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Manufacturing of PLA-based composites reinforced with cellulose fibers and fibrils

Master of Science Thesis in the Master Degree Program, Materials and Nanotechnology

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Manufacturing of PLA-based composites reinforced with cellulose fibers and fibrils

An approach to produce materials from sustainable resources

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Abstract

Over the last two decades the development in material engineering has increased exponentially. Much attention and research has been focused at multi-component materials or composites, typically containing a matrix reinforced with fibers. Composites are: light weight, low density, and thermal resistant materials with excellent mechanical properties. Parallel to development of composites, plastics, both thermosets and thermoplastics, have had a major impact on the packaging industry and has become an integral part of people's everyday life. Plastics are customizable, easy to process and cheap. Due to volatile oil prices and a growing environmental concern both from a consumer and an industrial point of view, plastic alone is not a sustainable option. For this reason, the demand is to find more environmentally friendly materials.

Extensive research has started to investigate cellulose as both a reinforcing agent and filler in thermoplastic based composites. Attention over recent years has been raised for micro-fibrillated (MFC) cellulose which is cellulose fibrils one step down in the hierarchical structure of wood fibers. MFC has a greatly expanded surface area thus exhibiting different properties compared to normal pulp. In previous studies MFC had been used as a reinforcing agent in bio degradable polylactic acid matrices which have shown a great improvement of properties, both thermally and mechanically. How different qualities of pulps alone or in combination are sufficient to achieve these improvements have not yet been fully investigated.

One of the goals of this study was to find a way to reduce the amount of plastic and substitute it with cellulose fibers in order to maintaining or improve the mechanical properties of the composite. The other goal was to develop and evaluate the most suitable method to produce the films.
The approach similar to that of papermaking proved to be the most efficient method. Following this method, composites with varying amounts of pulp/MFC/PLA content were produced. The qualities investigated were highly refined kraft pulp (HRKP), MFC, kraft pulp (BSKP), chemithermomechanical pulp (CTMP) and broke. Results showed no significant differences in tensile strength between the qualities at content up to 60 % cellulose. At higher cellulose contents, 70 % and above, HRKP followed by MFC were the most suitable reinforcements. When attempting to reinforce HRKP/PLA composites with small amounts of MFC (0-10%) no improvements on the tensile strength could be observed.

Acknowledgement

Innehåll

1   Introduction

1.1   The reduction of plastic waste: a future challenge

Plastics have had a major impact on people's everyday lives and paved the way for novel materials. It is assessed that the annual consumption in Western Europe adds up to as much as 60 million tons. As a consequence an estimated 23 million tons of plastic waste is produced annually. Around 63 wt. % of this comes from packaging (1). A majority of the plastics waste corresponds to thermoplastics such as PE, PP, PET and PVC and although they are recyclable the percentage of reused material is low due to complex waste streams and often these ends up as landfills (2).

1.2   Composites produced from a sustainable feedstock: a possible solution?

One of the major advantages with wood based raw materials is that it is produced from a renewable feedstock which makes it highly interesting along with today's increasing environmental awareness. Cellulose fibers have been used as a reinforcing agent in composites with matrixes ranging from plastics to concrete, but the improvement in mechanical properties has been limited and not been able to outshine the filler application as of yet. In the 1980's with the advent of Turbak's process to produce fibrillated cellulose out of pulp, suggested applications ranged from baking ingredients to a possible new super material. The attention of nano cellulose however died out due to the extreme energy consumption required during production. Much of the research that followed Turbak's patent was to facilitate the delamination of the fibrils in order lower the amount of energy used in production and due to much fortune with respect to this matter fibrillated cellulose has landed in the scientific spotlight once more.

Various methods to produce PLA based composites reinforced with fibrillated cellulose with interesting results with regards to mechanical properties have created a buzz in the scientific community over recent years but one problem however with these methods is that they often are limited to laboratory scale production and often suffers from time demanding treatments or processing steps. If a time efficient method with few to no intermediate steps could be established producing plastic based composites, fibrillated cellulose would be a supplement to both the carton and the plastic based packaging industries in order to create novel materials for a sustainable future.

1.3   Aim of project

- Produce manageable sheets of composites using PLA as matrix with a time efficient method with few to none intermediate steps.
- Determine whether only a minor addition of MFC in combination with finely refined pulp is sufficient to enhance mechanical properties in plastic resin composites.
- Investigate the possibility to reduce the amount of plastic by substituting the plastic content with e.g. 40 % cellulose fibers and/or MFC without compromising the integrity of the mechanical properties.
- Determine the mechanical properties of the sheets produced.
- Investigate structural differences for samples before and after heat treatment with SEM.

1.4   Thesis Outline

Initially this work consists of a literature study covering some basics theory about pulping processes, MFC, cellulose, PLA and composites. The results section begins with an experimental setup in order to give a detailed description of the methodology as well as materials and equipment that were used in this study. The results are then presented in the order; influence of methodology, SEM analysis and mechanical testing. The outcome of these results are discussed and summarized in the discussion section 5 and concluded in the conclusion section 6.

Parts of the literature study that was outside the scope of this thesis, but yet of interest, as well as experimental setups for other methods used in this study can be found in the Appendix.

2   Background

2.1   Pulp and pulping: different approaches

By mechanical and/or chemical treatment it is possible to liberate fibers and other lignocellulose materials that can be dispersed in water. The pulp can thereafter be reformed by web formation due to fiber-fiber interactions. The type of processes used to free discrete fibers, also referred to as pulp processes or pulping can be divided into three categories: chemical, chemical-mechanical and mechanical pulping. Chemical pulping is the process which relies on chemical treatment in order to free the fibers. This method tends to lower the total yield of the wood (40-50%) and removes the ligno-cellulosic compounds through chemical degradation. Moreover, fibers produced by chemical pulping remain their structural integrity. The removal of the lingo-cellulosic compounds that often covers the surface of fibers increase the amount of available hydroxyl groups, promoting fiber-fiber interaction. Mechanical pulping however, give rise to much higher yield (90-98%) of the wood but rely solely on physical action at the cost of more required energy and ruptured fibers packages (3).

2.2   Kraft Process

The Kraft Process (KP) is a pure chemical method and the dominant pulping process used today. It uses sodium hydroxide and sodium sulfide in alkaline conditions under moderate pressure and temperatures to dissolve the lignin and to separate the wood fibers. The process is applicable for both hard and softwood sources. What further gives the KP an advantage compared to other chemical processes, e.g. the sulfite process, is the possibility to recover and recycle its chemical constituents. Bleached kraft pulp is often used as starting material to produce micro-fibrillated cellulose (MFC) (3) (4).

2.3   Schopper-Riegler concept

The drainage of pulp is an important factor when it comes to the production of paper. Schopper-Riegler freeness (SR) is a method to measure drainage of 1 liter of 0.3 % pulp slurry through a calibrated screen. The drainage of the water will be dependent on the number of channels present in the fiber network. Small channels or low freeness will result in a high SR-value and correlates to finely coursed fibers and less refines fibers i.e. large channels or high freeness will result in a fast drainage of the pulp (3)

2.4   Cellulose structure and morphology

Cellulose is the most abundant macro molecule in the world with an estimated worldwide production between 10^{10} and 10^{11} tons annually (5). The hierarchical structure of cellulose fibers consists of β-1.4-linked anhydro-D-glucose repeating units in the order of 10000-15000. Each monomer has three hydroxyl groups that will cause intra-molecular hydrogen bonding. As a result of this, the micro fibrils will consist of amorphous and crystalline regions. The crystal unit cell is build up by five cellulose chains as depicted in Figure 1 with dimension of approximately 8*8*80 Å (3). The micro fibrils can be intertwined further, through intermolecular hydrogen bonding, into micro fibrillated cellulose (MFC) as illustrated in Figure 2 (4) (6). The abundance of hydrogen bonding both intra and intermolecular has been used to explain the fact that cellulose is insoluble in water. This has however been questioned by Lindman et al. that reported that cellulose displays amphiphilic, rather than hydrophilic properties and that the hydrophobic effect is integral instead. (7)
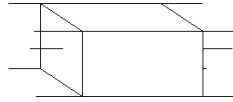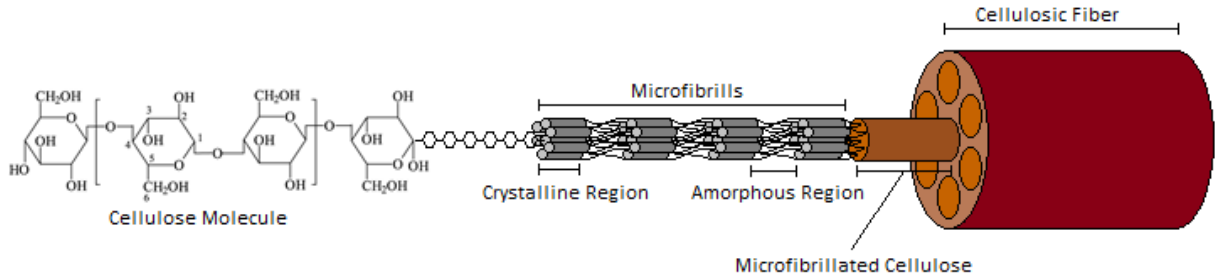
Figure 2 hierarchical structure of a wood from a cellulose molecule to a cellulose fiber.

2.5   MFC produced from wood-based materials now and then

The first patent regarding the extraction and production of MFC was released in 1983 by Turbak et al. (8). In that process pulp was passed through a narrow gap several times under high pressure. One drawback however, was that extensive amount of energy required. Therefore much of the research that has followed that of Turbak's has tried to establish new energy effective methods (9) (10). Today there are mainly three different techniques that disintegrate the cellulose fibers mechanically into MFC: the homogenizer, ultra-fine friction grinder and the micro-fluidizer from Microfluidics Corp (4).

With a fluidizer the fiber suspension is passed through a z-shaped channel under high pressure up to 3000 bar. This enables the production of polydispersed fibers with smaller dimensions than that of the homogenizer due to high shear rates (11). The most commonly used starting material to produce MFC is bleached chemical pulp that has its source from wood.

