DEVELOPMENT AND CHARACTERIZATION OF CHEMICALLY TREATED UNIDIRECTIONAL FLAX FIBRE COMPOSITES

by

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Abstract

In order to reduce the use of conventional, petroleum-based Fibre Reinforced Polymer (FRP) composites in construction, natural alternatives are being explored such as natural fibres and bio-based resins. However, there are several known disadvantages to natural fibre reinforced composites such as lower mechanical properties and a higher affinity for moisture absorption leading to limited applications.

In this study, three chemical treatments were chosen to address common issues associated with natural fibre composites: acetic anhydride, alkalization and amino-silane. These treatments were applied to unidirectional flax mats with a soaking time of 1 hour at low concentrations. Composite sheets were then fabricated with a commercial bio-based epoxy, and tested in standard tensile and lap-splice tests in order to evaluate their effect on mechanical properties. It was found that 2% acetic anhydride for 1 hour produced the best results, with a 72% increase in tensile strength and 2% amino-silane with a soaking time of 1 hour, produced a 20% improvement in shear strength.

A single fibre fragmentation test (SFFT) was also performed on the chemically treated flax fibres in order to get a better understanding of the flax/matrix interface. It was found that 2% Amino-Silane also showed the most improvement in micromechanical shear strength, supporting the lap-splice test results.

Finally, a moisture absorption test was performed on fully fabricated chemically treated flax fibre composites in order to determine the effect on moisture absorption. 1% acetic anhydride showed to be the most successful group with a 17% moisture resistance improvement.
Acknowledgements

I would like to firstly thank Dr. Duncan Cree for all his help and support throughout the duration of this research project. His knowledge and advice were an invaluable resource to me, and I am grateful to him to have provided me the opportunity to work with him.

None of this would have been possible without the constant encouragement of my parents, Philip and Anna, who also gave me the drive necessary to complete this project.

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Chapter 1

Introduction

1.1 General

Fibre reinforced polymer (FRP) composites are an essential part of several areas of construction and rehabilitation from Civil to Aerospace engineering. FRP composites have several advantageous properties such as a high strength-to-weight ratio, good stiffness and resistance to corrosion. FRP composites generally consist of a fibre reinforcement, glass and carbon being the conventional choice for Civil infrastructures, embedded in a protective thermoset matrix.

Since FRP composites are a heterogeneous material, different combinations of fibres and matrices provide a wide range of properties, hence their versatility in different areas of engineering. This ability to obtain different properties by varying constituents allowed the introduction of natural fibres as a reinforcing component. From their previous success in non-structural applications such as automobile interiors and tiling, the possibility of using non-petroleum based products is an attractive feature due to the environmentalfriendliness of the raw material itself, and the possibility of less harmful disposal methods of the finished product. Along with natural fibres, the use of bio-based resins and naturally extracted oils provide the grounds to produce a natural alternative to conventional structural materials.

Despite the incorporation of a wide variety of natural fibres in different conventional and non-conventional matrix systems, there is a general trend from the performance of natural fibre composites: lower strengths, variability, and an affinity for
moisture. To obtain an acceptable substitute for conventional materials, these issues need to be addressed. The use of chemical treatments on the natural fibres is one of the possible solutions where natural fibres are soaked or exposed to different chemicals before implementing in a matrix. There has been a variety of successes reported from these treatments which widens the range of the FRP properties further since there is an unlimited amount of combinations of chemical treatments, natural fibres and matrices. Each chemical treatment has its own reaction time, reaction temperature, concentration and use of co-agents.

The main goal of this research is to use three selected chemical treatments on one type of fibre (flax), and assess the effectiveness of fabricated composites through different tests. These tests are divided into three distinct phases: Phase 1 is the macromechanical tests including tensile and shear, Phase 2 is a micromechanical test where the fibre/matrix interface is assessed and Phase 3 is the environmental durability evaluation through a moisture absorption resistance test. This will give better insight on how a fibre’s properties can change by varying treatment conditions with the anticipation of improving its performance. This new knowledge on unidirectional flax fibre composites will contribute to the potential use of these natural fibre composites in a structural application.
1.2 Objectives

The objectives of the research are:

1. To determine the effect of three different chemical treatments at varying concentrations on flax composites based on mechanical properties
2. To examine the difference in micromechanical interaction between single flax fibres and the resin from chemical treatments
3. To determine the effect of the chemical treatments on moisture absorption of the flax composite
4. To provide an ideal chemical treatment method for unidirectional flax fibre composites which can be easily reproduced

1.3 Thesis Format

Chapter 1 provides a brief description of the current state of the field of natural fibre composites and how the research goals of this thesis will provide useful supplementation to data available. Chapter 2 is a literature review on work done leading up to the chemical treatment of natural fibres to be used in different composite applications. Chapter 3 outlines the development and final fabrication and testing methods. Chapter 4 shows relevant graphs and data obtained from the experimental procedures previously outlined. Finally, Chapter 5 gives main conclusions to be taken from this research and recommendations for future work.
Chapter 2

Literature Review

2.0 Introduction

Fibre reinforced polymer (FRP) composites are widely used in civil structural applications in areas of rehabilitation and new construction. This is due to the desirable properties of FRP composites such as high strength-to-weight ratio, resistance to corrosion, ease of installation and light weight. These composites have two homogeneous components, namely the fibre portion which provides the strength and stiffness, and the polymer matrix portion which protects the fibres from the environment and evenly distributes loads to the fibres.

2.1 Conventional Petroleum Based Fibre Reinforced Composites

Carbon fibre reinforced polymer (CFRP) composites and glass fibre reinforced polymer (GFRP) composites are the most common choices of FRP composites in current construction due to their high tensile strengths, reliable performance and environmental durability. However, in terms of recyclability carbon and glass are not sustainable materials and for the most part are expensive. In addition they also cause abrasive wear of the composite parts during the trimming and machining processes (Khairussshima et al., 2012) increasing overall operating costs. Glass fibres have a density of approximately 2.6 g/cm³ and costs between $1.30 and $2.00/kg whereas a natural fibre such as flax has a density of approximately 1.5 g/cm³ with a cost between $0.22 and $1.10/kg (Foulk et al., 2000). It was found that natural fibre composites have higher fibre content for the equivalent performance of glass fibre composites (Joshi et al., 2004). Therefore, an
overall lower amount of pollutants is potentially produced for the same project. At the end of their life cycle, the environmental impact of CFRP and GFRP composites is significant. Currently, the most common disposal method is direct land filling, producing 55 000 tons of GFRP waste per year in the UK alone (Broekel & Scharr, 2005). Alternative disposal methods are however being implemented, namely incineration with energy recovery and mechanical recycling. Due to the high energy content of thermosetting FRP’s, FRP waste is being used as an energy source for producing electricity by incineration. However, toxic emissions overwork the incinerating systems and additional ventilation systems are necessary, imposing extra costs on the process. Mechanical recycling is a process involving cutting and grinding FRP waste into a fine powder, and using the powder as a partial replacement for sand aggregates and filler in polyester based mortars (Ribeiro et al., 2013). In this method, toxic fumes are not produced and water pollution is avoided as the process is done mechanically without the use of extra chemicals. Mechanical recycling is currently the only responsible disposal process used for thermosetting polymers in a commercial scale (Correia et al., 2011; Hedlund-Ástrom et al., 2005).

2.2 Natural Fibre Reinforced Polymer Composites

In an effort to reduce the use of CFRP and GFRP composites in a large scale, natural fibre reinforced polymer (NFRP) composites are being considered as a potential total or partial replacement. These natural fibre composites represent an important fundamental step in putting into practice the ecological objective of closed-loop material systems. NFRP composites consist of a cellulosic material as the load-bearing material in
lieu of carbon or glass fibre, embedded in a reinforcing matrix. In literature, the matrix is typically a polyethylene-based resin or a bio-based resin to further decrease the overall environmental impact of the NFRP composite. Cellulose materials come with many advantages such as lower raw material cost, low abrasion during machining, low density, high abundance and lower environmental impact in waste disposal methods (Zafeiropoulos et al., 2002). Research so far has shown that these natural fibre composites have the potential to produce comparable properties to glass fibre composites (Hornsby et al., 1997). However, there are known disadvantages associated with natural fibre composites such as a higher affinity for moisture absorption (Li et al., 2007) and poor interfacial properties with matrices, which affect the properties of the heterogeneous material greatly (Zhandarov & Mäder, 2014). These disadvantages are influenced by the type of fibre and matrix chosen, and the manufacturing method; therefore NFRP composite properties tend to vary greatly.

2.3 Natural Fibre Morphology

There are many options to consider when selecting a natural fibre for a NFRP composite since each fibre type provides different physical and mechanical properties. Table 2.1 provides an overview of the most common natural fibres used to date, compared to E-glass fibre.
Table 2.1: Single Natural Fibre Properties (Wambua et al., 2003)

<table>
<thead>
<tr>
<th>Properties</th>
<th>Fibres</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E-Glass</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>2.55</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>2400</td>
</tr>
<tr>
<td>E-Modulus (GPa)</td>
<td>73</td>
</tr>
<tr>
<td>Specific (E/d)</td>
<td>29</td>
</tr>
<tr>
<td>Elongation at failure (%)</td>
<td>3</td>
</tr>
<tr>
<td>Moisture absorption (%)</td>
<td>-</td>
</tr>
</tbody>
</table>

Composites manufactured with these natural fibres tend to have lower strengths than conventional CFRP or GFRP composites due to the morphology of the natural fibre. Even under ideal fibre-matrix optimization, the irregular, hollow structure of the fibres and the natural occurring defects compromise strength (Van Den Oever et al., 2000). Flax is a good example to illustrate the structure of natural fibres. These fibres do not have a regular cross-section like their man-made counterparts. They consist of several cell wall layers bonded together by lignin and hemicellulose interphases (Figure 2.1) forming a hollow structure.
Each individual fibre can therefore be considered a composite, since it is not one homogenous material, but one which consists of several cellulosic structures. As seen in Figure 2.1, the layers of cell walls referred to as primary and secondary walls are held together by helically wound microfibrils with the main constituent of each individual microfibril being cellulose. Cellulose is a semi-crystalline polysaccharide \(((\text{C}_6\text{H}_{10}\text{O}_5)_n\) consisting of multiple cellulose microfibrils held together by hydrogen bonding. The cellulose microfibrils are bonded together with hemicellulose, a fully amorphous polymer with an open structure. Readily available hydroxyl and acetyl groups on the hemicellulose make this component soluble and hygroscopic (Frederick et al., 2004), affecting the entire fibre structure’s affinity for moisture.

