

ABSTRACT

Investigation of Interfacial Bonding in Banana Fiber-Reinforced Composites: Ascribing Global Economic Value to Unique Renewable Resources in Developing Countries

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Natural fibers have increased in popularity in the polymer composite industry, due to the steady rise of consumer pressure for biodegradable and environmentally-friendly products. However, the organic nature of these natural fibers causes poor interfacial bonding with the majority of thermoplastic polymers. As a result, the benefits of the increased composite stiffness and strength are greatly reduced. In order to increase this interfacial bonding, a variety of surface and chemical treatments have been explored, including fiber treatments such as alkaline and silane treatments as well as polymer additives such as maleic anhydride. This study seeks to compare the effectiveness of these treatments on the interfacial bonding as well as their effect on the mechanical properties of the fiber reinforced composite. Results reveal an increase in bonding and some benefit to the final composite properties for all treatments studied, though silane and maleic anhydride stand out as optimal treatment.

Investigation of Interfacial Bonding in Banana Fiber-Reinforced Composites: Ascribing
Global Economic Value to Unique Renewable Resources in Developing Countries

by

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A Thesis

Approved by the Department of Mechanical Engineering

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Submitted to the Graduate Faculty of
Baylor University in Partial Fulfillment of the
Requirements for the Degree
of

Master of Science in Mechanical Engineering

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August 2014

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ACKNOWLEDGMENTS

With the completion of this research, I would like to extend my personal gratitude to all those who have supported me, both academically and emotionally. These individuals, whom I would like to acknowledge below, have proven instrumental to the completion of this thesis and to the expansion of my academic knowledge during my time at Baylor University.

I would first like to acknowledge my advisor, Dr. William Jordan, for his support, encouragement, and guidance throughout this research and my time at Baylor. Dr. Jordan has never ceased to inspire and encourage me to recognize the potential social and economic impacts this field of engineering can have in communities of need.

I am also thankful for Dr. David Jack and Dr. Larry Lehr for serving on my thesis committee. I appreciate their willingness to serve in this capacity. I am especially grateful for the passion, academic insight, and experimental resources Dr. Jack has provided during this project.

I would also like to thank my classmates and colleagues for their contributions. Without the stimulating discussions and feedback about my research from Ben Lewis and Sarah Stair, this thesis would not nearly be as comprehensive.

Lastly, I want to thank my family for their invaluable support. I extend deepest thanks to my parents for their encouragement, and most especially to my wife, Megan, for her patience and never ending support.

CHAPTER ONE

Introduction

Section 1.1: Introduction

Part 1.1.1: Motivation

Motivated by the desire to support struggling communities in developing countries, this research seeks to provide a means in which stewardship of these communities can expand beyond that of meeting immediate needs through assistance technologies and micro-economic development and into long-term socio-economic growth. As a means to this end, an emphasis is placed on providing an opportunity for the developing country to enter into the global marketplace with a readily available and highly profitable export.

It is the stance of this research that natural resources, especially wasted material, found in developing countries can attain value in the global market through the demand of industry-leading applications. Based on this premise and current demands of modern society for biodegradable and environmentally-products, this research analyzes the use of banana pseudostem fiber, a natural resource commonly found in many developing countries, as a fiber-reinforcement in thermoplastic composites, an industry-leading innovation.

Part 1.1.2: Stewardship Model for Developing Countries

The classical engineering stewardship model for developing countries, shown in Figure 1, combines the use of humanitarian engineering and economic development to

meet immediate engineering needs while simultaneously addressing long-term financial development. Often referred to as appropriate technology, this method of stewarding developing communities into a sustainable future has effectively bridged modern and developing countries, sparking trends in sustainable development and socially-conscious products in the modern world, while providing the developing world with technological developments and financial means to meet everyday necessities.

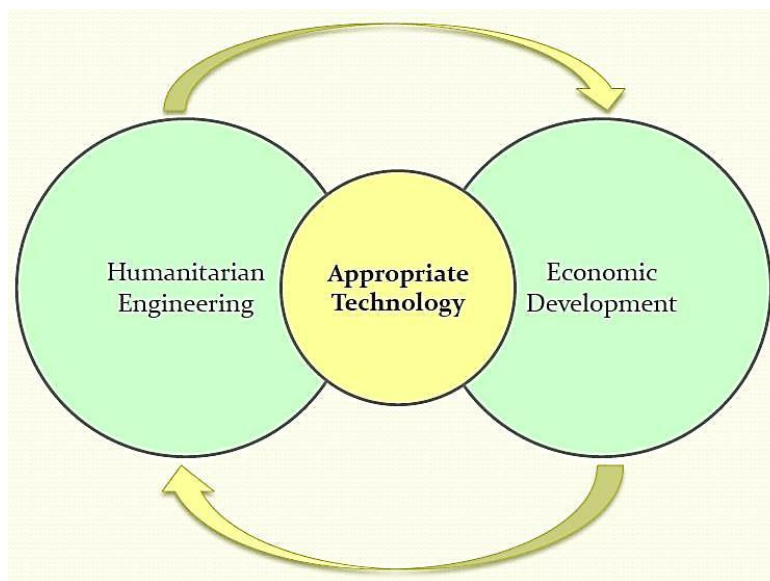


Figure 1 – Classical stewardship model for developing countries

Organizations such as Engineering for Change (E4C) LLC, founded by the American Society of Engineers (ASME) and supported by Engineers Without Borders-USA (EWB-USA) and the Institute of Electrical and Electronics Engineers (IEEE), join together communities of engineers around the world to improve the quality of life in developing countries “by facilitating the development of affordable, locally appropriate and sustainable solutions to the most pressing humanitarian challenges.”[1] This collaboration, often referred to as humanitarian engineering, is coupled with economic

development, such as micro-loans, in order to maintain sustainability. A prime example of this coupling is International Development Enterprises, founded by Paul Polak. This organization utilizes the economic development technique of micro-lending to provide small, low-interest loans to rural farmers, in order for them to purchase a unique, low-volume, drip-irrigation system, developed through humanitarian engineering.

Through this classical stewardship model, support for struggling communities in developing countries has not only risen in strength in the modern world, but it has also been extremely effective at making short-term impacts to immediate needs. However, the inability of the developing country to respond with its own export in the global market, providing a means for long-term economic growth, is found missing from this model.

It is proposed that through the addition of innovation in industry-leading fields directed towards the use of natural resources available in developing countries, an opportunity arises for these countries to enter into the global market and experience long-term economic growth. This modified model is shown in Figure 2.

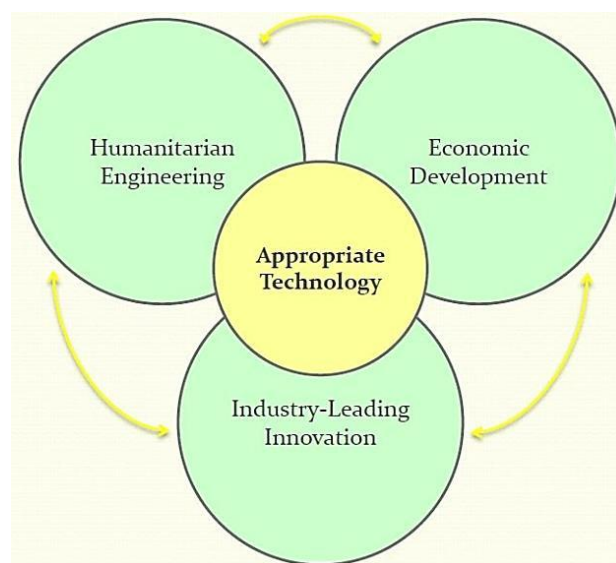


Figure 2 – Modified stewardship model for developing countries

For example, in the automotive industry, carbon-fiber reinforced composites are growing in popularity due to their high strength-to-weight ratio. If similar applications were to be found for natural-fiber reinforced composites, a demand would be placed on those fibers, ascribing global economic value to that natural resource.

Part 1.1.3: Banana Plant Physical Properties

One such natural resource found extensively in developing countries is the banana plant. While certainly not limited to developing countries, the banana plant is an excellent resource to consider due to its impressive mechanical properties and its abundance in the targeted communities, indicated in Figure 3.

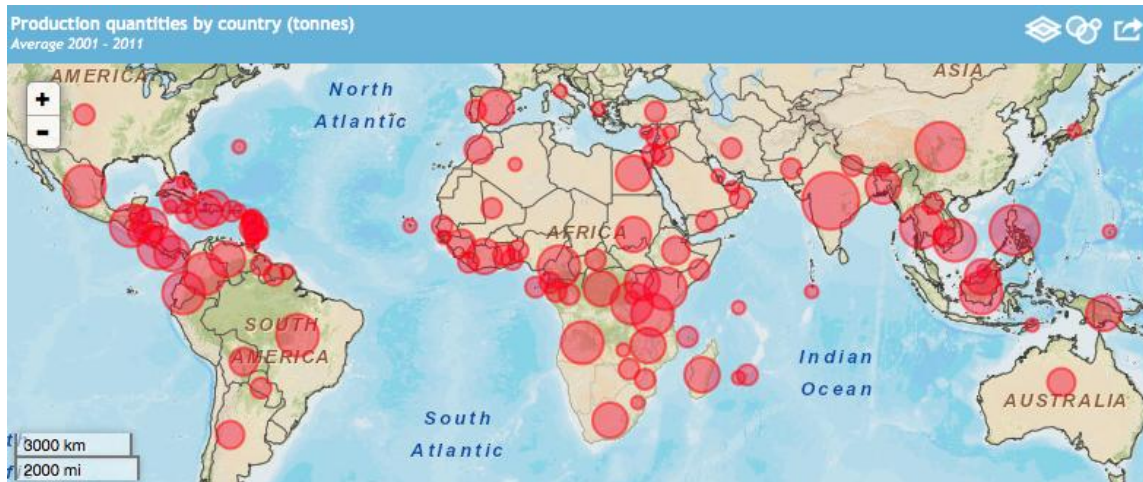


Figure 3 – World production of banana plant, courtesy Food and Agricultural Organization of the UN [2]

The banana plant, detailed in Figure 4, is unique in that instead of a tree trunk, the base of the plant consists of tightly packed sheaths, which make up the pseudostem. These sheaths are composed primarily of long fibers, which themselves are composed of concentric lignin and hemicellulose fibrils, detailed in Figure 5. These concentric

cellulose fibrils provide structural support for the fiber yielding considerable tensile strength.

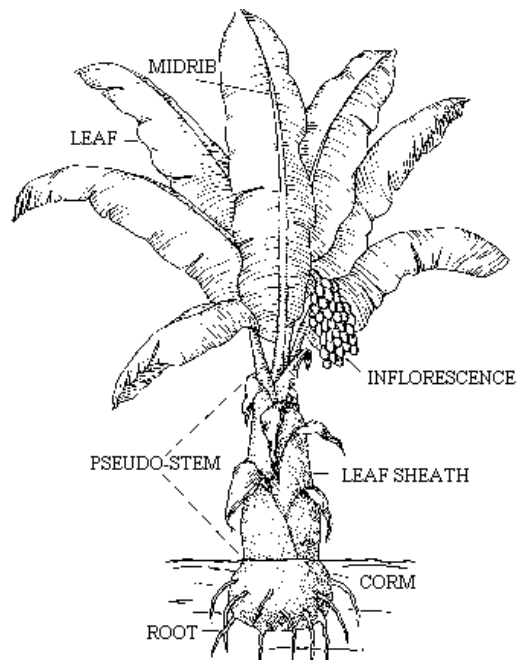


Figure 4 – Detailed image of banana plant, courtesy Devri Burdick [3]

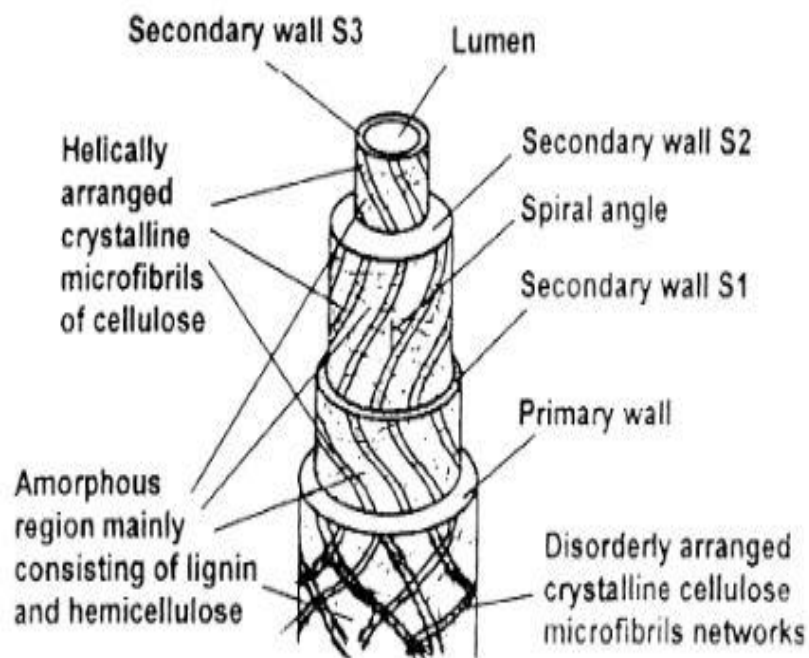


Figure 5 – Detailed image of lignocellulosic fiber [4]

Another unique aspect of the banana plant is its short life. The pseudostem of most banana plant species dies after just one bunch of bananas is grown. As a result, banana plants must be cut down and disposed of regularly.

Part 1.1.4: Current Uses of Banana Plant

With the regular disposal of banana plants, farmers have become extremely creative with using the plant. Aside from the obvious use of the fruit, the leaves are commonly used to cook, make hats, and even to make homemade soccer balls. The pseudostem, however, is largely unused and is considered waste material. In Figure 6, a rural farmer in Uganda is cutting up a pseudostem into its separate sheaths to feed to his cows.



Figure 6 – Rural Ugandan farmer disposing of banana pseudostem

Although the pseudostem is generally considered waste, fibers extracted from the pseudostem have begun to be used for a variety of products such as silk, clothing, and

even iPad cases [5]. One such company that supplies banana fibers for mats, bags, and even furniture is Banana Star, a banana fiber extraction company based in India [6]. This research seeks to provide an effective use to this wasted material through fiber-reinforced composites. The current extraction process includes separating the fiber from the pulp in the pseudostem by means of steel roller. These fibers are then allowed to dry in the sun prior to processing and shipment. Figure 7 exemplifies this process.



Figure 7 – Banana pseudostem fiber extraction process [7,8]

Section 1.2: Brief History of Thermoplastics & Fiber-Reinforced Composites

Part 1.2.1: Brief History of Thermoplastics & Fiber-Reinforced Polymer Composites

When looking for a source of industry-leading innovation to drive such research, one ought to highly consider the field of polymers, thermoplastics, and fiber-reinforced polymer (FRP) composites. A field that has integrated itself into nearly every aspect of

life, from chairs to aviation, plastics stretch back as early as the Ancient Egyptians and Greeks with their uses of resins – natural plastics such as shellac – to varnish sarcophagi and make jewelry [9]. However, the field of polymer science did not begin to take shape until the mid-Nineteenth and early-Twentieth centuries. The ‘first’ polymeric materials include nitrocellulose-based material invented by Parkes in 1862 and Hyatt in 1866 and phenol-formaldehyde, known as Bakelite, by Baekeland in 1907 [10]. These thermosetting polymers cure to form irreversible cross-linking between molecular chains, providing a great deal of mechanical strength while maintaining its light weight.

The first thermosoftening plastic, or thermoplastic, resulted from the addition of camphor to the nitrocellulosic material, and became known as celluloid [10]. Unlike thermosets, these thermoplastics do not cure, and so form irreversible cross-links, but rather soften with branches of molecular chains. Although this does not invoke as high of a mechanical strength, it does allow the plastic to be melted back down and re-used. Motivated to cut costs during the oil shortage of the 1970’s, cheap filler material began to be mixed with the plastic; surprisingly this often led to enhanced mechanical properties [11].

Part 1.2.2: Motivation for Fiber Reinforcement

Although thermoplastics provide a great alternative to the irreversibility of thermoset polymers and resulting low processing cost, the loss of mechanical strength is not insignificant. Especially as industries such as aerospace require high strength-to-weight materials, there is a great need to increase product strength, stiffness, and toughness. Fiber-reinforcement is an excellent method to improve these composites

without radically affecting processing methods. Ranging from 20 to 60 percent of composite volume filled with fiber, product cost can often drop proportionally.

Part 1.2.3: Brief History of Natural Fiber-Reinforced Composites

The increasing social pressure for biodegradable, sustainable, and environmentally-friendly products, coupled with their good processibility from their low density, nonabrasive, flexible, and cost-effective properties, has launched the use of natural fibers in FRP composites [12,13]. In fact, natural fiber-reinforced composites have already found their way into marketable products, such as in the automobile industry. For instance, interior panels and seat cushions originally made of glass mat FRP composites are now being made with natural fiber FRP composites, due to its high degree of flexibility, low density, and non-abrasive surface [14].

Section 1.3: Introduction to Interfacial Bonding Issue

The composition of lignocellulosic fibers, such as banana fibers, does cause significant limitations in the fibers' interfacial compatibility. This interfacial compatibility plays a primary role in the mechanical performance of a composite, and must be addressed. Lignocellulosic fibers are inherently polar and hydrophilic, meaning they readily absorb moisture. Since the majority of thermoplastic polymers are non-polar and hydrophobic, meaning polymers do not absorb or bond with water, the fibers and polymer are naturally incompatible and have inefficient fiber-matrix interfacial bonding [4]. A conceptual drawing of this poor interfacial bonding is shown in Figure 8, where black void is visible between the bulk matrix and bulk fiber.

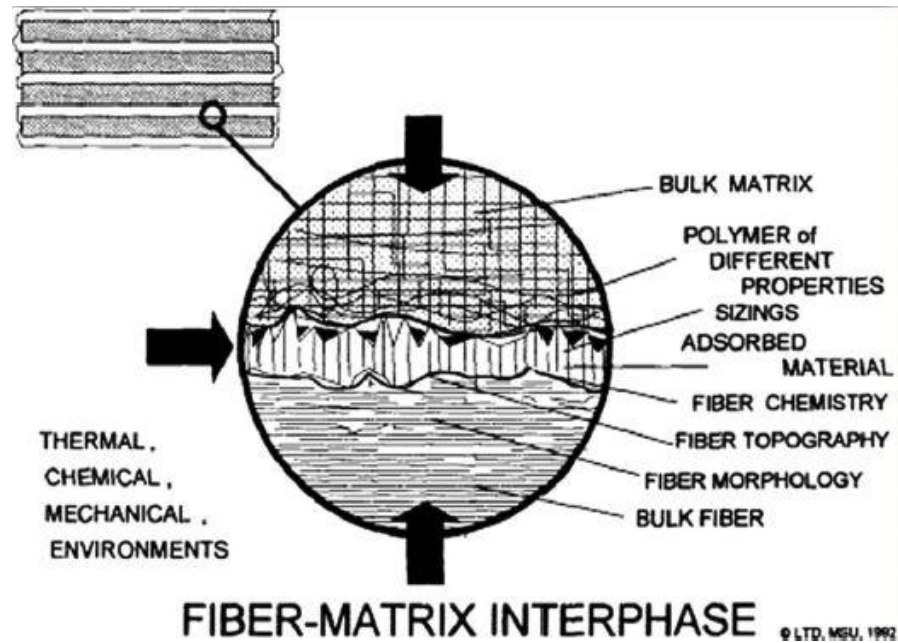


Figure 8 – Lignocellulosic fiber and hydrophobic polymer interfaphase, courtesy Jacob et al. [4]

This poor adhesion effectively dilutes the composite matrix and causes the fibers to act as flaws in the composite, greatly reducing the mechanical strength [15].

The aim of this study is to identify and optimize the interfacial bonding of banana fiber in a polymer matrix in order to both improve interfacial bonding as well as increase composite mechanical strength.

CHAPTER TWO

Literature Review

Section 2.1: Lignocellulosic Fibers in Thermoplastic Composites

Part 2.1.1: Natural Fibers Currently Used in Industry

As discussed in Part 1.2.3, natural fibers in fiber-reinforced thermoplastic composites are growing steadily in popularity in this field. These lignocellulosic fibers, fibers consisting of several microfibrils that run along the length of the fiber as seen in Figure 5, are often grouped into three types: seed hair, bast fibers, and leaf fibers [16]. Of these three types, bast and leaf fibers are more commonly used, such as jute, sisal, and kenaf fibers. Using classifications supplied from Mei-po et al. 2011 and data from sources listed, common natural fibers in these respective groups are congregated and their properties compared in the table below [15].

Table 1: Mechanical properties of common natural fibers used in natural FRP composites.

