MASTER'S THESIS

Sustainable Fillers for Paper

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Giving up is the ultimate tragedy

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Acknowledgement

Abstract

Development of biodegradable fillers for paper was aimed in this master's project. Three different types of starch were acetylated to high degree of substitution according to Wurzburg. Through a two-stage method, precipitated starch acetate fillers were manufactured. These manufactured PSA fillers were further investigated through characterization techniques. Handsheets containing these organic fillers were formed. Also PCC and GCC as two conventional mineral fillers were used in sheet-forming. Physical tests on the sheets were performed to investigate their physical properties. The fully organic sheets revealed lower structural density and higher surface roughness than mineral-containing sheets. Moreover they showed optical and mechanical properties almost the same as GCC-containing sheets. Paper grades comprising these starch-based fillers can either be biodegraded or combusted as fuel.

Table of Contents

1. Introduction

Nowadays printing paper grades and cardboards contain substantial amounts of minerals either as fillers or as coating pigments. As these minerals are less expensive than fibers and also contribute to give the paper high opacity, brightness and good printability the use of mineral has continuously been increasing.

However, sustainable development of paper industry demands that the rising trend in the minerals consumption should be reversed for the following reasons.

In Europe more than 50 % of the consumed paper is recycled and about 30 % of it is sent directly to final disposal (incineration or landfill) after the primary use. Recycling paper leaves 5 to 8 wt % as inorganic de-inking sludge. [1] In the case of incineration, the ash predominantly contains oxides such as alumina, silica, iron oxide, calcium oxide, and magnesium oxide, mostly from filler material and coating pigments. [2]

To increase the sustainability of the paper and board products the inorganic material should be replaced by organic materials. Paper grades containing such filler material are biodegradable and combustible and could be used as an energy source as well. Moreover this substitution leads to lighter final products since organic additives are expected to give lower structural densities to paper products compared to mineral additives. [1]

In order to switch to biodegradable paper, according to some scientists [3] starch is one promising organic material. Starch is a granular structure of amylose and amylopectin –carbohydrate polymers of anhydroglucose monomers- usually in 20:80 to 30:70 ratios. [4] Starch already has applications in the paper industry as retention aid, to improve internal sheet strength and in surface treatment [5].

Native starch is not suitable to be used as filler without any modifications since it lacks some desirable properties such as hydrophobicity and tolerance to heating in a hydrous environment. In order to attain such characteristics, modified starch or starch derivatives are employed. [6]

This project was offered by STFI-Packforsk AB aiming to investigate the possibilities to replace conventional inorganic fillers with sustainable organic material. The main focus was intended to be starch derivatives and in particular starch acetate as filler material.

STFI-Packforsk AB is one of the world's leading R&D companies in the fields of pulp, paper, graphic media, packaging and logistics. The activities range from basic research to direct commission, where expert skills and know-how are utilized to find solutions for customers to apply in their operations. [7]

2. Literature Review

2.1 Papermaking

Paper, the very ubiquitous material, is made by draining a dilute aqueous suspension of fibers through a web to lay down a mat of randomly interwoven fibers. The formed sheet had then to be dewatered through pressing and drying (**Fig. 1**). [8]
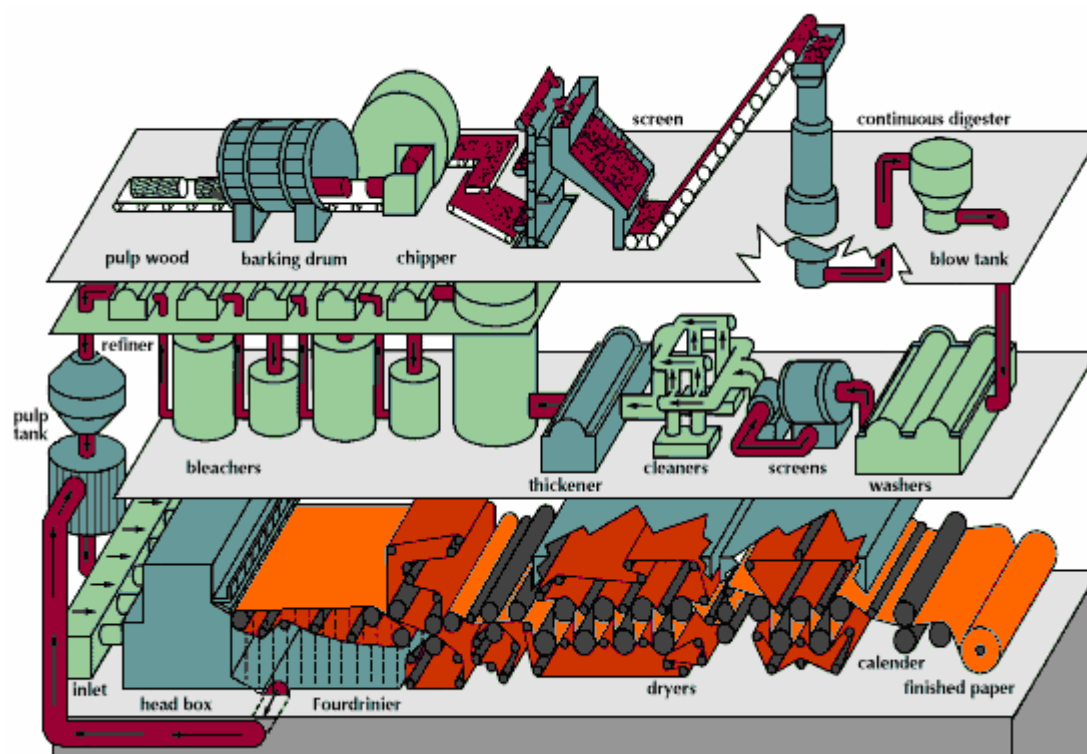
Fig. 1 Schematic diagram of a pulp and paper plant, showing the different units [9]

To further improve some desirable properties such as strength, printability, opacity and to decrease the manufacturing costs a continuous development of the process and products is undertaken.

Refining strategies and wet end chemistry strategies are intimately interconnected. Refining changes pulp properties by creating internal fibrillation, external fibrillation, fiber shortening, fiber straightening, and fine formation, which improves paper formation and other desirable properties of the final product, but at the same time decrease the dewatering capacity of the paper machine. Addition of paper chemicals can both increase the dewatering capacity as well as increase the strength properties of the paper. [10]

Almost all paper products require additives to reach desirable properties. Of course the amounts of these additives vary according to each grade and its requirements. Chemical additives can be categorized as:

- Compounds, which affect the properties of paper products, a.k.a. performance chemicals
- Compounds, which facilitate the process, a.k.a. process aids

"Performance chemicals" falls into subcategories as well. "Pigments and fillers" is one of the representatives. [10]

The main distinction between fillers and pigments is in their costs. Mineral pigments are mostly applied in writing and printing papers due to their rather high price. Fillers on the other hand are used in almost all paper grades. Not only they have substantial impact on paper quality, but also they improve the economy of the paper industry.

2.2 Conventional fillers

Fillers that are dominantly applied in the paper industry are mostly minerals. Their use saves up to 40% fiber material and enhances the economy of the paper industry in this way. In addition they improve surface smoothness and gloss of paper. Their use also leads to better printability. They increase the paper brightness and opacity. Their use facilitates drainage and drying of the formed sheets. The application of fillers also improves dimensional stability, paper's appearance, etc. However, there are disadvantages due to the use of too much filler. That is, the abrasive characteristic of mineral fillers increase wear to the wire on the paper machine and to the printing plates in the printing press, which leads to higher fine material content in the circulating water system. Moreover, the use of more filler lowers the bonding in the paper, thus increasing the dusting tendency. A final product of higher density is also a drawback.

In the following sections short introductions to conventional inorganic and organic fillers are given.

2.2.1 Inorganic fillers

The most dominant inorganic fillers used are kaolin a.k.a. clay, natural Ground Calcium Carbonate, chemically Precipitated Calcium Carbonate, and talc. Another noticeable material is titanium dioxide. Titanium dioxide is rarely applied, despite the good quality it gives due to its expensive price. The choice of material and the loading level are determined according to quality needs, logistical considerations, and cost. [11]

Clay

Kaolin clay is a naturally occurring mineral that is the most commonly used filler. The most typical kaolin is kaolinite formed from feldspar according to:

$$2KAlSi_3O_8 + 3H_2O \rightarrow Al_2((OH)_4 Si_2O_5) + 2KOH + 4SiO_2$$
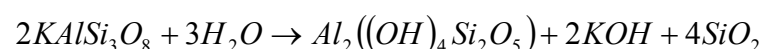
Crystals of kaolinite have the form of hexagonal plates and the chemical formula of $Al_2O_3.2SiO_2.2H_2O$. Therefore it is always found together with feldspar, quartz, and mica. [10]

Clay is mainly mined in Cornwall in England, in Georgia and South Carolina in the USA, and in Brazil. The English clay (**Fig. 2-b**) has a purity of 5-30% and is called "primary" because it is found at the site of formation. The American clay (**Fig. 2-a**) was eroded for the past millions of years and leached down its origin, the Piedmont Mountains, to the Southeast coast, where it is found today. That's why it is called "secondary" clay with purity of 95%. [10]

Generally kaolin treatment includes mechanical classification, grinding, leaching, magnetic separation, and floatation techniques. However depending on where the ore is mined the extraction process differs to some extent. [10]

Clay also can be calcined (**Fig. 2-c**) through a heating process to first lose 14% hydroxylation water at 500-700˚C. By continuing the heating particles then aggregate and agglomerate at 900-1000˚C. Eventually clay turns into a porous material with better light-scattering and opacity. [11]
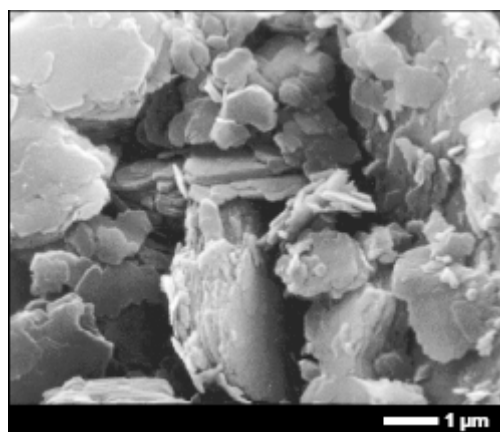
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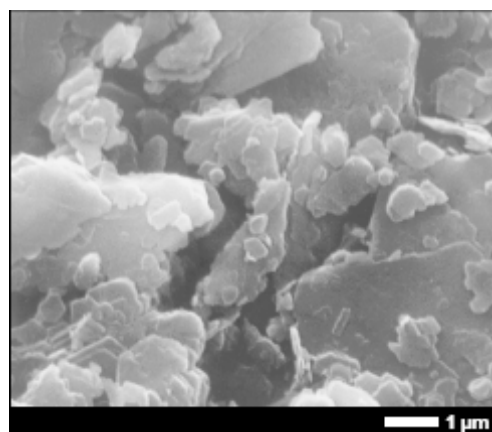
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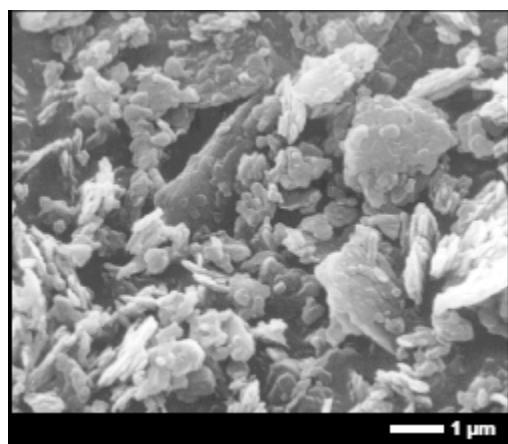
c)

Fig. 2 a: American clay, brightness 85%; **b**: European clay, brightness 80%; **c**: American calcined clay, brightness 92% [11]

Due to its plate-like structure, clay as a filler improves the smoothness, gloss and consequently, the printability of a paper. Clay improves the opacity by increasing the

light-scattering. Clay has the same refractive index as cellulose. The strength of paper is decreased by using clay, which is the case with all mineral fillers. The density of clay is higher than fiber. Sheets are more compressible at lower clay contents. Besides all the advantages and disadvantages, its low price in comparison with fiber is a good reason for its large use. [10], [11]

Talc

Talc is a natural hydrous magnesium silicate with the chemical formula of $3MgO.4SiO_4.H_2O$, which can be found almost everywhere throughout the globe (**Fig. 3**). It is very soft and low-abrasive material with plate-like particles.
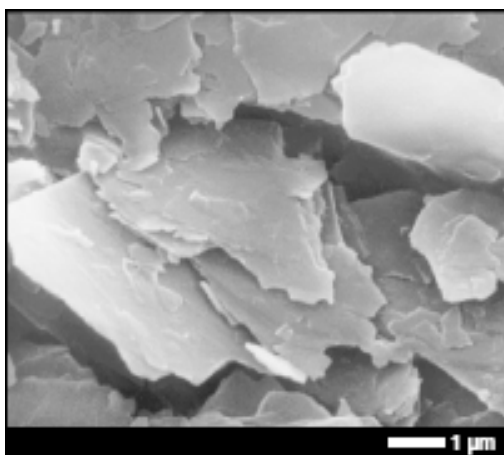

Fig. 3 European talc, brightness 84% [11]

Talc as a filler gives a good printability and brightness to paper, in addition to its positive economic impact. Also due to its oleophilic character, talc absorbs resin particles and other organic compounds and agglomeration is prevented. In this way talc keeps the wet-end system of the paper machine clean. Talc also has a good retention and softness and extends the lifetime of the wire on the paper machine. However, its higher dusting tendency during printing compared to clay has slightly reduced its application. [10], [11]

Natural Ground Calcium Carbonate

Natural calcium carbonate contributes to sedimentary rocks and constitutes about 1% of the earth crust. Chalk, the softest type, is still formed in the oceans through reactions of calcium salts with carbon dioxide (**Fig. 4-a**). It is then transformed into limestone and marble (**Fig. 4-b**) through geological modifications.
More than 50 plants around the globe supplying GCC in slurry form for the paper industry, which makes it is very dominant filler. [10], [11]
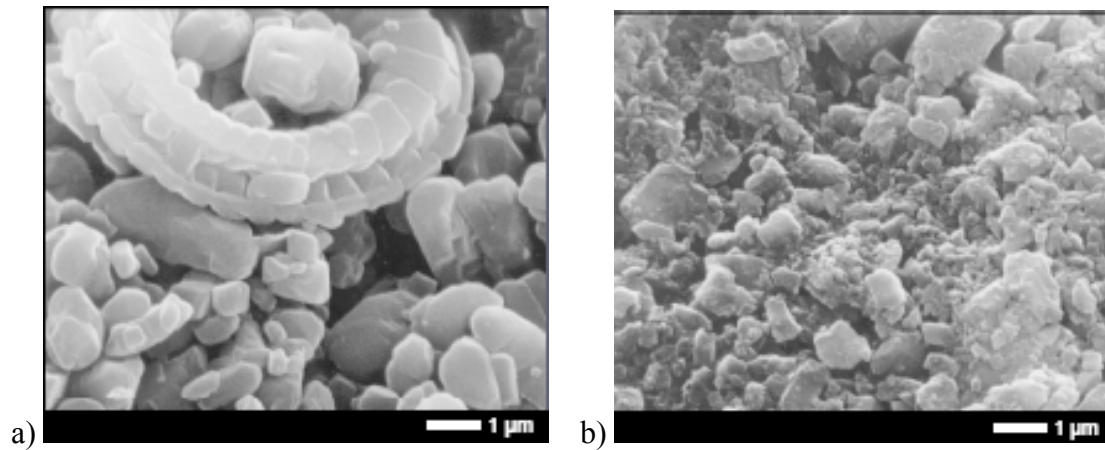
Fig. 4 a: Chalk, brightness 86% **b**: GCC (marble-based), brightness 95% [11]

Precipitated Calcium Carbonate

Limestone may be calcined at 800-900˚C to give CaO. The process is followed by the addition of water and carbonation to obtain precipitated calcium carbonate particles (**Fig. 5-a**). The process affects the particle fineness and shape. PCC producing sites are usually located on the paper mills.

