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TITLE PAGE

UNIVERSITI TEKNOLOGI PETRONAS

Mechanical and Water Absorption Properties of Oil Palm Empty Fruit Bunch-High Density Polyethylene Composites

By

Muhamad Fatikul Arif

A THESIS
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BANDAR SERI ISKANDAR,
PERAK

JUNE, 2008

DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UTP or other institutions.

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Date : 30 June 2008

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ABSTRACT

High density polyethylene (HDPE) composites were fabricated using oil palm empty fruit bunch (EFB) as the reinforcing material. The effect of fiber content and fiber type, EFB particulate and short fiber, on the mechanical and water absorption properties of the composites were investigated. EFB short fiber composites experienced higher tensile and flexural properties compared to that of EFB particulate composites at all fiber contents. For EFB short fiber composites, tensile modulus, flexural strength and flexural modulus increased as the EFB content increased. Unlike that of the EFB short fiber composites, the tensile modulus and flexural strength of the EFB particulate composites increased as the EFB content increased up to 20%wt, but decreased at 30%wt fiber content, while the flexural modulus constantly increased as the EFB content increased. The decrease in tensile strength was observed for both EFB particulate and short fiber composites as the EFB content increased. Study on water absorption of the composites revealed that EFB short fiber composites absorbed more water than that of EFB particulate composites. Both of EFB particulate and short fiber composites absorbed more water as the EFB content increased.

The effects of chemical treatments on the mechanical and water absorption properties of the 10%wt EFB short fiber composites were also investigated. Alkali, acrylation and two types of silane treatments, γ-methacryloxypropyltrimethoxysilane (MTS) and vinyltriethoxysilane (VTS) were employed. The optimum mechanical properties was achieved by treating the EFB with 10% alkali, 3% MTS, 3% VTS and 5% acrylic acid. Generally, the chemical treatments increased both of composite's tensile strength and tensile modulus. Among the four different types of treatments, the MTS treatment gave the highest increase in tensile strength of 9% compared to that of the untreated composites. To achieve the highest tensile modulus improvement, the acrylated treatment should be favored, with the increase of 10% compared to that of the untreated composites. The chemical treatments also increased composite's flexural strength and flexural modulus, except for the acrylation treatment, with an average increase of 6% and 18% compared to that of the untreated composites, respectively. The chemical treatments were found to decrease water absorption of the composites, with the highest water absorption resistance possessed by MTS treated composites, followed by VTS, acrylated and alkali treated composites.

It could be inferred that the EFB particulate and short fiber composites have a variety of attractive properties to be used in thermoplastic composites of at least moderate strength. The mechanical properties and water uptake behavior were found to be improved upon chemical treatments such as alkali, acrylated and silane treatments.

Keywords: oil palm empty fruit bunch, short fiber, particulate, composites, mechanical properties, water absorption, chemical treatment, alkali, acrylation, silane.

ABSTRAK

Komposit polietilena berketumpatan tinggi (HDPE) telah difabrikasi menggunakan tandan kosong buah sawit (EFB) sebagai bahan tetulang. Kesan kandungan serat dan jenis serat iaitu serat pendek EFB dan partikel EFB terhadap sifat-sifat mekanikal dan sifat serapan air kepada komposit telah dikaji. Komposit dengan kandungan serat pendek menunjukkan sifat regangan dan lenturan yang lebih tinggi berbanding komposit dengan kandungan serat partikel. Bagi komposit serat pendek, modulus regangan, kekuatan lenturan dan modulus lenturan meningkat apabila kandungan EFB meningkat. Tidak seperti komposit serat pendek, modulus regangan dan kekuatan lenturan komposit serat partikel meningkat apabila kandungan serat meningkat sehingga 20%wt tetapi berkekurangan pada kandungan serat 30%wt, manakala modulus lenturan sentiasa meningkat apabila EFB meningkat. Penurunan kekuatan regangan telah diperhatikan untuk kedua-dua komposit serat partikel dan serat pendek apabila kandungan EFB meningkat. Kajian terhadap sifat serapan air komposit membuktikan bahawa komposit serat pendek menyerap lebih banyak air berbanding komposit serat partikel. Kedua-dua komposit partikel dan serat pendek menyerap lebih banyak air apabila EFB meningkat.

Kesan rawatan-rawatan kimia terhadap sifat-sifat mekanikal dan sifat serapan air kepada komposit berkandungan 10%wt serat pendek EFB juga telah dikaji. Alkali, asid akrilik dan dua jenis rawatan silane, γ-methacryloxypropyltrimethoxysilane (MTS) dan vinyltriethoxysilane (VTS) telah diguna pakai. Secara umumnya, rawatan-rawatan kimia meningkatkan kekuatan regangan dan modulus regangan komposit. Antara empat rawatan yang tersebut, rawatan MTS menyumbangkan peningkatan tertinggi dalam kekuatan regangan iaitu 9% berbanding dengan komposit yang belum dirawat. Untuk mencapai peningkatan modulus regangan yang tertinggi, rawatan asid akrilik perlu dipilih, dengan peningkatan 10% berbanding dengan komposit yang belum dirawat. Rawatan-rawatan kimia juga meningkatkan kekuatan lenturan dan modulus lenturan komposit kecuali bagi rawatan asid akrilik dengan purata peningkatan masing-masing 6% and 18% berbanding dengan komposit yang belum dirawat. Rawatan-rawatan kimia tersebut juga telah didapati mengurangkan penyerapan air terhadap komposit dengan rintangan penyerapan air tertinggi diperolehi oleh komposit yang telah dirawat dengan MTS, diikuti oleh VTS, asid akrilik dan alkali.

Dapat disimpulkan bahawa komposit partikel dan serat pendek EFB mempunyai pelbagai sifat menarik untuk digunakan di dalam komposit termoplastik dengan berkekuatan sederhana. Sifat-sifat mekanikal dan sifat serapan air telah didapati meningkat apabila rawatan kimia seperti alkali, asid akrilik dan rawatan silane dijalankan.

Kata kunci: tandan kosong buah sawit, serat pendek, partikel, komposit, sifat mekanik, penyerapan air, rawatan kimia, alkali, asid akrilik, silane.

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LIST OF ABBREVIATIONS

3-APE	3-aminopropyltriethoxysilane
3-APM	3-aminopropyltrimethoxysilane
AA	Acrylic acid
APS	γ-aminopropyltriethoxysilane
BP	Benzoyl peroxide
DCP	Dicumyl peroxide
E-43	Epolene wax
EFB	Oil palm empty fruit bunch
EX	Extrusion
FFB	Oil palm fresh fruit bunch
HDPE	High density polyethylene
HDS	Hexadecyltrimethoxysilane
IM	Internal mixer
MA	Maleic anhydride
MA-PE	Maleic anhydride grafted polyethylene
MA-PP	Maleic anhydride grafted polypropylene
MA-PS	Maleic anhydride grafted polystyrene
MRPS	γ-mercaptopropyltrimethoxysilane
MTS	γ-methacryloxoproyltrimethoxysilane
PALF	Pineapple leaf fiber
PE	Polyethylene
PHA	Polyhydroxyalkanoates
PLA	Polylactic acid
PP	Polypropylene
PPAA	Poly (propylene-acrylic acid)
PPEAA	Poly (propylene-ethylene-acrylic acid)
PS	Polystyrene
RTM	Resin transfer molding
SEM	Scanning electron microscopy
SMA	Styrene-maleic anhydride copolymer

SMC	Sheet molding compound
UV	Ultraviolet
VTS	Vinyltriethoxysilane

LIST OF NOMENCLATURES

σ_t	Tensile strength
E_t	Tensile modulus
σ_f	Flexural strength
E_f	Flexural modulus
P	Force
L	Distance between the support span
b	Specimen width
d	Specimen thickness
E_f	Flexural modulus
m	Slope of the initial straight-line portion of the load-deflection curve.
Δl	Extension
l_o	Gage length

CHAPTER 1

INTRODUCTION

1.1 Background

The reinforced plastic industries for applications such as aerospace, transportation and construction have been established since the early 1960s. However, most of the traditional reinforcing fibers such as glass, carbon and aramid fibers are non-biodegradable and non-recyclable. The rapid change in environmental regulation and growing worldwide interest in bio-products have led material scientists and industries to develop environmental friendly composite materials. As a result, natural fibers are gaining ever increasing attention as reinforcement in polymer based composites. The advantages of natural fibers are low cost, low density, high strength to weight ratio, sustainable and biodegradable. Other advantages are good acoustic and insulating properties, low risk on health and skin irritations and low abrasive impact on processing tools. Furthermore, when natural fibers are burned at the end of their lifetime, the amount of CO_2 released to the environment is equal to the CO_2 intake during fiber growth, so the net release of CO_2 by natural fibers is zero [1, 2].

Currently, several natural fibers such as flax, hemp and kenaf are being utilized commercially as reinforcement materials for automotive applications. Some automobile industries like Daimler Chrysler, BMW and Audi have already started using natural fiber reinforced composites for various interior and exterior applications such as door panels, seat backs and floor panels [3-5]. When compared to glass fibers traditionally used in automotive, natural fibers demonstrate significant benefits, such as reduction in cost up to 50% cheaper than glass fiber composites, light weight (less than half the density of glass fibers) and safer crash behavior [6]. Natural fibers composites are also utilized as building materials and furniture. Wood-filled plastic composites are dominantly used for these applications. However, due to the scarcity of wood, non-wood natural fibers such as flax and hemp are also utilized as alternates to wood in reinforced plastic materials [6].

Although natural fibers posses many benefits, they also have several disadvantages. The potential use of natural fibers as reinforcement has considerably reduced due to their hydrophilic nature. The hydrophilic property of natural fibers is incompatible with the hydrophobic property of non-polar polymers. The reason is due to the big amount of hydroxyl group on the surface of the natural fibers. This incompatibility leads to poor wettability and inadequate adhesion between the fiber and the matrix, which result in poor mechanical properties of the composites. Other disadvantages of natural fiber composites are the sensitivity towards water and the relatively poor thermal stability. Water absorption of composites is a concern as the water absorbed by the natural fibers in the composites could lead to dimensional instability and loss of mechanical properties due to degradation of the natural fibers and deficiency of the fiber-matrix adhesion [7].

Therefore, physical and chemical methods to improve fiber-matrix adhesion of natural fiber composites have been developed. They optimize the interfacial characteristics and improve the properties of natural fiber reinforced polymer composites. Physical methods involve surface fibrillation and electric discharge such as corona, cold plasma and sputtering [8]. The purpose of the physical methods is to change the structural and surface properties of the fiber and thereby improve the adhesion between the fiber and the matrix.

Various chemical treatments on fiber surface have been employed to improve the performance of natural fibers and its composites. Chemicals may activate hydroxyl groups of the fiber and/or introduce new moieties that can effectively interlock with the matrix. Generally, chemical modifications can be employed by introduction of compatibilizers and coupling agents.

Compatibilizer, such as maleic anhydride (MA), enables to modify the polymer matrix and thereby improve the wetting efficiency between the fiber and the matrix. MA is grafted on the considered polymer (e.g. polypropylene (PP), polyethylene (PE) and polystyrene (PS)) to form copolymers such as MA-PP, MA-PE and MA-PS [9-11]. These copolymers are added to the fiber or the matrix before or during compounding. The coupling occurs at one side between acidic anhydride groups of MA and the hydroxyl groups of the natural fibers, while on the other side an entanglement occurs with the polymer.

Coupling agents, such as silanes and isocyanates are molecules possessing two functions. The first function is to react with the hydroxyl groups of the fiber and the second is to react with the functional groups of the matrix. All methods aimed to improve the composites interface characteristics, which will result in better dimensional stability, lower water uptake and improvement of the mechanical properties.

The old and widely used chemical treatment, with the mechanism slightly different from others, is alkali treatment. The nature of this treatment is only to modify the natural fiber surface without coupling effect to the polymer matrix. The introduction of alkali solution onto the fiber surface may activate or react with the hydroxyl groups of the fiber and thereby reduces the hydrophilic nature of the natural fiber.

1.1.1 Oil Palm Fiber and Its Composites

Amongst many types of natural fibers, oil palm fibers have gained many researchers interest in investigating the possibility of their utilization as reinforcement in polymer composites. Oil palm is perennial oil crop originated from the tropical forest of West Africa. Oil palm is grown mainly for its oil-producing fruit. The largest industrial cultivation is in Malaysia with a total of 3.87 million hectares of land planted with oil palm [12]. The average annual yield of fresh fruit bunches is 18.50 tones per hectares [12]. One of the major waste products of oil palm is the empty fruit bunches (EFB) which amounts to 30 million tones annually [12]. Other fibrous wastes are oil palm frond and mesocarp fibers. These fibrous wastes can create major environmental problems when simply left on the plantation fields. Some of the fibrous wastes are utilized as boiler feedstock in the oil mill which are also left to mulch and degrade as soil fertilizer in the field, while the majority of these wastes are not utilized [13, 14]. Utilization of these biomasses wastes will significantly reduce the environmental problems and increase the economical benefit. To accomplish the demand to utilize these fibrous wastes as filler in polymer composites, a systematic study is necessary to completely comprehend the behavior of oil palm fibers and their properties when incorporated into polymers.

There have been several studies on the performance of several by-products of the oil palm and their utilization as filler in polymer composites. The biomass wastes employed were EFB, oil palm frond [14] and mesocarp fiber [15], with the highest number of investigation were on the performance of EFB and its composites [14-22]. EFB is studied more than other oil palm by-products due to the fact that EFB is the major biomass waste and EFB possesses better mechanical properties and water absorption characteristic compared to that of mesocarp and oil palm frond [14, 15].

One important factor that needs to be investigated in order to achieve a sufficient level of adhesion between the fiber and the matrix in a composite is the chemical treatment. The efficiency of chemical treatment depends on the type and concentration of the chemicals, its temperature and duration of treatment. There have been several studies on chemical treatment of EFB fiber. Alkali treatment on EFB fiber results in significant improvement on tensile modulus and water absorption characteristic of the fiber [15, 19]. Coupling agents such as silane, acrylic acid and acetylation were also employed to improve mechanical properties of composites [16-18]. Usually, before the fiber-matrix compounding, chemical coupling agent solution is allowed to react with the hydroxyl groups of the natural fiber with specific operational conditions of the temperature, pH and solvent. Coupling effect with the polymer matrix is achieved during subsequent compounding process. Compatibilization methods such as the addition of polypropylene-acrylic acid, epolene and MA-PP during the fiber-matrix compounding also resulted in EFB composites with better mechanical properties [14, 16, 17].

1.2 Problem Statement

The utilization of oil palm fibrous wastes as reinforcing materials in polymeric composites promises many advantages, especially when ecology is a concern. A systematic investigation is necessary to fully describe the behavior of oil palm fibers and their composites.

Fiber content and fiber length are important parameters to be considered in order to achieve significant reinforcement in polymer composites. Longer fiber and higher fiber content in the composites usually lead to higher mechanical properties of the composites. However, the composite processing technology such as injection molding and extrusion limits the length and the content of natural fibers. The fiber content should be limited to a certain level of volume fraction and the fiber length should be short enough, with the length of 0.5-7.5 mm (short fiber) or shorter than 0.5 mm (particulate) in order to allow the melted material to flow. It should also be noted that during compounding and injection molding, fibers are damaged due to high fiber attrition, resulting in shorter fiber, or even become particulate [7, 23, 24]. Previous study on the EFB-HDPE composites performed by Rozman et al. [25] investigated the effects of different particulate size on the mechanical properties of the composites, with the result that the smaller particulate size possessed better mechanical properties compared to that of the higher ones. However, there is still lack of study to investigate the effect of fiber type, EFB short fiber and EFB particulate on the mechanical properties of the EFB-HDPE composites. The EFB short fiber composites may experiences fiber shorting during processing which may results in similar or comparable mechanical properties with EFB particulate composites. Therefore, investigation on the effect of fiber content and fiber type, EFB short fiber and EFB particulate on the mechanical properties of the composites is important to obtain optimum effect of reinforcement.

Treating the fiber chemically is one of the techniques employed to improve the interfacial properties of the natural fiber filled polymer composites. The study on the effect of various chemical treatments on the mechanical properties of EFB-HDPE composites was performed by Mohd Ishak et al. [16]. Two types of silane coupling agents, 3-aminopropyltrimethoxysilane (3-APM) and 3-aminopropyl-triethoxysilane (3-APE), and two types of compatibilizers, poly- (propylene-ethylene-acrylic acid) (PPEAA) and poly (propylene-acrylic acid) (PPAA), were used in their study. Generally, 3-APM and PPEAA were more effective in improving the filler-matrix interaction, with significant improvement was achieved for the tensile modulus value of the composites. The possibility of using silane with different organo- and silicon-functional groups and employing acrylic acid without any grafted polymer for the EFB-HDPE composites treatments are also of interest as the different functional groups of the silane and the acrylic acid without any grafted polymer may influence the effectiveness of the treatment. The incorporation of silane and acrylic acid treated EFB on HDPE may also be of advantage because according to the past research performed by Sreekala et al. [18], silane and acrylic acid treatments on EFB resulted in the optimum mechanical properties of the EFB fiber as compared with other treatments. Thus, its incorporation in HDPE matrix may significantly increase the mechanical properties of the composites. The use of alkali treatment on fiber also deserves further investigation. Even though Sreekala [18] reported that there was no improvement on the tensile strength of the EFB fiber occurred upon alkali treatment, it requires further study as the treatment could increase surface roughness of the fiber. This may result in better fiber-matrix mechanical interlocking behavior and thereby increase the mechanical properties of the composites. Furthermore, the removal of certain amount of impurities on the fiber surface upon the treatment might reduce the water uptake, hence improving the dimensional stability of the composites.

In order to promote the usage of natural fiber composites for engineering applications, environmental degradation issue of the composites need to be addressed. Under moist condition, the mechanical as well as the geometrical properties of natural fiber composites change, resulting in degradation, rotting and swelling. This has a great effect on the polymer matrix, which surrounds the fibers in the composite. Cracks can appear in a polymer around the fibers due to the swelling of the fibers and therefore worsen the mechanical properties of the composites. Water absorption of the natural fiber composites depends on the fiber content and fiber type. Higher fiber content in the composites usually leads to higher water uptake due to hydrophilicity of the natural fiber. Different fiber types, in the form of short fiber and particulate, may also result in different water uptake as they may differ in capillary mechanism. The water resistance of the natural fiber reinforced composites could be improved by the chemical modification of the natural fiber. Chemicals react with the hydroxyl groups on the fiber surface and thereby increase its hydrophobicity. Study on the effect of fiber content, fiber type and chemical treatments on the water absorption characteristics of composites is important in order to characterize the water absorption behavior of the EFB-HDPE composites.

1.3 Research Objectives

As the reinforcement effect of fibers in a composite is influenced by the fiber content and fiber type, it is the objective of the current study to investigate the effect of EFB fiber content and fiber types, EFB short fiber (5 mm) and EFB particulate (0.325-0.4 mm) on the mechanical properties and water absorption characteristic of the composites. The effects of various chemical treatments, namely alkali, silane and acrylation treatments on the tensile and flexural properties of the 10%wt EFB short fiber composites are also investigated. In addition, the influence of the chemical treatments on water uptake behavior of 10%wt EFB short fiber composites will also be determined. Results obtained will show the effectiveness of the chemical treatments to improve the mechanical properties and water uptake behavior of the composites.

1.4 Scope of Study

The investigation is focused on the properties of the EFB composites based on non-polar HDPE matrix. It involves the characterization of the fiber and its composites, specifically on the mechanical properties and water absorption properties of the composites.

Two different fiber types of EFB, namely short fiber (5 mm) and particulate (0.325-0.4 mm) are used as the reinforcing material in the HDPE matrix composites. The mechanical properties (i.e. tensile and flexural) and water absorption characteristics of the composites are studied. The EFB content is varied from 0 to 30%wt. The morphology of the EFB particulate and short fiber composites fractured surface are also examined to study the fiber-matrix adhesion characteristics of the composites.

To improve the fiber-matrix adhesion, chemical treatments (i.e. alkali, silane and acrylation) are performed on the EFB short fiber. Chemical concentration for each treatment is varied. The effects of these treatments on the mechanical properties and water uptake behavior of the HDPE composites filled with 10%wt EFB short fiber are examined. The morphology of the fiber surface and the composites fractured surface are also examined to study the effect of the treatments on the fiber surface and the fiber-matrix adhesion characteristics of the composites. The 10%wt of EFB is chosen because at lower EFB content, the EFB may well interact with the HDPE matrix without any significant void formation, thus the effects of the chemical treatments on the mechanical and water absorption properties will be easier to be understood.

1.5 Organization of the Thesis

Five chapters are presented subsequently to produce a systematic investigation on the EFB fiber and its composites. Chapter 1 describes the research background related to the possibilities and limitations of the natural fiber composites utilization, as well as the methods to overcome their limitations. Oil palm fiber composites utilization and the issues faced are also reviewed, followed by the research objectives and the scope of study.

Chapter 2 contains an extensive review on the chemical and physical composition of natural fibers. It also describes the processes involved in producing the fibers from their sources and the effects on the fiber properties. The properties of natural fiber composites and their processing technology, as well as methods of properties improvement are also presented. Literature review on the properties of natural fibers and their composites related to the current study are also reviewed to gauge the development of natural fiber composites research.

In chapter 3, details of the materials used, composites preparation and chemical treatments of the fiber are described. It also describes the mechanical properties, water absorption behavior and morphological studies involved.

Next, in chapter 4, analyses of the results obtained are presented. The tensile and flexural properties of the EFB particulate and short fiber composites, as well as the water absorption characteristics of these composites are discussed. The discussion then continues with the study on the effects of chemical treatments on the morphology of the fiber surface, as well as on the mechanical properties and water absorption characteristics of the EFB short fiber composites. The fractured surface of the composites is also discussed as qualitative method to assess the fiber-matrix bonding quality of the composites.

Finally, in chapter 5, conclusions on the mechanical properties and water absorption characteristics of the EFB particulate and short fiber composites are drawn. The effects of chemical treatments on the mechanical properties and water absorption characteristics of the 10%wt EFB short fiber composites are also summarized. Suggestions for future research are also given.

CHAPTER 2

THEORY / LITERATURE REVIEW

2.1 Natural Fiber

Natural fibers have attracted the attention of scientists and technologists due to its low-cost, low density, and high specific properties. They are sustainable, biodegradable and non-abrasive. Currently, natural fibers are being utilized commercially as reinforced plastics for automotive applications, building materials and furniture [3-5, 7]. There are some difficulties, however, in dealing with natural fibers. Natural fibers have large variation in mechanical properties and they are moisture and UV sensitive [8]. Therefore, some problems have to be resolved for successful application of natural fiber in composites.

2.1.1 Types of Natural Fiber

Depending on the part they are derived from, natural fibers can be broadly classified into two categories, namely wood and non-wood. Wood fibers are generally obtained from softwood and hardwood, whereas non-wood fibers are obtained from mono or dicotyledonous plants. Non-wood fibers can be subdivided into bast, leaf, grass, straw and seed/fruit fibers [5, 26, 27]. The classification of natural fibers derived from plants is presented in Figure 2-1.

All of the above-mentioned types of natural fibers in Figure 2-1 are currently available [5, 15, 28]. For example, flax and hemp are largely cultivated in Europe, Russia, Canada, Argentina and India. The largest producers of jute are India, China and Bangladesh. Ramie is cultivated mainly in Indonesia, China, Japan and India. Sisal is native to Mexico and Central America, but is now widely grown in tropical countries such as Africa, the West Indies and the Far East. Kenaf is a crop grown commercially in the United States. Oil palm is originated in the tropical forests of West Africa with major industrial cultivation in Malaysia and Indonesia.

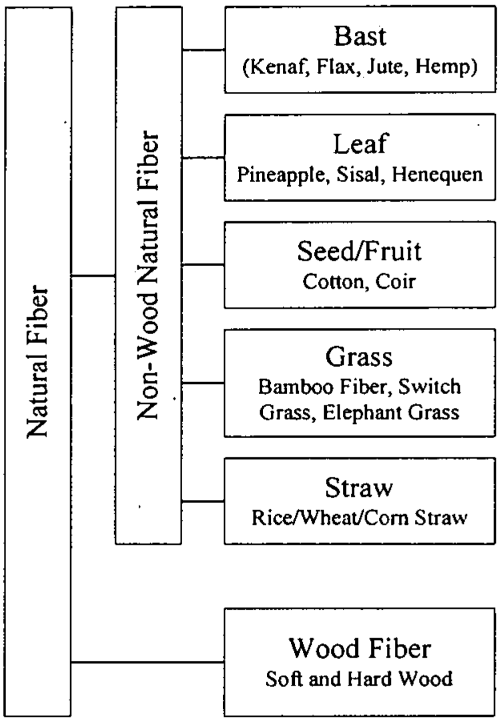


Figure 2-1 Classification of natural fibers derived from plants.

2.1.2 Chemical Composition of Natural Fiber

The age of the plant, climatic conditions and fiber processing techniques influence the structure of fibers as well as their chemical composition. The primary constituents of natural fibers are cellulose, hemicellulose, lignin and pectin. The minor components are waxes, silica and other water-soluble substances. Components of some natural fibers are presented in Table 2-1. The percentage and properties of each constituent contribute to the overall properties of the natural fibers.

Cellulose is the main component of natural fibers. These linear molecules consist of 3000 to 10000 glucose units linked together in long, unbranched chains, which aggregate through inter- and intra-molecular hydrogen bonding into highly ordered cellulose microfibrils. The highly ordered structure of the microfibrils results in high crystallinity. The crystalline regions make up 55-75% of the cellulose fibril, while the other 25-45% are regions with loosely packed molecules (amorphous regions). The hydroxyl groups in the amorphous regions are easily accessible and thus prone to chemical reactions. Those in the crystalline regions, on the contrary, are almost inaccessible. Due to the highly crystalline content, cellulose has a low solvent solubility in combination with high strength and stiffness properties [1, 5, 28, 29]. The molecular structure of cellulose is presented in Figure 2-2.