The structural hierarchy of a typical plant cell can be seen in Figure 2.2 below, showing the location of the elementary fibre in a wood tree stem. It can be seen that cellulose is
the basic structure of the natural fibre, which is located at different orders of magnification, from the molecular level in individual fibrils to the bonding components of the cell walls at the observable level with a light microscope.

![Diagram of plant cell composition](image)

**Figure 2.2: Composition of a Plant Cell (Feist et al., 1990)**

### 2.4 Applications of Natural Fibre Composites

Natural fibre reinforced polymer composites have been used commercially but in non-structural applications since 1986. The most common uses have been in the manufacturing of non-structural products such as paper weights and helmets (Satyanarayana et al., 1986). Currently, natural fibre reinforcements are being used in the automotive industry. Flax, sisal and hemp are being used in door cladding, seatback lining and floor panels of vehicles but the common drawbacks of moisture absorption, poor fibre-matrix interface and inconsistent performance are still prevalent (Holbery & Houston, 2006). Natural fibre composites have also been tested in biomedical applications in the form of wound sutures and scaffolds for tissue engineering, but due to
the poor interfacial bonding and stress transfer properties additional research is required before full implementation can be achieved (Cheung et al., 2009).

With more knowledge and experience handling natural fibre composites over the years, an increase in interest for potential structural and infrastructure applications can be seen. The environmentally friendly properties and lower costs of the NFRP composites are becoming an appealing selling point for material selection, along with acceptable strengths and performances. Projects with low to moderate design loads are therefore suitable for NFRP composites such as pedestrian bridge girders and composite sandwich beams (Ticoalu et al., 2010). For example acrylated epoxidized soy-bean oil as a resin matrix, with a variety of natural fibres such as flax and recycled paper were used to manufacture structural panels and beams for roof construction. These produced good results with the required structural performance, even exceeding conventional wood structure strengths (Dweib et al., 2004). Another type of beam where NFRP composites were successfully implemented was I-beams made of woven jute fabric and a soybean oil based resin to withstand structural loads (Alms et al., 2009). Once these proof-of-concept tests have been demonstrated to work properly, architects and contractors are more likely to use them in their design and construction projects, respectively.

2.5 Eco-Friendly Epoxy Resins

In addition to the implementation of natural fibers as an environmentally friendly alternative, bio-based polymer resins are being studied as a potential replacement for petroleum-based resins. Mahmoodul Haq et al. (2008) investigated the use of epoxidized soybean oil as a partial replacement of unsaturated polyester epoxy in manufacturing
hemp composites. It was found that the addition of the bio-resin lowered mechanical parameters but increased toughness properties such as impact strength and ductility. O’Donnell et al. (2004) also yielded similar results when testing flax and hemp composites with only acrylated epoxidized soybean oil as the resin component. These soy oil-based resin and cellulose fiber composites were successfully used to manufacture structural panels for roof structures (Dweib et al., 2006).

Partially natural epoxy resin systems have also proven to be a promising alternative to oil extracts. These resins have a large portion of the carbon content replaced by biomass origin, and the rest from petroleum-based sources. When compared to a conventional petroleum-based epoxy resins, two of these commercially available resins, Greenpoxy 55 and EcoPoxy (vegetable oil-based resins), outperformed in tensile and flexural composite tests. The eco-friendly flax fibre composites had a higher strength but the petroleum-based composites had favourable ductile properties (Bertomeu et al., 2012). Recycled waste products from industrial processes are also used to manufacture bio-based resins, such as Super Sap resin systems by Entropy Resins. These commercially available bio-based epoxies provide similar performance to conventional resins with up to 31 % bio-based products according to USDA certifications.
2.6 Flax Composites

Various natural fibres have proven to have the required mechanical properties to manufacture composites with acceptable strengths. Through comparison of results over several studies, flax fibres have been reported to have good composite properties such as high stiffness (15-39 GPa) and tensile strength (132 - 280 MPa) (Oksman et al., 2001). With small amounts of chemical treatment, Weyenberg et al. (2006) reported higher values of elastic modulus of 268 MPa and flexural properties of 237 to 283 MPa. Kong et al. (2014) reported values of 227.2 MPa in tension and 252.1 MPa in flexure for their flax/vinyl ester specimens. There are many factors to take into account when evaluating composite performance including volume fraction, type and origin of growth of flax fibre, epoxy resin and curing time.

Although flax composites have the potential to provide good properties, they can however differ greatly. As given in Table 2.2, mechanical properties obtained from different flax composites and different fibre volume fraction ($V_f$) are shown with standard deviations ($\pm$). Hermes, Andrea, Marylin and Ariane are four different flax varieties, in a Unidirectional (UD) woven mat fabricated with the same petroleum based epoxy resin. The two Hermes flax fibres were obtained from different sources and yielded different results.
Table 2.2: Flax composite mechanical properties compared with literature (Coroller et al., 2013)

<table>
<thead>
<tr>
<th>Material</th>
<th>Vf (%)</th>
<th>Young Modulus (GPa)</th>
<th>Strength at Break (MPa)</th>
<th>Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy Resin</td>
<td>0</td>
<td>3.3 ± 0.13</td>
<td>78 ± 6</td>
<td>3.1 ± 0.54</td>
</tr>
<tr>
<td>Epoxy/Hermes flax UD</td>
<td>22 ± 2</td>
<td>13 ± 0.3</td>
<td>208 ± 21</td>
<td>1.2 ± 0.20</td>
</tr>
<tr>
<td></td>
<td>42±1</td>
<td>22 ± 0.6</td>
<td>362 ± 19</td>
<td>1.3 ± 0.13</td>
</tr>
<tr>
<td></td>
<td>51±2</td>
<td>26 ± 2.0</td>
<td>408 ± 36</td>
<td>1.3 ± 0.05</td>
</tr>
<tr>
<td>Epoxy/Andrea flax UD</td>
<td>23 ± 1</td>
<td>11 ± 1.9</td>
<td>165 ± 11</td>
<td>1.1 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>36 ± 1</td>
<td>20 ± 3.0</td>
<td>207 ± 08</td>
<td>1.2 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>51 ± 4</td>
<td>28 ± 3.6</td>
<td>290 ± 22</td>
<td>1.1 ± 0.15</td>
</tr>
<tr>
<td>Epoxy/Marylin flax UD</td>
<td>36 ± 1</td>
<td>24 ± 1.8</td>
<td>271 ± 32</td>
<td>1.3 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>48 ± 2</td>
<td>31 ± 1.5</td>
<td>348 ± 28</td>
<td>1.2 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>54 ± 3</td>
<td>34 ± 3.0</td>
<td>364 ± 14</td>
<td>1.3 ± 0.01</td>
</tr>
<tr>
<td>Epoxy/Ariane flax UD</td>
<td>40</td>
<td>28</td>
<td>133</td>
<td>-</td>
</tr>
<tr>
<td>Epoxy/Hermes flax UD</td>
<td>19.7</td>
<td>12.4 ± 1.3</td>
<td>126 ± 14</td>
<td>3 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>20.1</td>
<td>16.7 ± 3.7</td>
<td>127 ± 14</td>
<td>0.9 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>19.8</td>
<td>11.1 ± 1.4</td>
<td>113 ± 11</td>
<td>1.5 ± 0.1</td>
</tr>
</tbody>
</table>
2.6.1 Fabrication Methods

The composite fabrication method is an important factor to consider when evaluating material properties as it affects the volume fraction and inclusion defects. There are two types of fabricating processes, namely open molding and closed molding (American Composites Manufacturers Association, 2014) each having their own variety of processing methods. The most common processing methods for open molding and closed molding in civil engineering applications are the hand lay-up method and vacuum bag molding, respectively. The hand lay-up method is a simple process which requires little investment on equipment. The procedure consists of applying the resin on the reinforcing fibres directly with rollers, spreading the resin while ensuring air bubbles are eliminated until all the fibres are thoroughly wetted. The wetted fibres are then allowed to air dry until the resin has cured. This process is versatile and can be used for different applications, especially those which require irregular shaped bodies. Vacuum bag molding follows a similar procedure to the hand lay-up method, but the finished wetted fibre material is placed in a vacuum bag and the vacuum pressure applied removes the excess resin and potential air bubbles. These two methods were compared when fabricating Kenaf/Polyester composites and it was found that the vacuum bag molding method produced samples with a higher fibre-resin ratio and superior mechanical properties (Mohd et al., 2010). These results agree well with the concept of the Rule of Mixtures which is used to predict composite properties based on the volume fraction (V) and modulus (E) of the reinforcing fibre (f) and matrix (m) (Smith & Hashemi, 2006) for a composite with fibres arranged in the longitudinal direction as given in Equation 1:

\[ E_c = E_f V_f + E_m V_m \] (1)
Since FRP composites always use a fibrous material stiffer than the reinforcing matrix, it can be seen that a higher fibre volume fraction will indicate a high overall composite stiffness. This was confirmed by tests done on three different natural fibres, Jowar, Sisal and Bamboo, by Prasad et al. (2011) where tensile strengths improved with volume fractions from 20 % to 40 % (the maximum V_f tested). Rao et al. (2010) also produced similar results on Vakka, Sisal, Bamboo and Banana composites where a linear increase in tensile strength was observed from 10 % to 40 % volume fraction. However, when tested at volume fractions higher than 40 %, Venkateshwaran et al. (2012), a sharp decrease in tensile strength was seen at 50 % in Banana/Sisal hybrid composites.

2.7 Natural Fibre Chemical Treatments

It is widely known that the main drawbacks of natural fibre composites are poor interfacial properties between fibre and matrix, their high affinity for moisture and inconsistent performance. Chemical treatments of natural fibres are often used as a solution to these disadvantages in an attempt to produce more reliable results from the composites manufactured. There are several chemical treatments but the most commonly used methods include the alkaline, silane, benzoylation, maleated coupling agents, and acetylation treatments. These treatments involve modifying the surface of the fibre, modifying the fibre chemical composition or introducing an intermediate agent between the fibre and matrix. Each of these methods is investigated in the following sections.
2.7.1 Alkaline Treatment

Alkaline treatment is the most common method in natural fibre composites. The main purpose of alkalization is improving interfacial interlocking of the fibre/matrix interface by increasing surface roughness of the fibre through the removal of natural waxes and oils on the external surface of the fibre cell wall (Mohanty et al., 2001) and exposing hydroxyl groups to chemicals such as resins (Mwaikambo & Ansell et al., 2002). With the improved resin uptake, water absorption is therefore reduced.