The fact that $CaCO_3$ is attacked by acids pushed papermaking processes to apply these types of fillers in neutral or slightly alkaline conditions. Their high brightness (90-95%) and with price the same as for clay motivated their vast application. [11]
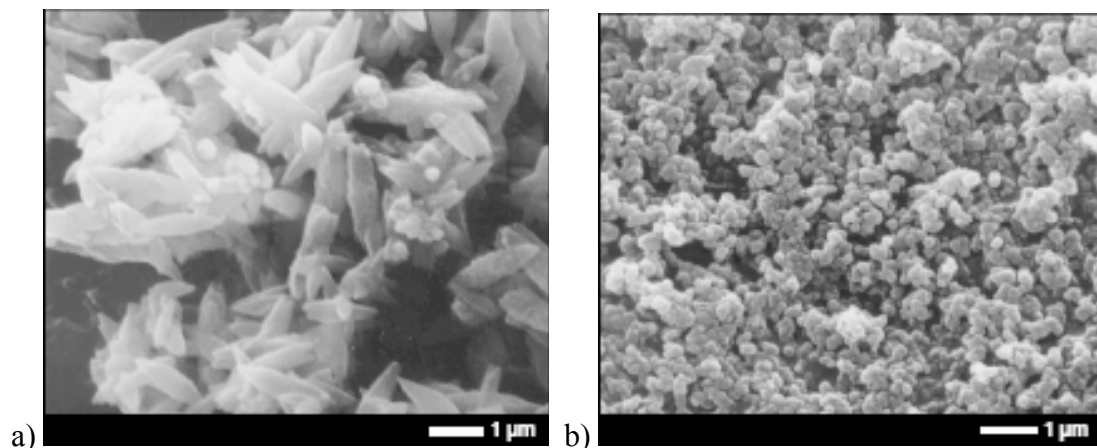
**Fig. 5 a**: PCC, brightness 95% **b**: Titanium dioxide, brightness 97% [11]

Titanium Dioxide

TiO_2 used to be consumed mostly in North America as filler (**Fig. 5-b**). Despite its considerable brightness (about 98%) and refractive index, being expensive restricted its application. [11]

2.2.2 Organic fillers

Having special applications such as in coated paper products having high gloss and brightness, fillers comprising organic polymers (plastic pigments) are in two main types, hollow micro-spheres, and porous pigments. The former is a low density material made out of vinylidene chloride/ acrylic nitrile copolymers, which gives good density properties to paper and board. Thus ultra-light papers can be produced. Porous pigments are usually made out of urea-formaldehyde resin agglomerates. They have the same brightness and opacity as for TiO_2 pigments. Definitely these organic pigments are suitable only for special applications because of their high price. [10]

2.3 Starch and starch derivatives

Starch is a granular polysaccharide of amylose and amylopectin molecules. Starch naturally occurs in seed and root crops. Amylose chains contribute to 20-50 wt % of starch grains. They are made up of up to 20,000 anhydroglucose units. Amylopectin molecules on the other hand are branched structures of anhydroglucose units. They contribute to the bulk of starch granules. [12]
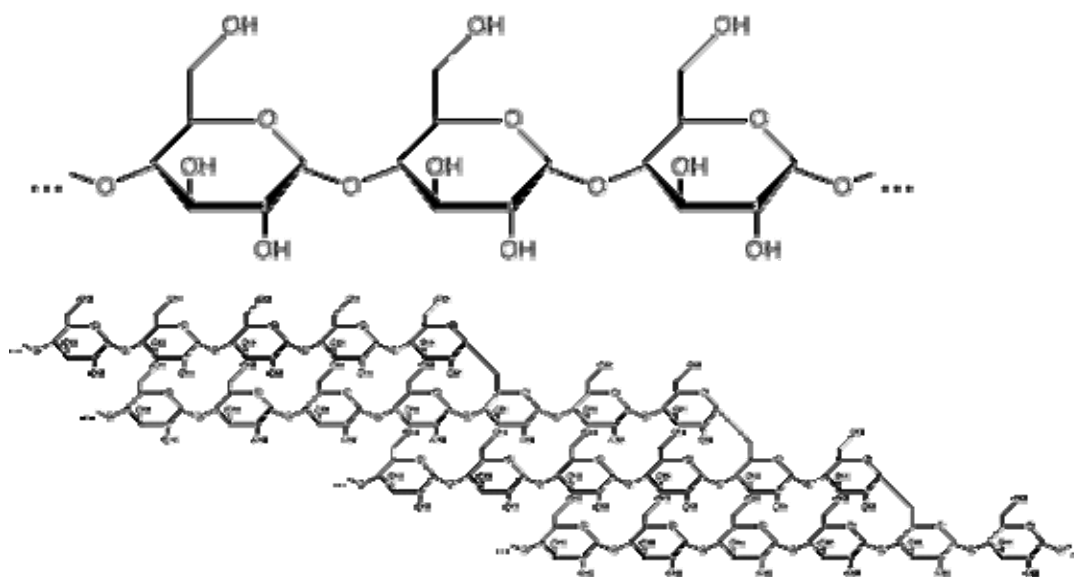
Fig. 6 Amylose (chain polymer) and amylopectin (branched polymer) [12]

There are two types of starch: native and modified. Native starch is separated from cereals and tuber vegetables and is mainly used in the food industry. Lack of some properties makes the use of native starch, say as filler material, impossible. For instance by heating native starch in water, granules hydrate, swell, and gelatinize. The viscosity of this paste is first increased by heating. After hitting a peak point it fall drastically. In addition to its poor stability, native starch has poor tolerance to acidity and low resistance to shear forces. Therefore native starch can be modified physically, chemically, and/or enzymatically to achieve materials of desirable characteristics. Some of these modifications are as follows:

7

Amylose or amylopectin molecules can be bound together (also called cross-linked) by covalent bonds. They can also be broken down to simpler molecules by heat, acids, or enzymes. [12]

There are three hydroxyl groups in each anhydroglucose unit (**Fig. 6**). Hydrogen atoms from these groups can be replaced by carboxyalkyl groups, a.k.a. etherification. Etherification makes starch more hydrophilic and less likely to be damaged by heat and microorganisms. Starch ethers are for instance applied in pharmaceutical industry. The viscosity, clarity, and whiteness of native starch can be altered through oxidization modification. Sodium hypochlorite is usually used as an oxidizing agent.

The hydroxyl groups of anhydroglucose units can be replaced in esterification reactions. Starch from a native starch source reacts with a carboxylic acid and leads to water and starch ester. Starch esters are hydrophobic and less likely to damage by heat. [12]

2.4 Starch acetate filler and its preparation

The reaction of starch (originating from any cereals or tuber vegetables) and acetic anhydride in front of a catalyst yields starch acetate.

The acetylation reaction can be carried out in the laboratory in two ways. High DS values (about 3) can be achieved through the reaction in anhydrous environment in presence of pyridine as the catalyst. Also the reaction can occur in an aqueous environment in presence of sodium hydroxide as the catalyst, which leads to low DS values at about 1 or so. [13]

The acetylation of starch can also be carried out in pilot plant under excess pressure of about 0.1-50 bar. The environment is needed to be as anhydrous as possible (10wt% water at the most) and the catalyst to this reaction can be sodium hydroxide, sodium acetate, or sulfuric acid. The inventors of this method claim that DS values up to 3 are attainable through this procedure. [14]

The starch acetate produced from either of the above methods is a white biodegradable polymer with a T_g value normally in the range of 150-170˚C. [1], [3]

The precipitation procedure starts by dissolution of the synthesized starch acetate in a volatile solvent such as acetone. It is desired to use the least possible amount of solvent in order to have a fast and convenient separation later. By adding a non-solvent phase such as water into the solution, starch acetate particles are precipitated. The solvent then has to be evaporated by fast heating. Otherwise the residual acetone in the solution dissolves the surface of the particles and reduces their porosity and eventually reduces the light-scattering property of the material. The newly formed starch acetate particles are coral-shaped with nano-porous structures in the range of 1-100 μm in diameter. However, the size distribution can be regulated by treating the suspension with mechanical or ultrasound energy. [3]

It is obvious that the nano-porous structure of the manufactured material improves its light-scattering. Therefore as filler it could improve the optical properties of paper.

Another advantage with these starch-based micro-particles is that they are capable of forming hydrogen bonds to fibers contrary to mineral fillers. In mineral fillers, the size, structure, and addition level of mineral fillers are quite influential on mechanical and optical properties of paper. The optimum particle size for mineral fillers falls between 1 to 10 μm depending on the filler type. However the starch-based material with several times larger particles may be used as filler without weakening the

mechanical properties of paper. It has also been observed that the mechanical properties of paper are not weakened by increasing the amount of the starch-based filler. [3], [15]

It is good to notice that the manufactured organic material is hydrophobe. Therefore it can reduce water absorption and increase dimensional stability of paper when used as filler. [16]

2.5 Retention of filler

Considering the size of filler particles and fibers, the mechanical entrapment of fillers in the paper web is quite poor. Poor retention means inefficient use of fillers and pigments and high concentrations of them in the white water. In order to efficiently retain fillers in the fiber network retention aids are used. Retention aids are chemical additives letting tiny particles aggregate through electrostatic forces and form lager units (a.k.a. flocculation), which are then bound to the fibers. There are different aggregation mechanisms. Retention aids fall into the following categories:

- Condensation products: polymers of low molecular weights and high charge densities
- Chain reaction polymers: polymers of high molecular weights and low degrees of substitution
- Neutral product derivatives: cationic, anionic, and amphoteric derivatives of for instance starch or galactomannan

Each of the above categories in turn comprises more subcategories. Cationic Polyacrylamide (C-PAM) is the dominant polymer in retention aid systems. Such systems take advantage of "bridging flocculation" mechanism. These polymers have molecular weight of 4-16 million Da. A charge density in such systems is between -4 to +3.4 meq/g. Further elaboration in this respect is far beyond the limits of this work. Furthermore, in order to have a good retention, high solid content suspensions, high sheet grammage, and high degree of beating also improve the filler retention. [10], [15]

2.6 The area's research leader

VTT technical research center of Finland is perhaps the pioneer in the field of starch-based material development. VTT's research activities are mainly on starch-based, bioplastics, dispersion products, adhesives, pigments and fillers, and materials for surface treatment of paper products.

VTT's publications about innovation and development of starch-based pigments and fillers were of our great interest. Moreover, a visit of their research center in Otaniemi and their pilot plants in Rajamäki was quite informative.

They produce starch esters and modified (transglycosylated) starch esters from different starch resources. In addition, they apply these materials to manufacture spherical nano-particles and coral-shaped micro-particles as pigments and fillers.

