



**Mittuniversitetet**  
MID SWEDEN UNIVERSITY

Thesis for the degree of Doctor of Technology, Sundsvall 2016

## **Mechanical Pulp-Based Nanocellulose**

**Processing and applications relating to paper and paperboard, composite  
films, and foams**

**Sinke Henshaw Osong**

Supervisors:

Prof. Per Engstrand

Dr. Sven Norgren

Department of Chemical Engineering  
Faculty of Science, Technology, and Media  
Mid Sweden University, SE-851 70 Sundsvall, Sweden


ISSN 1652-893X

Mid Sweden University Doctoral Thesis 245

ISBN 978-91-88025-64-7



**FSCN**

PART OF  MID SWEDEN UNIVERSITY

Akademisk avhandling som med tillstånd av Mittuniversitetet i Sundsvall framläggs till offentlig granskning för avläggande av teknologie doktorsexamen i kemiteknik, fredag, 22 april, 2016, klockan 09:15 i sal O102, Mittuniversitetet Sundsvall. Seminariet kommer att hållas på engelska.

## **Mechanical Pulp-Based Nanocellulose**

**Processing and applications relating to paper and paperboard, composite films, and foams**

**Sinke Henshaw Osong**

© Sinke Henshaw Osong, 2016

Department of Chemical Engineering, Faculty of Science, Technology, and Media  
Mid Sweden University, SE-851 70 Sundsvall  
Sweden

Telephone: +46 (0)771-975 000

Printed by Service and Maintenance Office, Mid Sweden University, Sundsvall,  
Sweden, 2016

## **Mechanical Pulp-Based Nanocellulose**

**Processing and applications relating to paper and paperboard, composite films, and foams**

**Sinke Henshaw Osong**

Department of Chemical Engineering, Faculty of Science, Technology, and Media  
Mid Sweden University, SE-851 70 Sundsvall, Sweden  
ISSN 1652-893X, Mid Sweden University Doctoral Thesis 245;  
ISBN 978-91-88025-64-7

### **ABSTRACT**

This thesis deals with processing of nanocellulose originating from pulps, with focus on mechanical pulp fibres and fines fractions. The nanocellulose materials produced within this research project were tested for different purposes ranging from strength additives in paper and paperboard products, via composite films to foam materials. TAPPI (Technical Association of Pulp & Paper Industry) has recently suggested a standard terminology and nomenclature for nanocellulose materials (see paper I). In spite of that we have decided to use the terms nanoligno-cellulose (NLC), microfibrillated cellulose (MFC), nanofibrillated cellulose (NFC) and nanocellulose (NC) in this thesis. It is well-known that mainly chemical pulps are used as starting material in nanocellulose production. However, chemical pulps as bleached sulphite and bleached kraft are quite expensive. One more cost-effective alternative can be to use fibres or fines fractions from thermo-mechanical pulp (TMP) and chemi-thermomechanical pulp (CTMP).

In paper II-IV, fractionation has been used to obtain fines fractions that can easily be mechanically treated using homogenisation. The idea with this study was to investigate the possibility to use fractions of low quality materials from fines fractions for the production of nanocellulose. The integration of a nanocellulose unit process in a high-yield pulping production line has a potential to become a future way to improve the quality level of traditional products such as paper and paperboard grades.

Paper III describes how to utilise the crill measurement technique as a tool for qualitative estimation of the amount of micro- and nano-material produced in a certain process. The crill values of TMP- and CTMP-based nanocelluloses were

measured as a function of the homogenisation time. Results showed that the crill values of both TMP-NLC and CTMP-NLC correlated with the homogenisation time. In Paper V pretreating methods, hydrogen peroxide and TEMPO are evaluated. Crill measurement showed that hydrogen peroxide pretreatment (1% and 4%) and mechanical treatment time did not improve fibrillation efficiency as much as expected. However, for TEMPO-oxidised nanocelluloses, the crill value significantly increased with both the TEMPO chemical treatment and mechanical treatment time. In paper V-VII TEMPO-mediated oxidation systems (TEMPO/NaBr/NaClO) are applied to these fibres (CTMP and Sulphite pulp) in order to swell them so that it becomes easy to disrupt the fibres into nanofibres with mechanical treatment.

The demand for paperboard and other packaging materials are steadily increasing. Paper strength properties are crucial when the paperboard is to withstand high load. A solution that are investigated in papers IV and VI, is to use MFC as an alternative paper strength additive in papermaking. However, if one wish to target extremely higher strength improvement results, particularly for packaging paperboards, then it would be fair to use MFC or cationic starch (CS). In paper VI CS or TEMPO-based MFC was used to improve the strength properties of CTMP-based paperboard products. Results here indicate significant strength improvement with the use of different levels of CS (i.e., 20 and 10 kg t<sup>-1</sup>) and 5% MFC. The strengthening impact of 5% MFC was approximately equal to that of 10 kg t<sup>-1</sup> of CS.

In paper VII, NFC and nanographite (NG) was used when producing composite films with enhanced sheet-resistance and mechanical properties. The films produced being quite stable, flexible, and bendable. Realising this concept of NFC-NG composite film would create new possibilities for technological advancement in the area of high-yield pulp technology. Finally, in paper VIII, a new processing method for nanocellulose is introduced where an organic acid (i.e., formic acid) is used. This eco-friendly approach has shown to be successful, a nanocellulose with a uniform size distribution has been produced.

**Keywords:** *mechanical pulp, thermo-mechanical pulp, chemi-thermomechanical pulp, fractionation, fines, homogenisation, nanocellulose, nano-ligno-cellulose, microfibrillated cellulose, nanofibrillated cellulose, paper, strength properties, crill, TEMPO, nanographite (NG), composite films*

## SAMMANDRAG

Avhandlingen presenterar arbetet med att tillverka nanocellulosa med till största delen mekaniska massor som ursprungsmaterial. Framtagna nanocellulosor provades med ett antal olika metoder för att utvärdera vilka användningsområden som kan vara lämpliga som t.ex. pappersadditiv, kompositfilmer eller skummaterial. Trots att TAPPI (Technical Association of Pulp & Paper Industry) nyligen har föreslagit en standardisering av terminologi samt nomenklatur inom nanocellulosa området har vi valt att använda oss av följande; nano-ligno-cellulosa (NLC), microfibrillerad cellulosa (MFC), nanofibrillerad cellulosa (NFC) och nanocellulosa (NC). Det är välkänt att de flesta som producerar nanocellulosa använder sig av kemisk massa. Ett kostnadseffektivt alternativ kan vara att använda fibrer eller fines från termo mekanisk massa (TMP) eller från kemi-termo mekanisk massa (CTMP). Hypotesen är att det i dessa processer finns fibrer/fines som ej bidrar till en bra slutprodukt och de kan istället fraktioneras och användas som startmaterial vid tillverkning av NLC eller NC.

