CHALMERS
UNIVERSITY OF TECHNOLOGY

Compression moulding of cellulose composites

The influence of additives

Master's thesis at INNVENTIA

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Helena Streitlien

Abstract

Several additives and their effect on an all-cellulose composite material have been studied. Different approaches for modification of additives were evaluated, physical and chemical modification. The objective was to find and evaluate additives that improve the mechanical properties of the of the all-cellulose composites, such as tensile strength and elastic modulus. An increased dimensional stability was also desirable.

Different types of additives were theoretically evaluated, those suitable for laboratory testing were carboxylic acids, starch, beta-glucan and fines enhanced fractions from Innventia.

Hand sheets were made, modified with additives, compression moulded at various temperatures from 130-170℃ into cellulose composites, and tensile tested. The additives were either mixed in the pulp prior to the sheet production, or sprayed together with sodium dihydrogen phosphate (NaH_2PO_4) as catalyst, on quaternary parts of already made hand sheets. Water retention value measures were performed on selected composite specimens after the tensile evaluation.

Mechanical properties were initially measured on premade sheets without any additives. The aim was to evaluate the precision of the method itself and how much it can differ depending on various equipment and other circumstances. This is valuable when considering the results from this project but also for future considerations. Results showed essentially no significant difference in comparison made from the same or different sheets made in the same way.

The chemical modification with carboxylic acids as cross linkers mainly resulted in decreased tensile strength, elastic modulus as well as elongation. The most significant differences occurred specifically for the sheets pressed at the higher temperatures (170℃), this may be due to chain cleavage of cellulose in the fibres caused by acid hydrolysis. Measures of the water retention value however, indicate that the crosslinking of cellulose decrease the water retention value and thereby also increase the dimensional stability.

The best results regarding the mechanical properties were achieved with physical modification by beta-glucan from oat, resulting in the highest ultimate tension value with a mean of 151 MPa, and for the elastic modulus mean value at 7.0 GPa.

Keywords: All-cellulose composite, compression moulding, additive, beta-glucan

Sammanfattning

Flera tillsatser och deras effekt på ett kompositmaterial baserat på enbart cellulosa har studerats. Olika metoder för modifiering av tillsatser utvärderades; fysisk och kemisk modifiering. Målet var att hitta och utvärdera tillsatser som förbättrar de mekaniska egenskaperna hos cellulosa-kompositer, såsom draghållfasthet och elasticitet. En ökad dimensionsstabilitet var också önskad.

Olika typer av tillsatser utvärderades teoretiskt, de som ansågs lämpliga för laboratorietester var olika typer av karboxylsyror, stärkelse, betaglukan och en finfraktionerad fiberblandning från Innventia.

Ark tillverkades och modifierades med tillsatser, formpressades vid temperaturer på 130-170 ℃ till cellulosakompositer och drag testades. Tillsatserna var antingen blandade i massan innan arkproduktionen, eller sprayade tillsammans med natriumdivätefosfat (NaH_2PO_4) som katalysator, på fjärdedelar av redan gjorda ark. Mätningar av vattenretentionstal utfördes på specifika kompositprover efter dragprovningen.

Mekaniska egenskaper utvärderades initialt på förtillverkade ark utan några tillsatser. Syftet var att utvärdera precisionen i själva metoden och hur mycket det kan variera beroende på olika utrustning eller andra omständigheter. Detta är värdefullt när man överväger resultaten från detta projekt och även viktigt att ha med sig i framtida mätresultat. Resultaten visade i huvudsak ingen signifikant skillnad inom eller mellan kompositer framställda på samma sätt.

Den kemiska modifieringen med karboxylsyror som tvärbindare resulterade främst i minskad draghållfasthet, elasticitetsmodul samt töjning. De mest väsentliga skillnaderna inträffade speciellt för arken pressade vid högre temperaturer (170 ℃). Mätningar av vattenretentionsvärden tyder dock på att tvärbindning av cellulosa minskar vattenkvarhållningsvärdet och därmed även ökar dimensionsstabiliteten.

De bästa resultaten angående draghållfastheten uppnåddes med hjälp av fysisk modifiering av betaglukan från havre, vilket resulterade i det högsta ultimata dragbrottsstyrkan med ett medelvärde på 151 MPa, och för elasticitetsmodulen med medelvärdet 7.0 GPa.

Nyckelord: Cellulosa-komposit, formpressning, tillsats, betaglukan

Table of contents

List of abbreviations

ACC	All-cellulose composite
BTCA	1, 2, 3, 4 Butanetetracarboxylic Acid
WRV	Water retention value
NCC	Nanocrystalline cellulose
NFC	Nanofibrillated cellulose
CI	Confidence interval
D	Chlorine dioxide
EP	Sodium hydroxide and alkaline hydrogen peroxide
P	Alkaline hydrogen peroxide
OO	O_2-treated
NMMO	N-Methylmorpholine N-oxide
LiCl/DMAc	Lithium Chloride/Dimethylacetamide

1. Introduction

Due to increased environmental concern, the desire to decrease the world’s petrochemical dependency is increasing. In order to build more sustainable and competitive alternatives to the crude oil products, processes and products from renewable raw materials need to be developed. Materials originating from the forestry are one example of a renewable raw material.

Cellulose is the major polymer in wood. In the Kraft process, wood chips are cooked in presence of hydrogen sulphide and alkali in order to produce paper pulp. The demand for pulp and paper production in the northern hemisphere has started to stagnate in the last couple of years. That is not only a result of increasing competition from eucalyptus based industries, but also due to increasing development and use of different kinds of new digital technologies as for instance smart mobile phones, tablets and E-books.

Newer, electronic equipment and diminishing market for traditional forestry products forces the forest industry to find new, wood-derived and value-added products. That counts especially for the cellulose in Kraft pulp. A possible solution to this problem can be to use the Kraft pulp not for paper but in the textile industry. Pure cellulose fractions called dissolving pulps can be used for the production of cellulosic textile fibres, in the same way as for cellulose from the sulphite process.

Wood fibre-based components have great potential when it comes to large volume production, if they can be used as engineering materials in different industrial applications (Vaca-Medina et al. 2013). By using more wood-based materials in the industries instead of crude oil-based, the environmental impact could be reduced. It would increase sustainability of our society and benefit both consumers and the environment.

A study of compression moulding of different kinds of cellulose sources, by the concept of all cellulose composites was performed by Helena Halonen in 2012 (Halonen 2012). Halonen reported promising mechanical properties for paper-grade Kraft pulps, with measured tensile modulus of 13.6 GPa and ultimate tensile strength of 131 MPa. The reinforcing agent and matrix in a composite material must adhere well at the interface. In all-cellulose composites, where the components are made of the same material, the adhesion is expected to be improved. In addition this construction also improves the recyclability of the material.

1.1. Objective

The aim with this thesis is to evaluate the possibilities and limitations for compression moulding of cellulose fibres from available, fully bleached pulp. This includes measuring of the tensile strength of so called all cellulose composite fibres, as well as a comparison and evaluation of the influence of different additives. The study focuses on evaluating the mechanical properties, such as dimensional stability and tensile strength.

Different kinds of additives will initially be evaluated in a literature study, before deciding the additives suitable for laboratory testing.

The work aims to evaluate whether any of the tested additives can be used for further development, especially when it comes to materials where sustainability is an important factor. Ultimately, this could lead to the development of an economically viable product that in the future could replace non-renewable materials and reduce our dependency of products from crude oil.

1.2. Thesis outline

A brief literature study was initially made in order to pinpoint possible additives for compression moulding of cellulose.

The process of composite-making was designed mainly after evaluating the literature study, enabling the knowledge of what additives to use. However, plain cellulose composites were also made for comparison.

The precision of the tensile test measurements made, i.e. the scattering of the method, was evaluated.

The finished composites, with and without additives went through tensile tests in order to compare and evaluate their mechanical properties. Selected composites also underwent analysis of the water retention value (WRV), which is an indirect measure of the dimensional stability.

2. Background

2.1. Wood polymers

Wood consists of elongated cells, connected to each other through openings called pits. The cell types vary in their shape and function and are the ones providing all necessary strength to the stem of the tree. These elongated cells also handle the liquid transport in the tree as well as the storage of nutrients supplies. The fibre cell walls of wooden cells have a layered structure, as indicated in figure 2-1. The layers are separated into the primary cell wall (P1), the outer secondary cell wall (S2) and the inner secondary cell wall (S3). The layers differ in both composition and structure and are made of complex bio composites made from cellulose aggregate. These aggregates are embedded in a matrix of hemicellulose and lignin.

Cellulose, hemicellulose and non-carbohydrates in form of lignin are the three most common components in wood and are briefly presented below.

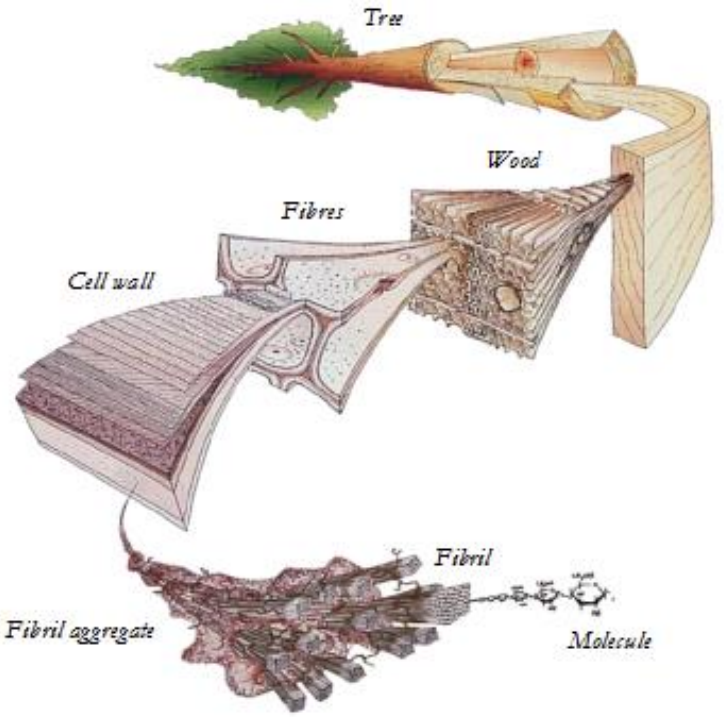


Figure 2-1. The hierarchical structure from the three to the cellulose molecule (Illustration: Airi Illistre) (Halonen, 2012).

2.1.1. Cellulose

Cellulose is a complex carbohydrate consisting of 3000, or more, glucose units. It is the most abundant biopolymer occurring on earth, and comprises about 33 % of all vegetable matter (Encyclopædia Britannica, 2014). Cellulose is not only found in plants but also in algae, fungi, bacteria and tunicates and is a linear polysaccharide, consisting of β-D-glucopyronase units linked with (1→4)-glycosidic bonds (Sjöström, Cellulose, 1993 a). The molecular structure of cellulose is shown in figure 2-2.The reactivity of the hydroxyl groups at the positions 2,3 and 6 of the glycosyl units offers a great variance of possibilities to make different useful derivates. The most reactive hydroxyl group is, as seen in figure 2-2 below, the one linked to a primary carbon, the C-6 OH-group.The less reactive is the C-2 OH and the C-3 OH is the weakest, for bending due to the forming hydrogen bond with the neighbouring oxygen (Rojas & Azevedo, 2011).

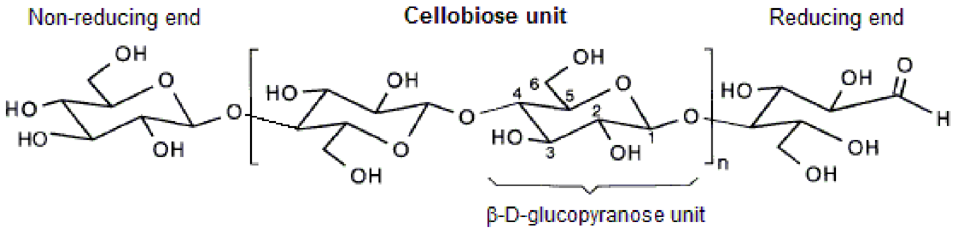


Figure 2-2. The molecular structure of cellulose (Halonen, 2012).

Cellulose is mainly used to produce paperboard and paper but also chemically modified to yield substances used in the manufacturing of plastics, films and rayon. Other applications of cellulose are different adhesives, thickening agents for foods and moisture-proof coatings.

The cellulose chains form strong inter- and intramolecular hydrogen bonds as well as hydrophobic interactions. Bundles of cellulose molecules are aggregated into the form of micro fibrils, closely packed into a crystalline structure. The crystalline structure formed can have more than one shape, meaning that cellulose is polymorphic. High tensile strength and insolubility in most solvents are consequences of the strong hydrogen-bonds in the fibrous structure of cellulose.

The crystalline form of native cellulose in wood is called cellulose I, a compound consisting of two crystalline forms with different bonding patterns; cellulose Iα and Iβ. The ratio between the two different forms of cellulose I depends on the variation within species. Cellulose Iα is dominant in algae, and bacterial cellulose and Iβ are dominated by the higher plants such as wood and cotton (Atalla & VanderHart, 1984).

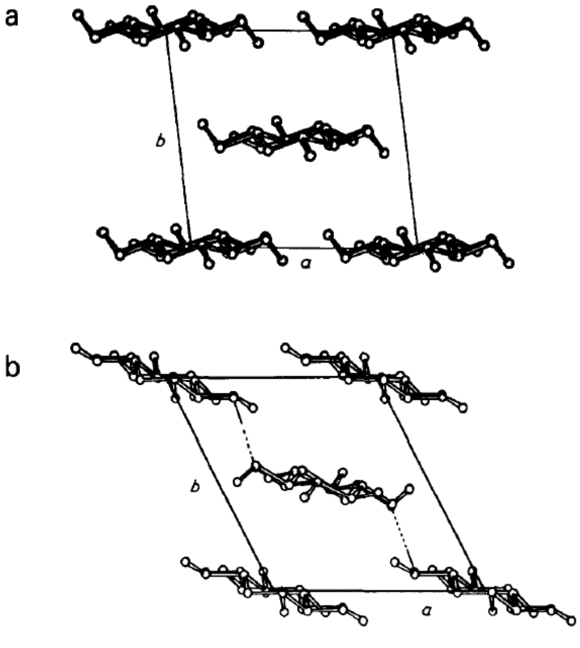


Figure 2-3. The axial projections of the a) native cellulose (cellulose I) and b) regenerated cellulose (cellulose II) (Sjöström, Cellulose 1993 a).

Regenerated cellulose, called cellulose II, has unlike cellulose I antiparallel chains and is formed whenever the lattice of cellulose I is disturbed. That could happen with for instance mercerization by intra crystalline swelling of native cellulose in alkali, or by dissolution and re-precipitation of cellulose i.e. regeneration (Zugenmaier, 2008). An accepted theory about the structural difference between cellulose I and II is that all the chains in native cellulose are parallel. That is while the cellulose II chains have an antiparallel arrangement, as seen in Figure 2-3.

2.1.2. Hemicellulose

Hemicellulose is any of several different hetero polymers that are present in almost all plant cell walls. The most common ones are xylans, xyloglucan and galactoglucomannans. Hemicellulose has, in contrast to cellulose, an amorphous structure with little strength and is easily hydrolyzed by dilute acid or base. The amount of hemicelluloses in wood is usually around 20-30%. The structure and composition of hemicelluloses differ considerably between soft- and hardwood, as well as between the branches, stem, roots and bark (Sjöström, 1993 b).

Galactoglucomannans are the most common hemicellulose that are present in softwood (around 20%), and around 5-10% are Arabinoglucoronoxylan. Apart from them, softwood also consists of other polysaccharides including starch (amylose and amylopectin) and pectin substances. The hemicellulose in hardwood on the other hand, consists instead mostly of glucuronoxylan and glucomannan (Sjöström, 1993 b).

2.1.3. Non-carbohydrates

Wood consists not only of cellulose and hemicelluloses, but also of non-carbohydrates such as different kinds of extractives; e.g. terpenoids, steroids, fats and waxes.

They are extractable by organic solvents such as ethanol or dichloromethane to produce the by-products of pulping such as turpentine and tall oil.

The proportions of these extractives vary in hardwoods and softwoods and also between species, but are usually less than 10% (Sjöström. 1993 d).

Lignin is another non-carbohydrate component, a complex polymer consisting of several different phenyl propane units, as seen in figure 2-4. The amount of lignin in different plants varies between species, and its main purpose in wood is to link cellulose together with covalent bonds, conferring mechanical strength to the cell wall and by extension the plant. Normal wood, a term referring to wood with desirable properties with straight grain, high density and high bending strength, is often mentioned in comparison with reaction and compression wood and is anatomically different (Gardiner et al., 2014). Normal softwood contains 26-32% lignin, compared to normal hardwood that

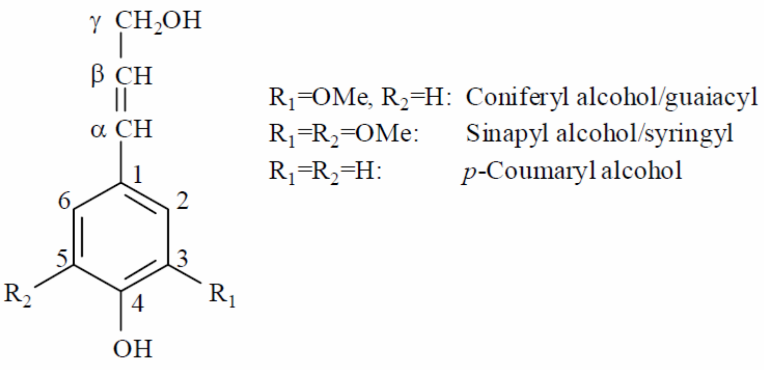


Figure 2-4. The three different phenyl propane monomers from which the lignin macromolecule is formed.

contains 20-25 %. Tropical hardwoods however, can have a lignin content exceeding 30% (Sjöström, 1993 c).