3. Materials and Methods

This part of the report describes materials used, experimental procedures, and performed analyses. In **Figure 7** the design of the experimental work is presented.
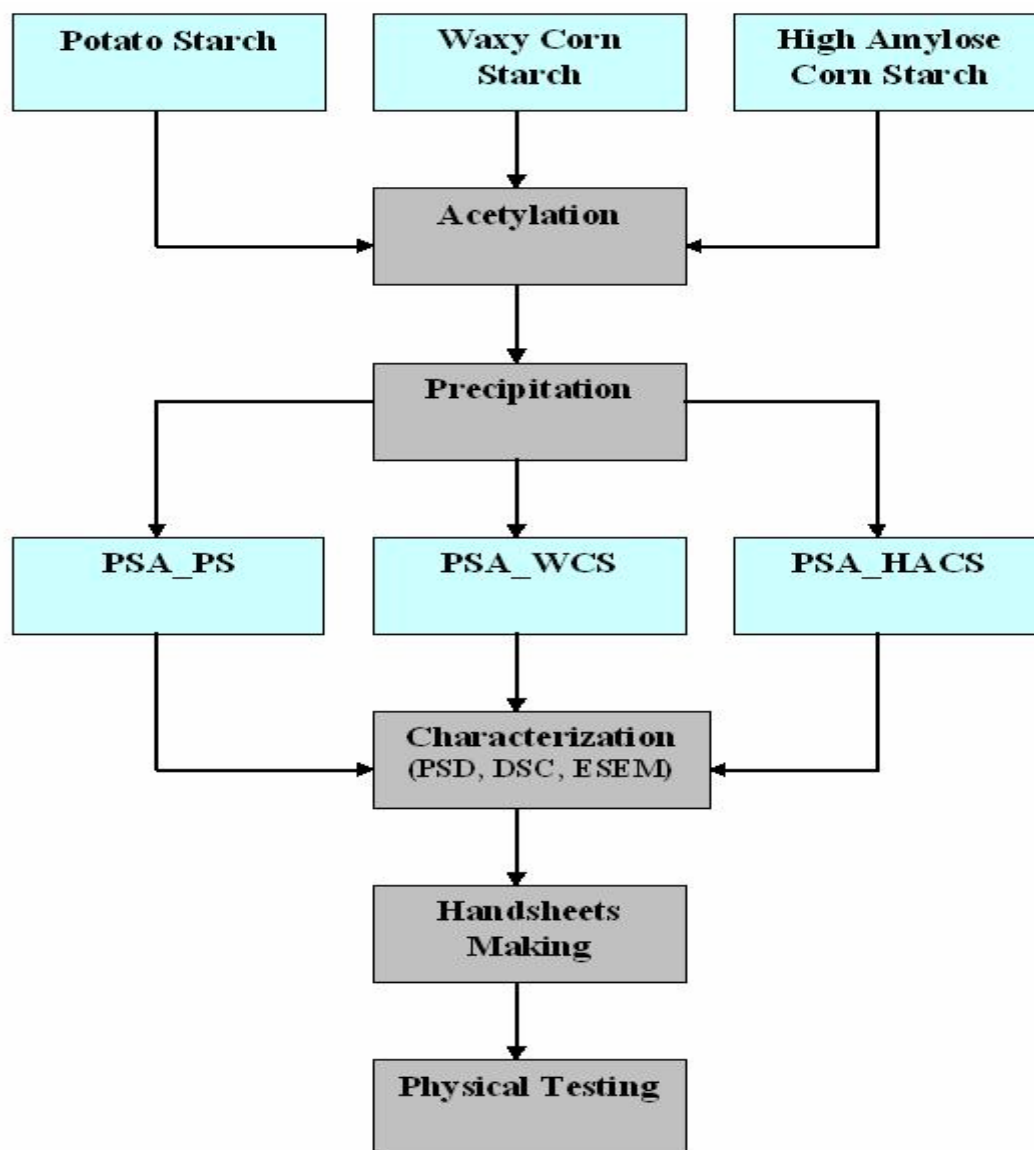
Fig. 7 The box diagram of the experimental steps

3.1 Acetylation

Acetylation of starch is generally formulated as follows:

$$(C_6H_7O_2)_x(OH)_{3x} + aAc_2O \xrightarrow{(NaOH+H_2O)or(pyridine)} (C_6H_7O_2)_x(OH)_{3x-a}(OAc)_a + aHOAc$$
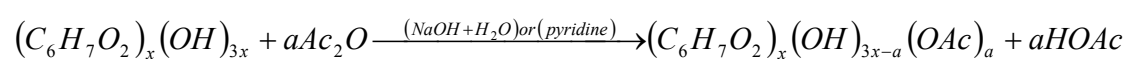
In this work laboratory-scaled starch acetates of high degrees of substitution were produced. The acetylation medium was anhydrous and pyridine was applied as the catalyst. The procedure was based on Wurzburg's recipe. [13]

Three different types of starch listed below, underwent the process.

- **Defatted (below 0.5 g in 100 g) potato starch (PS):** This type contains normally 30% amylose and 70% amylopectin

- **Waxy corn (maize) starch (WCS):** This contains 100% amylopectin supplied by SIGMA-ALDRICH

- **High amylose corn starch (HACS), a.k.a. Hylon VII:** This contains 70% amylose and 30 % amylopectin supplied by SIGMA-ALDRICH

Among the starch types, potato starch needed to be pretreated. By neglecting pretreatment of potato starch the reaction did not proceed at all even after 24 hr and starch granules remained unchanged (**Fig. 17**). In the pretreatment process 35 g starch was added to 700 ml of distilled water and mixed. The mixture was heated for one hour at 95-100˚C with constant stirring. Then the dispersion was agitated in a Waring Blendor at high speed for 20 min. When the ruptured dispersion reached a temperature of about 35˚C it was poured into a battery jar containing four liters of absolute ethanol (600 ml ethanol for every 100 ml of dispersion). Absolute ethanol washed the precipitating starch while a vigorous agitation by a large magnet stirrer. Separation of starch particles from the liquid phase was done by centrifuging the slurry at 10000 rpm for 20 min. The paste was then reslurried in 300 ml absolute ethanol, agitated, and centrifuged 2 more times. The treated starch was then left to be air-dried and even more dried under vacuum afterwards.

After this pretreatment, the acetylation procedure is the same for all the three types of starch. Each batch required 20 g (dry basis) starch. The reactor was a 500-ml three-necked round-bottomed flask, one neck of which was fitted to a stirrer, the second one to a reflux condenser, and the third neck to a stopper. Also the other side of the reflux condenser was sealed with a drying material. 160 ml pyridine and 65 ml acetic anhydride were added to the starch in the flask while stirring. The system was heated by an oil bath at 100˚C for 4 hr. **Figure 8** shows the acetylation construction.

When the time was up and the reactor had cooled down to room temperature, the jelly like content was transferred into another container. One liter absolute ethanol was added and the mixture was agitated. Absolute ethanol precipitated the starch acetate and washed undesired material away from the solid particles. The starch acetate was then filtered by a Büchner funnel on Whatman No. 4. Then the filter cake was reslurried in 150 ml absolute ethanol, mixed, and filtered out two more times to be washed up. The starch acetate was finally dried under vacuum.

According to Wurzburg this method of acetylation leads to triacetate. [13]. The DS was not determined, but there are techniques such as NMR to measure DS.

Fig. 8 The batch construction applied for the synthesis of starch acetate in laboratory

3.2 Precipitation of starch acetate

The procedure which is described in this section relates to preparation of nano-porous, coral-like fillers out of the synthesized starch acetates. A two-stage method was applied. That was, first dissolution of starch acetate in an organic solvent such as acetone, and then precipitation of the dissolved starch acetate by adding a non-solvent phase (hereafter only water). The process continued by removing the solvent from the suspension by evaporation. The removal of the solvent was performed to almost 100%. If residual acetone is present in the solution it dissolves the surface of the particles and reduces their porosity and eventually reduces the light-scattering property of the material.

Through each run in the laboratory 3 g starch acetate was dissolved in 75 ml acetone. By stirring the mixture at the room temperature a homogeneous paste was formed. Then 200 ml distilled water was instantaneously poured into the solution while strong agitation of the whole mixture. A milk-like suspension of precipitated starch acetate was thus formed. The suspension was then heated up to the boiling point of acetone, about 60˚C. The heating was kept until the temperature started to rise again and the volume of the suspension reached 200 ml. The acetone-free suspension was then left to be cooled down to room temperature. The particle size distribution can be controlled by applying mechanical or ultrasonic energies into an aqueous suspension of particles. In this work a high performance homogenizer (MICCRA D-8) was used to bring mechanical force into the suspension to break down coarser particles. The rotor of the homogenizer was working at 19,000 min^{-1} for 5 min per batch. In larger scales however it is more efficient to separate the particles from the slurry and dry and mill them to attain desired particle size distributions.

3.3 Material characterization

In order to study some characteristics of the manufactured materials the techniques that were applied are introduced under this section.

3.3.1 Particle size measurement

Particle size measurement was here based on laser diffraction technique. In this technique an emitted laser beam is diffracted by dispersed particles in a suspension and haloes of the diffracted rays are analyzed. The laser diffraction is particularly precise when particles are below 1 μm in diameter. [17]
The apparatus to measure PSD in this work was MasterSizer MS20 by MALVERN INSTRUMENTS.

3.3.2 Glass transition measurement

One of the best techniques to study the thermal transition of different materials particularly polymers is differential scanning calorimetry. In DSC two crucibles are placed in the apparatus chamber, one is occupied by a sample and the other one is left empty (the reference crucible). During a heating program the difference between the absorbed heats by the crucibles is measured and the sample's heat flow is plotted against temperature.
Q1000 DSC made by TA Instruments was used in this work. The heating range was from 50˚C to 350˚C with temperature increase rate of 30˚C/min. However in the case of starch acetate from waxy corn starch (SA_WCS) heating was performed up to 260˚C. The glass transition points of the manufactured materials were figured out by using the DSC plots.

3.3.3 Electron microscopy

Environmental scanning electron microscopy (Philips XL30) was applied to capture images of the manufactured materials. ESEM has a vast application in material characterization. It has overcome some of the limitations incorporated with SEM such as "no wet sample allowed in the SEM chamber" by using a differential pumping system.
Basically a beam of electron is emitted to a sample placed in the apparatus chamber. The sample's response to that emission in forms of secondary electrons, backscattered electrons, X-rays or whatsoever can be detected through different detectors depending on what is desired by the microscopist.
Thus an expert microscopist at STFI took over preparing the samples (by mounting them on ESEM sample holders and covering them by a thin layer of gold) and microscopy.

3.4 Sheet-forming

In this section the procedure to form handsheets is explained. The manufactured organic materials were used in handsheets as filler. Also conventional natural Ground Calcium Carbonate and Precipitated Calcium Carbonate fillers were used as reference fillers.

An aqueous suspension of fibers was prepared. The used pulp was a mixture of bleached, refined, 40wt % softwood (SR 28) and 60wt % bleached hardwood (birch) (SR 36) fibers. Handsheets with the area of 16.5×16.5 cm^2 and the grammage of 80 g/m^2 were to be produced. It was calculated that for a sheet containing 20wt % filler a total amount of 2.2 g fiber and filler was required. In other word 0.44 g filler and 1.76 g fiber were to be used for each handsheet.

A 12-liter aqueous suspension of the pulp with the dry content of 4.39 g/l was formed. Then 2 samples of 250 ml from the aqueous suspension were filtered through 2 dried filter papers. The filter papers containing the solid contents of the samples were left for 1 hr at 105˚C to be dried. Then they were weighed again and by knowing the initial weights of the dried filter papers, the solid contents of the samples were figured out. Their average gave the solid content of the mixture of pulp and water. As 1.76 g pulp per sheet was required, 400 ml of the pulp and water mixture was being used by the sheet-forming apparatus per handsheet. In addition an amount of filler slurry, containing 0.44 g filler was being added per handsheet. The whole mixture was being mixed by the automatic vertical mixer of the apparatus. After one minute an amount of C-PAM solution containing 1.081 meq/g was being added to the mixture as retention aid. The flocculating agents were cationic high-molecular-weight polyacrylamide polymers supplied by Allied Colloids under the trade mark **Percol 292**. The vertical mixer was being used again to homogenize the whole mixture. By pushing the drainage handle of the apparatus, a wet sheet was being laid down on the sheet-forming screen. In the end coded sheets were collected on top of each other one side of which stuck to a dewatering paper and the other side touching a wooden board. They were taken to "sheet press" to be pressed according to ISO 5269-1:2005 at 3.65 bar for 5.5 min and 2 min consecutively. Finally sheets were positioned separately all on top of each other isolated by special frames to be dried in a room at 50% humidity for 24 hr.

3.5 Physical tests

Physical testing of paper products are aimed to measure their physical properties. In this section those physical tests which are performed in this work are briefly introduced.

The **structural density (SCAN-P 88:01)** for a sheet of paper in kg/m^3 is the ratio of the **grammage (ISO 536:1995)** (g/m^2) to the **structural thickness** (μm) of the sheet.

Roughness PPS 1.0 (ISO 8791:2007) determines the roughness of sheet's surface in μm. In this test the values between 0.6 and 6 μm are numerically applicable. Generally a lower roughness value means a higher smoothness of the sample's surface.

"**Light-scattering coefficient (ISO 9416:1998)** is the fraction of light incident upon an infinitesimally thin layer of the material that is scattered backwards by that layer,

divided by the (infinitesimal) grammage of the layer" with the unit of m^2/kg. [18] A higher light-scattering coefficient means higher brightness for the sample.

The **Opacity (ISO 2471:1998)** of paper is a property that reveals the see-through of paper. The printing on one side of a paper with a higher opacity is less likely to be seen from the other side. Opacity test measures the ratio of the scattered or absorbed light to the radiated light in percentage.

The required force to break a strip of a paper is called **tensile strength (ISO 1924-3:2005)** (kN/m). The tensile strength divided by the grammage gives the **tensile index** in Nm/g. [19]

Strain at break (ISO 1924-3:2005), a.k.a. elongation at break, is the extension at break of a strip as a percentage of the free spam between the clamps of the extensometer. [19]

Tensile energy absorption (TEA) (ISO 1924-3:2005) in J/m^2 is the amount of work done to break a strip of a paper. TEA divided by the grammage is **TEA index** (J/kg). [19]

Tensile stiffness (ISO 1924-3:2005) is the required force at break times the free span between the clamps of the extensometer, divided by the extension at break times the strip's width, as it can be seen in the following formula.

$$TS = \frac{\Delta F . l_0}{b . \Delta l}$$

TS in (kN/m) divided by the grammage gives the **tensile stiffness index** (kNm/g). [19]

Formation analysis is done according to beta radiography technique based on STFI method, where a C-14 beta radiation source is used to emit through a sample sheet and transmitted radiations are recorded on an X-ray film. The radiograph is analyzed in a scanner using 300 dots per inch resolution and gray-scale values can be transformed to basis weight values by using a calibration scale. The formation analysis is performed by the machine's software to end up to formation spectra and formation numbers. Formation numbers are for small-scale formation in wavelength interval of 0.3-3 mm, for large-scale formation in wavelength interval of 3-30 mm, and for the combined scale in wavelength intervals of 0.3-3 mm, where wavelength corresponds to double floc size. [20]

4. Results and Discussion

The experiments and measurements can be categorized into two main groups. Material characterization is one of them, which is related to the characterization of the manufactured filler material. The other one, physical testing is related to the tests on the formed lab-sheets containing the fillers.

4.1 Material characterization

Here below are sections to present and discuss particle size distribution, glass transition temperature, and electron microscopy of the manufactured organic fillers and reference mineral fillers.

