

**Study of improving interfacial strength between matrix  
and reinforcement for green composites**

**Doctoral Thesis**

**By**

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# **Study of Improving Interfacial Strength between Matrix and Reinforcement for Green Composites**

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Recently, in the industrial field, there has been a lot of consideration for not only the development of the field itself but also for the environment. Therefore, the attention of the wide industry on the green composites was increased, however, the development of stable materials has yet to be elucidated and there are a lot of challenges that need to be solved. It is important to overcome the challenges of Green composite materials industry.

Previous research has shown that the interfacial shear strength is the key problem associated to composite properties. In particular, the interfacial strength between natural fiber and matrix is poor and unstable due to hydrophilic and hydrophobic problems between fiber and matrix and thus the fiber surface condition is not stable. In order to alter this characteristic, a previous study proposed the use of coupling agent and surface treatment.

The trend of the study for fiber analysis of natural fiber reinforced composite changed several times, because of accessibility and affordability reasons. Jute and kenaf are the most common resources in natural fiber reinforced composite so they were used to evaluate the effect of treatment methods. Bamboo fiber is a traditional material in Asia that has nice mechanical properties for composites. However, recently most of bamboo application has been replaced by plastic material so there is less competition on the market.

In this study, plasma polymerization and resin impregnation were used for the modification of kenaf, jute and bamboo fiber. The fibers were used for reinforced composites with polypropylene and poly lactic acid. Fiber tensile test, micro droplet test and microscope were used for fiber and tensile test and 3 point bending test and water absorption test were used for composites. Previous alkali treatment can modified adhesive strength between fiber and matrix but it can cause damages of fiber.

The plasma polymerization does not require water for treatment. In this study, plasma polymerization method charged acrylic acid at room temperature and room pressure. However, without alkali treatment, plasma polymerization damaged kenaf fiber and composite properties were not increased significantly, showing that when it is chopped for short fiber, the coated surface can be broken. So plasma polymerization is not very effective in this study. Therefore, fiber has to be chopped prior using plasma polymerization.

The resin impregnation method is coating fiber surface and rumen by low viscosity resin. In this study, polyvinyl alcohol(PVA) and phenolic resin were used for impregnation. This method fills up rumen and coated fiber surface, therefore, it reduces water absorption and changes fiber surface characteristic. PVA and phenolic resin

impregnation methods successfully increase fiber tensile strength. But phenolic resin impregnated fiber decreased inter facial shear strength, as when resin impregnation was used for fiber, it fixed the damages on fiber surface but the contact surface area was also decreased. So in the composites PVA impregnated composite can increase mechanical properties but phenolic resin impregnated fiber reinforced composite cannot. PVA impregnated bamboo fiber reinforced composite has higher mechanical properties, although, with this case it can also increase water absorption ratio. Therefore in this study, maleic anhydride grafted polypropylene(MAPP) were used for coupling agent with resin impregnation method. With MAPP the mechanical properties are similar with untreated, however, water absorption test showed that resin impregnated fiber reinforced composites have low absorption ratio than untreated. Especially PVA impregnated fiber was significantly decreased compared to without MAPP. Resin impregnation method is therefore a good material for MAPP/PP composites when considering lower water absorption.

In conclusion, plasma polymerization is good for fiber modification but it is hard to handle for chopped fiber reinforced composites made by an injection molding technic. Resin impregnation method increased fiber tensile strength, however, phenolic resin impregnated method can decrease interfacial shear strength. Thus, PVA impregnated bamboo fiber reinforced composite has increased mechanical properties but phenolic resin impregnated bamboo fiber has not. With MAPP and resin impregnation method water absorption ratio is reduced. It can be used to solve the challenge of natural fiber reinforced composites.

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# CHAPTER 1

## Introduction

### 1.1 Introduction

In the last century, the industry has to change the material needs of wood and steel with the structure of a polymer compound. These changes will have advantageous effects to a better mileage, mass production and cost reduction. Therefore, nowadays the polymer is one of the most important materials in industry[1,2].

Fiber-reinforced plastic composites, usually made of glass, carbon and aramid fiber reinforced with epoxy and unsaturated polyester, have played a dominant role during the last several decades in various applications because of their high mechanical strength and modulus. However, usage and disposal of these materials, especially glass-fiber-reinforced plastic (GFRP), have become critical because of their non-biodegradability, of the increasing environmental consciousness and demands of legislative authorities related to their recycling. Recently, completely biodegradable composites reinforced with natural fibers, which are called fully green composites, have attracted much interest to solve these problems[2].

To reduce the cost of composite fabrication and to make them light weight, wood flour and natural fibers were used as reinforcement or filler in early composites. In the 1980s, the synthesis of composites made of cellulosic fibers combined with thermoset resin began [3, 4]; then, in the 1990s, thermoplastic composites reinforced with wood flour were reported and extended to high-strength natural-fiber-reinforced thermoplastic composites [5, 6].

The specific properties of this natural product, namely low cost, lightweight, renewable character, high specific strength and modulus, availability in a variety of forms throughout the world, reactive surface and the possibility to generate energy, without residue, after burning at the end of their life-cycle, motivate their association with organic polymers to elaborate composite materials. The common thermoplastic materials that currently dominate as matrix materials for natural fibers are the polypropylene and polyethylene while phenolics and polyesters are also two widely used thermoset matrixes for the natural fibers [7, 8].

However, it is well known that different surface properties between the fiber and the matrix, i.e. the former is highly polar and hydrophilic while the latter is, generally, non-polar and relatively hydrophobic, impose that surface modification of the fibers surface can improve the fiber/polymer compatibility and their interfacial adhesion [9]. Without such a treatment, natural fibers embedded in a polymeric matrix generate unstable interfaces and the stress applied to the fiber/polymer composite is not efficiently transferred from the matrix to the fiber and the beneficial reinforcement effect of the fiber remains underexploited. Likewise, the poor ability of the polymer to wet the fiber hinders the homogeneous dispersion of short

fibers within the polymeric matrix [10]. Although the tensile strength and modulus of natural fibers are not as high as those for glass fiber, their specific tensile strength and modulus are close to the values of glass fiber, indicating the possibility that natural fibers can replace glass fiber as reinforcement in composites.

Recently, there is an increasing demand from automotive industries for materials with sound abatement capability as well as reduced weight for fuel efficiency. In automotive parts, such composites not only reduce the mass of the component but also lower the energy needed for production by 80%. Demands for natural fibers in plastic composites are forecast to grow at 15-20% annually in automotive applications and 50% are more in selected building applications [11]. Natural fibers possess excellent sound absorbing efficiency, are more shatter resistant and have better energy management characteristics than conventional fiber reinforced composites.

## **1.2 Motivation**

More recently, increasing environmental awareness, concern for environmental sustainability, and the growing global waste problem, initiation of ecological regulations and legislation such as the end-of-life vehicles regulation, the depletion of fossil fuels, and the increasingly higher price of crude oil have together created a groundswell of interest in renewable resources. Legislative pressures for greener technologies as well as the customer demands for more environmentally friendly consumer goods are forcing material suppliers and manufacturers to consider the environmental impact of their products at all stages of their life cycle, including materials selection processing, recycling, and final disposal. This and the worldwide availability of plant fibers [12] and other abundantly accessible agro-waste is responsible for this new research interest in the field of polymer science, engineering, and is responsible for a new interest in research in sustainable technology [13-15]. The development, processing and manufacturing, recycling, and disposal of “green composites” play as a circle of renewable resources. Consequently, a “cradle-to-grave” approach is emerging (Fig. 1.1).

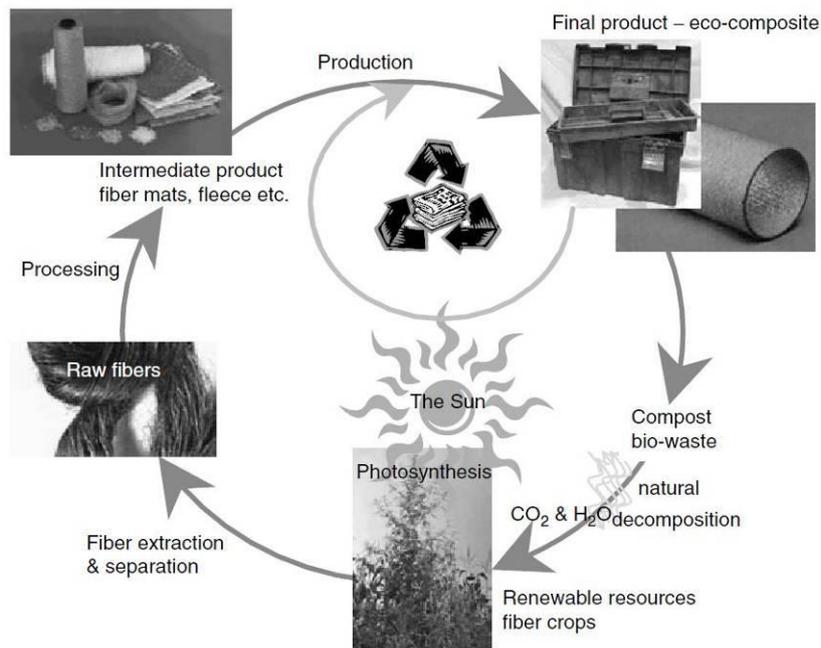


Fig. 1.1 Truly green composites in nature's circle of life

The increasing pressure on natural resources and the large amounts of energy required in glass fiber production has led to an upsurge in interest in the reinforcement potential of natural fibers. However, many researchers have reported disappointing levels of performance from their natural fiber composites which are significantly less than the level implied from such fiber property comparisons [15-20]. This disappointing level of reinforcement performance exhibited by many natural fibers is often discussed in terms of the challenges of obtaining good compatibility and adhesion between such fibers and polymer matrices. One of the generally accepted manifestations of 'adhesion' is in the mechanically measured value of interfacial shear strength (IFSS).

Particularly in thermoplastic matrix composites, reference is often made to the low level of chemical compatibility between polyolefin matrices and the polar materials found in natural fibers. The early history of the development of composite materials is dominated by the use of chemically reactive thermosetting polymers. A natural consequence of this fact is that much of the published work related to adhesion and stress transfer at the fiber-matrix interphase has been grounded in the assumption that chemical bonds play a key role. The hydrophilic character of cellulose is usually incompatible with the hydrophobic matrix material unless a compatibilizer or coupling agent is used [9]. This leads to poor interfacial adhesion between the fiber and matrix as well as poor fiber dispersion. An efficient utilization of the chemical modification of natural fiber surfaces or use of a proper compatibilizer or coupling agent are related to good wetting with the polymer matrix and homogeneous

dispersion of fibers in the matrix. Along with the two issues of compatibility and dispersion, a variety of further challenges must still be overcome to achieve high-performance natural fiber composites.

In the present time the limited use of cellulosic fiber composites in structural design is predominantly associated with disadvantages such as dimensional instability in humid environments, the lack of well defined fiber properties and the fiber's low ability to adhere to common matrix materials for efficient stress transfer. A better understanding of the dimensional stability and both the long term and short term mechanical performance of cellulose fiber composites are necessary if these materials are aimed to reach their full potential. To this end, computational modeling techniques can be an effective way to determine the mechanical properties of natural fiber composites. Computational modeling for the prediction of the mechanical properties of natural fiber composites can provide the flexibility of an efficient parametric study of the composites to then facilitate the design and development of the composite structures for engineering applications.

### **1.3 Research objectives**

The breakthrough for natural fiber composites in terms of usefulness in structural load bearing applications is yet to come. Some of the problem areas have been identified as: fiber-matrix adhesion properties, dimensional instability, fiber property variability, and micro-structural changes during the fiber extraction process and composite manufacturing. Currently many researchers are involved in the efforts to understand and solve these challenging tasks with the future goal to develop high performance green composites. Parallel to these efforts there is clear and distinct need for a broader knowledge-based understanding of the mechanical performance of natural fiber composites on several length scales. In light of this, the objectives of this research are summarized as follows:

- To develop and optimize the manufacturing method of natural fiber reinforced composites.
- To improve the physical and mechanical properties of the natural fiber reinforced composites by using different coupling agents and fiber surface treatments.
- To develop suitable for parametric studies of fiber's properties and their influence on composite's properties.

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# CHAPTER 2

## Background

### 2.1 Introduction

The use of natural fibers for reinforced plastics composites is one of the trends in composites materials. Their flexibility during processing, the highly specific stiffness, and low cost (on a volumetric basis) make them attractive to manufacturers. This century has witnessed ever-increasing demands for the utilization of plastics as important raw materials, more than 80% of which are thermoplastics. Natural fiber reinforced plastic composites are gaining more and more acceptance in structural applications[1].

Natural fiber reinforced composites can be applied in the plastics, automobile and packaging industries to cut down on material cost. Low density, low environmental impact and bio degradability are other important advantages of natural fibers. These advantages make natural fiber a replacement for glass fibers in composite materials. Mechanical properties of natural fibers, especially flax, hemp, jute and sisal, may compete with glass fiber in specific strength and modulus natural fiber reinforced polymeric composites have been developed for building, automobiles and most kind of polymeric applications[2-4].

Traditional fiber reinforced composites use various types of glass fiber, carbon fiber, aluminum oxide, and many others as the reinforcing component. To replace them, natural fibers, such as bamboo, hemp, jute, flax and many others were applied by researchers as fiber reinforcement for composites. In recent years, several methods to challenge the weak point of natural fiber composites fiber treatment methods were developed.

A better understanding of the chemical composition and surface adhesive bonding of natural fiber is necessary for developing natural fiber reinforced composites. The components of natural fibers include cellulose, hemi cellulose, lignin, pectin, waxes and water soluble substances. The composition of selected natural fibers is shown in Table 2.1. The composition may differ with the growing condition and testing methods even for the same kind of fiber. Low interfacial properties between fiber and polymer matrix often reduce their potential as

reinforcing agents due to the hydrophilic nature of natural fibers. Chemical modifications are considered to optimize the interface of fibers. Chemicals may activate hydroxyl groups or introduce new moieties that can effectively interlock with the matrix. The development of a definitive theory for the mechanism of bonding by chemicals in composites is a complex problem. Generally, chemical coupling agents are molecules possessing two functions. The first function is to react with hydroxyl groups of cellulose and the second is to react with functional groups of the matrix[5].

Table 2.1 Chemical composition of selected common natural fibers[5]

Type of fiber	Cellulose (%)	Lignin (%)	Hemi cellulose(%)	Pectin (%)	Ash (%)
Bast fiber					
Fiber flax	71	2.2	18.6-20.6	2.3	-
Seed flax	43-47	21-23	24-26	-	5
Kenaf	31-5	15-19	21.5-23	-	2-5
Jute	45-71.5	12-26	13.6-21	0.2	0.5-2
Hemp	57-77	3.7-13	14-22.4	0.9	0.8
Ramie	68.6-91	0.6-0.7	5-16.7	1.9	-
Core fiber					
Kenaf	37-49	15-21	18-24	-	2-4
Jute	41-48	21-24	18-22	-	0.8
Leaf fiber					
Abaca	56-63	7-9	15-17	-	3
Sisal	47-78	7-11	10-24	10	0.6-1
Henequen	77.6	13.1	4-8	-	-

In this chapter, limited chosen chapter undergone a partial review on the mechanism and utilization of treatments in fiber reinforced composites to advance the boundaries of application of natural fiber composites, focused on natural fiber and their modification technics.

## 2.2 Natural fiber

Natural fibers define the fibers which are not manmade. They can be sourced from not only plants but also from animals. Fibers obtained from animals are for example wool, silk, spider silk, and feathers. Fig 2.1 shows classification of natural fiber. These have something in common such as fast grow up, low cost, and high performance. Based on which part of the plant the fibers are sourced, the fibers can be classified into bast fibers (jute, flax, hemp, ramie and kenaf), leaf fibers (banana, sisal, agave and pineapple), seed fibers (coir, cotton and kapok), core fibers (kenaf, hemp and jute), grass and reed (wheat, corn and rice), and other types of fibers [1, 5-10]. Table 2.2 list of physical appearance of some natural fibers. Fig 2.2 shows some of plant fibers. Fig 2.3 is a dimension of specimen for fiber bundle tensile test. Table 2.3 lists of the mechanical properties of some natural and man-made fibers. Basically, natural fibers have been grown and used for life objects such as rope, bag, fishing net, housing and clothes [2-4].

