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TEMPO oxidation of cellulose pulp

Increasing mechanical properties of paper
using oxidised cellulose and additives

Materials chemistry

ELISABETH LILJENZIN

MASTER'S THESIS 2017

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Department of Chemistry and Chemical Engineering / Organic Chemistry
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2017

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Cover: SEM analyse of BAIB 1 oxidised cellulose pulp fibres, see Sections 3.2 and 4.4.

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Abstract

A cellulose pulp and MCC was oxidised using TEMPO/NaClO and TEMPO/BAIB. The cellulose pulp was oxidised and then analysed using FT-IR, WRV, SEM and conductometric titration.

The results of TEMPO/NaClO were 29.9% and 36.9% for the WRV and no distinct carboxylic acid peak could be seen in the FT-IR spectra. SEM results from the TEMPO/NaClO oxidised cellulose pulp showed a smooth fibre surface with few fibrils visible which suggest that the oxidation affects the entire fibre and that it included some level of polymeric degradation and possibly with less oxidation. Conductometric titration could not be done on the cellulose pulp oxidised with TEMPO/NaClO due to the initial sample pH being too high.

For TEMPO/BAIB, the FT-IR analysis showed a clear carboxylic peak at 1738 cm^{-1} and the WRV were 8.2% and 9.4%. SEM analyse shows a rougher surface with several fibrils protruding from the fibre, suggesting a more surface specific oxidation. Conductometric titration shows the total acidic group content of TEMPO/BAIB oxidised pulp to be $151.73\frac{\text{mmol}}{\text{gram}}$.

Based on surface specific oxidation of TEMPO/BAIB, handsheets were created containing 10% of cellulose pulp oxidised using TEMPO/BAIB. FeSO_4 , KHSO_5 , $\text{KAl}(\text{SO}_4)_2$, PAE, and surface modified CNC was added to the lab sheets and the mechanical properties of the handsheets containing additives were evaluated in terms of tensile index and tensile stiffness index. The sheets showed a lower density, but with similar tensile index. Handsheets with KHSO_5 and FeSO_4 as additives have a higher density but a lower tensile index.

Keywords: cellulose, pulp, chemical modification, TEMPO oxidation, BAIB, TEMPO, NaClO, oxidised cellulose pulp, additives, tensile index

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Contents

1	Introduction	1
1.1	Aim	1
2	Theory	3
2.1	Cellulose	3
2.1.1	Oxidised cellulose	4
2.2	Handsheets	6
2.3	Analysis	6
2.3.1	Fourier transform infrared (FT-IR)	6
2.3.2	Zeta-potential	6
2.3.3	Water Retention Value (WRV)	6
2.3.4	Scanning Electron Microscopy (SEM)	7
2.3.5	Conductometric titration method	7
2.3.6	Tensile strength index and tensile stiffness index	8
3	Methods	9
3.1	TEMPO NaClO	9
3.2	TEMPO BAIB	9
3.3	Handsheets	10
3.4	Additives	10
3.4.1	Sulfates	11
3.4.2	Polyamideamin epichlorohydrin (PAE)	12
3.4.3	Cellulose nanocrystals (CNC)	13
4	Results and discussion	15
4.1	Fourier transform infrared (FT-IR)	15
4.2	Zeta-potential	18
4.3	WRV	18
4.4	SEM	20
4.5	Conductometric titration method	23
4.6	Mechanical analysis	25
5	Conclusion	29
	Bibliography	31
A	TEMPO oxidation methods	I

Contents

B	Making handsheets	III
C	Weight tables	IX
D	Additive application	XIII

1

Introduction

Wood has been used as a material for thousands of years; it has been modified, refined and reworked for many areas of use with each one requiring a very specific set of properties. With the environmentally beneficial act of growing trees, the resource is both abundant as well as cheap. To more efficiently use the available wood resources, an increased functionality of the material could result in using less resources while still retaining a strong material. It also implicates a possible wider range of physical properties and also introduce new areas of use. [1, 2]

The production of materials from wood was initially on a larger scale and has over time slowly worked itself down to the main constituent of the wood fibre, the organic polymer cellulose. Cellulose is a light-weight material that is durable and recyclable, properties that give a wide range of use, from soft tissues to stiffer, stronger materials used for packaging.

Packaging material made out of paper is often designed to maximise the mechanical properties as well as chemical properties of the constituents. Even though packaging material today is often a combination of several different materials, cellulose still plays an important role in the mechanical stability of the end product. The paper industry produced a total of 403 million tons of paper in 2013, of which 13% was for packaging purposes [3]. At such large volumes, even a small decrease of material usage would make a huge impact on the paper industry and its use of resources. If 1% less material could be used for packaging material alone, that would mean an annual decrease of more than 500 000 tons of paper.

For this purpose, the chemical possibilities of modifying cellulose could be used in order to increase the mechanical properties of the fibre; an increase in the material's strength could lead to a decrease in use of resources without a decrease of the material's desired properties. As such, this potential resource optimisation as well as the chemical and mechanical versatility of cellulose is not only a vital part of its early success as a material, it is also what makes it a material of the future. [2, 4]

1.1 Aim

This work aims to increase the knowledge of how different oxidants in (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO) oxidation affect the cellulose fibres. It will also discuss how oxidised cellulose used together with an appropriate additive

1. Introduction

can improve the mechanical properties of cellulose. This work is to be a part of the scientific foundation needed to develop future advanced material concepts focusing on cellulose and its modifications.

2

Theory

The durability and strength of a paper material relies on the ability to keep its intended structure during the exposure to moisture, pressure and force. For paper to do so requires a consistent fibre structure and chemical modification should be done without affecting can be done without affecting the integrity of the fibre itself. Ideally, this can be done by keeping the modifications at a minimum and at the fibre surface level. With the introduction of a functional group to the surface of cellulose, there are possibilities to increase the interaction between the fibres that would allow for stronger bonds, thus affects the mechanical properties. [2, 5]

2.1 Cellulose

Cellulose is an organic polymer chain is a major component in the cell walls of plants and trees where it occurs as fibres. The fibres are 10-50 μm in diameter with a length of 1000-3000 μm . The fibres are comprised of fibrils that have a diameter less than 1 μm . Fibrils are made from microfibrils that are the smallest structure, being 2-20 nm in diameter and 100 - 40 000 nm long. [6, 7]

The cellulose in microfibrils consists of the repeating dimer of cellobiose. In the cellobiose there is two anhydroglucosic unit (AGU) and in each AGU there are three hydroxyl groups; two secondary alcohols at sites C2 and C3 and a primary alcohol at C6, see Figure 2.1 for numbering.

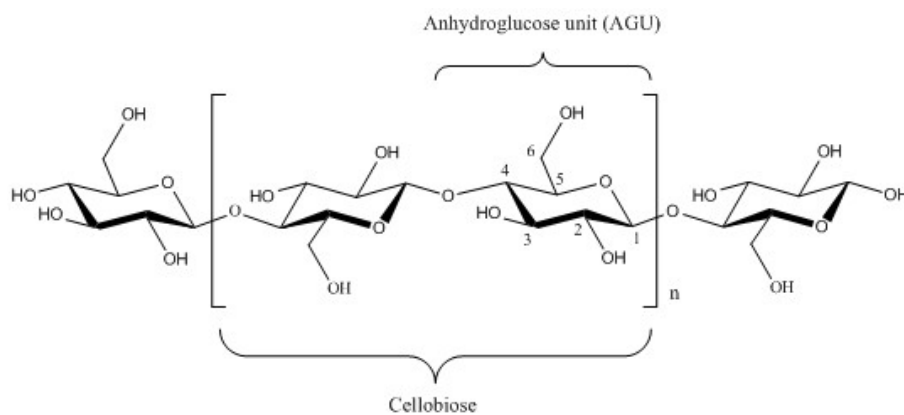


Figure 2.1: An anhydrogluconic unit (AGU) in a cellulose polymer chain.

In terms of modification, the hydroxyl groups are suitable for modification as they

are protruding from the structure and as such are less sterically hindered, C6 being less hindered than C2 and C3. The presence of these hydroxyl groups creates a relative reactive surface that can be used for modification that increases the fibre interaction. [2]

2.1.1 Oxidised cellulose

Oxidation of cellulose is when the functional group of carboxylic acid is replacing one or more of the hydroxyl groups positioned at C2, C3 or C6. Oxidised cellulose fibres have been shown to have higher sheet density and improved strength-related properties but only if the total carboxyl group content is less than 500 mmol/kg. [8]. See Figure 2.2 for oxidation of the primary alcohol on C6. [9, 10, 11]

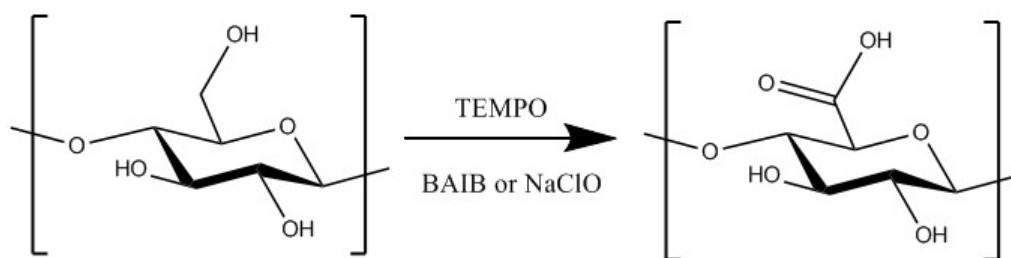


Figure 2.2: Oxidation of cellulose.

Even though there exists several possibilities for oxidation on an AGU, primary alcohols will in general be oxidised much faster than secondary alcohols. This, in combination with the reported chemoselectivity in oxidation of mixtures of primary and secondary alcohols, this suggests that it is primarily C6 that undergoes oxidation. [9]

In order to analyse the steric hinderance of cellulose, oxidation was also done on micro-crystalline cellulose (MCC). MCC is crystalline cellulose where the amorphous regions are removed using acid hydrolysis and the cellulose appears as a fine powder. MCC demonstrates excellent mechanical strength properties and, as it appears in powder form without the amorphous parts, the anhydroglucosic unit is less sterically hindered. [12]

One type of surface modification that has been explored in order to oxidise different types of polysaccharides is oxidation using (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO), see Figure 2.3. [9, 13, 14, 15, 16].

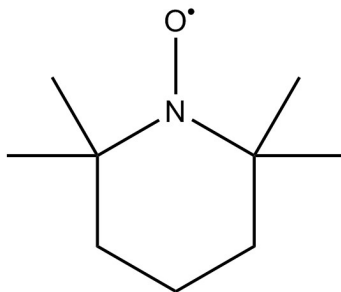


Figure 2.3: (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO).

TEMPO is a stable radical that can be oxidised to give a nitrosonium ion which is a strong oxidant that shows selectivity towards primary hydroxyl groups and as such is suitable for selective oxidation [9, 13, 15].

A common secondary oxidant is NaClO, see Figure 2.4, and there have been extensive reports on oxidation of cellulose using NaClO [10, 11, 17]. Even so, there have also been reports with trouble determining the carboxyl group content due to severe depolymerisation when using NaClO [18].

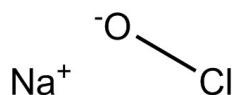


Figure 2.4: Sodium hypochlorite (NaClO).