This reaction is done through the ionization of the hydroxyl group to produce an alkoxide:

\[
Fibre - OH + NaOH \rightarrow Fibre - O^-Na^+ + H_2O + impurities
\]

This process depolymerizes the cellulose structure into short crystallites (Mwaikambo & Ansell, 2002). The fibre goes through fibrillation where larger fibre bundles are broken down into smaller fibres increasing effective surface area and improving mechanical interlocking potential with the matrix.

The most common method of alkaline treatment is the immersion of fibres in a sodium hydroxide (NaOH) solution over a certain period of time. Bismarck et al. (2001) treated coir and sisal fibres with 2 and 5 % NaOH solution for 30 min at 30 °C increasing the tensile strength of composites by 20 %. Similarly A.M. Edeerozey et al. (2007) investigated the effects on kenaf fibres and obtained optimum results with 6 % NaOH at 95 °C for 48 h, and no effective difference with 3 % NaOH. A. Arbelaitz et al. (2005) soaked flax fibres in 20 % NaOH for 1 h at room temperature but found a decrease in mechanical performance. Mishra et al. (2003) found agreeable results, where a higher
alkaline solution, above a 10% NaOH concentration, damaged the fibres drastically decreasing strength.

It can be seen the alkaline treatment of fibres using NaOH is a method that is very sensitive to concentration and soaking time. Therefore it must be optimized and selected appropriately based on the type of natural fibre since this method modifies the physical structure of the fibre.

2.7.2 Silane Treatment

Silane treatment uses the silane chemical compound SiH₄. This compound is used as a coupling agent, which is a molecule producing a cross-linked interface between the hydroxyl (-OH) groups of the fibre and the functional groups of the matrix (Bledzki et al., 1999). This reduces the number of cellulose hydroxyl groups, decreasing the hydrophilicity, thereby reducing any potential swelling and eventual rotting. This reaction occurs through hydrolysis of the silane agent producing silanols as given in Equation 3, which bond to the hydroxyl groups of the fibre through covalent bonding as given by Equation 4 (Agrawal et al., 2000). Van de Weyenberg et al. (2003) used three amino-propyl trimethoxy silane in a solution of acetone and water to treat flax fibre surface and found an increase in interfacial strength and higher tensile strength than alkaline treatments.

Formation of silanols:

\[
CH_2CHSi(OC_2H_5)_3 + H_2O \rightarrow CH_2CHSi(OH)_3 + 3C_2H_5OH
\]  

(3)
Reaction of silanols with fibre:

\[
CH_2CHSi(OH)_3 + Fibre - OH \rightarrow CH_2CHSi(OH)_2O - Fibre + H_2O
\]  \hspace{1cm} (4)

Since the main reaction of the silanols with fibres is the elimination of hydroxyl groups through covalent bonding, the silane treatment is a proven method to reduce moisture uptake. However, like any coupling agent reaction, the effectiveness of the treatment relies on two different reaction sites, namely the fibre and the matrix. Not only must the reactions be carefully optimized, but the reaction may not occur at all with certain epoxy resins, limiting the use of the treatment method.

2.7.3 Benzoylation Treatment

Benzoylation most often uses Benzoyl Chloride, which increases compatibility between the hydrophilic cellulosic fibre and the hydrophobic resin matrix (Joseph et al., 2000). This leads to a better interfacial interaction, improving composite strength. Nair et al. (2001) treated flax fibres with 18 % NaOH for 30 min, followed by a 10 % NaOH solution with benzoyl chloride for 15 min resulting in higher strengths.

Benzoylation is similar to the silane treatment where a compound reacts with an open hydroxyl (-OH) group, and to the alkaline treatment as waxes and oils on the surface of the fibre are removed.
2.7.4 Maleated Coupling Agent Treatment

The use of maleated coupling agents is common in improving the strength of composites where the chemical reaction occurs on both the fibre surface and the polymer matrix used. The coupling agent will form covalent and hydrogen bonds between the two materials improving interfacial adhesion (Gassan & Bledzki, 1997). Maleic anhydride is a widely used agent which first reacts with the matrix to produce a copolymer.

Polypropylene is a common resin used with maleic anhydride. The reaction which takes place is the cohesion between the maleic anhydride and polypropylene matrix, producing the copolymer, maleic anhydride grafted polypropylene (MAPP). The MAPP then reacts with the fibre surface through esterification- where the hydroxyl groups of the fibre surface are replaced by an alkyl group as illustrated in Figure 2.3 below.

![Chemical Formation of MAPP](image)

**Figure 2.3: Chemical Formation of MAPP (Bledzki, 1998)**

The surface energy of the fibres is then at a level closer to that of the matrix, resulting in better wettability and higher interfacial adhesion (Bledzki et al., 1998). T.J. Keener et al.
(2004) reported a 60% increase in tensile and flexural strengths when using maleated coupling agents in natural fibre/polyolefin composites. Similarly, Nachtigall et al. (2007) found improved mechanical properties of polypropylene/wood-flour composites and increased thermal stability.

The maleated coupling agent treatment is a two-part reaction where a compound is first formed with the matrix, which will then react with the fibre portion of the composite. Similar to the silane treatment, the reaction is matrix-specific therefore must be used appropriately.

2.7.5 Acetylation Treatment

Similar to the use of maleated coupling agents, acetylation reacts with the fibre through esterification. The hydroxyl groups are therefore replaced by the acetyl functional group \((CH_3COO^-)\) in the fibre structure. This decreases hydrophilicity and is said to cause plasticization of the cellulosic fibre. The reaction decreases the affinity for moisture absorption from the lowered availability of hydroxyl group, and also increases dimensional stability as the treated fibre does not shrink or swell as much as an untreated sample (Saheb & Jog, 1999). Acetylation has been shown to reduce moisture uptake of jute fibres by 50% (Bledzki et al., 1999) and enhance the interface in flax/polypropylene composites (Zafeiropoulos et al., 2002). Acetic anhydride \((\text{CH}_3\text{CO})_2\text{O}\) is a commonly used chemical for acetylation. The acetic anhydride reacts with the fibre surface through esterification, hydrolyzing into the acetyl functional group and acetic acid (Khalil et al., 1998) as shown in Equation 5.
\[ Fibre - OH + CH_3 - C(=O) - O - C(=O) - CH_3 \rightarrow Fibre - OCOCH_3 + CH_3COOH \]

2.7.6 Natural Fibre Chemical Treatment Summary

It can be seen that a wide variety of chemical treatments have been proven to be effective for different natural fibres through the same basic principles. The main focus is to target the open hydroxyl (-OH) groups on the fibre surface, improving interfacial properties leading to better mechanical properties, and reducing hydrophilicity. Thus creating better resistance to moisture uptake. These results can also be achieved through structure modification of the fibre as seen through the Alkalization process with sodium hydroxide.

The environmental benefits of using natural fibre may however be jeopardized if an extensive amount of chemicals are used for pre-treatment of fibres before the fabrication of composites. This indicates the need for optimization and thorough testing before large-scale implementation. In this study, a trial and error approach was used to optimize the concentrations and soaking times of these chemical treatments for small-scale flax/epoxy composite specimens.

2.8 Micromechanical Testing of Fibres

FRP composite performance is tested on a macromechanical scale through tensile, bending and lap-splice tests as the most common methods. However these tests tend to be affected by fibre volume fraction and the inclusion of voids (Taslica & Kusefoglu, 2010). The performance of the composite as a homogeneous unit is evaluated but it is difficult to
understand the fibre-matrix interaction and its role in the failure of the specimen. It is known that the four mechanisms involved in failure of composites are fibre/matrix debonding, matrix cracking, fibre pullout and fibre failure (Khan et al., 2010). Therefore the interface between the fibre and matrix is important to the strength of the composite and it is necessary to investigate the interface at a microscopic scale.

There are several techniques to measure the fibre/matrix interaction including the single-fibre pull out, single-fibre push out, and the fragmentation technique (Manoharan et al., 2009). The fibre pull out method is the most common technique used to determine interfacial strength where a single fibre embedded in a matrix is removed through tension. Based on the fibre’s embedded surface area and critical pull out load, the interfacial strength is calculated. The fibre pushout method uses a similar procedure to the pullout test. Both the pullout and push out methods produce good interfacial shear strength data but very large sample sizes are necessary as specimens vary greatly due to fibre breakage in tension instead of pull out failure.

The single fibre fragmentation test (SFFT) offers a simple method where the stress transfer mechanics can be easily observed (Manoharan et al., 2009) without an exposed fibre. This test involves pulling a polymer matrix sample containing a single fibre completely embedded through its centre, along the direction of the tensile load. If the strain is higher in the matrix than in the fibre, the stress will be transferred through the matrix to the single fibre causing it to fragment, due to its lower strain-to-break. The fibre fragments until the stress induced is no longer high enough for rupture. The smallest fragment left at this critical point is known as the critical fibre length, \( l_c \) as seen in Figure 2.4 below.
With knowledge of the critical fragment length, and the critical breaking stress, interfacial shear strength (IFSS) can be calculated with the relationship given in Equation 6 below based on the Kelly-Tyson equation:

$$\tau_c = \frac{\sigma_f d}{2 L_c}$$

(6)

Where $d$ and $\tau_c$ are the diameter and tensile strength of the fibre, respectively.

SFFT tests have been conducted on numerous fibre/matrix combinations. For example S. M. Lee et al. (1990) have been successful with the SFFT using carbon fibre sandwiched between thin, highly cross-linked resin films (Manoharan et al., 2009). Similarly, B. Taslica et al. (2010) used glass fibre and polyester resin. T. Huber et al. (2010) used the SFFT on natural fibres, flax and hemp, in polylactic acid (PLA) matrix samples, while A. Awal et al. (2011) studied flax fibres in polypropylene matrix. SFFT is seen to be a well-
established micromechanical test for interfacial shear strength of conventional fibres but it was observed that there are still difficulties when testing natural fibres such as their irregular shape and variability in results. SFFT can however provide sufficient comparative results for interfacial properties (Torres & Cubillas, 2005).

2.9 Environmental Durability of Natural Fibres

As previously discussed, one of the main drawbacks of natural fibres is their affinity for moisture absorption, which causes dimensional instability of the fibre structure and induces rotting. The most common method to test the environmental durability of natural composites is through soaking of composite samples in water and measuring water uptake. The mass difference indicates the amount of water absorbed by a sample and the rate of moisture absorption can also be measured. A. Stamboulis et al. (2000) tested the durability of flax composites in a polypropylene matrix by immersing samples in water for 60 days at room temperature. Similarly M. Assarar et al. (2011) investigated the moisture absorption of flax-fibre composites by immersion in a water bath at room temperature and measuring weight gain periodically.