Fiber Type	Density (g/cc)	Tensile Strength (MPa)	Young's Modulus (GPa)	Reference
<i>Seed Fibers</i>				
Cotton	1.5-1.6	285-597	5.5-12.6	[17]
Milkweed	-	234.4	-	[18]
Coir	1.39-1.52	95-174	2.5-4.5	[19]
<i>Bast Fibers</i>				
Flax	1.5	345-1035	27.6	[17]
Jute	1.3	393-773	26.5	[17]
Kenaf	-	930	5.3	[20]
Banana	1.4	468-1055	12-32.7	[21]
<i>Leaf Fibers</i>				
Sisal	1.5	511-635	9.4-22	[17]
Henequen	-	430-570	10.1-16.3	[12]
Pineapple	-	170-1627	6.0-8.2	[22]

Part 2.1.2: Applications

Natural fiber FRP composites are rising in popularity in industry and are being introduced in many applications. For instance, the aircraft and automotive industries are taking advantage of natural fibers such as hemp, flax, jute, kenaf, and coconut for trunk linings, seat cushions, and other interior applications [14,15,23]. The automotive industry has especially taken an interest in natural fiber FRP composites due to its relatively better finishing and ability to absorb high impact energy that might occur during a crash [14]. R. Zah et al. mention a European directive that mandates automotive manufacturers to reuse and recover at least 95% of material from end-of-life vehicles [24,25]. Natural fibers have a distinct advantage in this particular case.



Figure 9 – Mercedes-Benz components made out of natural-fiber FRP composites [26]

Other applications include thermal insulating materials for use in doors and wall panels, replacement for lumber, packaging, and consumer goods [27–29].

Section 2.2: Banana Fiber

Part 2.2.1: Botanical Description

As described in Part 1.1.3, the fiber, pictured in Figure 10, used in this research is banana fiber obtained from the pseudostem of the banana plant. Due to its organic and lignocellulosic nature, banana fibers are complex in structure. As a lignocellulosic fiber, banana fiber consists of core components such as cellulose, hemicellulose, and lignin. The hollow fibrils, as seen previously in Figure 8, consist of cellulose, which are held together by a lignin and hemicellulose matrix [30]. The cellulose content is directly proportional to the mechanical strength of the fiber, while the lignin and hemicellulose serve to resist natural decay, including thermal degradation [31]. The botanical composition of the banana fiber obtained by elemental analysis is given in Table 2, obtained by Bilba et al (2007).



Figure 10 - Photograph of dried, untreated banana fiber

Table 2: Botanical composition of banana psuedostem fiber [32]

Constituent	Composition (wt%)	95% confidence interval
Cellulose	31.27	3.61
Hemicellulose	14.98	2.03
Lignin	15.07	0.66
Extractives	4.46	0.11
Moisture	9.74	1.42
Ashes	8.65	0.10

Banana fibers have a relatively low cellulose and high lignin composition compared to other common natural fiber reinforcements, such as jute, which boasts cellulose of 71-74% but only 12% lignin, and sisal, which is composed of 60-75% cellulose and only 8% lignin [33]. Although the lack of cellulosic content has a negative impact on mechanical strength, the high lignin concentration contributes to a strong adhesion between fibers [34].

Part 2.2.2: Mechanical Properties

The mechanical properties of banana fibers have been thoroughly investigated in literature, such as in *Mechanical properties of banana fibres* by Kulkarni et al (1983). However, the exact ultimate tensile strength and initial tensile modulus reported for these fibers often does not agree. The reason for this lies with the definition of the cross-sectional area of the fiber.

As seen in the SEM image below, the banana fiber is extremely porous to all water to be disbursed throughout the tree. The amount of void in each banana fiber tested ranges from 30% – 60% volume fraction. In order to calculate the true stress of the individual fiber, these voids must be subtracted from the cross-sectional area. However, the typical size of these voids is 10µm in diameter, thus too small for the polymer to enter

into during processing. Thus, when calculating the total strength of a composite, these voids would continue to be voids, or spaces filled with air. In order to provide a more accurate ultimate tensile strength of the individual fiber for FRP composite calculations, the voids are included in the cross-sectional area.

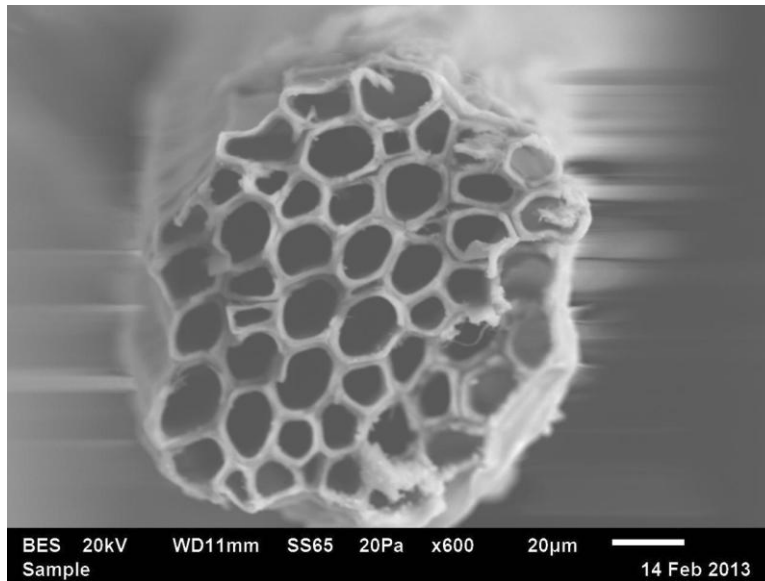


Figure 11 – Cross-sectional view of a single banana fiber taken with SEM at 600x magnification.

For instance, Kulkarni et al, who subtracts the voids from the fiber, reports an ultimate tensile strength of 711 – 789 MPa with an initial modulus of 27 – 32 GPa, while Joseph et al, who includes the voids, reports an ultimate tensile strength of 500 MPa and an initial modulus of 12 GPa [21,35]. For the purpose of this research for reasons specified above, the cross-sectional area will include both the fiber and voids.

Part 2.2.3: Chemical Description

Although an in-depth chemical characterization of banana fiber is not conducted in this research, a basic understanding of the chemical makeup of lignocellulosic fibers is helpful when considering fiber and polymer additives. Per previous discussion,

lignocellulosic fibers consist of cellulose, hemicellulose, and lignin. Cellulose is a semicrystalline polysaccharide with large amounts of hydroxyl groups, giving the fiber hydrophilic properties [36]. Hemicellulose is a branched, fully amorphous polymer with hydroxyl and acetyl groups, causing the fiber to be partly soluble in water [37]. Finally, lignin is an aromatic, amorphous polymer of phenylpropane, that attributes to the resistance of natural decay – such as thermal degradation [18].

Section 2.3: Interfacial Bonding

Part 2.3.1: Fiber Chemical/Surface Modification Treatments

Due to the hydrophilic nature of lignocellulosic fibers, such as banana fiber, they are often chemically treated in order to activate the fibers' hydroxyl groups or introduce mechanisms to effectively interlock with the polymer [36].

One such chemical treatment is mercerization, or alkali treatment, in which a certain amount of lignin and hemicellulose is removed and the cellulose is depolymerized through the disruption of hydrogen bonding [36]. As a result of this disruption, surface roughness of the fiber is significantly increased. Publications using alkali treatment include Ray et al (2001), who treated jute fibers with 5% sodium hydroxide. Ray et al reported a reduction in hemicellulose of approximately 10% by weight, contributing to a 20% improvement in flexural strength for a 35 wt. % jute reinforced vinylester composite [38].

Another chemical treatment includes silane treatment, in which hydrolysis allows for condensation to oligomers, which hydrogen bond with the hydroxyl groups of the fiber, allowing the treated fiber to form covalent bonds with inorganic polymer matrix [39]. This four-step process is depicted by Barry Arkles and reproduced in Figure 12.

Publications using silane treatment include Van de Weyenberg et al (2003), who treated flax fibers with 1% silane. Van de Weyenberg et al reported an approximate 5% tensile strength increase and 50% tensile modulus increase for a 40% by volume flax reinforced epoxy composite [40].

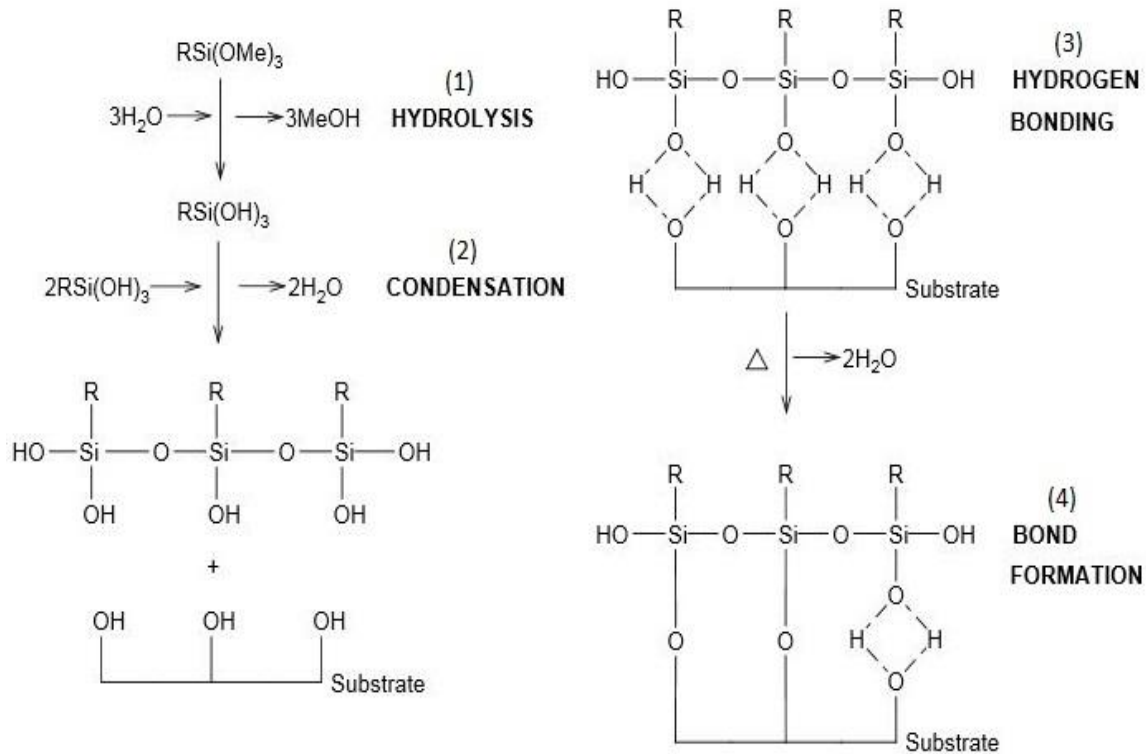


Figure 12 – Deposition of silanes [41]

Other, less common, chemical treatments include acetylation, in which the hydroxyl groups of the fiber cell wall is substituted with acetyl groups in order to cause the fiber to become hydrophobic, and benzylation treatment, in which benzoyl chloride reacts with the hydroxyl groups of the fiber to decrease the hydrophilic nature [36].

Part 2.3.2: Polymer Additives

Recent polymer science has focused on creating chemical and mechanical bonds between polar and non-polar surfaces through block copolymers. These block copolymers,

often grafted onto the original polymer matrix, form chain entanglements with the polymer matrix, while forming a strong bond with the polar fiber surface. One of these more recent grafted copolymers includes maleic anhydride, which forms ester linkages with the hydroxyl groups of the fiber while simultaneously forming entanglements with the polymer matrix [42]. Publications using maleic anhydride include Zhang (2005), who looked at the use of maleic anhydride to bond wood fibers with polypropylene and polyethylene. This bonding mechanism is shown in Figure 13, depicting maleic anhydride bonding a polymer with wood fiber.

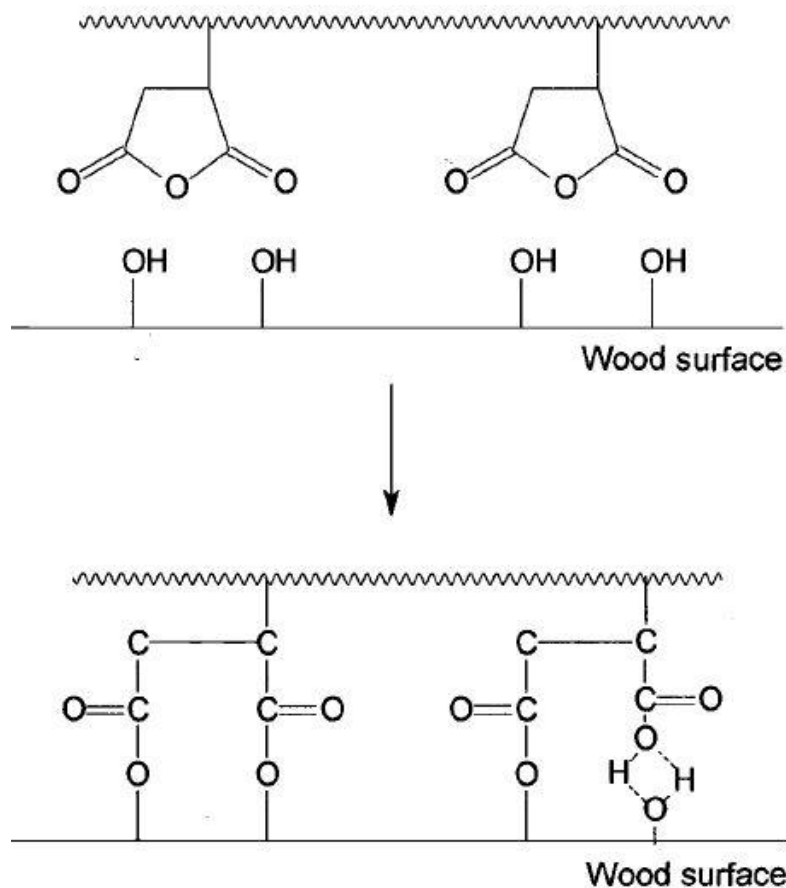


Figure 13 – General bonding mechanism of maleic anhydride with polymer matrix and wood fiber [42]

Section 2.4: Testing Methods

Part 2.4.1: Pull-Out Test

Of the experimental techniques to measure the interfacial bonding, the pull-out test is one of the most commonly accepted [43]. In the context of this study, one end of a single fiber is embedded a certain length into the polymer matrix. The free end of the fiber is then gripped and a tensile force is applied at a constant extension rate in order to pull it out of the matrix. A basic schematic of the pull-out test is shown in Figure 14.

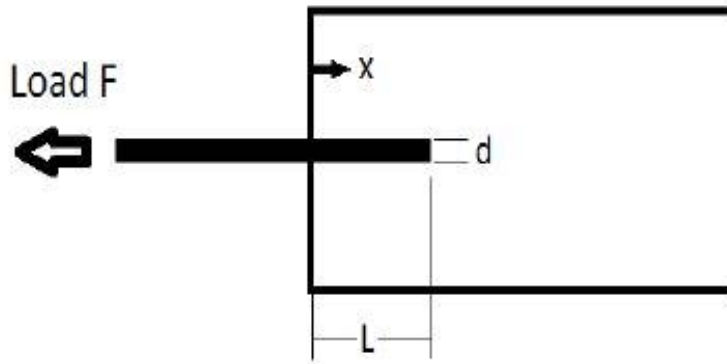


Figure 14 – Diagram of pull-out test sample

The maximum load measured just prior to debonding is measured and is used to calculate the interfacial shear strength, a quantification of the fiber-matrix interfacial bonding. Zhu et al (2012) show mathematically that the interfacial shear strength will decrease with the increase of fiber embed length [44]. The critical nature of the embed length will be discussed further in Part 4.2.4.

The simplicity of this micromechanical technique does require certain assumptions. This technique is only valid for constant cross-section across the length of the embedded fiber. As seen in Figure 15, a typical banana fiber can vary in size in a very

short span of length. Another assumption is that the fiber's surface is smooth. Unlike synthetic fibers, natural fibers can have fairly rough topographies. Lastly, the interfacial shear strength is typically calculated using the diameter of the fiber to find the surface area of the fiber.

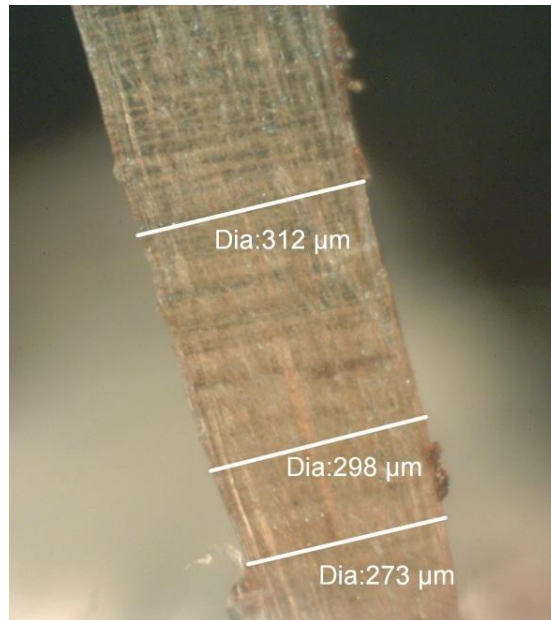


Figure 15 – Photograph of a typical banana fiber taken with an optical microscope

However due to the porous nature of the banana fiber, the fiber is often not perfectly circular and is prone to compressing during processing. In order to correct for this circular assumption, the perimeter of each fiber is measured via SEM, and the surface area is calculated from the perimeter. Valadez-Gonzalez et al shows that the perimeter of the fiber cross-section shows less deviation than that observed for the equivalent diameter of the cross-section [12].

Disadvantages of this technique include fiber breakage before the interface, sample preparation requires substantial time, and most importantly, the fiber-matrix

interface has different matrix geometry and residual stresses in single fiber tests samples than in composite parts [45].

Bannister et al (1995) provide an excellent schematic illustration of potential force-displacement curves for the single fiber pull-out test, which are reproduced below. In the first case, the fiber is extracted immediately after interfacial debonding, due to extremely weak interfaces. In the second case, frictional pull-out is visible following interfacial debonding, and is the most common. Finally, in the third case, multiple peaks form due to damage in the fiber caused by friction as the debonded region develops [46].

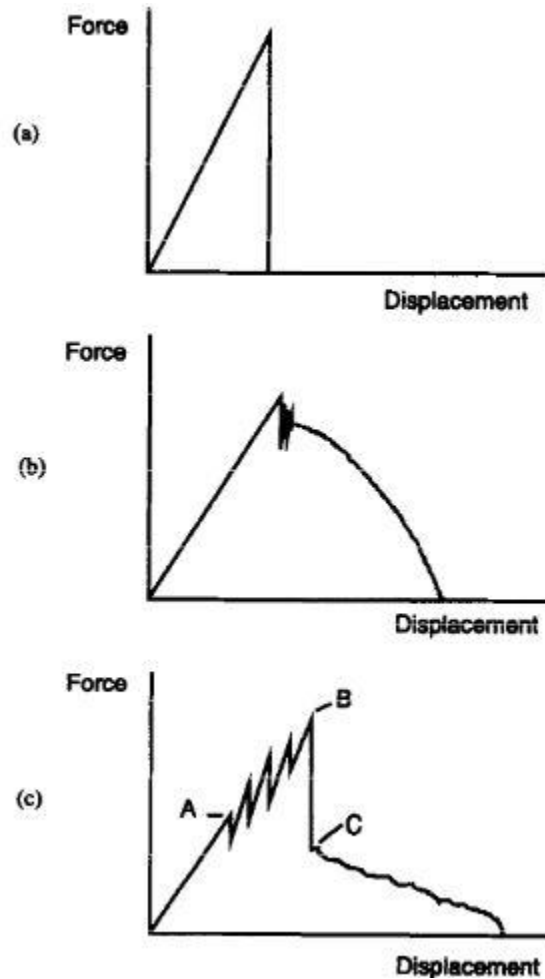


Figure 16 – Schematic of potential force-displacement curves of single-fiber pull-out test [46]

Part 2.4.2: Single-Fiber Fragmentation Test

Another common experimental technique to measure the interfacial bonding is the single-fiber fragmentation test. This technique involves embedding a fiber along the centerline of a polymer sample. The entire specimen is then strained along the fiber axis. As a result of this strain, the fiber fractures at its weakest point, and continues to fracture at different locations, until the fragments become so short that the shear transfer along the length of the broken fiber can no longer make the tensile strength higher to cause additional fractures [4]. The fragment length at the end of the test is known as the critical length, which is then used to calculate the interfacial shear strength. This test is depicted in the schematic below.