2.2. Wood pulping

The main purpose of wood pulping is to liberate the fibers, and that can be made either by chemical or mechanical treatment, or a combination of both. Chemical pulping methods rely on chemicals to separate the fibers, while the mechanical pulping methods mainly rely on physical action. The yield of pulp ranges from around 40 % by chemical methods to 95% by mechanical pulping (Biermann, 1996). Chemical processes are based on either acids (i.e. sulfite pulping) or alkaline including soda and Kraft processes, respectively. After the pulping process, the pulp is washed, thickened by removal of most of the water and bleached. Since Kraft pulp fibres are used in this project, the Kraft process will be further explained.

2.2.1. Kraft processing

The Kraft pulping process, or the sulfate process as it is also called, is the most commonly chemical pulp used globally. That is due to the easy recovery of chemicals and high fibre strength compared to, for instance, sulfite pulp (Sjöström, Cellulose, 1993 a). Kraft pulping is a process for conversion of wood into wood pulp with almost pure cellulose fibres. The process consists of several different steps; impregnation, cooking, recovery of chemicals, blowing, screening and washing.

2.2.2. Pulping reactions in Kraft cooking

The wood chips are initially wetted and preheated with steam. This treatment causes the air within the cavities of the wood to expand and push aside approximately 25% of the air away from the chips (Sjöström, 1993 e).

Kraft pulping is performed with a solution that consists of mainly sodium hydroxide (NaOH) and sodium hydrogen sulfide (NaHS) in water and this solution is called “white liquor”. The HS^- and ^-OH are the active components in Kraft pulping and the ones react during cooking. The chemical composition and properties of the white liquor are seen in the table below. According to the terminology all chemicals are calculated as sodium equivalents and expressed as weight of NaOH or Na_2O (Sjöström, 1993 e).

Table 2-1.The chemical composition and properties of the white liquor used in the Kraft pulping process.

Total alkali	All sodium salts
Titratable alkali	$NaOH + Na_2S + Na_2CO_3$
Active alkali (AA)	$NaOH + Na_2S$
Effective alkali (EA)	$NaOH + ½ Na_2S$
Causticity efficiency	$100\ \frac{NaOH}{NaOH + \ Na_2S}\ \%$
Sulfidity	$100\ \frac{Na_2S}{NaOH + \ Na_2S}\ \%$
Degree of reduction	$100\ \frac{Na_2S}{NaOH + \ Na_2SO_4}\ \%$

Figure 2-7 shows a simplified scheme of the liquor cycle in Kraft pulping. Black liquor is the resulting spent cooking liquor containing dissolved organic compounds and used inorganic cooking chemicals as well as inorganic compounds released from the wood. To transform the inorganic chemicals back to active cooking chemicals, the black liquor is evaporated and burnt, resulting in a smelt. This smelt is dissolved in water into green liquor, which with causticizing (calcium hydroxide) transforms into white liquor (Sjöström, 1993 e).

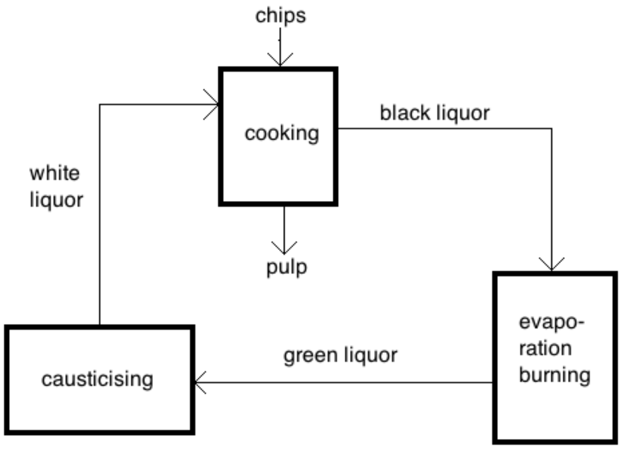


Figure 2-7. A simplified scheme of the liquor cycle in Kraft pulping.

2.2.3. Carbohydrate reactions

The primary aim of the chemical pulping is to remove lignin and liberate the fibres. No cooking chemical are however selective towards only lignin, but also the carbohydrates will be degraded and dissolved to a certain extent (Sjöström, 1993 e).

These carbohydrates are affected already at relatively low temperatures. The acetyl groups, found in galactoglucomannans in softwood and xylans of hardwood, are hydrolyzed and split of the respective polymer. The peeling reaction takes place at the reducing end group, where the end units of the carbohydrate chains are split off and dissolved, the yield of carbohydrates are decreased with approximately 20%. Due to the high degree of polymerization and the crystallinity of cellulose this decrease mainly affects hemicelluloses (Sjöström, 1993 a).

2.2.4. Delignification

The wanted reaction for the pulping process is the delignification of the wood, by degradation of and dissolution of the lignin. Simultaneously, carbohydrates are removed from the wood during pulping. The selectivity of the delignification is expressed as the weight ratio of the lignin and the carbohydrates removed, after a certain time. The higher the selectivity, the more carbohydrates are still remaining in the fibre wall. The removal of lignin during alkaline conditions occurs either in the pulping or in the oxygen treatment step and is depending on the cleavage of ether linkages, while the carbon-carbon linkages are essentially stable. Both hydroxyl and hydrogen sulfide ions promotes cleavage of ether linkages which results in increasing hydrophilicity of lignin due to the formation of phenolic hydroxyl groups. The degraded lignin dissolves as sodium phenolates in the cooking liquor (Sjöström, 1993 c).

The kappa number is a measure of standard potassium permanganate solution that the pulp will consume during bleaching, and is used for evaluation of the amount of residual lignin in the pulp, or the bleachability of the wood pulp. The kappa values range from 100 for very high yield pulp to as low as 1, as for fully bleached pulp. In fully bleached pulp with a kappa number lower than 1, double bonds are detectable but does not relate to "lignin" (Suess, 2010).

2.2.5. Oxygen delignification

Oxygen delignification is a relatively new process that removes the lignin from the pulp, this more effectively and by using fewer chemicals than the delignification method mentioned above. The pulp is treated with oxygen during pressure and high temperature under alkaline conditions. Commercial oxygen delignification are capable of removing approximately 50% of the lignin remaining after Kraft pulping, leading to a decreased need of bleaching (Carter et al., 1997).

2.2.6. Bleaching

One of the main uses of wood pulp is for papermaking. The color of the pulp is mainly associated with its lignin content. In order to increase the brightness of the paper, the residual lignin remaining after the delignification step must be removed. The goal with the bleaching process is often to remove all residual lignin, but bleaching is also performed in order to improve the cleanliness of the pulp by removal of extractives and other contaminants, such as bark residues. The bleaching is often performed not only in one step but with several different bleaching processes in different combinations. Common bleaching chemicals during the years are for instance chlorine dioxide; nowadays totally chlorine free bleaching is getting more and more common, mainly due to environmental reasons (Suess, 2010).

The brightness of bleached pulp is expressed as ISO brightness, the diffuse blue reflectance factor of the pulp.

2.3. All-cellulose composites

A composite or a composite material is a material consisting of two, or more, physically or chemically different materials. When these materials are combined, they form a material with different characteristics compared to the individual components. This new material formed can be beneficial in many ways, for instance with improved strength or lightness, or cheaper manufacturing compared to traditional materials. Some examples of common composite materials are cement, concrete and ceramic composites.

Composites can also be mono-material; made from only one material. This has been evaluated in all-polymer composites, for instance with all-polyethylene and all-polypropylene. The surface of the chosen polymeric material is in that case melted and recrystallized to form a matrix that binds the fibres together. This can also be made with cellulose as polymer, an all-cellulose composite (ACC).

The cellulose fibril is attractive as reinforcing agent in composite materials due to the high axial strength and length-to-diameter ratio. When the reinforcing agent and the matrix in a composite material are made of the same material, the adhesion at the interface is expected to be improved. With the same material serving as matrix and fibre, the recyclability is also improved.

Since cellulose is known not to melt, the all-cellulose composites (ACCs) have instead been created by use of dissolved cellulose to form the matrix, as a solution or as very swollen cellulose fibres, followed by precipitation. The dissolved cellulose is expected to improve the adhesion between the matrix and the fibres. That is by the inter diffusion of the cellulose molecules across the interface while maintaining the highly crystalline cellulose I core.

2.3.1. Compression moulding

Compression moulding is a process where materials (usually plastics) are both heated and compressed into a specific shape, at the same time. The initial form of the material is usually a molding powder or pellets, melted and poured into a mold. The mold is pressed and the material shaped into whatever shape desired. When the mold consists of flat plates, different materials can be molded together into laminated sheets. An example of a laminate of that kind is plywood, were layers of wood are adhered to one another. This is combined with an impregnation of urea-formaldehyde that forms a network of heating, combining the laminate to an intimately bound form (Encyclopaedia Britannica, 2015). Common examples of compression moulded manufacturing materials are for instance; electrical parts, buttons, buckles, flatware, electronic device cases and appliance housing. These types of products could also be made from cellulose composites instead of plastics, and thereby increase the recyclability of these items. That is a great potential for ACC compounds.

The compression moulding process of the ACC sheets takes place during high pressure (31.25 MPa) and high temperature (above 130℃). The pressing time used was 5-15 min and the sheet should have a dry content of at least 50%, prior to the compression-moulded step. The fibres are randomly oriented (isentropic) with a grammage of 200 g/m^2. The process of compression moulding is further and more carefully described in chapter 3.4.

The mono disperse fibrils in wood have widths of around 4 nm, but these are associated to form fibril aggregates with a mean of around 20 nm. Results from the study of Nilsson, et al (2010) showed that the fibril and fibril aggregate widths are highly affected of both pressing temperature and pressure at the compression moulding. An increasing pressing temperature also increases the fibril and fibril aggregation width, with a stabilization of growth around 170-180℃. Higher thermal energy should add more mobility to the fibrils by lowering the energy gap for formation or breaking of the hydrogen bonds. This will lead to strong and rigid formations of inter fibril fusion bonds during the compression moulding step, and thereby not affecting the ordered interior fibril structure (Nilsson, et al., 2010).

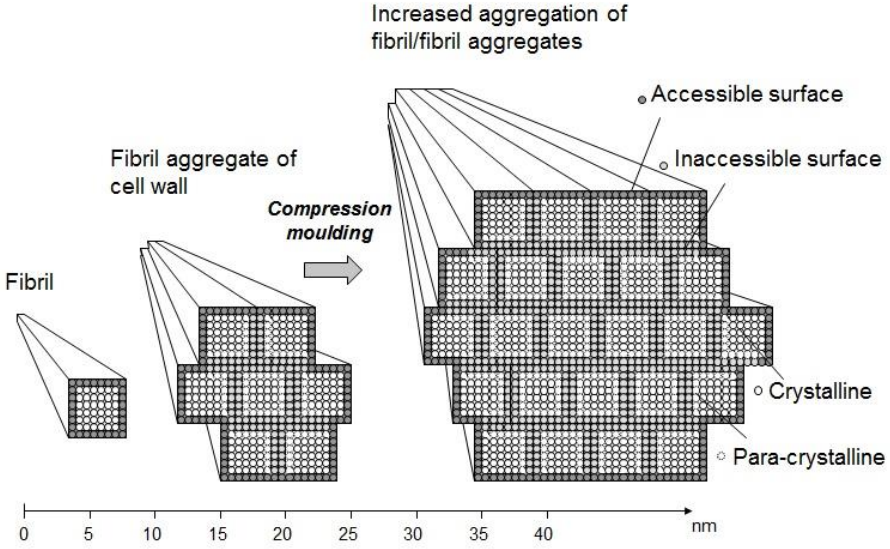


Figure 2-5. A representation of fibril (4 nm width) aggregation to larger fibril aggregates (mean width 20nm) (Halonen, 2012).

2.3.2. Mechanical properties

The mechanical properties can be evaluated using a tensile test, which is the most widely used material test (Emmens, 2011). The tensile test is also known as the tension test, and is measuring ultimate tensile strength (UTS), maximum elongation and area reduction. The ultimate tensile strength is a value of the maximum stress that a material can take while exposed to stress before breaking.

Increasing tension is applied to a specimen while measuring the applied load and the elongation of the specimen. From the values attain from the measurements, the stress and strain can be calculated and presented in a stress-strain curve, seen in figure 2-6. As seen in the figure the stress-strain curve has one linear region in which reversible deformation occurs (non-plastic), and a plastic region where the deformation is irreversible.

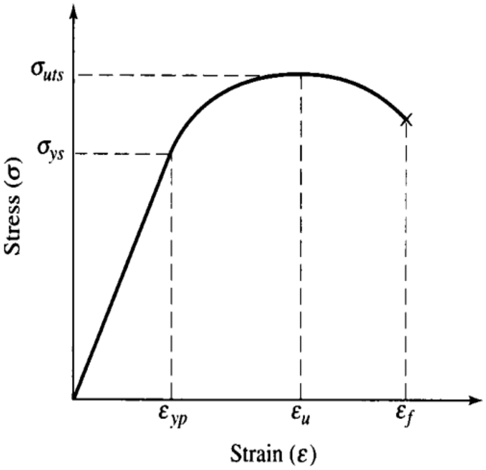


Figure 2-6. The stress-strain curve from a tensile test.

The initial slope, where the deformation is reversible corresponds to the modulus of elasticity, also known as Young’s modulus. It is defined as the ratio of the stress along an axis over the strain of the material and probably one of the parameters that can differ between instruments. It characterizes the stiffness of a material; a materials ability to resist extension and it is written as:

$$E = \frac{\sigma}{\varepsilon} \qquad \text{[Eq.1]}$$

where σ is the normal stress occurring in tension and ε represents the elongation that results from the stress. A material that has a very high Young’s modulus is very rigid, but that is not to be confused with strength or hardness.

Young’s modulus is a property of particular interest for all cellulose composites, since it more direct correlates with the composite structure and the bonds as compared to the measured strength (Halonen, 2012).

2.3.3. Dimensional stabilty

The dimensional stability of a material is stating the ability of the material to maintain its original dimensions, when subjected to change in humidity or temperature. One way to measure this is by determination of the water retention value (WRV). The water retention value is the ratio of the water mass retained after centrifugation under specified conditions by a wet pulp sample, to the oven dry mass of the same pulp sample. It is expressed in gram/gram according to this expression:

$$WRV = \frac{m1}{m2} - 1 \qquad \text{[Eq.2]}$$

Where m_1 is the wet test pad in grams, and m_2 is the mass of the same test pad after oven drying.

2.4. Additives to cellulose fibres

In order to change the mechanical properties of the all-cellulose composites, different additives was evaluated and tested. A literature study was performed in order to find possible additives that could have a positive effect on the mechanical properties of the ACCs. The different possible mechanisms that the additives would be implemented with were also studied.

Findings from the literature show that cellulose, with its derivatives, has been widely used in a lot of different kinds of products and industries. Common applications were for instance within plastics, paper, textiles, food and as a pharmaceutical additive (Rojas & Azevedo, 2011).

Several different types of additives were investigated and evaluated prior to choosing those suitable for lab tests. The additives that were evaluated but excluded from lab tests will however be mentioned here, as well as the reasons for excluding them.

In the literature study two different types of methods for additive addition was found; chemical and physical addition. Both methods are further described below.

2.4.1. Chemical modification

The structure of the cellulose molecule allows for a huge variety of morphological forms to be developed. They will all have different water solubility, porosity, mechanical strength and stability due to the pH and temperature of the reaction. The functionalization of cellulose is of great importance for its variability and proceeds mainly through esterification and etherification reactions.

The chemical modification procedure mainly reported in the literature was the crosslinking mechanism; a process where one polymer chain chemically bind to another. Crosslinking of cellulose have previously been made mainly within the textile industry, in order to improve for instance wrinkle resistance, wrinkle recovery, dimensional stability and crease retention.

To obtain a cross-linked cellulosic material, at least two hydroxyl groups in a cellulose molecule or between adjacent molecules must be combined. The crosslinking agent must be at least bi-functional, the reaction normally occurs in two chemical steps. The chemical reactions are typically initiated by heat and/or pressure.

Polycarboxylic acids esterify cellulose by dehydration of the carboxylic groups bound to the adjacent carbons in the backbone of the molecule, forming a five member cyclic anhydride. Polycarboxylic acids have been reported to increase the wet tensile strength and brittleness of cellulose fibres (Rojas & Azevedo, 2011). Studies also suggest that carboxylic acids together with the use of catalyst, such as sodium phosphate, can give cellulose fibers flame resistant properties. The mechanism for this is either low melting points for the phosphate salts, that produces a glassy coating over the substrate, or decomposition to non-flammable vapors that dilutes flammable gases; both effects results in retarding the flame (UDDIN, 2013).