The water absorption of natural fibre composites has been modelled as two-dimensional Fickian diffusion through the surface of the composite (Espert et al., 2004) as it is assumed that the surface area of the front and back of the composite are much higher than the thickness. The composite is also simplified to be one material during analysis. The moisture uptake initially follows a linear pattern and gradually plateaus at maximum saturation. Water absorption of jute and flax fibre composites with a bio-based
epoxy resin Super Sap TM 100/1000 also followed Fickian diffusion behavior in Dhakal et al. (2007) immersion tests at room temperature.

2.10 Research Goals

The goal of this research is to design, optimize and compare the performance of three chemical pre-treatments of flax fibres to be manufactured into composites using a bio-based epoxy resin and compared to a conventional epoxy resin as a control. These pre-treatment methods are to be designed with the intention of simplifying the process while still improving the performance of flax fibres with the goal of potential implementation in a large-scale civil engineering project. More importantly, the three pre-treatment methods chosen are based on their ease of implementation and use of minimal amounts of chemicals.

The effectiveness of each method will be compared using macromechanical tests (tensile, lap-splice) and micromechanical tests (Single Fibre Fragmentation Test- SFFT) and environmental durability (moisture absorption).

Chapter 3

Experimental Procedure

3.1 General

Natural fibres come with several well-known disadvantages: 1) lower strength 2) higher affinity for moisture 3) inconsistent mechanical properties 4) lower compatibility
with reinforcing matrices when compared to conventional man-made alternative such as carbon or glass. The purpose of this testing program is to address these concerns by performing three different chemical treatments on unidirectional flax fibres over a range of predetermined chemical concentrations and evaluate the efficacy of each treatment. The study aims to determine the ideal type of chemical treatment to improve upon as-received flax fibres when fabricated as a composite with a bio-based epoxy. The parameters studied were to optimize chemical concentration and reaction time. The chemical treatments are designed to be at low concentrations to minimize the use of potentially harmful chemicals, and at room temperature to allow potential implementation in a commercial setting where highly specialized equipment would not be required as these treatments are intended to be used in a civil engineering on-site application.

3.2 Materials

The natural fibre composites studied consisted of a unidirectional (UD) flax fibre mat and two epoxy resins: conventional and bio-based epoxies. Three types of chemicals were used for the treatment methods, each chosen to address different specific concerns with natural fibre composites. The hand lay-up and vacuum bagging fabrication techniques were used to produce the composites.

The flax mats used in this study were the Biotex Flax Unidirectional 275 gsm, obtained from Composites Evolution Ltd., Chesterfield, UK. These mats are sold as a 35 cm-wide roll. The supplier reports a tensile modulus, tensile strength and flexural strength of 18.8 GPa, 174 MPa and 196 MPa, respectively based on ISO 527-4 and ISO 14125 standards.
Carbon fibre used was the Unidirectional SikaWrap-300C from Sika Canada, Mississauga, Ontario, Canada. With a fibre density of 1.80g/cm\(^3\) sold in a 300 mm roll and reported fibre tensile strength and modulus of 3.9 GPa and 230 GPa respectively.

The conventional polypropylene epoxy resin used was Aeropoxy 2032 Laminating Resin with PH3630 hardening agent, from PTM&W Industries, Santa Fe Springs, California, USA. This epoxy resin is designed for glass, carbon and aramid composite part fabrication with structural applications. A mix ratio of 100:27 by weight is suggested, providing a tensile strength of 312 MPa, tensile modulus of 19.3 GPa and elongation of 1.91%.

The bio-based resin used was the Super Sap CPM/CPL resin system obtained from Entropy Resins Inc., San Antonio, USA. This resin is manufactured with co-products or waste products of other industrial processes, creating a 31% bio-based end product. The supplier reports a tensile strength of 62 MPa, tensile modulus of 3 GPa and elongation of 6% based on the ASTM D638 standard, with a mix ratio of 100:40 by weight.

For the Acetylation, Alkalization and Amino-Silane Treatments, the three chemicals used for the flax fibre were acetic anhydride (99.5%), sodium hydroxide and (3-aminopropyl)triethoxysilane (≥ 98%), respectively and were obtained from Sigma-Aldrich Canada Co., Oakville, Canada.

Materials used for the hand layup fabrication were two 19 mm (¾ inch) thick high density polyethylene plates for weight and stability, and clear 6 mm polyethylene sheets for a smooth finish. A 50 x 100 mm metal hand roller was used to remove excess resin and air bubbles.
The materials used for vacuum bagging were the Release Bag RBG-125, Econoweave 44 as the bleeder for excess resin, and Release Film 5200R for a smooth surface finish. All the materials were obtained from Composites Canada, Mississauga, Canada. The Heavy Duty Vacuum Pump E102 was obtained from CST Composites Store Inc., Tehachapi, USA to provide the suggested 20 to 30 in-Hg of pressure.

3.3 Test Program and Parameters

The test program was divided into three phases: 1) Macromechanical testing, 2) Micromechanical testing and 3) Environmental durability. Macromechanical testing in this case refers to test procedures on specimens obtained from fabricated flax composite coupons. Results from this phase indicate efficacy of chemical treatments on tensile and shear strength of composites. Micromechanical testing refers to the examination of the single flax fibre/matrix interface within a fabricated composite through Single Fibre Fragmentation Testing (SFFT). This phase indicates how chemical treatments affect the composite at a microscopic scale and the interaction between the fibre and matrix. The environmental durability phase indicates the performance of the flax composites in a fully saturated environment to determine moisture absorption resistance. The purpose of implementing three phases was to obtain a complete as possible analysis of the effect of the chemical treatments on the flax composites. The parameters studied were: 1) type of chemical treatment 2) reaction time and 3) chemical concentration.

A total of 310 coupons were fabricated and tested for the macromechanical testing phase. 150 tensile coupons double-layered (2-layer) and 158 single lap-splice coupons consisting of 4 layers (4-layer). Both tensile and shear strengths of the coupons were
determined through ASTM D3039 standard test using the Instron 8802 hydraulic testing system.

A total of 65 single-fibre dog-bone shaped epoxy samples were fabricated for the micromechanical testing phase. Each dog-bone sample contained a single fibre of flax carefully placed at the center, using the schematics of Bascom & Jensen (1986). The sample was slowly pulled in tension until the embedded fibre fractured, but leaving the matrix whole. Testing was conducted using a Zwick-Roell Z020 with a 20kN load cell.

A total of 13 sheets were fabricated and tested for the environmental durability phase according to ASTM D5229/D5229M-14. The sheets were left to soak in a distilled water bath for 15 days and moisture uptake was monitored every hour for the first 12 hours, then every 12 hours thereafter. The sheets were fabricated to represent the flax FRP composite if it were to be installed in a full-scale application.

3.4 Fabrication Procedure of Composite Sheets

For the vacuum bagging technique, the flax fibre mats were cut from a standard 350 mm wide roll in 350 mm lengths for 2-layer tensile specimens and 150 mm lengths for the 4-layer single lap-splice specimens. The mats were then carefully washed with distilled water to remove impurities, minimizing damage to the fibres. The clean mats were then placed in an oven at 105 °C for 8 hours, ensuring that the fibres were completely dry. It was important that the fibres be completely dry for all the chemical treatments as the presence of moisture can potentially affect chemical reactions. It also provided a standardized starting base material for all the treatments for the purpose of comparison. The fibres were therefore sealed in a moisture-resistant bag when transferring between work stations. The bio-based resin was then spread evenly on the
dried flax mats ensuring that the fibres were thoroughly wetted as seen in Figure 3.1. The required amount of wetted sheets were then layered as seen in Figure 3.2, then placed between layers of release film, bleeder fabric and Mylar and subjected to a 22-in Hg pressure with a regular vacuum pump for 24 hours as seen in Figure 3.3 and Figure 3.4.

Figure 3.1: Spreading Resin on a Dry Flax Mat
Figure 3.2: Layering Wetted Flax Mats

Figure 3.3: Placing Vacuum Bagging Films
Figure 3.4: Flax Mats under Vacuum Pressure

For the hand layup technique, the wetted flax mats were layered, and placed between two clear polyethylene sheets. Excess resin and air bubbles were then rolled out using a metallic roller. The sheets were allowed to set between two polyethylene plates with cinder blocks placed on top as weights.

Impregnated sheets for both techniques were then allowed to cure for 24 hours at room temperature, then at 82.2°C (180°F) for 20 min as suggested by the manufacturer for full cure, before cutting into 25 mm-wide coupons with a table saw.

The chemically treated sheets were soaked in their respective chemical solution for 1 hour, then rinsed with distilled water and dried again for 8 hours at 105 °C before impregnating with resin. The work flow of both procedures can be seen in Figure 3.5.
3.5 Tension Coupons

Tension coupons tested were obtained from the double-layered composite sheets cut in the longitudinal direction along the fibres using a table saw. Ten to twelve coupons were obtained per sheet, and the best ten (the ones with the least surface imperfections and straightest cuts) were selected to be tested. Coupons dimensions were obtained according to ASTM D3039 requirements. It is recommended that the minimum length be the gripping length at both ends, plus two times the coupon width plus gage length. The final coupon dimensions were then taken as 350 mm in length and 25 mm in width. The average thickness of the tension coupons was 1.48 ± 0.08 mm. CFRP end tabs were 40 mm long and 25 mm wide. End tabs were used as an extra precaution to reduce internal stress incurred by the gripping pressure of 2 MPa (300 psi). The coupon dimensions can be seen in Figure 3.6.
Figure 3.6: Final Dimensions of Tensile and Lap-Splice Coupons

Tension tests were performed on the Instron 8802 hydraulic testing system, with the wedge-type grips. The recommended strain rate of 2 mm/min was used. The strain data was acquired using a 25 mm gauge length extensometer. All data acquired, including load and stroke were through a high-level input card recorded using Vishay System 5000 Data Acquisition System (DAS). The Strain Smart™ software was used to store data.

3.6 Lap-Splice Coupons

Single-layer lap splice coupons were fabricated by partially overlapping two 4-layer flax sheets, according to ASTM D7616/ASTM D7616M as a guideline for dimensions. Since these standards do not address natural fibre composites, the suggested dimensions were used as a starting point, and reduced until the single-layer lap splice
coupons would fail by complete delamination in the overlapping portion. This ensured that the failure was shear critical and was not measuring the tensile strength of the coupon. The fabrication process was identical to that of the tensile coupons, using the vacuum bagging method. Three trials were needed to achieve the desired shear failure, including single-layered sheets with a 100 mm overlap as seen in Figure 3.7, double-layered sheets with a 100 mm and 76 mm overlap (Figure 3.8). Since none of the 30 specimens were close to failing by pure delamination, 4-layered sheets were used with a 25 mm single layer overlap to achieve the failure mode desired, as seen in Figure 3.9. The average thickness of the 4-layer lap-splice coupons was 3.48 ± 0.09 mm with an average overlap thickness of 5.78 ± 0.14 mm.