MFC consists of clusters of fibrils with varying dimensions; typically a diameter in the range of 20-60 nm and lengths of several microns. Klemm et al. has summarized different studies in his article that investigated the width of the fibrils. These studies indicated that MFC displays two hierarchical levels; one in the range of 15-20 nm and another in the range of 3-5 nm. The results corresponded well with the aggregation of cellulose fibrils as seen in **Figure 3** studied by Brändström et al. (12). MFC displays a high surface area with a factor of 10 compared to e.g. kraft pulp (4) meaning that more hydroxyl groups are able to form hydrogen bonds. As a consequence of this, MFC dispersed in water form gels even at low concentrations (13).
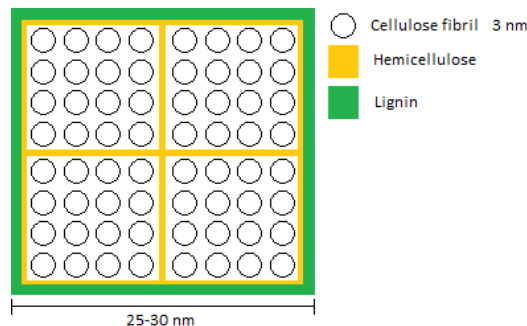
Figure 3 cellulose fibrils aggregate to form larger bundles of fibers creating a hierarchical structure (13).

2.6 Pre-treatments

2.6.1 Enzymatic treatment

To decrease the energy required when producing MFC the method of using enzymes as pre-treatment was investigated by Pääkkö et al. (10). This mild method hydrolyzed the fibers facilitating the mechanical disintegration and thus reducing the energy consumption during grinding. Enzyme treatment promotes cell wall delamination that facilitates the operation of the fluidizer. Henriksson et al. (9) investigated the differences between enzyme treatment and acid hydrolysis and studied the resulting MFC in atomic force microscopy (AFM) and showed that enzymatic treatment rendered fibers with a higher average molar mass and larger aspect ratio.

For more pre-treatments outside the scope of this thesis, see Appendix section 9 and 10.

2.7 Polylactic acid

Polylactic acid (PLA), see Figure 4, is biodegradable polyester prepared either through condensation of lactic acid or by ring-opening polymerization (ROP). Generally the monomers of PLA are obtained through fermentation of dextrose carried out by bacteria. PLA is therefore a polymer produced from a renewable rather than a petrol based feedstock (14).
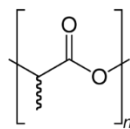
Figure 4 repeating unit of PLA

To produce 500,000 tons of PLA less than 0.5% of annual US corn crop is required. The impact that PLA has had on the market has been limited due to high production costs (more than 4 $ per kg) (14) but due to volatile crude oil prices the production of PLA has increased. Figures from 2009 shows that PLA stood for 5 % of the total world production of renewable biodegradable plastics. As illustrated in Figure 5; alongside with starch based plastics production of PLA has increased and is planned to grow even more in the future (15).
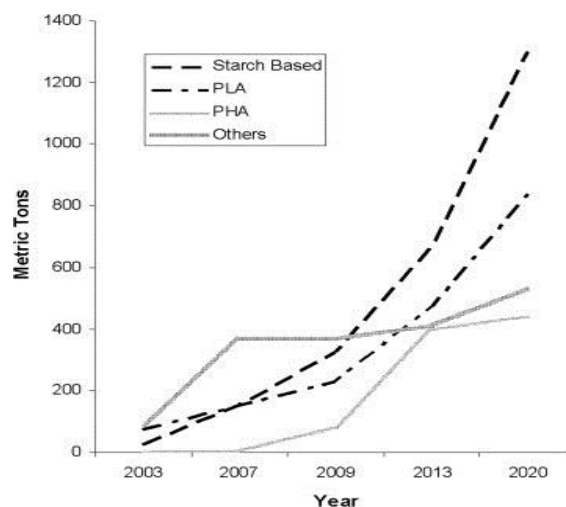
Figure 5 Previous and planned production of bio-degradable plastics in metric tons (16)

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2.8   Basic concept of composites

A composite is defined as a system of materials, a mixture of two or more physical phases, which in combination yields properties very different to that of each individual species alone (17). An example is wood where cellulose fibrils reinforce a matrix consisting of lignin and hemicellulose. Other occurring fiber reinforcements are glass or carbon dispersed in a polymer plastic matrix which gives rise to a resulting material that is stiffer and stronger. If the fibers are long enough and oriented, the stiffness and strength can be calculated by the rule of mixture:

$$E_{composite} = \phi_m E_m + \phi_f E_f \text{ (Pa)} \tag{1}$$

$$\sigma_{composite} = \phi_m \sigma_m + \phi_f \sigma_f \text{ (Pa)} \tag{2}$$

Where ϕ is the volume fraction of either the matrix (m) or fiber (f) and their respective σ strength and E modulus (Pa).

When load is applied, shearing forces within the matrix is transferred to the stiff fiber that will improve the mechanical properties of the final product. In terms of composites the concept of the critical fiber length is an important factor to consider when determining the properties of the resulting composite. The critical fiber length is defined as the length (of the fiber) at which the tensile stress is able to reach its maximum without compromising the structural integrity of the composite. When the length of the fiber is lower than the critical fiber length the stress applied might be higher than the interface between the fiber and matrix can sustain, resulting in failure within the material. Whereas when the length of the fiber is higher in comparison to the critical fiber length the load may be more than the fiber can sustain which causes it to break. Interfaces where weak interactions between the fiber and the matrix are present act as internal defects. The interfacial strength is however not the ultimate solution since this could render a brittle composite since cracks will not be hindered through branching or interfacial delamination. The optimal way is therefore to create a controlled interfacial strength rather than the strongest (18).

Composites are non-isotropic materials, meaning that they display directionality depending on the length and orientation of the fibers, see Figure 6. As a consequence of this, mechanical properties will be different depending on in which direction the test will be performed.
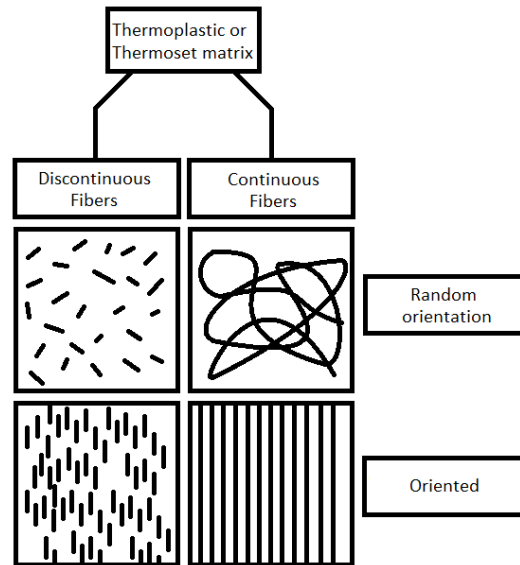
Figure 6 different dimensions and orientation of the reinforcing fibers in a composite (18). Combinations are possible as well.

2.9 Plastic based composites with MFC and cellulose fibers as reinforcing agents

Numerous studies have been carried out with MFC cellulose fibers as reinforcing agent in composites. In general the addition of MFC had a profound effect on the mechanical properties. Different sources to produce MFC from wood-based and non-wood materials; using various matrixes both thermoplastics and thermosets have been investigated. Efforts to produce bio-composites using biodegradable plastics such as PLA have been made as well (19). A study carried out by Nakagaito et al. produced MFC/PLA films by a method much like that of paper making. The results showed good dispersion of MFC, even at high amounts, and mechanical properties increased linear with increasing MFC content (20). A similar study was conducted by Larsson et al. that showed comparable results (21). The paper-like method seems to be the straightest forward in comparison to other procedures such as those reported by Mathew et al. and Iwatake et al. who produced PLA composites reinforced with cellulose nano whiskers[1], MFC and kraft pulp by mixing in a twin screw extruder (22) (23). Other bio-degradable matrixes like polyvinyl alcohol (PVOH) and starch (amylopectin) reinforced with MFC were reported to yield improved mechanical properties. When MFC and starch were combined MFC acted both as a reinforcing agent and a plasticizer which gave rise to stronger and less brittle films (24).

2.10 Scientific space from literature study

From the literature study both PLA and cellulose appears as interesting constituents with respect to sustainability. PLA, although its relative high production cost, is becoming more common on the market due to volatile oil prices and that it is produced from a renewable feedstock. Furthermore, new methods to refine cellulose pulp into something novel as MFC is always of interest to the paper and carton industry which is an industry with a slow rate of proactive development. Although MFC is a rather old concept, enzymatic pre-treatment presented by Pääkkö et al. and Henriksson et al. that decrease the amount of energy sheds new interest to fibrillated cellulose as a substitute or reinforcement to ordinary pulp (9)(10). Both promising as well as interesting results have been

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[1] CNW or cellulose nano whiskers are pretreated MFC where the amorphous regions have been hydrolyzed thus rendering crystalline cellulose tubes.

presented. When it comes to developing methods for producing composites with MFC as reinforcement agent, the works of Nakagatio et al. and Larssons et al. stands out in particular. Both reports showed results that MFC can greatly improve the mechanical properties in PLA/MFC composites. Moreover, with the fact that their method is simple as well as their use of PLA in the form of latex can facilitate a possible upscaling to industrial scale. The drawback to these methods however is that they involve time consuming intermediate steps, such as degasing and drying in vacuum. It would therefore be of interest to repeat the work of Larsson et al. by producing composites with varying MFC content in a PLA matrix with a method similar to that of paper making but to leave out the time consuming steps and evaluate if good results still could be achieved. Another issue of great interest, not covered by the works previously mentioned, is that regarding the choice to use MFC as a reinforcing agent rather than other types of pulps. To compare this could give indications whether it is economically viable to produce MFC for reinforcement in a PLA matrix, compared to either highly or less refined pulps such as HRKP, CTMP and kraft pulp.

3 Method and materials

3.1 Experimental setup and manufacturing of composites with a sheet former

Three different methods were evaluated; sheet former, Büchner funnel and Formette. The procedure explained in this section, i.e. the sheet former was the method of choice which proved to be the most effective one, see Figure 7 for illustration. The method is divided into three phases: wet, dry and melting step. No coupling agents or pre-treatments were used to enhance compatibility. Tensile strength and strain was evaluated and used as a parameter when comparing the different composites to each other. Description of the Büchner funnel and the Formette method, see Appendix section 11.1 and 11.4.

