Technical Analysis of Flax Reinforced Polypropylene

– Prerequisites for Processing and Recycling

Teknisk analys av linfiber förstærkt polypropen
– Förutsättningar för bearbetning och återvinning

Josephine Mattsson

Faculty of Health, Science and Technology
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Supervisor: Henrik Ullsten
Examiner: Lars Järnström
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Abstract
Nowadays, when environmental concerns are becoming increasingly important are there great interest in natural materials and recyclability. The possibility of reusing materials with maintained mechanical properties are essential for sustainability. Today produced approximately 90,000 tons of natural fiber reinforced composites in Europe of those are 40,000 tons compression molded of which the automotive industry uses 95%. Natural fiber reinforced composites is recyclable and therefore interesting in many applications. Also, natural fiber reinforced composites is inexpensive, light in weight and shows decent mechanical properties which makes them attractive to manufactures. However, the problem with natural fiber reinforced composites is the poor adhesion between fiber and matrix, the sensitivity of humidity and their low thermal stability. Those problems could be overcome by addition of compatibilizer and reactive filler. This study will examine the technical requirement in order to develop a sustainable and recyclable biocomposite. It investigates the composition of matrix (polypropylene), fiber (flax), compatibilizer (maleic anhydride grafted polypropylene) and reactive filler (CaO) in order to obtain various combinations of stiffness, strength and processability. The two main methods used for preparing samples were compounding and injection molding. Results shows that 20 wt% flax was the optimal fiber content and that maleic anhydride grafted polypropylene is a very good compatibilizer by enhancing the strength significant. Surprisingly was the strength impaired due to the addition of CaO. The composition of 20 wt% flax, 1 wt% maleic anhydride grafted polypropylene and 79 wt% polypropylene is the technically most favorable composition.

Keywords: Biocomposites, Natural fiber reinforced thermoplastics, Flax fiber reinforced polypropylene, Coupling agent, Maleic anhydride grafted polypropylene, Reactive filler, Calcium oxide, Adhesion, Mechanical properties, Compounding, Injection molding.
Summary

This study will examine the technical requirement in order to develop a sustainable and recyclable biocomposite. It will be investigated by examining the composition of matrix, fiber, compatibilizer and reactive filler in order to obtain various combinations of stiffness, strength and processability. Today, when environmental sustainability is of increasingly importance there is big interest in recyclable materials. Natural fiber reinforced composites is recyclable and therefore interesting in many applications. Also, natural fiber reinforced composites is inexpensive, light in weight and show decent mechanical properties which makes them attractive to manufactures. The drawback of such composites is their weak interfacial strength between fiber and matrix depending on their polar and non-polar characteristics. Poor interfacial strength leads to poor mechanical properties. This can be improved by using compatibilizer which have duo-polar character and can thus bind to both the fiber and the matrix leading to a material with good interfacial strength and good mechanical properties. The compatibilizer used in this study is maleic anhydride grafted polypropylene (MAPP).

Flax fibers are hydrophilic, making them very attracted to water. The water molecules binds to the hydroxyl group of the fibers by hydrogen bonds and do block the site so that the compatibilizer cannot bind there and thus lose its function as coupling agent. To overcome this problem calcium oxide (CaO) is added to the composite, calcium oxide absorbs the water (forming calcium hydroxide) so that MAPP can bind to the fibers. This study will examine the technical requirement in order to develop a sustainable and recyclable biocomposite.

The goal of the research work is to find answers for some unsolved problems regarding natural fiber reinforced composites.

- What is the optimal fiber amount?
- How much compatibilizer is optimal to add?
- How does CaO affect the biocomposite? Does CaO interact with the compatibilizer?

The material used was non-woven flax-polypropylene with 40 wt% flax fibers, fresh polypropylene (PP), maleic anhydride grafted polypropylene (MAPP) and calcium oxide (CaO).

The two main methods used was compounding in double screw extruder and injection molding. To be able to feed the non-woven to the extruder was it first cut into long strips, the strips were then fed by hand down a hopper to the screw. The additional additives and polypropylene were fed from a hopper with automatic feed. The output were then pelletized and dried before injection molding. The finished specimens were then evaluated in various testing methods such as tensile test were break at stress was measured, modulus test and charpy impact test, also analysis like TGA, FTIR and SEM was done.

The results are summarized in table I to table III.

<table>
<thead>
<tr>
<th>Polypropylene with different amount of flax fibers:</th>
<th>Tensile Strength [MPa]</th>
<th>E-Modulus [GPa]</th>
<th>Impact Strength [kJ/m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 wt% flax</td>
<td>26.0 ± -</td>
<td>1.4 ± -</td>
<td>6.5 ± 0.3</td>
</tr>
<tr>
<td>8 wt% flax</td>
<td>28.3 ± 0.38</td>
<td>2.2 ± 0.05</td>
<td>5.0 ± 0.3</td>
</tr>
<tr>
<td>18 wt% flax</td>
<td>37.7 ± 0.19</td>
<td>3.7 ± 0.19</td>
<td>6.1 ± 0.3</td>
</tr>
<tr>
<td>23 wt% flax</td>
<td>37.8 ± 0.18</td>
<td>4.2 ± 0.10</td>
<td>5.9 ± 0.3</td>
</tr>
<tr>
<td>30 wt% flax</td>
<td>36.3 ± 0.51</td>
<td>4.5 ± 0.09</td>
<td>5.1 ± 0.2</td>
</tr>
<tr>
<td>40 wt% flax</td>
<td>31.72 ± 1.52</td>
<td>4.8 ± 0.29</td>
<td>3.9 ± 0.3</td>
</tr>
</tbody>
</table>
The highest tensile strength is achieved round 20 wt% flax, as seen in Table I. The modulus is also increased by the reinforcement of fibers but the impact strength is decreased as the material becomes more brittle as flax fibers are more brittle than the matrix itself. Fiber reinforced composites are sensitive to heat and thus difficult to process as they become degraded if the temperatures rises above 200°C, than it loses its strength. 20 wt% is processable and shows good mechanical properties.

<table>
<thead>
<tr>
<th>Polypropylene with 20 wt% flax fibers and different amount of MAPP:</th>
<th>Tensile Strength [MPa]</th>
<th>E-Modulus [GPa]</th>
<th>Impact Strength [kJ/m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 wt% flax + 1 wt% MAPP</td>
<td>52.5 ± 0.37</td>
<td>4.2 ± 0.14</td>
<td>5.2 ± 0.3</td>
</tr>
<tr>
<td>20 wt% flax + 3 wt% MAPP</td>
<td>54.2 ± 1.46</td>
<td>4.0 ± 0.13</td>
<td>5.4 ± 0.1</td>
</tr>
<tr>
<td>20 wt% flax + 5 wt% MAPP</td>
<td>55.4 ± 0.35</td>
<td>4.2 ± 0.29</td>
<td>5.4 ± 0.3</td>
</tr>
<tr>
<td>20 wt% flax + 7 wt% MAPP</td>
<td>56.5 ± 0.48</td>
<td>4.3 ± 0.11</td>
<td>5.2 ± 0.4</td>
</tr>
</tbody>
</table>

Table II. Mechanical properties of flax fiber reinforced polypropylene with 20 wt% flax and different amount of MAPP.

There is a significant increase in strength with coupling agent, see Table II. From 37.8 MPa without MAPP to 52.5 MPa with 1 wt% MAPP. This result has proven the effect of having coupling agent present. The modulus is almost constant here, because it is the same fiber amount, stiffness is not affected by adhesion between fiber and matrix. Impact strength is slightly decreased depending on the better adhesion achieved. Having in mind here that MAPP is an expensive additive will influence the choice of amount, in industrial scale are 1 wt% the most economically favorable option. In this study is very small quantities produced and therefore is 3 wt% used in the next samples.