The most often mentioned poly-functional carboxylic acid in the literature is 1,2,3,4-butanetetracarboxylic acid (BTCA).
There are studies showing improved texture, high wrinkle resistance, water uptake and flexibility when crosslinking cellulose with BTCA as well as improved wet paper strength and dimensional stability. Reports about loss of original tensile strength as a consequence of the rigidity of the cellulose particle have also been reported (Mao & Yang, 1996). Typical curing temperatures reported for BTCA are 140-170℃ (Rojas & Azevedo, 2011). The reaction of BTCA during a crosslinking mechanism with cellulose is shown in figure 2-8.

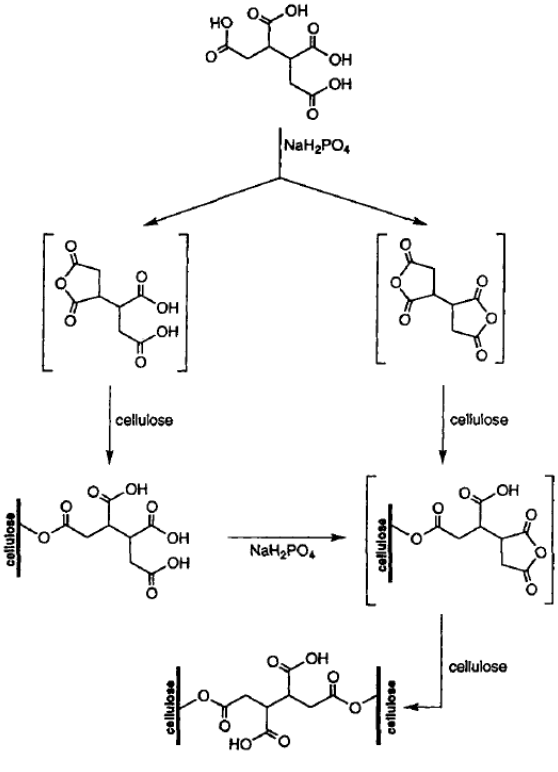


Figure 2-8. The reaction of BTCA during crosslinking with cellulose at 150°C in presence of NaH_2PO_4. (ZHOU, P. LUNER, & CALUWE, 1995)

Other acids mentioned as cross linkers for cellulose fibres are for instance succinic, maleic, polymaleic, itaconic, polyitaconic and citric acid, with results of affecting the tensile strength, flame resistant properties, wrinkle resistance, tenacity, flexibility and structure of the cellulose (Rojas & Azevedo, 2011).

The key to achieve a successful crosslinking process of cellulose with carboxylic acids is the addition of inorganic acids that both contains phosphorous, and are based on alkali metal salts.
A comparison was made of different catalysts, showing that the most effective ones where sodium dihydrogen phosphate (NaH_2PO_4) and sodium hypophosphite (NaH_2PO_2) (Luner et al, 1993). Since NaH_2PO_2 produces toxic phosphine gas when heated, and the difference in efficiency between the two catalysts was insignificant, NaH_2PO_4 was used as a catalyst during the crosslinking. That is together with all of the polyfunctional carboxylic acids used for this project. The concentration of the catalyst was 1:1 by weight of NaH_2PO_4 and the carboxylic acid, which in turn was added as weight percent of wood fibres.
Other catalysts mentioned as crosslinking catalysts were sodium hydrogen phosphate (Na_2HPO_4), sodium carbonate (Na_2CO_3), sodium dihydrogen phosphite (NaH_2PO_3) and tetra sodium pyrophosphate **(**$Na_4P_2O_7$) (Luner et al, 1993).

2.4.2. Physical modification

The additives mentioned here was the type of additive that contributes to the cellulose fibre through adhesion, which is further explained below.

Adhesion mechanism

The tendency of dissimilar particles or substances to attach to another is called adhesion. There are several different forces that cause this to happen. Examples of intermolecular forces are chemical, dispersive and diffusive adhesion. Mechanical adhesion is when an adhesive material fills the voids or pores of another material and in that way hold it together by interlocking. An example of a chemical adhesion is when two materials react somehow, when atoms of the two materials swap or share electron and the surface atoms form either ionic, covalent or hydrogen bonds. Surface molecules of both materials develop attractions, provided that these materials are thoroughly mixed and brought close together. That is since these attractive forces and covalent forces are effective only over very small distances.

Adhesion additives

One of the adhesion additives mentioned in several articles, proposed to improve the strength properties of paper via improving of the inter-fiber bonding was the nanocrystalline cellulose (NCC). In their article about specialty paper and their demand of high strength, Chaa et al mention the addition of carboxylated nanocrystalline cellulose (CNCC) as the explanation of improved strength properties of paper (Chaa et al., 2014).

Nanofibrillated cellulose (NFC), that has bigger dimensions compared to NCC , is also mentioned as an additive for composites with great potential of increasing physical and mechanical properties of paper (Kalia et al., 2014). NFC is suggested to have great potential in the field of paper and packaging and is reported to be able to, together with bio beating (enzymatic treatment of the fibres), enhance both mechanical and physical properties of the fibres (Gonzaléz et al., 2013).

Nanofibrillated cellulose has also been evaluated as additive in eucalyptus pulps. Beaten pulp was compared to unbeaten pulp treated with NFC and a slightly beaten pulp also treated with NFC. Results showed that the NFC addition on the unbeaten pulp gave mechanical and physical properties suitable for paper writing and printing, but that the best mechanical properties was achieved when the pulp was beaten prior to the addition of NFC (Gonzales et al., 2012).

Nanocelluloses have also some drawbacks, including that it can be a bit difficult to handle due to gelatinization of the pulp and slow dewatering process.

Starch is the additive that has been most widely used in the papermaking industry for a long time as an adhesive in the papermaking process. In the wet-end, cationic starch with a positive charge is often used, associating with the anionic or negatively charged cellulose fibers. Cationic starches increases both the wet and dry strength of the paper (Hedborg & Lindstrom, 1993). Starch is also used as binders in coating formulations that improve the smoothness, brightness, gloss and printing characteristics of the paper. Starch acetate however, has been reported to have little influence of the tensile strength (Matsui et al., 2004).

Hemicelluloses are known as one of the ingredients that by binding strength provide mechanical strength to the wooden cell wall. Glucomannan was suggested as more associated to cellulose, and xylan as more closely associated with a less-condensed type of lignin (Zhang et al., 2013). The affinity of hemicelluloses on all-cellulose composites should be high due to this.

Similar association is valid for other polysaccharides, such as for instance beta-glucan. Beta-glucan is polysaccharides made of D-glucose linked together by β-glycosidic bonds and can vary within different groups of molecules, with respect to molecular mass, solubility and viscosity. Beta-glucans occur in a lot of different species, commonly as cellulose in plants, cell wall of baker's yeast, bran of cereal grains, in some fungi, mushroom and also bacteria. Beta-glucan from oat consists mainly of the water soluble 1,3/1,4 bonding which makes it very similar to cellulose in structure, but soluble in water. Since beta-glucan is unbranched and has a very similar structure, compared to the cellulose molecule, one can expect that the affinity of beta-glucan on cellulose is high. This have also been examined in a recent study by Kiemle, et al.(2014) that confirms that this type of beta-glucan irreversibly binds to cellulose, and that longer reaction time has an increasing effect on the binding (Kiemle et al., 2014).

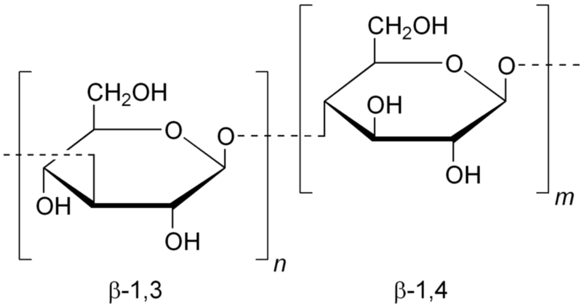


Figure 2-9. The structure of beta glucan commonly present in oat with β-1,3/1,4-glycosidic bonds.

Other additives mentioned in literature and used on cellulose fibres were also urea, ionic liquids and different combinations of plasma, NMMO and LiCl/DMAc treatments (Huber et al., 2012).

3. Experimental

3.1. Materials

3.1.1. Pulp fibres

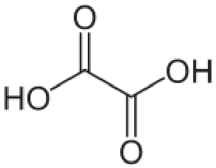
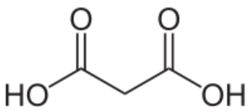
The material used was industrially produced, fully bleached softwood Kraft pulp. It was produced by applying the bleaching sequence (D-EP-D-P) on an OO-treated pulp and dried once. The relative carbohydrate composition was determined by acid hydrolysis and separation of the solubilized monosaccharides by ion chromatography. Detection was made using a pulsed amperometric detector. The following relative carbohydrate composition (%) was: glucose (85.8), xylose (7.1), mannose (6.1), arabinose (0.7), galactose (0.3).

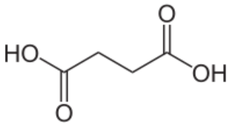
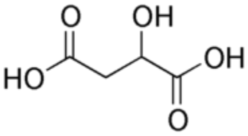
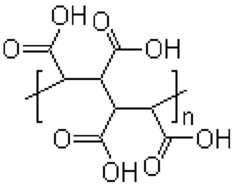
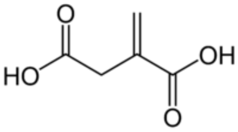
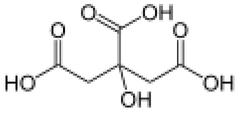
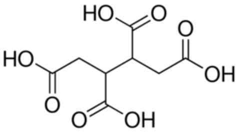
3.1.2. Chemicals for crosslinking

Table 3-1 shows all poly carboxylic acids used as cross linkers, together with their molecular formula, structure and weight as well as pKa values and the curing temperatures used for the crosslinking procedure (3-1). All acids, except polymaleic acid, were in solid form as sodium salts and therefore dissolved in deionized water together with NaH_2PO_4 as catalyst (1:1 w %), before sprayed on squared (80×80mm) ACC composites with approximately 50% dry content. The acids as well as the catalyst had a purity of >99% and were obtained from Sigma-Aldrich.

Other chemicals used were sodium hydroxide (NaOH), diluted with deionized water to a 1% solution, in order to adjust the pH of the pulp from ~5.6 to ~7 when needed (before starch addition).

Table 3-1. The table shows the names as well as the molecular formulas, structures, weight and pKa of the acids used. The curing temperatures stated are the ones applied during hot pressing in this project.

Additive	Molecular formula	Molecular structure	Molecular weight (g/mol)	pKa[a]	Curing temp. (℃)
Oxalic acid	$C_2O_2(OH)_2$		90.03 (anhydrous) 126.07 (dihydrate)	$pK_{a1} = 1.27$ $pK_{a2} = 4.06$	**170**
Malonic acid	$C_3H_4O_4$		104.06	$pK_{a1} = 2.83$ $pK_{a2} = 5.69$	**170**

Additive	Molecular formula	Molecular structure	Molecular weight (g/mol)	pKa[a]	Curing temp. (℃)
Succinic acid	$C_4H_6O_4$		118.09	$pK_{a1} = 4.21$ $pK_{a2} = 5.64$	**130, 150, 170**
Malic acid	$C_4H_3O_2(OH)_3$		134.09	$pK_{a1} = 3.40$ $pK_{a2} = 5.20$	**170**
(Poly)maleic acid[b]	$(C_4H_4O_4)_n$		800	$pK_{a1} = 1.93$ $pK_{a2} = 6.58$	**150**
Itaconic acid	$C_5H_6O_4$		130.10	$pK_{a1} = 3.85$ $pK_{a2} = 5.45$	**150**
Citric acid	$C_6H_8O_7$		192.12	$pK_{a1} = 3.13$ $pK_{a2} = 4.76$ $pK_{a3} = 6.40$	**170**
Butane-1,2,3,4–tetra carboxylic Acid (BTCA)	$C_8H_{10}O_8$		234.16	$pK_{a1} = 3.43$ $pK_{a2} = 4.58$ $pK_{a3} = 5.85$ $pK_{a4} = 7.16$	**130, 150, 170**

[a] pKa values are derived from (aquion.de, 2013).

[b] Added in liquid form.

3.1.3. Other polymer additives

The beta-glucan used was extracted from oat, which is a rich source of the water-soluble fibre (1,3/1,4) β-glucan. It came from Tate&Lyle under the name “Avenacare™ Oat Beta Glucan” as a 1% aqueous solution.

A (commercial) standard cationic wet-end starch called Amylofax PW (D.S=0.0035) with quaternary amino groups (2-hydroxy-3-trimethylammonium propyl starch) as the active component.

The fine fibres that in this report will be called “fines” were an enhanced fraction of fibres from Innventia produced from bleached softwood Kraft pulp through beating.

A combination of starch mixed with the pulp fibres and after sheet formation; sprayed with BTCA, was also made.

3.2. Sheet production

Isotropic sheets, that were to be hot-pressed into moulded ACCs, were made by putting 30 g (totally dry) fibres in deionized water for at least four hours, prior disintegration for 30,000 revolutions in a standard disintegrator (Noram model G3-13, Lorentzen and Wettre, Canada Inc.). When disintegrated, the pulp was dewatered by filtering in a Buchner funnel, reaching a level of approx. 10% dry content. After dewatering, deionized water was added and the pulp was beaten at 8000 revolutions, with the force per unit bar length of 3.33N/mm. Final concentration of the pulp was diluted until 3g/liter (dry pulp).

After beating, laboratory hand-sheets were prepared (ISO 5269-1:2005), with the dimensions of 165mm×165mm. The in-plane randomly oriented sheets were directly, after forming, cold-pressed in a PTI 40140 sheet press for 5 + 2 min under 0.6 MPa pressure to attain 50% dry content. These sheets were then kept sealed and stored in a refrigerator until used. All sheets (165×165mm) were labeled with a letter. When divided in smaller squared sheets the samples were numbered giving exact sample recognition (e.g. A1-4).

A reference sample of the sheet samples was dried in an oven over night at 105℃ in order to determine the total dry weight of the composite. At least one reference sample without additive per modification method were compression moulded for 15 min at the same temperature as the corresponding additive composite, from 130-170℃.

3.3. Fibre composite modification

The additives were either added directly to the project fibres prior to the sheet production process step for physical modification of the cellulose fibre surface or after the sheet production by spraying the additive directly on the sheet.

3.3.1. Chemical modification

The additives mentioned in table 3-1 were dissolved in deionized water with NaH_2PO_4 as catalyst (1:1 weight %). The concentration of the solutions was made high, in order to attain the target amount of acids in the sheets without the need of comprehensive drying prior to pressing. The small squared sheets were put on a lab bench and sprayed with the additive/catalyst solution on one side of the sheet, from a distance of approximately 20 cm, allowing the solution to impregnate the sheet completely. The hand sheet was weighted before and after spraying with the additive-solution, in order to keep track on the amount of additive applied on the sheet.

3.3.2. Physical modification

The additives for physical modification was mixed with the pulp fibres and absorbed during stirring at room temperature, for various amount of time depending on the additive. The "original" fibre slurry was divided into several different buckets (5.744 g dry solid each), put in room temperature overnight with a magnetic stirrer (ca 300 rev/min), at a temperature of approximately 22 °C. After that, the additives were added according to the description below.

Fines and starch

The fines was measured and mixed into the regular pulp at different concentrations and reaction times according to table 3-2 below. The concentration of the fines was varied between 5 and 10% of the fibre solutions and the reaction time varied between 1.5,3 and 4.5 hours.

The starch was gelatinized by dissolving 3g starch in 200 mL deionized water. The mixture was heated to 95 °C for 20 minutes before cooled to room temperature. The final concentration of the starch gel was 1.5%. All the fibre slurries where starch would be added, the initial pH on the fibre slurry was measured and found to be about 5.8, and adjusted to about 7.0 with 5 ml, 0.01 M NaOH solution. The concentration of starch relative fibres was 1 or 5% (w/w), and the slurry with starch was left standing for at least 15 minutes in room temperature. When both starch and fines were added, starch was added for the last 15 minutes of the "fine reaction-time".

Beta-glucan

The beta-glucan solution was applied directly on the fibre slurry at room temperature, in two different concentrations (3.5 and 7% of pulp fibres) for 4h.

After the addition of the additives, the slurry was diluted to a pulp concentration of 3g/l, in order to calculate how much slurry needed for a $200 g/m^2$ sheet. The hand sheets were made according to the default method in chapter 3.2.

3.3.3. Combination of chemical and physical modification

A combination of chemical modification together with physical modification was made. Two starch sheets with different concentrations (1 and 5%) were sprayed with BTCA (1%) prior to compression moulding.

3.4. Compression moulding

Squared parts of the hand-sheets (80×80mm) were compression moulded between blotters and wire in a PHI press model 0230H, at 170°C at 31.25 MPa for 5-15 min. Some of the crosslinking additives were pre-pressed at lower temperatures of 130 or 150°C. In that case the dry weight were not to exceed 90 % prior to hot press step (170°C), water was sprayed on the sheet between the pre-press compression step and hot press to make sure that the sheets would not be too dry entering the hot press.

The compression moulding resulted in composites. To limit warping during the cooling a pressure at 1.17 MPa was applied during cooling. The process route for the default method is presented in figure 3-1.