![Image](image.jpg)

**Figure 3.7: Single Layer Lap-Splice Specimen Failure (100 mm Overlap)**

It must be noted that ASTM D7616 gives the apparent shear stress of composite samples, and must therefore be interpreted in terms of a comparison point between treatment conditions.
3.7 Chemical Treatment of Fibre Mats

Chemical treatments of flax fibre mats were performed with the goal of addressing mechanical properties, fibre-matrix compatibility, and environmental durability. Three different chemical treatments were performed; Acetylation, Alkalization and Amino-Silane Treatment. Each treatment consisted of soaking the fibre mats in 177.8 x 279.4 mm (7 x 11-in) Pyrex glass trays for variable times as seen in Figure 3.10.

To obtain the different chemical solutions, a 2 L volumetric flask was used as the mixing container. The appropriate amount of each reactant was measured using a 10 mL
single channel pipette and added to the flask as seen in Figure 3.11, followed by either pure distilled water, or in the case of the amino-silane treatment, a 50/50 w/v (weight/volume percentage concentration) distilled water and ethanol solution. To minimize measurement errors, volumes of less than 5 mL were avoided when pipetting, therefore total volume needed was usually split into equal pipetting amounts. Concentrations reported were by mass. Using this method, 10 g of reactant in 1 L would be reported as a 1% solution. Sodium hydroxide pellets were weighed directly to 0.1 g whereas for liquid reactants, the reactant volume was calculated using the supplier’s reported density and volume needed to obtain concentration by mass.

Figure 3.10: Preparing Chemical Solution with Pipette
3.7.1 Acetylation

The acetylation process used 99% acetic anhydride solution from Sigma Aldrich Canada. The appropriate amount of reactant was measured and pipetted into a 2 L measuring flask. The flask was then filled with distilled water to produce the correct acid solution.

3.7.2 Alkalization

The Alkalization process used solid sodium hydroxide pellets from Sigma Aldrich Canada where the required amount was measured to 0.1 g accuracy using a balance scale and reacted with distilled water to produce the appropriate solution.
3.7.3 Silane Treatment

The Silane treatment process used > 98% (3-aminopropyl)triethoxysilane from Sigma-Aldrich Canada. The final solution was produced with the amino-silane and a 50/50 w/v distilled water-ethanol solvent in the 2 L measuring flask.

3.8 Single Fibre Fragmentation Test

The single fibre fragmentation test samples were fabricated by using a custom-made stainless steel mold. The specimen dimensions were based on Henstenburg and Phoenix (2004) simulation of interpreting single-filament composite tests. A gauge length of 25 mm with a thickness of 5 mm was used. A sketch of the mold can be seen below in Figure 3.12.

Figure 3.12: Sketch of SFFT Mold, Dimensions in mm.
A random single elementary flax fibre was carefully cut out of the flax mat and stretched across an individual mold slot. As seen in Figure 3.13, the fibre was carefully glued into place on the fibre slot then taped down ensuring enough tension in the fibre for it to remain straight when pouring the epoxy. The same procedure was followed for carbon fibre samples used as a second control group.

Figure 3.13: SFFT Mold with Single Fibres Placed in Slots

Before pouring into the mold, the bio-based epoxy was first placed in a Supersonic bath to remove air voids present for 5 min prior to pouring. Since this phase is at a microscopic scale, it was imperative to remove as many large air voids as possible to avoid skews in data. Figure 3.14 shows the difference in air bubble content between freshly mixed and degassed epoxy.
To ensure no air bubbles were introduced during pouring, the filled mold was then placed in the Branson Supersonic bath for another 5 min as seen in Figure 3.15.
The final specimen can be seen in Figure 3.16 below.

![Final SFFT Specimen](image)

Figure 3.16: Final SFFT Specimen

The specimens were removed by first heating the mold in order to expand the metal, then pouring cold water under each sample. The specimens were then individually pried out of each slot. Small release holes were also needed to push some specimens out of their slots. If the specimen was undamaged in the gauge length, with little to no air bubbles, it was deemed acceptable for testing.

### 3.9 Moisture Absorption Resistance

A total of 13 flax composite sheets were fabricated for the moisture absorption resistance test: four concentrations for each of the chemical treatments and one control. Each sheet was fabricated identical to the ones used to cut coupon specimens for tensile testing. The sheet dimensions were 350 mm by 350 mm.
All 13 sheets were immersed in a bath of distilled water as shown in Figure 3.17 for a total of 15 days and weighed to 0.01 g every hour for the first 12 hours, then every 12 hours thereafter to monitor moisture uptake rate and final full saturation mass.

Before each weigh-in, the specimens were wiped dry with a microfibre cloth towel and allowed to air dry for approximately 1 min to ensure that weight gain recorded was mainly from moisture absorbed into the bulk of the specimen instead of surface wetness.
Chapter 4

Results and Discussion

4.1 Tensile Coupons

A total of 150 specimens were tested in tension, including 30 control specimens, and 120 chemically treated specimens. Each variable had a test group of 10 specimens and the average mechanical properties and graphs are reported in the following sub-sections.

The control specimens consisted of unidirectional (UD) flax fibre composites fabricated with a bio-based epoxy and a UD flax fibre composite with a polypropylene epoxy matrix. Two different methods (hand layup and vacuum bagging) were investigated.

Also, 120 chemically treated specimens consisted of three different treatment methods at four different concentrations each having a sample size of 10 specimens.

A total of six measurements were taken for each coupon sample: the width and thickness at the top, bottom and mid-length. These measurements were averaged, and used to determine the average cross-sectional area to obtain the stress from load values of the tensile test.

4.1.1 Control Specimens

Two fabricating methods were compared in order to determine the more appropriate one to evaluate the performance of the UD flax fibre composites: vacuum
bagging and hand layup. Both methods are described in Chapter 3 under the Experimental Procedure. The two control groups were fabricated using a bio-based epoxy.

Figure 4.1 and Figure 4.2 display finished coupons from the vacuum bagging and hand layup fabricating methods.

Figure 4.1 (a): Vacuum Bagging Coupon (Top), (b): Hand Layup Coupon (Bottom)

Figure 4.2 (a): Thicknesses of Vacuum Bagging (Top), and (b): Hand Layup (Bottom) Coupons

It was first noted that the vacuum bagging coupons had a much rougher surface but did not contain large surface defects in the resin as seen in Figure 4.1. These surface defects originated from air bubbles during manual rolling of the resin-impregnated sheets. This proved to be a potential source of inconsistency and stress concentrations. Despite
the rough finish, the surface of the vacuum bagging coupons were uniform throughout the coupons and had consistent thicknesses measured along their lengths. The vacuum bagging coupons were also on average 34 % thinner. According to Rule of Mixtures, a higher fibre volume fraction produces more desirable mechanical properties with the added benefit of using less resin during the fabrication phase.

The stress-strain curves of the two fabricating methods for the flax fibre bio-resin composite can be seen in Figure 4.3. Each curve represents the average of 10 samples. The process of averaging the samples was done by averaging raw data values obtained and producing an average curve.

![Stress-strain curves](image)

**Figure 4.3: Control Specimens, Vacuum Bagging and Hand Layup Method (Bio-based Resin)**
The vacuum bagging method yielded more favourable results in terms of ultimate tensile stress due to the higher fibre volume fraction and less resin. A higher ultimate stress of $42.29 \pm 3.9$ MPa was obtained compared to that of the hand layup method of $32.41 \pm 5.5$ MPa. This suggests a 30% increase in tensile strength using the vacuum bagging technique. However, the latter method did show a lower modulus of elasticity of $3.20 \pm 0.7$ MPa compared to $8.20 \pm 0.5$ MPa. Due to the brittle nature of FRP composites, a lower modulus of elasticity is desirable to avoid catastrophic failure in a structural application. It was concluded that the vacuum bagging method was the better method for the remainder of the experimental procedure due to the mechanical properties of the coupons produced and the lower environmental impact.

A third control group was fabricated using UD flax fibres and the conventional polypropylene epoxy resin for comparison in the following sections. These coupons were fabricated using the vacuum bagging method.

Sections 4.1.2, 4.1.3 and 4.1.4 describe the tensile testing results of the three chemical treatments, Acetylation, Alkalization and Amino-Silane. These treatments were each done at four concentrations, and the composites were fabricated with the bio-based resin. The polypropylene epoxy resin was used only as a control, with untreated flax.

4.1.2 Acetylation Specimens

Four concentrations of acetic anhydride were chosen (1, 2, 3 and 4% named AA1, AA2, AA3 and AA4) as the first chemical treatment based on the work of L.Y Mwaikambo et al. (1999) where 10% acetic anhydride was used on Kapok, Sisal, Jute and Hemp fibres for 1 to 3 hours. A milder concentration range was used to adhere to the scope of this research project with the expectation of producing positive results. Figure
4.4 illustrates a peak tensile strength of 72.92 ± 4.0 MPa from a 2% anhydride treatment, using a 1 hour soaking time. This indicates an improvement of 72% and 22% compared to the control groups of bio-epoxy and polypropylene epoxy composites, respectively.

![Ultimate Tensile Strength of controls and Acetic Anhydride Specimens](image)

**Figure 4.4: Ultimate Tensile Strength of controls and Acetic Anhydride Specimens**

It is also noted that all the fibres treated with acetic anhydride improved in tensile strength. The trend from the four concentrations clearly indicates that the 2% is ideal due to the peak produced, indicating that increasing or decreasing the acid concentration within the 10% range, most likely would not significantly improve strength properties. In addition, any concentration higher than 4% is outside of the scope of this research as one of the main objectives is to design chemical treatments which would minimize use of potentially toxic chemicals. In addition, soaking for 1 hour and increasing the
concentration above 4% seems to indicate a reduction in strength as the concentration is increased.

Figure 4.5 shows the average stress-strain curves of the samples treated with acetic anhydride for 1hr with the bio-based resin.

![Stress-Strain Curve](image)

**Figure 4.5: Stress-Strain Curves of Acetic Anhydride (AA) and Control Specimens with Bio-Based Resin**

From Figure 4.5 it can be seen that all the AA treated samples displayed a consistent modulus of elasticity in the range of 4.6 to 5.4 MPa. Despite the significant improvement in tensile strength, a higher, less desirable moduli of elasticity were also produced but all 40 samples were in the same consistent range. The tensile modulus of elasticity values reported are based on the linear regression of each data set.
A sample of the most prominent type of failure of the acetic anhydride samples can be seen in Figure 4.6 below. All tensile coupons were tested in accordance to ASTM D3039/D3039M-14 as previously mentioned, and failure modes were also analyzed using the same standard’s three-part failure mode code. This code classifies each coupon failure based on location and type. The typical acetic anhydride coupon failure was identified as lateral, gage, middle (LGM) or angled, gage, middle (AGM).

