



TAMPEREEN TEKNILLINEN YLIOPISTO

KIRSTI ILOMÄKI
ADHESION BETWEEN NATURAL FIBERS AND THERMOSETS
Master Thesis

Examiners: Professor Pentti
Järvelä and Senior Research
Fellow Mikael Skrifvars
The thesis examiners and the
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PREFACE

This Master Thesis is part of the international ANACOMPO-project. In addition Tampere University of Technology also Ketek OY, SICOMP AB and Luleå University of Technology took part in this project. The supervisors and examiners of this thesis have been Prof. Pentti Järvelä and Senior Research Fellow Mikael Skrifvars.

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Tampere, January 2012

Kirsti Ilomäki

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TIIVISTELMÄ

TAMPEREEN TEKNILLINEN YLIOPISTO

Materiaalitekniikan koulutusohjelma

ILOMÄKI, KIRSTI: Luonnonkuitujen ja kertamuovihartsin välinen adheesio rakennekomposiiteissa

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Diplomityöni aiheena oli kehittää luotettava testausmenetelmä luonnonkuitukomposiittien adheesiointestaukseen. Kokeellisessa osassa materiaaleina on käytetty pellavakuitua, viskoosikuitua, kahdenlaista kertamuovihartsia ja kahta erilaista kemiallista pintakäsittelykemikaalia. Kertamuovihartseina käytettiin sekä biopohjaista että tavallista epoksia. Kemiallisen pintakäsittelyn tarkoituksena oli parantaa adheesiota kuidun ja hartsin välillä. Työ jakautui teoria- ja tutkimusosaan. Teoriaosassa tarkoituksena oli selvittää tekijät, jotka vaikuttavat luonnonkuitukomposiiteissa adheesioon, ja kuinka adheesiota voidaan parantaa ja testata.

Tutkimusosassa pyrittiin saamaan adheesiointestauksesta tuloksia, joita pystyttäisiin vertailemaan keskenään. Adheesiointestausmenetelmänä käytettiin mikrosidos menetelmää, jossa pieni hartsipisara valettiin kuidun pinnalle, mihin se sai kovettua. Hartsipisara vedettiin kuidusta irti työntömitan kärjessä olevan aukon avulla ennen testausta. Näyte asetettiin vetokonelaitteeseen, johon oli kiinnitettynä työntömitta. Vetokoneessa käytettiin pientä voimaselliä ja vetonopeutta, jotta kuidut eivät olisi rikkoutuneet testin aikana. Tämän lisäksi tutkimusosassa tehtiin yksittäisen kuidun lujuustestejä pellavakuidulle, viskoosikuidulle, lasikuidulle ja kemiallisesti käsitellyille pellavakuiduille. Yksittäisen kuidun lujuustestin perusteella voitiin todeta, kuinka kuidun lujuus kasvoi huomattavasti kemiallisella käsittelyllä. Adheesiointestaukseen käytetty mikrosidostesti osottautui käytännössä melko hankalaksi, sillä yksittäiset kuidut rikkoontuivat helposti testin aikana. Jokaisesta rinnakkaisnäytteestä onnistui kuitenkin riittävän monta, jotta pystyttiin laskemaan kuidun ja matriisin välisen rajapinnan leikkauslujuus. Adheesiointestauksen perusteella voitiin todeta, kuinka kemialliset pintakäsittelymenetelmät paransivat adheesiota kuidun ja matriisin välillä verrattuna käsittelemättömiin kuituihin.

ABSTRACT

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Key words: Adhesion, natural fiber composites, thermoset matrix, flax fiber, viscose fiber, micro-bond test, interfacial shear strength

The aim of my Master Thesis was developing a reliable adhesion testing method for natural fiber reinforced composites. Flax fiber, synthetic viscose fiber, two different thermoset matrix and chemical surface treatment were used in this investigation. Bio-based Epobiox and basic epoxy, Envirez G8600 INF-60, were used as thermoset matrix. Chemical surface treatment increased the adhesion between the natural fiber and thermoset resin. This Master Thesis was divided in theoretical part and experimental part. The purpose of the theoretical part was determining the factors affecting on the adhesion in natural fiber composites and how to improve the adhesion and how the adhesion can be tested.

The aim of the experimental part is to obtain adhesion testing results, which were able to compare with each other. Micro-bond test was used as an adhesion testing method in which small amount of thermoset resin was cured on the fiber surface. The droplet was pulled out of the fiber surface by micrometer, which was connected to the tensile testing machine. Low cross head speed and 1-5N load cell were used so that the fibers did not break during the test. The microbond test was difficult, because single fiber broke easily during the test. Only a few samples per each fiber-matrix combination were successful, where the interfacial shear strength, IFSS, can be calculated. A single fiber tensile test was done for alkali and silane treated flax fiber, non-treated flax fiber, viscose fiber and glass fiber. The test results show that fiber strength was improved with chemical surface treatment.

TERMS AND DEFINITIONS

(N/tex)	Tenacity, as the force per unit area expressed as the linear density at the break point
Δm	The change of mass before and after fiber is wetted in contact angle measurement
°	Contact angle
ADSA	Axisymmetric Drop Shape Analysis
ANACOMPO	Application of Natural Fiber Reinforced Composites in Harsh Environments
CO ₂	Carbon dioxide
d	Diameter of fiber
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimeter
Dtex	Fiber length as kilometer per kg of fiber
F	Fluor
F	The maximum load measured for debonding of the fiber
IFSS	Interfacial shear strength
l	Embedded length of microdroplet
N	Nitrogen
NaOH	Sodium hydroxyl
O	Oxygen
°C	Celsius
OH	Hydroxyl group
PP	Polypropylene
S	Sulphur
SEM	Scanning electron microscope
SSFT	Single fiber fragmentation test
TGA	Thermogravimetric analysis
UP	Unsaturated polyester
vdW	van Der waals forces
$\gamma(lv) \cos \alpha = \gamma(sv) + \gamma(sv)$	The Young equation
$\gamma(lv)$	Liquid- vapor surface tension
$\gamma(sv)$	Solid - liquid surface tension
$\gamma(sv)$	Solid- liquid surface tension
$IFSS = \frac{F}{\pi dl}$	Interfacial shear strength
$TS = \frac{F}{A}$	Single fiber tensile strength
$d = \frac{\sqrt{(4*10^{-6}*dtex)}}{\pi\rho}$	Fiber diameter from dtex-value
$\gamma(lv) \cos \alpha = \frac{\Delta mg}{\pi d}$	Willhelmy technique the wetting tension

1 INTRODUCTION

Natural fibers are being used as the reinforcement in the thermoset polymer matrix composites. The adhesion between the polymer matrix and the fibers affects the properties of the composites. A strong fiber-matrix interface bond is needed for high mechanical properties composites. The chemical surface treatment of fibers improves the fiber-matrix adhesion and tensile properties of the composites. The natural fibers are hydrophilic while polymer resins are hydrophobic in nature. This is reason for poor adhesion between them. The aim of my master thesis work is developing reliable and useful testing methods for measuring the adhesion between the fibers and the polymer resin. Master thesis work is done in ANACOMPO-project co-operation with Ketek Oy, Tampere University of Technology, Luleå University of Technology and SICOMP AB.

Flax fibers and viscose fibers are used this experimental investigation. Bio-based epoxy and basic epoxy are used as polymer resin. Fibers are separated from the bundle manually. Single fiber tensile testing is done for non-treated flax fiber, glass fiber and viscose fiber. The characterization of the interfacial shear strength between fiber and matrix is tested by the micro-bond test. Single fiber pull-out test, the fiber bundle pull-out test and the single fiber fragmentation test are also common micromechanical adhesion testing methods for the composites. Spectroscopic techniques are suitable for the surface characterization of the fiber before and after a surface modification or a micromechanical testing.

The micro-bond test involves the deposition of a small amount of resin on the surface of the fiber in the form of micro-droplet. The droplet size is about 100-250 μm . Typical droplet shape is ellipsoid because of uncured droplet surface energy. Samples are put on a paper framed so that they are easier to handle. Cured micro-droplet dimensions and the fiber diameters are measured with an optical microscope. The micro-meter is mounted on the crosshead of the testing machine with 5N load cell. The micro-meter is used as a small gap, from which samples are pulled through by the tensile testing machine. The gap between micro-meter is 50 μm . Cross head speed 0.5 mm/min is used.

2 NATURAL FIBER THERMOSET COMPOSITES

Natural fibers are being used as the reinforcement in thermoset polymer matrix composites. They are environmentally friendly, biodegradable and renewable fiber resources. Natural fibers are also CO₂- neutral, of a low-cost and they have rather good mechanical properties. Single fibers have high strength and stiffness in the fiber direction. The disadvantages are low compressive strength, poor thermal resistance, high moisture absorption and poor adhesion between the natural fibers and the matrix. High moisture content decreases the mechanical properties of the composite. The adhesion between the polymer matrix and the fibers affects the properties of the composite. Reliable and useful testing methods are needed for measuring the adhesion between the fibers and the polymer resin. [1]

The properties of natural fiber reinforced composites depend on the individual components, the fiber - matrix interfacial compatibility, the interfacial bond strength between the fibers and resin, the fiber orientation and the fiber length. A strong fiber - matrix interface bond is needed for high mechanical properties composites, because of the effective stress transfer from the matrix to the fiber. Pretreatment of fibers improves tensile properties owing to the improved fiber - matrix adhesion and the dispersion of the fibers in the matrix. [2]

Natural fiber can be grouped into bast, leaf, and seed or fruit fiber. Cellulose is the main component of the natural fiber. The elementary units of cellulose contain three hydroxyl groups. The cellulose backbone includes hydrogen bonds, and therefore all the natural fibers are hydrophilic in nature. This is the reason for poor adhesion, because hydrophilic fibers absorb moisture. A second factor is the incompatibility with resins which often are more hydrophobic in nature. An important parameter is the aspect ratio, which has influence on the mechanical properties of the composite. Cellulosic materials have amorphous and crystalline domains and the high degree of organization. Many hydroxyl groups interact with water molecules by hydrogen bonding. Cellulose fibers interact with water on the surface and the bulk. The water absorption depends on the raw cellulosic materials and the degree of crystallinity. Hydroxyl groups are more accessible to water in the amorphous phase than in the crystalline phase. All these factors play an important role when the fiber is in contact with the matrix. Strong adhesion is needed for the high modulus component. [3]

2.1 Thermosets

Thermosetting resins have low molecular weight and functional groups which are reacted in a cross-linking reaction leading to a giant, single macromolecule. The polym-

erization of thermosetting resins can occur by the addition reaction or the condensation reaction mechanism. Thermoset resins are divided in low and high viscosity liquids or solids. Low viscosity resins generally have a good wetting of the fibers, while high viscosity resins have poor wetting of the fibers. The wetting of fibers with high viscosity resins is possible by using high pressure or temperature. The good physical properties of thermoset resins are high glass transition temperature, high decomposition temperature, thermal and thermo - oxidative stability, the retention of properties in hot and wet environment, high ultimate tensile strength, high modulus, and elongation during break, high toughness and fatigue resistance, low water absorption, high flame resistance and the char yield. Thermoset are however brittle which results in poor resistance to crack propagation. This is due to high cross - link density and rigid molecular structure. [4]

Unsaturated polyesters (UP) and epoxy are the most used thermoset resins in natural fiber composites. Their chemical structures are shown in Figures 1 and 2. The mechanical properties of polyester and epoxy are shown in Table 1. UP resins are made from different unsaturated and saturated acids, glycols and styrene, which acts as a cross-linking monomer. These resins are easy to use and low - cost material. The molecular weight of the uncross-linked polyester is 1200 to 3000 g/mol. UP resins have only medium level mechanical properties and high cure shrinkage, but they are low viscosity which makes the processing easy. Polyesters are viscous liquid or brittle solid. They have a low degree of polymerization. The major problem with this resin is their high shrinkage during curing reaction. [3], [4], [5]

Table 1 The properties of Polyester resin and Epoxy resin [3]

Properties	Polyester	Epoxy
Density (g/cm ³)	1.2 - 1.5	1.1 - 1.4
Young's modulus (GPa)	2 - 4.5	3.0 - 6.0
Tensile Modulus (MPa)	40 - 90	35 - 100
Compressive strength (MPa)	90 - 250	100 - 200
Tensile elongation to break (%)	2	1.0 - 6.0
Cure shrinkage (%)	4.0 - 8.0	1.0 - 2.0
Water absorption 24h at 20 °C	0.1 - 0.3	0.1 - 0.4

Epoxy resins have good mechanical properties and resistance to environmental degradation. Adhesive properties and moisture resistance make them good resin materials for composites. The thermal resistance properties are very good and the cure shrinkage is low. Disadvantages are the high cost, and the resin component mixing must be done with great accuracy. These properties in an epoxy resin require a high crosslinking density, which usually results in brittle failure behaviour. Epoxies can be partially cured and stored in that state if kept cold, and they have the low shrinkage during the cure. The viscosity of epoxy is higher than polyester. Their major limitation is the long cure time and poor performance in hot and wet environments. [3], [4], [5]

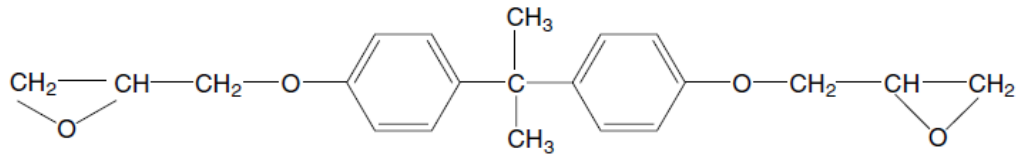


Figure 1 The chemical structure of epoxy resins [3]

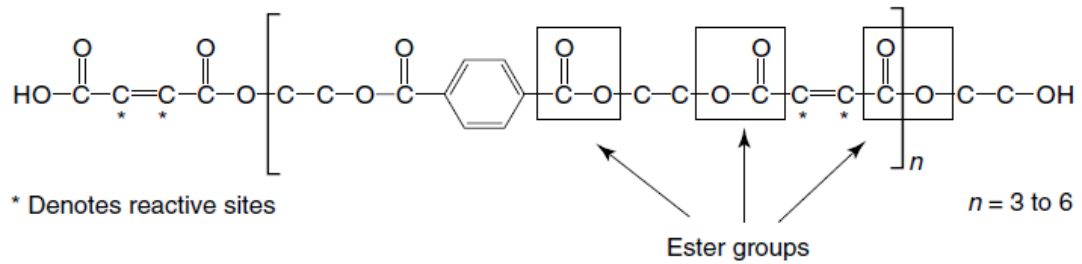


Figure 2 The chemical structure of a unsaturated polyester resin [3]

2.2 Natural fibers

Natural fibers are multicellular in nature, consisting of continuous honeycomb cells which have different sizes, shapes and arrangements in different types of fiber. These cells are cemented together by an intercellular substance, which is isotropic and noncellulosic in nature. Individual cells consist of the primary wall and the secondary wall which is shown in Figure 3. The layers differ in the composition and orientation of cellulosic microfibrils. The central cavity of each cell is named a lumen. The properties of single fibers depend on the crystallite content, their size, shape, orientation and thickness of cell walls. Natural fibers have discontinuous length and non-uniform diameter.

It is difficult to characterize the fiber properties regarding strength because of its large variations. The natural fibers have discontinuous length. The cross-sectional area of the single fiber is difficult to measure. A dimension related to the single fiber diameter which is often used is the linear density of the fiber. The parameter is expressed as “tex” in SI units, which is weight in grams of one kilometre of the fiber. The strength is expressed as the maximum force per unit area of fibers cross section which the fiber can sustain before the fracture. This is given as the tenacity (N/tex), which is defined as the force per unit area expressed as the linear density at the break point. [3, pages 8-12]

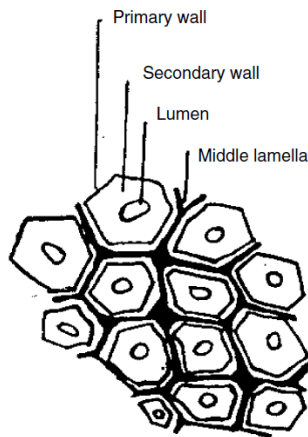


Figure 3 The structure of the natural fiber cell. [3]

The chemical composition of fibers is cellulose, hemicelluloses, lignin, pectin and waxy substances. The natural fibers cellulose acts as the main structural component. Lignin and hemicelluloses affects the characteristic properties of the fiber. Moisture from the atmosphere comes into contact with the fibers hydroxyl groups from hydrogen bonds with water molecules. Pectin and waxy substance hold these water molecules and hindering free hydroxyl groups to react with the polar matrix. Poor bonding between the hydrophobic matrix and hydrophilic fibers occurs. The problem can be solved by treating fibers suitable chemicals to decrease the hydroxyl group in the fibers. Chemical treatment reacts with hydroxyl groups of natural fiber and improves hydrophobic characteristic and make better bonding with thermoset matrix. [6]

The hemicellulose in the fiber is sensitive to the action of NaOH, acetic acid and acetic anhydride also reacts with the lignin and cellulosic compounds. The hydrophilic characteristics of the fiber is therefore reduced which results in improved fiber matrix adhesion characteristics of the composites. The effect of chemical treatment on the fiber can on the degree of adhesion between the fiber and the matrix can be determined through mechanical property testing and different adhesion testing methods. Mechanical properties improve with adhesion; therefore improved adhesion is commonly seen as improved mechanical properties. [6]

Table 2 is shown mechanical properties of natural fiber and they are compared to the properties of glass fiber in Table 3.