I artikel II-IV har fraktionering använts för att ta fram fraktioner som är lämpade för mekanisk bearbetning i en homogenisator. Idén är att använda lågkvalité fibrer från mekaniska massa processer och att förädla dem med mekanisk bearbetning i en homogenisator. Detta processteg kan vara möjligt att implementera i en befintlig produktionslinje.

Artikel III beskriver hur crillmätningar kan användas som ett verktyg för kvalitativa bedömningar av mängden micro/nano -material som produceras i ett process steg. Crillvärden mättes på nanocellulosor framtagna från TMP samt CTMP massor som en funktion mot bearbetningstid i homogenisator. Antalet Crill från både TMP-NLC och CTMP-NLC korrelerade väl med homogeiseringstid. Crill metodiken beskriven i artikel III användes i artikel V, detta för att utvärdera fibrilleringsgrad på framtagna nanocellulosor där väteperoxid eller TEMPO använts för att förbehandla massor innan den mekaniska bearbetningen med homogenisator. Crillanalysen visade att behandling med väteperoxid inte var så effektivt för att öka fibrilleringsgraden. Däremot ökade fibrilleringsgraden rejält för de prover där TEMPO använts.

Förbrukningen av kartong och förpackningspapper ökar stadigt. När utveckling av dessa produkter sker är pappersstyrke egenskaper viktiga att ta hänsyn till. Ett alternativ till att nå högre styrkor än traditionellt är att använda MFC som ett styrkeadditiv. Men för att nå ännu högre styrkenivåer är det relevant att

utvärdera tillsatser av MFC samt stärkelse med olika doseringar. I artikel VI studerades också tillsatser av stärkelse och TEMPO behandlad MFC för att förbättra pappersstyrkor på CTMP baserade kartongprodukter. Kombinationen av tillsatt stärkelse och MFC gav signifikant styrkeökning.

Artikel VII avhandlar framställande av kompositfilmer med höga styrkeegenskaper samt god resistans. Filmerna tillverkades av NFC och nanogرافit (NG). Framtagna filmer var stabila, flexibla samt böjbara. Tillverkning av kompositfilmer kan skapa nya möjligheter användning av hög utbytesmassor. Slutligen i artikel VIII beskrivs en ny miljövänlig förbehandlingsmetod med Myrsyra. Användning av Myrsyra metoden vid förbehandling före mekanisk behandling har visat sig ge en nanocellulosa med en jämn storleksfördelning.

**Nyckelord:** mekanisk massa, termomekanisk massa, kemitermomekanisk massa, fraktionering, homogenisering, nanocellulosa, nano-ligno-cellulosa, microfibrillerad cellulosa, nanofibrillerad cellulosa, papper, styrkeegenskaper, kryll, TEMPO, nanogرافit, kompositfilmer

## ACKNOWLEDGEMENTS

First, I would like to thank **God for God**. I must pay special tribute to my supervisors, **Prof. Per Engstrand** and **Dr. Sven Norgren**, whose teaching and coaching has been vital to my career development. You have given me the freedom, confidence, and time needed to grow as a scholar. Your valuable criticism and constructive input have enabled me to reach my current level. My dream of earning a Ph.D. would not have been achieved if it had not been for you, my supervisors. I owe you more than I can say.

As for all my **graduate course teachers**, in and out of Sweden, past and present, I would like to thank you all for a staggering level of professionalism: learning from you helped me reach the full stage to receiving a Ph.D.

To our able Centre Administrator at FSCN, **Anna Haeggström**, thanks so much for facilitating my travel arrangements and hotel reservations: you are indeed an asset to the research centre – continue your good work as always. I greatly appreciate the support you have provided over the years. To all my colleagues at FSCN-Mid Sweden University, past and present; Britta Andres, Majid Alimadadi, Alireza Eivazihollagh, Jiayi Yang, Ran Duan, Darius Zasadowski, Susanne Boija, and all those not listed here because of space limitations, you all are wonderful people, working in various respected research groups in which the learning and working atmosphere is graced with peace, joy, and happiness. **Karin Axell** and **Fiona Wait** (linguistic review), **Dr. Olof Björkqvist**, and **Prof. Myat Htun** (technical review) are specially acknowledged for the review of this thesis.

It would be a major oversight if I were to omit the name of our machinery guru, **Staffan Nyström**, working at the Material Testing building (“T-house”). Staffan has been the brains behind the design and maintenance of the T-house homogenising equipment that I used in my research. Words alone are unable to do justice to your good work – thanks so much, Staffan. **Andrew Butterworth**, working with the publishing group at Mid Sweden University Library, is gratefully acknowledged for the patent and article search related to microfibrillated cellulose.

The **European Union (EU)**, **Länsstyrelsen Västernorrland**, **KK Foundation**, and **Mid Sweden University** are gratefully acknowledged for their financial support. My thanks are also due to members of the **SCA R&D Centre** in Sundsvall.

**Bryan Dyson**, the former CEO of Coca Cola, once said, “Imagine life as a game in which you are juggling some five balls in the air. They are WORK, FAMILY, HEALTH, FRIENDS, and SPIRIT, and you’re keeping all of these in the air. You will soon understand that WORK is a rubber ball. If you drop it, it will bounce back. However, the other four balls – FAMILY, HEALTH, FRIENDS, and SPIRIT – are made of glass. If you drop one of these, they will be irrevocably scuffed, marked, nicked, damaged, or even shattered. They will never be the same. You must understand that”. The message as I see it is that one must work efficiently during office hours, spend enough time with one’s family and friends, and get proper rest.

I would like to say a big thank you to **Hans Höglund** and **Annette Höglund** for their unconditional support, kindness, and generosity. Our celebrations of midsummer’s eve (2014 and 2015), table tennis games, and great dinner conversations at Matfors are still fresh in my memory.

Accordingly, thanks to all my friends, in Sweden, Cameroon, and around the globe, for your support and encouragement, especially at difficult moments. I would also like to thank my parents, **Osong Vincent** and **Etoh Odilia**, for providing me with the fundamental guidance and support that enabled me to embark on many years of university education. They helped me understand the value of hard work, determination, and education. Finally, I want to use this medium to say *merci beaucoup* to my **wife Bam Christelle**, and my **son Dylan Sinke Jr.**: words cannot express my joy and happiness, and I am grateful that you have always stood by me through both thick and thin times.