Table 2-1 Chemical composition of natural fibers [28, 30].

Fiber	Cellulose (% wt)	Hemicelluloses (% wt)	Lignin (% wt)	Pectin (% wt)
Flax	71	18.6–20.6	2.2	2.3
Hemp	70–74	17.9–22.4	3.7–5.7	0.9
Jute	61–71.5	13.6–20.4	12–13	0.2
Kenaf	45–57	21.5	8–13	3–5
Ramie	68.6–76.2	13.1–16.7	0.6–0.7	1.9
Nettle	86			
Sisal	66–78	10–14	10–14	10
Henequen	77.6	4–8	13.1	
PALF	70–82		5–12.7	
Banana	63–64	10	5	
Abaca	56–63		12–13	1
Oil palm empty fruit bunch	49.6–65	18	19–21.2	
Oil palm mesocarp	60		11	
Cotton	85–90	5.7		0–1
Coir	32–43	0.15–0.25	40–45	3–4
Cereal straw	38–45	15–31	12–20	8

Hemicellulose is a polysaccharide like cellulose, but compared to the latter the chains are rather short and branched. Therefore, hemicellulose is amorphous and possesses a low molecular weight, which accounts for their low resistance to chemical attack. Hemicellulose is very hydrophilic and is largely responsible for the water sorption behavior of the fibers. Hemicellulose can be found in between the cellulose microfibrils, binding them together [5, 29].

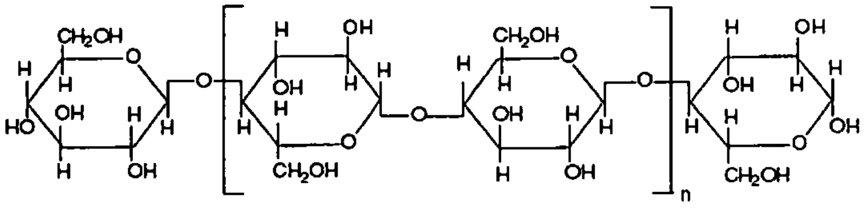


Figure 2-2 Molecular structure of cellulose [27].

Lignin, an amorphous structure with a high molecular weight, gives rigidity to the plant. It is a complex, three-dimensional, cross-linked, polyphenolic network which is situated between the hemicellulose regions surrounding the microfibrils. The exact chemical nature of this component still remains obscure due to the lack of a suitable method to isolate lignin in the native state from the fibers. However, it is believed that lignin gives a certain degree of hydrophobicity to the fibers, insoluble in neutral solvents, but can be degraded under acidic or alkali conditions [5, 29].

A fourth important component present in natural fibers is pectin. Pectin is a collective name for heteropolysacharides, which consist essentially of 1,4-linked galacturonic acid units, especially methyl esters of various sugar units. These are water soluble when they are partially neutralized with alkali or ammonium hydroxide [29].

Each of these constituents influences the fiber properties in various ways. The constituents that influence the fiber's strength, starting from the highest contribution are the crystalline cellulose, followed by non-crystalline cellulose, combination of hemicellulose and lignin as a composite and lignin [29]. The highly ordered structure of the cellulose microfibrils may contribute to the high strength of the fiber. The constituents that are responsible for moisture absorption of the fiber, starting from the highest contribution are hemicellulose, non-crystalline cellulose, lignin and pectin [29]. The very hydrophilic nature of hemicellulose causes this material to absorb more water compared to that of other constituents.

2.1.3 Cell Wall Structure of Natural Fiber

The cell wall structure of natural fiber is a composite. It consists of hollow cellulose fibrils held together by lignin and pectin in hemicellulose matrix. Each fibril has a complex, layered structure, consisting of a thin primary wall encircling a thick secondary wall as shown in Figure 2-3. The secondary wall is made up of three layers and the thick middle layer determines the mechanical properties of the fiber. The middle layer consists of series of helically wound cellular microfibrils formed from the long chain cellulose molecules [5, 28].

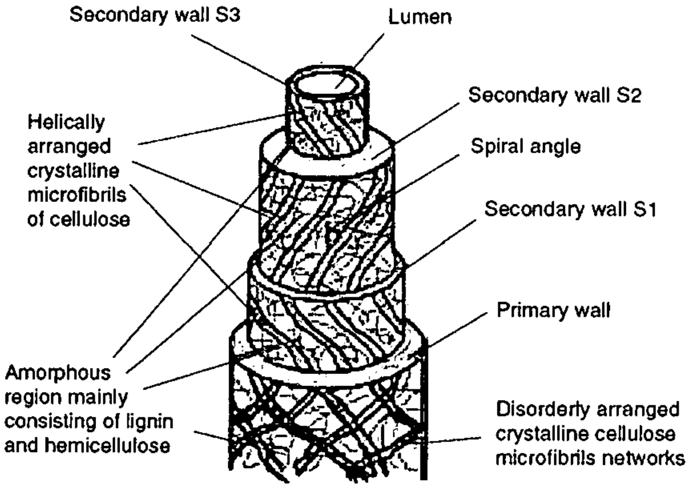


Figure 2-3 Structure of natural fibers [28].

2.1.4 Mechanical Properties of Natural Fiber

The mechanical properties of natural fiber are dependent on the cellulose content in the fiber, the degree of polymerization of the cellulose and the angle of the microfibrils. The microfibrillar angle is the angle between the fiber axis and the microfibril. Fibers with higher cellulose content, higher degree of polymerization and a smaller microfibrillar angle exhibit higher tensile strength and modulus. The physical and mechanical properties of selected natural fibers are given in Table 2-2.

Table 2-2 Physical and mechanical properties of selected natural fibers [28].

Fiber	Density ($g\ cm^{-3}$)	Diameter (μm)	Tensile Strength (MPa)	Young's Modulus (GPa)	Elongation at Break (%)
Flax	1.5	40–600	345–1500	27.6	2.7–3.2
Hemp	1.47	25–500	690	70	1.6
Jute	1.3–1.49	25–200	393–800	13–26.5	1.16–1.5
Kenaf			930	53	1.6
Ramie	1.55	–	400–938	61.4–128	1.2–3.8
Nettle			650	38	1.7
Sisal	1.45	50–200	468–700	9.4–22	3–7
PALF		20–80	413–1627	34.5–82.5	1.6
Abaca			430–760		
Oil palm EFB	0.7–1.55	150–500	248	3.2	25
Oil palm mesocarp			80	0.5	17
Cotton	1.5–1.6	12–38	287–800	5.5–12.6	7–8
Coir	1.15–1.46	100–460	131–220	4–6	15–40

2.1.5 Processing of Natural Fibers

Processing of natural fibers is required in order to obtain fibers from a plant in the form suitable for composites. Currently there are three main technologies: microbial deterioration (dew retting), hot water retting and steam explosion. Retting process separates the fibers from the woody stem by removing the non-fibrous cementing material that hold the fibers together (mainly pectin and hemicellulose), without damaging the fiber cellulose.

The traditional dew-retting is one of the most important and widely used methods. Freshly cut stems of a plant are left in the field for a certain period of time (maximum 6 weeks) and exposed under natural condition combining the deterioration of microbes, humidity and UV radiation. After that, the fibers reached the condition where they can be mechanically extracted from the stem, collected and transported to the subsequent processing stage. The resulting fibers may have large property variations and high moisture sensitivity due to non-optimal deterioration of the hemicellulose and pectin (both influencing the fibers separation) and variation in the degree of cellulose crystallinity (responsible for mechanical properties) [5, 29].

Hot water retting promises better retting quality than that of dew retting with shorter time of fiber extraction (several hours or days). However, this process requires high energy. The plants are processed in batches in hot water tanks. Then, the fibers are separated from the stems. This results in better mechanical properties of extracted fibers due to controlled processing conditions and therefore optimal pectin and hemicellulose degradation [5, 29].

In order to obtain even finer fibers the steam explosion can be applied to the fiber bundles. In this technique, lignocellulosics are subjected to steam treatment at high pressure and temperature in vertically mounted cylinder. At the end of the treatment, the biomass, which is at high pressure, is discharged from the cylinder. Saturated steam at high temperature (about 160°C) penetrates and softens the middle lamella of the fiber bundles and due to the sudden release of pressure, the material is mechanically separated into single fibers [29].

2.2 Natural Fiber Composites

Composite is a controlled combination of two or more materials, having properties which are superior to those of its constituents. In general, a composite consists of a matrix material like polymers and ceramics and a dispersed phase like fibers and particles. The matrix material acts as a load transferring medium between the fibers. Natural fibers can be used to reinforce both thermoset and thermoplastic polymer composites. Most commonly used natural fibers are listed in Figure 2-1.

2.2.1 Matrix Materials

Fibers can be combined with either thermosets or thermoplastic polymer to form composites. Most commonly used thermosets are epoxy, phenol-formaldehyde and unsaturated polyester [8, 31, 32]. In thermoplastics, mostly polyethylene, polypropylene, polystyrene and polyvinyl chloride are used as matrix due to their low melting point [8-11, 31-34]. The main limitation in choosing suitable thermoplastics for natural fiber impregnation is the processing temperature, which is limited to temperature below 200°C to avoid thermal degradation of the natural fibers.

Thermosetting materials have advantages and disadvantages over thermoplastics. Natural fiber composites based on thermosetting matrix usually have better mechanical performance over thermoplastic composites. It is due to the presence of polar groups in thermosets, which promotes better interaction with natural fibers. On the other hand, a thermoplastic is hydrophobic, which is incompatible with the hydrophilic properties of natural fiber. Even though thermoplastics have lower performance than thermosets, they offer other benefits, like low cost and easy processing, as well as possible reuse and recycling of the end-of-life material. Thermoplastics become viscous at higher temperatures and solidify at lower temperatures. Therefore, they can be reversibly shaped. Thermosets can flow only once and crosslink with the applied heat and curing agents. Thus, they can not be recycled.

Amongst polymers derived from petrochemical industry, thermoplastic and thermoset matrices derived from renewable raw materials are being considered for commercial applications. Materials such as starch, plant and animal oil are used for production of biopolymers. The key advantage of their use is that only small amount of minerals and fossil resources are used for their production [5]. Despite of their advantage, poor processing, high price and moisture sensitivity are the drawbacks, which still need to be overcome [35]. The performance of biopolymers as matrix in natural fiber composites has been investigated by many researchers [35-45]. Commercially available biopolymers are polylactic acid (PLA), polyhydroxyalkanoates (PHA) and starch-based polymers [38].

2.2.1.1 Polyethylene (PE)

PE is the simplest of all thermoplastic polymers, with just two carbons and four hydrogens in the basic polymer repeat unit, as shown in Figure 2-4. PE is characterized by its toughness, near-zero moisture absorption, excellent chemical resistance, excellent electrical insulating properties, low coefficient of friction and ease of processing.

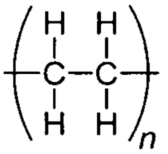


Figure 2-4 Molecular repeat unit of polyethylene.

PE is classified according to its density. PE with densities of 0.880 to 0.915 g/cm^3 can be categorized as ultra- or very low density, 0.910 to 0.925 g/cm^3 as low density, 0.926 to 0.940 g/cm^3 as medium density and 0.941 to 0.965 g/cm^3 as high density [46]. The primary differences among the various types are in their rigidity, heat resistance, chemical resistance and ability to sustain loads. In general, as density increases, hardness, heat resistance, stiffness and resistance to permeability will increase.

High density polyethylene (HDPE) will be used as the matrix for EFB composites in the current study. HDPE polymers are highly crystalline, tough materials that can be formed by most processing methods. The crystalline structure causes the product to have milky and translucent appearance. Within the density range of HDPE, they have good stiffness, tensile strength, melting point and chemical resistance. The low processing temperature of HDPE, which can be less then 180°C, makes this polymer suitable as a matrix material for natural fiber reinforced composites, as the low processing temperature will avoid thermal degradation of the natural fibers.

2.2.2 Composites Processing Technologies

The methods to produce thermoplastics composites are extrusion, compression and injection molding. Processing of natural fiber composites based on thermoplastic matrix involves compounding of the fiber and the matrix at the matrix melting temperatures in extruder or internal mixer, followed by a shaping operation such as injection molding or compression molding. The compounding and shaping operation performed by extrusion and injection molding are commonly used in industry due to their ability to produce plastic products in large volume and short production time. In order to produce composites with good quality, it requires certain viscosity to assure the flow ability of the fiber and melted polymer during processing. Therefore, there is a limitation on the amount of fibers and their length, especially in extrusion and injection molding processes.

2.2.2.1 Compounding

Compounding is the process of mixing polymer and fiber in a molten state to form a homogenous compound. The compounding is commonly carried out in extruder, which is the most common manufacturing process in thermoplastic products for high volume applications, such as plastic pipes, films, sheets, profiles and cable coatings [7]. The extruder consists of single or twin rotating screws placed inside a heated barrel. The mechanism of the extruder is by feeding the raw materials into a hopper, the screw accepts the materials in the feed section and conveys the material along the screw enclosed in the barrel. The conveying is forced by the rotation of the screw via a drive motor and gear reducer. The materials will be melted along the path of the extruder screw, although some instances the feed material is already in the melt form that the extruder screw needs only to convey it. The melting of the polymer is aided by heaters that tightly encapsulated the barrel outside diameter and are separated into several zones. These zones can be set at different temperatures to suit a particular process involved. The schematic diagram of an extruder is shown in Figure 2-5.

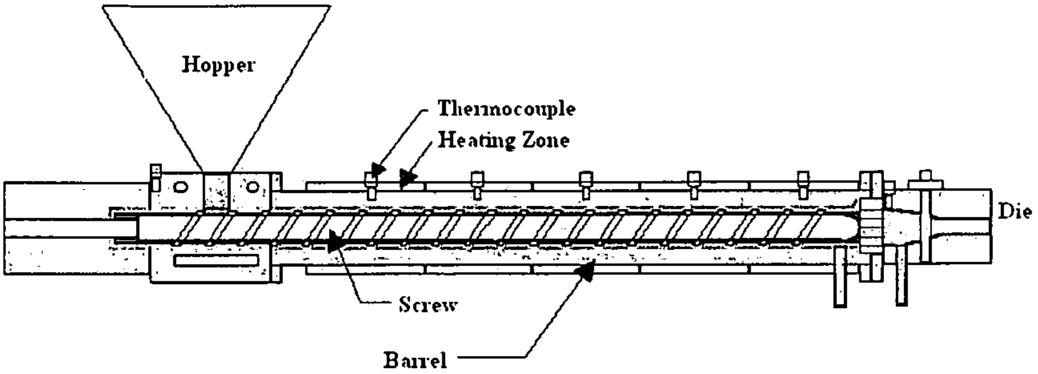


Figure 2-5 The schematic diagram of an extruder machine.

2.2.2.2 Injection Molding

Injection molding is a widely used polymer processing method with the specialty to produce complex geometry products in large series, short cycle-time production. Almost all thermoplastics and some thermosets can be injection molded. The schematic diagram of an injection molding machine is shown in Figure 2-6.

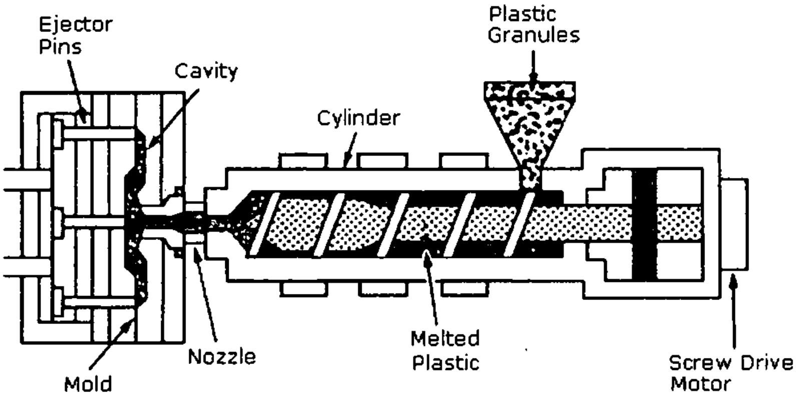


Figure 2-6 The schematic diagram of an injection molding machine.

The injection molding process starts with the plasticizing process, which involves heating and melting the plastics in the cylinder barrel, followed by injection process of the plastic melt from the barrel into a closed mold. The process then continues with after-filling process with the aim to maintain the injected material under pressure for a specified time to prevent back flow of the melt and to compensate for the decrease in volume of the melt during solidification. The subsequent step involves cooling of the thermoplastic molded part in the mold until it is sufficiently rigid to be ejected, or heating the thermoset molded part in the mold until it is sufficiently rigid to be ejected. The final step is the release of the molded-part, which involves opening the mold, ejecting the part and closing the mold so it is ready for the next cycle [47].

2.2.3 Particulate and Short Fiber Reinforced Polymer Composites

Compared to continuous fiber reinforced polymer composites, both particulate and short fiber reinforced polymer composites have much lower strength properties as well as modulus values. However, these two types of composites are used in larger quantities in various applications such as automotive structures, electrical components, machine components and consumer products. The reason for the widespread use of particulate and short fiber reinforced composites is because they can be mass produced using relatively easy processes such as injection molding and compression molding [48, 49].

Particulates are commonly known as fillers in the plastics industry. However, many of them served not only as fillers, but also as reinforcements in the sense that they increase the modulus and, in some cases, the strength of the polymer matrix to which they are added [48]. In the plastic industry, fillers are often used to control mold shrinkage, increase part stiffness and improve dimensional stability. The decrease in mold shrinkage is primarily due to a lower coefficient of thermal expansion for the filled polymer compared to the unfilled polymer. The coefficient of thermal expansion decreases with increasing filler volume fraction [48].

In general, the incorporation of short fibers into polymer increases its strength and modulus. The reinforcing effect of short fibers can be attained only if there is a significant stress transfer from the matrix to the fibers. This requires the fiber length to be greater than the critical fiber length. The critical fiber length is the minimum length necessary for effective transmission of stress from the matrix to the fiber. If the length of fiber in a composite is shorter than the critical length, failure in fiber-matrix interface can occur even at low stresses due to debonding, resulting in a weak composite. Whereas, if the fiber length is greater than the critical length, the load transfer is optimal, resulting in a strong composite [5, 50]. However, it is possible to decrease this critical length and yet maintain high composite strength by improving the interfacial bonds between the fiber and the matrix [51].

It should be noted that during compounding and injection molding, fibers are damaged resulting in shorter fiber lengths [7, 23, 24]. The amount of fiber attrition depends on the fiber content, viscosity of the polymer melt and the melt-flow velocity. The average fiber length remaining after processing is an important factor affecting the strength of a composite.

2.2.4 Mechanical Properties of Natural Fiber Composites

The mechanical properties of composites depend on those of the individual components and on their interfacial compatibility. The strength of composites is determined by the strength of the fiber and by the ability of the matrix to transmit stress to the fiber. Transmission of stress to the fiber is affected by fiber orientation, fiber geometry (e.g. length and diameter) and interfacial bonding between the fiber and the matrix [52]. A good interfacial bond is required for effective matrix-fiber stress transfer whereby maximum utilization of the fiber strength in the composite is achieved. Various methods of interfacial adhesion improvement are reviewed in the subsequent section. Higher fiber content and longer fiber usually lead to improvement in mechanical properties of composites [53-55]. However, the composite processing technology limits the length of natural fibers used. For example, in making composites using injection molding, fibers should be short enough in order to allow the flow of the melted matrix material. Long fibers, as well as high volume fractions, increase the viscosity of the melted composites and therefore might cause bad filling of mold and inhomogeneity of the structure. In other processing methods like compression molding, resin transfer molding (RTM) and sheet molding compound (SMC), there is no limitation on fiber length. However, the limitation of fiber volume fraction still remains. Therefore, a balance between the mechanical properties and the processability must be achieved [55, 56].

2.2.5 Moisture Sensitivity of Natural Fiber Composites

Natural fibers are hydrophilic and their properties are moisture sensitive. As they absorb water easily, their mechanical as well as geometrical properties change, resulting in degradation, rotting and swelling. This has a great effect on the polymer matrix, which surrounds the fibers in the composite. Cracks can appear in a matrix around the fibers due to the swelling of the fibers and, therefore, worsen the mechanical properties of the composite. Fibers on the surface of a composite are most affected by moisture content. Natural fiber composites with high fiber volume fraction have more fibers in the core of the composite as well as on its surface. Therefore, higher fiber volume fraction results in more moisture sensitive composite, because the fibers can absorb more moisture. The moisture absorbed by fibers on the surface can go deep into the composite due to capillary effect of interfacial areas [5]. Therefore, natural fiber composites should be prevented from moisture exposure by chemical treatments that react with the OH-groups present on the surface of the cellulose fibers and thereby increase its hydrophobicity.

2.3 Fiber-Matrix Adhesion and Methods of its Improvement

A major disadvantage of natural fibers is their highly polar nature, which makes them incompatible with non-polar polymers such as polyethylene and polypropylene. This results in poor matrix-fiber load transfer capability and therefore poor mechanical performance of the composites. Also, the poor resistance to moisture absorption makes the use of natural fibers less attractive for exterior applications. Therefore, to improve the fiber-matrix adhesion and to reduce the polarity of fibers as well, natural fibers must be physically or chemically modified.

2.3.1 Physical Modifications

Physical methods involve surface fibrillation and electric discharge such as corona, cold plasma and sputtering. Physical treatments change the chemical, structural and surface properties of the fiber and thereby influence the adhesion to the polymers [8]. Low-temperature plasma treatment causes mainly chemical implantation, etching, polymerization, free radical formation and crystallization which results in improvement of surface characteristics of the fibers and polymers [2, 50]. On the other hand, sputter etching brings about mainly physical changes such as surface roughness of fibers which leads to increase in fiber-matrix adhesion [2, 50]. Corona treatment is one of the most interesting techniques for surface oxidation activation. It changes the surface energy of the cellulosic fibers, which in turn affects the melt viscosity of composites. Corona treatment modifies the surface composition and therefore the surface properties of the composite components [50].

2.3.2 Chemical Modifications

2.3.2.1 Alkali Treatment

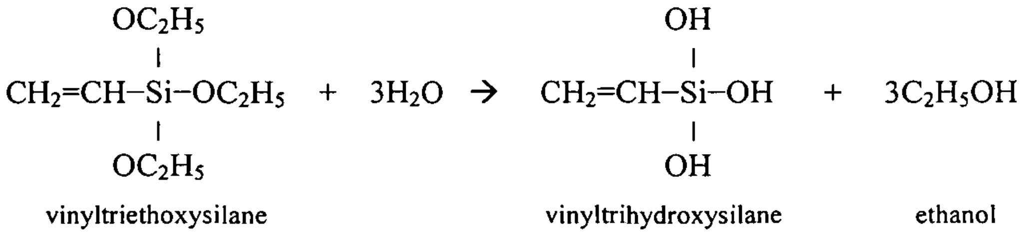
Alkali treatment or mercerization is one of the most used chemical treatments for natural fibers when used to reinforce thermoplastics and thermosets. The important modification done by alkali treatment is the disruption of hydrogen bonding in the network structure, hence increasing surface roughness [57]. The increase in surface roughness will result in better mechanical interlocking between fiber and matrix [49]. This treatment removes a certain amount of lignin, hemicellulose, wax and oils covering the external surface of the fiber cell wall [51, 57]. It increases the amount of cellulose exposed on the fiber surface, thus increasing the number of possible reaction sites. The treatment efficiency depends on the type and concentration of alkali solution, duration of treatment and temperature [50]. Eq. 2.1 represents the reaction as a result of the treatment with alkali:

$$\text{Fiber} - \text{OH} + \text{NaOH} \rightarrow \text{Fiber} - \text{O}^{-}\text{Na}^{+} + \text{H}_2\text{O} \qquad (2.1)$$

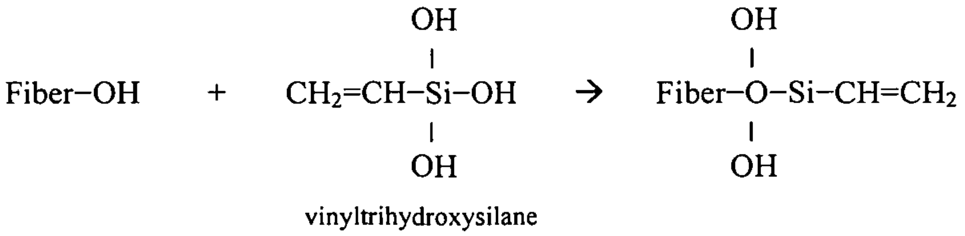
2.3.2.2 Silane Treatment

Organo-silane ($\text{R}-\text{Si}-(\text{OR'})_3$) is commercially available and widely used for modifying surface properties of inorganic substrates such as fiberglass or oxide filler [58-61]. Silane coupling agents bear alkoxysilane groups, which after hydrolysis are capable to react with OH-rich surfaces. Furthermore, there is a wide range of available functionalities for the R group. This R group is responsible to improve the compatibility between the reinforcing material and the matrix or even to establish covalent bonds between them [58]. Even though the beneficial effect on the adhesion between the fiber and the matrix is well established with fiberglass and inorganic fillers, their effects on the properties of lignocellulosic fibers reinforced composites are not formally established and still receive considerable attention [42, 62-69]. The reaction of silane coupling agents with lignocellulose fibers was found to be quite different compared to that observed between them and glass surface, in the sense that with cellulose macromolecules, only pre-hydrolyzed silanes undergone the reaction with cellulose surface [59].

The reaction schemes of the hydrolysis and silane treatment are presented in Eq. 2.2 and 2.3, respectively [70]. In the presence of moisture, hydrolysis of alkoxysilanes, e.g. vinyltriethoxysilane leads to the formation of silanols such as vinyltrihydroxysilane. The silanol then reacts with the hydroxyl group of the fiber, forming stable covalent bonds to the cell wall that are chemisorbed onto the fiber surface [71, 72].