<table>
<thead>
<tr>
<th>Polypropylene with 20 wt% flax, 3 wt% MA-PP and different amount of CaO:</th>
<th>Tensile Strength [MPa]</th>
<th>E-Modulus [GPa]</th>
<th>Impact Strength [kJ/m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 wt% flax + 3 wt% MAPP + 1 wt% CaO</td>
<td>48.5 ± 0.32</td>
<td>4.1 ± 0.16</td>
<td>5.0 ± 0.2</td>
</tr>
<tr>
<td>20 wt% flax + 3 wt% MAPP + 3 wt% CaO</td>
<td>49.0 ± 0.52</td>
<td>4.1 ± 0.14</td>
<td>5.0 ± 0.3</td>
</tr>
<tr>
<td>20 wt% flax + 3 wt% MAPP + 5 wt% CaO</td>
<td>48.4 ± 0.26</td>
<td>3.9 ± 0.12</td>
<td>4.7 ± 0.3</td>
</tr>
<tr>
<td>20 wt% flax + 3 wt% MAPP + 7 wt% CaO</td>
<td>49.4 ± 0.36</td>
<td>4.2 ± 0.18</td>
<td>4.5 ± 0.3</td>
</tr>
</tbody>
</table>

Table III shows the mechanical properties for samples containing CaO. The result is quite surprising because it was thought that the strength would be improved by the presence of CaO. The already high strength obtained with MAPP cannot be overcome as the specimen breaks because the fibers break and not because the adhesion between fiber and matrix is weak.

The composition of 20 wt% flax, 1 wt% MAPP and 79 wt% polypropylene is the economically most favorable.
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Karlstad, June 2014

Josephine Mattsson
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**Symbols and Abbreviations**

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<thead>
<tr>
<th>Symbol</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>Calcium oxide</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td>Calcium hydroxide</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>Calcium carbonate</td>
</tr>
<tr>
<td>CB</td>
<td>Carbon Black</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>ELV</td>
<td>End of life vehicles</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier infrared spectroscopy</td>
</tr>
<tr>
<td>FFP</td>
<td>Flax fiber reinforced polypropylene</td>
</tr>
<tr>
<td>GFP</td>
<td>Glass fiber reinforced composite</td>
</tr>
<tr>
<td>GPP</td>
<td>Glass fiber reinforced polypropylene</td>
</tr>
<tr>
<td>GPa</td>
<td>Giga Pascal</td>
</tr>
<tr>
<td>HPP</td>
<td>Homopolymer</td>
</tr>
<tr>
<td>ICP</td>
<td>Impact copolymer</td>
</tr>
<tr>
<td>J</td>
<td>Joule</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>kN</td>
<td>Kilo newton</td>
</tr>
<tr>
<td>MAPP</td>
<td>Maleic anhydride polypropylene</td>
</tr>
<tr>
<td>MPa</td>
<td>Mega Pascal</td>
</tr>
<tr>
<td>NFC</td>
<td>Natural fiber reinforced composite</td>
</tr>
<tr>
<td>NFT</td>
<td>Natural fiber reinforced thermoplastic</td>
</tr>
<tr>
<td>NRC</td>
<td>National Research Council of Canada</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>RCP</td>
<td>Random Copolymer</td>
</tr>
<tr>
<td>rpm</td>
<td>Rotates per minute</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetry Analysis</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra violet</td>
</tr>
<tr>
<td>wt %</td>
<td>Weight percentage</td>
</tr>
<tr>
<td>°C</td>
<td>Degree celsius</td>
</tr>
<tr>
<td>a</td>
<td>Impact strength</td>
</tr>
<tr>
<td>Cₚ</td>
<td>Heat capacity</td>
</tr>
<tr>
<td>d</td>
<td>Fiber diameter</td>
</tr>
<tr>
<td>Eₐ</td>
<td>E-modulus</td>
</tr>
<tr>
<td>l</td>
<td>Actual fiber length</td>
</tr>
<tr>
<td>lₙ</td>
<td>Critical fiber length</td>
</tr>
<tr>
<td>Tₐ</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>Tₘ</td>
<td>Melting point</td>
</tr>
<tr>
<td>μm</td>
<td>Micro meter</td>
</tr>
<tr>
<td>σₚ</td>
<td>Tensile strength</td>
</tr>
<tr>
<td>ΔH</td>
<td>Enthalpy change (amount of energy absorbed)</td>
</tr>
<tr>
<td>-ΔH</td>
<td>Enthalpy change (amount of energy released)</td>
</tr>
<tr>
<td>τₜ</td>
<td>Matrix/Fiber shear stress</td>
</tr>
</tbody>
</table>
1. Introduction
Nowadays, when environmental concerns are becoming increasingly important are there great interest in natural materials and recyclability. The possibility of reusing materials with maintained mechanical properties are essential for sustainability. Today produced approximately 90,000 tons of Natural Fibers Composites (NFCs) in Europe [1]. Of those are 40,000 tons compression molded of which the automotive industry uses 95%.

1.1 Natural Fibers as Reinforcement
Natural fibers are renewable, biodegradable, and have high strength to weight ratio. Its high stiffness and low cost makes them attractive to manufacturers [2]. Their light weight is of special significance in transportation application due to fuel savings [3]. The weakness of natural fibers is its hydrophilic character and low thermal stability [4].

1.2 Natural Fiber Reinforced Thermoplastics (NFTs)
Natural fiber reinforced thermoplastics (NFTs) have been of great interest in the last decade and several studies have been done in the area. The first natural fiber reinforced composites were based on thermosets matrixes, such as unsaturated polyester or phenolic resins, together with sisal and jute. More recently, developments shifted to thermoplastic matrixes due to its added advantage of recycling [5]. Also, thermoplastics are preferable as matrix in natural fiber reinforced composites due to its low cost and easiness in processing. Thermoplastics are very easy to melt down and reprocess unlike thermosets which cannot be melted. The most studied thermoplastic matrix is polypropylene (PP). The National Research Council of Canada (NRC) has carefully studied how the reinforcement of different fibers such as flax, hem and sisal affect the properties of the composite. When fibers are incorporated into a matrix to form a composite, the matrix serves to bind the fibers together, transfer loads to the fibers and protect them against environmental threats such as humidity. NFTs give raise to a composite having the best properties of each component. NFTs have both the strength and stiffness of natural fibers and the production easiness of thermoplastics [6][7]. NFTs have a widespread application due to their enhanced properties.

One crucial limitation of NFTs however is their weak interface between fiber and matrix. Since the fibers are hydrophilic and the matrix is hydrophobic they do not want to interact and it leads to poor mechanical properties [4]. As pointed out earlier the high sensitivity of fibers towards water and their relatively low thermal stability are other important disadvantages. Thus, water uptake can lead to swelling and dimensional instability, resulting in dramatic loss of mechanical properties. Thermal and mechanical degradation during processing may also affect the properties of the final product [4].

1.3 Additives in NFTs
Several studies made on NFTs shows that the addition of compatibilizer and reactive filler will enhance compatibility between fiber and matrix and also prevent water absorption and thermal degradation [8, 6, 9, 10, 11]. Maleic anhydride grafted polypropylene (MAPP) is a well-known compatibilizer used to improve the interfacial strength between natural fibers and polypropylene. It is a necessary additive in polypropylene composites and many studies have proven its effect [12, 6, 13, 14, 15]. Denault et al. was the first trying to add calcium oxide (CaO) to flax fiber reinforced polypropylene [8]. They showed in several studies that CaO is an advantageous additive, by absorbing water and neutralize acidity are increased tensile strength and modulus obtained.

1.4 Recycling of NFTs
Only few studies have been done on recycling of NFTs and the process needs improvement. Denault et al. concluded that flax fiber reinforced polypropylene can be recycled 3-5
times before a significant decrease in mechanical properties [16] [8].

This study examines the technical requirement in order to develop a sustainable and recyclable biocomposite. It investigates the composition of matrix, fiber, compatibilizer and reactive filler in order to obtain various combinations of stiffness, strength and processability.

The goal of the research work is to find answers for some unsolved problems regarding NFTs.

- What is the optimal fiber amount?
- How much compatibilizer is optimal to add?
- How does CaO affect the composite? Does CaO interact with the compatibilizer?

1.4 Materials

1.4.1 Polypropylene (PP)

Polypropylene (PP) is a thermoplastic polymer with the structure shown in figure 1-1. A thermoplastic is a polymer which becomes soft and moldable above a specific temperature and returns to a solid state upon cooling.

![Molecule structure of Polypropylene](image)

Figure 1-1. Molecule structure of Polypropylene [17].

There are numbers of ways producing PP but the most widely used in materials is the semi-crystalline structure and it is made with catalyst which will crystallize polymer chains into crystals. Semi-crystalline PP has good physical, mechanical and thermal properties and are called “isotactic” (crystallizable) PP, properties is seen in table 1-1 and 1-2. Another form of PP is a byproduct of semi-crystalline PP production, having very poor mechanical and thermal properties. This type of PP is very soft and is used in adhesives, sealants and caulk products. It is called “atactic” (noncrystallizable) PP [18].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_g$</td>
<td>-10°C</td>
</tr>
<tr>
<td>$T_m$</td>
<td>165°C</td>
</tr>
<tr>
<td>Density</td>
<td>900-910 kg/m$^3$</td>
</tr>
</tbody>
</table>

Table 1-1. Physical Properties of semi-crystalline polypropylene [19].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strength</td>
<td>25-35 MPa</td>
</tr>
<tr>
<td>E-modulus</td>
<td>1.4 GPa</td>
</tr>
<tr>
<td>Charpy Impact</td>
<td>6.5 kJ/m$^2$</td>
</tr>
</tbody>
</table>

Table 1-2. Mechanical Properties of semi-crystalline polypropylene [20].