## TABLE OF CONTENTS

ABSTRACT	II
SAMMANDRAG	IV
ACKNOWLEDGEMENTS	VI
LIST OF PAPERS	X
AUTHOR'S CONTRIBUTIONS TO THE PAPERS	XII
RELATED MATERIAL	XIII
ABBREVIATIONS AND ACRONYMS	XV
<b>1. INTRODUCTION</b>	<b>1</b>
1.1. MOTIVATION	3
1.2. BACKGROUND	4
1.3. MECHANICAL PULPING	5
1.4. RESEARCH OBJECTIVES	7
1.5. RESEARCH HYPOTHESIS	8
1.6. THESIS OUTLINE	9
<b>2. LITERATURE REVIEW</b>	<b>11</b>
2.1. NANOCELLULOSE	11
2.2. MECHANICAL TREATMENT OF PULP FIBRES TO FORM NANOCELLULOSE	20
2.2.1. <i>Homogeniser</i>	20
2.2.2. <i>Micro-fluidiser and micro-grinder</i>	21
2.2.3. <i>Cryo-crushing and super-grinder</i>	22
2.3. PRETREATMENT STRATEGIES	23
2.3.1. <i>Enzymatic pretreatment</i>	24
2.3.2. <i>Chemical pretreatment (TEMPO-mediated oxidation)</i>	25
2.4. ENERGY CONSUMPTION DURING NANOCELLULOSE PROCESSING	26
2.5. NANOCELLULOSE CHARACTERISATION	28
2.5.1. <i>Particle morphology</i>	28
2.5.2. <i>Atomic force microscopy (AFM)</i>	28
2.5.3. <i>Scanning electron microscopy (SEM)</i>	29
2.5.4. <i>Transmission electron microscopy (TEM)</i>	30
2.5.5. <i>Light microscopy</i>	31
2.6. NANOCELLULOSE AS A STRENGTH ADDITIVE IN PAPERMAKING	31
2.7. NANOCELLULOSE IN COMPOSITE FILMS	34
2.8. MARKET POTENTIAL OF NANOCELLULOSE AND PILOT PLANT FACILITIES	35
<b>3. MATERIALS AND METHODS</b>	<b>39</b>

3.1.	PULPS	40
3.2.	HOMOGENISER (PAPERS II–IV)	40
3.3.	PULP FRACTIONATION	41
3.3.1.	<i>Bauer-McNett classifier (BMcN) (paper II)</i>	42
3.3.2.	<i>Britt Dynamic Drainage Jar (BDDJ) fractionation (papers II–V)</i>	43
3.4.	FIBRELAB ANALYZER (PAPER II)	43
3.5.	MICROSCOPY TECHNIQUES	44
3.5.1.	<i>Light microscopy (paper II)</i>	44
3.5.2.	<i>Atomic force microscopy (AFM) (paper II)</i>	44
3.5.3.	<i>Scanning electron microscopy (SEM) (paper II)</i>	44
3.6.	RHEOLOGICAL PROPERTIES (PAPER II)	44
3.7.	CRILL INSTRUMENT (PAPERS III AND V)	45
3.8.	RAPID KÖTHEN SHEET FORMER (PAPERS IV AND VI)	46
3.9.	PULPS FOR CRILL SECTION (PAPER V)	47
3.10.	PULP WASHING (PAPER V)	47
3.11.	WING MILL REFINER (PAPER V)	47
3.12.	TRANSMISSION ELECTRON MICROSCOPY (TEM) (PAPER V)	48
3.13.	NFC PROCESSING USING THE TEMPO METHOD	48
3.14.	PREPARATION OF NANOGRAPHITE (PAPER VII)	50
3.15.	FILM CASTING (PAPER VII)	50
3.16.	SHEET RESISTANCE MEASUREMENTS (PAPER VII)	50
3.17.	NFC-NG MECHANICAL PROPERTIES (PAPER VII)	50
<b>4.</b>	<b>RESULTS AND DISCUSSION</b>	<b>51</b>
4.1.	SUMMARY OF APPENDED PAPERS	51
4.2.	FIBRE LENGTH DISTRIBUTION (PAPER II)	54
4.3.	MICROSCOPY (PAPER II)	56
4.4.	RHEOLOGY (PAPER II)	57
4.5.	CRILL (PAPER III)	58
4.6.	NANOCELLULOSE AS A STRENGTH ADDITIVE IN PAPER	60
4.7.	CRILL AS A QUALITATIVE METHOD TO CHARACTERISE NANOCELLULOSE	65
4.8.	NFC-NG COMPOSITE FILM (PAPER VII)	72
4.9.	ECO-FRIENDLY NANOCELLULOSE PROCESSING (PAPER VIII)	76
<b>5.</b>	<b>CONCLUSIONS</b>	<b>79</b>
<b>6.</b>	<b>RECOMMENDATIONS</b>	<b>81</b>
<b>7.</b>	<b>REFERENCES</b>	<b>82</b>

## LIST OF PAPERS

This thesis is mainly based on the following eight papers, herein referred to by their Roman numerals:

- |           |  |
|-----------|--|
| Paper I   | <b>Processing of wood-based microfibrillated cellulose and nanofibrillated cellulose, and applications relating to papermaking: a review</b><br><u>Osong, S. H.</u> , Norgren, S. & Engstrand, P.<br><i>Cellulose</i> , 2016, 23, 93–123     |
| Paper II  | <b>An approach to produce nano-ligno-cellulose from mechanical pulp fine materials</b><br><u>Osong, S. H.</u> , Norgren, S. & Engstrand, P.<br><i>Nordic Pulp and Paper Research Journal</i> , 2013, 28(4), 472– 479                         |
| Paper III | <b>Crill: a novel technique to characterize nano-ligno-cellulose</b><br><u>Osong, S. H.</u> , Norgren, S., Engstrand, P., Lundberg, M. & Hansen, P.<br><i>Nordic Pulp and Paper Research Journal</i> , 2014, 29(2), 190–194                  |
| Paper IV  | <b>Paper strength improvement by inclusion of nano-ligno-cellulose to CTMP</b><br><u>Osong, S. H.</u> , Norgren, S. & Engstrand, P.<br><i>Nordic Pulp and Paper Research Journal</i> , 2014, 29(2), 309–316                                  |
| Paper V   | <b>Qualitative evaluation of microfibrillated cellulose using the crill method and some aspects of microscopy</b><br><u>Osong, S. H.</u> , Norgren, S., Engstrand, P., Lundberg, M., Reza, M., & Tapani, V.<br>Submitted to <i>Cellulose</i> |
| Paper VI  | <b>The use of cationic starch and microfibrillated cellulose to improve strength properties of CTMP-based paperboard</b><br><u>Osong, S. H.</u> , Norgren, S., Engstrand, P., & Pettersson, G.<br><i>Manuscript</i>                          |

