Impact Behaviour of Hybrid Long Fibre Thermoplastic Composites

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Department of Chemical Engineering and Applied Chemistry
University of Toronto

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Abstract

Impact strength is a critical property of composites in the auto industry by way of product service life, safety, and liability. The aim of this project is to arrive at a hybrid biocomposites of hemp-glass fibre-PP with high toughness. Long glass fibres are believed to increase impact strength of composites, and current literature has mainly focused on hand layup process of laminates and mats to achieve long fibres, whereas this work investigates the use of extrusion and GF roving. The hypothesis being tested is that the energy absorption of hybrid composites can be improved by increasing glass fibre length using an extrusion process. Process optimization resulted in a hybrid composite with notched impact strength of $131 \pm 12$ J/m, tensile strength of $92 \pm 7$ MPa, and flexural strength of $160 \pm 15$ MPa produced at an optimum shear rate of $62$ sec$^{-1}$ while feeding glass fibre into a port before the vent. To enhance interaction of fibres and matrix, 5% MAPP coupling agent was added to the composite since the other examined surface treatments for natural fibres did not yield significant improvement of impact properties. The last objective for this thesis was to relate the work of fracture of hybrid composites to fibre and matrix properties using a theoretical model, since there is no experimental validation for the available models in literature. The model presented here uses the Rule of Mixtures model to incorporate matrix failure, fibre debonding and fibre pull out for short fibres, in addition to fibre stress redistribution for long fibres.
Good agreement between the presented model predictions and experimental data was observed. For the case of hybrid composites with long fibres, the dominant failure mechanisms were fibre stress redistribution and matrix failure, while for the case of short fibre composites fibre pull-out and matrix failure were dominant. In order to produce hybrid composites with high work of fracture, the focus should be on fibre processing to arrive at an optimum length, aspect ratio, volume fraction, and good dispersion.
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1 Introduction

1.1 Background

Different materials are often combined to produce composites which have the best qualities of the individual components. In fibre reinforced polymer composites, the matrix protects the fibres from the environment, and transfers applied stress to the fibres, which have better tensile, stiffness, and impact resistance properties. Traditional composites are made of synthetic fibres, such as carbon, aramid, and glass. These fibres have been proven to enhance the performance of composites, but unfortunately are not renewable. Advances in natural fibre and composite science have shown that natural fibres can be used to enhance composite performance. Biocomposites are composites in which at least one phase is a bio-based component. They have numerous advantages such as renewability and sustainability, eco-friendliness, lightweight design, low cost, sound abatement capability, and better crash resistance. The need for biocomposites has increased as the pressure of regulations pertaining to vehicle landfills and their recyclability has intensified worldwide.

Biocomposites have potential in various applications, especially in the automotive and aerospace industries. The primary goal of the automotive industry is weight reduction, cost efficiency, fuel savings, safety improvement, and recyclability after use. Biocomposites are highly suitable for the automotive industry as they can help manufacturers meet all these goals.

Impact strength is a critical property of composites in the auto industry as it relates to product service life, safety, and liability. The impact toughness of a composite is higher than either of its constituent phases due to the energy dissipating failure mechanism such as pull-out and debonding in the composite [1]. Unfortunately, impact properties of natural fibre reinforced composites cannot compete as well as their other mechanical properties with glass fibre reinforced composites [2]. Hence, hybridization (use of more than one fibre in matrix) can facilitate the achievement of
biocomposites with great load-carrying capacity and better impact energy absorption while being environmentally friendly. This thesis investigates the impact strength of a hybrid biocomposite made of long glass fibre, hemp fibre, and polypropylene. A hybrid composite has a higher strength and stiffness than a single fibre reinforced polymer; it also has a lower cost and leads to weight savings. Panthapulakkal et al. showed that hybridization with short glass fibre enhanced impact strength by 35% for a hemp-PP composite [3].

Long fibre thermoplastic are becoming more attractive as they have superior mechanical properties due to fibre’s higher aspect ratio [4-6]. Ability of long fibres to dissipate the force upon impact as oppose to localizing it makes them desirable. There are various methods available to achieve long fibre composites. Current literature has mainly focused on hand layup process of laminates and mats or fibre knitting for long fibre composites [7-10]. These methods result in high mechanical properties, however there is a gap in the literature in understanding flow behaviour of for long fibre plastics melt in commercial scale production through extrusion using continuous glass fibre. This work investigates commercial scale production of long fibre thermoplastic composites through Long Fibre Direct compounding and molding (LFT-D), and understanding the science behind energy absorbing mechanisms for hybrid long fibre composites. The challenge at hand is to reduce glass fibre content and add natural fibre to LFT-D method.

1.2 Hypothesis

The main hypothesis for this thesis is that the energy absorption of hybrid composites can be improved by increasing glass fibre length using extrusion process. Combination of MAPP coupling agent with other chemical surface treatment of natural fibres can also enhance the impact strength of hybrid biocomposites.
1.3 Objective

The overall objective is to develop a process to maximize fracture toughness of hybrid biocomposites through improved understanding of energy absorption behaviour of thermoplastic composites reinforced with organic and inorganic fibres.

The specific objectives are as follows:
1- To study the effectiveness of surface treatments of natural fibres
2- To optimize extrusion process parameters in order to disperse the fibres with minimum fibre breakage, to achieve a high toughness hybrid biocomposites
3- To develop a model for prediction of fracture toughness of hybrid composites
4- To validate the above predictive model
5- To develop prototype of hybrid composite with enhanced energy absorption behaviour

1.4 Thesis outline

This thesis attempts to find ways to enhance the toughness of hybrid composites and to relate the impact behaviour of hybrid composites to fibre and matrix properties using a theoretical model. Mechanical properties of biocomposites are dependent on their fibre-matrix interfacial properties. Thus, surface treatments of natural fibres are investigated to enhance the compatibility of fibre and matrix to improve the impact behaviour of composites. It is known that long fibre composites have better mechanical performance due to the higher fibre aspect ratio [4-6]. Hence, another way investigated to enhance the impact behaviour is to retain the length of the fibres in the system through varying operational conditions during compounding. Hybrid composites are processed following the new technology LFT-D (Long Fibre Thermoplastic Direct compounding and molding) in order to keep the length of the fibres. Although LFTs have been commercially in use for the automotive industry, little experimental and modeling work exists for these materials [11].

The theoretical modeling of work of fracture of hybrid composites is a useful and time-efficient method to understand the behaviour of composites. There are not many theoretical models
available for the work of fracture in comparison to well-established models available for tensile strength and modulus of composites. The problem with theoretical models, even the famous models such as Cox for stiffness, Kelly and Tyson for strength, and the Cottrell model for impact properties, is that most of them are not well verified by experiments except for the Cox model. As a result, critical properties determined by various models do not coincide well with experimental values [4]. Additionally, models that are available for work of fracture consider single fibre composites and do not deal with hybrid composites. This is primarily due to the complex nature of work of fracture, and the presence of too many variables for experimental validation such as the interaction of fibres with the matrix and with each other. This thesis investigates optimization of impact properties of a hybrid biocomposite and development of a model for work of fracture of hybrid composites.

The steps to achieve the objectives of this project are:

1. Enhancing impact properties of biocomposites by surface treatment of natural fibres and/or maintaining the length of the glass fibre

2. Developing a model which encompasses rigid glass fibre (GF) and flexible hemp microfibres with their parameters to enhance the impact strength - selection of set of controlling parameters

3. Validation of the model by experimental parameters

A brief summary of approach and findings in each chapter is presented here. Chapter two consists of the general literature background for this thesis; a specific literature review for each section is presented in the corresponding chapter for better flow of the thesis.

The incompatibility between hydrophilic fibres and hydrophobic matrices results in poor stress transfer in biocomposites. The surface treatment of natural fibres was investigated to enhance the impact properties and work of fracture of hybrid biocomposites (chapter three). This chapter
examine the necessity of surface modification for natural fibres to improve composites’ impact properties. The impregnation treatment or polymer coating of fibres with the matrix was carried out to increase the interface interaction between natural fibres and hydrophobic matrices. Polymer coating was compared to three treatment methods, acetylation, alkalization/acetylation, and silanization, to investigate its effectiveness as an alternative treatment method to those commonly used methods. It is hypothesized that there is a higher chance of mechanical interlocking with polymer coated fibres. All these treatments were combined with maleic anhydride polypropylene, MAPP, during compounding of composite to investigate effects of combination of natural fibre pre-treatment and coupling agent. Experimental results showed that surface treatments for hemp fibres did not improve the impact properties significantly, except for one case of unnotched impact strength of silanized hemp-PP composite. As a result, untreated hemp was used in all experimental work in chapters four and five in presence of 5% MAPP.

Another way to enhance impact properties of hybrid composites is through retaining the length of reinforcing fibres and finding the optimum process conditions (chapter four). The objective of this chapter was to arrive at the optimum operational conditions for the LFT-D process to create hybrid biocomposites with long glass fibres. Through optimization, it is desired to reduce shear and fibre breakage in the process while achieving good dispersion of fibres. The final product should meet the following requirements for the composites based on a Ford specification for interior parts: GF content of 20% or less, tensile strength of 50 MPa, flexural modulus of 2.5 GPa, and impact strength of 80 J/m [12]. Various parameters such as feeder speed, motor speed, position of fibre feeding, and diameter of glass fibre were changed to alter the amount of shear and fibre content in the system in order to find the optimum process conditions with the least fibre breakage, while providing good dispersion and mechanical properties - particularly impact strength. Shear in the extruder, length of fibres, and diameter of fibres are real challenges in this project.

Overall, the experimental work showed that it is possible to develop a process resulting in a hybrid composite exceeding the desired mechanical properties. As a result, the process optimization can
help as a guide to design process parameters for the LFT-D process to produce auto parts with high toughness. The optimum process with twin screw extrusion was carried out at a shear rate of 62 sec\(^{-1}\), a feeder speed of 10 rpm, temperature of 185°C, with no breaker and die. The main factors controlling the structure of hybrid composites were dispersion of fibres, fibre content, and GF length. The hybrid composite produced accordingly had the GF content of 20 wt% with an average length of 2.3 mm, and well dispersed fibres. Use of the smaller diameter GF (low tex\(^1\) GF) resulted in improvements in mechanical performance of hybrid composites. It also resulted in a lower GF content as there were fewer filaments in the GF roving with smaller diameter. Prototypes based on the optimum operational conditions for the LFT-D process determined here are currently being developed. The composites developed here were also used for the experimental validation of the developed model in chapter five.

The last objective for this thesis was to relate the work of fracture of hybrid composites to fibre and matrix properties using a theoretical model, and to find ways to enhance the toughness of hybrid composites (chapter five). Later, the model was experimentally evaluated by GF-hemp-PP hybrid composites. The goal of chapter five was to develop a model capturing the main experimental trends without making it unnecessarily complicated. The presented model for work of fracture was a modified Rule of Mixtures model accounting for matrix failure, fibre pull-out and fibre debonding for fibres shorter than the critical length\(^2\), with the addition of fibre stress redistribution for longer fibres. Comparison of the presented model against a prevalent model in literature showed better agreement with experimental values. Deviations between the experimental data and the model predictions were most likely because of errors in the determination of model parameters and simplifying-assumptions such as no fibre-fibre interaction, perfect adhesion and perfect fibre orientation in the system. Nevertheless, it was possible to observe some useful correlations between the work of fracture for hybrid biocomposites and the properties of fibres, matrix, and interface. For the case of hybrid composites with long fibres, the dominant failure

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\(^1\) The unit of tex is g/km. Lower tex glass fibre means less number of filaments in GF roving.

\(^2\) The critical fibre length is the shortest fibre length wherein \(\sigma_{\text{max}} = \sigma_{\text{fibre}}\).
mechanisms were fibre stress redistribution and matrix failure, while for the case of short fibre composites fibre pull-out and matrix failure were dominant. Increasing the length of fibres and achieving a fibre length around the critical length of the fibre leads to a maximum use of the fibres potential. This is important to note, because if the length is just below the critical length, pull out work is maximized and if it is above the critical length, stress redistribution is maximized for brittle fibres. In order to produce hybrid composites with a high work of fracture, the focus should be on fibre processing to arrive at an optimum length and aspect ratio, volume fraction, and good dispersion.
2 Literature Review

2.1 Biocomposites

Composites are engineered materials composed of different phases, combining the best properties of each phase. The reinforcing phase of fibre in a polymer matrix makes composites strong. Some of the required properties of fibres and matrices are as follows:

- Fibres should have a high ultimate strength and modulus of elasticity
- Fibres should be uniform with a low variation in mechanical properties
- Fibres should be stable and keep their strength during processing
- Matrices have to wet fibres completely and transfer the stress to fibres by adhesion
- Matrices have to be compatible with fibres and protect their surfaces from damage

Composites are used whenever high strength to weight ratio is necessary. Polymers have been used widely over the past few decades for various applications. However, the reinforcement with fibres is crucial for achieving high strength/high modulus specifications. In composites, stress exerted on the material is transferred from the polymer body to the strong fibres, having the benefits of both strength of fibres and ductility of polymers. Mechanical properties are greatly influenced by fibre concentration and dispersion, interfacial adhesion between fibre and matrix, and their properties.

Biocomposites are polymers reinforced with natural fibres which are the alternatives to artificial fibres such as aramid, carbon, and glass fibres. They have numerous advantages including renewability, sustainability, lightweight design, eco-friendliness, low cost, and sound abatement capability. Generally, plant fibres are used for polymer reinforcement [13]. The application of natural fibre-reinforced composites (biocomposites) has increased as they are replacing the depleting conventional petroleum derived reinforcing materials for various industries, such as building materials and structural parts for motor vehicles [14]. The need for biocomposites has increased as the pressure of regulations pertaining to vehicle landfills and their recyclability has
intensified worldwide. Additionally, the use of natural fibres has increased over the last few years due to their lower cost compared to conventional glass and aramid fibres, their recyclability, and their comparable strength per weight of materials [13]. Alves et al. have reported several social, environmental and economic advantages to incorporate natural fibre in automotive components [15].

2.1.1 Hybrid Composite

Hybrid composite, which is a mixture of two or more fibres in a single matrix, has a higher strength and stiffness compared to single fibre reinforced polymers. Hybridization facilitates the achievement of biocomposites with great load-carrying capacity and better impact energy absorption as it uses both brittle yet strong long glass fibres and ductile natural fibres. Hybrid composites are usually from a blend of synthetic and natural fibres in order to increase the renewable content of automotive parts. Combining natural fibre with glass fibre is finding more applications. Hybridization takes advantage of renewability, low cost, and low density of natural fibres and a higher performance of glass fibre. According to Pervaiz et al., net savings of approximately 50000 MJ, ~3 tonnes of CO$_2$ emissions, and ~1.19 million m$^3$ of crude oil can be obtained by replacing glass fibre (30 wt% fibre in thermoplastic) with hemp (65 wt% fibre) [16]. Moreover, reducing the weight of a vehicle by 10% can reduce fuel consumption by 1-4% (approximately 0.2-0.3 L/100 km) [17].

There is no agreed classification for hybrid composites, but they can be grouped into four categories, A-D. Type A is dispersed fibre which is a mixture of two or more types of fibres aligned, but randomly dispersed. Type B is dispersed fibre ply, which is a random or alternating mixture of two or more types of fibre ply. Type C is fibre skin and core where the stiffer fibre laminate is on skin on one or both sides of the fibre core. Type D is fibre skin, non-fibre core which is a sandwich structure, where fibre skin wraps a core of foam, resin, metal or wood [18]. The type of hybrid in this study is type A: two dispersed fibres in a single matrix. Hybrid composites offer more flexibility in a design combined with a higher weight and cost reduction.
It is expected to observe the enhancement in mechanical properties of natural fibre composites reinforced with glass fibres since glass fibre is stronger and stiffer than natural fibres. Kalaprasad et al. reported an 80% increase in tensile strength of oriented sisal polyethylene composite by hybridization with small amount of glass fibre, around 0.03 volume fraction [19]. Panthapulakkal et al. reported a 35% increase in impact strength of hemp fibre reinforced polypropylene due to the addition of 15% glass fibre [3]. In general, hybridization can further extend the use of natural fibres in applications requiring higher strength and stiffness [20]. It creates a wider range of options in design of composites, hence offering considerable cost reductions compared to single fibre reinforced composites.

2.2 Glass Fibre

The most common type of reinforcing synthetic fibre is glass fibre. Glass fibres are strong, but brittle. E-glass is boroaluminosilicate glass with a low alkali-metal content and a small amount of calcia (CaO) and magnesia (MgO). Glass fibre reinforced polymer has been used extensively in body panels in the automotive industry. Full potential of these composites is not discovered yet as they are mainly used for secondary structural elements and appearance parts [21].

The continuous glass fibre is formed by pulling molten glass through small orifices and winding them around a spool. The fibre diameter is a function of orifice size, winding speed and viscosity of molten glass. Glass fibres are categorized into three grades: E, C and S- representing for electrical, chemical/corrosion and structural respectively. E-glass fibres have good electrical insulation, good strength and Young’s modulus. C-glass fibres have a better resistance to chemical corrosion. S-glass fibres have higher strength and modulus (almost 20% greater) and are mainly used for military applications. The glass fibre used in this study is E-glass fibre and its modulus is 50-70 times higher than modulus of the polymer matrix used, polypropylene.
Table 1. Composition (wt %) of glass used for fibre manufacture [22]

<table>
<thead>
<tr>
<th>Elements</th>
<th>E-glass</th>
<th>C-glass</th>
<th>S-glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>52.4</td>
<td>64.4</td>
<td>64.4</td>
</tr>
<tr>
<td>Al₂O₃, Fe₂O₃</td>
<td>14.4</td>
<td>4.1</td>
<td>25</td>
</tr>
<tr>
<td>CaO</td>
<td>17.2</td>
<td>13.4</td>
<td>-</td>
</tr>
<tr>
<td>MgO</td>
<td>4.6</td>
<td>3.3</td>
<td>10.3</td>
</tr>
<tr>
<td>Na₂O, K₂O</td>
<td>0.8</td>
<td>9.6</td>
<td>0.3</td>
</tr>
<tr>
<td>Ba₂O₃</td>
<td>10.6</td>
<td>4.7</td>
<td>-</td>
</tr>
<tr>
<td>BaO</td>
<td>-</td>
<td>0.9</td>
<td>-</td>
</tr>
</tbody>
</table>

Although glass fibre has a much higher modulus compared to natural fibres, the specific modulus of some natural fibres is comparable to it due to a higher density of glass fibre (approximately double the density of most natural fibres) [23]. As shown in Table 2, some natural fibres such as hemp and flax have better specific modulus compared to glass fibre.

Table 2. Modulus comparison of E-glass and some natural fibres [23]

<table>
<thead>
<tr>
<th>Fibre Type</th>
<th>Density (g/cm³)</th>
<th>E-modulus (GPa)</th>
<th>Specific modulus (E-modulus/density)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-glass</td>
<td>2.55</td>
<td>73</td>
<td>28.6</td>
</tr>
<tr>
<td>Hemp</td>
<td>1.48</td>
<td>70</td>
<td>47.3</td>
</tr>
<tr>
<td>Flax</td>
<td>1.5</td>
<td>27.6-80</td>
<td>18.4-53</td>
</tr>
<tr>
<td>Jute</td>
<td>1.46</td>
<td>10-30</td>
<td>6.8-20.6</td>
</tr>
<tr>
<td>Sisal</td>
<td>1.45</td>
<td>9.4-22</td>
<td>6.5-15.2</td>
</tr>
<tr>
<td>Coir</td>
<td>1.2</td>
<td>4-6</td>
<td>3.3-5</td>
</tr>
<tr>
<td>Kenaf</td>
<td>1.45</td>
<td>53</td>
<td>36.5</td>
</tr>
</tbody>
</table>
Figure 1 shows the comparison of modulus/cost of several natural fibres vs glass fibre [24]. Kenaf, hemp and sisal fibres are just some of the alternatives that can be used to replace glass fibre with a higher strength/lower cost ratio.

![Comparison of modulus/cost of various natural fibres and glass fibre](image)

Lower density of natural fibres results in a mass reduction of components in the automotive industry. Approximately 75% of a vehicle’s energy consumption is related to its weight. Also, the replacement of glass fibre by natural fibre results in great reduction (about 80%) in energy required for production. For example, the energy required to produce 0.45 kg of kenaf is 6.8 MJ, almost four times less than the energy required to produce 0.45 kg of glass fibre (24.8 MJ) [25]. In general, glass fibre production requires 5-10 times more non-renewable energy than natural fibre production [26].
2.3 Natural Fibre

As explained before, currently there is a worldwide emphasis on replacing synthetic fibres by natural fibres. Natural fibres are categorized based on their source, namely plants, animals, and minerals. Generally, plant fibres are used for polymer reinforcement [13]. Plant natural fibres are divided into four categories based on their origin: i) Leaf: sisal, pineapple, henequen; ii) Bast: flax, hemp and jute; iii) Seed: cotton; iv) Fruit: coconut husk [27].

2.3.1 Advantages and Disadvantages

There has been extensive research and use of natural fibre composites in the past few decades. Some of the advantages of natural fibres are their low cost, low density, weight reduction (less fuel consumption for vehicles), great reinforcement by cellulose, high specific strength and modulus, renewability, recyclability, flexibility and non-abrasive behaviour during processing. In terms of fracture failure, natural fibres undergo non-brittle fracture on impact [28].

Some of the disadvantages of natural fibres are as follows: low thermal stability, tendency to form aggregates during processing, low resistance to moisture, non-uniform quality, poor adhesion between polar hydrophilic natural fibres and hydrophobic matrix. Surface modification can help to enhance the stress transfer from the matrix to the fibre by resolving the adhesion problems between hydrophilic fibres and the hydrophobic matrix.

The use of natural fibres can be justified by considering their advantages and disadvantages in comparison to synthetic fibres. Joshi et al. have reviewed a number of studies on life cycle assessment comparing natural fibre composites vs. glass fibre composites with similar mechanical performance. They have shown environmental superiority of natural fibres for all the cases under study [26]. In general, natural fibres result in less energy consumption for production, and less pollution except for nitrate emission to water due to fertilizer use during their cultivation.
2.3.2 Composition

Natural fibres are composed of cellulose, hemicellulose, lignin, pectin, waxes and water soluble substances. Cellulose is responsible for desired reinforcing properties of natural fibres. Cellulose is one of the most abundant organic materials in nature. Cellulose is a polydisperse linear homopolymer of D-glucopyranose units linked together by β-1,4-glycosidic bonds. The degree of polymerization is 10000-15000 and the structure is 40-65% crystalline.

![Figure 2. Structure of cellulose [29]](image)

According to the degree of polymerization ($P_n$), cellulosics are categorized into: α-cellulose: $P_n>150$, β-cellulose: $P_n$ 10-150, and γ-cellulose: $P_n <10$. Each unit has 3 hydroxyl groups positioned in the ring plane, leaving the hydrogen atoms in the vertical position. The hydrogen bond results in high tensile strength, high decomposition temperature, rigidity and insolubility of cellulose. A large amount of the hydroxyl group in the cellulose results in hydrophilic properties in natural fibres, thus poor compatibility with hydrophobic polymers. Cellulose has both intra- and intermolecular hydrogen bonding, based on X-ray, NMR and IR studies [30].

The conventional fibres such as glass, aramid, and carbon have fixed properties, while properties of natural fibres vary based on their plant type, age, location, and conditioning. It should be noted that mechanical properties of fibres are strongly related to their degree of polymerization. Lignocellulosic materials are the most abundant renewable biomaterials with production of $2x10^{11}$ tons of mass units per year compared to production of synthetic fibres which is $1.5x10^8$ tons per year [27].
Natural fibres are currently being used in the automotive industry. Ellison et al. have reported typical amounts of plant fibres used for various components of vehicles as follows: front door lines: 1.2-1.8 kg, rear door linens: 0.8-1.5 kg, boot linens: 1.5-2.5 kg, parcel shelves: up to 2.0 kg, seat backs: 1.6-2.0 kg, sunroof sliders: up to 0.4 kg, headliners: average 2.5 kg [31]. Wood fibres have more cellulose compared to agricultural fibres such as corn cobs, wheat straw, and rice straw, but these residues are inexpensive and abundant.

2.3.3 Hemp Fibre

Hemp fibre has excellent strength and is environmentally friendly, requiring few pesticides and no herbicides for growth. Hemp grows quickly and can reach heights of 3-3.5 m in 75-90 days [32].

![Image of hemp crop and hemp leaves and stem]

Figure 3. Hemp crop (a) and hemp leaves and stem (b) [33]

Hemp produces the highest fibre yield per hectare; it can produce 250% more fibre than cotton and 600% more fibre compared to flax [34]. Canada is one of the world’s largest hemp producing countries, after receiving authorization from Health Canada in 1998.
The chemical composition of hemp is presented in Table 3. A high cellulose content of hemp results in its good reinforcing qualities. Non-cellulosic content can be removed effectively by alkaline treatment [36].

Table 3. Chemical composition of hemp [27]

<table>
<thead>
<tr>
<th>Cellulose (wt%)</th>
<th>Lignin (wt%)</th>
<th>Hemicellulose (wt%)</th>
<th>Pectin (wt%)</th>
<th>Wax (wt%)</th>
<th>Moisture content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70.2-74.4</td>
<td>3.7-5.7</td>
<td>17.9-22.4</td>
<td>0.9</td>
<td>0.8</td>
<td>10.8</td>
</tr>
</tbody>
</table>

Traditionally, glass fibres have been used for the reinforcement of plastic, but the industry is moving towards more renewable materials. Some of the motivations for replacing glass fibre with hemp are its lower cost (~1/3 of E-glass fibre), lower density (~1/2 of E-glass fibre), specific mechanical properties, capacity for CO$_2$ sequestration, and biodegradability [28]. Some of the environmental parameters for production of 1 kg of hemp and glass fibres are shown in Table 4. The best method for the comparison is performing Life Cycle Inventory Analysis studies of hemp and glass fibre.

Figure 4. Hemp production trend in Canada 1998-2011 (Acres) [35]
Aside from reducing the carbon footprint of products, some of the benefits of biocomposites to the Canadian auto industry are job creation in the forest and agro sectors, lower material costs, less abrasive effects in handling and production, reduction in greenhouse gas emissions, and conservation of fossil resources.

### 2.4 Polymer Resin

Polymers can be reinforced with fibres in order to enhance their mechanical properties. Polymeric matrix in a fibre reinforced composite protects and aligns fibres. It also transfers stress to the strong fibres and from one fibre to another. In order to avoid degradation of lignocellulosic fibres, processing temperature should be below 200 °C. As a result, the choice of resin is usually limited to low melting polymers such as polypropylene, polystyrene, and polyethylene. Resins are generally categorized into two groups of thermoplastic and thermoset.

Fibre orientation in thermoplastic matrices is random and worse than in thermosets [37]. Some of the disadvantages of thermoplastic matrices (compared to thermosets) are reduced compression strength, stiffness, high processing temperature and pressures, and creeping - especially at high temperatures [38, 39]. Thermoplastics have high durability (impact resistance), unlimited shelf life, and simple recycling. Moreover, thermoplastics have a low processing cost, and flexibility in design and molding of complex parts, allowing simple methods such as extrusion and injection molding to be used for processing [11]. This project is based on polypropylene, a low cost
thermoplastic composite commonly used in the automotive industry. Properties of the polypropylene used in this study, PP 3622, are shown in Table 5 as provided by its producing company. It is worth noting that further replacement of polypropylene by biopolymers such as polylactic acid would result in a much more eco-friendly bio-composites.

Table 5. Properties of polypropylene- PP3622

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength (MPa)</td>
<td>35</td>
</tr>
<tr>
<td>Tensile Modulus (GPa)</td>
<td>1-1.6</td>
</tr>
<tr>
<td>Flexural Strength (MPa)</td>
<td>52</td>
</tr>
<tr>
<td>Flexural Modulus (GPa)</td>
<td>1.4</td>
</tr>
<tr>
<td>Notched Impact Strength (kJ/m²)</td>
<td>3-17</td>
</tr>
<tr>
<td>Flow Temperature (°C)</td>
<td>160</td>
</tr>
</tbody>
</table>

2.5 Coupling Agent

Natural fibres contain strongly polarized hydroxyl groups and are hydrophilic. Incompatibility between hydrophilic lignocellulosic fibres and hydrophobic matrices results in poor stress transfer in biocomposites. Mechanical properties of biocomposites are found to be dependent on its fibre-matrix interfacial properties. As a result, surface modification of natural fibres and or use of coupling agents are necessary for increased adhesion between phases and arriving at a material with desired properties.