4.1.1 Particle size measurement

There is always an optimum size for filler particles. For mineral fillers this value usually lies below 10 µm.
Figures 9 and **10** show the particle size distribution of precipitated calcium carbonate and ground calcium carbonate fillers used as reference mineral fillers. The figures reveal that the particles' diameters are mainly below 10 µm.
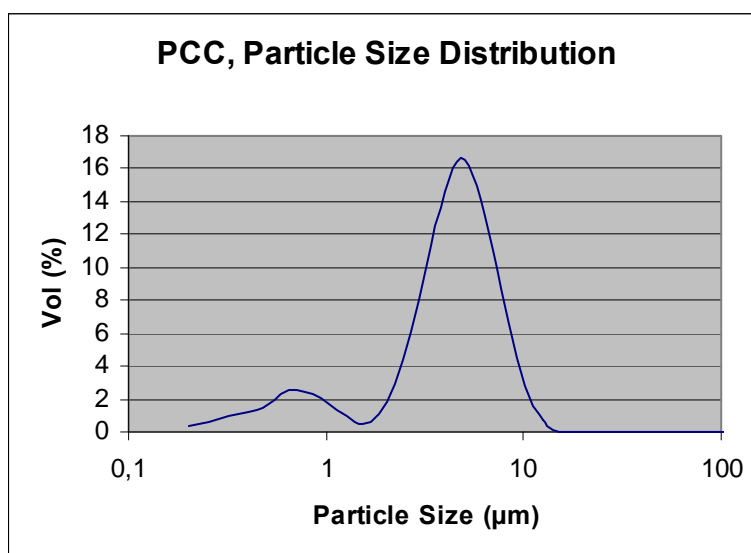
Fig. 9 Precipitated calcium carbonate particle size distribution
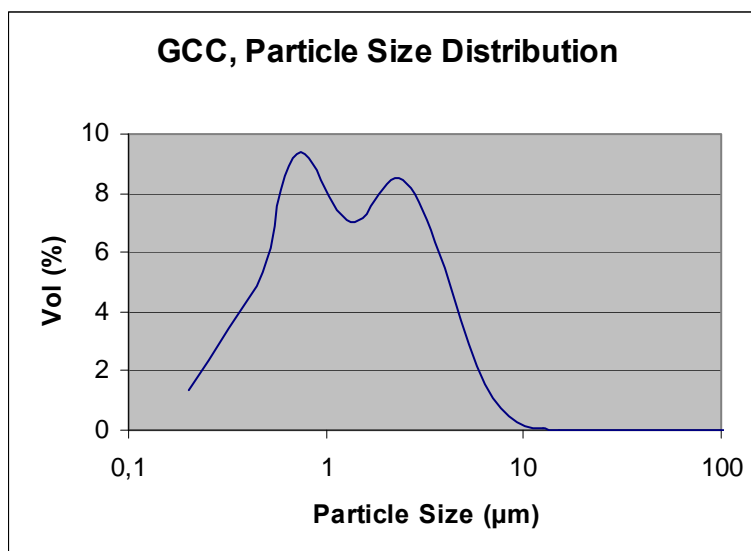
Fig. 10 Ground calcium carbonate particle size distribution

The particle size distribution of precipitated starch acetate fillers from potato starch, waxy corn starch, and high amylose corn starch are shown in **Figures 11**, **12**, and **13** respectively. Their particles were mainly between 10 to 100 μm in diameter, which is a bit too large compared to the optimum particle size which is normally below 10 μm. However, there are homogenizers available to further fine and homogenize the particles.
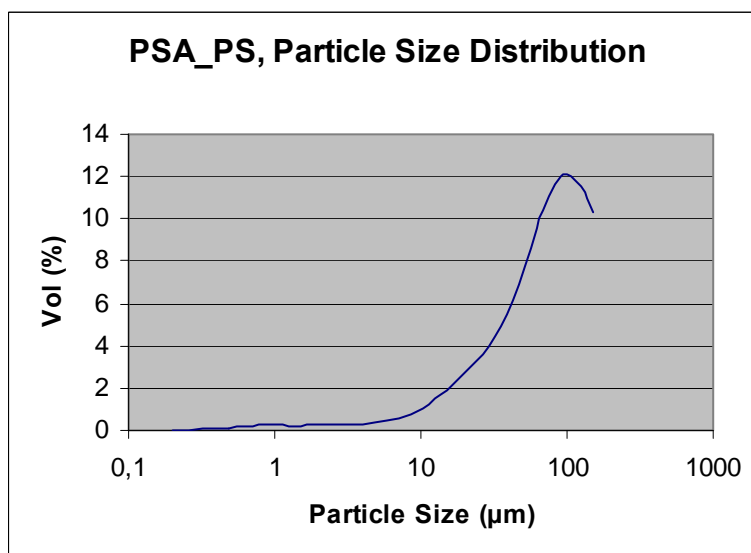
Fig. 11 Particle size distribution of precipitated starch acetate from potato starch
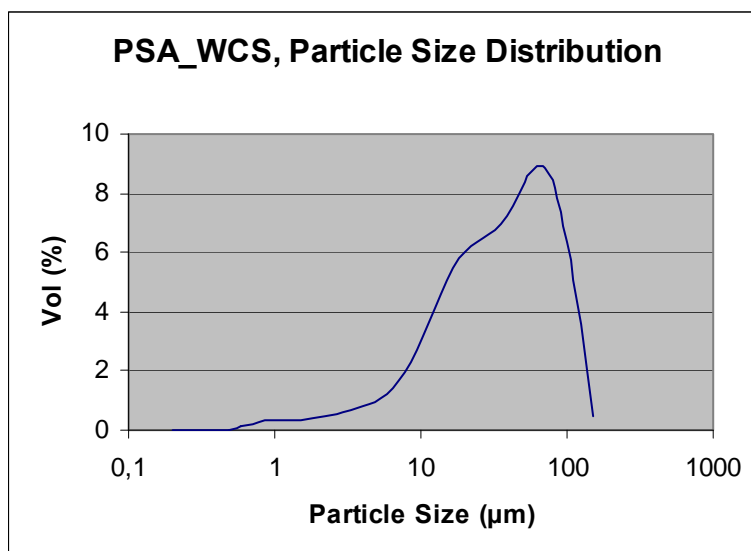
Fig. 12 Particle size distribution of precipitated starch acetate from waxy corn starch
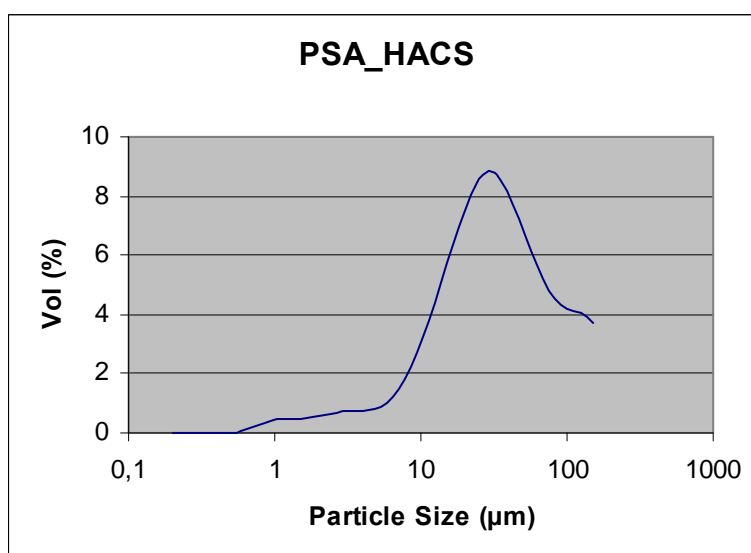
Fig. 13 Particle size distribution of precipitated starch acetate from high amylose corn starch

4.1.2 Differential Scanning Calorimetry

In order to make sure that the manufactured starch-based fillers withstand the occurring temperatures on the paper machine their glass transition temperatures were measured. These glass transition points are shown in the figures below. According to the **Figure 14** the T_g was calculated 161.28 ˚C for the synthesized starch acetate based on potato starch.

Sample: SA_PS
Size: 4.7250 mg

DSC

File: C:\TA\Data\DSC\amin\SA_B2_080519_Try1
Operator: Amin
Run Date: 19-May-2008 12:51
Instrument: DSC Q1000 V9.8 Build 296
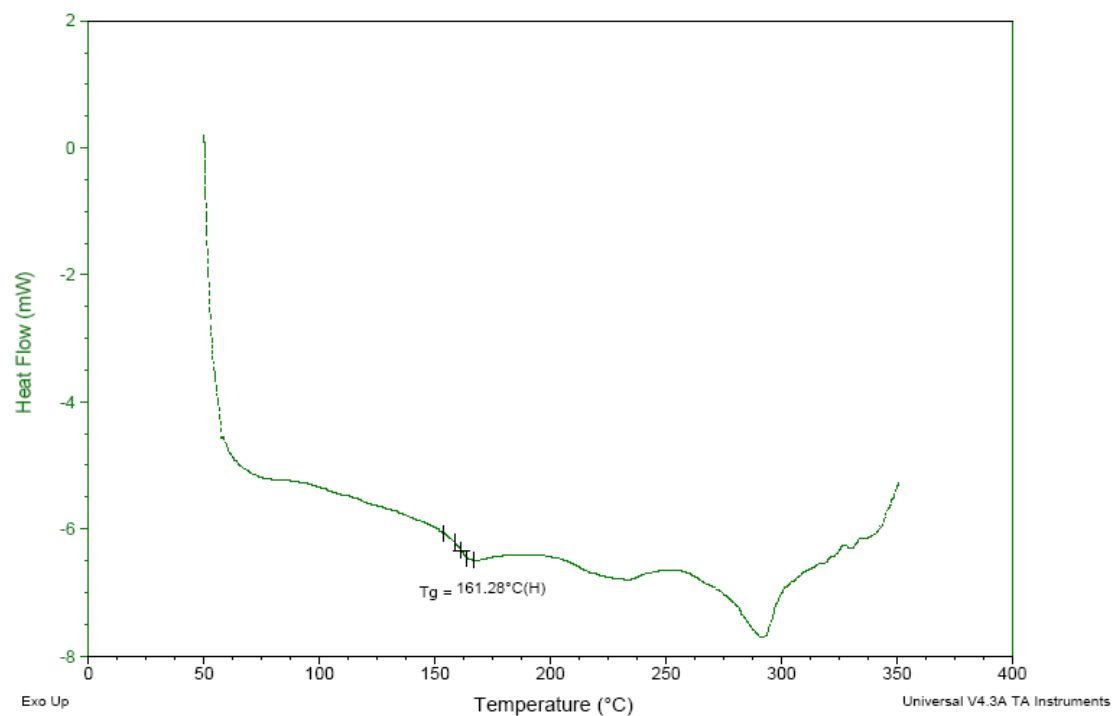
Fig. 14 The DSC pattern shows the heat flow (mW) vs. Temperature (˚C) for starch acetate from potato starch

Sample: SA_WCS
Size: 3.4030 mg

DSC

File: C:\TA\Data\DSC\amin\SA_B4_080519_Try1
Operator: Amin
Run Date: 19-May-2008 14:09
Instrument: DSC Q1000 V9.8 Build 296
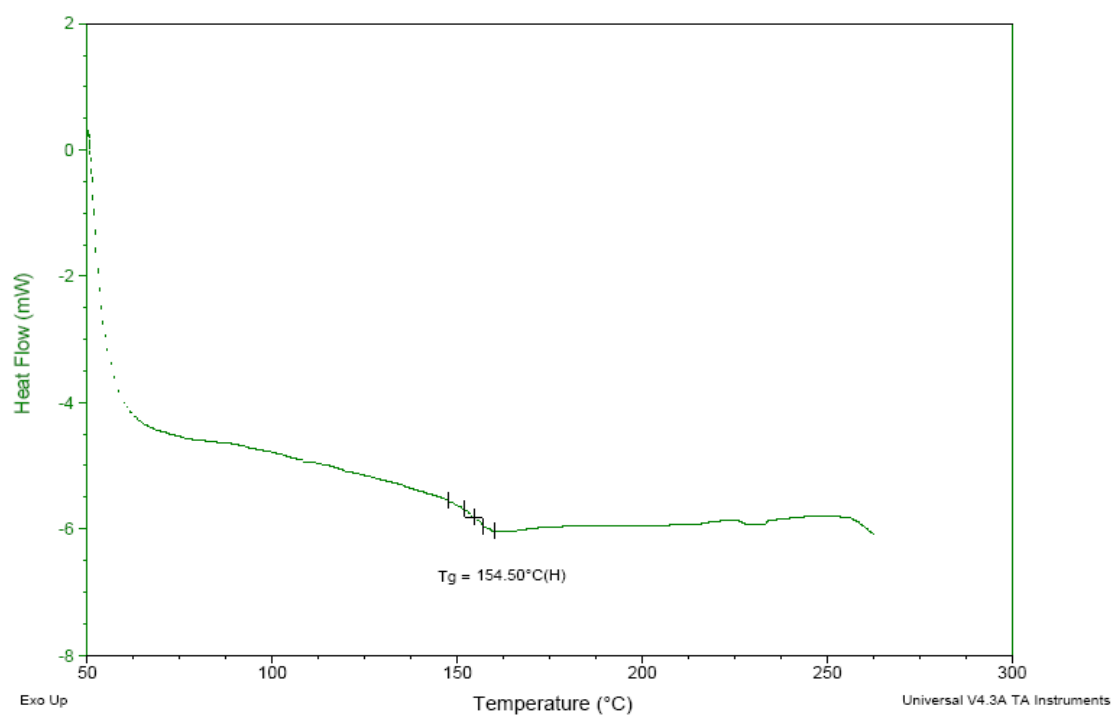
Fig. 15 The DSC pattern shows the heat flow (mW) vs. Temperature (˚C) for starch acetate from waxy corn starch