- Paper VII      **Nanofibrillated cellulose/nanographite composite films**  
Osong, S.H., Dahlström, C., Forsberg, S., Andres, B., Engstrand,  
P., Norgren, S., & Engström, A.-C.  
Submitted to *Cellulose*
- Paper VIII      **Eco-friendly design for scalable direct fabrication of  
nanocellulose**  
Afewerki, S., Alimohammadzadeh, R., Osong, S. H., Tai, C-W.,  
Engstrand, P., & Cordova, A.  
*Manuscript*

Paper I is reprinted with permission of Springer.

## **AUTHOR'S CONTRIBUTIONS TO THE PAPERS**

The author's contributions to the papers appended to this thesis are as follows:

Paper I	Principal author: performed literature review and wrote the paper
Paper II	Principal author: performed experimental work, interpreted results, and wrote the paper
Paper III	Principal author: performed experimental work, interpreted results, and wrote the paper; the crill measurements were performed by Mathias Lundberg (PulpEye), and part of the introductory section was written by Peter Hansen (Innventia AB)
Paper IV	Principal author: performed experimental work, interpreted results, and wrote the paper
Paper V	Principal author: performed all experimental work, except for acquiring the SEM images, and wrote the paper
Paper VI	Principal author: planned and performed all experimental work, interpreted results, and wrote the paper
Paper VII	Principal author: planned the experiment with Sven Forsberg, performed all the experimental work, except for preparing the nanographite and acquiring the SEM images, and wrote the paper
Paper VIII	Co-author: planned the experiment with Prof. Armando Cordova and Dr. Samson Afewerki, mechanically processed the nanocellulose, and produced the 3D-foam structure of freeze-dried nanocellulose



## RELATED MATERIAL

The following related material has been published and is referred to in this thesis:

### **A new concept to produce nano-ligno-cellulose materials by means of high-pressure homogenisation**

Osong, S. H., Norgren, S., & Engstrand, P.

Oral Presentation: 3rd International Cellulose Conference (ICC 2012), 10–12 October 2012, Sapporo, Japan

### **New products based on mechanical pulps: nano-ligno-cellulose (NLC)**

Osong, S. H., Norgren, S., & Engstrand, P.

Oral Presentation: 8th Fundamental Mechanical Pulp Research Seminar (FMPRS), 29 Jan 2013, Åre, Sweden

### **Mechanical properties of high-yield pulp handsheets, as affected by blends of nano-ligno-cellulose**

Osong, S. H., Norgren, S., & Engstrand, P.

Poster: 2013 TAPPI International Conference on Nanotechnology for Renewable Materials, 24–27 June 2013, KTH Royal Institute of Technology, Stockholm, Sweden

### **Nano-ligno-cellulose as strength enhancer in handsheets**

Osong, S. H., Norgren, S., & Engstrand, P.

Poster: Marcus Wallenberg Prize (MWP) 2013 – Young Researchers, 23–24 September 2013, Stockholm, Sweden

### **Technical problems with homogenising machines when producing mechanical pulp-based NLC**

Osong, S. H., Norgren, S., & Engstrand, P.

Oral Presentation: ERGS Technical Meeting, 31 May–1 June 2014, Vierumäki, Finland

### **Development of nano-ligno-cellulose produced from mechanical pulp**

Osong, S. H., Norgren, S., & Engstrand, P.

Oral Presentation: International Mechanical Pulping Conference (IMPC), 2–5 June 2014, Helsinki, Finland

**Recent developments in nano-ligno-cellulose production and the crill characterization technique**

Osong, S. H., Norgren, S., & Engstrand, P.

Oral Presentation: TAPPI International Conference on Nanotechnology for Renewable Materials, 23–26 June 2014, Vancouver, Canada

**Development of nano-ligno-cellulose produced from mechanical pulp**

Osong, S.H.

Oral Presentation: EFPRO-CEPI Seminar and CEPI European Paper Week, 25–27 Nov 2014, Thon Hotel EU, Brussels, Belgium

**Development of CTMP-based nanofibrillated cellulose/nanographite composites for paper applications**

Osong, S.H., Dahlström, C., Forsberg, S., Andres, B., Engstrand, P. Norgren, S., & Engström, A.-C.

Oral Presentation: 9th International Fundamental Mechanical Pulp Research Seminar, 19–20 May 2015, Trondheim, Norway

**Development of nanofibrillated cellulose/nanographite composites for paper applications**

Osong, S.H., Dahlström, C., Forsberg, S., Andres, B., Engstrand, P. Norgren, S., & Engström, A.-C.

Oral Presentation: TAPPI International Conference on Nanotechnology for Renewable Materials, 22–25 June 2015, Atlanta, GA, USA



## ABBREVIATIONS AND ACRONYMS

<b>AFM</b>	Atomic force microscopy
<b>BDDJ</b>	Britt dynamic drainage jar
<b>BJ30</b>	Britt jar 30 mesh screen
<b>BKP</b>	Bleached kraft pulp
<b>BMcN</b>	Bauer-McNett Classifier
<b>CSF</b>	Canadian standard freeness
<b>CTMP</b>	Chemi-thermomechanical pulp
<b>DTPA</b>	Diethylenetriamine penta-acetic acid
<b>FORE</b>	Forest as a resource
<b>FORIC</b>	Forest as a Resource Industrial Research College
<b>IR</b>	Infrared
<b>KFP</b>	Crill value
<b>MFC</b>	Microfibrillated cellulose
<b>NC</b>	Nanocellulose
<b>NG</b>	Nanographite
<b>NCC</b>	Nanocrystalline cellulose
<b>NFC</b>	Nanofibrillated cellulose
<b>NLC</b>	Nano-ligno-cellulose
<b>P-DADMAC</b>	Poly-diallyldimethylammoniumchloride
<b>SEM</b>	Scanning electron microscopy
<b>SP</b>	Sulphate pulp
<b>TEA</b>	Tensile energy absorption
<b>TEM</b>	Transmission electron microscopy