Another secondary oxidant for TEMPO-mediated oxidation is diacetoxyiodobenzene, BAIB, see Figure 2.5. Using BAIB to regenerate TEMPO is an efficient procedure with a high chemoselectivity in the presence of secondary alcohols and without creating inorganic salts. [15, 19]

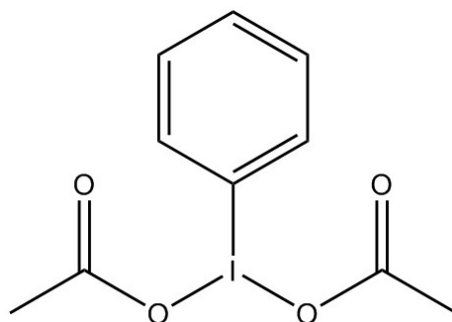


Figure 2.5: Diacetoxyiodobenzene (BAIB).

2.2 Handsheets

To study whether the oxidised cellulose could interact with additives in order to increase the mechanical properties, sheets made of cellulose pulp containing a percentage of oxidised cellulose was made. Recently developed oxidation methods show that there is only a percentage of the total material that oxidises [20, 21]. In combination with Ma et al. [8] reporting a loss of mechanical properties were reported when the carboxyl content increases, suggests that the sheets should contain a limited amount of oxidised cellulose. As such, the sheet used for mechanical analysis was made using 10wt% oxidised cellulose and 90wt% unmodified cellulose.

2.3 Analysis

The analyses were done at Chalmers University of Technology in Gothenburg with the exceptions of the mechanical analysis, which were done at Innventia in Stockholm.

2.3.1 Fourier transform infrared (FT-IR)

FT-IR is a spectroscopy method in which the sample is radiated with IR-radiation of different wavelengths. Different chemical bonds absorb electromagnetic radiation at different wavelengths, resulting in a transmission spectrum with values of the different absorbed wavelengths representative of the sample. In this particular study of cellulose oxidation, the wavelengths of interest will be that of carboxyl groups that appears at approximately around 1750 cm^{-1} in combination with a broad OH peak at $3400\text{ to }2400\text{ cm}^{-1}$. FT-IR analyses were made with a PerkinElmer Spectrum One FT-IR Spectrometer over an interval between $4000\text{--}400\text{ cm}^{-1}$ with a total of 16 scans collected. [22]

2.3.2 Zeta-potential

The amount and distribution of charges on a particle surface can be determined using zeta potential measurements. This can be done on functionalised surfaces to determine a change in surface charge that indicates the level of surface functionalisation. The measurements were done at a sample concentration of 0.05%, using a Malvern Zetasizer Nano ZS ZEN3600 at room temperature with a total number of 5 measurements. [23, 24]

2.3.3 Water Retention Value (WRV)

Water retention value (WRV) is used to examine how well a sample holds water. The sample is soaked for a certain amount of time and then centrifuged to remove excess water. The water remaining in the sample is the amount of water the sample can hold. By calculating the difference in weight between the damp sample, m_{damp} , and the dry sample, m_{dry} , the absorbed amount of water, m_{water} , is given.

The sample is then dried and the WRV is determined by

$$WRV = \frac{m_{\text{damp}} - m_{\text{dry}}}{m_{\text{dry}}} = \frac{m_{\text{water}}}{m_{\text{dry}}}. \quad (2.1)$$

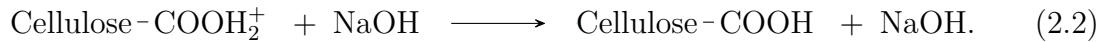
2.3.4 Scanning Electron Microscopy (SEM)

A SEM uses a focused beam of electrons to interact with the atoms in the prepared sample, producing various signals about the sample surface topography. By doing so, a SEM can produce a high resolution picture ($<1 \mu\text{m}$) of the sample surface. The SEM analysis was done using a LEO Ultra 55 FEG SEM. [25]

2.3.5 Conductometric titration method

The total amount of charged groups in cellulose pulps was determined using a conductometric titration method according to SCAN-CM 65:02, where the cellulose fibres are protonised as to interact with added NaOH. The titration starts at pH 3 and thus the sample is protonated as sodium chloride is added, liberating protons due to ion exchange. The amount of NaOH, μl , added plotted against the measured conductivity gives a plot with three distinct phases.

The transition between phase 1 and phase 2 is



Phase 1 has a conductivity decrease and represents strong acidic groups being neutralised by the NaOH. Phase 2 has no particular change of conductivity and as Na^+ are adsorbed as counter-ions to the carboxylic acidic groups and the dissociated protons are neutralised by the added OH^- .



is representing phase 2 and phase 3, where phase 3 causes increase of conductivity due to an excess of NaOH.

The total acidic group content, X , is calculated from Equation

$$X\left[\frac{\mu\text{mol}}{\text{gram}}\right] = \frac{C_t\left[\frac{\mu\text{mol}}{\text{L}}\right] \times V_2\left[\text{L}\right]}{m\left[\text{gram}\right]} \quad (2.4)$$

where C_t is the concentration of the NaOH in the solution, V_2 is the volume of consumed NaOH at the intersection between the 2nd and 3rd phase and m is the dry sample weight. For bleached softwood pulp, the total amount of acidic groups is around 40-180 $\frac{\mu\text{mol}}{\text{gram}}$. [5, 26]

2.3.6 Tensile strength index and tensile stiffness index

Information about a material's mechanical properties can be had from performing in-plane tensile measurement after constructing a test bar consisting of the sample material, the test bar is then pulled apart with a known speed and force. First, the material will be deformed and then there will be a break in the material. Values of the material's tensile strength, s , and the elastic modulus, e , can be calculated from the force-displacement curve. The tensile strength is the relation between the pulling force at the break, F , and the cross-sectional area, A , of the test bar:

$$s [\text{Pa}] = \frac{F [\text{N}]}{A [\text{m}^2]}. \quad (2.5)$$

The elastic modulus, e , is the ratio between the deformed material length at break and the non-deformed material length, L :

$$e = \frac{L[\text{mm}]}{L[\text{mm}]}. \quad (2.6)$$

Young's modulus, E , represents the slope of the force-displacement curve and is the ratio between the difference in tensile strength, Δs , and the difference of elastic modulus, Δe :

$$E = \frac{\Delta s}{\Delta e}. \quad (2.7)$$

Tensile stiffness index is the ratio of the pulling force to the elastic region of the tensile-strain and is numerically equivalent to $E \cdot t$, where t is the sample thickness. To calculate the tensile index, the tensile strength is divided by grammage of the paper. [27]

3

Methods

For the synthesis and analyses, deionised water was used. Regular tap water was used in creating the reference sheets containing 10% oxidised cellulose and additives. Procedure descriptions can be found in Appendix A.

3.1 TEMPO NaClO

The method used is from Saito and Isogai [10], which uses a NaClO solution of 11-14wt%. For the oxidation, 0.016 gram TEMPO and 0.1 gram of NaBr were added to a minimum of water and stirred with a magnetic stirrer. 1 gram of wet cellulose was added to the solution. The pH of 3.7 ml of NaClO was then adjusted to pH10 using 0.1 M HCl. The TEMPO-solution was then added at room temperature. The pH of the solution was kept at pH10 by adding 0.5M NaOH until no NaOH-consumption was observed. The cellulose was filtered and washed using a Büchner funnel.

Different amounts of NaClO and TEMPO were added to different types of cellulose, see Table 3.1.

Table 3.1: Amount of NaClO and TEMPO used for 1 gram of cellulose.

Name	Cellulose	NaClO [gram]	TEMPO [gram]
NaClO MCC	MCC	0.41	0.016
NaClO 1	pulp	0.41	0.016
NaClO 2	pulp	0.41	0.16

3.2 TEMPO BAIB

The oxidation was done to varying amounts using TEMPO and BAIB based on a method described by Nylander [28] and Epp and Widlanski [19] under the assumption that only the primary alcohol of cellulose was oxidised due to steric hinderance and the chemoselectivity of BAIB. [15]

For the different amounts of oxidants and cellulose type, see Table 3.2.

Table 3.2: Amount of BAIB and TEMPO used for 1 gram of cellulose.

Name	Cellulose	BAIB [gram]	TEMPO [gram]
BAIB MCC	MCC	11.91	0.47
BAIB 1	pulp	11.91	0.47
BAIB 2	pulp	11.91	0.16
BAIB 3	pulp	4.18	0.16

For the BAIB 1 oxidation, 1 gram of cellulose was mixed with a minimum of acetonitrile, was chilled to 0°C and stirred using a magnetic stirrer. The desired amount of BAIB and TEMPO were added to the solution and stirred for 2 hours at 0°C. After that, the solution was stirred for 4 hours at 25°C. The cellulose was then washed using a Büchner funnel, first with a small amount of diethyl ether and then with ethanol. If a yellow colour remained in the sample, the sample was transferred to an Erlenmeyer flask containing ethanol and then heated slightly to around 65°C while stirred until the cellulose looked white. Finally it was transferred to a Büchner funnel in order to remove the ethanol.

3.3 Handsheets

The oxidised cellulose of BAIB 1 and BAIB 2 were used to create handmade sheets containing 10% oxidised cellulose and 90% unmodified cellulose, to be used in combination with additives. The mixture of oxidised cellulose was made to be able to do all the planned additives for the mechanical analysis. The sheets were made with a radius of 8.5 cm to have a target grammage of $100 \frac{\text{gram}}{\text{cm}^2}$, though there is a variation in grammage due to the fibre nature. They were made using tap water and a sheet machine and dried on a drying disc in room temperature, see Appendix B.

To ensure that the additives were absorbed by the cellulose sheets in the water bath, reference sheets were made to estimate the average weight loss caused by washing away smaller fibres. The weight of the sheets were also measured before and after additives were applied in order to use the weight to confirm the presence of the additive, see Appendix C for weight tables and procedure.

3.4 Additives

The additives in question were chosen with aspects to their structure and their possibility to chemically react to improve the mechanical properties of the handsheets. More specifically, the additives have the possibility of radical recombination, cross linking or increased interaction between the fibres. [2]

To calculate the amount of sample to use of each additive, a molar ratio based on the mol of primary alcohol in the AGU:

$$3 \times \frac{1}{162 \frac{\text{gram}}{\text{mol}}} = 18.5 \text{ mmol} \frac{\text{OH}}{\text{AGU}}. \quad (3.1)$$

The ratios used for cellulose to additive were 1:0.1 and 1:0.2, see Table 3.3. For the additives that were available as dispersions, polyamideamin epichlorohydrin (PAE) and cellulose nanocrystals (CNC), the amount of additive was calculated as a weight% of the sheet weight. The CNC used was hydrolysed using sulphuric acid, see Section 3.4.3.

Table 3.3: Additives molar mass, molar ratio and wt%.

Additive	molar mass	molaratio	wt%
FeSO ₄	278,02	1:0.1	17
FeSO ₄	278,02	1:0.2	33
KHSO ₅	307,38	1:0.1	18
KHSO ₅	307,38	1:0.2	37
CNC	-	-	10
CNC	-	-	20
PAE	-	-	10
PAE	-	-	20
KAl(SO ₄) ₂	474,3884	1:0.1	17
KAl(SO ₄) ₂	474,3884	1:0.2	57

Application procedure used for the additives can be found in Appendix D.

3.4.1 Sulfates

Interesting additives would be those that could be used to interact with the fibre, either using hydrogen bonds or double bonds to be able to create radicals or crosslinking in a later stage of modification. An example of a well known chemical where both double bonds are present is iron (II) sulfate, see Figure 3.1. [29].