According to the **Figure 15** the T_g was calculated 154.5 ˚C for the synthesized starch acetate based on waxy corn starch. In the same way in the **Figure 16** the T_g was calculated 167.43 ˚C for the synthesized starch acetate based on high amylose corn starch.
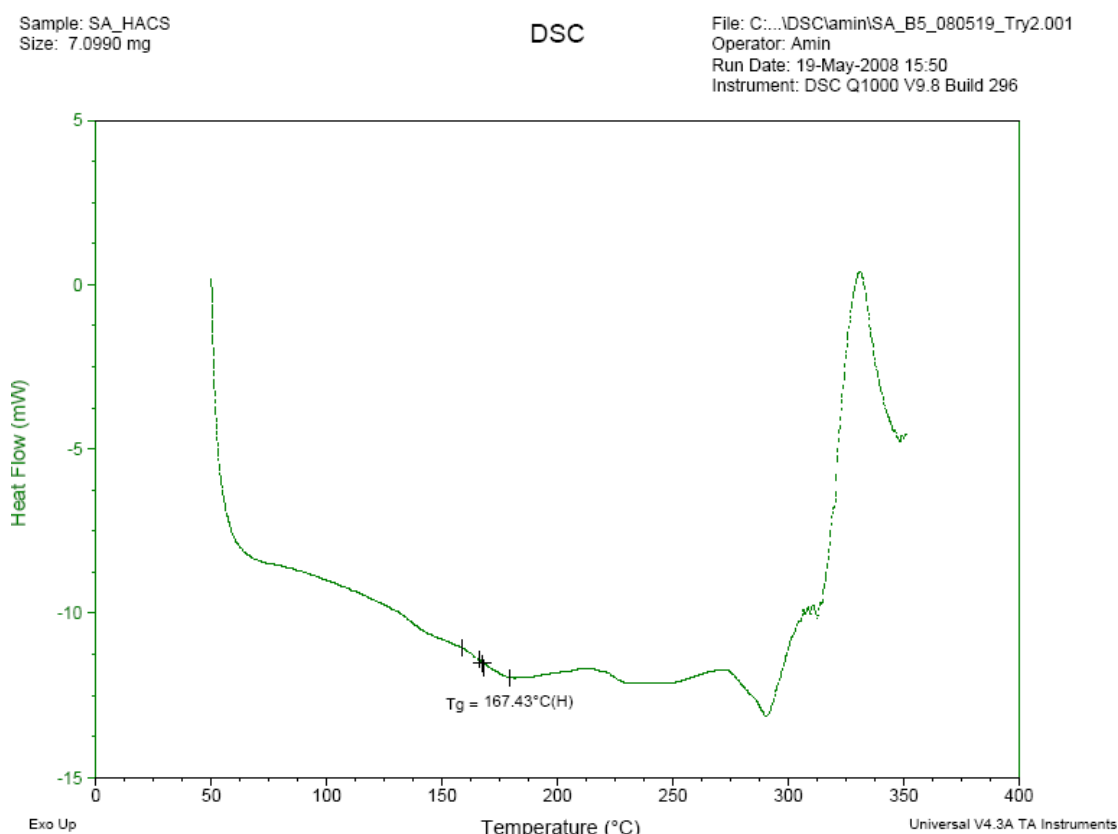
Fig. 16 The DSC pattern shows the heat flow (mW) vs. Temperature (˚C) for starch acetate from high amylose corn starch

The measured T_g values show that acetylation of the three investigated types of starch resulted in the starch acetates, which can tolerate the thermal conditions in the process of papermaking. The acetylation of the starch increased the T_g from below 100˚C depending on the starch source and its moisture content to above 150˚C.

4.1.3 Environmental Scanning Electron Microscopy

In this section before we get to ESEM images of the synthesized starch acetates and the manufactured organic fillers, we tend to show an image concerning our discussion about the importance of the pretreatment step in section 3.1.
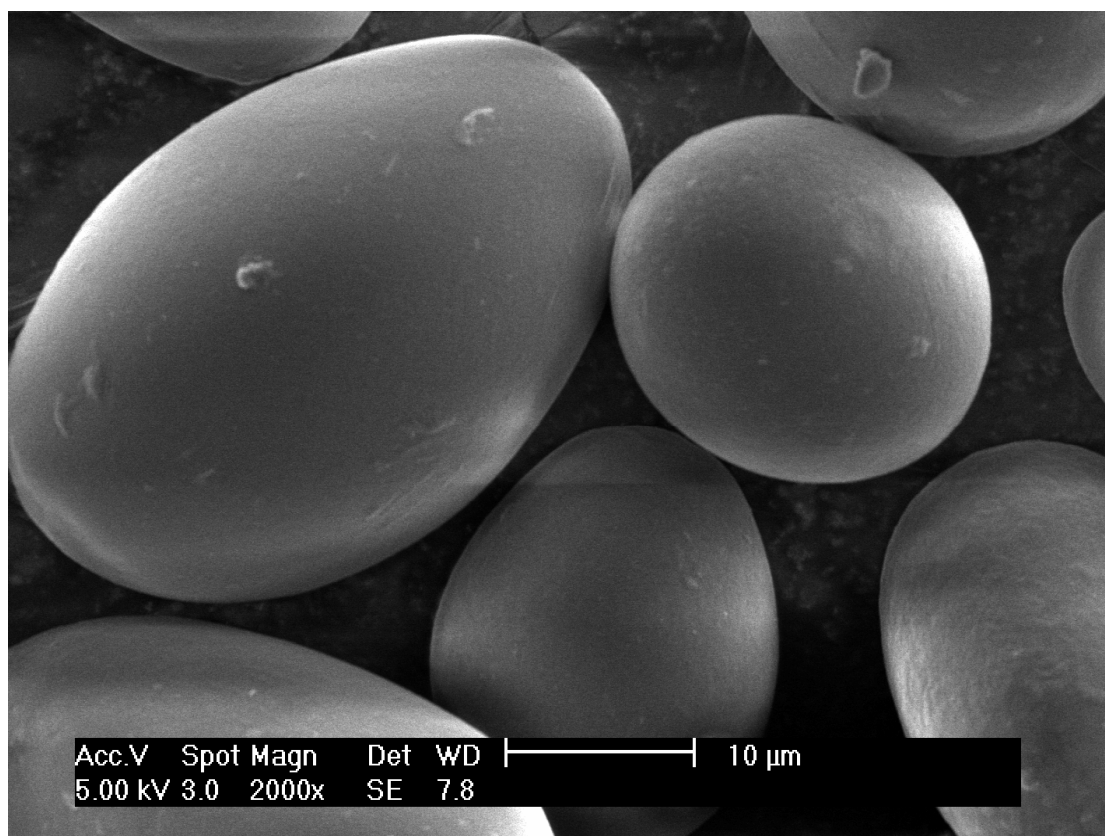

Fig. 17 Acetylated starch potato starch granules with no pretreatment

Figure 17 shows the structure of potato starch after an acetylation reaction time of 24 hours with no pretreatment of the potato starch. The figure clearly shows the unchanged and intact granule structure of potato starch. In other word the reaction did not progress. So it was experienced that the pretreatment of native potato starch according to section **3.1** is necessary so as it becomes susceptible of acetylation. It is inducted that the pretreatment step disrupts the reserved structure of native starch granules. Therefore the released polymer molecules are exposed to other reactants of acetylation reaction.
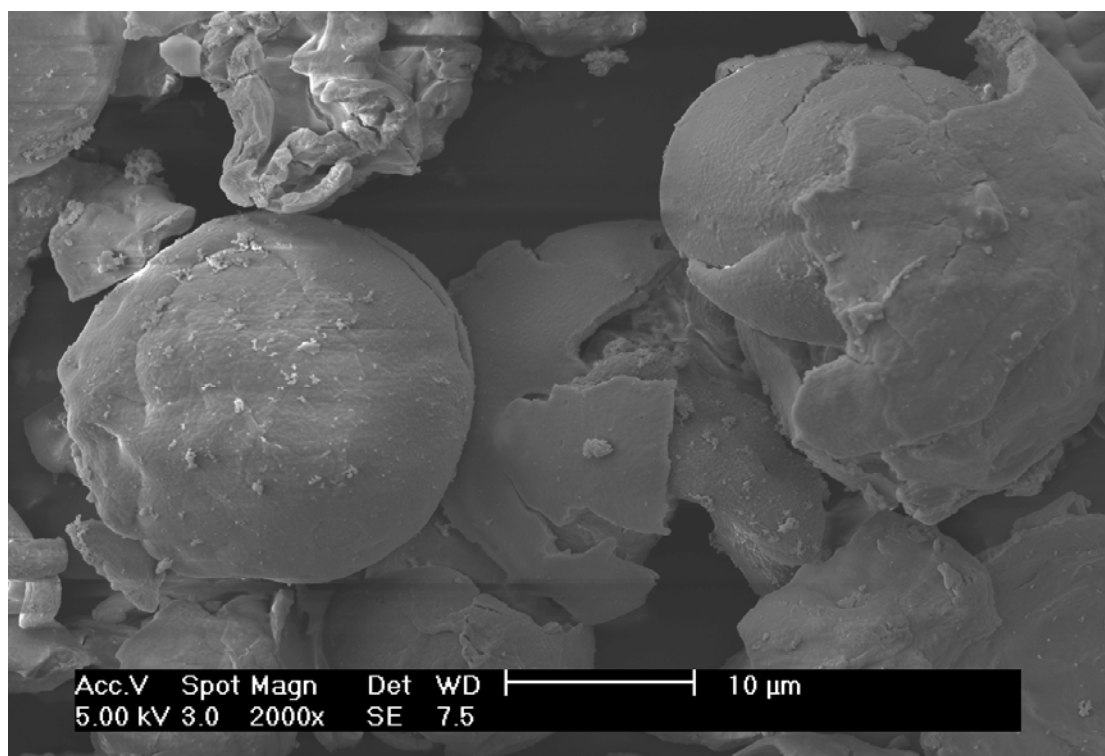
Fig. 18 Starch acetate from potato starch

Figure 18 shows the flakes of the (potato) starch acetate. **Figure 19** on the other hand displays precipitated (potato) starch acetate particles and their coral-shaped nano-porous structure.
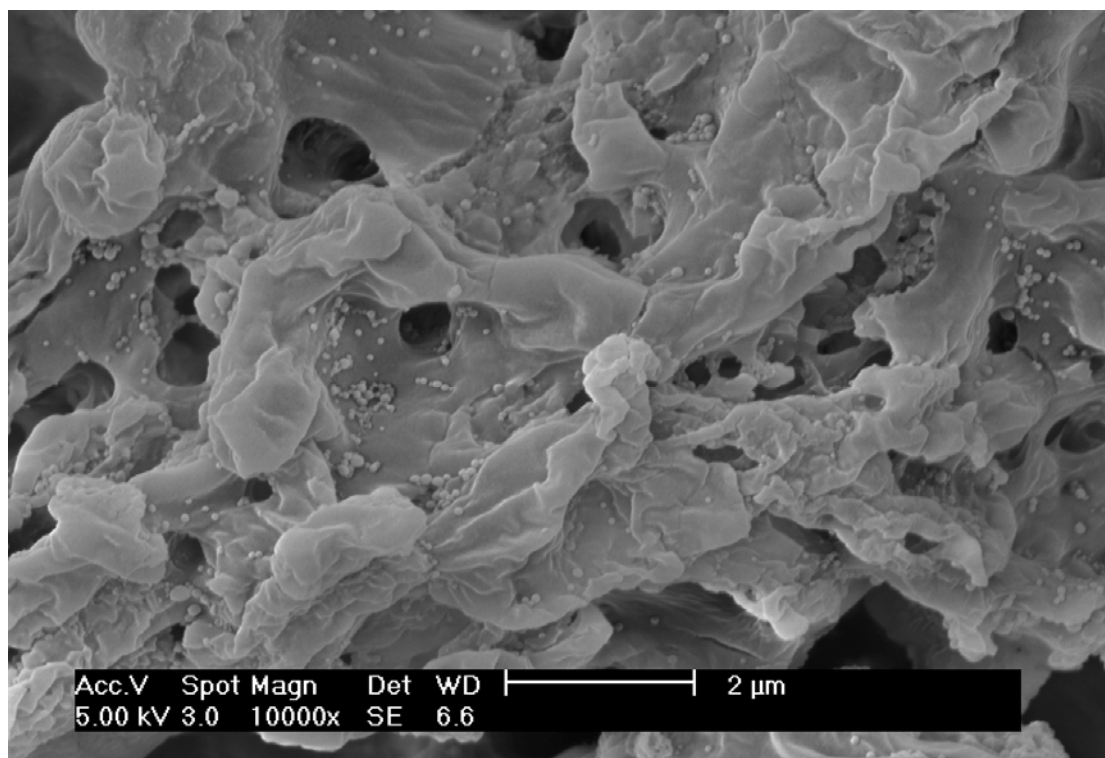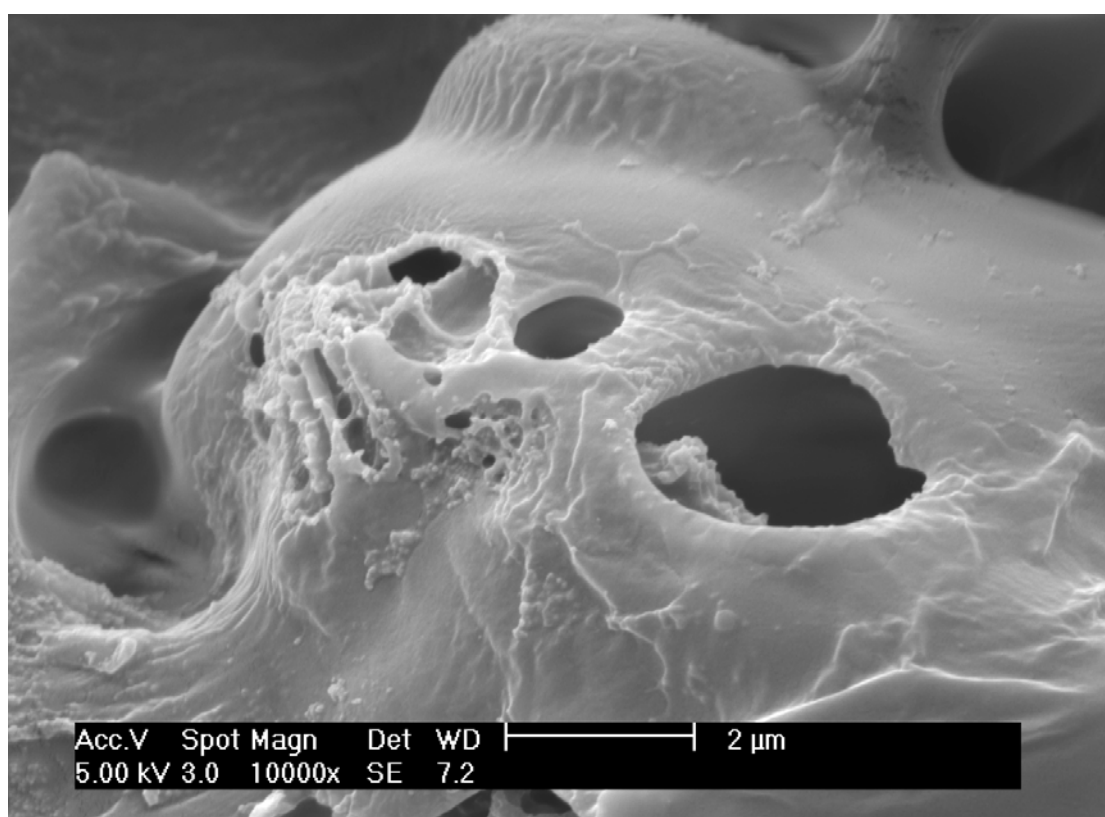