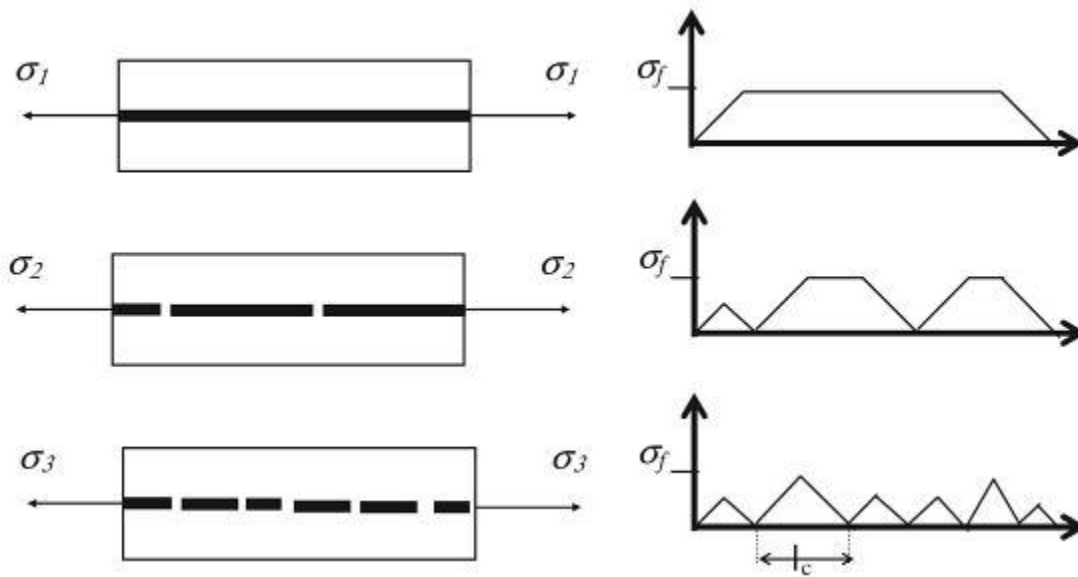


Figure 17 – Schematic of single-fiber fragmentation test [47]

Significant disadvantages of this method arise, however. Firstly, the failure strain of the polymer must be significantly larger than the failure strain of the fiber in order to promote multiple fragmentations of the fiber [4]. This is a major disadvantage for polymers which cannot undergo large deformation, such as LDPE. Another major

disadvantage is the role of friction. Unlike the pull-out test, where friction can be measured in two out of three cases, the coefficient of friction must be assumed. Lastly, sample preparation is very difficult, due to the single fiber needing to be embedded entirely within the matrix, which provides ample opportunity for air bubbles to form along the fiber during preparation, which largely disrupts the critical length during testing.

Part 2.4.3: Other Test Methods

Other experimental techniques include: spectroscopic techniques, such as x-ray photoelectron spectroscopy, laser Raman spectroscopy, and nuclear magnetic resonance, microscopic techniques to study morphological changes on the surface, as well as thermodynamic techniques, such as inverse gas chromatography [4]. All of these methods require very specific equipment, and many require expertise in other scientific fields, such as chemistry or spectroscopy.

CHAPTER THREE

Materials/Research Plan

Section 3.1: Materials

Part 3.1.1: Banana Pseudostem Fiber

The fiber used in this study is banana fiber extracted from the pseudostem of the banana plant. A profile of a typical banana fiber, photographed using a scanning electron microscope (SEM), is seen below. The white streak in this image is simply a result of charging while taking the photograph, and does not reflect pre-imaged fiber damage. However, one does note that there is damage to the fiber, especially along the edges. This damage, common to natural fibers, will play a key role in the high variation in the results of the mechanical properties of the fibers.

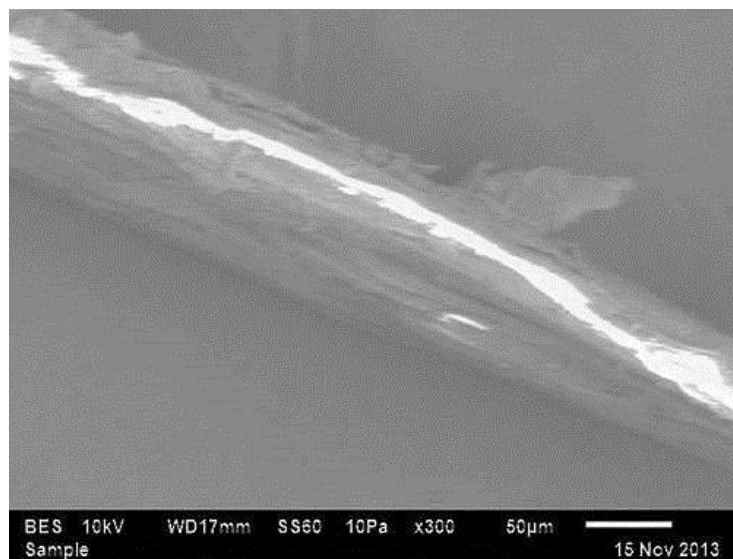


Figure 18 – SEM profile view of untreated banana fiber

Part 3.1.2: Low-Density Polyethylene

The polymer matrix used in this study is low-density polyethylene (LDPE), supplied by Plastic Solutions Inc. (Georgia, USA). As a branched, semi-crystalline thermoplastic, LDPE is an optimum commodity polymer which is used in a variety of packaging applications. Physical properties found from mechanical and thermal testing, following ASTM standards D638-03 and D790-07, are tabulated below.

Table 3: Low-Density Polyethylene (LDPE) physical properties found experimentally during thesis study.

Property	Experimental Value
Melt Flow Rate (g/10 min)	18.66
T _m (°C)	109.63
T _c (°C)	97.14
T _g (°C)	-127.36
T _{degrade} (°C)	287.32
Color	Translucent
Density (g/cm ³)	0.916
Processing Temp (°C)	200-215
Tensile Strength (MPa)	17.96
Tensile Modulus (MPa)	276.947

As seen in Table 3, the tensile strength and modulus of LDPE are extremely low compared to the banana fiber properties seen in Part 2.2.2. For this reason, banana fiber has the potential to be acceptable fiber reinforcement.

Low-Density Polyethylene has a wide variety of low strength, flexible applications. Used in Tupperware containers, lids, plastic wrap (shrink wrap), children's toys, playground slides, retail packaging, milk cartons, flexible pipe, and certain plastic bottles, LDPE is a very popular, low-cost, commodity polymer [48]. A significant contributor to its success is its processing capabilities. LDPE can be manufactured through film extrusion, injection molding, and compound injection molding [49]. Due to

this processing capability and its low melting and processing temperatures, so as to not degrade the natural fiber, LDPE is an excellent candidate to be used with natural fibers.

Part 3.1.3: (3-Aminopropyl) trimethoxysilane

One of the chemical treatments chosen for this research is $\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, (3-Aminopropyl) trimethoxysilane, obtained from Sigma-Aldrich, USA. Fibers treated with the aforementioned silane treatment are soaked for two hours in specified concentration – including 1%, 3%, and 5%, by volume, for this research – in a solution of acetone and water, 50/50, by volume. These soaked fibers are then dried in an oven for eight hours at 80°C. A SEM profile of a banana fiber treated with 1% silane is seen in Figure 19.

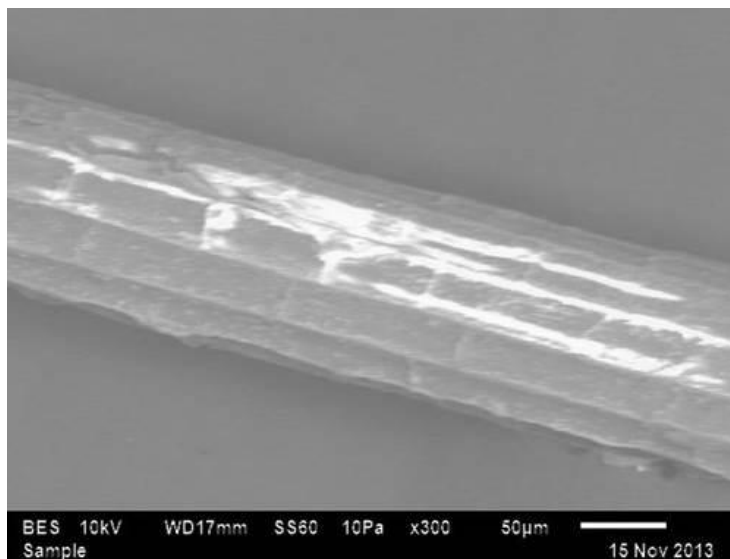


Figure 19 – SEM photograph of banana fiber treated with 1% silane

Comparing to Figure 18, the SEM profile view of untreated banana fiber, it is clear that the outer layer of cellulosic fibrils has been disrupted and a crystallized surface has taken shape.

Part 3.1.4: Sodium Hydroxide

The other chemical treatment chosen for this research is NaOH, sodium hydroxide solution, obtained from Sigma-Aldrich, USA. Fibers treated with the aforementioned alkaline treatment are soaked for four hours in specified concentration – including 4%, 6%, and 8%, by volume, for this research. These soaked fibers are then washed several times with fresh water to remove any NaOH sticking to the fiber surface, and then rinsed with distilled water. The fibers are then dried at room temperature for 48 hours followed by oven drying at 100°C for six hours. A SEM profile of a banana fiber treated with 8% NaOH is seen in

Figure 20. Note that in this case, the surface roughness is dramatically increased, as is typical of mercerization.

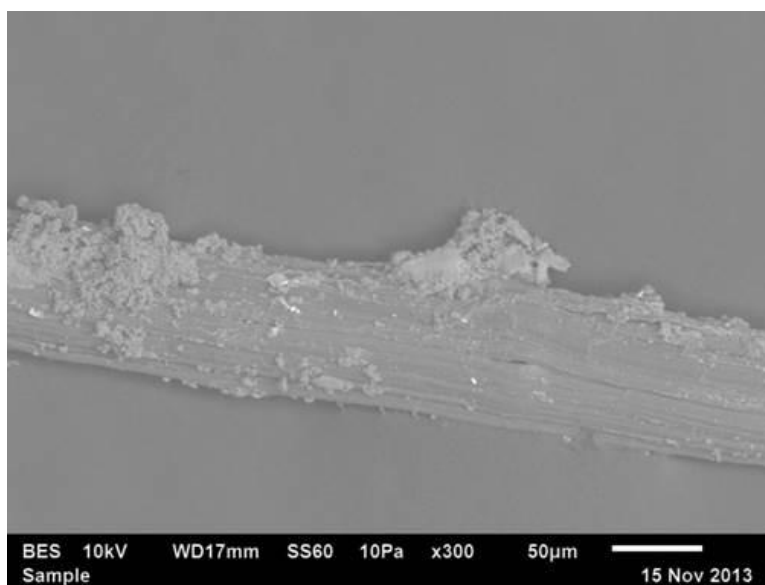


Figure 20 – SEM photograph of a banana fiber treated with 8% NaOH

Part 3.1.5: Maleic Anhydride

The form of polymer additive used for this research is polyethylene-graft-maleic anhydride (MaPE) obtained from Sigma-Aldrich, USA. Provided in pellets of 0.5 wt. %

maleic anhydride and polyethylene, the material has a viscosity of 500 cP, a density of 0.92 g/mL, and a melt temperature of 107 °C.

Polyethylene-graft-maleic anhydride is a chemical coupling agent, more specifically a block copolymer, which is combined with the polymer during processing in order to provide a polymer block capable of forming a bond with the polar fiber. Maleic anhydride consists of oxygen radical groups, which will tend to form covalent and hydrogen bonds with the hydroxyl groups on the polar fiber [11]. Grafted onto a polymer chain, this serves as a bridge between the polar fiber and the nonpolar polymer matrix. A diagram of a molecule of maleic anhydride grafted to polyethylene is shown below.

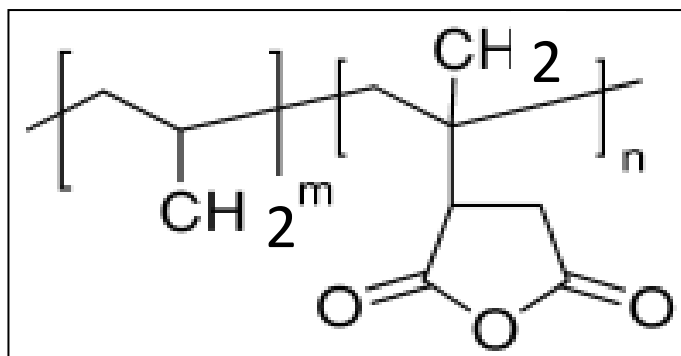


Figure 21 – Maleic anhydride molecule grafted to polyethylene [8]

Section 3.2: Research Plan

Part 3.2.1: Mechanical Strength of Banana Fiber/Effects of Chemical Treatments

Since the chemical treatments used in this research, such as the silane and alkaline treatments, modify the structure of the banana fiber, the first phase of this research is to determine and compare the effects of these treatments on the mechanical strength of the individual banana fibers. Per the typical measurement of mechanical strength of individual fibers, tensile tests were performed on individual fibers for untreated fibers,

silane treated fibers, and alkaline treated fibers. Both ultimate tensile strength and tensile modulus are calculated to determine the treatments' effect on both the total strength of the fiber as well as the stiffness of the fiber.

As well as determining the effect of the chemical treatment on the fiber strength, the tensile tests will determine the effect of varying amounts of chemical used. For each chemical treatment three varying volume percentages will be compared.

Part 3.2.2: Interfacial Bonding of Banana Fiber & LDPE/Pull-Out Test

The second phase of this research is to determine and compare the effects of the chemical treatments and polymer additive on the interfacial bonding of the banana fiber and LDPE. This is determined through the pull-out test, as described in Part 2.4.1. The pull-out test method is chosen to quantify interfacial bonding due to its repeatability, relative ease of sample preparation, and prevalence in literature. Other methods, such as the single-fiber fragmentation test, are very difficult to prepare samples for. For instance, when preparing samples for the single-fiber fragmentation test, air bubbles will often form along the length of the long fiber in the polymer matrix. As a result, test results are less accurate and significantly inconsistent.

The interfacial shear strength calculated from the peak debond force found during pull-out testing will act as a quantifiable measurement of the interfacial bonding of the fiber and polymer matrix. The same three varying volume percentages of each treatment used in the mechanical strength of the banana fiber are used in the pull-out testing.

Part 3.2.3: Banana Fiber Composite Testing

The final phase of this research is to determine and compare the effects of the chemical treatments and polymer additive on the mechanical properties of the final fiber-

reinforced polymer (FRP) composite. The mechanical properties of the FRP composite studied in this research include the tensile strength and tensile modulus. In this research phase, not only will the effect of reinforcing LDPE with banana fiber be determined, but the comparison of interfacial bonding improvement methods will be analyzed. For this phase, only the optimal volume percentage of each treatment will be used.

CHAPTER FOUR

Experimental Procedure

Section 4.1: Single-Fiber Tensile Testing

Part 4.1.1: ASTM standard/Test Procedure

Per the ASTM standard D3822-07, *Standard Test Method for Tensile Properties of Single Textile Fibers*, single untreated banana fibers were tensile tested at constant extension rates of 0.5 mm/min, 20 mm/min, and 100 mm/min with a sample size of 10 fibers per each extension rate. In order to test these individual fibers, square holes (20mm x 20mm) are first cut-out of cardboard squares (40mm x 40mm) and then an individual fiber (40mm) is affixed via super glue to the cardboard square such that 20mm of the fiber is exposed through the hole. Next, one side of the cardboard square is cut and then the cardboard square is placed in the grips of an Instron[®] 3344 Single-Column Testing Machine, pictured in Figure 22. Once gripped, the opposite side of the cardboard is cut, effectively setting a gage length of each sample to be 20mm. Finally, the test is performed at the designated constant extension rate, recording load and extension data at a frequency of 10Hz.

For the silane and alkaline chemically treated banana fibers, only a constant extension rate of 20 mm/min is used. Following the tensile test experiment, the cross-section of the fiber at point of fracture is imaged using a scanning electron microscope (SEM) to measure cross-sectional area. A discussion of whether or not to account for the

voids in the banana fiber, as seen in Figure 11, in the cross-sectional area using the SEM to calculate stress is found in Part 4.1.3.

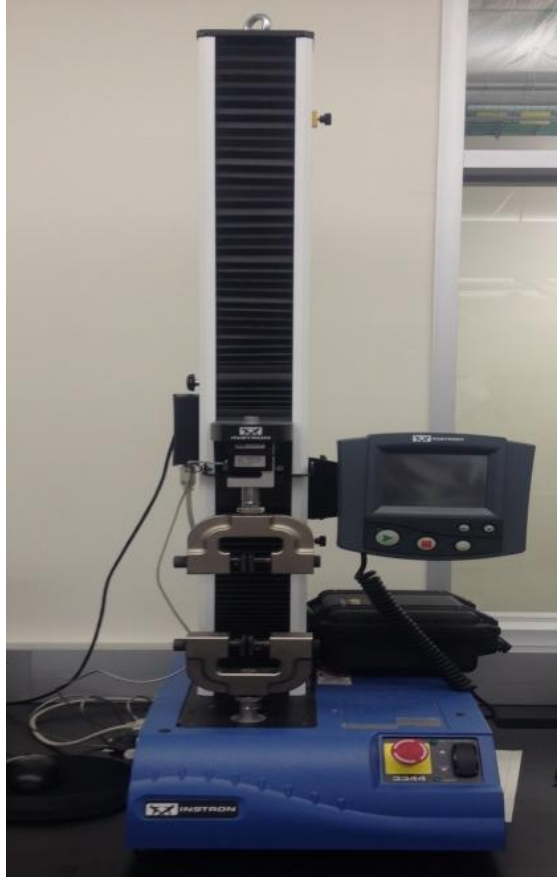


Figure 22 – Instron® 3344 Single-Column Testing Machine

Part 4.1.2: Mathematical Analysis

The mathematical analysis of the single-fiber tensile test consists of calculating stress, strain, and modulus. These simple calculations are performed on the load and extension data collected by the Instron® machine via MATLAB®. The strain is calculated by dividing the extension of the crosshead at each data point by the original gage length of 20mm. The stress is calculated by dividing the load at each data point by the cross-sectional area of the fiber, which, as discussed in Part 2.2.2, will include the voids in the fiber.

Section 4.2: Pull-Out Testing

Part 4.2.1: Sample Preparation

In order to prepare the samples for the pull-out test, bars of LDPE, approximately 40mm x 20mm x 0.4mm, are injection molded from the provided pellets. Fibers of length 40mm are independently placed between two bars of LDPE in an aluminum frame a certain embed length, where the remaining fiber is left free, or outside of the bars of LDPE. The specific embed lengths used for each sample are discussed in Part 4.2.5. The samples and aluminum frames are then pressed with a laboratory hot press at 200°C for 2 minutes. A manufactured sample ready for pull-out testing is seen in Figure 23.

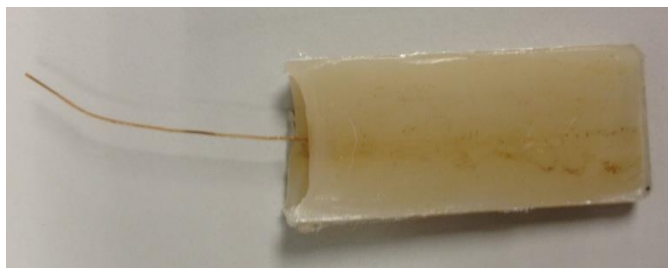


Figure 23 – Pull-out test sample

For the untreated and chemically treated fibers neat LDPE bars are used. For the maleic anhydride samples, the appropriate percentage of polyethylene-graft-maleic anhydride pellets – 2%, 4%, and 6% by weight – are hand-mixed with LDPE pellets and compounded with a single-screw extruder at the specifications listed in Table 4. The compound is then pelletized and injection molded into bars for sample preparation of the pull-out test. Finally, the free end of the fiber is affixed to a square of cardboard, much like in the single-fiber tensile testing, to improve gripping of the fiber end during testing.

Initially, tape was used to grip the fiber, but the fiber often slipped through the tape during testing.

Table 4: Single-Screw Extruder specifications for compounding MaPE/LDPE

Screw Property	Value
Screw Speed	20 RPM
Screw Diameter	25.4 mm
Dwell Time	113 seconds
Processing Temp	200°C
Feed-Type	gravity fed

Part 4.2.2: Test Procedure

Due to the lack of an ASTM standardized pull-out test procedure, the test procedure for the pull-out test follows the ASTM standard D3822-07 for tensile testing closely with only a change in the constant rate of extension. The cardboard, holding the free end of the fiber, is gripped on one end while the bar of polymer matrix is gripped on the other. A constant rate of extension of 1.2 mm/min is applied with the Instron[®] machine until the fiber completely pulls out of the polymer matrix. A slow constant rate of extension is chosen in order to avoid breaking the fiber before it has pulled out entirely. The load and extension data are recorded at a frequency of 10Hz. In order to ensure that the fiber completely pulls out of the polymer matrix, video is captured with a Scioscope Micro Zoom Video Inspection System. As discussed in Part 2.4.1, the interfacial shear strength of the pull-out test is more accurately calculated with measurement of the perimeter of the banana fiber using the SEM. So following the pull-out test, the banana fiber samples are measured for perimeter with the SEM. This perimeter measurement is performed on the side of the fiber that was embedded in the polymer matrix.