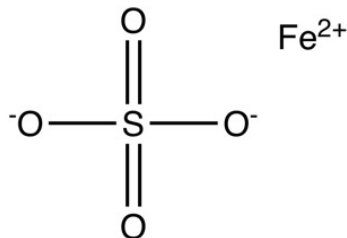


Figure 3.1: Iron (II) sulfate, FeSO₄.

Potassium monopersulfate has also been suggested to be able to form a radical, which could be used for creating crosslinks between the organic polymerchains, see Figure 3.2. [30]

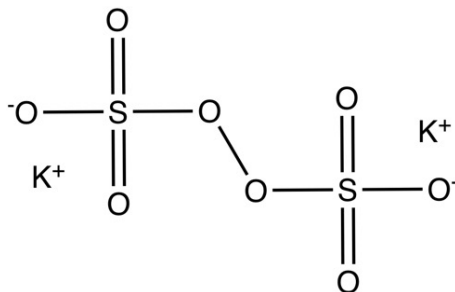


Figure 3.2: Potassium monopersulfate, KHSO_5 .

Potassium aluminium sulfate, see Figure 3.3, is a persulfate as well and is already in use in the paper industry as a pitch control, which makes it interesting to examine whether it could be of further use. [3, 29]

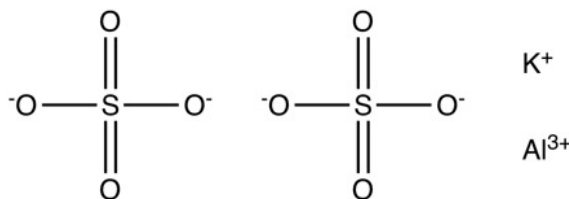


Figure 3.3: Potassium aluminium sulfate, $\text{KAl}(\text{SO}_4)_2$

3.4.2 Polyamideamin epichlorohydrin (PAE)

Polyamideamin epichlorohydrin (PAE), shown in Figure 3.4, is a well known wet strength additive for paper which has been shown to improve the tensile strength of wet paper as well as dry paper. [31, 32]

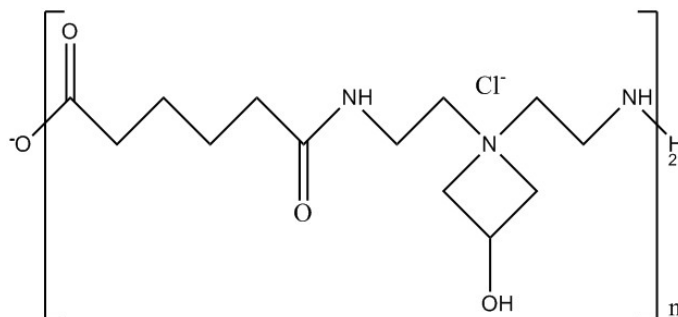


Figure 3.4: Polyamideamin epichlorohydrin (PAE).

3.4.3 Cellulose nanocrystals (CNC)

By removing the disordered part of a cellulose fibre, the remaining crystalline cellulose is referred to as cellulose nanocrystals. Cellulosic nanocrystals have a high crystallinity that results in a higher strength than natural cellulosic fibres, thus improves the material properties and mechanic properties. [2, 12, 23, 33]

In this work, the CNC used had been functionalised using sulphuric acid according to a method described by Hasani et al. [24], where MCC from Avicel was hydrolysed with 64% H_2SO_4 at 45°C for 2 hours. The CNC was dialysed in water to remove the reagents until the dialysis liquid had a conductivity $<5 \frac{\mu\text{S}}{\text{cm}}$ and the CNC was then sonicated to disperse the CNC.

In order to confirm the presence of sulphur groups in the functionalised CNC, an analysis of the zeta potential was made.

4

Results and discussion

Chemical analysis was done on pulps having different oxidation treatment, with a priority on BAIB 1 and NaClO 1 in order to compare the different methods. References were pure cellulose pulp. A reference sheet containing 10% oxidised cellulose in order to confirm the presence of oxidised cellulose in the sheets used with additives was also used as a reference.

4.1 Fourier transform infrared (FT-IR)

The FT-IR spectrum of oxidised MCC is presented in Figure 4.1, showing a distinct peak at approximately 1738 cm^{-1} that represents the carboxylic acid groups. In combination with a broad absorption for OH at $3400\text{--}2400\text{ cm}^{-1}$, this clearly indicates the presence of a carboxylic acid. [22].

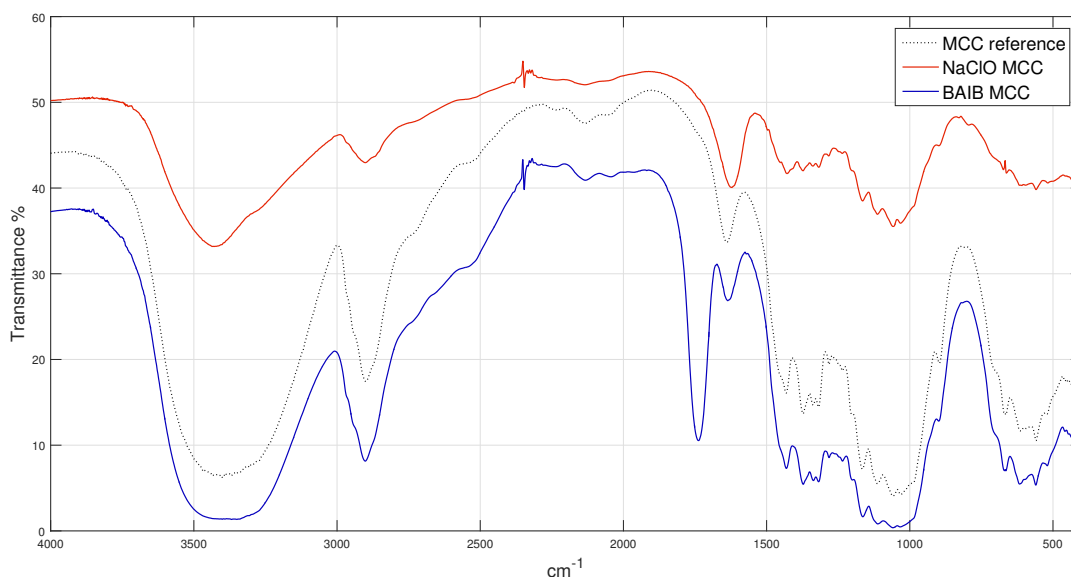


Figure 4.1: Cellulose oxidation on MCC using TEMPO and BAIB.

The complete absence of a carboxylic peak at around 1750 cm^{-1} in the TEMPO/-NaClO spectrum suggests that it might be that the carboxylic groups exists in a different variation then expected (e.g. a carboxylate) and as such has moved in the vibrational spectra and merged with the water peak at 1620 cm^{-1} . This could be examined further by drying the NaClO sample as to remove as much water as

possible. Nevertheless, even if water was completely removed from the sample, the peak intensity of TEMPO/NaClO at 1620 cm^{-1} is still less than the intensity of the peak for the carboxylic groups at 1738 cm^{-1} for TEMPO/BAIB, which indicates that a greater amount of cellulose has been oxidised for the TEMPO/BAIB compared to the TEMPO/NaClO.

Looking at the oxidation of the cellulose pulp using TEMPO/NaClO, no clear carboxyl peak can be seen, see Figure 4.2.

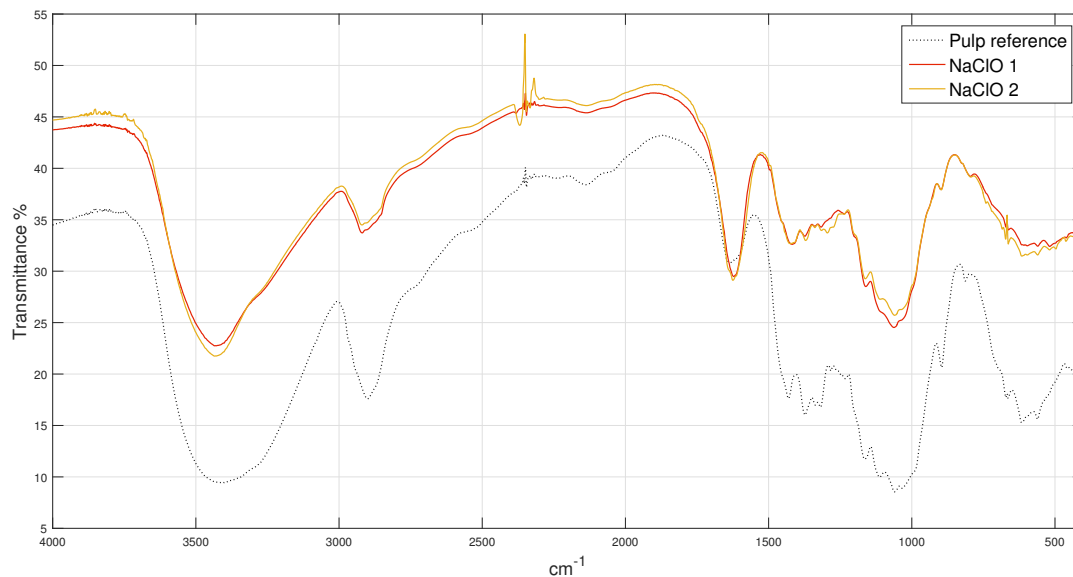


Figure 4.2: FT-IR spectra for cellulose oxidation on pulp using TEMPO and NaClO.

On the other hand, the FT-IR analysis of the oxidised cellulose pulps using BAIB 1, BAIB 2 and BAIB 3 exhibits clear carboxyl peaks at 1738 cm^{-1} for each sample, see Figure 4.3. It is suggested that the amount of TEMPO as well as BAIB greatly affects the level of oxidation.

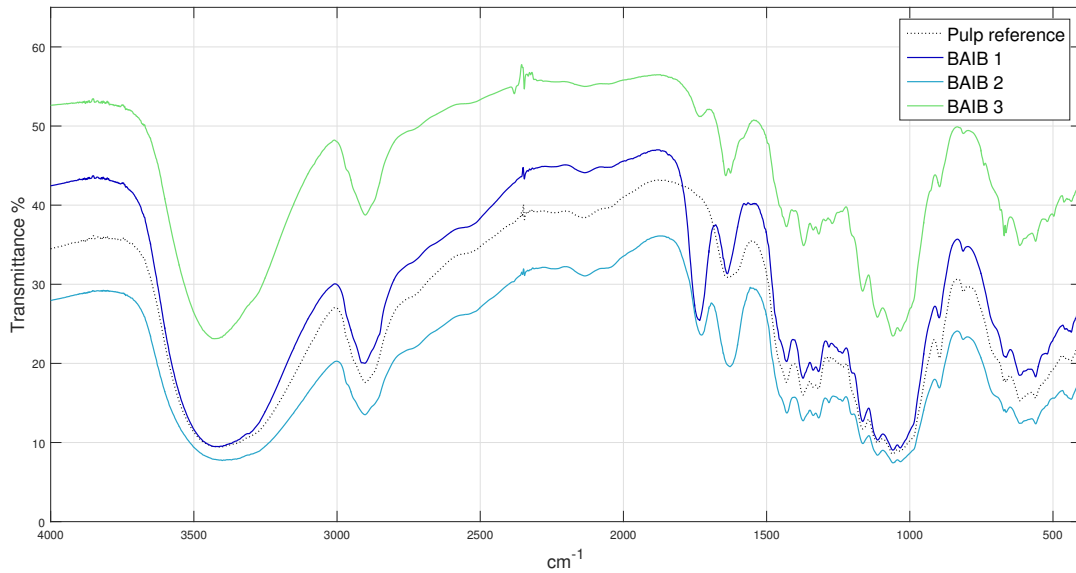


Figure 4.3: FT-IR spectra for cellulose oxidation on pulp using TEMPO and BAIB.