![Typical AA coupon failure](image)

**Figure 4.6: Typical AA coupon failure (Bio-based Resin)**

### 4.1.3 Alkalization Specimens

The range of sodium hydroxide concentrations used were 2% to 8% for 1hr, based on the studies done by Bismarck et al., A.M. Edeerozey et al. and A. Arbelaitz et al. on Sisal, Kenaf and Flax fibres, whose treatments ranged from 2% to 10% sodium.
hydroxide concentrations for 30 min to 48 hr with a variety of success. The tensile strengths of the alkalization coupons can be seen in Figure 4.7.

![Ultimate Tensile Strength of Control and NaOH Specimens](image)

**Figure 4.7: Ultimate Tensile Strength of Control and NaOH Specimens (Bio-Based Resin)**

Despite previous success with the treatment of natural fibres with sodium hydroxide, no positive results were obtained during this research. It can be seen that even a low concentration of 2 % (relative to concentrations reported in literature) caused a detriment to the strength of the composite in tension. As seen in Figure 4.8, this decrease in strength could be due to the structural integrity of the fibres themselves during the soaking phase or may require a shorter soaking time.

The type of specimens studied is a factor in the sodium hydroxide treatment method. Arbelaitz et al. (2005) obtained positive results with 20 % sodium hydroxide with a 1 hour soaking time, but an external mixer and extruder were used to first produce
compressed, dried pellets which were then fed to an injection moulding machine. The type of resin (thermoplastic versus thermoset) may have had a deciding factor. Since in this study unidirectional flax mats are being used to produce composite sheets, the structural integrity is essential in the resulting mechanical performance.

Figure 4.8 shows two samples of flax sheets which were both originally cut the same length with the sample on the left having been soaking for 10 min in 4 % acetic anhydride and the one on the right, 4 % NaOH.

Figure 4.8: Soaking UD Flax Fibres in 4 % AA (left) and 4 % NaOH (right)

A 40 % decrease in length was observed for the NaOH sample and can be attributed to the expected swelling of the fibre. This is due to the removal of surface waxes and consequent fibrillation of the fibres. The NaOH treatment was designed to
promote resin uptake, which would have been more effective with an injection molding process using a thermosetting resin as previously mentioned.

The typical failure of the NaOH coupon can be seen in Figure 4.9. The failure mode was identified as LGM or AGM, similar to the acetic anhydride samples. However, the surface shows more swollen and disorganized fibres in the mat structure, which could explain the low breaking stresses reported. Also the fibres within the bulk of the coupon do not seem to be fully saturated by the bio-based resin when compared to the acetic anhydride coupon as seen in Figure 4.6.

Figure 4.9: Typical NaOH Coupon Failure (Bio-based Resin)
The dry fibres in the bulk of the coupon could indicate the effectiveness of the moisture uptake resistance, making the alkalization treatment a viable option for low load applications with potential exposure to moisture, or simply an incompatibility with the bio-based resin.

The resulting stress-strain curves for the Alkalization coupons can be seen in Figure 4.10 where NaOH2, NaOH4, NaOH6 and NaOH8 are concentrations of 2, 4, 6 and 8 % NaOH, respectively soaked for 1 hour.

![Figure 4.10: Stress-strain curves of Alkalization coupons (Bio-based Resin)](image)
The curves obtained have a higher range of tensile strength and modulus of elasticity when compared the previous acetic anhydride treatment, showing less consistent results in addition to the lower strengths obtained. The stress-strain curves also did not show a consistent slope as expected from composites. Tensile strengths ranged from 16.9 MPa (NaOH8) to 43.9 MPa (NaOH2) with moduli of 1.6 to 4.6 MPa.

It can be seen that the damaged structural integrity of the flax fibres are affecting the performance of the composite and can be concluded that the NaOH treatment was ineffective overall unless used for a specific application.

4.1.4 Amino-Silane Specimens

A total of 40 specimens were treated with 3-aminopropyl-triethoxysilane with concentrations of 1 to 4 %, based on the work of Van de Weyenberg et al. and Valadez et al. where improved mechanical properties were reported with concentrations of 1 and 2 % on Flax fibres. Figure 4.11 and Figure 4.12 show the ultimate tensile strengths of the test specimens and their associated stress-strain curves respectively.
Figure 4.11: Ultimate Tensile Strength of control and Amino-Silane specimens (1 hour soaking time)

From Figure 4.11 it can be seen that the coupons soaked in 2% amino-silane for 1 hour produced the best improvement in tensile strength with an increase of 55% and 10% compared to the bio-based and polypropylene epoxy control composites, respectively.

All treated samples showed an improvement in tensile strength and similarly to the Acetylation treatment, a peak is shown at 2% therefore it was concluded to be the ideal concentration within the scope of this research. A decrease in tensile strength was observed for lower or higher concentrations of 2%.

Figure 4.12 shows the stress-strain curves of the treated coupons. Silane1, Silane2, Silane3 and Silane4 indicate concentration of amino-silane of 1, 2, 3 and 4%, respectively.
The resulting stress-strain curves were consistent and produced elastic moduli over a short range of 5.08 to 6.12 MPa, however values higher than the control specimen. Tensile strengths were also within a small range from 56.30 MPa (Silane3) to 68.62 MPa (Silane2).

Figure 4.13 shows a typical failure mode for the amino-silane coupons. These coupons displayed more angular lateral failures, sometimes outside of the gauge length of the extensometer used, classifying them as angled, gauge, middle (AGM), lateral, at grip/tab, top (LAT) or lateral, gauge, middle (LGM).
4.1.5 Tensile Coupon Summary

The control UD flax composite sheets were fabricated using the vacuum bagging method and it was determined that this was the best choice for all subsequent sheets in order to maintain uniformity and minimize surface defects.

Figure 4.14 shows a summary of the tensile coupons tested.
From the tensile tests performed, the group treated with acetic anhydride on average produced the best results, with 2% acetic anhydride being the ideal treatment method. Intermediate strengths resulted from the Silane treatment, while the least successful group was the sodium hydroxide treated fibres. These results were not expected as the Acetylation treatment was focused on improving moisture resistance, the Alkalization treatment method was intended to improve fibre/matrix interface and improve interfacial properties of the composite. The structural integrity of the fibre, fibre-resin compatibility and chemical concentrations may have affected the results. As seen in Figure 4.8, there is a large amount of swelling in fibres treated with sodium hydroxide, and acetic anhydride promotes dimensional stability due to the hydrolysis of open hydroxyl compounds, reducing water uptake in the fibres.
It can be seen that different factors must be taken into account when designing the ideal chemical treatment for natural fibres.

Table 4.1 below displays a summary of the tensile coupons tested along with reported mechanical properties. T/AA, T/SH and T/S indicating the tensile coupons for acetic anhydride, sodium hydroxide and amino-silane, respectively.

Table 4.1: Summary of Tensile Coupon Properties

<table>
<thead>
<tr>
<th>Coupon Type</th>
<th>Sample Size</th>
<th>Average Tensile Strength (MPa)</th>
<th>Standard Deviation (MPa)</th>
<th>Average Young’s Modulus (GPa)</th>
<th>Standard Deviation (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bio-based Epoxy (Vacuum Bag)</td>
<td>10</td>
<td>42.29</td>
<td>3.9</td>
<td>3.20</td>
<td>0.7</td>
</tr>
<tr>
<td>Bio-based Epoxy (Hand Layup)</td>
<td>10</td>
<td>32.41</td>
<td>5.5</td>
<td>8.20</td>
<td>0.5</td>
</tr>
<tr>
<td>Polypropylene Epoxy (Vacuum Bag)</td>
<td>10</td>
<td>59.91</td>
<td>8.9</td>
<td>2.30</td>
<td>0.5</td>
</tr>
<tr>
<td>Acetic Anhydride</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T/AA-1</td>
<td>10</td>
<td>67.67</td>
<td>5.5</td>
<td>5.30</td>
<td>0.5</td>
</tr>
<tr>
<td>T/AA-2</td>
<td>10</td>
<td>72.92</td>
<td>4.0</td>
<td>5.40</td>
<td>0.4</td>
</tr>
<tr>
<td>T/AA-3</td>
<td>10</td>
<td>69.13</td>
<td>7.8</td>
<td>4.60</td>
<td>1.9</td>
</tr>
<tr>
<td>T/AA-4</td>
<td>10</td>
<td>63.40</td>
<td>5.7</td>
<td>4.70</td>
<td>1.2</td>
</tr>
<tr>
<td>Acetylation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.2 Lap Splice Coupons

A total of 158 single overlap coupons were tested during this phase of the experimental procedure. Of which, 40 control specimens to finalize coupon dimensions since no standards are available for natural fibre specimens, and 118 chemically treated coupons.

The goal of the lap splice coupons phase was to determine the shear strength of the non-treated and treated coupons in order to assess the effect of the chemical treatments on the fibre-to-fibre interface. Similar to the tensile testing phase, an increase in shear strength was expected from the treatments, with one concentration being ideal.
The shear strength was calculated based on the peak tensile strength during a delamination type failure in only the overlapped area, as mentioned in Chapter 3. The following sections discuss the results of the tests.

4.2.1 Specimen Failure

Several trials were needed to obtain the final coupon dimensions of the lap-splice specimens. Full delamination was desired to ensure that the coupons were failing by shear force at the overlap area rather than the tensile strength outside the lap-splice region of the coupon. The typical failure of the final control four-layer, 25 mm overlap, lap-splice specimen with the bio-based resin can be seen in Figure 4.15 below.

![Figure 4.15: Full Delamination of Final Control Coupon](image)

Of the 10 samples tested for the control group, all failed by full delamination and was concluded to be a good comparison for treated samples.

The samples treated with acetic anhydride failed through two modes: full delamination (within the lap-splice region) and fibre-tear failure (in the lap-splice region...
and outside the lap-splice region) according to ASTM D7616/D7616M-11 as seen in Figure 4.16 and Figure 4.17 respectively.

Figure 4.16: Typical Delamination of Acetic Anhydride treated Sample
It was found that fibre-tear failure was found predominantly in 1 % acetic anhydride and 4 % acetic anhydride samples, however in no more than 4 samples out of the 10 tested per group. This could be the reason for higher shear strength values obtained as the fibres had to fail through tension, instead of the coupon failing by slipping.