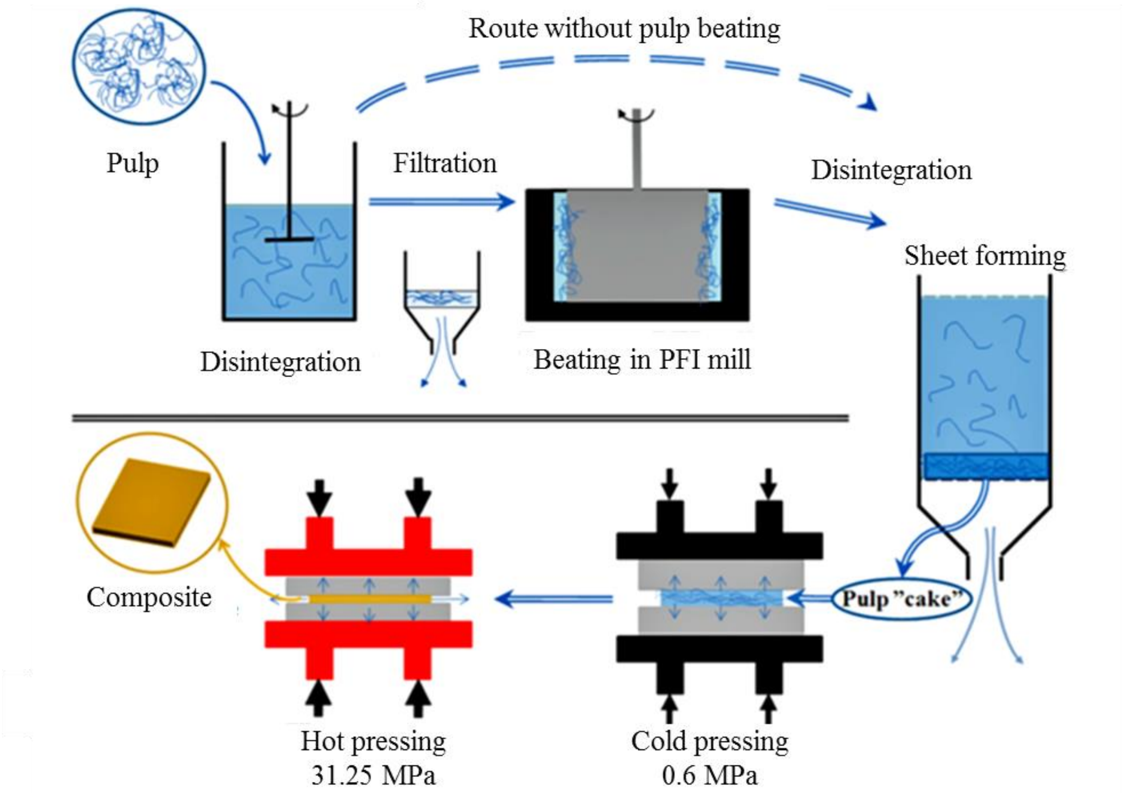


Figure 3-1. Shows a schematic picture of the process route from pulp to composite (Halonen, 2012).

3.5. Mechanical characterization (Tensile test)

The compression moulded cellulose composites were laser cut into dog-bone shaped samples (ISO 37-3, 4.2 mm wide) (Emmens, 2011). Prior to tensile testing on an Instron 5566, all samples were conditioned in a room at 23°C and 50% RH for at least 24 h. The Instron 5566 was equipped with a 500 N load cell and small clamps, with a crosshead speed of 4.8 N/mm. Eight samples was tested per material.

Ultimate tensile strength and yield strength as well as Young’s modulus and strain-to-failure were derived using a modified Matlab program. The material data inserted in the program were the number of samples (8), the length of the samples in mm (20), the width of the samples in mm (4.2) and the thickness mean of the samples. The data achieved from the tensile tests were converted from elastic modulus and max stress in N/mm^2 to ultimate stress in MPa and elastic modulus in GPa. These final data was exported to an excel file, resulting in table 4-3 for the crosslinking additives, and table 4-4 for the other additives. All data was also plotted according to figure A-1 in appendix A.

Two samples of the 400g/m^2 composites were sent to another laboratory for tensile tests, but the same data categories as above was measured. The specimens were not conditioned prior to the tensile tests, but the relative humidity in the room was 48-52%. A video extensometer was used during measures, ensuring more accurate elongation measures compared to the specimens tested at Innventia.

3.6. Water retention value

After the tensile tests, a physical characterization was made to measure the WRV of some selected samples.

A modified method of SCAN-C 62:00 was used, where selected samples were pre-swollen in deionized water for 7 days at ambient temperature in a vacuum desiccator. Centrifugation was performed of 50-60 mg samples at 3000×g for 15 min in a centrifuge tube filter
(Vectraspin™ 3, 0.45 µm Polypropylene Mesh 3 ml, Whatman International Ltd). After centrifugation, the samples were transferred to weighing bottles and weighted before and after drying in an oven over night at 105 ℃.

This method is measuring the water holding capacity of the compression moulded sample, and the WRV value is calculated as the ratio between the water mass retained in the fibers after centrifugation and the dry mass.

4. Results & Discussion

4.1. Evaluation of the used methods and materials

The value of 8000 revolutions for the disintegration in the sheet production step was used due to the results reported by Halonen, 2012, where mechanical properties from compression moulded Kraft paper grade pulp beaten at various revolutions were evaluated.

Different curing conditions for crosslinking of carboxylic acids have been described in the literature, mentioned for BTCA was 140-170 ℃. The curing in the literature was often made in an oven, but when pressure is added (compression moulded) the curing time needed for crosslinking should decrease. Since Halonen, 2012 found the optimal press temperature of all-cellulose composites to be 170℃, due to the thermal degradation of cellulose at higher temperature; this was the initial press temperature for all sheets. However, due to the increased brittleness in the cross-linked hand sheets, these temperatures were modified through the project.

Difficulties occurred during the addition of the crosslinking additives by spraying solution on each sheet. The challenge lied in the repeatability; to apply the same amounts of solution to the sheets. This is an explanation to the differences in the “higher” and “lower” concentrations of the composites, although the solution concentrations were the same. The initial target concentrations of additives on the sheets were 5 and 10%, relative fibre. Another difficulty was to achieve an even spraying of the sheet. Some sheets looked slightly stained after the compression moulding step, despite the fact that the impregnation seemed even prior hot-pressing.

For the tensile tests, an Instron without video extensometer were used. Since dog bone samples were used, a compromise was made in the Matlab program; calculations were set based on the length of 20 mm and width of 4.2 mm, despite the fact that the dog bone was measured over the entire length of 40 mm. No account was taken to the fact that the dog bone specimen elongates more on the narrow section than on the wider section (~20%), which lead to a deviation in accuracy of the measurements. This deviation is however considered minor.

4.2. Precision of the mechanical characterization methods

The mechanical properties were initially measured on reference samples in order to evaluate the precision of the mechanical determination. This is done in order to determine the repeatability of the method, and see if the data differs depending on various practitioners, equipment and other circumstances.

The tensile data achieved from the mechanical tests was evaluated by comparing the means of each sample quality. Error bars were projected at a 95% confidence interval using a Student's t-test, with the following equation:

$$t = \frac{x-\mu_0}{s/\sqrt{n}} \qquad \text{[Eq.3]}$$

where x=sample mean, μ_0 is a sample, s= the standard deviation and n=number of samples. This means that samples where the errorbars overlap eachorther, are not significantly different. A significant difference is valid only when the errorbars are not overlapping.

Pre-made 400g/m^2 and 200g/m^2 sheets were compression moulded at 170℃, 31.25 MPa and tensile tested. The results were evaluated both within and between different sheets. The samples from sheet A was prepressed at room temperature for 5 min at 0.78 MPa prior to hot-pressing at 170℃, 31.25 MPa, unlike the other reference sheets (F,G,H and L) that where directly hot-pressed.

The precision of the determination of the mechanical properties may be influenced by different execution between the samples, both during compression moulding and tensile testing; it can also be due to insufficient mixing of the pulp during the sheet production process.

4.2.1. Precision within reference sheets

Tensile tests were performed on 8 samples per quaternary part of two composites made from sheets with different grammages; A: 200 g/m^2 and B: 400 g/m^2. The tensile data for both sheets is presented in table 4-1 below. For the 400 g/m^2 sheet (B), an evaluation besides the precision within sheets, was also made on the potential impact due to use of different equipment. Two of the samples from sheet B, B6 and B7 were therefore analyzed at another lab. The results from both sheets are presented in figures 4-(1-6) below.

Table 4-1. The data from the tensile test on two composites made from sheets with two different grammages; 200 g/m^2 (A) and 400 g/m^2 (B), compression moulded at 170℃, 31.25 MPa for 15 min. The data is presented with the standard deviation in parenthesis, n=8.

Grammage (g/m^2)	Name	Thickness mean (μm)	Ultimate Stress in Tension (MPa)	Elastic Modulus (GPa)	Strain at Break (%)
200	A1	180 (7.3)	87 (7.7)	4.3(0.4)	6.3 (0.9)
200	A2	192 (10.8)	96 (6.7)	4.3 (0.3)	6.8 (0.4)
200	A3	185 (4.9)	74 (7.1)	4.2 (0.3)	5.8 (1.2)
200	A4	192 (6.8)	85 (9.5)	4.6 (0.4)	5.9 (1.1)
400	B5	349 (6.8)	92 (11.3)	4.8 (0.5)	6.9 (0.9)
400	B6[a]	N.A	78 (9.5)	6.7(3.0)	5.5 (0.7)
400	B7[a]	N.A	92 (10.8)	15.1 (5.5)	3.9 (0.8)
400	B8	336 (12.0)	96 (6.7)	6.9 (0.2)	6.2 (1.4)

[a] The tensile measures were performed at another laboratory.

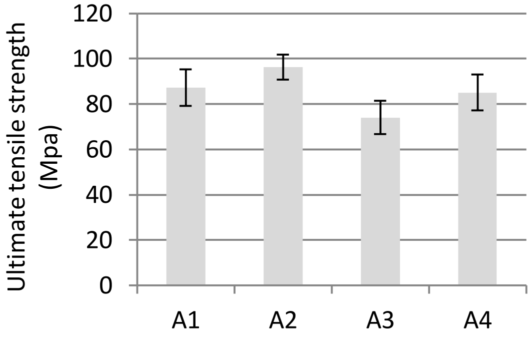


Figure 4-1. The ultimate tensile strength (MPa) values within sheet A, compression moulded at 170℃. The error bars are projected at a 95% CI, n=8.

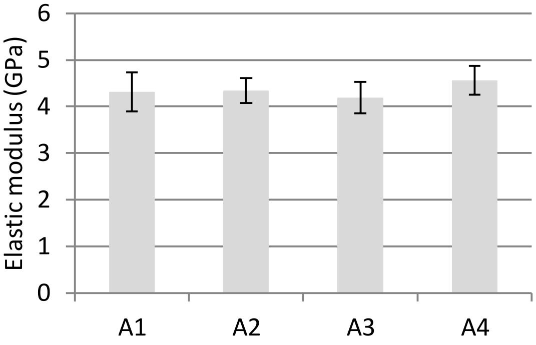


Figure 4-2. The module (GPa) within sheet A, compression moulded at 170℃. The error bars are projected at a 95% CI, n=8.

As seen in figures 4-(1-3), there are no significant difference within the 200g/m^2 sheets, with the exception of A2 and A3 for the ultimate tension (fig 4-1). All other error bars overlap to some extent.

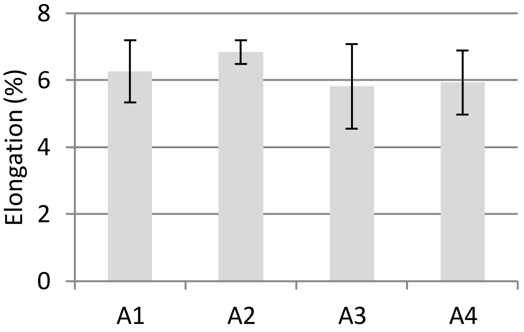


Figure 4-3. The elongation (%) within sheet A, compression moulded at 170℃. The error bars are projected at a 95% CI, n=8.

The results for sheet B (400 g/m^2) as seen in figure 4-(4-6) did not show significant differences between the two laboratories. The one sample that deviated the most however, was B7, one of the two samples tested using equipment at the external laboratory. This sample had a significant higher module mean ~15 MPa (as seen in figure 4-5) than the other test specimens in that category. The other specimens tested at the same lab (B6) were, on the other hand, at the same level as those measured at the external laboratory (B5 and B8). This strengthens the theory that the measures can be more dependent on the fibre distribution within the sheets than the testing conditions or the handling when performing the test.

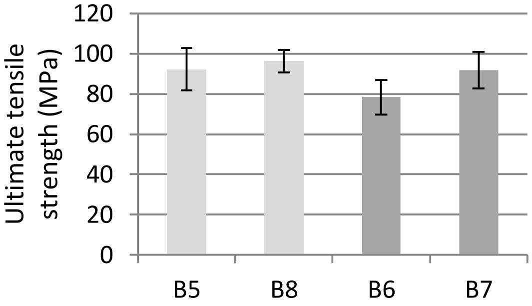


Figure 4-4. The ultimate tensile strength within sheet B, compression moulded at 170℃. The error bars are projected at a 95% CI. B5 and B8 are tensile tested at Innventia, and B6 and B7 at another laboratory, n=8.

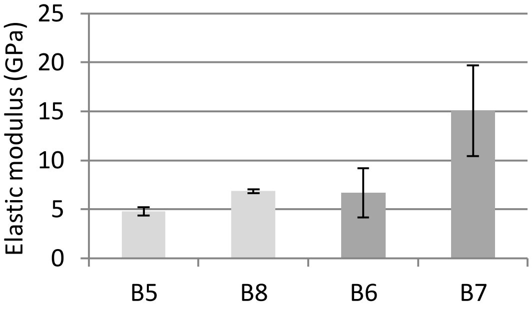


Figure 4-5. The module within sheet B, compression moulded at 170℃. The error bars are projected at a 95% CI. B5 and B8 are tensile tested at Innventia, and B6 and B7 at another laboratory, n=8.

Other significant variations were the ultimate tension of B6 that was slightly lower than B8, and B5 that had a lower modulus than B8. The conclusion is that differences in mechanical properties can occur within sheets made in the same way, something that should be kept in mind while evaluating the results on the sheets with additives. The differences within the sheets were suspected to be higher in sheets with higher grammage, due to the higher fibre content in the slurry. These fibres have a tendency to bundle up and create uneven fibre distribution with higher fibre content in certain parts of a sheet, where the corners are particularly subjected. This seems to be true according to the significant difference for the 400g/m^2 composite. One way to avoid this is to cut out one sample 8×8cm per sheet (in the middle) instead of dividing it in four parts.

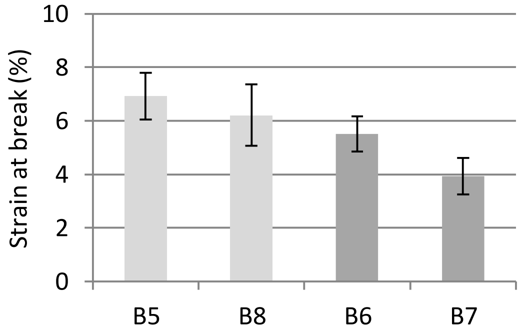


Figure 4-6. The elongation of composite specimens of sheet B, compression moulded at 170℃. The error bars are projected at a 95% CI. B5 and B8 are tensile tested at Innventia, and B6 and B7 at another laboratory, n=8.

For the composites made of 400 g/m^2 sheets, they were all pressed and tensile tested in the same way, but at two different laboratories with different equipment. The major difference was between two composites tested at the same location, which precludes this to be due to different instruments and handling. Therefore, uneven fibre distribution in sheet B is suspected to be the reason for the differences observed in the four composites B1-B4. However, even for the significant inequalities, the differences were relatively small.

4.2.2. Precision between reference sheets

A comparison between different sheets with the same grammage (200g/m^2) to be used as references in the project was also made. Quaternary parts of the sheets were compression moulded for 15 min at 170 ℃ and 31.25 MPa. The samples from sheet A were in addition prepressed at room temperature for 5 min and 0.78 MPa prior to compression moulding. 8 test specimens per composite sample were tensile tested, with the exception of 4×8 specimens for sheet A. Tensile testing values are presented in table 4-2 below.

Table 4-2. The results from the tensile tests performed on different 200g/m^2 sheets without additives. Compression moulded at 170℃, 31.25 MPA for 15 min. The data is presented with the standard deviation in parenthesis. Data for A is presented as the mean from the four composites A1-A4.

Name	n	Thickness mean (μm)	Ultimate Stress in Tension (MPa)	Elastic Modulus (GPa)	Strain at Break (%)
A[a]	32	180 (7.3)	86 (11.0)	4.4 (0.4)	6.2 (1.0)
F	8	193 (8.2)	88 (6.3)	5.6 (0.5)	4.3 (0.7)
G	8	192 (7.2)	83 (14.5)	5.5 (0.2)	4.0 (1.1)
H	8	183 (2.6)	94 (8.9)	5.6 (0.2)	4.9 (0.7)
L	8	181 (3.3)	109 (9.7)	6.2 (0.2)	5.0 (0.7)

[a] Pre-pressed at room temperature, 0.78 MPa for 5 min.