3.1.1 Materials

The latex used as matrix was PLA (Landy-1000 and -2000, Myioshi Oil & Fat Co. Ltd., Japan) with a mean particle size of 2 and 8 µm respectively. Five qualities of pulp were investigated; kraft pulp SR30, Broke SR24[2], CTMP[3] SR24, provided by Stora Enso Skoghall, highly refined kraft pulp (HRKP) SR90 from Imatra Finland and generation 1 MFC provided by Innventia (25), see section 2.3 for an explanation regarding SR.

3.1.2 Wet step

Samples prepared by the sheet former method were designed as a two layered composite that was formed on a filter membrane (Polyester 20 µm, MONODUR® Gråbo). The initial bottom layer consisted of pure HRKP with a grammage of 20 gm^{-2}. The second composite layer contained the composite in question with varying amounts of PLA and fibers/ fibrils with a grammage of 100 gm^{-2}, see Figure 1 for illustration. Deionized water was used in all solutions. The HRKP used for the bottom layer was diluted to 3gl^{-1} and stirred with a magnet for 30 seconds until the solution was free from flocculation which was otherwise removed with a spoon. The solution was then poured into the container of the sheet former followed by de-watering by vacuum. For the composite layer PLA and pulp was diluted to approximately 1 gl^{-1} followed by mixing with a magnetic stirrer (in this step some samples were reinforced with 0-10 wt. % MFC) and then poured on top of the bottom later followed by repeating the de-watering step.

3.1.3 Drying step

The monodur fabric with the moist sample was then pressed between blotting paper under 2 bar for 30 seconds to remove much of the moisture content. This procedure facilitated the removal of the composite film that was peeled from the monodur fabric and placed between dry blotting paper and left to dry under a constant pressure of 2 bar for 1 h.

3.1.4 Melting step

The dry sample was placed between two aluminum cylinders wrapped in aluminum foil to facilitate removal of the specimens and pressed for 5 minutes in 150° C. Prior to mechanical testing, samples were conditioned 24 h in dry environment followed by 24 h of conditioning in 50% humidity. Thickness was measured four times for each sample (TJT-Teknik AB STFI M201). The conditioned samples were then cut into three pieces with the dimensions 100x15 mm^{2}. Tensile-testing was

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[2] Broke is re-grinded carton board that is wasted during production and then recycled in the pulp chain. Broke is therefore often a mixture of different pulp qualities, both bleached and unbleached.
[3] CTMP or chemithermomechanical pulp is produced by a mild chemical treatment followed by immense mechanical grinding and contains high amounts of lignin and hemicellulose.

performed at 1 mms^{-1} (Zwik/ Roell Z010).

Prior to SEM analysis (Zeiss EVO MA10), samples were imbedded in epoxy resin and covered with gold.

Figure 7 A standard sheet former. A) the container in which the solution was poured in to B) regulation of vacuum
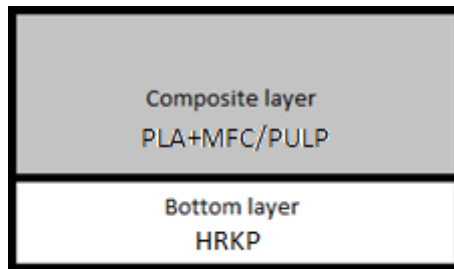

Figure 8 Illustration of the two layers formed through the two step approach: bottom layer and composite layer.

4   Results

4.1   Influence of methodology

The following sections 4.1.1 to 4.1.4 cover the outcome of the different methods evaluated in this study. The outcome was evaluated with respect to how much time that was put into making one film of composite, but other factors such as visible formation and appearances and how easy the samples were to handle was also taken into consideration.

4.1.1   PLA/MFC composites made by pre-drying in Büchner funnel

Films produced by following the procedure described in Appendix section 11.1 did not display satisfactory appearances when dried. The films shrunk considerably and as a result of this also crimped on the surface. Furthermore, no sample showed uniform surfaces due to major bubble formation within the matrix which resulted in small holes. Therefore the films could neither be analyzed mechanically nor used as reference later on in this study. This method was efficient but resulted in sheets of poor quality and appearance even though the blend of MFC and PLA appeared as homogenous gel prior to pressing.

4.1.2   Formette method

For sheets produced by the Formette methods, as described in Appendix section 11.4, 11.5 and 11.6, up to 90 % of the PLA content were lost in the process. The formed film comprised almost exclusively of fibers with small traces of PLA. The two-step approach applied on the Formette method decreased the loss of PLA marginally. The change of nozzle and the addition of retention agents had a minor impact on the amount of PLA that remained in final composite.

4.1.3   Fibers impregnated with alkyl ketene (AKD) without bottom layer

Films produced according to the approach described in section 11.2 resulted in films that were difficult to analyze. This was mostly due to the PLA latex diffusing in the fabric on which the films were vacuumed on, causing the film to stick. Furthermore, the loss of PLA was close to 40 %. Whether this was due the absence of the bottom layer was not further investigated.

4.1.4   MFC reinforced HRKP/ PLA composites with a bottom layer

Films produced by the method described in section 3 were easy to remove from the monodur fabric and displayed small to no crimping on the surface, making them suitable for analysis. The weight loss decreased dramatically from 40 % down to 5-15 % with the two step approach. However, bubble formation occurred for almost all samples.

4.2   SEM images

4.2.1   HRKP reinforced composites with a bottom layer before and after hot pressing

Figure 9 shows the presence of PLA in the form of latex marbles. As a result of the two-step approach with an initial addition of HRKP a distinct bottom layer separated by crack is present. The function of the bottom layer was two folded. Firstly the barrier property was to prevent PLA from being drained during an early stage of the vacuum filtration and secondly enable the PLA to diffuse slowly during vacuum filtration resulting in a gradient of PLA content internally. This was not achieved however, as illustrated in Figure 10 where no traces of PLA could be observed in bottom layer. Latex marbles appears to be fairly distributed in the composite layer but more represented further down in the composite layer.

11
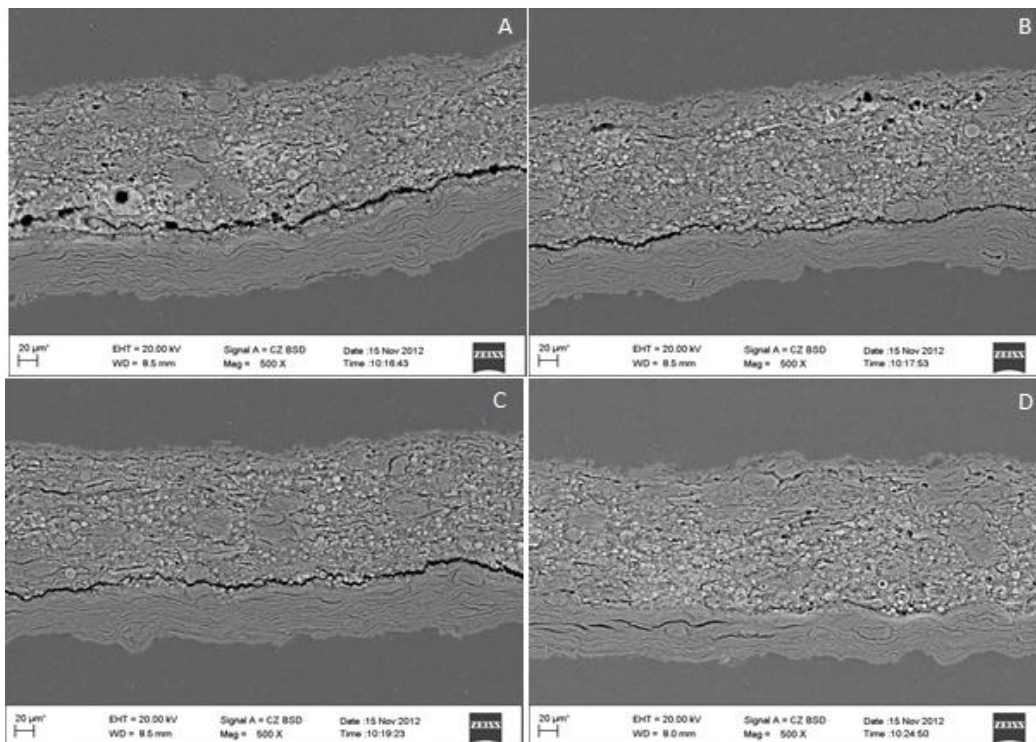
Figure 9 50/50 HRKP/PLA sample with a pure 20 gm^{-2} HRKP bottom layer not yet hot pressed. Latex marbles can be observed in the composite layer. Magnification 500x.
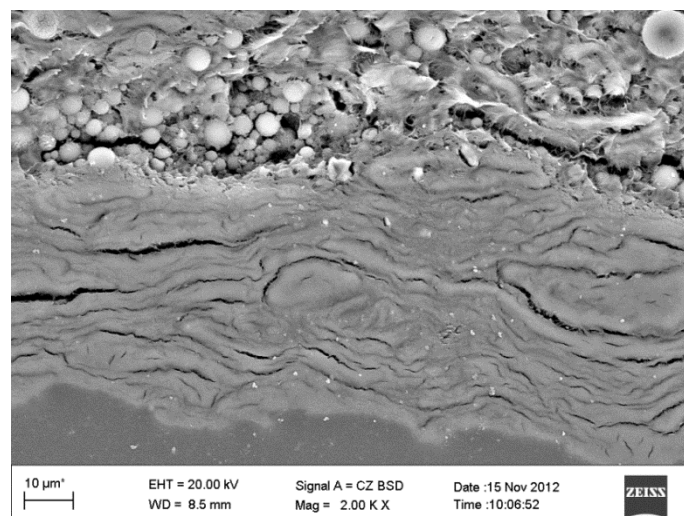
Figure 10 Magnified (2000x) of a 50/50 HRKP/PLA sample not yet hot pressed. No PLA appears to be present in the bottom layer.