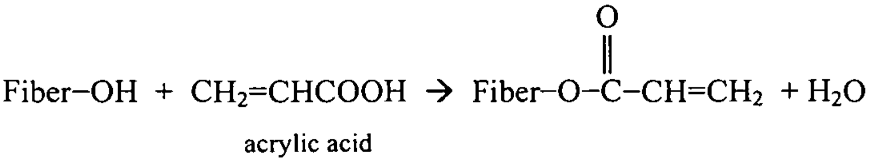
$$CH_2{=}CH{-}\underset{\underset{OC_2H_5}{|}}{\overset{\overset{OC_2H_5}{|}}{Si}}{-}OC_2H_5 + 3H_2O \rightarrow CH_2{=}CH{-}\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{Si}}{-}OH + 3C_2H_5OH \qquad (2.2)$$



$$\text{Fiber}{-}OH + CH_2{=}CH{-}\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{Si}}{-}OH \rightarrow \text{Fiber}{-}O{-}\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{Si}}{-}CH{=}CH_2 \qquad (2.3)$$

2.3.2.3 Acrylation

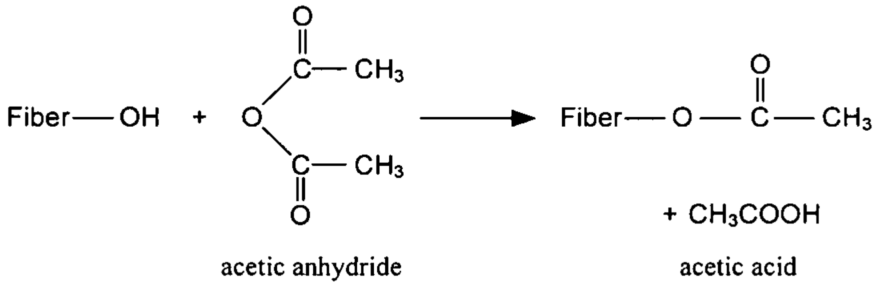
Another method used to treat fibers is by acrylation reaction. Acrylation reaction is initiated by free radicals of the cellulose molecule. The possible reaction between acrylic acid and hydroxyl groups of fibers is the esterification, as shown in Eq. 2.4 [73]. The treatment efficiency depends on the type and concentration of acrylic acid solution, duration of treatment and temperature [74].



$$\text{Fiber}{-}OH + CH_2{=}CHCOOH \rightarrow \text{Fiber}{-}O{-}\overset{\overset{O}{\|}}{C}{-}CH{=}CH_2 + H_2O \qquad (2.4)$$

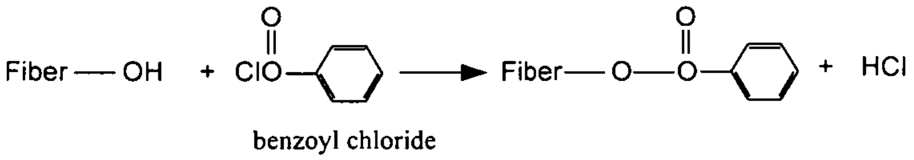
2.3.2.4 Other Chemical Treatments

Acetylation was used in surface treatments of natural fibers for use in polymer composites [75-79]. Acetylation describes a reaction involving acetic anhydride and the introduction of an acetyl functional group (CH_3COO–) into an organic compound. Acetylation of natural fibers is a well-known esterification method causing plasticization of cellulosic fibers. The reaction involves the generation of acetic acid as by-product which must be removed from the lignocellulosic material before the fiber is used. Chemical modification with acetic anhydride substitutes the polymer hydroxyl groups of the cell wall with acetyl groups, modifying the properties of these polymers so that they become hydrophobic [57]. The reaction of acetic anhydride with fiber is shown in Eq. 2.5 [78].



(2.5)

Benzoylation was also employed in surface treatments of natural fibers for use in polymer composites [33, 80, 81]. Benzoyl chloride is most often used in fiber treatment. Benzoyl chloride includes benzoyl ($C_6H_5C{=}O$) which is attributed to the decreased hydrophilic nature of the treated fiber. The reaction between the cellulosic hydroxyl group of the fiber and benzoyl chloride is shown in Eq. 2.6.



(2.6)

Maleated compatibilizing agents are widely used to improve the fiber-matrix adhesion in natural fiber composites [82-87]. Maleic anhydride (MA) is not only used to modify fiber surface but also the polymer matrix to achieve better interfacial bonding and mechanical properties in composites. First, the coupler is formed through the grafting of MA on the considered polymer chain (e.g. MA-PP, MA-PE or SMA). This coupler is added to the fiber or the matrix before or during compounding. The coupling occurs on one side through covalent and hydrogen bonds between the hydroxyl groups of the cellulosic fibers and the acidic anhydride groups of MA, while on the other side a co-crystallization and entanglement occurs with the polymer [1]. Figure 2-7 shows the schematic representation of the interaction between fiber, polymer matrix and compatibilizing agent.

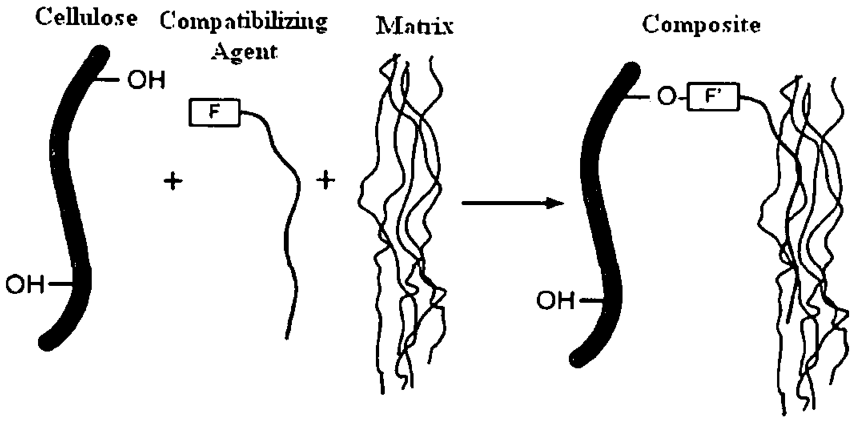


Figure 2-7 Schematic representation of the interaction between fiber, polymer matrix and compatibilizing agent [5].

Alternatively, permanganate treatment can be employed to improve the performance of the composites [18, 88, 89]. Permanganate is a compound that contains permanganate group MnO_4^-. Most permanganate treatments are conducted using potassium permanganate (KMnO4) solution. Another treatments usually employed is peroxide treatments. Benzoyl peroxide (BP) and dicumyl peroxide (DCP) are the chemicals that usually employed for peroxide treatments. In this treatment, fibers are coated with BP and DCP in acetone solution after alkali pre-treatment [18].

2.4 Literature Review

2.4.1 Past Research on the Natural Fiber Filled HDPE Composites

Published data showed that various natural fibers have good potential as reinforcements in HDPE composites. Several natural fibers such as EFB, henequen, jute, aspen and flax fiber have been used as fillers in HDPE composites [16, 25, 51, 63, 85]. The low processing temperature of HDPE, which can be less then 180°C, makes this polymer suitable as a matrix material for natural fiber reinforced composites, as the low processing temperature will avoid thermal degradation of the natural fibers. The studies performed were mostly about the effect of filler content and particle size [25], and the effect of chemical treatments [16, 49, 51, 81, 85] on the mechanical properties of the composites. The results on these investigations will be discussed in the subsequent sub-sections.

2.4.2 Effects of Fiber Content on the Mechanical Properties and Water Absorption Characteristics of EFB Composites and Other Natural Fiber Composites

Study on the effect of fiber content on the mechanical properties of the natural fiber composites was performed by many researchers [16, 25, 90]. Rozman et al. [25] reported that the tensile and flexural modulus of EFB-HDPE composites increased significantly with the increase in fiber content. Generally, samples with smaller particulate size displayed higher tensile and flexural modulus compared to that of the larger ones. Unlike the tensile modulus and the flexural modulus, the tensile strength decreased as more EFB was incorporated in the composites. Similar trends were also observed by Mohd Ishak et al. [16].

Karnani et al. [90] reported that flexural strength of kenaf fiber reinforced polypropylene composites increased as the fiber content increased. Al-kaabi et al. [91] reported that flexural strength of date palm fiber reinforced polyester composites increased as the fiber content increased up to 9%. However, further addition of fiber decreased the flexural strength of the composites.

Arbelaiz et al. [9] studied the effect of fiber content on the flexural properties and water uptake behavior of short flax fiber filled polypropylene composites. Results showed that flexural modulus of the composites increased as the fiber content increased. However, flexural strength of the composites remained constant with the increase in fiber content. Water uptake of the composites increased as the fiber content increased. Studies on water absorption at 28°C of the unmodified pineapple leaf fiber-low density polyethylene composites showed that water absorption of the composites increased with the increase in fiber content [92]. Similar results on other natural fiber composites were found by Chow et al. [93], Siriwardena et al. [94] and Joseph et al. [95].

2.4.3 Effects of Processing on the Final Fiber Length of Natural Fiber Composites

Processing affects the final fiber length and thus the mechanical properties of the composites. Processing techniques such as injection molding and extrusion can cause high fiber attrition and thereby reduce the final fiber length. The initial fiber length should also be short enough, with the length of 0.5-7.5 mm (short fiber) or shorter than 0.5 mm (particulate) in order to allow the flow of the melted composite. Doan [7, 24] reported that the fiber length of the jute fiber reinforced polypropylene composites experienced shorting to 0.25 mm during compounding in extrusion machine, whereas, no further fiber shorting was detected during injection molding. Similar phenomena was observed by Keller [56] in hemp fiber reinforced biodegradable matrix composites. The fiber length experienced shorting from 7.5 mm to 0.4 mm during compounding in extrusion machine and no further fiber shorting during injection molding. Moreover, there was no evidence that the fiber length had been influenced by fiber content.

2.4.4 Effects of Chemical Treatments on the Morphological Characteristics and Mechanical Properties of EFB Fiber

The study on chemical treatments of EFB fiber was performed by Sreekala [15, 18]. The chemical treatments employed were alkali treatment, silane treatment, acrylation, acrylonitrile grafting, permanganate treatment, acetylation and peroxide treatment. The alkali treatment removed the natural and artificial impurities of the fiber and thereby produced rough surface topography. Acrylation and silane treatments gave surface coating to the fibers. Fibrillation was observed on fiber upon treatment with acrylation and peroxide. Acrylonitrile grafted fiber showed fibrillated and porous structure. Waxy layer on the fiber was removed upon the acetylation treatment while porous structure was observed upon the permanganate treatment.

Optimum mechanical performances were observed for silane treated and acrylated fibers. Both tensile strength of silane and acrylated fiber were improved by 10%. Silane and acrylation led to strong covalent bond formation and thereby enhanced the strength of the fiber. However, many of the modifications decreased the strength properties. Alkali treatment reduced the tensile strength by 10%, whereas acetylation, peroxide treatment, permanganate treatment and acrylonitrile grafting significantly reduced the tensile strength compared to that of alkali treated fiber. It was due to the breakage of the bound structure and also due to the disintegration of the non-cellulosic materials. The tensile modulus of the acrylated fibers was improved by 65% upon acrylation reaction. The tensile modulus of silane treated fiber remained constant upon treatments, while acetylation, acrylonitrile grafting, permanganate and peroxide treatments reduced the tensile modulus of the fiber.

2.4.5 Effects of Chemical Treatments on the Mechanical Properties and Water Absorption Characteristics of EFB Fiber Filled Thermoplastic Composites

The study on the effect of various chemical treatments on the mechanical properties of EFB-HDPE composites was performed by Mohd Ishak et al. [16]. The EFB content was 40%. Two types of silane coupling agents, 3-aminopropyltrimethoxysilane (3-APM) and 3-aminopropyltriethoxysilane (3-APE), and two types of compatibilizers, poly-(propylene-ethylene-acrylic acid) (PPEAA) and poly (propylene-acrylic acid) (PPAA), were used in their study. Generally, 3-APM and PPEAA were more effective in improving the filler-matrix interaction. The tensile modulus and impact strength of the 3-APM composites increased up to 100% and 77% as compared with the untreated composites, respectively, while the tensile strength remained constant upon 3-APM treatment. For the PPEAA composites, the maximum increase obtained was 67% for the tensile modulus, while the impact strength remained constant and the tensile strength decreased upon treatment. In the case of PPEAA, the presence of ethylene groups was believed to be responsible in promoting better compatibility between EFB and HDPE.

The effect of chemical treatments with variation of compounding techniques on the mechanical and water absorption properties of the polypropylene composites filled with 40% EFB was investigated by Rozman et al. [17]. The chemical treatments employed were PPAA, 3-APE and epolene wax (E-43). The compounding techniques used were internal mixer (IM) and extrusion (EX). The incorporation of E-43 and 3-APE produced composites with improved tensile strength for both the EX and IM composites. The increase in tensile strength was 28% compared to that of the untreated composites for both the E-43 and the 3-APE treated IM composites. For the EX composites, the increase in tensile strength, compared to that of the untreated composites, was 70% for the E-43 treated and 24% for the 3-APE treated composites. In addition, all types of treatment for the EX composites resulted in comparable improvement on the tensile modulus of the composites, with the average increase of 80% compared to that of the untreated composites. All types of treatment for the IM composites also resulted in comparable improvement on the impact strength of the composites, with the average increase of 38% compared to that of the untreated composites. Water absorption tests revealed that only composites treated with 3-APE resulted in reduced water uptake.

2.4.6 Effects of Chemical Treatments on the Mechanical Properties and Water Absorption Characteristics of EFB Fiber Filled Thermoset Composites

The study on the effect of chemical treatments of EFB fiber on the mechanical properties of phenol formaldehyde (PF) composites reinforced with randomly oriented 40 mm length of EFB fiber was performed by Sreekala et al. [18]. The fiber treatments employed were alkali treatment, silane treatment, acrylation, acrylonitrile grafting, permanganate treatment, acetylation and peroxide treatment. Generally, the interaction between the untreated EFB fiber and the PF resin was excellent due to the hydrophilic nature of the cellulose and the PF resin, thus led to high compatibility between the fiber and the matrix. The incorporation of treated EFB fiber into PF matrix led to the decrease in tensile strength and tensile modulus of the composites. Significant decrease on tensile strength by 50% and tensile modulus by 35% were observed for acetylated, acrylated and silane treated composites. Fibers became more hydrophobic upon modifications which reduced the interaction with hydrophilic nature of the PF matrix.

2.4.7 Effects of Chemical Treatments on the Mechanical Properties and Water Absorption Behavior of Various Natural Fiber Composites

The effects of alkali treatment on the mechanical properties of natural fiber reinforced thermoplastic composites were investigated by many researchers. Herrera-franco et al.

[51] reported that the alkali treatment increased the tensile modulus by 8% for the henequen fiber-HDPE composites, while the tensile strength remained constant upon treatment. Mohanty et al. [85] reported that the alkali treatment on the jute fiber-HDPE composites increased the impact strength by 26% as compared with the untreated composites. However, there was only marginal increase in the flexural and tensile strength of 2% and 9%, respectively. The effects of alkali treatment on the mechanical properties of the natural fiber reinforced thermoset composites were also investigated by many researchers. Van de Weyenberg et al. [96] reported that alkali treatment increased the tensile strength and tensile modulus of the flax fiber-epoxy composites by 30%. Mishra et al. [97] reported that the 5% NaOH treated sisal fiber-reinforced polyester composite had better tensile strength than that of the 10% NaOH treated composites. Alkali treatment was also found to be effective in reducing the water uptake of the natural fibers [19, 91, 92]. This was due to the removal of certain amount of hemicellulose and pectin that has high tendency to absorb water.

The effects of silane treatment on the mechanical and water absorption properties of natural fiber reinforced thermoplastic composites were investigated by many researchers [58, 63]. Girones [58] modified the pine fibers using four types of silane, Hexadecyltrimethoxysilane (HDS), γ-methacryloxoproyltrimethoxysilane (MTS), γ-aminopropyltriethoxysilane (APS) and γ-mercaptopropyltrimethoxysilane (MRPS). Treatment with silanes led to a modest rise in tensile and flexural modulus of the pine fiber-polypropylene composites. Water uptake measurements revealed a low water absorption by the composites, consistently lower than 2%wt, which indicated a controlled dimensional stability. Colom et al. [63] modified the surface of aspen wood fibers with γ-methacryloxoproyltrimethoxysilane (MTS) to improve the interface adhesion between the fiber and the HDPE matrix. The tensile strength was reported to increase by 38% as compared with the untreated composites. Herrera-Franco et al. [51] reported that the silane treatment on the henequen fiber-HDPE composites increased the tensile strength by 19% compared to that of the untreated one, while the tensile modulus remained constant upon treatment.

Acrylic acid can be graft-polymerized to modify glass fibers [57]. The possibility of using this treatment on natural fiber composites was investigated by many researchers [74, 89].

Li et al. [89] reported that tensile strength of acrylic acid treated flax fiber–HDPE composites improved by 4% upon treatment. However, there was no improvement on the water absorption characteristic of the composites. Ganan et al. [74] investigated the effect of treating fique fibers with different acrylic acid concentration of 5, 10 and 15% on the mechanical properties of polyester based composites. 10% of acrylic acid demonstrated the best flexural properties with the increase of 20% and 13% for flexural strength and flexural modulus, respectively.

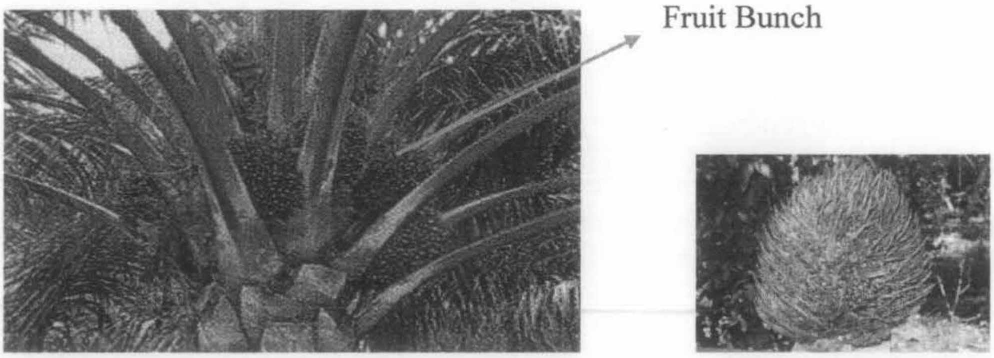
CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

3.1.1 Oil Palm Empty Fruit Bunch (EFB)

EFB is one of the major by product obtained from palm oil industry [12]. EFB fiber is obtained after the removal of oil seeds from fresh fruit bunch for oil extraction. EFB fiber is extracted by retting process of the EFB. Average yield of EFB fiber is about 400 g per bunch [15]. Photograph of oil palm tree and EFB is shown in Figure 3-1. In this work, EFB was obtained from Sabutek (M) Sdn. Bhd. in the form of pulverized and 5 mm average length of short fiber.



(a) (b)

Figure 3-1 Photographs of (a) oil palm tree and (b) oil palm empty fruit bunch.

3.1.2 High Density Polyethylene (HDPE)

HDPE used was from Titan Petchem (M) Sdn. Bhd. with a melt flow index and a density of 7 g/10 min and 0.961 g/cm^3, respectively.

3.2 EFB Preparation

Two different fiber types of untreated EFB, particulate and short fiber, were used in this study. The particulate size distribution and the average short fiber length were

0.325-0.4 mm and 5 mm, respectively. An Endeacotts Machine was used to obtain the specific particulate size distribution. To remove the moisture content, EFB was put in an oven at 80°C for 24 h.

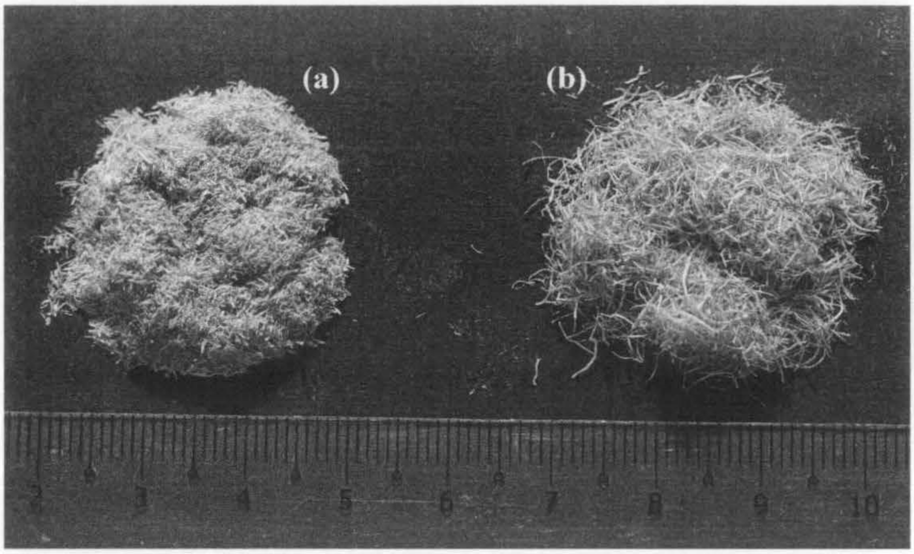


Figure 3-2 The photographs of (a) EFB particulates and (b) EFB short fibers.

3.3 Composite Preparation

The specimens were prepared in two steps: compounding and injection molding. The mixing of EFB and HDPE was carried out using the twin screw extruder Leistritz Type Mio27/Gl-32D at a screw speed of 50 rpm. Extruder temperatures were set at 160°C (zone 1 and 2), 170°C (zone 3 to 7) and 180°C (flange and die). The compounds were extruded through a single 2.5-mm rod die, cooled in a water bath and then pelletized. The compounded granulates were then transferred to the Tat Ming ME20 III injection molding machine at the injection pressure of 80 bar and the temperatures of 120°C (zone 1) and 180°C (zone 2 and 3) to produce the dog-bone shaped specimens (according to ISO 527-2, type 1B specimen) for subsequent mechanical testing. All the samples were set at similar injection molding parameters. The EFB content of the HDPE composites was varied from 0 to 30%wt. Higher EFB content were not analyzed due to the bad mold-filling problem and the failure to produce the samples with good surface appearance.

3.4 Chemical Treatment

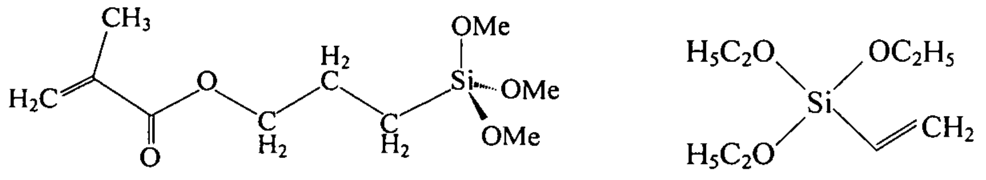
In order to modify the properties of the fiber and its composites, three chemical treatments, alkali, silane and acrylation were performed on the EFB short fiber. Only composites containing 10%wt of EFB short fiber were pre-treated.

3.4.1 Alkali Treatment

Alkali treatment of the EFB short fibers were performed by dipping them in a 2-10% NaOH solution for 24 h at room temperature. Then the fibers were washed thoroughly with purified water by Elga Purelab Option-S System. Subsequently, the fibers were dried in an oven at 80°C for 24 h.

3.4.2 Silane Treatment

The EFB short fibers were treated with 1, 3, 5 and 10%wt of the silane in an ethanol/water (60/40) solution for 1 h under agitation. The pH of the solution was adjusted to 3.5-4 with acetic acid. Subsequently, the fibers were dried in an oven at 80°C for 24 h. Two types of silane, γ-Methacryloxypropyltrimethoxysilane (MTS) and vinyltriethoxysilane (VTS) were used in this study. The silanes were supplied by Dow Corning Corp. The molecular stuctures of the silane used are shown in Figure 3-3.



(a) (b)

Figure 3-3 Molecular structures of (a) γ-Methacryloxypropyltrimethoxysilane and (b) vinyltriethoxysilane.

3.4.3 Acrylation

The EFB short fibers were treated with 5 and 10%wt of acrylic acid in purified water for 1 h under agitation. Then the fibers were washed thoroughly with purified water. Later, the fibers were dried in an oven at 80°C for 24 h.

3.5 Mechanical Testing

In this work, tensile and flexural testings were employed to investigate the mechanical performance of the composites. Both tensile and flexural tests were carried out using the LLOYD Instruments LR5K Universal Tensile Machine according to ISO 527-2 and ISO 178, respectively. The dog-bone shaped type 1B specimens with crosshead speed of 5 mm/min were used for the tensile testing. The value of tensile strength and tensile modulus of the composites were generated from the load vs. crosshead displacement curve. Due to the nature of this measurement technique, the elongation at break of the samples were not reported. The tensile strength was calculated using Eq. 3.1,

$$\sigma_t = \frac{P}{bd} \tag{3.1}$$

where σ_t is the tensile strength (MPa), P is the load (N), b is the specimen width (mm) and d is the specimen thickness. The strain was calculated using Eq. 3.2,

$$\varepsilon = \frac{\Delta l}{l_o} \tag{3.2}$$

where ε is the strain, Δl is the extension (mm) and l_o is the initial gage length (mm). The tensile modulus (E_t) is the slope of the stress vs. strain curve evaluated at initial strain, where the response is linear.