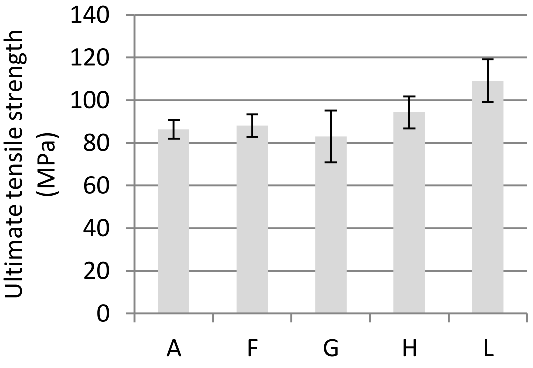


Figure 4-7. The ultimate tensile strength of 200 g/m^2 sheets, compression moulded at 170°C. The error bars are projected at a 95% C, n=8 apart from for A:n=32.

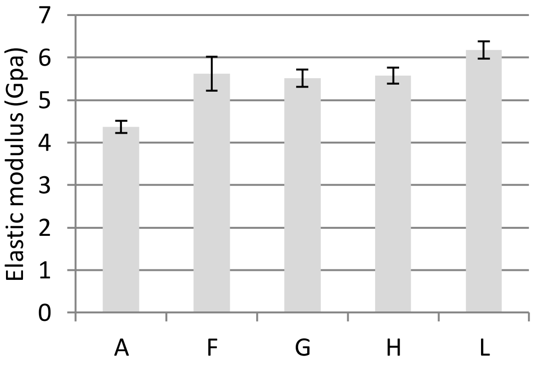


Figure 4-8. The module of 200 g/m^2 sheets, compression moulded at 170°C. The error bars are projected at a 95% CI, n=8 apart from for A:n=32.

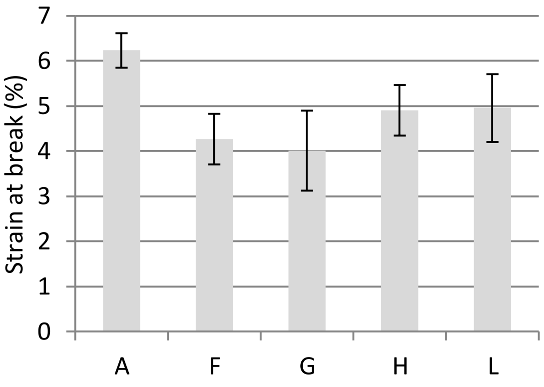


Figure 4-9. The elongation (%) of 200 g/m^2 sheets, compression moulded at 170°C. The error bars are projected at a 95% CI, n=8 apart from for A:n=32.

When comparing the different reference composites, the only significant difference for the ultimate tensile strength seem to be between composite A and L. A is significantly lower in elastic modulus than all other samples, which is confirmed with significantly higher elongation seen in figure 4-9. Sheet A was the only sheet that was pre-pressed at room temperature, a probable reason for deviation. When comparing the other samples to each other, no significant differences was observed except for the ultimate tension for sheet L, which is significantly higher than for F and G. However, the difference is small, as seen in figure 4-7.

The aim with this part of the project was to evaluate the magnitude of the precision in tensile testing, by subjecting the samples to the same treatment and measurements. This was made both between and within different sheets, the latter for 200 and 400 g/m^2. The results showed some scattering in mechanical data both within and between sheets.

For the composites made of 200 g/m^2 sheets, differences were observed in UTS, whereas the E-modulus was within the 95% confidence interval. The lower values for composite A could very well be caused by the cold-pressing step that was performed on that sheet, leading to lower water content during the subsequent hot pressing.

4.3. Crosslinking additives

The most promising carboxylic acids was chosen, both for improvement of the tensile strength and dimensional stability. A compilation of the mechanical test values for all sheets with crosslinking media are shown in appendix A2.

Methods for crosslinking mentioned in the literature are mainly impregnation and freeze drying prior to heating. The decision of spraying the sheets with the additive solution was made in order to simulate something that easily could be performed in an industrial scale, on the paper production path, for instance.

The initial samples of composites treated with crosslink media are presented in figure 4-10, some appear darker than others. The two darkest samples were the higher concentrations of malic acid and citric acid. These acids are also hydroxyl acids, as seen in table 3-1. The darkening is probably due to dehydration of the hydroxyl during the compression moulding step, which leads to the formation of chromophores and discoloring.

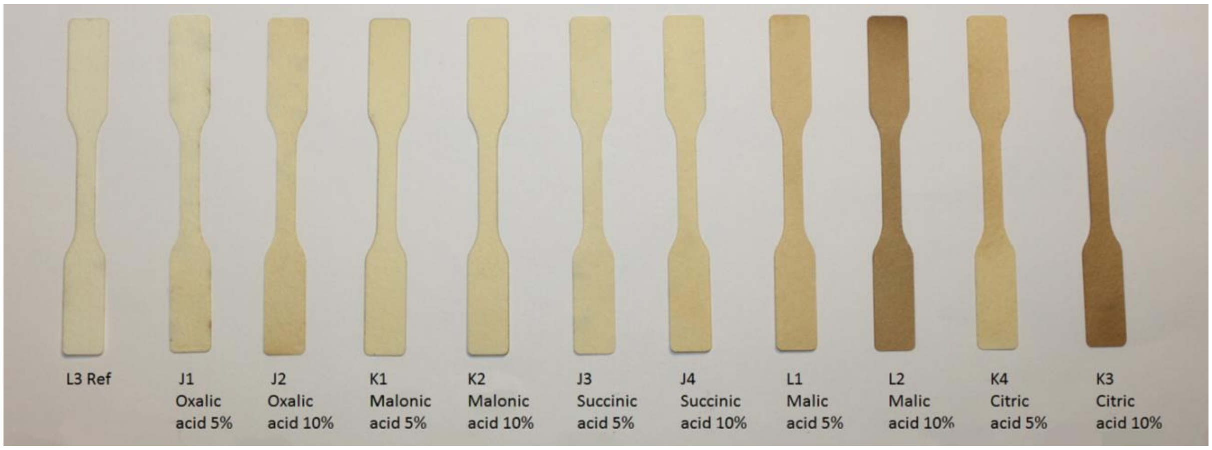


Figure 4-10. A picture of the first dog bone samples treated with carboxylic acids. Note that the concentrations here are the aimed concentrations for spraying; the real additive amount is seen in table 4-3.

Tensile tests were performed on the samples with a target concentration of 5% acid relative fibre, resulting in directly noticeable low tensile strength already at the lower concentrations seen in figure 4-11. The higher concentration samples with a 10% target concentration were therefore not even tensile tested.

This initial evaluation of the crosslinking method led to a revised process in the following crosslinking experiments with higher concentration of the spraying solutions in order reduce the additive solution needed for the target concentration and targeting the acid concentration relative fibre between 1-5%. The sheets where henceforward air dried to ~75% dry content prior to the spraying, in order to increase the absorption and avoid over wetting of the sheets. The sheets were also air dried after the additive spraying to ~50 % dry weight, prior to hot pressing. Lower hot-pressing temperature was also examined, to avoid decarboxylation and lower the risk for acid hydrolysis of the cellulose.

4.3.1. Hot pressing at high temperature

BTCA was together with the 5% target concentrations of oxalic, succinic, malonic, citric and malic acid pressed at a temperature of 170°C. The target for these concentrations was to be 5% weight relative to the fibres. As seen in figure 4-11, the actual amounts of the acids on the fibre were hard to control and turned out very different between the sheets. For some samples, even higher concentrations were obtained, even though the concentrations of the solutions were approximately the same.

The results from the tensile tests that followed are presented in the figures below. A big decrease in the tensile strength compared to the reference samples was noticed. The samples with the same additives but higher concentration did therefore not undergo further tensile tests. The results from the mechanical testing of the "lower concentration" samples are presented in figure 4-(11-13).

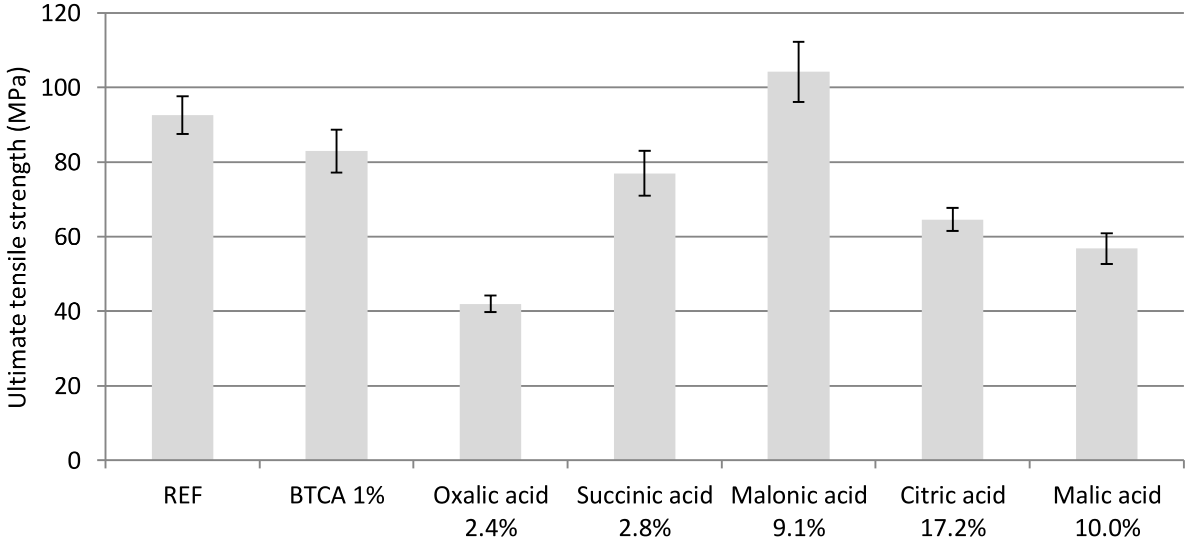


Figure 4-11. The influence of acid concentration on ultimate tensile strength of test composites hot pressed at 170℃, 31.25 MPa for 15 min, compared to untreated reference samples of all-cellulose composites(n=32). The error bars are projected at a 95% CI, n=8 for all acid-treated composites.

The ultimate stress measures were mostly significantly lower for the composites treated with the crosslinking additives, the exception was 9.1% malonic acid and 1% BTCA that was not significantly different from the reference sample. The highest value obtained was 104 MPa for malonic acid, 9.1 % weight relative fibre. No clear correlation between UTS and the pKa values of the acids could be observed, e.g. oxalic acid and malonic acid have the lowest pKa values (table 3-1). One possibility to a decrease in strength could be acid hydrolysis of cellulose leading to chain cleavage of the fibres.

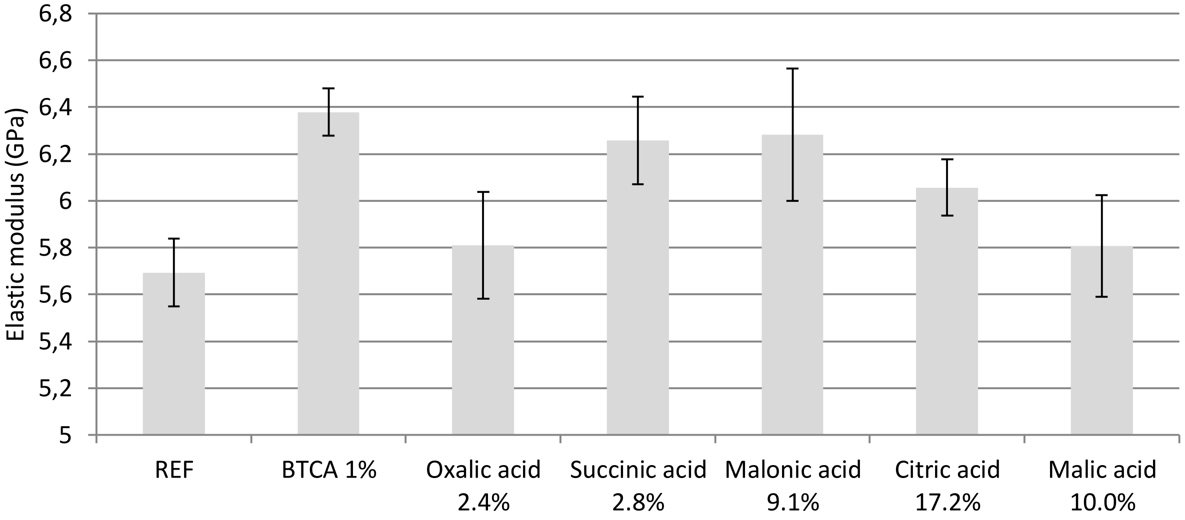


Figure 4-12. The influence of acid concentration on the elastic modulus values of test composites hot pressed at 170℃, 31.25 MPa for 15 min, compared to untreated reference samples of all-cellulose composites(n=32). The error bars are projected at a 95% CI, n=8 for all acid-treated composites.

The module values for the different sheets were a bit scattered, but all except oxalic and malic acid had a higher stiffness than the reference sample. No significant difference from the reference was measured for oxalic (2.4%) and malic acid (10%).

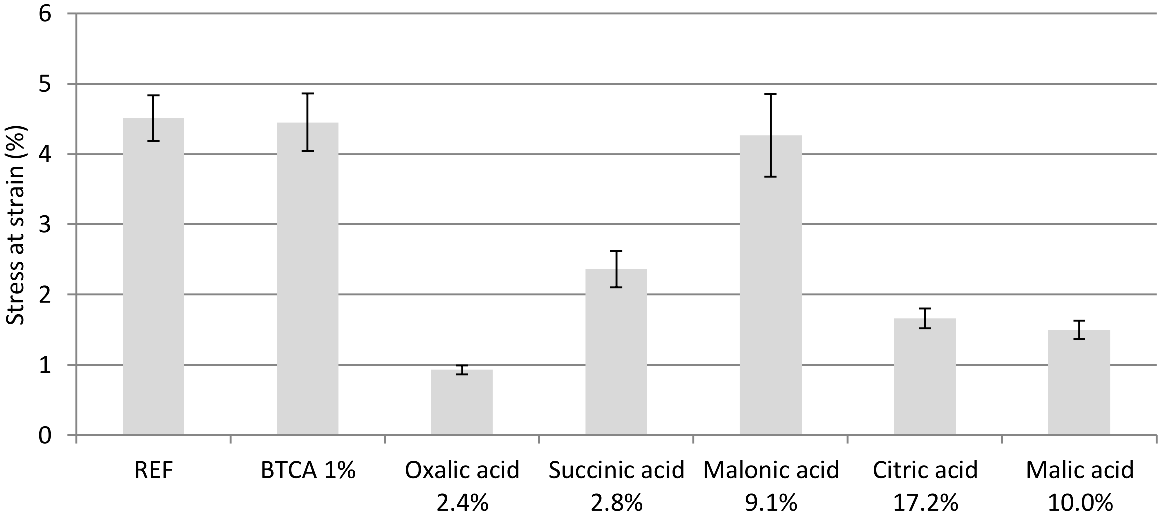


Figure 4-13. The influence of acid concentration on the elongation of test composites hot pressed at 170℃, 31.25 MPa for 15 min, compared to untreated reference samples of all-cellulose composites(n=32). The error bars are projected at a 95% CI, n=8 for all acid-treated composites.

The elongation values also showed big differences between the additives. Malonic acid and BTCA showed no significant difference from the reference sample, while the others were all significantly lower than the reference.

4.3.2. Hot pressing at moderate temperature

The following figures are the result of the compression moulded samples of BTCA and succinic acid at two lower levels of temperatures, 130°C and 150°C, compared to the 170°C made initially. The temperatures were lowered in an attempt to avoid the acid hydrolysis of the cellulose that occurred in the hot pressing at high temperature and to see if any improvement could be seen in mechanical properties.

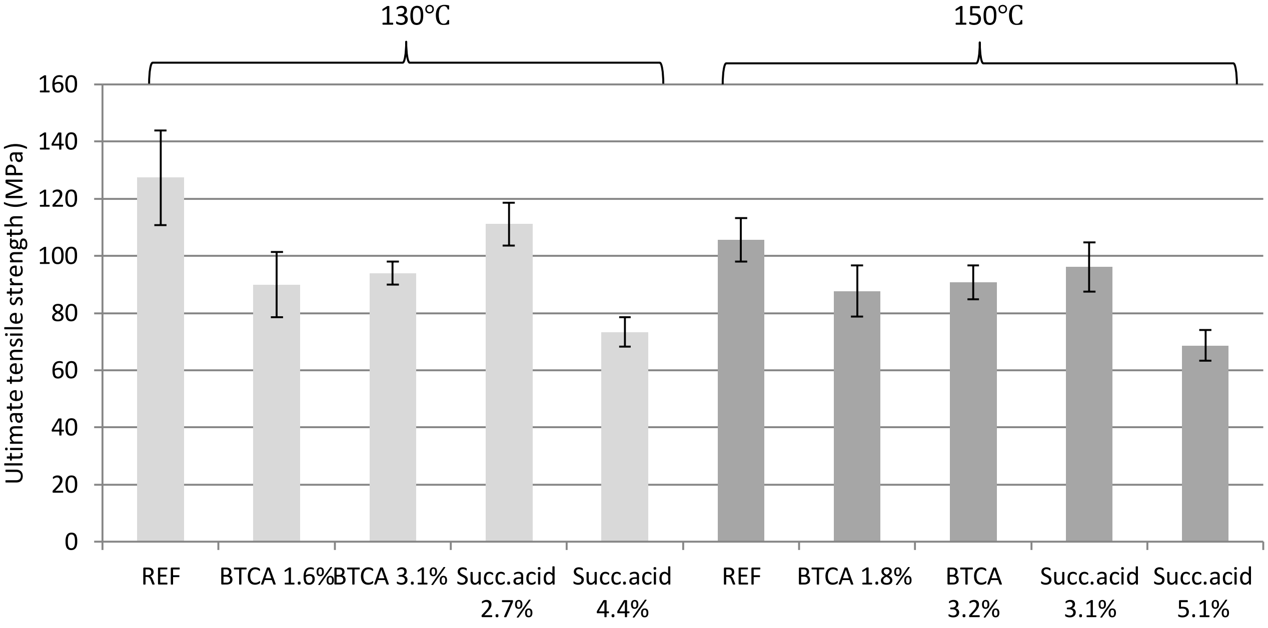


Figure 4-14. The influence of acid concentration on the ultimate tensile strength of test composites hot pressed at two temperature levels, 130 and 150°C at 31.25 MPa for 15 min, compared to untreated reference samples of all-cellulose composites(n=8). The error bars are projected at a 95% CI, n=8 for all acid-treated composites.