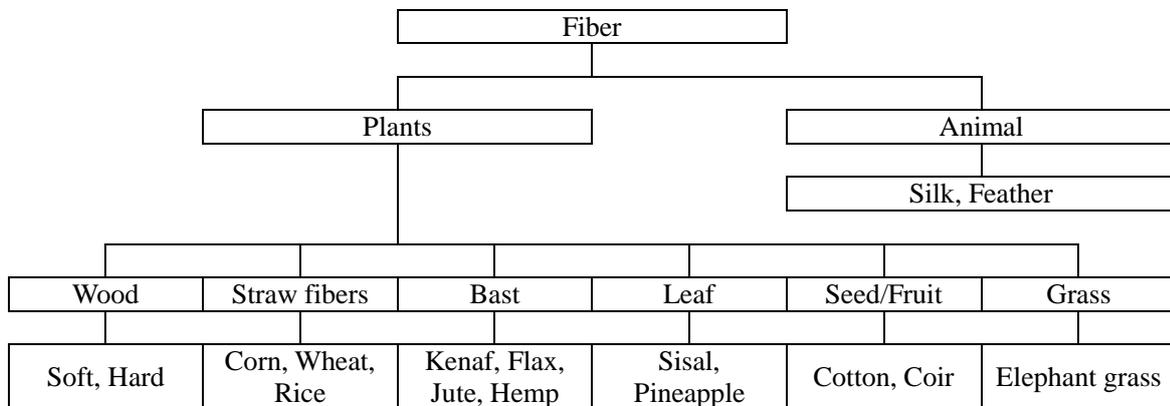


Fig 2.1 Classification of natural fibers[17]

Table 2.2 Physical appearance of some natural fibers[2]

Type of fiber	Diameter ( $\mu\text{m}$ )	Texture and color
Hemp	26.5	Silky-fine; White to light brown
Jute	25-200	Fine; Light brown
Sisal	50-200	Coarse-stiff; White
Coir	100-450	Coarse; White to brown
Gomuti	50-800	Coarse-stiff; Brown to black

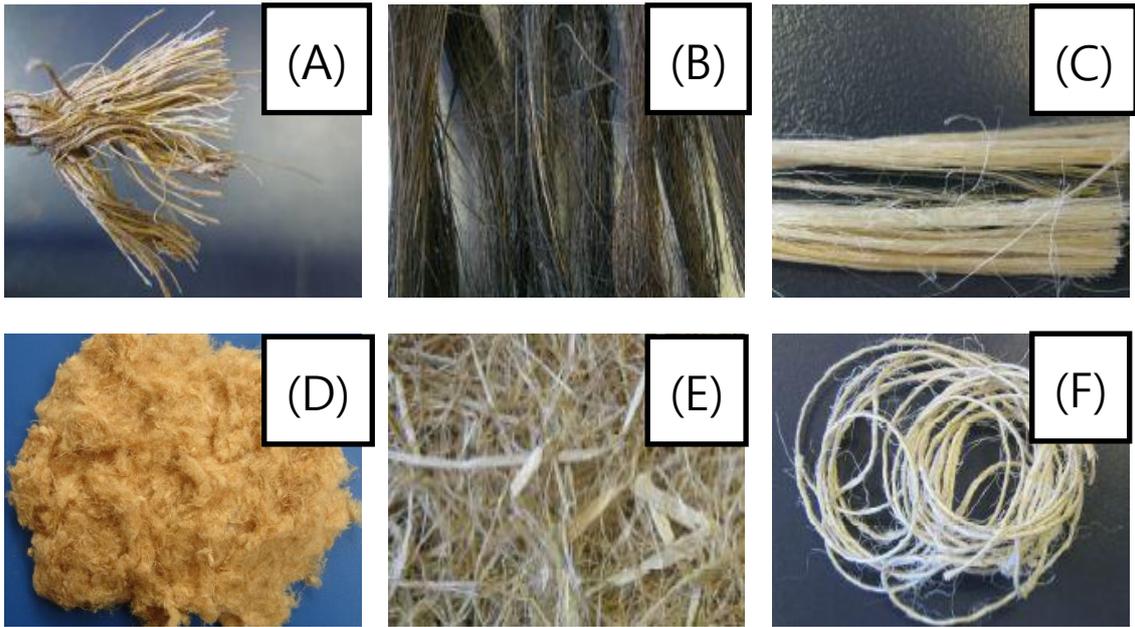


Fig 2.2 Pictures of several natural fibers; (A)coir, (B)gomuti, (C)jute, (D)bamboo, (E)sisal and (F)hemp[2]

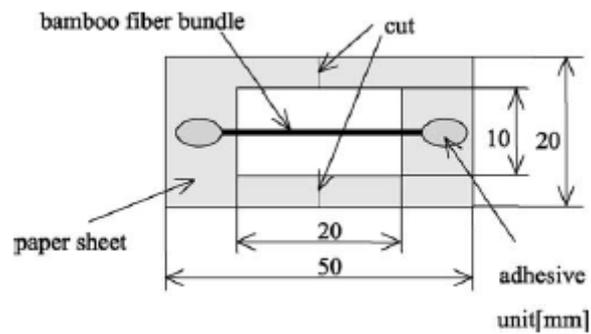


Fig 2.3 Dimensions of specimen for fiber bundle tensile test[25]

Table 2.3 Mechanical properties of natural fibers as compared to conventional reinforcing fibers [4-10]

	Specific gravity[g/cm <sup>3</sup> ]	Tensile strength[MPa]	Modulus of elasticity[GPa]
Sisal	1.370	347-378	15.2
Coconut	1.177	95-118	2.8
Bamboo	1.158	73-505	10-40
Hemp	1.500	900	34
Caesar weed	1.409	300-500	10-40
Banana	1.031	384	20-51
Piassava palm	1.054	143	5.6
Date palm	1.300-1.450	70-170	2.5-4
Cotton	1.5-1.6	287-597	5.5-12.6
Jute	1.3-1.46	393-800	10-30
Flax	1.4-1.5	345-1500	27.6-80
Coir	1.15	131-175	4-6
Pineapple	-	413-1627	0.24-0.40
Gomuti	1.29	190.29	3.69
Ramie	1.5	220-938	44-128
Softwood kraft	1.5	1000	40
E-glass	2.5	2000-3500	70
S-glass	2.5	4570	86
Aramid(normal)	1.4	3000-3150	63-67
Carbon(standard)	1.4	4000	230-240

## 2.3 Treatment of natural fiber

### 2.3.1 Alkaline treatment

Alkaline treatment or mercerization is one of the most used chemical treatments of natural fibers when used to reinforce thermoplastics and thermosets. The important modification done by alkaline treatment is the disruption of hydrogen bonding in the network structure, thereby increasing surface roughness. This treatment removes a certain amount of lignin, wax and oils covering the external surface of the fiber cell wall, depolymerizes cellulose and exposes the short length crystallites. Addition of aqueous NaOH to natural fiber promotes the ionization of the hydroxyl group to the alkoxide. Thus, alkaline processing directly influences the cellulosic fibril, the degree of polymerization and the extraction of lignin and hemi-cellulosic compounds. In alkaline treatment, fibers are immersed in NaOH solution for a given period of time. Treated jute and sisal fibers with 5% aqueous NaOH

solution for 2 to 72 h at room temperature were better than other conditions. It is reported that alkaline treatment has two effects on the fiber: First, it increases the surface roughness resulting in better mechanical interlocking. Second, it increases the amount of cellulose exposed on the fiber surface, thus increasing the number of possible reaction sites[5]. Alkaline treatment gave up to an increase in tensile properties (both strength and modulus) for flax fiber–epoxy composites and coincided with the removal of pectin. Alkaline treatment also significantly improved the mechanical, impact fatigue and dynamic mechanical behaviors of fiber-reinforced composites. Moreover, 5% NaOH treated sisal fiber-reinforced polyester composites had better tensile strength than 10% NaOH treated composites. This is because at higher alkali concentration, excess delignification of natural fiber occurs resulting in a weaker or damaged fiber. The tensile strength of the composite decreased drastically after certain optimum NaOH concentration [4, 11-15]. Figure 2.4 shows differences between treated and untreated. Treated fiber shows empty space suggesting impurity, fat etc. were removed.

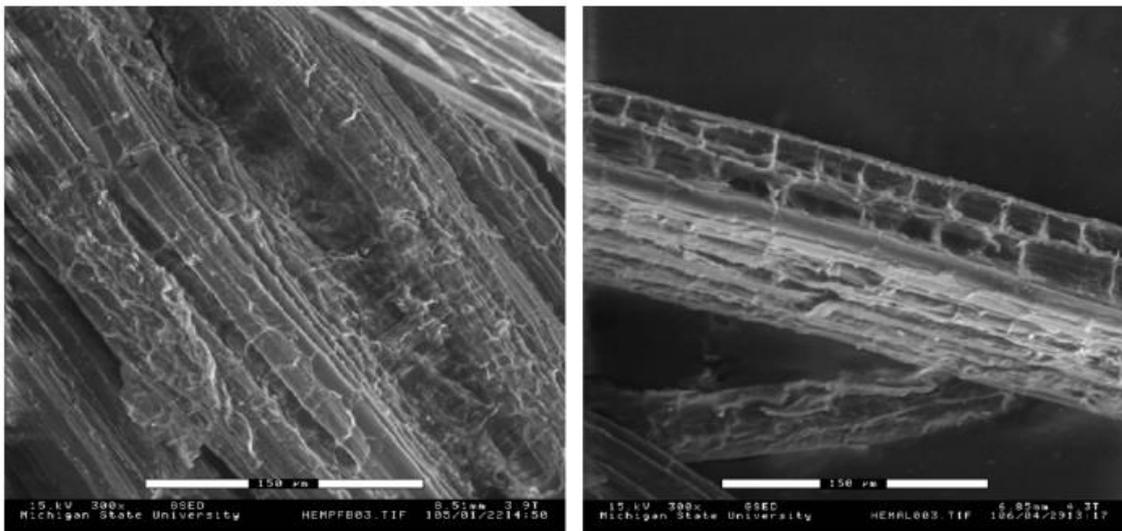


Fig 2.4 Left: untreated **hemp fiber**. Right: alkali treated hemp. Magnification  $\times 300$ [14]

### 2.3.2 Isocyanate treatment

Isocyanates are known in wood chemistry as wood binders with particle board. They are used for production of oriented strand board too. The mechanical properties of isocyanate treated fiber reinforced thermoplastics composites. Urethane derivatives of cardanol were treated with sisal fiber to improve the compatibility between fiber and matrix. Isocyanates are compounds containing the isocyanate functional group  $-N=C=O$ , which is highly reactive with hydroxyl groups in lignocellulose materials. It was discovered that blends of poly lactic

acid(PLA) with 45% wheat starch and 0.5% diphenylmethane diisocyanate(MDI) resulted in composites with the highest tensile strength. It was also shown that moisture absorption increased as a function of increasing starch content. Water absorption can influence the mechanical properties of the composite. The moisture in the composite can react with MDI, which can affect the interfacial interaction between starch mediated MDI with the PLA matrix by reducing the tensile strength or having a limited improvement. It was interesting to note that the highest strength was achieved at 45%. This can be attributed to two major reasons: the level of water in the blend can aid processing of the PLA, whereby the water behaves as a plasticizer, and secondly, the viscosity of the PLA at this level of water content maybe just sufficient to allow optimum dispersion of the starch particles within the PLA matrix. However, in order to utilize these materials in commercial applications such as for short term packaging these materials would require water proofing on the surface in order to prevent rapid degradation [4-6,15]. Fig 2.5 shows load deflection curves for composites with some compositions.

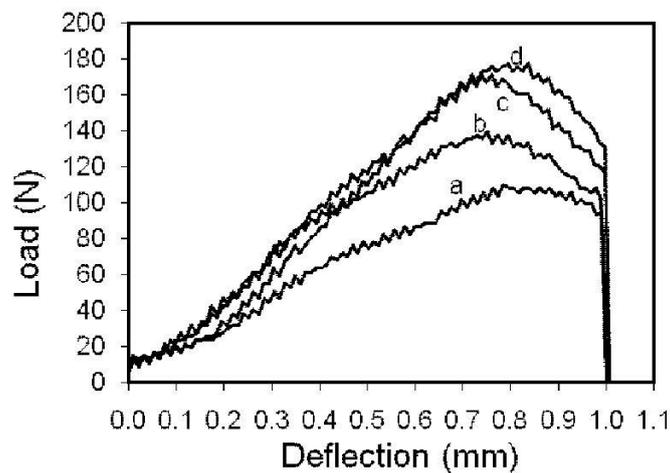


Fig 2.5 Load-deflection curves for a) PLA, (b) PLA/wood-flour, (c) PLA/wood-flour containing MDI, (d) PLA/wood-flour containing PEAA wood-flour content=20% w/w[15]

### 2.3.3 Silane treatment

Silane is a chemical compound that is used as a coupling agent to allow fiber adherence to a polymer matrix, stabilizing the composite material. Silane coupling agents may reduce the number of cellulose hydroxyl groups in the fiber–matrix interface. In the presence of moisture, hydrolysable alkoxy group leads to the formation of silanols. 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 [4-8]. Table 2.3 and Fig 2.6 show different treatment effects of silane treated fibers. Fig 2.7 is showing how one can prepare micro drop for thermo plastic matrix.

Table 2.4 Different fibers treatments applied to the henequen fibers[7]

Keyword	Surface treatment
FIB	No treatment
FIBNA	Treated with an aqueous alkaline solution
FIBNASIL	Treated first with alkaline solution and then with a silane coupling agent
FIBNAPRE	Treated with alkali and then impregnated with a dilute matrix solution

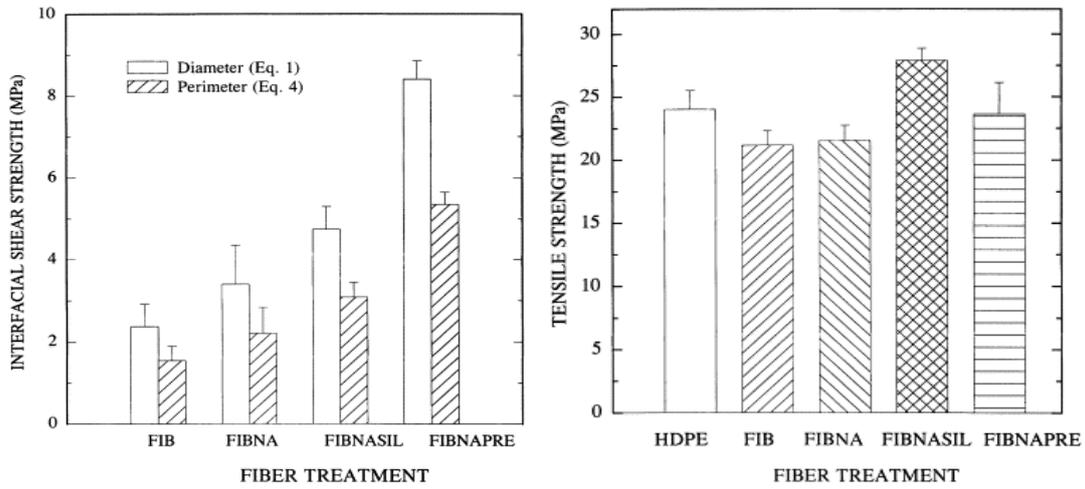


Fig 2.6 Left: interfacial shear strength and right: tensile strength of the henequen fibers[7]

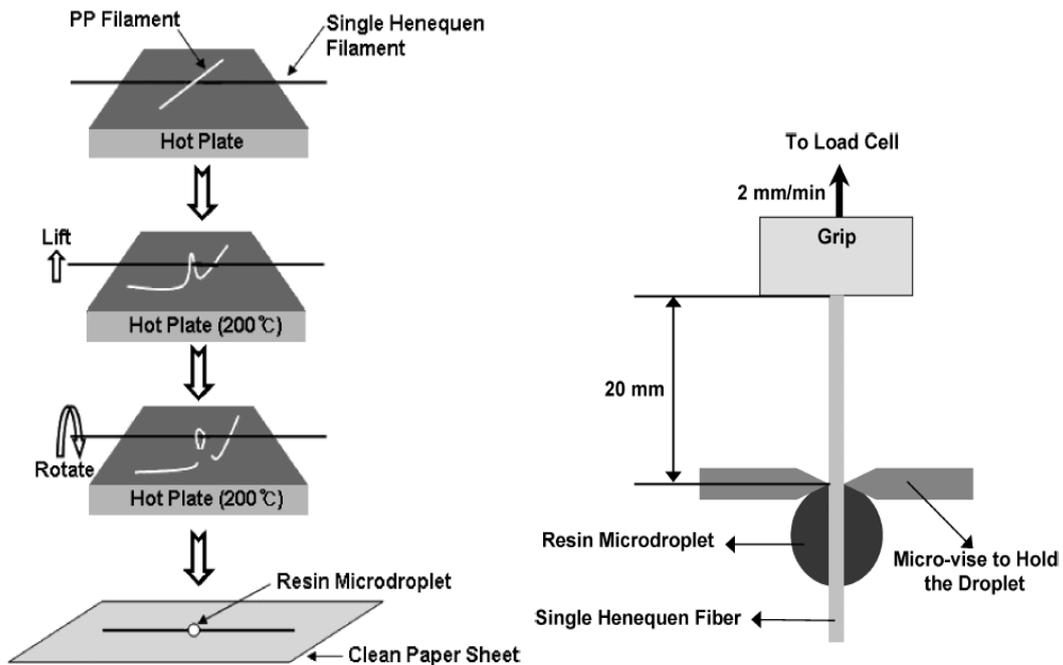


Fig 2.7 Left: Schematic of the experimental procedure forming a PP microdroplet around a single fiber. Right: Brief illustration of a single fiber microdroplet[18]

### **2.3.4 Impregnation of fibers**

A better combination of fiber and polymer is achieved by impregnation of the reinforcing fibers with polymer matrices compatible with the polymer. Fibers are impregnated in liquid monomer and then these monomers are polymerized in-situ using catalyst, heat or radiation. A wide range of composite properties is possible by changing the monomer with a crosslinking agent, and/or by changing the monomer filling method and the polymerization process. Improved dimensional stability of wood polymer composite using solvent exchange technique of impregnation was reported. It is known that the elevated viscosity of the matrix during processing the composite hinders the complete impregnation of the fibers which results in a low mechanical interaction with the matrix. Monomer solutions of low viscosity are used for the purpose [4,20,21].

### **2.3.5 Cross linked coated method**

The coated method to high-toughness thermoplastic composites is based on thermo plastic resin and thermosetting resin-coated cellulosic fillers. Dynamic cross-linking (during melt-mixing) of thermo plastic compatibilized and thermosetting resin-coated cellulose-filled thermoplastic composition produces a thermoplastic composite with tensile strength higher than that of unfilled PP and tensile toughness about as good as that of thermo plastic[21]. Table 4 shows the mechanical properties of different compositions cross-linked composites.

### **2.3.6 Electron beam irradiate**

Electron beam irradiate (EBI) treatment significantly influences the interfacial properties of henequen /poly (butylene succinate), and henequen/polypropylene natural fiber composites. They reported that EBI treatment on the henequen fiber surface with certain doses significantly contributes to the improvement of the interfacial property and the mechanical properties, as well as, the thermal stability of natural fiber composites [18]. Electron beam irradiation and alkali treatment effects on both the kenaf fiber and its bio composites were investigated to develop environmentally friendly bio composites with their corresponding manufacturing processes. Electron beam irradiation on kenaf fibers induced cellulose degradation resulting in a decrease of alpha cellulose content, lowering the maximum thermal decomposition temperature of cellulose, whereas little change of the functional groups for the kenaf fibers was noted [19].

