europe, then in North America, and now in Malaysia, featured natural fibre-reinforced thermosets and thermoplastics in door panels, package trays, seat backs and trunk liners. Likewise, the application of natural fibre reinforced composites as construction material holds enormous potential and is deemed to contribute to achieving sustainability. Due to their low density and their cellular structure, natural fibres possess very good acoustic and thermal insulation properties and demonstrate many advantageous properties over glass and rockwool fibres specifically during handling and disposal.

Natural Fibre and Sustainability

"Sustainability" means many things to many people, so any document on the subject must first define the operational meaning of the term. One intuitively considers the outputs of a given natural resource under current resource management practices as being "sustainable" if there is a good reason for believing that the rate at which the various outputs are produced can be continued indefinitely. Buried within such a definition are some assumptions that need to be stated explicitly as part of the definition. Among the assumptions that many people used are (Jan van Dam, 2008):

1. Supplies and prices of fossil fuels (needed for chemical feedstock, *etc.*) remain roughly constant indefinitely;

2. Long-term effects of climate change on growing conditions and precipitation are negligible;

3. Human population growth rates slow to zero by around the year 2050;

4. Technological advances do not substantively change the basic physical/ chemical process of photosynthesis, the process at the very bottom of the pyramid.

Among the assumptions, 1 and 4 relate directly to natural fibres which have significant influence on the development of bio-based industries such as biocomposites and biopolymers.

Depleting natural resources, regulations on using synthetic materials, growing environmental awareness, and economic considerations are the major driving forces to utilize annually renewable resources such as biomass for various industrial applications. Natural fibres are produced all over the world. Developed countries have important natural fibre industries, but in these large and diverse economies, the economic contribution

of natural fibres is minor compared to other industries. For some developing countries, however, natural fibres are of major economic importance: some examples are cotton in West African countries, jute in Bangladesh and sisal in Tanzania. In some cases, while fibres may look unimportant at the national level, they are of major local importance at the regional level, as is the case of jute in West Bengal (India) and sisal in North-Eastern Brazil.

There is a wide range of natural fibres, and their applications range from apparel to industrial applications. Consumers use natural fibres in a variety of ways. The biggest outlet is apparel, but other uses such as home furnishings and carpets are also significant. Some fibres have more industrial applications, traditionally in cordage and packaging, but increasingly more in a range of non-traditional uses such as pulp for paper and in composite materials. Aside from being renewable and biodegradable, as an engineering material natural fibre has excellent specific strength and high flexural and tensile modulus (up to five times that of base resin), high notched impact strength (up to two times that of base resin), reduces density of products, lowers cost, reduces tool wear, safe manufacturing processes (*e.g.,* no airborne glass particles, relief from occupational hazards, reduced dermal and respiratory irritation and no emission of toxic fumes when subjected to heat and incineration) (Rowell, 2013; Jan van Dam, 2008). In most of these applications, natural fibres are subject to competition from synthetic substitutes. Hence the only way for this industry to progress is to strengthen the quality of their production systems and to develop new products which will enable them to effectively compete with these synthetic products. Being natural, products from these fibres are more sustainable and healthy thus providing a vital key advantage in competing with the existing synthetic materials. High strength, greater durable and consistent quality are three major advantages of synthetic

materials which only through a systematic planting programme and processing methods could natural fibres compete with.

Plant fibres: Clockwise from top: Sisal, Kekabu tree, Coconut tree, Oil palm stems and Kenaf.

Realising the importance of natural fibres, the General Assembly of the United Nations has declared the year 2009 to be the International Year of Natural Fibres, with the main objective of promoting the use of natural fibres (both plant and animal fibres) in current and novel applications. Such efforts would not only increase the levels of income for fibre producers, processors and traders, but at the same time contribute to the increased use of environment friendly materials in those applications. Proceeds from the sale and export of natural fibres often contribute significantly to the income and food security of poor farmers and processors in the least developed countries. The promotion of the use of natural fibres as CO_2 neutral resource is believed to contribute to a greener planet. The Kyoto protocol on greenhouse gas reduction and CO_2 neutral production offers great prospects for natural fibre markets as the world transforms towards a bio-based economy and sustainable development.

NATURAL FIBRES

The Definition

Natural fibres can be defined as bio-based fibres or fibres of vegetable and animal origin. By definition, it includes all natural cellulosic fibres - wood, bamboo, rattan, palms, fibre biomass, cotton, jute, sisal, coir, flax, hemp, abaca, ramie*, etc.,* and protein-based fibres such as wool and silk. Excluded here are mineral fibres such as asbestos that occur naturally but are not bio-based. Asbestos containing products are not considered sustainable due to their well-known health risk which resulted in the prohibition of their use in many countries. On the other hand, there are manmade cellulose fibres (*e.g.,* viscose-rayon and cellulose acetate) that are produced with chemical procedures from pulped wood or other sources (cotton, bamboo). Similarly, regenerated (soybean) protein, polymer fibre (bio-polyester, PHA, PLA) and chitosan fibre are examples of semi-synthetic products that are based on renewable resources.

Wood has been known as the most abundant source of fibre. In most literature, wood fibres are not usually included in the group of natural fibres. There is no definite reason for this segregation, but in the author's opinion, it may be associated with the origin of the fibre. Wood is a hard, solid material formed from thousands to millions of fibres that have been layered together. Individual wood fibres can be obtained only after being reduced into individual cells *via* mechanical or chemical treatment. The same goes to bamboo and palm fibres but at a much less vigorous process. Fibres from agricultural crops such as kenaf, jute, sisal, coir, pineapple, hemp, and flax can be obtained directly from certain parts of the plant such as the leaf, stem, bast and seeds after retting or decortication. In other words, the latter can be found in the form of strands rather

than a solid, like wood an bamboo. The Oxford Dictionary defined wood fibre as "*fibre obtained from wood and used especially in the manufacture of paper*". The Canadian Terminology and Linguistic data bank (TERMIUM Plus©) defined wood fibre as "*a material in which the wood is reduced to predominantly individual fibres by mechanical or chemical means, or a combination of the two. It also noted that the word "fibre" is used as a general term of convenience for any long, narrow cell of wood or bast fibres (of the phloem), the former including both the tracheids of Gymnospermae (softwood) and libriform wood-fibres and fibre-tracheids of wood from Angiospermae (hardwood)*".

As mentioned earlier, plant fibres such as sisal, ramie, bamboo, kapok, pineapple, coir, hemp, jute, flax, and kenaf are generally classified by the part of the plant from which they are obtained, *i.e.,* leaf, seed, fruit, stem or bast. As its name implied, bast fibres are obtained from the outer layer, *i.e.,* the inner bark or phloem, of bast surrounding the plant stem. The fibres are usually very long (as long as the stem) and are relatively strong. For this reason, bast fibres are the most important fraction of any bast plants.

Plant biomass such as trees, energy crops and agriculture residues, is another source of natural fibres. It is defined as a biological material derived from living, or recently living plants and is usually referred to as lignocellulosic biomass. Biomass is carbon-based and is composed of a mixture of organic molecules containing hydrogen, oxygen, nitrogen and carbon. Because of these characteristics, plant biomass is usually used for energy conversion.

In this book, the term "natural fibres" is used interchangeably with fibres that are obtained from trees (*i.e.,* wood fibre), non-wood (*i.e.,* bamboo), fibre crops (*i.e.,* natural fibres) and plant biomass. In some instances, the terminology "plant fibre" is also used to describe all types of natural fibres originated from plants.

The Significance

While wood has been the most popular and used among plant resources for decades, the interest in natural fibres is relatively new. Natural fibre crops have been in existence for hundreds of years; however their commercial value has not been well developed. Practically everywhere and in almost all countries natural fibres are produced and used to manufacture a wide range of traditional and novel products ranging from textiles, ropes and nets, brushes, carpets and mats, mattresses, to paper and board materials. The long fibres are transformed into threads or yarns that are used to join, connect or attach and to form bonds, networks or weaves. In many instances, bast fibres are produced and used to manufacture a wide range of traditional and novel products from textiles, ropes and nets, brushes, carpets and mats, mattresses to paper and board materials. It can be used in many ways such as in the form of fine powder, short fibres as in random or non-woven mat, or long fibres as in woven mat, and for making biocomposite products. With the increasing consciousness to preserve the environment and the needs to recycle, there are renewed interests in using biocomposites to replace those of traditional composite structures, usually made of carbon, glass or aramid fibres. Composites made from natural fibres have useable structural properties at relatively low cost (Mohanty *et al.,* 2001). Advantages of natural fibres, particularly bast fibres, over the traditional reinforcing fibres such as glass and carbon include low cost, low density, high toughness, acceptable specific strength properties, ease of separation, enhance energy recovery, carbon sequestration and biodegradability. Long fibres offer greater flexibility for enhancement processes, particularly in woven and pultrusion composite industry (Paridah and Khalina, 2009). The long fibres are transformed into threads or yarns that are used to join, connect or attach to each other or hybrid with other synthetic yarns to form bonds, networks or weaved into textile.

The economic value of the fibre crop depends on its end-use market and costs of production. Fine and long fibres that can be spun into high counts of yarns are most appreciated and valued. On the other hand homogeneity is a prerequisite to efficient processing and high quality end-products. Lower quality shorter or coarser fibres are converted into nonwoven products, paper pulp or other materials. The lowest value of fibres is when it is left in the field as mulch to compost. However, the value of the end-product is not always reflected in the benefits for the agricultural production. In the production chain from farm to customer many steps are taken and quality improvement is attained at the cost of substantial losses. By-products, residues and wastes commonly are not contributing to the value addition. On the contrary, these may cause environmental pollution or add to costs for disposal.

The environmental impact of natural fibres accordingly also relies on how by-product management is organized. In principle, renewable resources will be fully bio-convertible and may be re-utilised as a source for carbon in the form of carbohydrates (sugars), lignin or protein (nitrogen) and minerals. For example, only 2-4% of the harvested biomass of sisal is of economic value. The rests are residues that can be utilised far better. Often agricultural production utilises only a small part of the total fixed carbon in the biomass produced or harvested.

Source of Lignocelluloses

All natural fibres are lignocellulosic in nature simply because they contain the three main chemical constituents, *i.e.,* cellulose, hemicellulose and lignin. Thus it is more accurate to call fibres that are obtained from any plants (including forest trees) as lignocelluloses. Forest and fibre crops are the two main producers of lignocelluloses. Both are renewable as they can be replaced by

natural ecological cycles or sound management practices, thus constantly associated with sustainability. Rowell (2006) estimated that about 4 billion metric ton of dry plant biomass is available annually in the world (Table 1). Wood contributes the highest, followed by agricultural residues in the form of straws and stalks. Although relatively much smaller, the amount of bamboo still looks significant when compared to natural fibres (cotton, kenaf, hemp,*etc.*). The following sections compare three classes of plant fibres: wood, bamboo and natural fibres, and highlight some of the results from our studies, in particular those relate to biocomposite research.

Table 1 Annual supply of plant biomass

Fibre Source	World (dry metric tons)
Wood	1,750,000,000
Straws	1,145,000,000
Stalks	970,000,000
Sugar cane bagasse	75,000,000
Reeds	30,000,000
Bamboo	30,000,000
Cotton staple	15,000,000
Core (jute, kenaf, hemp)	8,000,000
Bast (jute, kenaf, hemp)	2,900,000
Papyrus	5,000,000
Cotton linters	1,000,000
Esparto grass	500,000
Leaf (sisal, abaca, henequen)	480,000
Sabai grass	200,000
TOTAL	**4,033,080,000**

Source: Rowell (2006)

Wood

During the past few decades, production and trade in wood forest products have been mostly in the hands of European and North American countries. Countries such as Canada, USA, Finland, Germany and Japan have been large producers and important players in the international market. In spite of the fact that these traditional players are still important, some new emerging players have gained importance in the international market. Table 2 presents information on total exports of wood products of some selected countries (emerging and traditional players) and also their share in the international market over the last 15 years (1990 to 2005). Globalization and economic growth are collaborating to increase international trade of wood and wood products and the flow of capital into the forestry sector of emerging economies through new investments. Over the past 20 years, international trade of forest products, including pulp & paper, solid wood products and secondary processed wood products (SPWP) increased from US$60 billion to US$257 billion, an average annual growth of 6.6%, with wood panels and especially SPWP, growing above the average.

In the future, most of the wood supply will come from plantations. Forest plantations in the tropics are expanding rapidly and if current trend is maintained the annual potential sustainable production capacity of plantations will reach, in the year 2020, around 1.8 billion cubic meters, with more than 80% of this potential located in the tropics and other countries located in the southern hemisphere. This volume will be, in principle sufficient to supply most of global wood demand of the industry. Past decades production and trade of wood and wood products have been mostly in the hands of European and North American countries, but this is changing. In the last 15 years China has increased its share in the international trade of wood products from 1.5% to 7.2%, mainly

due to exports of SPWP. In wooden furniture, China displaced Italy, a long-time leader in furniture exports. China together with Brazil and Russia are expected to continue to gain market share and most probably will be among the major players in the international market by the year 2020. Under a conservative scenario, wood and wood products trade in the international market will reach around US$450 billion by the year 2020 (Anon, 2007). This means that countries and companies willing to maintain their market share in the international market will need to double exports in the next 10-15 years. In 2020 a large portion (40% or more) of the international trade is expect to be SPWP. The general trends and perspectives identified point out that a successful strategy to gain market share will need to consider investments in fast growing plantations and value added products, with a focus in the international market.

The diversity of tropical forest

Table 2 Exports and Share in the International Trade of Wood Products of Selected Countries

Country	1990 2005 Exports (USD Million)		1990 2005 Trade (%)	
Emerging Players				
Brazil	1,604	8,151	1.3	3.2
Chile	1,010	3,528	0.8	1.4
China	1,848	18,455	1.5	7.2
India	72	688	0.1	0.3
Indonesia	3,530	8,174	2.9	3.2
Malaysia	3,386	6,097	2.8	2.4
Russia	1,715	7,633	1.3	3.0
Vietnam	144	1,612	0.1	0.6
Traditional Players				
Canada	18,375	35,408	15.2	13.8
Finland	9,724	12,912	8.1	5.0

Source: FAO 2006, ITTO 2006 (from Anon, 2007)

Bamboo

Bamboo is a versatile plant that grows in many parts of the world, in particular the tropical and subtropical areas. About 65% of the area are dominated by Asia, mainly China and India (Figure 1). These two countries together have more than half the total bamboo resources globally (Figure 2). There are more than 70 genera and 1,450 species of bamboo available worldwide (Loretta *et al.,* 2008). Bamboo also has the potential to be used to address timber shortage in Malaysia. Recent studies carried out in 2009 estimated some 34 million bamboo culms are found in the natural forests of Peninsular Malaysia. The study also showed that bamboo has great potential to be used in the form of laminated products, particularly

as decking and flooring materials. The use of bamboo by the timber industry is still not widespread even though it has been proven to have comparable strength if not greater, to that of timber. Bamboo are mostly confined to making baskets for vegetables, handicrafts, bamboo cylinders and home construction for the aboriginal people. The stiffness of bamboo has been reported to be much greater than that of wood with flexural modulus of > 100 GPa as compared to 40-60 GPa for typical tropical medium hardwoods. Hence, through lamination process, bamboo strips can be converted into laminated products (parallel or cross laminated) easily and used as structural building components such as wall, flooring, beams or columns. Table 3 compares the strength of bamboo with wood, steel and concrete. Apparently it has the highest strength-to-weight by volume ratio; 0.17 based on ultimate strength, and 33 based on stiffness.
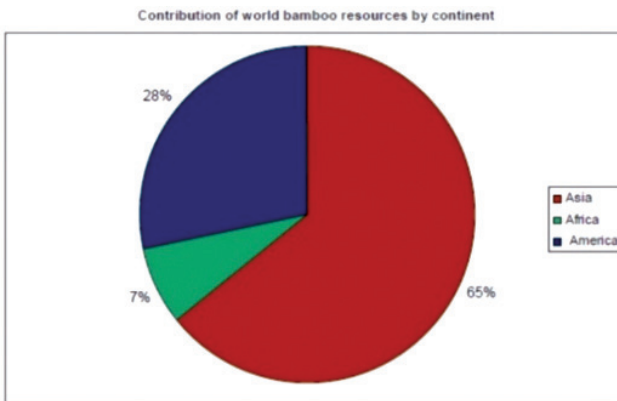

Figure 1 Bamboo resource according to continent
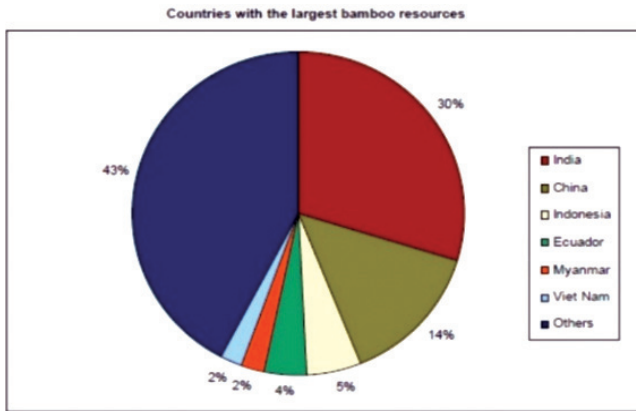
Figure 2   Bamboo resource according to country

From left Buluh Beting, Buluh Brang, Buluh Semantan - most popularly used by the bamboo industry in Malaysia

Table 3 Comparative strength of bamboo

Material	Weight by volume	Strength (Nmm^{-2})	Ratio*	Stiffness (Nmm^{-2})	Ratio*
Concrete	2400	8	0.003	25,000	10
Steel	7800	160	0.02	210,000	27
Wood	600	7.5	0.013	11,000	18
Bamboo	600	10	0.017	20,000	33

* *Note:* Ratio= Strength or stiffness/ weight by volume

(Source: Janssen, 1995)

Plant Fibres

Plant fibres are normally referred to as fibres that are obtained from agricultural crops such as sisal, ramie, bamboo, kapok, pineapple, coir, hemp, jute, flax, and kenaf, and are generally classified by the part of the plant from which they were obtained such as leaf, seed, fruit, stem, and bast. As its name implies, bast fibres are obtained from the outer layer, *i.e.,* the inner bark or phloem surrounding the plant stem. The fibres are usually very long (as long as the stem) and are relatively strong. For this reason, bast fibre is considered to be the most important fraction of any bast plant. Since all plant fibres are made up of mainly cellulose, they are categorised as "natural cellulosic fibres", which may consist of one plant cell or an aggregate of cells cemented together by non-cellulose materials. Thus, a cellulosic fibre can be either unicellular like wood and cotton, or multicellular like jute, hemp, flax, and kenaf (Sur, 2005). Jute, for example, has 5 to 15 cells, *i.e.,* the ultimate cell, which may be reduced upon storing or processing. Because of this characteristic, fibres that are separated from bast plants are often referred to as "crude fibres" (aggregates of single fibres bound together), which are usually much coarser and much longer, whilst those reported in many studies are defined based on scanning electron micrographs of microfibrils or single-strand fibre. Hence the reported average fibre lengths and widths are much smaller, *e.g.,* respectively 2.5 mm and 18 μm for jute (Sur, 2008), versus 2.3 mm and 16.1 μm for kenaf (Paridah *et al.,* 2009). The terminology is sometimes interchangeable, thus readers may have to make their own inferences based on the context of the discussion. Figure 3 shows examples of each classification of plant fibres based on its origin.
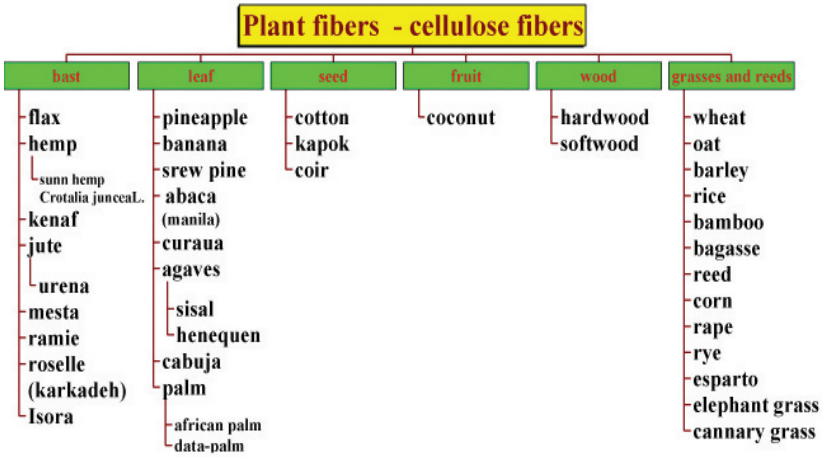
Figure 3 Classification of plant fibres by Kozlowski (2006)

Annual Production of Bast Plant Fibres

Detailed global supply/demand and price analyses for hemp, jute, flax, and kenaf are not available widely. The following statistics were taken from various sources, hence may have some discrepancies in the basis of calculations. Nevertheless, for comparison purposes the values are quoted as they appeared in the respective sources. Tables 4, 5, and 6 show the current world leading producers of jute, hemp and flax, and kenaf, respectively. Jute continues to dominate the natural fibre market with a continuous stable supply at 3,225,000 tonne, whilst hemp and flax together are close to 300,000 tonne, and kenaf is at an average of 400,000 tonne annually.