For flexural testing, specimens with dimensions of 80x10x4 mm^3 and crosshead speed of 2 mm/min were employed. The flexural strength (σ_f) was calculated using Eq. 3.3.

$$\sigma_f = \frac{3PL}{2bd^2} \tag{3.3}$$

where P is the force (N), L is the distance between the support span (mm), b is the specimen width (mm), and d is the specimen thickness (mm). The flexural modulus $\left(E_f\right)$ was calculated using Eq. 3.4.

$$E_f = \frac{L^3 m}{4bd^3} \tag{3.4}$$

where m is the slope of the initial straight-line portion of the load-deflection curve.

For all measurements, at least five specimens at each formulation were tested. The mean value and the associated standard deviation were then reported.

3.6 Water Absorption Test

The sample dimensions for water absorption experiments were 30x10x4 mm^3. A minimum of three samples were tested for each formulation. The samples were initially dried in an oven at 50°C for 24 h, cooled in a desiccator and weighed to the nearest 0.1 mg. Samples were then dipped in purified water at room temperature. The samples were removed at specified time intervals, blotted to remove the excess water on the surface and immediately weighed using a Mettler Toledo balance. The weight change during the water absorption test was determined by the difference between the mass after a specific period of immersion and the initial mass. The water absorption experiment setup is shown in Figure 3-4.

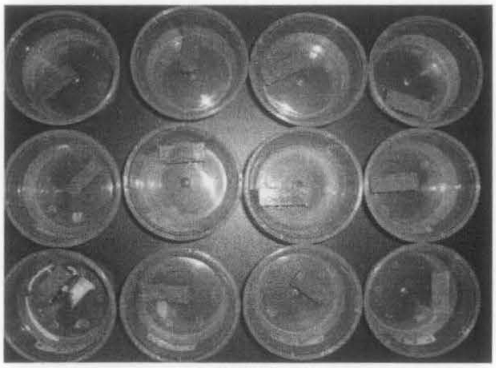


Figure 3-4 Photographs of water absorption test setup.

3.7 Morphology Study Using Scanning Electron Micrograph (SEM)

The fiber morphology and tensile-fractured surfaces of the composite samples were carried out using SEM, model Oxford Leo 1430. The specimens were mounted in aluminum stub and sputter-coated with a thin layer of gold to avoid electrostatic charging during examination. By means of this technique, it was possible to determine the fiber morphology characteristics and the adhesion quality between the fiber and the matrix.

CHAPTER 4

RESULTS AND DISCUSSION

This chapter is divided into two sections. In the first section, the tensile and flexural properties of EFB particulate and short fiber composites, as well as water absorption characteristics of these composites are discussed. The discussion then continues to the second section on the effects of chemical treatments on the mechanical properties and water absorption of the 10%wt EFB short fiber composites. The fractured-surface morphology for both untreated EFB particulate and short fiber composites, and also for the treated EFB short fiber composites are presented. The surface morphology of untreated and treated fiber are also presented.

4.1 Effects of EFB Fiber Content and Fiber Type

4.1.1 Effects of EFB Fiber Content and Fiber Type on the Mechanical Properties of the Composites

Two types of fiber, particulate with size distribution of 0.325-0.4 mm and short fiber with average fiber length of 5 mm were used as reinforcing material in this study. Figure 4-1 shows the effect of EFB content on tensile strength of the EFB-HDPE composites. It is observed that for both EFB particulate and short fiber composites, there is a decrease in the tensile strength values as the EFB content increases. The decrease is up to 12 and 22% for short fiber and particulate composites, respectively as the EFB content increases from 0 to 30%wt. The decrease in tensile strength of the composites as the EFB content increases could be attributed to poor adhesion between the EFB and the matrix, which promotes micro crack formation at the interface. Higher EFB content results in more void formation during processing, which leads to micro crack formation under lower loading and therefore reduces the tensile strength [98]. Higher EFB content also results in higher fiber agglomeration which reduces the adhesion between the EFB and the matrix.

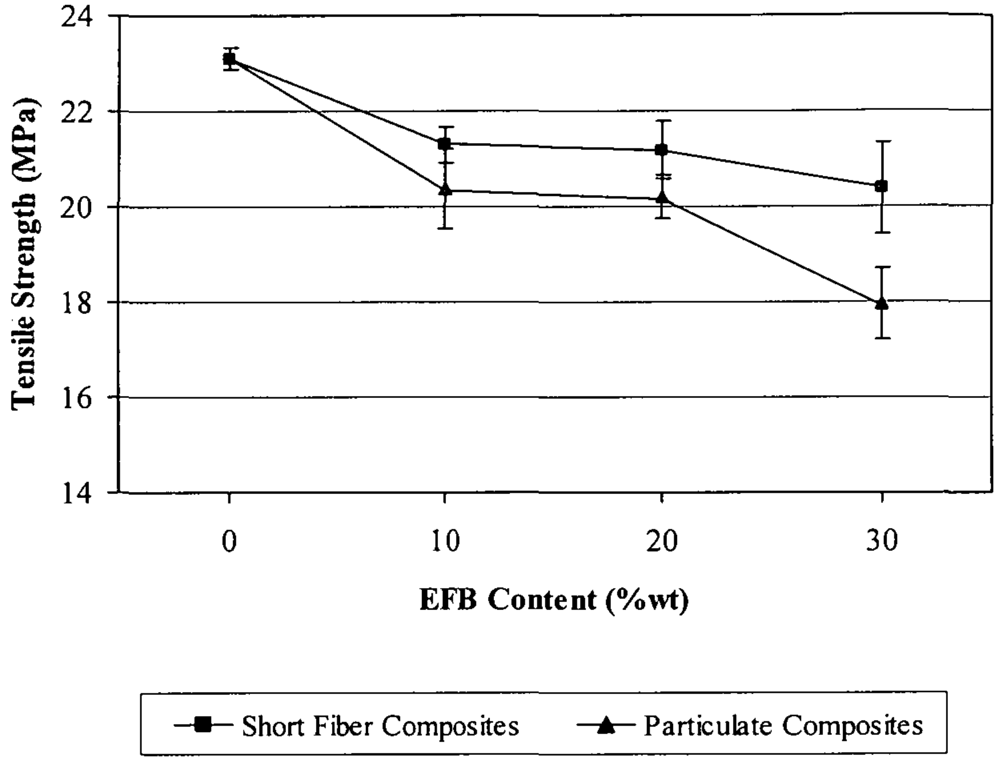


Figure 4-1 The tensile strength of untreated EFB particulate and short fiber composites at varying EFB content.

While the tensile strength decreases with the addition of fiber, the tensile modulus of EFB composites increases with the increase in EFB content as shown in Figure 4-2. As the EFB content increases, the increase in tensile modulus is up to 50% for the short fiber composites. For particulate composites, the tensile modulus increases up to 24% as the EFB content increases from 0 to 20%wt, and slightly reduces when the EFB content continues to increase to 30%wt. Generally, the presence of filler or reinforcing agent will increase the tensile modulus of the composites [48, 99]. The increase in tensile modulus indicates the ability of EFB to impart greater stiffness to the HDPE composites. The decrease in tensile modulus of the particulate composites as the EFB content increases to 30%wt may be due to the more void formation during processing as the EFB content increases. Another aspect is may be due to the maximum reinforcing ability that has already been reached by the EFB particulate.

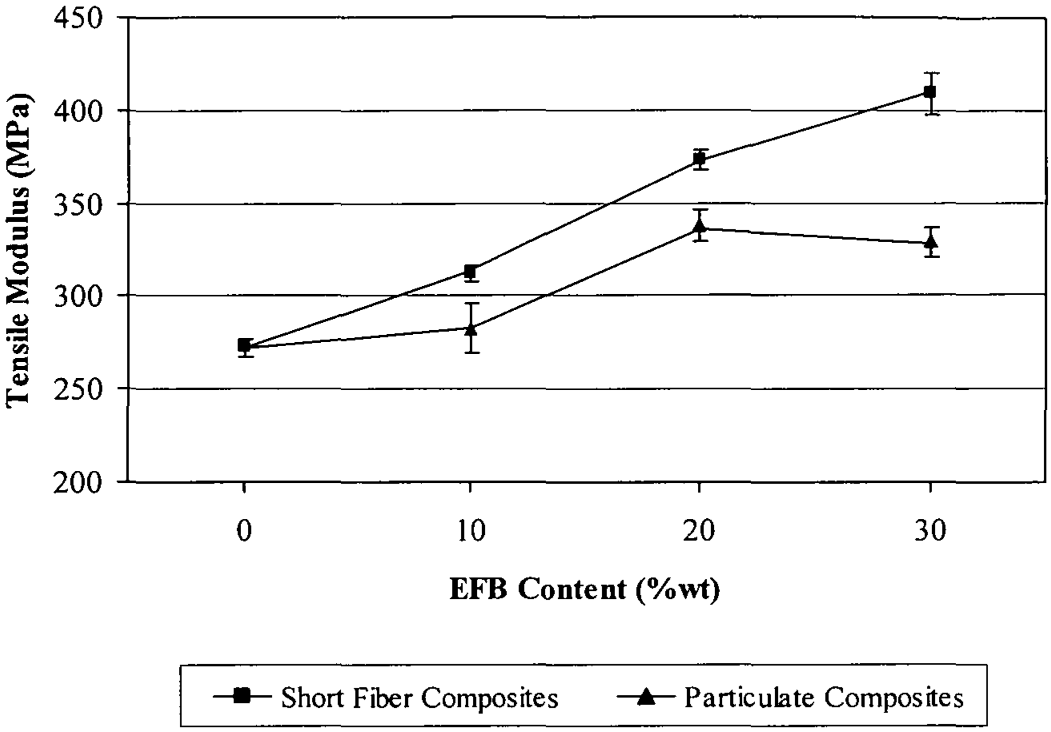


Figure 4-2 The tensile modulus of untreated EFB particulate and short fiber composites at varying EFB content.

The flexural strength of untreated EFB particulate and short fiber composites at varying EFB content are presented in Figure 4-3. Flexural strength of the short fiber composites increases up to 38% as the EFB content increases from 0 to 30%wt. For the particulate composites, the flexural strength increases up to 21% as the EFB content increases from 0 to 20%wt. The flexural strength then continues to decrease as the EFB content increases to 30%wt.

Unlike the flexural strength, the flexural modulus of both EFB particulate and short fiber composites continue to increase as the EFB content increases from 0 to 30%wt, as demonstrated in Figure 4-4. The increase amounted to 82% and 63% for short fiber and particulate composites, respectively for 30%wt EFB content. Flexural loading causes tensile, compression and shear forces to develop inside the material, as illustrated in Figure 4-5. The increase in flexural strength and flexural modulus of the composites may be due to the load that can be transferred into various forces inside the material, such as tension, compression and shearing, with different distribution at each layer, which makes the material's ability to withstand load improves. The decrease in flexural strength of the particulate composites at 30%wt EFB content and the decrease in the percentage of flexural modulus improvement of both particulate and short fiber composites at 30% EFB content indicate that the high amount of EFB may lead to agglomeration of the EFB fibers and thus reduces the flexural properties of the composites.

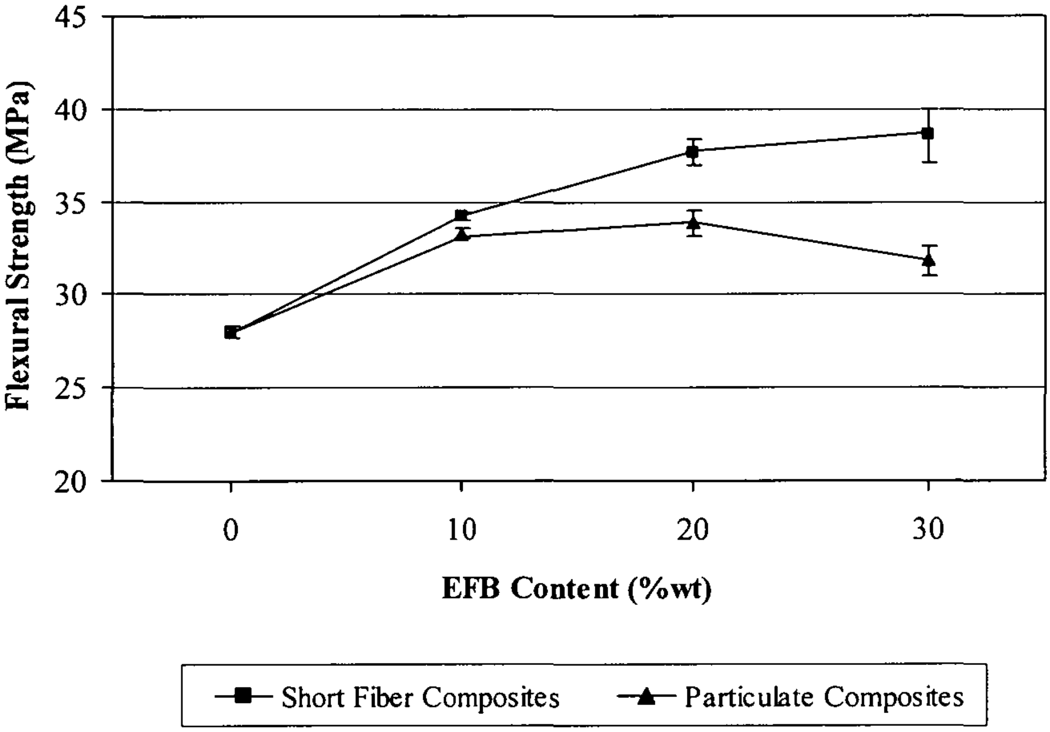


Figure 4-3 The flexural strength of untreated EFB composites varying EFB content.

It is observed that for both tensile and flexural properties, EFB short fiber composites experienced higher values compared to that of EFB particulate composites. For EFB particulates, due to their dimension, their capability to support load being transferred from the matrix is rather poor compared to that of short fibers. Thus, the mechanical properties improvement in the particulate composites is lower than that of the short fiber composites [16]. Other important factor that needs to be considered is the high fiber attrition during processing that may reduce the fiber length and thereby reduce the mechanical properties. As reported by Keller [56] and Doan [7, 24], short fiber in polymer composites experienced shorting to become particulate during compounding. According to the current results, EFB short fiber composites still possess higher mechanical properties compared to that of EFB particulate composites. It could be interpreted that not all of the EFB short fibers become particulate upon compounding and thus the remaining EFB short fiber inside the composites may give significant reinforcement effect on the composites.

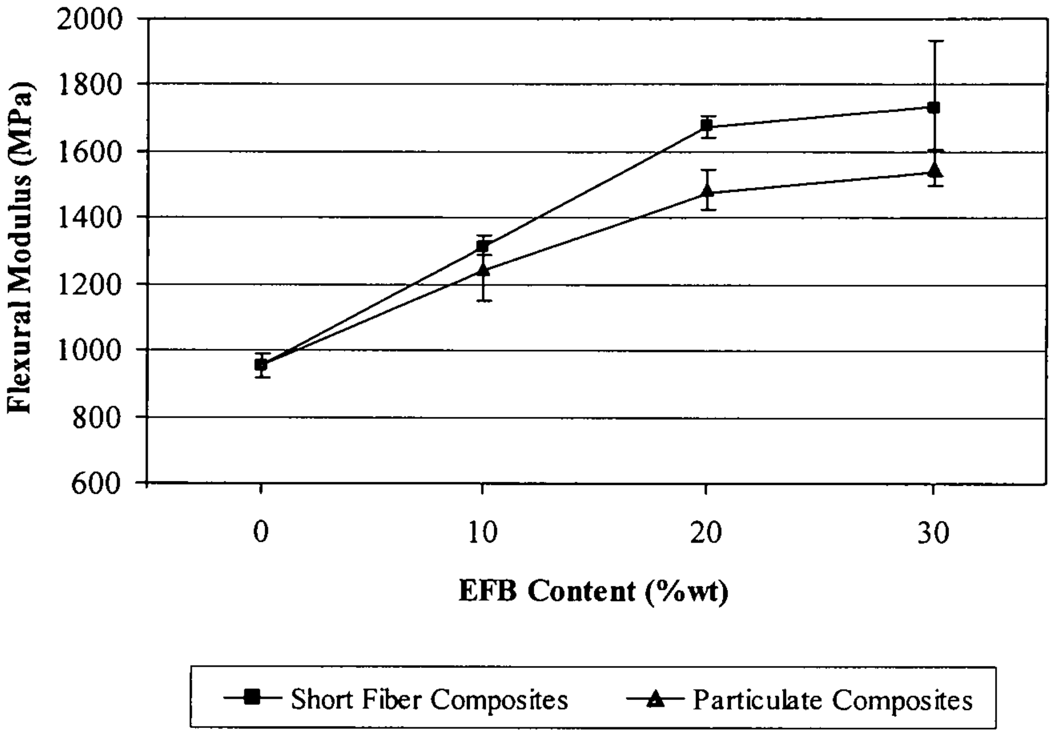


Figure 4-4 The flexural modulus of untreated EFB composites with varying EFB content.

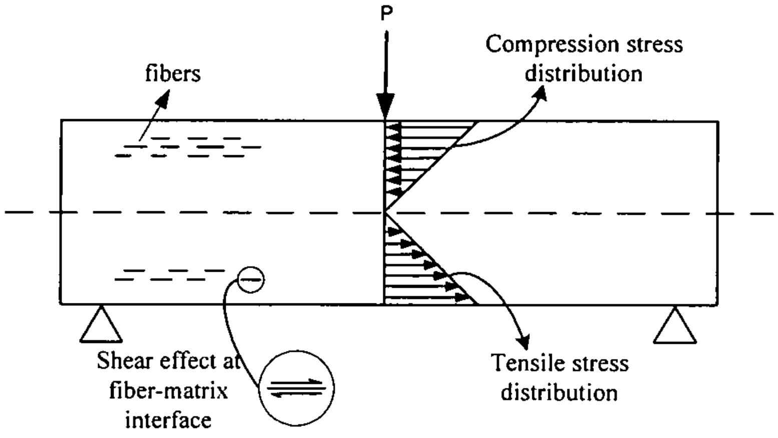


Figure 4-5 Schematic diagram of various forces developed inside the composites during flexural loading.

4.1.2 Morphological Studies on Fractured Surface of the Composites

According to the morphological studies of the tensile-fractured surface using SEM, the failure modes of the short fiber composites are dominated by fiber pullout and fiber debonding, as illustrated in Figure 4-6. Fiber pullout is the mechanism that the fiber is pulled out from the matrix. This mechanism is firstly initiated by the fiber debonding or loss of adhesion between the fiber and the matrix. For the particulate composites, plastic deformation in the form of matrix tearing is observed, as demonstrated in Figure 4-7.

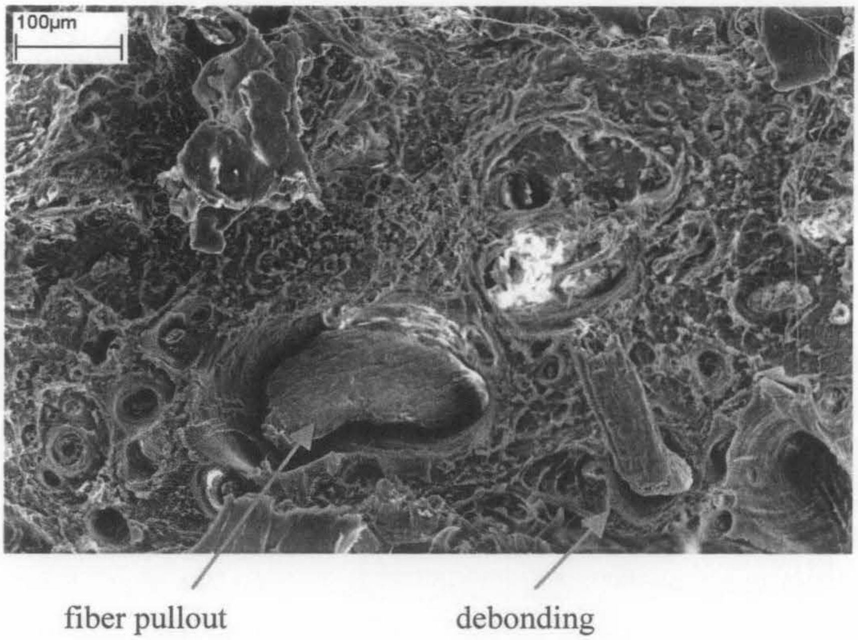


Figure 4-6 SEM micrograph of the tensile-fractured surface of the untreated EFB short fiber composites at 10%wt EFB content; magnification = 100 X.

It can be inferred that, even though short fiber composites experienced fiber pull out and debonding, the contribution of the fiber in improving the mechanical properties is still observed. The incidence of fiber pullout and debonding indicates that there is load being transferred to the fiber to a limited extent. As shown later, the ability of the fiber to transfer the load can be enhanced by fiber treatment by improving the fiber-matrix adhesion of the composites. Matrix tearing in the particulate composites indicates that the composites still possess ductile properties and the energy absorbed during mechanical testing is mainly transferred in matrix tearing formation. Thus, there is no significant reinforcing effect of EFB particulate since the stress or energy transferred to the particulate is limited.

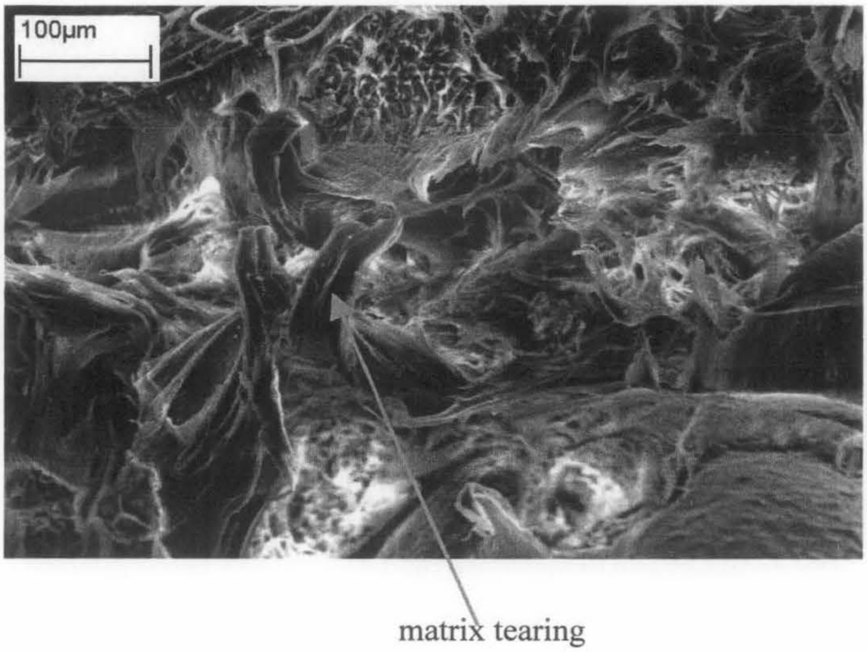


Figure 4-7 SEM micrograph of the tensile-fractured surface of the untreated EFB particulate composites at 10%wt EFB; magnification = 100 X.

4.1.3 Effects of EFB Fiber Content and Fiber Type on the Water Absorption of the Composites

A serious drawback related to the use of natural fibers in composites is their sensitivity to water, which reduces their mechanical properties. The water absorption characteristic of untreated EFB particulate and short fiber composites at varying EFB content is shown in Figure 4-8. For all composites, the amount of water absorption increases as the immersion time increases. It is due to the hydrophilic nature of EFB fibers, which means that EFB fibers possess high tendency to absorb water. After a period of time, the amount of water absorbed by the composites reaches a limiting value. This corresponds to the maximum amount of water that can be absorbed by the EFB fibers.

As the EFB content increases, water uptake of the composites also increases. The polar property of EFB leads to massive water absorption, whereas non-polar property of the HDPE makes this polymer highly resistant to water. Thus, higher EFB content in the composites will result in higher water uptake. Higher EFB content also contribute to the higher amount of EFB that is being exposed to the composites surface and thereby result in higher water uptake of the composites.

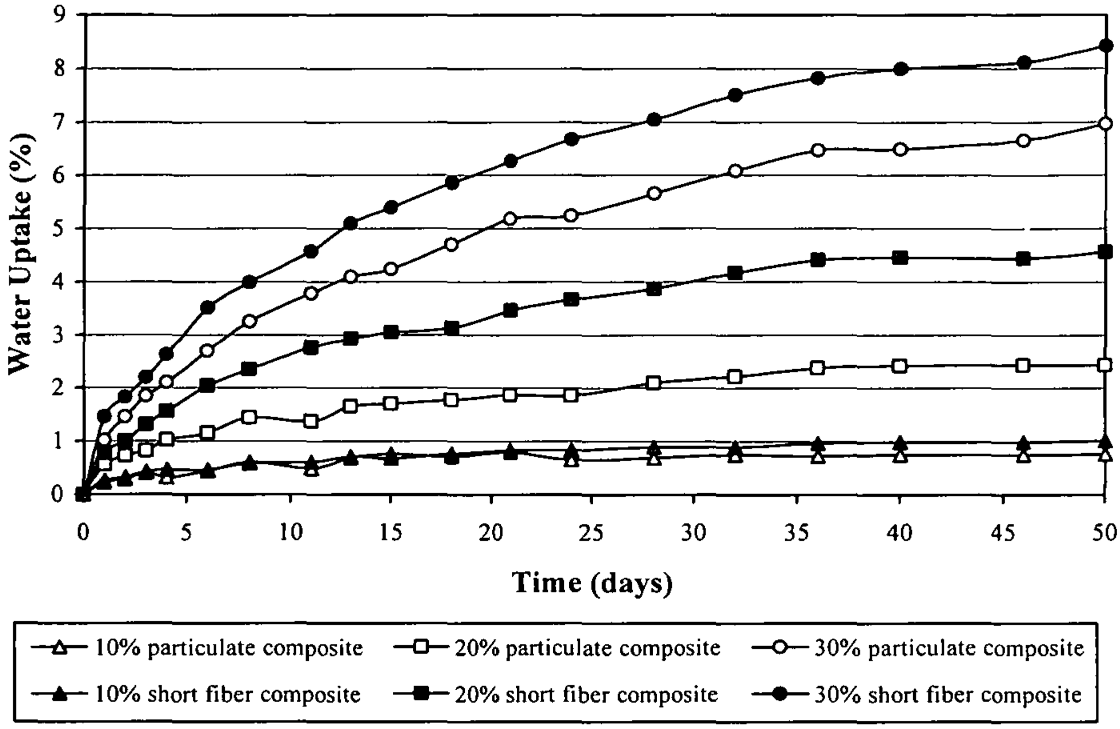


Figure 4-8 Water absorption characteristics of untreated EFB particulate and short fiber composites vs. immersion time at varying EFB content.