Table 2 Mechanical properties of natural fiber [10]

Properties	E-glass	Hemp	Jute	Ramie	Coir	Sisal	Flax	Cotton
Density (g/cm ³)	2.55	1.48	1.46	1.5	1.25	1.33	1.4	1.51
Tensile strength (MPa)	2400	590 - 900	400 - 800	500	220	600 - 700	800 - 1500	400
E-modulus (GPa)	73	70	10.0 - 30.0	44	6	38	60 - 80	12
Specific (E/d)	29	47	7.0 - 21.0	29	5	29	26 - 46	8
Elongation at failure %	3	1.6	1.8	2	15 - 25	2.0 - 3.0	1.2 - 1.6	3.0 - 10.0
Moisture absorption %		8	12	12.0 - 17.0	10	11	7	8.0 - 25.0

Table 3 The natural fibers compared to glass fibers [10]

Properties	Natural fibers	Glass fiber
Density	Low	Twice that of natural fibers
Cost	Low	Low, but higher than NF
Renewability	Yes	No
Recyclability	Yes	Yes
Energy consumption	Low	High
Distribution	Wide	wide
CO ₂ neutral	Yes	No
Abrasion to machines	No	Yes
Health risk when inhaled	No	Yes
Disposal	Biodegradable	Not biodegradable

2.3 The interface between the natural fiber and thermoset

Mechanical interlocking, attractive forces and chemical bonds between the natural fiber and the resin are the main factors that affect the bonding interfacial adhesion between the thermoset matrix and the natural fiber. Hydrogen bonds and van der Waals force are physical attractive forces which are importance in the interface. Natural fibers have hydroxyl groups and hydrogen bonds can therefore be formed to the surface of the natural

fiber. The unsaturated polyester resin does not have hydroxyl group in its backbone, and this is a reason for the weak bonds between natural fiber and the polyester. [3]

The bond strength in natural fiber - reinforced composites is decreased by the absorption of moisture. The hydrophilic fibers absorb the moisture from the environment, and hydrogen bonds are formed between the hydroxyl groups of the cellulose molecules and the absorbed water, as shown in Figure 4. The first water molecules are absorbed directly onto the hydrophilic groups of the fibers. The later absorbed water molecules are attracted to other hydrophilic groups on the cellulose back-bone. Moisture absorption affects also the dimensional stability of natural fibers. This results to poor adhesion between the resin and the matrix which causes debonding. Drying the fibers before the processing is very important, because it increases the mechanical properties of the composites. [3]

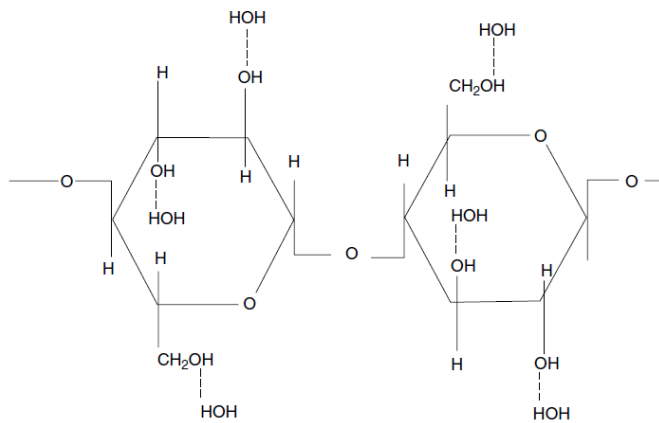


Figure 4 Absorption of moisture by natural fibers occurs because the hydroxyl groups of the cellulose molecules and the water forms hydrogen bond. [3]

Cellulose has many hydroxyl groups in its back – bone structure and they are available for interaction with water molecules by hydrogen bonding. Cellulosic fiber interacts with water on the surface and in the bulk. The water absorption depends on the purity of cellulose, the amount of amorphous and crystalline phase of cellulose and the total amount of cellulose in the natural fiber. The amorphous phase is more accessible to water, as the cellulose molecules are not tightly packed, as in the crystalline phase of the cellulose. Jute fiber has 45-63% cellulose, hemp fiber 57-77% and flax fiber 43- 47%. [3]

The main disadvantage of the natural fiber is their polar nature resulting in incompatibility with the nonpolar polymer matrix. Also the moisture absorption makes them less attractive for several applications. The stress transfer at the interphase between two different phases is determined by the degree of adhesion. An effective transfer of stress and load distribution throughout the interface is needed for strong adhesion. The chemical surface treatment reduces the moisture absorption and improves the me-

chanical properties of the composites. The chemical surface treatments, which consist of coupling agents or compatibilizing agents, introduce chemical bonds between the fiber and the matrix. [3]

The term interface is defined as two-dimensional region between the fiber and matrix having zero thickness. The properties of the interface are intermediate between those of fiber and matrix. Matrix molecules can be connected to the fiber surface by chemical reaction or absorption, and they determine the strength of interfacial reaction. The interface is different from interphase. The interphase determines the polymeric region surrounding the fiber. The interphase consists of polymeric material with a chemical interaction with the fiber and the matrix which has formed during the manufacturing process. Two major differences compare to the interface are the interphase physical dimensions and its effect on the bonds between the fiber and the matrix phases. The fiber - matrix interphase transfers external load over to the fibers. The effective load distribution is not achieved without a good interface and an ineffective load transfer leads to poor mechanical properties. A strong interface can ensure that external load can be distributed in the composite even if some fibers are broken. The adhesion between fiber and the matrix is the important factor in determining the response of the interface and its integrity under stress. [7]

The adhesion mechanism can be explained in several models. Mechanical interlocking can occur when the liquid polymer matrix is made to flow on the rough surface of a solid substrate. The interlocking is the result from solidification. The theory of absorption interaction is most often used to describe the adhesion in polymer composites. In this theory, primary and secondary forces create adhesion. The most important primary forces are the ionic, covalent and metallic bonds. The bonds formed by primary forces are strong in comparison with the secondary forces. The secondary bonds are created by van der Waals forces, induced dipole interaction, dispersion interaction, hydrogen bonds and acid-base interactions. [7]

3 CHEMICAL SURFACE TREATMENT

The adhesion between natural fibers and the hydrophilic thermoset resins can be improved by chemical surface treatment. The chemical pretreatments can clean the fiber surface, chemically modify the surface, stop the moisture absorption process and increase the surface roughness. The natural fibers are hydrophilic because they contain hydroxyl groups in their structure. Therefore, the natural fibers are incompatible with hydrophobic thermoset resins. It is reason for poor interfacial adhesion between the polar, hydrophilic fiber and the non-polar, hydrophobic matrix. Mixing is difficult because of the poor wetting of the fibers with the matrix which leads to a natural fiber reinforced composites with weak interface. Using right chemical surface treatment can be a solution for reduced moisture absorption. The chemical surface treatment makes the fibers more hydrophobic. Suitable treatment is needed for better fiber quality, increased fiber yield; reduced swelling and give better mechanical properties for composites. [2]

The constituents in natural fibers are cellulose, hemicelluloses, lignin and pectin. Cellulose is the main component in a natural fiber, and the cellulose is resistant to alkalis but hydrolyzed in acids. Hemicellulose acts as supporting matrix agents of cellulose. Lignins are amorphous network like polymers and hydrophobic in nature, and the lignins contain both aromatic and aliphatic constituents. Pectins are like the waxes providing flexibility. Natural fibers consist of OH group which lead to the moisture absorption and impairs the dimensional stability. Natural fibers do not efficiently adhere to non-polar resins due to these polar groups. This difficulty can be overcome by chemical modification. Chemically modified surfaces decrease moisture absorption, and increase tensile strength and wettability of fibers by matrix. [4], [8]

The hydroxyl groups reduce the interaction with the matrix. A chemical surface treatment activates these hydroxyl groups, thus giving a possibility to tailor the interaction, such as better interlock with the matrix. The typical chemical surface treatments are silane treatment, mercerization and acetylation. These methods have achieved improving fiber strength and improved fiber - matrix adhesion in the natural fiber reinforced composites. Chemical surface modification change surface tension and polarity of the fibers. The compatibility and dispersability of the natural fibers and the matrix can be improved by using a hydrophobic coating of a compatible polymer on the surface of fibers before being mixed with the polymer matrix. Coupling agents improve the stress transfer at the interface between the fiber and the matrix. Coupling agents react with the OH groups of cellulose and then they react with functional groups of the matrix. Interfacial bonding is improved and the moisture absorption is reduced. [2, pages 1-4], [3, p.12]

3.1 Silane treatment

Silane coupling agents improve the degree of cross-linking in the interface region and offer better bonding. Silane treatment is an effective method to modify the natural fiber-matrix interface. Silane treatment reduces the number of cellulose hydroxyl groups in the fiber- matrix interface. Stable covalent bonds are formed to the cell wall when hydroxyl groups react with the silane. [2]

Treatment of fibers with silane coupling agents significantly improves the interfacial adhesion and therefore the mechanical properties of the composites. The bifunctional silane molecules act as a link between the matrix and the cellulose. They form a chemical bond with the surface of cellulose through a siloxane bridge while its organofunctional group bonds to the matrix. The chemical formula of silane is a multifunctional, which consist of also reactive R- and X- groups. One end of it reacts with the cellulose fiber surface and the other and reacts with the polymer phase. [3]

The functional group of silane can react with the functional groups in the resin under given curing conditions. The X- groups of silanes can be hydrolyzed to allow reactions to take place between the silane and the OH group on the cellulose surface. The polysiloxane layer is formed between the silanol and OH groups on the cellulose fiber surface after the fibers are dried. Presence of catalyst or radical initiators is needed for the reactions. The polysiloxane layer is bonded to the cellulose surface. The silane coated cellulose surface gets in contact with the resin. The R groups on the fiber surface react with the functional groups in the matrix forming a covalent bond with the matrix. [3]

When the silane-coated cellulose surface gets in contact with the resin, the R-groups on the fiber surface react with the functional groups present in the polymer resin, forming a stable covalent bond with the polymer. When all these reactions occurs the bonding between the silane coupling agent, the cellulose and the polymer matrix is formed. The silane coupling agents forms the bridge to bond the cellulose fibers to the matrix with a chain of primary bonds. [3]

3.2 Mercerization

Mercerization, also called alkali treatment, is a common method to improve the properties of the natural fibers. Mercerization will break down the composite fiber bundles into smaller fibers with reduced fiber diameter. Therefore, the aspect ratio is increased and a rough fiber surface topography is developed. It makes the fiber - matrix adhesion better. Mercerization allows the fibers to wet better and increases the number of reactive sites on the fiber. The method will have an effect on the degree of polymerization, molecular orientation and chemical composition of the fiber. Lignin and hemicelluloses are

removed during the alkali treatment process. Mercerization has an effect on the mechanical behavior of fibers. The strength and the stiffness of the fibers are improved. [2]

The natural fibers are soaked in 2- 30 % NaOH- solution. The fibers are treated with NaOH solution for one to 8 hours at the temperature at 30 °C. The fibers are then dried at room temperature for 48 hours. After that, the oven drying takes 6 hours at 100 °C. The efficiency of the mercerization depends on the type and concentration of the alkaline solution, time of treatment, temperature and fiber tension. The immersion of alkaline leads to formation of high amounts of voids and makes the surface rougher. The effective surface area is increased which improves the adhesion between the fibers and the matrix. The alkali treated fibers have better tensile properties compared to the untreated fibers. The presence of crystalline celluloses is higher in treated fibers. The alkali treated natural fibers have good mechanical properties which are comparable to the man-made fibers. [2], [3], [8]

3.3 Acetylation

Acetylation involves the esterification of the hydroxyl groups on the fiber surface. Acetylation is applied to improve moisture absorption, dimensional stability and environmental stability. The fibers become hydrophobic, because they are treated with acetic anhydride substitutes. The polymer hydroxyl groups react with the acetyl groups. Acetylation is based on reaction between the cell wall hydroxyl groups and acetic or propionic anhydride at elevated temperature. Lignin and hemicelluloses have also hydroxyl groups that react with the reagent from the treatment. The hydroxyl group of cellulose are being closely packed with hydrogen bonds. [2]

The acetylation is an effective way to reduce moisture absorption. In acetylation acetic acid or acetyl chloride are heated in the presence of a solvent. Acetylation is possible to speed up by using a catalyst. The hydroxyl groups are acetylated in different ways. The moisture absorption of the cell walls is reduced, if the hydroxyl groups in the cellulose are substituted with acetyl groups. [9]

4 TESTING AND CHARACTERISTIC METHODS

The characterization of the interface between fiber and matrix gives information about their interactions and the adhesion strength between them. Common methods available for the characterization of the interface are micromechanical techniques such as the single fiber pull - out test, the fiber bundle pull- out test, the single fiber fragmentation test and the micro bond test. Spectroscopic techniques are suitable for surface characterization of the fiber before and after a surface modification or a micromechanical testing. Microscopic methods are scanning electron microscopy, optical microscopy and stereo microscopy. They can be used to study morphological changes on the surface which can be related to the strength of adhesion at the interface. Contact angle measurement can be used for wettability and surface energy investigations of fiber surface. [7]

The mechanical properties of natural fiber reinforced composites depend on the stability of the interfacial region. The characterization of the interface is therefore of great importance. All micro-mechanical techniques evaluate the bonding strength between the fiber and matrix. The pull-out test is considered to be a good method of evaluating the interfacial shear load. The method will directly measure the interfacial shear strength between the fiber and matrix, independent of their properties. The interfacial shear strength is a critical which controls the mechanical properties and interlaminar shear strength for composite materials. [7]

4.1 Adhesion testing

The degree of adhesion can be determined indirectly by measuring mechanical properties like tensile strength, flexural strength and impact strength of the natural fiber reinforced composites. The degree of adhesion is increasing when these mechanical properties are improved. DSC and TGA analyses were used to characterize fibers to determine chemical changes in their structure included by different chemical surface treatment methods. The mechanical properties of the natural fibre reinforced composites have typically values which are almost half of the values for the corresponding properties of the synthetic fibre composites. Chemical surface treatment can improve the level of adhesion and reduce moisture adsorption near to the synthetic fibres. Microscopic analysis show that the used chemical surface treatment resulted reduction in void size which improves the adhesion level. [9], [12]

Wettability can affect the interfacial adhesion between fiber and matrix. The incomplete wettability may lead to low interfacial shear strength. Better wetting can enhance the interfacial shear strength by improving the work of adhesion. It is determined by polar and dispersive surface free energy. The mechanical interlocking and surface

roughness are parameters that also have a influence on the degree of interfacial shear strength. [5]

4.1.1 Single fiber pull-out test

The adhesion in natural fiber - thermoset matrix composites can be measured using single fiber pull - out test. The interfacial shear strength, IFSS, can be calculated from the measured force and the fiber diameter. One end of the fiber is embedded in a block of cured polymer matrix. A force is then applied to the free end of the fiber to pull it out of the matrix while the force is continuously recoded and monitored. The average IFSS, be calculated from the equation:

$$IFSS = \frac{F}{\pi dl} \quad (1)$$

In this equation F is the maximum load measured for debonding of the fiber, d is the fiber diameter and l is the fiber embedded length. The embedded length of the fiber has to be short enough to avoid fiber fracture below the surface. The load and the displacement are monitored during the pull-out process. The failure load is converted to interfacial shear strength. The shear stress is uniformly distributed along the embedded length. [3], [7]

There can be some variations in the testing details in various testing protocols. The most used methodology is pulling a single fiber out of the block of the matrix, which is around the single fiber. This single fiber pull- out test method is shown in Figure 5. Fibers are cut in long fragments and attached to frame using high adhesive tape. The fibers are then placed in the matrix and the mold is heated above the curing temperature and then cooled to room temperature. The single fiber is therefore oriented along the main axis of the rectangular fiber – matrix sample. The force is applied by holding the cured resin plate piece fixed and pulling from the free end of the fiber. The embedded length and the diameter of the fiber are measured by using an optical microscope before testing. A cross- head speed from 0.1 – 1.0 mm/min is typically used and a tensile load force displacement curve is then recorded by a PC.. For single fiber pull - out test a tensile testing machine with a 1- 10 N load cell is typically used. [7], [10], [13]

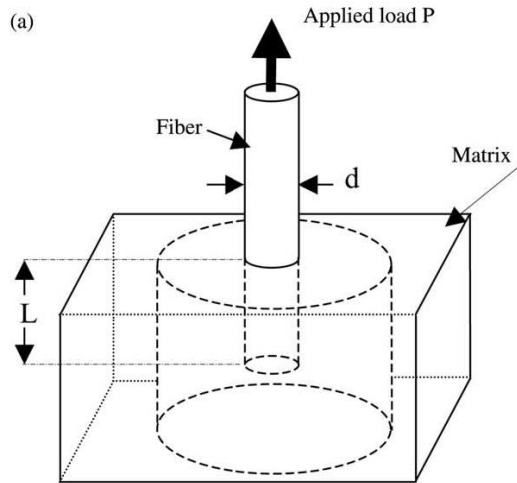


Figure 5 The single- fiber pull-out test. [13]

The bonding strength between the matrix and the fiber is calculated by measuring a required force to pull- out the single fiber out of the embedded matrix. The interfacial shear strength is criterion for the fracture. The shear stress on at the interface is not constant when load is applied to single fiber composites. The interfacial debond occurs when the interfacial shear strength exceeds the ultimate shear strength of the interface. The debond initiate at the loaded fiber end or at the embedded fiber end. The maximum debonding force increases with the embedded fiber length. [11]

For statistical reasons 20 - 30 samples are commonly tested and the average values of testing results are then calculated. From the geometry of the droplet on the fiber surface it is also possible to determine the work of adhesion of the matrix to the fiber, which gives an indication of the good adhesion between the fiber and resin. The fiber is pulled out of the matrix, which can be a block of resin, a disc or a droplet. The test samples were made using compression molding at a pressure and the curing temperature [14], [13]

The single fiber pull - out test is relatively simply and the test specimen preparation is not difficult. The pull-out test is considered as a good method to measure the interfacial shear load. It can directly measure the interfacial shear strength between the fiber and matrix independent of their properties. The measurement is expected to give realistic information. The pull- out test has two features. The debonding destroys the bond between fiber and matrix. The recovered fiber is inspected in the SEM to measure the fiber diameter and the resin embedded fiber length. SEM measurement also ensures that the fiber does not fail inside the resin button. [7]

The shape of the force/ -displacement curves in the pull- out test depends on the characteristics of the interface. Immediate extraction follows the interface failure. The second type of graph occurs with the weakly bonded interface and short enough free

length. The fiber can be extracted progressively after the interface has failed. The friction is measured up to the final point. The embedded length and the friction load can be recorded along with maximum debonding load. The interfacial shear strength of the fiber - matrix interface is a key property when investigating the micro - mechanical behaviour of the composites. [7]

The single fiber pull-out-test involves only a single fiber. The role of neighbouring fibers is not taken into account, thus stresses and polymer morphology are not the same as in real natural fiber composites. The embedded length of the fiber cannot exceed the range 0.07- 1.0 mm. It is difficult to keep the embedded length short value, handle the test specimens and measure the strengths. [7]

The single fiber pull- out test sample preparation is shown in Figure 6.