The use of coupling agents, such as maleic anhydride polypropylene (MAPP), improves composite strength by enhancing the adhesion between the natural fibre and the polymer. It has been reported in the literature that the addition of MAPP significantly improves the mechanical properties of
natural fibre-polypropylene composites and reduces water uptake [40]. The improvement in composite strength is due to the formation of ester bonds between the anhydride carbonyl groups of MAPP and the hydroxyl groups of the natural fibre [41]. As a result, sites that otherwise would be taken by moisture get occupied [13, 42]. As MAPP attaches to both polypropylene and wood fibre, it enhances adhesion between the fibre and the PP matrix.

The chemical reaction mechanism for such interfacial bond formation between fibre and matrix is shown in Figure 5. The peroxide catalyst facilitates radical formation of polypropylene by hydrogen abstraction (transfer) and chain scission [43]. The radical then reacts with maleic anhydride to form maleated polypropylene, which then bonds with natural fibre.

![Chemical reaction mechanism of the natural fibre and MAPP matrix](image)

Figure 5. Chemical reaction mechanism of the natural fibre and MAPP matrix [43]

MAPP has a lower molecular weight compared to polypropylene and its addition can cause plasticization. Plasticization occurs due to compounding with a lower molecular weight matrix.
which can increase chain flexibility and reduce rigidity. Use of high amounts of MAPP can have negative effects on tensile strength and flexural modulus of composite due to plasticization [44]. Various studies have shown MAPP concentration of 3-5% results in optimum mechanical properties [45-48]. Arbelaitz et al. showed addition of 5% MAPP resulted in better bonding for fibres in glass fibre-flax-PP hybrid composite [46]; hence 5% MAPP was added to the matrix for all samples in this work.

2.6 Impact Damage Behaviour

Impact strength is a critical property of composites as it is related to a product’s safety, liability and service life. The impact strength of a composite, which is a measure of resistance to fracture failure under stress applied at high speeds, is directly related to toughness, which is a measure of the energy a material can absorb before it breaks. The impact in the automotive industry may vary from the accidental drop of a tool to a high speed collision with another vehicle. Impact testing measures the applied energy up to failure under rapid loading. The most common test types are Izod and Charpy, where energy to break is measured from the loss of kinetic energy of a hammer like weight hitting a specimen. The results are usually expressed as energy lost per unit of thickness at the notch (J/m). Impact strength can also be calculated from the area under stress-strain curve in high speed tensile tests. The notched impact test is commonly used and can give insight about the in-service performance of composites [49, 50]. In the Izod test, a pendulum strikes the specimen in the center. In these tests, there is a possibility of overestimating impact energy due to the following reasons: i) stored elasticity in the test specimen prior to failure, ii) dissipation of energy in different forms (thermal, acoustic, and kinetic energy of failed parts, etc.).

The work of fracture is the work required to propagate a crack through the unit area of a material with units of kJ/m². It is equal to the area under load deflection curve. One simple method to characterize the total work of fracture is through use of an impact tester which uses the following equation to calculate impact energy [51]:
\[ U = \frac{E}{b(d-c)} \]  

Equation 1

Where \( U \) is the impact energy, \( E \) is the energy registered in the test, \( b \) is the breadth of specimen, \( d \) is the depth of specimen, and \( c \) is the depth of notch.

Although the impact strength is not an accurate measure of work of fracture, it is still widely used in industry and academia due to its convenience. Impact strength overestimates fracture toughness as it includes some extra energy such as kinetic energy of the broken pieces. In this work, the impact test has been used in the preliminary work to find the optimum processing condition for LFT-D, and later for the model development work of fracture is calculated for the composite samples.

Energy required to initiate damage can be found by integration of the area under the load-displacement curve, up to the maximum load at first failure. Energy required to propagate damage, \( E_p \), is related to initiation energy, \( E_i \), by the ductility index, \( D \) [51]. Ductility index of zero is associated with a completely brittle material, while larger \( D \) values mean that more energy is used in propagating failure than its initiation.

\[ D = \frac{E_p}{E_i} \]  

Equation 2

Mechanism of energy absorption of composites can be categorized into five groups: fibre breakage or failure, matrix cracking, debonding between fibre and matrix, delamination of adjacent plies in a laminate, and fibre pull-out from the matrix [50]. The matrix may deform and undergo fracture in an area in front of the crack tip. Additionally, fibre debonding may occur as the applied load exceeds the strength of fibre matrix interface. Even in a debonding scenario, the transfer of stress to a debonded fibre is possible through frictional forces along the interface. Moreover, fibres may
fracture and pull out as the applied load exceeds the fibre strength. Fibre pull-out is an important energy dissipation mechanism in long fibre reinforced composites [4].

Impact strength of a fibre reinforced composite is higher than its components due to energy absorption as a result of fibre pull-out and debonding [1]. Very strong or very weak interaction between fibre and matrix is not desired as the former results in brittle failure while the latter results in easy fibre pull-out. Good impact strength can only be achieved when optimum interaction exists between well dispersed fibres and matrix [52]. Thomason et al. showed a linear increase of impact strength with fibre concentration for glass fibre reinforced polypropylene. They also concluded that the rate of increase in impact strength is dependent on the fibre length, with long fibres having a much higher enhancement. Similar trends were found from Charpy impact tests at two temperatures of 23 °C and -30 °C [4].
3 Surface Treatment

3.1 Introduction

As mentioned before, the application of natural fibres has increased over the last few years due to the fact that natural fibres have many advantages over conventional glass and aramid fibres. Cellulose is renewable, biodegradable, and available worldwide. In addition, natural fibres offer reduction in weight and density, and have thus become important in the automotive and aerospace industries. Financially speaking, natural fibres are less expensive than conventional synthetic fibres and their recyclability and biodegradability makes them an inevitable choice due to current environmental regulations and landfill concerns. Furthermore, their excellent structural properties allow them to compete with synthetic fibres.

However, natural fibres have several drawbacks such as incompatibility with matrix, high degree of moisture uptake, and inconsistency in fibre properties. They are polar and hydrophilic hence, if untreated, have poor adhesion with hydrophobic polymers. This incompatibility results in inadequate dispersion of fibres in the matrix and thus reduces stress transfer from the polymer to the fibres. Furthermore, cellulose has poor dimensional stability due to swelling by water under humidity.

Extensive research has been carried out to achieve the desired polymer reinforced composites [24, 53, 54]. Many studies have been conducted to optimize mechanical properties of biocomposites by improving surface interaction of fibres with polymer, and enhancing fibre dispersion in the polymer matrix [14]. El-sabbagh examined MAPP percentage with respect to type and content of natural fibre, and determined the optimum ratio to be between 10 to 13.3% depending on the investigated property (stiffness, strength and impact) [53]. In this work, the effect of combination
of MAPP and a number of other surface treatments on impact properties of composites is investigated as a technique to enhance the performance of hybrid composites.

3.2 Literature Background

Two natural fibres are investigated here: hemp, a common Canadian natural fibre, and sisal, a common Brazilian natural fibre. Hemp is a bast fibre while sisal is a leaf fibre. Hemp fibres contain 70.2-74.4% cellulose, 3.7-5.7% lignin, 17.9-22.4% hemicellulose, 0.9% pectin, and 0.8% wax; while sisal fibres contain 67-78% cellulose, 8-11% lignin, 10-14.2% hemicellulose, 10% pectin, and 2% wax [27].

It is very clear nowadays that incompatibility between hydrophilic fibres and hydrophobic matrices results in poor stress transfer in biocomposites. Mechanical properties of biocomposites are found to be dependent on their fibre and matrix interfacial properties. Physical and chemical treatments are the alternatives used for surface modification of natural fibres, improving adhesion between phases to arrive at a material with the desired properties. Main physical methods are surface fibrillation, and electric discharge - corona, cold plasma. Change in structure, and thus surface properties of fibres due to physical treatments, affect the mechanical bond of fibres and matrix [55]. The most promising approach is chemical treatment where covalent bonds are formed between fibre and matrix. In general, chemical coupling agents, like silanes, have two functionalities: (a) reacting with hydroxyl group of cellulose and (b) reacting with matrix, acting like a bridge to join different polarities (i.e. the hydrophobic matrix and the hydrophilic fibre).

Different mechanisms of coupling in materials are listed by Bledzki et al. as follows: elimination of weak boundary layers, generation of a tough and flexible layer, formation of a highly cross-linked interphase region with a modulus in-between polymer and fibre, enhancement of wetting
between fibre and matrix, formation of covalent bonds with both fibre and matrix and change of acidity of fibre surface [56].

Several studies show enhancement in mechanical performance after fibre surface treatment, however this observation is not always consistent. Abdelmouleh et al. studied effect of different structures of silane coupling agents and determined a 6-26% increase in tensile strength and 6-17% in tensile modulus in 50wt% short natural fibre reinforced polyethylene. The lack of consistent enhancement was attributed to inability of some silane coupling agents to bring about covalent boding with matrix [57]. Ganan et al. observed a 12% increase in flexural strength of silanized fibre composites [58]. Sawpan et al. carried out single fibre tensile measurements for silane and acetylated hemp fibres and found that the average tensile strength of treated fibres slightly decreased compared to untreated fibres, while the average Young’s modulus increased for treated fibres [59]. In a study by John et al., no significant effect on the flexural properties of sisal/glass hybrid composites was found after silane treatment, while small increase in flexural properties by alkaline treatment was observed [60]. This study was carried out to determine whether indeed surface treatment of natural fibres would be beneficial for impact properties of composites.

Another method to improve the fibre-matrix interface was investigated in this work by using a polymer coating based on an acrylic derivative to cover the fibres’ surface to improve the properties of the composites. A variety of polymer solutions can be prepared by changing monomer types and polymerization techniques. It is hypothesized that there is a higher chance of occurrence of mechanical interlocking and physico-chemical interaction during compounding for polymer coated fibres. Theoretically, carboxylic acid in coating may result in better adhesion of natural fibres as they react with the hydroxyl group, resulting in ester and water.
To increase the interface interaction between sisal and hemp fibres and hydrophobic matrices, three treatment methods - acetylation, alkalization/acetylation, and silanization - are being compared to a polymer coating or impregnation treatment of fibre with matrix prior to compounding to investigate its effectiveness as an alternative treatment method to the commonly used methods. The intention of combining alkalization and acetylation was to investigate the influence of partial removal of lignin and insertion of hydrophobic acetyl group in the natural fibres used. The objective of this work was to investigate the effect of surface treatment methods for hemp and sisal fibres on their physical and thermal properties, surface morphology, and chemical composition. The ultimate goal was to use modified fibres for long fibre thermoplastic direct compounding process to reduce glass fibre content, if shown modifications enhance impact properties of composites.

**Alkalization**

Alkalization or alkaline treatment is one of the most common surface modification techniques. Factors affecting alkalization are the type and concentration of the alkaline solution, the time of treatment, and the temperature. In this treatment, fibres are immersed in the alkaline solution for a specified period of time. Alkaline treatment reduces the cementing material (lignin and hemicellulose) as well as volatile products with the rupture of bonds.

Very different techniques have been used by various authors, between 0.5 to 29% NaOH and between 20 minutes to 8 hours with various temperatures [59, 61-64]. El Oudiani et al. concluded that NaOH concentration higher than 2% (at 30°C for 1 hour for agave fibres) results in a significant decrease of crystallinity index and hence the reinforcement of fibres [65].

As a result of the alkaline treatment, hydrogen bonding is disrupted, and cellulose becomes more amorphous. This treatment eliminates some of lignin, wax and oils of the fibres. It depolymerizes
cellulose, and increases fibre defibrillation, exposing more contact area between fibre, matrix and sites for reaction. Increase in the amount of exposed cellulose means an increase in the amount of possible sites for reaction. Moreover, surface roughness increases due to the disruption of hydrogen bonding, and thus better mechanical interlocking is achieved between fibre and matrix, resulting in a higher mechanical resistance of the composites.

In alkaline treatment, the hydroxyl group is ionized to the alkoxide as a result of the addition of aqueous sodium hydroxide, as shown below by Equation 3.

\[ \text{Fibre-OH} + \text{NaOH} \rightarrow \text{Fibre-O-Na} + \text{H}_2\text{O} \quad \text{Equation 3} \]

**Acetylation**

Acetylation of natural fibres is a well-known esterification method to stabilize the cell wall against moisture absorption. The addition of acetic anhydride (CH$_3$-C(=O)-O-C(=O)-CH$_3$) to lignocellulosic fibre results in the replacement of the hydroxyl group with the acetyl group (CH$_3$COO$^-$), as shown in Equation 4, making fibres more hydrophobic and less polar. Thus, esterification of natural fibres causes cellulosic fibres to be more compatible with hydrophobic polymer matrices. In addition, acetylation can reduce moisture absorption of natural fibres, and thus enhance dimensional stability of composites.

\[ \text{Fibre-OH} + \text{CH}_3\text{-C(=O)-O-C(=O)-CH}_3 \rightarrow \text{Fibre-O-C(=O)-CH}_3 + \text{CH}_3\text{C(=O)-OH} \quad \text{Equation 4} \]
**Silanization**

Silanes are commonly used as coupling agents for the enhancement of glass fibres’ adherence to the polymer matrix and stabilizing the glass fibre composites. A coupling agent is a chemical containing both polar and non-polar groups in their structure to improve compatibility between hydrophilic natural fibres and hydrophobic matrix by reacting with the OH group of the fibre and the functional group of matrix. The most common coupling agents are silanes, isocyanates, and titanate-based compounds [55].

According to Bledzki and Gassan, coupling mechanisms include removal of a weak boundary layer, formation of a tough and flexible layer, formation of a highly cross-linked interphase region with a modulus in between the polymer and the fibre, formation of covalent bond between phases, and improvement of wetting between phases [66]. Silane can form a chemical bond with the surface of cellulose via a siloxane bridge, while its organofunctional groups bond to the polymer matrix [55], thus reducing cellulosic hydroxyl groups present in the fibre matrix interphase. Bonding between a silane coupling agent, cellulose and polymer resin is shown in Figure 6.
In a silane treatment, the hydrolysable alkoxy group reacts to form silanol, in the presence of moisture. The silanol then reacts with the hydroxyl group of the fibre, forming stable covalent
bonds to the fibre surface. As a result of this modification, the swelling degree reduces in composites. A general representation of this reaction can be given by vinyltriethoxysilane in Equation 5 and Equation 6, as follows:

\[
\text{CH}_2\text{CHSi(OCH}_3\text{)}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{CHSi(OH)}_3 + 3 \text{C}_2\text{H}_5\text{OH} \quad \text{Equation 5}
\]

\[
\text{CH}_2\text{CHSi(OH)}_3 + \text{Fibre-OH} \rightarrow \text{CH}_2\text{CHSi(OH)}_2\text{O-Fibre} + \text{H}_2\text{O} \quad \text{Equation 6}
\]

**Polymer Coating**

Based on the hypothesis that a polymer coating could improve the compatibility of fibres with matrix, the fibres were coated with a resin composed of ethyl acrylate, acrylic acid, and styrene. The carboxylic acid group in polymer solution is responsible for better adhesion of the natural fibre to matrix as it reacts with the hydroxyl group of fibre. A variety of polymer solutions can be prepared by changing monomer types and polymerization techniques. It is hypothesized that, with polymer coated fibres, there is a higher chance of mechanical interlocking and physical interaction during compounding. Theoretically, carboxylic acid in coating may result in better adhesion of natural fibres as they react with the hydroxyl group, resulting in ester and water. A general presentation of the reaction in polymer coating is given by Equation 7.

\[
\text{Fibre-OH} + \text{HOOC-(CH}_2\text{=C(CH}_3\text{)=COOCH}_3\text{)}_x(\text{C}_6\text{H}_5\text{CH}=\text{CH}_2)_y(\text{CH}_2\text{=CH-COO(CH}_2\text{)}_3\text{-CH}_3)_z \rightarrow \text{Fibre-O-CO-C-(CH}_2\text{=C(CH}_3\text{)=COOCH}_3\text{)}_x(\text{C}_6\text{H}_5\text{CH}=\text{CH}_2)_y(\text{CH}_2\text{=CH-COO(CH}_2\text{)}_3\text{-CH}_3)_z + \text{H}_2\text{O} \quad \text{Equation 7}
\]
3.3 Experimental Section

3.3.1 Materials

Hemp fibres used in this study were untreated native hemp grown in Ontario obtained from Hempline Inc. Untreated hemp fibres with size of 8.25 cm were reduced in size by passing through a refiner. The refiner is composed of two rigid metal plates which crush the material to a smaller size based on the gap setting value between the plates. Hemp fibres were passed through a refiner at gap 20, i.e. gap value of .5 mm, arriving at a fibre length of 1.28 mm and an aspect ratio of 80. Sisal fibres were obtained from UNESP, Brazil and were cut to a length of 2 cm to provide fibres with good aspect ratio (L/D=100). It is optimal to keep the fibre aspect ratio in the range of 100-200 for efficient composites, by conserving the length of fibre through processing [67].

3.3.2 Surface Treatments

The following surface treatments were carried out: acetylation, alkalization/acetylation, silanization, and polymer coating treatment.

*Acetylation*

A ratio of 1:1.5 of acetic anhydride to acetic acid was prepared. Acetic acid is known to enhance the swelling of fibres, resulting in higher accessibility of hydroxyl groups of fibres [59]. A few drops of sulfuric acid were added to enhance the reaction. Fibres were immersed in the stirring solution for 2 hours at 90 °C in a reflux experimental setup. Fibres were washed with distilled water and oven dried at 60 °C for 24 hours.
**Alkalization/Acetylation (A/A)**

In this work, natural fibres were submerged in a 2% NaOH solution for 20 minutes [61, 65, 68], then washed thoroughly with tap water until the pH was neutralized. A weak sodium hydroxide solution was used for alkalization to partially remove lignin from fibre without resulting in any degradation. Following this, the natural fibres were oven dried at 60 °C for 24 hours. Afterwards, acetylation was carried out as explained above.

**Silanization**

A solution of 1wt% silane in ethanol:DI-water (1:1 ratio), (adjusted pH to 4 by adding 2% acetic acid) was stirred for 2 hours in a closed lid plastic container under the hood to complete hydrolysis [69]. Afterwards, fibres were submerged in the solution for 1.5 hours, and subsequently oven dried at 60 °C for 24 hours.

**Polymer Coating**

Through emulsion polymerization, a solution was prepared in the lab with the following components: mixture A (46% acrylic acid (C₅H₈O₂), 8% styrene(C₈H₈), 42% water, 1.5% itaconic acid(C₅H₆O₄), and 2.5% anionic surfactant (alkyl diphenyl oxide disulfonate) at 90 °C); and mixture B (7.5% sodium persulphate and 92.5% water) were prepared. In a reflux set up, polymer solution was prepared composed of 12% mixture A, 1% mixture B, 1% anionic surfactant, and 86% water through mixing at 14000 rpm, 82-84 °C for 3 hours.

Itaconic acid has two carboxylic acid functional groups which can replace hydroxyl group of natural fibres. Finally, natural fibres were impregnated in 3% polymer solution for 30 minutes and, after filtration, were oven dried at 60°C for 24 hours.
3.3.3 Fibre Characterization

*Fourier Transform Infrared Spectroscopy (FTIR)*

FTIR was performed to study the nature of bonds and determine chemical changes in functional groups of fibres before and after treatment to evaluate the efficiency of each treatment. A Thermo Scientific Nicolet 6700 model was used. A minimum of 32 scans were run in the range of 675-4000 cm\(^{-1}\), with a resolution of 4 cm\(^{-1}\).

*X-ray Diffraction (XRD)*

X-ray Diffraction was conducted to determine if the different chemical treatments could affect the crystallinity of the natural fibre. XRD was performed using a Philips Analytical X-ray of X`pert MPD model, employing CuK\(\alpha\) (\(\lambda = 1.54\)) radiation with a voltage of 40 KV and a current of 40 mA. Fibres were cut and placed into a disk using a cylindrical steel mold (D=15mm). The diffraction intensity was in the range of 5°-60° of 2\(\Theta\) with scanning speed of 0.02°/s.

The crystallinity index, I\(_c\), of fibres was measured using the Segal empirical method [62, 70]. The crystallinity index measures the orientation of cellulose crystals in a fibre to the fibre axis. X-ray diffraction counts at a 2\(\Theta\) angle close to 18° and 22° were used to calculate the crystalline index. The counter reading at peak intensity at 22° represents the crystalline materials and intensity at 18° represents amorphous materials in cellulose. Use of Equation 8 requires the two peaks to be well separated [70], which was the case in this analysis.

\[
I_c = \frac{I_{002} - I_{am}}{I_{002}} * 100
\]

Equation 8

*Where I_{002} is the maximum intensity of diffraction of the (0 0 2) lattice peak at 2\(\Theta\) angle between 22° and 23°, while I_{am} is the intensity of diffraction of amorphous material which is the minimum at 2\(\Theta\) angle between 18° and 19°.*
Scanning Electron Microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS)

The surface morphologies of treated and untreated fibres were investigated using a Scanning Electron Microscope with Energy Dispersive Detector X-ray - SEM/EDS (Leo electron microscopy 440i for SEM, and 6070 for XPS) with an accelerating voltage of 5 kV and a beam current of 50 mA to obtain the micrographs. Prior to SEM, surfaces were coated with gold using a Sputter Coater POLARON (VG Microtech SC7620).

Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) was employed to investigate the thermal stability of fibres before and after treatment. The heating was carried out at 10 °C/minute and from 25 °C to 600 °C in N₂ and air using a TA instruments model SDT 2960 machine. TGA figures show a variation of sample weight and derivative weight with temperature.

Water Absorption

The water absorption test was carried out according to the ASTM D570-98. Six compression molded specimen for various treated and untreated composites -15% NF- were first oven dried at 105 °C for 2 hours. Afterwards, they were placed in desiccators until they reached room temperature and then were weighed. Tensile fractured specimens of composites were used for this test. Specimens were submerged in water at room temperature. The samples were taken out periodically and weighed after wiping out the water on the surface, using a balance. The percentage of water uptake was calculated based on the following equation:

\[
\text{Water absorption (\%)} = \frac{W_t - W_0}{W_0} \times 100
\]

Equation 9

where \( W_t \) is the weight of the sample at time \( t \), and \( W_0 \) is the initial weight of the sample.
Mechanical Properties of composites

The objective of the surface treatment of natural fibres was to enhance the mechanical performance of composites for the auto industry. In this work, natural fibres were treated by acetylation, alkalization/acetylation, silanization and polymer coating, while the matrix was treated with coupling agent of maleic anhydride polypropylene - MAPP. Numerous researchers have reported benefits of the addition of MAPP for natural fibre composites [47, 53, 71]. The addition of MAPP significantly improves the mechanical properties of natural fibre-polypropylene composites and reduces water uptake [40]. There are also various studies presenting positive effects of MAPP on modifying the matrix and its interaction with glass fibre [48, 72]. As a result, MAPP was added to all samples of treated and untreated natural fibre composites to study effect of combination of natural fibre pre-treatment and coupling agent. Similarly, El-sabbagh et al. investigated combination of alkaline treatment and MAPP addition in flax-PP compounds and showed 210% increase in strength [72]. Another study by El-sabbagh et al. also suggested that the addition of MAPP was more effective for pre-treated fibres due to removal of surface impurities in alkalized fibres [53]. Pan et al. also studied effect of combination of fibre treatment with addition of MAPP [73].

Hemp and sisal fibres and the coupling agent -MAPP- were oven dried for 1 hour at 105 °C. Composites of 15% natural fibre were prepared using a high shear mixer. For compounding, first PP and MAPP were melted in the mixer, and then natural fibres were added. Each run was carried out for a 50 g batch which was mixed for 20 seconds, with a water cooling system running to avoid overheating of the machine. Right after compounding, composites were pressed in a hot press at 180 °C for 5 minutes under 5 tons of pressure, followed by 2 minutes of cooling under the same pressure. Afterwards, tensile and impact specimens were cut from the pressed sheets.
3.4 Results and Discussion

After the chemical treatment of the natural fibres, they were analyzed in their physico-chemical, morphological and thermal aspects using several techniques presented as follows.

3.4.1 FTIR

The FTIR spectra of the untreated and treated hemp fibres are shown in Figure 7. The C-H symmetrical stretch around 2919 cm\(^{-1}\) is present in all fibers examined. The strong peak at 3340 cm\(^{-1}\) is also present in all fibers corresponding to axial stretching of hydroxyl group (-OH), very common in natural fibers and attributed to hydrocarbon constituents [59].
FTIR for untreated hemp commonly shows the following functional groups: COO$^-$ of pectin, present in natural fibres, at 1650 cm$^{-1}$[74]. The peak at 1422 cm$^{-1}$ presents the existence of CH$_2$ symmetric bending of cellulose, as detected by others [59, 64, 74]. The 1317 cm$^{-1}$ and 1159 cm$^{-1}$ wave numbers are attributed to the CH$_2$ wagging and C-O-C asymmetric bridge stretching of cellulose, respectively [74]. The presence of lignin was detected at the peak at 1250 cm$^{-1}$ which represents the C-O stretching of the acetyl group [59]. The C-C stretching at 1059 cm$^{-1}$ and the asymmetric out of phase ring stretching of cellulose at 898 cm$^{-1}$ were also detected and related to the β-glucosidic linkages between the sugar units in hemicellulose and cellulose [59]. In general, the region of 700-900 cm$^{-1}$ is for the CH$_a$ functional group of natural fibres.
The spectra for both cases of hemp acetylation (with and without alkalization) showed the peak at 1740 cm\(^{-1}\), which corresponds to C=O stretching of ester. Acetylation also resulted in the reduction of intensity of peak at 3340 cm\(^{-1}\) for hydroxyl group. FTIR did not show any significant difference in the case of silanized fibres, but similar observations were encountered by other researchers [63, 64]. According to Sawpan et al., peaks at 780 cm\(^{-1}\) for Si-C symmetric stretching, at 708 cm\(^{-1}\) for Si-O-Si symmetric stretching, and at 1203 cm\(^{-1}\) for Si-O-C stretching should be observed after reaction between hydrolysed silane and cellulose of natural fibres [59]; however no peaks around these wavenumbers were observed in this study. Untreated hemp had a peak at 1204 cm\(^{-1}\) which was shifted to 1197 cm\(^{-1}\) for silanized hemp. This shift toward a lower wave number could be due to the change of the C-O-C bond of lignin in untreated fibre to C-O-Si in silanized hemp since the latter has a lower bond energy. To verify the presence of silicon on silane treated fibre, elemental analysis was carried out. As shown later, XPS spectra verify the presence of silicon on silanized fibres which indicates the occurrence of silanization. It is possible that the concentration of silane on the fibre surface was too small to be detected by FTIR.

In the case of polymer coated hemp fibres, absorption at 1730 cm\(^{-1}\) appeared which was due to the carbonyl group, C=O stretch, in the coating.
Figure 8 shows FTIR of treated and untreated sisal fibres. The peak at 1240 cm\(^{-1}\) is attributed to C-O stretch of the acetyl group of lignin. The band for 1736 cm\(^{-1}\) is attributed to the C=O stretching of the acetyl groups of hemicelluloses and pectin for sisal fibres [58]. This band disappeared in alkalized sisal due to the removal of hemicelluloses from the fibre surface.

In the alkalized/acetylated (A/A) sisal the band at 1736 cm\(^{-1}\) reappeared after fading away in alkalized sisal. This is only attributed to C=O bonds due to acetylation, further confirming successful acetylation. For acetylation and A/A (alkalization plus acetylation), the peak of the
carbonyl group at 1736 cm\(^{-1}\) appeared, indicating that the acetylation in fact occurred. In the case of silanized sisal, significant differences were not observed similar to hemp fibres. In the case of polymer coating of sisal, the same peak at 1736 cm\(^{-1}\) appeared for the carbonyl group in the coating.