Depending on application are different properties desired and it can simply be varied by altering the chain regularity (tacticity) content and distribution, the average chain lengths or incorporate a co-monomer such as ethylene into the polymer chains. The different product types are described below [18].

1.4.1.1 Homopolymer (HPP)

PP containing only polypropylene monomer in the semi-crystalline solid form is referred to as HPP. HPP is a two-phase system consisting both crystalline and non-crystalline structures. The non-crystalline or amorphous regions are composed of both isotactic PP and atactic PP. HPP is the most widely used in materials such as natural fiber reinforced composites [18].

1.4.1.2 Random Copolymer (RCP)

RCP are made by copolymerizing PP and small amounts of ethylene, about 1-8%. The properties are significantly changed by the addition of ethylene. The result is better impact properties, improved clarity, decreased hazed, decreased melting point and enhanced flexibility. The ethylene monomer in the PP chains is affecting the crystallizability negatively and thus lowers the melting point of the polymer [18].
1.4.1.3 Impact Copolymer (ICP)
ICP or a heterophasic copolymer is a mixture of HPP and RCP. The ethylene content in the RCP part is between 40-65%. The RCP part is called the rubber phase. As the rubber phase in the ICP is increased, so is the impact resistance, but it is at the expense of the stiffness of the product. The impact of the ICP is dictated by the RCP phase and the stiffness is dictated of the HPP phase. This is why ICPs have great impact resistance in low temperatures, especially in freezer temperatures or below [18].

1.4.1.1 Crystalline and Amorphous Structures
Polymers are either amorphous or semi-crystalline. Semi-crystalline is a mixture of amorphous and crystalline structure, see figure 1-2. The polymers are entangled and disorganized in the amorphous phase unlike the crystalline phase were the polymers are strictly ordered. The composition of amorphous and crystalline phase is very important for the properties of the polymer. The crystal phase is much stiffer and has great impact on the mechanical properties such as strength and modulus of the material [21].

1.4.1.2 Glass Transition Temperature, $T_g$
$T_g$ is the temperature when an amorphous polymer transitioning from a stiff to a more rubber like state. The modulus of the polymer is significantly lower with temperatures over $T_g$ and thus makes the polymer useless in many applications. Semi-crystalline polymers have both amorphous and crystalline structure, when transitioning at $T_g$ the amorphous part become rubber like. The polymer is still relatively stiff because of its strong crystalline part, which is not affected by the transition. This explains why polypropylene and other semi-crystalline polymers with $T_g$ under room temperature can be used in various applications [19].

1.4.1.3 Melting Temperature, $T_m$
$T_m$ is defined as the temperature at which the last crystalline part melts in a semi-crystalline polymer. Here, ”the last” is important as the melting process occurs over a wide temperature range. The slow melting process in semi-crystalline polymers is because their various-sized crystals which melts at different temperatures. Melting is an endothermic transition which means that the polymer absorbs heat. As the crystalline parts only characterizes by $T_m$, it will not be affected by $T_g$. However, no polymers are 100% crystalline and thus all polymers will undergo glass transition and melting. $T_g$ is always lower than $T_m$ and none of the temperatures are affected by fiber reinforcement [19].

1.4.1.4 Recrystallization, $T_c$
When processing a semi-crystalline polymer at temperatures over $T_m$ are all crystals melted and the polymer becomes a viscous liquid. After processing, the temperature will decrease and at a certain temperature $T_c$, the polymers start to crystallize again. The recrystallization starts around discrete points called nuclei, the crystals grows around the nuclei and form what is called a spherulites. When all spherulites are big enough to meet their neighbor, the crystallization is completed. Crystallizing is an exothermic transition and the polymers give off heat. $T_c$ will vary depending of fillers, initial temperature and rate of cooling [23].
Semi-crystalline homopolymer PP is the primary thermoplastic used in NFTs, due to its desirable physical, mechanical and thermal properties in room-temperature. It has low cost, low density and low processing temperature which is essential because of the relatively low thermal stability of natural fibers (200-250°C) [24]. It has also good chemical resistance and can be processed using a wide variety of manufacturing techniques such as extrusion, injection and compression molding etcetera. However, the weak UV stabilization of PP limits its application areas. The use of UV stabilizer has proven to be very effective [25].

1.4.2 Flax Fibers
Flax fiber is a stem fiber and originates from the flax plant Linum Utitatissimum. Flax fibers mainly consist of cellulose, hemi-cellulose and lignin. Flax has high tensile strength and good resistance to abrasion, see properties in table 1-3 and 1-4.

<table>
<thead>
<tr>
<th>Table 1-3. Physical properties of flax fiber [26].</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical fiber length 8 – 69 mm</td>
</tr>
<tr>
<td>Fiber diameter 5 – 30 μm</td>
</tr>
<tr>
<td>Density 1,450 g/cm³</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 1-4. Mechanical properties of flax fiber [26].</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength 500-1500 MPa</td>
</tr>
<tr>
<td>E-modulus 50 GPa</td>
</tr>
</tbody>
</table>

Flax fibers can be used in a wide range of applications, especially in automotive products but also in furniture, sports equipment, luggage and musical instrument etcetera.

There are a lot of advantageous reasons why [27]:

- Cost effective.
- Bio-degradable.
- High stiffness and tensile strength.
- Lighter products.
- Good replacement for glass- and carbon-fiber.
- Suits for needle punched non-woven products.
- Can be used in different manufacturing systems such as extrusion, compression molding and injection molding.
- Reduces molding time.

Flax is the most important and demandable fibers in Europe. Approximately 80% of all flax production is in France, Spain, Belgium, UK and Netherlands [28]. The thermal stability of flax fibers are relatively low about 200-250°C and need to be considered when processing composites containing flax fibers [24].

1.4.2.1 Critical Fiber Length (l_c)
In order to strengthen the composite, the reinforcing fibers need to be of specific length. The adhesion between fiber and matrix are critical for a strong material and the longer fibers, the better adhesion. The function of reinforcing fibers is to support the load through shear in the matrix. If fibers are longer or equal to the critical length (l_c) are they able to support load and when the load is high enough will fiber breakage occur. Short fibers (l < l_c) cannot support load from the matrix and does not function as amplifier. When the load is high enough, fiber pull-out will occur [29].

The critical fiber length depends on:

- The fiber tensile strength, σ_t.
- The fiber diameter, d.
- Matrix/fiber shear strength, τ_c.

It is calculated by equation 1 [29].

\[ l_c = \frac{\sigma_t \cdot d}{2 \cdot \tau_c} \]  

(1)

Furthermore, τ_c has been determined to 8 MPa for flax reinforced PP [24] [30].
1.4.3. Maleic Anhydride Polypropylene (MAPP)

Maleic anhydride polypropylene (MAPP) is primarily used as a coupling agent or a compatibilizer in immiscible materials. MAPP has the ability to bind between cellulosic fibers and thermoplastic matrixes because of its dual polarity. It has one hydrophobic part which binds to the thermoplastic matrix and one hydrophilic part which binds to the cellulosic fiber, see figure 1-3.

Several studies show the compatibilizing effect of different coupling agents in NFTs, of which MA-PP is the most effective for polypropylene composites [12]. However, the compatibilizing effect is affected by water. When water is present on the fiber surface, MA-PP cannot bind covalently to its hydroxyl group, instead MA-PP binds to the water by hydrogen bond, see figure 1-4.

1.4.4 Calcium Oxide (CaO)

Calcium oxide (CaO), also called quicklime or burned lime, is a white alkaline crystalline solid. CaO is very reactive and reacts vigorously with water forming calcium hydroxide (Ca(OH)₂). Reaction with carbon dioxide forms calcium carbonate (CaCO₃), which is commonly used as a mineral filler in PP. However, what occurs when adding CaO to NFTs is not clear. Authors do agree that CaO will enhance the mechanical performance of the composite through absorption of water and neutralization of acidity but how that is done are they not agreed about.