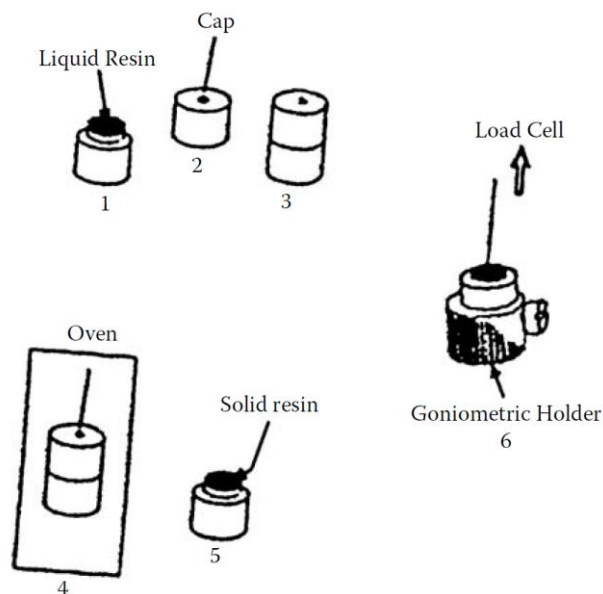


Figure 6 Pull- out test preparation. [7]

A drop of liquid resin is spread in the small aluminium holder. A cap with a 0.5-mm central hole containing the fiber is then placed over the holder with the fiber end entering the 10–1000 μm thick resin layer around the fiber. All the required samples can be prepared at the same time. All the cylinders are then transferred to an oven and the resin properly cured. After cooling and removing the cap, each sample is fastened by a screw to a goniometric holder on the cross head of the tensile testing machine. The fiber is aligned with the loading direction. The cross head is moved upward to introduce the free fiber end into a 200 -mm diameter hole drilled in the brass part on a heating head connected to the load cell. [7]

4.1.2 Fiber bundle pull-out test

The fiber bundle pull-out test is similar with the single fiber pull-out test, but a fiber bundle is used instead of a single fiber. A coupon is fabricated where a bundle of fibers are embedded in the matrix. Transverse notches are cut into the coupon near the end of the fiber bundle. The coupon is loaded in tension with the load applied parallel to the fiber axes. The load vs. displacement curve is monitored and the debonding point is detected. The interfacial shear strength between the bundle of fibers and matrix can then be calculated. A typical fiber bundle pull - out test and the load vs. displacement curve is shown in Figure 7. [11]

The fiber bundle pull - out test is used to determine the interfacial parameters between fiber bundles and the matrix. The fiber – matrix interface plays a key role in the fracture process. The test is done with the aid of jig metal frame which is equipped with strain gauges and thus acts as a load cell. The bottom part of the specimen, from which the single fiber bundle is pulled out, is fixed by a metal frame. The pull-out test is performed in a tensile testing machine. The load cell is larger than single fiber pull - out test. A typical load cell for the fiber bundle pull- out test is about 1000 N. The load/displacement curves are recorded during the tests. The experiments are carried out with a constant cross-head speed of either 0.02 to 0.05 mm/min. The tests were stopped as soon as the top of the samples were separated from the base plate. [15], [16]

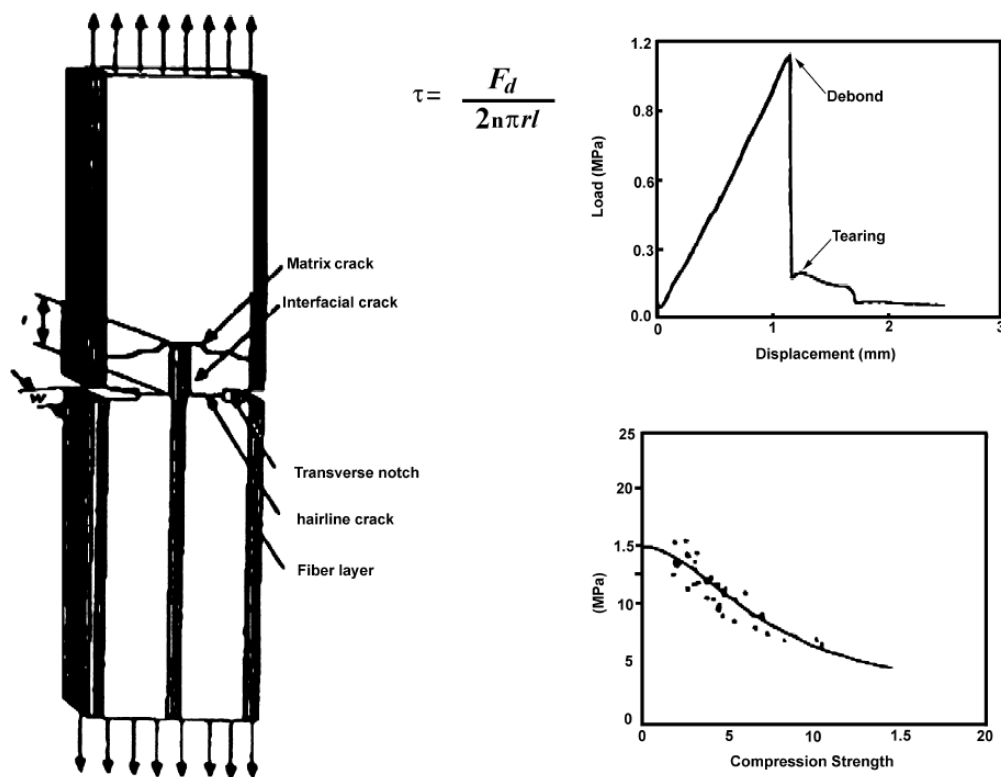


Figure 7 Fiber bundle pull-out test. [11]

The influence of the displacement rate of the pull - out behaviour is measured. The data of the cross head displacement, the load required for pull-out and the perpendicular load were recorded. After reaching the maximum value of load, the load rapidly decreases to reach a smaller decreasing rate when the bundle is pulled -out over their overall length. The peak load corresponds to a debonding over the whole embedded fiber length. It is then possible to evaluate the effective interfacial shear stress. The interfacial shear strength can be calculated from the measured maximum force, fiber embedded length and the fiber diameter. The fiber parameters are measured by an optical microscope before the testing. The fiber bundle- matrix interface is characterized by a scanning electron microscope after testing. [15], [16]

4.1.3 Single-fiber fragmentation test, SSFT

Single-fiber fragmentation test, SSFT, is used to calculate the interfacial shear strength. A single fiber is embedded in a dog bone-shaped tensile coupon, which in turn is subjected to a tensile load. Tensile forces are transferred from the matrix to the fiber and tensile stresses build up in the fiber. The tensile strength in the fiber achieves at some point a value where stress concentration is high enough for it to fracture. This loading process continues until the fiber fragment lengths are so small that the tensile stresses induced in the fiber can no longer fracture the fiber and the fiber fragmentation process ceases. The final fiber fragment length is referred to as the critical fiber length. The ratio the fiber critical length per its diameter can be good indicator of the fiber- matrix adhesion bond strength. From this value of the critical length, the IFSS can be calculated from the equation. The single fiber fragmentation test is shown in Figure 8. [3]

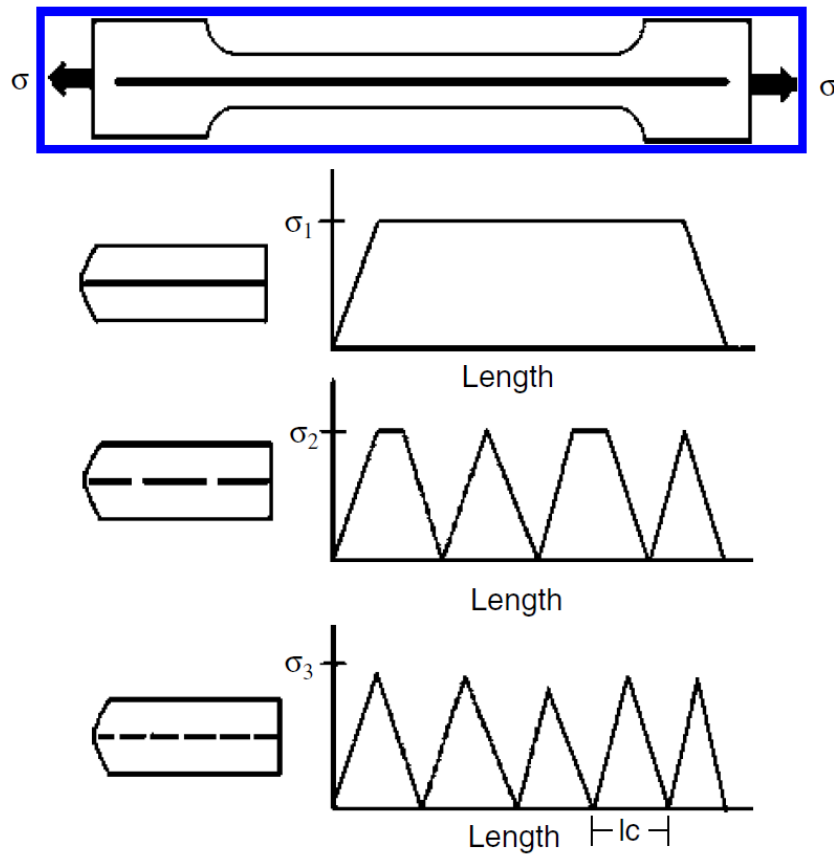


Figure 8 Single fiber fragmentation test method. [3]

In this method, a fiber is embedded in a matrix material such that the strain the failure of the matrix is at least three times higher than that of the fiber. The single fibre fragmentation test advantages are the simplicity in the sample preparation and creation large number of fragments from a single specimen. The interfacial shear strength can be characterized successfully. The interface has an important role in transferring the stress from the matrix to the fiber. There is a need to be able to characterize the interface and the level of adhesion to properly understand the performance of the composite. The single fiber fragmentation test is commonly used. [10]

Traditionally the single fiber fragmentation test is a low – strain - rate test. A high strain rate test is used for the investigation of composite materials intended for crash and impact applications. The single fiber fragmentation test done at low strain rate is used study the fiber- matrix interface. It is a useful method, because only a small amount of material is needed. Traditional low strain rate single fiber fragmentation tests were performed on specimens of exactly the same dimensions as the high strain rate specimens. [17], [18]

The single fiber fragmentation specimen consists of a single fiber, centrally embedded in a dog bone of the polymer matrix. Tensile load is applied to the specimen as a

whole, and this load is transferred from the matrix to the fiber, through the interface. The single fiber fragmentation testing is shown in Figure 9. If the matrix is more extensible than the fiber, the load will cause the fiber to break into fragments while the matrix continues to extend without breaking. The fiber fragmentation stops when the fragments have become so short that further increases in applied load cannot be effectively transferred to them. The stop of the fragmentation is called saturation. The length of the fragments at saturation is the central experimental quantity in the test. The fragment length at saturation will correlate with the quality of the interface. [17], [18]

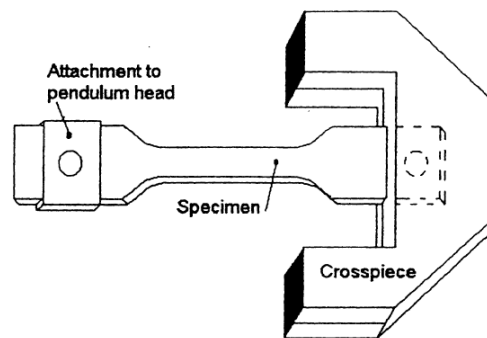


Figure 9 Test specimens lay-out [17]

At first rectangular coupons are cut, washed in a detergent and vacuum dried. One PP sheet with the thickness of 0.10–0.14 mm is fixed on the flat surface of Teflon-sheet on one side by an adhesive tape. Also others resins can be used in this method. Single fiber filaments are separated manually before attachment to the Teflon sheet. Fiber length is 10-20 mm. Sample set-up is shown from above in Figure 10. A single fiber is centered lengthwise between two coupons in a sandwich style. Then the specimens are placed in a heated press and held at touch pressure until the polymer coupons fused together. Each fused specimen is then cut into a dog bone shape. The single fiber fragmentation process is then observed closely at different test speeds and strain rates. Loading is stopped if the specimen fails, or when the fragmentation saturation level is achieved. In this situation, the fragments are not long enough to receive at the interface an axial load sufficient to cause subsequent fiber breakages. In most cases, the above described saturation length is not reached during the test. Instead, a series of cracks appear which arise from the ends of the fiber fragments and grow through the matrix or the interface. The low-rate test is performed on a testing machine at cross head speed of 0.050 mm/s. Each test specimen was examined in the microscope for determination of its average fragment length. [17], [18], [19]

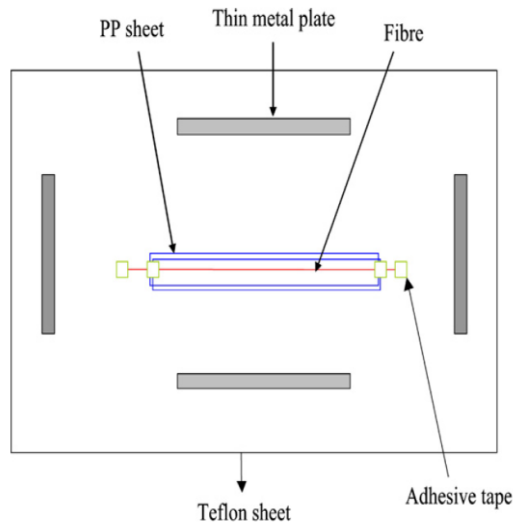


Figure 10 Sample preparations [18]

4.1.4 Micro-bond test

The micro-bond technique has been developed for studying the interfacial adhesion between fibers and matrix. The procedure involves the deposition of small amounts of matrix on the surface of a fiber in the form of discrete micro-droplets. The droplets form around the fiber the shape of an ellipsoid and it retain the shape after curing. The micro-droplet dimensions and the fiber diameter are measured with the aid of an optical microscope. The embedded length is fixed by the diameter of the micro-droplet along the fiber axis, which is dependent on the amount of resin deposited on the fiber. The practical minimum limit for the embedded length using this technique is 40 μm . [7] Interfacial shear strength is calculated from micro-bond test from equation (1):

$$IFSS = \frac{F}{\pi dl}, \quad (1)$$

where F is maximum load from micro-bond test, d is fiber diameter and l is embedded length of the droplet.

One end of each fiber specimen is glued to a metal tab and it is connected to a load cell. A small amount of matrix is allowed to come into contact with the fiber. Usually two droplets are placed on each fiber and about ten fibers are mounted on each template. The fibers are pulled out of the micro-droplets at rate of 0.5mm/ min using a tensile tester. The plates of the vice are first positioned above the droplet, and the slit is narrowed until the plates make contact with the fiber. As the shearing plates continue to move downward, they make contact with the resin and a downward force is exerted on the droplet. The shearing force at the interface is then transferred to the fiber through the fiber–matrix interfacial bond and is recorded by the load cell. The pull - out occurs when the shearing force exceeds the interfacial bond strength. The absence of large resin fragments on the surface of the fiber after the pull-out demonstrates that cohesive failure of the matrix does not occur. Two droplets per fiber are a practical amount. Two pull-out results are obtained from one fiber specimen. The microbond testing system is shown in Figure 11. [7]

The interfacial shear strength depends on mechanical locking and chemical bonding. Hydrogen bonding is possible between ester groups in the resin and - hydroxyl groups in the fiber cellulose. The interfacial shear strength is mainly attributed the high surface irregularity of fibers and the resulting mechanical interaction. The specimen preparation for the micro - bond test is difficult. The shape of the droplet affects the reliability of the test result. A symmetric and round droplet is easier to test and analyze than droplets with flat surfaces. The size of the droplet is also critical. If the length of the droplet exceeds a critical value, the fiber will fracture before debonding and the pull-out occur. [7]

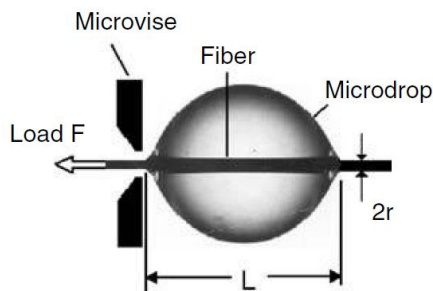


Figure 11 Microbond techniques [7]

The main problem in the micro-bond testing is that if the required force for pulling out the fiber is too high, the fiber will break. For fibers, whose diameter ranges from

5 to 50 μm , the maximum embedded length that can be used should be in the range of 50 to -200 μm . It is difficult to keep the embedded fiber length small enough and handle test specimens. A small amount of matrix is deposited on the fiber in the form of a micro droplet. A micro vise is used to grip the droplet and the fiber is then pulled out. [20]

Symmetrical droplets are selected for testing. The droplet/ fiber specimen attached at one end to a tensile tester with a 5 N load cells. The free length of fiber is as short as possible. A typical cross head speed is about 0.5mm/ min. The force/ extension curve is then created in a PC. The force/ -extension curve is presented in Figure 13. Tests are typically conducted until 30-40 debonded specimens are obtained. At least a 10 mm distance is left between the tabs and the droplet. The mixture of the epoxy and the curing agent are placed in vacuum at 50 °C to remove gas bubbles introduced during the mixing. An axially symmetric drop of the matrix is then placed on the fibers using a thin steel needle. The prepared specimens are cured for 2h hour at 75- 135 °C. [20], [21]

In the micro-bond technique it is assumed that the interfacial shear strength is uniformly distributed along the embedded length of the fiber. The average shear stress is calculated by dividing the maximum force of debonding by the embedded fiber length area. A change in the shape from a spherical micro droplet to an elliptical droplet does not affect much the state of stress along the embedded length of the fiber. The presence of a meniscus formed by the matrix at its point of contact with the fiber affects the interfacial stress distribution and failure mode. During the experiment, the matrix is held fixed against the stop system, which the fiber can only pass. At the point of contact at two diametrically located contact points, a stress concentration exists and the state of stress around the fiber is not axisymmetric. [11]