<b>TEMPO</b>	2,2,6,6 –tetramethyl-piperidine-1-oxil
<b>TMP</b>	Thermo-mechanical pulp
<b>UV</b>	Ultraviolet
<b>WP</b>	Whole Pulp

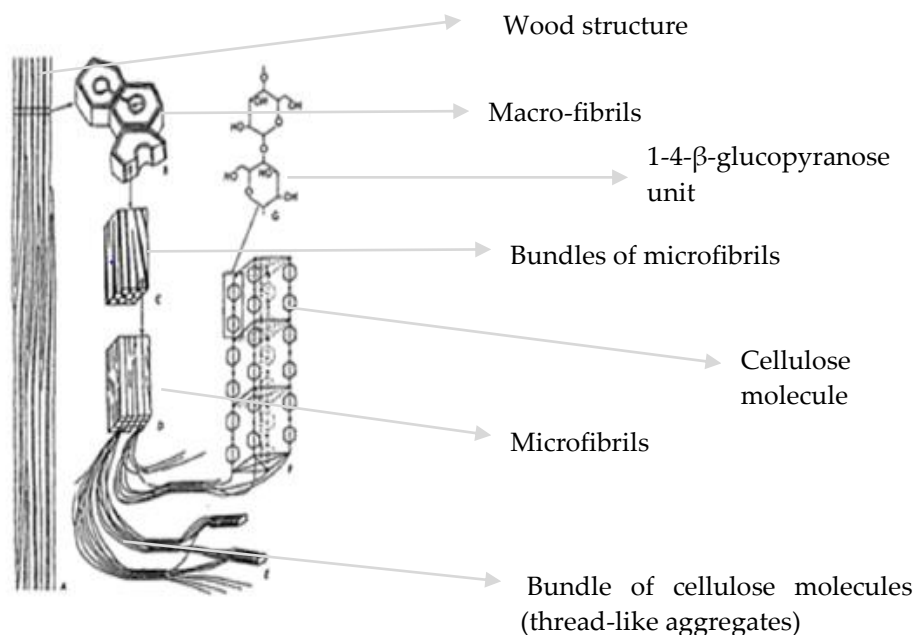
## 1. INTRODUCTION

Sweden is approximately 50% covered in forest. The pulp and paper industry forms part of the forest-based bio-economy, and this sector is important to the Swedish economy. Forest-based industry has played a pivotal role in ensuring sustainable development and has been a major source of Sweden's export income.

There are basically two types of pulping process: chemical and mechanical pulping. In mechanical pulping systems, considerable attention is paid to the fractionation in screens and cleaners as well as to optimising process conditions in order to refine the rejected fractions. The fraction rejected for further treatment can range from 10 to 50%, depending on the process strategy and the final product (e.g., paper or paperboard) and its qualities. In practice, it is common for approximately 10% of the pulp fibres and a large part of the fines fraction to have unsatisfactory properties for the final products. The less useful part of the fines fraction could instead be used to produce mechanical pulp-based nanocellulose, referred to as nano-ligno-cellulose (NLC), which can be of high value either in the main product or when used for completely different purposes.

The mechanical pulp and paper industry is now being subjected to economic pressures, radical changes, and challenges at both the local and international levels. The demand for mechanical pulp fibres, especially of newspaper grades, and for coated and uncoated paper products is in rapid decline based on the electronic media preferences of the present generation of end-users. The industry is now struggling with declining profitability, which is affecting final product performance. This emerging drawback means that a paradigm shift is needed in process technology in forest-based industry.

Innovation-led and sustainable research into nanotechnology for renewable fibre-based products is the main research source of new ideas for improving the strength of the entire forest-based bio-economy. The application of nanocellulose in pulp and paper products is gaining in importance because of the high strength-to-weight ratio, renewability, and environmental friendliness of this biomaterial.



**Figure 1.** Detailed microscopic model of cellulose; the arrows indicate the composition of each wood sub-section (adapted from Esau 1977)

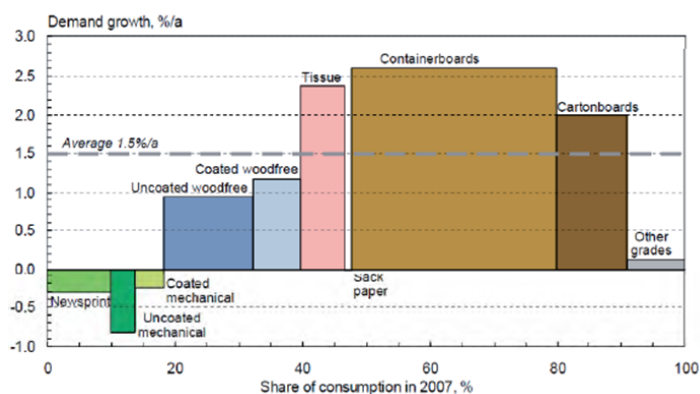
Wood is a biodegradable biopolymer and consists mainly of three chemical components: cellulose, hemicelluloses, and lignin. Several published articles, including those by Sjöström (1993), Fengel and Wegener (1989), and Levin and Goldstein (1991), have presented detailed findings pertaining to these wood components. The hierarchical structure of wood is presented in Figure 1, which shows both the macroscopic and microscopic structure of wood from the fibre level to the 1-4- $\beta$ -glucopyranose units. The carbohydrates of wood are made of cellulose and hemicelluloses, which are polysaccharides, and the lignin is made of phenylpropanoic units. Different types of lignin precursors include coniferyl-, sinapyl-, and coumaryl-alcohol groups. In these various lignin precursors, the coniferyl alcohol groups are more closely related to softwood lignin while the guaiacyl and sinapyl groups are more closely related to hardwood lignin. Hemicelluloses are composed of galactoglucomannans, arabinoglucuronoxylan and glucuronoxylan. Cellulose, which is the most abundant biopolymer on earth, is composed of crystalline and amorphous regions. In addition, the cellulose molecule can be chemically functionalised and engineered for various applications ranging from papermaking, films, coatings, and nanocomposites to pharmaceutical and biomedical engineering applications. As shown in Figure 1, the idea in this thesis is to extract the microfibrils from pulp fibres. In this thesis the terms nano-ligno-cellulose (NLC), nanocellulose (NC), microfibrillated cellulose (MFC), and nanofibrillated cellulose (NFC) are used to describe pulp fibre nanoparticles. We

chose to use mechanical pulp fibres to produce nanocellulose so that we could apply our knowledge of wood polymer-related research and, in addition, learn how to extract fibre materials to form micro- or nanofibrils under 200 nm wide. More specifically, we chose to exploit the ionic polymer and softening aspects of the amorphous wood polymers hemicellulose and lignin to enhance the delamination of the fibrillar structure during homogenisation.