### 3.4.2 XRD

To verify any possible changes in the crystallinity of fibres after chemical treatment, their XRD spectra were investigated. It is expected to observe higher crystallinity for alkalization treatment as it removes some lignin, and wax from fibres. Figure 10 and Figure 11 show that all treated and untreated fibres have two very distinct peaks: one at 2\(\Theta\) between 22° and 23°, characteristic of cellulose I, which corresponds to (002) crystallographic plane [70]. The other peak is observed as one broad peak around 15°-16° and is actually divided into two distinct peaks at 15.2° and 16.6°, which accordingly correspond to (101) and (10\(\bar{1}\)) crystallographic planes, as shown in Figure 9 [59]. The latter two peaks are more distinct when the crystalline cellulose content is high, and for amorphous compounds (such as lignin, hemicelluloses, pectin and amorphous cellulose), they appear as one broad peak as observed in this thesis [62]. The crystallinity index was calculated from the height ratio between the intensity of the crystalline peak (\(I_{002}-I_{AM}\)), and total intensity (\(I_{002}\)); where \(I_{002}\) is the maximum intensity of diffraction of the (002) lattice peak at 2\(\Theta\) angle between 22° and 23°, while \(I_{AM}\) is the intensity of diffraction of amorphous material which is the minimum at 2\(\Theta\) angle between 18° and 19° [75].
Figure 9. Typical X-ray diffraction spectra [75]

Figure 10. X-ray diffraction of untreated and treated hemp fibre
The crystallinity index of untreated and treated fibres was calculated using Equation 8, and the results are summarized in Table 6. Overall, hemp fibres had higher crystallinity index compared to sisal fibres which was expected since they have lower lignin, pectin, and wax content.
Troedec et al. reported an increase in the crystallinity index after surface treatment of hemp fibres [70], while Sawpan et al. observed a reduction in the crystallinity index after the hemp fibre treatment except for the alkalized ones [59]. In this study, it can be seen that fibre treatment led to an increase in the crystallinity index in the case of hemp fibre, with the alkalized/acetylated treated fibres having the highest crystallinity index followed by acetylated and polymer coated fibres. However, in the case of sisal fibres, treatment resulted in a decrease in the crystallinity index again with the exception of alkalized/acetylated and alkalized sisal. Increase in crystallinity index for alkalized fibres has been observed by other researchers as well [59, 62]. This increase in crystallinity is due to better packing of cellulose as a result of partial removal of pectin and other impurities after treatment. Overall, treatment for sisal fibres led to little impact in crystallinity. It is worthy of note that irreversible conversion from cellulose I (metastable) to cellulose II (stable) is linked to decrease in the crystallinity index, and hence mechanical properties of fibre [65].

Tserki et al. also reported in their literature review both cases of increase and decrease in crystallinity index after acetylation [76]. According to Shiriashi et al., the explanation for the decrease in the crystallinity index after treatment is as follows: due to reaction of reagent with

<table>
<thead>
<tr>
<th>Hemp</th>
<th>I_am</th>
<th>I_002</th>
<th>I_c</th>
<th>Sisal</th>
<th>I_am</th>
<th>I_002</th>
<th>I_c</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>202</td>
<td>1030</td>
<td>80.4</td>
<td>F</td>
<td>180</td>
<td>671</td>
<td>73.2</td>
</tr>
<tr>
<td>B</td>
<td>202</td>
<td>1318</td>
<td>84.7</td>
<td>G</td>
<td>219</td>
<td>812</td>
<td>73.0</td>
</tr>
<tr>
<td>C</td>
<td>228</td>
<td>1806</td>
<td>87.4</td>
<td>H</td>
<td>188</td>
<td>724</td>
<td>74.0</td>
</tr>
<tr>
<td>D</td>
<td>199</td>
<td>1246</td>
<td>84.0</td>
<td>I</td>
<td>174</td>
<td>630</td>
<td>72.4</td>
</tr>
<tr>
<td>E</td>
<td>225</td>
<td>1444</td>
<td>84.4</td>
<td>J</td>
<td>199</td>
<td>697</td>
<td>71.4</td>
</tr>
<tr>
<td>*</td>
<td>237</td>
<td>1673</td>
<td>85.8</td>
<td>#</td>
<td>199</td>
<td>1069</td>
<td>81.4</td>
</tr>
</tbody>
</table>

A, untreated hemp; B, acetylated hemp, C, alkalized/acetylated hemp; D, silanized hemp; E, polymer coated hemp; *, alkalized hemp; F, untreated sisal; G, acetylated sisal, H, alkalized/acetylated sisal; I, silanized hemp; J, polymer coated sisal; #, alkalized sisal
chain ends of crystalline region, as it cannot diffuse to crystalline region itself, some of the hydrogen bonded cellulose chains get opened. The reagent then diffuses to this newly generated amorphous cellulose and consequently more amorphous cellulose is generated, and the crystallinity index reduces [77]. On the other hand, the case of increase in the crystallinity index can be attributed to the treatment that possibly has partially removed the fibre amorphous contents such as pectin, and lignin [78].

3.4.3 SEM

The SEM images below (Figure 12 and Figure 13) show the differences in the surface morphologies of hemp and sisal fibres after various treatments. Significant differences were observed for the case of alkalized fibres, where surface impurities were removed as similarly observed by other researchers [62, 70, 76]. Thus, treatment with 2% NaOH was an effective and easy method for removing waxes and additives from natural fibres.
20 µm —, Magnification: 1.00 K X

Figure 12. SEM micrographs of untreated hemp (A), acetylated hemp (B), alkalized/acetylated hemp (C), silanized hemp (D), polymer coated hemp (E), and alkalized hemp (*)
Images (B) and (C) in Figure 12 show that acetylation removed nearly all the impurities from the fibre surface, making it smooth. During this process, waxy substances of fibres are removed and hydroxyl groups are replaced by acetyl groups. Tserki et al. concluded that acetylation removed noncrystalline constituents of natural fibres through SEM analysis [76].

The SEM images of fibres before and after silane treatment, (A) and (D), were not significantly different, as was the case for alkalization. Interestingly, similar results were reported in studies on silanization, whose silane was deposited on the fibre surface without significant changes to the surface morphology [59, 63]. It should be noted that elemental analysis of silanized fibres in this thesis showed the existence of silicon in the fibres after treatment, while no conclusion can be made about bonding of silicon in the fibres after treatment (see Table 7 and Table 8) as a proof of its impregnation. Sawpan et al. suggested that the smooth surface of silanized hemp fibres can be due to the deposition of siloxane on the surface [59]. Finally, a micrograph of polymer coated hemp, Image (E), shows fibres with rough, although cleaner surfaces, suggesting the possibility of a good mechanical interlocking during compounding.
40 µm, Magnification: 400 X

Figure 13. SEM micrographs of untreated sisal (F), acetylated sisal (G), alkalized/acetylated sisal (H), silanized sisal (I), polymer coated sisal (J), and alkalized sisal (#)
Similarly, in the case of sisal fibres, most external impurities were removed from the surface after treatment, leaving a clean surface. Comparing SEM micrographs of alkalized sisal and alkalized/acetylated sisal (Figure 13, H and #), it is clear that alkalization resulted in a smooth surface which, once more, became rough after acetylation. This behaviour, also noted by Li et al. [66], is due to esterification resulting in higher surface roughness and surface area of treated fibres. This cleaner surface is expected to result in better bonding with the coupling agent during composite manufacturing [62].

3.4.4 XPS

X-ray photons can eject inner-shell (core) electrons of surface atoms. Kinetic energy of ejected electrons was measured in X-ray photoelectron spectroscopy and spectra were obtained for treated and untreated hemp and sisal fibres. All fibres contained carbon, oxygen and calcium while potassium, silicon, and magnesium were detected in some samples. Elemental composition of treated and untreated hemp and sisal fibres are presented in Table 7 and Table 8. It should be noted that any signal from hydrogen overlaps with signals from excitation of valence electrons from other surface atoms. Hence it is not possible to distinguish between H 1s valence electron and valence electrons of other elements and hydrogen is not shown in the elemental composition obtained from XPS [79]. This analysis was mainly carried out to verify the presence of silicon in silanized fibres as FTIR did not show distinct peaks for silicon bond. XPS spectra clearly verified the presence of silicon in silanized hemp and sisal.

Table 7. Elemental composition (%) of surface treated hemp fibres

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>O</th>
<th>Ca</th>
<th>K</th>
<th>Na</th>
<th>Cl</th>
<th>Si</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>42.67</td>
<td>55.69</td>
<td>0.75</td>
<td>0.88</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>48.11</td>
<td>50.11</td>
<td>1.07</td>
<td>-</td>
<td>0.38</td>
<td>0.15</td>
<td>0.1</td>
<td>0.08</td>
</tr>
<tr>
<td>C</td>
<td>49.20</td>
<td>50.48</td>
<td>0.32</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>D</td>
<td>42.76</td>
<td>51.55</td>
<td>1.36</td>
<td>1.24</td>
<td>-</td>
<td>-</td>
<td>2.87</td>
<td>0.22</td>
</tr>
<tr>
<td>E</td>
<td>48.49</td>
<td>51.15</td>
<td>0.36</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

A, untreated hemp; B, acetylated hemp; C, alkalized/acetylated hemp; D, silanized hemp; E, polymer coated hemp
Table 8. Elemental composition (%) of surface treated sisal fibres

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>O</th>
<th>Ca</th>
<th>K</th>
<th>Si</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>48.18</td>
<td>50.47</td>
<td>1.00</td>
<td>0.27</td>
<td>-</td>
<td>0.08</td>
</tr>
<tr>
<td>G</td>
<td>48.11</td>
<td>51.60</td>
<td>0.29</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H</td>
<td>46.32</td>
<td>52.71</td>
<td>0.98</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>I</td>
<td>44.37</td>
<td>52.08</td>
<td>2.6</td>
<td>0.15</td>
<td>0.80</td>
<td>-</td>
</tr>
<tr>
<td>J</td>
<td>46.79</td>
<td>52.55</td>
<td>0.66</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

F, untreated sisal; G, acetylated sisal; H, alkalized/acetylated sisal; I, silanized hemp; J, polymer coated sisal

3.4.5 TGA

TGA results for hemp and sisal in nitrogen (Table 9 and Table 10) and air medium (Table 11 and Table 12) are presented in this section. TGA results show the process of weight loss for various fibres. Considering the case of inert atmosphere for hemp (Figure 14), the first weight loss region below 100 °C is due to the release of moisture present in natural fibre attributed to the hydrophilic characteristic of natural fibres. The other weight loss regions between 210° - 480 °C are attributed to the decomposition of hemicellulose, cellulose and lignin [58]. In specific, the weight loss between 272° - 351 °C is due to the thermal decomposition of hemicelluloses and the break of the glycoside link of the cellulose molecules [80]. Moreover, this loss can be attributed to the break of α and β aryl-alkyl-ether linkages from thermal degradation of lignin.

Table 9. Thermogravimetric results for surface treated hemp fibres in N2 environment

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Max. degradation temp (°C)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10% wt loss</td>
<td>20% wt loss</td>
</tr>
<tr>
<td>A</td>
<td>349</td>
<td>247</td>
</tr>
<tr>
<td>B</td>
<td>362</td>
<td>275</td>
</tr>
<tr>
<td>C</td>
<td>339</td>
<td>244</td>
</tr>
<tr>
<td>D</td>
<td>357</td>
<td>272</td>
</tr>
<tr>
<td>E</td>
<td>355</td>
<td>285</td>
</tr>
<tr>
<td>*</td>
<td>361</td>
<td>283</td>
</tr>
</tbody>
</table>

A, untreated hemp; B, acetylated hemp; C, alkalized/acetylated hemp; D, silanized hemp; E, polymer coated hemp; *, alkalized hemp
In the case of hemp fibres in a nitrogen environment, all treatments, except alkalization/acetylation, showed a higher temperature at each increment of weight loss percentage. This means a higher thermal stability was achieved after surface treatment. Furthermore, all treatments (except for alkalization/acetylation) showed a higher maximum degradation temperature. This may relate to the presence of new groups on the surface of treated fibres which can increase restriction on the segmental mobility of molecules and hence increase thermal stability of treated fibres [58]. Figure 14 shows thermogravimetric curves for surface treated and untreated hemp fibres in a nitrogen environment.

Figure 14. TGA of surface treated hemp fibres in N$_2$ environment

In the case of sisal fibres, the results are summarized in Table 10 for N$_2$ environment and in Table 12 for an oxidative atmosphere.
Table 10. Thermogravimetric results for surface treated sisal fibres in N\textsubscript{2} environment

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Max. degradation temp (°C)</th>
<th>Temperature (°C)</th>
<th>10% wt loss</th>
<th>20% wt loss</th>
<th>30% wt loss</th>
<th>40% wt loss</th>
<th>50% wt loss</th>
<th>60% wt loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>348</td>
<td></td>
<td>258</td>
<td>308</td>
<td>327</td>
<td>338</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>G</td>
<td>343</td>
<td></td>
<td>260</td>
<td>284</td>
<td>325</td>
<td>331</td>
<td>336</td>
<td>-</td>
</tr>
<tr>
<td>H</td>
<td>344</td>
<td></td>
<td>246</td>
<td>316</td>
<td>328</td>
<td>334</td>
<td>242</td>
<td>-</td>
</tr>
<tr>
<td>I</td>
<td>353</td>
<td></td>
<td>268</td>
<td>326</td>
<td>341</td>
<td>343</td>
<td>346</td>
<td>349</td>
</tr>
<tr>
<td>J</td>
<td>358</td>
<td></td>
<td>260</td>
<td>285</td>
<td>335</td>
<td>341</td>
<td>348</td>
<td>-</td>
</tr>
<tr>
<td>#</td>
<td>342</td>
<td></td>
<td>261</td>
<td>304</td>
<td>322</td>
<td>332</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

F, untreated sisal; G, acetylated sisal; H, alkali/acid nitratized sisal; I, silanized hemp; J, polymer coated sisal; #, alkali nitratized sisal

In the case of sisal fibre in a nitrogen environment, surface treatments resulted in a slightly more stable thermal behaviour.

Figure 15. TGA of surface treated sisal fibres in N\textsubscript{2} environment
In air medium, TGA curves for sisal and hemp show another distinct weight loss at 351°-410°C due to decomposition of cellulose oligomers which turn to levoglucosans and low molecular weight volatile compounds such as ketone, aldehydes, furans, and pyrans [80]. Additionally, TGA in air medium resulted in lower residues for both fibres.

Table 11. Thermogravimetric results for surface treated hemp fibres in air environment

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Max. degradation temp (°C)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>10% wt loss</td>
</tr>
<tr>
<td>A</td>
<td>314</td>
<td>244</td>
</tr>
<tr>
<td>B</td>
<td>347</td>
<td>265</td>
</tr>
<tr>
<td>C</td>
<td>310</td>
<td>245</td>
</tr>
<tr>
<td>D</td>
<td>333</td>
<td>260</td>
</tr>
<tr>
<td>E</td>
<td>328</td>
<td>275</td>
</tr>
<tr>
<td>*</td>
<td>334</td>
<td>273</td>
</tr>
</tbody>
</table>

A, untreated hemp; B, acetylated hemp; C, alkalized/acetylated hemp; D, silanized hemp; E, polymer coated hemp; *, alkalized hemp

Surface treatment resulted in an increase in the maximum rate of decomposition temperature of hemp fibres, except for the case of alkalized/acetylated fibres. This observation in both air and nitrogen environment indicates that all surface treatments, except for alkalization/acetylation, led to the enhancement in thermal stability of the fibres. In other words, surface treatment of fibres had enhanced the onset of degradation, except for the A/A fibres.
Figure 16 shows an increase in temperature for the second distinct peak for derivative weight vs. temperature plot, indicating that the treatment resulted in higher thermal stability in the region attributed to cellulose oligomers decomposition. A similar observation was shown for sisal fibres in Figure 17.
Table 12. Thermogravimetric results for surface treated sisal fibres in air environment

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Max. degradation temp (°C)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10% wt loss</td>
<td>20% wt loss</td>
</tr>
<tr>
<td>F</td>
<td>324</td>
<td>249</td>
</tr>
<tr>
<td>G</td>
<td>315</td>
<td>254</td>
</tr>
<tr>
<td>H</td>
<td>325</td>
<td>246</td>
</tr>
<tr>
<td>I</td>
<td>330</td>
<td>261</td>
</tr>
<tr>
<td>J</td>
<td>330</td>
<td>240</td>
</tr>
<tr>
<td>#</td>
<td>333</td>
<td>253</td>
</tr>
</tbody>
</table>

F, untreated sisal; G, acetylated sisal; H, alkalized/acetylated sisal; I, silanized hemp; J, polymer coated sisal; #, alkalized sisal

Figure 17. TGA of surface treated sisal fibre in air
Figure 17 shows that surface treatment has an increased onset of degradation except for the acetylated sisal. All treated fibres (except acetylated sisal) had a higher temperature at 20% weight loss, indicating higher thermal stability. Acetylated sisal had a lower thermal stability while the other treatments led to a slightly higher thermal stability for sisal fibres based on TGA in the air.

Comparing the TGAs in nitrogen and in the air environment for all fibres, it is clear that the fibres started degradation earlier in an oxygen atmosphere, as expected. Additionally, it should be noted that for hemp fibres in an air environment, the acetylation treatment was the most effective against fibre degradation under heating. The replacement of the hydroxyl groups of the cell wall by acetyl groups could enhance fibre matrix adhesion and increase stability of composites. On the other hand, sisal fibres were more protected against heating after silanization. Despite two exceptions, alkalized/acetylated hemp in nitrogen and acetylated sisal in air, the hemp and sisal fibre treatments were effective against their heat degradation in air and in an inert atmosphere.

3.4.6 Water Absorption

Composites of 15% NF (treated and untreated) - 5% MAPP - 80% PP were evaluated for water absorption at room temperature. MAPP was added to composites to study effects of combination of natural fibre pre-treatment and coupling agent. This study was carried out for 6 months and % change in weight of treated and untreated hemp and sisal composites are summarized in Table 13 and Table 14.
Table 13. Water absorption of surface treated hemp-PP composites

<table>
<thead>
<tr>
<th>Hemp Treatment</th>
<th>% change in weeks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>week 1</td>
</tr>
<tr>
<td>MAPP</td>
<td>2.7±0.9</td>
</tr>
<tr>
<td>Acetylated + MAPP</td>
<td>2.9±2.1</td>
</tr>
<tr>
<td>A/A + MAPP</td>
<td>2.3±0.8</td>
</tr>
<tr>
<td>Silanized + MAPP</td>
<td>1.5±0.2</td>
</tr>
<tr>
<td>Polymerized + MAPP</td>
<td>2.7±0.5</td>
</tr>
</tbody>
</table>

Results are also shown graphically in Figure 18 and Figure 19 for easier comparison. Statistical analysis was performed using t-test to assess significance within the data. Sgriccia et al. showed that silane treated fibres absorb less water compared to alkaline treated fibres [64]. However, paired t-test analysis of the data showed no significant improvement in water resistance of hemp-MAPP-PP composites after different treatments of hemp fibre.

Figure 18. Water absorption of surface treated hemp-PP composites
For the case of sisal-PP composite, alkalization and acetylation (A/A) treatment of sisal fibres in addition to MAPP treatment led to a significant enhancement in water resistance behavior of natural fibre composites. Polymerization also led to significant improvement for weeks 2 to 20 based on a paired t-test analysis. The replacement of the hydroxyl groups of the cell wall by acetyl groups reduced polarity of fibres, enhanced fibre matrix adhesion and hence increased water resistant characteristic of composites.

![Figure 19. Water absorption of surface treated sisal-PP composites](image)

Table 14. Water absorption of surface treated sisal-PP composites

<table>
<thead>
<tr>
<th>Sisal Treatment</th>
<th>% change in weeks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>week 1</td>
</tr>
<tr>
<td>MAPP</td>
<td>4.2 ± 1.3</td>
</tr>
<tr>
<td>Acetylated + MAPP</td>
<td>3.4 ± 1.2</td>
</tr>
<tr>
<td>A/A + MAPP</td>
<td>2.4 ± 1.7</td>
</tr>
<tr>
<td>Silanized + MAPP</td>
<td>2.9 ± 1.3</td>
</tr>
<tr>
<td>Polymerized + MAPP</td>
<td>4.0 ± 1.2</td>
</tr>
</tbody>
</table>
3.4.7 Mechanical Testing

Tensile strength and modulus of surface treated hemp-PP composites are presented in Figure 20. As cited earlier, various studies have shown MAPP concentration of 3-5% results in optimum mechanical properties of composites [45-48]. Treatment of cellulose fibres with MAPP copolymers creates covalent bonds [66]. For hybrid composites, Arbelaitz et al. concluded that the addition of 5% MAPP resulted in better bonding for fibres in flax-glass fibre-PP hybrid composite [46]. As a result, 5% MAPP was added to all samples. Possible enhancement in mechanical properties of composites due to combination of MAPP with other surface pre-treatment methods was investigated in this work as it has been suggested in the literature [53, 72, 73].

Unpaired t-test of unequal sample sizes and variances with a confidence limit of 95% (a=0.05) was carried out for evaluation of the effect of combination of surface treatments on mechanical performance of natural fibre composites. Results showed that additional treatment of fibres did not enhance the tensile properties of composite for the case of 15% hemp-5% MAPP-PP composite, indicating that stress could not transfer from matrix to fibres which is an indication of poor interface between fibres and the matrix. Similarly, Sawpan et al. observed a reduction in tensile strength of silanized and acetylated fibres as a result of decrease in cellulose crystallinity [59].
Tensile strength and modulus of surface treated sisal-PP composite are presented in Figure 21. A slight improvement in the tensile strength and modulus was observed for the silanized and A/A pre-treated sisal-PP composite compared to treatment with MAPP alone. Increase in the Young’s modulus of treated fibres could be attributed to densification of fibre cell walls due to removal of non-cellulosic components during treatment [59].
Figure 21. Tensile properties of surface treated sisal-PP composites

Tensile strength and modulus along with notched and unnotched Izod impact strength for surface treated hemp-PP composites are presented in Table 15. T-test did not show a significant difference for impact strength of hemp-PP composites after any of treatments combined with MAPP. This suggests that combination of the surface treatments was ineffective for hemp fibres. The hemp used in this study was refined - explained in section 4.3.2.1-, and thus cellulose was more exposed during treatments. It is possible that there were not enough reagents for the number of exposed hydroxyl groups, and hence pre-treatment was not effective. Moreover, it is probable that parts of the strong hemp microfibres were lost during pre-treatments, hence reducing the composite performance for pre-treated hemp fibres combined with MAPP compared to MAPP treated alone.
Table 15. Mechanical properties of surface treated hemp-PP composites

<table>
<thead>
<tr>
<th>Hemp-PP</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Notched Izod Impact (J/m)</th>
<th>Unnotched Izod Impact (J/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPP</td>
<td>31.0 ± 1.6</td>
<td>1.8 ± 0.2</td>
<td>20.7 ± 2.5</td>
<td>118.3 ± 19.7</td>
</tr>
<tr>
<td>Acetylated + MAPP</td>
<td>28.3 ± 1.8</td>
<td>1.7 ± 0.1</td>
<td>19.2 ± 1.0</td>
<td>98.6 ± 6.5</td>
</tr>
<tr>
<td>A/A + MAPP</td>
<td>26.5 ± 1.3</td>
<td>1.8 ± 0.2</td>
<td>19.4 ± 1.4</td>
<td>108.0 ± 9.1</td>
</tr>
<tr>
<td>Silanized + MAPP</td>
<td>30.3 ± 2.1</td>
<td>1.8 ± 0.1</td>
<td>20.4 ± 2.5</td>
<td>132.1 ± 21.1</td>
</tr>
<tr>
<td>Polymerized + MAPP</td>
<td>26.5 ± 1.5</td>
<td>1.8 ± 0.1</td>
<td>18.4 ± 1.6</td>
<td>94.3 ± 23.9</td>
</tr>
</tbody>
</table>

Figure 22. Impact strength of surface treated hemp-PP composites

Tensile strength and modulus, and notched and unnotched Izod impact strength for surface treated sisal-PP composites are presented in Table 16. Polymerization of sisal fibres combined with MAPP led to significant enhancement of the notched Izod impact strength of sisal-PP composites. Alkalization/acetylation pre-treatment displayed the best performance for unnotched Izod impact strength followed by silanization and polymerization pre-treatments (Figure 23). Overall, some improvements were observed for sisal-PP composites, but not for hemp-PP composite which is the main focus of this thesis. This study investigated the effect of addition of MAPP to pre-treated...
fibres in hopes to further enhance impact properties, but the results showed that MAPP treatment alone was more effective for hemp-PP composite. MAPP treatment alone would also be more economical and suitable for commercial scale production of hybrid composite.

Table 16. Mechanical properties of surface treated sisal-PP composites

<table>
<thead>
<tr>
<th>Sisal-PP</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Notched Izod Impact (J/m)</th>
<th>Unnotched Izod Impact (J/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPP</td>
<td>22.6 ± 1.0</td>
<td>1.7 ± 0.1</td>
<td>25.5 ± 4.3</td>
<td>53.5 ± 11.5</td>
</tr>
<tr>
<td>Acetylated + MAPP</td>
<td>22.0 ± 1.0</td>
<td>1.7 ± 0.1</td>
<td>24.9 ± 4.2</td>
<td>52.6 ± 14.8</td>
</tr>
<tr>
<td>A/A + MAPP</td>
<td>23.6 ± 0.9</td>
<td>1.8 ± 0.1</td>
<td>24.8 ± 2.9</td>
<td>75.3 ± 5.7</td>
</tr>
<tr>
<td>Silanized + MAPP</td>
<td>24.8 ± 0.9</td>
<td>1.8 ± 0.1</td>
<td>28.8 ± 2.9</td>
<td>73.0 ± 13.0</td>
</tr>
<tr>
<td>Polymerized + MAPP</td>
<td>22.3 ± 0.9</td>
<td>1.6 ± 0.1</td>
<td>30.3 ± 2.6</td>
<td>65.4 ± 11.5</td>
</tr>
</tbody>
</table>

Figure 23. Impact strength of surface treated sisal-PP composites

There are few factors contributing to the differences in performance of treated hemp and sisal fibres. Though both fibres had similar aspect ratios (length to diameter ratio), but hemp fibres used
here were refined to microfibres, while sisal fibres were regular fibres cut to 2 cm. Consequently, more cellulose was exposed on hemp microfibres compared to sisal fibres, and ineffectiveness of additional pre-treatments could suggest that not enough reagents were available for treatment of all those exposed hydroxyl groups. Moreover, it is probable that parts of the strong hemp microfibres were lost during pre-treatments, hence reducing the composite performance for treated hemp fibres.

Results showed that surface pre-treatment was more effective for unrefined fibres – sisal fibres. Since microfibres were the focus of composite production in this thesis, fibre surface pre-treatment was not carried out for natural fibres. Consequently, only coupling agent MAPP was added to the hybrid composite to modify matrix and enhance bonding for both natural and synthetic fibres.

### 3.5 Conclusions

Renewable and biodegradable lignocellulosic fibres are currently used to achieve low-cost, low-density composites with improved characteristics. The enforced stress on the composites is to be transferred from matrix to these fibres, thus compatibility and interface between fibres and resin is very important for composites. There is poor compatibility between polar hydrophilic fibres and hydrophobic polymer matrix in the biocomposites. In order to enhance adhesion between fibre and matrix, treatment of fibre surface (before compounding) was investigated.

Silanization did not show a significant difference in FTIR, but XPS confirmed the placement of silicon on the silanized fibres. Overall, hemp fibres had a higher crystallinity index compared to sisal fibres, which was expected since they have a lower lignin, pectin, and wax content. The crystallinity index slightly increased for treated hemp fibres due to partial removal of amorphous pectin and lignin. Combination of alkalization and acetylation led to the highest degree of increase
in the crystallinity. In general, all SEM micrographs of treated fibres showed cleaner surfaces due to the removal of waxy substances and lignin during treatments and washing with distilled water. TGA showed an increase in thermal stability in treated fibres, except for the alkalized/acetylated fibres in both mediums.