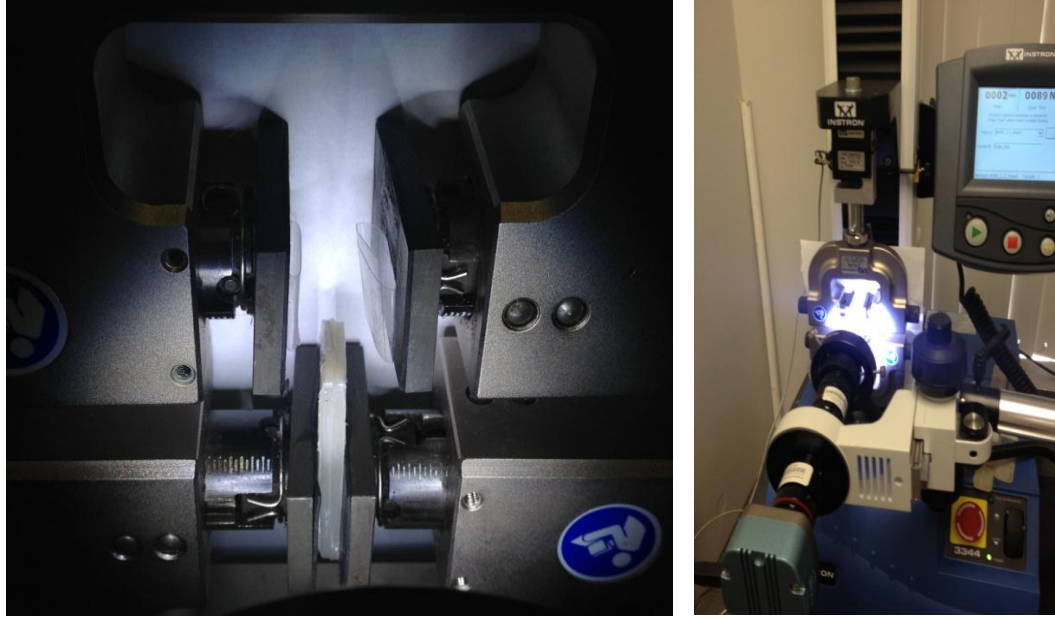


Figure 24 – Initial method of gripping fiber with tape for pull-out test

Part 4.2.3: Mathematical Analysis

As defined in Part 2.4.1, the interfacial shear strength is the shear stress at failure, or debonding. The general equation is shown in equation 1.

$$\tau = \frac{F_d}{A_c} \quad (1)$$

where τ is shear stress (MPa), F_d is the peak force measured just prior to debonding (N), and A_c is the cross-sectional area parallel to the applied force (mm^2). In this context, the cross-sectional area parallel to the applied force is the surface area of a cylinder.

The surface area of the cylinder is found using the perimeter rather than the diameter as discussed previously.

$$A_c = pL_e \quad (2)$$

Where p is the perimeter of the cylinder (mm) and L_e is the length of the cylinder in contact with the applied force, or embed length (mm). This embed length plays a

critical role in the measurement of the interfacial shear strength, and is discussed in Part 4.2.4.

Finally, the interfacial shear strength is determined using equation 3.

$$\text{---} \quad (3)$$

Part 4.2.4: Critical Embed Length

In order to obtain an accurate debond force, F_d , the fiber needs to completely pull-out of the polymer matrix. If the fiber breaks inside of the matrix, there is no way to ensure that the fiber debonded from the matrix prior to reaching fiber failure. With the micromechanical stresses exerted on the fiber by the polymer matrix, a maximum embed length can be determined to ensure complete fiber pull-out. Kim and Mai (1998) derive this maximum embed length from the micromechanical stresses acting on the fiber in their book, *Engineered Interfaces in Fiber Reinforced Composites*, which is shown in equation 4 [50].

$$\text{---} \quad (4)$$

where λ is a frictional component (approximately $\frac{1}{2}$ the coefficient of friction), σ is the asymptotic debond stress at which the fiber would completely pull out of the polymer matrix, σ_1 is the crack tip debond stress at which the fiber would fracture inside the polymer matrix before complete pull-out, σ_{TS} is the fiber tensile strength, z_{max} is the embed length minus the partially debonded region (assumed to be 10% of the embed length), and ω is a component of matrix-fiber moduli ratio, Poisson's ratio and fiber volume fraction. This ω component is shown in equation 5 [50].

$$\omega = \frac{\alpha v_f}{\alpha v_f + \gamma v_m} \quad (5)$$

where α is the modulus of the matrix divided by the modulus of the fiber, γ is the fiber volume fraction, and v_f and v_m are Poisson's ratios of the fiber and matrix, respectively [50].

Initially, samples of the untreated banana fiber in neat LDPE were prepared with an embed length of approximately 10mm. The embed lengths are approximate due to movement of fibers during the pressing stage of manufacturing. Exact embed lengths are determined by subtracting the elastic extension of the fiber from the total extension recorded during each pull-out test. The stress-strain results from these initial experiments, both of those that completely pulled out as well as those that did not, provided the necessary values to calculate the maximum embed length of untreated banana fiber in neat LDPE. This calculated maximum embed length is 7.39mm. All remaining results of untreated banana fiber in neat LDPE are from samples prepared with an approximate embed length of 5mm to ensure complete pull-out.

While this approximate embed length allowed for a much greater prevalence of accurate samples for the untreated banana fiber in neat LDPE, the treated fibers and polymer modified samples continued to see failure of the fiber inside the polymer matrix. The maximum embed length was recalculated with the unique fiber tensile strengths of the banana fibers as well as the new asymptotic and crack tip debond stresses of each modification. The maximum embed length dropped to an average of 4.47mm for the modifications. As a result, the embed lengths of the fibers for the modified samples were prepared at an embed length of approximately 2mm.

Section 4.3: Composite Testing

Part 4.3.1: Sample Preparation

In order to prepare the banana fiber-reinforced low-density polyethylene composites, the banana fiber is hand-mixed with LDPE pellets, or polyethylene-graft-maleic anhydride pellets, in order to achieve a fiber volume fraction of 30%, and compounded with a single-screw extruder at the specifications listed in Table 4 in Part 4.2.1. The compound is then pelletized and injection molded using a DSM Xplore Micro 10cc Injection Molding Machine, shown in Figure 25. This machine was used to injection mold the composite pellets into ASTM standard D638-03 Type 1 tensile ‘dog-bone’ bars. The ASTM tensile ‘dog-bone’ mold is shown in Figure 26, and its dimensions are found in Table 5.

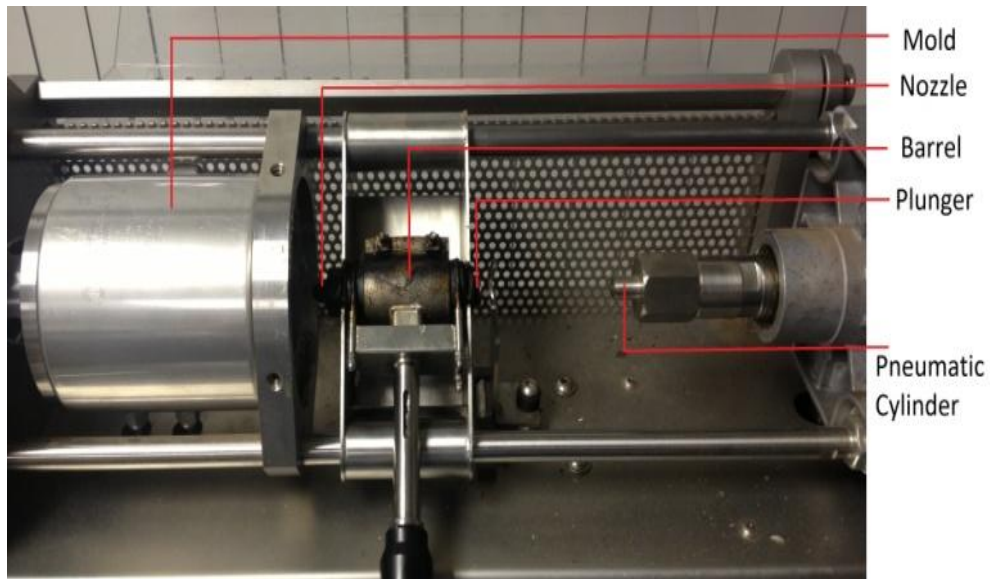


Figure 25 – DSM Xplore Micro 10cc Injection Molding Machine



Figure 26 – ASTM D638-03 Type 1 tensile ‘dog-bone’ bar mold

Table 5: ASTM dimensions of tensile ‘dog-bone’ bar mold

Mold Dimension	Value (in)
Width of narrow section	0.5
Length of narrow section	2.25
Total width	0.75
Total length	6.5
Thickness	0.125
Radius of fillet	3

Part 4.3.2: Tensile Testing

The tensile tests were performed according to the ASTM standard D638-03 on a tensile testing machine. At least five tests are performed at each strain-rate per the ASTM standard. The loading rate is strain-controlled because it is safer and easier to monitor due to its lack of need for an external feedback loop control. The strain rate is measured using crosshead motion at a constant rate of extension of 20 mm/min. The load and extension data are recorded at a frequency of 10Hz.

CHAPTER FIVE

Strength Of Individual Banana Fibers

Section 5.1: Results of Tensile Test: Untreated Fibers

As described in Part 4.1.1, tensile test performed on the untreated banana fibers include constant rates of extension of 0.5 mm/min, 20 mm/min, and 100 mm/min, per ASTM standard D3822-07. These results all use the full SEM measured area – including the voids in the fiber – as discussed in Part 2.2.2. For the sake of validation, however, a batch of samples was tested and calculated for true stress – subtracting the voids in the fiber – and compared with published data from Kulkarni et al. These results are shown first, in Figure 27.

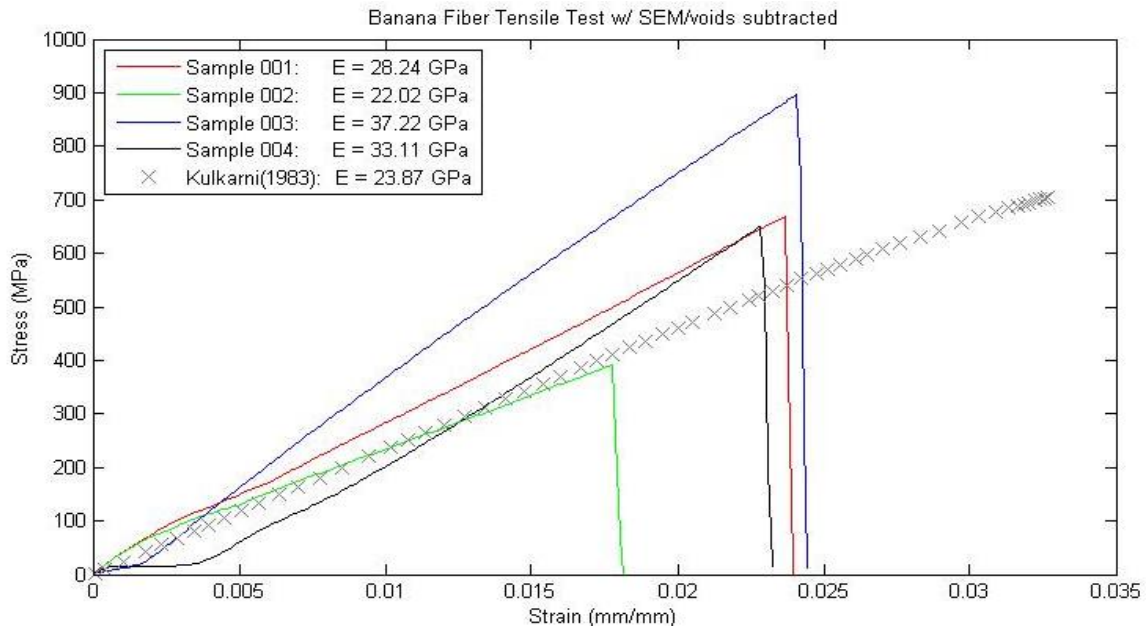


Figure 27 – Banana fiber tensile test comparison with published data from Kulkarni et al [21]

As seen above, the tensile test results of this batch – ran at a constant rate of extension of 0.5 mm/min – match closely with the published data. There is, however, significant variability with a standard deviation of 6.54 GPa. This large deviation will continue to be apparent throughout the mechanical testing results for the banana fiber. This is due largely to the complex, organic nature of the natural lignocellulosic fiber. For instance, moisture content can be significantly different fiber-to-fiber, as well as its botanical composition. Another significant contributor to the high variation in results is the damage within a single fiber, as was shown in Figure 18. This damage is rampant in natural fibers, and affects the effective diameter – the diameter calculated from the true cross-sectional area, as measured by SEM – of the fiber. For this reason, the assumption of a constant cross-sectional area throughout the span of the fiber for calculating stress is poor. Although the ASTM standard only calls for five samples, additional samples are tested to calculate as accurate an average for each batch as possible.

The next three figures contain the stress-strain curves for the three batches of samples at the specified rates of extension, per the ASTM standard. In Figure 28 and Figure 29 – CRE of 0.5 mm/min and 20 mm/min, respectively – the fibers clearly exhibit a linearly elastic, brittle response, which one would expect to observe in a single fiber. Figure 30 – CRE of 100 mm/min – however, exhibits more ductile responses indicating these fibers are sensitive to strain rate at higher rates of extension.

Table 6 summarizes the averages of each batch of tests and includes their standard deviations. These results will serve as the baseline when comparing the effects of the chemical treatments and polymer additive.

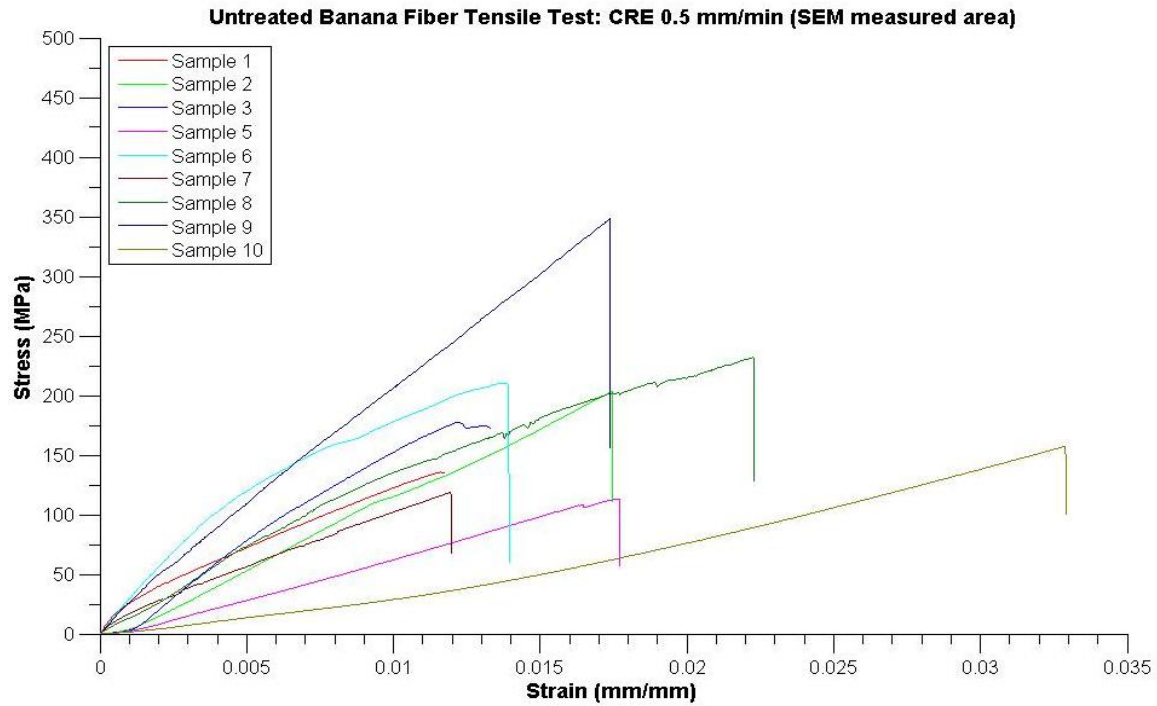


Figure 28 – Untreated banana fiber tensile test results for a constant rate of extension of 0.5 mm/min

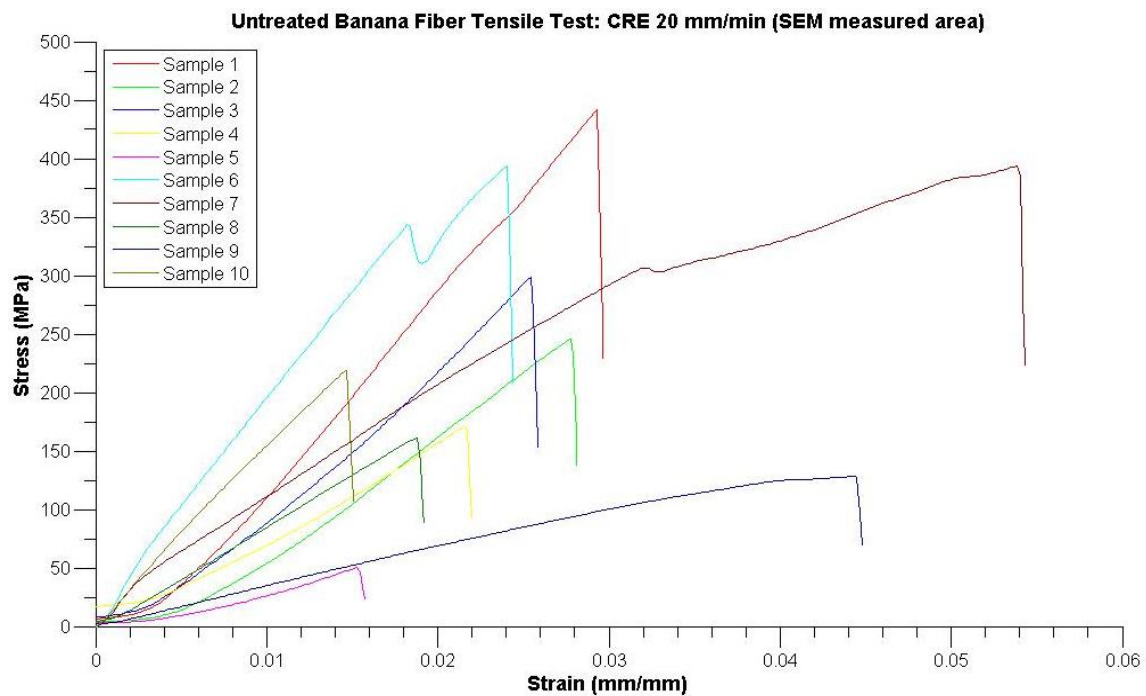


Figure 29 – Untreated banana fiber tensile test results for a constant rate of extension of 20 mm/min

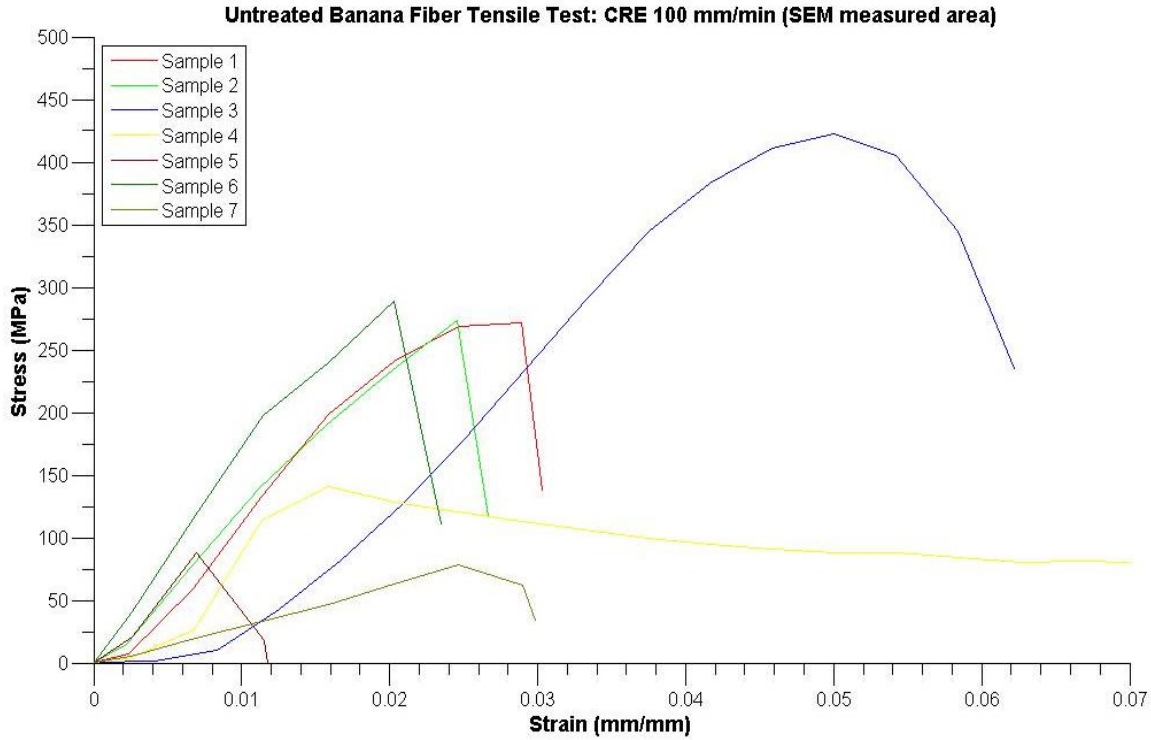


Figure 30 – Untreated banana fiber tensile test results for a constant rate of extension of 100 mm/min

Table 6: Average untreated banana fiber tensile properties with varying rates of extensions

Constant Rate of Extension (mm/min)	Ultimate Tensile Strength (MPa)	Strength Standard Deviation	Tensile Modulus (GPa)	Modulus Standard Deviation
0.5	188.47	72.91	11.79	4.73
20	272.14	160.18	13.33	5.74
100	204.57	128.07	9.08	3.73

Section 5.2: Results of Tensile Test: (3-aminopropyl) Trimethoxysilane Treated Fibers

Part 5.2.1: 1% Results

Due to the higher ultimate tensile strength average at the constant rate of extensions of 20 mm/min, this is the only CRE used for the remaining tensile tests. For the banana fibers treated with 1% by volume (3-aminopropyl) trimethoxysilane – henceforth referred to as silane treatment – it should be noted that some samples are

visually more degraded than others. This is thought to be a result of insufficient drying, possibly due to these fibers not fully separated prior to drying. Another possibility is that the fiber was damaged in its original, untreated state. However, a fiber's structure was not followed from its untreated state through its treated state, and would be an excellent study for future work.