Micro- bond tests have advantages and limitations. The major advantages are that the force of debonding can be measured and that this technique can be used for almost all fiber - and matrix combinations. There are also limitations to the micro - bond methods. The debonding force is the function of the fiber embedded length. When using a small fiber diameter, the fiber embedded length has to be also very small. Longer embedded length can cause fiber failure during the test. The small size of micro droplet makes the failure difficult to observe. The state of stress on the droplet varies both with size and with support conditions at the points of contact between the blades and the micro droplet. A large scatter in the test data is obtained from the micro - bond test, because of the testing parameters such as a position of a micro droplet in the loading direct, droplet gripping and measurement of the fiber diameter. The variations in the chemical, physical and morphological nature of the fiber affect also the testing results. [5]

For the micro droplet test, several factors cause the large variation in test data and the interfacial shear strength. These factors are the tip geometry being in contact with a

droplet, the gap size between the vise tips and thickness and the property of the inter-phase layer. The gap between the micro-vise tips is about $20\mu\text{m}$ considering the size of the droplet and the fiber diameter. The gap is present in Figure 12. The centre of a single fiber is positioned at the centre of the gap between the vise tips. After fixing the specimens, the micro - vise jaw was moved to load the droplet with a displacement rate of 0.1 mm/min . 50 specimens are tested and their embedded lengths are from 50 to $150\ \mu\text{m}$. The microbond testing system is present in figure 14. [22]

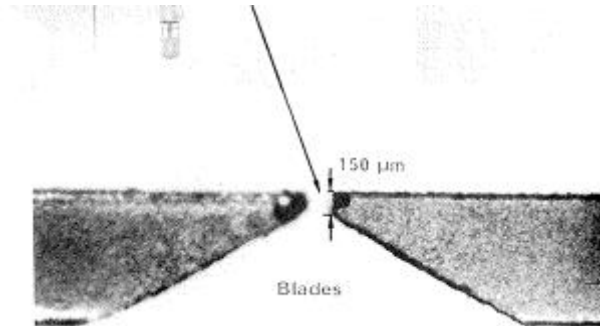


Figure 12 The gap between blades. [22]

The obtained curve of load versus displacement measurement from the micro droplet test is a measurement for the microbond test result. The load almost linearly increased up to the maximum load, and then decreased to the lower level of frictional load. After the maximum load is reached, the interfacial failure occurs between the fiber and droplet. Between the matrix and the fiber, some frictional load is maintaining during the test of the debonded droplet along the fiber. The curve of load versus displacement measured from the microbond test is shown in Figure 13. [22]

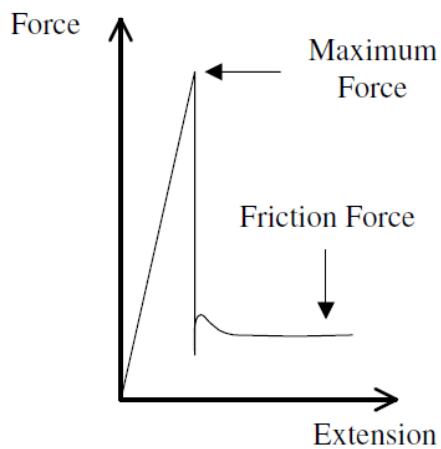


Figure 13 A typical microbond curves

The maximum load versus embedded fiber lengths can also be expressed as a graph in the microbond test. The maximum load has a tendency to increase with the embedded length of the fiber. If the embedded length is over 120 μm , fiber fracture will occur instead of the interfacial fracture. The critical minimum length of the embedded fiber is about 120 μm . [22]

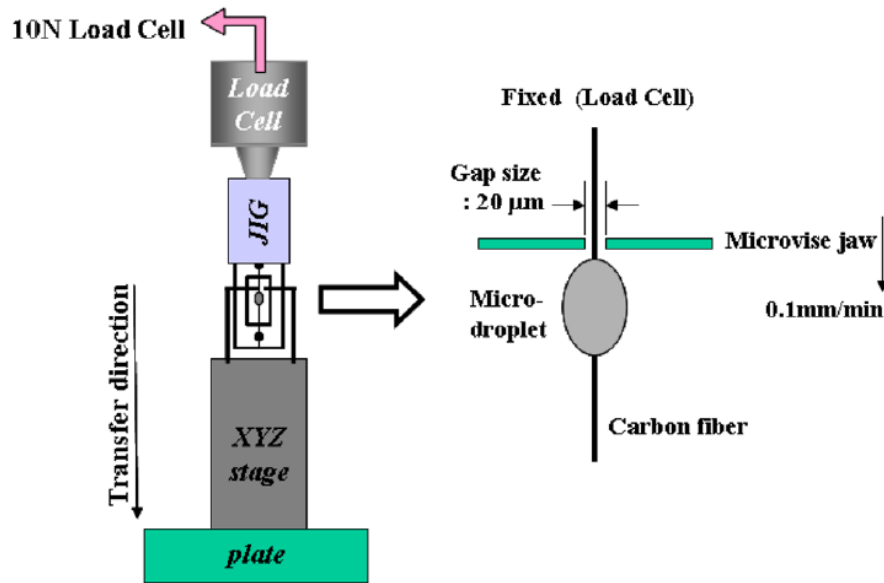


Fig. 2. Experimental arrangement for the microdroplet test.

Figure 14 Microbond testing. [22]

4.2 Contact angle measurement

Understanding the nature of the interaction of fibers with various liquids is important when developing new polymeric composite materials for different applications. The contact angle measurement gives information about the surface wettability and surface energies. This is important for the surface modification of the fiber surface state and when choosing the suitable rheological properties of the wetting matrix or polymer melt. Solid surface tension is calculated from measured contact angles and surface polarity. These parameters are used to estimate the expected interfacial adhesion between the fibers and the matrix. The wetting behaviour depends on surface chemistry, the surface roughness and the level of adhesion. Contact angle measurement is suitable for characterizing the changes in the surface characteristics with a high degree of accuracy. Load stress must be transferred from the matrix through the interphase into the reinforcing fiber. The wettability of fibers by polymer melts is a needed property. The result of good wetting is a greater contact area between the fiber and the matrix. The poor wetting of the fibers can lead the formation of voids in the interphase, which reduce the strength of the composites. The liquid matrix is wetted by reinforced fibers, this occurs when the surface tension of the fiber is higher than the surface tension of the matrix. The wetting of fibers is characterized by using the Willhelmy method. [23]

The major problem when measuring the contact angle between the polymer melt and the fiber is the high melt viscosity. Measurement of wettability and surface energies of fiber and the matrix are measured by the contact angle measurement method. The contact angle is one of the main parameters controlling the final mechanical behavior of the natural fiber composites. The adhesion is controlled by complete adherence between fiber and matrix and their wettability. These parameters can be characterized directly by contact angle measurement. The contact angle is directly related to wettability and the adhesion strength. The contact angle can be calculated for untreated and treated fibers, and then the results can be compared. The difference between the maximum and minimum contact angle values is called the contact angle hysteresis. This value can be useful when determining the surface roughness. [4], [24]

The contact angle is an important parameter in surface science. It is defined as the angle formed between the liquid - vapor and the liquid- solid interfaces, and at the solid – liquid - vapor three-phase contact line. The contact angle is also a common measure of the hydrophobicity of a surface. It provides information about surface energies, surface heterogeneity and surface roughness. Contact angle measurement is a simple and straightforward technique to estimate solid surface tensions. There are different ways to measure the contact angle which are depending on the size and the shape of the sample. If the liquid drop is strongly attracted to the solid surface, the droplet will spread out on the surface. The contact angle is in this case near to 0 °. Solid surface is then highly hydrophilic. If the solid surface is hydrophobic, the contact angle will be larger than 90°. The shape of a liquid drop is determined by a combination of surface tension and gravity effects. Surface forces tend to make drops spherical, whereas gravity tends to elongate a pendant drop or flatten a sessile drop. The Young equation governs the equilibrium or Young contact angle of a liquid drop on a solid one. The relationship is given in the equation:

$$\gamma (lv) \cos \alpha = \gamma(sv) + \gamma(sv) \quad (2)$$

In this equation $\gamma (lv)$ is liquid - vapor surface tension, $\gamma (sv)$ is the solid- liquid surface tension and $\gamma (sv)$ is the solid - liquid surface tension. The contact angle system is present in Figure 15. The solid surface is smooth, homogenous and rigid. The Young equation is expected for a given system liquid drop on the solid surface. [25]

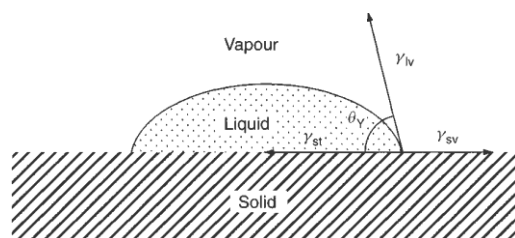


Figure 15 Schematic of a sessile drop contact angle system [25]

Many techniques are developed for the measurement of contact angles, but only a few are widely used. For flat solid surface geometry, the sessile drop method is the most common way to determine the contact angle. The contact angle of a sessile drop can be measured from the drop profile. Direct contact angle measurement from a drop profile can be measured by the conventional goniometer - telescope or axisymmetric Drop Shape Analysis (ADSA). [25], [26]

The contact angle is measured by using a contact angle goniometry. The contact angle can be read directly from the scale of the goniometer- telescope device. In this technique, the tangent is determined at the point of contact with a solid surface. The tangent aligning is easily done with a telescope equipped on the goniometer eyepiece. The tangent is aligned to the profile at the contact point and the contact angle is measured. Relatively high magnifications are used. The sessile drop slowly grows to a diameter of 5 mm using a syringe. The goniometer technique is easy to implement and straightforward to use. Contact angles with the accuracy of $\pm 2^\circ$ is possible be achieved. [26]

The most used method is the direct contact angle measurement of a sessile drop, which can be simply carried out by aligning a tangent to the sessile drop profile at the point where three interfaces meet. The contact angle of a liquid drop on a solid can be measured, either directly by using a telescope equipped with a goniometry eyepiece or from a photograph of a drop profile. [25]

The Wilhelmy balance is the most suitable method for measuring the contact angle in single fiber of a known diameter. The positions of the fibers affect the apparent contact angle. A qualitative measurement for the fibers wettability is commonly used. The modified Wilhelmy technique is a suitable method for measuring contact angles between the fibers and the liquid polymer matrix. This method is sensitive to measure the contact angle between fibers and low- viscose liquids. Before measuring contact angles, fiber diameters are measured by a scanning electron microscope or an optical microscopy. The diameter can be measured easily with the Wilhelmy method using a test liquid. Wilhelmy technique is shown in Figure 16. The fiber is attracted to the arm of a high-precision ultra- microbalance placed on an anti vibration table in an enclosed measuring chamber. The fibers can be immersed and withdrawn from the test liquid using a reversible elevator platform carrying the beaker containing the liquid, and the mass change detected at the balance will be recorded using a computer. The Wilhelmy method is very accurate, because a balance can be exactly calibrated using calibration weights. Using the Wilhelmy technique the wetting tension can be calculated from the equation: [23], [26]

$$\gamma(lv)\cos \alpha = \frac{\Delta mg}{\pi d} \quad (3)$$

In this equation Δm is the change of mass before and after fiber is wetted in the liquid, and d is the fiber diameter.

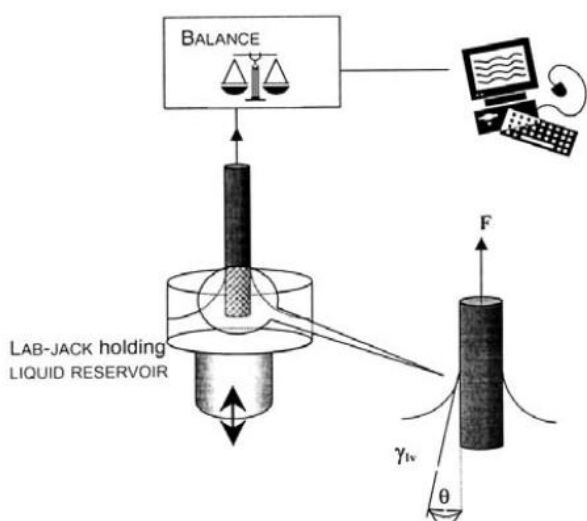


Figure 16 Willhelmy technique is used for measuring contact angle in fiber- matrix system. [23]

The modified Willhelmy technique can be used to measure either static or dynamic contact angles. In the static mode, the fiber is immersed in the test liquid only by a few millimetres in order to avoid possible end effects. The fiber is held stationary until a constant mass is measured so that the contact angle can be calculated. In the dynamic mode, however, the mass change is recorded during the whole fiber immersion-emersion cycle at a constant stage velocity. Contact angles can be calculated using the Willhelmy equation from the mass changes. The mass changes are detected during the immersion and emersion of the fibers. The dynamic contact angle measurement is used to characterize a large area of surface of fibers and detect changes in the wetting behaviour. Advancing and receding contact angles gives information about the chemical surface heterogeneity and roughness. The accuracy of the contact angles measured using the Willhelmy method depends on the accuracy of the fiber diameter. In case of natural fiber, the shape and diameter have a variation which must be considered. [23]

The contact angle is determined by a computer program in the Axisymmetric Drop Shape Analysis. The accuracy of this method is 0.2° . Application of ADSA includes the measurement of different modes of contact angles including static, advancing- and receding angles, contact angles on nonideal surfaces and contact angles on wetting surfaces. Determination of the liquid surface tension and the contact angle in ADSA is based on the drop shape. [26]

A low energy surface is more hydrophobic and a high energy surface is more hydrophilic. The effect of the water droplet to equilibrate with different surfaces is shown Figure 17. Polymers have relatively low surface energies, which lead to poor wettability

and moderate hydrophobicity. The hydrophilic surface area can be defined as the contact angle less than 45 degrees. The hydrophobic surface could be defined as the surface having a contact angle of water greater than 90 degrees. The conventional polymers have the contact angle of water between 45 degrees to 90 degrees. [27]

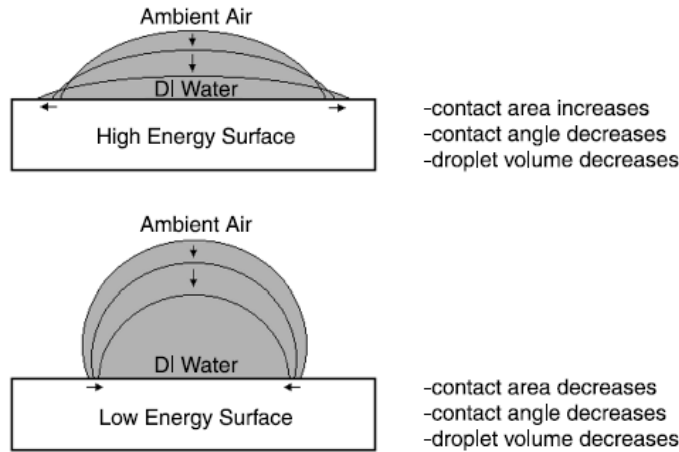


Figure 17 The effect of the water droplet to equilibrate with a different surface [27]

4.3 Microscopic Technique

Optical microscopy, stereo microscopy and scanning electron microscope are used for the characterisation of the fiber - matrix surface before and after micromechanical testing. The diameter of the fiber and the embedded length is measured by the optical microscope or the stereo microscope. The optical microscope picture is more reliable. The fracture mechanism and mode are investigated by the scanning electron microscope after micromechanical testing.

4.3.1 Scanning electron microscope (SEM)

The failure surfaces for sheared specimens can be used to illustrate the effect of the different fiber surface treatments and their effect on the effective properties of the composite. Scanning electron microscopy (SEM) studies of the composite failure surfaces can also be used to indicate if there is an improved adhesion between fiber and matrix. Examination of the failure surfaces also indicated differences in the interfacial failure mode. With increasing fiber–matrix adhesion the failure mode is changed from interfacial failure resulting in a considerable the fiber pull-out from the matrix. [13]

The anisotropy and heterogeneity in these composite systems make the fracture phenomena very complex. The other factors that contribute to this complexity are interfacial adhesion, wetting, fiber alignment, stress concentration at the fiber ends, the overlap of adjacent fibers, and different modes of fracture of the fibers and the matrix. In composites with brittle matrixes, the ductile fibers do not result in a

significant increase in elongation during break. However, this can be increased by reducing the adhesion between the fibers and matrix. The impact strength of fiber reinforced polymer composites is more complex than that of matrix polymers due to the role of the fibers and the interface. During an impact, the fibers may pull out of the matrix and dissipate the energy by mechanical friction thus preventing the localization of stresses along the fiber. Composites show a reduction in elongation during break and a reduction in the area under the stress - strain curve. This in turn reduces the impact strength or toughness of the composite. In conventional composites, the poorer adhesion of fibers to the matrix has higher impact strength than those with higher adhesion. [19]

The tensile properties of natural fiber reinforced polymers are mainly influenced by the interfacial adhesion between the matrix and the fibers. In general, the tensile strengths of the natural fiber reinforced polymer composites increase with fiber content, up to a maximum or optimum value, after that the value will then drop. Fiber surfaces have waxes and other non - cellulosic substances such as hemi cellulose, lignin and pectin, which create poor adhesion between the matrix and the fibers. In order to improve and develop natural fiber reinforced polymer composites with better tensile properties, it is necessary to increase the fibers hydrophobicity by surface chemical modification on the natural fibers. The fiber modification is attempted to improve fibers hydrophobic, interfacial bonding between the matrix and fiber, roughness and wettability, and decrease moisture absorption, leading to the enhancement of the tensile properties of the composites. [20]

The chemical coupling method is also one of the important chemical methods, which improve the interfacial adhesion. In this method, the fiber surface is treated with a compound that forms a bridge of chemical bonds between fiber and matrix. After the full extraction has been achieved, the recovered fiber is inspected in the SEM to measure both the fiber diameter and the embedded length, l_e , with l_e given by the distance between the remaining marks of the junction line with the resin (often as a broken wetting cone) and the fiber end. [7], [20]

4.3.2 Optical microscope

The optical microscope is used for fiber diameter and the embedded length measurement. The optical microscope uses visible light and a system of lenses to magnify the picture of small samples. Basic optical microscope is easy to use and simple, but there are also complex designs which aim to improve the quality of the picture. Microscopic studies such as optical microscopy can be used to study the morphological changes on the surface and can predict the strength of mechanical bonding at the interface.