Table 2.5 Properties of cellulosic filled cross linked composites[21]

	Weight ratio PP/SD/Coated SD/ MAHPP	Average fiber size(mm)	Yield strength (MPa)	Yield strain (%)	Young's modulus (GPa)	Tensile toughness (MPa)	Impact strength (kJm <sup>2</sup> )
1	65/35/0/0	1.20	17.3(1.2)	2.1	1.1	0.42	11.1
2	65/35/0/0	0.63	20.8(1.1)	2.9	1.2	0.40	10.8
3	65/35/0/0	0.50	22.0(0.7)	3.7	1.5	0.51	10.6
4	65/35/0/0	0.27	22.1(0.6)	7.4	1.64	0.69	9.2
5	55/45/0/0	0.28	16.5(0.5)	3.0	1.78	0.49	8.9
6	65/26/9/0	0.29	23.2(1.1)	4.8	1.73	0.51	10.9
7	65/18/17/0	0.32	22.3(1.2)	7.0	1.50	0.60	9.9
8	65/9/26/0	0.33	21.7(1.1)	5.6	1.74	0.49	8.4
9	65/0/35/0	0.36	22.9(1.7)	6.6	1.25	0.59	9.5
10	55/35/0/10	0.28	39.0(1.6)	5.9	1.68	1.45	10.3
11	55/0/35/10	0.34	40.0(1.1)	8.5	1.53	2.21	11.7
12	60/0/30/10	0.50	36.6(1.3)	5.1	1.31	1.21	11.8
13	55/0/45/0	1.17	16.6(1.1)	1.9	1.48	0.29	12.4
14	55/0/45/0	0.33	26.9(1.7)	7.1	1.51	0.85	7.9
15	50/0/45/5	0.32	37.1(1.6)	5.3	1.89	1.05	6.3

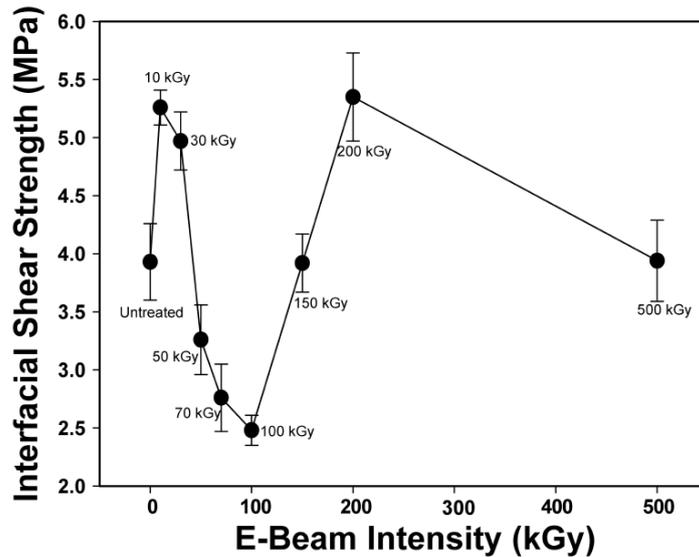


Fig 2.8 Variation of the interfacial shear strengths of henequen/PP composites as a function of E-beam intensity[18]

### 2.3.7 Plasma polymerization

Surface modification by discharge treatment such as low temperature plasma,

sputtering and corona discharge is of great interest in relation to the improvement in functional properties of vegetable fibers. Low temperature plasma treatment causes mainly chemical implantation, etching, polymerization, free radical formation, crystallization, whereas sputter etching brings about chiefly physical changes such as surface roughness and this leads to an increase in adhesion and a decrease in light reflection. Low temperature plasma is a useful technique to improve the surface characteristics of the fiber and polymeric materials by utilizing ingredients such as electron, ion, radical and excited molecules produced by electrical discharge. Low temperature plasma can be generated under atmospheric pressure in the presence of helium. This technique reports high tensile strength and low water absorption than raw or NaOH treated fibers [22, 23]. Fig 2.9 shows the tensile strength curve for NaOH treated, plasma treated and raw rice husk fiber reinforced composites. Fig 2.10 shows that plasma polymerization decreased the water absorption rate.

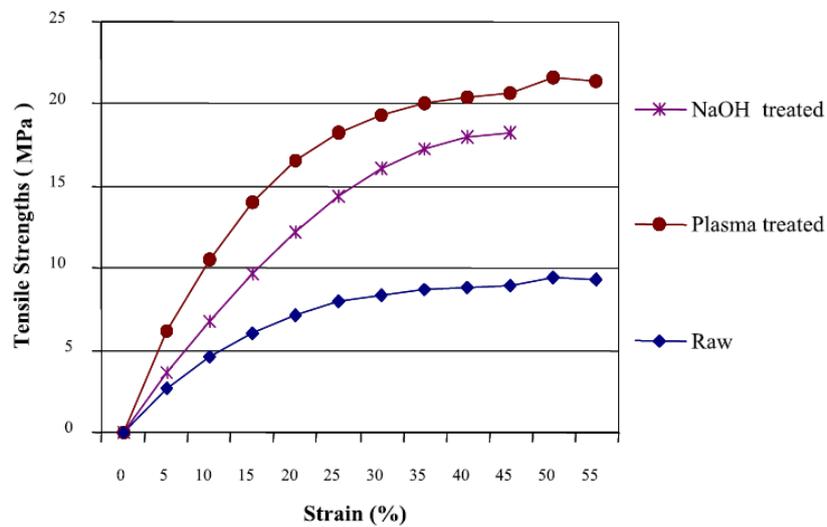


Fig 2.9 Tensile strengths of Rice Husk(RH)/PP composites[23]

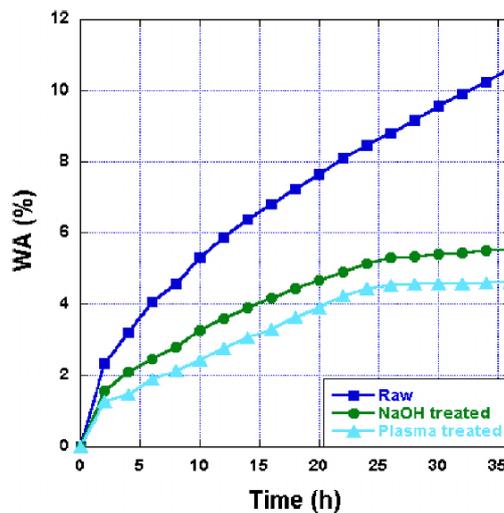


Fig 2.10 water absorption of RH/PP composites[23]

### 2.3.8 Stream explosion

Steam-exploded filament (SEF) a bamboo tree is firstly steam-exploded to easily separate fibers (lignin and hemi-cellulose in parenchyma cells are hydrolyzed as well as in fiber bundles). Cut bamboo cylinders are put into a steam chamber. Then, the chamber is filled with over-heated steam. After keeping them in this steam condition for 60 min, the steam explosions are occurring in the cells. The chamber is refilled with steam, and the pressure is successively released. This cycle is repeated for 11 times to assure the sufficient fracture of cell walls. Then, separated fiber bundles are treated with sodium hydroxide solution (1 N) at 100°C for 15–20 min. Finally, steam-exploded filaments are obtained after mixing with water. Most of the parenchyma cells are removed from the surface due to steam explosion [24, 25]. Fig 2.11 shows the exploded effect on bamboo fiber reinforced composites.

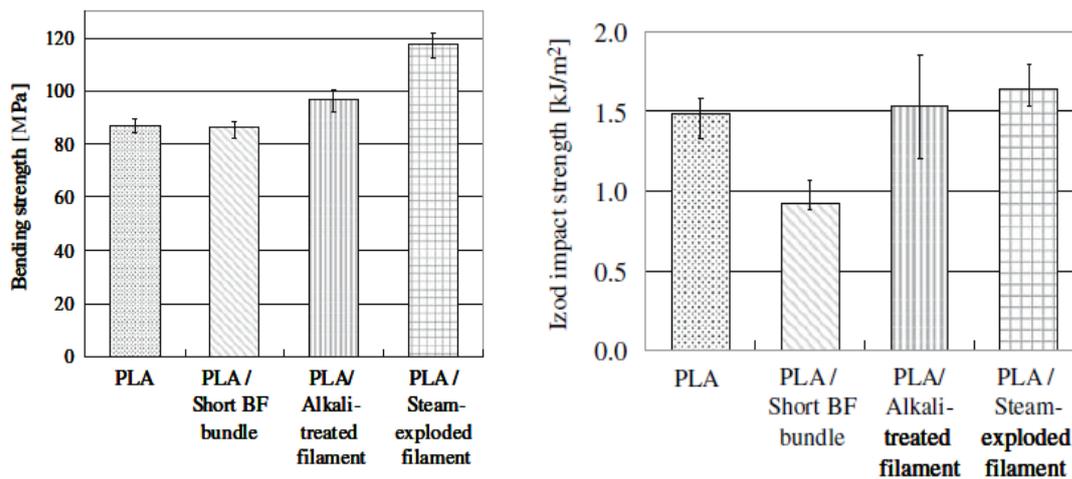


Fig 2.11 Left: Bending strength Right: Izod impact strength of PLA and PLA/bamboo fiber composites[24]

### Maleated coupling agents

Grafting is an effective method for the modification of natural fibers. Grafting on the cellulose fiber may take place before or during compounding. In the former case, pretreatment of fibers by compatibilizing agents generally occurs in solution. In the latter case, treatment during compounding occurs at the mixing temperature of the matrix. Grafting efficiency, grafting proportion and grafting frequency determine the degree of compatibility of cellulose fibers with a polymer matrix. The grafting parameters are influenced by the type and concentration of initiator, the monomer to be grafted and the reaction conditions [4-6].

Maleated coupling(MA) agents are widely used to strengthen composites containing

fillers and fiber reinforcements. The difference with other chemical treatments is that maleic anhydride is not only used to modify the fiber surface but also the PP matrix to achieve better interfacial bonding and mechanical properties in composites. Fig 2.12 shows Maleic anhydride effect on composites. Maleic anhydride treatment reduced the water absorption to a great extent in banana, hemp and sisal fiber-reinforced novolac composites. Mechanical properties like Young's modulus, flexural modulus, hardness and impact strength of plant fiber-reinforced composites were increased after maleic anhydride treatment [26, 27].

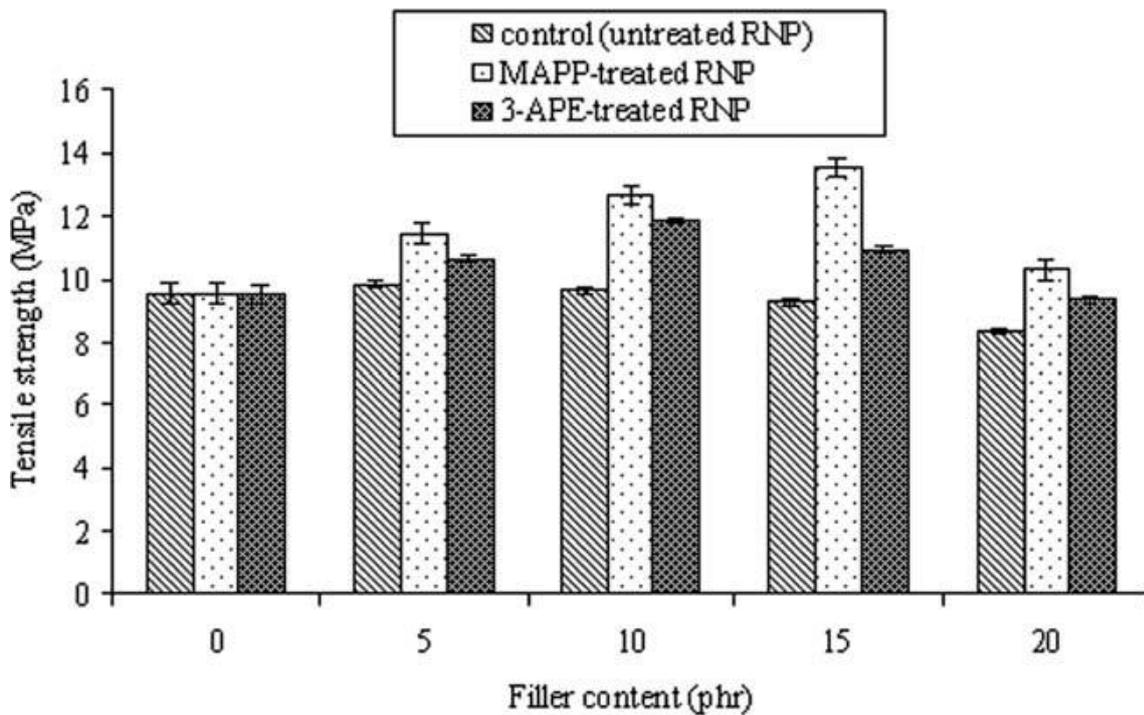


Fig 2.12 Effect of MAPP, 3-APE, and filler content on tensile strength of RNP-filled PP/NR composites[26].

## 2.4 Conclusions

Natural fiber composites have developed significantly over the past years because of their significant processing advantages, low cost, recyclable, low density and eco-friendly. Their application area also increases more and more. Natural fiber has some limitations, such as the interfacial strength between fiber and matrix which is one of the key issues in term of overall performance when produced final products. Many studies and going on research, are examining and reviewing points to improve the interfacial strength.

Further research is required in order to overcome limits such as moisture absorption, chemical absorption, long term stability, increasing life term.

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## **CHAPTER 3**

# **Surface treatment influence on the mechanical behavior of jute fiber reinforced composites**

### **3.1 Introduction**

Nowadays, the growing environmental awareness, new rules and regulations are forcing the industries to seek more ecologically friendly materials for their products. So, considerable research and development have been expanded in natural fibers as reinforcement in thermoplastic resinous matrix. The various advantages of natural fibers are low cost, low density, reduced energy consumption. In addition, the specific mechanical properties of natural fibers are comparable to those of traditional reinforcements. However, one primary disadvantage is poor interfacial adhesion and dispersion in olefinic thermoplastic matrix materials due to the hydrophilic character of cellulose[1-12]. Almost plant fibers are covered with pectin and waxy substances, thus hindering the hydroxyl groups from reacting with polar matrices, and forming mechanical interlocking adhesion with non-polar matrices. The poor moisture resistance of natural fibers leads to incompatibility and poor wet ability with hydrophobic polymers, and this reposes the interaction bonding at fiber/matrix interface. There are various methods for promoting interfacial adhesion in systems where lingo cellulosic materials are used as fillers [13-18].

The present research aims to study the effect of a solvent free, catalyst free, anhydride treatment on different lingo cellulosic materials, in order to produce cost effective totally biodegradable composites. Two different methods such as alkali treatment and plasma treatment were investigated in this study[20-26]. The formal technique was performed in room temperature conditions varying the weight percentage of sodium hydroxide (NaOH) and the later method was carried out to make a uniform deposition of rectangle hole free thin film over jute fibers. Surface morphology was investigated by Scanning Electron Microscopy (SEM) methods. At last, fiber specimens were made for tensile test and flexural test.

## 3.2 Experiments

### 3.2.1 Materials

#### Jute

Jute is a plant of the Malvaceae family. It is one of the cheapest natural fibers and after cotton the most used natural fiber. The downside of jute plants is that they only grow under monsoon climates (temperatures from 20°C to 40°C and a relative humidity of 70%–80%), so cultivation of jute plants is difficult to perform outside monsoon climate areas. However, the reason that jute fibers are cheap is because the plants grow fast and can be harvest 3 to 4 times a season. In this study, jute fiber was gathered from jute string. Because it is one of most common material for natural fiber reinforced composites and it means easy to compare with other treatment method. Fig 3.1 shows material of in this study.

#### Poly lactic acid(PLA)

Poly(lactic acid) or polylactide (PLA) is a biodegradable thermoplastic aliphatic polyester derived from renewable resources, such as corn starch (in the United States), tapioca roots, chips or starch (mostly in Asia), or sugarcane (in the rest of the world). In 2010, PLA had the second highest consumption volume of any bio plastic of the world. In this study PLA, which was produced by Miyoshi Oil and Fat Co.(PL-1000), was used for matrix because it is fully biodegradable and thermoplastic so it can be use recycle material.



(a)

(b)

Fig. 3.1 Used in this study (a)PLA, (b)jute fiber

### 3.2.2 Surface treatment

#### Alkali treatment

In this process untreated jute fibers were dipped in 1–7wt% of NaOH solutions at ambient temperature (22°C) for a 24 h duration maintaining fiber weight to alkali volume ratio of 1:50. Commercially available NaOH pellets of 98% purity were used in alkali treatment of jute fibers. After treatment, jute fibers were washed with distilled water thoroughly. Washing was stopped when pH value reached a neutral value nearly level 7. Finally, all fibers were dried at 80°C for 24 h[34, 35].

#### Plasma treatment

Plasma treatment technology, a dry process, is very simple and cost effective. In addition, this treatment produces no environmental pollution. Plasma treatment has been applied to recover inactivated jute surfaces for better adhesion and bonding and to increase wet ability. Helium was used as a plasma gas and plasma frequency and voltage were applied 20KHz and 3 KV, respectively during experiment. Effects of surface modification of jute fibers have been observed by changing the plasma treatment time. Fig 3.2 shown process of treatment for fiber.