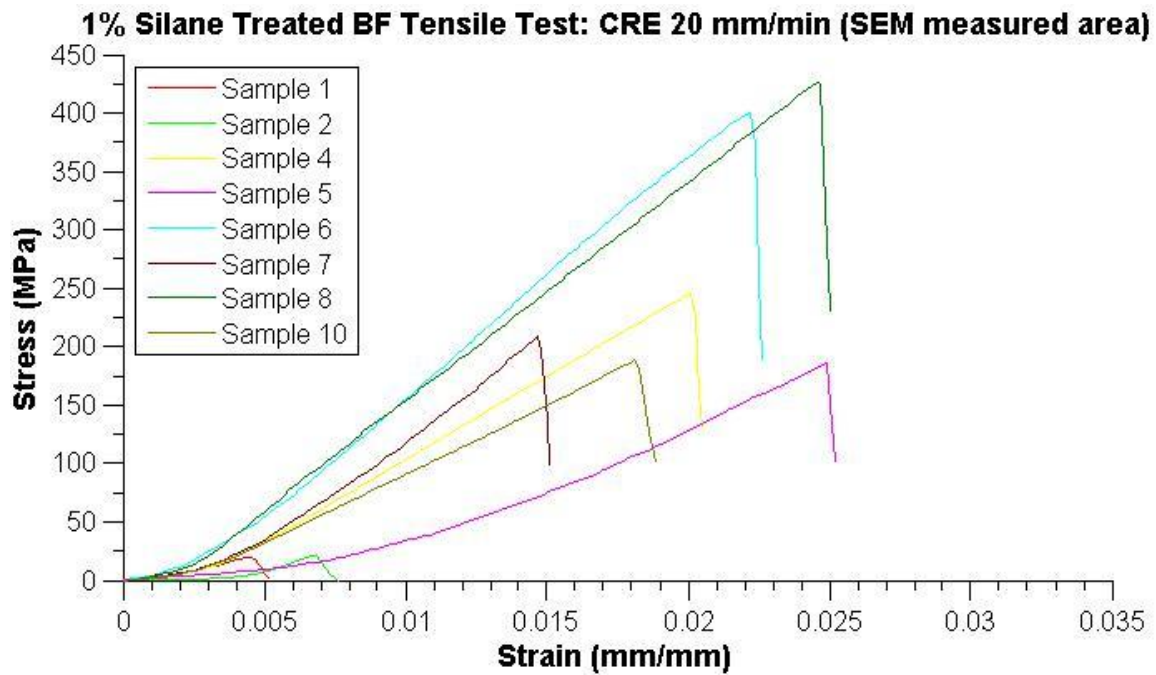


Figure 31 – 1% (3-aminopropyl) trimethoxysilane treated banana fiber tensile test results

The significance of initial fiber damage is critical. For instance, sample 1, as seen in Figure 31, has a very low ultimate tensile strength and modulus, while sample 6 has a dramatically higher ultimate tensile strength and modulus. SEM photographs of both samples at approximately 300x magnification were taken prior to tensile testing for damage effects consideration.

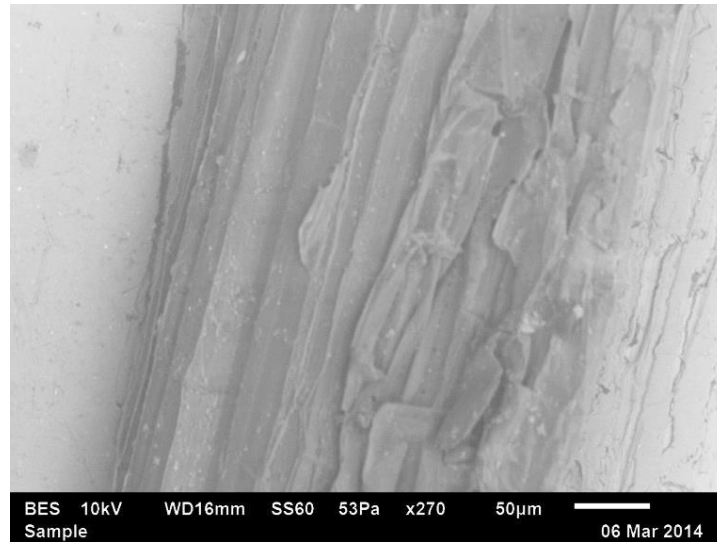


Figure 32 – SEM photograph of sample 1, 1% silane treated banana fiber, at 270x magnification

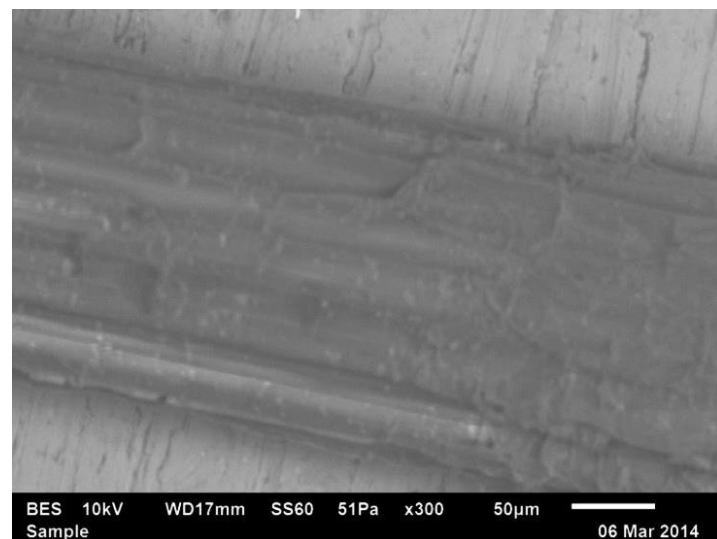


Figure 33 – SEM photograph of sample 6, 1% silane treated banana fiber, at 300x magnification

Visual damage is clearly seen in sample 1, while sample 6 is more typical of a clean, silane treated sample (similar to that seen in Figure 19). Although this damage significantly affects the average tensile properties and significantly contributes to the standard deviation, these samples remain in the results, as it would simply be too costly to separate damaged fibers from undamaged fibers prior to processing.

Part 5.2.2: 3% Results

Figure 34 displays the stress-strain curves for samples treated with 3% silane. It is again noted that two samples are measured to be much greater in strength than the remaining samples. This is again attributed to pre-existing damage in the fiber.

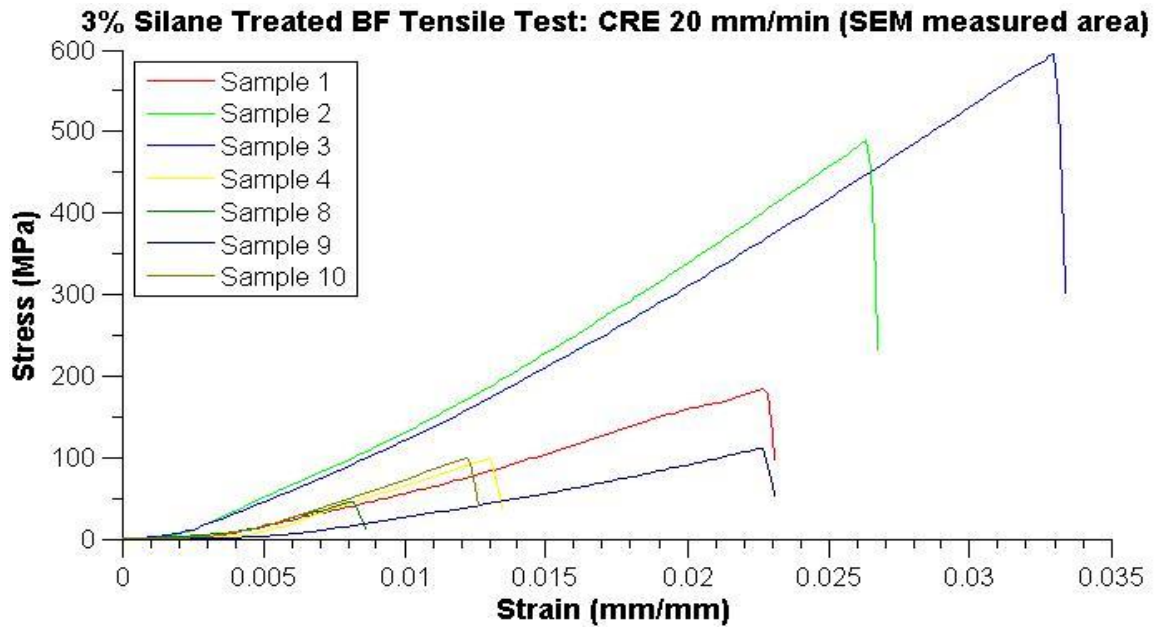


Figure 34 – 3% (3-aminopropyl) trimethoxysilane treated banana fiber tensile test results

Part 5.2.3: 5% Results

Figure 35 displays the stress-strain curves for samples treated with 5% silane. An observation of all the silane treated fiber tensile test results, although especially pronounced in the samples treated with 5% silane, is the less linear elastic behavior. Rather than being purely linear elastic, such as the low strain rate untreated fiber results, the fibers treated with silane tend to exhibit nonlinear elastic behavior near the fracture point. The cause of this nonlinear behavior could be contributed to the increase in hydrogen bonding as an effect of the silane treatment. As the stress on the fiber increases,

the weak hydrogen bonding fails initially, causing an increase in modulus near the fracture point of the stress-strain curve.

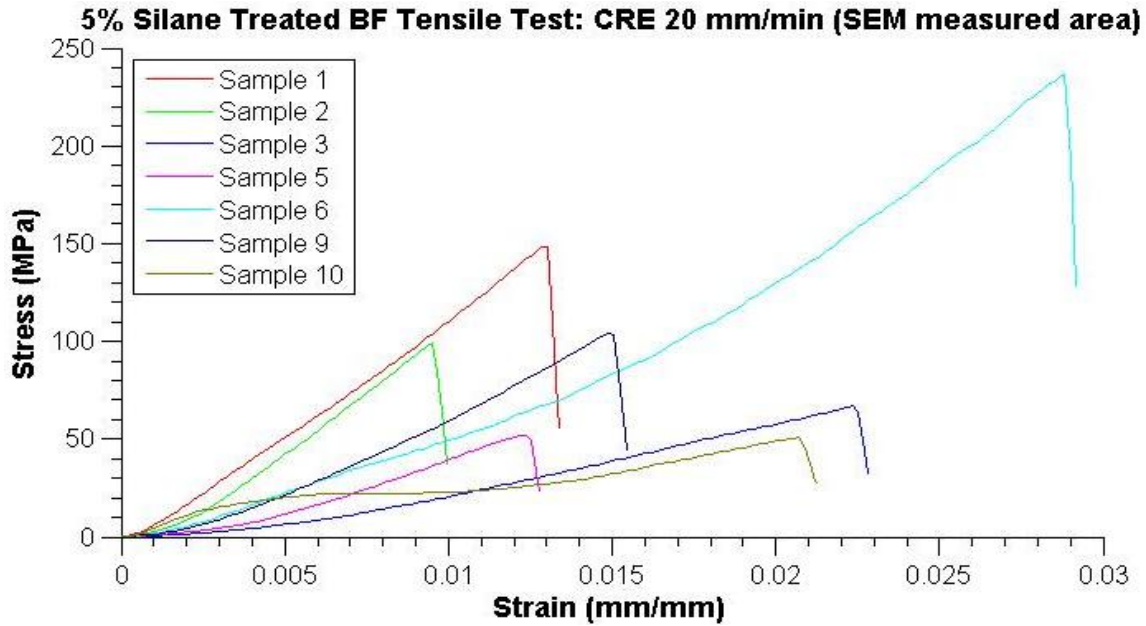


Figure 35 – 5% (3-aminopropyl) trimethoxysilane treated banana fiber tensile test results

Part 5.2.4: Comparison

Table 7: Average silane treated banana fiber tensile properties with varying concentrations

vol. % of Silane	Ultimate Tensile Strength (MPa)	Strength Standard Deviation	Tensile Modulus (GPa)	Modulus Standard Deviation
1	192.02	140.63	10.27	5.77
3	192.98	180.35	9.11	4.85
5	115.39	66.25	7.76	4.26

From Table 7, a summary of the average results for various concentrations of silane treatment, there is a significant decrease in both strength and modulus as the concentration reaches 5% by volume, while there is no statistically different change between 1% and 3%. The significant decrease in strength is expected as the chemical treatment significantly modifies the structural surface of the fiber.

Section 5.3: Results of Tensile Test: Sodium Hydroxide Treated Fibers

Part 5.3.1: 4% Results

Through the process of mercerization, the reduction of lignin and hemicellulose in the fiber structure along with the additional fiber damage, or increased roughness, to the fiber's surface, is thought to significantly decrease the mechanical strength of the fiber. This hypothesis is verified through the tensile tests of sodium hydroxide treated banana fibers in concentrations of 4%, 6%, and 8% by volume. In Figure 36, the tensile tests results of the 4% sodium hydroxide treated fibers, there are significantly low strength results with a few outlying, high-strength, tests. With the increased fiber damage and surface roughness, it is reasonable to observe a higher deviation in results, due to the lack of uniformity in fiber surface erosion during the treatment process.

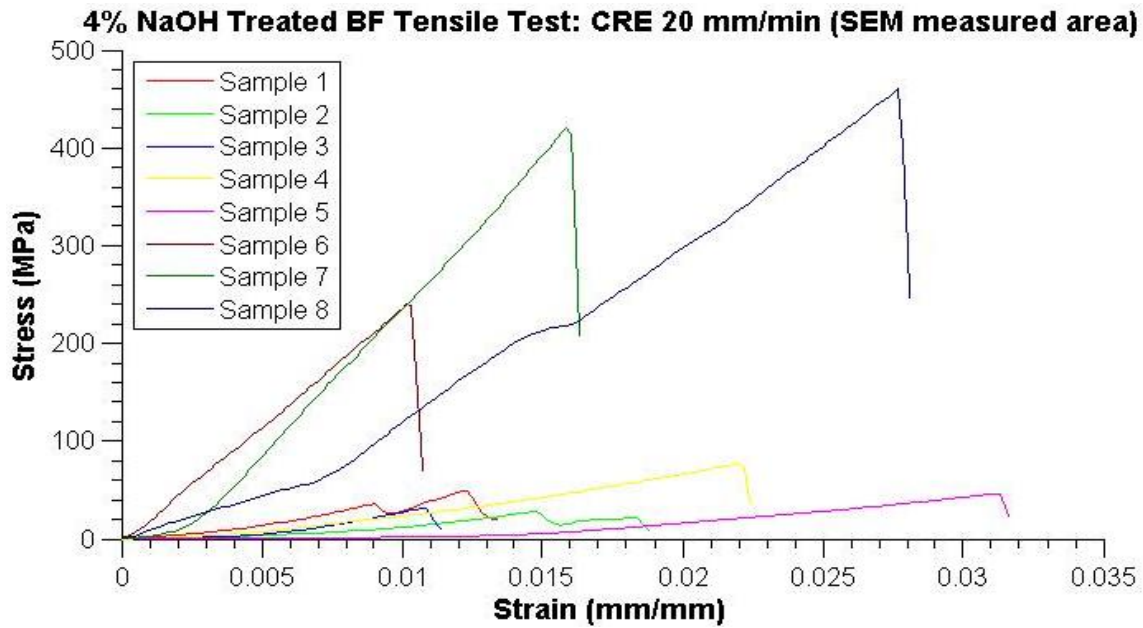


Figure 36 – 4% sodium hydroxide treated banana fiber tensile test results

Part 5.3.2: 6% Results

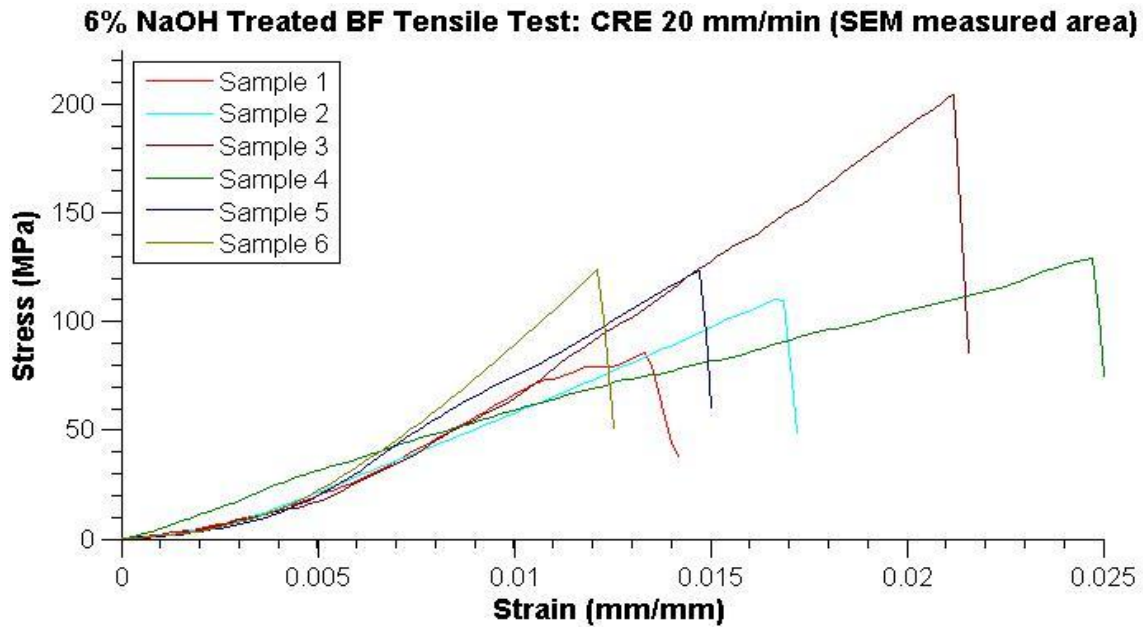


Figure 37 – 6% sodium hydroxide treated banana fiber tensile test results

Uniquely, the 6% sodium hydroxide treated banana fiber resulted in a dramatically reduced standard deviation. These treated fibers exhibit merely an approximate 40 MPa deviation in tensile strength compared to a more typical 130 MPa standard deviation in untreated fibers. A possibility of this consistency is a lack of initially damaged fibers in the sample population, as well as an even distribution of chemical treatment to the fibers.

Part 5.3.3: 8% Results

Similar to the high concentration of silane treatment, the highest concentration of the sodium hydroxide treatment results in a typical nonlinear elastic behavior. Again, the effect of the chemical treatment on the fiber surface properties is attributed to this nonlinear elastic response. Through increased surface roughness, reduction of the lignin and hemicellulose, as well as polymerization of the surface, these highly concentrated

sodium hydroxide treated banana fibers exhibit relatively high tensile strengths and moduli.