A FT-IR analysis was also done on the reference sheet containing different ratios of additives, which is shown in Figure 4.4.

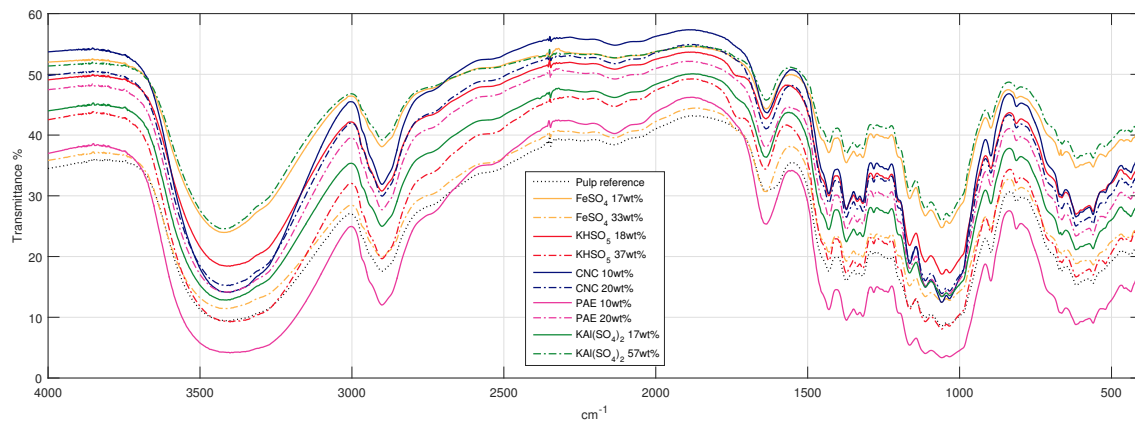


Figure 4.4: Analysis of reference sheets containing additives.

No clear level of oxidation can be seen, however, there is a small deviation to be noted in the samples containing FeSO_4 and KHSO_5 , see Figure 4.5. This suggests increased level of oxidation in samples used with these additives; further analyses would be necessary to confirm this.

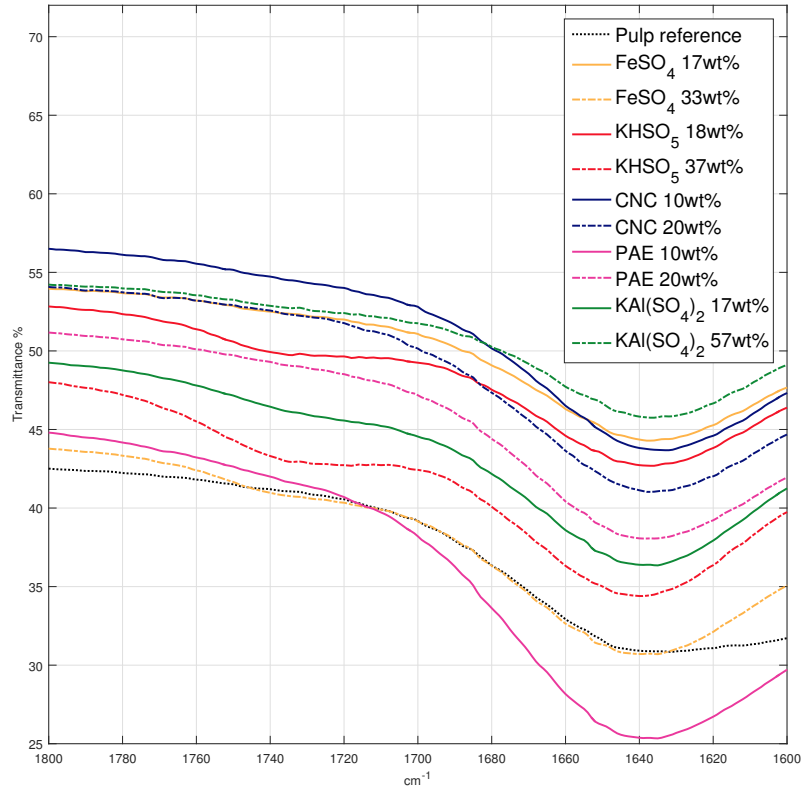


Figure 4.5: Close up of the suggested carboxyl peaks of the additives.

4.2 Zeta-potential

A difference in zeta potential exists between the reference sample of unmodified CNC and the surface modified CNC which confirms the surface modification, see Table 4.1. 4.1.

Table 4.1: Average value of the zeta potential measurements.

Sample	Zeta potential [mV]
Reference CNC	-54.8
Surface modified CNC	-75.3

4.3 WRV

The cellulose samples were dried after centrifugation in room temperature for approximately 24 hours and then oven dried at 105°C for 24 hours. The WRV of

references and different oxidations is given in Figure 4.6. There is a remarkable difference between the WRV of TEMPO/NaClO and TEMPO/BAIB. The TEMPO/BAIB, with its values between 7.9-9.4%, is similar to the reference of 9.0% while the TEMPO/NaClO is about three times higher with values of 29.9-36.9%. According to Saito and Isogai [10], WRV is influenced by the content of fine fibres and degree of fibrillation of the longer fibres.

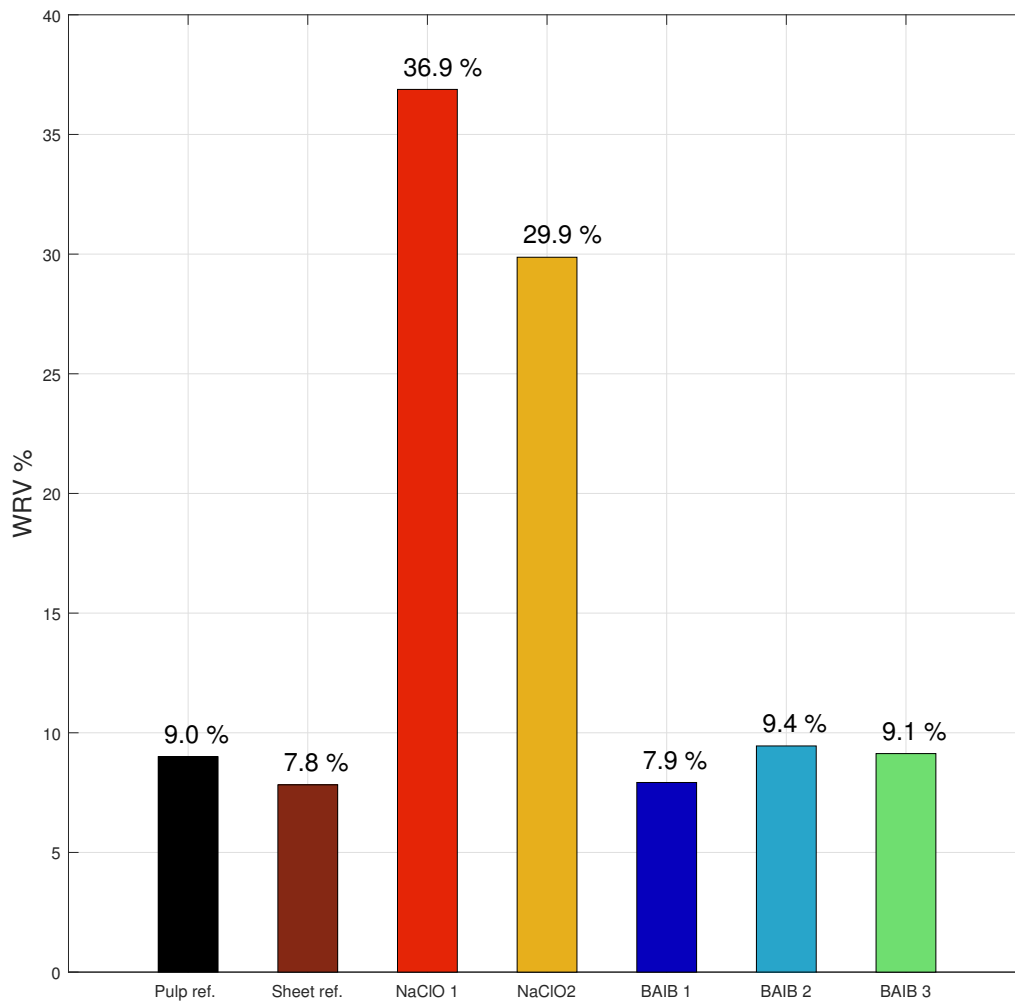


Figure 4.6: Water retention values.

4.4 SEM

Analysis was done on the cellulose pulp reference, NaClO 1 and BAIB 1. The samples was dried in room temperature and then sputtered with a gold layer of 10 nm. The fibres of the cellulose pulp reference looks linear and well separated with the occasional microfibrils protruding from the longer fibres, see Figure 4.7.

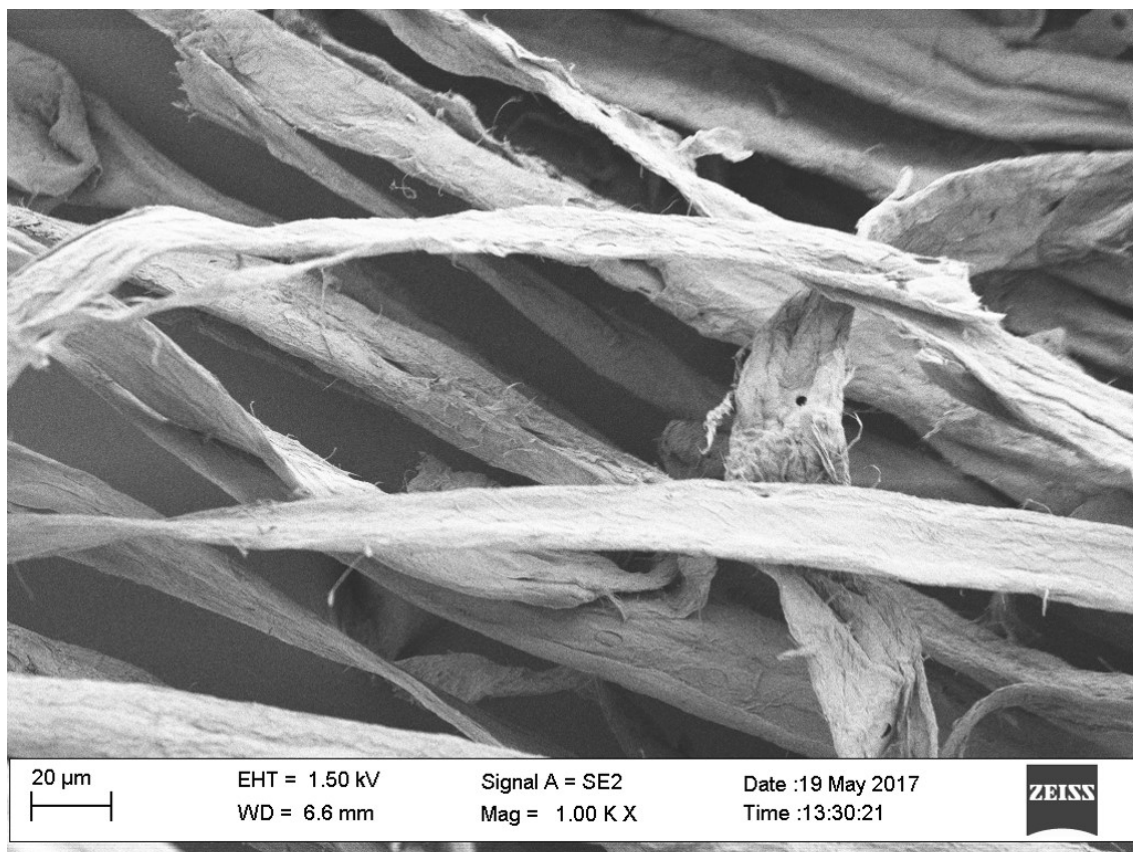


Figure 4.7: Pulp reference.