Table 4 Top World Jute Producers in 2008 by Country

Country	Production (x 10^3 tonnes)
India	2,1401
Bangladesh	8001
People's Republic of China	992
Côte d'Ivoire	401
Thailand	311
Myanmar	301
Brazil	26.712
Uzbekistan	201
Nepal	16.782
Vietnam	111
World	3,225.49

Source: Food And Agricultural Organization of United Nations: Economic and Social Department: The Statistical Division, 2008 (from Paridah et al., 2011)

Table 5 Top World Flax and Hemp Producers in 2005

Country	Production (x 10³tonnes)			
	Flax			Hemp
	Long Flax fibre [tonnes]	Short Flax fibre [tonnes]	Total	
Belgium	19 .03	11.89	30.92	-
Czech Rep	2 .93	3.55	6.48	. -
Germany	0.11	0.12	0.23	2.36
Spain	-	-	-	1.7
France	105	75	180	14
Italy	-	0.13	0.13	0.42
Lithuania	0.32	0.75	1.07	-
Latvia	2.54	3.80	6.34	-
Hungary	-	-	-	0.94
The Netherlands	4.52	3.33	7.85	0.08
Austria	82	0.13	82.13	0.44
Poland	0.15	0.12	0.27	0.14
Finland	-	0.10	0.10	0.008
UK	-	0.12	0.12	1.58
People's Republic of China	25	-	25	43
Total			**340.64**	**64.67**

Source: Food And Agricultural Organization of United Nations: Economic And Social Department: The Statistical Division, 2008. Note: Values were rounded to two decimals (from Paridah *et al.,* 2011).

Table 6 Top World Kenaf Producers

Country	Production (x 10^3 tonnes)				
	2004	2005	2006	2007	2008
India	198.00	203.20	202.14	198.70	156.40
People's Republic of China	125.90	136.00	155.00	165.00	86.92
Thailand	29.60	29.50	41.00	57.00	35.66
Vietnam	11.30	14.60	20.50	21.00	14.20
Brazil	7.30	7.20	10.20	10.90	12.65
Cuba	10.00	10.00	10.00	10.00	10.00
Indonesia	7.00	7.00	6.82	7.00	7.00
Myanmar	1.63	3.73	9.45	11.27	5.26
Cambodia	0.20	0.20	0.50	0.50	0.65
World	**390.93**	**411.43**	**481.37**	**481.07**	**328.74**

Source: Food And Agricultural Organization of United Nations: Economic And Social Department: The Statistical Division, 2008. Note: Values were rounded to two decimals (from Paridah *et al.,* 2011).

Table 7 shows the world annual production and prices for hemp, jute, flax, and kenaf. Both hemp and flax have been dominated by the European countries, whilst jute and kenaf by the Asia. The prices of bast fibres from these stems range from USD$0.60 to 0.90 per kilogram, with jute maintaining reasonably high prices. These are the prices officially quoted by various reports up to the preparation of this book. As indicated in Table 7, among the four bast fibres, kenaf seems to be more economically favourable, producing reasonably high yield with a good selling price. Kenaf prices have escalated between five to eight times as a result of new demands

by composite industries that include building, automotive, defence, and aerospace in their efforts to combat the current environmental issues, and in meeting government policies. The Malaysian climate, with its abundant sunshine, together with availability of rainfall throughout the year offers a suitable environment for kenaf. In such a climate, kenaf is able to grow all year round and can be harvested twice a year. Other Asian countries that fall under the same category are Thailand, Indonesia, Myanmar, and Vietnam. Between 1990 and 2002, Thailand used to be the major producer and consumer of kenaf (Anon, 2003); however this scenario has changed due to competition with other crops as well as environmental issues due to water retting.

Table 7 Annual Production and Prices of Hemp, Jute, Flax and Kenaf

Fibre type	Botanical name	Family	Main sources	Stem production (10³ Tonnes) per hectare	Prices ($/kg) of dry bastfibre	References
Hemp	*Cannabis sativa* L.	Cannabaceae	Germany, UK, France and possibly Romania	214	0.7-0.8	1,2,5,6
Jute	*Corchoruscapsularis* and *Corchorusolitorius*	Tiliaceae	Bangaladesh, India	2850	0.8-0.9	5,6,7
Flax	Linum usitatissimum	Linaceae	France, Spain, UK, Belgium, Lithuania	830	0.6-0.8	1,2,3, 4,5,6
Kenaf	*Hibiscus cannabinus*	Malvaceae	Bangaladesh, China	970	0.7-0.8	1,2,5,6

1 Rebson *et al*., 1993; 2 Rowell and Han, 2000; 3 Semder and Liljedahl, 1996; 4 Karus and Kaup, 2002; 5 Mwaikambo *et al*., 1999; 6 Ilison and McNaught, 2000; 7 Riccio and Orchard, 1999 (from Paridah *et al*., 2011).

Plant Biomass

Biomass is biological material derived from living, or recently living organisms. When associated with energy production, it is often used to mean plant based material, but biomass can equally be applied to both animal and vegetable derived materials. Biomass is carbon based and is composed of a mixture of organic molecules containing hydrogen, usually including oxygen, often nitrogen and also small quantities of other elements, including alkali, alkaline earth and heavy metals. These metals are often found in functional molecules such as porphyrins which include chlorophyll which contains magnesium. The concept of biomass for energy substitution is simple. The carbon used to construct biomass is absorbed from the atmosphere as carbon dioxide (CO_2) by the plants, using energy from the sun. The plants may subsequently be eaten by animals and thus converted into animal biomass. However, the primary absorption is performed by plants. If plant material is not used, it is generally either broken down by micro-organisms or burned:

- If broken down, it releases the carbon back to the atmosphere, mainly as either carbon dioxide (CO_2) or methane (CH_4), depending upon the conditions and processes involved.

- If burned, the carbon is returned to the atmosphere as CO_2.

These processes have happened for as long as there have been plants on earth and is part of what is known as the carbon cycle. Fossil fuels such as coal, oil and gas are also derived from biological material, the difference is that the CO_2 has been absorbed from the atmosphere many millions of years ago. As fuels they offer high energy density, but making use of that energy involves burning the fuel, with the oxidation of the carbon to carbon dioxide and the hydrogen to water (vapour). Unless they are captured and stored, these combustion products are usually released to the

atmosphere, returning carbon sequestered millions of years ago and thus contributing to increased atmospheric concentrations.

The difference between biomass and fossil fuels

The vital difference between biomass and fossil fuels is one of time-scale. Biomass takes carbon out of the atmosphere while it is growing, and returns it as it is burned. If it is managed on a sustainable basis, biomass is harvested as part of a constantly replenished crop. This is either during woodland or arboriculture management or coppicing or as part of a continuous programme of replanting with the new growth taking up CO_2 from the atmosphere at the same time as it is released by combustion of the previous harvest. This maintains a closed carbon cycle with no net increase in atmospheric CO_2 levels.

Categories of plant biomass materials

Within this definition, biomass for energy can include a wide range of materials. There are huge resources of residues, co-products and wastes, which can potentially become available in quantity, at relatively low cost, or even negative cost where there is currently a requirement to pay for their disposal. There are five categories of plant biomass:

- **Virgin wood**, from forestry, arboriculture activities or from wood processing

- **Energy crops**: high-yield crops grown specifically for energy applications

- **Agricultural residues**: residues from agriculture harvesting or processing

- **Industrial waste and co-products:** from manufacturing and industrial processes.

As there is wide diversity in the characteristics and properties of these different classes of plant biomasses and their various sub-groups, there is also a wide range of conversion technologies to make optimum use of them, which include both thermal and chemical conversion technologies.

Oil Palm Biomass

Oil palm contributes significantly in the Malaysian biomass scenario. Both plantations and palm oil industries generate thousands of tonnes of biomass daily in the form of residual fibres, leaves, shell and effluent. Malaysia generates approximately 30 million tonnes of oil palm residues annually which can be the source of fibre raw materials for various industries, such as the biocomposite industry, pulp & paper, bioenergy, composting. Anis (2007) estimated the amount of biomass generated by the oil palm industries and classified them under (1) plantation residues comprising oil palm trunk (OPT) and fronds (OPF), and mill residues including empty fruit bunch (EFB), shell, and effluent as follows:
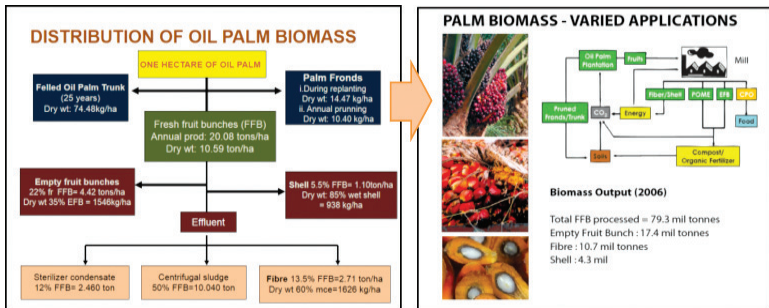
She also claimed that among the available biomasses, EFB has the highest potential as BioEnergy source (Table 8).

Table 8 Total potential for mesocarp fibre, EFB and PKS as BioEnergy

Fuel type	% to FFBC*	Lower calorific value KJ/kg	Energy in MJ	MJ at 25% thermal efficiency	Total MWh	Power plant capacity (MW)
Mesocarp fibre	13	17,344	584,423,424	146,105,856	40,585	6.95
EFB	23	17,050	956,836,800	239,209,200	66,447	11.38
PKS	6	18,660	290,200,320	72,550,080	20153	3.45

*Note: Estimated FFB projection is 259,200 tonnes per year with working period of 16 hours/day.
(Source: Anis, 2007)

ANATOMICAL STRUCTURE

We have studied several types of plant fibres and used them in our composite research. These include fast growing tropical hardwoods (*e.g.,* sentang, *Acacia mangium*, macaranga, kelempaian), bast fibres (kenaf, jute), leaf fibres (pineapple) and biomass (oil palm trunk, empty fruit bunch, rice husks). These fibres are "cellulose fibre reinforced materials" as they consist of microfibrils in an amorphous matrix of lignin and hemicelluloses that run all along the length of the fibre. The hydrogen bonds and other linkages provide the necessary strength and stiffness to the fibres. Inside the microfibrils there are nanofibrils with diameters that range from 2 to 20 nm, and a length of more than a few micrometers (Figure 4). These nanometer-sized single crystals of cellulose are commonly referred to as nanofibrils, whiskers or nanocrystals (Winandy, 1994, 2013). The cell wall of wood fibres consists of repeated crystalline structure resulting from the aggregation of cellulose chains. Over the past decades, researchers have successfully found ways to remove the hemicelluloses and lignin to give rise to a new class of fibres, nanocellulose, with enhanced performance (Rowell, 2013).

The chemical component of natural fibres varies, depending upon the type of fibres. As shown in Figure 4, all fibres or lignocellulosic materials consist of three types of chemicals; approximately half of which is cellulose and approximately a quarter thereof is hemicelluloses and lignin that are strongly intermeshed and chemically bonded by non-covalent forces and by covalent cross-linkages. Other extractives present in plant sources include pectin and waxes. The differentiation of non-wood and wood cell is illustrated in Figure 5.
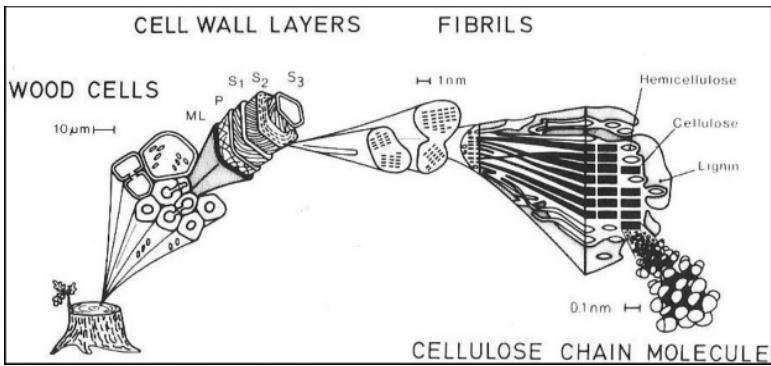
Figure 4 The structure of plant fibre
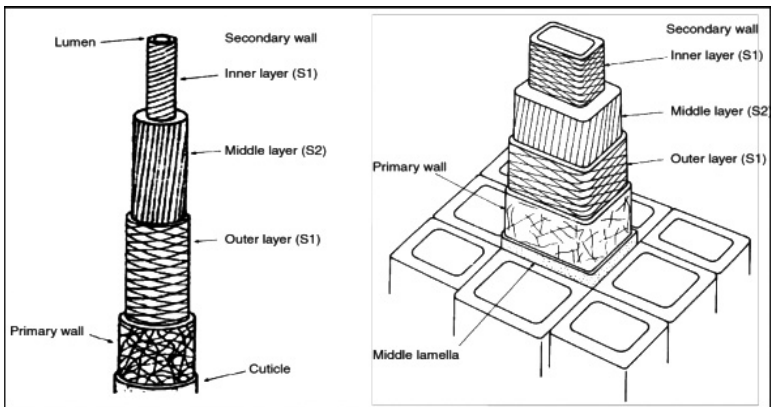(*Source:* Nabi Saheb and Jog, 1999)

Figure 5 Schematic diagram of the morphological architecture of (a) a cotton fibre and (b) a delignified spruce wood
(*Source*: Nabi Saheb and Jog, 1999)

Wood

The primary structural building block of wood is the tracheids (in softwood) or fibre cells (in hardwoods). For easy reference the term "fibre" is used to describe both elements. The cells (each cell

representing a strand of fibre) vary from 16 to 42 μm in diameter and from 870 to 4000 μm long. Thus a cubic centimetre of wood can contain more than 1.5 million wood fibres (Rowell *et al.,* 1994). When packed together they form a strong composite. Because of this reason, wood is constantly separated from other natural fibres such as those of bast fibres (kenaf, hemp, flax, jute, ramie), or from others like abaca, sisal, pineapple, bamboo, straws, oil palm biomass, *etc.* Each individual fibre is structurally advanced because it is actually a multilayered, filament-reinforced, closed-end tube rather than just a homogeneous-walled, non-reinforced straw. Each individual cell or fibre has four distinct cell wall layers (Primary, S1, S2, and S3). This is the point of similarity with other natural fibres. Each layer is composed of a combination of three chemical polymers: cellulose, hemicellulose, and lignin (Figure 6). Cellulose and hemicellulose are linear polysaccharides (*i.e.,* hydrophilic multiple-sugars), and lignin is an amorphous phenolic (*i.e.,* a three dimensional hydrophobic adhesive). Cellulose forms long unbranched chains, while hemicellulose forms short branched chains. Lignin encrusts and stiffens these polymers. The difference between **softwood** and **hardwood** is found in the microscopic structure of the wood. Softwood contains only two types of cells: longitudinal wood fibres (or tracheids) and transverse ray cells. Hardwoods have vessel elements for water transport that softwoods lack; these vessel elements are evident in hardwoods as pores. SEM images show the presence of pores in hardwoods, which are absent in softwoods. In softwood, water transport within the tree is *via* the tracheids only.
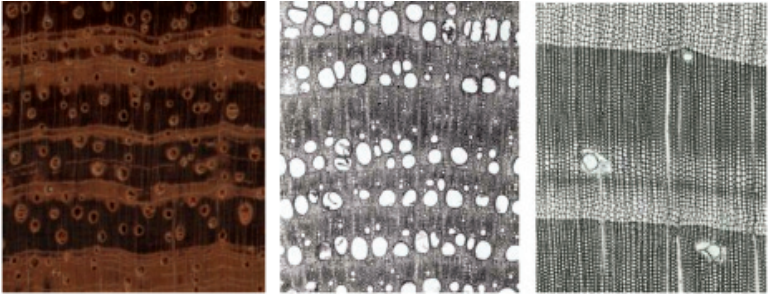
Figure 6 Images showing the presence of vessels in hardwoods (tropical hardwood (Resak, left) and (Oak, centre) which are absent in softwood (Pine, right)

Bamboo

There are several differences between bamboo and wood. In bamboo, there are no rays or knots, which results in stresses being distributed far more evenly throughout its length. Bamboo is a hollow tube, sometimes with thin walls, and consequently it is more difficult to join bamboo than pieces of wood. Bamboo does not contain the same chemical extractives as wood, and can therefore be glued very well (Jassen 1995). Bamboo's diameter, thickness, and internodal length have a macroscopically graded structure while the fibre distribution exhibits a microscopically graded architecture, which lead to favourable properties of bamboo (Amada *et al.,* 1998).

The bamboo culm is divided into segments by diaphragms or nodes. The nodes separate the culm into several sections termed internodes. The culm's outermost layer, the bark, consists of epidermal cells that contain a waxy layer called cutin. The innermost layer is wrapped by sclerenchyma cells. The tissue of the culm contains parenchyma cells and the vascular bundles (Figure 7). Vascular bundles are a combination of vessels and sieve tubes, with companion cells and fibres. The vascular bundle in bamboo culm

consists of the xylem with one or two smaller protoxylem elements and two large metaxylem vessels (40 - 120 μm) and the phloem with thin walled unlignified sieve tubes connected to companion cells.

The anatomical characteristics in relation to the mechanical properties of Malaysian bamboos have been studied by Abd. Latif *et al.* (1999). They concluded that vascular bundle size (radial/ tangential ratio) and fibre length correlated positively with modulus of elasticity (MOE) and stress at proportional limit. The authors implied that the increase in the size (mature stage), and fibre length could be accompanied by an increase in strength properties; larger size vascular bundle has longer fibres thus is stiffer. The correlation between fibre length and shear strength, however was negative. Fibre wall thickness correlates positively with compression strength and MOE, but negatively with modulus of rupture (MOR). There was also an inverse correlation between lumen diameter and all the mechanical properties, except compression strength.
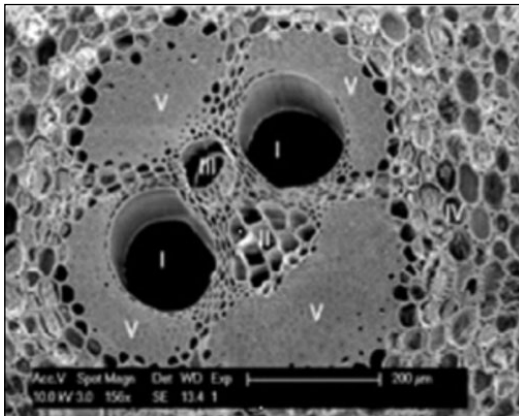

Figure 7 Transverse section of Bamboo: V vascular bundles; l lumen or metaxylem. (*Source*: Anwar *et al*., 2006).