## 1.1. Motivation

The pulp and paper industry is now attempting to emulate an existing concept from the petro-chemical industry, in which energy and petrochemicals have been co-produced for hundreds of years. In the pulp and paper industry, the term “biorefinery” has gained significance in recent years, and now traditional pulp fibres, newly engineered fibres (i.e., nanocellulose), dissolved lignin, hemicelluloses, and energy are being co-produced in the same industry. One difference between the petrochemical and pulp and paper industries is that the latter can produce large amounts of physical and biodegradable products aligned with “green” legislation in support of renewable bio-materials and bio-economic policies. Based on the declining growth in demand for newspaper grades and for both coated and uncoated papers, as shown in Figure 2 (Johnsson 2013), the research interest of most pulp and paper mills has shifted towards newly engineered fibres such as nanocellulose. Nanocellulose has been demonstrated to be a potential candidate for renewable nanotechnology applications in forest-based industry.

Global growth in demand 2007-2025



**Figure 2.** Use of printing papers is declining, so high-yield pulp development is focusing more on board grades (Johnsson 2013)

The world's current population is estimated to be 7.12 billion people, with China (approximately 1.36 billion people) and India (almost 1.27 billion) accounting for 36.9% of the total (2.63 billion people as of 2013; [http://en.wikipedia.org/wiki/List\\_of\\_countries\\_by\\_population](http://en.wikipedia.org/wiki/List_of_countries_by_population)). It is strongly believed by many that Asia is an emerging market for paper and paperboard products. Although demand for newspaper grades and for coated and uncoated papers is declining in the western world, there is a strong belief that demand for these will soon increase in the Asian markets as their industrialisation increases. The idea of integrating a miniature nanocellulose plant within a mechanical or chemi-mechanical pulp mill in order to improve the quality of paper currently produced should prove to be an asset, as the market for low-grade paper products is expected to grow while global demand for board and carton board products continues its steady increase, see Figure 2.

## **1.2. Background**

Almost all research into biorefinery concepts is based on chemical pulping processes and ways of using lignin, hemicelluloses, and extractives as well as part of the remaining cellulose for the production of nanomaterials in order to create more valuable products. In the Forest as a Resource research programme at the Fibre Science and Communication Network (FSCN), Mid Sweden University we are examining the whole chain of unit processes from forestry to final products, such as paper and board; and our research focuses on high-yield pulp processes such as TMP and CTMP. As these process solutions preserve or only slightly change the properties of the original wood polymers and extractives, the idea is to find high-value-adding products designed by nature.

The FSCN research centre is currently running an industrial research school known as the Forest as a Resource Industrial Research College (FORIC), which is striving to develop a biorefinery concept using all sorts of forest resources to enable the sustainable development of both new and existing products. In addition, before the commencement of FORIC, the Forest as a Resource (FORE) project was financed by the European Regional Development Fund from 2011 to 2014. The overall aim of FORE was to identify and investigate synergetic opportunities related to forest industry production systems, with a focus on improved efficiency and on developing a large range of sustainable bio-material-based new and existing products (Björkqvist et al. 2010) (see Figure 3). One sub-objective of this work was to use low-quality fibres in a mechanical pulp and paper mill to produce new products and/or improve the product quality of traditional products.

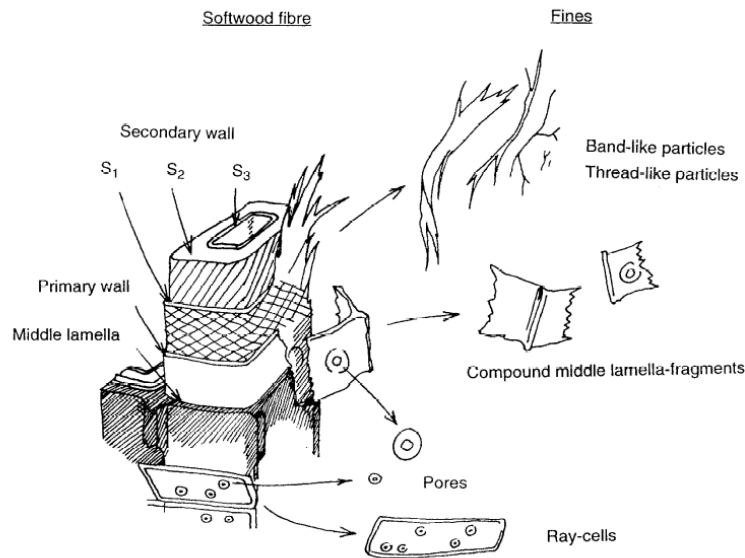


**Figure 3.** FORE concept at Mid Sweden University

### 1.3. Mechanical pulping

This occurs when wood is mechanically disintegrated into fibre particles by the repeated action of a refiner plate or a grinder. The term “mechanical pulp” applies to a number of pulps, including: stone groundwood, pressure groundwood, super pressure groundwood, thermo-groundwood, refiner mechanical, pressure refiner mechanical, thermo-mechanical, chemi-mechanical, and chemi-thermomechanical pulps (Sundholm 1999).

Thermo-mechanical pulp (TMP) and chemi-thermomechanical pulp (CTMP) are the two main pulps of interest in this study. Stone groundwood is noted for the similar proportions (i.e., 50/50) of its fines and fibre fractions, whereas thermo-mechanical and chemi-thermomechanical pulps have somewhat larger fibre fractions, with the fines content being in the range of 30% (Giertz 1973). Chemical pulps (sulphite and sulphate) and mechanical pulps (TMP and CTMP) differ significantly in terms of both their manufacturing processes and yields (the yield of chemical pulp is approximately 45–50% and of mechanical pulp is approximately 90–95%). Figure 4 shows the structural and morphological appearance of the fibre wall of a TMP fibre.



**Figure 4.** Structural appearance of thermo-mechanical pulp fines (Rundlöf 2002)

Fines are known to have more anionic groups than do fibres, due to the significantly larger amounts of pectin in fines than in fibres. Fines are said to be more charged than fibres because the fines contain more fatty acids and extractives, the latter also being a source of carboxyl groups. It is worth noting that fines consist of a wide range of particles, including flakes or lamellae, thread-like bands or fibrils, tori from bordered pits, parenchyma cells, and ray cells. Hill and Eriksson (1973) were of the same opinion as Giertz (1973), stating that the fines and fibre fractions are of great importance for mechanical pulps. The fines are noted for their light-scattering ability and the longer fibres have a strengthening effect. Dillen et al. (1973) also commented on the fact that the geometrical dimensions of mechanical pulp fibres (including fines, fibres, fibre aggregate, and fibre fragments) are vital for the process of papermaking.