4.4 Dynamic mechanical analysis (DMA)

The influence of cyclic loading on the interfacial properties of the composites can be determined by a dynamic mechanical analysis, DMA. Different fibers and thermoset matrices can be studied by the DMA techniques. The effect of the chemical surface treatment is used and the results are compared to each other. Usually the chemically surface treated fibers have better interfacial shear strength which is shown in the results of the DMA testing. The fiber - matrix interfacial degradation was characterized with various load levels. The cyclical fatigue loading affects the fiber - matrix interfacial properties. The force and the displacement values are recorded during the test. The average shear strength and energy absorbed are determined during the debonding and frictional sliding in the micro - debonding process. The strength and energy - absorption of the interphase are sensitive to the loading rate. [7]

The dynamic mechanical analysis is used to analyze the interfacial adhesion in natural fiber reinforced thermoset composites. The additional peak in tan delta curve is due to an additional polymer layer in the interphase. The storage modulus increased with treatment. Storage modulus is found to be directly relation to the interfacial strength of the composite. Glass transition temperature was found to shift to higher temperatures for treated composites indicative of good interfacial adhesion. The loss energy is a good parameter to characterize the fiber- matrix adhesion. The loss energy is higher with good adhesion interface than composites with good adhesion level. The poor adhesion composites consume more energy during a stress- strain loop. [7]

DMA is an analytical and non-sample destructive technique in which an oscillating stress is applied to a sample. The resultant strain measured as functions of both oscillatory frequency and temperature. The relationships between the various parameters such as storage moduli, loss moduli, mechanical damping parameter (tan delta), dynamic viscosity and temperature can be determined. DMA has been used to quantify the storage and loss moduli of polymers, polymer damping properties, glass transition temperatures, rate and extent of the curing of the polymers and identification of the polymer- polymer compatibility. [29]

The DMA can be used for fibers determining the effect of different chemical surface treatment. The chemical treated fibers composites show better properties than untreated fibers composites. DMA is an important method to analyze the effect of temperature and mechanical properties of the natural fiber reinforce composites. The effects of temperature and fiber loading on the storage modulus, the fiber length and the fiber orientation on the damping behaviour of the composites can be investigated. The storage modulus of modified fiber composites is higher than that of untreated fiber composites. This can be explained by better level of fiber- matrix adhesion. Thermal analysis for natural fiber reinforced composites is an important method in analyze the structure-

Figure 18 The variation of dynamic modulus as a function of temperature for the treated and untreated fibres. [31]

The loss modulus curve shows an interesting trend with two peak regions in all the fibre filled samples, which is shown in Figure 19. The surface area of the fiber changes, which in turn leads to improved fibre- matrix adhesion.

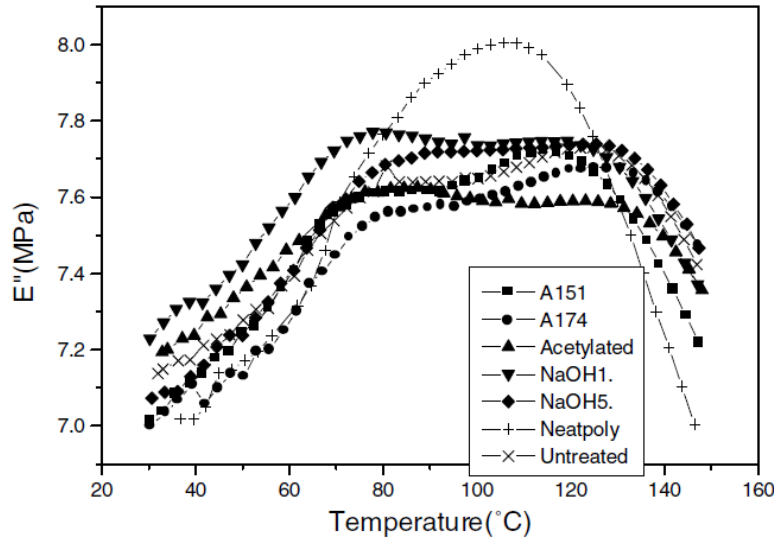


Figure 19 Effect of temperature on the loss modulus curves of the treated and untreated fibre composites. [31]

The shift in the Tg values in tan delta curves is shown in Figure 20. The shift in the curve indicated the improved fiber- matrix adhesion. Good adhesion between the fiber and the matrix leads to high level of dynamic modulus. The fiber surface is roughness which increases the adhesive bonds and makes the interface mechanically strong. [31]

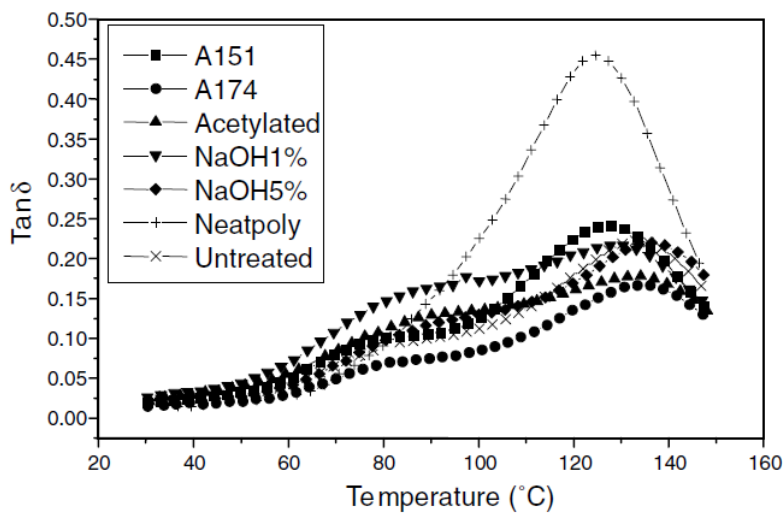


Figure 20 Effect of temperature on the damping curves of the treated and untreated fibre composites. [31]

4.5 Single fiber tensile testing and linear density determination

The diameter measurement is complicated with natural fibers because the diameter varies along the length and from fiber to fiber. A linear density parameter is related to the fibers diameter. The linear density of the fiber means its weight in grams per length in meters. The d-tex parameter is the weight in grams of 10 000m of fiber. The fiber diameter can be calculated from the d-tex parameter in equation:

$$d = \frac{\sqrt{(4 \cdot 10^{-6} \cdot dtex)}}{\pi \rho} \quad (4)[35]$$

The single fiber tensile testing is done by Lenzing instruments' Vibroskop and Vibrodyn tensile testing machine. The instrument measures of the linear density (dtex) of single fibers. The instrument determine of the linear density, fineness, denier and dtex parameters. The appropriate pretension weight has to be chosen and set on instrument. The mass of pretension depends on the fiber dtex parameter. The fiber is set into vibration by an electronic impulse. The parameters are derived from the fibers vibration frequency. [33]

Vibroskop instrument is used in combination with tensile tester Vibrodyn. The fiber with pretension weight is loaded into instrument. The instrument is shown in Figure 21a and 21b. The tenacity tests results are recorded by the computer in relation to the linear density. The results reports include tenacity, elongation, force and young modulus with graphics. [34]



Figure 21 Vibrodyn and Vibroskop instrument for fibers tensile testing

Single fiber tensile strength, TS, can be calculated from equation:

$$TS = \frac{F}{A} \quad (5)$$

In this equation, F is force from the single fiber tensile test and A is the cross-sectional area of the fiber.

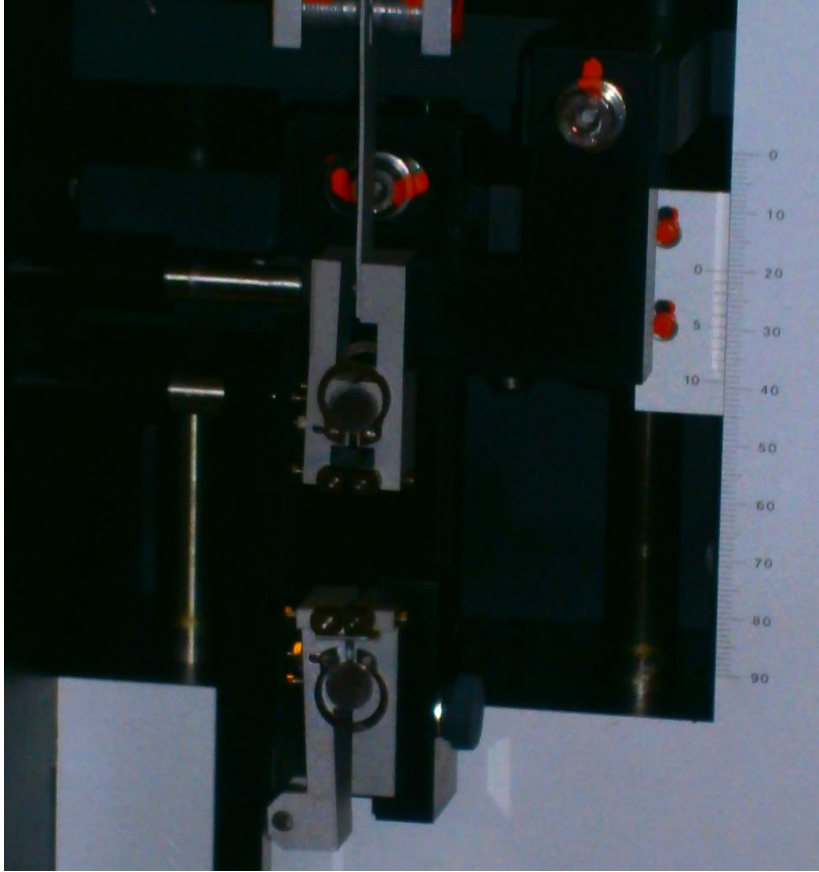


Figure 21b Fiber is attached to the machine

5 ADHESION BETWEEN NATURAL FIBERS AND MATRIX

Adhesion is defined as how well two different materials tend to stick together, and an adhesion measurement is giving an indication of the force required to separate them. The adhesion between the reinforcing fibres and the matrix plays an important role in the final mechanical properties. The load transfers between the matrix and the fibres. The adhesion is characterized by calculating the interfacial shear strength, which is measured by micromechanical testing. [1]

Mechanical interlocking, primary bonding, absorption, interdiffusion and electric theories describe the adhesion phenomenon. Adhesion is a thermodynamic event and there is a thermodynamical need to decrease the interfacial tension at interfaces. Good wetting is a requirement for good adhesion. It can occur if the surface energy of the wetting substance is lower than that of substrate. Wetting and the surface energy can be determined by measuring the contact angle. [3]

The basic types of adhesion are fundamental adhesion, thermodynamically adhesion and practical adhesion. Fundamental adhesion refers to the basic intermolecular forces that occur when two materials are close together. The intermolecular forces that act between the surfaces are called surface forces. The adhesion is based on surface forces. These forces are always present. Surface forces are classified as short - range and long - range surface forces. Short-range surface forces are those that act between atoms and molecules that are in contact within 0.1 or 0.2 nm of each other. Covalent bonds and hydrogen bonds are short- range surface forces, and they are stronger than long- range surface forces. [12]

Thermodynamic adhesion refers to the free energy when an interface is formed. The adhesion is defined in terms of surface energy, interfacial energy and work of adhesion. Surface energy is the work required to create a unit area of new surface. When a solid surface is not in the vacuum but is in contact with a liquid or vapour, it is considered in terms of interfacial energy. The surface tension of a liquid can be measured directly. Solid-liquid and solid-vapour surface energies are related to the liquid surface tension and the contact angle made by the liquid on the solid through Young's equation. [12]

The reinforcing ability of the fibers depends on the mechanical properties of the fibers, the polarity of the fiber and surface characteristics. All these factors control interfacial interaction between fiber and the matrix. The mechanical properties of the natural fibers composites depend on the degree of the interfacial bond strength, fiber strength,

and modulus and fiber orientation. Better mechanical properties with adhesion level can be explained by the changes in chemical interactions at the fiber- matrix interface. Impact strength is defined as the ability of a material to resist the fracture under stress applied at high speed. Natural fibers have effect impact properties. Good matrix-fibers interfacial adhesion is required to achieve moderate impact strength. The impact properties of the composites relate its toughness, which means the ability to absorb the energy. The impact strength of the composites depends on fiber rigidity, interfacial stress resistance and the fiber aspect ratio. The weakest part of the composites is related to the failure process. It is noted that the interfacial adhesion strength is dependent on the roughness of the fiber surface. A smooth fiber surface may lead to the lower interfacial adhesion strength. [14], [17], [25]

A combination of different adhesion mechanisms is often required to explain the adhesive bonding. The role of each mechanism varies for the different interfacial adhesion system. The adhesion interactions are divided into microscopic, macroscopic, atomic and molecular scale interactions. The mechanical interlocking is a microscopic parameter. Diffusion and wettability are atomic and molecular scale interactions. If an adhesive wet a solid surface, the adhesive should have a lower surface tension than the critical surface tension of the solid. Therefore, the fiber is wetted by the matrix and the fiber has lower surface tension. This is the reason for surface treatment for the fibers, which increases their surface energy and polarity. [28]

5.1 Adsorption theory

Adsorption theory is the most applicable theory of adhesion. Primary and secondary forces create the adhesion according to this theory. It contributes to all adhesive bonds. The most important primary forces are the ionic, covalent, and metallic bonds. The bonds formed by these forces are very strong. The strength is between 60–80 kJ/mol for covalent bonds and 600–1200 kJ/mol for ionic bonds. [22], [32]

The adsorption theory is also based on van der Waals forces, vdW, which occur between all atoms and molecules when they are closed together. They called secondary forces. Van der Waals forces are the weakest of all intermolecular forces. The strengths are adequate to account for the strengths of adhesive joints. Van der Waals is the forces of attraction between molecules with permanent dipoles, the forces between a permanent dipole and nonpolar molecule and the forces between nonpolar molecules. The strongest van der Waals forces are those between molecules which have permanent dipoles. The weakest van der Waals forces, so called dispersion forces, are formed between non- polar molecules. [22], [32]

5.2 Chemical bonding theory

The chemical bonding theory of adhesion involves the formation of covalent, ionic, hydrogen bonds and acid-base interactions between the interfaces. Covalent and ionic bonds are the chemical bonding, which provides much higher adhesion strength than secondary forces. The covalent bonds are often formed by silane coupling agents. The silane coupling agent is considered to be chemically reacting with both substrate and adhesive which are forming covalent bonds across the interface. The covalent bonds are strong and durable. The fibers are first treated by the silane coupling agent, and then dipped in the polyester and epoxies liquid to make composite. The ionic bond is the strongest chemical bond. [28], [32]

Hydrogen bonds are weak and they are easily broken and readily formed. The hydrogen bond consists of a hydrogen atom which is bonded to two other atoms. Two other atoms are bridged by a hydrogen atom. The hydrogen bond formed only atoms which are electrostatic (O, N, F and S). The strongest bonds are made with fluorine, because it is the most electronegative. The hydrogen is unique in forming bonds because it can approach other atoms closely on account of its small size. The bond does not have to be linear as the electrostatic force is not directional. [32]

Dipole – dipole forces means intermolecular forces, which is the result from the tendency of polar molecules to align themselves such that the positive end of one molecule is near the negative end of another. Dispersion forces are intermolecular forces resulting from the small, instantaneous dipoles that occur because of the varying positions of the electrons during their motion about the nuclei. [28]

5.3 Diffusion theory

In the diffusion theory molecules in contact may diffuse, and the initial boundary is removed. Adhesion is developed through the diffusion of molecules in between the adhesive and the adherent. The adhesion is caused by the mutual diffusion of the molecules of the interacting surfaces. The diffusion can occur only if the molecule chains are compatible and moveable. The use is limited when the solid surface is in contact. The diffusive interfacial layer typically has a thickness in the range of 1 – 100 nm [7], [28], [32]

5.4 Mechanical interlocking

Adhesive enter irregularities prior to the hardening if the substrate has an irregular surface. Adhesion occurs by the penetration of the liquid matrix into pores, cavities, and other surface irregularities on the surface of the fiber. Mechanical interactions can occur when a liquid polymer matrix is made to flow on the rough surface of a solid substrate. The theory contributes to adhesive bonds with porous materials. The extent of mechani-

cal interlocking depends on the porosity, the viscosity of molten adhesive, pressure and duration of bonding. [7], [28], [32]

The adhesive bond strength is resulting from the mechanical interlocking of the fiber and the matrix. Adhesives frequently form stronger bonds to porous abraded surfaces than they do to smooth surfaces. Good adhesion is possible also on the smooth surface. Enhanced adhesion after abrading the surface of an adherent may be due to mechanical interlocking, the formation of a clean surface, the formation of a highly reactive surface, and an increase in contact surface area. The changes in the physical and the chemical properties of the adherent surface produce an increase in adhesive strength. Mechanical interlocking, increase in the adhesion contact surface area, wetting or extensive chemical bonding are factors that explain the increased level of adhesion. [28]

6 EXPERIMENTAL

Micro-bond test was done for nine different natural fiber-thermoset combinations in order to determine the level of adhesion. It is possible to characterise changes in the physical and chemical structure of the interface between the fiber and the matrix by micro-bond technique. The aim of this investigation was to show that the micro-bond test is a useful method for characterising adhesion at the interface.

The interfacial shear strength (IFSS) can be calculated from micro-bond tests. Alkalization and Silylation was used in modification of fiber surface to improve adhesion between the fiber and the matrix. Single fiber tensile testing was done for glass fiber, flax fiber, viscose fiber and alkali-treated flax fiber. Single fiber tensile test shows that 4% NaOH treated fiber had the highest strength. Therefore, 4% alkali-treated flax fibers were chosen for micro-bond test. The aim of micro-bond test was to compare IFSS results between biobased epoxy and polyester resins.