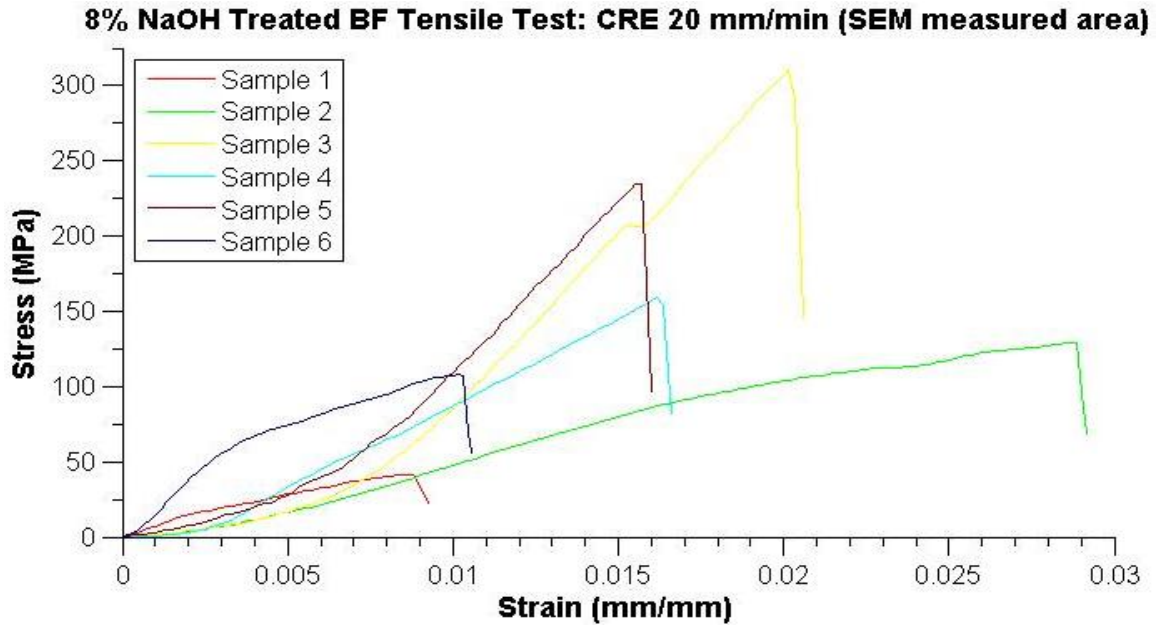


Figure 38 – 8% sodium hydroxide treated banana fiber tensile test results

Part 5.3.4: Comparison

Table 8: Average sodium hydroxide treated banana fiber tensile properties with varying concentrations

vol. % of NaOH	Ultimate Tensile Strength (MPa)	Strength Standard Deviation	Tensile Modulus (GPa)	Modulus Standard Deviation
4	162.56	150.81	9.02	8.73
6	129.40	39.87	7.75	1.97
8	175.73	112.55	7.48	4.90

Unlike the silane treatment results, there is not a noticeable trend in the sodium hydroxide treatment results, shown in Table 8. With the high standard deviation, it is difficult to assert any statistically significant distinction between the concentrations of the sodium hydroxide treatment.

Section 5.4: Comparison of Tensile Test Results for Various Treatments

A full comparison of the ultimate tensile strength results are shown in Figure 39 and the full comparison of the initial tensile modulus results are shown in Figure 40. The error bars shown on these figures are the 95% confidence intervals, or standard error measurements (SEM) for each sample population for each treatment concentration. Although these error bars or significant and overlap, it is important to remember that the large deviation occurs from damaged fiber pre-processing.

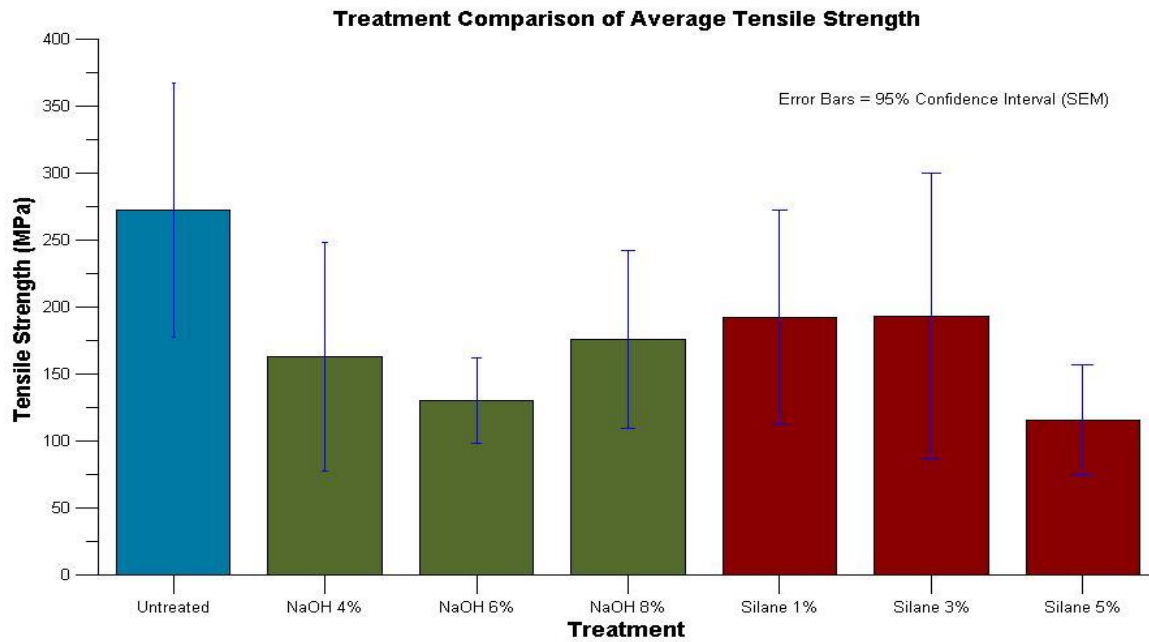


Figure 39 – Comparison of tensile strength for various fiber chemical treatments

Concerning the comparison of the tensile strength averages, one can note immediately that although the confidence intervals overlap for a number of treatments, both of the chemical treatments seem to decrease the ultimate tensile strength of the individual banana fibers. For instance, the 6% sodium hydroxide treatment saw a

decrease of 52.5% from untreated banana fiber in ultimate tensile strength, while the 5% silane treatment saw an even greater decrease of 57.6%.

This trend is also apparent in the initial tensile modulus comparison. Both chemical treatments reduce the modulus of the untreated banana fiber to a significant extent. An interesting trend that is clearly shown in the figure below includes a distinctive reduction of modulus with higher volume concentration of the treatment. For instance, the 1% silane treatment reduced the modulus of the banana fiber by 22.9%, while the 5% silane treatment reduced the modulus by 41.8%. This trend is consistent with the idea that additional alteration of the fiber's surface or reduction in key structural composition reduces the fiber's stiffness.

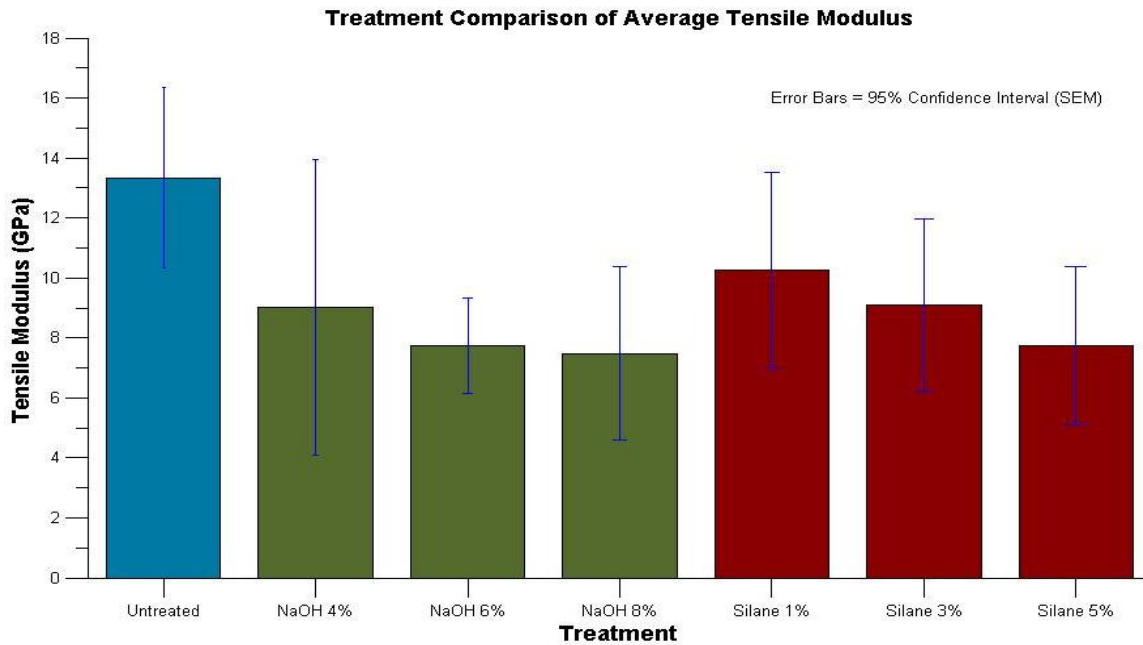


Figure 40 – Comparison of tensile modulus for various fiber chemical treatments

CHAPTER SIX

Interfacial Bonding Of Banana Fiber & Low-Density Polyethylene

Section 6.1: Results of Pull-Out Testing for Untreated Fibers

Part 6.1.1: Initial Untreated Results

The typical load-extension curve for the pull-out test is shown in Figure 41. The curve exhibits a non-linear behavior, which is consistent with a ductile matrix. The immediate drop-off from the peak load is attributed to the failure of the interfacial bond. After this failure, a steady decreasing slope reveals the measurement of friction as the fiber is pulled the rest of the way out of the matrix.

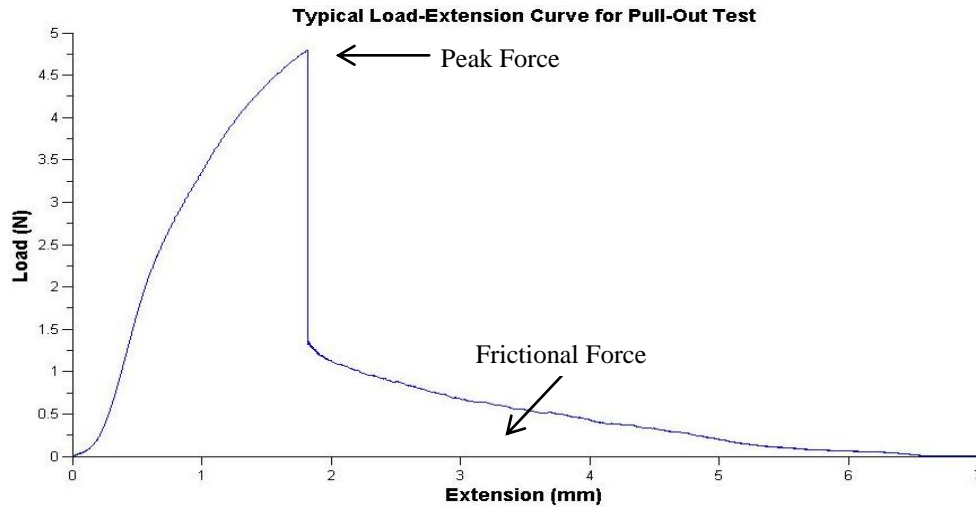


Figure 41 – Typical load-extension curve for pull-out test

The peak load, just prior to debonding, is used for the interfacial shear strength calculations. The embed length of the fiber in the polymer matrix can also be measured

with this curve by subtracting the extension due to the elasticity of the fiber from the total extension recorded prior to the load going to zero.

In order to determine the maximum, or critical, embed length, per equation 4 in Part 4.2.5, the asymptotic debond stress and the crack tip debond stress are assumed to be the peak stress found in experiments that completely pulled out and the peak stress found in experiments that prematurely fractured in the polymer matrix, respectively. An initial batch of tests was run of the untreated samples with embed lengths of approximately 10 mm. Of these initial six samples, only sample 6 completely pulled out of the matrix. The average peak stress of the previous five samples was found to be 160.56 MPa, which is then assumed to be the crack tip debond stress. The peak stress of sample 6 was found to be 147.17 MPa, which is assumed to be the asymptotic debond stress. These stresses are used in equation 4 to determine a maximum embed length of 7.39 mm for untreated banana fiber in neat LDPE.

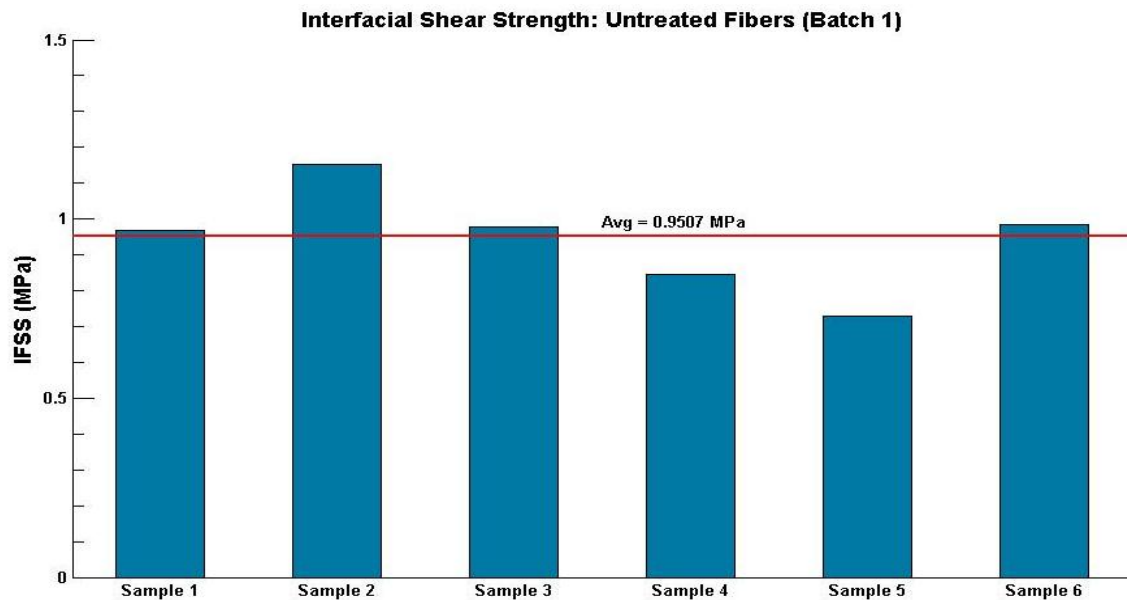


Figure 42 – Interfacial shear strength of untreated banana fiber in LDPE at embed length of approx. 10mm

Although only one sample in this first batch completely pulled out, the interfacial shear strengths are shown above for comparison.

Part 6.1.2: Untreated Results w/ Critical Embed Length

With the calculated maximum embed length, a second batch of untreated samples were run with an approximate embed length of 5 mm, of which all samples that did not break during processing completely pulled out. The IFSS results for these samples are shown in Figure 43.

It is noted that the average interfacial shear strength does not rise significantly between the two batches of samples. This can possibly be attributed to some of the fibers in batch 1 fracturing in the matrix during the friction stage – after debonding from the polymer matrix – causing the IFSS to be near the actual value. The important observation, however, is the significantly low IFSS value. The IFSS value of approximately 1 MPa reveals an extremely poor interfacial bonding between the untreated banana fiber and the neat LDPE.

Compared to other IFSS studies of natural fiber in similar polymer matrices found in literature, this IFSS is quite low. Figure 44 shows a comparison of the average IFSS of untreated banana fiber in LDPE with henequén fiber in high-density polyethylene (HDPE) from Valadez et al (1999), as well as with untreated banana fiber in polyurethane (PU) from Merlini et al (2011). The relatively low calculated IFSS confirms a poor interfacial bonding between the fiber and the polymer matrix. This IFSS value will serve as a baseline for interfacial bonding improvement as a result of modification. Table 9 summarizes the results for each of these four samples in batch 2 of the untreated banana fiber in neat LDPE.

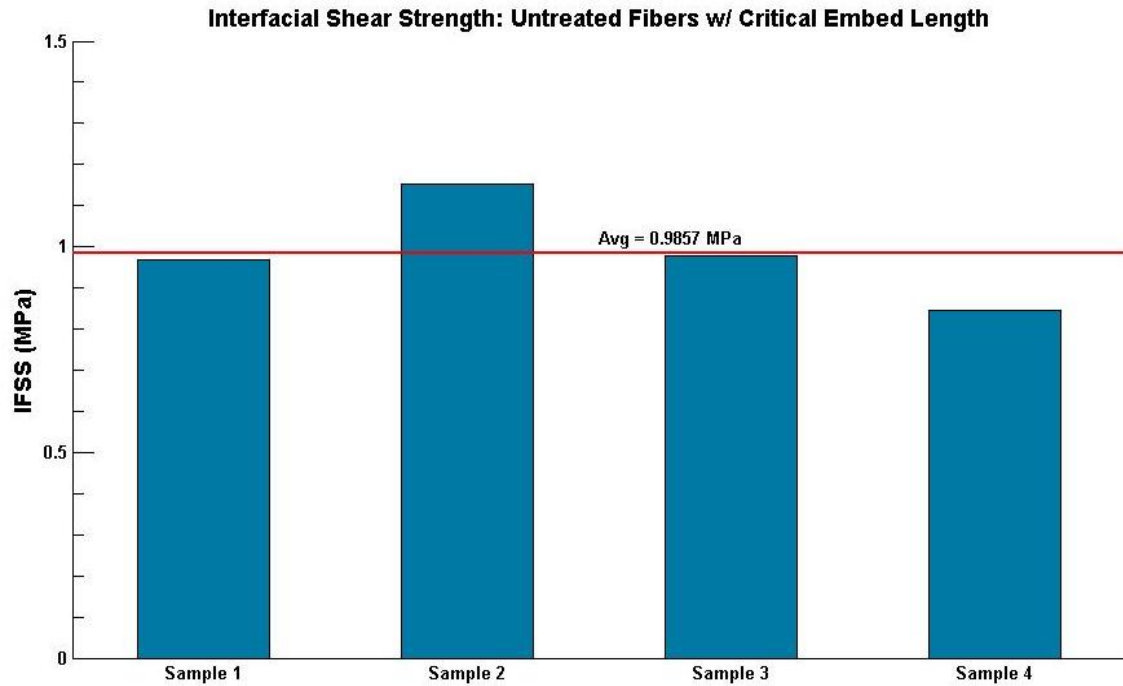


Figure 43 – Interfacial shear strength of untreated banana fiber in LDPE at embed length of approx. 5mm

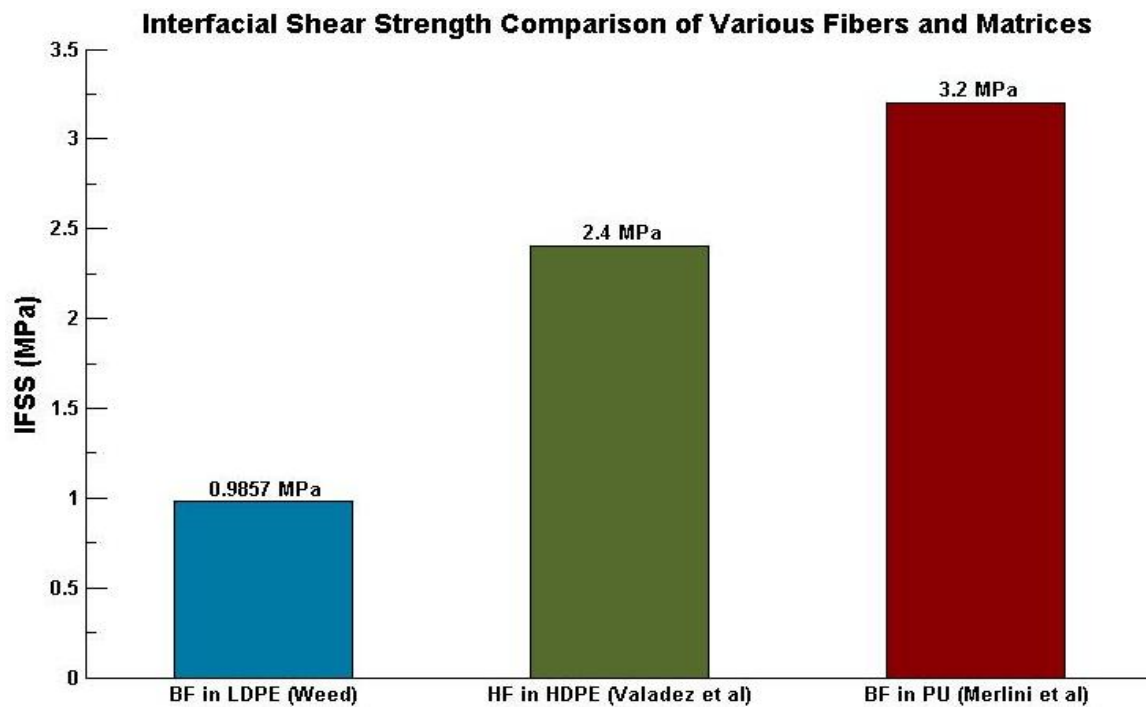


Figure 44 – IFSS comparison of banana fiber in LDPE, henequén fiber in HDPE from Valadez et al [12], and banana fiber in castor oil polyurethane from Merlini et al [43]

Table 9: Summary of untreated banana fiber in LDPE pull-out test results

Sample #	Perimeter (μm)	Embed Length (mm)	Peak Force (N)	IFSS (MPa)
1	779.2	6.69	5.05	0.968
2	639.8	6.50	4.79	1.152
3	1099.3	0.70	0.75	0.978
4	1106.0	1.56	1.45	0.845
Avg. IFSS		Std. Dev.	= 0.126	

Section 6.2: Results for (3-aminopropyl) Trimethoxysilane Treated Fibers

Part 6.2.1: 1% Results

For the banana fibers treated with 1% silane treatment, the average IFSS increased by 89%. The results are shown in Figure 45 and summarized in Table 10.