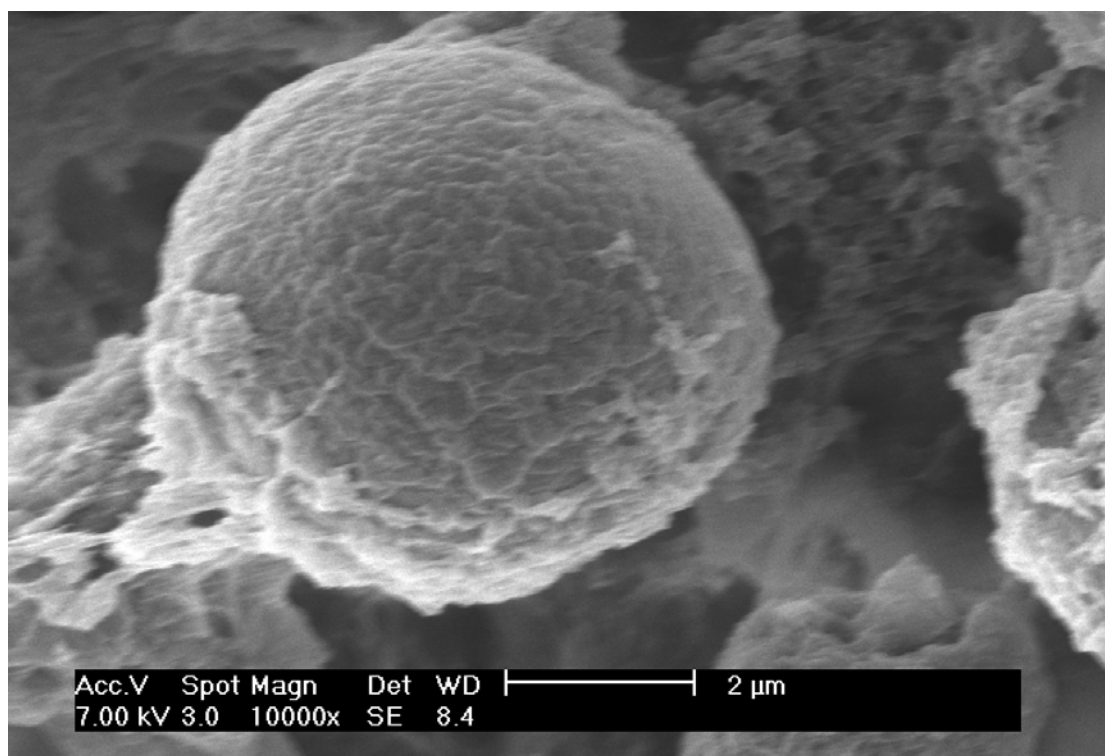**Fig. 19** Precipitated starch acetate from potato starch

Fig. 20 Starch acetate from waxy corn starch

Figure 20 shows the granules of waxy corn starch acetate. Then **Figure 21** reveals that the precipitation process confers hallow structure and nano-pores to the particles.
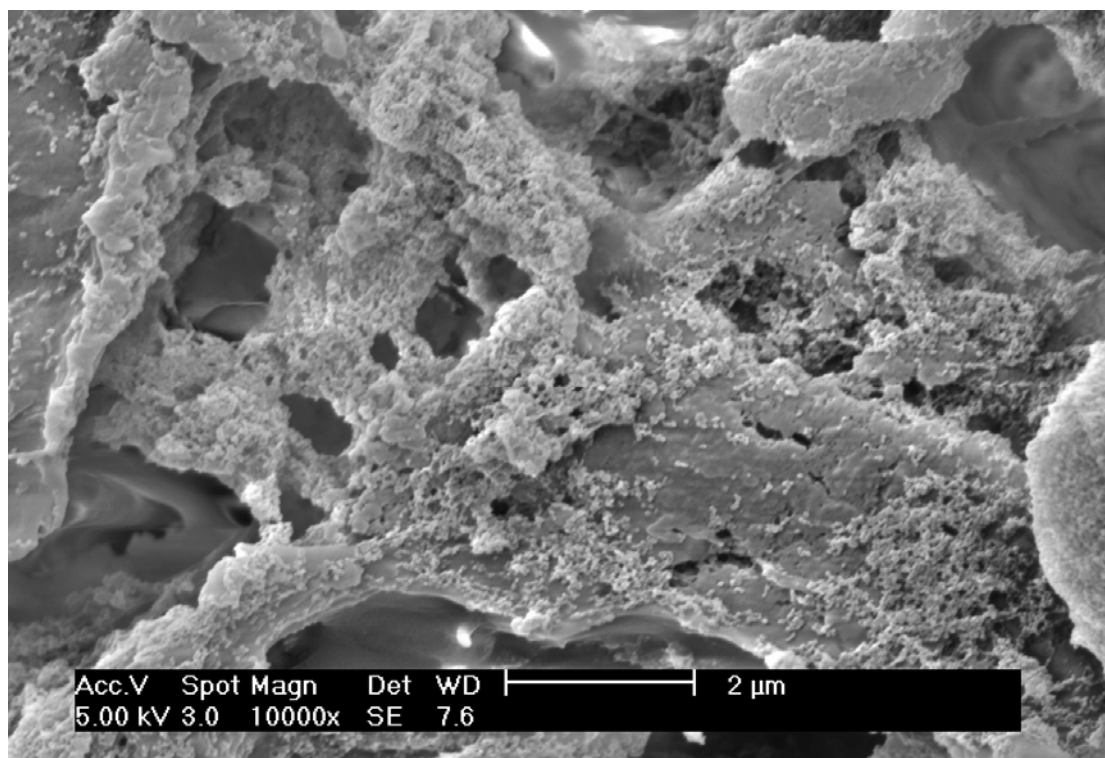

Fig. 21 Precipitated starch acetate from waxy corn starch

Fig. 22 Starch acetate from high amylose corn starch

Figure 22 shows granular shape of a random (high amylose corn) starch acetate particle. It is possible to estimate the particle size to about 7 µm in diameter. **Figure 23** on the other hand shows that the precipitation process confers coral-shaped and nano-porous structure to the granular particles.

Fig. 23 Precipitated starch acetate from high amylose corn starch

To sum up, the ESEM images reveal that the precipitation process manufactures hollow micro-particles with nano-scale and micro-scale cavities in their coral-shaped structure. This porosity in turn increases light scattering. Therefore the application of precipitated starch acetate as filler material confers improved optical properties to paper products.

4.2 Physical testing

In this work a series of physical tests were conducted to reflect some properties of the manufactured organic fillers. In order to make comparisons PCC and GCC were applied as reference mineral fillers. The results of these measurements were plotted and categorized in 3 main groups to be further investigated as follows:

4.2.1 Structural properties

Structural density and roughness plots are presented under the structural properties category.

Figure 24 shows, the lab-sheets containing PSA_PS (precipitated potato starch acetate) had the lowest structural density. The mean density values for the handsheets with PSA_WCS (precipitated waxy corn starch acetate) and PSA_HACS (precipitated high amylase corn starch acetate) was about 610 kg/m^3 and 630 kg/m^3 respectively. The reference sheet containing PCC and GCC had values at about 700 kg/m^3 or even more.
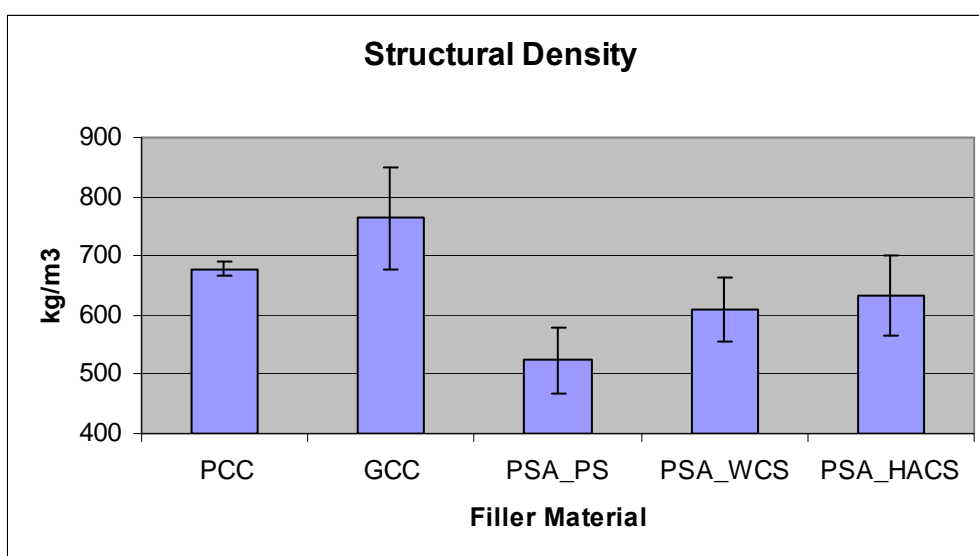
Fig. 24 Structural density chart of the measured values (including 95% confidence interval) for the lab-sheets containing different fillers.

These results show that at a constant grammage, sheets containing starch-based fillers are bulkier (having a lower density) than those containing mineral fillers. Moreover sheets comprising PSA_PS was the bulkiest of all.
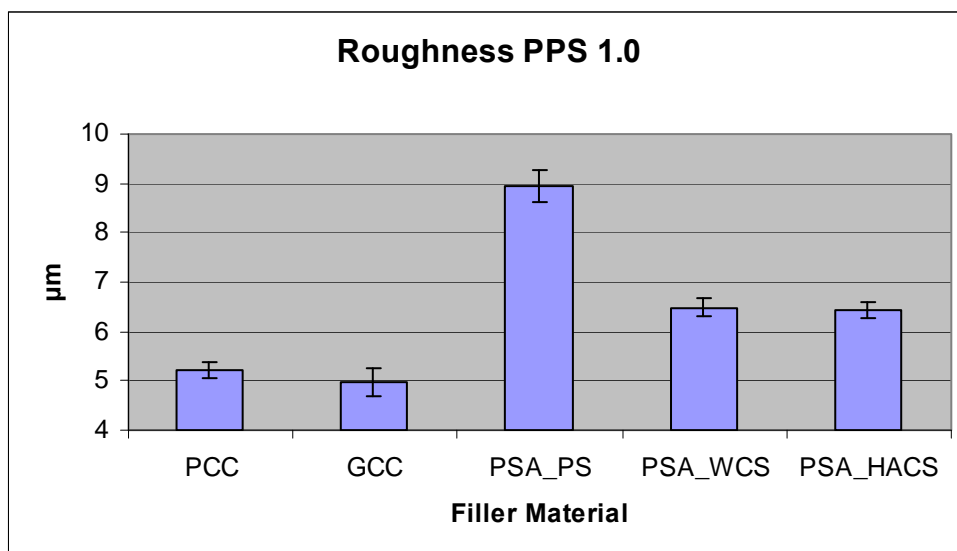
Fig. 25 Roughness PPS 1.0 chart of the measured values (including 95% confidence interval) for the lab-sheets containing different fillers

The column chart above (**Fig. 25**) shows that the sheets containing PSA_WCS and PSA_HACS were almost of the same surface roughness while those containing PSA_PS had a much higher roughness. The sheets containing organic fillers had all a higher surface roughness than the reference sheet.
Note that the roughness PPS 1.0 measurements (ISO 8791-4:2007) only are valid between 0.6 and 6 μm according to the standard.
As the size of the particles have an impact on the surface roughness, the larger roughness values for the sheets containing organic fillers are very probable to originate from the size of the organic fillers. It is also noticeable when visually looking at the sheets that the manufactured organic fillers seem to be thermoplastic.