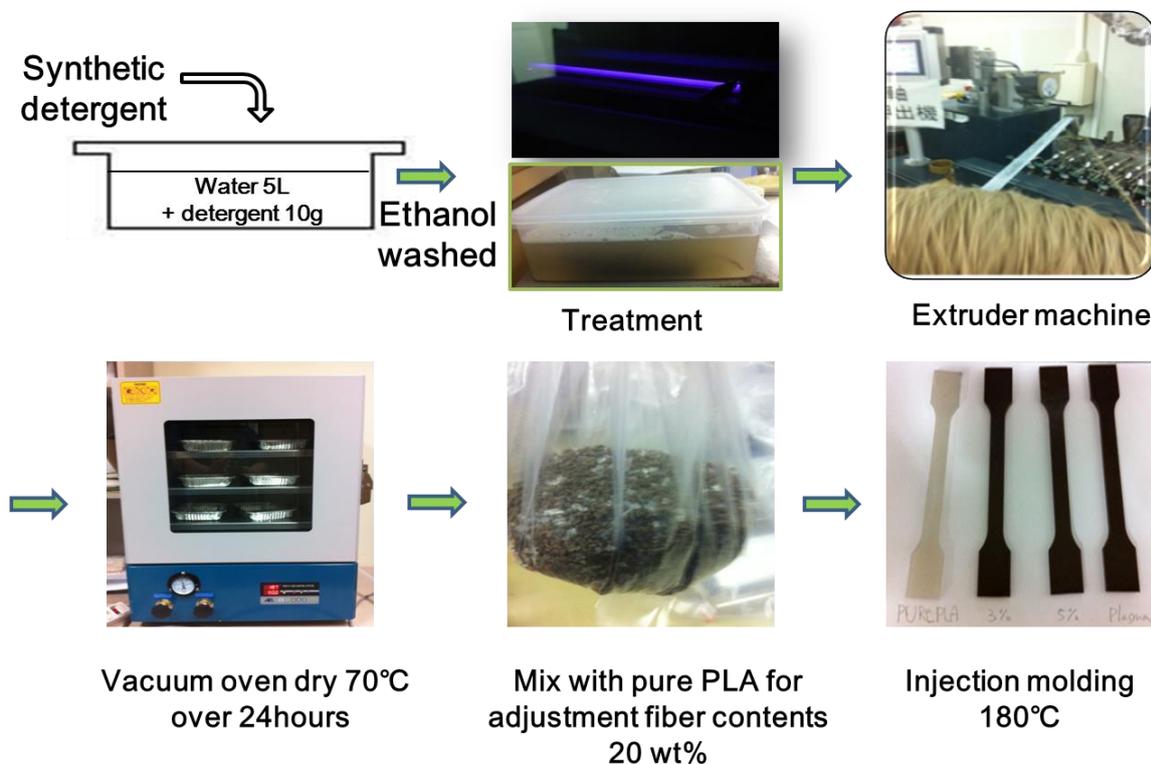


Fig. 3.2 Jute fiber surface treatment process of NaOH treatment and plasma polymerization.

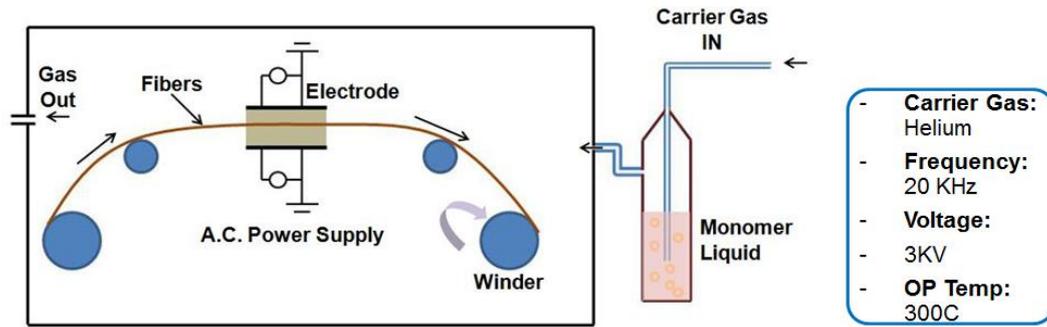


Fig. 3.3 Schematics of plasma polymerization process[18].

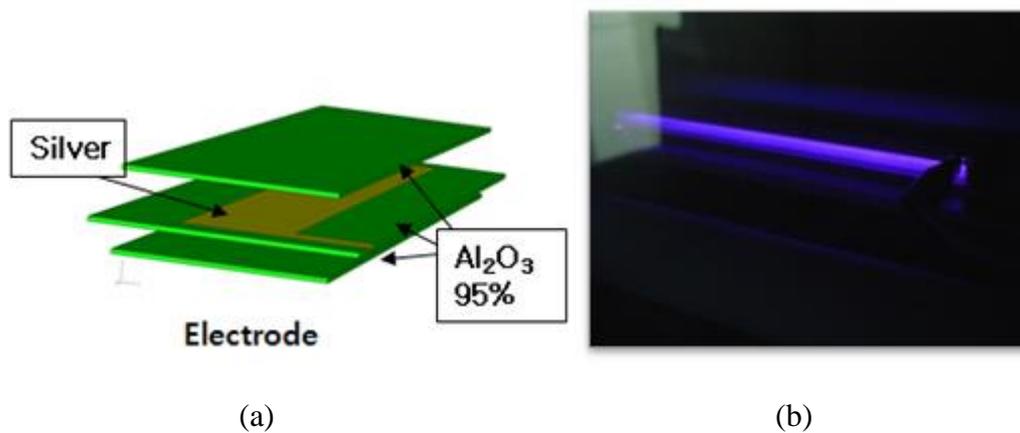


Fig. 3.4 Plasma polymerization electrode (a)schematic drawing and (b) setup[19].

### 3.2.3 Composites fabrication

Treated jute fibers were chopped into short length of about 2-3 mm for easy blending in extruder machine. The chopped jute fibers and polypropylene(PP) were then compounded with the coupling agent by a kitchen blender. The mixed blends were molded pellets type of diameter 2mm in twin screw extruder (PRIM TSC 16TC, Thermo Electron Corp.) by using the melt mixing process. The temperatures of five extruder sections from the first heating zone to the die were set as 180, 200, 210, 200, and 180 °C, respectively. The hopper rate, the screw speed, and the speed of roll were adequately adjusted for this process. For proper and uniform mixing between reinforcement and matrix the cycle was repeated three times. After extrusion, rods were cut into pellets. Pellets were dried in vacuum oven at 70°C for 24h. The dried pellets were used to prepare the dog bone specimens for tensile testing in accordance to the American Society for Testing and Materials(ASTM) standard using an injection molding equipment.



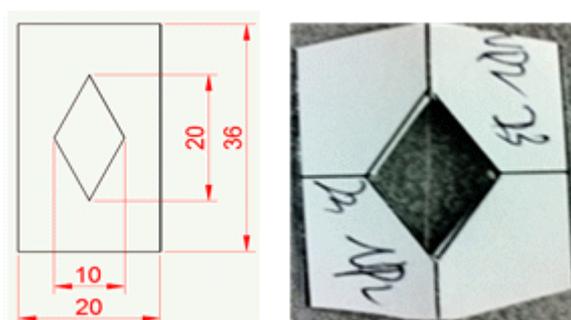
(a)

(b)

Fig. 3.5 Manufacture process (a)twin screw extruder machine and continuous manufacture,  
(b)jute reinforced PLA pellet.

### 3.2.4 Bundle fiber tensile test

The single fiber tests were carried out using a Universal Testing Machine (R&B 301Unitech, Korea). Crosshead speed was 1 mm/min. The effects of surface modification of jute fibers have been observed by changing the plasma treatment time and combining treatment through single fiber test. Untreated and treated jute fibers were treated by 3%, 5% NaOH solutions and 30sec, 1mins, 2mins plasma treatments.



(a)

(b)

Fig. 3.6 Bundle fiber test specimens (a)schematic drawing and (b) setup.



Fig. 3.7 Fiber tensile tester (Microload system, R&B, Korea).

### 3.2.5 Micro droplet test

For the micro droplet test conclaves were made with the following dimensions: outside  $50 \times 50 \text{mm}$ , inside  $40 \times 20 \text{mm}$ . After gluing the micro droplet specimens, PP fibers were used to create the micro drop. This was done by carefully making a small knot on the glued fiber. After that the fibers were put in the oven on  $180^\circ\text{C}$  for 1 h, this causes the PP fibers to melt, creating a micro drop on the natural fiber[19, 27-33].

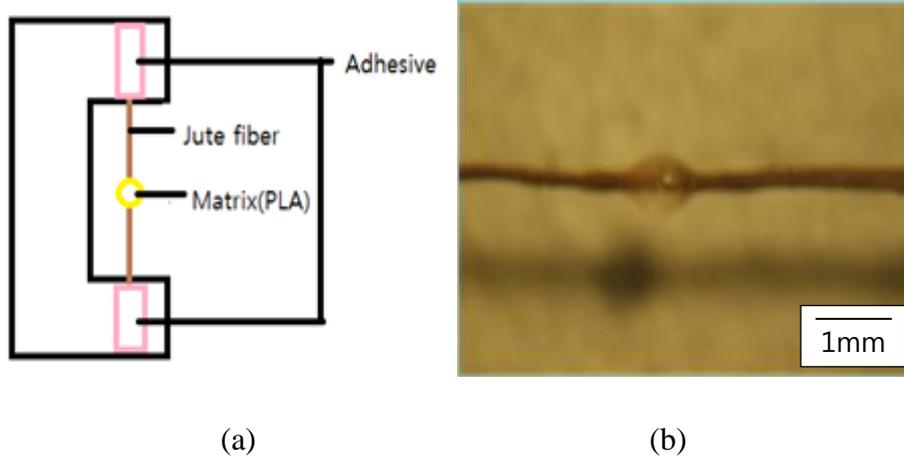


Fig. 3.8 Micro droplet test specimens (a)schematic drawing and (b) setup.

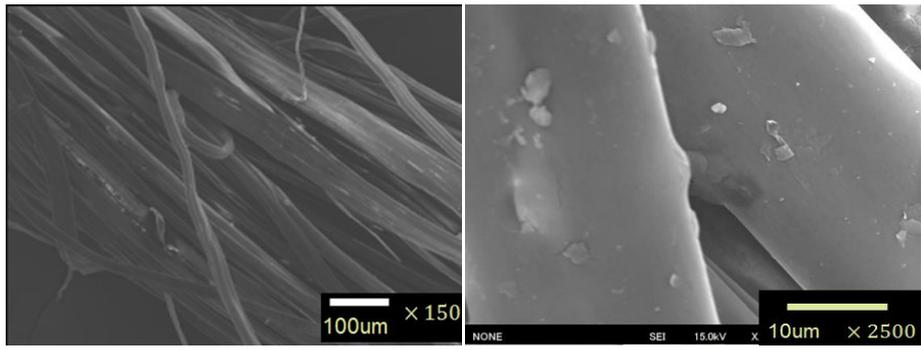
### **3.2.6 Composite mechanical test**

Untreated and treated jute fibers, which were treated by 1 wt.%, 3 wt.%, 5 wt.%, 7wt.% NaOH solutions and 2mins plasma treatments, were chopped into short lengths about 2mm to insure an easy blending for both manual and twin screw extrude processes. A 10 wt % chopped jute fibers, 2 wt.% MA, and 88 wt.% PP were compounded in a manual mixer. The blends were molded in a twin screw extruder (PRIM TSC 16TC, Thermo Electron Corp.) to form rods of diameter 1.0mm by using the melt mixing process. The tensile and flexural test were carried out on a computer controlled closed loop servohydrauli Universal Testing Machine(R&B 301 Unitech) and performed on dog-bone specimens(ASTM D 638 Type I standard) and rectangle specimens (ASTM D 790), respectively. Crosshead speed was 2.50 mm/min while extension meter, having 25 mm gauge length, was used for measurement of the change of strain.

## **3.3 Results and discussion**

### **3.3.1 Bundle fiber morphology**

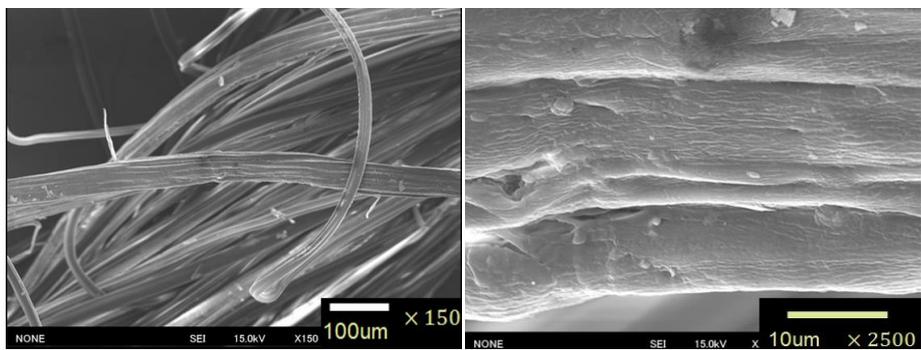
SEM images of untreated and esterified jute fibers are shown in Fig. 3.9. Significant changes in surface morphologies were observed after alkali treatment in Fig. 3.10-3.11. It shows that the untreated fibers are covered with a layer, which was mainly composed by waxy substances. After alkali treatment the surface of jute fibers became cleaner due to the removal of waxy substances. In case of alkali treatment with over the 2% NaOH, the results show a better removal of wax and rougher surface compared with untreated and others treated cases. Fig. 3.12 shows SEM images of plasma treated and hybrid treated (plasma treated after alkali treatment) jute fibers. In this case, it is shown that opposed to alkali treatment, the untreated fibers are smoother than plasma treated jute fibers. After Plasma treatment was carried out the surfaces of jute fibers were covered with carboxyl group. Hybrid treatment surface of jute fibers are smoother than plasma treatment. 3% alkali treatment was chosen since this concentration gave the highest bundle fiber test result.



(a)

(b)

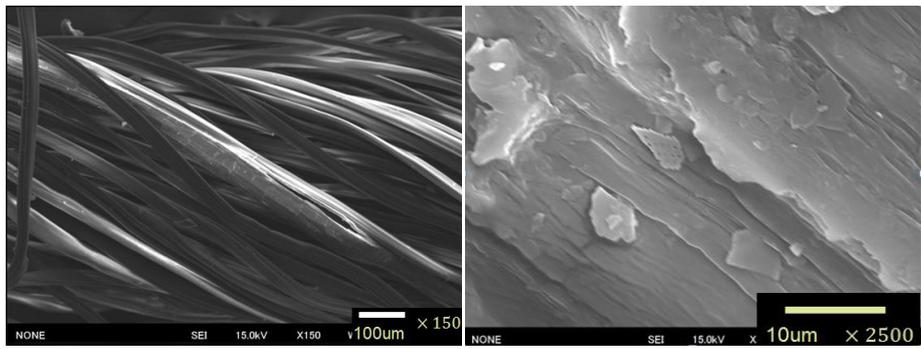
Fig. 3.9 Morphology of untreated jute fiber surface (a)×150 (b)×2500



(a)

(b)

Fig. 3.10 Morphology of 3% NaOH treated jute fiber surface (a)×150 (b)×2500



(a)

(b)

Fig. 3.11 Morphology of 5% NaOH treated jute fiber surface (a)×150 (b)×2500

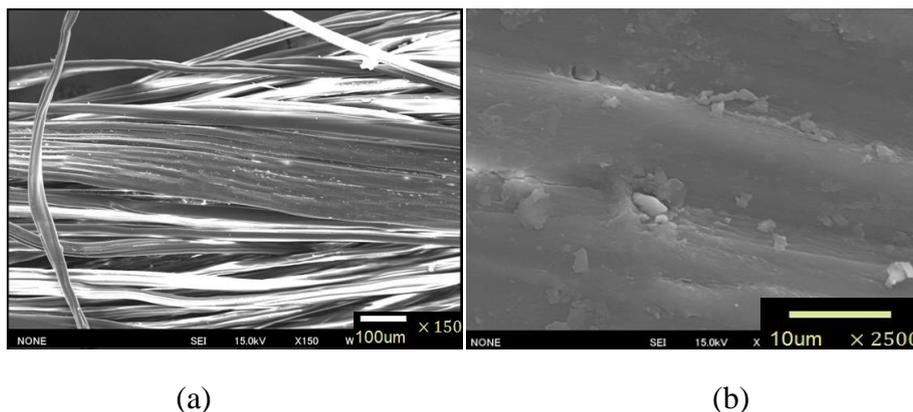


Fig. 3.12 Morphology of plasma polymerized jute fiber surface (a)×150 (b)×2500

### 3.3.2 Bundle fiber tensile test

Fig.3.13 shows that after the alkali treatment than plasma treatment case was followed in an attempt to obtain a better value for the fiber surface treatment. Raw means untreated fiber, 3% NaOH and 5% NaOH are 3% and 5% NaOH alkali solution treated fiber, plasma means plasma polymerization fiber and N+P30s, N+P 1min and N+P 2min are first 3% of NaOH treated and 30s, 1min and 2mins plasma polymerization fiber. Fig 3.13.(A) shows that 3% alkali treatment has the highest tensile strength value in the single fiber test of only alkali treatment. Through this result it is known that high percentage solution treatment can damage the fiber surface and thus reduce the tensile properties. in this study 5% NaOH solution is maximum percent of alkali solution. This is demonstrated in the graph below. So, after 3% of alkali treatment, plasma treatment was performed at 30sec, 1min, 2min, respectively. Fig.3.13(B) shows that hybrid treatment has an effect on increasing tensile strength. N+P means alkali treated with plasma polymerization. When only used plasma polymerization fiber properties was decreased, and this trend can be observed in E-beam irradiated fiber. So in these treatments were assumed high charged energy damaged on fiber. Small size impurities and fat can burn on fiber surface so alkali treatment was used for remove that. 3% of the alkali treatment and 2min plasma treatment fiber produced the highest tensile strength. It guessed after alkali treatment, plasma treatment did not make damaged on surfaced.