Water uptake of the short fiber composites is higher than that of the particulate composites. The amount of water absorbed by the composites at 30%wt EFB content are 8.5% and 7% for EFB short fiber and particulate composites, respectively. For the composites with 20%wt EFB content, the water absorbed are 4.5% and 2.5% for short fiber and particulate composites, respectively. However, the amount of water absorbed by the composites containing 10%wt EFB is similar between particulate and short fiber composites, which are lower than 1%.

The shape of the EFB short fiber leads to greater capillary action of water compared to that of the EFB particulate. When water reaches the EFB short fiber, it will easily flow along the fiber. However, the particulate composites experience more difficulty in water uptake. Due to the small shape of the particulates, the amount of water that they can absorb is limited. Capillary action to other particulates is also hindered by the presence of HDPE as the matrix.

For the composites containing 10%wt EFB, the relatively small fiber mass fraction may be almost completely surrounded by the HDPE matrix which limits the water being absorbed by the fiber. This may explain the minimal difference in the amount of water uptake between the particulate and the short fiber composites.

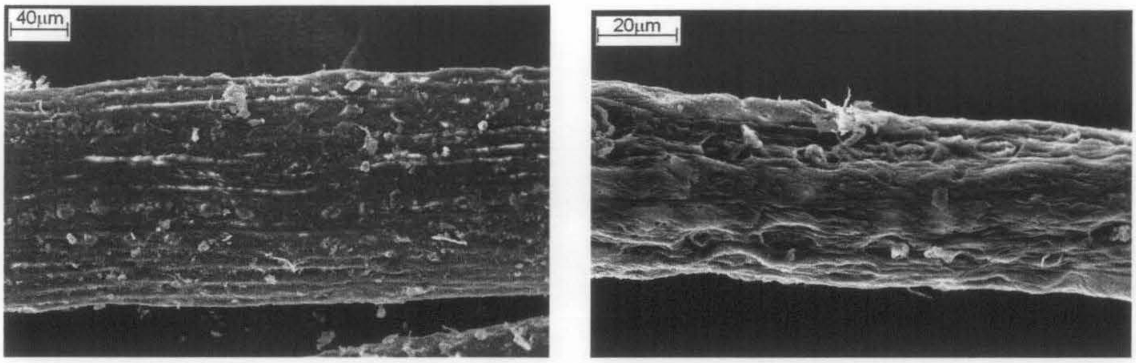
For all the composites, the highest rate of water uptake was in the first 4 days of water immersion of the composites. After 4 days, the amount of water absorbed continues to increase. The amount of water absorbed by the particulate and short fiber composites containing 10%wt EFB reaches a limiting value after 35 days of water immersion, as shown in Figure 4-8. The limiting amount of water absorbed by the 20%wt particulate and short fiber composites are reached after 40 days of water immersion. However, the particulate and the short fiber composites containing 30%wt EFB do not exhibit similar limiting value in water uptake. In fact, even after 50 days, the amount of water absorbed continues to rise. Generally, it can be inferred that as the EFB content increases, the time required to reach the limiting value of water uptake also increases. The higher the EFB content means the more water is able to be absorbed by the composites and the longer the time required to reach the maximum or limiting value of water absorbed.

4.2 EFB Short Fiber Composites: The Effects of Chemical Treatments

Fiber surface modifications were attempted to improve the fiber-matrix compatibility of the composites. Chemical treatments such as alkali, silane and acrylation were performed on the EFB short fiber. The effects of fiber surface modifications on the mechanical properties and water absorption characteristics of the 10%wt EFB short fiber composites are discussed. Fiber surface morphology and fiber fractured surface of the 10%wt EFB short fiber composites upon treatments are presented first as the morphological characteristics may provide insights to explain the trends observed on the mechanical properties and water absorption behavior of the composites.

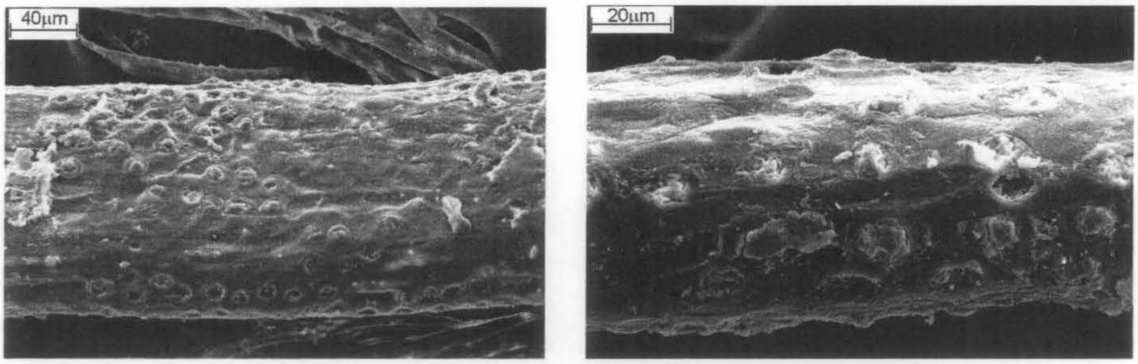
4.2.1 Morphology of the Short Fiber Surface

Chemical treatments modify not only the chemical nature but also the morphology of the fibers. Hence, it is necessary to study the fiber surface morphology using SEM. As shown in Figure 4-9(a–e), the scanning electron micrographs of the untreated and treated fiber surfaces revealed the changes in the structure of the fibers.



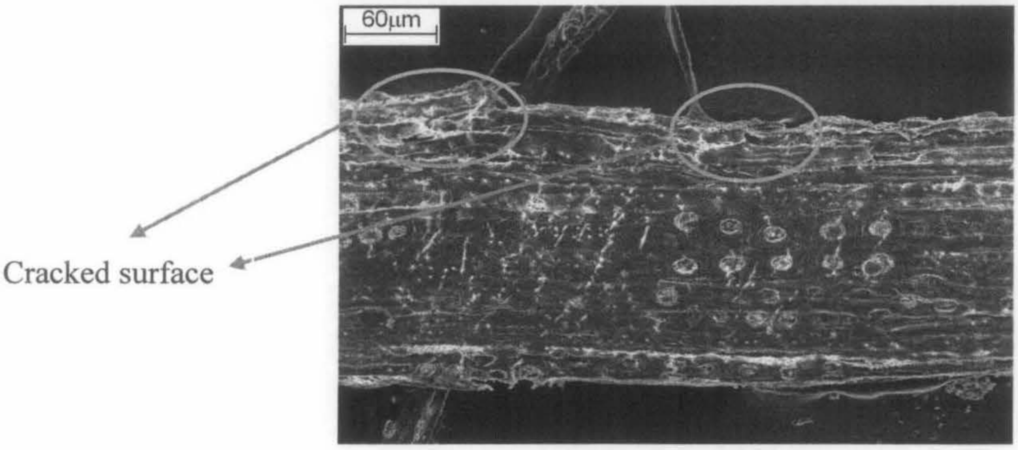
a) Untreated fiber.

b) Alkali treated fiber.



c) MTS treated fiber.

d) VTS treated fiber.



e) Acrylated fiber.

Figure 4-9 Scanning electron micrographs of short fiber surfaces.

Clean and smooth fiber surface is observed for the untreated fiber as shown in Figure 4-9a. After the alkali treatment, the fiber surface morphology shows more texture. There has been removal of the waxy epidermal tissue of the fiber, as illustrated in

Figure 4-9b. The removal of surface impurities on plant fibers is advantageous for fiber-matrix adhesion as it facilitates both the mechanical interlocking and the bonding reaction due to the exposure of the hydroxyl groups to the chemical used in the treatment.

Surface coating on MTS and VTS treated fiber revealed that the coupling agents are successfully grafted on the short fiber surface, as shown in Figure 4-9c and 4-9d, respectively. Since the EFB short fiber demonstrates micropores on their surface, the coupling agents can penetrate into the pores and form a mechanical interlocking coating on the surface. Both MTS and VTS show similar phenomena since both coupling agents are silane-based compounds. The difference is on the functional groups born by each silane, as illustrated in Figure 3-3.

Figure 4-9e shows that the waxy layer on the fiber surface is partly removed after the acrylation treatment. Cracks on the surface are also observed, which may be induced by the strong acid characteristic of the acrylic acid. It may also be detrimental if the fiber is over exposed to the solution.

4.2.2 Morphology of the Fractured Surface of the 10%wt Short Fiber Composites

Scanning electron micrographs of the cross section of the tensile-fractured specimen for selected composites containing 10%wt EFB short fiber were carried out as an attempt to evaluate the failure mechanism and the quality of the fiber-matrix bonding. It was observed that the interfacial adhesion between the fibers and the matrix of the untreated composites was poor, as demonstrated in Figure 4-6. Indeed, fiber debonding and fiber pull out were observed.

When using alkali treatment, the surface seems to be clean and free from any adhering polymer, as illustrated in Figure 4-10. Void at the fiber-matrix interface was also observed from the micrograph. As discussed earlier, the alkali treatment has removed the natural and artificial impurities on the fiber surface and increased its surface roughness as demonstrated in Figure 4-9b. The chemical reaction between the NaOH and the hydroxyl group of the fiber is proposed to occur, as illustrated in Eq. 2.1, thus decreasing the hydrophilic property of the fiber and consequently improved the fiber-matrix compatibility to some extent.

Figure 4-10 Scanning electron micrograph of the fractured surface of the composites filled with the alkali treated fibers; magnification = 100 X.

It should be noted that, based on the nature of the alkali chemical, there is no chemical coupling between the fiber and the matrix. The alkali treatment has only reduced the hydrophilicity of the fiber and thus results in improved fiber-matrix compatibility and wetting. It can be inferred that any mechanical properties improvement of the alkali treated composites may be vastly contributed by the mechanical interlocking mechanism between the fiber and the matrix, as illustrated in Figure 4-11, and to a lesser extent contributed by the chemical interaction between the fiber and the matrix.

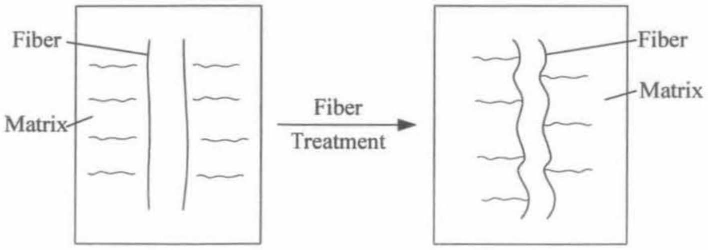


Figure 4-11 The schematic model of mechanical interlocking mechanism between the fiber and the matrix.

For MTS and VTS fiber treated composites, the matrix is observed to be adhered to the fiber surface, as illustrated in Figure 4-12 and 4-13, respectively. Both MTS and VTS fiber treated composites show similar behavior. This is because both MTS and VTS are silane-based coupling agents with differing functional groups. The observation from both Figure 4-12 and 4-13 indicates the improved fiber-matrix compatibility of the composites upon both of the silane treatments.

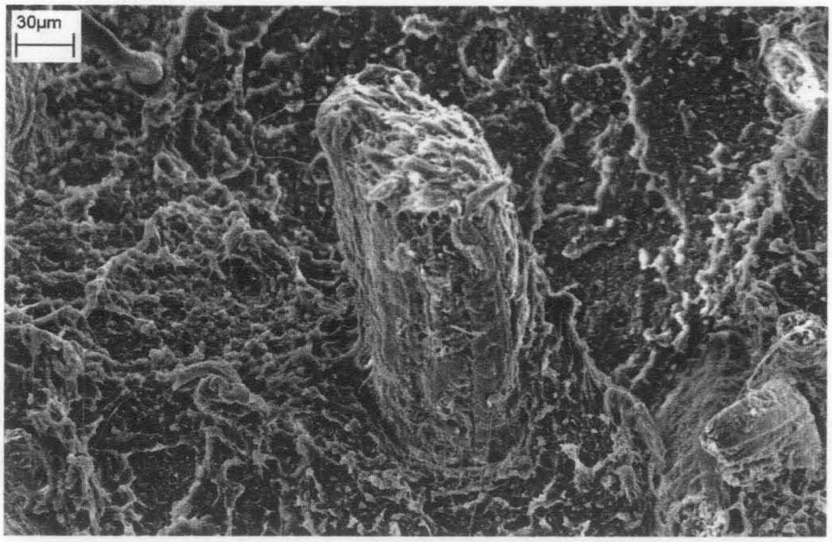


Figure 4-12 Scanning electron micrograph of the fractured surface of the composites filled with the MTS treated fibers; magnification = 200X.

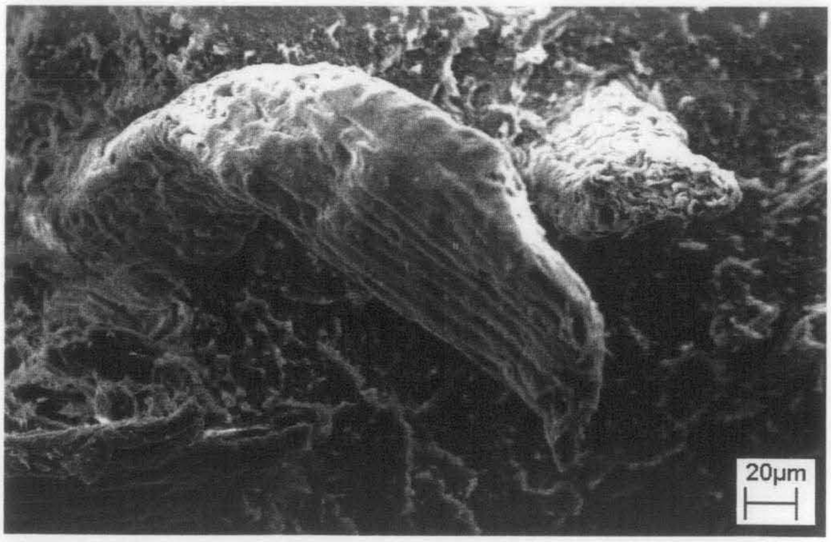


Figure 4-13 Scanning electron micrograph of the fractured surface of the composites filled with the VTS treated fibers; magnification = 200 X.

During the compounding process, the matrix may have chemically reacted with the organic functionality of the silane coupling agents adhering to the treated fiber, leading to the enhanced adhesion and compatibility of the fiber-matrix interface. This is depicted in Figure 4-12 and 4-13 where the polymer matrix is seen to adhere well to the fiber surface. The improved interaction between the fiber and the matrix after these silane treatments may contribute to improved mechanical properties of the composites.

For the composites filled with acrylated fiber, the fiber in the composites broke into smaller fiber diameter, as demonstrated in Figure 4-14. It may be due to the strong acid characteristic of the acrylic acid which has the ability to dissolve the pectin adhesive in the fiber. In addition, the fiber splitting effect may have been worsened by the shearing effect during the compounding and injection molding processes.

Figure 4-14 Scanning electron micrograph of the fractured surface of the composites filled with the acrylated fibers; magnification = 40 X.

According to its chemical formula, acrylic acid (CH_2=CHCOOH) is characterized by the presence of carboxylic group (-COOH) and the short unsaturated carbon chain (CH_2=CH-). Upon acrylation treatment, the hydroxyl group of the fiber is proposed to react with the carboxylic group of the acrylic acid and thereby reduce the hydrophilic property of the fiber, as shown in Eq. 2.4. At the same time, the carbon chain of the acrylic acid may interact with the polymer matrix during processing and thereby establishes chemical coupling effect between the fiber and the matrix. The presence of chemical coupling between the fiber and the matrix should be evidenced by the presence of the polymer on the fiber surface. However, referring to Figure 4-14, the presence of polymer on the fiber cannot be ascertained clearly. It may be due to the nature of the short carbon chain of the acrylic acid that has relatively low reactivity towards the matrix.

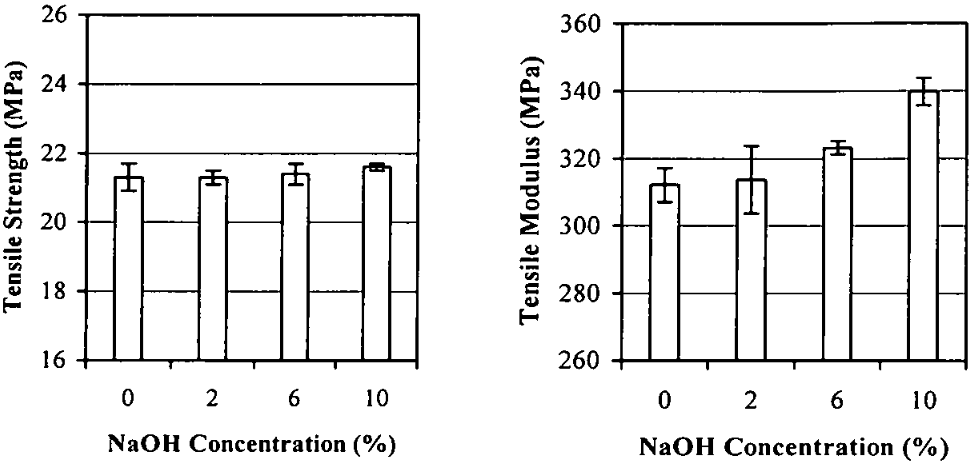
The mechanical properties of the acrylated fiber composites may be affected by the fiber splitting phenomenon as it leads to higher fiber aspect ratio. The brittle nature of the acrylated fiber may also influence the mechanical properties of the composites.

4.2.3 The Mechanical Properties of the 10%wt EFB Short Fiber Composites

4.2.3.1 Alkali Treatments

The tensile strength and tensile modulus of the 10%wt EFB short fiber composites subjected to alkali treatment are shown in Figure 4-15. The tensile strength of the composites does not vary noticeably by applying the alkali treatment. Increase in tensile modulus is observed in the composites treated with 6% and 10% NaOH solution. The increase in tensile modulus reached a maximum of 9% for the composites with fibers treated using 10% NaOH solution. The tensile modulus is predicted to increase when the NaOH concentration is increased. However, the addition of more than 10% concentration of NaOH with respect to the amount of water is excessive enough and unsuitable in terms of economical point of view.

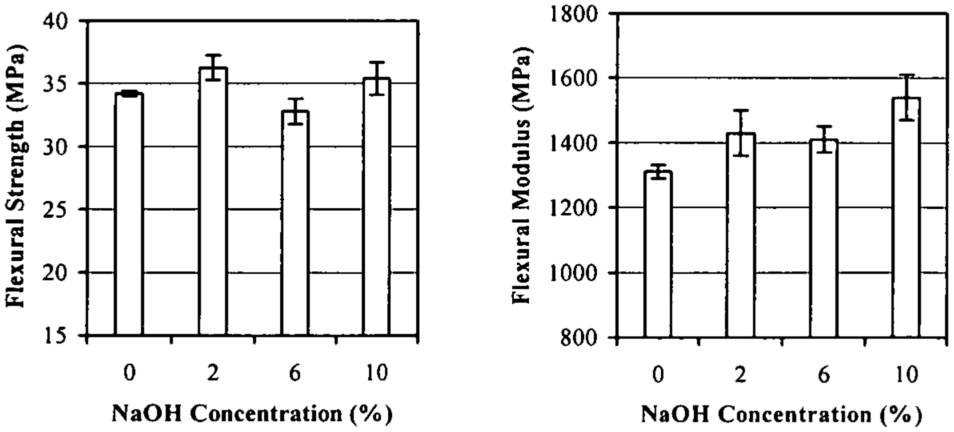
The alkali treatment removes the impurities on the fiber surface and thus increases the fiber's surface roughness. However, as there is no polymer sticking to the fiber surface, the bonding mechanism between the fiber and the matrix are vastly contributed by the mechanical interlocking mechanism and to a lesser extent by the chemical interaction between the fiber and the matrix, as illustrated in Figure 4-11. Nonetheless, the mechanical interlocking interaction between the fiber and the matrix is of low strength and could not effectively transfer the load from the matrix to the fiber. This is evidenced by the insignificant increase in the tensile strength values of the composites despite the alkali treatment on the short fibers. The removal of waxy cuticle layer and amorphous hemicellulose on the fiber surface upon the alkali treatment may result in stiffer fiber and thus the incorporation of the fiber into the HDPE matrix may improve the tensile modulus of the composites. However, as the mechanical interlocking mechanism is relatively weak, the increase in the tensile modulus is also relatively small.



(a) (b)

Figure 4-15 The effects of alkali treatments on the tensile properties of the EFB short fiber composites; (a) tensile strength and (b) tensile modulus.

Flexural strength does not show any systematic trends as the NaOH concentration increases, as demonstrated in Figure 4-16. There is no significant change in the flexural strength values upon alkali treatments. Unlike the flexural strength, the flexural modulus of the composites seems to increase upon the alkali treatments. The increase in tensile modulus reached a maximum of 18% at 10% NaOH solution. The rough surface of the fiber upon treatment combined with high shear resistance during flexural loading may contribute to the increase in the flexural modulus.



(a) (b)

Figure 4-16 The effects of alkali treatments on the flexural properties of the EFB short fiber composites; (a) flexural strength and (b) flexural modulus.

4.2.3.2 Silane Treatments

There were two kinds of silane R-Si(OR')$_3$ used in this study, vinyltriethoxysilane (VTS) and γ-Methacryloxypropyltrimethoxysilane (MTS).

4.2.3.2.1 MTS

As shown in Figure 4-17, increase in tensile strength is observed as the MTS concentration increases up to 5%, but decreases upon treatment with the 10% concentration of MTS. The maximum tensile strength measured is 13% at 5% MTS concentration. Tensile modulus of the composites increases upon treatment with the MTS at all concentrations, although not systematic. The maximum increase in the tensile modulus is 6% at 10% MTS concentration while the lowest increase is for the composites treated with 5% MTS concentration.

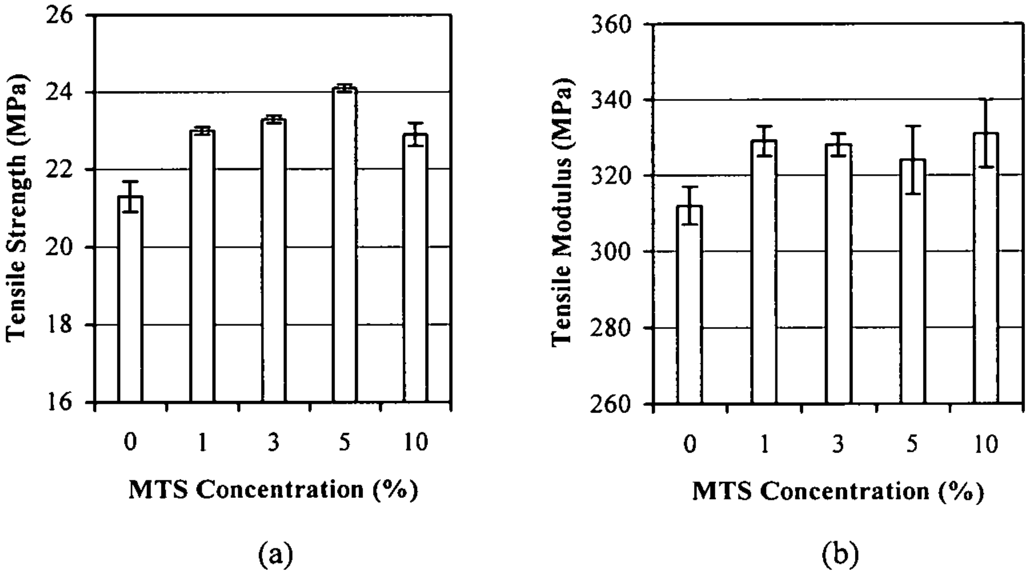


Figure 4-17 The effects of MTS treatments on the tensile properties of the EFB short fiber composites; (a) tensile strength and (b) tensile modulus.

As previously discussed, the presence of thin layer on the fiber surface and the polymer matrix adhering to the fiber surface were observed upon the MTS treatment. These morphological evidences indicate the improved fiber-matrix compatibility of the composites upon the MTS treatment. The increase in the fiber-matrix compatibility may explain the increase in the tensile strength values of the composites.

The increase in fiber-matrix compatibility may be induced by the nature of the MTS that have two reactive functional groups. On one hand, MTS bears alkoxysilane groups OR' that are capable to react with the fiber surface. In the presence of moisture, hydrolysis of alkoxysilanes leads to the formation of silanols $R\text{-}Si(OH)_3$. The silanol then reacts with the hydroxyl group of the fiber, as illustrated in Eq. 2.2 and 2.3, forming stable covalent bonds to the cell wall. On the other hand, organofunctional groups R on the MTS are capable to improve the compatibility, or even react with the matrix, thus enhancing the interfacial adhesion between the two phases. This coupling effect may have positive impact on the tensile strength of the composites. The schematic illustration of the fiber-matrix chemical coupling and the interfacial zone formed are shown in Figure 4-18.