The fibres oxidised with NaClO 1, which can be seen in Figure 4.8, have a seemingly fused appearance as compared to the reference picture.



Figure 4.8: NaClO 1.

No fibrils can be seen extending from the fibres and the surfaces looks uniform in their appearance.

The surface of the fibres oxidised using BAIB 1, see Figure 4.9, looks ragged and the fibres look in general more crumpled and non-linear than the reference sample.

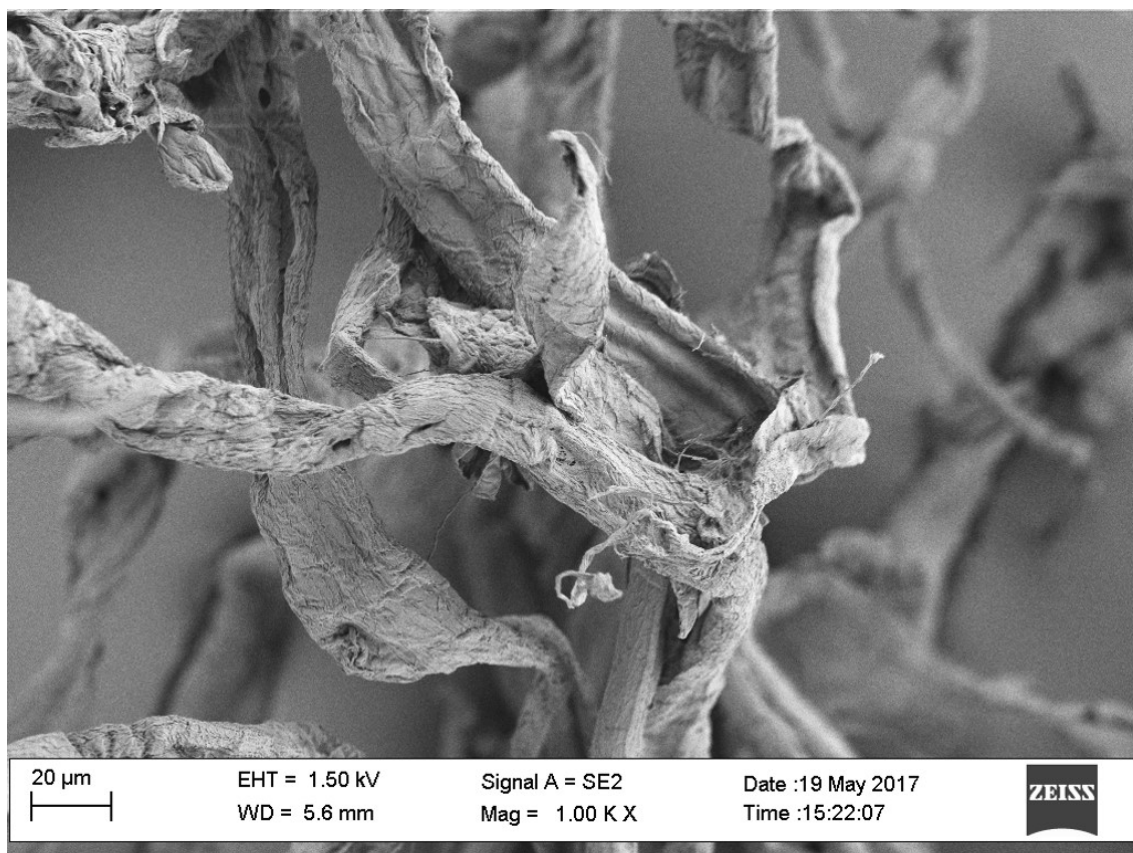


Figure 4.9: BAIB 1.

The difference in fibre structure of both the oxidised cellulose samples as well as the cellulose pulp reference suggests that the oxidation has been on different levels. The NaClO 1 oxidation allowing for water being held at a more in-depth level of the fibre compared to the BAIB 1 in which the oxidation seems to primarily have affected the fibre surface.

4.5 Conductometric titration method

Conductometric titration was used to measure the total acid group content on pulp reference, sheet reference and BAIB 1, see Figure 4.10. The

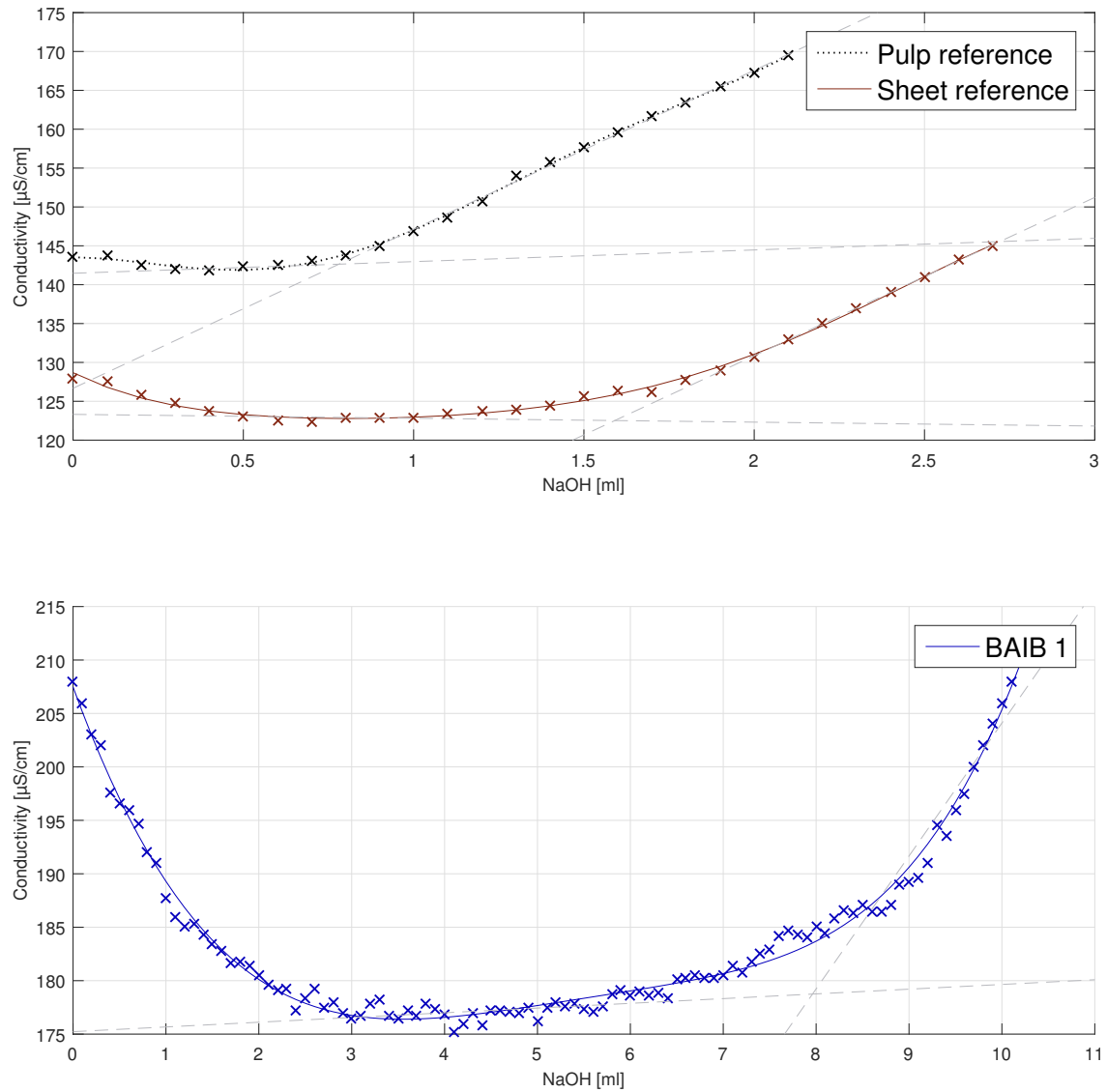


Figure 4.10: Conductometric titration curves.

The acidic group content was calculated using equation 3.1 and is presented in Table 4.2. Phases were visually identified in each graph and data was extrapolated from each phase accordingly in order to estimate the point of each phase change. The total amount of NaOH used for phase 1 and 2 represents the acidic group content of the sample.

Table 4.2: Total acidic group content.

Sample	NaOH [mL]	Acidic group content $\frac{\mu\text{mol}}{\text{gram}}$
Pulp reference	0.78	82
Sheet reference	1.59	287
BAIB 1	7.97	151730

Figure 4.10 and Table 4.2 shows that there is a great increase of acidic groups in the oxidised cellulose which is due to the level of oxidation in the sample. The conductometric titration curves also shows the presence of acidic groups in the sheet reference and as such, the oxidised cellulose in the reference sheet can possibly affect the properties of the hand sheets used for mechanical analysis.

The same conductometric titration method was applied to NaClO 1 but the initial pH at 7-8 was too high to get a representative titration curve.

4.6 Mechanical analysis

For the mechanical analysis there is also a reference for dry pulp and a once wet sample that have been wet and then dried in order to simulate the drying procedure of sheets containing additives.

A general figure of the mechanical data of references and sheet with additives showing sheet density against tensile index can be seen in Figure 4.11. The handsheets shows a decreased density but with a similar tensile index. Handsheets with FeSO_4 and KHSO_5 as additives shows a increased density but a decreased tensile index. Increased tensile index was instead had by handsheets containing PAE and CNC.