4.2.2 Optical properties

Light-scattering coefficient and opacity plots are presented under the optical properties category.
According to the **Figure 26** the lab-sheets containing PSA_PS and PSA_WCS had a light-scattering coefficient of about 33 m^2/kg and the value for PSA_HACS was 36 m^2/kg. For the reference sheets, the light-scattering coefficient was 33 m^2/kg for GCC and for the PCC-containing paper 56 m^2/kg. So the light scattering coefficient was approximately the same for all the fillers except for sheets made with PCC.
It is known that PCC have a good light-scattering capacity compared to GCC. Although the organic filler particles were considerably larger than mineral particles, their light-scatterings are the same as GCC or even slightly higher. This can be explained by the conclusion that was made in section **4.1.3** about the hollow structure of the precipitated starch acetate particles and their improved light-scattering capacity
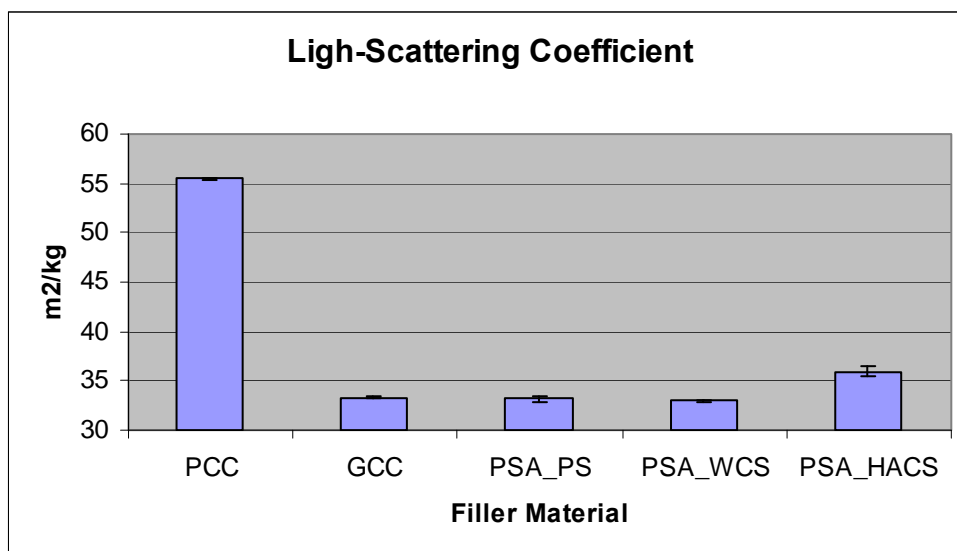
Fig. 26 Light-scattering coefficient chart of the measured values (including 95% confidence interval) for the lab-sheets containing different fillers

When it comes to opacity the trend is almost the same. **Figure 27** shows that the lab-sheets containing the starch-based organic fillers have values at about 79% for those containing PSA_PS and PSA_WCS and 81% for those with PSA_HACS. Sheets comprising GCC have the opacity values at about 77% and those with PCC have the highest opacity at about 86.5%.
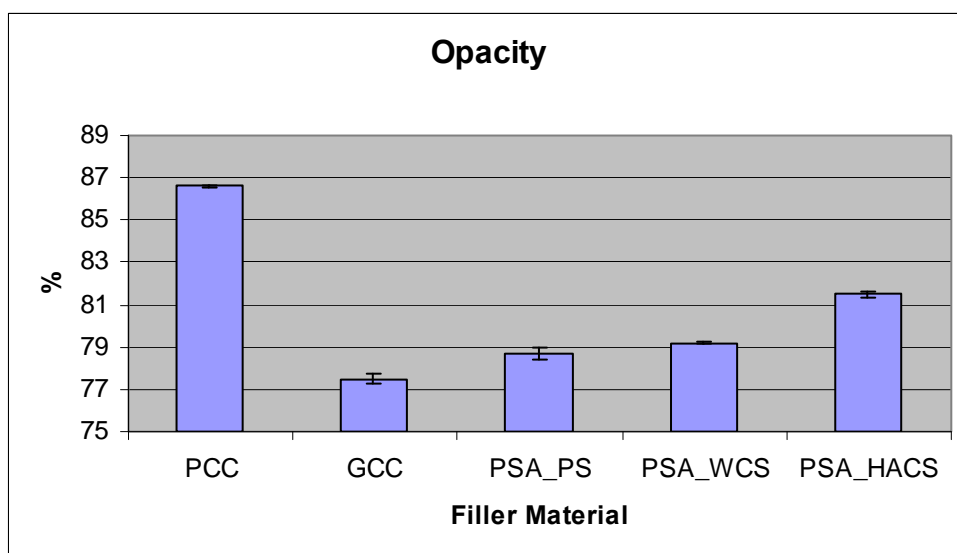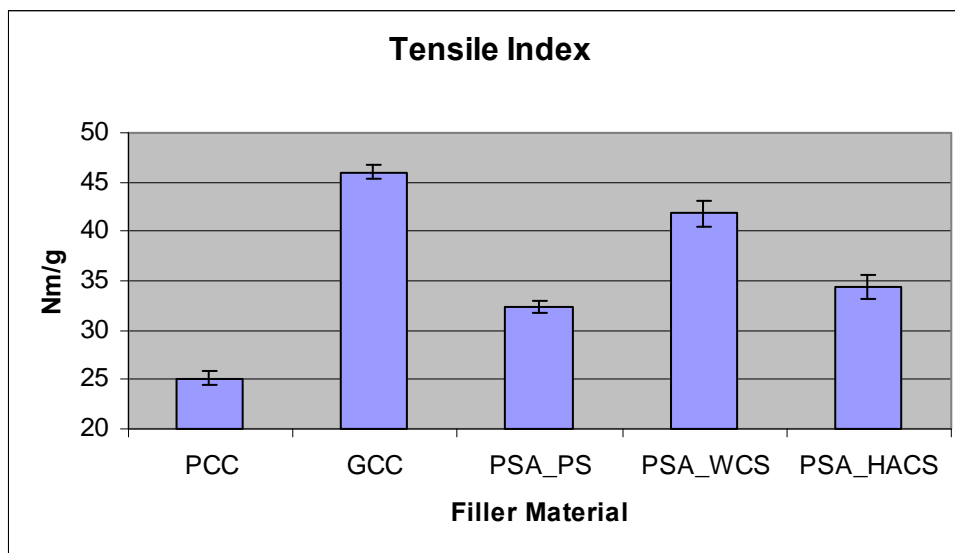

Fig. 27 Opacity chart of the measured values (including the 95% confidence interval) for the lab-sheets containing different fillers

Overall the use of the organic fillers results in opacity values higher than for those containing GCC and less than for those containing PCC.

4.2.3 Mechanical properties

In this section a few mechanical properties of the lab-sheets containing the organic fillers are investigated. This may give an understanding on how the starch-based fillers will affect the mechanical properties of the paper.
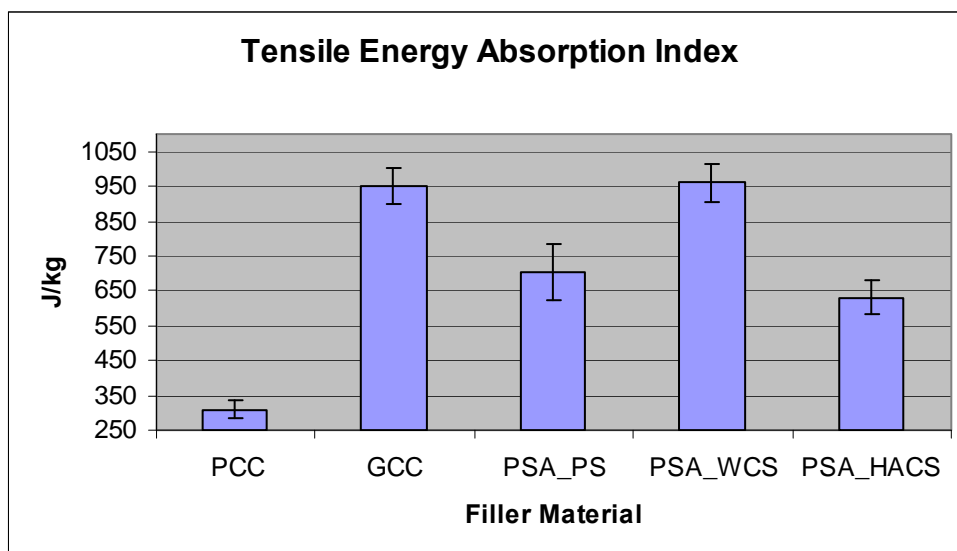

Fig. 28 Tensile index chart of the measured values (including 95% confidence interval) for the lab-sheets containing different fillers

Figure 28 shows, of the sheets containing the starch-based organic fillers, PSA_WCS had the highest tensile index. The sheets with PSA_HACS and PSA_PS had a somewhat lower tensile index. The lowest tensile index was obtained for sheets with PCC and the highest for sheets with GCC.
The reason for the lower values of the sheets with PCC than with GCC is probably due to differences in their formation. Visually the formation of PCC handsheets was worse than for the other sheets and the formation data is discussed in 4.4.4.

Fig. 29 Tensile energy absorption index chart of the measured values (including 95% confidence interval) for the lab-sheets containing different fillers.

The second chart in this section (**Fig. 29**) demonstrates tensile energy absorption index values. Again the same trend as in tensile index chart is seen. The lab-sheets containing PSA_WCS have TEA index values at about 950 J/kg. PSA_PS and PSA_HACS-containing sheets have TEA index values in the range of 550-800 J/kg. Among the mineral-containing sheets, those with PCC have the lowest TEA index values at below 350 J/kg. GCC-containing sheets reveal TEA index values the same as for PSA_WCS at about 950 J/kg.
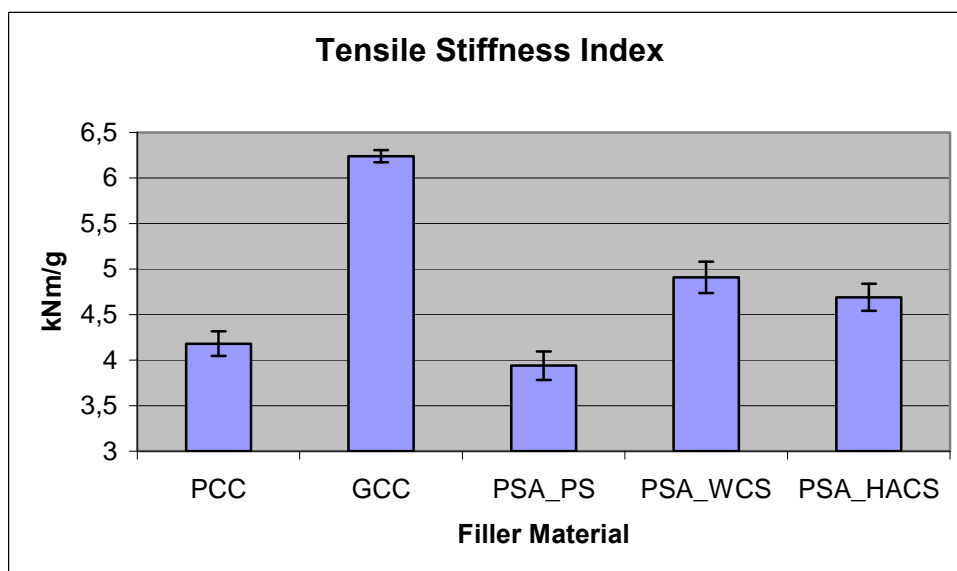
Fig. 30 Tensile stiffness index chart of the measured values (including 95% confidence interval) for the lab-sheets containing different fillers

Figure 30 shows that sheets containing PSA_WCS have tensile stiffness index values about 5 kNm/g. PSA_PS and PSA_HACS-containing sheets own less values at 4 and

4.8 kNm/g respectively. PCC-containing sheets have tensile stiffness index at 4.2 kNm/g. Once again GCC-containing sheets are on top with values at 6.3 kNm/g.
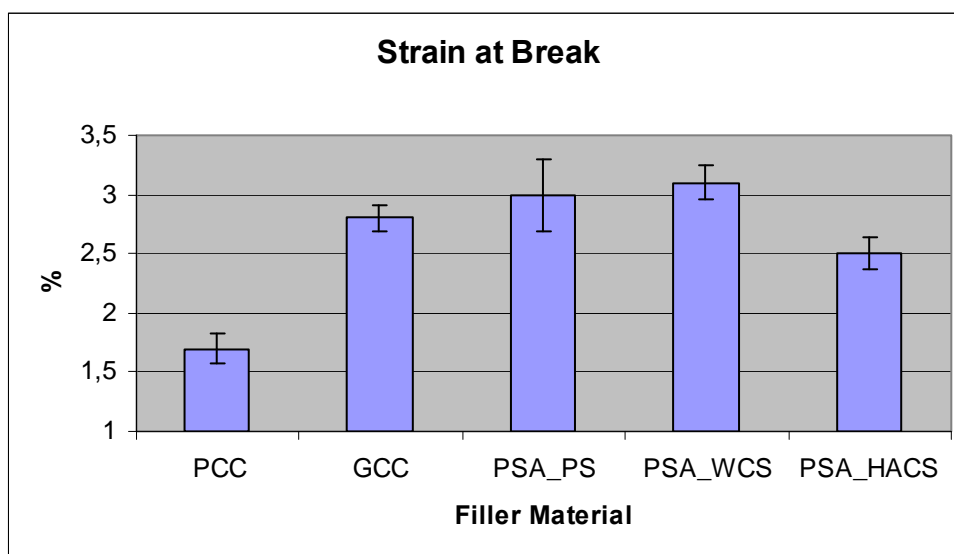
Fig. 31 Strain at break chart of the measured values (including 95% confidence interval) for the lab-sheets containing different fillers

The last chart in this section demonstrates strain at break of the lab-sheets (**Fig. 31**). Among the fully organic samples, PSA_WCS-containing sheets stand on top with about 3.2% strain at break. Sheets with PSA_PS and PSA_HACS fillers own lower values about 3 and 2.5% respectively. Again PCC-containing sheets take the lowest value about 1.7% and GCC-containing sheets have strain at break values about 2.8%.

Overall the lab-sheets containing PCC revealed the lowest mechanical properties. The sheets containing GCC and PSA_WCS stood on top and the samples with the other two starch-based fillers were intermediate.

4.2.4 Formation analysis

Considering the results and observations of the previous analyses it was found interesting to also carry out formation analysis on the lab-sheets.
Table 1 shows normalized formation numbers [%] of the lab-sheets for three wavelength intervals [mm]. The formation spectra for each sample accompanied with the relevant formation numbers graph, is presented in the appendix at the end of the report.
 The formation numbers given for the wavelength intervals clearly demonstrate that large flocs dominate in the PCC-containing sample. In other word PCC-containing sheets have the poorest formation and GCC-containing sheets have the most even formation. Among the starch-acetate-containing sheets the one with PSA_HACS has the best formation.

Filler	F(0.3-3.0mm)	F(3.0-30mm)	**F(0.3-30mm)**
GCC	8.3	8.0	**11.5**
PCC	8.7	12.0	**14.9**
PSA_PS	8.7	9.4	**12.8**
PSA_WCS	8.1	10.2	**13.0**
PSA_HACS	8.5	9.1	**12.5**

Table 1 Normalized formation numbers [%] of the lab-sheets for three wavelength intervals [mm]

The data from formation analysis confirm that the poor mechanical properties of PCC-containing sheets arise from their poor formation. The good mechanical properties for the GCC-containing samples may also be partially due to their good formation. Moreover the sheets containing the starch-based fillers revealed intermediate formation and mechanical properties. No optimization work for the retention of the fillers was made and the used retention aid was a conventional one designed for conventional fillers. However, this retention aid may not be the best choice for the organic fillers used in these experiments.