The samples that were hot pressed appear as one phase, as illustrated in Figure 11, in contrast to the sample dried at room temperature, see Figure 9. Higher magnification reveals two distinct phases that could be observed as illustrated in Figure 12. Although morphologies are different between the two layers, no boarder or crack separates the two phases which suggest good adhesion.
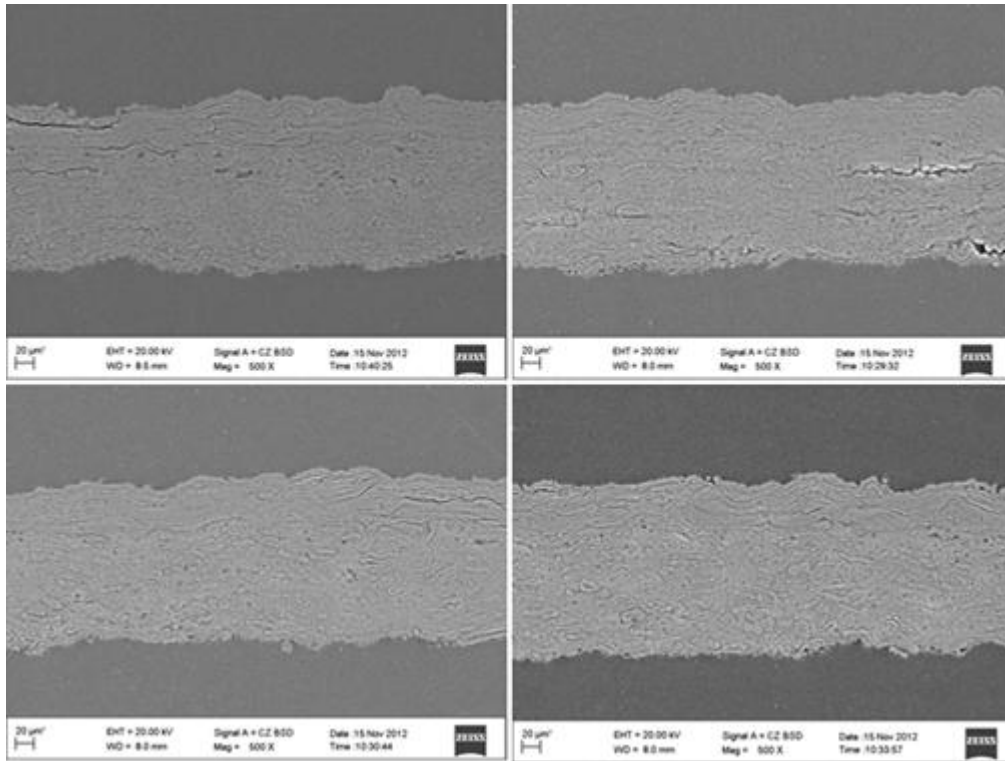
Figure 11 Hot pressed 50/50 HRKP/PLA composites. Mag 500x.
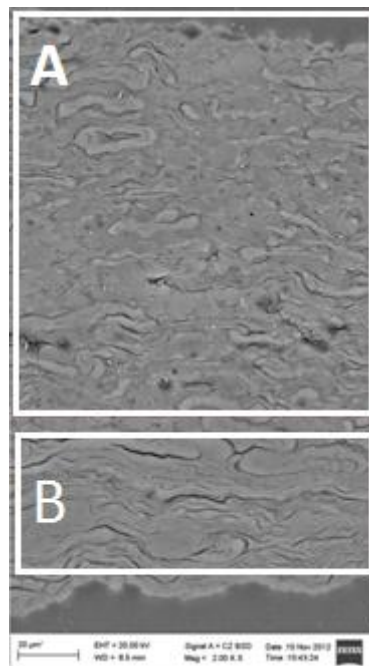
Figure 12 Magnification (2000000x) of a hot pressed 50/50 HRKP/PLA sample. Two distinct phases can be observed. A) Marks the composite layer containing both HRKP and PLA. B) Marks the bottom layer comprising pure HRKP.

4.2.2   Kraft pulp reinforced composites and pure kraft pulp film

SEM images for the kraft pulp/PLA samples showed fairly good dispersion for 50/ 50 samples, see Figure 13. This was in contrast to the samples containing pure kraft pulp sample which had major defects and voids internally, see Figure 14.
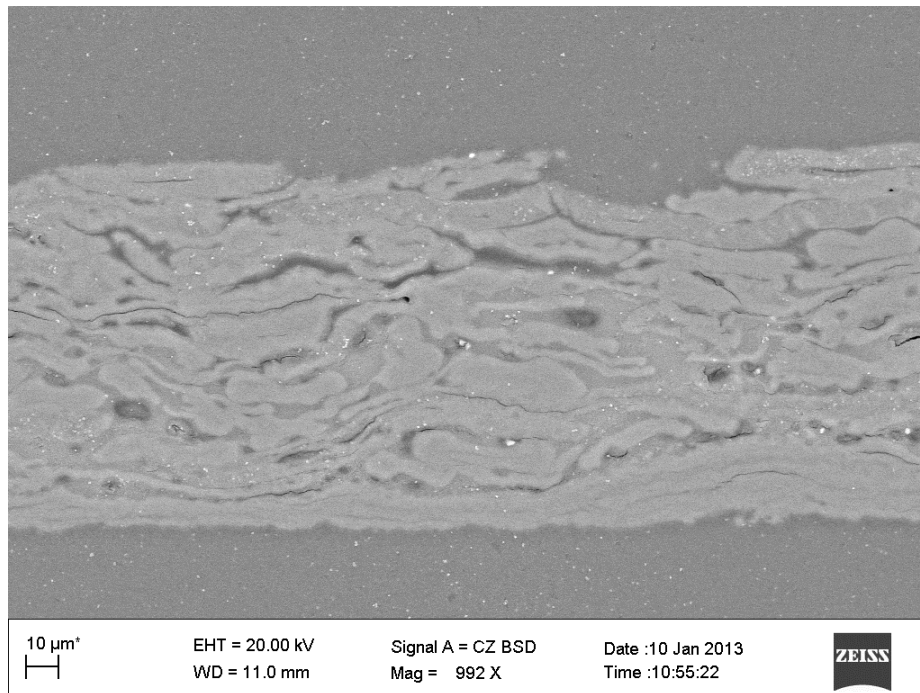
Figure 13 50/ 50 kraft pulp/ PLA composite. Dispersion is limited between the two species. Magnification 992x.
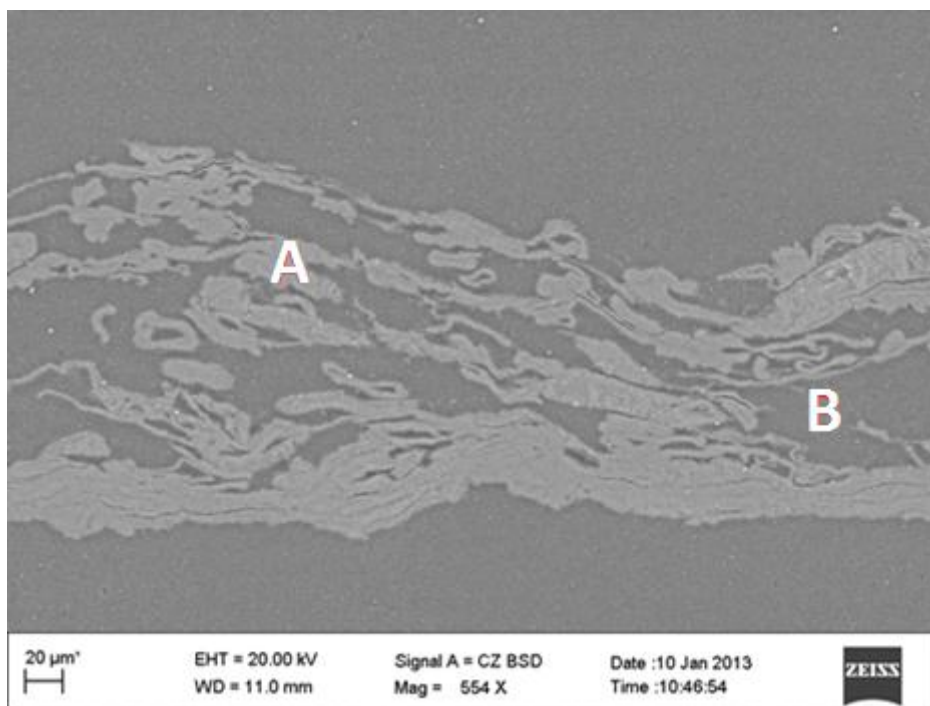
Figure 14 Sample of pure kraft pulp with A) fiber aggregation and B) void/ defects. Magnification 554x.

4.2.3   HRKP reinforced composites with small additions of MFC

Figure 15 shows SEM images of a sample comprising 60 wt. % PLA and 40 wt. % HRKP with varying amounts of MFC: 0, 2, 4 and 6 wt. % respectively prepared as described in section 3. Sample B and C containing 2 and 4 wt. % MFC respectively appeared as semi-transparent films without formations of

bubbles which can be observed in Figure 15 picture B and C. However, inhomogeneous morphology with clusters of either cellulose or PLA is present which indicate poor dispersion. The characteristic morphology was present in all four samples and appears to be more occurring near the surfaces but is best observed for sample A Figure 15 which suggests that the amount of MFC added had no effect on the overall dispersion.
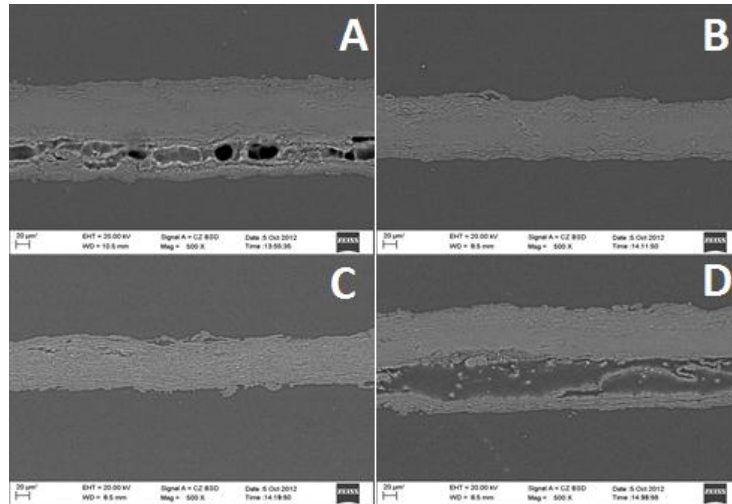
Figure 15 MFC reinforced 40/60 HRKP/PLA composites. Major defects can be observed in picture A and D. Samples shown in picture B and C appeared as smooth samples.