Got et al. (2000) was studying the effect of adding basic oxides such as CaO to wood reinforced polypropylene due to its ability to absorb water [34]. Humidity is a problem in wood and natural fiber reinforced composites as the cellulose is highly hydrophilic. When water penetrates into the wood/fibers, it is likely to swell, swelling can damage the matrix and thereby the composite. Also, wood and fibers containing water have lower stiffness and strength, thus affecting the mechanical performance of the composite negatively. According to Got et al., water is produced from the wood when the composite is compounded due to the high temperature and the added CaO going to chemically react with the water forming Ca(OH)₂. Ca(OH)₂ serves to neutralize acids included in the water and as a result, MA-PP is polarized to increase the adhesion between the wood and the matrix. However, according to the authors is the CaO amount added very important and is recommended to not exceed 10 wt% of total composite weight thus the non-reacted CaO will absorb water contained in the air and react chemically therewith after completing the compounding, leading to deformation of the resulting composite [34]. Adding CaO will replace the otherwise needed drying process.

Denault et al. (2007) mean that CaO will enhance the strength and stiffness of the composite by binding to the coupling agent, increase its molecular weight and thus improving the composite performance. They also agree that CaO will absorb water and neutralize acidity due to its alkalinity and thereby minimize degradation during processing [8]. Russel et al. and have earlier studied molding
compositions containing crosslinks and concluded that it is formed by the reaction of MAPP and CaO [35], see figure 1-5.

CaO is also reactive with organic materials and can thus react with cellulosic fibers [36]. These theories lead to figure 1-6.

CaO is one of the top fillers for cellulose composites due to its high reactivity and low cost. Although the addition of CaO is advantageous it needs to be handled with care, it reacts vigorously with water and forms calcium hydroxide which is corrosive. Contact with skin, eyes or inhalation is dangerous. Protective wear, goggles and respirator is highly recommended [37].

1.5 Processing

1.5.1. Extrusion

Extrusion is a process which can be used both for mixing and to produce plastic components with a fixed profile, such as a pipe, sheet or film. The plastic mass is loaded in the feed hopper which feed the plastic down to the screw, where it is heated and melted. The screw is usually divided in three sections:

- Feed zone - the plastic mass is still solid.
- Melting zone - mixture of solid and melt.
- Metering zone - all plastic is melted.

The screw is pressing the melt forward at constant speed to the die. The plastic is pressed through the die and are immediately cooled down to maintain its profile [38]. An extruder is shown in figure 1-7. There are two types of extruders, single- and twin-screw extruders, where the twin screw extruder has two screws instead of one, see figure 1-8.
1.5.2 Injection Molding

Injection molding is one of the most common methods of producing goods from thermoplastics, thermosets and rubber. There are three main tasks for injection molding [38]:

- Raise the temperature of the plastics until it is molten.
- Insert the melted plastic to the mold and cool.
- Open the mold and eject the finished product.

![Figure 1-9. Injection molding machine](image1)

The injection molding machine is divided in two parts, the injection unit and the clamping unit. The injection unit prepares the plastic for injection to the mold through heating the plastic to the temperature at which it has suitable viscosity. The plastic is moving forward towards the nozzle by the rotation of the screw. The nozzle is filled with plastic and force the screw backwards, when it is totally filled the rotation is stopped and it force the screw forward again which presses the melt into the mold.

The clamping unit is responsible for closing and opening the mold and yields enough clamping pressure during injection (about 300-2000 bar). The clamping unit is either mechanical or hydraulic [38]. The production rate needs to be as high as possible to yield a profitable process. The mold temperature and the thermal conductivity of the material are critical [38]. The injection pressure is desired to be as low as possible, high injection pressure is costly and it causes tool wear [42].

![Figure 1-10. Compression molding](image2)

1.5.3 Compression Molding

Compression molding is an old and relatively simple method. The compression molding machine consists of two heated pressing plates with a mold in between, see figure 1-10. The material is placed in the mold and when the plates are pressed together the material will spread in the cavity. The material is usually heated in oven first because it takes amount of time to heat it in the mold. When cooled down, the shaped material is removed from the mold [43].

1.6 Analytical Methods

1.6.1 Scanning Electron Microscopy (SEM)

Unlike light microscopy, scanning electron microscopy are using electrons instead of light to form an image and are able to detect levels of details and complexity inaccessible by light microscopy. The signals that detected from electron-sample interactions give information about the sample including texture, chemical composition, crystalline structure and orientation of materials in the sample [45]. The combination of the ease of observation, good resolution, high magnification and fine resolution makes SEM one of the most widely used equipment [46].

A beam of electrons is produced by an electron gun at the top of the microscope, the electron beam follows a vertical path through the microscope and travels through lenses and electromagnetic fields which will focus the
beam towards the sample. Once the beam hit the sample, electrons are scattered, detected and converted into signals which will finally produce the image of the sample, see figure 1-11.

Figure 1-11. SEM set-up [47].

Figure 1-12. Illustration of scattered electrons [48].

Figure 1-12 shows an illustration of the scattered electrons when the electron beam strikes the sample. Secondary and backscattered electrons are mostly used for imaging samples. Secondary electrons are most valuable for showing morphology and topography on samples. Secondary electrons is produced when electrons of the incident beam excites electrons in the atomic orbitals, if the excited electron have sufficiently energy to excite the surface it becomes a secondary electron [46].

The primary backscattered electrons (BSE) are produced when high energetic electrons rebound elastically from the sample surface. Backscattering depends on the atomic number. The number of electrons detected is proportional to the mean atomic number of the sample. BSE provides very high-resolution images where the brighter areas correlates with greater atom number and the darker areas have lower atom number. BSE images are helpful for quick distinguish of different phases and the composition in a sample [49].

X-rays is produced by inelastic collisions with the incident electrons and the electrons within the atomic orbital in the sample. As the excited electrons return to a lower energy state, they yield x-rays of different wavelengths depending of which element the sample is [45].

An auger electron is an electron excited by the energy released from an electron transition downwards. The incident high speed electron knocks out an inner shell electron, leaving a vacancy. An upper electron will drop to the vacancy to fulfill the inner shell, leading to either emittance of light (photon) or excitation of the outer electron, if the outer electron is excited is it called an auger electron [50].

1.6.2 Differential Scanning Calorimetry (DSC)

“Differential scanning calorimetry (DSC) is a thermal analysis technique that looks on how a materials heat capacity (C_p) is changed by temperature” by PerkinElmer 2013 [51].

DSC measures the amount of energy required to increase the temperature of the material. The temperature program for a DSC analysis is designed such that the temperature of the sample will increase linearly. The amount of energy needed to raise the temperature is compared with a reference. Samples undergoing phase transition needs less or more energy to keep the same temperature as the reference depending on the phase transition is endothermic (require more energy, like glass and melt-transition) or exothermic (require less energy, like crystallization). These deviations from the reference will be revealed in a plot where the temperatures $T_g$, $T_m$, $T_c$ and the
amount of energy either absorbed (melting, $\Delta H$) or released (crystallizing, $-\Delta H$) can be read [52].

1.6.3 Thermogravimetric Analysis (TGA)

“TGA is a technique in which, upon heating a material, its weight increases or decreases” by PrekinElmer. TGA is used for material characterization. The instrument determines the degradation of materials when heated. The instrument can quantify loss of water, solvent, weight % filler, oxidation, etcetera [53]. The analysis is done to determine the thermal stability of the flax fibers.

1.6.4 Fourier Transform Infrared Spectroscopy (FTIR)

An infrared spectrometer is an instrument measuring an infrared spectrum. FTIR is a specific type of infrared spectrometer and can tell what molecules are present in the sample and at what concentrations [54]. In infrared spectroscopy, IR radiation is passed through a sample. Some of the radiation is absorbed by the sample and some of it is passed through. The resulting spectrum is very information rich. The peak position give the structures of the molecules in a sample, the peak intensities give the concentration of molecules in a sample and the peak widths are sensitive to the chemical matrix of the sample including pH and hydrogen bonding. The instrument detects vibrations arising from molecules absorbing infrared light. Individual atoms and monatomic ions cannot be detected as they have no vibrations nor infrared spectrum [54].

1.6.4 Mechanical Properties

The mechanical performance of biocomposites is greatly influenced by the processing technique and processing conditions, fillers and additives. It is also influenced by the crystallinity, cross-linking and branching of the polymer matrix. These aspect need to be considered when developing useful biocomposites. NFTs require certain properties to compete with glass fiber reinforced composites [25]. The purpose with fiber reinforced composites is to achieve a stronger and stiffer material than the matrix itself. Polypropylene is used because of its cheapness and good processability but is limited in many applications due to its poor properties. By adding fibers with high strength and stiffness becomes the matrix reinforced and more useful in applications that require high performance materials.