Combination of surface pre-treatment with MAPP treatment showed some improvements in mechanical performance for sisal-PP composites, but failed to enhance composite performance for hemp fibre which was the focus of this thesis. Coating with acetyl group in polymer coating method only improved impact strength for sisal fibres. As a result, fibre pre-treatment was not considered for enhancement of impact properties of hemp-GF-PP hybrid composites in this thesis and only addition of MAPP alone was selected as the best modification to enhance fibre-matrix interaction. Another method to enhance impact properties of hybrid composites is through changing processing conditions to reduce breakage of glass fibre, and arrive at composites with long fibres. As will be discussed in the next chapter, processing of hybrid composites in order to attempt to maintain length of glass fibre in the hemp-GF-PP composites was investigated.
4 Processing LFT-D

In composites, stress exerted on the material is transferred from the polymer body to the strong fibres, having the benefits of both strength of fibres and ductility of polymers. Mechanical properties are greatly influenced by process conditions. The process optimization for production of a tough hybrid biocomposite through Long Fibre Thermoplastic Direct compounding and molding process (LFT-D) was investigated in this chapter with an ultimate goal of high impact strength. High shear mixing -twin screw extrusion- and low shear mixing -single screw extrusion- methods were used for the production of tough hybrid composites. The objective of this chapter is to arrive at optimum operational conditions to create hybrid biocomposite with long glass fibres which meets the following requirements: GF content of 20% or less, tensile strength of 50 MPa, flexural modulus of 2.5 GPa, and notched impact strength of 80 J/m [12].

4.1 Introduction

Thermoplastic composites are produced by various conventional processing methods such as single screw extrusion, twin screw extrusion, injection and compression molding. Shear force exerted by the screws in the extruder results in fibre breakage and length variation, aside from dispersion of fibres and bonding fibre and matrix. Greater fibre length and better fibre dispersion are crucial for composite performance. Length of fibres is a key parameter for enhancing strength and toughness, while dispersion of fibres enhances stiffness [81, 82]. Different compounding conditions were investigated to find the optimal balance of fibre length and dispersion.

The experimental approach here was to use both low shear mixing (single screw extruder), and high shear mixing (twin screw extruder) to develop long fibre thermoplastic direct compounding and molding process (LFT-D). Various parameters such as feeder speed, motor speed, and position of fibre feeding along diameter of glass fibre were changed to alter the amount of shear and fibre
content in the system in order to find the optimum conditions with the least fibre breakage while providing good dispersion and mechanical properties, particularly impact strength. In the twin screw extruder, motor speed influences shear rate and amount of GF entering the system, while feeder speed impacts composition of product as it controls addition of hemp-PP granulates. The main factors controlling the structure of hybrid composites are dispersion of fibres, fibre content, and GF length. The same amount of hemp was compounded in the rotary mixer (plasticorder) for all runs - since surface treatment was not effective in enhancing impact properties, untreated refined hemp fibre was used here with addition of MAPP.

The preliminary manner to investigate dispersion of fibres was through mechanical properties. Subsequently SEM was carried out to make a stronger conclusion about the dispersion of fibres and mechanisms of composite failure. Further validation was carried out by GF length distribution.

4.2 Literature Background

4.2.1 Composite Manufacturing

Matrix, fibre(s) and other additives are compounded through different methods to form composite. The extruder provides shear force and heat to melt polymer and facilitates dispersion of fibres within. Compounding is mixing that is dispersed (homogenously mixed) and compatible. As mentioned before, natural fibres are temperature sensitive and the process temperature should be kept below 200 °C at all times, thus making the control of shear and heat in the system very crucial for WPCs (Wood Plastic Composites).

The polymer is partially melted by the heated barrel but mostly the heat generated from friction of the shear between the rotating screw and stationary barrel results in polymer melting. The extruder
is usually divided into three sections: feed, compression and metering. The polymer is conveyed from hopper to the screw channels in the feed section, and is melted in the compression section. In metering section polymer melt is homogenized and is pumped out of the extruder due to pressure built up. In this project, as will be demonstrated later in this chapter, the best results are obtained when glass fibre is introduced in the metering section to the molten polymer.

a)

![Extruder sections](image)

b)

![Screw section](image)

Figure 24. a) Extruder sections b) Screw section showing channel depth, H, and screw diameter, D [83]

The shear in the extruder results in polymer melting and dispersive mixing of fibres in composite. Shear rate in an extruder screw channel is determined as follows:
\[
\gamma(\text{screw channel}) = \frac{\pi DN}{60H} \quad [84] \quad \text{Equation 10}
\]

Where \( \gamma \) is the shear rate in screw channel; \( D \) is screw diameter in mm; \( N \) is screw speed in revolutions/minute; \( H \) is screw’s channel depth in mm (distance from top of the flight to root of screw). The channel depth between the screw and the barrel, \( H \), varies along the length of the extruder in order to facilitate melt and flow of the polymer. The channel depth in the metering section affects the shear rate screw channel in extruders. Viscosity can be determined from shear rate vs. viscosity plot for the composite.

There are two main types of extruders: single screw extruder and twin screw extruder. Some of the disadvantages of a single screw extruder are lower output rates and greater risk of burning fibres especially at the screw tip at high screw RPMs. In the case of twin screw extruders, a good dispersion is achieved due to intermeshing, though the temperature must be controlled carefully since rapid heating can be problematic.

Twin screw extruders are widely used in the industry for WPCs, although there are different options available [42, 85]. Bledzki et al. explored the effect of the compounding process on wood fibre damage, dispersion, and size distribution. WPCs were compounded using three techniques of two roll mill, high speed mixer, and twin screw extruder. The twin screw extruder resulted in the lowest amount of absorbed moisture, and the best mechanical strength [86].

Extruder parameters such as compression ratio, screw speed, and barrel temperature are important factors influencing compounding of WPCs. Zhang et al. evaluated uniformity at four speeds of 50, 100, 150, and 200 rpm. The lowest speed of 50 rpm was ineffective and as speed increased, shear rate increased and dispersion was enhanced. However at higher speeds, 200 rpm, shear heating increased, and fibre degradation occurred as wood fibres are temperature sensitive [85].
After compounding, composites are commonly manufactured through injection or compression molding. Injection molding is a process of manufacturing thermoplastic composites where composite pellets are molten and pushed through a barrel using a screw/piston through a nozzle (injection gate) and fill a cold mold that keeps the shape of product to be made. A gate is an inlet port to the mold cavity connecting the runner and mold cavity. Runners are channels distributing materials which have more surface area compared to gates and facilitate pressure development. Having gates after runners, it is possible to fill cavity with same pressure from runner at different points. The gate thickness is usually 50-75% of the part thickness to develop pressure to push materials in before gate freezing. Once the part temperature is well below the polymer solidification temperature, the part is ejected.

Compression molding is the process wherein composites are shaped in a mold as they are in contact with hot plates under pressure. Compression molding can be carried out at different pressures and temperatures. After compression, the mold is cooled to room temperature under the molding pressure, and then the composite is removed from the mold. It is important to note that impact resistance of compression molded parts is 50% higher than injection molded ones, as shown on tests of large LFT-D body panels [87].

4.2.2 Long Fibre Thermoplastic Direct Compounding and molding Process (LFT-D)

Fibre length is governed by the original length and concentration of fibres, equipment design and processing conditions [88]. It is known that Long Fibre reinforced Thermoplastics (LFTs) have better mechanical performance due to their higher aspect ratio. LFTs have good impact strength due to their energy dissipating mechanisms of fibre debonding and pull-out. However, processing becomes much more difficult as the length of the fibres increases, and theoretically it is not clear whether there is an optimum length of fibres or not [4]. Fibre length retention is a hard task to accomplish as fibre length reduces during the mixing process. Fibre length distribution depends
on the type of matrix and its rheological properties, fibre content, and their interactions [14, 27]. Gibson et al. have shown that there is a limit to the maximum aspect ratio of fibres at a particular volume fraction for the case of glass reinforced polyester. The implication is that if volume fraction is to increase, the aspect ratio has to decrease to allow fibres to pack in the space [89].

The long fibre composite industry has come to believe in the necessity of wetting of glass fibre filaments before extensive mixing to preserve fibre length [90]. The in-line compounding of long fibre reinforced polymers provide this impregnation as shown in Figure 25. The LFT-D process is a promising technology for long fibre composites. In the LFT-D, thermoplastic polymer pellets are fed into the resin hopper where they melt in a resin shooter. Continuous glass or other fibres are pulled into the process die by the high pressure flow of molten polymer. An in-line chopper cuts the fibre imbedded in the molten polymer as it exits the viscous entrainment die. Cut lengths of 6 - 25 mm are possible [90].

Figure 25. Schematic diagram of in-line molding system [90]
Some of the advantages of inline compounding process are as follows: i) the resin is melted before mixing with glass fibre, thus fibre length preservation is maximized, ii) resin is only melted once thus degradation is minimized and physical properties are improved, iii) screw and barrel wear are minimized due to the elimination of partially melted resin pellets and glass fibre. Costs of raw materials can be 30-50% lower than using pre-compounded pellets with using pushtrusion system [90].

4.2.3 Mechanical Performance of Hybrid Composites

Long fibre thermoplastics are becoming more attractive as they have superior mechanical properties due to fibre’s higher aspect ratio. Long fibres enable composite to dissipate the force upon impact as oppose to localizing it. There are various methods available to achieve long fibre composites. Current literature has mainly focused on hand layup process of laminates and mats, pultrusion and fibre knitting [7-10]. For example, pultrusion of continuous GF in engineering thermoplastic polyurethane (73% GF) resulted in impact strength of 4.1 KJ/m and tensile strength of 1000 MPa [91]; hand layup of 3 cm sisal-GF-PP, where three out of five layers were GF mats, resulted in impact strength of 18 J and tensile strength of 176 MPa [9]; and fibre knitting of 52%GF-PP with various knitting techniques resulted in impact strength of 40-200 KJ/m² and tensile strength of 50-350 MPa [92]. It can be seen that these methods result in high mechanical properties, but there is a research gap for long fibre thermoplastics compounding through extrusion. This work investigates commercial scale production of long fibre thermoplastic composites and explores the science behind energy absorbing mechanisms for hybrid long fibre composites. Mechanical properties of hybrid NF-GF-PP composites found in literature are presented in Table 17 and are compared with product specification and the final product developed from this work.
<table>
<thead>
<tr>
<th>Molding technique</th>
<th>Natural fibre (wt%, type)</th>
<th>GF (wt%)</th>
<th>Tensile strength (MPa)</th>
<th>Flexural Modulus (GPa)</th>
<th>Impact strength (J/m)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injection</td>
<td>25, hemp</td>
<td>15</td>
<td>59</td>
<td>5.4</td>
<td>54</td>
<td>[3]</td>
</tr>
<tr>
<td>Injection</td>
<td>20, sisal</td>
<td>10</td>
<td>29.6</td>
<td>4.03</td>
<td>16.7</td>
<td>[40]</td>
</tr>
<tr>
<td>Injection</td>
<td>15, sisal</td>
<td>15</td>
<td>31.5</td>
<td>4.04</td>
<td>18.3</td>
<td>[40]</td>
</tr>
<tr>
<td>Compression</td>
<td>15, banana</td>
<td>15</td>
<td>61</td>
<td>2.5</td>
<td>64</td>
<td>[93]</td>
</tr>
<tr>
<td>Compression</td>
<td>15, bamboo</td>
<td>15</td>
<td>58.2</td>
<td>2.7</td>
<td>72</td>
<td>[94]</td>
</tr>
<tr>
<td>Injection</td>
<td>20, vakka</td>
<td>10</td>
<td>20</td>
<td>1.6</td>
<td>59</td>
<td>[71]</td>
</tr>
<tr>
<td>Injection</td>
<td>35, corn stalk</td>
<td>10</td>
<td>26.8</td>
<td>3.6</td>
<td>26</td>
<td>[95]</td>
</tr>
<tr>
<td>Injection</td>
<td>35, bagasse</td>
<td>10</td>
<td>26.3</td>
<td>3.52</td>
<td>26</td>
<td>[95]</td>
</tr>
<tr>
<td>Compression</td>
<td>25, hemp</td>
<td>20</td>
<td>92</td>
<td>7.5</td>
<td>131</td>
<td>Current work</td>
</tr>
</tbody>
</table>

The comparison for hemp-GF-PP shows significant enhancement in impact strength, tensile strength and flexural modulus due to use of the LFT-D method under the determined optimum operating conditions in this work. It should be noted that the glass fibre roving was used in this work to better mimic industrial facilities. Improvement in mechanical properties can be attributed to both long and short fibres in the composite. This chapter explains the process optimization to arrive at hybrid composite with enhanced mechanical properties through extrusion.
4.3 Experimental Section

4.3.1 Materials

Hybrid composite in this project is composed of hemp and glass fibre in the polypropylene matrix with addition of MAPP as a coupling agent. Hemp fibres used in this study have an original length of approximately 8 cm, and are untreated native hemp grown in Ontario obtained from Hempline Inc., Ontario.

There are two different glass fibre rovings in this project, both excellent for long fibre-polypropylene processes such as LFT-D. The difference is in the fibre tex (g/km) or the number of filaments in the strand and their diameter. High tex glass fibre roving (chemically sized with a coating to enhance processability and mechanical properties) with a tex of 2200 and a filament diameter of 22 µm is from Johns Manville, Star Roving LFT 840. Silane treated (0.4%) low tex glass fibre roving with a tex of 1100 and filament diameter of 17 µm is from PPG, TufRov® 4599.

Polypropylene PP3622 with a density of 0.905 g/cc and melt flow index of 12 g/10 min is obtained from Arkema, Canada, which is good for extrusion and injection molding. The coupling agent is maleic anhydride polypropylene, MAPP OREVAC-CA100 from Arkema, Canada. It has been shown in the literature that the addition of 5% coupling agent can significantly improve strength and stiffness properties, as it results in better adhesion between matrix and fibres [96].

4.3.2 Methodologies

The objective of these experiments is to find the operating conditions which result in hybrid biocomposites with the best mechanical properties and fibre dispersion while having acceptable
glass fibre content (< 20%). As surface treatment of hemp fibre did not result in significant enhancement in the impact properties, untreated hemp was used for all experiments while keeping its amount constant at 30 wt%. High natural fibre content in the hybrid composite was desired to reach a more environmentally friendly and lighter product. However, in order to avoid common problems of high wood content polymer composites such as increase in viscosity, and agglomeration of wood fibre and poor dispersion [86], this amount was limited to 30 wt%. The hemp fibre content was based on earlier studies at the Centre for Biocomposites and Biomaterials Processing at University of Toronto to determine influence of fibre content on mechanical properties of hybrid hemp-GF-PP composite with short glass fibres [3]. The fibre content is also in agreement with the optimum content determined in the work of Nestore et al. who examined influence of fibre content in hemp-LDPE composite [97].

Hemp was compounded in a rotary mixer, Brabender Plasticorder, for all runs. Variations in processing conditions were made to vary length, content and dispersion of glass fibres in the composite. Two processing methods of single screw extrusion (low shear) and twin screw extrusion (high shear) were used for hybrid compounding and their resulting composites were compared with each other based on GF content, mechanical properties, fibre dispersion and length distribution. The preliminary manner to investigate dispersion of fibres in composites was through mechanical properties. Further investigation was carried out using SEM.

Experimental work in this chapter can be divided into three parts: i) experiments on hemp fibre selection; ii) experimental design to process hybrid composite by LFT-D process; iii) mechanical testing and characterization of composites. In order to arrive at a successful model in chapter five, knowledge of mechanical properties of fibre, matrix and composite is required. Some of the parameters that need to be determined are fibre length, fibre diameter and fibre concentration.
4.3.2.1 Hemp Fibre Preparation

Untreated hemp fibres with size of 8.25 cm were reduced in size by passing through a refiner. The refiner is composed of two rigid metal plates which crush the material to a smaller size based on the gap setting value between the plates. Refining allows mechanical alteration in the structure of fibres and fibre fibrillation. Fibre fibrillation increases the specific area and enhances ability of fibres to bond [98]. The first trial for refining was a wet refining, where hemp fibres were soaked in deionized water overnight at 15% consistency (85% water). Wet fibres were then passed through the refiner 20 times at gaps 4 to 1, while additional water had to be added to the system to ease the flow in the refiner. After refining, some water was separated by draining, but most of the water was air dried from the refined hemp of 22% consistency before use in composite compounding. The problem with wet grinding was that the refined hemp would agglomerate upon drying and form very hard pieces despite well spreading of refined fibres prior to drying. Hemp and MAPP were oven dried at 105 °C for 1 hour prior to mixing to remove moisture. The dried refined hemp was mixed with PP and MAPP in a rotary mixer, Brabender Plasticorder, at 170 °C and 60 rpm for 5 minutes. Refined hemp fibres were not uniformly distributed despite heating and mixing in the mixer, leaving chunks of hemp in the composite.

To overcome the distribution problem, untreated hemp fibres were dry ground in the refiner. The refiner plate gap was placed at different settings of 5, 20, 80 and 120 resulting in gap values of 0.125, 0.5, 2, and 3 mm. Consequently, hemp fibres with different lengths and diameters were obtained. In order to find the optimum grade of refining, mechanical properties of hemp-PP composites were investigated. Hemp-PP composites were produced by mixing hemp with polypropylene and MAPP in a Brabender Plasticorder mixer. The formulation of composites was 30% hemp - refined at different gaps, thus different fibre lengths, 65% PP, and 5% MAPP mixed at 170 °C for 5 minutes. Hemp and MAPP were oven dried at 105 °C for 1 hour prior to mixing to remove moisture. Then composites were compression molded at 180 °C, for 5 minutes at low pressure (1.5 MPa), then 1 minute at 8.5 MPa pressure, followed by cooling to room temperature under 8.5 MPa pressure to produce approximately 3 mm thick hemp-PP sheets. Rectangle shaped
specimen were cut from the sheets with the width and length in accordance to ASTM D638 and ASTM D256. First, impact and then tensile properties of the hemp-PP composites with varying hemp fibre length were investigated. The refining gap resulting in the highest mechanical properties for hemp-PP was selected to refine the hemp required for hybrid compounding. Statistical analysis was performed using ANOVA to assess significance within the data.

It is noteworthy to mention that once during the refining process, the refined fibres in the bag caught fire. To avoid such incidents, 8.25 cm hemp fibres were slightly dampened and cut by a cutter before grinding for the rest of the experiments - hemp fibres were placed in sealed bags with the addition of 20% water for 24 hours prior to refining.

4.3.2.2 Composite Preparation

4.3.2.2.1 Extrusion
To achieve long fibre reinforced composites, a Long Fibre Thermoplastic Direct compounding and molding process (LFT-D) was designed in this study. The LFT-D process consists of hemp-PP compounding, extrusion with GF, and compression molding of hybrid composite. Hemp, polypropylene, and MAPP were melt blended in 60 g batches using a Brabender Plasticorder at 170 °C and at 60 rpm for 5 minutes. The melt blended materials were later granulated so that they could be fed into the extruder. Glass fibre was then added to hemp-PP granulate in the extruder to obtain the long GF-hemp-PP hybrid composite. Glass fibre roving was used to mimic commercial facilities. It is expected that a better dispersion will be achieved when roving is used in a commercial facility, compared to the small extruder used in these experiments.
The single screw extruder has a length to diameter ratio (L/D) of 25:1, and a diameter of 19.05 mm. It has a compression ratio (channel depth in feeding section over channel depth in metering section at end of extruder) of 3:1 with a feed depth of 3.8 mm. The single screw extruder has four heating zones and was operated at a speed of 20 rpm without a die at the end of the machine. The glass fibre can only be fed into the machine at the hopper in the first zone, along with hemp-PP granulates. The screw speed was kept at 20 rpm after attempting to run at different speeds to prevent machine’s torque to rise too high causing damage to the machine. Using Equation 10 and knowing channel depth at metering section, shear rate can be calculated as follows:

\[
\gamma = \frac{3.1416 \times 19.05 \times 20}{60 \times 1.3} = 15.3 \text{ sec}^{-1}
\]

The co-rotating twin screw extruder, ONYX TEC 25/40, has a length to diameter ratio (L/D) of 40, and a diameter of 25 mm. It has a channel depth of 2.1 mm, a throughput capacity of 2-15 kg/h and a main motor power of 5.5 kW. Parameters that can be changed in the extruder are as follows: the main motor speed - speed of rotation of the screw; the feeder speed - the speed at which the
materials from the hopper enter the extruder body; temperature in each of eleven zones; the feeding position of the glass fibre; and keeping the breaker and die in place or removing them. The temperature in all zones was kept constant at 185 °C for all runs with the twin screw extruder to assure complete melting of the resin and good flow of the composite in the extruder, while avoiding overheating of natural fibres during compounding.

Glass fibre needs to be distributed in the composite from the original roving bundle, while the length is kept at its maximum size possible under the processing condition. Two feeding positions in the extruder have been investigated for the glass fibre to arrive at the desired length with acceptable wetting and dispersion. The extruder under study has three ports other than the hopper, one in the middle, one before the vent port toward the end, and the vent port at the end. The positions that have been investigated are the middle port, and the one before the vent port. The vent port of the extruder was not considered for GF feeding as venting is necessary for biomaterials since organics can cause a material to be porous, and can cause it to undergo a hydrolysis reaction and degrade the polymer. Thus, venting of evaporated moisture and non-condensable organics from the system is crucial. Additionally, the vent port is very close to the end of the extruder, thus it would be unlikely to achieve the necessary wetting for the glass fibre in the composite using the vent port.

To find the optimum operating conditions for the twin screw extruder, the operating parameters were varied to create different scenarios as shown in Table 18. Initially, pure PP was introduced into the system instead of a hemp-PP composite as it is time-consuming to make large amounts of composite; the batches are limited to 60 g in the plasticorder. Thus, in the initial trials, the composite contained only PP and glass fibre. Since glass fibre was introduced after the hopper in the twin screw extruder, main motor speed determined the amount of glass fibre that was pulled into the system, and thus affecting the concentration of glass fibre. The feeder speed determined how much polymer entered the system, and eventually controlled the amount of hemp-PP component of the hybrid composite. To reduce the pressure on the composite and breakage of
fibres, the breaker which is a square block with a number of holes to direct the fibres in the composite, and the die were removed from the end of the extruder.

Table 18. Operating conditions for twin screw extrusion of GF-PP composite

<table>
<thead>
<tr>
<th>Shear Rate (sec(^{-1}))</th>
<th>Feeder Speed (RPM)</th>
<th>Breaker</th>
<th>Die</th>
<th>GF Feeding Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>93</td>
<td>20</td>
<td>Yes</td>
<td>Yes</td>
<td>+</td>
</tr>
<tr>
<td>78</td>
<td>15</td>
<td>Yes</td>
<td>Yes</td>
<td>+</td>
</tr>
<tr>
<td>62</td>
<td>10</td>
<td>Yes</td>
<td>Yes</td>
<td>+</td>
</tr>
<tr>
<td>62</td>
<td>10</td>
<td>No</td>
<td>No</td>
<td>+</td>
</tr>
<tr>
<td>50</td>
<td>10</td>
<td>Yes</td>
<td>Yes</td>
<td>+</td>
</tr>
<tr>
<td>50</td>
<td>8</td>
<td>No</td>
<td>No</td>
<td>+</td>
</tr>
</tbody>
</table>

Main motor speed controls the shear rate and amount of glass fibre entering the extruder. The shear rate in the extruder was varied by change of motor speed from 80-150 rpm. Using Equation 10, shear rate in screw channel was calculated, ranging from 50-93 sec\(^{-1}\). Lower shear rates result in higher aspect ratio of fibres which is desired. If the shear rate is too low, fibre agglomeration can be problematic, and if shear rate is too high, fibre breaking and reduction in aspect ratio can reduce fibre strength. Moreover, high flow velocity would reduce melt residence time, resulting in a weak skin and a blistered surface [99]. The optimum shear rate of 62 sec\(^{-1}\) resulted in optimum mechanical properties and was the most repeatable run. Hence, all twin screw extruder samples were produced at this optimum shear rate.

Factors influencing the optimum operating conditions for twin screw extrusion of GF-PP composite were the mechanical properties of composites, length and concentration of GF. The glass fibre content for each run was determined by isolating the glass fibre from the composite via pyrolysis in a muffle furnace, in which the polymer was burned and the glass fibre was left intact. A sample of composite was placed in a crucible and then placed in an oven at 600 °C for 3 hours.
Accordingly, only the glass reinforcement was left behind. Measuring the weight of the crucible before and after the test helped determine the glass fibre content.

After determining the optimal conditions for twin screw extrusion with GF and PP, hemp was introduced into the system. There was an attempt of feeding the refined hemp fibre along with PP and MAPP pellets through the hopper to be mixed in the extruder, in hope of reducing the compounding step of the mixing in the plasticorder. Although the horizontal agitator in the hopper promoted flow of natural fibres to create consistent flow to the extruder, the fluffy nature of the refined hemp made it impossible for it to enter the extruder. As a result, there was no option other than compounding hemp, PP, and MAPP in advance in the rotary mixer (Brabender Plasticorder) and later feeding the composite granulates to the extruder through the hopper. Runs for hemp-PP granulates with GF under optimum conditions determined for PP, resulted in very different product specifications. This can be explained by the differences in viscosity and shear behavior of two systems. Introduction of natural fibre to the system increased the viscosity of the material in the extruder, hence resulting in more fibre breakage. As a result, the hybrid compound of hemp-GF-PP had a 60% increase in GF concentration and a 23 times reduction in GF length compared to single fibre GF-PP composite. GF length and concentration were determined after pyrolysis of composite in the muffle furnace. As a result, new set of investigations were needed to be carried out with hemp-PP granulates to find the optimum conditions. Nevertheless, the runs with GF-PP determined optimum GF feeding position, and the necessity for the removal of die and breaker from the end of the extruder. Table 19 shows various operating scenarios of changing shear rate and feeder speed investigated after the addition of hemp to the composite. Motor speed affects GF content as speed of screws determines how much GF is pulled into the system, and feeder speed affects hemp content. These findings were implemented in the runs for hybrid compounding. The twin screw extruder had great difficulty functioning in cases where the ratio of the feeder speed to the main motor speed was not close to 1:10. As a result, only small samples for each run were collected to determine glass fibre concentration in order to find optimum process condition for hybrid composite.
Table 19. Various operating conditions for extrusion of hemp-GF-PP hybrid composite

<table>
<thead>
<tr>
<th>Run</th>
<th>Shear rate (sec(^{-1}))</th>
<th>Motor Speed (RPM)</th>
<th>Feeder Speed (RPM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>80</td>
<td>13</td>
</tr>
<tr>
<td>2</td>
<td>56</td>
<td>90</td>
<td>14</td>
</tr>
<tr>
<td>3</td>
<td>62</td>
<td>100</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>62</td>
<td>100</td>
<td>12</td>
</tr>
<tr>
<td>5</td>
<td>62</td>
<td>100</td>
<td>14</td>
</tr>
<tr>
<td>6</td>
<td>62</td>
<td>100</td>
<td>16</td>
</tr>
<tr>
<td>7</td>
<td>62</td>
<td>100</td>
<td>18</td>
</tr>
<tr>
<td>8</td>
<td>62</td>
<td>100</td>
<td>20</td>
</tr>
</tbody>
</table>

4.3.2.2.2 Challenges with the Twin Screw Extruder

The twin screw extruder continuously stopped working at runs where the ratio of the feeder speed to the main motor speed was not close to 1:10. At low shear rates (< 45 sec\(^{-1}\)) some materials came out of the extruder’s open ports in the middle and end of it. These limitations should be considered when designing the experiment and varying control variables for composite preparation.

4.3.2.2.3 Injection Molding

Materials out of the extruder are molded to provide final products and mechanical testing specimen in order to check the mechanical properties of the composite. Injection molding was carried out under the processing conditions listed in Table 20.

Table 20. Injection molding processing conditions

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Injection Time (Sec)</th>
<th>Cooling Time (Sec)</th>
<th>Mold Open Time (Sec)</th>
<th>Ejector counter</th>
<th>Pressure (Tons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>204</td>
<td>8</td>
<td>38</td>
<td>2</td>
<td>1</td>
<td>28</td>
</tr>
</tbody>
</table>
To arrive at samples with longer glass fibre length, GF-PP extruded rods were cut to 2.5 cm and were fed to the injection molding machine. Glass fibres of the injection molded samples were very short; as the fibres broke inside the machine or at the gate, where materials had to pass through a number of 90 degree turns in the mold. Breakage of glass fibre during plastication and injection could be due to shear force of the mixing screw as well. It was concluded that it is not possible to keep the length of fibres in the current injection molding machine. As a result, compression molding was carried out instead.