Bast Fibres

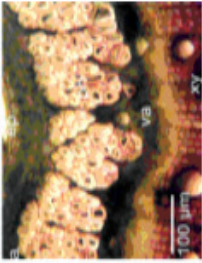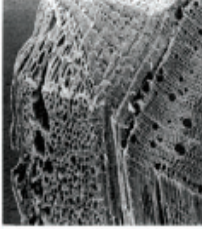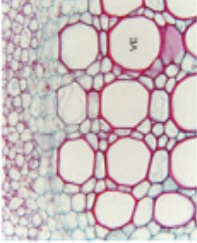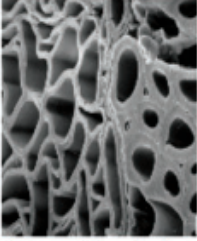Most of our work has been on the use of kenaf and pineapple fibres in particleboard, medium density board (MDF), fibre reinforced composites (FRC), pulp & paper and woven composites (Juliana *et al.,* 2012; Aisyah *et al.,* 2012; Ahmad *et al.,* 2012; Arib *et al*., 2004; Mohieldin *et al*., 2011; Azizi Mosello *et al.,* 2010). We have also extensively studied the retting process of kenaf stem using water, chemicals and microbes for the production of long fibres (Paridah *et al*., 2011). Generally, kenaf and other bast fibre bundles are composed of elongated thick-walled ultimate cells that are joined together both end-to-end and side-by-side, forming aggregates of fibre bundles along the height of the plant stem. During the growing period of the stem, a circumferential layer of primary fibres are developed from the protophloem, but, as vertical growth ceases in the lower parts, the secondary phloem fibres (where the bast fibres can be obtained) are developed as a result of cambial activity. Figure 8 shows the stem and cell structure of hemp, jute, flax and kenaf. Unlike cotton which is unicellular, these fibres have multi-cellular cell types. The cross section of a jute cell is polygonal with slightly rounded corners and a medium-sized lumen. Retted jute fibres normally contain 15 to 30 fibre cells (Sur, 2005) whilst the number of fibre bundles in the stem of flax ranges from 15 to 40. Each bundle contains between 12 and 40 ultimate fibres. The ultimate fibres consist of pointed cells with very thick walls and very small lumens. Goodman *et al.* (2002) investigated each flax fibre bundle using light microscopy and revealed that flax fibres originate from primary phloem tissues which are located between the outer cortical tissue and the secondary phloem tissues. Each fibre contains 30 to 40 ultimate fibres. In another study, Oliver and Joynt (1999) clearly observed the cross-section of hemp stem and found that its bast fibres are composed of 'primary bast fibres', which are

long and low in lignin content, and 'secondary bast fibres', which are intermediate in length and higher in lignin content.

Depending on the location in the stem, kenaf contains three types of fibre: bast, core, and pith. The fibres from the bast are long and have thick cell walls, whilst the core fibres are thinner with much shorter fibre length (Paridah *et al.,* 2008). The core fibres appear as wedge-shaped bundles of cells intermingled with parenchyma cells and other soft tissue. The pith consists exclusively of parenchymatous cells, which are not typically prismatic but polygonal in shape. In mature plants, kenaf can reach a height of 2.5 to 3.5 m (Rowell and Stout, 1998). Zhang (2003) reported that the kenaf fibres are shorter at the bottom of the stalk and longer at the top. The increase in length from the bottom to the top was found not to be gradual, but S-shaped (Rowell and Han, 1999). It was reported that the fibre length increases during the early part of plant growth, and decreases again as the plants mature (Chen *et al.,* 1995). Kenaf single fibres are only about 1 to 7 mm long and about 10 to 30 microns wide, thus too short for textile processing (Calamari, 1997). Compared with cotton fibre, these fibres are coarse, brittle, and non-uniform, which makes them difficult to be processed using conventional textile or nonwoven fabric equipment. Table 9 compares the morphology of natural cellulosic fibres against other types of bast plants.

Figure 8 Stems and cell structure in, hemp, jute, flax, and kenaf fibre (after Paridah *et al.*, 2011)

	Type of plant			
	Hemp	**Jute**	**Flax**	**Kenaf**
Stems				
Cells	Cross-section of hemp bastfibres.[6]	Jute stem (combined transverse section and longitudinal section).[5]	Flax stem in transverse section.[4]	Bark (lower part) and core (upper part) in transverse section.[3]

[1](Goodman *et al.*, 2002), [2](Voulgaridiset *al.*, 2000), [2](Oliver and Joynt, 1999), [3]www.sbs.utexas.edu/, mausethweblab/, webchap5scier/ 5.1-4. htm. [5]Rowell and Stout, 1998), [6](Tavisto et al., 2002).

Table 9 Morphology of Natural Cellulosic Fibres

Type of fibre	Cell type	Cross-sectional shape of ultimate cell
Jute Mesta Kenaf	Multicellular	Polygonal with slightly rounded corners and medium-sized lumen
Ramie	Multicellular	Elongated ellipse with collapsed elongated lumen
Flax	Multicellular	Appreciable roundness in the corners and medium size lumen
Hemp Pineapple	Multicellular	Oval cross-section with collapsed small size lumen
Sisal	Multicellular	Polygonal with sharp corners and medium to large size lumen
Coir	Multicellular	Polygonal with rounded corners and large size lumen
Cotton	Unicellular	Peanut-shaped cross-section of each fibre with elongated collapsed lumen

Source: Sur (2005)

Other Agricultural Fibres

Lignocellulosic agricultural byproducts are abundant and is a relatively cheap source of cellulose fibres. Agro-based biofibres have the composition, properties and structure that make them suitable for uses such as composites, textile, pulp & paper manufacture. Like other natural fibres, agro-based fibres can also be used to produce fuel, chemicals, enzymes and food. Byproducts produced from the cultivation of corn, wheat, rice, sorghum, barley, sugarcane, pineapple, banana and coconut are the major sources of agro-based biofibres (Reddy and Yang, 2005).

The dimensions of the individual cells or 'ultimates' in natural fibres are dependent on the species, maturity and location of the fibres in the plant, and also on the fibre extraction conditions (Paridah *et al.,* 2011). For instance, individual cells in pineapple and banana fibres are relatively longer and therefore these sources can produce long fibres. The widths of individual cells in rice straw, wheat straw and corn husk are smaller and can therefore form relatively finer fibres. As shown in Figure 9, coir has thick individual cells and therefore cannot form fine fibres. When used for applications such as textiles and paper, the length-to-diameter ratio (l/d) of individual cells in a fibre affects the flexibility and resistance to rupture of the fibres and products made from them (Kirby, 1963; Maiti, 1997). Wheat and rice straw have high l/d ratios and are therefore more commonly used in the manufacturing of paper.
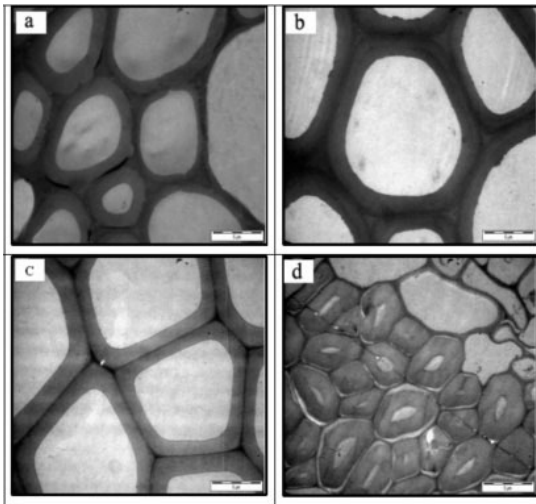

Figure 9 Transmission electron micrograph of the Malaysian agro-fibres (a) Oil palm frond, (b) Coconut (Coir), (c) Banana stem (d) Pineapple leaf (Khalil *et al.,* 2006).

PROPERTIES OF NATURAL FIBRES

Chemical Composition

In 1893, the presence of cellulose in plant cell walls was first discovered by Anselm Payen. A natural polymer consisting of D-glucose ($C_6H_{12}O_6$) monomer units, cellulose contains glucose units which link together to form long unbranched chains (Figure 9a). There are roughly 4,000 to 8,000 glucose molecules strung together. The polymer chains in cellulose have a linear structure due to the 1,4- -glycosidic linkages. Cellulose is largely crystalline, organised into microfibrils and is very stable in normal environments. The H-bonding of many cellulose molecules to each other results in the formation of microfibres that can interact to form fibres. Cellulose fibres usually consist of over 500,000 cellulose molecules. So, if a fibre consists of 500,000 cellulose molecules with 5,000 glucose resides/cellulose molecules, the fibre would contain about 2.5 billion H-bonds. Even if a H-bond has about 1/10 the strength of a covalent bond, the cumulative bonding energy of 2.5 billion of them is incredible. It is the H-bonding that forms the basis for the high tensile strength of cellulose (Biagiotti*et al.,* 2008).

Hemicellulose consists of short, highly branched chains of sugars. It contains five-carbon sugars (usually D-xylose and L-arabinose), six-carbon sugars (D-galactose, D-glucose and D-mannose) and uronic acid. The sugars are highly substituted with acetic acid. Its branched nature renders hemicelluloses amorphous and relatively easy to hydrolyse to its constituents. When hydrolysed, the hemicellulose from hardwood releases products high in xylose (a five-carbon sugar). The hemicellulose contained in softwood, in contrast, yields more six-carbon sugars. In contrast to cellulose, which is crystalline, strong and resistant to hydrolysis, hemicellulose has a random, amorphous structure with little strength. It is easily

hydrolysed by dilute acid or base, but nature provides an arsenal of hemicellulase enzymes for its hydrolysis. These enzymes are commercially important because they open the structure of wood for easier bleaching leading to the alternative and better methods of bleaching, thus avoiding the consumption of large amounts of chemicals dangerous for the environment, such as chlorine. Figure 10 illustrates the structure of (a) a cellulose chain in glucose, and (b) five common sugars found in hemicellulose.

(a)
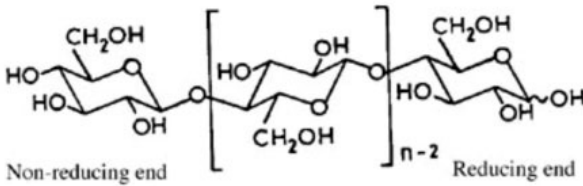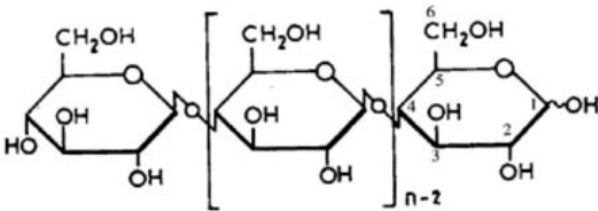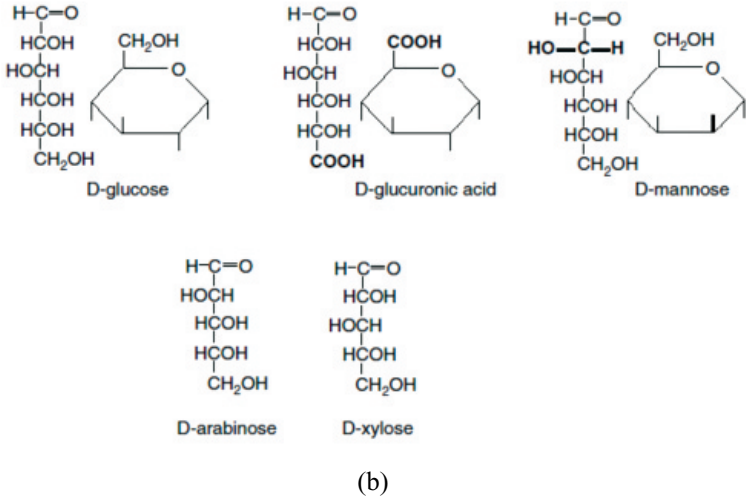
Figure 10 (a) Structure of cellulose and (b) Some monomers of hemicelluloses

Lignin is formed by the removal of water from sugar to create an aromatic structure. Lignin is isopolyphenolic in nature,(Figure 11) which explains why sometimes it is isolated as a brown powder, but more often it is a gummy mixture of lignins with a wide range of molecular weights. Lignin resists attack by most microorganismsm, and anaerobic processes tend not to attack the aromatic rings at all. The aerobic breakdown of lignin is slow and may take months. Lignin together with hemicellulose is nature's cement in the exploitation of the strength of cellulose while conferring flexibility. The chemical compositions of some plant-fibres are shown in Table 10.

Figure 11   Typical structure of lignin found in plants

Table 10 Chemical composition of natural plant fibres (from Kozlowski, 2008)

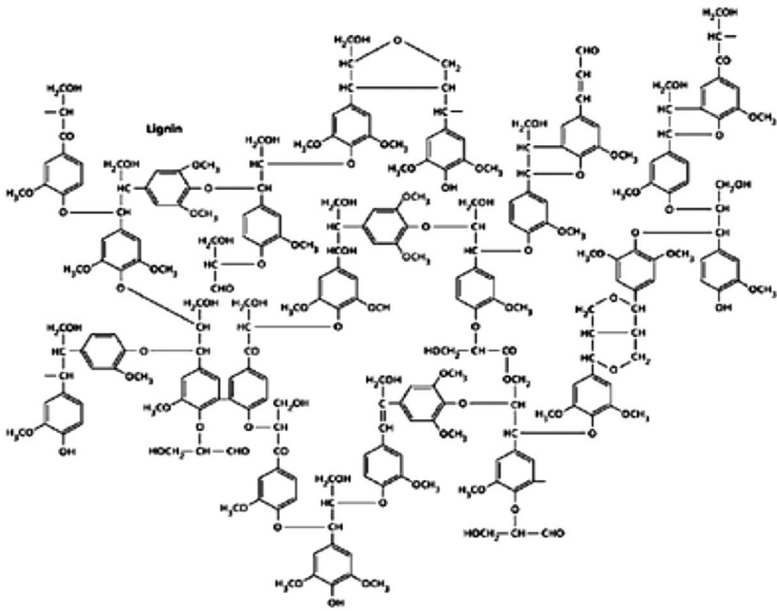| Fibre	Latin name	Cellulose (wt.%)	Hemicellulose (wt.%)	Lignin (wt.%)	Pectin (wt.%)	References*
Flax	*Linum usitatissimum*	60-81	14-18.6	2-3	1.8-2.3	1
Jute	*Corchorus capsularis, C. olitorius*	51-72	12-20.4	5-13	0.2	2
Abaca	*Musa textilis*	60.8-64	21	12	0.8	3
Sisal	*Agave sisalana Perrine*	43-88	10-13	4-12	0.8-2	4
Kenaf	*Hibiscus cannabinus*	36	21	18	2	5
Ramie	*Boehmeria nivea Gaud, variety tenacissima*	68.6-76	13.1-15.0	0.6-1	1.9-2	6
Hemp	*Cannabis sativa* L.	70-78	17.9-22	3.7-5	0.9	7
Cotton	*Gossypium spp.* (commonest *G. hirsutum*)	82.7-92	2-5.7	0.5-1	5.7	8
Coir	*Cocos nucifera* L.	43	0.3	45	4.0	9
Banana	*Musa acuminata* L.	60-65	6-19	5-10	3-5	10
Henequén	*Agava fourcroydes Lemaire*	60-78	4-28	8-13	3-4	5
Bagasse	*Saccharum officinarum* L.	40	30	20	10	5
Pineapple	*Acanas comosus*	80-81	16-19	12	2-2.5	11
Wood	-	45-50	23	27	-	11

*1. (Gassan, Chate and Bledzki 2001; Smeder and Liljedahl 1996; Bledski and Gassan 1999; Bledski, Reihmana and Gassan 1996 ; Mwaikambo and Ansell 2002).
2. (Gassan, Chate and Bledzki 2001; Smeder and Liljedahl 1996; Bledski and Gassan 1999; Bledski, Reihmana and Gassan 1996).
3. (RunCang Sun et al. 1998; Rowell et al. 1997).
4. (Joseph et al. 2002; Bledzki and Gassan 1999; Rowell et al. 1997; Bledski, Reihmana and Gassan 1996; Mwaikambo and Ansell 2002).
5. (Klemm, Schmauder and Heinze 2001).
6. (Bledski and Gassan 1999; Bledski, Reihmana and Gassan 1996; Mwaikambo and Ansell 2002).
7. (Bledski, Reihmana and Gassan 1996).
8. (Smeder and Liljedahl 1996; Bledski and Gassan 1999; Mwaikambo and Ansell 2002; Klemm, Schmauder and Heinze 2001).
9. (Gassan, Chate and Bledzki 2001; Bledski, Reihmana and Gassan 1996).
10. (Gassan, Chate and Bledzki 2001; Smeder and Liljedahl 1996).
11. (Gassan, Chate and Bledzki 2001).

Fibre Morphology

Fibre extraction procedures depend on the type of plant and portion thereof from which the fibres are derived (*e.g.,* bast, leaves, wood), as well as the required fibre performance and economics. Fibre bearing plants have very different anatomies (*e.g.,* trees versus herbaceous plants) and often fibres are derived from agricultural residues or by-products from industry. Consequently, the processing needs can differ greatly. Wood is primarily composed of hollow, elongated, spindle-shaped cells (called tracheids or fibres) that are arranged parallel to each other along the trunk of the tree. These fibres are firmly cemented together and form the structural component of wood tissue. Fibres are extracted from wood by mechanical or chemical means during the pulping process.

Bast fibres, such as flax or kenaf have considerably different structures compared to wood and consequently, are processed quite differently. They are found in the inner bark of the stems and typically account for less than 30% of the stem weight. Inside the inner bark is a woody core (called the "shive") with much shorter fibres. Fibre strands are removed from the bast. These fibre strands are several meters long and are actually fibre bundles of overlapping single ultimate fibres. Table 11 compares different dimension of fibres according to fibre types and parts from where they are obtained.

Mechanical Properties

The range of plant fibres is fairly broad. Included are very short wood fibres from both deciduous and coniferous sources, used as fillers in extruded plastic lumber and moulding compounds. Also represented are straw from corn, wheat and rice crops, and various natural grasses. Prof. Drzal, Director of the Composite Materials

and Structures Center at Michigan State University (East Lansing, Mich.) classified the natural fibres into three types: "Bast" fibres, such as flax, hemp, jute and kenaf, are noted for being fairly stiff when used as a composite reinforcement. Leaf fibres, including sisal, henequen, pineapple and banana, are noted for improving composite toughness with somewhat lower structural contribution. Finally, seed or fruit fibres — cotton, kapok and coir (from coconut husks), which demonstrate elastomeric type toughness, but are not structural (Drzal *et al.,* 2005).

The properties of some natural fibres are presented in Table 11. The tensile strength of glass fibres is substantially higher than that of natural fibres even though the tensile modulus is of the same order. However, when the specific tensile modulus of natural fibres (tensile modulus/specific gravity) is considered, the natural fibres showed values that are comparable to, or better than those of glass fibres. These higher specific properties are one of the major advantages of using natural fibre composites for applications where the desired properties also include weight reduction.