1.6.4.1 Tensile Strength, $\sigma$

Tensile strength is the maximum applied load or stress a specimen can withstand before breaking. The tensile test measures the force needed to pull a specimen until it breaks. The tensile strength highly depends on the adhesion between fiber and matrix, fiber length and fiber loading [25]. It is important for a material that going to be stretched or subjected to tension.

1.6.4.2 E-modulus, $E$

When applying a load on the material it undergoes elastic deformation initially. Elastic deformation is not permanent and the deformation will return when the load is released. In this region are the E-modulus (elastic modulus) measured as the ratio between stress and strain, it measures the stiffness of the material. Addition of fillers increases the E-modulus which makes the material stiffer [25]. Stiffness is important in products which can only be deflected by a certain amount. In transportation applications stiffness is required at minimum weight.

1.6.4.3 Impact Strength, $\alpha$

Is the capability of withstand a sudden applied load. Measure the amount of energy absorbed by a material during impact before it fractures [55]. Impact toughness is important for components subjected to shock loading and measures the brittleness of the material.

1.7 Recycling

Today when sustainability and environmental safety are becoming increasingly important are recyclability a hot topic on the market, materials that can be recycled are therefore
desirable. There is three ways of recycling: mechanically, chemically and thermally.

1.7.1 Mechanical Recycling
Mechanical recycling is mostly preferred because it is a very easy and cheap process. The relatively low melting point of polypropylene makes it possible to melt the composite without damaging the fibers. The most obvious technique for recycling NFT is to mechanically break down the material to granules and re-run the original process [56]. However, the problem is that the fibers will be shortened in the reprocessing and eventually lose its mechanical properties as they act as fillers only. Also, repeated processing of thermoplastics will result in weak properties and thus limit its applications. The quality and cost of the recycled material are key issues in recycling of NFTs. The reprocess needs further improvement [57].

Thermal and chemical recycling are alternative methods to mechanical recycling, although the recoved value is usually significantly lower. [19].
2. Experimental Part

In this chapter, raw materials needed for the experiments, composite preparation methods and testing methods are introduced. Figure 2-1 shows a schematic representation over the work plan.

![Schematic representation over the Work plan.](image)

**2.1 Materials**

Non-woven flax-polypropylene, supplied by Libeltex Sweden with fiber content of 40 wt%. To obtain a processable composite were additional fresh polypropylene necessary, supplied by Borealis, Sweden (BH345MO, \( \rho = 904 \text{ g/cm}^3 \)). Maleic anhydride polypropylene (MAPP), supplied by Eastman (G-3216, \( M_w = 60,000 \text{g/mol} \)). CaO supplied by Sagitta Pedagog AB.

**2.2 Specimen Preparation**

Samples were prepared as described in section 2.2.1 and 2.2.2, the fiber content was varied from 10-40 wt%.

**2.2.1 Compounding**

Non-woven with additives (PP, MAPP and CaO) was compounded in a twin-screw extruder Coperion ZSK 26 K 10,6, see figure 2-2. The screw configuration used is shown in figure 2-3.

The condition used for compounding:
- Temperature in zone 1: 165°C
- Temperature in zone 2-11: 190°C
- Screw speed: 150 rpm

The non-woven were cut into strips and fed by hand to the screw, fresh polypropylene, MAPP and CaO was fed automatically from the feed hopper. The out-put were pelletized and dried in 60°C about 20 hours.

![Coperion ZSK 26 K 10,6 twin-screw extruder.](image)

![Screw configuration. Kneading and shredding elements was placed at 52, 60, 65, 75,5 and 79 cm according to the scale. Also in Appendix as figure 7-1.](image)
Table 2-1. Composition of samples.

<table>
<thead>
<tr>
<th>Designation of samples</th>
<th>Fiber [wt%]</th>
<th>MAPP [wt%]</th>
<th>CaO [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NF8</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NF18</td>
<td>18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NF23</td>
<td>23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NF30</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NF40</td>
<td>40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NF20MA1</td>
<td>20</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>NF20MA3</td>
<td>20</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>NF20MA5</td>
<td>20</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>NF20MA7</td>
<td>20</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>NF20MA3CaO1</td>
<td>20</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>NF20MA3CaO3</td>
<td>20</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>NF20MA3CaO5</td>
<td>20</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>NF20MA3CaO7</td>
<td>20</td>
<td>3</td>
<td>7</td>
</tr>
</tbody>
</table>

2.2.2 Injection Molding

Tensile bars were prepared by an injection mold ENGEL ES 200/100 HL-V, see figure 2-4.

- Cylinder temperature: 185°C
- Mold temperature: 40°C
- Injection pressure: Between 20-165.5 MPa
- Melt pressure: Differ with the fiber content.

![Figure 2-3. ENGEL ES 200/100 HL-V.](image)

2.3 Mechanical Characterization

The test specimens were investigated at room temperature (23±2°C), at least 5 repetitions were done in each series and standard deviations were obtained from the measurements.

2.3.1 Tensile Test

The tensile test was done by using a MTS 20/M with standard ISO 527, the load cell was 10 kN and the crosshead speed was 50 mm/min. Size of tensile bar is shown in figure 2-6.

![Figure 2-6. Schematic representation over a tensile bar.](image)

2.3.2 E-Modulus Test

The modulus test was done by using a MTS 20/M with standard ISO 527, the load cell was 1 kN and the crosshead speed was 1 mm/min. The selected speed of testing shall provide a strain rate as near as possible 1% of the gauge length per minute. Same size of specimen was without having to apply a too high pressure. The structure of a coil is shown in figure 2-5.

![Figure 2-5. Image of a coil.](image)
used for measurements of modulus, see figure 2-6.

**2.3.3 Impact Test**
The Impact test was done by using an Instron 7614.000/23334 CEAST 9050 with standard ISO 179. Hammer energy: 0.5 J. Specimens with 2 mm V notch (45°C) were applied. Size of specimen is shown in figure 2-7.

![Figure 2-7. Schematic representation over a Notched specimen for impact test.](image)

**2.4 Scanning Electron Microscopy (SEM)**
The fracture surface of specimens was analyzed by using a JEOL JSM-6610LV. Overviews and close-ups of the samples were taken, fiber pull-out and fiber breakage was studied.

**2.4.1 Critical Fiber Length**
The critical fiber length was measured using a digital measuring tool named Engauge Digitizer.

**2.5 Differential Scanning Calorimetry (DSC)**
$T_p$, $T_m$ and $T_c$ of the samples were measured by METTLER TOLEDO DSC 1 STAR® system. The measurements was made in a temperature range between 23-200°C, first heating to 200°C and then cooling to 23°C.

**2.6 Thermogravimetric Analysis (TGA)**
The thermal stability of the composite was evaluated using METTLER TOLEDO TGA/DSC 1 Star® system. Two different methods was used, TGA 50-900, N2, -blank dt 1.00 s and TGA 50-500, 500 15 min, 500-900 subtrac dt 1.00 s. The first method is only nitrogen based and the second method is both nitrogen and air based, changing at 500°C.

**2.7 Fourier Transform Infrared Spectroscopy (FTIR)**
Spectrum from the composite with three different compositions was evaluated by transmission, NF20, NF20MA3 and NF20MA3CaO5. The machine used was BRUKER TENSOR 27, TGA-IR.
3. Result and Discussion

Results from evaluated samples are presented in this chapter.

3.1. Mechanical Properties

The result of mechanical properties on flax fiber reinforced polypropylene with additional coupling agent and reactive additive are shown in the next coming sections.

3.1.1 Flax Fiber Reinforcement

Tensile Strength
The reinforcing effect of flax fibers on tensile strength can be seen in figure 3-1. To achieve significant reinforcement flax load of 10 wt% were needed. Maximum tensile strength is achieved at 20 wt% flax, then the strength decreases with increasing fiber content, indicating poor load transfer between fiber and matrix.

![Figure 3-1. Measurements of tensile strength with different amount of flax fibers, without coupling agent present. The standard deviation is less than 4.7% and cannot be seen in the chart.](image)

The result from figure 3-1 is also presented in table 3-1.