4.3 Mechanical testing

4.3.1 HRKP/ PLA composites with varying pulp content and relative bottom layer thickness

Tensile strength of prepared samples with an increasing HRKP content (30-100 wt. %) and relative bottom layer (see Appendix section 11.3) was fairly constant up to 70 %. Further addition gave rise to a more pronounced increase in tensile strength. The low value from the 50% samples was due to poor quality of the produced sheets. Moreover, the tensile strength for the 100% samples varied greatly ranging from 60-110 MPa. Comparing the strain curves an increasing pulp content give rise to a more distinct plastic region, see Figure 19. The elastic contribution remains constant independent of the amount in the composite. However, the strain behavior changed dramatically with increasing content as shown in Figure 17. The effect could be observed for samples containing 70 % pulp and showed an even more pronounced effect for pure HRKP samples. Composites containing less than 70% HRKP resulted in similar stiff materials with low percentage of elongation.
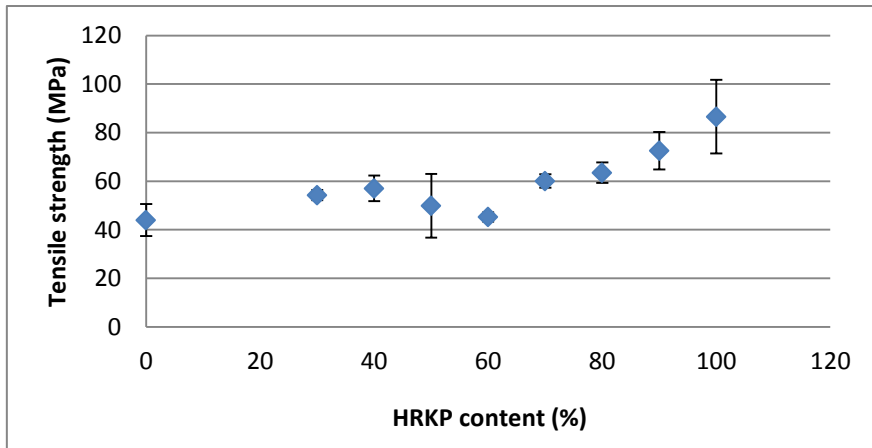
Figure 16 Tensile strength for PLA composites reinforced with varying amounts of HRKP
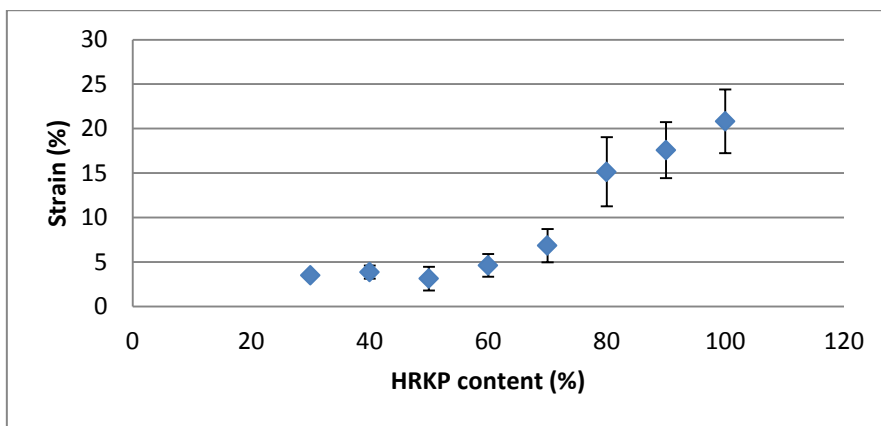
Figure 17 Strain plotted against increasing HRKP content
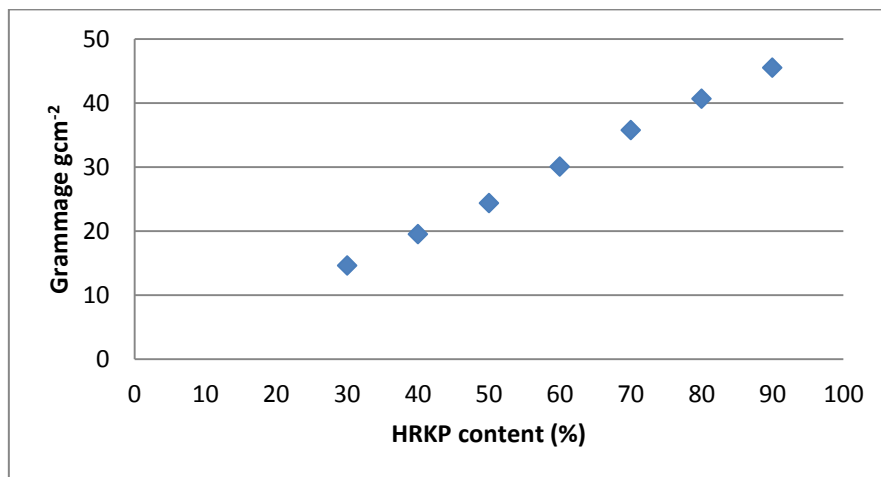
Figure 18 since 50 % of the total HRKP content was added as a bottom layer the grammage increased relative to total amount of pulp present in the composite.
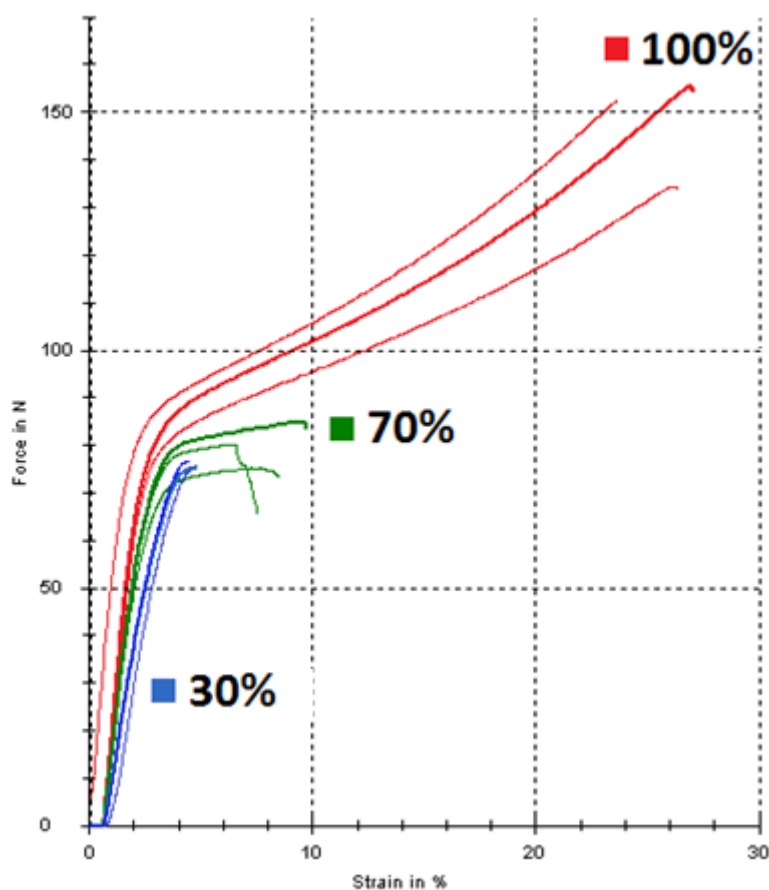
Figure 19 Stress strain curves of HRKP/ PLA composites: 100/0 in red, 70/30 green and 30/70 blue

4.3.2   PLA Composites with constant bottom layer containing refined pulps: HRKP and MFC

Samples with a constant bottom layer were prepared accordingly to procedures described in section 3. The tensile strength increased with increasing amount of HRKP added up to 70 %. Overall the tensile strength was higher for all samples in comparison to the samples made where the bottom layer was relative to the amount HRKP added, Figure 16 and Figure 20.
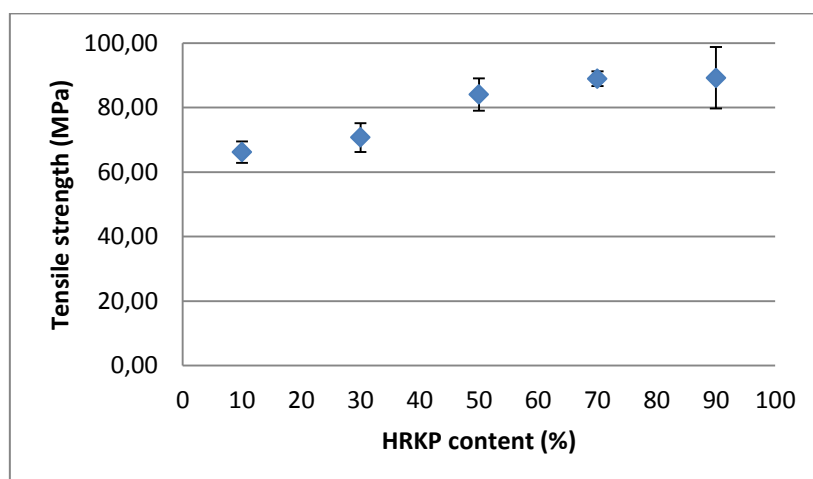
Figure 20 Tensile strength for HRKP/ PLA composites with constant bottom layer plotted against increasing HRKP content