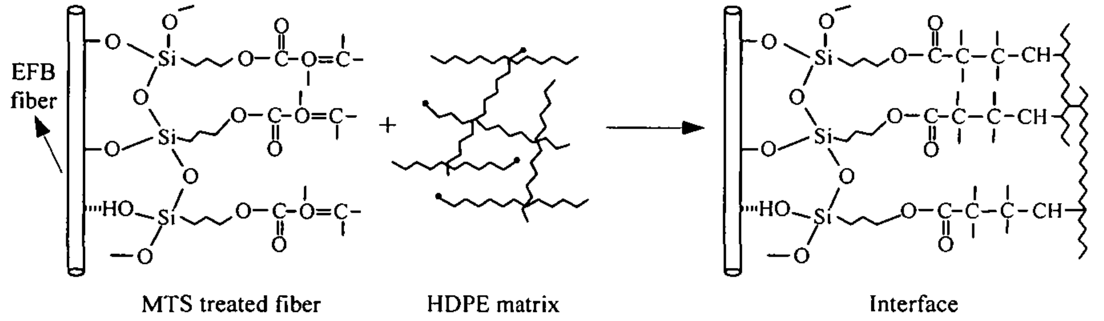
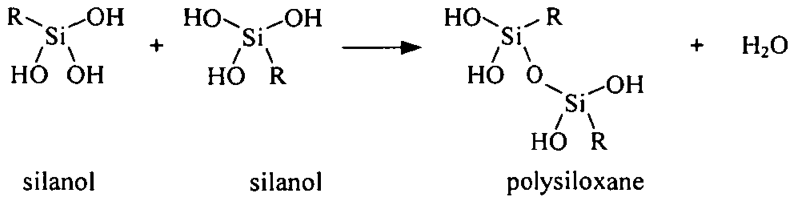
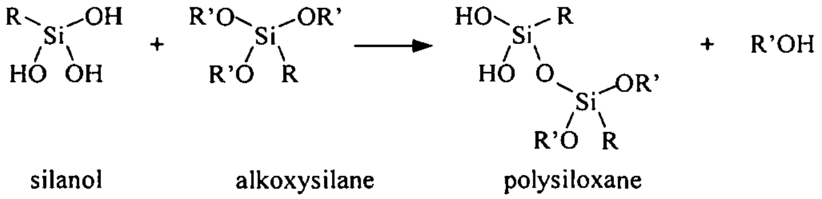


Figure 4-18 Schematic illustration on the interfacial zone formed in the HDPE based composites containing MTS modified fiber [59].

The decrease in the tensile strength of the composite treated with 10% MTS concentration may be related to the treatment effectiveness. The effectiveness of silane treatment depends on the silane solubility level in the medium, thickness of the film formed on the surface and the extent of the silane wettability of the fiber surface. It can be achieved by controlling the extent of hydrolysis and condensation reaction. After solvent evaporation, the residual silanol groups may undergo further condensation reaction with the hydroxyl groups of the fiber. The residual silanol groups may also undergo self condensation or react with residual alkoxy groups to form a polysiloxane network on the surface, as illustrated in Eq. 4.1. and Eq. 4.2, respectively [100].



(4.1)



(4.2)

Further condensation reactions lead to gel-like networks which precipitate in the form of colloidal particles and thereby reduce the fiber-matrix compatibility. By optimizing these reactions, which can be studied by varying the functional groups of the silane and the composition medium such as temperature, pH, concentration, amount of water and catalyst, the optimal properties of the composites will be obtained. According to the tensile strength result of the composites, it can be inferred that 5% MTS was the optimum concentration to bring about the optimum chemical coupling between the fiber and the matrix. Further increase of MTS concentration may lead to a further condensation reaction of the residual silanol groups and thus reduce the tensile strength of the composites.

Marginal increase in the tensile modulus was observed in this study, with the lowest increase of 4% was observed for the composites treated with 5% MTS, as illustrated in Figure 4-17. Generally, the presence of fibers in a polymer based composite increases the composite's tensile modulus. In contrary, the high extent of chemical coupling interaction between the fiber and the matrix due to the MTS treatment may reduce the matrix molecular arrangements and hence the matrix crystallinity. Molecular disorderness reduction may lead to the decrease in tensile modulus of the composites. Although the tensile strength measured at the 5% concentration of MTS is the highest, the tensile modulus measured is the lowest among the four different MTS concentration. This may be attributed to the effective reaction of the MTS with the matrix. This interaction may attribute to a plasticization effect of the matrix which reduce the matrix crystallinity and hence the tensile modulus value. The lowest value in tensile modulus of the composites treated with 5% MTS may be attributed to this high chemical interaction between the fiber and the matrix and the reduced matrix crystallinity.

Generally, the MTS treatment has not significantly modified the composite's flexural strength except for composites treated with 3% MTS concentration as shown in Figure 4-19a. Unlike that in the flexural strength, the trend observed in the flexural modulus of the composites is different. The flexural modulus of the composites increases steadily at 1% and 3% concentration of MTS. At 5% concentration of MTS, the flexural modulus value decreases by 7% compared to that of the untreated composites, while the flexural modulus at 10% concentration of MTS is similar with that of the untreated composites.

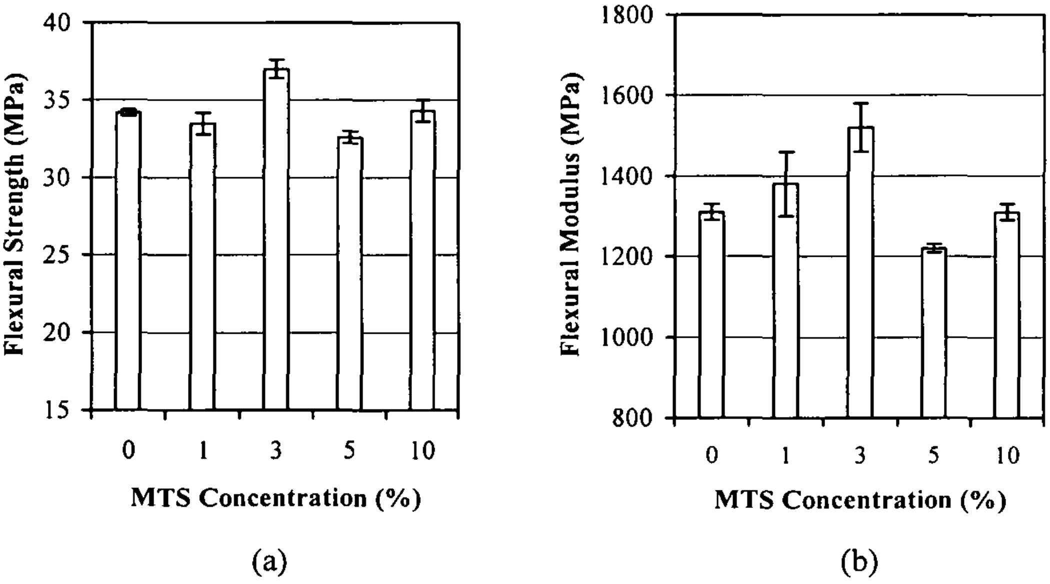


Figure 4-19 The effects of MTS treatments on the flexural properties of the EFB short fiber composites; (a) flexural strength and (b) flexural modulus.

As discussed earlier, the optimum chemical interaction condition was achieved for the composites treated with the 5% concentration of MTS. This optimum condition may contribute to the decrease in flexural strength and flexural modulus of the composites, as the optimum condition of chemical coupling may lead to the decrease in matrix molecular perfection. It can be inferred from these phenomena that in order to obtain better overall mechanical properties, the silane reaction must be optimized so that the silane reaction with the fiber and the silane reaction with the matrix are controlled to an optimum level.

According to the results on the flexural properties of the composites, the maximum flexural properties are achieved at 3% MTS concentration. At this concentration, MTS may react with the fiber effectively without reducing the matrix molecular perfection or crystallinity.

4.2.3.2.2 VTS

As shown in Figure 4-20, the increase in tensile strength is observed as the VTS concentration increases up to 5% but it remains unchanged at 10% concentration of the MTS treatment. The maximum tensile strength measured is 8% at 5% and 10% concentration of VTS. The tensile modulus of the composites also increases upon the VTS treatments. The maximum increase in the tensile modulus is 9% at 10% VTS concentration and the lowest increase is 4% at 5% VTS concentration.

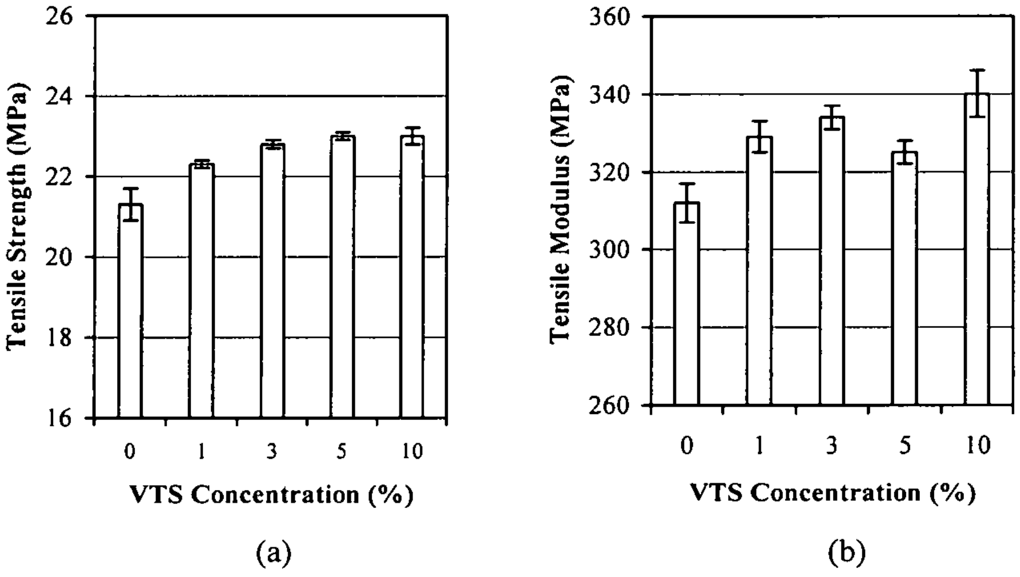


Figure 4-20 The effects of VTS treatments on the tensile properties of the EFB short fiber composites; (a) tensile strength and (b) tensile modulus.

According to the morphological studies on the VTS fiber surface and the fractured surface of the composites, it was observed that a thin layer was formed around the fiber surface and polymer was adhering to the fiber surface of the composites. These mean that the fiber-matrix compatibility of the composites has increased upon the VTS treatment. The increase in fiber-matrix compatibility of the VTS treated composites may lead to the increase in tensile strength, as observed in Figure 4-20a. The maximum tensile strength is achieved at 5% VTS concentration. Further increase in VTS concentration may decrease the tensile strength or at least remain constant, which attributed to the possibility of further condensation of VTS.

The tensile modulus of the composites treated with 5% VTS concentration experience the lowest value compared to that treated at other VTS concentration. It may be due to the organofunctional groups of the VTS that effectively react with the polymer matrix at 5% VTS concentration. This interaction may attribute to a plasticization effect of the matrix and thereby reduce the matrix molecular perfection. This reduction may lead to the decrease in the tensile modulus of the composites.

Generally, the VTS treatment has not significantly modified the composite's flexural strength and flexural modulus except for composites treated with the 3% VTS concentration as shown in Figure 4-21. The increase in flexural strength and flexural modulus of the composites treated with the 3% concentration of VTS are 6% and 18%, respectively. Treating the composites with the 3% concentration of VTS may lead to the optimum condition of the treatment. At this concentration, VTS may react with the fiber effectively without reducing the matrix molecular perfection or crystallinity.

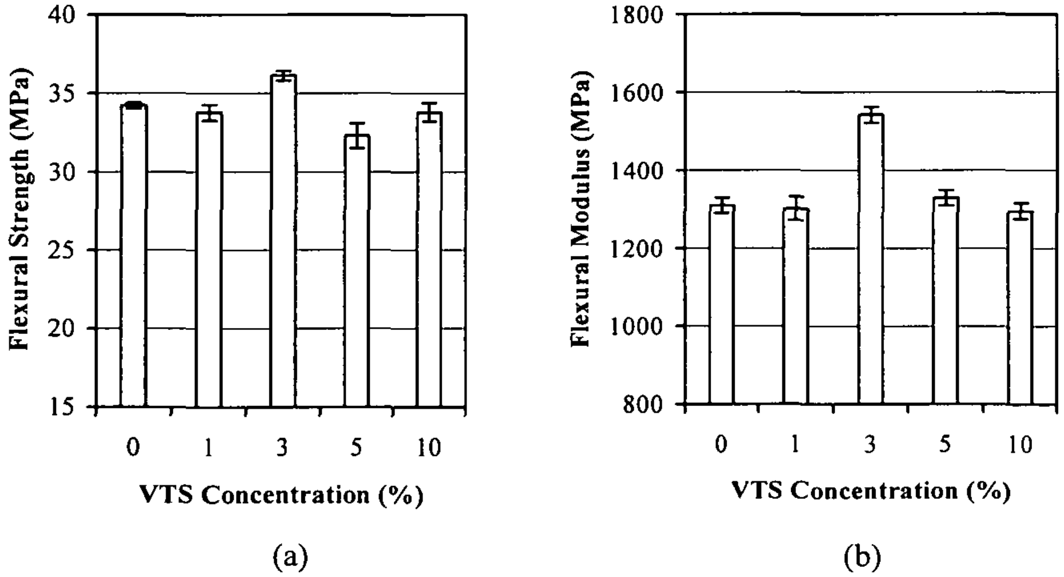


Figure 4-21 The effects of VTS treatments on the flexural properties of the EFB short fiber composites; (a) flexural strength and (b) flexural modulus.

4.2.3.2.3 Overview of the Effects of MTS and VTS Treatment on Mechanical Properties

Based on the results obtained, it can be concluded that the effects of MTS and VTS treatments on the mechanical properties of the composites showed similar trends. The optimum overall mechanical properties of the composites were obtained by treating the fibers with 3% MTS and VTS concentration. The optimum condition could be achieved by controlling the silane concentration so that the reaction of the silane with the fiber and the silane with the polymer matrix are at an optimum level.

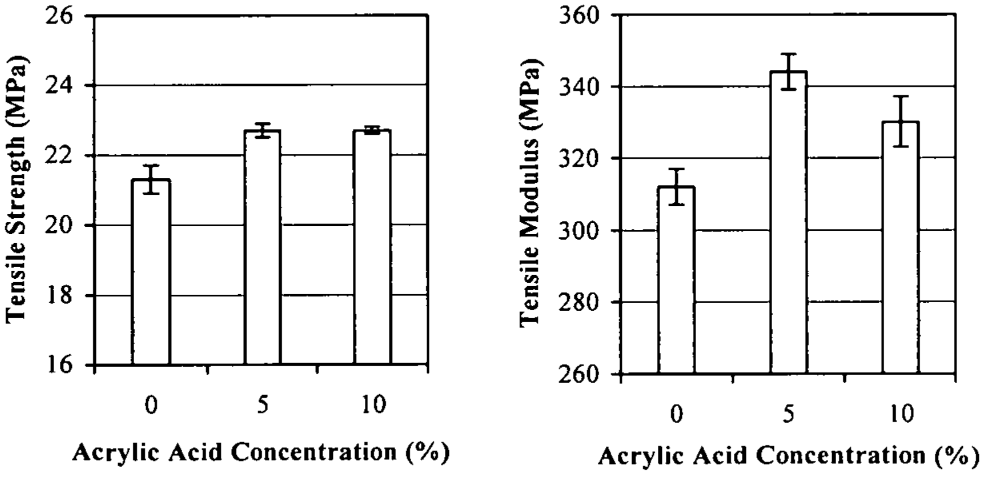
Looking at the chemical formula of the MTS and VTS, both coupling agents possess silicon-functional and organofunctional groups. Silicon functional group of MTS and VTS are methoxy and ethoxy, respectively, while organofunctional group of MTS and VTS are methacrylic and vinyl, respectively. The nature of these chemicals may contribute to the different treatment effectiveness between the MTS and VTS.

According to the organofunctional groups possessed by the coupling agents, MTS is more reactive than VTS. Methoxy have higher hydrolysis rate than that of ethoxy [101]. Higher hydrolysis rate increases the possibility to produce greater silanol formation. It indicates that good mechanical properties of the composites may be easier to obtain. However, it should be noted that greater silanol formation may results in higher possibility of further condensation taking place. In addition, MTS yields longer non-polar organofunctional groups compared to that of VTS, which gives rise to better compatibility with the matrix. Methacrylic double bond in the MTS also participates in the free radical polymerization with the matrix, which may contribute to a strong chemical bonding between the fiber and the matrix.

This analysis supports the trends observed for the tensile properties of the composites. As observed in the tensile strength of the composites, the 5% MTS treated composites have higher tensile strength values compared to that of the 5% VTS treated composites. On the other hand, further addition of MTS concentration decreased the composite's tensile strength, while further addition of VTS concentration resulted in the composites with unchanged tensile strength values. The decrease in tensile strength indicated that further condensation reactions were more intense in MTS compared to that in VTS. For the tensile modulus, the VTS treated composites showed higher values than that of the MTS treated composites. This suggested that the degree of reaction between the MTS and the matrix was higher than that between the VTS and the matrix. Thus, the matrix molecular arrangement in the MTS treated composites was less orderly than that in the VTS treated composites. The phenomena observed for the tensile properties were similar to that of the flexural properties. The flexural strength of the MTS treated composites was higher than that of the VTS composites, while the flexural modulus showed the opposite trend.

4.2.3.3 Acrylations

It can be seen from Figure 4-22 where acrylations have improved the tensile strength and tensile modulus of the EFB short fiber composites. The increase in tensile strength is 7% for both composites treated with the 5% and 10% concentrations of acrylic acid (AA). The highest increase in the tensile modulus measured is 10% for the composites treated with the 5% AA concentration. However, as the concentration of AA increases to 10%, the tensile modulus decreases by 4% compared to that at 5% AA concentration.



(a) (b)

Figure 4-22 The effects of acrylation treatments on the tensile properties of the EFB short fiber composites; (a) tensile strength and (b) tensile modulus.

Upon acrylation, waxy layer is partly removed from the surface and the fiber splits into smaller diameter, as seen in Figure 4-9e and Figure 4-14, respectively. The strong acid characteristic of AA might have resulted in the removal of the adhesive pectin of the fiber and thereby splitting the fiber into smaller diameter. The fiber splitting effect may have been worsened by the shearing effect during the compounding and injection molding processes. The smaller diameter gives rise to a higher fiber aspect ratio, which contributes to the tensile properties improvement. In addition, the increase in the tensile properties may also be influenced by the decrease in hydrophilic character of the fiber, which brought about better compatibility with the matrix, as proposed by the reaction in Eq. 2.4.

For the flexural properties, the flexural strength of the composites decreases as the AA concentration increases. The maximum decrease observed is 10% for the composites treated with the 10% AA concentration. Similarly, the flexural modulus also decreases as the AA concentration increases with a maximum decrease of 18% for the composites treated with the 10% AA concentration.

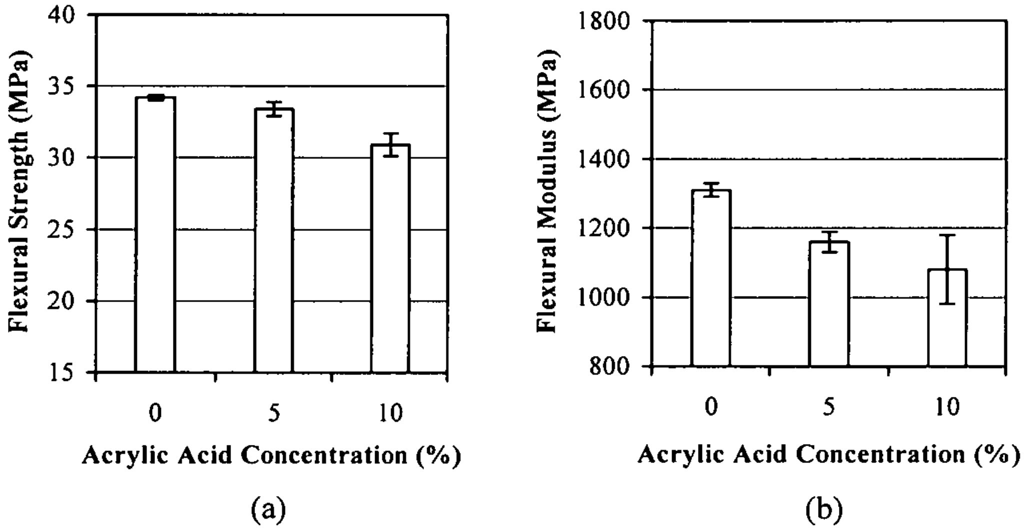


Figure 4-23 The effects of acrylation treatments on the flexural properties of the EFB short fiber composites; (a) flexural strength and (b) flexural modulus.

The high fiber aspect ratio of the composites may results in the decrease in the flexural properties of the composites. Unidirectional composites usually have good tensile strength but poor in compression strength as the fiber can only effectively transfer the load from the matrix in tensile loading. The fiber orientation in injection molding is presumably unidirectional since the fiber is oriented in the direction of the polymer flow as it exits the die. Due to the unidirectional property of the composites, the higher fiber aspect ratio results in composites with higher tensile properties but lower compressive properties. The decrease in the flexural properties of the composites treated with acrylic acid may be due to the poor compressive properties as the flexural loading comprises both tensile and compression modes.

4.2.3.4 Overview of the Effects of Various Chemical Treatments on the Mechanical Properties

The mechanical properties of the composites resulted from the selected optimum chemical treatments of the fibers are compared as shown in Figure 4-24 and 4-25. It can be concluded that the chemical treatments of the fibers have increased both of the composites tensile strength and tensile modulus. Among the four different types of treatments, the 3% MTS treatment gave the highest increase in tensile strength of 9% compared to that of the untreated composites. The least increase in the tensile strength of 2% compared to that of the untreated composites resulted from the 10% alkali treatment. To achieve the highest tensile modulus improvement, the 5% acrylated treatment should be favored, with the increase of 10% compared to that of the untreated composites.

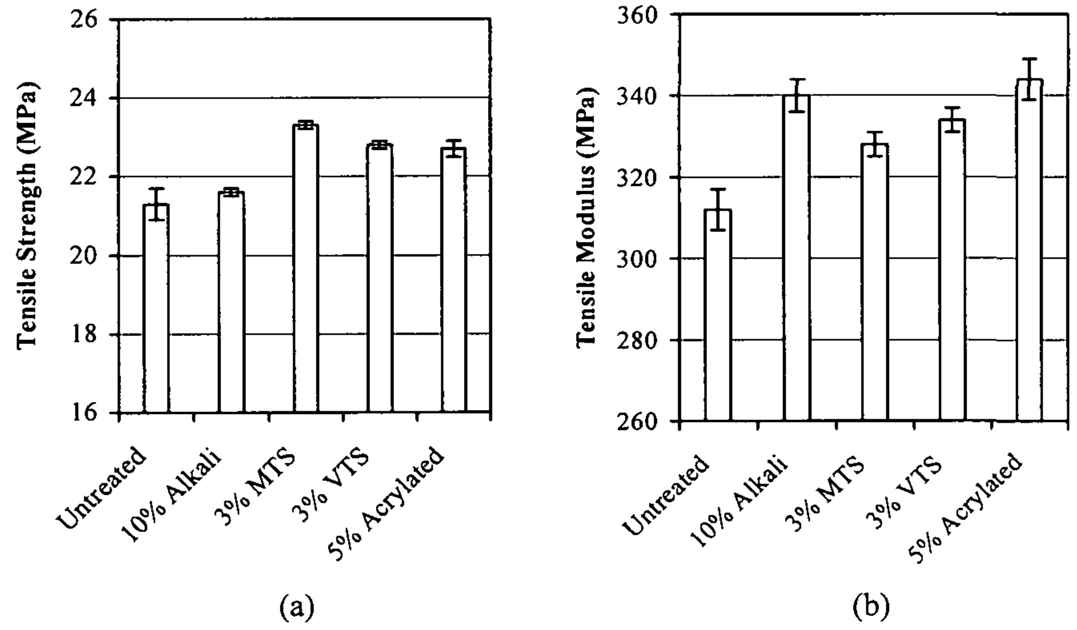


Figure 4-24 The tensile properties of composites treated with various chemical treatments at their optimum concentration; (a) tensile strength and (b) tensile modulus.

From Figure 4-25, it is obvious that all the chemical treatments increased the composites flexural strength and flexural modulus except for the 5% acrylated treatment. For the 10% alkali, 3% MTS and 3% VTS, they all resulted in comparable improvement on the flexural strength and flexural modulus with an average increase of 6% and 18% compared to that of the untreated composites, respectively.

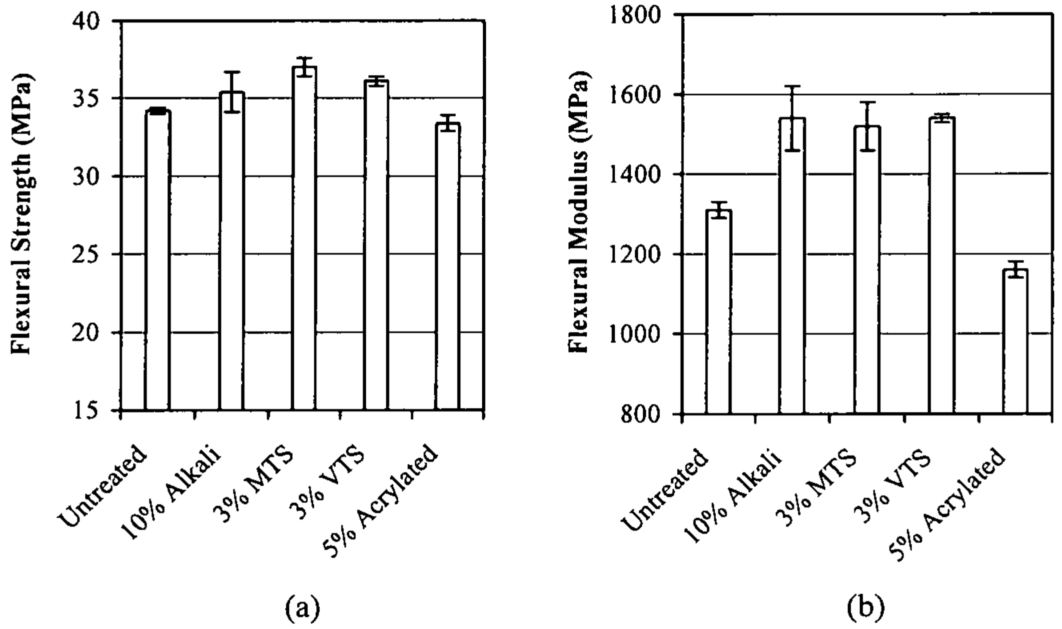


Figure 4-25 The flexural properties of composites treated with various chemical treatments at their optimal concentration; (a) flexural strength and (b) flexural modulus.