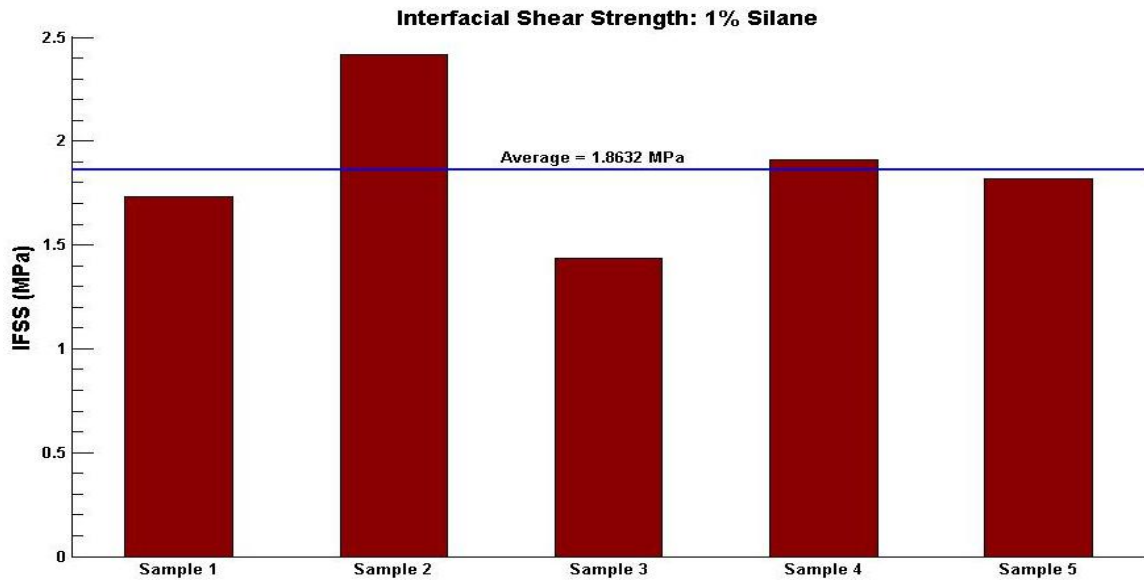


Figure 45 – Interfacial shear strength of 1% silane treated banana fiber in LDPE

Table 10: Summary of 1% silane treated banana fiber in LDPE pull-out test results

Sample #	Perimeter (μm)	Embed Length (mm)	Peak Force (N)	IFSS (MPa)
1	694.1	7.84	9.43	1.733
2	499.7	4.73	5.72	2.416
3	735.2	6.10	6.45	1.438
4	494.1	9.00	8.49	1.910
5	638.2	10.63	12.35	1.821
Avg. IFSS		Std. Dev.	= 0.356	

Although the critical embed length is calculated to be 7.39 mm for untreated banana fiber in neat LDPE, it is noted that this is not the same critical embed length for the 1% silane treated fibers. For instance, Sample 5, as seen in Table 10, has an embed length of 10.63mm. This is due to the change in mechanical properties of the fiber as a result of the treatment. In fact, each treatment along with each concentration of each treatment corresponds with a unique critical embed length, due to its unique micromechanical stresses placed on the single fiber in the polymer matrix.

Part 6.2.2: 3% Results

As the concentration of the silane treatment is increased to 3%, there is virtually no change in average interfacial shear strength; however, there is a significantly larger deviation between samples. As seen in Table 11, there is not necessarily a correlation between either the perimeter, embed length, or peak force and the interfacial shear strength. Rather, the significant deviation is attributed to manufacturing process, as often fibers tend to not embed straight in the polymer matrix. It is also possible that some fibers are more exposed than others to the silane treatment during soaking.

Table 11: Summary of 3% silane treated banana fiber in LDPE pull-out test results

Sample #	Perimeter (μm)	Embed Length (mm)	Peak Force (N)	IFSS (MPa)
1	506.7	1.69	1.96	2.289
2	1400	3.00	4.53	1.078
3	574.7	0.62	0.45	1.270
4	620.5	0.45	0.69	2.450
5	671.6	0.58	0.41	1.042
6	738.5	2.38	5.46	3.111
Avg. IFSS	= 1.873	Std. Dev.	= 0.863	

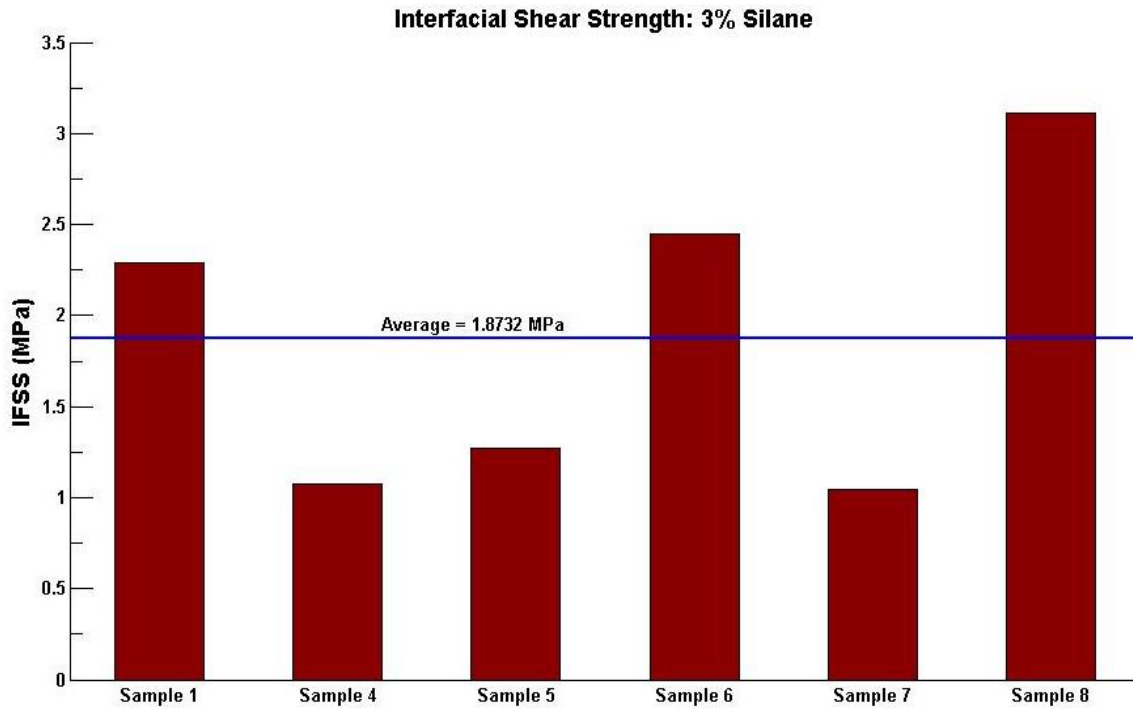


Figure 46 – Interfacial shear strength of 3% silane treated banana fiber in LDPE

Part 6.2.3: 5% Results

The results of the highest concentration of silane treatment tested, 5% by volume, are seen in Figure 47 and Table 12. An interesting observation concerning these results is the significant increase in interfacial bonding. While 1% and 3% silane treatment resulted in similar IFSS, 5% silane almost quadrupled in shear strength. This substantial increase is attributed to the presence of additional functional groups which bond with both the fiber and the polymer matrix. Another interesting object to note is the extremely low embed length for these samples. Due to the significant increase in IFSS, the critical embed length for the pull-out test is considerably smaller.

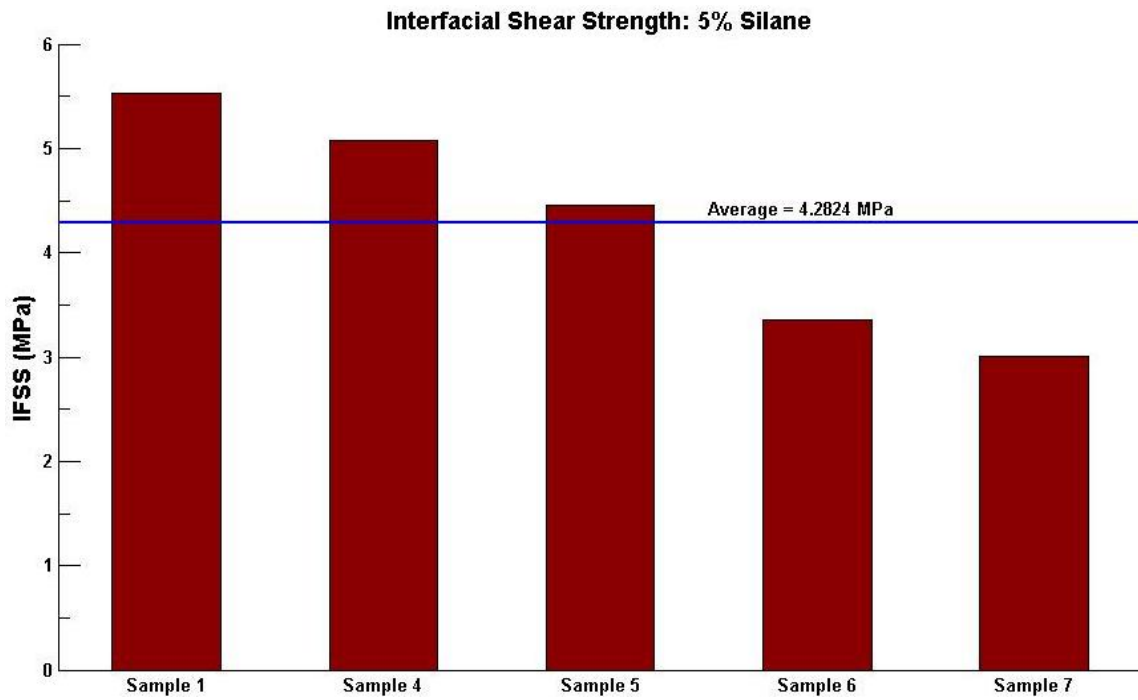


Figure 47 – Interfacial shear strength of 5% silane treated banana fiber in LDPE

Table 12: Summary of 5% silane treated banana fiber in LDPE pull-out test results

Sample #	Perimeter (μm)	Embed Length (mm)	Peak Force (N)	IFSS (MPa)
1	767.1	0.55	2.32	5.527
2	572.6	0.31	0.91	5.069
3	820.0	0.43	1.57	4.452
4	1385	0.41	1.88	3.353
5	1026	0.50	1.55	3.011
Avg. IFSS		Std. Dev.	= 1.082	
			= 4.282	

Section 6.3: Results for Sodium Hydroxide Treated Fibers

Part 6.3.1: 4% Results

As was the case for the tensile test results of the sodium hydroxide treated fibers, the pull-out test results for these specific treated fibers have a high standard deviation. This is largely attributed to the variation in the surface roughness created and amplified

by the presence of sodium hydroxide. Due to both this surface roughness as well as the lower tensile properties of the treated fibers, the peak force and critical embed length must be relatively small, as compared to untreated fiber in neat LDPE, in order to avoid fiber fracture prior to pull-out. The results of the pull-out tests for sodium hydroxide, 4% by volume, treated fibers are found in Figure 48 and Table 13, below.

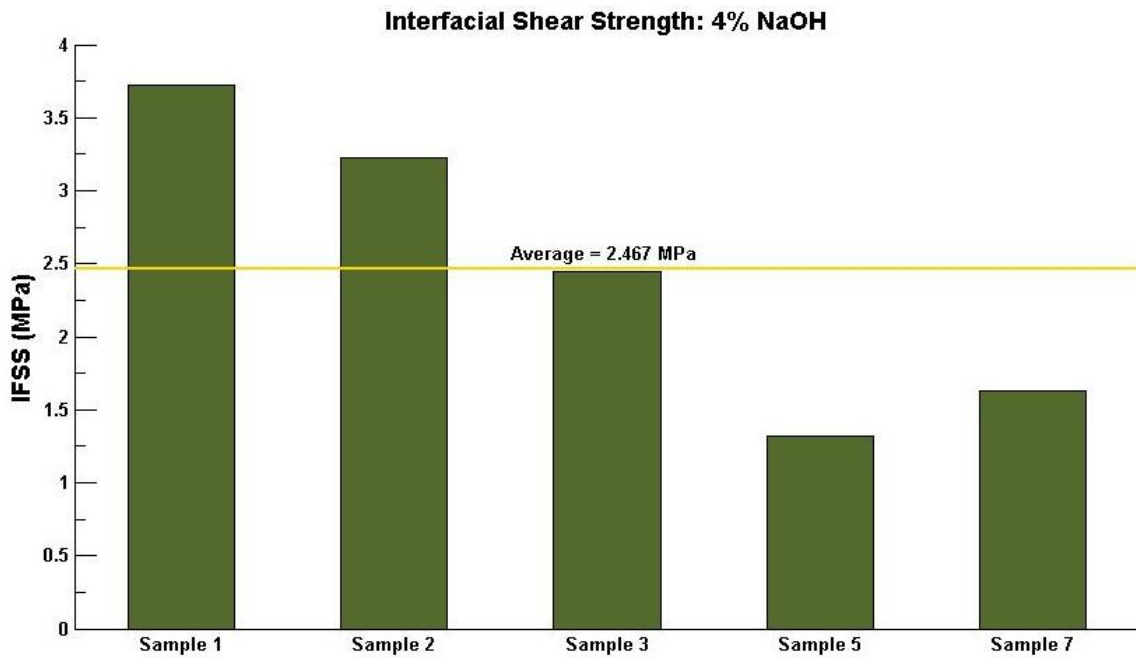


Figure 48 – Interfacial shear strength of 4% NaOH treated banana fiber in LDPE

Table 13: Summary of 4% NaOH treated banana fiber in LDPE pull-out test results

Sample #	Perimeter (μm)	Embed Length (mm)	Peak Force (N)	IFSS (MPa)
1	598.0	2.20	4.90	3.720
2	411.1	3.82	5.06	3.226
3	559.3	1.66	2.27	2.444
4	512.5	1.06	0.72	1.319
5	611.5	2.07	2.05	1.625
Avg. IFSS		Std. Dev.	= 1.021	
			= 2.467	

Part 6.3.2: 6% Results

The results of the 6% silane treated fiber pull-out tests are seen in Figure 49 and Table 14. The results are typical of the sodium hydroxide treated fiber pull-out tests. Both the results and sources of deviation are similar to the 4% concentration.

Table 14: Summary of 6% NaOH treated banana fiber in LDPE pull-out test results

Sample #	Perimeter (μm)	Embed Length (mm)	Peak Force (N)	IFSS (MPa)
1	996.6	2.00	3.45	1.731
2	748.7	2.00	2.00	1.337
3	838.5	3.00	2.47	0.984
4	360.2	2.14	1.79	2.327
5	634.9	2.99	3.50	1.843
6	1231	2.90	5.74	1.609
7	425.1	2.00	2.34	2.755
Avg. IFSS		Std. Dev.		= 0.594

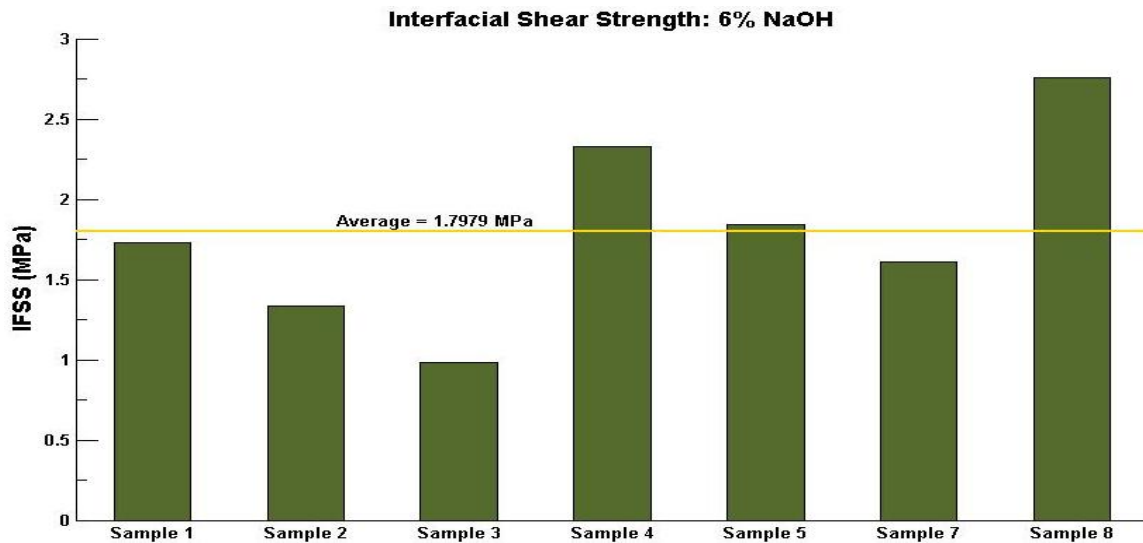


Figure 49 – Interfacial shear strength of 6% NaOH treated banana fiber in LDPE

Part 6.3.3: 8% Results

The results of the 8% silane treated fiber pull-out tests are seen in Figure 50 and Table 15. It should be noted that the fibers at this high of sodium hydroxide concentration

begin to lose substantial mechanical structure. Due to the weaker tensile properties of the treated fiber, the critical embed length and peak force is forced to maintain a low range. Another effect of this weaker fiber tensile strength is the large deviation, as have seen be typical of sodium hydroxide treated fibers.

Table 15: Summary of 8% NaOH treated banana fiber in LDPE pull-out test results

Sample #	Perimeter (μm)	Embed Length (mm)	Peak Force (N)	IFSS (MPa)
1	1428	2.00	8.28	2.901
2	2000	0.80	2.42	1.510
3	3500	1.17	5.13	1.254
4	1587	0.69	3.60	3.299
5	800	0.55	0.77	1.749
6	358.5	1.05	1.70	4.550
7	1012	1.01	2.80	2.736
8	1114	1.61	2.52	1.404
Avg. IFSS		Std. Dev.		
= 2.425			= 1.153	

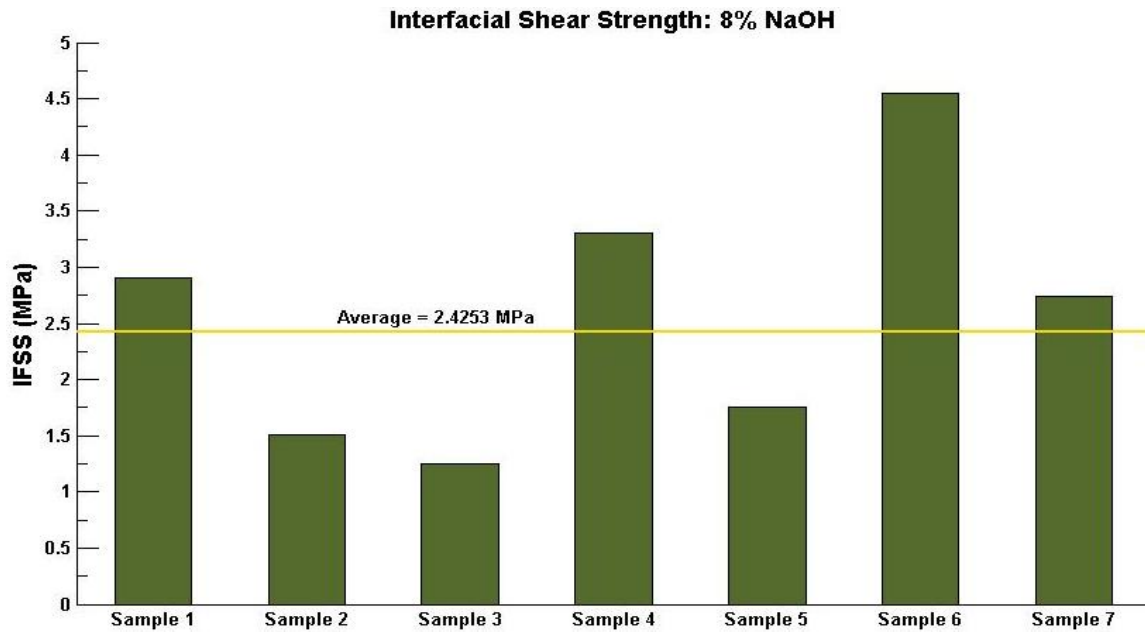


Figure 50 – Interfacial shear strength of 8% NaOH treated banana fiber in LDPE

Section 6.4: Results for Maleic Anhydride Polymer Additive

Part 6.4.1: 2% Results

Unlike the previous results for silane and sodium hydroxide treatments, which are chemical treatments for the fibers themselves, the following results are of untreated fibers in LDPE compounded with maleic anhydride, a polymer additive, as discussed in Part 2.3.2. Since the individual banana fibers for these tests are untreated, there is less concern for fiber fracture caused by reduced fiber tensile strength. This allows for easier sample preparation and pull-out testing. The results for 2% MaPE are seen in Figure 51 and Table 16. Deviation in results for samples prepared with maleic anhydride can be contributed to damage within individual fibers as well as possible non-uniform compounding of maleic anhydride with the low-density polyethylene.