5. Conclusion

This work shows that precipitated starch acetate is feasible of being used as filler in paper products. This could, in turn, give a fully biodegradable paper product.

The obtained hollow-structured fillers had nano-scale and micro-scale cavities in their coral-shaped structure. Their primary size fell in the wide range of 1-100 μm.
These starch-based fillers gave a lower structural density and a higher surface roughness than PCC and GCC. The higher surface roughness of paper probably originates from the size and structure of the organic fillers. Papers containing these organic fillers have optical properties resembling paper containing GCC. Considering the large particle size of the starch acetate fillers compared to conventional fillers, they had good formation and mechanical properties probably due to their capacity of hydrogen bonding to fibers.
The produced fully organic paper is biologically degraded or can be fully combusted as fuel. However, the use of starch-based fillers may be suppressed for economical reasons.

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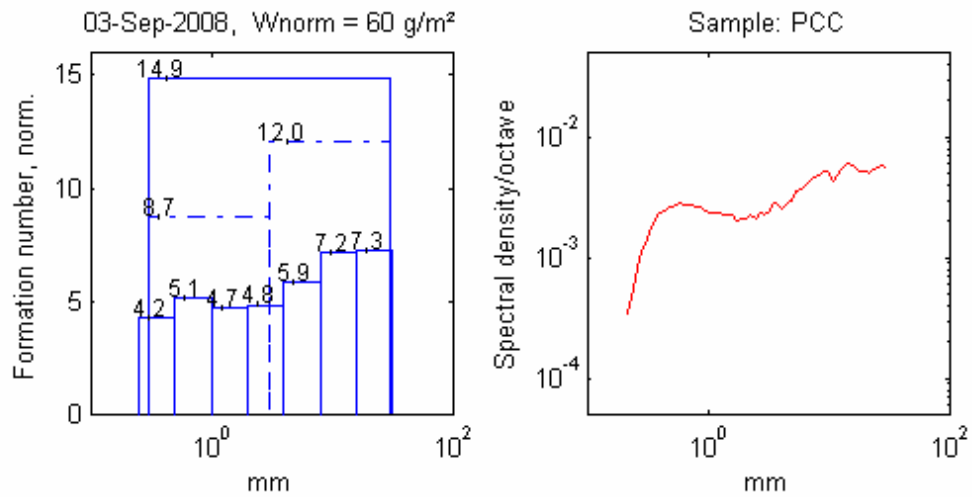
Appendices
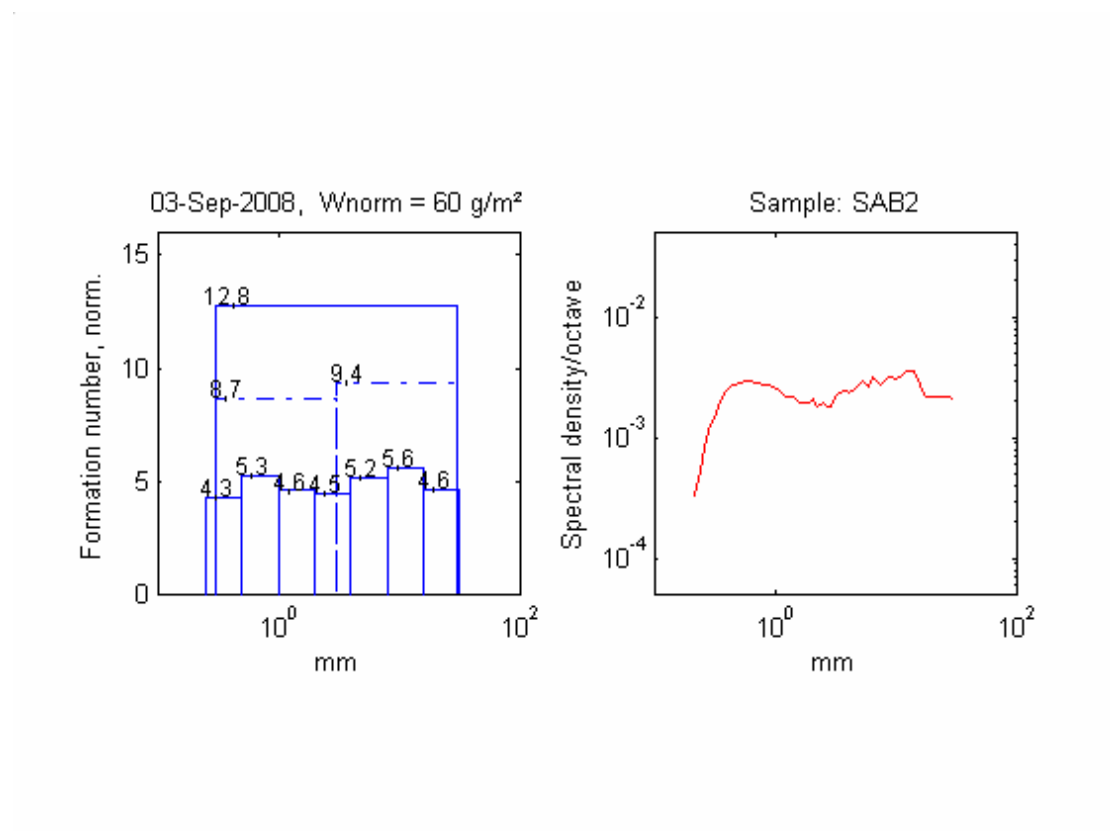
Formation analysis data for samples individually

A.1
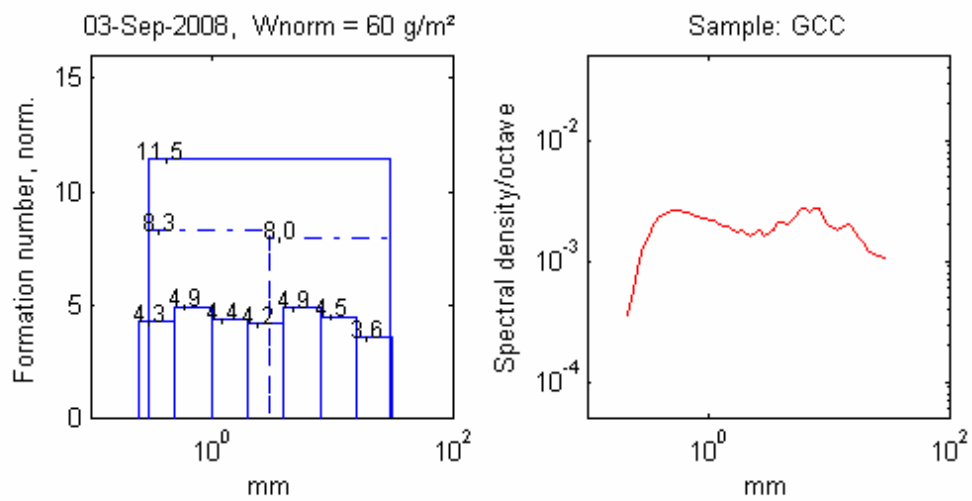
Sample: GCC-containing lab-sheet; **Left**: Normalized formation number for different wavelength intervals; F=11.5%; F(0.3-3)=8.3%; F(3-30)=8.0%; **Right**: Formation spectra at 60 g/m^2

A.2

Sample: PCC-containing lab-sheet; **Left**: Normalized formation number for different wavelength intervals; F=14.9%; F(0.3-3)=8.7%; F(3-30)=12.0%; **Right**: Formation spectra at 60 g/m^2
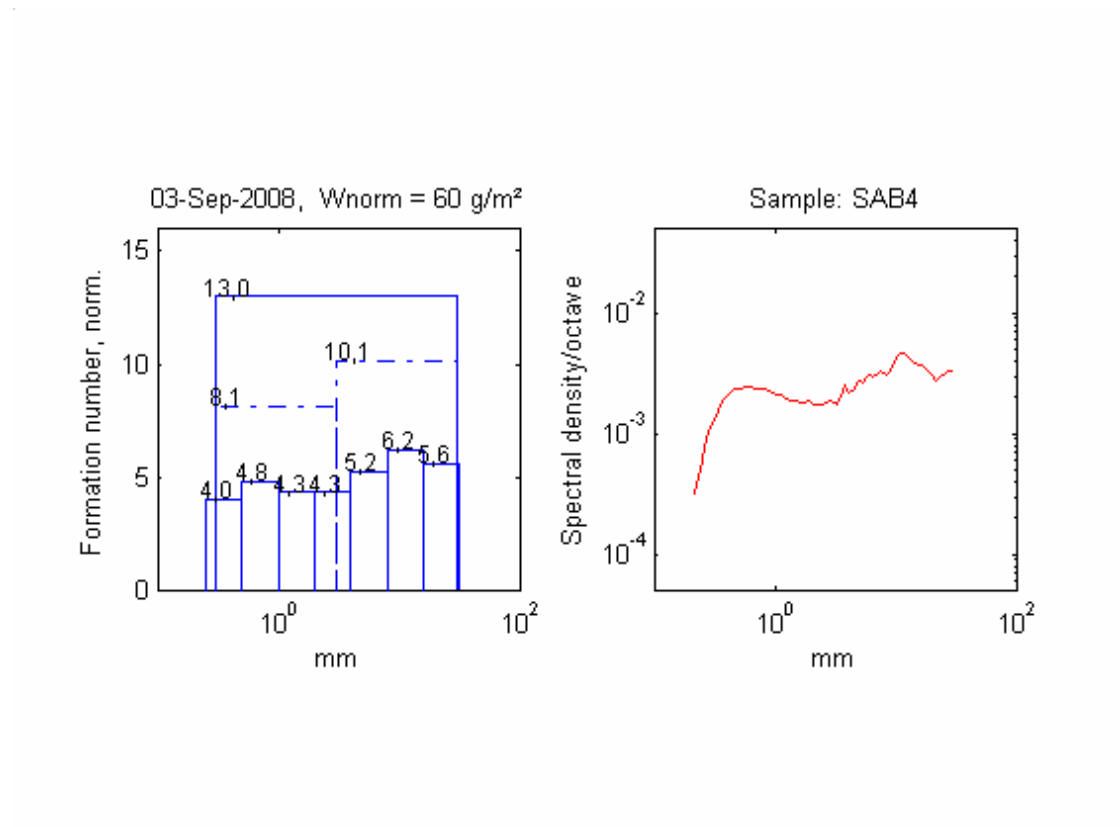
A.3

Sample: Potato precipitated starch acetate (PSA_PS)-containing lab-sheet; **Left**: Normalized formation number for different wavelength intervals; F=12.8%; F(0.3-3)=8.7%; F(3-30)=9.4%; **Right**: Formation spectra at 60 g/m^2
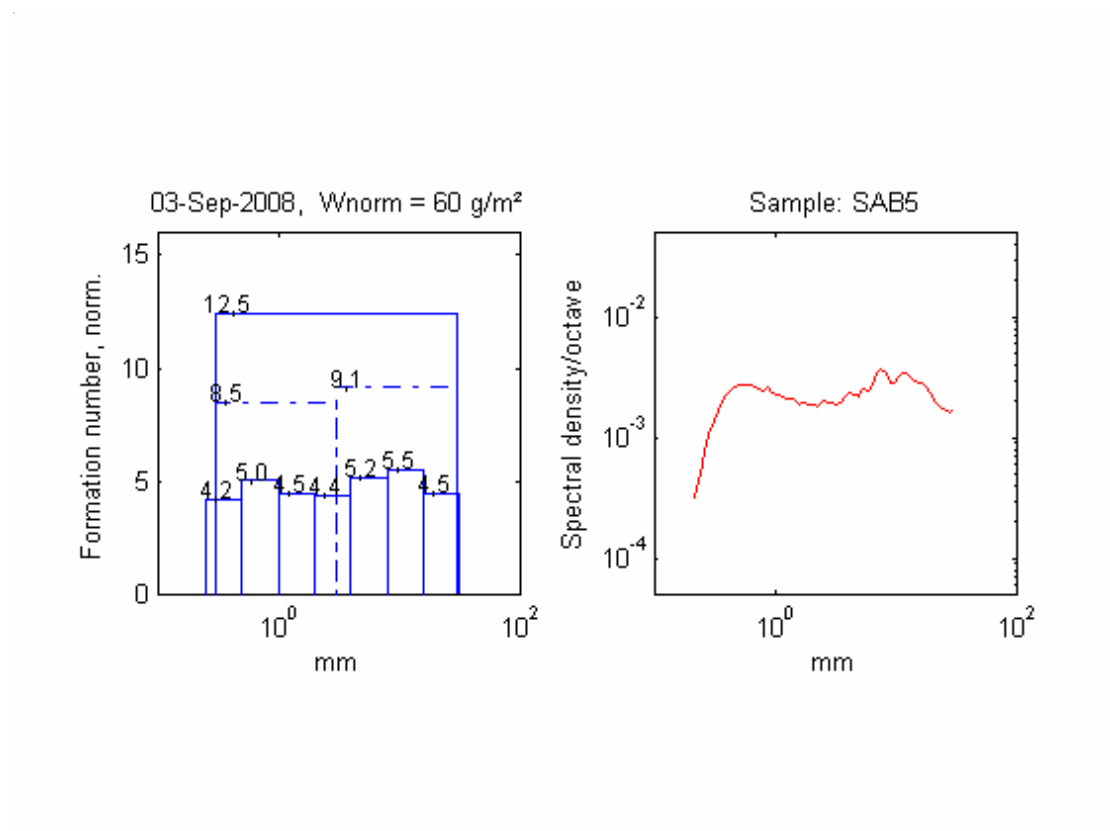
A.4

Sample: Waxy corn precipitated starch acetate (PSA_WCS)-containing lab-sheet; **Left**: Normalized formation number for different wavelength intervals; F=13.0%; F(0.3-3)=8.1%; F(3-30)=10.1%; **Right**: Formation spectra at 60 g/m^2

A.5

03-Sep-2008, Wnorm = 60 g/m²

Sample: SAB5

Sample: High amylose corn precipitated starch acetate (PSA_HACS)-containing lab-sheet; **Left**: Normalized formation number for different wavelength intervals; F=12.5%; F(0.3-3)=8.5%; F(3-30)=9.1%; **Right**: Formation spectra at 60 g/m^2