As seen in figure 4-14, the ultimate stress levels of composites from the BTCA and succinic acid treated sheets are similar or significantly lower than the reference samples. When comparing the two reference samples (130 and150°C), the result indicates that higher temperature decreases the ultimate tensile strength.

The elastic modulus values for these samples are seen in appendix B, and there was hardly any significant difference between the samples. The exception was succinic acid 5.1 and 2.7%, cured at 130°C and 150°C, respectively.

The values of the elongation were significantly lower than the reference samples for all additive samples except for the composites of succinic acid (2.7%) treated sheet pressed at 130°C.

The target for the concentrations of the carboxylic acids here was to be lower and more even than in the initial tests presented in chapter 4.3.1. Despite intermediate pressing temperatures (130,150°C), the carboxylic acids used have significantly affected the mechanical properties of the composites, mainly by lowering the tensile strength. Further exploring of some of these samples was therefore made by measures of the water retention value (section 4.4).

4.3.3. Hot pressing at intermediate temperature

Composites of polymaleic and itaconic acid treated sheets were also made by hot pressing at 150°C.

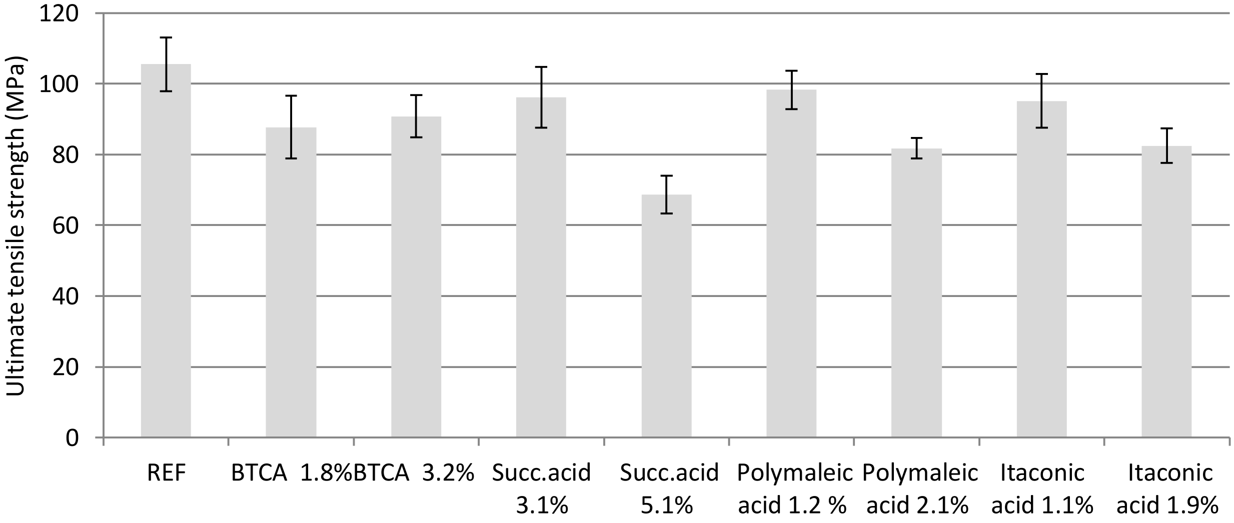


Figure 4-15. The influence of acid concentration on the ultimate stress values of test composites hot pressed at 150°C. The error bars are projected at a 95% CI, n=8.

The carboxylic acids are compared together with the reference samples in figure 4-15, showing that the ultimate tension were not significantly different from the reference sample, except for succinic acid (5.1%), polymaleic acid (2.1%) and itaconic acid (1.9%). The value is significantly lower for these three, even though that the difference from the reference is not that big.

The elastic moduli, seen in appendix B have hardly any significantly different values between the samples whilst succinic acid (5.1%) was the only sample significantly lower than the reference sample. For the elongation it was the other way around, almost all samples were significantly lower than the reference sample, which is reasonable due to the higher stiffness at the lower elongation values. The exceptions were the lower concentrations of polymaleic (1.2%) and itaconic acid (1.1%), which are not significantly different, seen in appendix B.

The method that was used for the chemical modification of the cellulose composites was by spraying the additives dissolved in water in presence of a catalyst on the cellulose sheets. This turned out to be a method with low repeatability as indicated by the uneven results. It was hard to control the spraying distance as well as to perform an even distribution of additive on the sheets. This probably resulted in sheets with different additive content, making a real comparison hard to do.

The uncertainty in these results is therefore high. An alternative way to apply these types of additives could in the future be by impregnation by immersion, in order to achieve a more even absorption and increase the repeatability.

4.4. Effect on water uptake

The composites subjected to water retention value (WRV) measure were from acid treated sheets for crosslinking. Three different levels of curing temperatures for the additive sheets: 130, 150 and 170°C were evaluated as well as reference sheets from each temperature.

The water retention value, where a decreased value correlates to higher dimension stability, is a way of indirectly estimating the dimensional stability. Fibril aggregation leads to decreased WRV by reduction of the fibril area accessible to the water (Halonen, 2012). The samples chosen for evaluation were those that had a significant lower elongation compared to the reference. Low elongation values might indicate that the fibres have been affected by the crosslinking and potentially should also be more dimensional stable.

Determinations were made in duplicates for each sample; the mean was calculated as well as the standard deviation. Since only two test points per sample was measured, the t-test evaluation was omitted. The error bars in figure 4-16 therefore represents the standard deviation. The results from this measure indicate that some decrease in water retention value is obtained compared to the reference samples; differences are observed for both BTCA and succinic acid pressed at 150°C, and for starch combined with BTCA pressed at 170°C. Despite these indications of increasing dimensional stability, no significant differences in WRV were observed. Further tests would preferable be made on more replicates, to confirm or to contradict the results.

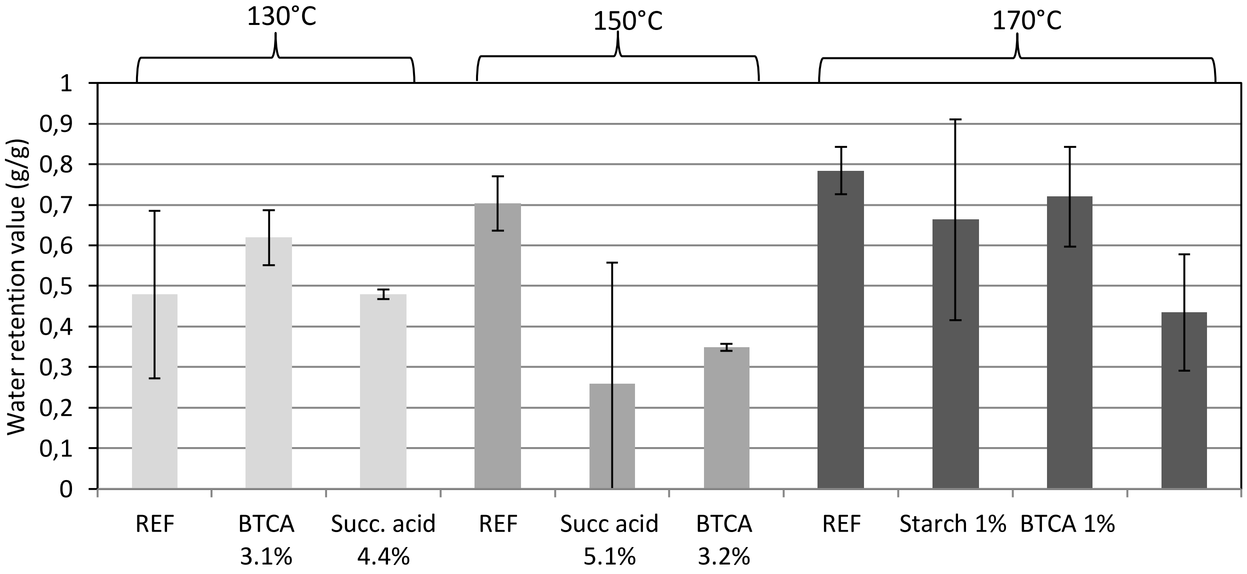


Figure 4-16. The water retention at three different temperature levels for curing at 15 min: 130°C (light gray), 150°C (medium gray) and 170°C(dark gray). Duplicates of each quality were made (n=2), and the error bars shows the standard deviation.

4.5. Fines & starch

The evaluation made for the sheets modified by physical modification was made in the same way as for the crosslinking sheets. The major difference between them was that the fines and starch sheets were modified already prior to the sheet forming step. Since no water or any additives were added to the sheets prior to the compression moulding step, it was a lot easier to make sure that all sheets had ~50% dry content prior to the compression moulding. The pressing temperature of 170℃ was used here.

Nanocellulose was considered as an additive, but due to its potential problems with dewatering during the sheet production process, the decision was instead to use "fines"; an enhanced fraction of fibers made at Innventia. These fibres were not as micronized as NCC, but significantly a lot more finely grounded than the regular ACC fibres, these fines were expected to have similar properties as NCC, considering the expected improvement of the inter-fibers bonding.

Starch adsorption has been proved to be favored by a neutral or preferentially an alkaline solution, therefore, the pH was adjusted to around 7 prior the starch addition in these samples (Shirazi et al., 2003).

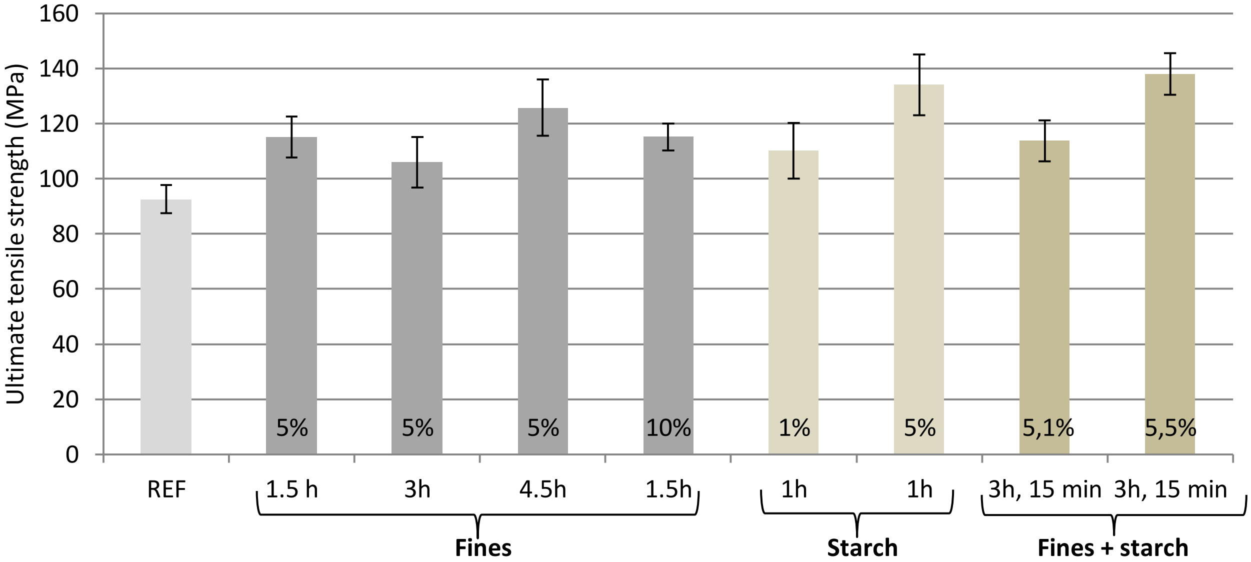


Figure 4-17. The ultimate tensile strength (MPa) obtained from the physical modification by starch and fines, compression moulded at 170℃. The error bars are projected at a 95% CI, n=8 apart from the reference sample where n=32.

As shown in figure 4-17, all samples except 5% fines, 3h have significantly higher ultimate tension than the untreated sample. The highest value obtained was 138 MPa, for 5% fines + 5% starch. Interesting is that no significant difference is measured between the different fines samples at 5 and 10% and for 1.5,3 and 4.5 h. It seems like neither the higher concentration of 10% nor the longer reaction time of 3 and 4.5 h increases the tensile strength significantly. For the cationic starch that binds to the cellulose due to its slightly negative charge, it seems like the concentration, rather than reaction time, matter. The higher concentration of 5% starch shows significantly higher tensile strength than for the low concentration of starch at 1%.

According to literature, starches preferentially adhere to fines as compared to cellulose fibre surfaces (Hedborg & Lindstrom, 1993). The starch was expected to mainly stick to the fines, rather than the cellulose fibres. The fines would have a more reachable negative charge than the origin fibres and therefore attract the starch. Since the structure of starch can not only be linear but also branched, this might include a steric obstacle for the starch sticking to the origin pulp.

Two concentrations of starch (1 and 5%) were combined with 5% of fines. However, no significant improvement in UTS was observed for these blends compared to the corresponding starch addition, though the adsorption time was considerably shorter (15 min vs. 60 min). The highest mean obtained was 138 MPa for the combination of 5% fines and 5% starch, but it did not differ significantly from the 5% starch sample.

The data for the modulus shows a bit more modest increase for the modified samples. The ones with significant increased modulus are fines 5% for 1.5 and 4.5h, as well as 5% starch sample and both combination of starch and fines. This can be seen in appendix B.

For the elongation values, the fines with concentration of 10% and 5%, the latter for 4.5h reaction time, were slightly but significantly higher than the reference.

4.6. Beta-glucan

The results for the beta-glucan additive are presented below. The samples with two different concentrations of beta-glucan added during the same amount of treatment time (4h) showed both significant increase for ultimate tension and elastic modulus. The highest values were obtained from the 7% solution of beta-glucan; 151 MPa for the ultimate tension, and 7.0 GPa on elastic modulus. For the elongation, no significant differences from the reference samples were attained.

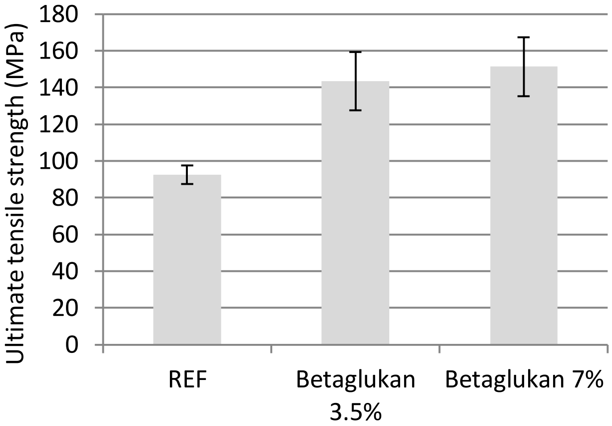


Figure 4-18. The ultimate tensile strength (MPa) obtained from the physical modification by beta glucan, compression moulded at 170℃. The error bars are projected at a 95% CI, n=8 apart from for the reference where n=32.

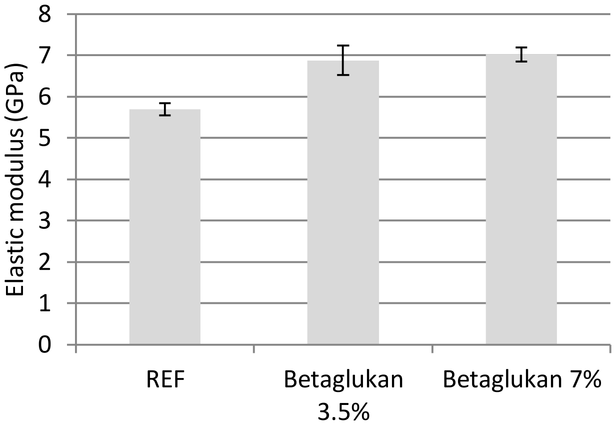


Figure 4-19. The modulus (GPa) obtained from the physical modification by beta glucan, compression moulded at 170℃. The error bars are projected at a 95% CI, n=8 apart from for the reference where n=32.

Beta-glucan from oat was used, having a similar structure compared to cellulose, meaning that the affinity was expected to be high. This is also indicated by the results. Why the beta-glucan showed more improvement than for instance the starch, could be due to the structural differences of the polymers. Since beta-glucan is linear as cellulose, it might be easier for it to bind to the cellulose. As seen in all figures, no significant differences occur between the two concentrations of beta-glucan, 3.5 and 7%. This indicates that 3.5% or even lower concentration could be enough to achieve desired effect. The reaction time of 4 could also be longer than necessary and shorter treatment times should be investigated to settle the optimum time.