Table 11 Dimensions of different natural fibres

Parts where fibres are obtained	Property (mm)	Types of Fibre			
		FLAX	**HEMP**	**JUTE**	**KENAF**
Bast	Length	4-69	5-55	0.7-6	2-11
	Diameter	8-31	16	15-25	13-33
Core	Length	0.2	0.7	1.06	0.6
	Diameter	-	-	26	30
		ABACA	**SISAL**	**PALM**	
Leaf	Length	2-12	0.8-7	1.2-2.53	
	Diameter	6-40	8-48	18	
		COIR	**COTTON**		
Seed	Length	0.2-1	10-50		
	Diameter	6.24	12-25		
		CORN	**RICE**	**WHEAT**	
Straws/Stalk (Cereal fibres)	Length	1.0-1.5	0.65-3.48	1.5	
	Diameter	20	5-14	15	
		BAGASSE	**BAMBOO**		
Stem (Grass fibres)	Length	2.8	2.7-4		
	Diameter	34.1	15		
		RUBBER-WOOD	**RADIATA PINE**		
Wood2	Length	1.15-1.34	2.6-3.7		
	Diameter	0.12-0.28	0.37-0.43		

Source: [1]Jusoh (2008); [2]Naji *et al.* (2012) ; [3]Ghosh *et al.* (2006)

The chemical constituents and complex chemical structure of natural fibres also affect the properties considerably. Coir shows the lowest tensile strength among all the natural fibres listed in Table 12, which is attributed to a low cellulose content and considerably high microfibrillar angle (Mohanty *et al.*, 2001). The high tensile strength of flax may be attributed to its high cellulose content and comparatively low microfibrillar angle. However, it is not possible to correlate the fibre strength exactly with cellulose content and microfibrillar angle because of the very complex structure of natural fibres. Filament and individual fibre properties can vary widely depending on the source, age, separating technique, moisture content, speed of testing, history of fibres, *etc.* The lignin content of the fibre influences its structure, its properties and morphology. The waxy substances of natural fibres generally infuences the fibre's wettability and adhesion characteristics (Frihart 2005). In terms of specific strength, natural fibres can be compared with glass fibres. On the other hand, the low temperature limit for use of natural fibres does not allow an arbitrary choice of polymers as matrix materials. For manufacture of composites with suitable matrix systems, it is very important to consider the degradation of the fibre's mechanical properties when they are exposed to composite processing temperatures between 180–200±°C.
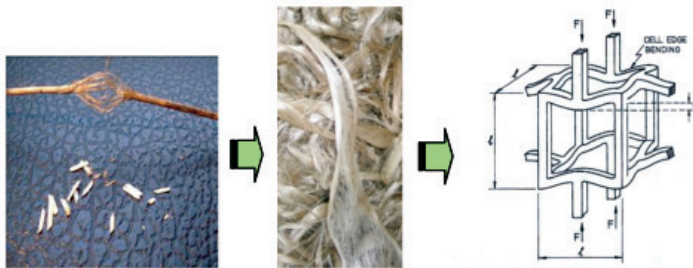

Figure 12 Natural fibre has high tensile strength due to the presence of intra H-bonds: (a) showing cell edge bendingduring linear-elastic deformation, (b) continuous fibre bundles and (c) the web structure in fibres increases the breaking tenacity, greater than steel

Table 12 Mechanical properties of natural fibres

Fibre	Density (g/cm³)	Elongation (%)	Tensile strength (MPa)	Young's modulus (GPa)	Reference
NATURAL FIBRES					
Cotton	1.5-1.6	7.0-8.0	287-597	5.5-12.6	Mohanty et al., 2001
Jute	1.3	1.5-1.8	393-773	26.5	Mohanty et al., 2001
Flax	1.5	2.7-3.2	345-1035	27.6	Mohanty et al., 2001
Hemp		1.6	690		Mohanty et al., 2001
Ramie		3.6-3.8	400-938	61.4-128	Mohanty et al, 2001
Sisal	1.5	2.0-2.5	511-635	9.4-22.0	Mohanty et al., 2001
Coir	1.2	30.0	175	4.0-6.02	Mohanty et al., 2001
Viscose (cord)	1.4	11.4	593	11.0	Mohanty et al, 2001
Softwood kraft	1.5		1000	40.0	Mohanty et al., 2001
Kenaf		1.5	930	53	Simpson & Crawshaw, 2002
Abaca			430-760		Simpson & Crawshaw, 2002
Oil palm	0.7-1.55	3.2	248	25	Simpson & Crawshaw, 2002
Pineapple		2.4	170-1627	60-82	Zahn et al., 1980
Wool		25-35	120-174	2.3-3.4	Zahn et al., 1980
Spider silk		17-18	875-972	11-13	Zahn et al., 1980
Tussah silk	1.32	33.48	248.77	5.79	Feughelman, 1997

MAN-MADE FIBRES

E-glass	2.5	2.5	2000-3500	70	Mohanty et al., 2001
Aramid	1.4	3.3-3.7	3000-3150	63-67	Mohanty *et al.*, 2001
Carbon	1.4	1.4-1.8	4000	230-240	Mohanty *et al.*, 2001

*Source:* Extracted from Ho *et al.*, 2012

BONDING MECHANISM

A strong fibre–matrix interface bond is critical for high mechanical properties in composites. In polymer matrix composites, there appears to be an optimum level of fibre–matrix adhesion, which provides the best composite mechanical properties (Drzal and Madhukar, 1993). Physical properties of natural fibres are basically influenced by the chemical structure such as cellulose content, degree of polymerization, orientation and crystallinity, which are affected by conditions during growth of the plants as well as extraction methods used. There is an enormous amount of variability in fibre properties depending upon from which part of the plant the fibre is taken, the quality of the plant and location. Different fibres have different lengths and cross-sectional areas and also different defects such as micro compressions, pits or cracks. To obtain uniformity and flexibility, some researchers conduct surface modification on the fibres by dissolving the microfibrils in solvents followed by precipitation under controlled conditions, or by increasing the wettability of the fibre surfaces through pre-treatment with chemicals, or by adding coupling agents.

The natural fibre–polymer interface presents a formidable challenge. Due to the presence of hydroxyl and other polar groups in various constituents of natural fibres, the moisture absorption in biocomposites is high, which leads to weak interfacial bonding between fibres and matrix polymer. Natural fibres have a strong polar character that renders hydrophilic property, whilst thermosetting and thermoplastic matrices are hydrophobic in nature. Hence, when both are combined, it is necessary to make use of compatibilizers or coupling agents in order to improve the adhesion between fibre and matrix (Bledzki and Gassan 1999). Unlike wood, bonding of most fibre crops such as kenaf and jute, and agro-fibres from coir and empty fruit bunch (EFB), is relatively more difficult mainly due

to lower wettability. A typical example is demonstrated in Figure 11 which shows a poor interfacial bonding occurring between coir fibre and epoxy. Mohanty and co-workers made a comprehensive review of the influence of various surface modifications of natural fibres like henequen, jute and coconut (coir) fibres and their effects on performance of biocomposites. According to them, the main drawback of natural fibres is their hydrophilic nature, which lowers their compatibility with hydrophobic polymer matrices. The hydrophilic nature of biofibres leads to biocomposites having high water absorption characteristics that reduce their usefulness in many applications. The presence of a natural waxy substance on the fibres surface contributes immensely to ineffective fibres to polymer matrix bonding and poor surface wetting. The presence of free water and hydroxyl groups, especially in the amorphous region, reduces the ability of natural fibres to develop acceptable adhesive characteristics with most binder resins. High water and moisture absorption of the fibres causes swelling and a plasticising effect resulting in dimensional instability and poor mechanical properties. Research on low cost surface modification of natural fibres is a necessity since the main attraction of today's market of biocomposites is the low cost of biofibres. Among the various low cost surface modifications, alkali treatment and ammonia fibre explosion (AFEX) are very attractive and promising (Mohanty *et al.,* 2000). Although maleated polypropylene (MAPP) is a very attractive coupling agent for natural fibre–PP based biocomposites, the use of organic solvent like toluene, to dissolve the coupling agent (such solution is usually required for the sizing of natural fibres) may be costly or may not be environmentally acceptable. Recent findings of water emulsion based maleated polypropylene may kindle renewed interest as a very promising coupling agent in natural fibre–thermoplastic composite technology.

Similar observation was made by Keener *et al.* (2004).The physical properties of natural fibre/polyolefin composites can be greatly enhanced by MaPO coupling agents. Maleated polyethylene (MaPE) couplers have been developed and used for some time and has been shown to be superior to other potential polyolefin coupling agents. Results indicate that the new polyethylene couplers can double the tensile strength and triple the impact properties compared to non-coupled blend of wood and polyethylene. Figure 13 shows the differentiation of agro-fibre with and without coupling agent. Untreated natural fibres are usually covered with a layer, whose composition is probably mainly waxy substances (Zafeiropoulos *et al.,* 2008). Such layer is not evenly distributed along the fibre surface, and its thickness varies from point to point. Studies by Sreekala *et al.* (1997) showed that the surface of the esterified materials became smoother as compared to that of untreated materials. Removal of the waxy substances on the surface of lignocellulosic materials causes the smoothening of the fibre surface after esterification (Figure 14).
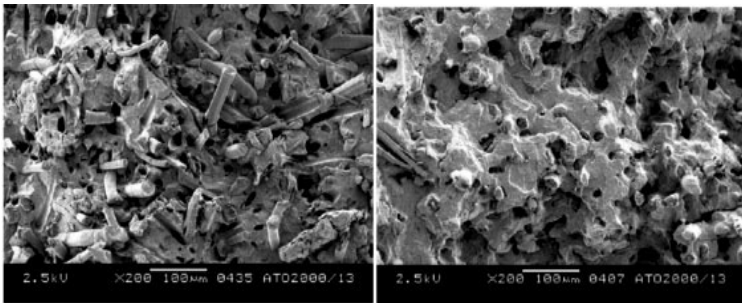
(a)   (b)

Figure 13 SEM 200x of 30 wt% agrofibre/PP composite (a) without coupler: shows voids and pull outs (b) with 3% Epolenee G-3015 coupler shows good fibre wetting and interblocking (Keener *et al*., 2004).
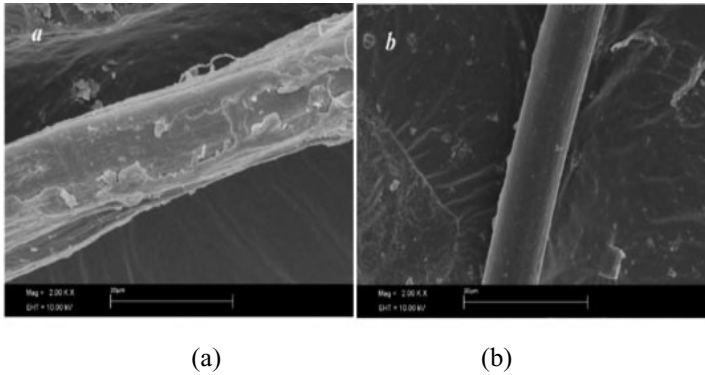
(a)   (b)

Figure 14 SEM micrographs of untreated and esterified hemp fibre: (a) untreated, (b) acetylated (*Source*: Tserki *et al.,* 2005)

Our study (Norul Izani *et al*., 2013 a and b) on the pre-treatment of oil palm empty fruit bunch fibres (EFB) shows a tremendous improvement in fibre surfaces once treated with NaOH. The SEM micrographs of untreated and treated fibres (Figure 15) clearly show fibrils that are aligned together forming a packed structure. The untreated fibre shows a much rougher surface with layers of impurities covering the surfaces which are suspected to be lignin and wax. The fibre surfaces of the NaOH-treated fibres are cleaner with almost all impurities being removed. Some degree of hydrolysis however seems to have occurred based on the roughness of the fibre surface. Researchers (Rowell, 2013, Paridah *et al.,* 2011; Khalil *et al*., 2001; Rowell and Stout, 1998) associated this to hydrolysis of some of the hemicellulose, lignin and cellulose, including the amorphous waxy layer. As a result, more reactive hydroxyl group are exposed on the fibre surfaces making them more hydrophilic. Such a condition provides a more conducive environment for adhesive-fibre interactions through better mechanical interlocking, adsorption and diffusion processes.
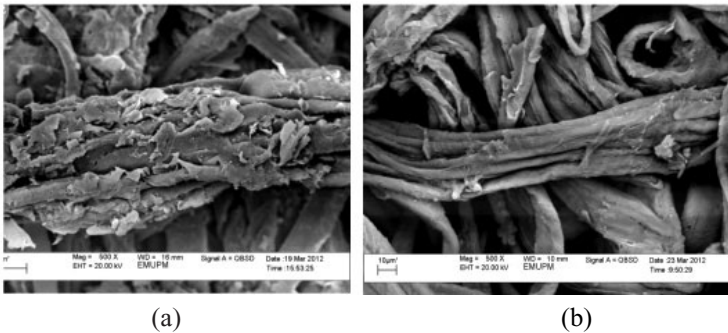
(a)   (b)

Figure 15 SEM micrograph of EFB fibre (a) Untreated and (b) after soaking in NaOH (500x magnification). *Source*: Norul Izani *et al.* (2013a)

Bonding Mechanism in Natural Fibre

Adhesion mechanisms have been known to be dependent on the surface characteristics of the materials. The past 30 years have shown tremendous increase in the understanding of adhesion mechanisms particularly after aggressive efforts by both the automotive and aerospace industries in seeking lighter and cheaper alternatives to metals and metal components. This drive has been the major influence in the need to understand polymer adhesion and to resolve the debate over how the interfaces are actually adhering (Awaja *et al.,* 2009). Being porous, the bond formation in natural fibres involves generally three main adhesion mechanisms: mechanical interlocking, adsorption theory and chemical bonding. The following sections give a brief overview of adhesion mechanisms in relation to bonding of natural fibres.

Adhesion principle

Adhesion is the state that in which ***two surfaces*** are ***held*** together by ***interfacial forces*** which may consist of valence forces and/or interlocking actions. These forces of attraction are caused by the presence of interactions between molecules, atoms or ions, on the two surfaces involved in the adhesion process. Three major components in gluing are substrate, adhesive and interface:
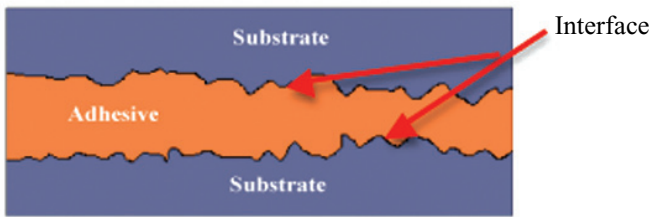
There are several theories attempting to explain the phenomenon of adhesion of the adhesive/matrix on the substrates, however, there is currently no unified theory to justify all cases. Nevertheless there are four theories mostly applied to describe this phenomenon: (i) Mechanical interlocking (ii) Adsorption (iii) Chemisorption (iv) Diffusion, and (v) Chemical bonding. In most cases, these theories are combined to describe the actual bonding process in natural fibres.

(i) Mechanical interlocking

The mechanical interlocking adhesion mechanism is based on the adhesive being deposited in the voids of any porous substrate that once cured, form an anchor between the adhesive and the substrate. Any type of material when observed at the microscopic level has a surface composed of valleys and ridges. This surface topography allows the adhesive to penetrate and fill the valleys,

resulting in anchorage areas between the adhesive and substrate. Like wood, other types of fibre such as agro-fibres and plant biomass, experience the same adhesion mechanism. The mechanical interlocking begins with the adhesive first being spread onto the surface of the porous substrate (Figure 16), forming interface layers between the adhesive and the substrates. Because the substrates are porous, the adhesive (normally in liquid form) flows through the cell wall and into the lumen while at the same time forming several layers: (i) boundaries between interface and substrate, (ii) interface and (iii) boundaries between interface and adhesive. These layers depend upon each other like a chain; if one layer breaks, the whole bonding collapses. Such incidence can be represented by a nine-chain concept (Marra, 1992).

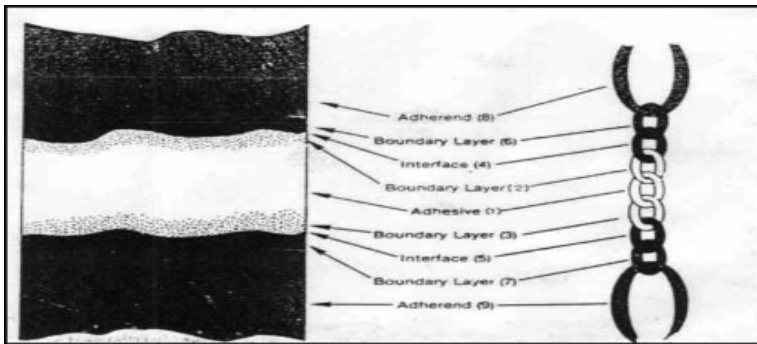**Figure 16** Illustration of mechanical interlocking between two substrates

Apart from the roughness and porosity of the substrate surface, it is necessary that the adhesive/matrix has a good filling power (*i.e.,* suitable viscosity), and can penetrate into the valleys and pore substrate surface to generate adhesion anchor points. Mechanical adhesion theory does not account for the incompatibility that may

exist between the adhesive and the substrate, it only takes into account the topography of the substrate and adhesive filling power, and so this theory cannot explain the adhesion between surfaces with low roughness or smooth, nor the lack of adhesion between rough substrates incompatible with adhesives.

(ii) Adsorption Theory

The adsorption theory or model explains the phenomenon of adhesion based on concepts such as contact angle, wet ability (also denoted as wettability) and surface tension. When the adhesive has a lower surface tension compared to the substrate surface energy, it is capable of wetting the surface, generating a contact angle less than 90°, thus generating the adhesion between the adhesive and substrate. Against the mechanical model and the model of diffusion, adsorption model explains the phenomenon of adhesion without penetration by the adhesive to the substrate; the adhesion is generated by the contact between the adhesive and substrate.

(iii) Chemisorption theory

Chemisorption theory is an extension of the adsorption theory of adhesion, in which the adhesive has properly wet the substrate; the adhesion phenomenon arises when generating intermolecular or Van der Waals forces and chemical bonds between the adhesive and substrate. This theory is very much suited to elucidate the use of compatible agents in fibre reinforced composites.

(iv) Diffusion theory

The diffusion model explains the concept of adhesion by the compatibility between polymers and the movements that occur in the polymer chains. When two polymers are compatible,

their polymer chains are able to mix between them, resulting in partial penetration between the two materials; as a result of these penetrations anchorage areas and adhesion points are formed. The mobility and degree of penetration of the polymers are determined directly by their molecular weight, so that short polymer chains have high mobility and penetrate into the other material before long polymer chains (see below).
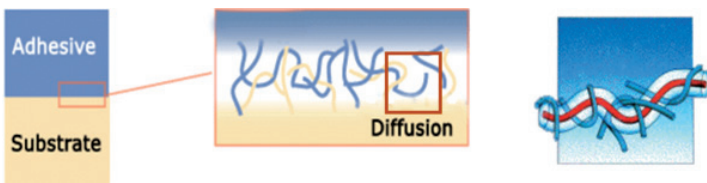
This theory can explain the phenomenon of adhesion that occurs between polymeric materials, plastic welding and plastic binding with adhesives.

(v) Chemical bonding

Chemical bonding is the most widely accepted mechanism for explaining adhesion between two surfaces in close contact. It entails intermolecular forces between adhesive and substrate such as dipole-dipole interactions, van der Waals forces and chemical interactions (that is, ionic, covalent and metallic bonding). This mechanism describes the strength of the adhesive joints by interfacial forces and also by the presence of polar groups (Awaja *et al.,* 2009). Chemical bonding mechanisms require an intimate contact between the two substrates as shown in Figure 17. Among the types or classes of chemical bonds mentioned above, the covalent bond is the one that takes place in the adhesive joints using organic adhesives based on polymers.
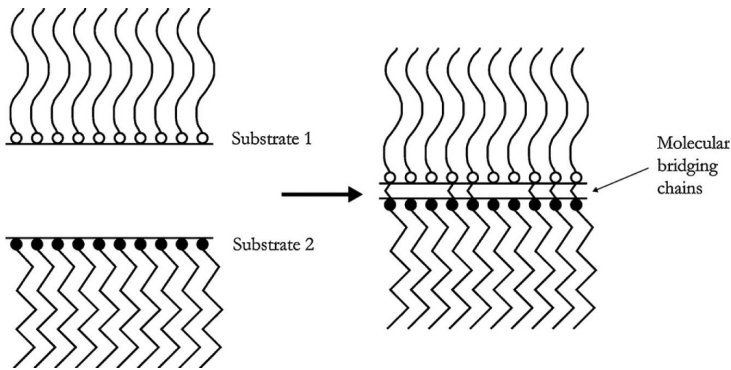
Figure 17 Schematic of the molecular bonding between substrates
(Awaja *et al.,* 2009).