Results presented in Figure 21 compare the tensile strength of composites reinforced with the refined pulps: MFC and HRKP. Overall, the tensile strength increased for both qualities with an

increasing amount of reinforcement. HRKP samples performed better compared to MFC samples at low to intermediate (10-90%) pulp concentrations but equally well for pure pulp films. Furthermore, as displayed in Figure 21 bottom picture tensile strength could be increased with 80 % and 35 % for 50/50 samples of HRKP and MFC respectively compared to pure PLA films.
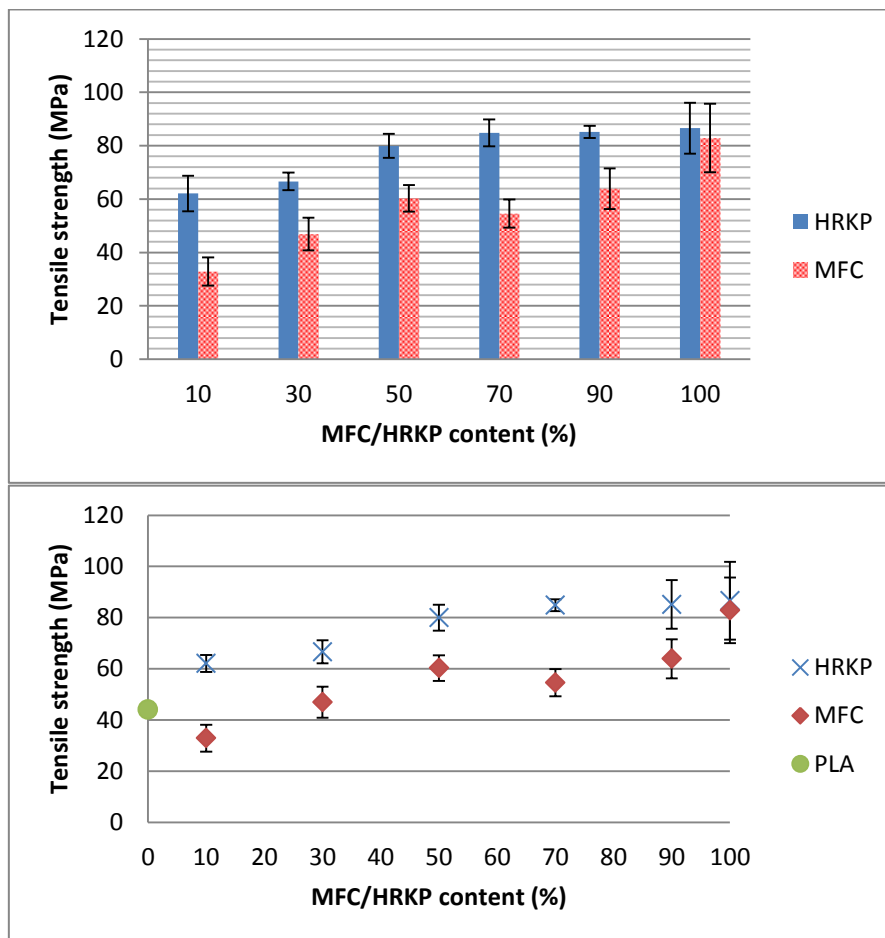
Figure 21 Comparison of tensile strength of HRKP and MFC composites with increasing pulp content. Note the pure PLA.

4.3.3 PLA composites with a constant bottom layer containing less refined pulps: kraft pulp, CTMP and broke

Less refined pulps showed similar trends to that displayed in Figure 21. Tensile strength increased with an increasing amount of pulp but started to decrease when pulp content reached 80 % and more. Overall, broke displayed the highest tensile strength followed by CTMP and lastly kraft pulp.
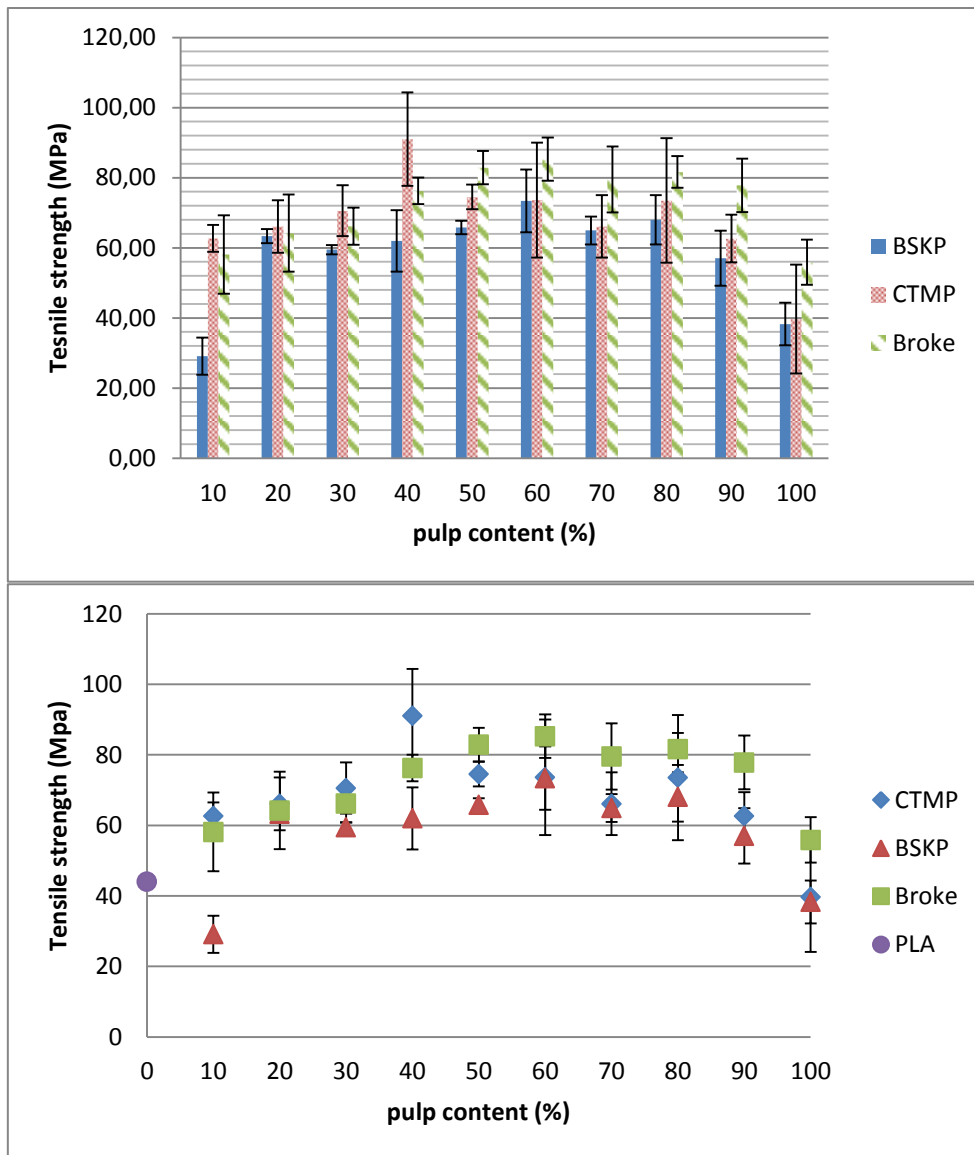
Figure 22 Comparison of tensile strength of BSKP, CTMP and broke composites with increasing pulp content

4.3.4 MFC reinforced HRKP/ PLA composites (i)

Results from the first attempt to determine whether minor addition of MFC to a HRKP/PLA 50/50 composite had an impact on the average tensile strength showed no correlation. Although values varied between species the tensile strength only ranged from around 45 to 65 MPa, see Figure 23.
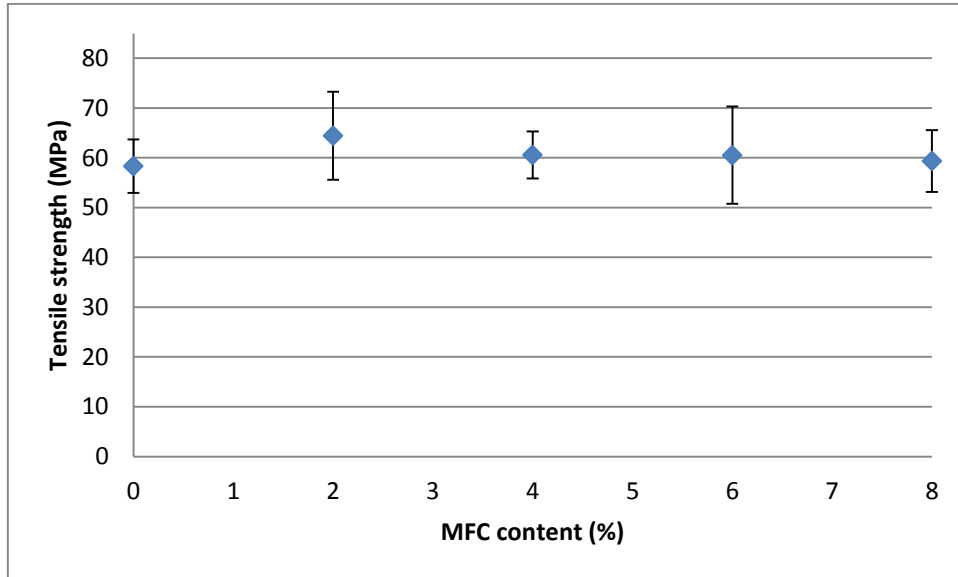
Figure 23 tensile strength of 50/50 HRKP/PLA composites reinforced with 0, 2, 4, 6 and 8 % MFC. No correlation between the amount of MFC added and the tensile strength could be observed.

4.3.5 MFC reinforced HRKP/ PLA composites (ii)

Similar results to that described in section 4.3.4 was obtained. The tensile strength appears independent of the amount of MFC added to the composite.
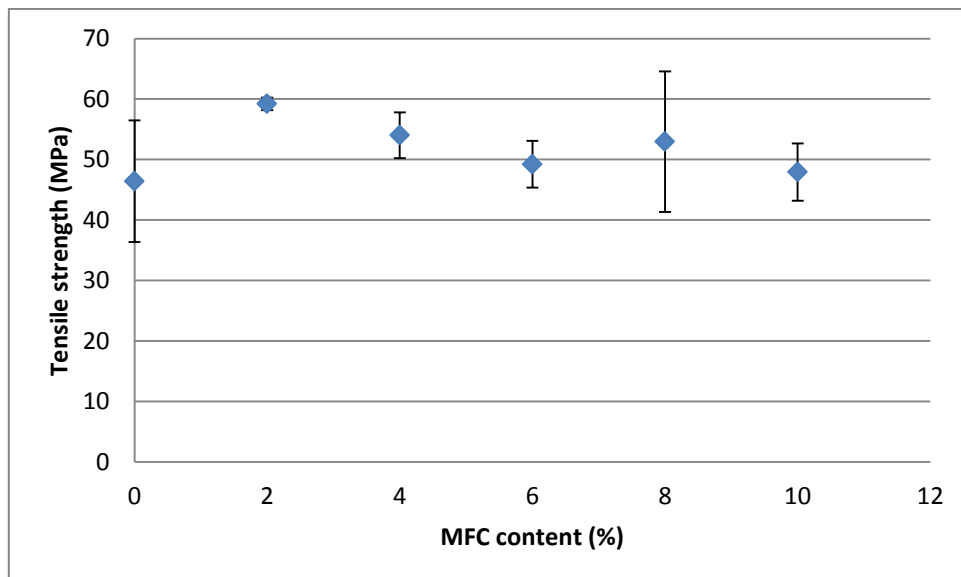
Figure 24 tensile strength of 50/50 HRKP/PLA composites reinforced with 0, 2, 4, 6, 8 and 10 % MFC. No correlation between the amount of MFC added and the tensile strength could be observed.