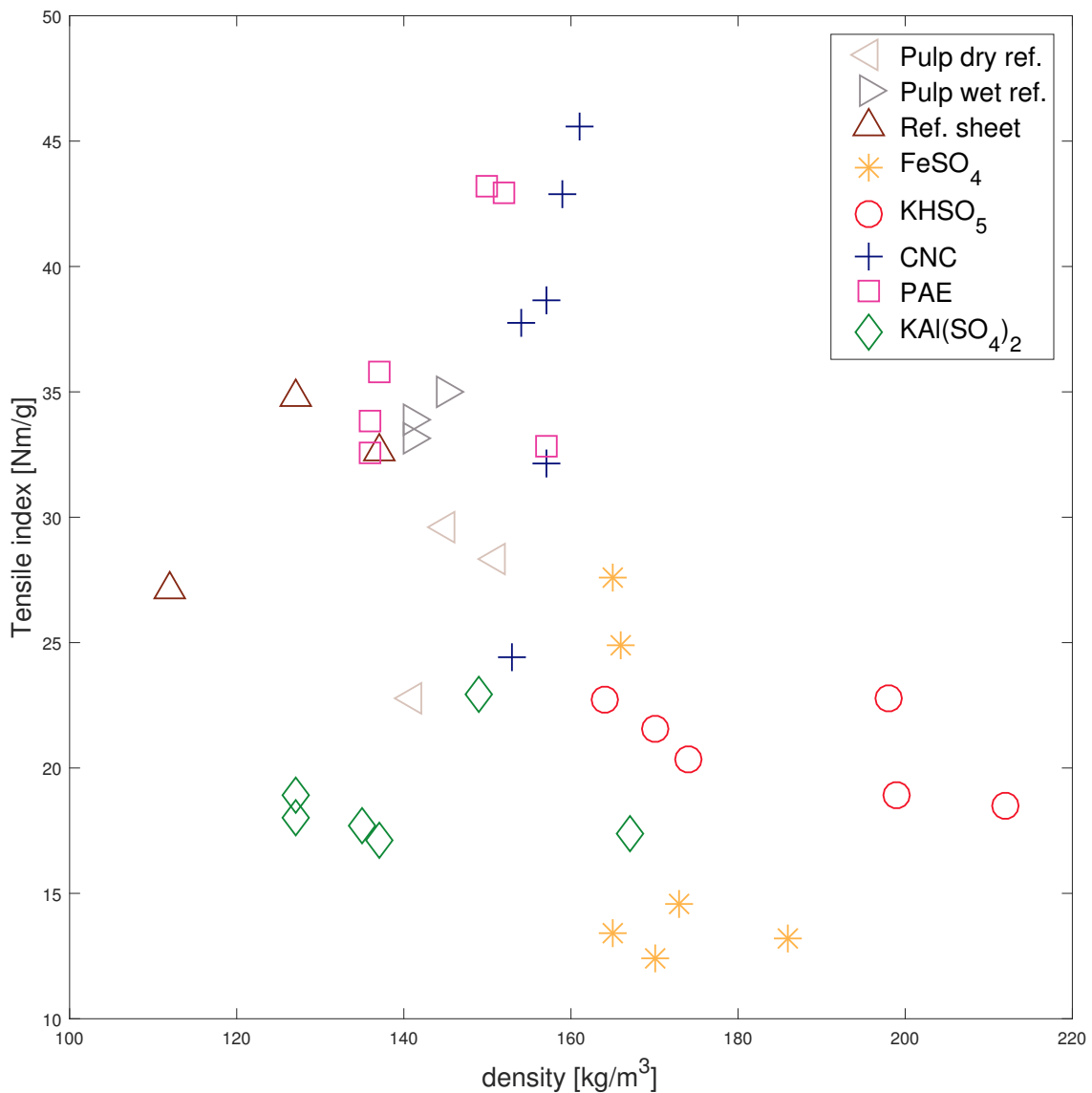


Figure 4.11: Tensile index of reference sheet containing additives.

Handsheets with FeSO_4 and KHSO_5 as additives shows a increased density but a decreased tensile index, see Figure 4.14.

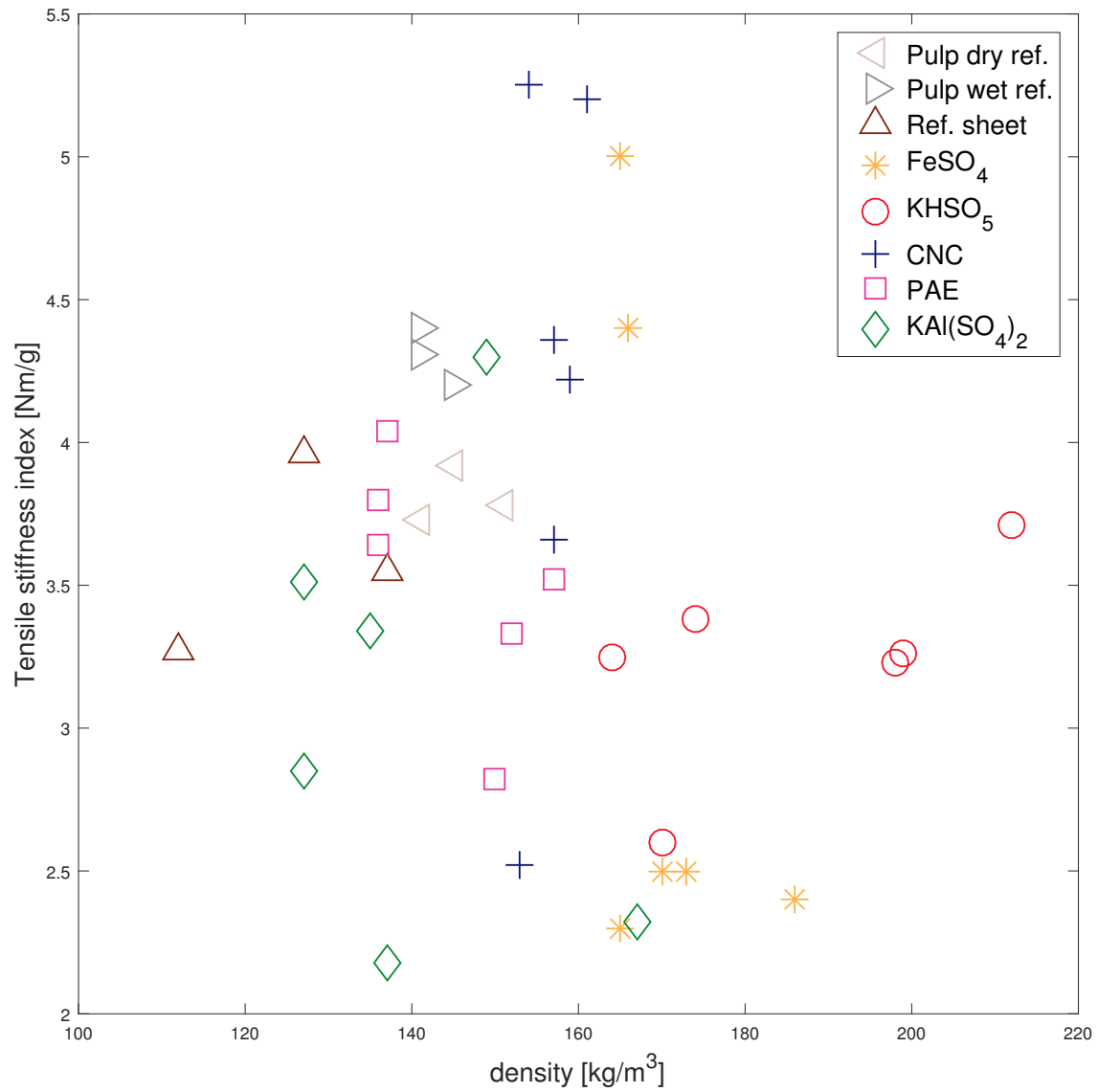


Figure 4.12: Tensile stiffness index of reference sheet containing additives.

Figure 4.13 suggests that a higher weight ratio of FeSO_4 and KHSO_5 gives a higher tensile index. The higher rates for CNC is also shown to increase. Concerning density, it seems like a higher weight ratio for KHSO_5 increases the density as well. The higher rates for CNC is also shown to increase.

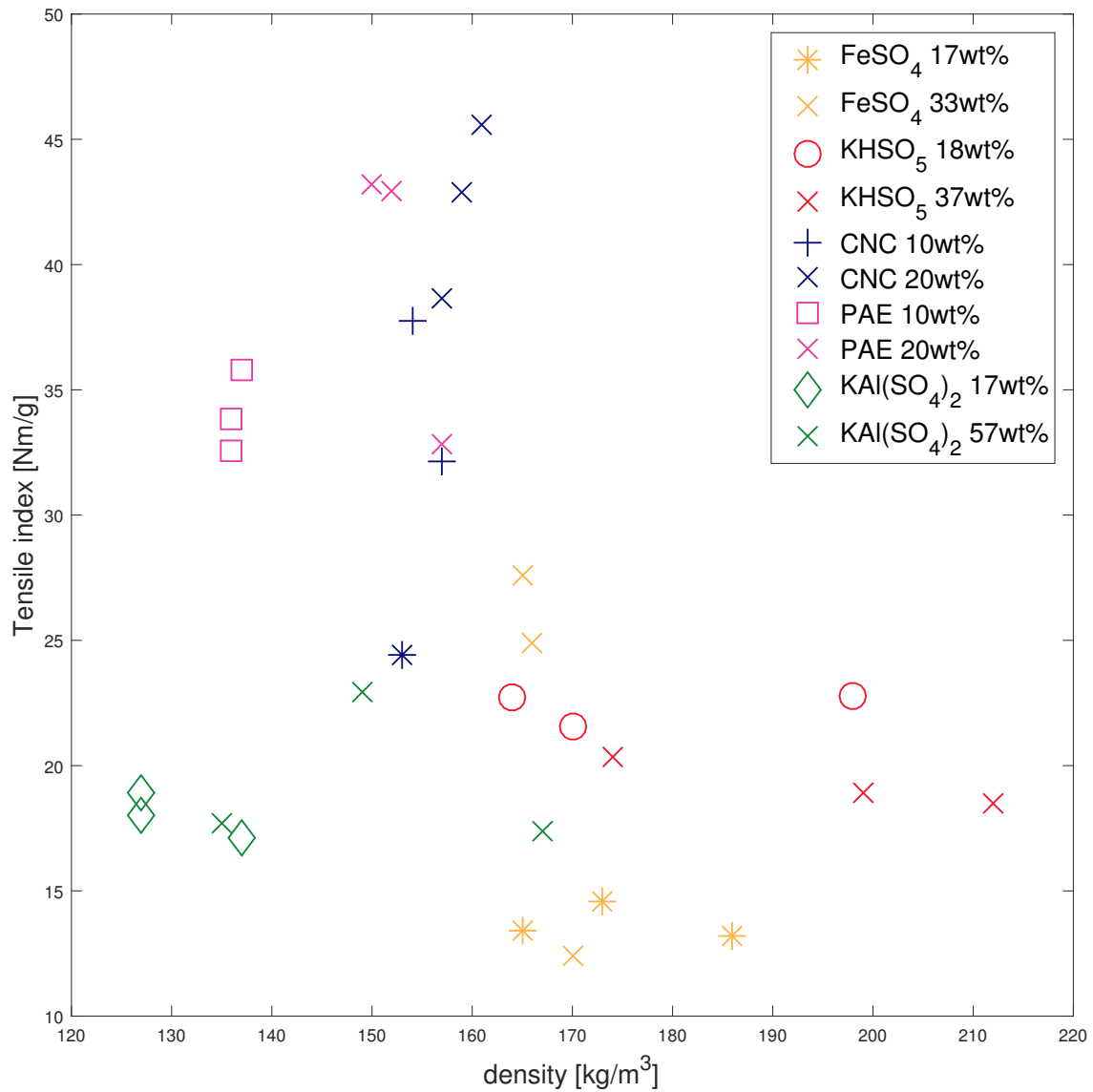


Figure 4.13: Tensile index for the different additive ratios.

It is clear that, the weight ratios in relation to tensile stiffness index, are similar to the tensile index with the exception of FeSO_4 , see Figure 4.14.