None of the coupons treated with sodium hydroxide failed by pure delamination. Perhaps a smaller lap-splice length is required for Alkalization treatments of flax fibres and could be conducted in future work. All 40 of the coupons tested failed by fibre-tear failure as seen in Figure 4.18 and Figure 4.19 below.
Figure 4.18: Typical Fibre-tear in Alkalization treated Sample (in Lap-Splice region)
Despite the fibre-tear failure mode, the alkalized samples on average produced lower shear strengths when compared to the other treatment methods. This may be due to the lower tensile strengths reported in Section 4.1.3.

All the amino-silane samples failed by pure delamination, as seen in Figure 4.20 and Figure 4.21 below.
Figure 4.20: Typical Delamination of Amino-Silane Treated Sample

Figure 4.21: Typical Side view of Amino-Silane Treated Sample
It can be seen that there is minimal damage to the fibres in the overlapped portion, resulting in a delamination failure mode.

### 4.2.2 Shear Strengths

Figure 4.22 below shows the average shear strengths of the tested sample groups.

![Figure 4.22: Shear Strength of Tested Coupons](image)

The control samples with the bio-based resin produced an average strength of $8.13 \pm 0.7$ MPa. The acetic anhydride samples have higher shear strengths for the 1% and 4% concentration groups, with improvements of 11.8% and 12.4% respectively. However, these values may be overinflated due to tensile strength as seen via their failure mode. Stress was transferred to the bulk of the fibres, causing rupture and increasing the
breaking strength. It is expected that the fibre strength was higher than the overlap shear strength. The 2 % and 3 % groups were mainly failure by delamination (7-9 out of 10) and showed significantly lower shear strengths by approximately 25 %. A larger sample size may have improved results.

Lower shear strength values can also be seen in the Alkalization (NaOH) groups despite all the coupons failing by partial fibre-tear. This further confirms the detrimental effect of the sodium hydroxide on the fibres as higher shear strengths would have been expected with only fibre-tear failures.

All the amino-silane samples failed by delamination and increased in strength in the order of 2 % and 3 % concentration groups can be seen by 20 % and 18 %, respectively. These are the only groups which can be concluded to be successful due to the lack of failure through the bulk of the coupon and still providing an increase in strength.

4.2.3 Lap-Splice Summary

The 2 % amino-silane was determined to be the ideal concentration from the lap-splice testing phase. The results however may not be representative of each chemical treatment method’s influence on shear strength due to variability in failure modes. Ideally, each coupon would fail by pure delamination for best comparison purposes but more insight is provided on the effect of the fibre integrity. From the previous section, it was supposed that sodium hydroxide affects the fibre structure, weakening composite strength, which was supported in this section.

A summary of the tested coupons can be seen in Table 4.2 below. With LS indicating a Lap-Splice sample group, T indicating a Tensile sample group with AA, SH
and S being acetic anhydride, sodium hydroxide and amino-silane. The indicated numbers show concentrations by mass used.

Table 4.2: Summary of Lap-Splice Coupons Properties

<table>
<thead>
<tr>
<th>Coupon Type</th>
<th>Sample Size</th>
<th>Average Shear Strength (MPa)</th>
<th>Standard Deviation (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Control</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bio-based Epoxy</td>
<td>10</td>
<td>8.13</td>
<td>0.7</td>
</tr>
<tr>
<td>LS/T-1</td>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>LS/T-2</td>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>LS/T-3</td>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Acetic Anhydride</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LS/AA-1</td>
<td>10</td>
<td>9.09</td>
<td>1.2</td>
</tr>
<tr>
<td>LS/AA-2</td>
<td>10</td>
<td>6.05</td>
<td>0.5</td>
</tr>
<tr>
<td>LS/AA-3</td>
<td>8</td>
<td>5.92</td>
<td>0.6</td>
</tr>
<tr>
<td>LS/AA-4</td>
<td>10</td>
<td>9.14</td>
<td>0.9</td>
</tr>
<tr>
<td><strong>Acetylation</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LS/SH-2</td>
<td>10</td>
<td>7.66</td>
<td>1.2</td>
</tr>
<tr>
<td>LS/SH-4</td>
<td>10</td>
<td>6.01</td>
<td>0.9</td>
</tr>
<tr>
<td>LS/SH-6</td>
<td>10</td>
<td>7.18</td>
<td>2.8</td>
</tr>
<tr>
<td>LS/SH-8</td>
<td>10</td>
<td>8.28</td>
<td>1.6</td>
</tr>
<tr>
<td><strong>Amino-Silane</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LS/S-1</td>
<td>10</td>
<td>6.96</td>
<td>0.6</td>
</tr>
<tr>
<td>LS/S-2</td>
<td>10</td>
<td>9.82</td>
<td>2.3</td>
</tr>
<tr>
<td>LS/S-3</td>
<td>10</td>
<td>9.54</td>
<td>1.2</td>
</tr>
<tr>
<td>LS/S-4</td>
<td>10</td>
<td>7.31</td>
<td>1.0</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td></td>
<td>158</td>
<td></td>
</tr>
</tbody>
</table>
4.3 Single Fibre Fragmentation Testing (SFFT)

4.3.1 Initial Testing

Initial testing of the SFFT’s was conducted using three trials due to the equipment available in the laboratory. The first trial for the SFFT was done on the Instron 8802 hydraulic testing system. As seen in Figure 4.23, the hydraulic grip pressure of 3.5 MPa (500 psi) created a high stress concentration point between the gauge length and the gripping area, which was observed to cause bending of the specimen.

![Figure 4.23: Digital Image of the SFFT Sample in Instron 8802](image)

It can be seen from Figure 4.24 that this stress concentration is clearly due to the compression of the entire gripping area of the samples.
Figure 4.24: Digital Image of the Compression of SFFT Sample Gripping Area
Despite reducing the grip pressure to 0.7 MPa (100 psi) (the lowest grip pressure available on this Instron model), much lower than the recommended pressure, stress was still created under the gripping point, eventually resulting in total failure of the grip area.

One possible solution was to tab the gripping area of the SFFT specimens with CFRP tabs identical to those used for tensile coupons, however specimens still fractured before any tests could be initiated, deeming the Instron 8802 inappropriate for the SFFT.
4.3.2 Second Testing

From this learning curve, the Zwick-Roell Z020 was used instead of the Instron 8802 as its mechanical grips and 20 kN load cell compared to the Instron’s 250 kN were more appropriate for small-scale material testing.

A cross-head distance of 20 mm with a strain rate of 0.5 mm/min was used for all specimens reported. The setup can be seen in Figure 4.30 below.

![Figure 4.26: SFFT Sample in Zwick-Roell](image-url)
The mechanical grips did not damage the samples during testing, as can be seen in Figure 4.27 below. A total of 65 Single Fibre dog bone samples were tested during this phase: 15 untreated flax fibres, 15 carbon fibres, 15 fibres treated with 2% acetic anhydride, 15 fibres treated with 2% amino-silane and 15 fibres treated with 2% NaOH. The concentrations selected for this phase represented the best conditions for each treatment methods based on the previous tensile and lap-splice tests.

![Figure 4.27: Undamaged SFFT Sample in Zwick-Roell](image)

The goal of the SFFT was to examine the micromechanical interaction between the fibre and reinforcing bio-based epoxy. As previously mentioned, this was done by drawing comparative results from the tests through the number of fragments produced from a single tensile test. A sample with a high number of fragments indicates more
slipping resulting in local fracturing due to less effective stress transfer between the bulk of the epoxy dog bone to the single fibre. A sample with no fragments is theoretically ideal as this indicates that the fibre would fragment only at the break point of the dog bone sample.

Fragments were counted manually with the use of the Olympus SZX series stereomicroscope with a 20 x 0.8 magnification, equipped with an Infinity 2 camera software. Fragments were defined by clear breaks in the fibre as seen in Figure 4.28 for a carbon fibre sample. Air voids can also be seen but are away from the fibre and are circled for clarity. In addition, the air voids did not affect the SFFT testing as no local crack formations were observed.

![Figure 4.28: Carbon Fibre SFFT Sample showing Breaks (arrows) and Air Voids (circles)](image)

Based on average fragments, the carbon fibre samples had the least, with 13.13 ± 2.0. It was also noted that the breaks were at fairly regular lengths, as expected from the man-made fibre. The flax fibres displayed more random fragment lengths due to fraying, as opposed to slipping as can be seen in Figure 4.29 for the 2% amino-silane sample.
As indicated on Figure 4.29 with arrows, large, non-distinct breaks can be seen in various sections of the SFFT sample. This was prevalent in several flax samples and can be due to the variety in fibre diameters and natural imperfections. During fabrication, the smallest, elementary fibre was always chosen to prepare a sample, but from handling and the nature of the natural fibre, it was impossible to collect 50 identical fibres in diameter. Human error could be the cause of random data spread. Additionally, there is a prevalent variability in single fibre to single fibre due to a variety of reasons including climate, soil conditions, water supply and temperature throughout the growing season. For example, the same plot of land can yield different fibres if one flax plant grows in the shade or in moist soil compared to a dryer soil. Basically the growing conditions from plant to plant can affect the single fibre morphology. A way to mitigate this is to increase the sample test size. Figure 4.30 illustrates an untreated flax sample, while Figure 4.31 shows a treated fibre where a clear difference is visible in the size of the two fibres.
Figure 4.30: Control SFFT Sample

Figure 4.31 and Figure 4.32 show examples of acetic anhydride and NaOH samples respectively.

When compared to other treated samples, the sodium hydroxide samples had high variations of fragments with an average of 15.93 ± 3.0. Several samples had more than 20 fragments as seen in Figure 4.32 below, whereas some would have as few as 10 fragments.
The variation in fragments from the sodium hydroxide samples can be due to damage in the structure of the fibre as discussed in the macromechanical test results, explaining the samples with more than 20 fragments. In addition, the samples with very few fragments can be potentially due to a successful treatment in terms of increasing surface roughness, one of the treatment’s reported benefits.

The average elongation of the samples was 3.6 ± 0.57 mm, an elongation of 6.5 ± 1 %, within range of the manufacturer’s reported expected elongation of 6 % for homogeneous epoxy resin samples. Figure 4.33 illustrates the results for the Single Fibre Fragmentation Testing.
Similar to the lap-splice test done prior, it is difficult to distinguish a conclusive trend among all 65 samples. There is no clear ideal chemical treatment that can be seen from Figure 4.33 as the number of fragments varied across all samples from a range of 10 to 22. These values are within range of similar studies performed by Awal et al. (2011) on Flax and Ramie fibres in a polypropylene matrix. The study yielded mean fragments of 10.0 and 17.3 for 30.0 and 70.0 mm gauge lengths respectively.