## 1.4. Research objectives

The main objectives of this research are as follows:

- To use mechanical pulp fibres/fines to produce nanocellulose and use the nanocellulose as a paper strength additive, in composite films, and in foams.
- To study the possibility of using cationic starch and MFC for paper strength improvement.
- To study the possibility of co-utilising NFC and NG in composite film applications.
- To use the crill measurement technique in qualitatively evaluating the fibrillation efficiency of nanocellulose.
- To study new possibilities for processing nanocellulose using organic acids.

This thesis focuses on the processing of nanocellulose – also termed microfibrillated cellulose (MFC), nanofibrillated cellulose (NFC), and nano-lignocellulose (NLC) – originating from pulp fibres, specifically mechanical pulp fibres. It is worth noting that the TAPPI and ISO naming standard proposes using cellulose nanofibrils (CNF) and cellulose microfibrils (CMF) as standard terminology; however, in this thesis we have decided to use the terms NFC and MFC, except in papers II–IV, in which we used the term NLC.

The chemical pulping process has been a dominant driver of the biorefinery concept in the pulp and paper industry. From an economic perspective, the production of nanocellulose from chemical pulp is quite expensive, as the pulp must either be enzymatically pretreated (e.g., using mono-component endoglucanase) or chemically oxidised using the 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation method.

In mechanical pulping processes such as TMP and CTMP, it is possible to use low-quality material fractions as alternatives for producing nanocellulose. The integration of a nanocellulose production unit in a mechanical pulping operation could become a way of using suitable fractions of mechanical pulp, as the nanocellulose thus produced could improve the quality of traditional products such as paper and paperboard grades. The aim of this research is by exploring this concept, to create a knowledge base supporting the development of a low-cost nanocellulose production method that can feasibly be implemented.

This work sought to develop a methodology for producing mechanical pulp-based nanocellulose from fibres and fines fractions and to optimise the usage of nanocellulose in order to improve the strength properties of paper and paperboard

products. However, producing nanocellulose from mechanical pulp fibres and/or fines and characterising its microfibrils as part of a broader mapping of the evolution of this unique product are challenging tasks. Another sub-aim of the research was to build our knowledge of mechanical pulp-based nanocellulose by supporting the development of a new production method and/or improving the current state-of-the-art method for microfibril characterisation. In addition, while striving to develop completely new products, in order to widen the application of high-yield pulp fibres, we have studied the possibility of co-utilising NFC and NG in composite film applications.

### **1.5. Research hypothesis**

The main hypothesis of this work was that the softening and swelling properties of lignin and hemicellulose can be used to enhance the delamination of fibrils during the homogenisation of mechanical pulps. The technical aim was to produce nanocellulose from a mechanical pulp fines fraction by means of mechanical homogenisation combining two different chemical pretreatment strategies (i.e., hydrogen peroxide pretreatment and TEMPO oxidation) with high-shear homogenisation. The TEMPO-mediated oxidation systems (TEMPO/NaBr/NaClO) are applied to these fibres (i.e., CTMP and sulphite pulp) to swell the fibres so that they become easy to disrupt into nanofibres. Figure 5 shows how we can reduce the fibres to the size of microfibrils

It is also well-known that mechanical pulp fibres and fines, as well as other cellulosic materials, derive their charges from the dissociation of acidic groups, and that the weak carboxylic acid groups are the ones contributing the most to the total negative fibre charge. However, in the case of CTMP and sulphite pulp fibres, the strong sulphonate acid groups also contribute to the total charge of the fibres. It is worth noting that the total charges of fibres and of MFC contribute significantly to paper strength improvement, as these charges strengthen the ion-ion interactions between pulp fibres and nanocellulose, and between pulp fibres and cationic starch.

The technical concept of this thesis was to produce nanocellulose from mechanical pulp fibres and the fines fraction by means of mechanical homogenisation, using different chemical pretreatment strategies (i.e., hydrogen peroxide and TEMPO oxidation) combined with high-shear homogenisation. One plausible explanation as to why TEMPO-based MFC acted as a strength additive in paper VI is that MFC is gel-like and highly swollen. It therefore helps improve the fibre-fibre joint strength of the CTMP fibres, as the soft and gel-like MFC facilitates good bonding between the fibres during papermaking and drying process. Figure 5 shows how we can reduce fibres to the size of cellulose microfibrils.

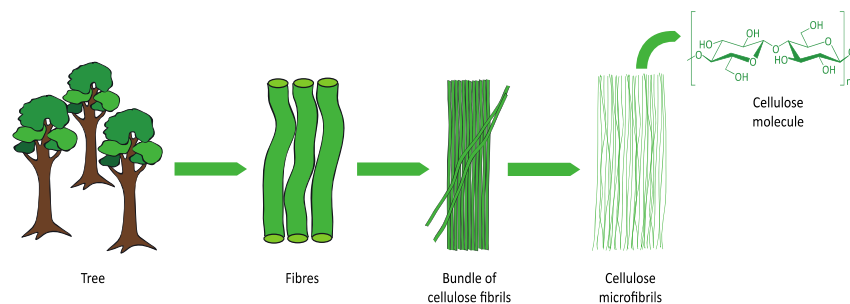


Figure 5. Top-down approach to the processing of cellulose nanofibres

## 1.6. Thesis outline

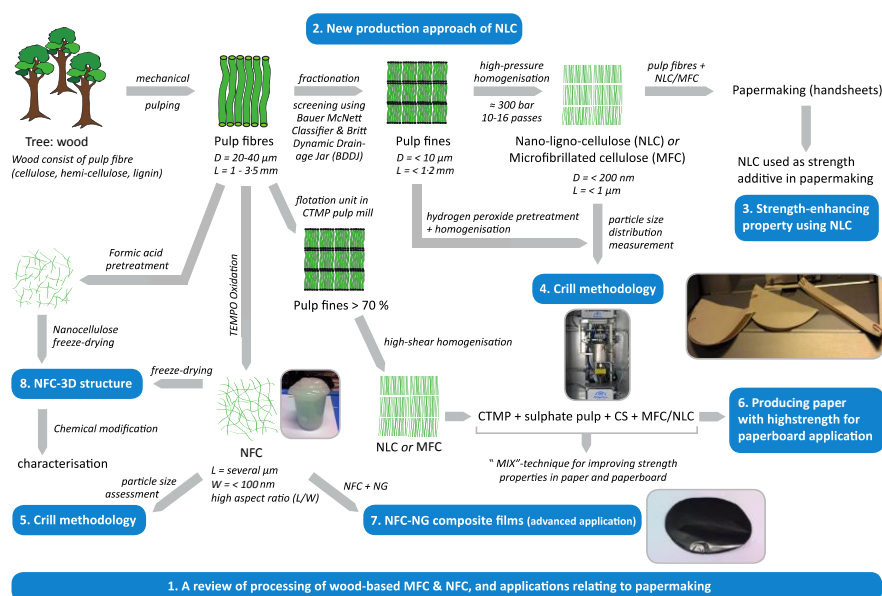


Figure 6. Schematic of the entire doctoral project in relation to nanocellulose processing and applications