While the current study on the effects of silane and acrylic treatments on the mechanical properties of the composites resulted in the composites with increased both tensile strength and tensile modulus, the previous studies on the EFB-HDPE composites performed by Mohd Ishak et al. [16] showed different results. The silane treatments increased the tensile modulus by 100% as compared with the untreated composites, while the tensile strength remained constant upon treatments. The addition of acrylic acid based compatibilizers also increased the tensile modulus by 67% as compared with the untreated composites, while the tensile strength decreased upon treatments. The higher improvement on the composite's tensile modulus compared to that of the current study is due to the higher EFB content (40%wt) incorporated into the HDPE matrix and the use of compression molding that has higher degree of compaction compared to that of the injection molding. Another factor is due to the different chemicals for the treatment. The current study showed that using lower EFB content (10%wt) resulted in the improvement of both the tensile strength and tensile modulus upon treatments with silanes and acrylic acid. The trends on the mechanical properties of the composites with variations in chemical concentrations are also easier to comprehend as lower EFB content will result in lower void formation at the fiber-matrix interface of the composites and thus results in better interfacial interaction.

4.2.4 The Effects of Chemical Treatments on Water Sorption Characteristic of the Composites

It can be observed from Figure 4-26 that the chemical treatments have led to the decrease in the water absorption of the EFB short fiber composites. The lowest water uptake measured is the MTS treated composites, followed by the VTS, the acrylic acid and the alkali treated composites. The maximum water uptake of the MTS treated composites is 0.6%, while that of the VTS treated composites is 0.63%. For the acrylated and alkali treated composites, the maximum water uptake are 0.77% and 0.9%, respectively. All the composites absorbed water rapidly during the first four days of water immersion, and continue to absorb more water until they reached steady state condition about 35 days after immersion.

The significant decrease in water uptake for the composites treated with MTS and VTS is due to the formation of thin water resistant layer on the fiber surface upon treatments. The silanes alter the water-soluble characteristic of the fiber as a consequence of the hydrolysis process and the formation of silanols. MTS yields slightly better resistant to water absorption. It may be due to the silicon-functional groups of the MTS that have higher hydrolysis rate compared to that of the VTS [101]. Higher hydrolysis rate increases the possibility to produce greater silanols formation. These Si–OH functional groups are very reactive in establishing a covalent bond between the fiber and the silane. Higher amount of silanols results in more hydrophobic property of the fiber and thus reduces the water uptake of the fiber.

The decrease in water uptake of the acrylated composites may be due to the esterification reaction, which causes the reduction of hydroxyl group on the fiber surface. For the alkali treated composites, the decrease in water sorption is mainly due to the removal of the waxy epidermal tissue which absorbs more water than that of the cellulose.

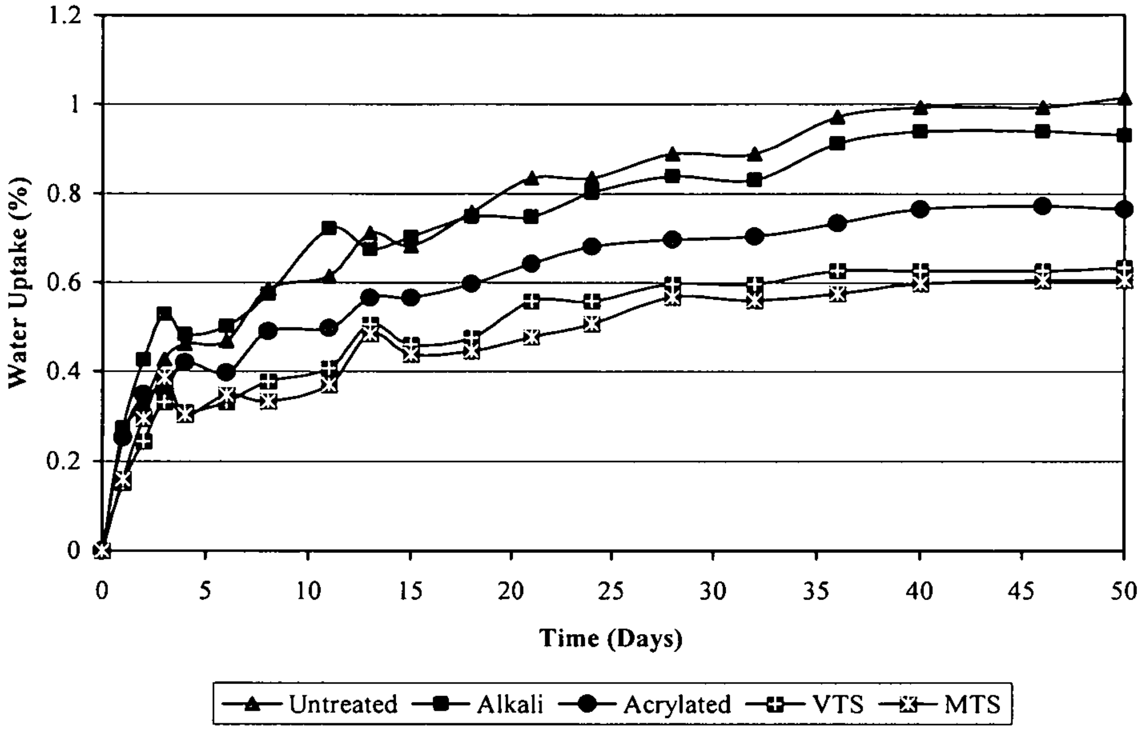


Figure 4-26 The effects of chemical treatments on water absorption characteristic of the EFB short fiber composites.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The mechanical properties and water absorption characteristics of the EFB particulate and short fiber composites were examined. Results showed that the EFB short fiber composites experienced superior tensile and flexural properties compared to that of the EFB particulate composites. It could be interpreted that for the EFB particulate, its capability to support load transfer from the matrix was rather poor compared to that of the short fiber. Thus, the mechanical properties enhancement in the particulate-matrix composites is lower than that of the short fiber composites.

The tensile modulus, flexural modulus and flexural strength of the EFB short fiber composites increased as the EFB content increased. Unlike that of the EFB short fiber composites, tensile modulus and flexural strength of the EFB particulate composites increased as the EFB content increased up to 20%wt, and continued to decrease at 30%wt, while flexural modulus constantly increased as the EFB content increased. The decrease in tensile strength was observed for both EFB particulate and short fiber composites as the EFB content increased. Results obtained indicated the ability of the EFB to impart greater mechanical properties, with the expense of reduction in the composite's tensile strength due to the poor adhesion between the EFB and the matrix. The decrease in tensile modulus and flexural strength of the particulate composites at 30%wt EFB content compared to that at 20%wt EFB content indicated that the excessive amount of EFB may have led to agglomeration of the EFB and thus decrease the ability of EFB to impart greater tensile modulus and flexural strength of the EFB particulate composites.

As the EFB content increased, water uptake of the EFB particulate and short fiber composites also increased due to the polar property of the EFB that led to high amount of water absorption. Water uptake of the EFB short fiber composites was higher than that of the EFB particulate composites. It was due to the fiber shape of the short fiber that allowed higher capillary action of water than that of the particulate.

The effects of chemical treatments on the mechanical properties and water absorption characteristics of the 10%wt EFB short fiber composites were also investigated. The optimum mechanical properties was achieved by treating the EFB with 10% alkali, 3% MTS, 3% VTS and 5% acrylic acid. The chemical treatments increased both of the composites tensile strength and tensile modulus. Among the four different types of treatments, the MTS treatment gave the highest increase in tensile strength of 9% compared to that of the untreated composites. To achieve the highest tensile modulus improvement, acrylated treatment should be favored, with the increase of 10% compared to that of the untreated composites. The chemical treatments also increased the composites flexural strength and flexural modulus of the composites except for the acrylated treatment. Alkali, MTS and VTS resulted in comparable improvement on the flexural strength and flexural modulus of the composites, with an average increase of 6% and 18% compared to that of the untreated composites, respectively.

The chemical treatments led to the decrease in water absorption of the EFB composites. The lowest water uptake was observed for the MTS treated composites, followed by the VTS, acrylic acid and alkali treated composites. The maximum water uptake of the untreated composites was 1%. It decreased to 0.60%, 0.63%, 0.77% and 0.93% for the MTS, VTS, acrylated and alkali treated composites, respectively. The decrease in water sorption in alkali treated fiber was mainly due to the removal of the waxy epidermal tissue. The successful esterification reaction was the key factor in the reduced water uptake of the acrylated composites. The presence of silanes has altered the water-soluble characteristic of the fiber as a consequence of the hydrolysis process and the formation of silanols.

It could be concluded that EFB particulate and short fiber composites possessed a variety of attractive properties to be used in thermoplastic composites of at least moderate strength. Based on the mechanical properties and cost consideration, EFB short fiber demonstrated more promising mechanical and physical properties compared to that of EFB particulate as filler in composite materials. The price of EFB short fiber is cheaper than that of particulate due to simpler processing route. With their low cost and sustainability, this by product could serve as an alternative filler to wood composites. The proper introduction of various chemical treatments such as alkali, acrylic acid and silane treatments could result in improvement on the mechanical and water absorption properties of the composites and hence might be favored in real applications of the composites. The silane treatments may serve as the best chemical treatments as both MTS and VTS treatments resulted in the composites with improved mechanical and water absorption properties at reasonable values.

5.2 Recommendations for Future Work

The above results show that the research on natural fiber composites is far from complete. Further research and development need to be carried out so that these composites might become a potential substitute for synthetic fibers such as glass and carbon fibers. To achieve this, it is important to limit the variability on the fiber properties as much as possible. It can be realized by processing and handling the fibers with care, so no additional damage is introduced.

Further studies on the processing parameters may result in composites with better mechanical properties. The research on temperature variation and feeding speed in the extrusion process could be carried out to obtain better degree of compounding between the fiber and the matrix. The possibility to increase the EFB content to more than 30%wt can be explored further as the higher content of EFB can reduce the overall cost of composites production. It could be achieved by investigating the effects of injection molding process parameters such as injection pressure, temperature and degree of specimen cooling. The optimum parameters may result in higher degree of compaction between the fiber and the matrix and thus the maximum EFB content filled in the polymer matrix could be increased.

The fiber shortening phenomena during processing could be investigated further. It could be carried out by boiling the composites in xylene and the fiber then extracted. Image analysis to measure the fiber length using automatic two point measuring mode may serve as the best method as it can generate more accurate and statistically representative data.

The internal adhesion and the interface between the fiber and the matrix should be studied further. Investigation on the adhesion mechanism of a single fiber with the matrix needs to be performed to reveal the adhesion mechanism in the smallest scale.

Producing composites product prototypes and examining their mechanical and environmental properties are important for assessing the possibility of the natural fiber composites to be employed in the real applications.

REFERENCES

1. I. Van de Weyenberg, *Flax fibres as a reinforcement for epoxy composites.* Department of Metallurgy and Materials Engineering, Katholieke Universiteit Leuven, 2005. PhD Thesis.

2. G. Shi, *Effect of surface chemistry on the interfacial adhesion and mechanical properties of natural fiber reinforced polymer composites.* Department of Chemical Engineering and Materials Science, Michigan State University, 2003. PhD Thesis.

3. T.P. Schloesser, *Natural fiber reinforced automotive parts*, in *Natural Fibers, Plastics and Composites*, F.T. Wallenberger and N. Weston, Editors. 2004, Kluwer Academic Publishers. p. 275-285.

4. G. Marsh, *Next step for automotive materials*, in *Materials Today.* 2003. p. 36-43.

5. K.G. Kavelin, *Investigation of natural fiber composites heterogeneity with respect to automotive structures.* Delft University of Technology, 2005. PhD Thesis.

6. B.C. Suddell and W.J. Evans, *Natural fiber composites in automotive applications*, in *Natural Fibers, Biopolymers, and Biocomposites*, A.K. Mohanty, M. Misra and L.T. Drzal, Editors. 2005, CRC Press. p. 231.

7. T.-T.-L. Doan, *Investigation on jute fibres and their composites based on polypropylene and epoxy matrices.* Faculty of Mechanical Engineering, Technischen Universität Dresden, 2006. PhD Thesis.

8. A.K. Bledzki and J. Gassan, *Composites reinforced with cellulose based fibres.* Progress in Polymer Science, 1999. 24: p. 221-274.

9. A. Arbelaiz, B. Fernández, J.A. Ramos, A. Retegi, R. Llano-Ponte and I. Mondragon, *Mechanical properties of short flax fibre bundle/polypropylene composites: Influence of matrix/fibre modification, fibre content, water uptake and recycling.* Composites Science and Technology, 2005. 65: p. 1582–1592.

10. S. Mohanty, S.K. Verma and S.K. Nayak, *Dynamic mechanical and thermal properties of MAPE treated jute/HDPE composites.* Composite Science and Technology, 2006. 66: p. 538–547.

11. K.C.M. Nair, S. Thomas and G. Groeninckx, *Thermal and dynamic mechanical analysis of polystyrene composites reinforced with short sisal fibres.* Composites Science and Technology, 2001. 61: p. 2519-2529.

12. [cited 2006 June, 23]; Available from: http://www.fibre-x.com/.

13. A.H. Abu Bakar and H.P.S. Abdul Khalil, *Lignocellulose-based hybrid bilayer laminate composite: Part I - Studies on tensile and impact behavior of oil palm fiber-glass fiber reinforced epoxy resin.* Journal of Composite Materials, 2005. 39(8): p. 663-684.

14. H.D. Rozman, Z.A. Mohd Ishak and U.S. Ishiaku, *Oil palm fiber - thermoplastic composites*, in *Natural Fibers, Biopolymers, and Biocomposites*, A.K. Mohanty, M. Misra and L.T. Drzal, Editors. 2005, CRC Press. p. 407.

15. M.S. Sreekala, M.G. Kumaran and S. Thomas, *Oil palm fibers: morphology, chemical composition, surface modification, and mechanical properties.* Journal of Applied Polymer Science, 1997. 66: p. 821-835.

16. Z.A. Mohd Ishak, A. Aminullah, H. Ismail and H.D. Rozman, *Effect of silane-based coupling agents and acrylic acid based compatibilizers on mechanical properties of oil palm empty fruit bunch filled high-density polyethylene composites.* Journal of Applied Polymer Science, 1997. 68: p. 2189-2203.

17. H.D. Rozman, G.B. Peng and Z.A. Mohd Ishak, *The effect of compounding techniques on the mechanical properties of oil palm empty fruit bunch–polypropylene composites.* Journal of Applied Polymer Science, 1998. 70: p. 2647–2655.

18. M.S. Sreekala, M.G. Kumaran, S. Joseph, M. Jacob and S. Thomas, *Oil palm fibre reinforced phenol formaldehyde composites: Influence of fibre surface modifications on the mechanical performance.* Applied Composite Materials, 2000. 7: p. 295-329.

19. M.S. Sreekala and S. Thomas, *Effect of fibre surface modification on water-sorption characteristics of oil palm fibres.* Composites Science and Technology, 2003. 63: p. 861-869.

20. H.D. Rozman, G.S. Tay, R.N. Kumar, A. Abusamah, H. Hanafi and Z.A. Mohd Ishak, *Polypropylene-oil palm empty fruit bunch-glass fibre hybrid composites: a preliminary study on the flexural and tensile properties.* European Polymer Journal, 2001. 37: p. 1283-1291.

21. M.S. Sreekala, J. George, M.G. Kumaran and S. Thomas, *The mechanical performance of hybrid phenol-formaldehyde-based composites reinforced with glass and oil palm fibres.* Composite Science and Technology, 2002. 62: p. 339-353.

22. H.D. Rozman, G.S. Tay, A. Abubakar and R.N. Kumar, *Tensile properties of oil palm empty fruit bunch-polyurethane composites.* European Polymer Journal, 2001. 37: p. 1759-1765.

23. W. Liu, L.T. Drzal, A.K. Mohanty and M. Misra, *Influence of processing methods and fiber length on physical properties of kenaf fiber reinforced soy based biocomposites.* Composites Part B: Engineering, 2007. 38: p. 352-359.

24. T.-T.-L. Doan, S.-L. Gao and E. Mäder, *Jute/polypropylene composites I. Effect of matrix modification.* Composites Science and Technology, 2006. 66: p. 952–963.

25. H.D. Rozman, H. Ismail, R.M. Jaffri, A. Aminullah and Z.A. Mohd Ishak, *Mechanical properties of polyethylene-oil palm empty fruit bunch composites.* Polymer-Plastic Technology Engineering, 1998. 37(4): p. 495-507.

26. D. Gulati, *Modification of interface in natural fiber reinforced polymer composites.* Graduate Department of Chemical Engineering and Applied Chemistry, University of Toronto, 2005. MSc Thesis.

27. A.K. Mohanty, M. Misra, L.T. Drzal, S.E. Selke, B.R. Harte and G. Hinrichsen, *Natural fibers, biopolymers, and biocomposites: An introduction*, in *Natural Fibers, Biopolymers, and Biocomposites*, A.K. Mohanty, M. Misra and L.T. Drzal, Editors. 2005, CRC Press. p. 1.

28. A. Bismarck, S. Mishra and T. Lampke, *Plant fibers as reinforcement for green composites*, in *Natural Fibers, Biopolymers, and Biocomposites*, A.K. Mohanty, M. Misra and L.T. Drzal, Editors. 2005, CRC Press. p. 37.

29. M. Sain and S. Panthapulakkal, *Green fibre thermoplastic composites*, in *Green composites*, C. Baillie, Editor. 2004, Woodhead Publishing Ltd & CRC Press LLC. p. 181-206.

30. H.P.S. Abdul Khalil, S. Hanida, C.W. Kang and N.A. Nik Fuaad, *Agro-hybrid composite: The effects on mechanical and physical properties of oil palm fiber (EFB)/glass hybrid reinforced polyester composites.* Journal of Reinforced Plastics and Composites, 2007. 26(2): p. 203-217.

31. K. Joseph, R.D. Tolêdo Filho, B. James, S. Thomas and L. Hecker de Carvalho, *A review on sisal fiber reinforced polymer composites*, in *Revista Brasileira de Engenharia Agrícola e Ambiental.* 1999: Campina Grande. p. 367-379.

32. Y. Li, Y.-W. Mai and L. Ye, *Sisal fibre and its composites: A review of recent developments.* Composites Science and Technology, 2000. 60: p. 2037-2055.

33. K.C.M. Nair, S.M. Diwan and S. Thomas, *Tensile properties of short sisal fiber reinforced polystyrene composites.* Journal of Applied Polymer Science, 1996. 60: p. 1483-1497.

34. H. Djidjelli, A. Boukerrou, R. Founas, A. Rabouhi, M. Kaci, J. Farenc, J.-J. Martinez-Vega and D. Benachour, *Preparation and characterization of poly(vinyl chloride)/virgin and treated sisal fiber composites.* Journal of Applied Polymer Science, 2007. 103: p. 3630-3636.

35. K. Oksman and J.-F. Selin, *Plastics and composites from polylactic acid*, in *Natural Fibers, Plastics and Composites*, F.T. Wallenberger and N. Weston, Editors. 2004, Kluwer Academic Publishers. p. 149-165.

36. Z.S. Petrovic, A. Guo, I. Javni and W. Zhang, *Plastics and composites from soybean oil*, in *Natural Fibers, Plastics and Composites*, F.T. Wallenberger and N. Weston, Editors. 2004, Kluwer Academic Publishers. p. 167-192.

37. E. Frollini, J.M.F. Paiva, W.G. Trindade, I.A. Tanaka, Razera and S.P. Tita, *Plastics and composites from lignophenols*, in *Natural Fibers, Plastics and Composites*, F.T. Wallenberger and N. Weston, Editors. 2004, Kluwer Academic Publishers. p. 194-225.

38. D. Plackett and A. Vazquez, *Natural polymer sources*, in *Green composites*, C. Baillie, Editor. 2004, Woodhead Publishing Ltd & CRC Press LLC. p. 123-153.

39. E. Bodros, I. Pillin, N. Montrelay and C. Baley, *Could biopolymers reinforced by randomly scattered flax fibre be used in structural applications?* Composites Science and Technology, 2007. 67: p. 462-470.

40. L.Y. Mwaikambo and M.P. Ansell, *Hemp fibre reinforced cashew nut shell liquid composites.* Composites Science and Technology, 2003. 63: p. 1297–1305.

41. S.-H. Lee and S. Wang, *Biodegradable polymers/bamboo fiber biocomposite with bio-based coupling agent.* Composites: Part A, 2006. 37: p. 80–91.

42. A. Maffezzoli, E. Calo, S. Zurlo, G. Mele, A. Tarzia and C. Stifani, *Cardanol based matrix biocomposites reinforced with natural fibres.* Composites Science and Technology, 2004. 64: p. 839–845.

43. M.Q. Zhang, M.Z. Rong and X. Lu, *Fully biodegradable natural fiber composites from renewable resources: All-plant fiber composites.* Composites Science and Technology, 2005. 65: p. 2514–2525.

44. A. O'Donnell, M.A. Dweib and R.P. Wool, *Natural fiber composites with plant oil-based resin.* Composites Science and Technology, 2004. 64: p. 1135-1145.

45. K. Oksman, M. Skrifvars and J.-F. Selin, *Natural fibres as reinforcement in polylactic acid (PLA) composites.* Composite Science and Technology, 2003. 63: p. 1317-1324.

46. M.L. Berins, *SPI plastics engineering handbook.* 5th. ed. 2000: Kluwer Academic Publisher.

47. D.V. Rosato, D.V. Rosato and M.G. Rosato, *Injection molding handbook.* 3rd ed. 2000: Kluwer Academic Publisher.

48. P.K. Mallick, *Particulate and short fiber reinforced polymer composites.* Comprehensive Composite Materials, 2000. 2: p. 291-331.

49. A. Valadez-Gonzalez, J.M. Cervantes-Uc, R. Olayo and P.J. Herrera-Franco, *Effect of fiber surface treatment on the fiber–matrix bond strength of natural fiber reinforced composites.* Composites: Part B, 1999. 30: p. 309–320.

50. P. Herrera-Franco and A. Valadez-Gonzalez, *Fiber-matrix adhesion in natural fiber composites*, in *Natural Fibers, Biopolymers, and Biocomposites*, A.K. Mohanty, M. Misra and L.T. Drzal, Editors. 2005, CRC Press. p. 177.

51. P.J. Herrera-Franco and A. Valadez-Gonzalez, *A study of the mechanical properties of short natural-fiber reinforced composites.* Composites: Part B, 2005. 36: p. 597–608.

52. P. Peltola, *Alternative fibre sources: paper and wood fibres as reinforcement*, in *Green composites*, C. Baillie, Editor. 2004, Woodhead Publishing Ltd & CRC Press LLC. p. 81-99.

53. P. Wambua, J. Ivens and I. Verpoest, *Natural fibres: Can they replace glass in fibre reinforced plastics?* Composites Science and Technology, 2003. 63: p. 1259–1264.

54. G. Kalaprasad, K. Joseph, S. Thomas and C. Pavithran, *Theoretical modelling of tensile properties of short sisal fibre-reinforced low-density polyethylene composites.* Journal of Materials Science, 1997. 32: p. 4261-4267.

55. B.M. Dabade, G.R. Reddy, S. Rajesham and C.U. Kiran, *Effect of fiber length and fiber weight ratio on tensile properties of sun hemp and palmyra fiber reinforced polyester composites.* Journal of Reinforced Plastics and Composites, 2006. 25(16): p. 1733-1738.

56. A. Keller, *Compounding and mechanical properties of biodegradable hemp fibre composites.* Composite Science and Technology, 2003. 63: p. 1307-1316.

57. X. Li, L.G. Tabil and S. Panigrahi, *Chemical treatments of natural fiber for use in natural fiber-reinforced composites: A review.* Journal of Polymers and the Environment, 2007. 15: p. 25-33.

58. J. Girones, J.A. Mendez, S. Boufi, F. Vilaseca and P. Mutje, *Effect of silane coupling agents on the properties of pine fibers/polypropylene composites.* Journal of Applied Polymer Science, 2007. 103: p. 3706–3717.

59. M. Abdelmouleh, S. Boufi, M.N. Belgacem and A. Dufresne, *Short natural-fibre reinforced polyethylene and natural rubber composites: Effect of silane coupling agents and fibres loading.* Composites Science and Technology, 2007. 67: p. 1627–1639.

60. G.W. Lee, N.J. Lee, J. Jang, K.J. Lee and J.D. Nam, *Effects of surface modification on the resin-transfer moulding (RTM) of glass-fibre/unsaturated-polyester composites.* Composites Science and Technology, 2002. 62: p. 9-16.

61. H.-Q. Xie, S. Zhang and D. Xie, *An efficient way to improve the mechanical properties of polypropylene/short glass fiber composites.* Journal of Applied Polymer Science, 2005. 96: p. 1414-1420.

62. M. Abdelmouleh, S. Boufi, M.N. Belgacem, A. Dufresne and A. Gandini, *Modification of cellulose fibers with functionalized silanes: Effect of the fiber treatment on the mechanical performances of cellulose-thermoset composites.* Journal of Applied Polymer Science, 2005. 98: p. 974–984.