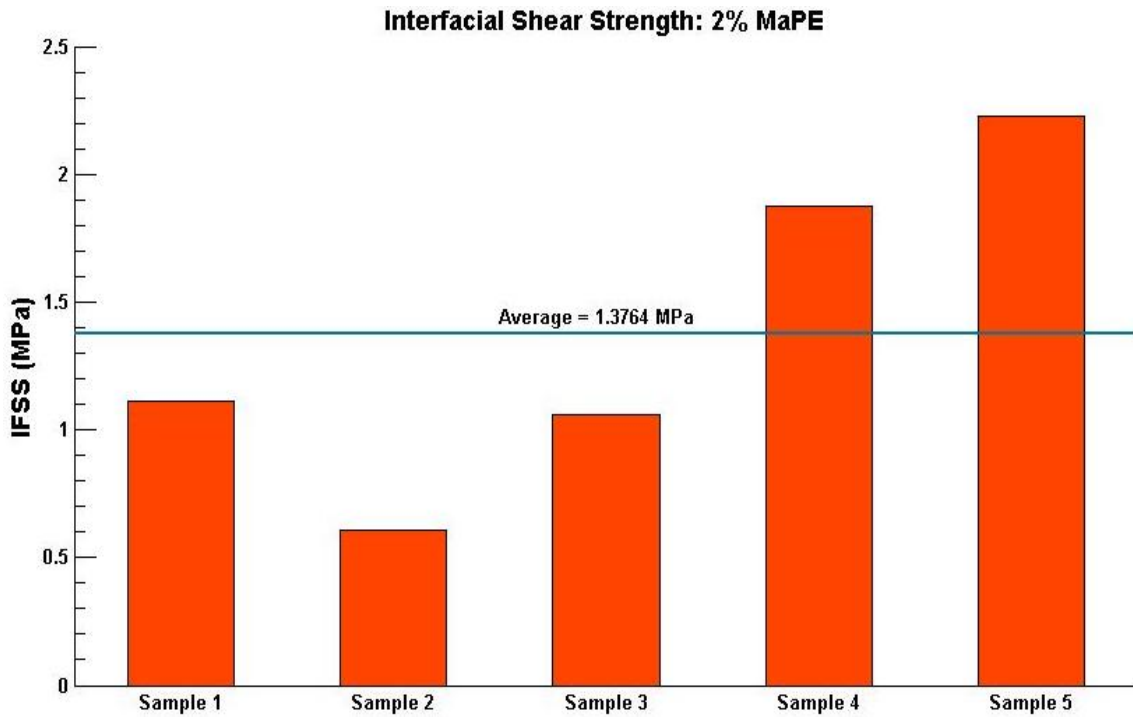


Figure 51 – Interfacial shear strength of untreated banana fiber in 2% MaPE/LDPE

Table 16: Summary of untreated banana fiber in 2% MaPE/LDPE pull-out test results

Sample #	Perimeter (μm)	Embed Length (mm)	Peak Force (N)	IFSS (MPa)
1	448.5	4.36	2.17	1.112
2	365.8	13.57	3.02	0.608
3	402.7	7.04	3.01	1.061
4	360.0	2.96	0.68	1.876
5	391.3	6.07	5.29	2.224
Avg. IFSS	= 1.376	Std. Dev.	= 0.657	

Part 6.4.2: 4% Results

The results of the 4% MaPE pull-out tests are seen in **Error! Reference source not found.** and **Error! Reference source not found.**. The results are typical of the sodium hydroxide treated fiber pull-out tests. Both the results and sources of deviation are similar to the 2% concentration.

Table 17: Summary untreated banana fiber in 4% MaPE/LDPE pull-out test results

Sample #	Perimeter (μm)	Embed Length (mm)	Peak Force (N)	IFSS (MPa)
1	547.8	0.86	1.44	3.076
2	798.2	1.20	4.30	4.492
3	538.3	0.34	0.54	2.957
4	576.5	0.24	0.54	3.948
5	949.7	0.29	0.79	2.820
Avg. IFSS	= 3.459	Std. Dev.	= 0.727	

Part 6.4.3: 6% Results

The results of the 6% MaPE/LDPE pull-out tests are seen in Figure 52 and Table 18. In this case, the interfacial shear strength dramatically increases beyond that of any other treatment with very little deviation. This dramatic increase in IFSS and decrease in deviation is attributed to the high concentration of maleic anhydride. With the increase of maleic anhydride concentration, the compounded additive is more likely to be uniform

across the polymer matrix; and thus increasing the number of functional groups which bond to the polymer matrix covalently and to the banana fiber through hydrogen bonding.

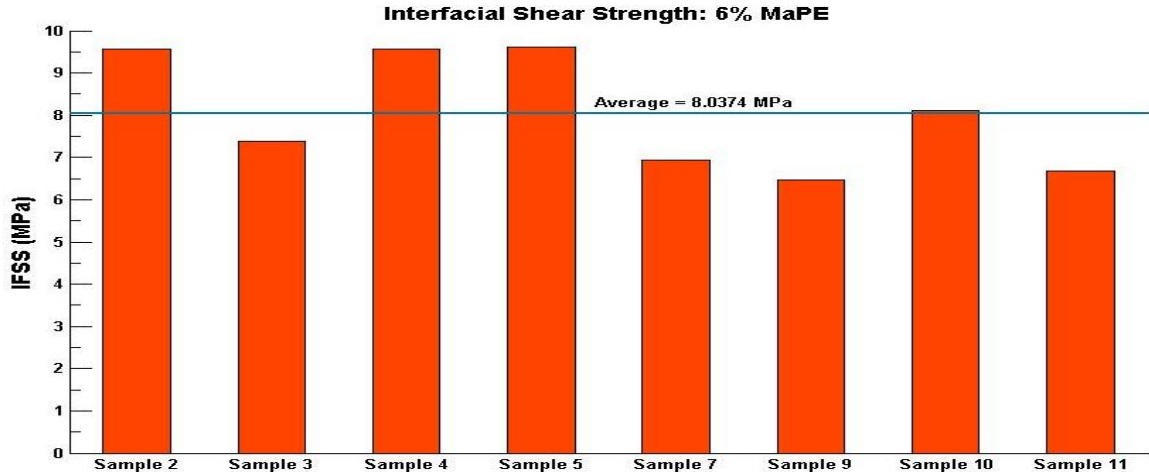


Figure 52 – Interfacial shear strength of untreated banana fiber in 6% MaPE/LDPE

Table 18: Summary of untreated banana fiber in 6% MaPE/LDPE pull-out test results

Sample #	Perimeter (μm)	Embed Length (mm)	Peak Force (N)	IFSS (MPa)
1	466.6	1.34	5.96	9.559
2	870.8	0.41	2.65	7.373
3	541.6	1.38	7.18	9.577
4	397.4	1.10	4.19	9.608
5	1128	0.64	4.99	6.926
6	1301	0.94	7.87	6.464
7	1102	1.05	9.40	8.113
8	1305	0.60	5.25	6.680
Average IFSS	= 8.037	Std. Dev.	= 1.371	

Section 6.5: Comparison of Pull-Out Test Results for Various Treatments

A full comparison of the interfacial shear strength, as measured via the pull-out test, is shown in Figure 53. The error bars shown on these figures are the 95% confidence intervals for each sample population for each treatment concentration. In the case of this comparison, there is very little overlap in the confidence intervals, thus allowing for more valid conclusions to be made about the improvement of interfacial bonding through the various treatments listed.

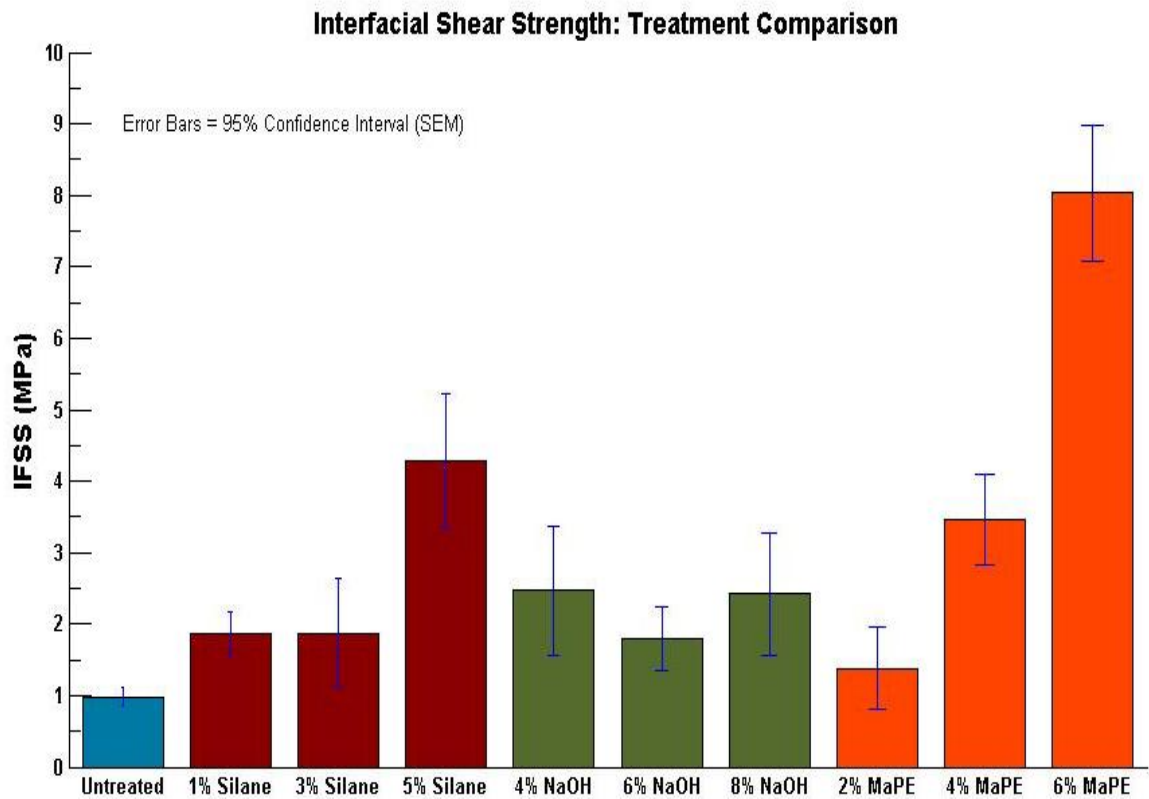


Figure 53 – Comparison of interfacial shear strength for various fiber treatments and polymer additive

As seen above, all of the various fiber treatments and the polymer additive significantly increased the interfacial bonding of the banana fiber in low-density polyethylene. While the chemical treatments, silane and sodium hydroxide, were

relatively close in comparison, the polymer additive, maleic anhydride dramatically outperformed all other treatments at the highest concentration tested.

Table 19: Comparison of interfacial shear strength for various fiber treatments and polymer additive

Treatment	Average IFSS (MPa)	95% confidence	Percent Difference (compared to untreated)
<i>Untreated</i>	0.986	0.12	-----
<i>Silane</i>			
1%	1.863	0.31	89.0%
3%	1.873	0.76	90.0%
5%	4.282	0.95	334.5%
<i>NaOH</i>			
4%	2.467	0.90	150.0%
6%	1.798	0.44	82.4%
8%	2.425	0.85	146.0%
<i>MaPE/LDPE</i>			
2%	1.376	0.58	39.6%
4%	3.459	0.64	250.9%
6%	8.037	0.95	715.4%

CHAPTER SEVEN

Banana Fiber Low-Density Polyethylene Composite

Section 7.1: Discussion of Optimal Composite Designs Chosen

As shown in Table 19, all treatments including silane, sodium hydroxide, and maleic anhydride substantially increase the interfacial bonding of banana fiber in low-density polyethylene. However, in order to determine the optimal treatment for composite design, both the effect of the treatment on the improvement of interfacial bonding, as well as the effect of the treatment on fiber mechanical properties must be taken into account.

In the case of the silane treatment, the 5% by volume concentration has the most negative effect on fiber tensile properties, decreasing modulus by 41.9%; however, the treatment provides an overwhelming 334.45% increase in interfacial shear strength. Since the interfacial bonding improvement of the 5% concentration is roughly three times that of the other silane concentrations, it is argued that the benefit of improved bonding outweighs the hindrance of the weakened fiber tensile strength and modulus.

In the case of the sodium hydroxide treatment, the 8% by volume concentration has the least negative effect on fiber tensile properties. Concerning the improvement of interfacial bonding, both the 4% and 8% have similar increase of approximately 150%. Taking both of these into account, 8% sodium hydroxide will be used in composite testing.

Concerning the case of the maleic anhydride, only the pull-out test results are considered. Due to the dramatic increase of 715%, the 6% MaPE was chosen as the design for composite fabrication.

All composite samples were prepared per the method described in Part 4.3.1.

Section 7.2: Discussion of Sample Preparation Complications

During sample preparation of the banana fiber-reinforced low-density polyethylene composite, regardless of surface treatment or polymer additive, a significant complication arose in the injection molding stage. As the composite pellets were melted in the barrel of the desktop injection molding machine, the composite experienced rapid expansion, seen in Figure 54.



Figure 54 – Expansion of banana fiber LDPE composite during processing

This rapid expansion is attributed to the evaporation of water, which is thought to be absorbed by the composite material during the cooling stage of the compounding process. Currently, as the hot composite material leaves the single-screw extruder, it is cooled in a cold water bath before entering the pelletizer to be processed into composite

pellets. It is during this cooling step that the natural fiber composite is thought to be absorbing large amounts of water, which boils out when melted in the barrel of the injection molding machine.

As a result of this rapid expansion, the composite is left with significant voids where the water previously took up space, thus significantly affecting the composite's mechanical properties. This processing issue was temporarily resolved through repeatedly melting the composite material in the barrel until a sufficient amount of the moisture content had evaporated, allowing the plunger to be properly set. The complication that arises with this solution, however, is the possible degradation of the banana fiber at the high temperature for prolonged duration. Although this processing issue arose, composite parts were still able to be injection molded, allowing for tensile testing to occur, though the validity of the results is a point of discussion.

Processing of natural composites is outside the scope of this thesis research, therefore resolutions to these complications are an excellent opportunity for future work in this research topic.

Section 7.3: Results of Tensile Testing

As described in Part 4.3.2, tensile tests are performed on banana fiber-reinforced low-density polyethylene composite tensile bars at a constant rate of extension of 20 mm/min, per ASTM standard D638-03. The results for the ultimate tensile strength for the composites of varying interfacial bonding treatments are shown in Figure 55 and Table 20, while the results for the tensile moduli are shown in Figure 56 and Table 21.

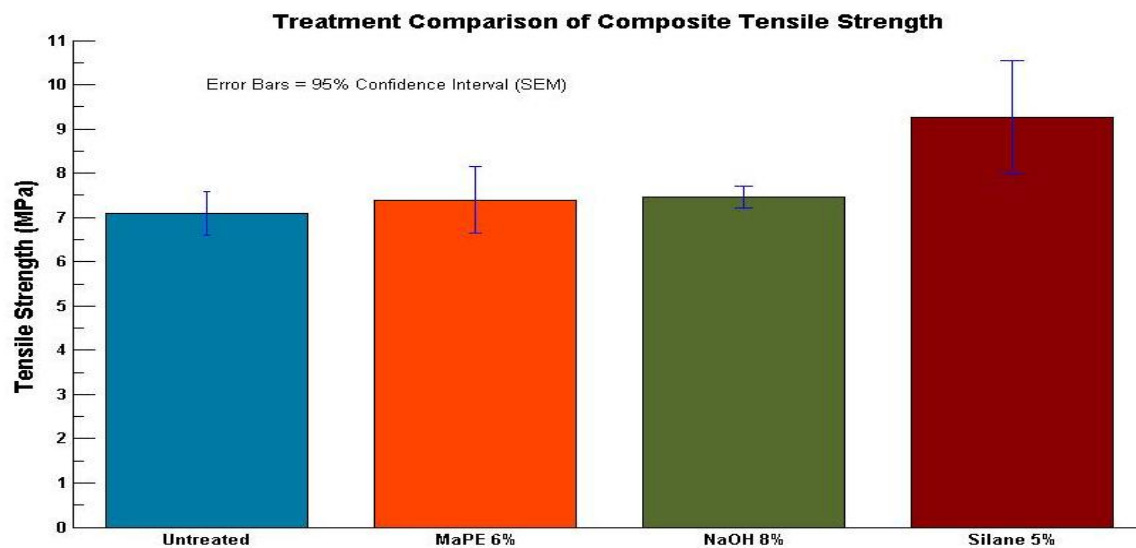


Figure 55 – Comparison of effects of interfacial bonding treatments on composite strength

Table 20: Comparison of interfacial shear strength for various fiber treatments and polymer additive

Treatment	Tensile Strength (MPa)	95% confidence	Percent Difference (compared to untreated)
Untreated	7.09	0.50	-----
MaPE/LDPE	7.40	0.75	4.27
NaOH	7.46	0.24	5.14
Silane	9.26	1.28	30.55

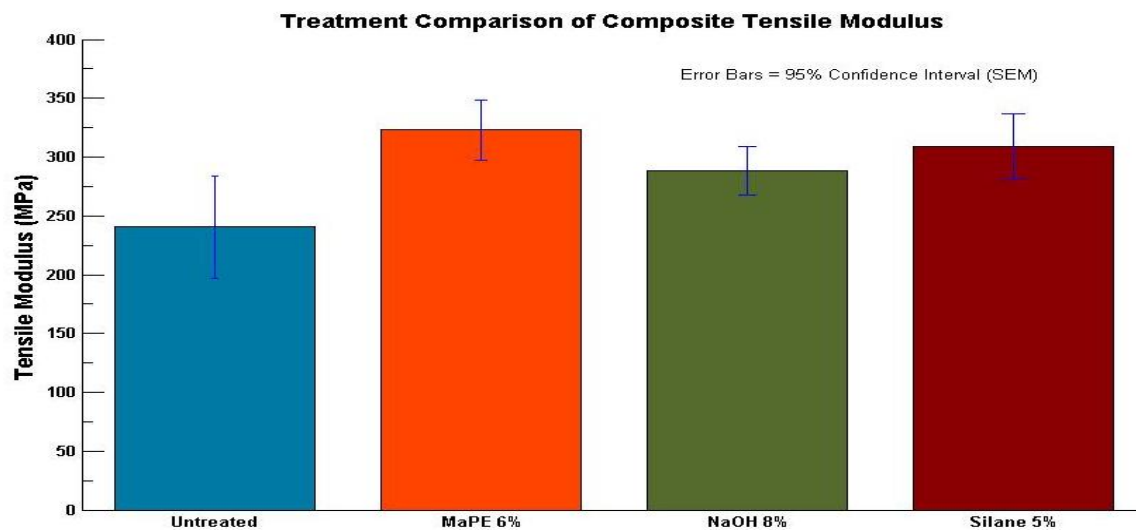


Figure 56 – Comparison of effects of interfacial bonding treatments on composite modulus

Table 21: Comparison of interfacial shear strength for various fiber treatments and polymer additive

Treatment	Tensile Modulus (MPa)	95% confidence	Percent Difference (compared to untreated)
Untreated	240.40	43.44	-----
MaPE/LDPE	323.05	25.76	34.38
NaOH	288.11	20.54	19.85
Silane	308.97	28.22	28.52

At first look, these results match the effects of the treatments on interfacial bonding and fiber tensile properties quite closely. The sodium hydroxide treatment improves the composite mechanical properties beyond that of the untreated relatively well. However, the silane treatment and maleic anhydride treatment show dramatic improvement, much like the results seen for the interfacial shear strength. It is interesting to note that although the maleic anhydride increases the interfacial bonding considerably more than the silane treatment, it does not have as similar of an effect in the composite testing. This could possibly be attributed to the effect of the maleic anhydride on the mechanical properties of the low-density polyethylene. A study on this particular effect would provide another excellent avenue for future work.

It is important to note, however, that these results are considerably lower than the properties of the neat LDPE. Considering the fiber volume fraction used and the considerable strength of the banana fiber in comparison to the neat polymer, the composite properties should be greater than that of the neat polymer. This discrepancy is attributed to the high moisture and void content discussed in Section 7.2. Although the values of these tensile tests are much lower due to the processing issue, the improvement of composite tensile properties from the surface and polymer treatments still warrants recognition, if nothing more than the validity of using these various treatments to improve on the composite properties exhibited by the untreated composite.

CHAPTER EIGHT

Final Conclusions On Interfacial Bonding Research

This research focused on identifying a natural resource found in developing countries and ascribing global value to that resource through industry-leading innovation. Due to its prevalence, current lack of use, and surprising mechanical properties, banana fiber, extracted from the banana plant's pseudostem, was identified as having excellent potential for use as fiber reinforcement in thermoplastic composites. A common deterrent for the use of natural fibers such as banana fiber in fiber-reinforced composites is the poor interfacial bonding that arises from combining a hydrophilic fiber with a hydrophobic polymer matrix. This research evaluated the effects of two chemical treatments, silane and mercerization, and a polymer additive treatment, maleic anhydride, on the mechanical properties of individual banana fibers, on the interfacial bonding between a single fiber and the polymer matrix, and on the composite mechanical properties.

The results revealed that while all of the treatments studied provided some increase in interfacial bonding and some benefit to the final composite properties, the silane treatment and maleic anhydride additive provided substantially better improvement. The maleic anhydride shows dramatic improvement in the interfacial bonding, while the silane treatment shows the best overall increase in composite strength.

There is a large potential for future work in this area including resolving composite processing issues, such as moisture intake, as well as in depth study on the full banana fiber-reinforced polymer composite.

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