<table>
<thead>
<tr>
<th>Flax fiber [wt%]</th>
<th>Tensile Strength [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>26 ± -</td>
</tr>
<tr>
<td>8</td>
<td>28 ± 0.4</td>
</tr>
<tr>
<td>18</td>
<td>38 ± 0.2</td>
</tr>
<tr>
<td>23</td>
<td>38 ± 0.2</td>
</tr>
<tr>
<td>30</td>
<td>36 ± 0.5</td>
</tr>
</tbody>
</table>

The poor strength obtained in figure 3-1 can be explained by the theory about critical fiber length. The fiber length needed for good load transfer (critical fiber length) between fiber and matrix is calculated below ($l_c$) and are compared with the experimental fiber length ($l_{exp}$).

\[ l_c = 2.812 \text{ mm} \]
\[ l_{exp} = 2.413 \text{ mm} \]

The experimental fiber length is based on assumptions of chemical interactions between fiber and matrix, described in section 1.4.2.1 so some uncertainty exists. Here, the experimental length is shorter than the critical length meaning that the prepared samples should have poorer mechanical properties than it would have if the fibers were longer than the critical length. Since the fibers were much longer before processing, it is obvious that fiber degradation has occurred. The reason why 30 wt% and 40 wt% flax has lower strength than 20 wt% is probably because the high fiber content has caused more degradation during processing. When composites are compounded, friction between fibers leads to increase in temperatures. The more fibers there are in the composite the more friction occurs which leads to more degradation. Flax fibers have low thermal stability and will be degraded when temperature is above 200°C, resulting in losing its strength. Another possible explanation why 30- and 40 wt% flax fiber would have weaker strength than 20 wt% is that there is poor wetting with matrix which can wet all the fibers. If partly no matrix the fibers in those areas will not be applied with load (as it is the matrix which receives the load and transfer it to the fibers) and thus not help to reinforce the matrix, instead the strength becomes poor. This is has also affected the result in figure 3-2 were the stiffness decreases at fiber load of 20 wt% or more.
**E-Modulus**

The tensile modulus of the composite with different amount of flax fiber is shown in figure 3-4 and table 3-4. There is a huge increase in modulus from having no fibers up to 20 wt%, from 1.4 GPa to 4 GPa respectively. The growth slows down after 20 wt% and the increase from 20 wt% to 40 wt% is less than 1 GPa. This is illustrated by the red lines in the chart, the optimal amount of flax fibers is in the breakpoint, round 20 wt%.

![Figure 3-2](image)

Figure 3-2. Measurements of tensile modulus with different amount of flax fiber, without coupling agent present. The standard deviations is less than 6.1% and can slightly be seen in the chart.

The result from figure 3-2 is also presented in table 3-2.

<table>
<thead>
<tr>
<th>Flax fiber [wt%]</th>
<th>E-modulus [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.4 ± _</td>
</tr>
<tr>
<td>8</td>
<td>2.2 ± 0.1</td>
</tr>
<tr>
<td>18</td>
<td>3.7 ± 0.2</td>
</tr>
<tr>
<td>23</td>
<td>4.2 ± 0.1</td>
</tr>
<tr>
<td>30</td>
<td>4.5 ± 0.1</td>
</tr>
<tr>
<td>40</td>
<td>4.8 ± 0.3</td>
</tr>
</tbody>
</table>

Table 3-2. Measured E-modulus at different weight percentage of flax fiber.

The result from figure 3-2 was partly expected. It was known that reinforcement of flax fibers would give a stiffer composite but the stiffness was not expected to slow down after 20 wt% fiber. The stiffness was expected to increase linearly to 40 wt%. This is yet another result of poor load transfer between fiber and matrix from degraded fibers. This means that there is no great advantageous to reinforce the composite by either 30 wt% or 40 wt% flax fibers because the stiffness is not improved much. It also has lower strength than 20 wt% flax, as seen in figure 3-1.

**Impact Strength**

Adding flax fiber to polypropylene makes it more brittle, this is shown in figure 3-3. The impact strength of the composite decreases continuously with increased fiber content, most likely is that all data points should follow the trend but 8 wt% flax fiber deviates.

![Figure 3-3](image)

Figure 3-3. Measurements of impact strength with different amount of flax fiber, without coupling agent present. The standard deviations is less than 5.0% and can slightly be seen in the chart.

The result in figure 3-3 is also presented in table 3-3.

<table>
<thead>
<tr>
<th>Flax fiber [wt%]</th>
<th>Impact Strength [kJ/m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6.5 ± 0.3</td>
</tr>
<tr>
<td>8</td>
<td>5.0 ± 0.3</td>
</tr>
<tr>
<td>18</td>
<td>6.1 ± 0.3</td>
</tr>
<tr>
<td>23</td>
<td>5.9 ± 0.3</td>
</tr>
<tr>
<td>30</td>
<td>5.1 ± 0.2</td>
</tr>
<tr>
<td>40</td>
<td>3.9 ± 0.3</td>
</tr>
</tbody>
</table>

Table 3-3. Measured Impact Strength at different weight percentage of flax fiber.

Polymers are durable and are quite impact resistant, fibers or filler on the other hand are more brittle and is not very impact resistant. Reinforcement of fibers makes the composite more brittle. Most brittle is the 40 wt% flax fiber reinforced polypropylene, 20 wt% flax is round 6 kJ/m² which is close to the impact resistance of polypropylene. Meaning that 20
wt% fiber or below does not affect the impact resistant much. Once again can one show that 20 wt% is the optimum fiber amount. As mentioned earlier did 8 wt% deviate from the trend, the result was not expected but can be explained by poor dispersion of fibers in the melt. The amount of fresh polypropylene, added to dilute the fiber content is very high at 8 wt%, see table 2-1. Because of that cannot the high-viscous melt with 40 wt% flax fiber be mixed properly with the additional fresh polypropylene and the material will lose its impact strength. In fact, the strength and stiffness seems to be affected by this too as we can see that 8 wt% deviates in all tests.

Results from all testing methods shows that 20 wt% is the most favorable fiber content.

3.1.2 Effect of MAPP

**Tensile Strength**

Figure 3-4 and table 3-4 shows the strength achieved by adding different amounts of MA-PP. From 0 wt% to 1 wt% MA-PP is a significant increase in strength, from 38 MPa to 52 MPa. The more MA-PP is added the stronger composite, up to 56 MPa with 7 wt%.

<table>
<thead>
<tr>
<th>MAPP [wt%]</th>
<th>Tensile Strength [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>38 ± 0.2</td>
</tr>
<tr>
<td>1</td>
<td>52 ± 0.4</td>
</tr>
<tr>
<td>3</td>
<td>54 ± 1.5</td>
</tr>
<tr>
<td>5</td>
<td>55 ± 0.4</td>
</tr>
<tr>
<td>7</td>
<td>56 ± 0.5</td>
</tr>
</tbody>
</table>

MAPP has proven to be a very effective coupling agent for flax fiber reinforced polypropylene. However, MAPP is an expensive additive and this need to be considered. The small increase in strength that is seen from 1 wt% to 7 wt% is not good enough compared to how much the price of the composite increases. 1 wt% therefore seems to have the best strength to price ratio. If less than 1 wt%, the risk of losing the effect of coupling agent and the strength are likely to happen. Addition of MAPP enhances the interfacial shear strength, \( \tau_c \) between fiber and matrix and thus leads to a shorter critical fiber length. This means that fibers can be shorter than the critical length calculated in the previous section and still show good strength. The prepared samples have fibers shorter than the critical length but after the addition of MAPP are the critical length reduced and the fibers are now long enough to result in a strong composite. If longer fibers could be maintained during processing less coupling agent would be needed to obtain sufficient strength. That would be economically favorable as MAPP is expensive, but is outside the scope of this study.

**E-Modulus**

Again, MAPP will enhance the adhesion and also the modulus, see figure 3-5. There is an increase in modulus from 3.74 GPa without MAPP to 4.16 GPa with MAPP, the growth is slight but it is a significant increase and worth noting. The amount of MAPP seems to have little impact on tensile modulus as the modulus is quite constant after 1 wt% MAPP.
Figure 3-5. Measurements of tensile modulus with different amount of coupling agent, 20 wt% flax fiber and 3 wt% MA-PP. The standard deviation is less than 6.7% and can slightly be seen in the chart.

The result from figure 3-5 is also presented in table 3-5.

Table 3-5. Measured E-modulus at different weight percentage of MAPP.