Intimate contact alone is often insufficient for good adhesion at the interface due to the presence of defects, cracks and air bubbles. The molecular bonding mechanism is not yet fully understood and there have been many theories proposed to explain it. Chen *et al.,* (2007) who investigated the shear strength of aluminium–polypropylene lap joints found that the overriding adhesive mechanism was the chemical interaction between the functional groups at the interface and also concluded that excessive chemical bonding at the adhesive interface could have a negative effect on the interface strength. Such condition may occur as the number of chemical bonds increase at the contact zone, adhesion strength passes through a maximum value. Once the number of chemical bonds increases past this value, the concentration of the mechanical stresses at the interface leads to a decrease in adhesion strength due to the excessive increases in the size of the interfacial effect. The fact that adhesion strength depends also on the thickness of the adhesive layer for composite interfaces, such explanation is valid. Interfacial bonding strength increases as the thickness of the adhesive layer is

reduced (thinner glueline) as stress is able to dissipate through the interface with greater ease.

Surface Energy, Contact Angle and Wetting

Adhesive bonding is being used in biocomposites for various applications like construction, transportation, aeronautical, sports and even repairs. Because all plant fibres are made up of layers of naturally occurring cellulose-hemicellulose-lignin polymers, the variations on the fibre surfaces are inevitable, thus preparation of natural fibres is a critical step. Good bonds are produced but questions remain: What are the appropriate techniques to inspect surfaces? What are the key factors deciding a good/poor bond? How to predict material and surface preparation compatibility? Investigations into the effect of various surface preparation procedures and material systems on the adherent surface chemistry/ structure and its relation to subsequent bond performance can be performed using various techniques such as surface appearance/ topography, surface chemistry, surface energy/wetting, and fracture evaluation. Wetting and fracture are most easily adapted to laboratory assessment, factory inspection and repair settings. The following sections review surface tension theory and its relation to surface wetting. Some of the work on wetting and buffering capacity of wood, kenaf, oil palm fibres and bamboo conducted at our laboratory are also discussed.

Surface Energy and Contact Angle

This theory considers the inter-action of surface energy of the substrate and the adhesive in relation to bond quality (Sharfrin *et al.,* 1960). Surface energy is normally used to indicate the ease of bonding of a surface. This theory involves Young's equation, where θ is an angle between the horizontal plane of a substrate and the

contact line of a droplet, denoted as contact angle (Figure 18). Contact angle is defined as the angle formed by a drop of liquid/adhesive in contact with the surface of the substrate; the value of this angle will indicate the degree of wettability and therefore the adhesion of the adhesive on the substrate.
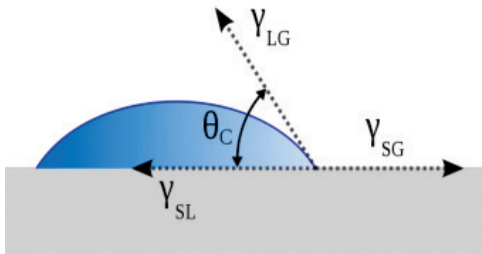

Figure 18 Schematic illustration of a liquid drop showing the quantities in Young's equation

Adhesive forces between a liquid and solid cause a liquid drop to spread across the adhesive forces between the surfaces. Cohesive forces within the liquid cause the drop to ball up and avoid contact with the surface. The contact angle (θ), as seen in Figure 18, is the angle at which the liquid–vapour interface meets the solid–liquid interface. The contact angle is determined by the resultant adhesive and cohesive forces. As the tendency of a drop to spread out over a flat, solid surface increases, the contact angle decreases. Thus, the contact angle provides an inverse measure of wettability.

A contact angle of less than 90° (low contact angle) usually indicates that wetting of the surface is very favourable, and the fluid will spread over a large area of the surface. At this state, the adhesive wets the substrate causing adhesion between both materials. A complete wetting means θ approaches zero. On the other hand, contact angles greater than 90° (high contact angle)

generally means that wetting of the surface is unfavourable, so the fluid will minimize contact with the surface and form a compact liquid droplet. Under this condition, it is said that the adhesive does not wet the substrate - it does not generate any adhesion between the adhesive and the substrate. Contaminants usually lower the solid's surface energy (increase θ). The contact angle of an adhesive on any substrate can be determined by using specific devices such as goniometers or by applying specific software.

For water, a wettable surface may also be termed hydrophilic and a non-wettable surface hydrophobic. Super hydrophobic surfaces have contact angles greater than 150°, showing almost no contact between the liquid drop and the surface. This is sometimes referred to as the "Lotus effect". For non-water liquids, the term lyophilic is used for low contact angle conditions and lyophobic is used when higher contact angles result. Similarly, the terms omniphobic and omniphilic apply to both polar and a polar liquids.

Wetting

Wetting is the ability of a liquid to maintain contact with a solid surface, resulting from intermolecular interactions when the two are brought together. Intermolecular forces are defined as the set of attractive and repulsive forces that occur between the molecules as a result of the polarity of the molecules. Intermolecular forces acting between the molecules are classified as:

1. Permanent dipoles
2. Induced dipoles
3. Dispersed dipole
4. Hydrogen bonds

Within these four groups, the most important forces are the first three, also known as Van der Waals forces. The binding energies generated by the intermolecular forces are smaller than the energies generated in the chemical bonds, but exist in greater numbers compare with the number of chemical bonds, so overall they play a very important role. Compared to covalent bonds, the binding energies of Van der Waals is 0.1 to 10 kJ/mol, compared to those of covalent bonds, which is 250-400 kJ/mol. Table 13 compares intermolecular forces and chemical bonds.

Table 13 Comparison between intermolecular forces and chemical bonds

Intermolecular Forces	Chemical bonds
1. Intermolecular forces depend on the temperature; an increase of the temperature produces a decrease of the intermolecular forces.	1. Chemical bonds do not depend so much on the temperature.
2. They are weaker than chemical bonds, order of 100 times lower	2. They are stronger than intermolecular forces
3. The bond distance is at the level of microns	3. The bond distance is very small, in terms of Angstroms
4. Unions are not directed.	4. Unions are directed

Wetting is important in the bonding or adherence of two materials. The degree of wetting is determined by a force-balance between adhesive and cohesive forces. Wetting deals with the three phases of materials: gas, liquid and solid. It has become a topic of interest in nanotechnology and nano-science studies due to the advent of many nano-materials in the past two decades

(*e.g.,* graphene, carbon nano-tube). Wetting and the surface forces that control wetting are also responsible for other related effects, including the so-called capillary effects. Regardless of the amount of wetting, the shape of a liquid drop on a rigid surface is roughly a truncated sphere. Various degrees of wetting can be obtained depending on the surface tension of the liquid and the substrate. Some examples of the degree of wetting is shown in Table 14. Figure 19 demonstrates the wetting process of kenaf core (Paridah *et al.,* 2009).

Table 14 Relationships between contact angle and the degree of wetting

Contact angle	Degree of wetting	Strength of:	
		Solid/liquid interactions	Liquid/liquid interactions
θ = 0	Perfect wetting	strong	weak
0 < θ < 90°	high wettability	strong	strong
		weak	weak
90° ≤ θ < 180°	low wettability	weak	strong
θ = 180°	Perfectly non-wetting	weak	strong

Source: Eustathopoulos et al. (1999)

Figure 19 Wetting of kenaf core surface - A water droplet after 30 sec.(left); 1 min. (centre) and 5 min. (right). *Source*: Paridah *et al.* (2009)

Wettability and Buffering Capacity

Our research has shown that wetting is a necessary but not always sufficient for a strong bond, and that contact angle has been shown to detect changes in surfaces due to contamination or chemical modification. Adhesion properties such as wettability, pH, and buffering capacity of wood and non-wood are among the factors influencing the properties of most composite panel. Marra (1992), stated that the five steps of adhesive bond formation in a wood substance are: flow, transfer, penetration, wetting, and solidification. Wettability is one of the indicators of how well the substrate reacts with liquid. It is a quick method for predicting the gluability of an unknown species. Wetting of the surface by an adhesive is a necessary prerequisite to bond formation. A convenient method to measure wetting of a solid surface is through the determination of contact angle of a liquid. The wettability is a fast method for predicting the gluability of unknown wood and plant fibres which can be measured by determining the contact angle between the solid-liquid interface and liquid-air surface (Blomquist *et al.*, 1981). Another property that has great influence on the glueline formation is pH and buffering capacity. Buffer capacity measures the resistance of wood to change its pH level either in acid or in alkaline (Paridah *et al.,* 2001). This characteristic is very important for bonding of porous materials like plant fibres as it influences the pH of the adhesive/matrix at the boundary layers which eventually affects the rate of curing of the adhesive/matrix.

In conventional biocomposite manufacturing, thermosetting resin, namely urea formaldehyde (UF), melamine urea formaldehyde (MUF), and phenol formaldehyde (PF), are commonly use as binders. These adhesives are sensitive to the pH of the substrate since the rate of cross-linking of most thermosetting adhesives is pH-dependent (Blomquist *et al.*, 1981). Therefore, the formulation

of most adhesives is adapted to the acid range and buffer capacity of the substrate. According to John and Niazi (1980), the gelation time of UF resin is directly correlated to pH and is inversely dependent on acid buffering capacity. Thus, as pH is closely related to adhesive bond quality and total manufacturing cost, it must be considered as one of the more important factors in determining the suitability of the raw material. The effect of wood pH and buffering capacity has also been extensively studied in wood composite manufacture because of its effect on the curing of resins. For example, UF resin can decrease the gelation time when in contact with excessively acidic wood (Freeman and Wangaard, 1960). Similarly, the curing of PF resins is negatively affected by wood with high alkaline buffering capacity. It was reported that the pH and acid buffering capacity of aqueous extracts from crop materials were significantly higher than those of softwoods, and in the presence of such materials, resin gel time increased greatly (Wellon, 1980).

While contact angle indicates the ease of a liquid to spread and wet the surface, buffering capacity is a measure of resistance of wood or fibre to change in its pH level, either acidic or alkaline. Both the pH and buffering capacity significantly influence the rate of curing of the resin particularly at the interface and the boundary layers. In our study, the bonding characteristics of rubberwood (*Hevea brasiliensis*), sentang (*Azadirachta excelsa*), kenaf (*Hibiscus cannabinus*), oil palm (*Elaeis guineensirom)* fibres - from the stem and empty fruit bunch, and bamboo (*Gigantochloa scortechinii)* were evaluated by determining the (1) Wettability through contact angle measurement, and (2) Buffering capacity. Table 15 presents results of wettability and buffering capacity of rubberwood (RW) and different parts of kenaf - outer core, inner core, outer bast and inner bast.

Table 15 pH, wettability and buffering capacity of some natural fibre

Natural Fibre	Treatment/Part	pH	Initial contact angle (°)	Buffering Capacity (HCl)*	Buffering Capacity (NaOH)**
Rubberwood[1]	Untreated	5.49	58.6	10.5	6.4
	Whole stem	6.55	-	15.5	-
	Core	6.82	-	7.4	11.7
	Outer core	-	52.0	-	2.4
	Inner core	-	44.5	-	-
Kenaf[2]	Bast	7.94	-	24.8	5.9
	Outer bast	-	68.0	-	-
	Inner bast	-	60.7	-	-
Empty Fruit Bunch (EFB)[3]	Untreated	4.26	-	2.4	8.8
	NaOH soaking	7.80	-	13.2	8.4
	Water boiling	4.53	-	1.6	12.4
	NaOHsoaking+boiling	7.07	-	6.6	11.8

Untreated	5.6	-	-	-
Outer	-	47	1.5	9
Inner	-	46	3	10
LMwPF	6.5	-	-	-
Outer	-	79	7	6
Inner	-	92	7	8
MMwPF	6.6	-	-	-
Outer	-	62	9	6
Inner	-	67	7	5
Oil Palm Stem (OPS)[4] Commercial PF	7.8	-	-	-
Outer	-	50	11	5
Inner	-	52	12	5
Untreated:	6.42	-	7.5	1.0
Outer	-	15.3	-	-
Inner	-	14.6	-	-
Bamboo[5] (*Gigantochloascortechinii*) PF-treated	5.87	-	7.4	1.1
Outer	-	42.5	-	-
Inner	-	42.5	-	-

Note: [1] Paridah *et al.*, 2001; [2] Juliana *et al.*, 2012; [3] Norul *et al.*, 2013; [4] Norhafizah *et al.*, 2012; [5] Anwar *et al.*, 2006

Wettability

Kenaf

Figures 20 and 21 show that contact angle of wettability reduces as a function of time; a high contact angle was obtained at the initial liquid droplet as measured in 0.1 N HCl and 0.1 N NaOH. The trend is the same for all types and origin of fibre, *i.e.,* rubberwood, outer core (KOC), inner core (KIC), outer bast (KOB), and inner bast (KIB). Initially, KOB has the highest contact angle, followed by KIB, RW, KOC, and KIC. KIC has a low contact angle, revealing that it has high wettability, as evidently shown by spontaneous wetting which happens within 1 minute. This is due to the low specific gravity of the kenaf core plus the large number of voids in it. Meanwhile, RW took about 8 minutes for a complete wetting. It is obvious that kenaf fibres obtained from the bast have different bonding properties than those obtained from other parts of the stem. Fibres from this part appear to be low in wetting thus some manipulation in resin viscosity and/or incorporation of a coupling agent may be required to help adhesive/matrix penetration.

The fibres behaved differently when exposed to acid and alkali. KOB was observed to be stable in both acidic and alkaline conditions, although it seems to be relatively more sensitive in the latter (as shown by much gradual decrement of contact angle over time). In the case of KIB, KIC and KOC, they behave like rubberwood irrespective of the level of acidity. Like KOB, the decline in contact angle is much faster in alkaline than in acidic condition. This condition may be attributed to the higher amount of extractives in the bast which acts as a blockage at the openings between the cells, thus penetration of a droplet is inevitably prevented through the surface of the fibre. Abdul Khalil *et al.,* (2009) also reported that the amount of extractive is higher in kenaf bast (5.5%) than in the core (4.7%).

One of the contributing factors for the lack of wetting in KOB fibres is its relatively thicker cell walls.   As shown in Figures 22 (a-d), vast differences were observed for the cell wall thicknesses of respectively, KOB, KIB, KOC, and KIC parts. Other studies have reported similar observations; both KOB and KIB showed a wide variation of small-sized lumens [4.60–33.63 μm (Ali Ashori *et al.,* 2006) and 2.80 μm (Abdul Khalil *et al.,* 2010)],while KOC and KIC have bigger sized lumens [8.38–45.65 μm (Ali Ashori *et al.,* 2006) and 6.70 μm (Abdul Khalil *et al.,* 2010)]. The presence of vascular bundle gives some advantages for water transportation, or in this case, resins penetration. Conversely, bast fibres may have some difficulties in resin penetration due to the less porous cells available that limit the penetration of the resin adhesive.
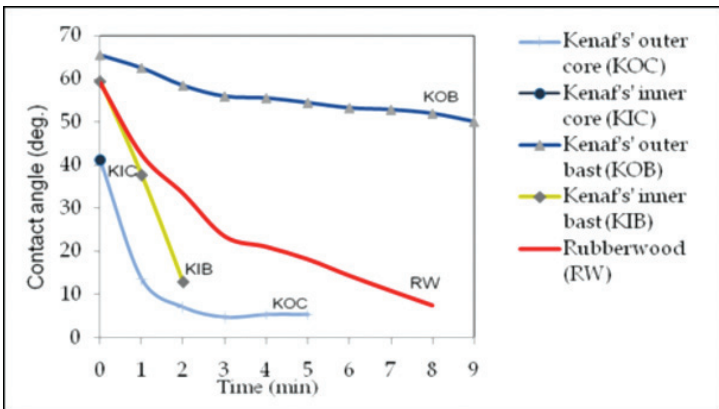

Figure 20 Contact angles of 0.1 N HCl solutions on different substrates as a function of time
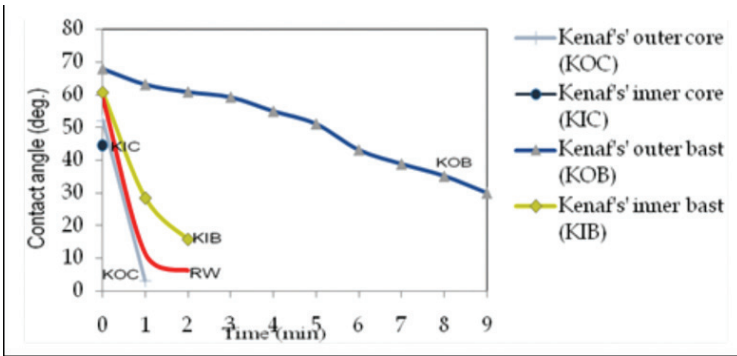
Figure 21 Contact angles of 0.1 N NaOH solutions on different substrates as a function of time
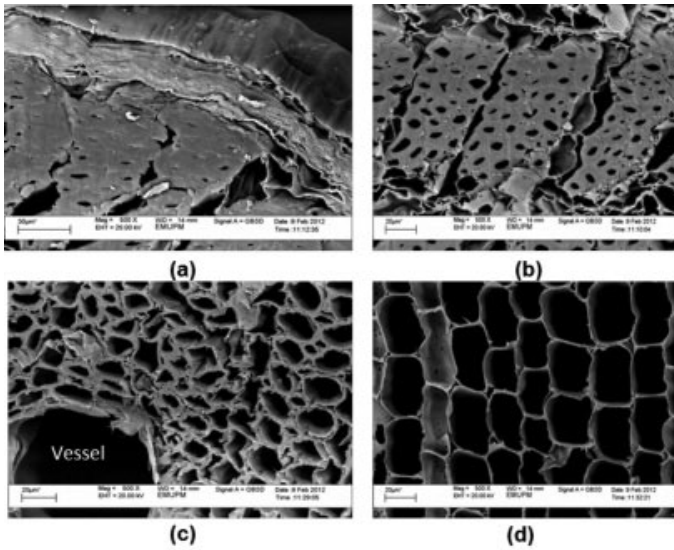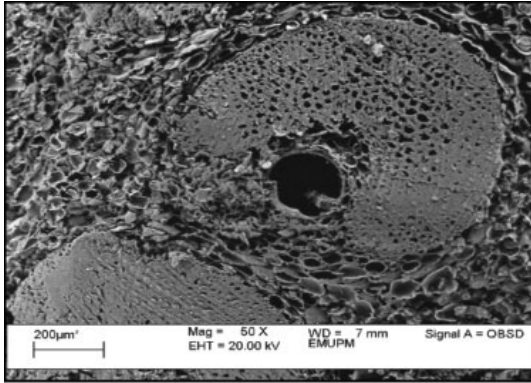

Figure 22 SEM of cross-sections of kenaf parts under 500x magnification: (a) Outer bast, (b) Inner bast, (c) Outer core and (d) Inner core (Juliana *et al.,* 2012)

Oil Palm Stem

The stem of an oil palm tree contains two distinct substances: solid vascular bundles and loose parenchyma cells (see below).

SEM of a cross section of oil palm stem

The two components not only vary in their anatomical structures, but also in density, which is the main factor that underlies various other problems such as in drying, machining, gluing, dimensional stability, and eventually the strength of the resulting products. One potential use of OPS is in plywood manufacturing, due to its long straight bole of almost cylinder shape, which can reach up to 8 m height. The difference in density throughout the tree stem generates very coarse veneer surfaces, which significantly contribute to adhesion problems, such as over penetration, uneven spreading, high resin consumption, and starved joints during plywood manufacturing (Loh *et al*., 2011).