4.3.2.2.4 Compression Molding

Long glass fibre-PP composite strands were cut roughly about 17.8 cm as exiting the extruder to fit in the 17.8 x 17.8 cm$^2$ mold for compression molding. A sheet of composite was prepared by heating the mold filled with extruded materials under pressure. Materials were placed in the mold between two mylar sheets and were heated at 170 °C for 1 hour prior to compression molding. Two 2 mm thick stainless steel sheets were placed at the top and the bottom of the mold to arrive at a product sheet with thickness of approximately 3 mm - in accordance with ASTM standards for mechanical testing. Compression molding conditions are presented in Table 21.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time at Low Pressure (min)</th>
<th>Time at 8.5 MPa Pressure (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>5</td>
<td>1</td>
</tr>
</tbody>
</table>

The low pressure is the minimum pressure on the machine which is near 1.5 MPa. After pressing for 5 minutes at low pressure, the pressure was raised to 8.5 MPa. After 1 minute, the mold was cooled under the 8.5 MPa pressure to room temperature and the sheet of composite was taken out of the mold. Afterwards, the shapes of mechanical testing specimen were traced over the composite sheet, and were cut accordingly.
4.3.3 Characterizations

4.3.3.1 Hemp fibre Extraction

Hemp fibres were extracted from the hybrid composites by dissolving the matrix in boiling xylene, C₆H₄(CH₃)₂, using reflux method. Roughly 2 grams of a compression molded sample was placed in a round bottom flask containing 100 ml of xylene and attached to a water cooled condenser to prevent loss of solvent during heating. The flask was heated for one hour at 140 °C, and solid fibres were left at the bottom of the flask and then separated by vacuum filtering. This was repeated twice more to ensure the removal of all resin from fibres, leaving a mixture of hemp and glass fibres, which was suspended in acetone for 12 hours. Microscopic picture of fibres were obtained using a Leica DM LM microscope where pictures were analyzed by Leica QWin Standard software. Length distribution of the hemp fibres was obtained by using ImageTool analysis of microscopic pictures of the fibres.

4.3.3.2 Hemp Fibre Characterization

For the case of extracted hemp fibres, optical microscopy was used to determine length distribution of fibres. For the case of refined hemp fibres, the length was analyzed by Fibre Quality Analyzer (FQA). The FQA rapidly and automatically measures fibre length and shape (curl and kink) for fibres up to 10 mm long [100]. A dilute suspension of fibres was passed through the optical and imaging system and then was grouped into various length classes.

In order to determine the diameter of refined fibres, a few drops of hemp fibres in water solution were placed on a stub. The stub was oven dried at 105°C for 1 hour. Then SEM was carried out, using a scanning electron microscope (model Hitachi S-2500, Tokyo, Japan). Prior to the SEM observations, all samples were sputter-coated with gold. SEM images were analyzed using an image analysis software package, UTHSCSA, which was downloaded from
The diameter of the hemp fibre was obtained based on the average of over one hundred readings.

4.3.3.3 Glass Fibre Length Distribution

Glass fibres were separated from hybrid composite by burning samples in the muffle furnace for 3 hours at 600°C. Composite samples used for length distribution studies were at least 6 cm long. Visual observation of glass fibres showed a wide range from powder to more than 2 cm long fibres. Unlike the case for natural fibres, FQA (which was used to measure length of hemp refined at various gaps in the refiner) cannot be used for glass fibres since they are brittle and would break in the machine. Thus, microscopic images of glass fibres were obtained to study their length. It must be noted that the diameter is constant for synthetic fibres. It was not possible to measure the length of long fibres with a microscope as they did not fit in the screen shots even at lowest magnification. Thus fibres were divided into two categories of short and long by using a 50 mesh sieve with a 0.297 mm opening. Glass fibres were weighed before sieving and then the two portions were weighed to determine the percentage of short and long fibres in the sample. This was repeated three times to get an average for the fraction (percentage) of short and long fibres. The length of short fibres was measured by a Leica DM LM microscope where pictures were analyzed by a Leica QWin Standard software and later the length of fibres were determined using ImageTool software. For the longer fibres a few methods were investigated, such as taking picture of the fibres against dark backgrounds, scanning the fibres, and dying the fibres to make them more visible. However, none of those images gave satisfactory contrasts. As a result, long fibres (n > 200) were manually traced by hand on a dark sheet and then lengths of traced lines were measured by a ruler after removing the fibres. The average length of the fibres was determined by considering the weight fraction of short and long portions of the fibres.
4.3.3.4  Mechanical Tests

Tensile and flexural properties were measured on a standard computerized testing machine (Instron 3367). Tensile properties were measured in accordance with the ASTM D638 procedure at a crosshead speed of 12.5 mm/min, with a span of 100 mm. Flexural properties were measured using the three-point bending method specified by ASTM D790 at a crosshead speed of 12.5 mm/min, with a span of 50.8 mm. Impact tests followed ASTM D256 procedure using a pendulum type impact machine, a Tinius Olsen Model 892 impact tester. Samples were notched according to the ASTM specifications. Tests were carried out on 6-10 specimens to obtain a reliable average and standard deviations. All tests for mechanical properties were performed at room temperature.

4.3.3.5  Water Absorption Test

A water absorption test was carried out according to the ASTM D570-98. Eight compression molded specimens for various hybrid composites were submerged in water at room temperature. The samples were taken out periodically and weighed after wiping off the water on their surfaces. The percentage of water uptake was calculated based on Equation 9.

4.3.3.6  Thermal Test

Thermogravimetric Analysis (TGA), measurement of weight change of composites in relation to temperature, was employed to investigate the thermal stability of composites processed under different conditions. The heating was carried out at rate of 10 °C/min and from 25 °C to 900 °C in N₂ using a TA Instrument Q500 machine. TGA figures show variation of sample weight and derivative weight with temperature.
4.3.3.7 Morphological Analysis

Characterization of fibre surface morphology, fibre fracture, fibre distribution and the appearance of the fibre-resin interface was carried out using scanning electron microscopy. SEM of the fracture surface of fibre composites helped to observe fibre fracture, debonding and pull-out. Scanning electron microscopy fractographic studies were carried out on the impact fracture surfaces of composites using scanning electron microscope (model Hitachi S-2500, Tokyo, Japan). Prior to SEM observations, all fractured surfaces of the impact specimens were sputter-coated with gold.

4.4 Results and Discussion

4.4.1 Hemp Fibre Selection

To select the optimum length of hemp fibres, they were refined at different gaps and impact strength of hemp-PP was compared for composites made from hemp of different lengths. Hemp composite with the highest impact strength would determine the optimum refining gap and hence the length of hemp. The fibre content was 30% for all samples, with the addition of 5% MAPP to improve the interfacial adhesion between the natural fibre and the matrix. Figure 27 shows notched impact strength of hemp-PP composites with hemp refined at various gaps (i.e. hemp with different lengths). Hemp refined at gap 120 produced the composite with the highest impact strength.
Figure 27. Notched impact strength of 30% hemp-PP composite of hemp refined at various gap sizes

Statistical analysis was performed using ANOVA to assess the significance of the data. ANOVA checks if the means of more than two populations are the same; it uses a F distribution to determine whether the variability within and between groups is significant. Based on the ANOVA studies (Table 22), the increase in impact strength was not significant as the null hypothesis of equal means was not rejected up to the 25% significance level since $F_{\text{stat}} < F_{\text{table}}$. ($F_{0.25, 3, 32}=1.44$)

Table 22. ANOVA table for impact strength of hemp-PP with hemp refined at gaps 5, 20, 80, and 120

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>Degrees of Freedom</th>
<th>Mean Square</th>
<th>F-statistics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Between samples (explained)</td>
<td>45.38</td>
<td>3</td>
<td>15.13</td>
<td>1.42</td>
</tr>
<tr>
<td>Within samples (unexplained)</td>
<td>341.57</td>
<td>32</td>
<td>10.67</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>386.94</td>
<td>35</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Similarly, Nechwatal et al. showed flax fibre length variation from less than 1 mm to over 10 mm, led to a slight difference in Charpy impact strength of 30% flax-PP composites [101]. This result is surprising since a great amount of work is involved in breaking of hollow natural fibres and splitting and crumpling of cellulose walls. Negligible effect of length of natural fibres on toughness may be due to an increased chance of entanglement for longer fibres because of curl of natural fibres. As a result, there will be poor dispersion of the fibres in matrix for longer fibres, and hence no improvement in impact properties.

Since notched impact strength was not affected by length of hemp, tensile strength, as the next important parameter for hemp-PP composite with different refining gaps, was investigated. Figure 28 shows the variation in the tensile strength of hemp in hemp-PP composites refined at different gaps. Initially, the tensile strength increased as the length of the fibre increased, but after a certain point, it decreased whilst increasing hemp length. Hemp refined at gap 20 produced composites having the maximum tensile strength. The tensile strength of PP was 34.95 MPa but reinforcing the matrix with 30% hemp refined at gap 20 increased the tensile strength to 37.62 MPa.

Figure 28. Tensile strength of 30% hemp-PP composite of hemp refined at various gap sizes
Based on the ANOVA studies (Table 23), the increase in the tensile strength for hemp refined at gap 20 is statistically significant. The null hypothesis of equal means was rejected at the 2.5% significance level since $F_{\text{stat}} > F_{\text{table}} (F_{0.025,4, 25} = 3.35)$. This shows that the means are not equal and the difference is significant. Thus, the difference between groups was significant, and hemp refined at gap 20 was the optimum hemp for compounding with the matrix.

Table 23. ANOVA table for tensile strength of hemp-PP with hemp refined at gaps 5, 20, 80, 120, and unrefined hemp

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>Degrees of Freedom</th>
<th>Mean Square</th>
<th>F-statistics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Between samples (explained)</td>
<td>88.42</td>
<td>4</td>
<td>22.10</td>
<td>4.10</td>
</tr>
<tr>
<td>Within samples (unexplained)</td>
<td>134.64</td>
<td>25</td>
<td>5.38</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>223.06</td>
<td>29</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fibre quality analysis (FQA) provided fibre length of hemp refined at different gaps (Table 24). Looking at length of fibres at various gaps of the refining machine, it is clear as the gap opening of the two disks increased, fibre length increased.

Table 24. Hemp fibre length determined by fibre quality analyzer

<table>
<thead>
<tr>
<th>Refining Gap</th>
<th>5</th>
<th>20</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fibre Length (mm)</td>
<td>0.94</td>
<td>1.28</td>
<td>1.44</td>
</tr>
<tr>
<td>Fibre Count</td>
<td>4754</td>
<td>3253</td>
<td>2304</td>
</tr>
</tbody>
</table>

FQA analysis determined an average length of 1.28 mm for hemp refined at gap 20. SEM studies, Figure 29, showed that hemp refined at gap 20 had an average diameter of $16 \pm 8 \mu m$, resulting in an aspect ratio of 80. Pervaiz et al. reported that hemp in polypropylene matrix has a critical length
of 3.4 mm, with a critical aspect ratio of 52 [102]. Hence, the refined hemp at gap 20 exceeds the critical aspect ratio of hemp in polypropylene, and should provide reinforcement.

Figure 29. SEM micrographs of hemp fibres refined at gap 20

4.4.2 Analysis of Operational Optimum Conditions

Main motor speed, feeder speed, temperature, and glass fibre feeding port were varied in the twin screw extruder in order to find the optimum shear rate and operational condition to obtain long glass fibre-PP composite. The smoothest runs –where the extruder did not frequently go out of service - were at a shear rate of 62 sec\(^{-1}\) and a feeder speed of 10 rpm. Other runs, especially when the feeder speed was over 14, led to frequent shut down of the extruder.

Feeding the GF before the vent resulted in long and short fibres, while feeding in the middle of the extruder resulted in only short fibres. GF content and length were determined after isolating the
glass fibre out of the composite using the muffle furnace. Since the goal of this project is to achieve long fibres, the optimum feeding port for GF was selected as the one before the vent, where continuous GF is pulled into process by the high pressure flow of molten PP, and fibres broke less as they spent less time under shear in the extruder. The optimum conditions of the twin screw extruder for GF-PP composite production were set as follows:

- Shear rate screw channel: 62 sec\(^{-1}\)
- Feeder speed: 10 rpm
- Temperature in all zones: 185 °C
- GF introduced to molten composite before the vent port
- No breaker, no die

These conditions resulted in GF-PP composite with an average glass fibre content of 18.3%.

Introducing hemp-PP granulate composite to the hopper of the extruder, under the optimum conditions found for GF-PP led to different GF content and length for hybrid composite. This is because viscosity is different in the two systems. Introduction of the hemp-PP composite resulted in many problems for the twin screw extruder, forcing it to shut down frequently especially at high feeder speeds. In order to reduce the pressure in the extruder, the end of the extruder was opened, but still the flow was not satisfactory. Under optimum operational conditions determined for GF-PP, the hybrid composite had a GF content of 29.3%. This is much higher than the product specification of 20% GF for this project.

Motor speed affects the GF content as it determines how fast GF is pulled into the extruder by rotating screws as it is introduced at a port before the vent. Additionally, feeder speed determines the amount of hemp and PP in the composite, hence affecting ratio of GF in the hybrid composite and product composition. Arriving at a desired GF content was very difficult due to operational limitations of the extruder. One approach for reducing the glass fibre content is to reduce the motor speed - pulling in less GF, and/or increase the feeder speed - have more PP vs. GF. However,
changing the shear rate and/or feeder speed is a delicate matter, and it is important to follow the suggested ratio of 1 to 10 for the feeder speed to the main motor speed for the twin screw extruder in use. For the case of the hemp-GF-PP composite, it was found impossible to run at low shear rates (motor speeds of 70, 80, and 90 rpm). Since reducing the motor speed was not possible, increasing feeder speed and in turn the amount of hemp and PP in the hybrid composite was investigated to reduce the GF content. Running the extruder at a shear rate of 62 sec$^{-1}$, with feeder speeds of 10, 12, 14, 16, 18, and 20 rpm were explored. GF content of various runs is shown in Table 25 for comparison. The extruder went out of service frequently when the speed ratio of 1:10 was not followed, especially with feeder speed greater than 14. Thus, although theoretically it was possible to reduce GF content by increasing feeder speed, in practice limitations of the extruder prevented this.

Table 25. Feeder speed and glass fibre content of the hybrid composite at a shear rate of 62 sec$^{-1}$, feeding the GF before the vent, with no breaker and die

<table>
<thead>
<tr>
<th>Feeder Speed (rpm)</th>
<th>GF Content (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>29</td>
</tr>
<tr>
<td>12</td>
<td>37</td>
</tr>
<tr>
<td>14</td>
<td>27</td>
</tr>
<tr>
<td>16</td>
<td>19</td>
</tr>
<tr>
<td>18</td>
<td>17</td>
</tr>
</tbody>
</table>

Another way to reduce GF content is to carry out the experiment with a GF roving having less GF strands in the bundle. To reduce glass fibre content, a new GF roving with lower tex (i.e. less number of GF strands in bundle) was used. From this point on, to differentiate two types of GF used in this project, “high tex” and “low tex” terms have been added, where low tex GF has a smaller number of filaments in its roving, hence permitting it to arrive at a composite with a lower GF content under similar conditions.
The moisture content of the GF-PP composite was determined by drying samples at 105 °C for two hours. Samples were compounded under the following conditions: a shear rate of 62 sec\(^{-1}\); a feeder speed of 10 rpm; and a temperature of 185 °C in all zones. It was found that the moisture of the extruded GF-PP is negligible, since it was less than 0.01%.

4.4.3 Fibre Length Distribution

4.4.3.1 GF of Twin Screw Extruded GF-PP Composite (High tex GF)

In the early trial runs to determine optimum operational conditions, high tex glass fibre (2200) was added to the molten polymer in the twin screw extruder before the vent port. Glass fibre, separated from composite by pyrolysis, was analyzed by manually tracing the fibres on a black sheet as they were too long to fit under a microscope. Fibres were between 0.1 to 25 mm, with an average of 6.9 ± 5.4 mm. As shown in Figure 30, 77% of the fibres have a length of less than 10 mm.

Figure 30. Glass fibre length distribution for twin screw extrusion of GF-PP composite
4.4.3.2 GF of Twin Screw Extruded Hybrid Composite (High tex GF)

The addition of high tex glass fibre (2200) in the twin screw extruder before the vent resulted in fairly short fibres based on naked-eye observation. Glass fibre separated from hybrid composite was analyzed with the use of a microscope and ImageTool software. The average length of fibres was found to be $0.30 \pm 0.27$ mm, ranging from 9 μm to 1.39 mm. As shown in Figure 31, 60% of the fibres have a length of less than 0.3 mm. Aside from the short length of fibres, this composite had a high glass fibre content (29 wt%) and thus was not an acceptable final product.

![Figure 31. Glass fibre length distribution for Twin screw extrusion of hybrid composite (High tex GF)](image)

4.4.3.3 GF of Single Screw Extruded Hybrid Composite (High tex GF)

As explained in section 4.3.3.3, glass fibres were divided into two fractions since it was not possible to measure the length of the longer fibres with a microscope. The sieving method divided fibres into two groups of short (43%) and long (57%) fibres. The length distribution of each
fraction is shown in Figure 32 and Figure 33. The overall average, considering the appropriate fractions, was found to be 5.72 mm. Thus, single fibre extrusion resulted in longer GF in hybrid composites as it lacked the intermeshing of the screws in the twin screw extruder and had a lower shear rate (15 sec\(^{-1}\) vs. 62 sec\(^{-1}\)). Single screw extrusion led to low GF content and long fibres, and the next step is to evaluate fibre dispersion and mechanical properties of the composites to complete evaluation of process operation for low shear mixing in the single screw extruder.

Figure 32. Length distribution of fraction of short GF extracted from single screw extruded hybrid composite determined by ImageTool (High tex GF)
4.4.3.4 GF of Twin Screw Extruded Hybrid Composite (Low Tex GF)

Similarly, glass fibres were divided into two fractions for the case of low tex glass fibre hybrid composite - twin screw extruded. The sieving method determined that 76% of fibres were short fibres, and 24% long fibres. The length distribution of each fraction is shown in Figure 34 and Figure 35. The overall average, considering the appropriate fractions, was determined to be 2.28 mm.
Figure 34. Length distribution of fraction of short GF extracted from twin screw extruded hybrid composite determined by ImageTool (Low tex GF)

Figure 35. Length distribution of fraction of long GF extracted from twin screw extruded hybrid composite determined manually (Low tex GF)
In summary, the average glass fibre lengths along with minimum and maximum values for different composites are reported in Table 26. All average lengths were below the glass fibre critical length. Wide distribution of length of extruded GF, from powder to over 2 cm long fibres, has caused high standard deviation values for the average GF lengths.

Table 26. Average glass fibre length in different composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Extruder</th>
<th>Avg length (mm)</th>
<th>Min-Max (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GF-PP (High tex)</td>
<td>Twin screw</td>
<td>6.93 ± 5.4</td>
<td>0.1 – 25</td>
</tr>
<tr>
<td>GF-Hemp-PP (High tex)</td>
<td>Twin screw</td>
<td>0.29 ± 0.27</td>
<td>0.009 – 1.39</td>
</tr>
<tr>
<td>GF-Hemp-PP (High tex)</td>
<td>Single screw</td>
<td>5.72 ± 3.67</td>
<td>0.011 – 25</td>
</tr>
<tr>
<td>GF-Hemp-PP (Low tex)</td>
<td>Twin screw</td>
<td>2.28 ± 1.61</td>
<td>0.013 – 24</td>
</tr>
</tbody>
</table>

4.4.3.5 Hemp Fibre from Twin Screw Extruded Hybrid Composite (Low Tex GF)

During compounding, both in the plasticorder mixer and in the extruder, refined hemp experienced shear which resulted in breakage of the fibre. Xylene extraction of hemp from hybrid composite resulted in isolation of fibres from the matrix. Figure 36 shows a microscopic view of extracted hemp fibres from the hemp-GF-PP composite with low tex GF - Twin screw extrusion. Comparison of microscopic picture of extracted hemp to SEM figure of hemp fibres before compounding - presented in Figure 29 – shows extent of length reduction during composite production.
Microscopic pictures determined the average length of hemp fibres in the hybrid composite to be $0.17 \pm 0.12$ mm ($n=168$), where 76% of the fibres had a fibre length of less than 0.3 mm. This means shear in the plasticorder and the extruder resulted in approximately 85% reduction in length of hemp fibres. The length distribution of extracted hemp from hybrid composite (hemp-GF-PP) is shown in Figure 37.
Accordingly, aspect ratio ($S_c$) of hemp fibre reduced to 10 from $S_c$ of 80 during processing. These values suggest that practically hemp may be acting as filler in the final hybrid composite. To further investigate this matter, hemp fibres were replaced with hemp dust filler in similar processing conditions. Mechanical properties of a hybrid composite with low tex GF and hemp dust, filler with core or inside stem fibre grade and size of 10 mesh from Hempline Inc., were investigated to study the effect of hemp fibre in mechanical properties of the hybrid composite.

### 4.4.4 Tensile, Flexural and Impact Properties

In injection molding, specimens are shaped by filling cavities designed according to ASTM standards. However, for the compression molded samples, simple and reproducible shapes as shown in Figure 38 were drawn on the composite sheet and cut accordingly. Convenient specimen geometry was used for cutting samples. The shape of the cut samples was rectangular with similar
lengths and widths as the ASTM standard, but without the arch for the tensile test due to difficulties in getting consistent arch cuts.

Figure 38. Specimen configurations, a) Tensile strength specimen, b) Flexural strength specimen, c) Impact strength specimen *The thickness of compressed sheets was roughly 3.2 mm

4.4.4.1 GF-PP Composite

4.4.4.1.1 Injection Molded Composite

Tensile and flexural properties of polypropylene and GF-PP composites with high tex GF fed in the middle and before the vent port of the extruder are shown in Table 27. Based on strength and modulus data in Figure 39 and Figure 40, it is clear that the addition of glass fibre has enhanced mechanical properties of PP as expected. Also, introducing GF later in the extrusion process...
(before the vent) resulted in better mechanical properties. This could be due to the greater length of glass fibres as they experienced less shear force since they traveled less distance with the extruder screws.

Table 27. Tensile and Flexural properties for injection molded specimens (High tex GF – Twin screw extruded)

<table>
<thead>
<tr>
<th>Injection Molded</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Flexural Strength (MPa)</th>
<th>Flexural Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP 3622</td>
<td>31.8 ± 0.5</td>
<td>1.6 ± 0.1</td>
<td>49.7 ± 0.9</td>
<td>1.3 ± 0.1</td>
</tr>
<tr>
<td>GF-PP-Mid Fed</td>
<td>38.2 ± 0.3</td>
<td>3.9 ± 0.1</td>
<td>63.0 ± 0.4</td>
<td>3.0 ± 0.1</td>
</tr>
<tr>
<td>GF-PP-Before Vent Fed</td>
<td>40.5 ± 0.1</td>
<td>3.5 ± 0.1</td>
<td>64.5 ± 0.5</td>
<td>2.8 ± 0.1</td>
</tr>
</tbody>
</table>

Figure 39. Tensile and flexural strength for injection molded specimens (High tex GF – Twin screw extruded)
Impact properties of injection molded GF-PP are shown in Table 28 and Figure 41. It was expected to observe an increase in impact properties due to the addition of reinforcing fibres, however the addition of short GF (length reduction due to injection molding), resulted in a reduction of unnotched impact properties. This may be due to experimental errors, but the results were not checked again since it was decided to exclude the injection molding technique and only carry out compression molding to better retain the length of fibres. The goal was to find the optimum concentration and length of fibres in PP to achieve high impact properties while having good tensile and flexural properties. Strong adhesion between fibre and matrix results in high tensile strength and lower impact strength, since most fibres break rather than being pulled out when there is good adhesion between fibres and matrix. In order to enhance impact properties, it is necessary to optimize adhesion in a way that impact strength is maximized while tensile strength is satisfactory. In order to explore this area, type and concentration of compatibilizer can be changed to investigate adhesion between fibres and matrix which is beyond the scope of this work.
Table 28. Impact strength of injection molded specimens (High tex GF – Twin screw extruded)

<table>
<thead>
<tr>
<th>Injection Molded</th>
<th>Notched Izod Impact (J/m)</th>
<th>Unnotched Izod Impact (J/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP 3622</td>
<td>18.4 ± 2.2</td>
<td>421.5 ± 181.0</td>
</tr>
<tr>
<td>GF-PP-Mid Fed</td>
<td>37.2 ± 2.3</td>
<td>208.0 ± 35.2</td>
</tr>
<tr>
<td>GF-PP-Before Vent Fed</td>
<td>49.6 ± 2.7</td>
<td>181.2 ± 15.5</td>
</tr>
</tbody>
</table>

Figure 41. Impact strength for injection molded specimens (High tex GF – Twin screw extruded)

4.4.1.2 Compression Molded Composite

Since it was determined that the optimum location to feed the glass fibre is before the vent, the remainder of the studies were carried out only for this condition. As mentioned in section 4.4.4.1.1, in order to keep the length of the GF in a hybrid composite, compression molding was carried out instead of injection molding. Mechanical testing was carried out on samples cut out of GF-PP sheets. Figure 42 shows a photograph of the failure surfaces of tensile tested GF-PP. As it can be seen, the network of fibres was very strong, and despite the force exerted on the test specimen, glass fibres still held the specimens in one piece after failure. Equivalent photo for hemp-PP is also
presented in Figure 42 for comparison, with the mechanical properties presented in the previous chapter, section 3.4.7.

Figure 42. Photographs of the failure surface of tensile tested GF-PP specimens (High tex GF – Twin screw extruded) and hemp-PP specimens

Tensile and flexural strength and modulus of pure polypropylene and glass fibre reinforced polypropylene are presented in Table 29, Figure 43 and Figure 44. Compression molded samples of long GF-PP composite had higher tensile and flexural properties compared to the pure polymer. This was due to the presence of strong and long glass fibres in the polymer matrix. There was about 18 wt% glass fibre present in the GF-PP composite.
Table 29. Tensile and flexural properties of compression molded specimens (High tex GF – Twin screw extruded)

<table>
<thead>
<tr>
<th>Compression Molded</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Flexural Strength (MPa)</th>
<th>Flexural Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP 3622</td>
<td>34.9 ± 1.4</td>
<td>1.7 ± 0.1</td>
<td>64.7 ± 3.4</td>
<td>2.2 ± 0.1</td>
</tr>
<tr>
<td>GF-PP-Before Vent Fed</td>
<td>58.2 ± 4.1</td>
<td>3.9 ± 0.1</td>
<td>97.9 ± 7.3</td>
<td>4.4 ± 0.4</td>
</tr>
</tbody>
</table>

Figure 43. Tensile and flexural strength of compression molded specimens (High tex GF – Twin screw extruded)
4.4.4.2 Fibre Orientation and Length

Since composite strands were placed manually in the mold for compression, it was possible to control the fibre orientation to some extent. By cutting the impact specimens in longitudinal and transverse direction to the mold, composites with long and short glass fibre strands in resin were obtained. Thus, impact strength was measured in both parallel and perpendicular to the fibre orientation for the compression molded samples. This allowed investigating the effect of both length and orientation of glass fibres on impact properties of composite. Results showed that long fibres formed a network which was harder to destroy. The significant differences between longitudinal and transverse properties of composites are shown in Table 30, justifying the importance of considering fibre orientation and length. Composites show better impact resistance when the applied stress is in fibre direction, and are generally weaker in other directions [50]. However, impact strength was higher when the force was applied perpendicular to long fibres rather than parallel to short fibres, emphasizing importance of fibre length for composite toughness. Figure 45 shows the impact strength of pure resin and long GF-PP (longitudinal cut of composite sheet).
Table 30. Impact strength of compression molded specimens (High tex GF – Twin screw extruded)

<table>
<thead>
<tr>
<th>Compression Molded</th>
<th>Notched Izod Impact (J/m)</th>
<th>Unnotched Izod Impact (J/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP 3622</td>
<td>26.6 ± 1.9</td>
<td>181.3 ± 50.2</td>
</tr>
<tr>
<td>GF-PP-Before Vent Fed (Long GF)</td>
<td>345.5 ± 108.0</td>
<td>459.6 ± 153.2</td>
</tr>
<tr>
<td>GF-PP-Before Vent Fed (Short GF)</td>
<td>123.1 ± 31.1</td>
<td>168.8 ± 45.1</td>
</tr>
</tbody>
</table>

Figure 45. Impact strength of long GF-PP compression molded specimens (High tex GF – Twin screw extruded)

4.4.4.3 Hybrid Composite

Two mixing methods of twin screw extrusion (high shear) and single screw extrusion (low shear) were used for hybrid compounding. In the twin screw extrusion, hybrid composite was obtained by feeding glass fibre before the vent to the compounded hemp-MAPP-PP granulates which were fed in the hopper of the extruder. In single screw extrusion, GF and hemp-MAPP-PP pellets were all fed simultaneously in the hopper. Next, for both cases, hybrid composites were pressed in a hot mold to roughly 3 mm sheets which were later cut for mechanical testing.
4.4.4.3.1 Twin Screw Extrusion (High Tex GF)

Twin screw extrusion with glass fibre with a tex of 2200 was carried out under optimum operational conditions found for the GF-PP system (shear rate: 62 sec\(^{-1}\), feeder speed: 10 rpm, feeding glass fibre before the vent port, no breaker, no die). Tensile and flexural strength and modulus of compression molded pure polypropylene and hemp-GF-polypropylene composites are presented in Table 31, Figure 46 and Figure 47. Compression molded samples of hemp-GF-PP composite had higher tensile and flexural properties compared to the pure PP polymer. This is due to the presence of strong glass fibres in the polymer matrix. A muffle furnace experiment determined the glass fibre content to be about 29 wt% in the hybrid composite. As this project demands a lower GF content (below 20%), other processing options should be explored in order to reduce the glass fibre content in the hybrid composite.