63. X. Colom, F. Carrasco, P. Pages and J. Canavate, *Effects of different treatments on the interface of HDPE/lignocellulosic fiber composites.* Composites Science and Technology, 2003. 63: p. 161-169.

64. J. George, I. Van de Weyenberg, J. Ivens and I. Verpoest, *Mechanical properties of flax fibre reinforced epoxy composites*, in *2nd International Wood and Natural Fibre Composites Symposium* 1999: Kassel/Germany.

65. P. Herrera-Franco, A. Valadez-Gonzalez and M. Cervantes-Uc, *Development and characterization of a HDPE-sand-natural fiber composite.* Composites: Part B, 1997. 28B: p. 331-343.

66. M. Bengtsson and K. Oksman, *Silane crosslinked wood plastic composites: Processing and properties.* Composites Science and Technology, 2006. 66: p. 2177–2186.

67. N. Sombatsompop and K. Chaochanchaikul, *Average mixing torque, tensile and impact properties, and thermal stability of poly(vinyl chloride)/sawdust composites with different silane coupling agents.* Journal of Applied Polymer Science, 2005. 96: p. 213-221.

68. M. Bengtsson, P. Gatenholm and K. Oksman, *The effect of crosslinking on the properties of polyethylene/wood flour composites.* Composites Science and Technology, 2005. 65: p. 1468–1479.

69. H. Ismail, S. Shuhelmy and M.R. Edyham, *The effects of a silane coupling agent on curing characteristics and mechanical properties of bamboo fibre filled natural rubber composites.* European Polymer Journal, 2002. 38: p. 39-47.

70. R. Kozlowski and M. Wladyka-Przybylak, *Uses of natural fiber reinforced plastics*, in *Natural Fibers, Plastics and Composites*, F.T. Wallenberger and N. Weston, Editors. 2004, Kluwer Academic Publishers. p. 249-274.

71. R. Agrawal, N.S. Saxena, K.B. Sharma, S. Thomas and M.S. Sreekala, *Activation energy and crystallization kinetics of untreated and treated oil palm fibre reinforced phenol formaldehyde composites.* Materials Science and Engineering, 2000. A277: p. 77–82.

72. R. Agrawal, N.S. Saxena, M.S. Sreekala and S. Thomas, *Effect of treatment on the thermal conductivity and thermal diffusivity of oil-palm-fiber-reinforced phenolformaldehyde composites.* Journal of Polymer Science: Part B: Polymer Physics, 2000. 38(7): p. 916-921.

73. A. Vazquez, V.A. Dominiguez and J.M. Kenny, *Bagasse fiber-polypropylene based composites.* Journal of Thermoplastic Composite Materials, November 1999. 12: p. 477.

74. P. Ganan and I. Mondragon, *Fique fiber-reinforced polyester composites: Effects of fiber surface treatments on mechanical behavior.* Journal of Materials Science, 2004. 39: p. 3121-3128.

75. A. Paul, K. Joseph and S. Thomas, *Effect of surface treatments on the electrical properties of low-density polyethylene composites reinforced with short sisal fibers.* Composites Science and Technology, 1997. 57: p. 67-79.

76. M.Z. Rong, M.Q. Zhang, Y. Liu, G.C. Yang and H.M. Zeng, *The effect of fiber treatment on the mechanical properties of unidirectional sisal-reinforced epoxy composites.* Composite Science and Technology, 2001. 61: p. 1437-1447.

77. Salmah, H. Ismail and A. Abu Bakar, *Effects of chemical modification of paper sludge filled polypropylene (PP)/ethylene propylene diene terpolymer (EPDM) composites.* Journal of Reinforced Plastics and Composites, 2005. 00(00).

78. A. Bessadok, S. Marais, F. Gouanve, L. Colasse, I. Zimmerlin, S. Roudesli and M. Metayer, *Effect of chemical treatments of alfa (stipa tenecissima) fibres on water-sorption properties.* Composites Science and Technology, 2007. 67: p. 685-697.

79. H.P.S. Abdul Khalil, H. Ismail, H.D. Rozman and M.N. Ahmad, *The effect of acetylation on interfacial shear strength between plant fibres and various matrices.* European Polymer Journal, 2001. 37: p. 1037-1045.

80. B. Wang, *Pre-treatment of flax fibers for use in rotationally molded biocomposites.* Department of Agricultural and Bioresource Engineering, University of Saskatchewan, 2004. MSc Thesis.

81. B. Wang, S.A. Panigrahi, L.G. Tabil and W. Crerar, *Pre-treatment of flax fibers for use in rotationally molded biocomposites.* Journal of Reinforced Plastics and Composites, 2007. 26(5): p. 447-463.

82. J. Zhang, *Accelerated weathering performance of natural fiber plastic composites and its effect on the efficacy of the maleated anhydride coupling agents.* Graduate Department of Forestry, University of Toronto, 2005. MSc Thesis.

83. Z. Lu, *Chemical coupling in wood-polymer composites.* School of Renewable Natural Resources, Lousiana State University, 2003. PhD Thesis.

84. M. Sain, P. Suhara, S. Law and A. Bouilloux, *Interface modification and mechanical properties of natural fiber–polyolefin composite products.* Journal of Reinforced Plastics and Composites, 2005. 24(2): p. 121-130.

85. S. Mohanty and S.K. Nayak, *Mechanical and rheological characterization of treated jute–HDPE composites with a different morphology.* Journal of Reinforced Plastics and Composites, 2006. 25(13): p. 1419-1439.

86. G. Cantero, A. Arbelaiz, F. Mugika, A. Valea and I. Mondragon, *Mechanical behavior of wood/polypropylene composites: Effects of fibre treatments and ageing processes.* Journal of Reinforced Plastics and Composites, 2003. 22(1): p. 37-50.

87. D. N.-S. Hon and S. Ren, *Interfacial phenomena of newspaper fiber-reinforced polypropylene composite, Part I: The development of interfacial interaction.* Journal of Reinforced Plastics and Composites, 2003. 22(11): p. 957-971.

88. P.V. Joseph, K. Joseph and S. Thomas, *Effect of processing variables on the mechanical properties of sisal-fiber-reinforced polypropylene composites.* Composites Science and Technology, 1999. 59: p. 1625-1640.

89. X. Li, S.A. Panigrahi, L.G. Tabil and W.J. Crerar, *Flax fiber-reinforced composites and the effect of chemical treatments on their properties*, in *2004 North Central ASAE/CSAE Conference.* 2004: Winnipeg, Manitoba, Canada.

90. R. Karnani, M. Krishnan and R. Narayan, *Biofiber-reinforced polypropylene composites.* Polymer Engineering and Science, 1997. 37(2).

91. K. Al-Kaabi, A. Al-Khanbashi and A. Hammami, *Date palm fibers as polymeric matrix reinforcement: DPF/polyester composite properties.* Polymer Composites, 2005. 26: p. 604-613.

92. J. George, S.S. Bhagawan and S. Thomas, *Effects of environment on the properties of low-density polyethylene composites reinforced with pineapple-leaf fibre.* Composites Science and Technology, 1998. 58: p. 1471-1485.

93. C.P.L. Chow, X.S. Xing and R.K.Y. Li, *Moisture absorption studies of sisal fibre reinforced polypropylene composites.* Composites Science and Technology, 2007. 67: p. 306-313.

94. S. Siriwardena, H. Ismail and U.S. Ishiaku, *A Comparison of the mechanical properties and water absorption behavior of white rice husk ash and silica filled polypropylene composites.* Journal of Reinforced Plastics and Composites, 2003. 22(18): p. 1645-1666.

95. P.V. Joseph, M.S. Rabello, L.H.C. Mattoso, K. Joseph and S. Thomas, *Environmental effects on the degradation behaviour of sisal fibre reinforced polypropylene composites.* Composite Science and Technology, 2002. 62: p. 1357-1372.

96. I. Van de Weyenberg, J. Ivens, A. De Coster, B. Kino, E. Baetens and I. Verpoest, *Influence of processing and chemical treatment of flax fibres on their composites.* Composites Science and Technology, 2003. 63: p. 1241-1246.

97. S. Mishra, A.K. Mohanty, L.T. Drzal, M. Mishra, S. Parija, S.K. Nayak and S.S. Tripathy, *Studies on mechanical performance of biofibre/glass reinforced polyester hybrid composites.* Composites Science and Technology, 2003. 63: p. 1377-1385.

98. M.M. Thwe and K. Liao, *Effects of environmental aging on the mechanical properties of bamboo-glass fiber reinforced polymer matrix hybrid composites.* Composite Part A, 2002. 33: p. 43-52.

99. R.R. Rothon, *Particulate-filled polymer composites.* 2nd ed. 2003: Rapra Technology Limited.

100. M.-C. Brochier Salon, M. Abdelmouleh, S. Boufi, M.N. Belgacem and A. Gandini, *Silane adsorption onto cellulose fibers: Hydrolysis and condensation reactions.* Journal of Colloid and Interface Science, 2005. 289: p. 249-261.

101. M. Xanthos, *Functional fillers for plastics.* 2005: WILEY-VCH Verlag GmbH & Co KGaA.

APPENDIX A

The Mechanical Properties of Composites

Table A-1 The mechanical properties of pure HDPE.

pure HDPE		tensile properties		flexural properties	
		strength [1]	modulus [1]	strength [1]	modulus [1]
		23.2	270	27.6	988
		23.2	266	28.4	944
		23.4	281	28.4	997
		22.8	273	27.9	913
		22.9	270	28.0	917
	Mean	23.1	272	28.1	952
	STD[2]	0.2	5	0.3	35

Table A-2 The mechanical properties of untreated EFB particulate composites with varying EFB content.

EFB particulate content		tensile properties		flexural properties	
		strength [1]	modulus [1]	strength [1]	modulus[1]
10%wt		21.0	265	33.0	1260
		21.7	300	33.1	1320
		19.4	288	33.1	1050
		19.6	291	33.4	1320
		20.2	270	33.8	1290
	Mean	20.4	283	33.3	1250
	STD[2]	0.8	13	0.3	100
20%wt		20.5	330	34.9	1570
		19.5	340	33.5	1470
		20.7	353	33.6	1520
		20.5	337	34.3	1390
		19.9	330	32.9	1480
	Mean	20.2	338	33.8	1490
	STD[2]	0.5	9	0.7	60
30%wt		17.6	333	32.7	1580
		17.8	335	31.3	1450
		17.3	337	30.8	1590
		17.6	315	32.9	1580
		19.4	325	31.3	1560
	Mean	18.0	329	31.8	1550
	STD[2]	0.7	8	0.8	50

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[1] The unit for both strength and modulus are MPa.

[2] STD = Standard Deviation.

Table A-3 The mechanical properties of untreated EFB short fiber composites with varying EFB content.

EFB short fiber content		tensile properties		flexural properties	
		strength [1]	modulus [1]	strength [1]	modulus [1]
10%wt		20.8	319	34.2	1340
		21.3	313	33.8	1310
		21.8	308	34.4	1310
		21.6	308	34.2	1270
		20.9	318	34.4	1320
	Mean	21.3	312	34.2	1310
	STD[2]	0.4	5	0.2	20
20%wt		20.0	381	36.6	1680
		21.2	376	37.6	1720
		21.6	366	38.1	1710
		21.8	369	37.5	1630
		21.3		38.7	1650
	Mean	21.2	373	37.7	1680
	STD[2]	0.6	6	0.7	30
30%wt		21.4	429	39.4	2010
		21.4	408	36.5	1540
		19.5	395	40.0	1540
		19.1	411	37.1	1620
		20.5	404	39.8	1940
	Mean	20.4	409	38.6	1730
	STD[2]	0.9	11	1.5	200

[1] The unit for both strength and modulus are MPa.

[2] STD = Standard Deviation.

Table A-4 The mechanical properties of composites treated with varying alkali concentration.

alkali concentration		tensile properties		flexural properties	
		strength [1]	modulus [1]	strength [1]	modulus [1]
2%		21.2	299	35.9	1540
		21.2	315	36.6	1420
		21.2	310	37.3	1380
		21.7	313	34.6	1330
		21.3	331	36.9	1480
	Mean	21.3	314	36.3	1430
	STD[2]	0.2	10	1.0	70
6%		21.2	323	33.5	1420
		21.1	324	33.4	1330
		21.1	323	31.2	1460
		21.9	321	32.1	1410
		21.4	326	33.8	1410
	Mean	21.4	323	32.8	1410
	STD[2]	0.3	2	1.0	40
10%		21.4	342	33.4	1440
		21.6	343	34.9	1610
		21.5	340	35.7	1480
		21.8	340	37.4	1580
		21.7	333	35.7	1590
	Mean	21.6	340	35.4	1540
	STD[2]	0.1	4	1.3	70

[1] The unit for both strength and modulus are MPa.

[2] STD = Standard Deviation.

Table A-5 The mechanical properties of composites treated with varying MTS concentration.

MTS concentration		tensile properties		flexural properties	
		strength [1]	modulus [1]	strength [1]	modulus [1]
1%		23.0	326	32.6	1310
		22.8	327	33.7	1360
		23.1	334	34.6	1530
		23.0	324	33.5	1360
		23.1	335	33.1	1350
	Mean	23.0	329	33.5	1380
	STD[2]	0.1	4	0.7	80
3%		23.4	328	37.5	1440
		23.3	334	35.9	1500
		23.3	328	36.7	1600
		23.1	324	37.1	1480
		23.1	326	37.5	1560
	Mean	23.3	328	37.0	1520
	STD[2]	0.1	3	0.6	60
5%		24.0	314	32.8	1230
		23.9	321	32.0	1230
		24.2	334	33.3	1240
		24.1	316	32.6	1200
		24.2	335	32.3	1200
	Mean	24.1	324	32.6	1220
	STD[2]	0.1	9	0.4	10
10%		23.2	320	35.1	1320
		22.7	336	35.1	1320
		23.0	340	33.6	1340
		22.3	321	33.5	1300
		23.1	339	34.4	1280
	Mean	22.9	331	34.3	1310
	STD[2]	0.3	9	0.7	20

[1] The unit for both strength and modulus are MPa.

[2] STD = Standard Deviation.

Table A-6 The mechanical properties of composites treated with varying VTS concentration.

VTS concentration		tensile properties		flexural properties	
		strength [1]	modulus [1]	strength [1]	modulus [1]
1%		22.3	321	33.2	1350
		22.2	329	33.9	1300
		22.2	334	33.2	1290
		22.5	329	33.8	1320
		22.3	331	34.6	1250
	Mean	22.3	329	33.8	1300
	STD[2]	0.1	4	0.5	30
3%		23.0	333	36.1	1540
		22.7	335	35.8	1570
		22.7	329	35.9	1510
		22.8	338	36.8	1560
		22.8	337	36.1	1540
	Mean	22.8	334	36.1	1540
	STD[2]	0.1	3	0.3	20
5%		23.1	326	33.5	1330
		23.0	327	31.0	1320
		22.7	324	32.7	1360
		23.0	328	32.5	1320
		22.9	320	31.8	1320
	Mean	23.0	325	32.3	1330
	STD[2]	0.1	3	0.8	20
10%		22.6	338	33.3	1290
		23.2	342	34.0	1280
		23.1	329	33.3	1290
		22.9	344	33.4	1300
		23.2	345	34.9	1330
	Mean	23.0	340	33.8	1300
	STD[2]	0.2	6	0.6	20

[1] The unit for both strength and modulus are MPa.

[2] STD = Standard Deviation.

Table A-7 The mechanical properties of composites treated with varying acrylic acid concentration.

acrylic acid concentration		tensile properties		flexural properties	
		strength [1]	modulus [1]	strength [1]	modulus [1]
5%		22.9	343	33.8	1130
		22.5	339	33.7	1170
		22.5	352	33.4	1180
		22.7	346	32.5	1200
		23.0	340	33.6	1120
	Mean	22.7	344	33.4	1160
	STD[2]	0.2	5	0.5	30
10%		22.9	320	31.3	1260
		22.5	325	30.3	987
		22.5	331	32.4	1130
		22.7	332	30.1	992
		22.7	340	30.5	1050
	Mean	22.7	330	30.9	1080
	STD[2]	0.1	7	0.8	100

[1] The unit for both strength and modulus are MPa.

[2] STD = Standard Deviation.

APPENDIX B

The Water Absorption Properties of Composites

The weight unit used in the water absorption tables is “gram” and the data selected for analysis are the “sample 1” data.

Table B-1 The water absorption properties of untreated short fiber composites with varying EFB content.

		16-Aug	17-Aug	18-Aug	19-Aug	20-Aug	22-Aug	24-Aug	27-Aug	29-Aug	31-Aug
		0	1	2	3	4	6	8	11	13	15
10%wt untreated short fiber composites	sample 1	1.4496	1.4534	1.4544	1.4558	1.4563	1.4564	1.4581	1.4585	1.4599	1.4595
	sample 2	1.4386	1.4422	1.4429	1.4430	1.4437	1.4456	1.4476	1.4502	1.4505	1.4491
	sample 3	1.3737	1.3764	1.3773	1.3782	1.3788	1.3827	1.3830	1.3813	1.3857	1.3823
20%wt untreated short fiber composites	sample 1	1.4343	1.4454	1.4486	1.4532	1.4567	1.4635	1.4680	1.4739	1.4762	1.4780
	sample 2	1.3990	1.4079	1.4126	1.4156	1.4168	1.4239	1.4289	1.4302	1.4335	1.4348
	sample 3	1.4606	1.4721	1.4768	1.4796	1.4831	1.4899	1.4977	1.5055	1.5066	1.5102
30%wt untreated short fiber composites	sample 1	1.4365	1.4575	1.4628	1.4680	1.4743	1.4869	1.4937	1.5021	1.5097	1.5140
	sample 2	1.4729	1.4890	1.4933	1.4985	1.5041	1.5135	1.5224	1.5258	1.5288	1.5328
	sample 3	1.4448	1.4600	1.4671	1.4716	1.4779	1.4881	1.4943	1.5019	1.5043	1.5092

		3-Sep	6-Sep	9-Sep	13-Sep	17-Sep	21-Sep	25-Sep	1-Oct	5-Oct
		18	21	24	28	32	36	40	46	50
10%wt untreated short fiber composites	sample 1	1.4606	1.4617	1.4617	1.4625	1.4625	1.4637	1.4640	1.4640	1.4643
	sample 2	1.4477	1.4490	1.4490	1.4499	1.4499	1.4508	1.4508	1.4508	1.4508
	sample 3	1.3823	1.3830	1.3835	1.3842	1.3842	1.3853	1.3854	1.3864	1.3864
20%wt untreated short fiber composites	sample 1	1.4792	1.4839	1.4869	1.4898	1.4941	1.4974	1.4981	1.4980	1.4997
	sample 2	1.4373	1.4425	1.4436	1.4460	1.4499	1.4560	1.4540	1.4562	1.4583
	sample 3	1.5152	1.5199	1.5238	1.5294	1.5342	1.5402	1.5405	1.5442	1.5487
30%wt untreated short fiber composites	sample 1	1.5207	1.5266	1.5323	1.5376	1.5444	1.5488	1.5514	1.5531	1.5574
	sample 2	1.5381	1.5451	1 5492	1.5556	1.5620	1.5690	1.5680	1.5714	1.5788
	sample 3	1.5132	1.5199	1.5240	1.5301	1.5368	1.5425	1.5450	1.5479	1.5549

Table B-2 The water absorption properties of untreated particulate composites with varying EFB content.

		16-Aug	17-Aug	18-Aug	19-Aug	20-Aug	22-Aug	24-Aug	27-Aug	29-Aug	31-Aug
		0	1	2	3	4	6	8	11	13	15
10%wt untreated particulate composites	sample 1	1.3953	1.3984	1.3994	1.4009	1.3998	1.4014	1.4038	1.4021	1.4049	1.4059
	sample 2	1.4722	1.4750	1.4773	1.4773	1.4778	1.4788	1.4817	1.4815	1.4828	1.4849
	sample 3	1.3936	1.3970	1.3994	1.4004	1.4016	1.4051	1.4083	1.4115	1.4139	1.4135
20%wt untreated particulate composites	sample 1	1.3501	1.3577	1.3600	1.3613	1.3639	1.3657	1.3696	1.3687	1.3725	1.3731
	sample 2	1.4974	1.5041	1.5064	1.5091	1.5137	1.5182	1.5201	1.5232	1.5243	1.5252
	sample 3	1.4429	1.4520	1.4529	1.4528	1.4543	1.4561	1.4585	1.4612	1.4611	1.4601
30%wt untreated particulate composites	sample 1	1.4648	1.4797	1.4861	1.4919	1.4955	1.5043	1.5124	1.5203	1.5248	1.5268
	sample 2	1.4829	1.5004	1.5057	1.5032	1.5094	1.5196	1.5244	1.5321	1.5356	1.5425
	sample 3	1.4564	1.4688	1.4787	1.4850	1.4927	1.5006	1.5121	1.5206	1.5251	1.5311

		3-Sep	6-Sep	9-Sep	13-Sep	17-Sep	21-Sep	25-Sep	1-Oct	5-Oct
		18	21	24	28	32	36	40	46	50
10%wt untreated particulate composites	sample 1	1.4053	1.4065	1.4044	1.4050	1.4058	1.4054	1.4058	1.4058	1.4059
	sample 2	1.4834	1.4854	1.4851	1.4855	1.4858	1.4872	1.4876	1.4878	1.4878
	sample 3	1.4146	1.4175	1.4186	1.4217	1.4245	1.4272	1.4290	1.4303	1.4315
20%wt untreated particulate composites	sample 1	1.3741	1.3754	1.3753	1.3785	1.3800	1.3822	1.3828	1.3830	1.3830
	sample 2	1.5263	1.5277	1.5280	1.5313	1.5332	1.5348	1.5348	1.5371	1.5371
	sample 3	1.4614	1.4655	1.4654	1.4666	1.4674	1.4680	1.4682	1.4687	1.4688
30%wt untreated particulate composites	sample 1	1.5337	1.5406	1.5416	1.5476	1.5540	1.5596	1.5599	1.5624	1.5667
	sample 2	1.5469	1.5520	1.5544	1.5594	1.5635	1.5650	1.5654	1.5660	1.5701
	sample 3	1.5362	1.5419	1.5420	1.5528	1.5602	1.5635	1.5630	1.5680	1.5713

Table B-3 The water absorption properties of 10%wt EFB short fiber composites treated with various chemical treatments.

		16-Aug	17-Aug	18-Aug	19-Aug	20-Aug	22-Aug	24-Aug	27-Aug	29-Aug	31-Aug	3-Sep	6-Sep	9-Sep	13-Sep	17-Sep	21-Sep	25-Sep	1-Oct	5-Oct
		0	1	2	3	4	6	8	11	13	15	18	21	24	28	32	36	40	46	50
Alkali	sample 1	1.0960	1.0990	1.1007	1.1018	1.1013	1.1015	1.1023	1.1039	1.1034	1.1037	1.1042	1.1042	1.1048	1.1052	1.1051	1.1060	1.1063	1.1063	1.1062
	sample 2	1.3702	1.3743	1.3743	1.3764	1.3766	1.3782	1.3795	1.3826	1.3830	1.3799	1.3818	1.3815	1.3824	1.3810	1.3826	1.3839	1.3841	1.3842	1.3842
	sample 3	1.2550	1.2587	1.2610	1.2620	1.2614	1.2636	1.2646	1.2653	1.2666	1.2674	1.2686	1.2701	1.2689	1.2680	1.2696	1.2705	1.2706	1.2709	1.2713
MTS	sample 1	1.3207	1.3228	1.3246	1.3258	1.3247	1.3253	1.3251	1.3256	1.3271	1.3265	1.3266	1.3270	1.3274	1.3282	1.3281	1.3283	1.3286	1.3287	1.3287
	sample 2	1.3879	1.3905	1.3919	1.3919	1.3924	1.3925	1.3932	1.3938	1.3952	1.3952	1.3940	1.3944	1.3954	1.3963	1.3959	1.3964	1.3966	1.3969	1.3971
	sample 3	1.4773	1.4800	1.4831	1.4850	1.4824	1.4826	1.4838	1.4837	1.4864	1.4840	1.4837	1.4847	1.4852	1.4864	1.4858	1.4863	1.4865	1.4865	1.4866
VTS	sample 1	1.3236	1.3256	1.3268	1.3280	1.3277	1.3280	1.3286	1.3290	1.3303	1.3297	1.3299	1.3310	1.3310	1.3315	1.3315	1.3319	1.3319	1.3319	1.3320
	sample 2	1.4116	1.4139	1.4167	1.4155	1.4162	1.4165	1.4174	1.4189	1.4201	1.4185	1.4185	1.4197	1.4195	1.4201	1.4198	1.4201	1.4206	1.4208	1.4211
	sample 3	1.3040	1.3055	1.3071	1.3074	1.3096	1.3084	1.3089	1.3104	1.3103	1.3107	1.3094	1.3103	1.3108	1.3116	1.3116	1.3117	1.3120	1.3119	1.3123
Acrylated	sample 1	1.3070	1.3103	1.3116	1.3117	1.3125	1.3122	1.3134	1.3135	1.3144	1.3144	1.3148	1.3154	1.3159	1.3161	1.3162	1.3166	1.3170	1.3171	1.3170
	sample 2	1.3439	1.3470	1.3486	1.3488	1.3514	1.3488	1.3501	1.3520	1.3507	1.3508	1.3507	1.3514	1.3517	1.3524	1.3530	1.3530	1.3533	1.3536	1.3537
	sample 3	1.3424	1.3457	1.3475	1.3470	1.3486	1.3489	1.3499	1.3527	1.3510	1.3508	1.3508	1.3527	1.3532	1.3536	1.3550	1.3550	1.3549	1.3549	1.3549