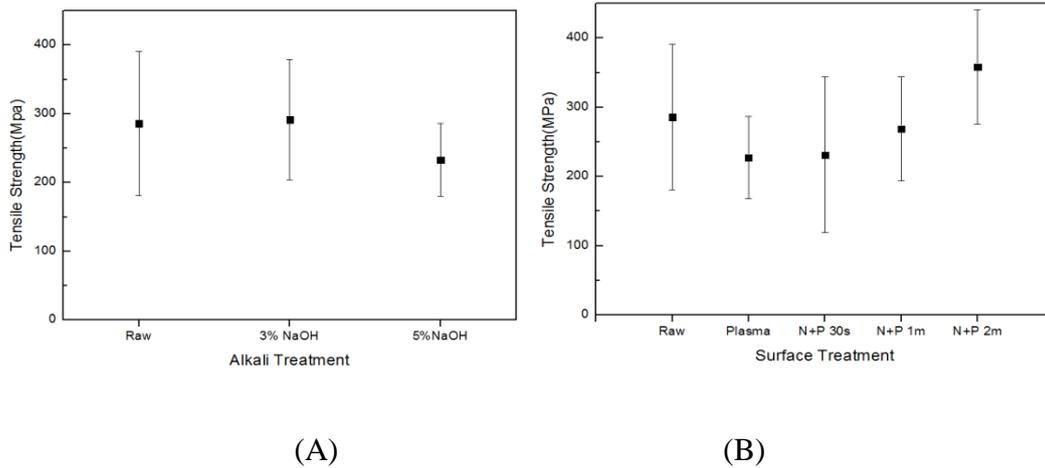


Fig.3.13 Result of (A) alkali treated jute fiber, (B) Plasma treated jute fiber.

### 3.3.3 Composite mechanical test

The Fabrication of composites is based on Single Fiber test. Figures 3.14-16 show that treatment did not have obvious effect on increasing tensile and flexural test on strength comparing raw composites, which used untreated fiber for reinforcement, results. Raw mean untreated fiber reinforced composites 1%NaOH, 3%NaOH, 5%NaOH and 7%NaOH mean 1%, 3%, 5% and 7% NaOH alkali solution treated fiber reinforced composites and plasma means plasma polymerization fiber reinforced composites. Flexural strength is stable raw to 5% NaOH treated fiber reinforced composite however, flexural strength decreased when 7% NaOH was utilized. Figures 3.17-20 are SEM image of composites cross section area. With untreated and 3% alkali treatment, fiber was pulled out from matrix. 5% alkali treatment and plasma case, fiber was broken near cross section. These can show IFSS strength and fiber tensile strength valance. Untreated and 3% alkali treated fiber have lower IFSS so fiber pull out from matrix and 5% alkali treated and plasma polymerization fiber tensile strength lower so broken near the cross section or cause increasing IFSS. In test, 1~7% NaOH alkali solution treated fiber were used. Because it expected be show fiber tensile strength effect. When fiber tensile strength was increased but composites did not show enough to increase. It caused reinforced fiber ratio(20%) was too low so effect is not so significant.

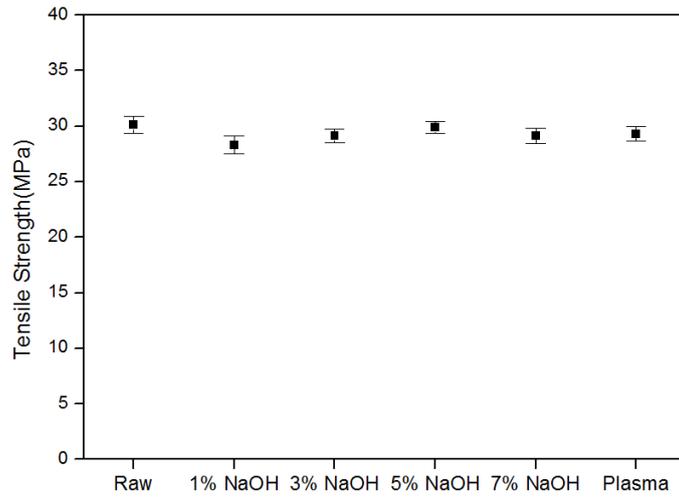


Fig.3.14 Tensile strength for jute fiber reinforced composites.

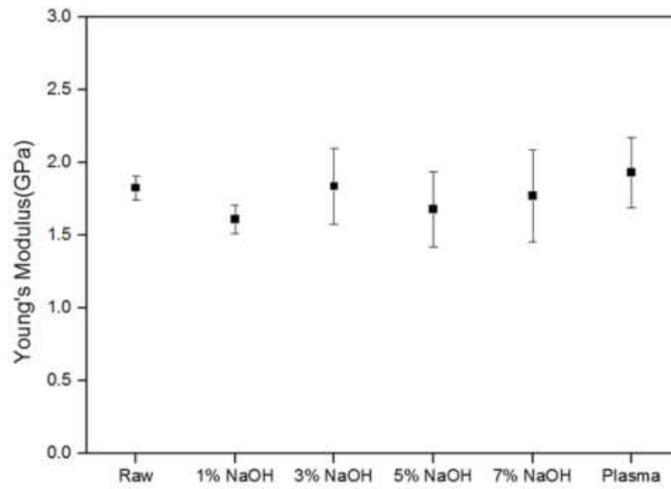


Fig.3.15. Tensile modulus for jute fiber reinforced composites.

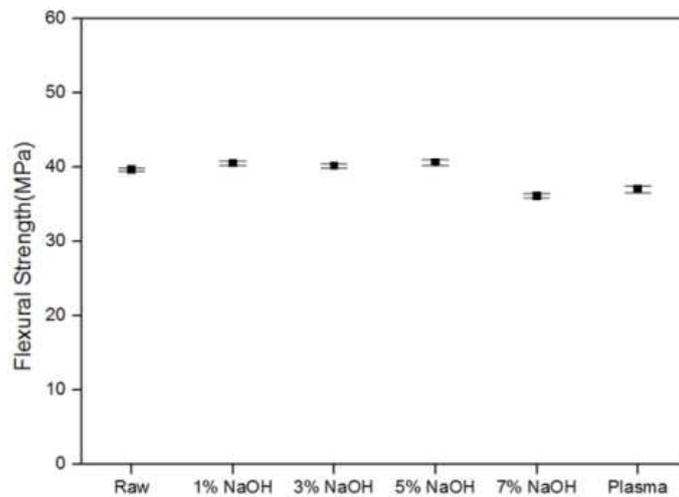
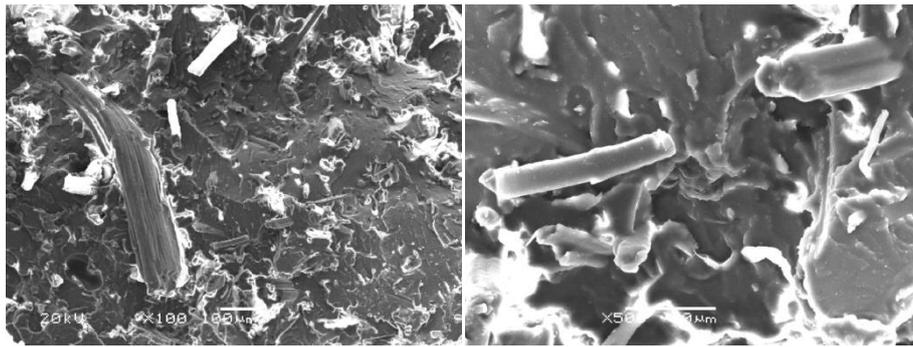


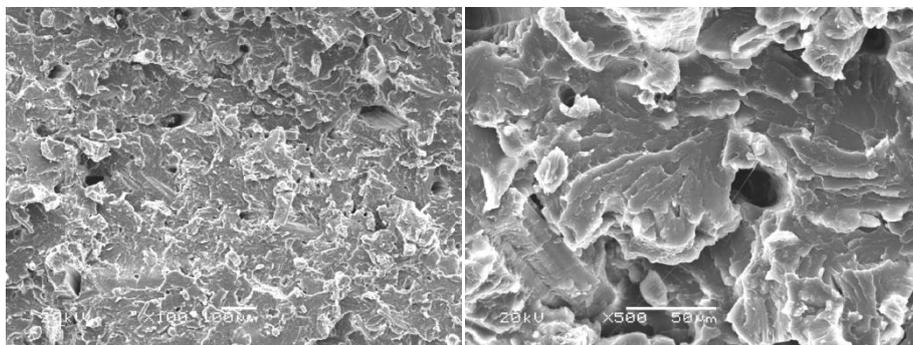
Fig.3.16. Flexural Strength for jute fiber reinforced composites.



(a)

(b)

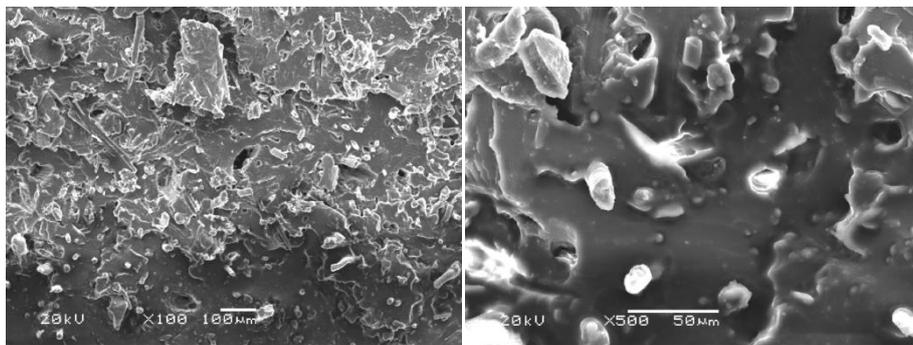
Fig. 3.17 Fracture morphology of untreated JFRC fracture surface (a)×100 (b)×500.



(a)

(b)

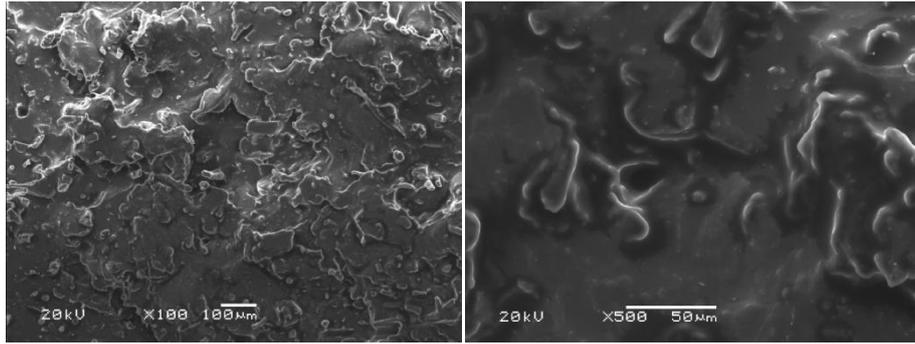
Fig. 3.18 Morphology of 3% NaOH treated JFRC fracture surface (a)×100 (b)×500.



(a)

(b)

Fig. 3.19 Morphology of 5% NaOH treated JFRC fracture surface (a)×100 (b)×500.



(a)

(b)

Fig. 3.20 Morphology of plasma polymerized JFRC fracture surface (a)×100 (b)×500.

### 3.4 Conclusions

1) Through SEM analyses it was observed that the surface of the untreated fibers is rich in waxes and wax like substances, and the treatments altered the fiber surface characteristics, by removing the outer surface layer and producing a smoother fiber surface with alkali treatment. But using 5% NaOH solution shows fiber surface was damaged.

2) However 3% of the alkali treatment fiber has the highest value of single fiber tensile strength in alkali treatment. Because high percentage solution treatment can cause damage on fiber surface. Plasma treatment has been conducted in atmospheric conditions to recover inactivated jute surfaces for better adhesion and bonding between fiber and matrix in composites. In hybrid treatment, and more specifically after 3% of the alkali treatment and 2min plasma treatment the fiber was found to have the highest tensile strength. The more the plasma treatment time is increased from 30sec to 2min, the higher the value of single fiber tensile strength.

3) Composite containing 20% of jute fiber produced a tensile and flexural experiment. But the result of the composite's mechanical test is different than that obtained for the single fiber test. The improvement of tensile strengths and modulus of the composites could not be observed. It was not found that the addition of NaOH contents as a treatment solution could improve the composite performance by enhancing the adhesion between jute fibers and PP. Also, composites have a relatively low jute contents. In addition, plasma coating is considered broken in fibers that were chopped after treatment.

Therefore, modification of this experiment is necessary. 7% NaOH treated fiber reinforced composite flexural strength is less than 5% treated (worse than raw). This suggests that dipping the jute fiber in 7% NaOH solution for 24h is too strong to be used for reinforced composite since it damages the fiber conditions.

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# CHAPTER 4

## Strength effects of resin impregnation on natural fibers

### 4.1 Introduction

The Green composites are alternatives for previously used petroleum base composites. These plastics were one of the great inventions in human history. Production and use of these plastics may exist primarily due to their cheap cost. However, it has been known that such synthetic plastics cause a high rate of CO<sub>2</sub> emissions and require the use of fossil fuel for disposal. Therefore new, renewable materials must be found. Plant based resources are increasing being harnessed to produce materials that are aimed at replacing fossil origin resources. Environmental and cost concerns are at the center of extensive research which is currently being undertaken worldwide to develop new materials that would replace the fossil origin materials. Green composites can reduce CO<sub>2</sub> emissions and can be used as sustainable materials [1, 2]. Currently green composites are not used in common industrial materials due to a lack of stability and durability for industrial level. This study carried out on green composites in an attempt to develop them as new materials and also to modify their character and make them suitable for industrial level use.

Kenaf is a seasonal fiber crop closely related to cotton and jute. Historically, kenaf has been used as a cordage crop to produce twine, rope and sackcloth. There are now various new applications for kenaf including paper products, building materials, absorbents and animal feeds [3]. Bamboo is an abundant natural resource in Asia and South America due to its fast growing nature. Bamboo has been traditionally used to construct various living facilities and tools. Bamboo poses a high strength to weight ratio, because its fibers are longitudinally aligned in its body [4]. Recently the use of thermoplastic resins has been increasing [5]. This is directly related to their ease of recycling and mass production. However thermoplastic resins having high viscosity liquid form or solid form are more difficult to permeate into reinforced materials. Consequently, this can cause void content problems, low adhesive strength and water absorption problems. One idea was to reinforce fiber by the liquid type resin and then use the fiber for composites [6]. With fiber treatment, it will be possible to control damage, as well as improve the composite and waterproof properties [7]. The natural plants fiber poses a tube for water transpiration. This feature can be used with low viscosity liquid, enabling the liquid to be absorbed into the fiber. Therefore permeated fiber using low viscosity liquid resin will be easier to work with a micro sized composite than permeated fiber using a different composite. It can be lighter than a matrix particle and fiber already filled up with resin will decrease water absorption. This method does not require high cost

equipment or complex process. In the study, resin impregnation as the treatment method was attempted. Alkali treatment and resin impregnation method were also used. Kenaf and bamboo bundle fibers were tested with these methods of treatment as well as fiber reinforced composites.

## **4.2 Experiments**

### **4.2.1 Materials**

#### **Kenaf**

Kenaf is a plant in the Malvaceae category and it is related to Cotton and Ökra, the kenaf plant is build up of 40 % bast fibers which have a fiber length between 2 to 6 mm. The other 60% are core fibers, these are a lot smaller and have an average length of 0.5 mm. The fibers can be roughly compared to softwood fibers and they can be used as a replacement for Jute fibers since the characteristics are very similar.

#### **Bamboo**

Bamboo is a plant of the grass family Poaceae and falls inside the sub family of bambusoideae. The benefit of bamboo is that it is an abundant natural resource in Asia and Middle & South America, and it is almost certainly the last sustainable plant resource that not has been massively used as a natural fiber. Especially for Japanese companies, bamboo is a good solution since bamboo grows in Japan and its possible application would allow Japan to produce its own fibers and not be dependent on other countries.

#### **Sodium hydroxide(NaOH)**

Sodium hydroxide is a popular and most commonly used surface treatment agent for natural fibers. This treatment is most commonly referred to as an alkaline treatment. With the use of an alkaline treatment the fibers are actually cleaned, removing lignin and impurities. This is very important and is especially needed to create space for the next treatments. Several studies are investigating the influence and the best way to use an alkaline treatment. The importance of cleaning the natural fibers is explained in several studies. [3, 6, 7,] Recent studies have shown that the interfacial strength between fiber and matrix is poor when they are used without treatment. With the use of an alkaline treatment a huge part of the lignin inside of the fibers is removed which subsequently causes the cellulose to be exposed to the surface. Since cellulose has a better adhesion with the matrix material the interfacial strength

increases. However, in the same studies it was found that the alkaline treatment also damages the fibers and therefore reduces the tensile strength of the fiber. During a long time of testing and studies, various methods are developed for applying an alkaline treatment. This study chooses the most commonly used technique, and that is submerging the fibers inside the alkaline treatment for a period of time.

### **Polyvinyl Alcohol (PVA)**

PVA was also used as a resin since it has high tensile strength and flexibility. The adhesion between PVA and natural fibers is high. The downside is that the properties are highly dependent on the moisture content. This means that if it would be used as a resin with natural fibers the composite is highly dependent on the humidity where it is used, since both products easily absorb water. Previous studies showed that if the fibers are impregnated with PVA and used in a composite the adhesion between fiber and matrix increases in comparison with untreated fibers. The PVA properly bonds with the fiber and the PVA also bonds with the matrix material and hence the adhesion increases. The advantage is that the humidity doesn't influence the mechanical properties of the composite anymore.

### **Phenolic resin**

Phenol has many applications and is therefore an important industrial commodity. For a lot of plastic and compound products it is one of the basic products. Also for epoxy resins it is a precursor and therefore an important product in the composite industries. Since the viscosity of phenol is easy to control it is perfect to use as a treatment. The downside of phenol is that in contrary to PVA. Phenol is toxic. It is corrosive for eyes and skin, which can cause second and third degree burns, or several diseases. Therefore using phenol requires a special work environment and special disposal of the old phenol treatment. The way phenol is used is exactly the same as with the PVA treatment. It will not change the chemical composition of the fibers but the fibers are impregnated with a phenol solution.

### **Polypropylene(PP)**

The thermoplastic polymer PP, used as a matrix material, was supplied by the Primepolymer (Japan). It has a specific gravity of 0.90 - 0.91, melting temperatures of 165°C - 171°C and crystallinity of 82%. PP is one of cheap and low density material so many of application in industry, so in this study use PP for matrix of composites.