Table 31. Tensile and flexural properties of twin screw extruded hybrid composite (High tex GF)

<table>
<thead>
<tr>
<th></th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Flexural Strength (MPa)</th>
<th>Flexural Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP 3622</td>
<td>34.9 ± 1.4</td>
<td>1.7 ± 0.1</td>
<td>64.6 ± 3.4</td>
<td>2.2 ± 0.1</td>
</tr>
<tr>
<td>GF-PP</td>
<td>58.2 ± 4.1</td>
<td>3.9 ± 0.1</td>
<td>97.9 ± 7.3</td>
<td>4.3 ± 0.4</td>
</tr>
<tr>
<td>GF-hemp-PP</td>
<td>51.9 ± 19.5</td>
<td>7.1 ± 0.6</td>
<td>145.1 ± 11.7</td>
<td>9.3 ± 1.1</td>
</tr>
</tbody>
</table>

It is clear that the addition of hemp to the GF-PP composite resulted in an increase in the flexural properties. This could be explained by further orientation of the fibres at the surface of the composite due to the addition of hemp fibres.
Impact properties of compression molded pure polypropylene, GF-PP, and hemp-GF-PP composites are shown in Table 32 and Figure 48. Hemp-GF-PP had a higher notched impact strength compared to pure PP, as the presence of reinforcing fibres resulted in more fibre pull-out and higher work of fracture. GF-PP composite had superior impact properties compared to the
hybrid composite. The addition of hemp to GF-PP composite led to the reduction in impact properties due to an increase in the amount of fibre ends because of presence of short fibres. Short fibres act as stress concentration points while the long glass fibres allow dissipation of energy along their length.

Table 32. Impact strength of twin screw extruded hybrid composite (High tex GF)

<table>
<thead>
<tr>
<th></th>
<th>Notched Izod Impact (J/m)</th>
<th>Unnotched Izod Impact (J/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP 3622</td>
<td>26.6 ± 1.9</td>
<td>181.3 ± 50.2</td>
</tr>
<tr>
<td>GF-PP</td>
<td>345.5 ± 108.0</td>
<td>459.6 ± 153.2</td>
</tr>
<tr>
<td>GF-hemp-PP</td>
<td>99.7 ± 26.9</td>
<td>185.6 ± 38.6</td>
</tr>
</tbody>
</table>

Figure 48. Impact strength of twin screw extruded hybrid composite (High tex GF)

4.4.4.3.2 Single Screw Extrusion (High Tex GF)

Due to the high glass fibre content in the twin screw extrusion compounding of hybrid composite, single screw extrusion was investigated as an alternative compounding mode of LFT-D. Attempts to feed the glass fibre at any port other than the main hopper was unsuccessful as the pressure was
not enough to push the material forward to the die, hence they would exit from that feeding port. As a result, glass fibre was fed at the hopper with hemp-MAPP-PP granulates, running the extruder at 20 rpm and 180 °C, without die.

Single screw extrusion reduced the glass fibre content in the hybrid composite to 9.3 wt% compared to 29 wt% by twin screw extrusion for high tex GF. Tensile and flexural properties of the hybrid composite is shown in Table 33, Figure 49 and Figure 50. The addition of reinforcing fibres to the matrix by single screw extrusion resulted in a slight increase of modulus, without affecting the tensile and flexural strengths in comparison to the pure polypropylene.

Table 33. Tensile and flexural properties of single screw extruded hybrid composite (High tex GF)

<table>
<thead>
<tr>
<th></th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Flexural Strength (MPa)</th>
<th>Flexural Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP 3622</td>
<td>34.9 ± 1.4</td>
<td>1.7 ± 0.1</td>
<td>64.6 ± 3.4</td>
<td>2.2 ± 0.1</td>
</tr>
<tr>
<td>GF-hemp-PP</td>
<td>32.5 ± 2.0</td>
<td>2.9 ± 0.1</td>
<td>66.9 ± 6.2</td>
<td>2.9 ± 0.2</td>
</tr>
</tbody>
</table>
Figure 49. Tensile and flexural strength of single screw extruded hybrid composite (High tex GF)

![Graph showing tensile and flexural modulus of single screw extruded hybrid composite (High tex GF)](image)

Figure 50. Tensile and flexural modulus of single screw extruded hybrid composite (High tex GF)

Impact properties of hybrid composite from single screw extrusion is shown in Table 34 and Figure 51. Although the addition of fibres resulted in an increase of notched impact strength, unnotched impact strength was reduced. Ineffectiveness of reinforcement by single screw compounding was due to lack of good dispersion of fibres in the resin during extrusion.

Table 34. Impact strength of single screw extruded hybrid composite (High tex GF)

<table>
<thead>
<tr>
<th></th>
<th>Notched Izod Impact (J/m)</th>
<th>Unnotched Izod Impact (J/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP 3622</td>
<td>26.6 ± 1.9</td>
<td>181.3 ± 50.2</td>
</tr>
<tr>
<td>GF-hemp-PP</td>
<td>45.9 ± 9.7</td>
<td>101.6 ± 18.7</td>
</tr>
</tbody>
</table>
4.4.4.3 Twin Screw Extrusion (Low Tex GF)

Despite the reduction of glass fibre content using single screw extrusion, twin screw extrusion with a glass fibre with low tex was carried out to investigate the possibility to improve impact properties of hybrid composite while having low glass fibre content. Low tex glass fibre (GF tex 1100) was fed according to the optimum conditions found for the twin screw extrusion. The glass fibre content in the hybrid composite with low tex GF was determined to be 20.1%, which is in agreement with the guidelines of this project. Tensile and flexural properties of the hybrid composite of low tex glass fibre are shown in Table 35, Figure 52 and Figure 53. The addition of low tex glass fibre and hemp fibre to the matrix resulted in a significant increase in tensile and flexural properties.
Table 35. Tensile and flexural properties of twin screw extruded hybrid composite (Low tex GF)

<table>
<thead>
<tr>
<th></th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Flexural Strength (MPa)</th>
<th>Flexural Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP 3622</td>
<td>34.9 ± 1.4</td>
<td>1.7 ± 0.1</td>
<td>64.6 ± 3.4</td>
<td>2.2 ± 0.1</td>
</tr>
<tr>
<td>GF-hemp-PP</td>
<td>92.1 ± 6.9</td>
<td>6.1 ± 0.2</td>
<td>159.8 ± 14.9</td>
<td>7.5 ± 0.6</td>
</tr>
</tbody>
</table>

Figure 52. Tensile and flexural strength of twin screw extruded hybrid composite (Low tex GF)

Figure 53. Tensile and flexural modulus of twin screw extruded hybrid composite (Low tex GF)
Notched and unnotched impact properties of this compounding condition were higher compared to the pure polypropylene and previous hybrid composites. Although the impact strength of the hybrid composite was less than the GF-PP composite, it exceeded the requirement for this project (80 J/m). Good impact resistance can be attributed to good absorption of impact energy and slow propagation of crack.

Table 36. Impact strength of twin screw extruded hybrid composite (Low tex GF)

<table>
<thead>
<tr>
<th></th>
<th>Notched Izod Impact (J/m)</th>
<th>Unnotched Izod Impact (J/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP 3622</td>
<td>26.6 ± 1.9</td>
<td>181.3 ± 50.2</td>
</tr>
<tr>
<td>GF-hemp-PP</td>
<td>131.4 ± 12.4</td>
<td>324.9 ± 68.0</td>
</tr>
</tbody>
</table>

Figure 54. Impact strength of twin screw extruded hybrid composite (Low tex GF)

Complete comparison of mechanical properties of low tex GF-hemp-PP hybrid composite (lower GF content) to high tex GF-hemp-PP hybrid composite (higher GF content) is shown in Figure 55 and Table 37. Composites compounded in a twin screw extruder showed better mechanical properties due to higher dispersion of fibres in the matrix. Low tex GF-hemp-PP composite
exhibited great impact strength without compromising tensile and flexural properties. Aside from good dispersion, this composite had long fibres as well. Greater length of glass fibre below the critical length resulted in a higher energy dissipation of the transferred stress to the fibres as it had higher area. The processing conditions used for the low tex GF-hemp-PP hybrid composite in the twin screw extruder are being applied for production of prototype of this project.

Figure 55. Overall comparison of impact strength for the matrix, single fibre and hybrid composites
4.4.4.3.4 Hemp dust - Low Tex GF Hybrid Composite

As shown in section 4.4.3.5., aspect ratio of hemp fibres was greatly reduced during processing. To evaluate reinforcing role of hemp fibres, they were replaced by hemp dust fillers in production of the low tex GF hybrid composite under similar processing conditions. After compression molding of composite, tensile, flexural and impact specimen were cut to investigate mechanical properties and effect of hemp fibre. Tensile and flexural properties are presented in Table 38, Figure 56 and Figure 57, while impact properties are presented in Table 39 and Figure 58.

| Table 37. Overall comparison of mechanical properties for matrix and hybrid composites |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                                 | Tensile strength (MPa) | Tensile modulus (GPa) | Flexural strength (MPa) | Flexural modulus (GPa) | Notched Izod Impact strength (J/m) | Unnotched Izod Impact strength (J/m) |
| PP 3622                         | 34.9 ± 1.4          | 1.7 ± 0.1        | 64.6 ± 3.4          | 2.2 ± 0.1          | 26.6 ± 1.9        | 181.3 ± 50.2     |
| GF-PP twin screw (high tex)     | 58.2 ± 4.1          | 3.9 ± 0.1        | 97.9 ± 7.3          | 4.3 ± 0.4          | 345.5 ± 108.0     | 459.6 ± 153.2    |
| Hybrid single screw (high tex)  | 32.5 ± 2.0          | 2.9 ± 0.1        | 66.9 ± 6.2          | 2.9 ± 0.2          | 45.9 ± 9.7        | 101.6 ± 18.7     |
| Hybrid twin screw (high tex)    | 51.9 ± 19.5         | 7.1 ± 0.6        | 145.1 ± 11.7        | 9.3 ± 1.1          | 99.7 ± 26.9       | 185.6 ± 38.6     |
| Hybrid twin screw (low tex)     | 92.1 ± 6.9          | 6.1 ± 0.2        | 159.8 ± 14.9        | 7.5 ± 0.6          | 131.4 ± 12.4      | 324.9 ± 68.0     |

| Table 38. Tensile and flexural properties of twin screw extruded hybrid composite with hemp dust filler replacing reinforcing hemp fibre (Low tex GF) |
|---------------------------------|-----------------|-----------------|-----------------|
|                                 | Tensile Strength (MPa) | Tensile Modulus (GPa) | Flexural Strength (MPa) |
| PP 3622                         | 34.9 ± 1.4          | 1.7 ± 0.1        | 64.6 ± 3.4          |
| GF-hemp-PP                      | 92.1 ± 6.9          | 6.1 ± 0.2        | 159.8 ± 14.9        |
| GF-hemp dust-PP                 | 59.8 ± 6.2          | 4.6 ± 0.5        | 104.5 ± 4.8         |
Figure 56. Tensile and flexural strength of twin screw extruded hemp dust and hemp fibre hybrid composite (Low tex GF)

Figure 57. Tensile and flexural modulus of twin screw extruded hemp dust and hemp fibre hybrid composite (Low tex GF)
It is clear that although hemp fibre suffered significant reduction in aspect ratio, it still contributed as a reinforcing agent in the hybrid composite. This is because a great amount of work is involved in breaking of hollow natural fibres which have walls with spiral structure. Splitting and crumpling of the cellulose walls can enhance toughness of composites [103]. Hemp microfibre absorbed energy due to its cellulose walls and reinforced the composite while hemp dust only acted as filler.

Table 39. Impact strength of twin screw extruded hybrid composite with hemp dust filler replacing reinforcing hemp fibre (Low tex GF)

<table>
<thead>
<tr>
<th></th>
<th>Notched Izod Impact (J/m)</th>
<th>Unnotched Izod Impact (J/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP 3622</td>
<td>26.6 ± 1.9</td>
<td>181.3 ± 50.2</td>
</tr>
<tr>
<td>GF-hemp-PP</td>
<td>131.4 ± 12.4</td>
<td>324.9 ± 68.0</td>
</tr>
<tr>
<td>GF-hemp dust-PP</td>
<td>117.2 ± 24.9</td>
<td>196.1 ± 39.7</td>
</tr>
</tbody>
</table>

Figure 58. Impact strength of twin screw extruded hemp dust and hemp fibre hybrid composite (Low tex GF)
4.4.5 Water Absorption

Presence of water in the environment can cause microcracking and debonding in composites, and hence it is desired to reduce water absorption in the composites. GF-PP and hybrid composites extruded under different conditions were evaluated for water absorption at room temperature. This study was carried out for two months and percentage changes in weight of composites are summarized in Table 40.

Table 40. Changes in water absorption of hybrid composites at room temperature

<table>
<thead>
<tr>
<th>Composites</th>
<th>% change in weight</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>week 1 week 2 week 3 week 4 week 5 week 6 week 7 week 8</td>
</tr>
<tr>
<td>GF-PP twin screw (high tex)</td>
<td>0.14 ± 0.15 ± 0.12 ± 0.12 ± 0.15 ± 0.08 ± 0.11 ± 0.12 ±</td>
</tr>
<tr>
<td></td>
<td>0.06 0.03 0.04 0.03 0.04 0.01 0.04 0.02</td>
</tr>
<tr>
<td>Hybrid twin screw (high tex)</td>
<td>2.1 ± 3.2 ± 3.8 ± 4.4 ± 4.5 ± 4.6 ± 4.6 ± 4.7 ±</td>
</tr>
<tr>
<td></td>
<td>0.19 0.26 0.32 0.27 0.22 0.11 0.07 0.06</td>
</tr>
<tr>
<td>Hybrid twin screw (low tex)</td>
<td>1.6 ± 2.3 ± 2.8 ± 3.2 ± 3.6 ± 3.8 ± 4.0 ± 4.0 ±</td>
</tr>
<tr>
<td></td>
<td>0.20 0.25 0.22 0.23 0.21 0.17 0.09 0.10</td>
</tr>
<tr>
<td>Hybrid single screw (high tex)</td>
<td>2.1 ± 3.1 ± 3.9 ± 4.6 ± 4.8 ± 4.8 ± 4.9 ± 4.9 ±</td>
</tr>
<tr>
<td></td>
<td>0.31 0.31 0.33 0.41 0.36 0.30 0.24 0.23</td>
</tr>
</tbody>
</table>

The comparison of the water absorption of three hybrid composites to the GF-PP composite showed that the addition of natural fibre to the matrix greatly increased water absorption. The hemp fibre content of the hybrid composites was in a close range between 21-27 wt%, and it is reasonable to expect a similar behavior from all hybrid composites. However, low tex GF hybrid composites showed a better resistance to water absorption based on the t-test analysis. The use of low tex glass fibre led to significant enhancement in water resistance behaviour in hybrid composites. This could be explained by better wetting of hemp fibres in the twin screw extrusion with lower GF content.
A paired t-test analysis for high tex GF hybrid composite in single and twin screw extrusion showed that twin screw extrusion led to a significant improvement for weeks 5 to 8. Increased water resistant characteristic of composites for twin screw extrusion in the long term could be attributed to the higher shear in twin screw extrusion which led to better distribution of fibres and better wetting of natural fibres.

4.4.6 TGA

Thermogravimetric results for composites processed under different conditions are presented in Table 41. The first region of weight loss, below 100 °C, was due to the release of moisture present in natural fibre, hence this value was zero for pure PP, and highest for the case of hemp-PP. The addition of GF, especially the low tex GF, to hemp-PP composite has reduced the moisture content. All composites showed a lower onset of degradation temperature compared to pure PP. This can be explained by the lower thermal stability of natural fibres.
Table 41. Thermogravimetric results for composites

<table>
<thead>
<tr>
<th>Composites</th>
<th>wt loss % up to 100°C</th>
<th>Onset of degradation temperature (°C)</th>
<th>Max. degradation temperature (°C)</th>
<th>Temperature at 50% wt loss (°C)</th>
<th>Residue at &gt; 800°C (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>0</td>
<td>367</td>
<td>448</td>
<td>434</td>
<td>0.2</td>
</tr>
<tr>
<td>Hemp-PP</td>
<td>0.7</td>
<td>271</td>
<td>462</td>
<td>450</td>
<td>1.2</td>
</tr>
<tr>
<td>Hybrid twin screw (high tex)</td>
<td>0.49</td>
<td>255</td>
<td>462</td>
<td>446</td>
<td>31.3</td>
</tr>
<tr>
<td>Hybrid single screw (high tex)</td>
<td>0.49</td>
<td>253</td>
<td>461</td>
<td>443</td>
<td>5.6</td>
</tr>
<tr>
<td>Hybrid twin screw (low tex)</td>
<td>0.29</td>
<td>265</td>
<td>464</td>
<td>449</td>
<td>21.6</td>
</tr>
</tbody>
</table>

Figure 60 shows the temperature dependence of the sample mass for different composites. As it can be seen polypropylene degrades in a single step that begins around 300 °C and reaches zero mass at 470 °C. For the composites, the weight loss region between 210° and 480 °C are attributed to the decomposition of hemicellulose, cellulose, and lignin in hemp [58].

The addition of fibres makes the plastic more stable as all composites have a higher maximum degradation temperature compared to pure PP. Increase in the maximum degradation temperature in composites could be explained by higher restriction for mobility of molecules due to the addition of glass and hemp fibres.
Higher temperature in each weight loss increment means a higher thermal stability. Composites showed a higher temperature at 50% weight loss compared to pure polypropylene; ergo the addition of fibres increased the thermal stability. The amount of residue after 800 °C represents the glass fibre content in composites. The GF content results from TGA were in good agreement with GF content findings from pyrolysis of composite in the muffle furnace.

4.4.7 SEM

SEM micrographs of fracture surfaces of failed impact specimens were investigated to gain a better understanding of energy absorbing mechanisms and to determine failure mechanisms. SEM also helped to arrive at a stronger conclusion about dispersion of fibres.
Figure 61. Failed impact specimens of high tex long GF-PP tested at room temperature, 3&8) Notched Izod Impact, 11&12) Unnotched Izod Impact

The holes in fracture surfaces of GF-PP specimen in Figure 62 and Figure 63 indicate some fibre pull-out during impact test. Pull-out is a desired mode of fracture as it absorbs large amounts of energy. The length of the fibre has to be less than its critical length for fibre pull-out to occur instead of fibre breaking. Fibre pull-out also suggests that adhesion between fibre and matrix is not strong. Gaps between the fibre and polymer at interface can arise during manufacturing or mechanical testing.
Figure 62. SEM micrographs of fracture surfaces of failed notched Izod impact specimens of long GF-PP composites tested at room temperature (High tex GF)

SEM micrographs of fracture surfaces of failed unnotched Izod impact specimens, Figure 63, revealed substantial fibre pull-out. Unnotched Izod specimens had more fibre pull-out, while notched specimens had more fibre breakage.
Figure 63. SEM micrographs of fracture surfaces of failed unnotched Izod impact specimens of long GF-PP composites tested at room temperature (High tex GF)

Fracture surface of Izod notched and unnotched impact specimen of hybrid composites prepared by single screw extrusion, twin screw with high tex glass fibre and twin screw with low tex glass fibre are shown in Figure 64. In general, more fibre pull-out was observed for the case of Izod unnotched specimen.
Figure 64. SEM micrographs of fracture surface of failed specimen from single screw high tex GF Izod notched (a), single screw high tex GF Izod unnotched (b), twin screw high tex GF Izod notched (c), twin screw high tex GF Izod unnotched (d), twin screw low tex GF Izod notched (e), twin screw low tex GF Izod unnotched (f)
It can be seen that single screw extruded hybrid composites lacked a good dispersion of glass fibres, though it had a lower glass fibre content. Low shear mixing in the single screw extruder, shear rate of 15 sec$^{-1}$, resulted in a poor interface between fibre and matrix as indicated by gaps at interface. Based on SEM results, it can be concluded that a high shear mixing method, i.e. twin screw extrusion, resulted in better dispersion of fibre in matrix. Moreover, SEM examination reveals twin screw extrusion resulted in better alignments of glass fibres in hybrid composites.

### 4.5 Conclusions

The optimum extrusion conditions for producing hemp-GF-PP using the LFT-D process were different from those for producing GF-PP. There was higher shear in the system when the second fibre (hemp) was present, resulting in a higher fibre breakage and a higher glass fibre content. High shear mixing -twin screw extrusion- and low shear mixing -single screw extrusion- methods were investigated. Twin screw compounding significantly increased the tensile, flexural and impact properties. More length retention was achieved in low shear mixing, but reinforcing with the single screw extruder was not as effective. This ineffectiveness was attributed to the lack of good dispersion of fibres in the resin during extrusion and its low GF content. Based on SEM results, it can be concluded that a high shear mixing method resulted in better dispersion of fibres in the matrix.

Mechanical tests showed that unnotched Izod specimens had higher impact strength compared to the notched Izod. SEM micrographs of those fracture surfaces showed more fibre pull-out for the unnotched Izod specimens accordingly. This observation is in agreement with the literature that fibre pull-out is the most energy absorbing failure mechanism and thus the desired one in this study.

Overall, the experimental work carried out here showed that it is possible to develop a process resulting in a hybrid composite exceeding the desired mechanical properties. As a result, the process optimization can help as a guide to design process parameters for the LFT-D process to
produce auto parts with high toughness. The optimum process with twin screw extrusion was carried out at shear rate of 62 sec$^{-1}$, the feeder speed of 10 rpm, temperature of 185$^\circ$C, with no breaker and die with low tex GF. Toughness was influenced by fibre concentration, length and dispersion, and the hybrid composite produced accordingly had a GF content of 20 wt% with an average length of 2.3 mm, and well dispersed fibres. Use of the smaller diameter GF (low tex GF) resulted in an improvement in mechanical performance of hybrid composite and a lower GF content. The twin screw extruder in use continuously stopped working as the motor and feeder speed ratio varied from 10:1. Further investigations using extruders with different designs that would allow changing shear rate and composition may help develop products with longer fibre length and lower GF content. Overall, careful selection of a processing method, processing parameters and type and amount of fibres in the matrix can improve the impact strength and work of fracture of the composites. For the commercial use of these composites as auto parts, reproducibility and economical production become important as well. Prototypes based on the optimum operational conditions for the LFT-D process determined here are currently being developed. The composite developed here was also used for the experimental validation of the developed model in the next chapter.
5 Theoretical Model

The theoretical modeling of work of fracture of hybrid composites is a useful method to help understand the behaviour of composites. There are not many theoretical models available for work of fracture in comparison to well-established models available for tensile strength and modulus of composites. The problem with theoretical models, even the famous models such as Cox for stiffness, Kelly and Tyson for strength, and Cottrell model for impact properties, is that most of them are not well verified by experiments except for the Cox model; and critical properties determined by various models do not coincide well [4]. Additionally, models that are available for work of fracture consider single fibre composites and do not deal with hybrid composites. This is primarily due to the complex nature of work of fracture, and the presence of far too many variables for experimental validation such as the interaction of fibres with the matrix and with each other. In this chapter, some of the available models for work of fracture of single fibre composites are reviewed and a model for work of fracture of hybrid composites is presented. Later, the model is experimentally evaluated by GF-hemp-PP hybrid composites.

5.1 Introduction

Work of fracture is the total energy absorbed during the fracture of a composite. Work of fracture is equal to the area under the load-displacement curve with units of kJ/m². The most common method to investigate work of fracture is the Izod impact test, though this test tends to overestimate the fracture toughness. This is because in addition to the crack opening energy; the impact strength also includes some extra energy such as inelastic collision energy, and the kinetic energy of the broken pieces [104]. Fracture toughness is sometimes measured in terms of the critical stress intensity factor, $K_c$ (MPa.m$^{1/2}$), which is based on the linear elastic fracture mechanism [105]. The initiation of fracture can be described in terms of $K_c$ and the critical energy release rate, $G_c$. However, for ductile polymers such as polypropylene and polyethylene, the total work of fracture is not a material constant since most of the plastic flow work at the crack tip is not directly
associated with the fracture process. In the case of ductile polymers, \( K_c \) and \( G_c \) cannot be used, and only the work dissipated at the fracture process zone is a material constant [106].

Since the impact strength is not an accurate measure of the work of fracture, and \( K_c \) cannot be used for a ductile matrix, the “essential work of fracture” has been proposed for micromechanical modeling. The essential work of fracture is a material property first suggested by Broberg (1968) to describe the toughness of relatively ductile materials. The best method to determine fracture toughness of ductile polymers is through the Essential Work of Fracture (EWF) concept. According to this theory, the energy dissipation upon fracture of a tough material occurs across two parts: the crack tip process zone \( (W_e) \), and an outer plastic zone \( (W_p) \). If a deep edge notched specimen completely yields before fracture, the plastic region is almost circular, with a diameter equal to the ligament length, as shown in Figure 65 [107]. The essential work of fracture is proportional to the ligament length, \( l \), while the work in the plastic region is proportional to \( l^2 \). The work of fracture \( (W_f) \) can be written as follows:

\[
W_f = lt w_e + \beta l^2 t w_p \quad [107, 108] \quad \text{Equation 11}
\]

where \( W_f \) is the work of fracture; \( w_e \) is the essential work of fracture; \( l \) is the ligament length; \( t \) is the specimen thickness; \( \beta \) is a shape factor; and \( w_p \) is the plastic work.

![Figure 65. Test specimen (with thickness of 3 mm) for the essential work of fracture test](image)
The essential work of fracture is the positive intercept of the plot of the specific work of fracture \( w_f \) (the work of fracture divided by \( lt \)) versus the ligament length, \( l \) [108]. The above equation is valid only when there is complete yielding of the ligament before crack initiation. Thus, there is an upper and lower limit for the ligament:

\[
(3 - 5)t \leq l \leq \min\left(\frac{w}{3} \text{ or } 2r_p\right) \quad [109]
\]

where \( t, l, \) and \( w \) are the specimen thickness, ligament length, and specimen width, respectively, and \( 2r_p \) is the size of the plastic zone.

Determination of valid ligament lengths for the EWF test is very crucial as it is one of the biggest sources of error of this theory [110]. The width of specimen needs to be at least three times greater than the ligament length to confine the plastic region sufficiently, thus \( W > 3l \) [111].