5   Discussion

Regarding the methods of producing manageable sheets PLA composites reinforced with pulp, the approach described in section 3 resulted in the best samples.

Other methods used in this study i.e. to dewater a mixture of PLA and cellulose in Büchner funnel to a specific dry content and then press it, resulted in poor sheets with immense bubble formation both internally and on the surface.

When using PLA in the form of latex as in this study it enables the normally hydrophobic polymer to mix with water. A drawback however with the latex was that the PLA tends to be lost in the dewatering step when using the sheet former, Büchner funnel or Formette method. This caused the majority of the added PLA to be drained during vacuum resulting in a composite with just a fraction of the intended PLA content. In prevention the two-step method was implemented for all samples which proved to be very effective. This was confirmed both by weighing the samples after melting and by looking at SEM images prior to melting, see Figure 10 section 4.2. Although this initial step proved to be effective in preventing loss of PLA the initial intention for it was to act as filter in which the PLA could diffuse into. The SEM pictures in Figure 10 section 4.2, shows that no diffusion did occur and thus the composites produced contained two layers: one with pure HRKP and the other with a mixture of PLA and pulp/ MFC. In contrast to the method used by Larsson et al. (21) the MFC and PLA did not go through the fluidizer prior to mixing. Therefore poor mixing was achieved in comparison which might explain why the two-step method was a mandatory step to produce composites with satisfactory quality.

One of the main challenges when producing MFC and PLA composites was to achieve regular results with as little variation as possible. This was however often the case when comparing results from the mechanical testing. The French paper process using the Formette method posed as good candidate to produce composites with excellent formation and thus minimizing dissimilarities between species. The dewatering step was however too harsh and most of the added PLA was therefore lost in this step. The two-step approach was also used but the PLA content did not increase in the resulting composite. Other more delicate modifications were attempted e.g. to use a nozzle in the second step that sprayed the mixed PLA/pulp/MFC suspension on a sheet of pure HRKP. This caused the good formation that often is achieved through this method to be lost.

In the first attempt to produce sheets with increasing amount of HRKP the tensile strength was fairly constant ranging between 45-55 MPa, see Figure 16 section 4.3.1. At around 70 % and up to 100 % HRKP content the tensile strength increased. This was in contrast to the work of Larsson et al. (21) which showed a linear increase in tensile strength when increasing the MFC content. If this was due to the differences in the pulp quality, was not investigated. However, an explanation to the no-linear increase could be that the bottom layer of pure HRKP was not kept constant as described previously. The bottom layer was therefore thickest for the sample containing 90 % HRKP and thinnest for the sample containing 30% HRKP see Figure 18 section 4.3.1 for clarification. The contribution to the tensile strength from the bottom layer would therefore increase by increasing its grammage.

The same experiment showed that the percentage of elongation increased with increasing HRKP content. Similar results were shown by Larsson et al. Results are presented in Figure 17 and Figure 19 section 4.3.1 and shows elongation for pure HRKP samples could up to 20 %. The reason to this could

be that the cellulose fibers align and crystallize when samples is strained thus explaining the increase in work needed. This is common for amorphous polymers (25).

The results from the experiments where the bottom layer was kept constant at 20 gm^{-2} are presented in Figure 20 section 4.3.2. Since differences in dispersion and bubbles formation between samples seem to be frequent results tend to vary. This becomes obvious when comparing the tensile strength from Figure 16 section 4.3.1 and Figure 20 4.3.2 where the 10% samples in Figure 20 have a higher tensile strength than all the samples from 30 to 80 %. At higher MFC compositions, 80 and 90 %, the values are similar. When comparing the more refined pulps MFC and HRKP, see Figure 21 section 4.3.2, composites reinforced with HRKP showed better results over all compared to those reinforced with MFC. This could be explained by the fact that composites containing MFC were hard to de-water. The prolonged time to remove water caused bubbles to form for some of the samples. Another explanation which is linked to that previously mentioned is that MFC fibrils interaction is too strong, due to the increased surface area and thus has a tendency to agglomerate rather than dispersing evenly in PLA matrix. This will cause defects rather than the desired network of cellulose.

The results presented in Figure 22 section 4.3.3 compares the tensile strength for composites reinforced with kraft pulp, CTMP and broke. In comparison to composites comprising HRKP and MFC in the composite layer, tensile strength reaches a maximum at around 60 %. After further addition the tensile strength drops dramatically. At higher concentrations of pulp an insufficient amount of PLA is added to achieve a good composite. The thickness increased for samples around 70 % and above which suggest that considerable amount of air is trapped during composite preparation which would yield thicker composites with a lower density. The increasing thickness did not occur when using HRKP or MFC .The effect can be observed for a pure kraft pulp sample in Figure 14 section 4.2 and is presumed to be similar for pure broke and CTMP samples. As a result of these defects, composites containing a high amount of less refined pulp will appear as a less strong. Apart from this, the results from the tensile testing show that kraft pulp, broke and CTMP in a PLA matrix yields similar tensile strengths as those made of HRKP even though latter quality seems to exhibits better dispersion when comparing the SEM image in Figure 11 and Figure 13 section 4.2. By looking at the tensile strength for different pulp-qualities in Figure 22 section 4.3.3 broke seem to be slightly better than CTMP followed by kraft pulp. This can be explained by the fact that the broke and CTMP pulp used in this study were unbleached which yields fiber with natural resins covering the surfaces of the fibers. This will render less hydrophilic fibers and thus facilitating the dispersion in the hydrophobic PLA matrix. Bleached kraft pulp fibers however, have no resin on their surface which renders fibers similar to that of HRKP and MFC.

In the two attempts to determine the impact on the tensile strength when adding small amounts of MFC to 50/50 HRKP/PLA composites results showed that the tensile strength was independent of the MFC content, see section Figure 23 and Figure 24 section 4.3.4 and 4.3.5 respectively. There are both reports and patents that have shown that tensile strength can be increased by adding MFC to regular paper and board (26) (27). The reason to this is that the MFC fills up internal voids that are present in films made of less refined pulp, see Figure 14. In the case of HRKP, kraft pulp has been refined mechanically to such an extent that the impact of MFC addition becomes limited. The two options to avoid the empty voids in e.g. a BSKP/PLA composite are to refine the BSKP further to achieve higher SR numbers similar or close to that of HRKP or to add MFC and maintain a low SR number on the kraft pulp.

Lastly, results showed that addition of AKD to the composite mixture, did not simplify the separation of the wet sample from the monodur fabric after the dewatering step. It did however prevent the PLA to produce foam when mixed with MFC that resulted in a reduction of bubbles that would otherwise be formed internally in the composite. The added AKD did also melt during the heating step which prevented the composite to stick to the aluminum cylinders when pressing the films. No results indicated that the dispersion or interaction between PLA and MFC did improve. AKD still pose as a good additive because of the advantages previously described.

6 Conclusion

The composites produced in the sheet former in combination with an initial layer proved to be the best method of choice due to a lean de-watering and prevention of PLA-losses. In contrast, the Formette method resulted in excellent formation of the fiber/fibril content but lacked in PLA content due to a harsh de-watering step. Another conclusion that could be drawn with respect to methodology is that the method of choice and including intermediate steps will have a huge impact on the resulting material. It is therefore necessary to weigh economical and time factors versus desired mechanical properties.

Composites containing broke, kraft pulp and CTMP displayed satisfactory tensile strength compared to both HRKP and MFC. The tensile strength increased with the amount of pulp added to the composite. In the case of MFC and HRKP the increase was maintained even at high concentrations. As for broke, kraft pulp and CTMP the tensile strength passed through a maximum as the fiber concentration increased. Broke preformed best, at intermediate concentrations, followed by CTMP and kraft pulp. Similar to composites reinforced with HRKP, composites reinforced with around 50-60 % Broke, kraft pulp and CTMP almost doubled the tensile strength compared to pure PLA films. MFC showed poor tensile strength relative to the other pulps. Given the high cost of producing both MFC and HRKP, these are not cost effective enough as reinforcing agents when using the method used in this study, see section 3. The plastic content can therefore be substituted with at least 50 % up to 70 % without compromising the tensile strength or the management of the composite. Minor additions (2-10%) of MFC to HRKP composites did not improve the tensile strength. This downgrades the possibility to use MFC as co-reinforcing agent in combination with HRKP or similar refined pulps. It is therefore preferable, from an energy and time perspective, to grind more on a less refined pulp in order to obtain a more refined pulp than to reinforce a pulp that has been moderately grinded.

SEM images showed major voids and defects in composites containing high amounts or only kraft pulp. SEM images also showed good dispersion of PLA in the fibril network and more aggregated in a fiber network before and after hot pressing.

7   Future development

For future work it would be of great interest to study the interaction between PLA and cellulose in detail in order to tailor the interfacial properties with better precision. To control the integrity and assembly of the cellulose network is important in order to be able to produce better composites. Furthermore, although MFC has gathered considerable buzz in the scientific community and reports have presented promising results certain aspects remain to be investigated before being industrially applicable; one being the high water content which results in extremely time demanding de-watering steps. To evaluate methods to decrease the time aspect would therefore be of great interest as well.

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Appendix

The appendix covers parts of the literature study that was outside the scope of this work. Introductory sections briefly explain some of the physical and chemical methods to improve compatibility. This is followed by the sections covering the basic theory of silane and maleated coupling agents. Lastly, the methodology regarding the Büchner funnel and Formette are explained.

9 Modification of cellulose fibers

A common occurring problem when mixing an inorganic and an organic compound is the difficulty to achieve proper blending and dispersion. This is due to that one has to rely on dipol-dipol bonds or lewis acid interaction when making composites. However, major differences in chemical reactivity and composition often results in repulsive rather than attractive interaction. Alteration of the two species is therefore an important intermediate step prior to mixing and processing (26). Moreover is the level of treatment to the surface of the fibers significant to both the impact resistance as well as the composites residual load-carrying capability. In general large areas of delamination in the interphase occur to untreated fibers reinforced in a composite. When fibers are treated however the internal damages are more localized thus rendering a more durable material (27).