<table>
<thead>
<tr>
<th>MAPP [wt%]</th>
<th>E-modulus [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.7 ± 0.2</td>
</tr>
<tr>
<td>1</td>
<td>4.2 ± 0.2</td>
</tr>
<tr>
<td>3</td>
<td>4.0 ± 0.1</td>
</tr>
<tr>
<td>5</td>
<td>4.2 ± 0.3</td>
</tr>
<tr>
<td>7</td>
<td>4.3 ± 0.1</td>
</tr>
</tbody>
</table>

The stiffness was expected to increase additional with the addition of MAPP as the interfacial strength between fiber and matrix was strengthened. The result in figure 3-5 indicates a small increase in stiffness from 0 wt% to 1 wt% coupling agent. Higher amount of MAPP does not seem to affect the stiffness much. This indicates that we achieve good load transfer between fiber and matrix by addition of small amount of MAPP.

Impact Strength
The addition of MAPP lowers the impact strength slightly, regardless the amount of MAPP, see figure 3-6.

Figure 3-6. Measurements of impact strength with different amount of coupling agent and 20 wt% flax fiber. The standard deviation is less than 7.6% and can slightly be seen in the chart.

The result in figure 3-6 is also presented in table 3-6.

Table 3-6. Measured Impact strength at different weight percentage of MAPP.

<table>
<thead>
<tr>
<th>MAPP [wt%]</th>
<th>Impact Strength [kJ/m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6.1 ± 0.3</td>
</tr>
<tr>
<td>1</td>
<td>5.2 ± 0.3</td>
</tr>
<tr>
<td>3</td>
<td>5.4 ± 0.1</td>
</tr>
<tr>
<td>5</td>
<td>5.4 ± 0.3</td>
</tr>
<tr>
<td>7</td>
<td>5.2 ± 0.4</td>
</tr>
</tbody>
</table>

When good adhesion is achieved are the applied load transferred from the matrix to the fibers. As the fibers are more brittle than the matrix itself are the material become more brittle. Therefore increased adhesion leads to decreased impact resistant.

3.1.3 Effect of Reactive Filler

Tensile Strength
Surprisingly, the strength was negatively affected by the presence of CaO, see figure 3-7 and table 3-3. Here, the strength is lower for the samples containing CaO. The amount of CaO seems to not affect the strength at all, indicating that the CaO acts as a crack initiator.
CHAPTER 4. RESULT & DISCUSSION

The result from figure 3-7 is also presented in table 3-7.

Table 3-7. Measured tensile Strength at different weight percentage of CaO.

<table>
<thead>
<tr>
<th>CaO [wt%]</th>
<th>Tensile Strength [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>54 ± 1.5</td>
</tr>
<tr>
<td>1</td>
<td>49 ± 0.3</td>
</tr>
<tr>
<td>3</td>
<td>49 ± 0.5</td>
</tr>
<tr>
<td>5</td>
<td>48 ± 0.3</td>
</tr>
<tr>
<td>7</td>
<td>49 ± 0.3</td>
</tr>
</tbody>
</table>

The assumption about CaO interacting with the coupling agent to strength the adhesion between fiber and matrix seems incorrect according to results in figure 3-7, were the strength of the composite is reduced by addition of CaO. The specimen breaks because the fibers break and not because the adhesion between fiber and matrix is weak. Result from studies by Denault et al. shows great increase in both strength and stiffness when adding CaO to their flax reinforced polypropylene composites. Their composite have, however, not nearly as high strength as ours has with no coupling agent or additive. It may be because they mix together flax and polypropylene in the compounding step which can lead to poor dispersion, while we already have a well-dispersed material (non-woven) from the beginning. An inhomogeneous composite loses its strength and stiffness as it only has the reinforcing fibers in some areas. Therefore are their composite improved with CaO. We have already good adhesion and CaO does not affect the result.

**E-Modulus**

CaO does not seem to have an influence on the modulus, there is no significant change from 0 wt% to 7 wt%, see figure 3-8.

Table 3-8. Measured E-modulus at different weight percentage CaO.

<table>
<thead>
<tr>
<th>CaO [wt%]</th>
<th>E-modulus [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.0 ± 0.1</td>
</tr>
<tr>
<td>1</td>
<td>4.1 ± 0.2</td>
</tr>
<tr>
<td>3</td>
<td>4.0 ± 0.1</td>
</tr>
<tr>
<td>5</td>
<td>3.9 ± 0.1</td>
</tr>
<tr>
<td>7</td>
<td>4.2 ± 0.2</td>
</tr>
</tbody>
</table>

As we have very good compatibility between fiber and matrix with the addition of MAPP is the stiffness of the fibers the limiting factor. Thereby, the addition of CaO will not affect the modulus.

**Impact Strength**

Here, additional decrease in impact strength is obtained by the addition of CaO. From 5.4 kJ/m² to 4.5 kJ/m² with 7 wt% CaO as seen in figure 3-9.
CHAPTER 4. RESULT & DISCUSSION

Figure 3-9. Measurements of impact strength with different amount of CaO, 20 wt% flax fiber and 3 wt% MA-PP. The standard deviations is less than 6.6% and can slight be seen in the chart.

The result in figure 3-9 is also presented in table 3-9.

Table 3-9. Measured Impact strength at different weight percentage of CaO.

<table>
<thead>
<tr>
<th>CaO [wt%]</th>
<th>Impact strength [kJ/m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.4 ± 0.1</td>
</tr>
<tr>
<td>1</td>
<td>5.0 ± 0.2</td>
</tr>
<tr>
<td>3</td>
<td>5.0 ± 0.3</td>
</tr>
<tr>
<td>5</td>
<td>4.7 ± 0.3</td>
</tr>
<tr>
<td>7</td>
<td>4.5 ± 0.3</td>
</tr>
</tbody>
</table>

Fillers like CaO do also decrease the impact strength of the composite by acting as crack initiator. When adding CaO is certain amount of PP replaced and results in a more brittle material. The more CaO added to the composite the lower the impact strength.

3.2 Microstructure

The fracture surface of flax fiber reinforced polypropylene without coupling agent is shown in figure 3-10.

Images of the fracture surfaces clearly show the effect of coupling agent. The sample in figure 3-10 has no coupling agent and the fibers were pulled out the matrix as expected, its fibers are shorter than the critical length and the interfacial strength is thereby low. It is clearly visible in figure 3-10b), where the fibers are not adjacent the matrix.

Figure 3-11 shows the fracture surface of flax fiber reinforced polypropylene with MAPP.
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Figure 3-11. SEM images a) Overview of the surface fracture of 20 wt% flax reinforced polypropylene composite with 3 wt% MAPP. A clear reduction of fiber pull-out is seen. b) Close-up image of 20wt% flax reinforced polypropylene with 3 wt% MAPP.

The sample in figure 3-11 has coupling agent present and the fracture is very smooth as expected. The good interfacial shear strength is high, making the critical fiber length, $l_c$, shorter which means that the fibers in the samples are now longer than the critical length resulting in better adhesion and fiber breaking instead of pull-out. It is clearly seen in figure 3-11b) were the fibers are adjacent the matrix and no fiber pull-out have occurred.

Figure 3-12 shows a magnification of two samples. To the right, the sample with MAPP and to the left, the sample without MAPP. It is clearly visible even at this magnification that the sample to the right has higher adhesion between fiber and matrix as there are no visible fibers at the surface.

Figure 3-12. To the left, flax reinforced polypropylene without coupling agent. To the right, flax reinforced polypropylene with coupling agent.

The fracture surface in figure 3-13 is very similar to figure 3-11, indicating the good adhesion between fiber and matrix achieved with MAPP. The difference is the white spots found at the surface. It is clear that the interfacial strength has not been improved with the addition of CaO.

Figure 3-13. SEM image of the surface fracture of 20 wt% flax fiber reinforced polypropylene with 3 wt% MAPP and 7 wt% CaO.

3.2.1 Chemical Analysis
The spectrum in figure 3-14 is a chemical analysis of the white spots in figure 3-13. Here, the peaks indicate that the sample contains calcium carbonate (CaCO$_3$). The high C-peak comes from surrounding PP.
Figure 3-14. Identification of the components present in the white dots by SEM. Also in Appendix as figure 7-2.

Figure 3-15 shows the three different compositions. First, the red curve shows the spectrum of NF20. The blue curve corresponds to NF20MA3 and the green curve to NF20MA3CaO5. The curves is pretty much the same except the green curve which have an intense peak at 3642 cm\(^{-1}\), this corresponds to Ca(OH)\(_2\).