5.2 Micromechanical Models (Background)

Although experimental research provides valuable information on composites and their mechanical properties, the dynamic properties and failure behaviour of biocomposites are very complex. Hence, theoretical modeling can be an effective tool to investigate composite behaviour. Micromechanics study mechanical properties of the basic components of a composite, the fibre and the matrix, their interactions, and mechanical properties of the end product. A number of these models for prediction of work of fracture are briefly described below.
5.2.1 Rule of Mixtures

The Rule of Mixtures (ROM) is the simplest model that can predict properties of composite based on properties of fibre and matrix and their respective volume fractions. It assumes fibres to be aligned and oriented in the loading direction. To calculate any material property, the following formula can be applied:

\[ P_c = P_f V_f + P_m V_m \]  

where \( P_c \) is any composite property, \( V_f \) and \( V_m \) are volume fractions of fibre and matrix respectively.

It is worthy of note that \( V_f + V_m = 1 \), under the assumption of no void in composites.

5.2.2 The Cottrell Model

The Cottrell model is commonly used for prediction of work of fracture for unidirectional reinforcement. It is divided into two parts based on the critical length of fibre. The critical length of fibre, \( L_c \), is the shortest fibre length wherein the maximum stress \( \sigma_{\text{max}} = \sigma_{\text{fibre}} \) and is presented by Equation 14. Fibres shorter than the critical length tend to fail by debonding and pull-out, while fibres longer than the \( L_c \) tend to fail under load by breaking.

\[ L_c = \frac{\sigma_f D}{2\tau} \]  

where \( L_c \) is the critical fibre length; \( \sigma_f \) is the fibre strength; \( D \) is the fibre diameter; \( \tau \) is the interfacial strength.
Based on the Cottrell model, work of fracture for a composite is equal to:

\[
\text{when } L < L_c \quad U_c = (1 - V_f)U_m + \left[ \frac{V_f L U_d}{D} \right] + \left[ \frac{V_f L^2 \tau_f}{6D} \right]
\]

Equation 15

\[
\text{when } L > L_c \quad U_c = (1 - V_f)U_m + \left[ \frac{V_f (L - L_c)U_f}{L} \right] + \left[ \frac{V_f L_c^2 U_d}{DL} \right] + \left[ \frac{V_f L_c^3 \tau_f}{6DL} \right]
\]

where \( U_c \) is the work of fracture of composite; \( D \) is the fibre diameter; \( \tau \) is the interfacial strength; \( V_f \) is the volume fraction of fibres; \( L \) is the fibre length; \( U_m,d,f \) is the fracture energy of matrix, interface and fibre respectively; \( \tau_f \) is the interfacial friction during fibre pull-out; and \( L_c \) is the critical fibre length [4]

The first term in both scenarios of the above equation accounts for matrix fracture. For the case of length smaller than the critical length, the second term represents the energy dissipated by fibre debonding, and the third term covers fibre pull-out. For the case of fibres longer than the critical length, the second term is for fibre fracture, while the third and fourth terms are fibre debonding and pull-out respectively applicable only to the portion of fibres that are shorter than the critical length. The Cottrell model is described as a pull-out dominated model by Thomason et al. [4].

Value of \( \tau_f \), interfacial friction during fibre pull-out, can be calculated based on the following equation:

\[
\tau_f = \rho \sigma_R
\]

Equation 16

where \( \rho \) is the coefficient of friction; \( \sigma_R \) is the radial stress due to thermal shrinkage.
Radial stress due to thermal shrinkage, $\sigma_R$, can be calculated according to Equation 17. Values of $E_m$ and $\alpha_m$ can be obtained from DMA (Dynamic Mechanical Analysis) and TMA (Thermo Mechanical Analysis) measurements.

$$\sigma_R = \frac{(\alpha_m - \alpha_f)(T_s - T_t)E_f E_m}{(1 + \nu_f + 2\nu_f)E_f + (1 + \nu_m)E_m} \tag{Equation 17}$$

where $\sigma_R$ is the radial stress due to thermal shrinkage; $\alpha$ is the thermal expansion coefficient; $T_s$ is the matrix solidification temperature; $T_t$ is the testing temperature; $\nu$ is Poisson's ratio; and $E$ is the Young's modulus.

The problem with the Cottrell model is that experimental data does not support it, with the exception of the work on epoxy composite with copper wires as fibres conducted by Cooper [112]. Thomason et al. justify this problem by lack of experimental research due to difficulty of arriving at composite with defined fibre lengths [4].

5.2.3 Fibre Strain Energy Model

Another way of computing work of fracture of composite is using the fibre strain energy model which suggests fibre fracture as the main energy absorbing mechanism. This model considers unidirectional continuous fibre reinforced composites. In this model, the fracture energy of fibres, $U_f$, based on the fibre strength measurement is given by:

$$U_f = \frac{\sigma_f^2 L_d}{2E_f} \tag{[50]} \tag{Equation 18}$$

where $L_d$ is the length of the fibre debonding prior to fibre fracture; $\sigma_f$ is the fibre strength; $E_f$ is the fibre Young’s modulus.
Composite fracture energy, $U_c$, can be presented in a simple form involving matrix fracture, $U_m$, and a term $U_x$ covering all the fibre-related energy dissipation mechanisms:

$$U_c = U_m + V_f (U_x - U_m)$$  \hspace{1cm} \text{Equation 19}$$

$U_x$ can be determined from the slope of the line in impact strength vs. fibre volume fraction plot. As fibre length increases value of $U_x$ increases until it reaches a plateau at long fibre lengths. Assuming fibre fracture as a dominant energy absorption mechanism, $U_x$ is:

$$U_x = U_f \left( \frac{L}{L + L_c} \right)$$ \hspace{1cm} \text{[50] Equation 20}$$

It is known that strength of glass fibres increases with decrease of temperature.

$$\frac{dU_f}{dT} = \frac{2U_f}{\sigma_f} \frac{d\sigma_f}{dT}$$ \hspace{1cm} \text{Equation 21}$$

By substituting Equation 18, Equation 20, and Equation 21 into Equation 19 the following expression is obtained:

$$U_c = V_f \left( \frac{\sigma^2 f L_d}{2E_f} \right) \left( \frac{L}{L + L_c} \right) + (1 - V_f)U_m$$ \hspace{1cm} \text{[50] Equation 22}$$

where $L_d$ is the length of fibre debonded prior to fibre fracture in a composite containing continuous fibres.
The fracture energy is proportional to the amount of fibre (volume fraction), fibre strength or its square, and the length of fibre pulled out. Garkhail et al. reported that the experimental validation of this model shows a good agreement for the case of a debond length of 12 mm in a GF-PP composite. However, the debond length loses its physical meaning due to fitting procedure of the model, as there were some cases where the debond length was higher than the fibre length [113].

The Cottrell model suggests fibre pull-out as the dominant energy absorption mechanism while the Fibre Strain Energy model ignores contribution of fibre pull-out and assumes fibre fracture as the dominant energy absorption mechanism. Fibre pull-out is one of the main energy absorption mechanisms for composites as it accounts for reinforcing role of fibres in preventing brittle rupture of materials, hence disregarding it is not reasonable. In any case, neither of the models are supported by experimental data in the literature and there exists a need for a model for work of fracture of hybrid composites that covers all important energy absorbing mechanisms.

5.3 Model Development for Work of Fracture of Hybrid Biocomposites

The work of fracture can be calculated based on the sum of micro-failure mechanisms. According to the literature, the main failure mechanisms are: fibre and matrix breakage, fibre debonding, and fibre pull-out [50]. The Fibre Strain Energy model is only based on fibre fracture, while the Cottrell model is based on fracture, pull-out and debonding. In this work, aside from considering the major energy absorption mechanisms known in literature, stress redistribution for long fibres was also included in the model. Furthermore, this work deals with hybrid composite of organic and inorganic fibres while most models deal with single fibre composites.

The model developed for the work of fracture uses the Rule of Mixtures model to incorporate the contribution of each of these failure mechanisms for each fibre. Equation 23 presents the preliminary model developed for the work of fracture of hybrid biocomposites. A good model of
the work of fracture of a hybrid composite can give insight into effectiveness of each fracture toughness method. Later, experimental validation is carried out to verify the proposed model.

\[ U_c = (1 - V_{f1} - V_{f2})U_m + U_{po1} + U_{po2} + U_{f1} + U_{f2} + U_{d1} + U_{d2} + U_{sr2} \]  

Equation 23

where \( U_c \) is the total work of fracture of composite; \( V_{f1} \) is the volume fraction of hemp fibres; \( V_{f2} \) is the volume fraction of glass fibres; \( U_m \) is the fracture energy of matrix; \( U_{po1,2} \) is the fracture energy of fibre pull-out; \( U_{f1,2} \) is the fracture energy of fibre fracture; \( U_{d1,2} \) is fracture energy of fibre debonding; and \( U_{sr2} \) is the fracture energy due to stress redistribution in long fibres.

The work of fracture model presented in this thesis connects the following units in series: matrix fracture, fibre pull-out, fibre fracture, fibre debonding, and fibre stress redistribution. Fibre stress redistribution was only considered for the portion of glass fibres that were longer than the critical length. For these fibres, it is possible for the stress to be distributed along the length of the fibre. Furthermore, when the long fibre breaks at a weak point, the fibre instantly relaxes back as its ends are gripped by the matrix [105]. As a result, the strain energy is redistributed from the fibre to the matrix after fracture.

Not all mechanisms necessarily occur in one failure situation; for example fibre fracture is negligible for brittle fibres, as well as in the case of crack propagation of a crack parallel to the fibres in a unidirectional composite [103]. It should be noted, depending on the characteristics of the fibre and the matrix, one or more of the failure mechanisms can be dominating. Equations relating specific work of fracture for different failure mechanisms to properties such as: volume fraction, fibre strength, fibre length and diameter, Young modulus, interfacial shear strength, fibre critical length, and fibre debonding length are available in the literature. There are models available for each mode of failure. Typical formulas for fibre pull-out, fibre fracture, stress redistribution and fibre debonding are presented in Table 42. It can be seen that important factors are fibre
volume fraction, fibre length and fibre strength. As an example, formula derivation for pull-out failure is shown in the appendix to better understand the concept behind energy absorption equations.

Table 42. Summary of failure mechanisms in fibre reinforced composites

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fibre pull-out</td>
<td>( U_{po} = \frac{V_f L^2 \tau_f}{6D} ) [4, 105]</td>
</tr>
<tr>
<td>Fibre fracture</td>
<td>( U_f = \frac{V_f (L - L_c) U_{fr}}{L} ) [4, 105]</td>
</tr>
<tr>
<td>Fibre debonding</td>
<td>( U_d = \frac{V_f \sigma_f^2 L_d}{2E_f} ) [105]</td>
</tr>
<tr>
<td>Fibre stress redistribution</td>
<td>( U_{sr} = \frac{V_f \sigma_f^2 L_c}{3E_f} = \frac{V_f \sigma_f^3 D}{6E_f \tau_f} ) [105]</td>
</tr>
</tbody>
</table>

where \( U_{po} \) is the fracture energy of fibre pull-out; \( U_f \) is the fracture energy of fibre fracture; \( U_d \) is fracture energy of fibre debonding; \( U_{sr} \) is the fracture energy due to stress redistribution in long fibres; \( V_f \) is the volume fraction of fibre; \( L \) is the length of fibre; \( \tau_f \) is the interfacial strength; \( D \) is the fibre diameter; \( L_c \) is the critical length of fibre; \( \sigma_f \) is the fibre strength; \( L_d \) is the debonding length of fibre; \( E_f \) is the Young’s modulus of fibre

5.4 Measuring Model Parameters

Four composites were prepared for experimental validation of the work of fracture model. The composites were produced using the twin screw extruder. The first two composites are the hybrid composites discussed in chapter four. The last two composites were produced under similar
conditions as composites I and II, but at a feeder speed of 7 rpm resulting in a slightly different composition. Glass fibre type, content and length of the composites are presented in Table 43.

Table 43. List of different hybrid composites prepared at shear rate of 62 sec\(^{-1}\) for experimental validation of the work of fracture model

<table>
<thead>
<tr>
<th>Hybrid Composites</th>
<th>GF Type</th>
<th>GF Content (V(_f)% )</th>
<th>Hemp Content (V(_f)% )</th>
<th>GF Length (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>High tex</td>
<td>15.1 ± 4.0</td>
<td>18.7 ± 0.9</td>
<td>0.3 ± 0.3</td>
</tr>
<tr>
<td>II</td>
<td>Low tex</td>
<td>9.7 ± 0.3</td>
<td>19.9 ± 0.1</td>
<td>2.3 ± 1.6</td>
</tr>
<tr>
<td>III</td>
<td>High tex</td>
<td>17.4 ± 0.2</td>
<td>18.2 ± 0.1</td>
<td>0.7 ± 0.4</td>
</tr>
<tr>
<td>IV</td>
<td>Low tex</td>
<td>10.1 ± 0.6</td>
<td>19.8 ± 0.1</td>
<td>1.4 ± 1.6</td>
</tr>
</tbody>
</table>

5.4.1 Essential Work of Fracture

GF-hemp-PP (four types as listed in Table 43), and pure PP were compression molded to 3 mm thick plates after extrusion. Specimens with a width of 2 cm, and a length of 12 cm were cut from compression molded plates. A notch was made in the middle of each specimen using a thin circular blade with a thickness of 0.25 mm. A minimum of 18 specimens per material was prepared for each sample of PP and hybrid composite, with ligament lengths of 6, 8, and 10 mm. The geometry of the specimens used in these experiments is shown in Figure 65. Flexural testing was carried out on the specimens using the three-point bending method specified by ASTM D790 at a crosshead speed of 2 mm/min, with a span of 80 mm -four times the width of specimen.
Work of fracture was calculated as the area under the load-displacement curve which was obtained from this test. Furthermore, the intercept of the plot of work of fracture vs. ligament length is the essential work of fracture ($W_e$) as shown in Figure 66 for the case of PP.

![Work of Fracture vs. Ligament Length Plot](image)

\[ y = 0.1738x + 1.7876 \]
\[ R^2 = 0.9844 \]

Figure 66. Work of fracture vs. ligament length plot for polypropylene for the $W_e$ test

The EWF values for polypropylene and hybrid composites are listed in Table 44. These values are later used as the actual energy required for the composite to fail under impact to validate the theoretical model for the work of fracture of hybrid composites. The matrix fracture is determined by ductility of the matrix, loading rate, and temperature [22]. For composites, aside from these parameters, strength of fibre, dispersion, and interface between fibre and matrix are important parameters.
Table 44. Essential work of fracture values

<table>
<thead>
<tr>
<th>Composites</th>
<th>( W_e ) (J/m(^2))</th>
<th>( \beta W_p ) (kJ/m(^2))</th>
<th>( R^2 ) (Coefficient)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>1788 ± 392</td>
<td>0.1738</td>
<td>0.98</td>
</tr>
<tr>
<td>I</td>
<td>3333 ± 902</td>
<td>0.2704</td>
<td>0.81</td>
</tr>
<tr>
<td>II</td>
<td>3446 ± 792</td>
<td>0.1274</td>
<td>0.99</td>
</tr>
<tr>
<td>III</td>
<td>3474 ± 1483</td>
<td>0.2358</td>
<td>0.62</td>
</tr>
<tr>
<td>IV</td>
<td>3158 ± 1911</td>
<td>0.2593</td>
<td>0.98</td>
</tr>
</tbody>
</table>

5.4.2 Single Fibre Strength Test

Single fibres of hemp, high tex GF, and low tex GF were separated from the batch and were glued in the middle of a paper frame with a slit dimension of 10 mm x 10 mm. Fibres with a length higher than 2 cm were selected and the diameter of the hemp fibres were measured using a calibrated eyepiece microscope. For the case of hemp fibres, five points were measured to find the average diameter of each fibre, whereas the diameters of the glass fibres were obtained from their producer. The strength and modulus of fibres were determined using the Instron tensile machine with load cell of 2 kN, gage length of 10 mm, and test speed of 2 mm/min. Before testing, the edges of paper frames were cut so the entire load was carried by the fibre and not the paper frame.

In the single fibre strength test, the maximum load, maximum stress, and Young’s modulus were measured. The experiment was repeated for approximately one hundred fibres for each case and the average values are shown in Table 45. Comparing the experimental results in Table 45 to the literature values in Table 46 and Table 47 shows that the results are comparable to the values found in the literature. It should be kept in mind that the low tex glass fibre has a smaller diameter in comparison to the high tex glass fibre.
Table 45. Summary of results for the single fibre strength test

<table>
<thead>
<tr>
<th>Fibres</th>
<th>Tensile strength (MPa)</th>
<th>Tensile modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GF (low tex)</td>
<td>2463 ± 727</td>
<td>62.5 ± 50.9</td>
</tr>
<tr>
<td>GF (high tex)</td>
<td>2659 ± 564</td>
<td>47.3 ± 23.0</td>
</tr>
<tr>
<td>Hemp fibre</td>
<td>257 ± 230</td>
<td>8.4 ± 8.7</td>
</tr>
</tbody>
</table>

Values for critical length and interfacial shear strength of glass and hemp fibres were borrowed from literature considering the diameter of the fibres used in the studies. A critical length of 1.96 mm for glass fibre and 2.5 mm for hemp fibre were used in this study based on interpolation of the collected data. Interfacial shear stress was assumed to be 6.5 MPa for glass fibre in PP and 3.43 MPa for hemp fibre in PP. The values for fibre strength and modulus are presented here for comparison to the measured values for the fibres used in this study.

Table 46. Literature values for fibre strength, interfacial shear strength and critical length of GF in PP

<table>
<thead>
<tr>
<th>D (µm)</th>
<th>τ (MPa)</th>
<th>σ (MPa)</th>
<th>Lc (mm)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.8</td>
<td>15.2</td>
<td>1956</td>
<td>0.889</td>
<td>[114]</td>
</tr>
<tr>
<td>11</td>
<td>3.8</td>
<td>-</td>
<td>-</td>
<td>[34]</td>
</tr>
<tr>
<td>12.2</td>
<td>4.07</td>
<td>1401</td>
<td>2.1</td>
<td>[115]</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>3450</td>
<td>0.885</td>
<td>[116]</td>
</tr>
<tr>
<td>-</td>
<td>53-83</td>
<td>1200-1900</td>
<td>-</td>
<td>[50]</td>
</tr>
<tr>
<td>17.5</td>
<td>3 to 6</td>
<td>1500</td>
<td>2.2</td>
<td>[117]</td>
</tr>
<tr>
<td>13.7</td>
<td>-</td>
<td>1657</td>
<td>-</td>
<td>[118]</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>3530</td>
<td>.95</td>
<td>[119]</td>
</tr>
<tr>
<td>11</td>
<td>3.8</td>
<td>1818</td>
<td>2.6</td>
<td>[4]</td>
</tr>
<tr>
<td>13.7</td>
<td>10</td>
<td>2600</td>
<td>1.8</td>
<td>[4]</td>
</tr>
<tr>
<td>-</td>
<td>3.5</td>
<td>2378</td>
<td>-</td>
<td>[120]</td>
</tr>
</tbody>
</table>
Table 47. Literature values for fibre strength, interfacial shear strength, critical length and Young’s modulus of hemp fibre in PP

<table>
<thead>
<tr>
<th>D (µm)</th>
<th>τ (MPa)</th>
<th>σ (MPa)</th>
<th>L_{c} (mm)</th>
<th>E (GPa)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>65</td>
<td>4.7</td>
<td>2140</td>
<td>3.4</td>
<td>-</td>
<td>[102]</td>
</tr>
<tr>
<td>10.86</td>
<td>6</td>
<td>2099</td>
<td>2.5</td>
<td>-</td>
<td>[43]</td>
</tr>
<tr>
<td>10.86*</td>
<td>3.43</td>
<td>381</td>
<td>1.9</td>
<td>-</td>
<td>[43]</td>
</tr>
<tr>
<td>50.6</td>
<td>-</td>
<td>-</td>
<td>2.81</td>
<td>-</td>
<td>[115]</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>962</td>
<td>-</td>
<td>-</td>
<td>[63]</td>
</tr>
<tr>
<td>25-35</td>
<td>-</td>
<td>132</td>
<td>-</td>
<td>11.1</td>
<td>[121]</td>
</tr>
<tr>
<td>26.5</td>
<td>-</td>
<td>514</td>
<td>-</td>
<td>24.8</td>
<td>[122]</td>
</tr>
</tbody>
</table>

Note: * case is with the addition of 5% MAPP

5.4.3 Length of Debonding

Wells et al. investigated the relationship between the average pull-out length and debond length by varying several parameters [1]. Figure 67 shows a schematic drawing to give a better idea of the length of fibre debonding. They found an experimental correlation between average fibre pull-out and fibre debond length for the case of glass and Kevlar reinforced composites.

\[ l_{p} = l_{d} / 6.8 \]  \hspace{1cm} [1]  

Where \( l_{p} \) is pull-out length and \( l_{d} \) is final debonded length on both sides of the matrix

This approximation is accurate within ± 10% for \( l_{p} < 0.3 \) mm (or \( l_{d} < 2.1 \) mm) [1]. Average pull-out length can be determined from averaging out the length of the glass fibre pulled out from SEM images of the fractured surface. Using SEM pictures of composites to investigate a few hundred pulled out fibres is the most common method to determine fibre pull-out length [123]. Using the above equation, debond length can be determined, and thus the work of debonding can be calculated.
Accordingly, debonding length was determined to be $0.016 \pm 0.013$ mm for composite I, and $0.015 \pm 0.010$ mm for composite II, based on SEM analysis.

### 5.4.4 Fibre Volume Fraction Calculation

The fibre volume fraction was calculated from weight measurement using the following equation.

$$V_{f1} = \frac{W_{f1}}{\rho_{f1}} \frac{W_{f1}}{\rho_{f1}} + \frac{W_{f2}}{\rho_{f2}} + \frac{W_m}{\rho_m}$$

Equation 29

Where $V_{f1,2}$ is the volume fraction of fibres; $W_{f1,2}$ is the weight of fibres; $W_m$ is the weight of matrix; $\rho_{f1,2}$ is the density of fibres; and $\rho_m$ is the density of matrix.

Calculations for the volume fraction of hemp and glass fibres are shown in Table 48. Fibre density values were provided by their suppliers. Mass of composite was calculated based on the weight of
the empty crucible and then with a small sample of hybrid composite. Samples were weighed before and after burning in the muffle furnace for 3 hours at 600°C. Both matrix and hemp fibres were completely removed in the muffle furnace, leaving only the glass fibres behind. Subtraction of the mass of glass fibre from the mass of composite results in the mass of hemp, polypropylene and MAPP together. Mass of hemp and PP were calculated based on the weight fraction used during compounding the composite. Knowing the mass and the density of hemp, glass fibre, and PP, along using Equation 29 allowed for the calculation of the volume fractions of fibres.

Table 48. Volume fraction for hemp-GF-PP hybrid composite II

<table>
<thead>
<tr>
<th>No.</th>
<th>Mass of Composite (M&lt;sub&gt;c&lt;/sub&gt;) (g)</th>
<th>Mass of GF (W&lt;sub&gt;f2&lt;/sub&gt;) (g)</th>
<th>Mass of PP + Hemp + MAPP (g)</th>
<th>Mass of Hemp (W&lt;sub&gt;f1&lt;/sub&gt;) (g)</th>
<th>Mass of PP (W&lt;sub&gt;m&lt;/sub&gt;) (g)</th>
<th>V&lt;sub&gt;f&lt;/sub&gt;(GF) (%)</th>
<th>V&lt;sub&gt;f&lt;/sub&gt;(Hemp) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.47</td>
<td>2.32</td>
<td>9.15</td>
<td>2.75</td>
<td>5.95</td>
<td>9.74</td>
<td>19.87</td>
</tr>
<tr>
<td>3</td>
<td>9.96</td>
<td>2.06</td>
<td>7.90</td>
<td>2.37</td>
<td>5.14</td>
<td>10.01</td>
<td>19.81</td>
</tr>
<tr>
<td>4</td>
<td>21.07</td>
<td>4.25</td>
<td>16.82</td>
<td>5.05</td>
<td>10.93</td>
<td>9.71</td>
<td>19.87</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>9.67</td>
<td>19.88</td>
</tr>
</tbody>
</table>

The average volume fractions of fibres obtained based on similar calculations, using at least three samples, are listed in Table 49.

Table 49. Average volume fractions of glass fibre and hemp fibre for three hybrid composites

<table>
<thead>
<tr>
<th>Composite</th>
<th>V&lt;sub&gt;f&lt;/sub&gt;(GF) (%)</th>
<th>V&lt;sub&gt;f&lt;/sub&gt;(Hemp) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>15.1 ± 3.9</td>
<td>18.7 ± 0.9</td>
</tr>
<tr>
<td>II</td>
<td>9.7 ± 0.3</td>
<td>19.9 ± 0.1</td>
</tr>
<tr>
<td>III</td>
<td>17.4 ± 0.2</td>
<td>18.2 ± 0.1</td>
</tr>
<tr>
<td>IV</td>
<td>10.1 ± 0.6</td>
<td>19.8 ± 0.1</td>
</tr>
</tbody>
</table>
5.5 Derivation of Work of Fracture Model for Hybrid Composites

The following assumptions were made to arrive at the theoretical model:

- A perfect bonding exists at the fibre-matrix interface, implying stress transfer is occurring without any yield or slip.
- There is no fibre-fibre interaction between hemp and glass fibres.
- The Rule of Mixtures applies.
- Interfacial shear stress, \( \tau \), is constant during fibre pull-out [103].
- Straight fibres are perfectly elastic up to their breaking point, \( \sigma_f \) (true for GF) [103].
- The matrix is assumed to be entirely elastic [103].
- Fibre length distribution is normal.
- Fibres are aligned in the matrix and thus, there is no need to consider fibre orientation.
- Aligned fibres have the same aspect ratio, identical in shape and size [103].

The failure mechanisms can be classified into three terms: matrix related; fibre related- fracture, stress redistribution; and interface related- pull-out and debonding. A model for the total work of fracture using the Rule of Mixtures, and assuming that the main fracture mechanisms are matrix fracture, fibre pull-out, fibre fracture, fibre debonding, and fibre stress redistribution is presented here (Equation 23):

\[
U_C = (1 - V_{f1} - V_{f2})U_m + U_{Po1} + U_{Po2} + U_{f1} + U_{f2} + U_{d1} + U_{d2} + U_{sr2}
\]

Glass fibres with a length less than the critical length would fail through pull-out, while longer fibres fail through fracture and stress redistribution of fibres after fracture. For the glass fibre component in the model, work of fibre fracture was assumed to be zero due to the brittle nature of glass fibres [103]. The work of debonding was found based on Equation 26 in section 5.3, using the length of debonding. The length of debonding for glass fibres was found based on the fibre pull-out length as explained in section 5.4.3. The work of fibre pull-out was calculated based on
Equation 24 for the short portion of fibres. For example, in the case of composite II 48% of glass fibres were short (L < Lc) with an average length of 0.3 mm, while 52% were long (L > Lc) with an average length of 9 mm. The work of stress redistribution was calculated based on Equation 27, only accounting for the long glass fibres.

Fibre fracture for hemp was assumed to be zero as all hemp fibres had a length much below the critical length, and thus all fibres were expected to be pulled out. According to Piggott, work of fibre fracture is negligible when S < S_c - for the case of short fibres [103]. Work of debonding for hemp was assumed to be negligible. The reason for this was that the calculated work of debonding for glass fibre was about 140 J/m^2, and since hemp fibres were much shorter than glass fibres, they would have lower work of debonding in comparison to GF. Therefore, it is reasonable to neglect this term for hemp as it will hold a very small value. The best manner in which to calculate debonding energy is to use length of debonding that can be related to pull-out length which is obtained from SEM of fractured specimen; however, as mentioned, due to the small size of hemp fibres and low contrast in SEM for hybrid composites, it was not possible to find these values from SEM as was the case for the glass fibre. Thus, the total work of fracture can be estimated based on the following equation which is a modified ROM model for work of fracture of hybrid composites:

\[
U_c \simeq (1-V_{f1}-V_{f2})U_m + \frac{V_{f1}L_{1}^2\tau_{f1}}{6D_1} + \frac{aV_{f2}L_{2}^2\tau_{f2}}{6D_2} + \frac{aV_{f2}\sigma_{f2}^2l_{d2}}{2E_{f2}} + \frac{bV_{f2}\sigma_{f2}^3D_2}{6E_{f2}\tau_{f2}}
\]

Equation 30

Where \( U_{c,m} \) are the work of fracture of hybrid composite and matrix; \( V_f \) is the volume fraction of fibres (\( f_1 \) is hemp, and \( f_2 \) is GF); \( a \) is the % of short portion of glass fibres (L < Lc); \( b \) is the % of long portion of glass fibres (L > Lc); \( L \) is the fibre length; \( \tau_f \) is the interfacial friction during fibre pull-out; \( D \) is the fibre diameter; \( \sigma_f \) is the fibre strength; \( l_{d2} \) is the GF debonding length; \( E_{f2} \) is the GF Young’s modulus
The above equation was developed for unidirectional fibres and the effect of fibre orientation was not taken into consideration. What is clear is that the work of fracture is dependent on the volume fraction of fibres, length of fibres, diameter of fibres, square of fibre strength, interfacial strength, and fibre’s Young’s modulus.