Owing to its high porosity, OPS absorb water instantly. As shown in Figures 23 and 24, the untreated OPS veneer (control) experienced a spontaneous wetting, *i.e.,* $\Theta = 0$ within 15 s. Veneers from the inner section of the stem relatively were much faster

(within 10 s), almost instantaneously. NorHafizah *et al.* (2012) treated the OPS veneers with phenol formaldehyde resin and pre-cure the veneers to control the adhesive penetration. They claimed that this method was able to reduce the wettability of the surface by at least 100%. As can be seen in the figures, the longer and less steep trend lines indicate a significant reduction in the rate of absorption by the phenolic-treated surfaces.
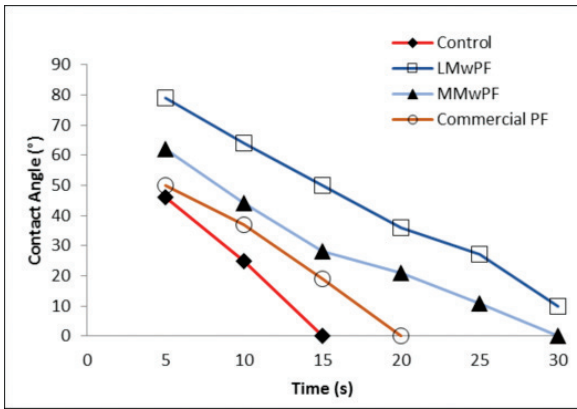

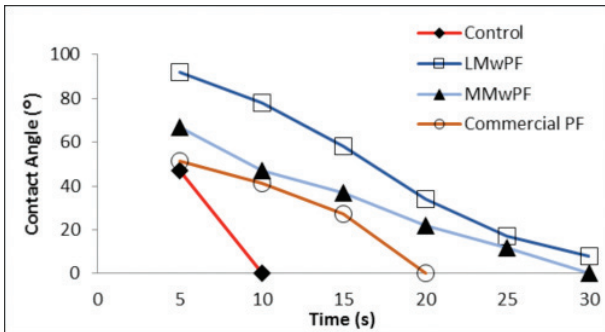**Figure 23** Contact angle of distilled water on outer section of OPS Veneer as a function of time

Figure 24 Contact angle of distilled water on inner section of OPS veneer as a function of time
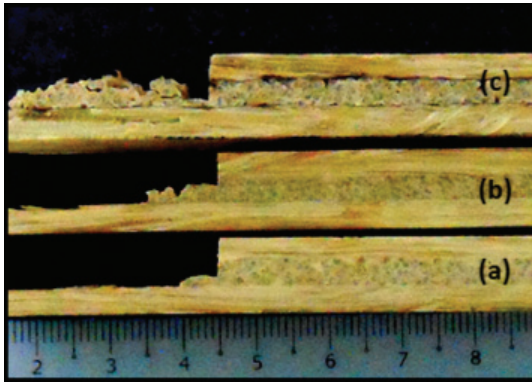
Figure 25 Differentiation of glueline in phenolic treated 3-ply palm plywood
(a) LMwPF, (b) MMwPF and (c) commercial PF resin
(NorHafizah *et al.,* 2012).

Bamboo

Bamboo strips usually generate smaller contact angle within a short time due to higher surface wettability (Mansur, 2000; Anwar, 2003; Seyoum, 2005). This statement is not usually true for some bamboo. Ahmad and Kamke (2003) claimed that contact angle does not really depend on the density of the material. They found the contact angle of water droplet on Calcutta bamboo (density 630 kg/m³), yellow poplar (380 kg/m3),and white oak (710 kg/m3) were 52°, 51° and 50° respectively. They also found that the buffering capacity and contact angle of Calcutta bamboo are very similar to those of wood. Conversely, Anwar *et al.,* (2003) reported that the wettability of Semantan bamboo is much higher than that of rubberwood which posed a problem in gluing. To overcome this problem, they soaked bamboo strips in low molecular weight phenol formaldehyde resin and pre-cured it prior to a normal gluing. Such treatment has successfully reduced the wettability of the bamboo

to an acceptable rate. The remarkably improved rate of wetting for phenolic-treated samples is due to the partially cured LMwPF resin that remained on the surface, which also filled the parenchyma cells of the bamboo preventing the water to instantly penetrate the cells. Figure 26 demonstrates the wettability of outer and inner surface of untreated and phenolic-treated bamboo strips. Both outer and inner surfaces behaved similarly as the contact angles of water droplet gradually decreased within 1 minute in untreated, and > 30 min in phenolic-treated strips.
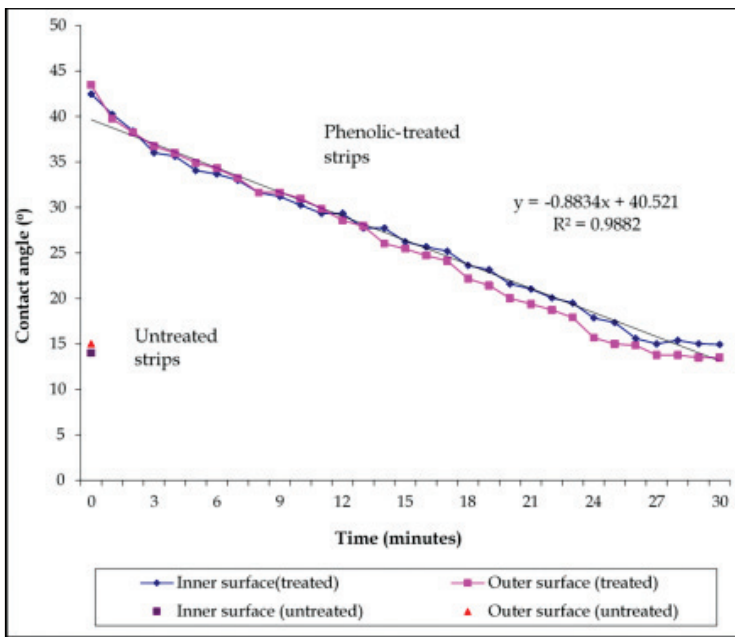

Figure 26   Contact angle vs. time (minutes) of phenolic-treated and untreated strips (Anwar *et al.,* 2003)

Buffering capacity

Buffering capacity measures the sensitivity or stability of the fibre to change in pH, either in acid or in base/alkali. Maloney (1993) defined buffering capacity as the resistance of wood or woody material to the change in its pH level. A low buffering capacity indicates the fibre material is less stable or sensitive towards a change in pH. As wood and plant fibres are porous materials, the adhesive flows into the surface and form an interface between the substrate and liquid. As the liquid adhesive penetrates further into the wood cells, the voids will be filled with liquid adhesive which eventually form two types of boundary layer: (i) between adhesive and interface - denoted as rings number 2 and 3 and (ii) between wood cells and interface - rings number 6 and 7 (refer Figure 15). If the substrate has low buffering capacity, the pH at these layers as well as that of interface will be changed easily which can either accelerate or impede the curing of the binders. On the other hand, when the substrate possesses a high buffering capacity the pH will not change easily unless a larger quantity of acid catalystis added to decrease the pH to the level for an ideal resin cure (Maloney, 1993). Depending on the species and type of fibre, the pH of the resin could significantly drop when in contact with the wood surface. Different types of fibres have different level of buffering capacity (in acid or base), thus assessment of this property for each type of fibre is crucial to ensure sufficient curing of the resin so that good bonding can be formed.

Wood

Knowledge of the pH and buffering capacity of wood is fundamental for the efficient use of wood in gluing and coating processes particularly where the resin polymer used is pH-sensitive. Wood acidity varies between trees of the same species, within a tree,

and the location along the tree stem. Generally, most resin binders used in wood composite cure at the rate governed by the pH at the glueline. Any changes in pH at the glueline will significantly affect the rate of curing, and consequently, the resulting bond strength. For instance, urea formaldehyde resin is acid catalysed, and cannot be used to an optimum state-of-cure in a low acid environment. The ability of the adhesive to cure on a substrate depends greatly on the condition of the wood surface. Since the rate of cross-linking of most thermosetting adhesives is pH-dependent, these adhesives will be sensitive to the pH of the substrate. In order for the resin binders to cure properly in the furnish (mixture) of a board, an appropriate acidity must be established. Urea-formaldehyde (UF) and melamine urea formaldehyde (MUF) resins are accelerated in an acidic environment, but most phenolic resins used for wood-based composite require a base environment for cure. Hence the formulation of most adhesives is adapted to the acid range of the substrate, and a wide deviation of this value will create difficulties in providing a superior adhesive bond. Thus, pH value and buffering capacity of any material intended for the manufacture of an adhesively-bonded composite have to be known. A single species of wood, or any woody material, that possesses high variability of buffering level could be an important issue, and this problem is magnified when multiple species are used.

Hernandez (2011) investigated the effects of age and location in stem on the pH and buffering capacity of radiata pine sapwood. Experimental results support the hypothesis that these chemical properties can change significantly in trees of the same specie harvested at different ages and within samples extracted from different locations in the same tree. General trends showed that juvenile wood tend to be more acidic than mature wood in 25 and 30 year-old trees. Variations with the age revealed that while

mature wood decreased its acidity, showing no relevant changes in its buffering capacities, juvenile wood increased both its acidity and buffering capacities. In terms of height, mature and juvenile wood tend to be more acidic in the lower sections of the trees, but differences in buffering capacity were observed only in juvenile wood.

Paridah *et al.* (2001) studied the wettability of rubberwood and sentang wood and found that the former has a higher degree of wetting. Since the vessel size and the amount of extractives in both rubberwood and sentang are almost similar (Goh, 1996), the fast absorption by rubberwood can be attributed to the capillary action generated by the moisture in the wood cells. Adsorption can occur in rubberwood (EMC 12%) much easier than in the wetter sentang (EMC 13.5%). The higher wettability of rubberwood suggests that it requires shorter assembly time during bonding process since the adhesive could easily spread and penetrate into the wood surface. If the surface is left open for a relatively longer period (longer assembly time) most of the adhesive would be absorbed into the wood, leaving a starved joint thus lowering the bond quality. Sentang apparently requires a slightly longer assembly time during the bonding process than does rubberwood.

Kenaf

Table 16 represents the pH and buffering capacity values for the extracts of kenaf whole stem (KWS), kenaf core (KC), kenaf bast (KB) and rubberwood (RW). Both pH and buffering capacity are important factors influencing the curing behaviour of a resin. The extracts of almost all these materials were found to be acidic. According to Mantanis and Young (1997), all the wood surfaces have a very strong acidic characteristic because the strongest interactions occurred with formamide, which is a basic probe,

while much weaker interactions occurred with ethylene glycol which is an acidic probe. This behaviour can be explained by the presence of acidic-type functional groups, specifically, carboxylic acid groups, on the surfaces of the fibres. As shown in Table 16, crop fibre such as kenaf exhibits higher pH value than the control RW samples, indicating that RW has more acidic properties than kenaf. The control RW samples gave a strong acid value of pH 5.49. Kenaf has been identified as a non-wood material, which commonly possesses higher pH than softwoods and hardwoods. KWS gives higher acidity properties as compared to the KC and KB with the pH value of 6.55, 6.82, and 7.94, respectively. Studies by many researchers found that most field crops and biomasses are less acidic than wood; the pH of wheat straw was 6.83 (Zhang *et al.,*2003).

Figures 27 and 28 compare the buffering capacities of KWS, KC, KB, and RW in both acidic and alkaline conditions. The choice of pH condition depends on the type of adhesive use, *i.e.,* acid-curing resin like aminoplasts or alkali-curing resin like the phenolics. The study indicates that KWS, KC, and KB are more stable in acidic than in alkaline conditions since it required more amount of acid to reach pH 3.0 compared to the amount of NaOH required to reach pH 10.0. Whole stem kenaf (bast and core parts are intact) was observed to be more resistant in both acid and alkali than in separated form – bast and core. KB appears to be more stable in acid as shown by the significantly longer trend lines and a gradual slope (Figure 27) which is opposite to that of alkali (Figure 28).

Table 16 The pH and buffering capacity values of kenaf whole stem, kenaf core, kenaf bast, and rubberwood

Materials	pH	Acid* 0.1N (HCl) (ml)	Alkali** 0.1N (NaOH) (ml)
Kenaf whole stem (KWS)	6.55[c]	15.5[b]	11.7[a]
Kenaf core (KC)	6.82[b]	7.4[d]	2.4[d]
Kenaf bast (KB)	7.94[a]	24.8[a]	5.9[c]
Rubberwood (RW)	5.49[d]	10.5[c]	6.4[b]

Note: Values are average of samples.

* The amount of acid needed to reach pH3.0

** The amount of alkali needed to reach pH10.0

Means followed by the same letters [a,b,c,d] in the same column are not significantly different at p≤0.05 according to Least Significant Difference (LSD) method. (from Juliana *et al*., 2013)

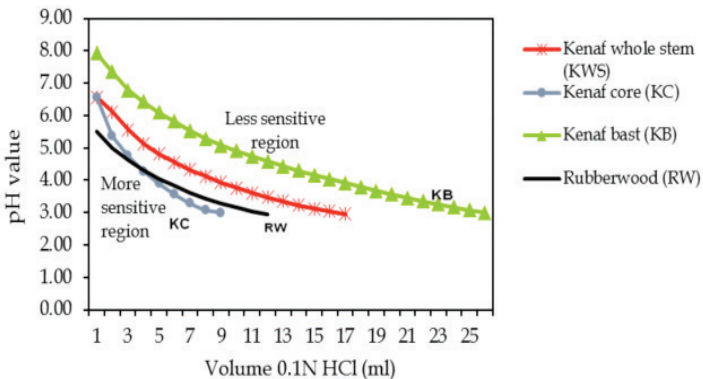**Figure 27** Comparative stability of different parts of kenaf stem and rubberwood in acidic liquid. (from Juliana *et al.,* 2013)
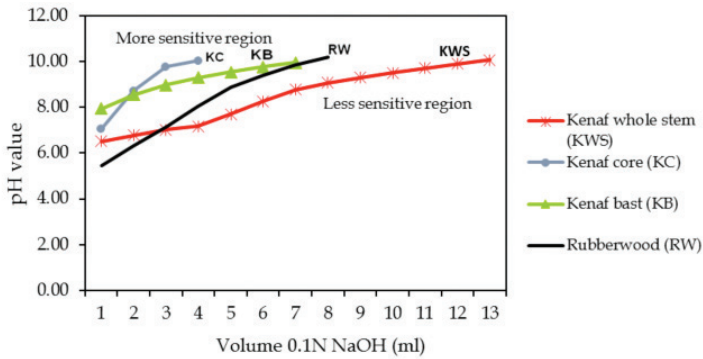
Figure 28 Comparative stability of kenaf stem and rubberwood in alkaline liquid (from Juliana *et al.,* 2013)

Apparently, KWS and RW produced almost a similar trend in acidic condition. High acidity properties in KWS helps to better cure the aminoplast resins (urea formaldehyde or melamine urea formaldehyde), resulting in relatively higher bond strength. According to Juliana *et al.* (2012) and Han *et al.* (2001), better acidity properties of the treated wood/straw particles help improve the bondability between these particles and acid-setting UF resin, and thus the performance of the resulting particleboards. Meanwhile, KC has been observed to be the most sensitive kenaf parts towards both acid and alkali. As seen in both figures, KC has much steeper and shorter slopes thus its buffering capacity is low. The results suggest that bonding of KC with either aminoplast or phenolic resins requires an addition of buffering agent to control the curing rate.

Empty Fruit Bunch (EFB)

Oil palm empty fruit bunch (EFB) fibres are residues from palm oil mills which are generated after steaming and oil extraction

processes. Inevitably, the amount of residual oil retained in EFB is about 2-3 % (w/w), sufficient to affect the gluing properties of this fibre, in particular the pH and buffering capacity. Norul Izani *et al.* (2013a) reported that EFB, without any pre-treatment is sensitive to acid but quite stable in alkali. As shown in Figure 29, the rate of change in acidic pH was greater in untreated fibres as shown by a steeper slope as compared with other treated fibres. Boiling was found not to be effective in improving the acidic buffering capacity of EFB. While soaking in NaOH increases the buffering capacity significantly, soaking in NaOH followed by boiling in water generates fibres of medium level of buffering capacity.
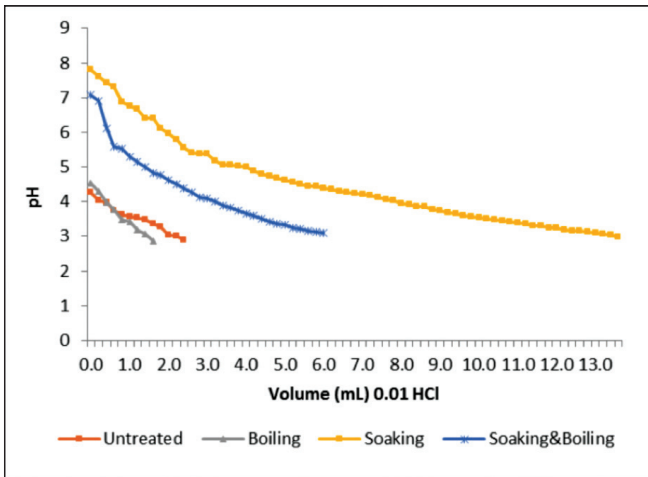

Figure 29 Comparative stability of different EFB fibre treatments under acidic conditions (NurulIzani *et al.,* 2013a).
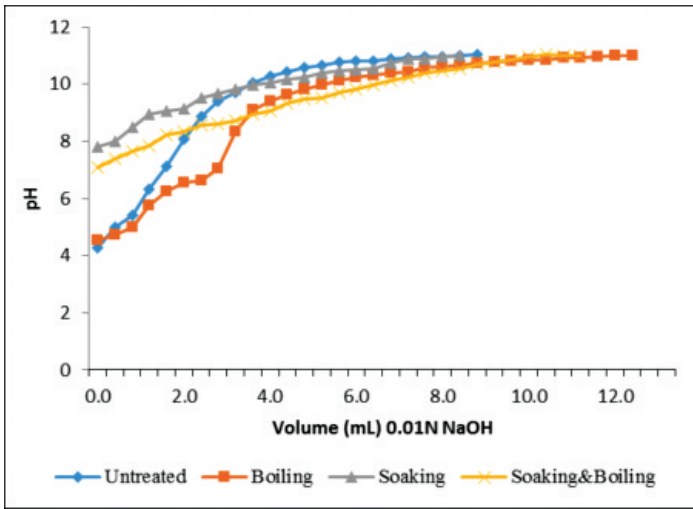
Figure 30 Comparative stability of different EFB fibre treatments under alkaline conditions (Norul Izani *et al.,* 2013a).

Oil Palm Stem (OPS)

Like many other lignocellulosic materials, oil palm stems are slightly acidic (pH 5.6), which is quite similar to some wood such as rubberwood and bintangor (*Calophyllum* spp.). Such a characteristic is not unusual, since the oil palm tree was reported to be tolerant of high acidity and is able to grow well under a broad range of soil pH, from 4.0 to 5.5. Because of it's anatomical structure, OPS is relatively poorer in properties. Thus several researchers has used phenolic resin to enhance it's strength and durability. Such treatment, however changes the buffering capacity of the OPS material.

Norhafizah *et al.* (2012) reported that after being soaked in PF resin (initial pH 8.5 to 12.7), the pH values of phenolic-treated OPS veneers ranged from 6.5 (using low molecular weight PF - LMwPF),

and to 7.8 (commercial PF). The pH values of untreated and phenolic-treated oil palm stem (OPS) veneers during the addition of alkali and acid are shown in Figures 31 and 32, respectively. Observation of the trends revealed that the untreated and phenolic pre-preg OPS veneers behaved differently towards alkali and acid. The inner section veneers treated with medium molecular weight PF (MMwPF) resin and both sections of OPS veneers treated with commercial PF resin were sensitive to alkali; it required 5.0 mL of NaOH to reach a pH of 11.0 (Figure 31). This is probably due to the high pH values of alkaline PF resin (pH 9.7 for MMwPF resin, and pH 12.7 for commercial PF resin) when compared to LMwPF resin (pH 8.5). The outer layer veneers treated with MMwPF resin and the inner section treated with LMwPF resin presented similar trends with slightly different volumes; it required a mere 6.0 mL NaOH to reach a pH of 11.0.