## **4.2.2 Fiber treatments**

### **Alkali treatment**

In this process untreated jute fibers were dipped in 3wt% of NaOH solutions at ambient temperature for a 2h duration maintaining fiber weight to alkali volume ratio of 1:50. Commercially available NaOH pellets of 98% purity were used in alkali treatment of jute fibers. After treatment, jute fibers were washed with distilled water thoroughly. Washing was stopped when pH value reached a neutral value nearly level 7. Finally, all fibers were dried at 80°C for 24 h.

### **PVA treatment**

One of the other treatments is the PVA treatment. This treatment is made using water and PVA powder, at a weight ratio of 3%. To mix the two components together a magnetic stirrer was used. This machine uses a magnet to create a vortex in the water which results in mixing the PVA with the water. It is also possible to increase the heat of the water using induction, using more heat allows the PVA to dissolve more easily with the water. So basically the magnetic stirrer is set so that the magnet spins with a speed that it creates a vortex inside the measuring cub. The temperature is increased; in this study it is set on 65 degrees Celsius. Since the temperature is increased the cub is covered with tinfoil so the vaporized water drips back in the cub. After 24 hours on the machine the PVA is solved and the mixture can be used for the treatment. In both cases, single fiber tests and composite tests, the fibers are submerged in the PVA solution for 2 hours. After that fiber was hanging drying rack. Afterwards the fibers were allowed to dry, in case of the single fibers the specimens were done and were ready for testing.

### **Phenolic resin treatment**

The Phenolic resin treatment is made using ethanol and phenol powder, in this study 9% was used. The components were mixed using a homogenizer for 15 minutes. After these 15 minutes the mixture was clear and yellow, and was ready to be used as a treatment. Also for this treatment the fibers were submerged in the mixture for 2 hours. After that fiber was hanging drying rack 24h. When the fibers were treated they were put in the oven on 180 degrees Celsius, this is needed for the phenol to crystallize. This crystallization gives the fibers more stiffness; nevertheless it also has the disadvantage of making the fibers brittle.

### 4.2.3 Manufacturing of specimens

This chapter provides insight about the used specimens and explains how the specimens are made. With this information it is possible to reproduce the specimens. During this study a code was made for identifying the specimens, during and after testing (Table 4.1). First it is explained how the preparations are done and afterwards the production itself. For the production of the composites polypropylene (PP) pellets was used.

Table 4.1 Codex specimens

Fiber	Untreated	Alkali treated	Alkali+PVA	Alkali+Phenolic
Kenaf	UK	NK	PVK	PHK
Bamboo	UB	NB	PVB	PHB

#### **Bundle fiber tensile test specimens**

For testing the single fiber's strength paper concaves was used. This provided the possibility to hold the fibers in a tensile tester. The concaves were made by hand using thick pieces of paper. After the making of the conclaves the fibers where glued inside of them using water resistant superglue. The water resistance was needed since a part of the fibers still needed to be treated. For the tensile test conclaves with the following dimensions were used: outside 40×30 mm, inside 20×10mm. Fig 4.1 shows a bundle fiber tensile specimen set on the tester.

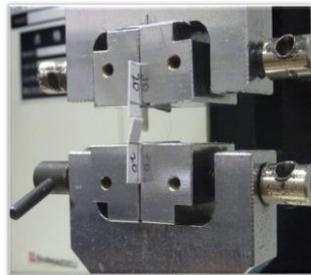


Fig 4.1 Conclave fixated in tensile tester

### Micro droplet test specimens

For the micro droplet test conclaves were made with the dimensions: outside 50×50mm, inside 40×20mm. After gluing the micro droplet specimens PP fibers were used to create the micro drop. This was done by carefully making a small knot on the glued fiber. After that the fibers were put in the oven on 180°C for 1 hour, this causes the PP fibers to melt, creating a micro drop on the natural fiber.

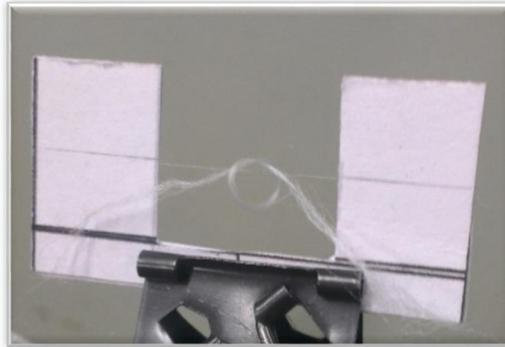


Fig 4.2 Making a PP knot



Fig 4.3 PP knot



Fig 4.4 Micro droplet

## Composites specimens

With the use of an injection molding machine the composite specimens were made. Fiber contents are 30wt% of composites. During this study an injection molding machine off brand Toyo model ET-40V was used. The mold that was used produces specimens according to the Japanese Industrial Standard, specifically the JIS K 7139 standard. This standard is determined by the Japanese standards association and is widely used in Japan.

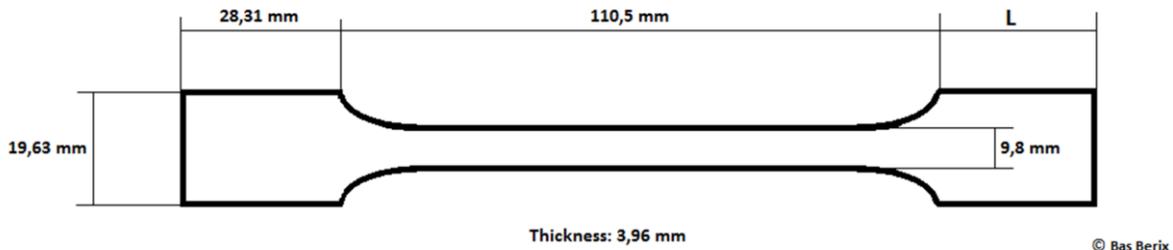


Fig 4.5 Specimens dimensions

## 4.2.4 Test

### Fiber tensile

The meaning of the fiber tensile test is to provide information about the strength of the bundle fibers. The testing itself is carried out by placing a concave with a fiber in the tensile tester. After the conclave is fixated in the clamps the middle part is cut. This was particularly done so that the fiber was vertical. Before the tests were performed the thickness of the specimens was measured first using an optical microscope. Since the fibers are natural and have a lot of variation the fibers were measured on ten places. Afterwards the average thickness of the fibers could then be calculated. For testing a tensile tester from the brand Shimadzu model EZ-test-500N was used. For this reason, the test speed in the standard was too high and was eventually set on 0.5 mm/min.

### Micro droplet test

The reason to perform a micro droplet test is to determine the interfacial shear strength between the fibers and the matrix material. The test was done as follows, a droplet of matrix material was put on a fiber, then two knives were placed just against the fiber. When the machine was turned on, the knives tear off the matrix. The force that was necessary to debond the droplet was measured, and using the Quote 4.1 the interfacial shear strength could be calculated.

#### Quote 4.1 Interfacial shear strength

$$\text{IFSS} = \frac{F}{\pi \times d \times L}$$

IFSS = interfacial shear strength

F = measured force

d = average diameter of fiber

L = length of microdrop

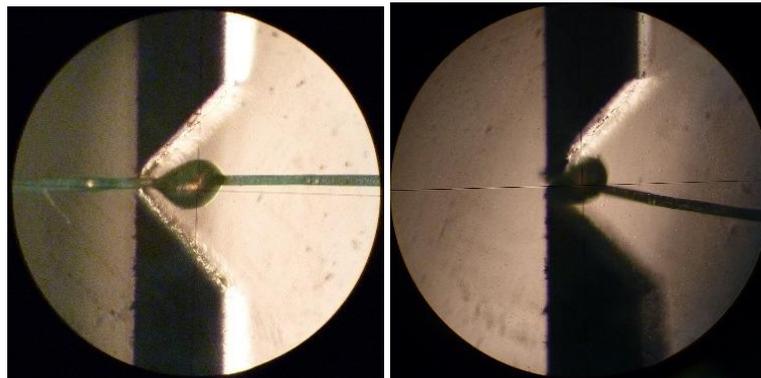


Fig 4.6 Micro drop let test

### Composite tensile test

The tensile tests were performed following the ASTM D3039/D 3039 - 001 standard[9]. Using the tensile tester of Shimadzu model AG-I 100KN, the force was measured with a load cell (type SLFL-100KN) and recorded with a computer. The tests were conducted with a head speed of 2 mm/min and the average room temperature was 25°C. To obtain statistically significant results for each case, a minimal of 30 specimens were tested to evaluate the mechanical properties.

### Composite bending test

The ASTM D790 standard was used as a guide line for the bending test. With the use of the tensile tester and special equipment for a 3-point bending test was used. This test has a few variables which first have to be determined for setting the equipment. Determining these values was done with formulas found in the ASTM standard[10].

#### Quote 4.2 Crosshead motion

Calculate the rate of crosshead motion as follows and set the machine for the rate of crosshead motion as calculated by Eq. 1:

$$R = \frac{ZL^2}{6d} \quad (1)$$

where:

R=crosshead speed, mm(in.)/min

L=support span, mm(in.)

d=depth of beam, mm(in.) and

Z= rate of straining of the outer fiber, mm/mm/min (in./in./min). Z shall be equal to 0.01.

In no case shall the actual crosshead speed differ from that calculated using Eq. 1, by more than  $\pm 10\%$ .

#### Quote 4.3 Settings bending test

Materials 1.6mm (1/16 in.) or Greater in Thickness- For flatwise test, the depth of the specimen shall be the thickness of the material. For edgewise tests, the width of the specimen shall be the thickness of the sheet and the depth shall not exceed the width (see Notes 4 and 5). For all tests, the support span shall be 16 (tolerance  $\pm 1$ ) times the depth of the beam. Specimen width shall not exceed one fourth of the support span for specimens greater than 3.2 mm(1/8 in.) in depth specimens 3.2 mm or less in depth shall be 12.7 mm (1/2 in.) in width. The specimen shall be long enough to allow for overhanging on each end of at least 10% of the support span, but in no case less than 6.4 mm (1/4 in.) on each end. Overhang shall be sufficient to prevent the specimens from slipping through the support

The support span is determined from following equation:

$$\begin{aligned} &16 \text{ times the thickness of the specimen} \\ &16 \times 3.96 = 63.36(\text{mm}) \end{aligned}$$

Since the calculated value is difficult to set and a tolerance of  $\pm 1$  thickness is allowed the support span is set on 64 mm. In the quote it is also mentioned that the width of the specimens must not exceed one fourth of the support span. This is checked and it fulfills the demands as seen in the following constrain:

$$\begin{aligned} \frac{\text{Support span}}{4} &\geq \text{with specimen} \\ \frac{64}{4} &= 16 \geq 9.8(\text{mm}) \end{aligned}$$

Because the specimens are made in a T-bone shape there is enough overhang of the specimen. With the support span known the crosshead speed is calculated below:

$$\begin{aligned} R &= \frac{Z \times L^2}{6 \times d} \\ R &= \frac{0.01 \times 64^2}{6 \times 3.96} \doteq 1.73 \\ 10\% &= \pm 0.173(\text{mm}/\text{min}) \end{aligned}$$

The calculation shows a max speed of 1.903 mm/min, however, due to previous studies and the amount of specimens the crosshead speed is set on 2mm/min. This provides less test information since the sampling rate of the test equipment stays the same. For this study this provided no issues since the sampling rate of the equipment was 20Hz.

## 4.3 Results and discussion

### 4.3.1 Bundle fiber morphology

Scanning electron microscopy (SEM) provides an excellent examination of the surface morphology of untreated and treated kenaf fibers[8]. It is expected that the surface morphology of untreated fiber will be different to that of treated fiber particularly in terms of

their level of smoothness and roughness. Therefore studies of the fiber surface topography could provide vital information on the level of interfacial adhesion that would exist between the fiber and the matrix, when used as reinforcement fiber with and without treatment. All micrographs in this work were taken with 1000 times ( $\times 1000$ ) magnification. Fig 4.7 shows the SEM micrograph of an untreated kenaf fiber. Clearly, UK and NK have fiber column consisting of many vascular bundles and xylem. Yet, PVA and phenolic resin impregnated fiber cases were filled up capillary tube with thermosetting resin. After resin impregnation, the weight of fiber was increased. In Table 4.2, the main characteristics of the resin are reported as specified by the manufacturer.

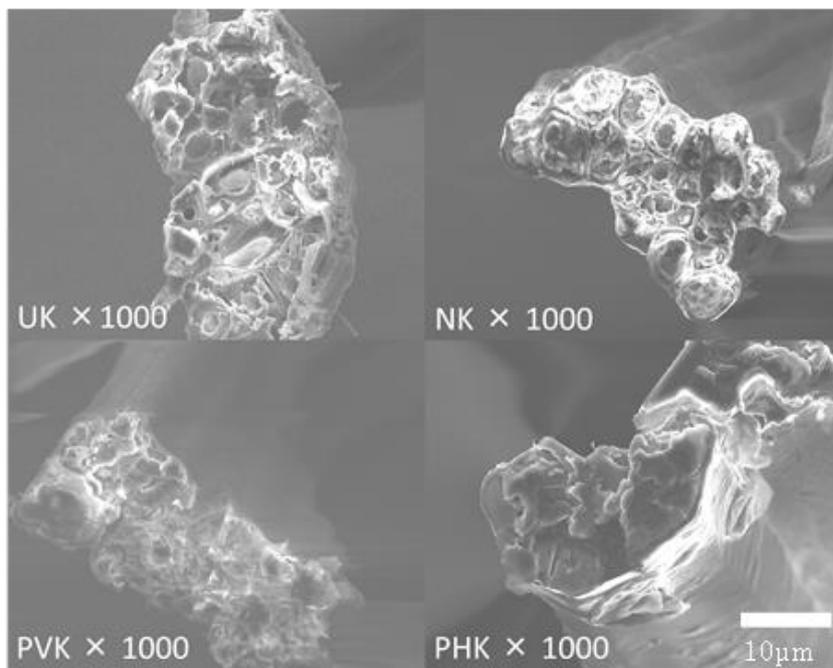
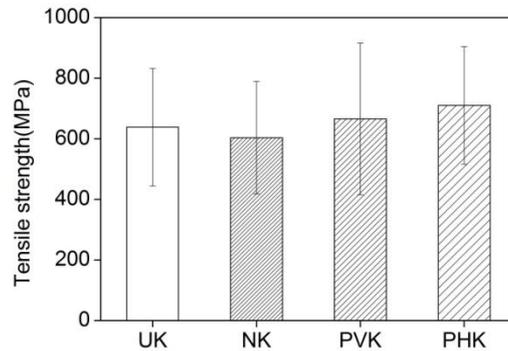


Fig 4.7 Cross sectional SEM images of kenaf fiber

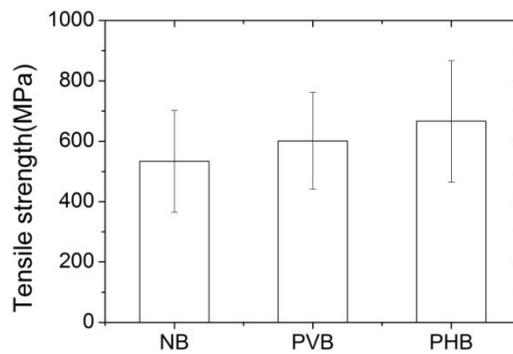
### 4.3.2 Bundle fiber tensile test

Fiber bundle tensile strength of different treated kenaf fiber bundles has been measured and the results are shown in Fig 4.8. The average unit break for every set of treatment, which represents the bundle fiber tensile strength, was summarized in Fig 4.8. From the figure, it can be seen that the average unit break of the bundle of PHK fiber and PVK fiber are higher than UK and NK. This is explained by the resin impregnation method that contributes to the increase in strength. However in the case of alkali treated fiber, the fiber bundle tensile strength was decreased. An alkali treatment, which remove not only impurity, hemi cellulous,

fat and protein base material, would certainly damage the fiber and consequently reduce the tensile strength of the fiber. Bamboo bundle fiber tensile strength trend is also similar with kenaf. Resin impregnated fiber is higher than untreated and phenolic resin impregnated fiber has highest tensile strength. Because surface and rumen were fill up by PVA or phenolic resin. It can cure damages on fiber and enhanced fiber. In this test, fiber diameter was measured in 2D and the supposed fiber shape is cylindrical.



(A)



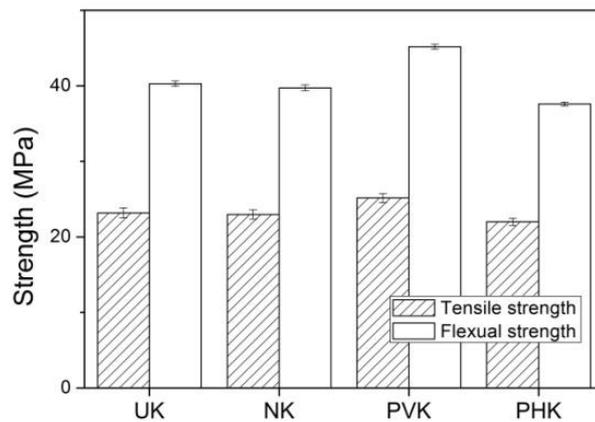
(B)

Fig. 4.8 Resin impregnated bundle kenaf(A) and bamboo(B) fiber tensile test

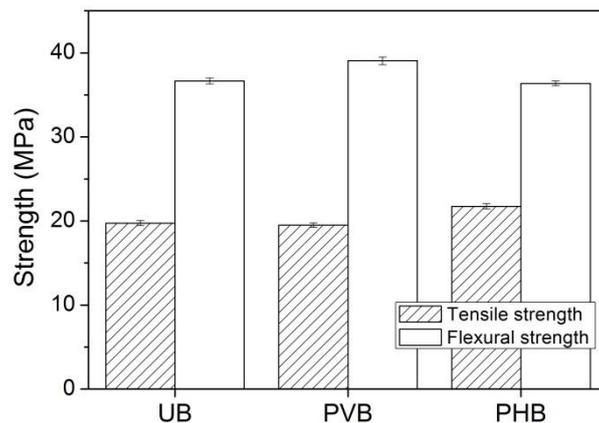
### 4.3.3 Mechanical testing for composites

The influence of fiber treatment on the tensile modulus and the tensile strength are illustrated in Fig 4.9. In Fig 4.9(A), it can be seen that the tensile strength of the kenaf/PP composites increases with resin impregnation; whereas the strength of the kenaf/PP composite does not vary significantly with treatment. In contrast slightly PVA impregnation

method case is higher than others. Bending test results shows that the PVA impregnation case is clearly 10% higher than others. It can be seen in Fig 4.9(B) that the tensile strength of the bamboo/PP composites decreases with alkali treatment. This is because the alkali solution was used when the bamboo fiber was manufactured. So the alkali treatment caused critical damage on fiber [9, 10]. Then resin impregnation method repaired fiber which is not enough to go over the untreated fiber reinforced composites. With both of resin impregnation fiber tensile strength was increased. But only PVA resin impregnation fiber reinforced composites increased mechanical properties, it caused interfacial shear strength(IFSS) between fiber and matrix. PVA can increased IFSS, but phenolic resin did not increased IFSS between fiber and matrix[11].