9.1 Physical methods

Corona and plasma treatment are two straight forward techniques to raise the surface energy through oxidation of e.g. yarns and films composed of cellulose. Ragoubi et al. reported improved mechanical and thermal properties when corona treated hemp (28) and miscanthus[4](29) fibers were dispersed in PLA and PP matrixes. The effect on the surface when using physical treatments are in its nature two folded; physical etching of the fiber surface which leads to increased surface area and addition of functionalized oxygen groups . The combined effect enhances the fiber/matrix interaction. These methods, especially corona, do however pose the difficulty to treat three dimensional objects.
Treatment with regards to plasma treatment poses a much larger variety of possible modifications. In general studies using plasma treatment did not show as noticeable differences in mechanical properties as for those using corona treatments. (30)

9.2 Chemical methods

One of the most commonly used chemical treatments is to impregnate the fibers under alkaline conditions (31) (32). Masuda et al. reported that both silane and alkali treated fibers yielded superior PLA composites compared to neat PLA. One suggestion to the improved properties is removal of residue i.e. lignin and hemi cellulose and thus recovering otherwise hindered hydroxyl groups. Due to the straight forward as well as cheap approach that alkaline treatment offers it is suitable in combination with coupling agents or other chemical subsequent steps.

Another route to yield less hydrophilic fibers is through an acetylation reaction that functionalizes the hydroxyl groups. In a study by Bledzki et al. acetylation, up to 18 %, of flax fibers increased flexural as well as tensile strength for PP/ flax composites (33). Acetylation beyond 18 % caused degradation of the fibers which resulted in subpar composites. It further showed that an increasing

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[4] A type of grass

degree of acetylation improved the moisture resistance. The resistance towards moisture is a significant property with regards to bio-degradability since the presence of water hastens the hydrolysis and thus the degradation of polymers.

Bledzki et al. used enzyme treatment to remove residue from abaca fibers thus making them smother. This resulted in increased tensile and flexural strength for PP/ abaca composites (34). Enzyme treatments, unlike alkali and acetylation treatment, offer very specific reactions.

Carlmark et al. (35) reported the possibility of grafting organic chains through ring opening polymerization and thus functionalizing the cellulose fibers. This procedure leads to amphiphilic block-copolymers, that when integrated in a matrix forms three dimensional networks. Furthermore, this approach also proved to effectively produce hydrophobic cellulose fibers that could be dispersed in tetrahydrofuran (THF). Another advantage is that the ROP is initiated by hydroxyl groups that are in abundance with regards to cellulose and thus no prior treatment is needed. The possibility to disperse the fibers in a satisfactory fashion is a key aspect for the cellulose fibers to form a web-like structure rather than aggregates. This was indeed suggested by Lönnberg et al. (36) that investigated the influence of the concentration and the length of the grafted chains and how this altered the mechanical properties.

10 Coupling agents

The coupling agent acts as bridge between the species rendering them miscible in combination. The most commonly used coupling agents used for commercial plastics, are organofunctionalized silanes, but titan and carboxylate based agents are used as well. (37) (41)

Monomeric organosilanes has the chemical formula illustrated in Figure 25, where R1, R2, R3 and R4 can either be the same or four different substituents. Possible substituents are chlorine, amine, methoxy, acetoxy or hydroxyl groups. Due to silicon's electropositive nature the substituents are reactive towards compounds containing hydroxyl groups i.e. water or cellulose. When this occurs the unstable silanol reacts with another silane to condense to form a –Si-O-Si-, reaction 1 Figure 26. Furthermore a methoxysilane, CH_3O-Si-R can react with other methoxysilane to also form –Si-O-Si- or react with available hydroxyl groups on a surface interface, reaction 2 Figure 26. The R group can be an arbitrary alkyl group to match the polymer chemistry that will give good interaction.

$$
\begin{array}{c}
R1 \\
| \\
R2 - Si - R3 \\
| \\
R4
\end{array}
$$

Figure 25 silane monomer with the functional groups R1, R2, R3 and R4.

$$RSiX_3 + H_2O \longrightarrow RSi(OH)_3 \longrightarrow R(OH)_2Si\text{-}O\text{-}Si(OH)_2R \quad (1)$$
$$\longrightarrow R(OH)_2Si\text{-}O\text{-}(\text{species surface}) \quad (2)$$

$X = Cl, CH_3O$
$R = alkyl, aryl, organofunctional$

Figure 26 reaction paths for an organosilanes; either it reacts with another silane (1) or with a hydroxyl group at surface (2).

10.1 Maleated coupling

Similar to silane and titan based coupling agents; maleated coupling with maleated anhydride (MAH) does not only alter the surface of the fibers but also the polymeric matrix. This has proven to be a very effective way to increase the dispersion in bio based composites. A study carried out by Lei et al. investigated the impact of different compatibilizers and showed that impact strength could be increased by raising the compatibilizer content of maleated polyethylene (MA-PE) (39). Yang et al. investigated different MAHs both MA-PP and MA-PE which showed improved morphology and mechanical properties (40) (41). Another important observation that Yang reported was that MA-PP treated fibers mixed in a PE matrix were not optimal with regards to morphology. One conclusion that could be made from this is that the choice of coupling agents has to be tailored to the matrix to acquire a good composite.

Gao et al. tried to blend PP, PE and fibers (70 wt. %) in different ratios in order to simulate recycled thermoplastic mixtures (42). Untreated neat mixtures display poor mechanical properties due to insufficient dispersion. The study showed that MAH is a suitable candidate to improve interfacial bonding.

11 Other methods used in this study

11.1 Büchner funnel method

A first attempt to fabricate films was initiated by mixing small batches varying the MFC content from 30, 50 and 80 wt. %. In advance the dry content of the pure MFC and PLA mixtures were established to 2.3 and 30 % respectively, by using a Mettler Toledo HR73 halogen dryer. The batches were initially stirred by hand to achieve fairly good mixing between the species, followed by circulation in a Microfluidizer® Processor M-110EH, provided by Microfluidics, with a pressure of 1500 bar for 15 minutes. The next step was to dry the fluidized mixtures in a Büchner funnel to preferred dryness. An amount of 1-2 grams dried blend was then applied evenly in the middle of circular Teflon sheet that had been glued to a firm plate of rubber followed by a film of polyethylene plastic over the specimen to cover it. Extra attention had to be put on removing the bubbles, which appeared between the mixture and the PE-film, by gently pressing on the sample. Finally, another rubber form was put on top and then pressed under 2 bars for five seconds. This resulted in a circular gelatinous sheet of the specimen between the Teflon sheet and the PE-film. The PE-film was then removed with great care to ensure that the composite-mixture remained on the Bytac® sheet. The sample was dried in an oven at 30°C for 5 hours.

11.2 Impregnation of fibers/ fibrils with AKD

Three master batches containing varying amounts of PLA, HRKP and AKD: 2, 6 and 10 wt. %. The solutions were then stirred and stored at 7° C for 24 hours. The films was then manufactured accordingly to the Büchner funnel method, see Appendix section 11.1.

11.3 Composites with a relative bottom layer

Films consisted of a bottom layer and a composite layer similar to that displayed in Figure 8 but instead of a constant $20gm^{-2}$ grammage on the bottom layer, 50 wt. % of the total HRKP content was used instead. This caused the bottom layer thickness and grammage to be relative to the total amount of HRKP, see figure Figure 18.

11.4 Formette® method

A batch containing 40% HRKP and 60% PLA was diluted in tap water to a concentration of 3 g/l. A plastic wire was placed inside the drum for support followed by a wire of MONODUR® on which the paper was to be formed on, see Figure 27. The mixture was then sprayed onto the wire accordingly to the Formette® procedure; see Figure 28 and Figure 29. The formed composite was peeled off from the wire and placed between two sheets of blotting paper. A weight was then rolled over once. The moist blotting papers were exchanged with a pair of dry sheets. The package was then pressed with 1 bar one way and 5 bar one way. Blotting papers were changed and replaced with dry papers once more followed by an additional pressing procedure. The sample was then dried in 100°C for 10 minutes.
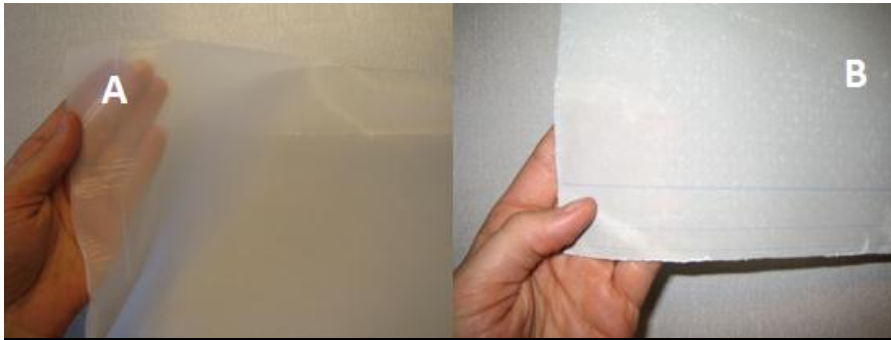

Figure 27 A: monodur fabric used on which the composite was formed upon. B: The wire used as support on which the monodur fabric was attached to.

Figure 28 the support wire was placed inside the drum of the Format. A: The nozzle that sprayed the mixture on the monodur fabric. B: Edges of the support wire intertwined which enabled the monodur fabric to remain fixed.

Figure 29 left picture: the drum in which the mixture was poured and pumped to the nozzle. Right picture: Inside of drum without wire. B: rotational direction of drum. C: Vertical direction of the nozzle.

11.5 Formette method with a bottom layer

The same setup and drying procedure as described in section 11.4 was used. Similar to the method described in section 11.3, half of the HRKP content was diluted separately to a concentration of 3 g/l and the other half was mixed with PLA and diluted to 6 g/l to form an initial layer.

11.6 Formette method using retention agents and a spray nozzle

The same setup as described in section 11.5 was used. In the second step where PLA and pulp mixture retention agents[5]: bentonite and PL1310 were added to the PLA/pulp mixture under stirring. The nozzle with a narrower hole was used which contributed to a less aggressive application of the mixture.

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[5] Retention agents are used to prevent the added substances e.g. PLA or cellulose of being drained during de-watering step