As can be seen in Figure 32, when exposed to acid conditions, both control outer and inner sections of OPS veneers were more sensitive to acid; respectively 1.5 mL and 3.0 mL HCl were used to reach a pH of 3.0. Among phenolic-treated OPS veneers, both sections of OPS veneers treated with LMwPF resin were more sensitive to acid, which needed 7 mL HCl to reach a pH of 3.0.
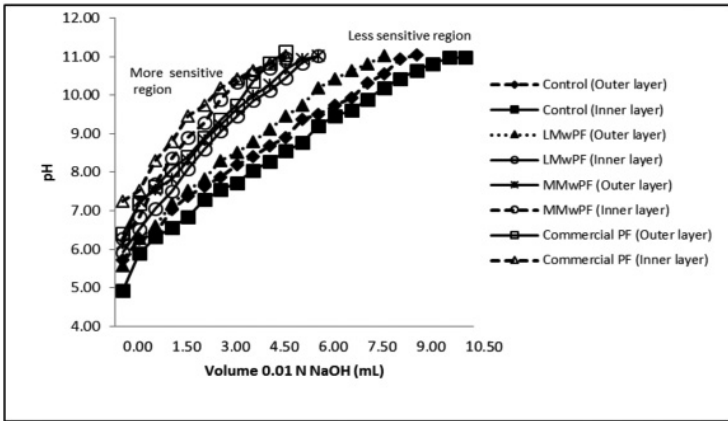
Figure 31 Changes in pH of oil palm stem veneers during alkali addition
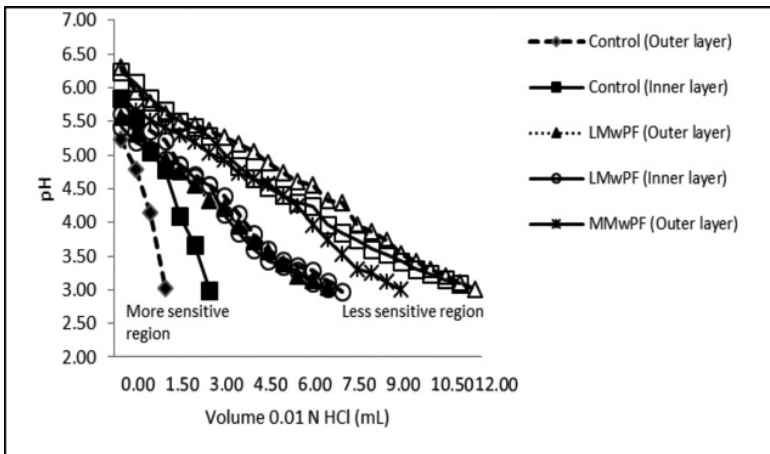
Figure 32 Changes in pH of oil palm stem veneers during acid addition

Bamboo

Figures 33 and 34 illustrate the trend of buffering capacity on untreated and phenolic-treated strips of bamboo *(G. scortechinii).* Similarly with OPS, bamboo is a monocot, thus the presence of parenchyma tissues in the cell anatomy creates instability of the material. Anwar et al. (2012, 2006) treated bamboo strips with LMwPF and observed the buffering capacity. They found that the buffering capacity of both untreated and phenolic-treated strips of *G. scortechinii* did not differ much (Figures 32 and 33). Between the two conditions, it appears that bamboo is slightly more sensitive towards acidic condition (as shown by the more curvilinear trend lines).
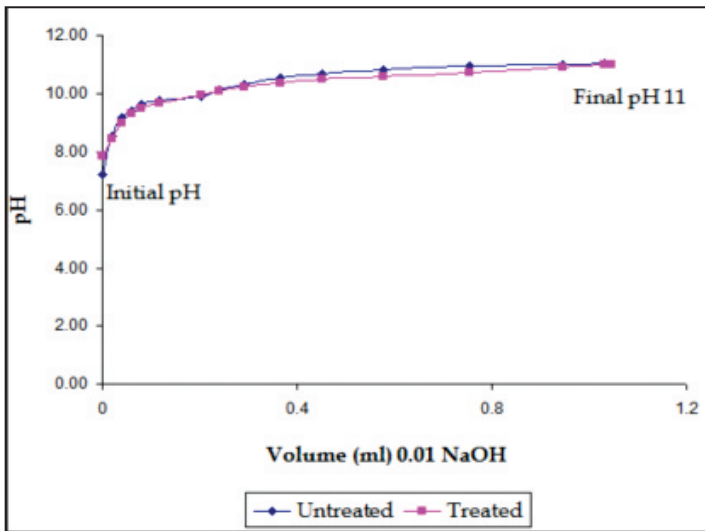
Figure 33 Buffering capacity of bamboo strips in alkaline condition
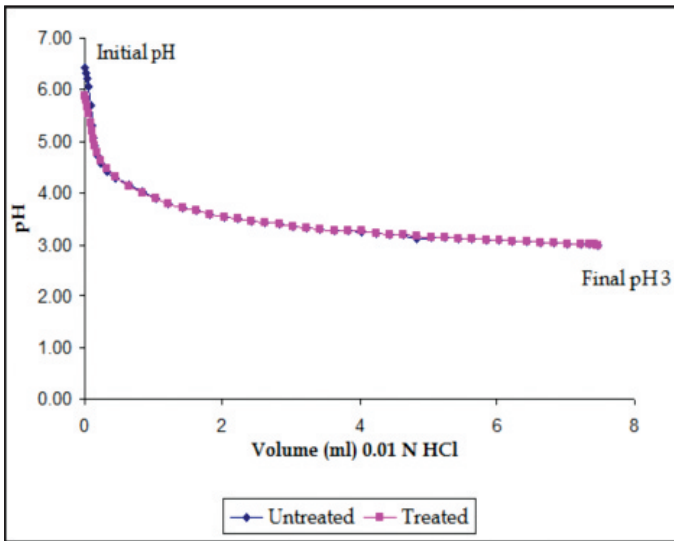
Figure 34 Buffering capacity of bamboo strips in acidic condition

The finding on buffering capacity of bamboo strip is in good agreement with Zaidon *et al.* (2004). They suggested that when an alkaline resin (i.e., phenol formaldehyde) is spread onto the bamboo surface, the adhesive at the boundary layers change its pH to slightly lower than normal, just enough to slow down the curing rate of the PF resin, which normally occurs between pH 11 to 12. This would not happen if the binder is an acid curing resin, *i.e.,* aminoplast resin, since *G. scortechinii* is stable in acid. In general, our studies show that the pH values of rubberwood, kenaf, EFB, OPS and bamboo are on the acidic side, except for kenaf bast (pH 7.94). Among the fibres studied, kenaf bast (KB) appears to be the most stable in either acid or alkali conditions.

Adhesion Problems in Natural Fibre

Inorganic adhesion resembles synthetic resin adhesion, where the interfacial bonding between two different materials may involve chemical or physical bonding mechanisms as well as mechanical interlocking (Frihart, 2013). The formation of hydrogen bridges can be proven by testing wet and dry composite samples. Dry composites usually showed high strength properties, which can be explained by a high number of hydrogen bonds or hydroxyl bridges. On the other hand, the hydrogen bonds of the wet samples are destroyed by the insertion of water molecules between the bridging hydroxyl groups due to the pressure of the swollen cellulosic fibres, and thus, development of frictional forces between the fibres and binders.

Depending on the cells fracture, processing of wood/fibres into particles or pulp can create many types of surface attributes as illustrated in Figure 35, Frihart, (2013). When the cell walls are cleaved in a longitudinal trans-wall fashion, the lumen will be the large part and main bonding surface in all natural fibres, especially for early wood cells of softwoods, and vessel elements in hardwoods, kenaf core, and metaxylem in palm and bamboo fibres. The composition of lumen walls can vary between being highly cellulosic, to not, especially if the S3 layer is exposed to high lignin, or if they are covered by a warty layer. The middle lamella is also found to be rich in lignin. However, for the most part it is difficult to know when the walls are fractured if the cleavage plane runs through any of the three main fractions or between the lignin-hemicellulose boundaries, which may be the weakest link in the wood cellular structure. The most complicated issue of the bonding surface is the typical mechanical way of providing binding surfaces that cause a lot of fragmentation and smearing of the cell wall components. The clean splitting of the cell walls can only be

viewed by applying a careful microtome sectioning, while, other techniques give surfaces that are less intact (Frihart, 2013). Thus, the theory of many open lumens into which the adhesive can flow is not always correct, and this can be proven by the fact that penetration of the adhesive into the lumens is not always that fast. The major factors that influence the interaction between fibres and matrix are the matrix composition (cracked or uncracked), fibres geometry, fibres type, fibres surface characteristics, fibres orientation, fibres volume, and the overall durability of the composite.
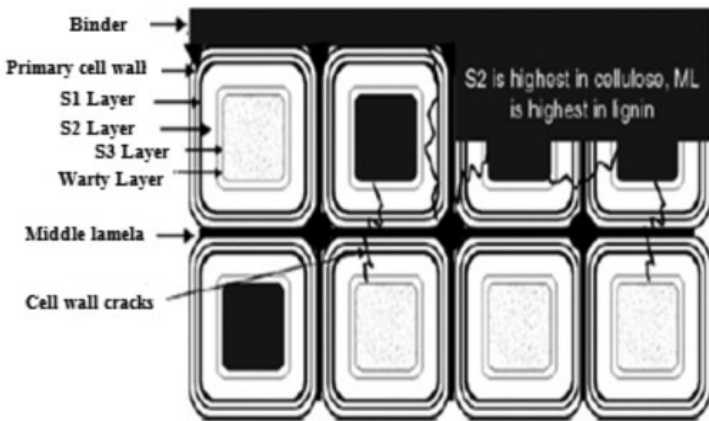
Figure 35 Illustration of a transverse section of wood showing fracture points of the wood cellular structure and surfaces available with which binders can interact, assuming clean fractures are occurring
(*Source*: Frihart, 2013)

Surface Inactivation and Adhesive Bonding

From the instant an adhesive/matrix is applied to natural fibres (wood and other plant fibres) until the adhesive/matrix cures (*i.e.,* setting into solid), several important steps must take place in order

for a good bond to occur. In the majority of bonding processes, adhesive/matrix is normally applied onto the surfaces of the fibres using various techniques that suit the manufacturing process and products. Regardless of the technique used, the most important criterion is that the adhesive/matrix must flow and transfer properly to achieve a glue line which uniformly covers the surfaces of the fibres. Also, the adhesive/matrix must penetrate into the fibre surfaces, filling the small voids caused by pores, checks, and other anatomical features. One step further than penetration is wetting. While penetration allows the resin polymer to contact the fibre deep in the crevices on the fibre surface, wetting involves the attraction of the liquid adhesive/matrix to the fibre surface *via* molecular forces. Finally, the adhesive/matrix must solidify. If any of these actions do not occur, the glue bond will be faulty. Such is the case when gluing fibre which is surface inactivated. The definition, causes, and prevention of surface inactivation in natural fibres (including wood and plant fibres) will be discussed below. Some of the discussion refers to bonding of wood however the explanation can also be applied to other plant fibres.

Lack of adhesion in MDF made from empty fruit bunch (EFB) fibres caused by low surface wetting (Norul Izani *et al.*, 2013).

Surface Inactivation

Inactivation of surfaces occurs when the fibre will not allow wetting to happen. An attempt to glue surface inactivated fibre results in weak glue bonds. The poor bonding can evidently be seen from a broken glue line with either the imprint of the opposite surface

and an occasional loose fibre embedded in the glue – in the case of laminated fibre composite, or protruding fibres – in the case of homogeneous fibre reinforced composites. The appearance of the opposite surface would indicate that penetration took place (the adhesive/matrix filled the voids on the fibre surface), however, if the fibre is surface inactivated, the adhesive/matrix would not be attracted to the fibre molecularly, thus a weak bond occurred at the binder-fibre interface.

To better understand how to prevent problems associated with surface inactivated fibres, a simplified explanation of the wetting phenomenon is presented. The components which make up natural fibres are held together by strong molecular forces. When wood and plant fibres are processed, essentially what happens at the molecular level is the breaking of the bonds between fibre components. Where molecules once joined are now open bonding sites which possess strong attractive forces (open bonding sites are unstable and molecules desire stability). The higher the number of available bonding sites, the greater will be the total attraction. It is this attraction which gives freshly machined wood and plant fibres its wettability (Frihart, 2013). Water, gases, microscopic dust and dirt particles, extractives in the fibres, and adhesives are all likely candidates for open bonding sites. The longer freshly machined wood is exposed to the atmosphere, the more of these bonding sites will be taken by gases and pollutants, and less will be available for the adhesive/matrix. This is why wood and plant fibres lose its wettability over time and the surface becomes inactivated.

Heat is another factor that increases the chance of an inactivated surface. Heat increases the movement of extractives which exist in the natural fibres, increasing the chance that they will move to the fibre's surface and attach to open sites. In addition, severe heat

can actually alter the chemistry of fibre components, destroying available bonding sites. Such is the case with wood lumber or veneer that has been dried too harshly, a condition often erroneously referred to as casehardening in the wood-based industry.

Fibre may easily be tested for surface inactivation simply by placing a drop of water (using an eye dropper) gently on the surface of the fibre. If the drop sits high on the surface and retains a round shape, surface inactivation is suspected. If the drop sits flat on the surface and begins to take on an oblong shape parallel to the grain, the fibre surface is not inactivated. Another test is to time how long it takes for the drop of water to absorb into the fibre. If the fibre surface is not inactivated, the drop will absorb in several minutes or less. In severely surface inactivated fibre, the water will actually evaporate before it can be absorbed.

NATURAL FIBRE COMPOSITE

The term "Biocomposite" is used mainly to describe composites that are made up of natural fibres such as wood and other plant fibres, and a resin polymer as a binder/matrix. Wood composites like plywood, glulam, laminated veneer lumber (LVL), laminated board, oriented strand board (OSB), particleboard, medium density fibreboard (MDF) are traditional composites which comprise between 87-97% (w/w) wood or other plant fibres, while the rest is the binder. The strength of these biocomposites depends very much on the wood/ fibre properties which varies from non-structural (as in furniture parts for particleboard and MDF) to high load structural loading (as in beam and columns for LVL and glulam). The binders used for these biocomposites are mainly formaldehyde-based resins such as urea formaldehyde, melamine formaldehyde, phenol formaldehyde, resorcinol formaldehyde either in pure and fortified forms.

Wood plastic composite (WPC) on the other hand, are composite materials made of wood fibre/wood flour and thermoplastic or thermoset resins. Some examples of thermoplastics include polyester (PE), polypropylene (PP) and polyvinyl chloride (PVC), and those of thermosets are epoxy and the phenolics. Since The first oil crisis in 1973, WPC have become engineering materials with a very wide range of properties. The first generation WPCs uses recycled woodchips/flour and polymer binder, designed for undemanding applications. The new generation WPCs, are high performance products, with good mechanical strength, high dimensional stability, having complex shapes of high dimensional tolerance. This new generation WPCs are produced by mixing wood flour or fibre and plastics to produce a material that can be processed like a conventional plastic and has the best features of wood/fibre and plastic. The main reason for using wood/fibre (in the form of powder or fibre) in WPC is to modify the mechanical strength of the plastic. In this case the role of wood is twofold: as fillers, similar to talc and calcium carbonate, and as reinforcements, like glass and carbon fibres. Being of lower density than the inorganic fillers and reinforcements, WPC has many advantages; lighter, lower cost in transportation, attractive appearance, and can be labelled as 'green' materials. WPC offers a wide range of products for industries such as automotive, building, furniture, house-hold goods, *etc.* Key to this advancement is the development in compounding equipment and additives to suit many sources of fibre materials. Both process technology and materials are continually improving and new compositions and processes are being intensively researched, developed and applied. The times of simply mixing plastics with natural waste fillers and characterising their main properties are gone.

Natural Fibres *versus* Synthetic Fibres

The engineering applications of polymer matrix composites involve the use of a variety of short or continuous fibres bound together by an organic polymer matrix. Unlike a ceramic matrix composite, in which the reinforcement is used primarily to improve the fracture toughness, the reinforcement in FRC provides high strength and stiffness. A fibre reinforced polymer composite (FRPC) is a composite material consisting of a polymer matrix imbedded with high-strength fibres, such as glass, aramid and carbon (Rowell, 2013. Mohanty *et al.*, 2001). Unlike the conventional wood composite or wood plastic composite, the "new" generation of FRPC uses short or long fibres that can be arranged in many ways: uni- or multi-directional lamination, woven and non-woven and pultruded yarn. The new advance composites offer wider range of products and applications. Kozlowski (2006) prioritised the uses according to their costs as follows:

Hierarchy of Uses and Costs

Market Sector	Costs
– Space	– Nano tubes
– Military	– Metal alloys
– Recreation	– Carbon fibers
– General construction	– Ceramics
– Housing	– Glass fibers
– Misc	– Synthetic polymers
	– Inorganics
	– Plastics
	– Biomass
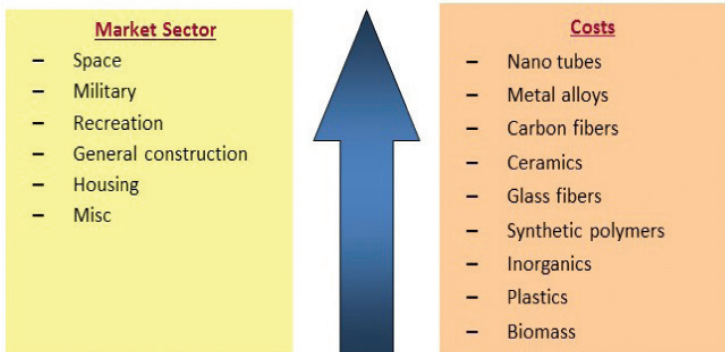
Courtesy by Kozlowski, 2006

The distinction between reinforced and "advance" fibre reinforced composites is based on the level of mechanical properties (usually strength and stiffness); however, there is no clear line separating the two. Reinforced plastics, which are relatively inexpensive, typically consist of polyester resins reinforced with low-stiffness glass fibres. Carbon and aramid fibres are normally used in advanced composites; having superior strength and stiffness, relatively expensive and used primarily in the aerospace industry. Their main advantage is light weight coupled with high stiffness and strength along the direction of the reinforcement. This combination is the basis of their usefulness in aircraft, automobiles, and other moving structures. Other desirable properties include superior corrosion and fatigue resistance compared to metals.

Many of these FRCs are designed so that the mechanical loads to which the structure is subjected in service are supported by the reinforcement. The function of the matrix is to bond the fibres together and to transfer loads between them. Thus an efficient bond formation between the two components is a challenge. The aim is to get a high strength engineering composite and to reach the level of glass fibre composite (GFC), or even to substitute GFC in near future. Some of these properties can be achieved by using natural fibres as a replacement for glass fibres and aramid (see Table 12). Ashby and Cebon (2002) mapped the Young's modulus against density for different classes of materials (Figure 36) and claimed that wood and fibre materials have much higher specific modulus when compared to ceramic and metals.

Nevertheless natural fibres are not without disadvantage when compared to synthetic fibres. There are limits that natural fibre can do due to its' characteristics as listed in Table 17.
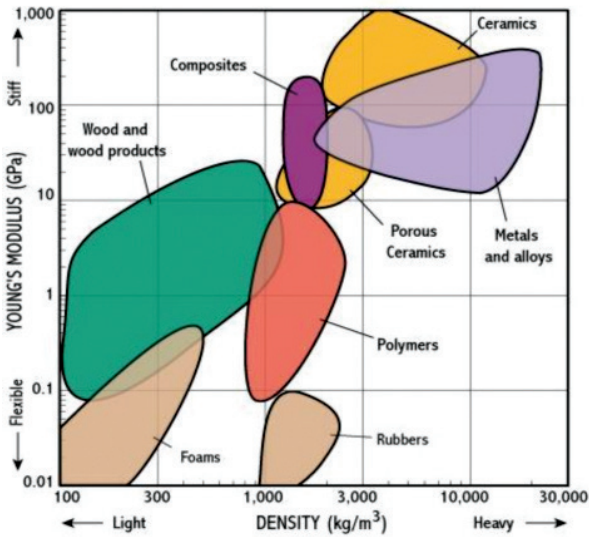
Figure 36 Young's modulus against density
(Ashby and Cebon, 2002)

Table 17 Some advantages and disadvantages of natural fibres

Advantages	Disadvantages
• Low specific weight, which results in a higher specific strength and stiffness than glass. This is a benefit especially in parts designed for bending stiffness	• Lower strength properties, particularly its impact strength
	• Restricted maximum processing temperature
• It is a renewable resource, the production requires little energy, CO2 is used while oxygen is given back to the environment	• Moisture absorption, which causes swelling of the fibres

• Producible with low investment at low cost, which makes the material an interesting product for low-wage countries	• Variable quality, depending on unpredictable influences such as weather
• Friendly processing, no wear of tooling, no skin irritation	• Lower durability, fibre treatments can improve this considerably
• Thermal recycling is possible, where glass causes problems in combustion furnaces	• Price can fluctuate by harvest results or agricultural politics
• Good thermal and acoustic insulating properties	• Poor fire resistance

Challenges in Natural Fibre Composites

Increasing the use of natural fibre composites (NFC) has significant potential for positive environmental outcomes, but achieving this will require addressing major challenges, as well as choosing the right applications in the short term. Some of the challenges are listed below.