(A)



(B)

Fig. 4.9 Mechanical properties of Kenaf(A) and Bamboo(B)PP composites

Table 4.2 Effect of natural fiber reinforced polypropylene composite using resin impregnation

	Bundle fiber tensile strength(MPa)	Composite tensile strength(MPa)	Composite flexural strength(MPa)
Untreated Kenaf(UK)	638.43	23.20	40.29
Alkali treated Kenaf(NK)	603.66	22.97	39.75
PVA impregnated Kenaf(PVK)	665.66	25.15	45.19
Phenolic resin impregnated Kenaf(PHK)	710.33	22.00	37.59
Untreated Bamboo(UB)	533.86	19.74	36.66
PVA impregnated Bamboo(PVB)	601.55	19.50	39.06
Phenolic resin impregnated Bamboo(PHB)	666.47	21.73	36.37

### 4.3.4 Water absorption

The water absorption of composites is related to properties of composites such as dimensional stability. The results of the water absorption tests are summarized below in Fig 4.10. It can be observed that the phenolic resin treated caused a decrease in the water absorption ratio but PVA treated caused an increase in the absorption ratio. This is because PVA resin is a hydrophilic material and can be bind to water. Much lower values than these are obtained for composites than for fibers themselves, because cellulose fibers are covered by PP layers which slow down the diffusion of water.

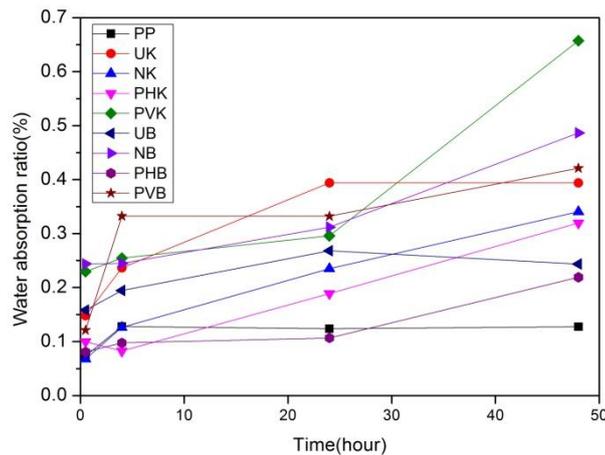


Fig. 4.10 Water absorption test resin impregnated fiber with bamboo/PP and kenaf/PP composites

#### **4.4 Conclusions**

It was observed that resin impregnation fiber can increase tensile strength and flexural strength of composites due to the fact that the fiber capillary tubes are filled. As for the kenaf fiber reinforced composites, the PVA impregnated kenaf fiber had a higher effect on the mechanical properties than phenol resin impregnation. For the bamboo fiber reinforced composites, the phenol resin impregnated fiber had a higher effect on the mechanical properties than the PVA impregnation. It is also known that alkali treatment can cause damage to the fiber. In conclusion resin impregnation can improve the mechanical properties of the natural fibers while alkali treatment should be excluded.

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## **CHAPTER 5**

# **Study of maleic anhydride grafted polypropylene effect on resin impregnated bamboo fiber polypropylene composite**

### **5.1 Introduction**

Nowadays, high demand and increase in more mature and eco-friendly lifestyle, along with limitation of petroleum industry due to global warming, waste problem and exhaustion of resource, have alerted a number of researchers around the world to seek for the development of much more sustainable composite materials compared to conventional glass fiber reinforced plastics. Most of green composite are made from yearly renewable materials, and thus disposing treatments of the green composites become easier and environment friendly. For these reasons, natural fiber composites have already been applied for fabricating some products such as furniture and architectural materials[1, 2]. Recently they have gained widespread use in the automobile industry. In their application, synthetic resins such as polypropylene and polyethylene are commonly used as a matrix for natural fiber composites. However, those composites often have problems of fiber-matrix compatibility which result in a decrease in mechanical properties. Therefore, in order to improve the interaction between fiber and matrix, surface treatments are necessary for modifying fibers' morphology [1-6].

Natural fiber is a traditional material which has been used throughout human history to produce cloth and fabric. Natural fiber is gathered from animal and plants. Generally plant fiber is used in green composite research for reinforcement. This is because the plant fiber has benefits such as easily renewable substance, mass gathering and low cost. With FRP method, polymer can get more functional properties but established reinforcement fibers have high price or pollution problems. Natural fiber can replace established fiber for eco-friendly, density and cost. Previously chapters, jute, kenaf, hemp and flax are used for composite.

Bamboo is one of the common materials used in human history but lately in Far East Asia, most of bamboo materials are replaced with plastics. This means that it does not need to compete with other, against jute, kenaf and hemp. Also bamboo fiber is one of the strongest natural fibers, which has near or over tensile strength than mild steel. Moreover bamboo is one of the fast growing plants and has high mechanical properties.

Resin impregnation method using PVA or phenolic resin has been applied for impregnation. Resin impregnation method for fiber has recovered the fiber damage on

surface and filled fiber rumen. It can increase the fiber mechanical properties and decrease the water absorption ratio.

Maleic anhydride grafted polypropylene (MAPP) is a common modified for thermoplastic polymer. It can usually improve inter-facial shear strength (IFSS) between fiber and matrix and increase the mechanical properties of composites.

Due to the expansion of the green composite field, assignments to find cost efficient, more stable and better water absorbing materials were given. Previous PVA resin impregnation method with PP composites increased water absorption ratio and phenolic resin impregnation method with PP composites decreased the IFSS and the mechanical properties. In this paper, PP and MAPP combination was used as one of the common methods for improving PP composites. Fiber tensile strength, inter-facial share strength between fiber and matrix, tensile and flexural strength, impact test and water absorption ratio were considered.

## **5.2 Experiments**

### **5.2.1 Materials**

The thermoplastic polymer PP, used as a matrix material, was supplied by the Primepolymer (Japan). It has a specific gravity of 0.90 - 0.91, melting temperatures of 165°C - 171°C and crystallinity of 82%. The Bamboo fiber used as reinforcing fiber was collected from China. Raw bamboo fiber obtained from bamboo was boiled with alkali solution. It was washed with fluid water to remove impurities, such as; dust, bamboo powder and NaOH on the fiber surface. Then it was dried with a fan for over 2 days. MAPP was used to modify PP matrix [7].

### **5.2.2 Resin impregnation method**

In this study two kinds of materials were used for resin impregnation method. PVA impregnation method was used on PVA produced by NACALAI TESQUE.INC (Japan). PVA solution was made with a stirrer and a 80°C water based 3% solution mixed for over a 24hour period. The fiber was to immerse natural fibers for two hours at room temperature. After that fiber was hanging drying rack. The Phenol resin treatment uses a 9% ethanol based solution. The components of the mix used a homogenizer for 15 minutes. The fiber was to immerse natural fibers for two hours at room temperature. After that fiber was hanging drying rack. Raw bamboo fiber (UB), phenol resin impregnated bamboo fiber (PHB) and PVA impregnated bamboo fiber (PVB) were used for testing and manufacturing. Resin impregnated fiber was dried with a fan for over 2 days.

### **5.2.3 Bundle fiber and micro drop let test specimens**

The bundle fiber tensile specimens and micro drop lets specimens were made with paper frame with washed fiber. With a paper frame fiber specimens were impregnated solutions. Micro drop lets specimens were knotted by PP (or MAPP/PP) fiber and finally they were put in 180°C oven for 30 minutes. Phenolic resin impregnated bundle fiber specimens were put in the oven for 10 minutes for thermosetting. Diameter and drop lets size of specimens were measured by optical. Bundle fiber tensile specimens have 10 mm gage length.

### **5.2.4 Fabrication of composites and test specimens**

The composite specimens were prepared by using an injection molding machine. Before using the injection molding machine, fiber and matrix were mixed in twin screw extruder machine twice. This happened inside the blocks which were heated at 170°C. Both materials were added to the machine at the same time with a weight ratio of 3:10 (natural fiber: PP). MAPP was physically mixed with PP. As a result, 100% PP, 10% MAPP/PP and 100% MAPP were prepared. The mold used to produce specimens were prepared according to the Japanese Industrial Standard, specifically the JIS K 7139 standard. The tensile, flexural, impact, and water absorption tests were conducted. Each type of composites was tested and its average values were reported. For tensile and flexural tests, 15 and 10 specimens were used for each test and were conducted with a speed of 2 mm/min and the average room temperature was 25°C.

### **5.2.5 Water absorption test**

The water absorption test used 5 specimens for each case and it followed the standard of room temperature. Before the test, specimens were dried in an oven at 70°C for 24 hours. Then, specimens were sodden into the water. For a total of 1, 3, 24, 48, 96, 196, 288 and 384 hours after, sodden specimens were taken out from the water and the weight of specimens was measured. Prior the weight measurements were acquired, the water on the surface of specimens was removed by paper towels [8-10].

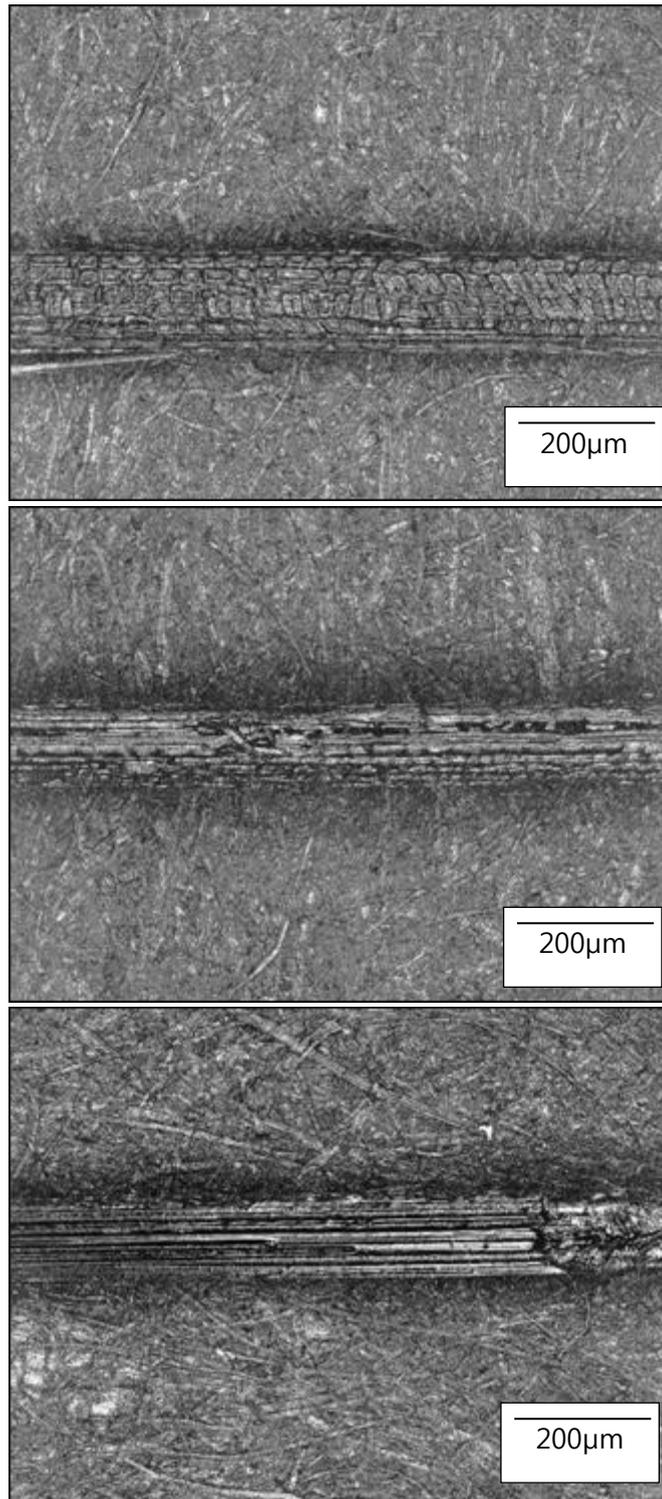


Fig 5.1 Laser micro scope images of bamboo fiber (top), bamboo fiber with phenolic resin impregnated bamboo fiber (middle), and bamboo fiber with PVA impregnated bamboo fiber(bottom).

## 5.3 Results and discussion

### 5.3.1 Bundle fiber tensile test

The fiber surface was coated by resin impregnation. Fig 5.1 shows the surface morphology of untreated and resin impregnated fibers. The fiber bundle tensile which treated with different strength bamboo fiber bundles has been measured and the results are shown in Fig 5.2. In this Fig. untreated, PVA impregnated fiber and phenolic resin impregnated bamboo fiber used. It was explained by the fact that the resin impregnation method contributes to an increase in the tensile strength of fiber [10]. When bamboo fiber was manufactured, a process which used alkali solution for separation of fiber from bamboo, the most successful rate was shown. However, the alkali solution can cause a decrease in the tensile strength of natural fiber. As reported by Mwaikambo and Ansell [11], the alkali treatment would certainly damage the fiber and consequently reduce the tensile strength of the fiber. The resin impregnation method can fix and increased the tensile strength of fiber. In this test, fiber diameter was measured by 2D, and it was supposed that the fiber shape is cylindrical which caused a huge error in Fig 5.2. In this study over 50 specimens were examined and we can conclude that the bundle fiber tensile strength was improved. With resin impregnation fiber rumen and creak or damages on fiber surface fixed and between single fiber and single fiber enhanced by resin. So bamboo bundle fiber increased their tensile strength.

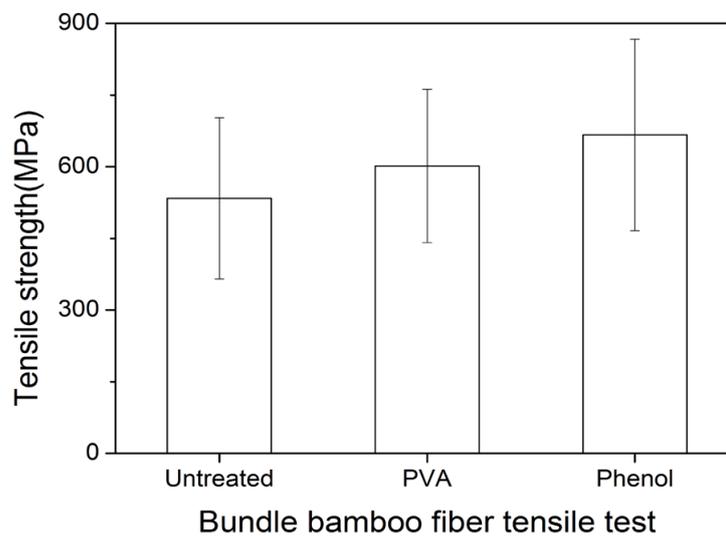


Fig 5.2 Resin impregnated bundle bamboo fiber tensile test.

### 5.3.2 Micro droplet test

The resin impregnation filled up and covered fiber's rumen and surface. When fiber's surface was coated, it fixed the fiber crack on the surface but at the same time it also caused the surface area to be decreased. Inter-facial shear strength between phenolic resin

impregnated bamboo fiber and PP was lower than untreated. It was guessed that first the physical shape was changed to a simple one and this reduced its contact area between fiber and matrix, and secondly the inter facial shear strength between fiber and phenolic resin is not so high [12]. PVA impregnated fiber was increased than untreated; this is based on the chemical bonding between fiber and matrix. Fig 5.3 is a laser micro scope image of bamboo fiber on PP droplet for the micro droplet test.

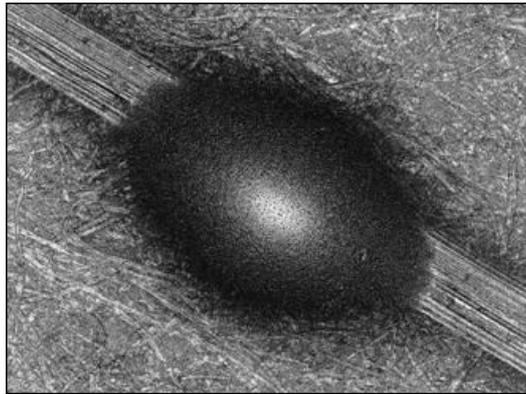


Fig 5.3 Laser micro scope image of micro droplet specimen.