Figure 3-15. FTIR spectrum of three different material compositions. Red curve: 20 wt% flax. Blue curve: 20 wt% flax and 3 wt% MAPP. Green curve: 20 wt% flax, 3 wt% MAPP and 5 wt% CaO. Also in Appendix as figure 7-3.

Figure 3-16. Enlarged image of the peak round 3642 cm\(^{-1}\) from FTIR spectrum in figure 3-15.

Ca(OH)\(_2\) forms when CaO reacts with water, remember the purpose of adding CaO was to eliminate the excess water that could block the binding between MA-PP and fiber. During time will Ca(OH)\(_2\) react with carbon dioxide (CO\(_2\)) and form CaCO\(_3\) which is shown in figure 3-14. During the formation of CaCO\(_3\) is water going to be released and stay in the composite. By this result can the assumption of CaO interacting with MA-PP be eliminated. The different result from SEM and FTIR can be explained. Ca(OH)\(_2\) do react with carbon dioxide forming CaCO\(_3\) but it takes time before all Ca(OH)\(_2\) has react as the most CaO is sealed by the plastic matrix. Carbon dioxide will eventually react with all Ca(OH)\(_2\) as it slowly penetrates into the matrix. The analysis in SEM is done at the fracture surface which have been exposed to air for a certain amount of time and the Ca(OH)\(_2\) at the surface has being converted to CaCO\(_3\). When doing the analysis in FTIR was a small piece of the sample taken, probably from the core which have not been exposed for air. The result of FTIR showed that the sample contained Ca(OH)\(_2\) as shown in figure 3-15 and 3-16.

The explanation above can be strengthened by means of TGA, figure 3-17 and 3-18 will show that water have disappeared from the sample including CaO. Figure 3-17 shows that the sample includes about 1 wt% water which is
released round 100°C. Figure 3-17 is also shown in Appendix as figure 7-4.

Figure 3-17. TGA of 20 wt% flax fiber reinforced polypropylene with no additives. Also in Appendix as figure 7-4.

Figure 3-18 is an enlargement of the box in Figure 3-17 in order to show more clearly that there was water in the sample.

Figure 3-18. Enlargement of the area marked in figure 3-16.

Figure 3-19 shows that the sample contains no water as there is no step at 100°C, this is a proof of CaO absorbing water. Figure 3-19 is also shown in Appendix as figure 7-5.

Figure 3-19. TGA of flax fiber reinforced polypropylene with addition of CaO. Also in Appendix as figure 7-5.

Figure 3-20 is an enlargement of the box in Figure 3-19 in order to show more clearly that there was no water in the sample.

Figure 3-20. TGA of flax fiber reinforced polypropylene. Also in Appendix as figure 7-6.

CaO could be used as drying agent in natural fiber reinforced composites. Usually, drying takes long time and the production process could be shortened if the drying step was removed.

3.4 Degradation during Processing

As noted in section 3.1 Mechanical properties is the strength of the composite highest at 20 wt% fiber, that is a surprising result. In theory should both strength and stiffness be improved by adding more fiber as fibers are the stronger and stiffer component in the composite. However, the assumption of fibers being degraded during compounding leads to this part. The degradation of the composite was studied using TGA, figure 3-20 describes the process up to 900°C. Worth noting is the temperature at which the flax fibers starting to degrade (200°C), which will affect the fibers negatively.

When compounding the non-woven flax/polypropylene with 40 wt% fibers, the temperature increased above 225°C due to friction between fibers in the melt, more fibers leads to more friction and thus higher temperature. The high temperature made the
fibers brittle, resulting in a weak composite. Figure 3-21 shows the fracture surface of the composite with 40 wt% flax fibers and it is clearly visible that the fibers have been degraded.

Figure 3-21. SEM image of 40 wt% Flax fiber reinforced polypropylene processed with temperatures above 225°C a) Overview of the fracture surface. b) Close-up image of the fracture surface.

The temperature range between the melting point of polypropylene and the temperature were the fibers starts to degrade are short, making it difficult to process the composite. By slowing down the rotation of the screw can the friction can be reduced but it complicates the process as the material is likely to stick in there if the screw is feeding it to slow through the die.

3.5 Processability

An issue in processing is the injection pressure which needs to be kept low for a profitable process. The pressures used when injection molding is seen in table 3-10, the pressure increases with the fiber content.

<table>
<thead>
<tr>
<th>Fiber content [wt%]</th>
<th>Injection pressure [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>20-50</td>
</tr>
<tr>
<td>8</td>
<td>54</td>
</tr>
<tr>
<td>18</td>
<td>99</td>
</tr>
<tr>
<td>23</td>
<td>112</td>
</tr>
<tr>
<td>30</td>
<td>140</td>
</tr>
<tr>
<td>40</td>
<td>165</td>
</tr>
</tbody>
</table>

The difficulty in flax fiber reinforced polypropylene is that the fibers will increase the viscosity of the melt and the flow of the resin is retarded. The alternative is to increase the injection pressure but it is costly, since it causes machine wear. Both 30 and 40 wt% does need high injection pressures, way over 100 MPa and is not considered as optimal injection molding compounds. However, the composite with 20 wt% flax is easy to process and shows great strength and stiffness as seen in section 3.1.1 Flax Fiber Reinforcement.

The coil test was done to evaluate the flowability of the melt and is summarized in table 3-11. This is a very useful hands-on test to compare the viscosity of different materials, knowing in what application the material can be used.

<table>
<thead>
<tr>
<th>Melt pressure [MPa]</th>
<th>8 wt% [mm]</th>
<th>18 wt% [mm]</th>
<th>23 wt% [mm]</th>
<th>30 wt% [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>251</td>
<td>134</td>
<td>99</td>
<td>63</td>
</tr>
<tr>
<td>75</td>
<td>359</td>
<td>213</td>
<td>158</td>
<td>112</td>
</tr>
<tr>
<td>100</td>
<td>465</td>
<td>275</td>
<td>224</td>
<td>162</td>
</tr>
<tr>
<td>125</td>
<td>540</td>
<td>337</td>
<td>277</td>
<td>218</td>
</tr>
<tr>
<td>150</td>
<td>616</td>
<td>400</td>
<td>326</td>
<td>270</td>
</tr>
</tbody>
</table>

Materials with a greater flowability can fill more detailed molds without having to apply to high pressures. 20 wt% needs an injection pressure about 100 MPa and it floats round 250 mm, this is normal injection pressure for natural fiber reinforced composites. 8 wt% has also good flowability and is easy to process.
however, it has significantly lower mechanical properties and because of that is its application area limited. 30 wt% is considered as non-profitable due to its high injection pressures and poor flowability.

### 3.6 Plans for Future Research

By doing a literature survey were several unsolved problems found about NFTs. The results of this diploma work offer answers for them but during the examinations some other new questions were born. Time and volume of the work limited the investigations of these problems.

- Are the mechanical properties affected by the use of already compression molded composite? Is the material going to have inferior properties after compression molding?
- How many times can the composite be reprocessed before starting to degrade?
5. Conclusion

The study shows that:

- 20wt% flax is the most favorable fiber content. There is no great advantageous of reinforce the composite by either 30 wt% or 40 wt% flax fibers because the composite will be difficult to process without degradation.

- MAPP proves its strength as a coupling agent, 1 wt% MAPP is enough to improve the composites mechanical properties significantly.

- CaO could be used as drying agent in biocomposites. Usually, drying takes long time and the production process could be shortened if the drying step was removed. However, CaO does not improve the mechanical properties, depending on the already good adhesion obtained with the addition of MA-PP.

The composition of 20 wt% flax, 1 wt% MAPP and 79 wt% polypropylene is the technically most favorable.
6. References


2013.


[31] R. Anandjiwala and E. Erasmus, "Enhancement of mechanical properties and interfacial adhesion by chemical modification of natural fiber-reinforced


7. Appendix

Figure 7-1. Screw configuration, specially constructed for flax fiber composite. Kneading and shredding elements was placed at 52, 60, 65, 75.5 and 79 cm according to the scale.
Figur 7-2. Inducation of compounds in the white dots, analysis in SEM.
Figure 7.3. FTIR spectrum of three different compositions. Red curve: 20 wt% flax. Blue curve: 20 wt% flax and 3 wt% MAPP. Green curve: 20 wt% flax, 3 wt% MAPP and 5 wt% CaO. Also in Appendix.
Figure 7.4. TGA of flax fiber reinforced polypropylene with no additives.
Figure 4-5. TGA of flax fiber reinforced polypropylene with addition of CaO.
Figure 7-6. TGA of flax fiber reinforced polypropylene.