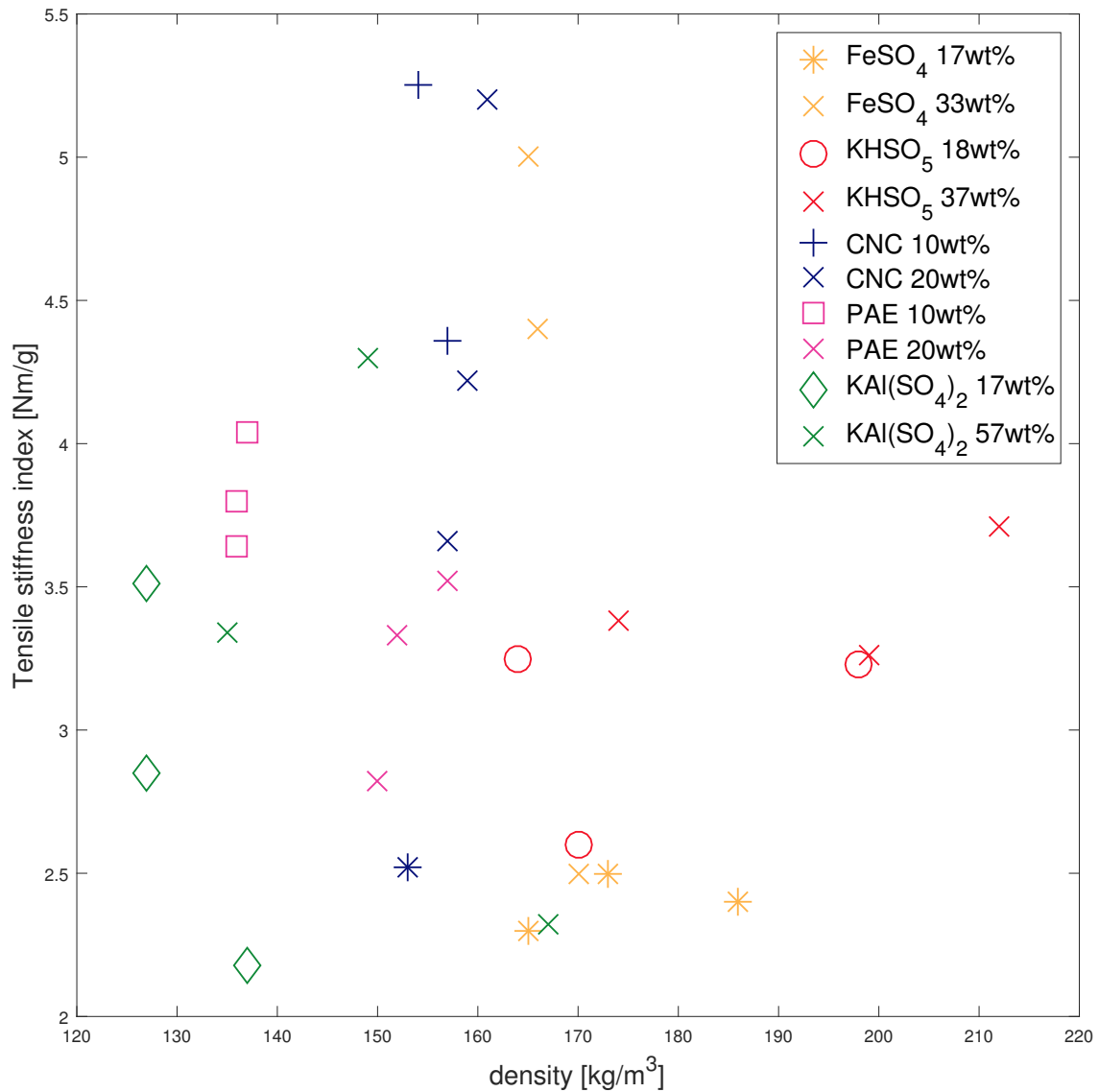


Figure 4.14: Tensile stiffness index for the different additive ratios.

Concerning the mechanical results it can be said that there are some additives that could be interesting to explore further. CNC shows some improvement in the tensile index but the results are not consistent. In comparison to both FeSO_4 and KHSO_5 , they have the largest deviation from the references in aspects of density and that of tensile stiffness index.

5

Conclusion

Cellulose oxidation using TEMPO/BAIB shows that the oxidation is affected by sterical hinderance of the cellulose fibre and that the level of oxidation is greatly affected by the amount of secondary oxidant present during the reaction.

The results reported here suggests that oxidation of cellulose using TEMPO/NaClO affects the cellulose fibre structure differently than oxidation done using TEMPO/BAIB. The SEM analyse suggests a more in depth level of oxidation using TEMPO/NaClO because of the fibres merged appearance which could be due to the fibres ability to hold a lot of water, which is confirmed by the WRV. As such the cellulose fibre structure is greatly affected when said water evaporates. This indicates that oxidation using a TEMPO/NaClO comes with some polymeric degradation which allows the oxidation to happen at microfibril level. Compared to the the TEMPO/BAIB where the FT-IR shows a large presence of carboxylic acid which shows that the level of oxidation can be assumed to be greater, while the SEM-analysis shows that the TEMPO/BAIB oxidised cellulose still regains a lot of its fibre structural integrity which indicates that the oxidation is generally taking place on the surface of the fibre.

The mechanical analysis for the cellulose pulp sheets containing 10% TEMPO/BAIB oxidised cellulose shows an increase of mechanical properties and it implies a density difference in most of the samples containing FeSO_4 and KHSO_5 . This recommends both FeSO_4 and KHSO_5 for further research concerning strength additives in paper sheets.

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A

TEMPO oxidation methods

The oxidations were done using deionised water.

TEMPO-oxidation using NaClO

1 gram cellulose
H₂O
0.016 gram TEMPO 0.1 mmol
0.1 gram NaBr 0.1 mmol
3.7 ml 11-14 wt% NaClO 5.0 mmol
0.1 M HCl
0.5 M NaOH

1. Add 0.016 gram TEMPO and 0.1 gram of NaBr to a minimum of water
2. Add 1 gram of wet cellulose to the TEMPO-solution
3. Adjust pH of NaClO to pH10 using 0.1 M HCl
4. Add NaClO to TEMPO-solution and stir in room temperature
5. Maintain pH10 by adding 0.5M NaOH until no NaOH-consumption is observed
6. Filter and wash cellulose in H₂O

TEMPO-oxidation using BAIB

1 gram cellulose
11.91 gram BAIB
0.47 gram TEMPO 0.1 mmol
CH₃CN-H₂O, acetonitrile, at a 3:1 ratio
(C₂H₅)₂O, diethyl ether
C₂H₆O, ethanol

1. Cellulose was mixed with a minimum of acetonitrile and was chilled to 0°C and stirred using a magnetic stirrer.
2. 11.92 gram of BAIB and 0.47 gram of TEMPO was added.
3. Stirred for 2 hours at 0°C.
4. Stirred for 4 hours at 25°C.
5. The cellulose was washed using a Büchner funnel, first with a small amount of diethyl ether then with ethanol. If a yellow colour remained in the sample, the sample was transferred to an erlenmeyer flask containing ethanol and then

heated slightly to around 65°C while stirred until the cellulose looked white. Then it was transferred to a Büchner funnel in order to remove the ethanol.

B

Making handsheets

The hand sheets made was circle formed and had a radius of 8.5 cm and an approximate weight of $100 \frac{\text{gram}}{\text{cm}^2}$ and a sheet machine.

1. The dry content of the pulp was determined using an IR-scale and used to calculate the correct amount of pulp to be used for each sheet.
2. The pulp was suspended in 1.5 L tap water and then disintegrated using a pulp disintegrator until all fibres was dispersed.



Figure B.1: Fibre dispersed in water.

B. Making handsheets

3. The sheet machine was closed and filled with water to the first line in the container, then the slurry was added and then water was added up to the second line of the container. The water-cellulose mix was stirred using a perforated stirrer that was moved up and down five times and then removed slowly from the suspension.



Figure B.2: Mixing used perforated stirrer.

4. The water was then drained through the sheet and after 3 seconds after the machine was opened and the water was drained during approximately 5 seconds and then waited another additional 5 seconds before the drain was closed.



Figure B.3: Draining of water.



Figure B.4: Sheet drained of water.

B. Making handsheets

5. A standard blotting paper was placed with its smooth side against the sheet, see Figure B.5, and then a weight was placed upon it for 20 seconds, see Figure B.6.

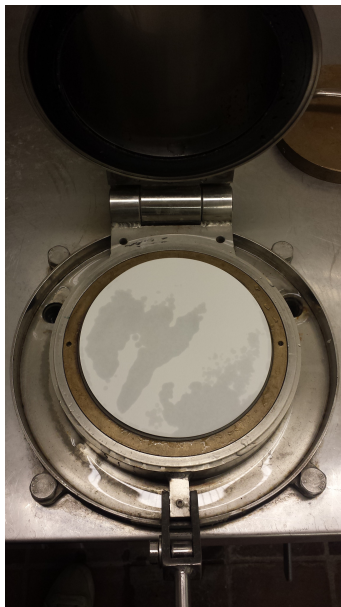


Figure B.5: Sheet with blotting paper.



Figure B.6: Sheet with blotting paper and additional weight.

6. The weight was then removed and a copper couch roll was used to gently roll the blotting paper 3 times and the sheet together with no pressure being applied except from the weight of the roll, see Figure B.7. The roll was then used to roll the blotting paper and sheet off the wire and put to dry in room temperature on a drying disc with the blotting paper facing upwards, see Figure B.8.

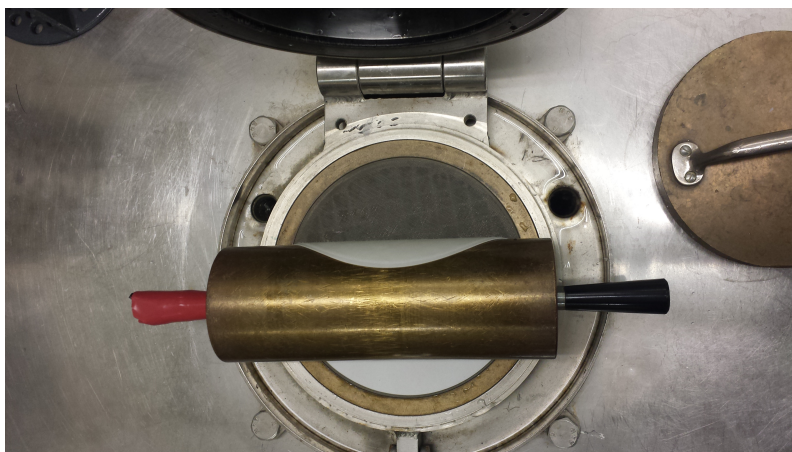


Figure B.7: Rolling off the sheet.

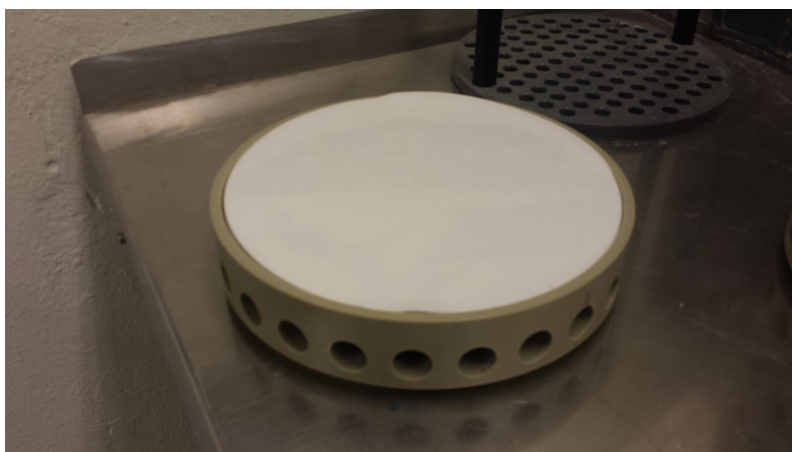


Figure B.8: Drying paper sheet using a drying disc.