6.1 Materials

Used natural fiber types are untreated flax, untreated viscose fiber, alkali and silane treated flax fiber. Viscose fiber was from Cordenka, Germany. Flax fiber was taken from Safilin Ltd low twist roving from France. Envirez G8600 INF-60 and Epobiox are used as thermoset resins. Envirez G8600 INF-60 is biobased polyester and EpobioX LV (low viscosity infusion resin) is biobased epoxy resin. Biobased resins are formulated using recyclable and renewable raw materials. EpoBioX LV was ordered from Amroy Europe Oy in Lahti, Finland. Envirez G8600 INF-60 was ordered from Ashland from Porvoo, Finland. Alkalization was made from pellet form Sodium hydroxide, which was taken from Merck. Silane treatment, 3 aminopropyltriethoxy silane, 99%, was taken from Acros Organics. Fiber-resin systems with their curing methods are listed in table 4. Samples with Envirez G8600 INF-60 are cured at first 2-3hours at 23 °C and then at 70 °C for 5 hours. EpoBioX LV samples are cured at first for 2hours at room temperature and then at 80 °C for 2-3 hours.

Table 4 Natural fiber, resin and curing

Sample	Natural fiber type	Resin	Curing
1	Untreated flax	Envirez G8600 INF-60	2-3 h at 23 °C. 70 °C for 5 h
2	Untreated viscose	Envirez G8600 INF-60	2-3 h at 23 °C. 70 °C for 5 h
3	4 % 30 min alkali- ne treated flax	Envirez G8600 INF-60	2-3 h at 23 °C. 70 °C for 5 h
4	5 % silane treated flax	Envirez G8600 INF-60	2-3 h at 23 °C. 70 °C for 5 h
5	4 % 30 h alkaline treated flax	Envirez G8600 INF-60	2-3 h at 23 °C. 70 °C for 5 h
6	Untreated flax	EpoBioX LV (CA35 TG 30 %)	2 h at 23 °C and then curing for 2–3 h at 80 °C
7	Untreated viscose	EpoBioX LV (CA35 TG 30 %)	2 h at 23 °C and then curing for 2–3 h at 80 °C
8	4 % 30 min alkali- ne treated flax	EpoBioX LV (CA35 TG 30 %)	2 h at 23 °C and then curing for 2–3 h at 80 °C
9	4 % 30 h alkaline treated flax	EpoBioX LV (CA35 TG 30 %)	2 h at 23 °C and then curing for 2–3 h at 80 °C
10	5 % silane treated flax	EpoBioX LV (CA35 TG 30 %)	2 h at 23 °C and then curing for 2–3 h at 80 °C

6.2 Chemical surface treatment

Fiber surface modifications such as alkali treatment and silane treatment are done to improve the fiber-matrix interactions. Flax fiber was subjected to alkalization and silylation before single fiber tensile testing and micro-bond test.

6.2.1 Alkali treatment

Flax fibers were treated with 1 - 6% concentration of NaOH for different time interval (30min and 30 hours) at room temperature. Flax fibers were soaked in the NaOH solution for designated time interval. Then fibers were washed under running tap water and finally with distilled water until neutral. Fibers were dried in an oven for 24 hours at 70 °C.

6.2.2 Silane treatment

Silylation of flax fiber was done with 2% and 5% of 3-aminopropyltriethoxysilane. Deposition from aqueous alcohol solutions is the most facile method for preparing silylated surfaces. A 95% ethanol / 5% water solution is adjusted to pH 4.5–5.5 with acetic acid. Silane is added with stirring to yield a 2% (APS 1 & APS 2) and 5% (APS 3) concentration. Solution was left open for hydrolysis and silanol formation to occur. In APS 1 the above step was 5 minutes and for APS 2 and APS 3 was 15 minutes. After hydrolysis flax yarn was dipped in the beaker for 5 minutes and then kept for air drying for 30 minutes. Finally fibers were dried in an oven for 2 hour at 70°C.

6.3 Testing methods

The adhesion between natural fiber and thermoset resins is measured by microbond test. Microbond test was done in Luleå University of Technology. Single fiber strength is determined by single filament tensile testing. Single fiber tensile testing was done in Tampere University of Technology.

6.3.1 Single fiber tensile testing and linear density determination

Single fiber tensile testing was done for flax fiber, glass fiber and two types of viscose fibers. The difference between viscose fibers was the level of twist. The fibers were separated from the bundle manually the day before the test. The single filaments were separated manually with good light which is shown in figure 20. The fibers stayed in testing temperature and atmosphere in laboratory for 24 hours before the testing because of drying. The tension speed was 1 mm/min, the used pretension weight was 200 mg and the gauge length was 200mm for each fibers.



Figure 22 Single fiber separations from the bundle.

Linear densities (dtex) of the fibers were measured by Lenzing Vibroskop instrument. Linear density parameter was related to the fibers diameter. The fiber diameter can be calculated from the dtex parameter in equation (1). Single fiber tensile strength was calculated from the equation (4). Single fiber tensile test was done by Lenzing Vibrodyn instrument.

6.3.2 Microbond test

This work aimed to characterize the level of adhesion between the natural fiber and bio-based resin by microbond technique. A small amount of matrix was deposited on the fiber in the form of microdroplet. Fiber diameter and droplet size (embedded length) were measured by optical microscope before testing. The diameter was calculated in different points and average value was calculated from these three points. Samples were taped to paper frame, because they were easier to measure, handle and connect to the tensile testing machine. Microbond sample with paper frame was shown in figure 23. Paper frame was cut away before testing when sample was connected to the tensile testing machine. Microbond technique with vernier calliper and Instron 4411 tensile testing machine with 5N load cell were shown in figure 24a. The gap between vernier calliper's knives was set 50 μm , which is shown in figure 24b.

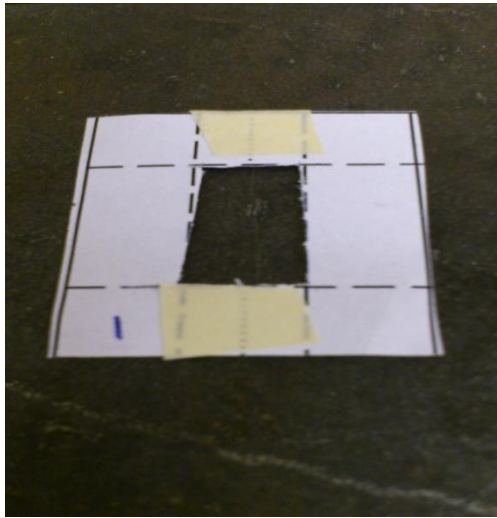


Figure 23 Microbond test sample is taped in paper frame

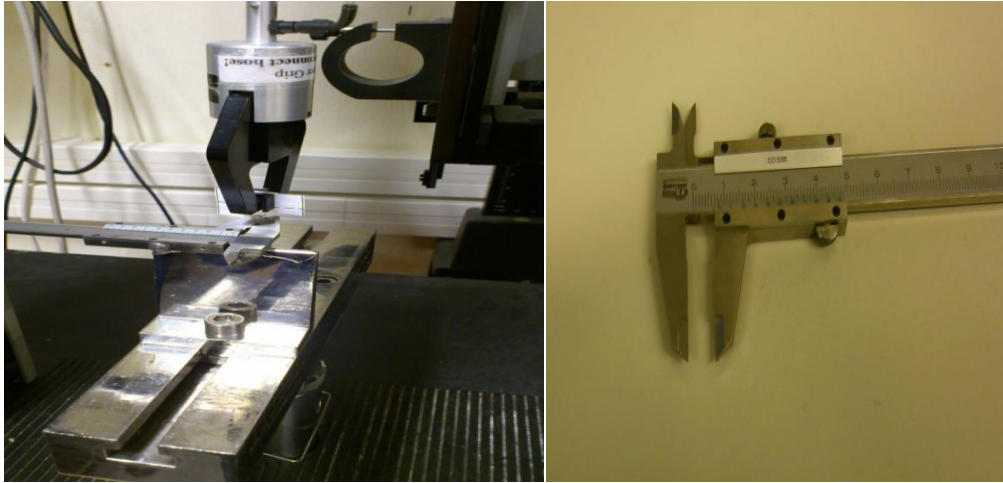


Figure 24 a) Microbond test b) Vernier calliper

Special care was taken to obtain samples with a free length as short as possible. Tests were performed at a cross-head speed of 0.5mm/min. The diameter was calculated in different points and average value was calculated. The pictures of measured samples before and after were shown in figure 25.

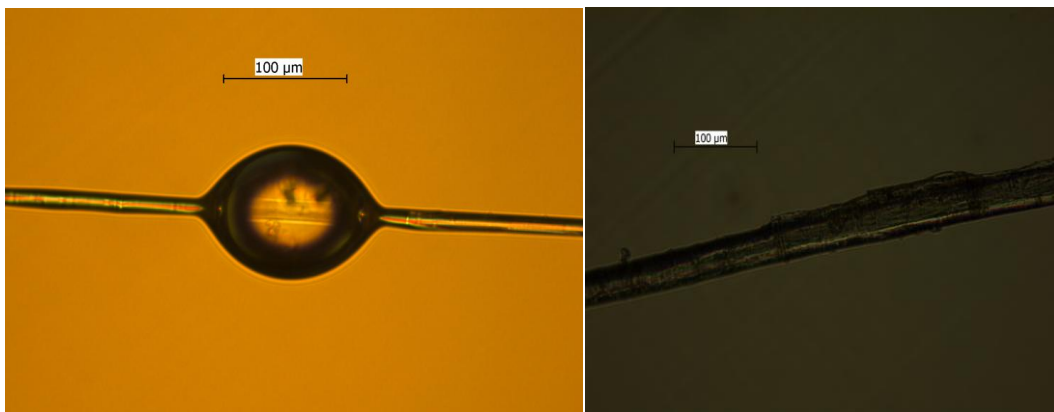


Figure 25 Microbond sample before and after the test

7 RESULTS AND DISCUSSION

Force-extension graphs, interfacial shear strength results and single fiber tensile strength test results are presented in this chapter.

7.1 Microbond test results

Microbond test results are presented in figure 27 and table 5. IFSS is calculated from the test results. Load-extensions curves are shown in figure 28-36. Droplet size, diameters, maximum load and the IFSS from each sample are presented in table 6-14. Fiber diameters, droplet size, young modulus of matrix and residual stresses affect the level of adhesion and therefore the value of IFSS. Residual stresses plays important role in the failure initiation, which is one reason for so many broken fibers. Optical microscope was used to examine the fiber surface after the test.

7.1.1 Interfacial shear strength, IFSS

Interfacial shear strength was calculated from the test results. Only a few samples per each fiber-matrix combinations succeed. A considerable amount of samples broke during the test or setting sample to the tensile testing machine. If the force required for pulling out was too high, the fiber broke. Average IFSS and standard deviation was calculated in table 5. The results are shown in figure 27. The results were difficult to compare because standard deviations were so high. High standard deviation from the results is typical for natural fiber characterization, because fibers diameters, and therefore also the fiber strength vary a lot. The accompanying variability in the fiber diameter and the embedded length means that it was difficult to screen out the samples that will break before shear debonding can occur. If the fiber has an increased cross-sectional area below the droplet, or if there is an irregularity in the fiber surface within the embedded part of the droplet, a larger force will be required to give shear debonding. The fiber is then likely to break instead. The test requires the shearing plates of the micrometer to be bought together to make contact with the fiber surface. The micrometer gap has to set to be slightly wider than the fiber but still small enough to prevent passage of the droplet. This test used the gap 50 μm which could not adjust during the test, because the gap is made by 50 μm thin metal. The positioning of the plates can significantly affect the stress distribution along the length of the interface. The gap width needs to be as small as possible according to the fiber diameter. [36]

One reason for high standard deviation was that only a few measurements per fiber-matrix combinations were successful. Samples were made about 20-25 per each combination, of which 10-15 was able to test. About 2-8 per tested samples were possible to calculate the IFSS. This means that about 50 samples must be prepared in order to ob-

tain 10-20 samples which are able to calculate the IFSS. The IFSS was calculated from equation (1):

$$IFSS = \frac{F}{\pi dl}$$

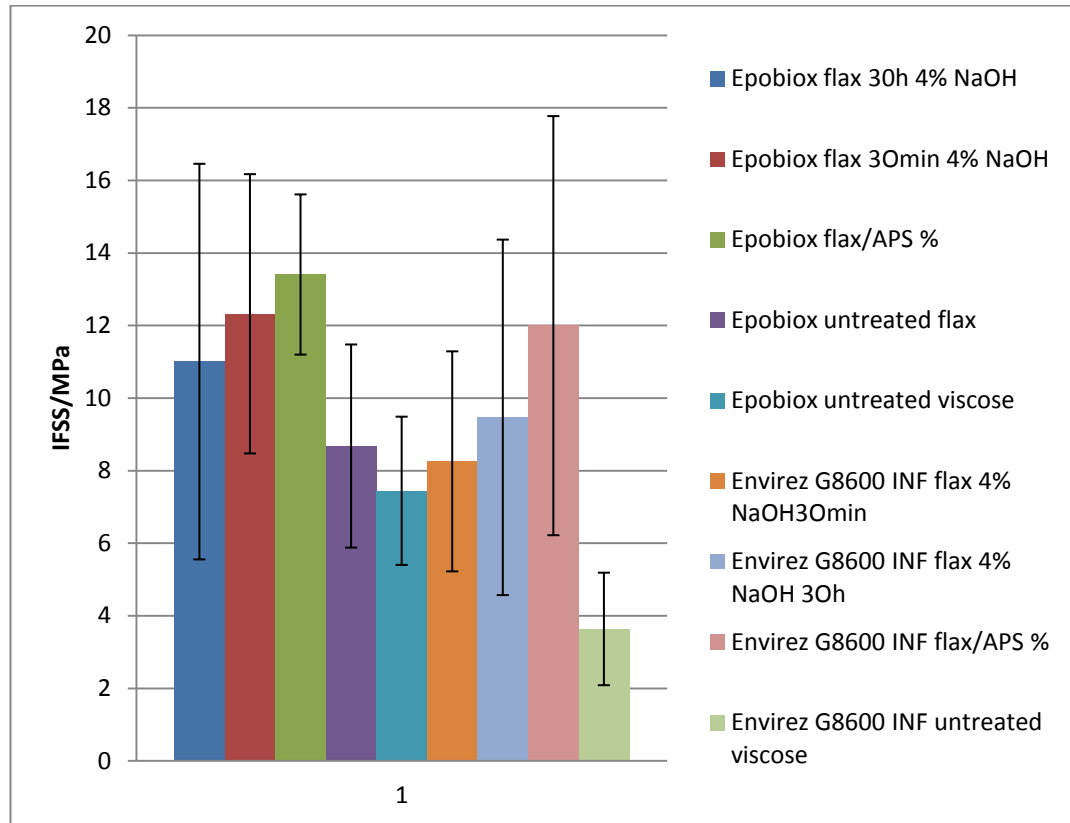


Figure 27 IFSS with standard deviation per each fiber/matrix/treatment systems

The highest value of the IFSS was silane treated flax fiber with Epobiox and the second was silane treated flax fiber with Envirez G8600 INF. Standard deviation is much higher with Envirez G8600 INF flax/APS % because IFSS can be calculated only per two samples. The lowest value of IFSS is samples with untreated flax and viscose fiber with both matrix, Epobiox and Envirez G8600 INF. In order to test results can be considered reliable; the standard deviation should be lower and more samples should be measured successfully.

The adhesion between Epobiox and flax fiber was improved with alkalization and silane-treatment, even if standard deviation was relatively high. The IFSS with untreated flax fiber was lower than treated ones. According to the results, the adhesion between Epobiox and flax fiber was better than adhesion between untreated viscose fiber and Epobiox. Micro-bond test failed with untreated flax fiber and Envirez G8600 INF resin. For this reason, it is not possible to evaluate the level of adhesion between treated and untreated flax fiber with Envirez G8600 INF resin. The IFSS with treated flax fiber were higher than the IFSS with untreated viscose fiber. In conclusion, the adhesion be-

tween Epobiox and natural fiber was better than the adhesion between natural fiber and Envirez G8600 INF resin.

Table 5 Interfacial shear strength and standard deviation measured in micro-bond test in various combinations

Sample	Fiber/matrix/treatment systems	IFSS/MPa	STDEV/MPa
1	Epobiox flax 30h 4% NaOH	11.00	5.45
2	Epobiox flax 30min 4% NaOH	12.32	3.84
3	Epobiox flax/APS %	13.40	2.20
4	Epobiox untreated flax	8.67	2.79
5	Epobiox untreated viscose	7.44	2.04
6	Envirez G8600 INF flax 4% NaOH30min	8.25	3.03
7	Envirez G8600 INF flax 4% NaOH 30h	9.46	4.89
8	Envirez G8600 INF flax/APS %	11.99	5.77
9	Envirez G8600 INF untreated viscose	3.63	1.55

Standard deviation is typically high for flax fiber, which is also shown in S. Wong, R.A. Shanks and A. Hodzic investigation. The IFSS was evaluated by single fiber pull-out test, which was done flax fiber and biopolymer with different chemical treatment. According to their results from the test, standard deviation was also relatively high when calculating the IFSS. [38]

7.1.2 Load-extension curves from the micro-bond test

Epobiox with 4% NaOH-treated flax fiber load-extensions graphs are seen in figure 28. Droplet size, fiber diameter, maximum load and IFSS are calculated in table 6. The effect time of alkali treatment was 30h.

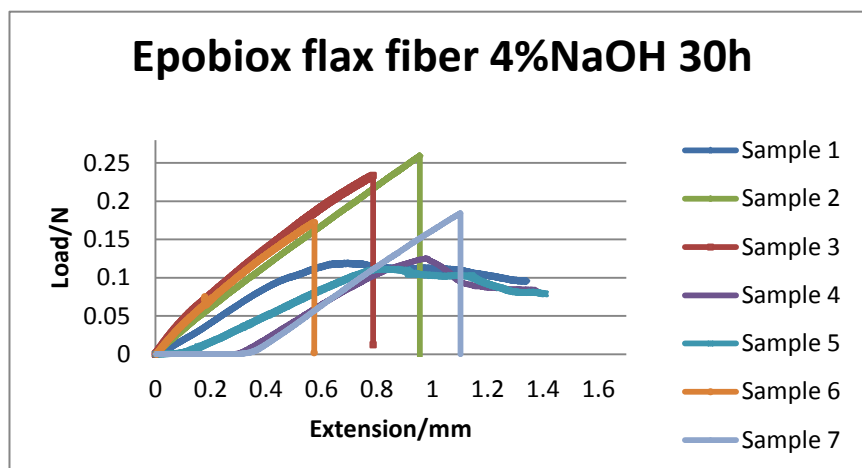


Figure 28 Load-extension graphs for 4% NaOH-treated flax fiber with Epobiox matrix. Alkali-treatment effect time is 30h.