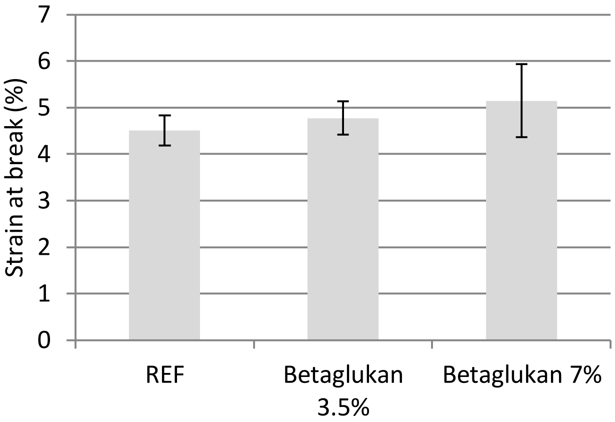


Figure 4-20. The elongation (%) obtained from the physical modification by beta-glucan, compression moulded at 170℃. The error bars are projected at a 95% CI, n=8 apart from for the reference where n=32.

4.7. Starch + BTCA

Two quaternary parts of the starch sheets used for evaluation of composites in chapter 4.4 were also sprayed with BTCA prior to the compression moulding step. This was made in order to evaluate if the starch containing composites were more efficiently cross-linked by the BTCA addition, compared to the sheets without polymer addition. Percentages mentioned below are weight% relative cellulose fibre.

Samples with starch (1 and 5%) and BTCA (1%) are in the figure below compared to reference samples without additive, samples with only starch (1 and 5%) and with only BTCA (1%).

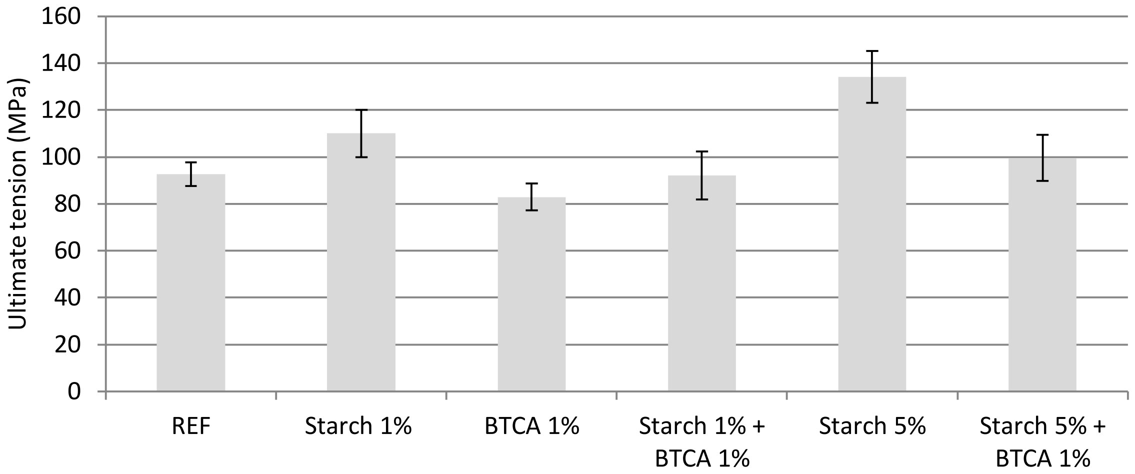


Figure 4-21. The ultimate stress data (MPa) obtained from the physical modification by starch, combined with the chemical modification of BTCA, compression moulded at 170℃. The error bars are projected at a 95% CI, n=8 apart from for the reference where n=32.

The samples with significantly higher UTS than the ACC reference sample were the two starch samples, as shown before. The BTCA seem to have a decreasing effect on the tensile strength, independently if starch is present or not. There is however a slight indication that the starch has a positive effect on the strength even when BTCA is present, seen when comparing the neat BTCA sample to those containing both 1 and 5% of starch. The increase is not a significant difference though.

As for the modulus data that are shown in figure B2-3 in appendix B2, no significant differences from the reference were obtained. There is however, an indication of an increase in modulus for samples containing 1% BTCA as well as 5% starch.

No significant deviation from the reference was obtained in the elongation of the modified composites (fig B2-4 in appendix B2).

5. Conclusions

The evaluation of the precision of the mechanical testing method showed that there are essentially no significant differences within or between composites made in the same way. The handling of sheets during production process as well as tensile testing can affect the results and small differences was revealed; pre-pressing prior to the compression moulding step indicates a decrease in modulus.

The chemical modification with the crosslinking additives mainly resulted in decreased tensile strength, elastic modulus and elongation. The temperature conditions are critical, the most significant differences occurred for the sheets pressed at the higher temperatures (170℃).

Measures of the water retention value slightly indicate that the crosslinking of cellulose decrease the water retention and thereby also increase the dimensional stability.

Modification by addition of fines, starch and beta-glucan resulted in similar or significant increase in mechanical properties. The best results were achieved for the beta-glucan; both for UTS (151 MPa), and for the elastic modulus (7.0 GPa), which looks promising for future developments.

The combination of both chemical and physical modification with starch and BTCA did not improve the mechanical properties, even if starch seems to slightly increase the tensile strength in the combined samples compared to the pure BTCA composites. The starch + BTCA samples showed decreased water retention, which could be a possible development of a material with retained tensile strength and increased dimensional stability.

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A. Appendix A: Tensile test data plot and data

A1. Tensile test data plot

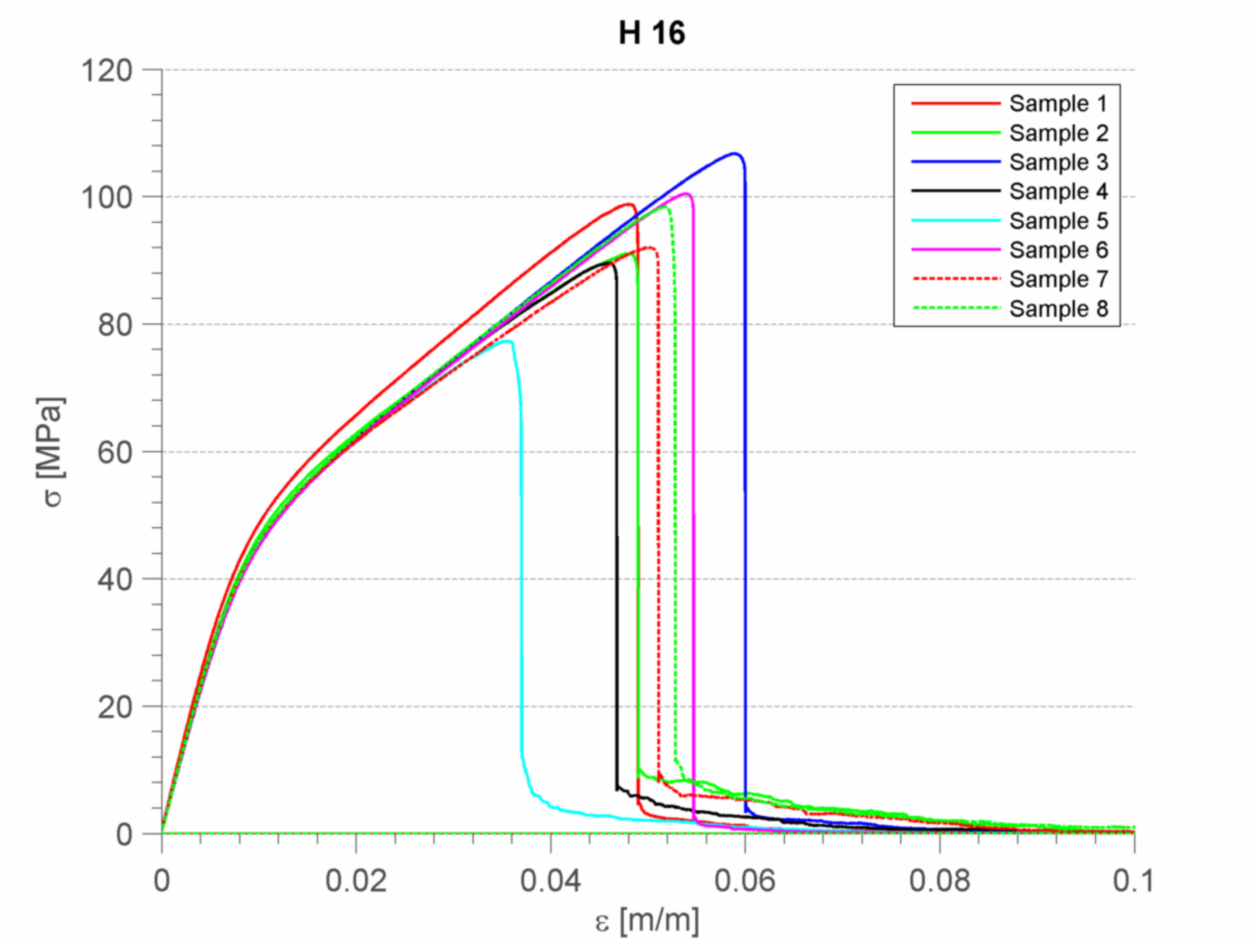

Figure A-1. An example of the plot resulting from the tensile test data converted by Matlab. The data was also exported to an excel file, resulting in table A-1 for the crosslinking additives, and table A-2 for the other polymers.

A2. Tensile test data: Carboxylic acids and references

Table A-1. Shows the conditions and results of the tensile tests for the different sheets where cross linkers were added as an additive in alphabetical order together with reference sheets.

Additive	% (w/w)	Name	Thickness mean (µm)	Ultimate Stress in Tension (MPa)	Elastic Modulus (GPa)	Strain at Break (%)	Compression temperature 15 min (℃)
Carboxylic acids							
BTCA	0.95	I1	178 (4.7)	97 (6.6)	5.6 (0.2)	4.2 (0.7)	170
BTCA	0.88	I3	178 (5.4)	68 (5.3)	5.6 (0.3)	2.2 (0.5)	170
BTCA	0.76	I4	178 (4.5)	95 (10.5)	5.6 (0.3)	4.3 (0.4)	170
Oxalic acid	2.4	J1	178 (4.9)	42 (2.7)	5.8 (0.3)	0.9 (0.1)	170
Succinic acid	2.8	J3	177 (7.5)	77 (7.2)	6.3 (0.2)	2.4 (0.3)	170
Malonic acid	9.1	K1	175 (5.1)	104 (6.5)	6.3 (0.2)	4.3 (0.5)	170
Citric acid	17.2	K4	179 (5.9)	65 (3.7)	6.1 (0.1)	1.7 (0.2)	170
Malic acid	10.0	L1	179 (5.9)	57 (5.0)	5.8 (0.3)	1.5 (0.2)	170
BTCA	1.6	N1	176 (5.9)	90 (13.6)	6.1 (0.5)	3.1 (0.5)	130[b]
BTCA	1.8	N2	176 (8.7)	88 (10.7)	6.4 (0.4)	2.6 (0.5)	150[b]
BTCA	3.1	N3	178 (4.8)	94 (4.8)	6.2 (0.3)	3.1 (0.3)	130[b]
BTCA	3.2	N4	173 (4.0)	91 (7.1)	6.5 (0.4)	2.6 (0.2)	150[b]
Succinic acid	4.4	O1	177 (4.4)	73 (73.4)	5.5 (0.5)	3.0 (0.3)	130[b]
Succinic acid	5.1	O2	174 (4.1)	69 (6.5)	5.6 (0.2)	2.4 (0.4)	150[b]
Succinic acid	2.7	O3	174 (6.2)	111 (9.0)	6.4 (0.1)	4.4 (0.5)	130[b]
Succinic acid	3.1	O4	170 (5.8)	96 (10.3)	6.7 (0.5)	3.1 (0.3)	150[b]
Polymaleic acid	1.2	Q1	174 (3.9)	98 (6.5)	6.4 (0.2)	3.5 (0.5)	150
Polymaleic acid	2.1	Q2	180 (4.5)	82 (3.5)	6.0 (0.2)	2.9 (0.2)	150
Itaconic acid	1.1	Q3	177 (4.8)	95 (9.1)	6.7 (0.2)	3.3 (0.7)	150
Itaconic acid	1.9	Q4	175 (4.0)	82 (5.9)	6.1 (0.3)	3.0 (0.3)	150
References							
ACC[a]	-	M4	179 (3.8)	126 (17.6)	6.6 (0.4)	4.7 (1.0)	130[b]
ACC[a]	-	P1	173 (5.6)	106 (9.1)	6.5 (0.4)	4.2 (0.5)	150[b]
ACC	-	F,G,H,L	187 (5.4)	93 (13.6)	5.7 (0.4)	4.5 (0.9)	170

[a] Sprayed with deionized water and air-dried prior to compression, in order to be compared with the carboxylic acid sheets.

[b] This compression temperature was followed by a curing temperature of 170 ℃ for 5 min.

A3. Tensile test data: Polymers, fines and references

Table A-2. Shows the conditions and results of the tensile tests for the sheets that were physically modified by addition of different additives, together with reference sheets.

Additive	% (w/w)	Reaction time (h)	Name	Thickness mean (µm)	Ultimate Stress in Tension (MPa)	Elastic Modulus (GPa)	Strain at Break (%)	Compression temperature 15 min (℃)
Fines, starch, beta-glucan								
Fines	5	1.5	S1	183 (6.0)	115 (8.8)	6.5 (0.2)	4.6 (0.6)	170
Fines	5	3	T1	178 (3.8)	106 (11.0)	6.1 (0.2)	4.6 (0.8)	170
Fines	10	1.5	U1	180 (4.8)	115 (5.9)	6.1 (0.4)	5.3 (0.5)	170
Starch	1	1	V1	172 (7.0)	110 (12.0)	6.0 (0.4)	5.1 (0.7)	170
Starch + BTCA	1,1	0.25	V2	175 (6.8)	92 (12.2)	5.7 (0.5)	3.7 (0.6)	170
Starch	5	1	W1	178 (5.4)	134 (13.2)	6.3 (0.1)	5.4 (0.8)	170
Starch + BTCA	5,1	0.25	W2	182 (5.1)	100 (11.7)	6.0 (0.3)	3.2 (0.4)	170
Beta-glucan	3.5	4	X1	182 (3.4)	143 (19.0)	6.9 (0.4)	4.8 (0.4)	170
Fines + starch	5,1	0.25	Y1	188 (5.9)	114 (9.0)	6.2 (0.2)	4.9 (0.8)	170
Fines +starch	5,5	0.25	Z1	191 (3.4)	138 (8.2)	6.7 (0.3)	4.6 (0.6)	170
Beta-glucan	7	4	Ä1	189 (5.1)	151 (19.1)	7.0 (0.2)	5.2 (0.9)	170
Fines	5	4.5	Å1	192 (7.9)	126 (12.3)	6.6 (0.4)	5.3 (0.5)	170
References								
ACC [a]	-		M4	179 (3.8)	126 (17.6)	6.6 (0.4)	4.7 (1.0)	130[b]
ACC [a]	-		P1	173 (5.6)	106 (9.1)	6.5 (0.4)	4.2 (0.5)	150[b]
ACC	-		A	180 (7.3)	86 (10.9)	4.4 (0.4)	6.2 (1.0)	170[c]
ACC	-		L3	181 (3.3)	109 (9.7)	6.2 (0.2)	5.0 (0.7)	170
ACC	-		F14	193 (8.2)	88 (6.3)	5.6 (0.5)	4.3 (0.7)	170
ACC	-		G15	192 (7.2)	83 (14.5)	5.5 (0.2)	4.0 (1.1)	170
ACC	-		H16	183 (2.6)	94 (8.9)	5.6 (0.2)	4.9 (0.7)	170
ACC [a]	-		I2	176 (4.3)	80 (15.7)	5.5 (0.4)	3.6 (1.2)	170[b]

[a] Sprayed with deionized water and air-dried prior to compression, in order to be compared with the carboxylic acid sheets.

[b] This compression temperature was followed by a curing temperature of 170 ℃ for 5 min.

[c] Pre-pressed at 0.78 MPa in room temperature for 5 min prior hot-pressing.