Characteristics of the Natural Fibres

Of all the natural fibres available, bamboo and bast plants may probably have the most potential to replace GRF and aramid simply because they have sufficient individual fibre length and the strength. Wood and plant fibres are hierarchical, thus require a combination of processes - natural (known as retting but is not applicable to wood), mechanical and chemical to separate the fibres. During these processes inevitably some high value fibres are being removed. Bos *et al.* (2006) described the hierarchy of fibres and fibrils found in the flax fibre as in Figure 36.
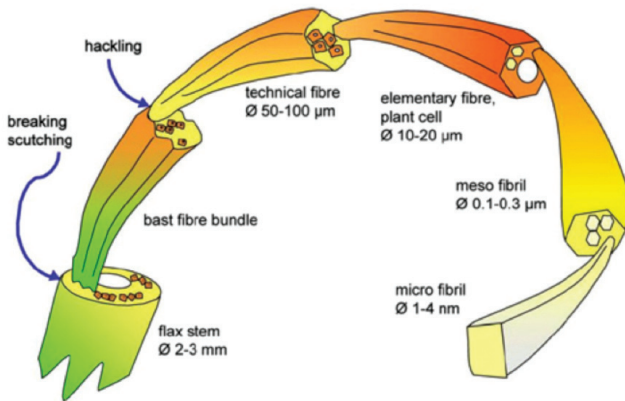
Figure 36 Hierarchy of flax fibres (Bos et al., 2006)

Depending on the technique used, some elementary fibres can be economically processed into smaller diameter similar to synthetic fibres. Fibres are variable due to factors such as whether they were derived from the top or the bottom of the plant. They also have flaws based on growth patterns and harvesting. For these reasons, quoted performance values in the literature are widely scattered.

Moisture Absorption

Another feature of natural fibre is their hollow nature which is responsible for moisture absorption. As mentioned earlier, natural fibres primarily consist of: cellulose, hemicelluloses, pectin and lignin. The individual percentage of these components varies with different types of fibres. Cellulose is a semicrystalline polysaccharide and is responsible for the hydrophilic nature of natural fibres. Hemicellulose is a fully amorphous polysaccharide with a lower molecular weight compared to cellulose. The amorphous nature of hemicelluloses results in it being partially soluble in water and alkaline solutions (Winandy, 2013). Pectin,

whose function is to hold the fibre together, is a polysaccharide like cellulose and hemicellulose. Lignin is an amorphous polymer but unlike hemicellulose, lignin is comprised mainly of aromatics and has little effect on water absorption (Rowell, 2013; Winandy, 2013).

Geographical Availability

Availability and geographical location are another factors need to be considered in using natural fibres. The low cost of these fibre raw materials can be easily cancelled out if they must be transported over long distances. For instance, flax is cultivated and used a lot in the more humid areas of Northern Europe, whereas jute, sisal or kenaf are found in the more arid parts of the world. Hemp has an advantage over other plants in that it is easily cultivated pretty much everywhere from Canada to South Africa, including Europe and China. Within their respective areas of production, all of these fibres are comparably priced (Paridah *et al*., 2011; Mougin, 2006).

Sustainability in Supply

The future of a natural product is always a question of its availability over time, and more particularly of the ability of its producers to meet the demand, especially in an upbeat market. This is not really a problem for natural fibres, however, because for all plants considered, there are enough cultivable areas in all the production countries to follow market trends. To keep up with the growing market, you must not only increase the surface cultivated, but also create facilities for processing the plants so the fibres can be used. Such facilities are relatively costly.

Consistent Fibre Quality

The composition of natural fibres is not the same, even when they are of the same species – it varies not only from one type of fibre to another, but also as a function of how and where the plant is cultivated. The first constraint in producing natural-fibre reinforced composites is the ability to control plant-related parameters and to influence the properties of the final composite.

The Compatibility of Natural Fibres and Polymers

Cellulose, the main component of natural fibres, is completely incompatible with the majority of polymers. This fact has been reported by many studies. Our recent study (Paridah *et al.,* 2012) using unsaturated-polyester-kenaf-pultruded-composite shows that while the weight of this composite reduced markedly, the mechanical properties also declined (Figures 38 and 39). A significant observation on the failed specimens confirmed the lack of adhesion between the fibres and the matrix as compared to that having 100% glass fibres (Figure 38a). Between PE and the phenol formaldhyde (PF), the latter appears to have lower wettability. Ku *et al.* (2011) associated this instance as incompatibility between the hydrophilic natural fibres and the hydrophobic thermoplastic matrices which led to poorer properties of the composites. Malkapuram *et al. (*2008) asserted that it is necessary to modify the fibre surface by employing chemical modifications to improve the adhesion between fibre and matrix.

Durability

Natural fibres are not inert materials and they react with their environment under certain conditions such as moisture or relative humidity, temperature and weathering. Natural fibres can absorb a certain amount of water, a phenomenon that many consider as a

degradation of the fibres. Because of the nature of its components, a natural fibre cannot be brought up to temperatures higher than 220-230°C without involving a degradation of its components. Thus, composites containing natural fibres cannot be processed at temperatures higher than 230°C. In addition, some plastics converters complain about a strong odour generated by fibres during and after the processing of composites, particularly when higher temperature is used. Excessive heat also causes a carbonization of pectins and other weak components of fibres such as hemicellulose which may be the cause of such smell.
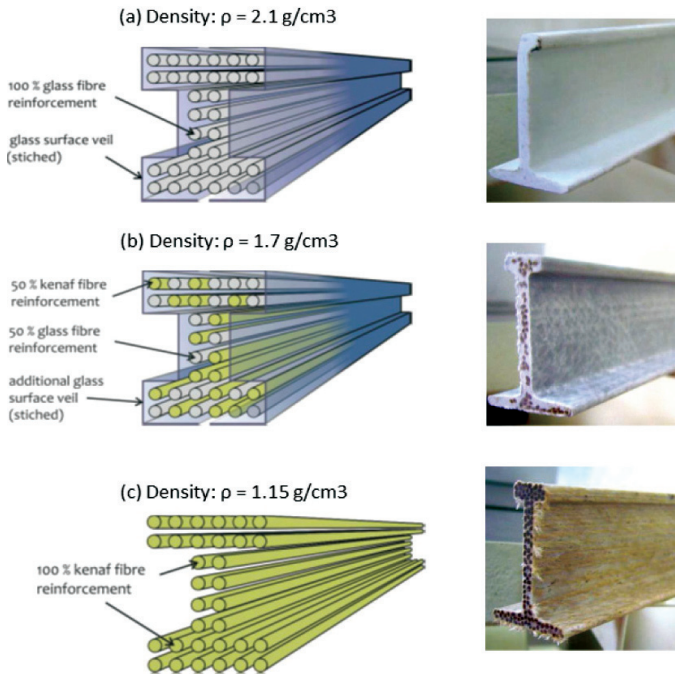
Figure 38 Replacement of glass fibres with kenafbast fibres inunsaturated polyester-pultruded composites : (a) 100% glass fibre, (b) 50% kenaf, and (c) 100% kenaf (Paridah *et al.*, 2012).
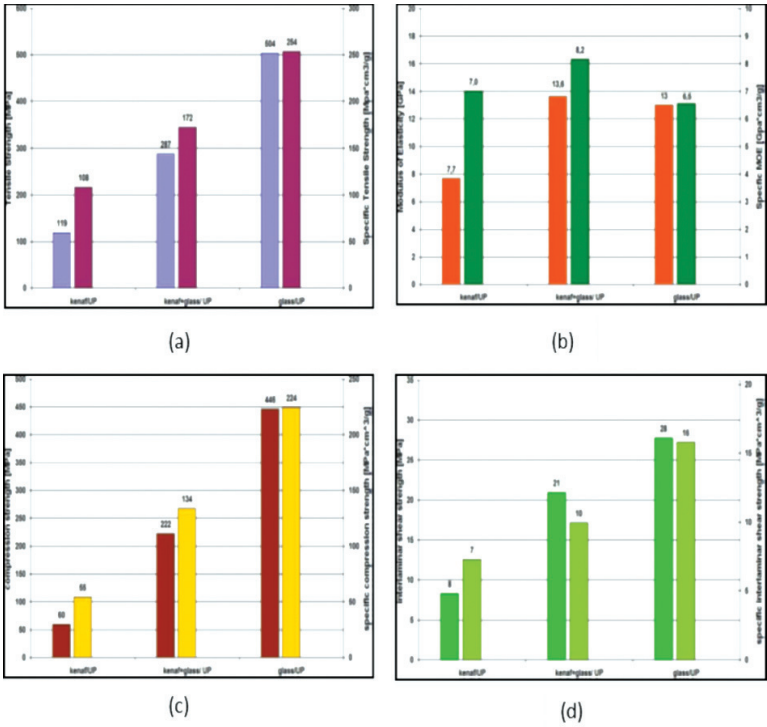
Figure 39 Comparison between mean (left bar) and specific strength (right bar) properties of kenaf-glass fibre pultruded composite (a) Tensile strength, (b) Tensile Modulus, (c) Compressive strength and (d) Interlaminar shear (Paridah *et al.*, 2012).

WAY FORWARD

The need for renewable fibre reinforced composites has never been as prevalent as it currently is. Natural fibres offer both cost savings and a reduction in density when compared to glass fibres. Although the strength of natural fibres is not as great as glass, the specific properties are comparable.

Currently natural fibre composites have two issues that need to be addressed: resin compatibility and water absorption. The R&D sector had come up with several innovative solutions focusing on these novel materials with specific properties. The use of new additives, *e.g.,* coupling agents or new high-quality preparation methods for natural fibres enabled more reproducible properties and allowed better processing control. The understanding of the influence of factors such as moisture, fibre type and content had improved the composites' mechanical properties and their end-product quality. Moreover development of new moulding technologies had increased the process efficiency significantly. Today, NFC have much improved properties than those of several years ago. To satisfy the various needs, many companies offer more additives and auxiliary supplies. Different ones are chosen depending on their applications and compounding methods. In this field, knowledge of chemical interactions (matrix/fibre) and the action mechanisms of additives is necessary. Coupling agents combine fibres and resin, lubricants increase the throughput and improve the surface quality, colourants and UV stabilisers prevent the polymer degradation and increase visual perception. Biocides can prevent biological decomposition, especially at a higher fibre content.

Surface interaction between resin polymer matrix and natural fibres is an area that requires more concerted efforts. As natural fibres vary from one another, and within each plant, the variability

is tremendous. The characterization of the interface between fibre and matrix provides information on the adhesion strength. This evaluation can be done through several techniques such as:

- Micromechanical techniques: Single fibre pull-out test, fibre bundle pull-out test, single fibre fragmentation test & micro bond test

- Spectroscopic techniques: Surface characterization of the fibre (before and after treatment)

- Microscopic techniques: SEM, optical microscopy & stereo microscopy

- Contact angle measurement: Wettability & surface energy

Many companies such as Mercedes Benz, Toyota and DaimlerChrysler have already incorporate natural fibres in their products. Two major factors currently limit the large scale production of natural fibres composites. First, the strength of natural fibre composites is very low compared to glass. This is often a result of the incompatibility between the fibre and the resin matrix. The wettability of the fibres is greatly reduced compared to glass and this constitutes a challenge for scale up productions. Though when comparing specific strengths, natural fibres are not much less than glass fibre composites.

The second factor limiting large scale production of natural fibre composites is water absorption. Natural fibres absorb water from the air and through direct contact with the environment. This absorption deforms the surface of the composites by swelling and creating voids. The result of these deformations is lower strength and an increase in mass. Additionally, with water absorption rates as high as 20 % (w/w) the light weight advantage is often nullified. The treatment of fibres is currently an area of research receiving

significant attention. The absorption of water is commonly thought to occur at the free hydroxyl groups on the cellulose chains. With a ratio of 3 hydroxyl groups per glucose repeat unit the amount of water that can be absorbed is substantial. By capping the hydroxyl groups this ratio can be reduced. There are several promising techniques that have been studied by various groups (Rowell, 2013). Among these treatments, mercerization (alkaline) treatment has had the most reviews. Utilizing silanes as coupling agents is a treatment commonly used in glass composite production and is starting to find uses in natural fibre composites. Acetylation is another treatment that is common with cellulose to form a hydrophobic thermoplastic and has the potential to have the same results on natural fibres.

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BIOGRAPHY

Paridah Md. Tahir was born on 29 June 1959 in Ipoh, Perak, Malaysia. She is married to Zaidon Ashaari and has four children. Paridah started her primary education at Sekolah Kebangsaan Kampong Pandan, Kuala Lumpur. She attended her secondary education first at Sekolah Menengah (P) Putri Jaya, Pudu and later at Sekolah Menengah Perempuan (P) Jalan Kolam Air (now Sekolah Menengah Seri Puteri, Cyberjaya). She then attended Universiti Putra Malaysia (then Universiti Pertanian Malaysia), Semengok Campus and obtained a Diploma in Forestry in 1980. In August 1981, she was employed by the Malaysian Timber Industry Board (MTIB) as the first female Assistant Utilisation Officer (AUO). Paridah was awarded a Public Service Department-UPM (SLAB) Scholarship to pursue her Bachelor and Masters degrees at Mississippi State University, USA. In recognition of her achievements, she received a "Best Senior Achievement 1987" and an "Outstanding Graduate Student 1989" from the Forest Products Department, Mississippi State University. She completed her Masters Science in Wood Science and Technology in March 1989 and joined the Faculty of Forestry as a lecturer. She pursued her Ph.D at the Department of Chemistry, University of Aberdeen, Scotland in October 1992 and graduated three years later. She resumes her duty as a lecturer at the Faculty of Forestry, UPM in January 1996. Family comes first; Paridah started late in her career as an academician. She was only promoted to Associate Professor in 2003 and to a full Professor in 2011. Administratively, she was appointed as a Programme Manager at the Bio-Engineering Laboratory, Institute of Advanced Materials UPM in 2005. In June 2006. she became the Head, Laboratory of Conventional Biocomposite, Institute of Tropical Biocomposite, UPM. In February 2007, Paridah was appointed as

Deputy Director of INTROP and in April 2009, she becomes the second director of INTROP until today.

As a lecturer, Paridah has taught various courses related to wood science but is known for her expertise in wood adhesive, bonding, surface coating and biocomposite.

Paridah's involvement in wood-based sector particularly in the area of Biocomposite, has been extensive. Her knowledge and commitment have been acknowledged by other organizations where she has been appointed as technical assessor/expert to evaluate projects such as Industrial Grant Scheme (IGS), MOSTI, R&D in Biocomposite, Ministry of Plantation Industries and Commodities (MPIC), Technology Park Malaysia, Economic Planning Unit, Lembaga Perindustrian Kayu Malaysia, JKR and Lembaga Kenaf dan Tembakau Negara. She sits in the National Technical Committee for Timber and Timber products, National Kenaf R&D Committee, Steering Committee for Kenaf Road Map, Technical Committee for Natural Stand Bamboo Road Map, Chairman of Sub-Committee for Timber, and leads several other Working Groups for timber standards. She has represented Malaysia in two important ISO standards annual meetings – ISO TC 218: Timber and ISO TC 89: Wood-Based Panels, since 2006 until present. She was elected as a convener for ISO TC 218, WG 4 - Test methods in 2007; is responsible to revise 16 existing standards. Most recent she has been asked to lead the discussion on developing ISO standard for oil palm plywood in the ISO TC 89 Plenary meeting in Salzburg, Austria in March 2013 which was attended by 23 countries.

Paridah has supervised more than 150 students at both undergraduate and graduate levels and most of these works have been published. To date, she has published more than 90 articles in numerous journals, more than 200 appeared in International and National proceedings, chapter in book, technical reports, as well as

a number of consultation reports. To date she has received more than 50 awards on her research works. In 2009 she was elected as The Best Woman Inventor 2009 in the Malaysian Technology Expo (MTE).

Paridah has led her team in receiving more than RM 10 million including RM 2.1 million from Common Funds for Commodities (CFC) and RM 26,000 from Korea University. Other than fundings from MoHE and MOSTI, EPU has also allocated RM 5 million to research on the potential downstream products from kenaf. In addition, she has been involved in a number of consultancy projects for both government and industry such that with The Sarawak Government (by-products from sago), Heveaboard Sdn. Bhd. (Oriented Strand Board (OSB) from rubberwood TNBRD Berhad (wooden cross-arms), ECER (Kenaf business strategies), MTIB (RRIM 3000 clone study, R&D on palm plywood, pre-commercialisation of palm plywood), Perak SADC (EFB potential in panel industry) RCP Technologies (effects of stimulants on rubberwood strength), and others like Robin Fiberboard (board manufacture), Evergreen Fiberboard (Kenaf board), Dong Wha Fiberboard (rubberwood supply). Her enthusiasm in fostering creativity and innovation are well known among the students which fits well with her motto **"*You never change things by fighting the existing reality. To change something, build a new model that makes the existing model obsolete"*** (taken from Richard Buckminster Fuller).

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A sincere appreciation also goes to my colleagues and collaborators: Dr. NorYuziah Mohd. Yunus, Prof. Dr. Desa Ahmad, Prof. Dr. Sapuan Salit, Prof. Dr. Luqman Chuah Abdullah, Prof. Dr. Awang Abd. Ghani, Prof. Ali Karimi, Prof. Dato' Dr. Nik Muhamad Nik Majid, Prof. Datuk Dr. Mohd Khalil Shawkatali, Prof. Dr. Sarani Zakaria, Prof. Mohd Shahwahid Othman, Dr. Khamuruddin Mohd. Noor, Assoc. Prof. Dr. Zakiah Ahmad, Assoc. Prof. Dr. H'ng Paik San, Assoc. Prof. Dr. Edi Suhaimi Bakar, Assoc. Prof. Dr. Ahmad Ainuddin Nuruddin, Assoc. Prof. Dr. Hazandy Abd. Hamid, Assoc. Prof. Dr. Rosfarizan Mohamad, Dr. Azmah Hanim Mohamed Ariff, Assoc. Prof. Dr. Shukri Mohamed, Assoc. Prof. Khalina Abdan, Assoc. Prof. Dr. Edi Syam Zainuddin, Assoc. Prof. Dr. Zaiton Samdin, Dr. Farideh Namwar, Dr. Mohamad Jawaid, and Dr. Mahnaz Abadi.

I wish to express my sincere appreciation to the Management and staff of Universiti Putra Malaysia, in particular the Faculty of Forestry and Institute of Tropical Forestry and Forest Products (INTROP) who have been supporting my career in many ways. My deepest gratitude to Azira for her efficient work and multi-tasking skills that have made me more ingenious.

I am greatly indebted to my parents, Tahir bin Abd. Hamid (Allahyarham) and Puteh binti Daud (Allahyarhamah) for their undying love and inspirations. Not to forget my parent-in-law Hj. Ashaari Jaman and Hajah Puziah Ketik, for your love, support and prayers. To my siblings, Kak, Barin, Nor, Icam, Adik and their families, my in-laws and their families, thank you very much for being there for me. To my children, Zahira, Zuheir, Zulfa and Zafira, all my prayers for you and thank you for being such an understanding daughters/son, especially during my absence which is quite frequent.

Most importantly to my husband, Prof. Dr. Zaidon Ashaari, you have been everything to me – a husband, partner, colleague, rival, advisor, boss and inspiration throughout my journey to this feat. Thank you, thank you and thank you.

LIST OF INAUGURAL LECTURES

1. Prof. Dr. Sulaiman M. Yassin
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