5.6 Experimental Validation

It is expected that the presented theoretical model, Equation 30, would not be exact as it assumes perfect interfacial properties among a number of other simplifying assumptions. To validate the model, hybrid composites with different GF lengths and concentrations were tested for work of fracture. GF length and concentration were determined after pyrolysis of the hybrid composite. Through production of hybrid composites under different conditions, GF length and concentration were varied as much as possible under the limitations of the extruder and the LFT-D process. Two different GF diameters were used as part of model validation (high tex GF had a higher diameter). The experimental values for total work of fracture, and matrix work of fracture were determined by the EWF test. Parameters used in theoretical model which were measured experimentally are listed in Table 50.

Table 50. Experimental parameters used for the calculation of work of fracture of hybrid composites

<table>
<thead>
<tr>
<th>Composites</th>
<th>GF diameter (µm)</th>
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<th>GF strength (MPa)</th>
<th>GF modulus (GPa)</th>
<th>GF debonding length (µm)</th>
<th>Work of composite fracture (J/m²)</th>
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Two simplifications were applied during experimental validation of the work of fracture model: a) GF debonding length for composites III and IV were assumed to be equal to composites I and II respectively and SEM analysis was not carried out for them. Composites I and III, and composites II and IV were only slightly different in composition due to change of the feeder speed (10 rpm vs. 7 rpm). In any case, this assumption had negligible effects since debonding energy of fibres held a small value. b) the value for interfacial shear strength was borrowed from the literature. As shown in Table 46 and Table 47, there is a wide range of data for this value in various sources. Considering the fibre diameter, an average was interpolated and used for the model prediction. Clearly, accuracy of this value along with other experimentally measured values will affect the model prediction.

The work of fracture for hybrid composites extruded under different conditions was calculated according to the model presented in this thesis. Model predictions were compared to the experimental values determined from the EWF test for hybrid composites.
The presented model predicts an increase in work of fracture as GF length increases. Having longer fibres results in presence of larger effective area for stress redistribution which act as the stress release points hence enhances energy absorption capacity of composites. The predicted work of fracture for GF length below 0.3 mm was underestimated by the model. This could mean that there were other failure mechanisms involved that were not accounted for in the model. Also, this sample was the only case where stress redistribution was not included and all fibres were shorter than the critical length. On the other hand, the predicted work of fracture for the composite with the average GF length exceeding the $L_c$, i.e. $\bar{L}=2.3$ mm, was overestimated. Although model prediction shows dependence between work of fracture of hybrid composite and glass fibre length, the experimental data do not show any dependence of fibre length for glass fibre length up to 2.3 mm. This could be due to poor dispersion of long fibres in the matrix, which leads to poor interface between fibres and matrix and hence not a good transfer of load from matrix to fibres. Consequently, the matrix probably failed before full potential of reinforcement by fibres was appreciated; hence, in practice less energy was required for failure.
As discussed earlier, the developed model does not consider fibre orientation and interaction. Considering that composites were compression molded, fibres should be fairly well oriented, hence the insight we gain from the discrepancies between the predicted and experimental values is that fibre interaction needs to be considered to get better prediction agreement for GF length. Other factors resulting in the difference were simplifying model assumptions and possible errors in estimation of model parameters. Here fibres were assumed to have normal length distribution with a small standard deviation, while samples of residual glass fibres obtained from the composite showed a wide range of length distribution with high standard deviations. In practice there is a wide distribution in length of fibres, therefore accounting for distribution in fibre length can further improve the model. It should be remembered that the objective of this work was to develop a model capturing the main experimental trends without unnecessarily complicating the predictions and these issues are out of scope of this study.

5.7 Theoretical Predictions

To better understand failure mechanisms, theoretical percentage contributions to the total work of fracture based on the presented model are shown in pie charts, Figure 69. Here $U_m$ is the matrix fracture, $U_{po1}$ is the hemp pull-out, $U_{po2}$ is the GF pull-out, $U_{d2}$ is the GF debonding, $U_{sr2}$ is the GF stress redistribution. For the case of composite I, the model predicted the matrix fracture as the governing failure mechanism, followed by fibre pull-out. Fibre pull-out held about 24% of the total work of fracture for composite I.
There is a competition between matrix deformation and fibre-related toughening. Matrix deformation plays an important role in the hybrid composites analyzed here, ranging from 26 to 65%. This can be explained by relatively low concentrations of rigid glass fibre which allows matrix deformation. Similar observations were made by Tjong et al. for hybrid composites containing less than 15wt% GF, while fibre pull-out and debonding mechanisms dominated for hybrid composites with short glass fibre content greater than 20wt% [116].
For the case of composite II and IV, the model predicted the stress redistribution of long glass fibres and matrix fracture as the governing failure mechanisms. As composite II and IV had longer fibres, it was possible for the stress to be distributed along the length of the fibres. Here when the long fibres broke at weak points, fibres instantly relaxed back as their ends were gripped by the matrix, and strain energy was redistributed from the fibres to the matrix after the fracture. Higher work of fracture of composite II compared to IV despite their similar GF content is attributable to its longer fibres. Long fibres with $L > L_c$ facilitated stress redistribution for GF while fibre fracture was not considered due to the brittle nature of GF.

Comparing the work of debonding of glass fibres between high tex and low tex GF twin screw extruded composites (I and II); it can be seen that as the number of fibres and fibre diameter increased in roving in high tex GF, higher values of fibre debonding were achieved as there were more fibres available for debonding. This observation is in good agreement with the results from the work of Beaumont et al. [123]. Additionally, when low tex GF was used, the length of fibres was better preserved and the work of fracture for composite II with 50% less GF content was even higher than that for composite I due to presence of fibres with greater length and lower diameter.

Both composites I and III were reinforced with high tex GF and had similar GF content, but composite III had slightly higher work of fracture due to its longer glass fibres. For both composites, the average length of fibres was less than the critical length of GF, but having longer short fibres enhanced the work of pull-out for composite III. As expected, the main failure mechanism for composite III after matrix fracture was fibre pull-out. In the literature, the energy dissipated by the matrix is usually small as presence of fibres prevents large deformations by the matrix [4]. Here the model has predicted the matrix fracture as one of the dominant failure mechanisms. This energy dissipation by the matrix could be due to the ductile nature of polypropylene.
Aside from predicting the percentage contribution for each failure mechanism, the developed model was used to predict how the work of fracture would be affected by changes in parameters. By varying one parameter while keeping the rest constant, the effect of that parameter on the work of fracture was determined. Using the presented model, effects of change in diameter, and volume fraction on the work of fracture of hybrid composite were investigated. The presented model for work of fracture was compared against the Cottrell model using experimental data from four hybrid composites.

*Diameter of Glass Fibre*

![Graph showing effect of diameter of glass fibre on the work of fracture of hybrid composite](image)

Figure 70. Model prediction for the effect of diameter of glass fibre on the work of fracture of hybrid composite

Figure 70 shows the prediction of the developed model for diameter of GF as well as experimental data for the hybrid composites. As GF diameter increases from 10 to 35 µm, the presented model
predicts approximately a 30% reduction in the work of fracture while the Cottrell model predicts a 53% reduction. An increase in the glass fibre diameter means a decrease in its aspect ratio, hence its reinforcing ability. Furthermore, as the fibre diameter increases so do the chances of the fibre having defects. The presence of defects and micro cracks in the system causes the system to fail under smaller loads, hence a lower work of fracture. Moreover, an increase in the diameter can also facilitate debonding, which is a low energy dissipating mechanism. As fibre diameter decreases, more energy is required for fibre debonding, and fibre pull-out. Since the fibre pull-out is responsible for much of the toughness in the composite, varying the glass fibre diameter affects work of fracture. An examination of Equation 24 shows an inverse relationship between work of pull-out and the fibre diameter.

*Volume Fraction of Glass Fibre*

![Graph showing the effect of volume fraction of glass fibre on the work of fracture of hybrid composite](image)

Figure 71. Model prediction for the effect of volume fraction of glass fibre on the work of fracture of hybrid composite
The dependence of the work of fracture of hybrid biocomposites to volume fraction of GF is shown in Figure 71. For an increase in the GF volume fraction from 5 to 30%, the presented model predicts nearly 175% increase in the work of fracture of hybrid composites; while the Cottrell model exhibits over 300% increase in the work of fracture. On the other hand, the experimental data did not show a dependence on GF volume fraction which could be due to poor dispersion of fibres as volume fraction increases. It is well known that the amount of fibres in a matrix affects their reinforcing properties in a composite. Here as the volume fraction of GF increases, the matrix contribution to the work of fracture reduces, while the contribution of fibre pull-out, debonding and stress redistribution increase. Overall, an increase in volume fraction of glass fibre leads to an increase in the work of fracture of the composite due to high strength of this synthetic fibre. However, as the objective of this project was to minimize the use of synthetic fibres, this option would not be considered for an enhancement of the work of fracture of the hybrid composite.

*Volume Fraction of Hemp Fibre*

![Graph](image)

Figure 72. Model prediction for the effect of volume fraction of hemp fibre on the work of fracture of hybrid composite
Negligible hemp content dependence was predicted for the hybrid composites as shown in Figure 72. According to the presented model, an increase in the volume fraction of hemp fibre from 10 to 35% leads to less than 5% reduction of the total work of fracture. On the other hand, the Cottrell model shows a 3% increase in the work of fracture as hemp content increase from 10 to 35%. Higher hemp contents result in products that are lighter, less expensive, and more environmentally friendly. Further experimental investigation needs to be carried out to validate this correlation for hybrid biocomposites since fibre-fibre interaction was not accounted for in the derived model, and increasing volume fraction of hemp can change the conditions of the system.

Overall, the presented model was in better agreement with the experimental data when compared to the Cottrell model in predicting the work of fracture of hybrid thermoplastic composites containing organic and inorganic fibres. This comparison showed benefits of the addition of stress redistribution of long fibres.

5.8 Conclusions

Developing an analytical model can help save time and experimental costs by assisting in the selection of fibres and process specifications to achieve the desired toughness properties. The objective of the current study was to develop a simple model for work of fracture of hybrid composites. Major energy absorbing failure mechanisms were fibre stress redistribution, matrix fracture and fibre pull-out. The developed model shows work of fracture depends on fibre length, volume fraction, diameter, strength and interfacial properties of the composite.

The objective of this chapter was to develop a model capturing the main experimental trends without over-complicating it. The presented model for work of fracture is a modified ROM accounting for matrix failure, fibre pull-out and fibre debonding for fibres shorter than critical length, with addition of fibre stress redistribution for longer fibres. The presented model has some
limitations due to its assumptions. There are some deviations between the experimental data and model predictions which are probably due to errors in estimation of model parameters and simplifying assumptions such as no fibre-fibre interaction, perfect adhesion and dismissing fibre orientation in the system. Nevertheless, it is possible to observe some useful correlations between the work of fracture for hybrid biocomposites and properties of fibres, matrix, and interface. For the case of hybrid composites with long fibres, dominant failure mechanisms are fibre redistribution and matrix failure, while for the case of short fibre composites fibre pull-out and matrix failure are the dominant ones.

A number of recommendations for the production of tough hybrid biocomposites can be drawn based on the derived theoretical model. For example, experimental studies showed a lower diameter leads to a higher work of fracture for the same processing condition. The model predicts approximately a 30% reduction in the work of fracture when the GF diameter increases from 10 to 35 µm. The model predicts a 175% increase in the work of fracture of hybrid composites as GF volume fraction increases from 5 to 30%. On the other hand, increasing the content of natural fibre from 10 to 35% leads to less than 5% decrease in the work of fracture. Minor effects of increasing the natural fibre volume fraction on toughness of hybrid composites allows production of more economical, lighter weight and environmentally friendly composites by increasing the NF content. Theoretically, improvement in the work of fracture can be observed by increasing the length of glass fibre. Fibre ends act as stress concentrator points, hence toughness can increase with increasing the length of fibres. It can be concluded that increasing the length of fibres and achieving a fibre length around the critical length leads to the maximum use of fibre potential. Seeing as, if the length is below the critical length, pull out work is maximized and if it is above the critical length, stress redistribution dissipates the energy along the brittle fibres. In general, higher aspect ratio fibres can enhance the work of fracture of hybrid biocomposite as shown experimentally and theoretically. In order to produce hybrid composites with high work of fracture the focus should be on fibre processing to arrive at an optimum length and aspect ratio, volume fraction, and good dispersion.
6 Conclusions and Recommendations

6.1 Conclusions

The following conclusions were drawn from the various results discussed in this thesis.

- Hemp fibres had a higher crystallinity index compared to sisal fibres, which was expected since they have a lower lignin, pectin, and wax content.
- The crystallinity index of hemp slightly increased after surface treatments due to partial removal of amorphous pectin and lignin.
- TGA showed an increase in thermal stability in treated hemp fibres, except for the alkalized/acetylated fibre in both mediums.
- Combination of surface pre-treatment with MAPP treatment showed some improvements in mechanical performance for sisal-PP composite, but failed to enhance composite performance for hemp-PP composite which was the focus of this thesis. As a result, untreated hemp fibres were used for compounding with GF-PP with addition of 5% MAPP to enhance fibre-matrix interaction.
- Single screw extrusion – low shear mixing- led to longer GF length, lower GF content, but poor dispersion of fibres in the matrix, hence a low work of fracture. Twin screw extrusion – high shear mixing- produced composites with higher toughness, and better fibre dispersion as shown by SEM.
- SEM micrographs of fracture surfaces showed more fibre pull-out for unnotched Izod specimens.
- Process optimization led to production of a hybrid hemp-GF-PP which significantly exceeded the desired mechanical properties with notched impact strength of 131 ± 12 J/m, tensile strength of 92 ± 7 MPa, and flexural strength of 160 ± 15 MPa.
- Compounding was carried out at an optimum shear rate of 62 sec⁻¹ with no breaker and die while feeding glass fibre into a port before the vent.
• Toughness was influenced by fibre concentration, length and dispersion, and the hybrid composite produced accordingly had well dispersed fibres with a GF content of 20 wt% and an average length of 2.3 mm.

• Replacement of hemp fibre by hemp dust to evaluate reinforcing role of hemp fibre in hybrid hemp-GF-PP composite showed that using hemp with a longer length enhanced the mechanical properties of composite.

• Use of low tex GF with a smaller diameter led to a lower GF content and longer GF length, and improvement in mechanical performance compared to high tex GF.

• For the case of hybrid composites with long fibres, dominant failure mechanisms are fibre redistribution and matrix failure, while for the case of short fibre composites fibre pull-out and matrix failure are the dominant ones.

• The work of fracture model presented in this thesis was a modified ROM accounting for matrix failure, fibre pull-out and fibre debonding for short fibres and fibre stress redistribution for long fibres.

• The presented model showed that the work of fracture depends on fibre length, volume fraction, diameter, strength and interfacial properties of the composite.

• The model predicted approximately a 30% reduction in the work of fracture when the GF diameter increased from 10 to 35 µm.

• The model predicted a 175% increase in the work of fracture of hybrid composites as GF volume fraction increased from 5 to 30%.

• The model suggested that increasing the content of natural fibre from 10 to 35% led to less than 5% decrease in the work of fracture. The minor effect of increasing natural fibre volume fraction on toughness of hybrid composites allows the production of a more economical, lighter weight, and environmentally friendly composite by increasing the NF content without sacrificing work of fracture of hybrid composite. Some problems could rise from high wood content in polymer composites such as agglomeration and poor dispersion of fibres, burning of fibres, and increase in viscosity. A study should be carried out to find the optimum maximum fibre loading in the hybrid composite.

• Increasing the length of glass fibre and achieving a fibre length around the critical length of fibre leads to the maximum use of fibre potential, since if length is below the critical
length, pull out work is maximized and if above the critical length, energy is dissipated through stress redistribution for brittle fibres. The focus should be on fibre processing to arrive at optimum length and aspect ratio, volume fraction, and good dispersion.

6.2 Recommendations

This study achieved hemp-GF-PP hybrid composites with very high toughness values using LFT-D process and feeding glass fibre roving at various positions. Shear rate was varied and effects of fibre length and fibre-matrix interaction were studied. This work resulted in significantly superior mechanical properties compared to other studies available for hybrid composite produced through extrusion and compression molding. Process optimization resulted in retaining length of glass fibre, and dispersion of micro and long fibres in resin led to a tough hybrid composite. The study also established that use of MAPP coupling agent alone is the best treatment for hemp micro-fibres.

Number of experimental data points to validate the model was limited due to restrictions of the extruder machine. The twin screw extruder continuously stopped working as motor and feeder speed ratio varied from 10:1. The motor speed controlled shear rate and the feeder speed controlled product composition. Further investigations using extruders with different designs that would allow changing shear and composition may help to produce more experimental points for model validation.

The dominant factors governing the work of fracture of hybrid composites are fibre length, diameter, content, dispersion and interfacial properties. The following recommendations were made based on the modeling of work of fracture for hybrid composites to further enhance toughness:
a) Increasing the length of hemp fibre can enhance the work of fracture. This is because a great amount of work is involved in the breaking of hollow natural fibres which have walls with a spiral structure. Splitting and crumpling of the cellulose walls can enhance the toughness of composites [103]. Hence, incorporating long hemp fibres which would break as they fail would enhance work of fracture. Since in this project natural fibres were much shorter than the critical length and were all pulled out, the benefit of this toughening mechanism may have not been fully used, and it is something that may be further investigated. It may also be that entanglement and poor dispersion of long natural fibres negatively affects its potential to increase toughness as length of fibres increase.

b) Decreasing the diameter of GF and increasing its length would enhance toughness. For example, composite II with a smaller diameter and a longer length, had a higher work of fracture although it had 50% less GF content compared to composite I. GF diameter does not vary during its production, but length of GF can change substantially by varying shear rate and composition. In this case, due to limitations of the extruders, screw design needs to be varied to allow greater fibre length in the system.

c) According to Piggott, pull-out work and stress redistribution work can be very large [103]. Accordingly, the best solution seems to be having long fibres with average length close to the critical length. If the length is above the critical length, then stress redistribution would dissipate energy along the fibre. On the other hand, if the length is below the critical length, pull-out is maximized as fibres with a higher length would require more energy to be pulled out. As an example composite III had a higher work of pull-out compared to composite I, even though both mainly had short fibres. Composite III had longer short fibres (L=0.6 mm) in comparison to composite I (L=0.3 mm). In general, the incorporation of fibres with higher aspect ratios (L/D) in composites results in an improvement in the work of fracture.

d) Using stronger fibres and better sizing agents could enhance the work of fracture. The enforced stress on composites can be better transferred from matrix to fibres, when a suitable sizing agent is used due to better adhesion between fibres and matrix. It should be noted that a strong adhesion
between fibre and matrix results in a higher tensile strength and a lower impact strength. This is because most fibres break rather than being pulled out when there is good adhesion between fibres and matrix. In order to enhance impact properties, it is necessary to optimize adhesion in a way that the impact strength is maximized while tensile strength is satisfactory. In order to explore this area, type and concentration of GF sizing agent and compatibilizer used for natural fibre can be changed to investigate adhesion between fibres and matrix which is beyond the scope of this work.

e) Increasing hemp volume fraction is predicted to have minor effects on the toughness of composites. The production of natural fibres consumes less energy compared to synthetic fibres and is more economical and environmentally friendly. Their application also results in weight savings for the final product which subsequently results in fuel saving for the auto industry. As a result, an increase in hemp fibre content can be beneficial, but further experimental investigation needs to be carried out to validate this correlation for hybrid biocomposites as fibre-fibre interaction was not accounted for in the developed model. Some problems could rise from high wood content in polymer composites such as agglomeration and poor dispersion of fibres, burning of fibres, and increase in viscosity. A study should be carried out to find the optimum maximum fibre loading in the hybrid composite. Ashori et al. suggested a 35 wt% fibre loading for effective stress transfer in hybrid NF-GF-composites and reported a decrease in impact strength as fibre loading increased beyond this point [95].

f) Increasing volume fraction of GF would enhance toughness, but product specifications should be considered regarding the GF content. This project required GF content below 20%, and thus this root cannot be tested. It should be noted that as GF content increases, GF length may decrease after a certain point due to fibre-fibre interaction. Thus, there might be a maximum GF volume fraction for the system which could be determined experimentally.

g) Aside from fibres, the matrix also has a critical role as it protects the fibres and transfers stress from one fibre to another. Reducing the damage to the matrix can enhance the performance of a composite. A number of techniques can be applied to improve the toughness of matrix in composite such as the use of plasticizing modifiers, and the addition of rubber particles (ex. carboxyl
terminated butadiene) [124]. For the case of toughened matrix, it is necessary to improve the fibre-matrix bond strength as well to reduce material failure at the interface before the full benefit of toughened matrix is realized [50]. On the other hand, it is desired to increase probability of fibre pull-out as it is one of the main sources of fracture toughness. To promote fibre pull-out, it would be necessary to have high frictional shear strength, $\tau_f$, as well as weak interfacial bond strength, $\tau_b$. Thus, a balance needs to be reached for optimum composite. If the interface is too strong, brittle fracture with relatively low energy absorption would dominate, whereas if the interface is weak, high energy absorbing mechanism such as fibre pull-out and debonding dominate composite failure [22].

As part of the future work, fibre-fibre interaction and fibre length distribution can be investigated. Effects of pre-treatment can be further studied by increasing concentration and time of treatments for hemp microfibres since it is possible that there were not enough reagents for the exposed hydroxyl groups in refined hemp microfibres. A cost analysis for surface treatment has to be studied as well.

The engineering contribution of this work is production of long glass fibre hybrid biocomposites through LFT-D that exceeds the desired mechanical properties. The most important scientific contribution of this research is understanding microfibre dispersion in relation to glass fibre length preservation. Application of energy principles has led to production of a hybrid composite with high energy absorbing capacities designed through incorporation of short and long fibres. Long fibres can dissipate energy along their length and short fibres can have more influence in bridging of micro-cracks. Short fibres are expected to be better oriented due to limitations of space for their rotation imposed by longer fibres.
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Appendices

Appendix 1 - Formula Derivation

Details of the calculation to derive the work of fibre pull-out for fibres with a length of 2L as discussed by Piggott is presented here as an example of formula derivation for the equations listed in Table 42 [103]. As shown in Figure 73, the tensile strength of fibres are governed by an interfacial shear stress parallel to fibre surface, which has a constant value, $\tau$, near the ends and is zero near the centre. It is assumed that the fibres are aligned and have same aspect ratio.

Figure 73. Single fibre embedded in matrix (a) unstressed and (b) stressed. (c) shows the fibre-matrix interfacial stress and the fibre internal stress for stress transfer by slip [103]
Fibre with an aspect ratio less than $S_c$ will pull out and $\sigma_f$ decreases linearly with embedded length. Force required to pull out the fibre with embedded length $l$ is $\tau_i\pi Dl$ (see Figure 74).

![Figure 74. Fibre pull-out stresses [103]](image)

The work of pull-out for one fibre is

$$W_{po} = \int_0^l \sigma_f \, dx = \int_0^l \tau_i\pi D \, dx = \tau_i\pi D \frac{l^2}{2}$$  \hspace{1cm} \text{Equation 31}

The work of pull-out for different distribution of fibres with $0 < L < L_c$ is

$$U_{fp} = \int_0^{kc/2} W_{po}(L) \, dl = \int_0^{kc/2} \tau_i\pi D \frac{l^2}{2} \, dl = \tau_i\pi D \frac{l^3}{6}$$  \hspace{1cm} \text{Equation 32}

Assuming there are $N$ fibres crossing the unit area of the crack, the number with an embedded length between $l$ and $l+dl$ on one side of the crack is $Ndl/L$ where $2L$ is the fibre length. Assuming parallel fibres which are randomly dispersed. Work of pull-out is $G_{fp}/2$, since we are considering one side only.
\[ G_{fp} / 2 = \int_{0}^{L} \frac{NU_{fp} dL}{2L} \]  

Equation 33

Since \( V = N\pi r^2 \) and \( S = L/r \), \( D = \) fibre diameter = \( 2r \), work of fracture for pull-out is

\[
G_{fp} = \int_{0}^{L} \frac{2N\tau rDL^3}{12L} dL = \int_{0}^{L} \frac{N\pi 2rL^2}{6} dL = \int_{0}^{L} VjS^2\tau r^3 dL = VjS^2\tau D \]

Equation 34

Since in this work fibre length is \( L \) and not \( 2L \), the work of fibre pull-out for fibres with length \( L \) becomes

\[ G_{fp} = Vj\pi L^2 / 6D \]  

Equation 35

Appendix 2 - Confidence Interval for a Single Data Point

The EWF concept divides the work of fracture to two parts of crack tip process zone (\( w_c \)) and an outer plastic zone (\( w_p \)):

\[ W_f = W_c + \beta W_p l \]

The essential work of fracture, \( W_c \), is the intercept of plot of specific work of fracture vs. ligament length, \( l \). To determine confidence interval for this single set of data a basic regression model is considered:

\[ w_{fl} = \beta_0 + \beta_1 l_i + \varepsilon_i \]
where $w_{i}$ is the specific work of fracture in the ith trial, the intercept $\beta_0$ and the slope $\beta_1$ are unknown regression coefficients and are equivalent to $w_c$ and $\beta w_p$, $\varepsilon_i$ is a random error with mean zero and (unknown) variance $\sigma^2$.

The least squares estimates of the intercept and slope in the simple linear regression model are

$$\hat{\beta}_0 = \bar{y} - \hat{\beta}_1 \bar{x}$$

$$\hat{\beta}_1 = \frac{\sum_{i=1}^{n} y_i x_i - \left(\sum_{i=1}^{n} y_i\right) \left(\sum_{i=1}^{n} x_i\right)}{n} \frac{\sum_{i=1}^{n} x_i^2 - \left(\sum_{i=1}^{n} x_i\right)^2}{n}$$

where $\bar{x}$ and $\bar{y}$ are the mean value for ligament length and specific total work of fracture.

The fitted or estimated regression line is therefore

$$\hat{y} = \hat{\beta}_0 + \hat{\beta}_1 x$$

And the error in the fit of the model to the ith observation $y_i$ is the residual, $e_i$.

In simple linear regression the estimated standard error of the slope and the estimated standard error of the intercept are respectively

$$se(\hat{\beta}_1) = \frac{\hat{\sigma}^2}{\sqrt{S_{xx}}}$$

$$se(\hat{\beta}_0) = \sqrt{\hat{\sigma}^2 \left[\frac{1}{n} + \frac{\bar{x}^2}{S_{xx}}\right]}$$

where $\hat{\sigma}^2$ is the variance of the error term $\varepsilon$. The residuals $e_i = y_i - \hat{y}_i$ are used to obtain an estimate of $\sigma^2$. 
Under the assumption that the observations are normally and independently distributed, a 100\((1-\alpha)\)% confidence interval on the slope \(\beta_1\) is

\[
\hat{\beta}_1 \pm t(\alpha/2; \ n - 2)se(\hat{\beta}_1)
\]

Similarly, a 100\((1-\alpha)\)% confidence interval on the intercept \(\beta_0\) is

\[
\hat{\beta}_0 \pm t(\alpha/2; \ n - 2)se(\hat{\beta}_0)
\]

For 95% confidence limits values of \(t(0.025, \ n - 2)\) are read from t-table.

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