12 samples have been tested, of which 7 was able to calculate the IFSS. 5 samples broke during the test. Fiber broke during the test before the droplet pull-out. In this case, the required force was too high, which made fiber breaks. Average IFSS was 11.002 MPa and standard deviation of the IFSS was 5.45 MPa.

Table 6 IFSS for Epobiox with 4% NaOH-treated flax fiber. Alkali-treatment effect time was 30h.

Sample	Droplet/ μm	Diameter/ μm	F/N	IFSS/MPa
1	295.00	22.40	0.11	5.72
2	187.00	19.80	0.25	22.28
3	237.00	27.10	0.23	11.57
4	224.00	20.30	0.12	8.78
5	329.00	24.60	0.11	4.39
6	225.00	21.60	0.17	11.27
7	207.00	21.82	0.18	12.98

Epobiox with 4% NaOH-treated flax fiber load-extension curves is shown in figure 29. Droplet size, fiber diameter, maximum load and IFSS are calculated in table 6. The effect time of alkali-treatment is 30min. 6 samples have been tested, one samples broke and the IFSS is calculated from 5 samples. Average IFSS was 12.32 MPa and standard deviation was 3.849 MPa.

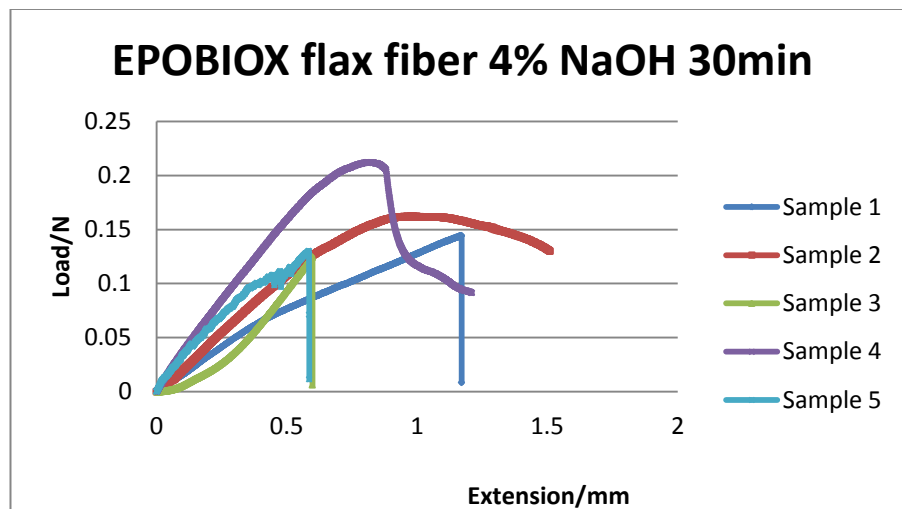


Figure 29 Load-extension graphs for 4% NaOH-treated flax fiber with Epobiox matrix. Alkali treatment effect time is 30min.

Table 7 Interfacial shear strength for Epobiox 4% alkali-treated flax fiber. The effect time is 30min.

Sample	Droplet/ μm	Diameter/ μm	F/N	IFSS/MPa
1	134.48	19.87	0.14	17.18
2	172.41	19.36	0.16	15.45
3	163.79	18.63	0.12	12.99
4	251.00	29.54	0.21	9.10
5	327.00	18.45	0.13	6.86

Epobiox with silane-treated-flax fiber load-extensions graphs are seen in figure 30. Droplet size, fiber diameter, maximum load and IFSS are calculated in table 8. Three samples of 8 were successful. Average IFSS was 13.403 MPa and standard deviation was 2.208 MPa. The highest IFSS with treated flax fiber with Epobiox resins was 13.403 MPa. Generally, all the treated fibers with Epobiox had the IFSS in same level.

Epobiox with untreated flax and viscose fiber load-extension curves are shown in figure 31 and 32. Their droplet size, fiber diameter, maximum load and IFSS are listed in table 9 and 10. The average IFSS for untreated flax fiber was 8.675 MPa and standard deviation was 2.79 MPa. Five samples per 15 samples were successful tested. This shows that the adhesion between flax fiber and EpobioX lv was improved by silane and alkali treatment. The average IFSS for untreated viscose fiber with EpobioX LV was 7.4416 MPa and standard deviation is 2.043 MPa. Silane coupling agent improves the adhesion between flax fiber and Epobiox, because hydrogen bonds and silane bond are provided between them. [39], [40]

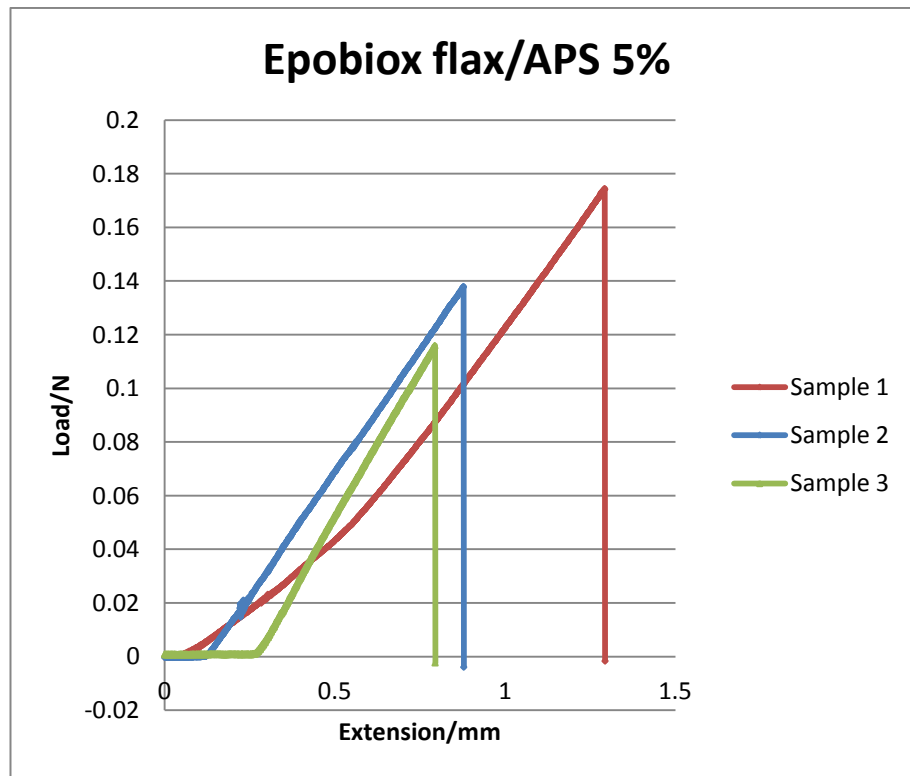


Figure 30 Load-extension graphs for silane-treated flax fiber with Epobiox matrix

Table 8 Interfacial shear strength for Epobiox with silane treated flax fiber

Sample	Droplet/ μm	Diameter/ μm	F/N	IFSS/MPa
1	181.03	20.08	0.17	15.28
2	155.17	19.34	0.13	14.62
3	211.00	16.98	0.11	10.30

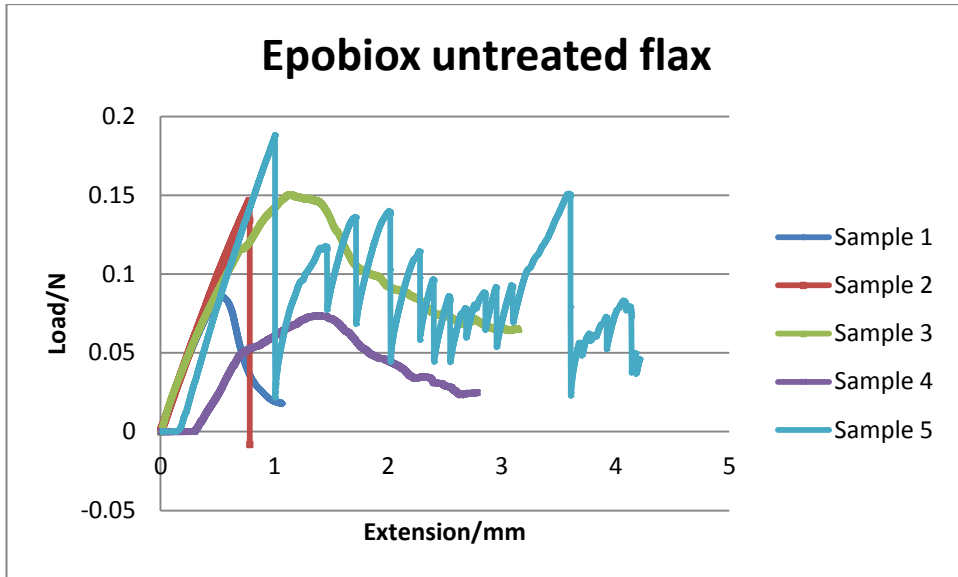


Figure 31 Load-extension graphs for Epobiox with untreated flax fiber

Table 9 Interfacial shear strength for Epobiox with untreated flax fiber

Sample	Droplet/ μm	Diameter/ μm	F/N	IFSS/MPa
1	186.0	22.41	0.08	6.51
2	227.0	20.13	0.14	10.21
3	295.0	26.65	0.15	6.09
4	150.0	23.98	0.07	6.52
5	200.0	21.36	0.18	14.03

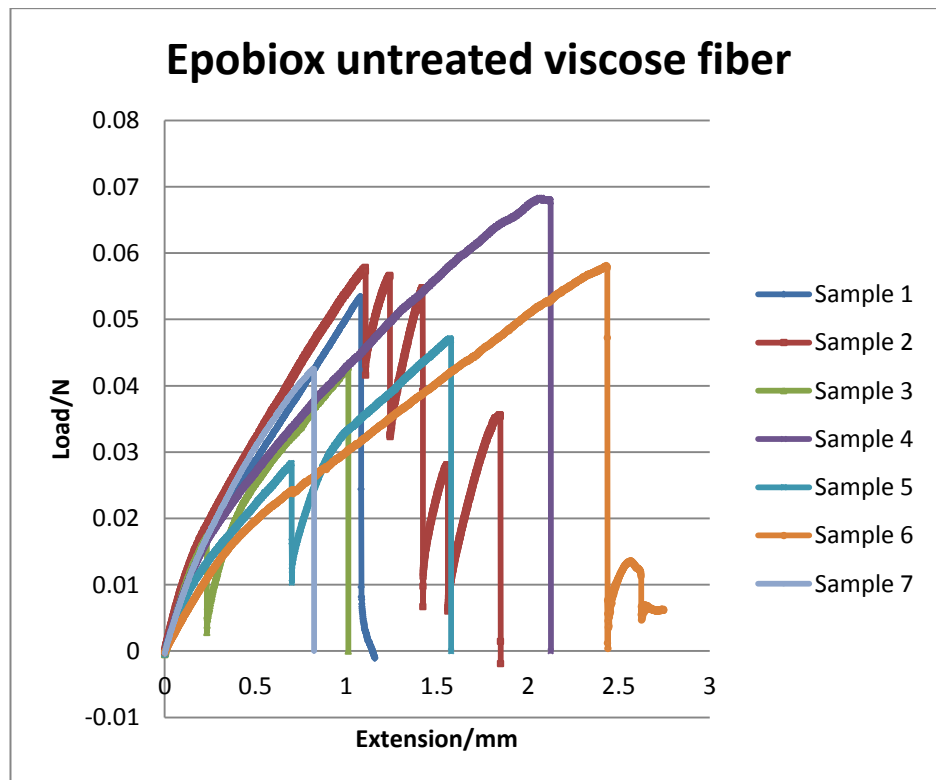


Figure 32 Load-extension graphs for Epobiox with untreated viscose fiber

Table 10 Interfacial shear strength for Epobiox with untreated viscose fiber

Sample	Droplet/ μm	Diameter/ μm	F /N	IFSS /MPa
1	181.25	16.67	0.053	5.63
2	168.75	15.10	0.057	7.23
3	150.00	14.95	0.043	6.09
4	128.13	15.30	0.068	11.09
5	190.63	14.74	0.047	5.33
6	148.44	13.90	0.057	8.86
7	168.75	15.05	0.042	7.83

Envirez G8600 INF with untreated flax fiber did not get results, because all the samples failed during the test. Untreated flax fiber with Envirez G8600 INF was tested first, and therefore this combination failed. It took time to samples adjust the micro-bond test method.

The average IFSS for Envirez G8600 INF with 4% NaOH-treatment was 8.253 MPa and standard deviation was 3.032 MPa. The results are shown in figure 33 and table 11. The chemical surface effect time was 30min. Only three samples per 14 were successfully tested. Rest of the samples failed during the test when the fiber broke before the droplet pulled out.

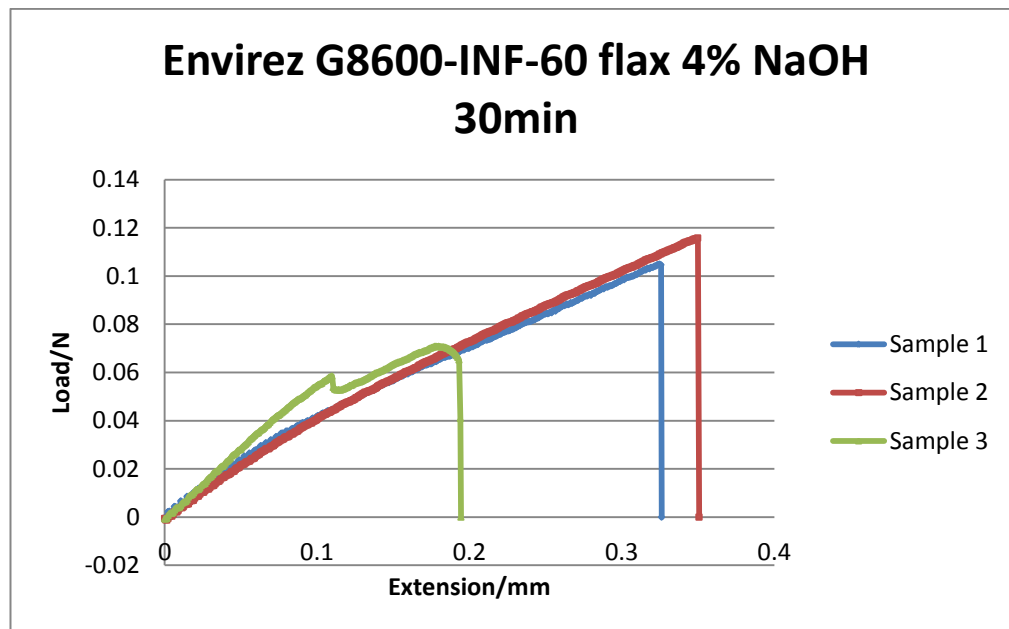


Figure 33 Load-extension graphs for Envirez G8600 INF-60 and 4% NaOH-treated flax fiber. The treatment effect time is 30min.

Table 11 Interfacial shear strength for Envirez G8600 INF-60 and 4% NaOH-treated flax fiber. The treatment effect time is 30min.

Sample	Droplet/ μm	Diameter/ μm	Load/N	IFSS/MPa
1	210.00	15.79	0.105	10.07
2	198.00	17.40	0.116	10.69
3	226.00	25.09	0.071	3.98

The IFSS for same fiber-matrix combination and 4% NaOH-treatment with 30h effect time was 9.466 MPa. Standard deviation was 4.899 MPa. The results are shown in figure 34 and 12. Seven samples from the 15 measured samples were successfully measured.

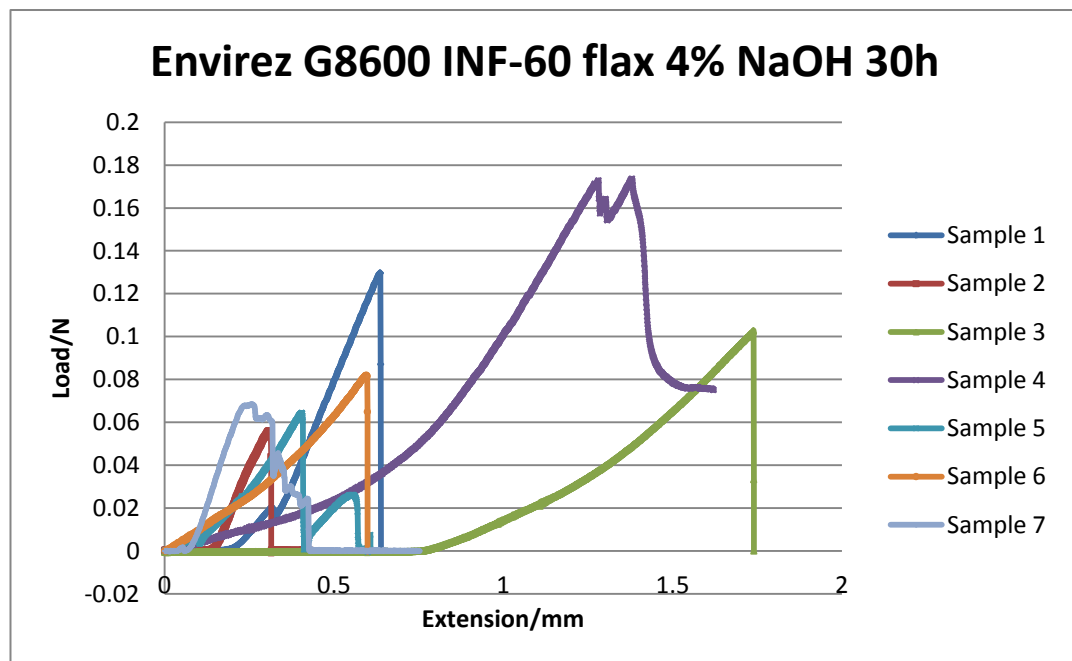


Figure 34 Load-extension graphs for Envirez G8600 INF-60 and 4% NaOH-treated flax fiber. The treatment effect time is 30h.