C

Weight tables

Table C.1: Additives, molratio, wt% and sample names for paper sheets consisting of 10% oxidised cellulose.

Additive	molar mass	molratio	wt%	sample names
FeSO ₄	278,02	1:0.1	17wt%	A01, A02, A03
FeSO ₄	278,02	1:0.2	33wt%	A04, A05, A06
KHSO ₅	307,38	1:0.1	18wt%	B01, B02, B03
KHSO ₅	307,38	1:0.2	37wt%	B04, B05, B06
CNC	-	-	10wt%	C01, C02, C03
CNC	-	-	20wt%	C04, C05, C06
PAE	-	-	10wt%	D01, D02, D03
PAE	-	-	20wt%	D04, D05, D06
KAl(SO ₄) ₂	474,3884	1:0.1	17wt%	E01, E02, E03
KAl(SO ₄) ₂	474,3884	1:0.2	57wt%	E04, E05, E06

Average weight loss for the procedure of wetting and drying the handmade sheets with an average density of $150 \frac{\text{kg}}{\text{m}^3}$ is estimated to be approximately 3%.

Table C.2: References for the weight loss related to the wetting of paper with an average density of $150 \frac{\text{kg}}{\text{m}^3}$.

Name	Initial weight [gram]	End weight [gram]	Difference [gram]
RW1	1.21	1.18	-0.3
RW2	1.08	1.05	-0.03
RW3	1.1	1.06	-0.04

Table C.3: Sample weight before and after additive for paper sheets consisting of 10% oxidised cellulose with an average density of $150 \frac{\text{kg}}{\text{m}^3}$.

Name	Initial weight [gram]	End weight [gram]	Difference [gram]
A01	1.02	1.09	0.07
A02	1.14	1.21	0.07
A03	1.12	1.19	0.07
A04	1.06	1.17	0.11
A05	1.2	1.34	0.14
A06	1.28	1.36	0.08
B01	1.15	1.29	0.14
B02	1.15	1.27	0.12
B03	1.22	1.4	0.18
B04	1.22	1.65	0.43
B05	1.17	1.47	0.3
B06	1.17	1.67	0.5
C01	1.2	1.25	0.05
C02	1.17	1.22	0.05
C03	1.08	1.12	0.04
C04	1.06	1.18	0.12
C05	1.1	1.21	0.11
C06	1.16	1.27	0.11
D01	1.15	1.14	-0.01
D02	1.2	1.23	0.03
D03	1.2	1.22	0.02
D04	1.25	1.34	0.09
D05	1.25	1.33	0.08
D06	1.15	1.27	0.12
E01	1.09	1.25	0.16
E02	1.16	1.37	0.21
E03	1.1	1.29	0.19
E04	1.09	1.37	0.28
E05	1.1	1.4	0.3
E06	1.18	1.52	0.34

Table C.4: FTIR samples weight before and after additive paper sheets consisting of 10% oxidised cellulose with an average density of $150 \frac{\text{kg}}{\text{m}^3}$.

Name	Initial weight [gram]	End weight [gram]
oxref	0.1	0.098
A10	0.15	0.15
A20	0.2	0.2
B10	0.25	0.25
B20	0.25	0.25
C10	0.26	0.26
C20	0.26	0.26
D10	0.26	0.26
D20	0.22	0.23
E10	0.21	0.21
E20	0.12	0.12

D

Additive application

1. Add about 45-50 ml of tap water was added and then slightly stir for about 1 minute so that the additive is dissolved in the water, for example see Figure D.1.

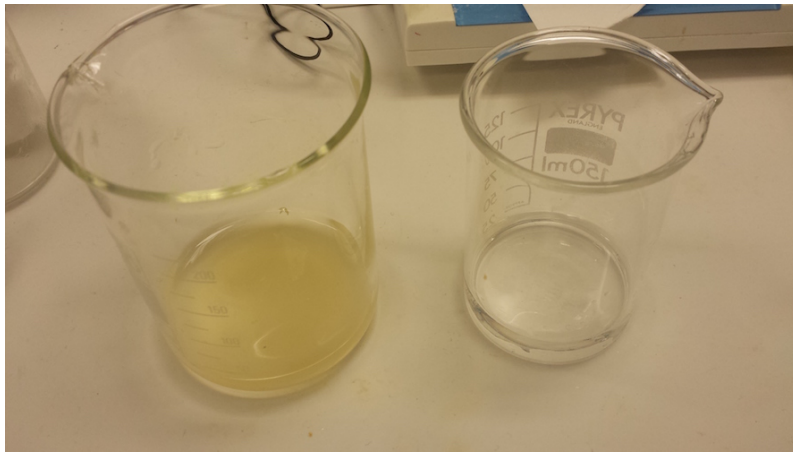


Figure D.1: Additives dissolved in water, FeSO₄ to the left and MPS to the right.

D. Additive application

2. Then add the solution to a container large enough so that the paper sheet can be completely submerged and the total level of liquid in the container should be enough to just submerge the paper sheet. Add additional water if necessary. Setup example can be seen in Figure D.2.

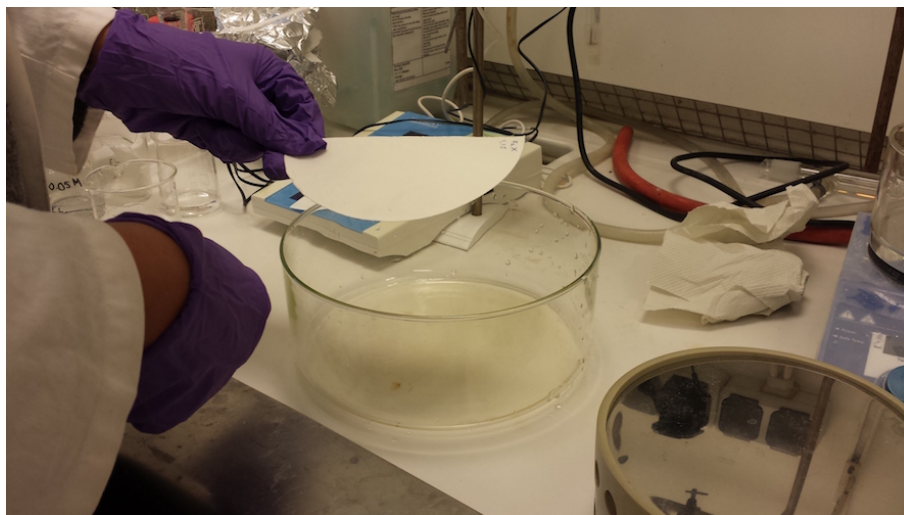


Figure D.2: Setup.

3. Place the sheet carefully in the bath, see Figure D.3.

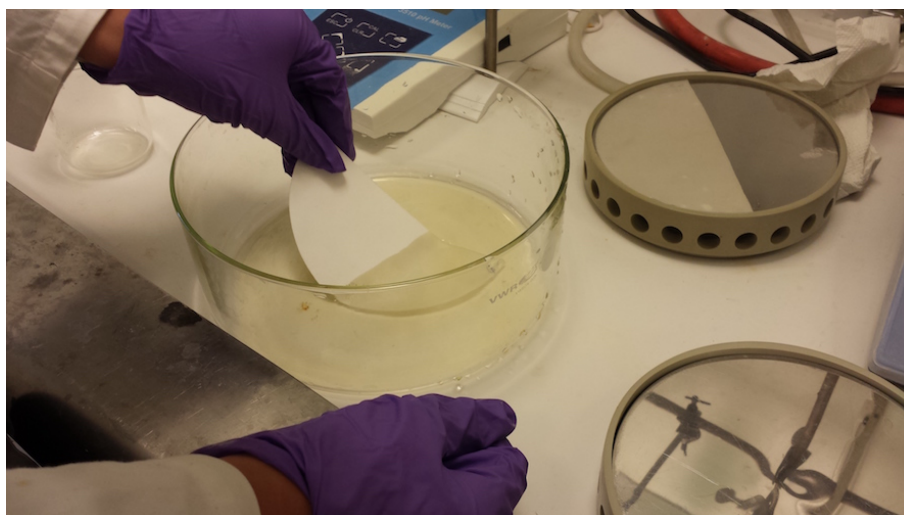


Figure D.3: Sheet submersion.

Fully submerge the sheet in the solution, see Figure D.4. The time of submersion affects the integrity of the sheets fibre structure and as such increases the chance of tearing the sheet when removing it from the solution; and as such, the time of submersion is recommended as short as possible while still allowing for the paper sheet to be soaked, around 10-20 seconds.

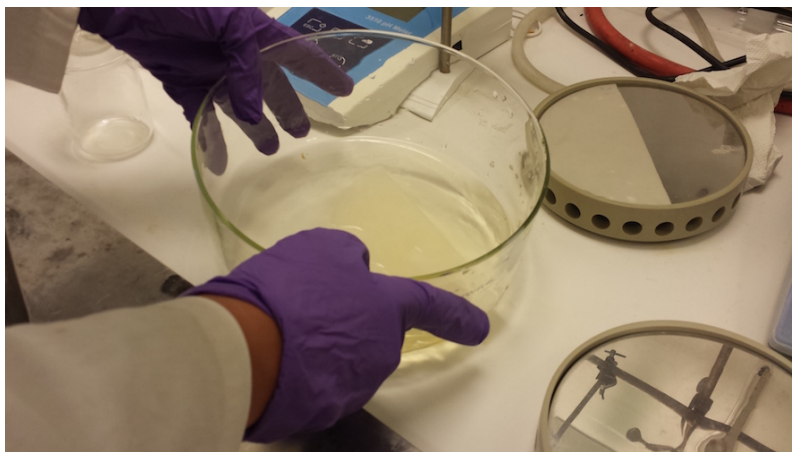


Figure D.4: Sheet submerged in solution.

4. Carefully remove the sheet from the bath as to avoid tearing and stretching and then place it on a drying disc, see Figure D.5.

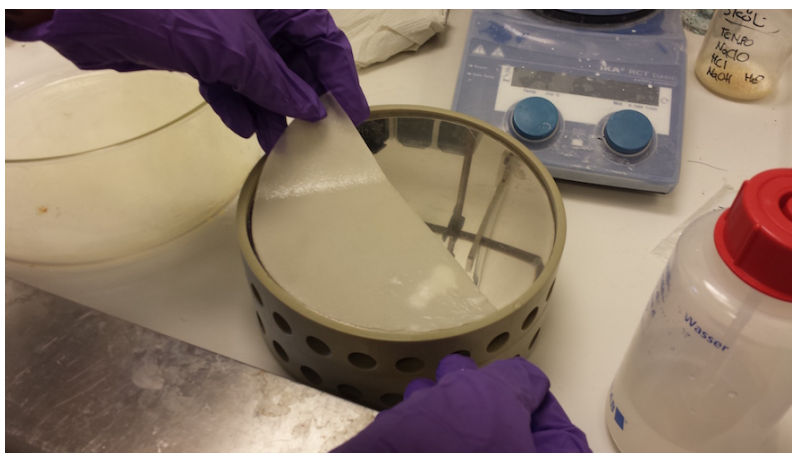


Figure D.5: Wet sheet being placed on metal sheet for drying.

Directly after the putting the first sheet on the dryer, the procedure was repeated for the second sheet of using the same solution and method.