The mean fragments of each group of fibres tested can be seen in Figure 4.34 below.
Figure 4.34: Mean Number of Fragments of SFFT Samples

It can be seen that there is a slight decrease in number of fragments observed in the treated flax samples compared to the untreated fibres, indicating an improvement in fibre/matrix adhesion. When comparing the treated flax fibres to the conventional carbon fibre sample group, it can be seen that Silane 2 yielded very comparable results with a mean number of 12.80 ± 2.1 compared to 13.13 ± 2.0. This does indicate an improvement in interfacial bonding between the natural fibre and matrix compared to its petroleum-based counterpart. However since it is such a small difference at this scale, measurement error should be taken into account.

The tests were successful due to the ability to detect distinct fragments and draw a conclusion from data acquired but much larger sample sizes are recommended for future work. The SFFT tests showed the three chemical treatments were able to improve the fibre-resin adhesion for single fibres.
4.4 Moisture Absorption

The effectiveness of moisture uptake resistance of each chemical treatment method was evaluated by monitoring water uptake rate and absorption quantity over 15 days. Water absorption was measured by weighing samples at set time intervals and presented as a percent of their original mass as seen in Figure 4.35 below.

![Figure 4.35: The % Moisture Absorbed by Chemically Treated and Control Specimens](image)

All treated samples showed an improvement to moisture resistance when compared to the control, with 1 % acetic anhydride and 8 % sodium hydroxide treatments being the most effective with 15.4 % and 15.9 % moisture absorbed compared to the 25.5 % of the control sample. This is a moisture intake reduction of 40 % and 38 %, respectively. The least effective treatment for moisture resistance is the Alkalization method NaOH4 where the sample showed a similar water uptake as the control. Moisture uptake rates can be seen in subsequent sections for each chemical treatment.
4.4.1 Acetic Anhydride

The acetylation process or acetic anhydride treated flax fibre results are provided in Figure 4.36.

![Figure 4.36: Moisture Absorption of acetic anhydride Group](image)

The control, 1, 2, 3 and 4 % acetic anhydride specimens had an initial linear water uptake up from 0 to 25 hours, with rates of 4.64, 2.08, 2.35, 3.04 and 3.03 %/h\(^{1/2}\) respectively. The time is shown as square-root hours simply for display purposes. It can be seen that all the samples treated with acetic anhydride outperformed the control specimen in terms of initial rate of absorption and weight gain percentage, with 1 % acetic anhydride being the ideal concentration. This sample represents a significant 40 % improvement of moisture resistance.

One of the main advantages of using the Acetylation method was the plasticization of fibres by replacing open hydroxyl groups with acetyl groups, decreasing
moisture affinity. Based on the results obtained from the four concentrations tested, 1% acetic anhydride was the most effective in plasticizing process. This however does not agree with predicted results as a higher concentration would imply a faster rate of plasticization from basic chemistry principles. Since the range of moisture absorbed is only 15.4% to 19.6%, fabrication imperfections could have heavily influenced results which holds true for the two other chemical treatments.

4.4.2 Alkalization

The alkalization results are shown in Figure 4.37.

![Figure 4.37: Moisture Absorption of Sodium Hydroxide Group](image)

The initial linear water uptake rates were 4.58, 4.26, 3.43 and 3.15%/h^{1/2} for 2%, 4%, 6% and 8% NaOH samples, respectively. It can be seen that despite 2% sodium hydroxide performing closely to the control sample, all the treated specimens were successful. There is a larger spread in performance with the four different concentrations
used, compared to the acetic anhydride group with a range from 15.9 to 25.0 % moisture absorbed.

It was however expected for the alkalized samples to be outperformed by the acetylated samples based on the interaction between sodium hydroxide and the fibre surface. In theory, the sodium hydroxide removes waxes and oils on the surface of the fibre, simultaneously exposing hydroxyl groups to the reinforcing matrix to improve adhesion. The main advantage of alkalization is therefore theoretically fibre/matrix interface resulting in improved strengths and not moisture resistance through direct fibre modification. It can therefore be supposed that the bio-based epoxy chosen did not fully absorb into the fibre as intended, which would have been the mechanism through which moisture resistance would be achieved.

4.4.3 Amino-Silane

The Amino-Silane results are given in Figure 4.38. Initial linear water uptake rates of 3.29, 3.29, 2.83, 3.21 %/h\(^{1/2}\) were obtained from the 1 %, 2 %, 3 % and 4 % Amino-Silane samples, slightly higher numbers than the Acetylated samples including moisture absorption percentage. But the treated samples did outperform the control sample by 17, 27, 19 and 21 % with 2 % amino-silane being the most successful concentration and 1 % being the least.
It is known that the success of the amino-silane treatment depends on two separate but dependent reactions as follows: first is the formation of silanols, then the attachment of these silanol compounds to the fibre surface as outlined in Chapter 2 in more detail. This attachment of the silanol compounds is the driving mechanism behind moisture resistance as hydroxyl groups are targeted and bonded thus reducing affinity for moisture. Similar to the acetic anhydride process, as was expected the 4% amino-silane sample yielded the best results based on a theoretical higher availability of silanols produced. Again, the discrepancy between the expected results and the results obtained may be due to fabrication or measurement errors. The difference between the best and worst samples was 1.7% for a difference of 4.3 g.

4.4.4  Moisture Absorption Conclusions
It can be concluded that 1% acetic anhydride, 8% sodium hydroxide, and 2% amino-silane were the most successful concentrations in each of their respective chemical treatment methods, with 1% acetic anhydride being the ideal of all treated sheets. This represents a 40% moisture absorption resistance improvement.

A summary of the samples tested can be seen in Table 4.3 below. With the identifying code M for moisture and AA, SH and S for acetic anhydride, sodium hydroxide and amino-silane.

<table>
<thead>
<tr>
<th>Sheet Type</th>
<th>Initial Weight (g)</th>
<th>Max Weight (g)</th>
<th>% Moisture absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Control</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bio-based Epoxy</td>
<td>105.74</td>
<td>141.90</td>
<td>25.5</td>
</tr>
<tr>
<td><strong>Acetic Anhydride</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M/AA-1</td>
<td>145.53</td>
<td>173.30</td>
<td>15.4</td>
</tr>
<tr>
<td>M/AA-2</td>
<td>143.99</td>
<td>172.15</td>
<td>16.3</td>
</tr>
<tr>
<td>M/AA-3</td>
<td>122.28</td>
<td>152.00</td>
<td>19.6</td>
</tr>
<tr>
<td>M/AA-4</td>
<td>124.31</td>
<td>151.35</td>
<td>17.9</td>
</tr>
<tr>
<td><strong>Alkalization</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M/SH-2</td>
<td>123.80</td>
<td>165.12</td>
<td>25.0</td>
</tr>
<tr>
<td>M/SH-4</td>
<td>129.60</td>
<td>168.89</td>
<td>23.3</td>
</tr>
<tr>
<td>M/SH-6</td>
<td>135.50</td>
<td>165.26</td>
<td>18.0</td>
</tr>
<tr>
<td>M/SH-8</td>
<td>147.12</td>
<td>174.9</td>
<td>15.9</td>
</tr>
<tr>
<td><strong>Amino-Silane</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>------</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>M/S-1</td>
<td>125.81</td>
<td>159.63</td>
<td>21.2</td>
</tr>
<tr>
<td>M/S-2</td>
<td>130.37</td>
<td>159.89</td>
<td>18.5</td>
</tr>
<tr>
<td>M/S-3</td>
<td>126.82</td>
<td>159.85</td>
<td>20.7</td>
</tr>
<tr>
<td>M/S-4</td>
<td>130.32</td>
<td>163.18</td>
<td>20.1</td>
</tr>
</tbody>
</table>
Chapter 5
Conclusions and Future Work

5.1 Conclusions

The goal of this research was to design and optimize chemical treatments on unidirectional flax fibre composites in an effort to improve mechanical properties and reliability. Three chemical treatments were chosen based on previous success: acetic anhydride, alkalization and amino-silane. These treatments were each evaluated through their performance as a fabricated composite with a bio-based epoxy and as individual fibres.

The first testing phase was the macromechanical tests which consisted of tensile testing and lap-splice testing of composite coupons. It was found that the fibres soaked in 2% acetic anhydride for 1 hour produced the best results, with a tensile strength of 72.92 ± 4.0 MPa compared to the control’s 42.29 ± 3.9 MPa. This represented an improvement of 72%. A 22% improvement was also found when comparing to a conventional polypropylene epoxy. The lap-splice results indicated that control samples with the bio-based resin produced an average shear strength of 8.13 ± 0.7 MPa and the ideal chemical treatment was 2% amino-silane with a soaking time of 1 hour, producing an average shear stress of 9.82 ± 2.3 MPa, representing a 20% improvement.

The second test phase was a micromechanical test, called the Single Fibre Fragmentation Test. This test was a tensile test performed on single fibres embedded in dog bone epoxy specimens. By analyzing the number of fragments obtained within each sample, comparative conclusions can be drawn on the fibre/matrix interface. It was found
that 2% amino-silane produce the least amount of fragments, 12.80 ± 2.1, compared to the untreated flax control’s 15.93 ± 3.0 and the carbon fibre’s 13.13 ± 2.0.

The final testing phase of this research was a moisture absorption test where the absorption rates and magnitudes were analyzed when composites were exposed to a fully saturated environment. All the treated samples showed moisture resistance improvement, with 1% acetic anhydride being the most successful group with a 17% moisture resistance improvement.

5.2 Future Work and Recommendations

Based on the results obtained throughout the course of this research project, it is suggested that:

1. Single Fibre Fragmentation tests be performed with similar chemically treated flax fibres, but with larger samples sizes of at least 50 fibres per variable in order to obtain more definitive conclusions in the flax/matrix interface in an effort to reduce the effects of human error and natural fibre variability.

2. Commercially available and natural oil-based resins be compared with the three different treatments.

3. Different reaction times (soaking times) be tested for all three chemical treatments.

4. Impact Charpy and three-point bending tests be performed to obtain an even more complete properties profile of the flax fibre composites.

5. Different bio-based epoxy composites moisture absorption performance be compared to conventional epoxy composites.
6. The flax composites performance be evaluated in larger scale tests, as beam or column reinforcement.
References


Joseph, K., Mattoso, L.H.C., Toledo, R.D., Thomas, S., de Carvalho, L.H., Pothen, L., Kala, S., James, B. (2000). *Natural Polymers and Agrofibers Composites*. São Paulo State University, Brazil.