Table 12 Interfacial shear strength for Envirez G8600 INF-60 and 4% NaOH-treated flax fiber. The treatment effect time is 30h.

Sample	Droplet/ μm	Diameter/ μm	F/N	IFSS/MPa
1	105.58	20.10	0.129	19.43
2	124.13	21.69	0.056	6.62
3	120.69	19.31	0.103	14.04
4	240.00	29.40	0.174	7.84
5	183.00	23.90	0.064	4.69
6	183.00	21.46	0.082	6.65
7	159.00	19.60	0.069	6.99

The results from Envirez G8600-INF-60 resin with silane-treated flax fiber micro-bond test are shown in figure 35 and table 13. Only two samples of the twelve tested successfully. The average IFSS was 11.993 MPa and standard deviation was 5.776 MPa. The IFSS value is high compared to other samples, but more successfully tested samples is needed to confirm the result.

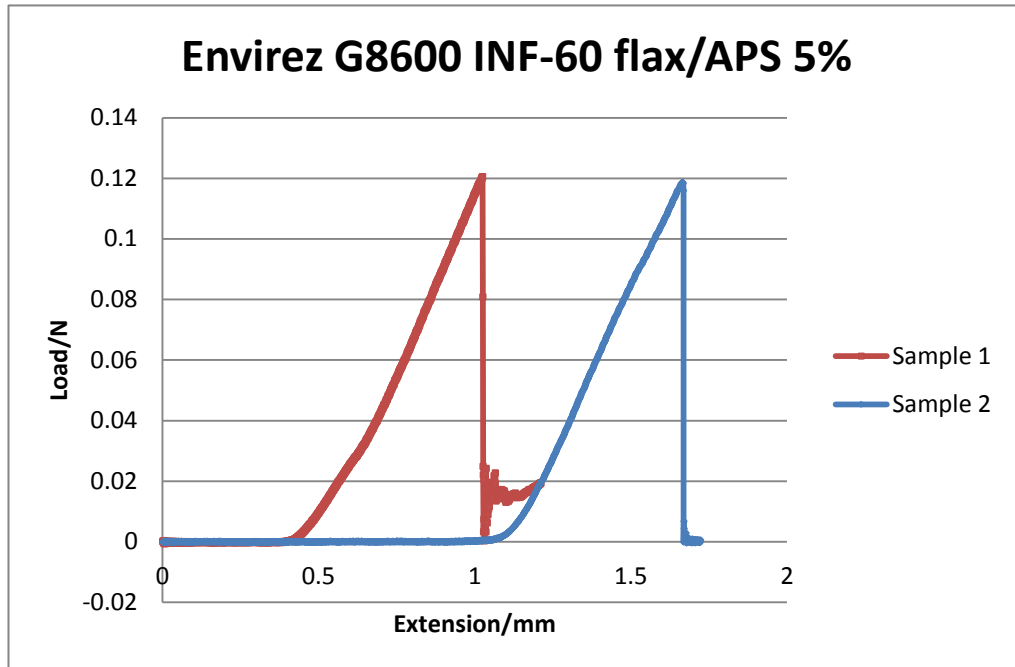


Figure 35 Load-extension graphs for Envirez G8600 INF-60 and silane-treated flax fiber

Table 13 Interfacial shear strength for Envirez G8600 INF-60 and silane-treated flax fiber

Sample	Droplet/ μm	Diameter/ μm	F/N	IFSS/MPa
1	151	14.3	0.1205	17.768
2	225	27	0.1187	6.217

The load-extension graph and test results from Envirez G8600 INF-60 resin with untreated viscose fiber are shown in table 36 and 14. Five samples of the twelve samples were tested successfully. The average IFSS was 3.634 MPa and standard deviation was 1.551 MPa. The IFSS was the lowest of the all fiber-matrix-surface treatment combinations. This result shown that the adhesion between untreated viscose fiber and Envirez G8600 INF-60 was weak compared to the other systems.

Table 14 Interfacial shear strength for Envirez G8600 INF-60 and untreated viscose fiber

Sample	Droplet/ μm	d/ μm	F/N	IFSS/MPa
1	171.87	13.57	0.01073	1.46447
2	146.87	14.33	0.02765	4.18195
3	150.00	17.90	0.02174	2.5773
4	231.58	14.27	0.06281	6.0501
5	178.23	15.68	0.03422	3.89777

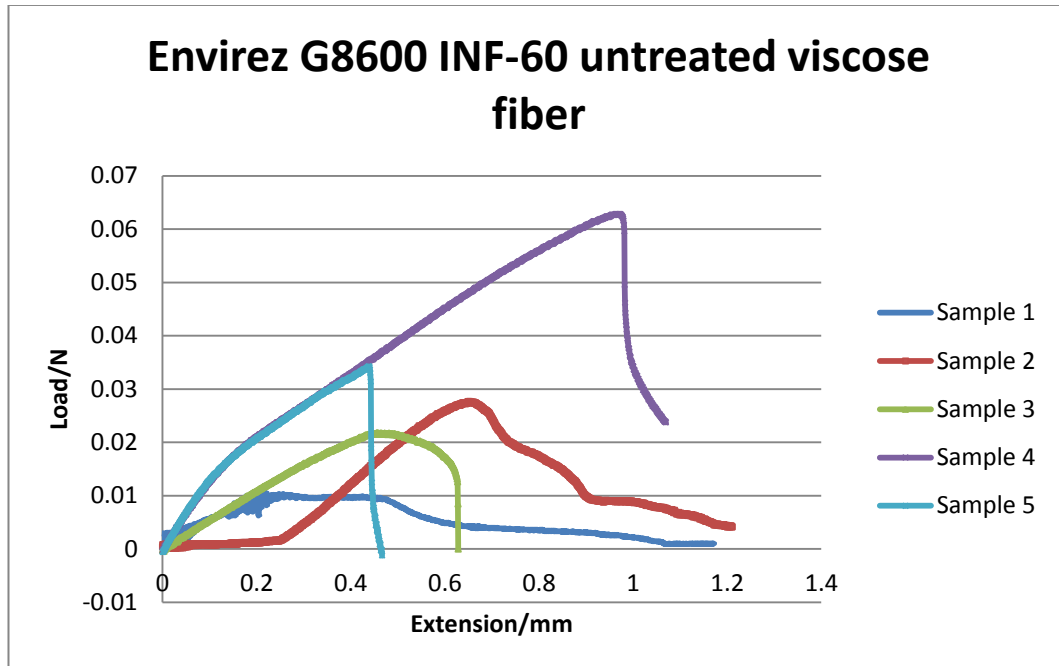


Figure 36 Load-extension graphs for Envirez G8600 INF-60 and untreated viscose fiber

7.2 Single fiber tensile test

The single fiber tensile testing was done by Lenzing instruments' Vibroskop and Vibrodyn tensile testing machine. Vibroskop was an instrument for measuring of the linear density (dtex) of single fibers. The instrument determine of the linear density, fineness, denier and dtex parameters. Fiber diameters were calculated from equation (3) and fibers strength were calculated from equation (4). Tensile testing results are shown in figure 37 and 38. The effect of chemical treatment on flax fiber was studied by using single fiber tensile test. According to the figure 37, glass fiber has highest strength compared to natural fibers. Flax fiber has remarkably higher single fiber tensile strength compared to viscose fiber.

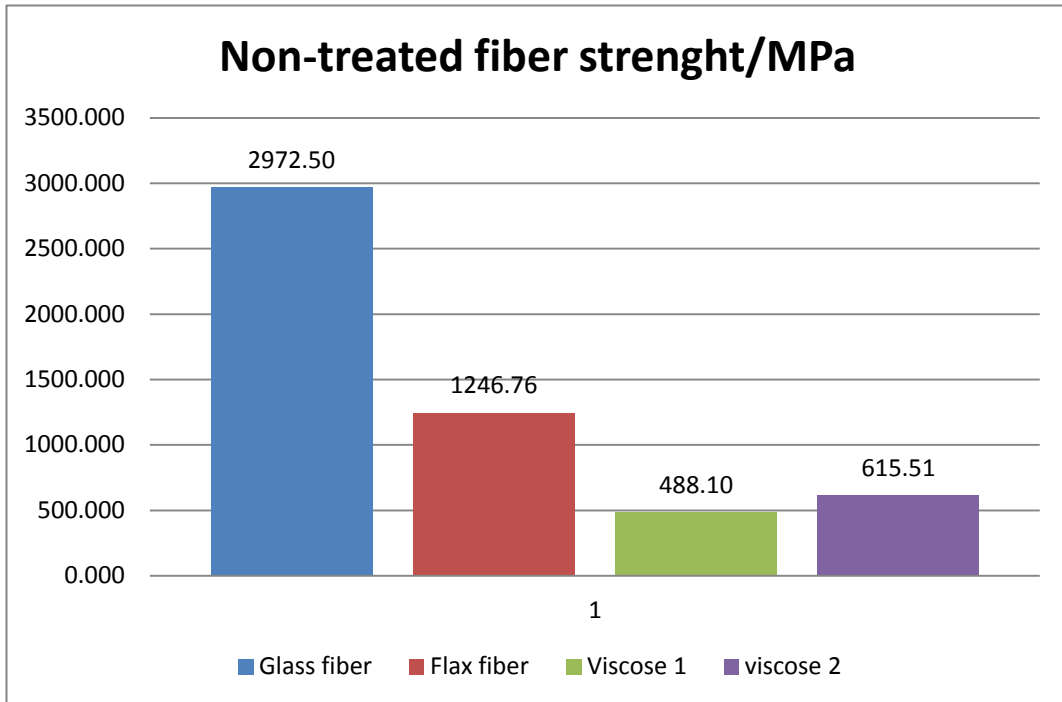


Figure 37 Single fiber tensile testing results for non-treated fiber

The results from the alkali-treated tests are listed in table 15. Tensile strength of treated flax fiber seems to increase when compared to untreated flax. Flax fiber with 3% and 4% NaOH concentration had the highest tensile strength. Tensile strength almost doubled from 1364 MPa for untreated flax to 2954 MPa for 4% alkali treated flax. Viscose fiber has the lowest tensile strength.

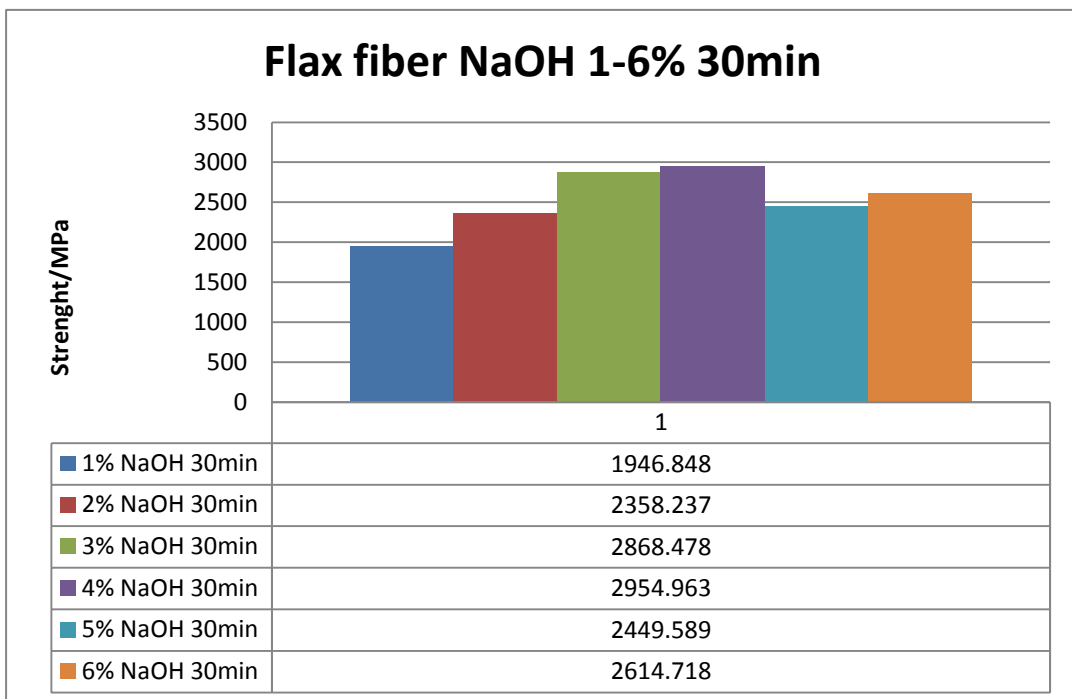


Figure 38 Single fiber tensile testing results for 1-6% NaOH-treated flax fiber

Table 15 Single fiber tensile testing results for 1-6% NaOH-treated flax fiber

NaOH (%)	Dtex	Elongation (%)	F/cN	Diameter (μm)	Strength (MPa)
0	4.82	2.52	43.87	20.23	1364
1	1.85	3.7	23.51	12.4	1946
2	1.70	3.85	26.36	11.93	2358
3	1.50	3.95	28.31	11.21	2868
4	1.37	3.81	26.62	10.71	2954
5	1.17	4.34	19.20	9.99	2449
6	1.34	4.21	23.03	10.59	2614

Results from single fiber tensile tests are relatively high. The fiber diameters should be determined by an optical microscope instead of calculating from the d-tex value. Fiber diameters are measured by the optical microscope before the micro-bond test. When comparing diameters value from the table 15 and 4% NaOH-treated flax fiber diameters from the table 6, 7, 11 and 12, it is shown that diameters are remarkably lower than in table 5. Therefore, tensile strengths are higher than normally.

8 CONCLUSION

This Master Thesis was divided in theoretical and experimental part. At first in theoretical part, the aim was finding knowledge and information about adhesion testing between natural fibers and thermoset resins. Different micromechanical tests were used in adhesion testing. Typical techniques are the micro-bond test, single fiber fragmentation test and single fiber pull-out test. In these cases, interfacial shear strength, IFSS, was calculated from the fiber diameter, embedded length and debonding force. The IFSS is parameter evaluating the level of adhesion the bond strength between natural fiber and thermoset resins. Reliable adhesion testing method is necessarily when choosing the most suitable combination of the treatment, natural fiber type and thermoset resin for structural composites. Adhesion testing is especially important when characterising the improvement of chemical surface treatment. When load is applied to a single-fiber composite, it is generally accepted that interfacial debonding takes place when the interfacial shear stress exceeds the ultimate shear strength of the interface. As the crosshead moves upward, the resin bead comes into contact with the blades. As the interface fails at the maximum load, F , the fiber begins to pull out from the droplets. A stress concentration is caused in the droplet by the blades.

Micro-bond technique is a popular method in order to measure the adhesion between the fiber and the matrix conventional fibers; like carbon fiber and glass fiber. In natural fiber case, there are some problems with micro-bond test. A considerable amount of samples broke during the test or setting sample to the tensile testing machine. If the force required for pulling out is too high, the fiber broke. According to the single fiber tensile strength results, flax fiber had much lower tensile strength than glass fiber. That is why flax fibers easily break before the debonding occurs. The IFSS and standard deviation was calculated only a few samples per each fiber-matrix combination. Therefore, standard deviations were high and the results were not able to compare reliable. High standard deviation is typical for natural fibers, because their diameters and therefore fiber tensile strength vary a lot. This is also shown in S. Wong, R.A. Shanks and A. Hodzic investigation, where the IFSS for natural fiber was evaluated by single fiber pull-out test. According to their results from the test, standard deviation was also relatively high. [38] It is difficult to determine poor samples out that will break during the test before pull-out occur. According to the results, some samples with high diameter and embedded length were successful.

The highest value of the IFSS was silane treated flax fiber with Epobiox and the second was silane treated flax fiber with Envirez G8600 INF. The adhesion between Epobiox and flax fiber was improved with alkalization and silane-treatment, even if standard deviation was relatively high. The IFSS with untreated flax fiber was lower than treated ones. According to the results, the adhesion between Epobiox and flax fiber was better than adhesion between untreated viscose fiber and Epobiox. Micro-bond test

failed with untreated flax fiber and Envirez G8600 INF resin. For this reason, it is not possible to evaluate the level of adhesion between treated and untreated flax fiber with Envirez G8600 INF resin. The IFSS with treated flax fiber were higher than the IFSS with untreated viscose fiber. In conclusion, the adhesion between Epobiox and natural fiber was better than the adhesion between natural fiber and Envirez G8600 INF resin. Same kind of results can be found in literature, that the adhesion is improved with chemical surface treatment and especially silane coupling agent. Hydrogen bonds and silane bonds are formed between natural fiber and thermoset resins which are one reason for improvement adhesion level. [39], [40]

One basic assumption of micro-bond method is that there is a constant shear stress at the fiber-matrix interface. In reality, non-linear shear stress is exhibited at the regions near the fiber ends. This non-linear shear stress can be reason for high standard deviation. [37] About 50 samples must be prepared in order to obtain 10-20 samples which are able to calculate the IFSS. Reliable results can't be calculated only a few samples. If the fiber has an increased cross-sectional area below the droplet, a larger force will be required for pull-out occur. If there is an irregularity in the fiber surface within the embedded part of the droplet, a larger force is needed for debonding. In both cases, the fiber is likely to break instead of pull-out. The micrometer gap has to be set wider than the fiber but small enough to prevent passage of the droplet. The positioning of the plates can significantly affect the stress distribution along the length of the interface. The gap width needs to be as small as possible according to the fiber diameter. [36] The micro-bond test method can be improved by using an adjustable micrometer gap.

Single fiber tensile strength results for alkali-treated fibers shows that fiber strength is highest with 3% and 4% NaOH concentration treated flax fiber. Tensile strength almost doubled from 1364 MPa for untreated flax to 2954 MPa for 4% alkali treated flax. Viscose fiber has the lowest tensile strength. Results from single fiber tensile tests are relatively high. The fiber diameters should be determined by an optical microscope instead of calculating from the d-tex value. Single fiber tensile test with Vibrodyn was able to compare the strengths fibers, although the results were relatively high. This method makes it possible to determine the effect of the chemical treatment of fiber strength.

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