### 5.3.3 Mechanical testing for composites

As it can be seen in Fig 5.4, UB is untreated bamboo fiber, PVB is PVA impregnated bamboo fiber and PHB is phenolic resin impregnated bamboo fiber. And it tested with 3 different composition of matrix. The tensile strength and flexural strength of the bamboo/MAPP/PP composites are not so different from resin impregnation, whereas the strength of the bamboo/MAPP/PP composite does not vary significantly even after treatment. A different trend without MAPP is seen. In the case of PP with the PVA impregnation, it is slightly higher than others. However with MAPP, untreated and resin impregnated cases have enough strength of IFSS. Bending test results show the same trend with the tensile test as it can be seen, in Fig 5.4. In this test the fiber diameter was also measured by 2D, assuming that the fiber shape is cylindrical. It caused a huge error in Fig 5.4. In this study, over 50 specimens were checked and this allows us to conclude that the bundle fiber inter facial shear strength was improved. The influences of the fiber treatment on the tensile strength and flexural strength are illustrated in Fig 5.5, in the top UBPP is untreated bamboo fiber with PP composites, PVBPP is PVA impregnated bamboo fiber with PP composites and PHBPP is phenolic resin impregnated bamboo fiber with PP composites, in the middle, UBMA is untreated bamboo fiber with 10%MAPP and 90% PP composites, PVBM is PVA impregnated bamboo fiber with 10%MAPP and 90% PP composites and PHBM is phenolic resin impregnated bamboo fiber with 10%MAPP and 90% PP composites and in the bottom , UB is untreated bamboo fiber with MAPP composites, PVB is PVA impregnated bamboo fiber with MAPP composites and PHB is phenolic resin impregnated bamboo fiber with MAPP composites. And Young's modulus are shown in Fig 5.6 UB is untreated bamboo fiber, PVB is PVA impregnated bamboo fiber and PHB is phenolic resin impregnated bamboo fiber.

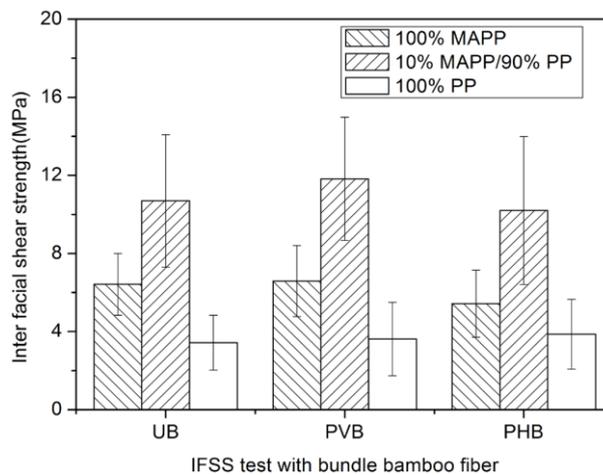


Fig 5.4 Micro drop let test for resin impregnated bamboo fiber and MAPP/PP.

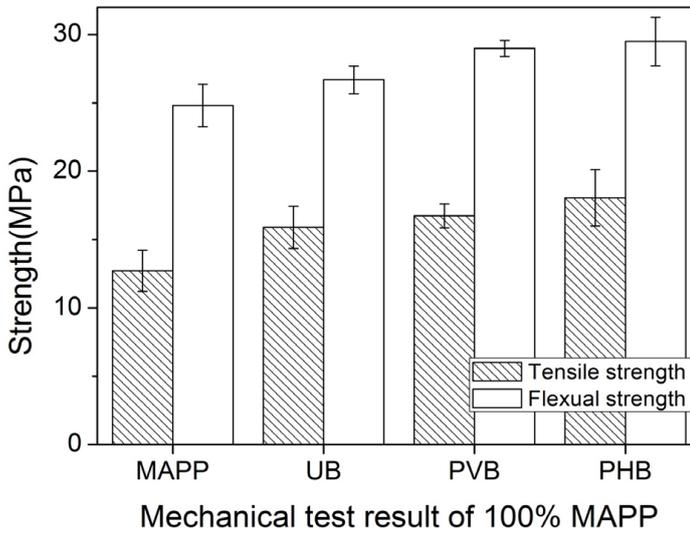
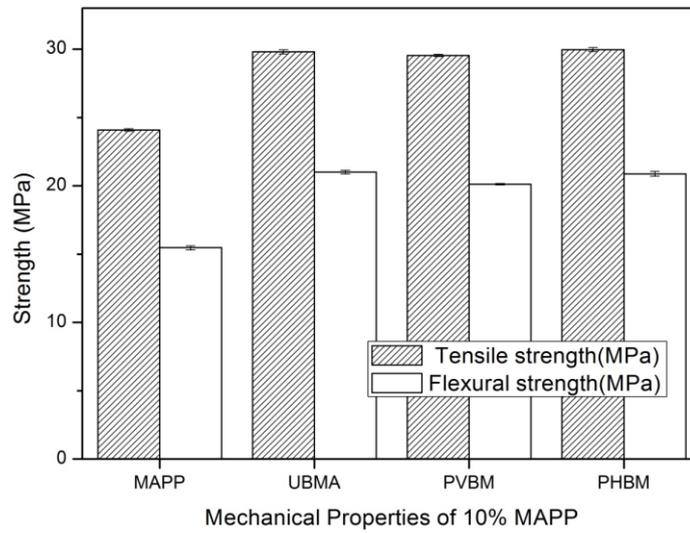
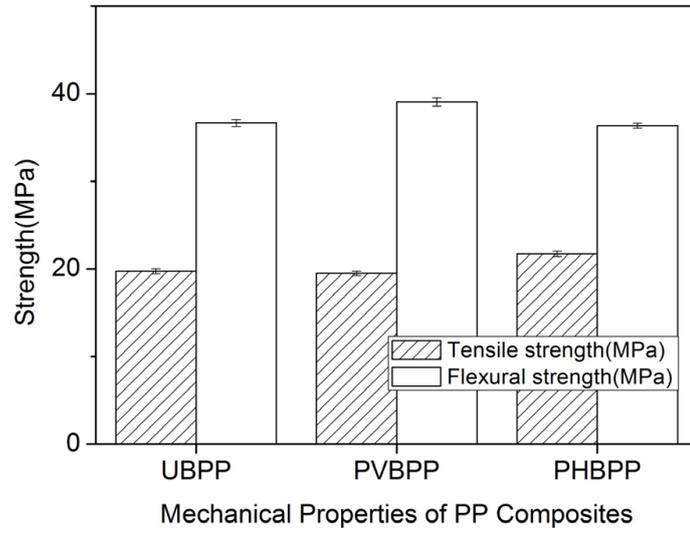


Fig 5.5 Mechanical properties of PP (top), 10% MAPP/PP (middle), 100% MAPP (bottom) composites.

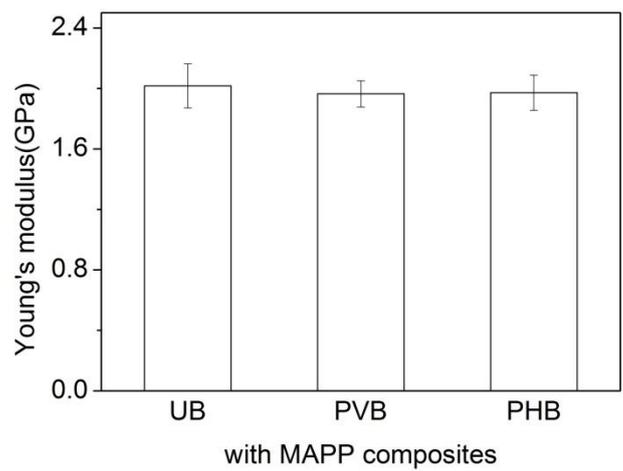
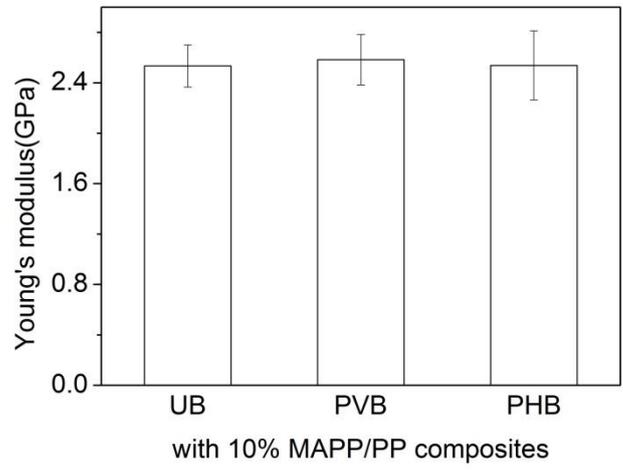
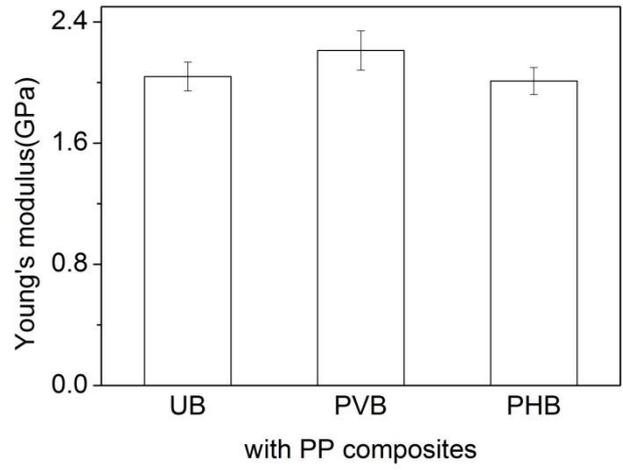


Fig 5.6 Young's modulus of PP (top), 10% MAPP/PP (middle), 100% MAPP (bottom) composites.

Table 5.1 Tensile test results with resin impregnation method

		UB	PVB	PHB
PP	Tensile strength(MPa)	19.74	19.50	21.73
	Young's Modulus(GPa)	2.04	2.01	2.21
10% MAPP	Tensile strength(MPa)	29.80	29.54	29.97
	Young's Modulus(GPa)	2.53	2.58	2.55
MAPP	Tensile strength(MPa)	15.90	16.74	18.06
	Young's Modulus(GPa)	2.02	1.96	1.97

Table 5.2 Bending test results with resin impregnation method

		UB	PVB	PHB
PP	Flexural strength (MPa)	36.66	39.06	36.37
	Flexural Modulus (GPa)	2.58	2.83	2.43
10% MAPP	Flexural strength (MPa)	21.00	20.12	20.88
	Flexural Modulus (GPa)	2.79	2.72	2.96
MAPP	Flexural strength (MPa)	26.68	28.99	29.50
	Flexural Modulus (GPa)	2.61	2.40	2.51

Table 5.1 and 5.2 shown mechanical test result of bamboo fiber reinforced composites.

10% MAPP 90%PP, matrix composites show higher Young's modulus and tensile strength but in this case fiber treatments did not show different between others. It guessed MAPP effect to coupling agent so IFSS increasing effect is stronger than fiber surface treatment. IFSS between Pure PP and phenolic resin worse but fiber tensile properties was increased so composites properties can increase. MAPP can increase IFSS between fiber and matrix but mechanical properties of pure MAPP is lower than PP so 100% MAPP composites show lower tensile strength and flexural strength than others.

### 5.3.4 Water absorption test

Fig 5.7 shows the water absorption ratio of PP and MAPP/PP composites with resin impregnated bamboo fiber, PP is pure PP, MA and MAPP is 10% MAPP with 90% PP specimens, UB is untreated bamboo fiber reinforced composites PVAB is PVA resin impregnated bamboo fiber reinforced composites, PHB is phenolic resin impregnated bamboo fiber reinforced composites. The water absorption characteristics of the manufactured composites are related to the fiber treatment method. In PP composites case, the water absorption (%) decreased with phenolic resin impregnated fiber. The phenolic resin impregnated fiber reinforced composites had lower water content compared to the raw fiber reinforced composites. This may be due to the effect of the fiber surface being coated. But PVA resin impregnated fiber reinforced composite was higher than raw fiber reinforced composite. This can be explained because phenolic is a hydrophobic material but PVA is a hydrophilic material. As a result, phenolic resin impregnated fiber reinforced composites absorbed less water which might improve the dimensional stability of the composites. PP mixed 10% MAPP shows a different trend than pure PP composites. Pure PP and MAPP have similar water absorption ratio. But fiber MAPP mixed composites have a lower water absorption ratio than PP matrix composites. In the case of PP matrix, PVA impregnated fiber reinforced composites have high water absorption ratio, but in MAPP mixed PP matrix composites, untreated fiber reinforced composites have the highest ratio of all. The water absorption ratio of PVA impregnated fiber reinforced composites shows similar result with phenolic resin impregnated fiber reinforced composites.

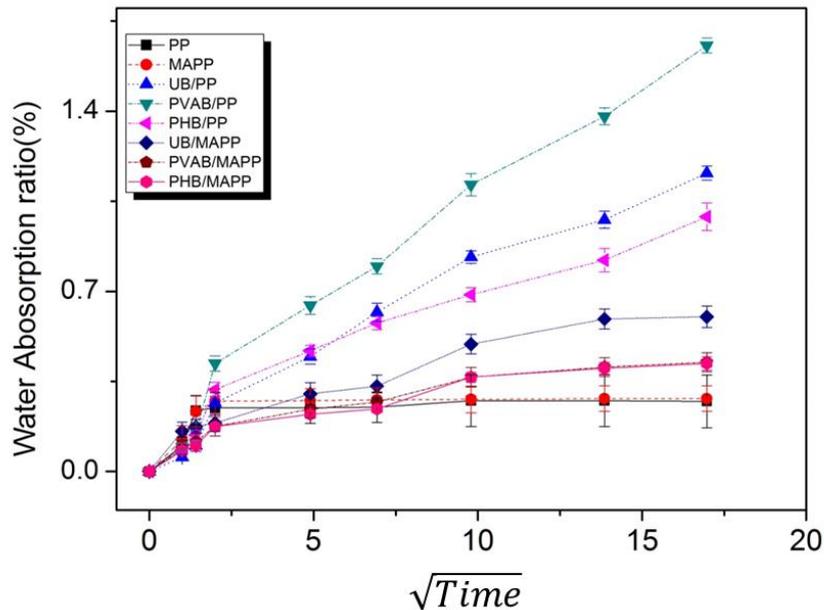


Fig 5.7 Water absorption test resin impregnated fiber with bamboo/PP and bamboo/MAPP/PP composites.

## 5.4 Conclusions

In this study, bamboo fiber reinforced PP, MAPP/PP and MAPP composites were manufactured using twin screw extruder and injection molding method. Raw bamboo fiber was resin impregnated and manufactured composites were resin impregnated with phenolic resin and PVA to increase the compatibility of the bamboo fiber with the 100% PP matrix 10% MAPP/ 90% PP matrix and 100% MAPP matrix. A significant effect of the PVA impregnated on the water absorption properties has been observed. Pure PP and phenolic resin impregnated bamboo fiber reinforced composites had lower water absorption properties than PVA impregnated bamboo case, but MAPP/PP matrix cases showed even much lower result. Unexpectedly bamboo fiber did not significantly improve the mechanical properties with resin impregnation. However with resin impregnation method, the composite can reduce the water absorption ratio. In conclusion, the resin impregnation method is effective for MAPP/PP composites from the point of view regarding water absorption properties.

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## **CHAPTER 6**

### **Final Remarks**

In this thesis, the investigation of the treatment methods for natural fiber bundles, consolidation method for natural fiber reinforced composites and enhanced interfacial strength was introduced. Chapter 1 and 2, reviewed recently green composites and chosen fiber coated method for modified green composite, because it can be cheaper and more environmental friendly increased composites mechanical properties. In chapter 3, plasma polymerization and electron beam irradiated method was studied it is dry method so it can be avoid water pollution which usually chemical treatment methods have. But these high energy treatment also has disadvantage. They need high energy and special equipment. So chapter 4 tried to use resin impregnation method one of cheapest method coating on fiber surface. And chapter 5 tried to use bamboo for composite. Previously, reinforcement material such as jute and kenaf have to use traditional objects, so it can cause to increase market price. But bamboo case almost lost their traditional object. And it is one of very fast grow up plants it is expectant material so tried resin impregnation. Namely plasma polymerization, alkali treatment and resin impregnation were used as modifier for polypropylene (PP) and poly lactic acid (PLA). Moreover, the resin impregnated method and maleic anhydride grafted polypropylene were fabricated mixed with polypropylene and were used together to modify bamboo fiber reinforced composites. Some major conclusions obtained from this work are listed as follow:

1. Plasma polymerization effected on jute fiber, but it needs preprocessing. 3% alkali treatment fiber with plasma treatment 2 minutes gave the highest value of single fiber tensile strength. Plasma treatment has been conducted in atmospheric conditions to recover inactivated jute surfaces for better adhesion and bonding between fiber and matrix in composites. After 3% of the alkali treatment, 2min plasma treatment fiber had the highest tensile strength in the case of hybrid treatment. Composite containing 20% jute fiber was used to perform the tensile and flexural experiments. The improvement in tensile strength and modulus of the composites could not be observed. Therefore, further modification is needed for experiment.

2. Resin impregnation can increase fiber tensile properties and IFSS and also mechanical properties of composites were increased. It was observed that the resin impregnation method can increase the tensile strength, flexural strength of composites due to the fact that the fiber's capillary tubes become filled. With regards to the kenaf fiber reinforced composites, the PVA impregnated kenaf fiber had a higher effect on the mechanical properties than phenol resin impregnation. For the bamboo fiber reinforced composites, the phenol resin impregnated fiber had a higher effect on the mechanical properties than the PVA impregnation. It is also known that the alkali treatment can cause damage to the fiber. In conclusion resin impregnation can improve the mechanical properties of the natural fibers while alkali treatment should be excluded.

3. MAPP enhanced composites tensile strength of composites and reduced water absorption ratio. Bamboo fiber reinforced PP, MAPP/PP and MAPP composites were manufactured using a twin screw extruder machine and injection molding method. Raw bamboo fiber was resin impregnated and manufactured composites were resin impregnated with phenolic resin and PVA to increase the compatibility of the bamboo fiber with the 100% PP matrix 10% MAPP/PP matrix and 100% MAPP matrix. A significant effect on the PVA impregnated on the water absorption properties has been observed. Pure PP and phenolic resin impregnated bamboo fiber reinforced composites were lower compared to PVA impregnated bamboo case, but MAPP/PP matrix cases showed a much lower result. Unexpectedly, from the results obtained by this study it can be concluded that the bamboo fiber did not significantly improve the mechanical properties with resin impregnation. However with resin impregnation method, the composite can reduce the water absorption ratio. Thus, resin impregnation method is a good material for MAPP/PP composites in terms of reducing the water absorption property.

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