B. Appendix B: Elastic and modulus data

B1. Carboxylic acids and references

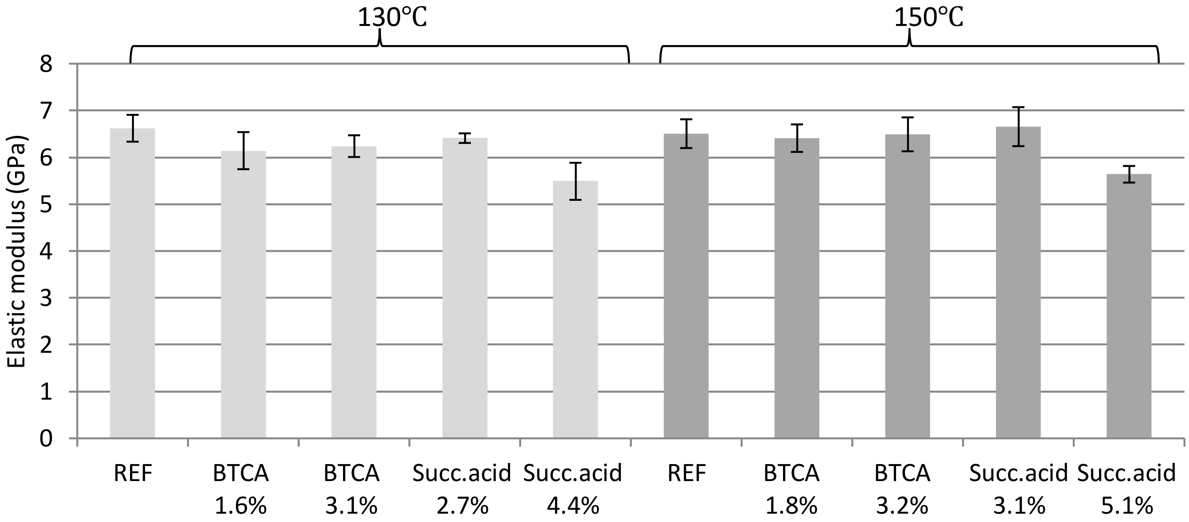

Figure B1-1. The influence of acid concentration on the elastic modulus values of test composites hot pressed at two temperature levels, 130 and 150℃ at 31.25 MPa for 15 min, compared to untreated reference samples of all-cellulose composites(n=8). The error bars are projected at a 95% CI, n=8 for all acid-treated composites.

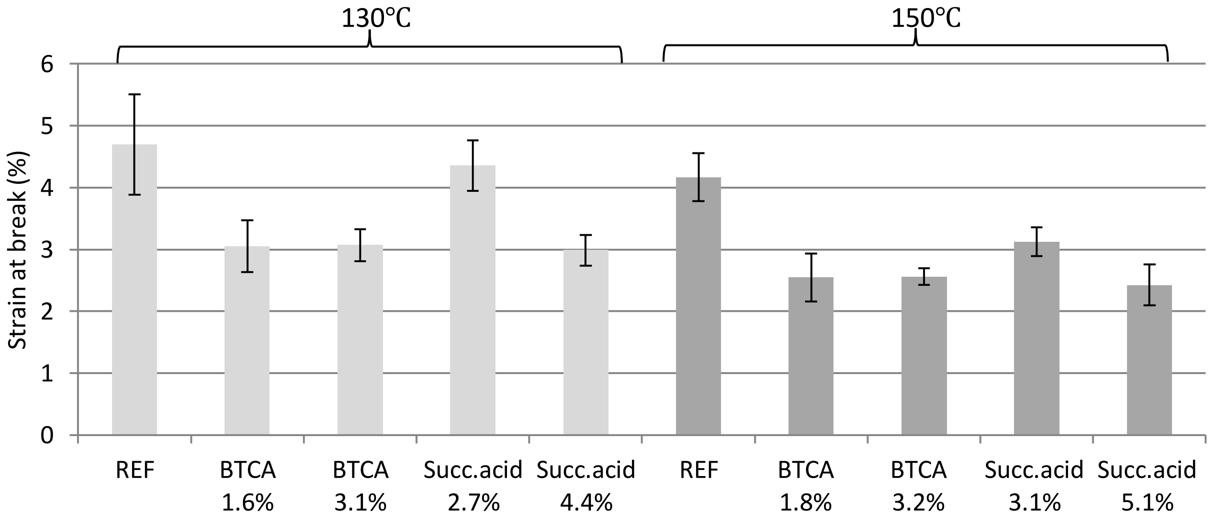

Figure B1-2. The influence of acid concentration on the elongation values of test composites hot pressed at two temperature levels, 130 and 150℃ at 31.25 MPa for 15 min, compared to untreated reference samples of all-cellulose composites(n=8). The error bars are projected at a 95% CI, n=8 for all acid-treated composites.

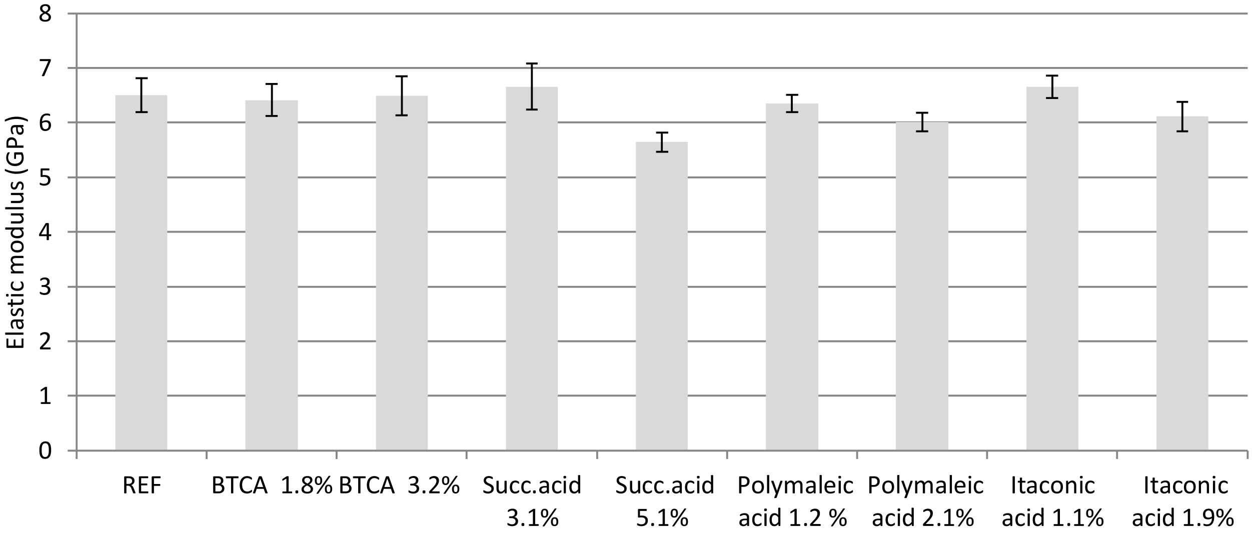

Figure B1-3. The influence of acid concentration on the elastic modulus values of test composites hot pressed at 150℃ at 31.25 MPa for 15 min, compared to untreated reference samples of all-cellulose composites(n=8) . The error bars are projected at a 95% CI, n=8, for all acid-treated composites.

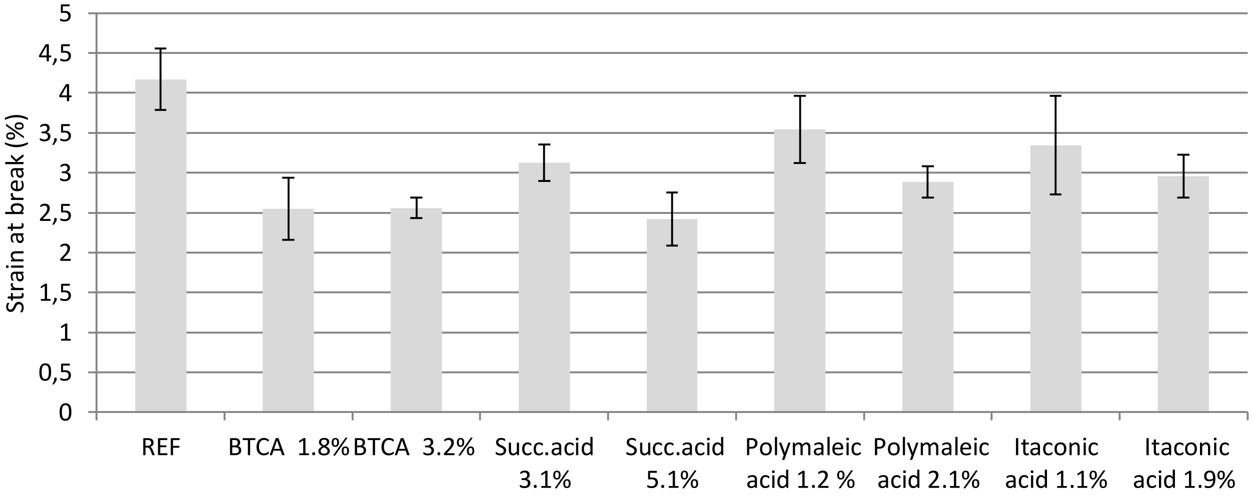

Figure B1-4. The influence of acid concentration on the elongation values of test composites hot pressed at 150℃ at 31.25 MPa for 15 min, compared to untreated reference samples of all-cellulose composites(n=8) . The error bars are projected at a 95% CI, n=8, for all acid-treated composites.

B2. Polymers, fines and references

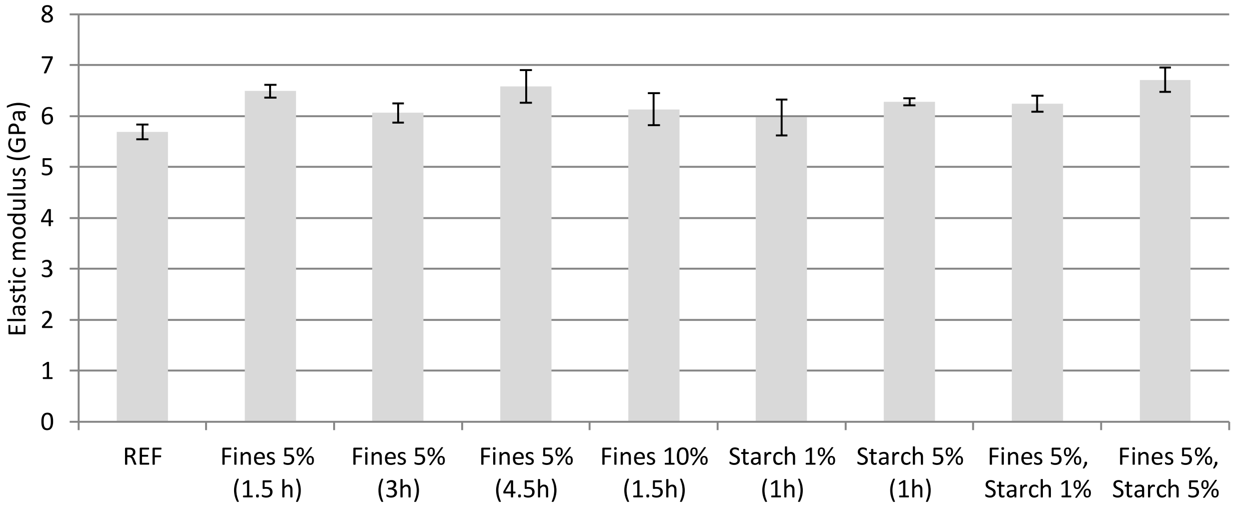

Figure B2-1. The values of modulus (GPa) obtained from the physical modification by starch and fines compression moulded at 170℃ at 31.25 MPa for 15 min, compared to untreated reference samples of all-cellulose composites(n=32) . The error bars are projected at a 95% CI, n=8, for all additive-treated composites.

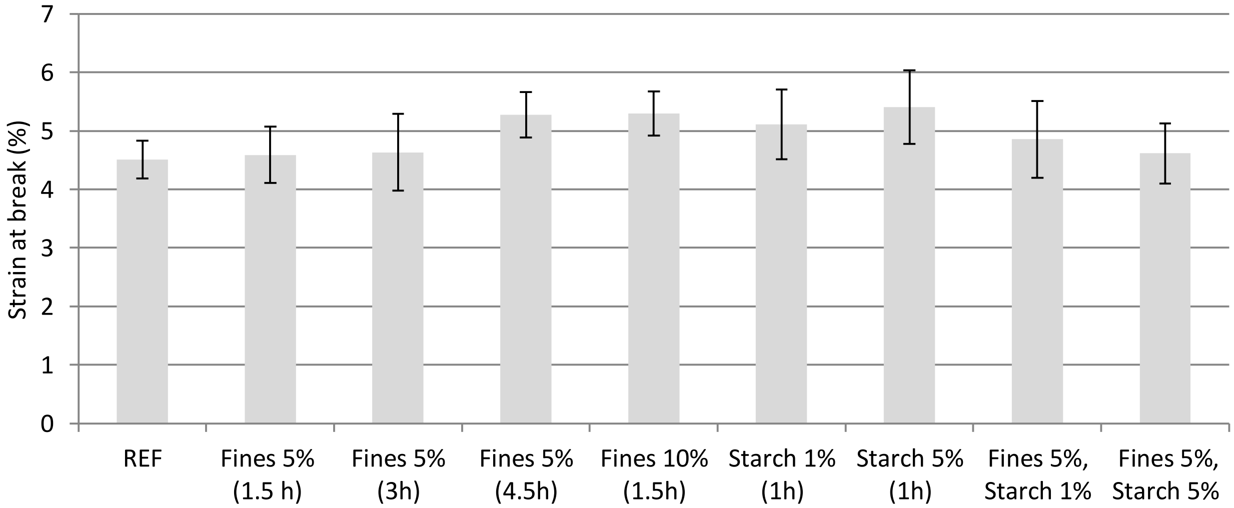

Figure B2-2. The values of elongation (%) obtained from the physical modification by starch and fines compression moulded at 170℃ at 31.25 MPa for 15 min, compared to untreated reference samples of all-cellulose composites(n=32) . The error bars are projected at a 95% CI, n=8, for all additive-treated composites.

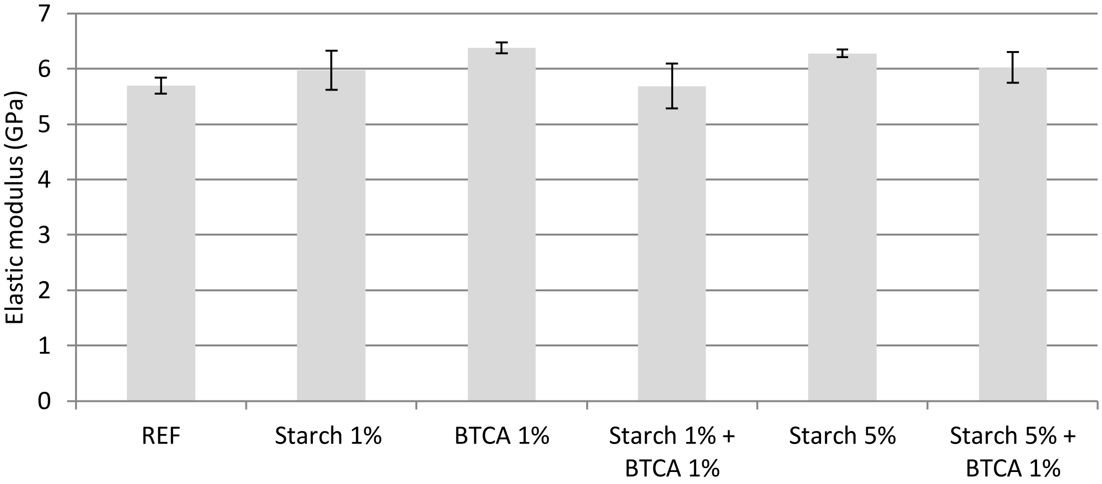

Figure B2-3. The elastic modulus (GPa) obtained from the physical modification by starch, combined with the chemical modification of BTCA, compression moulded at 170℃ at 31.25 MPa for 15 min, compared to untreated reference samples of all-cellulose composites(n=32) . The error bars are projected at a 95% CI, n=8, for all additive-treated composites.

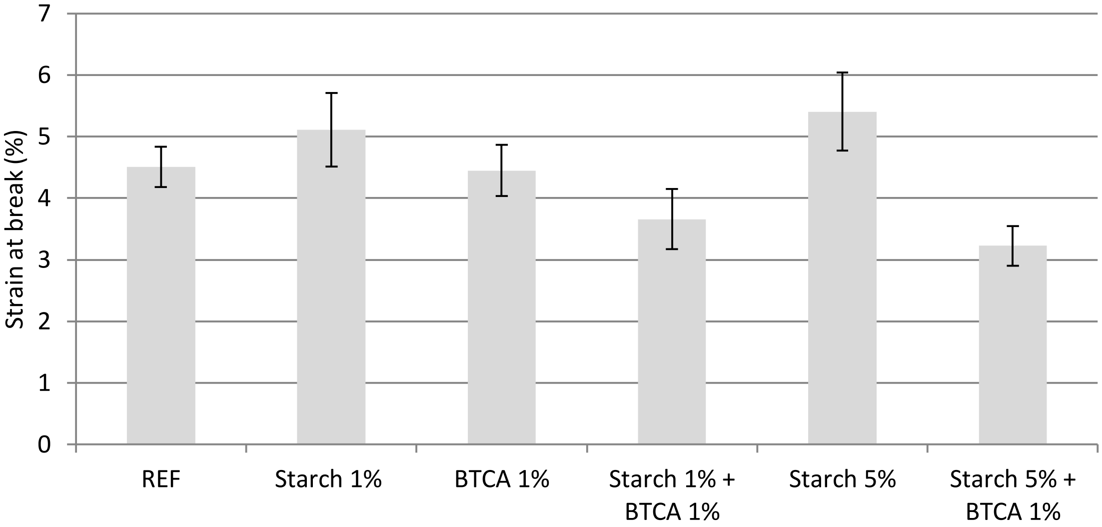

Figure B2-4. The elongation (%) obtained from the physical modification by starch, combined with the chemical modification of BTCA, compression moulded at 170℃ at 31.25 MPa for 15 min, compared to untreated reference samples of all-cellulose composites(n=32) . The error bars are projected at a 95% CI, n=8, for all additive-treated composites.