Most of this work was performed using CTMP and TMP (Figure 6), though sulphite pulp-based nanocellulose was also produced in papers V–VII to permit comparison of both pulp raw materials for nanocellulose production. This thesis is organised as follows: chapter 1 briefly introduces the study, motivation, background, mechanical pulping, research objectives, and research hypothesis. Chapter 2 describes the review of literature related to nanocellulose, types of nanocellulose, mechanical treatment of pulp (using a homogeniser, micro-fluidiser, micro-grinder, and super grinder), pretreatment strategies (i.e., enzymatic and chemical, such as TEMPO oxidation), energy consumption during nanocellulose processing, nanocellulose characterisation, nanocellulose as a strength additive in papermaking, nanocellulose in composite films, the market potential of nanocellulose, and pilot plant facilities. Chapter 3 presents the material and methods. Chapter 4 presents, discusses, and interprets the main results achieved during the work. Chapters 6 and 7 present recommendations and references, respectively.

## **2. LITERATURE REVIEW**

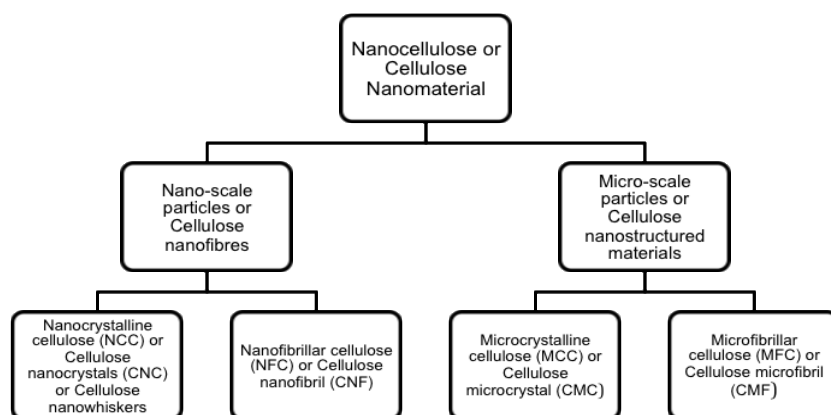
The relevant literature is surveyed to gain an understanding of what has occurred in the field of forest nanotechnology using renewable materials.

### **2.1. Nanocellulose**

The term nanocellulose is often used to refer to nanoscale cellulosic material. A cellulosic material is considered to be in the nanoscale range if the fibril particle width is less than 100 nm. Figure 7 shows the different groups of nanocellulose. So far, there is no specific nomenclature for nanocellulose. Several schools of thought have referred to nanocellulose as microfibrillated cellulose, nanocellulose, microfibrillar cellulose, microfibrillized cellulose, nanofibrillated cellulose, nanofibrillar cellulose, nanoscale fibrillar cellulose, and cellulosic fibrillar fines (Hubbe et al. 2008, Eichhorn et al. 2010, Siqueira et al. 2010, Siro and Plackett 2010, Klemm et al. 2011, Moon et al. 2011, Charreau et al. 2013).

More recently the TAPPI organisation has formulated new standard terminology and nomenclature for nanocellulose and indicated that nanocellulose can be categorised into cellulose nanofibres and cellulose nanostructured materials. Cellulose nanofibres are sub-divided into nanocrystalline cellulose (or cellulose nanocrystals or cellulose nanowhiskers) and nanofibrillar cellulose (NFC) (or cellulose nanofibrils – CNF). Cellulose nanostructured materials are sub-grouped into microcrystalline cellulose (or cellulose microcrystals) and microfibrillar cellulose (MFC) (or cellulose microfibrils – CMF) (TAPPI WI 3021).

It is worth noting that MFC comprises very heterogeneous pulp fibre particles produced by means of mechanical disintegration, as reported by Turbak et al. (1983) and Herrick et al. (1983), and that the term MFC or CMF has been inconsistently used by most scholars to refer to NFC, CNF, and other similar fibre materials resulting from various disintegration procedures. The structure of MFC and NFC is often referred to as spaghetti-like, comprising both crystalline and amorphous regions. Great disparities are found in the particle size distribution of cellulose nanomaterials (Table 1), as has been confirmed by microscopy and image analysis (Mörseburg and Chinga-Carrasco 2009).



**Figure 7.** Hierarchical levels of nanocellulose (adapted from proposed new TAPPI Standard WI 3021)

**Table 1.** Cellulosic nanomaterial dimensions (adapted from proposed new TAPPI Standard WI 3021)

Terminology and nomenclature of cellulose nanomaterials	Width (nm)	Length (nm)	Aspect ratio (length/width)
Cellulose nanofibril (CNF), Nanofibrillar cellulose (NFC)	2–10	>10,000	>1000
Cellulose nanocrystals (CNC) Nanocrystalline cellulose (NCC) Cellulose nanowhiskers	2–20	100–600	10–100
Cellulose microcrystal (CMC) Microcrystalline cellulose (MCC)	>1000	>1000	≈ 1
Cellulose microfibril (CMF) Microfibrillar cellulose (MFC)	10–100	500–10,000	50–100
Bacterial cellulose (BC) Microbial cellulose	10–40	>1000	100–150

There are three kinds of nanocellulose, namely, MFC and/or NFC, NCC and/or CNC, and bacterial nanocellulose (BNC) (Klemm et al. 2011). NCC is obtained by acid hydrolysis, while BNC is formed by bacterial synthesis. However, in this thesis, the focus is on MFC and/or NFC, with very little attention paid to NCC/CNC or BNC. The IUPAC definition of nanoparticles or nanomaterials refers to these as particles of any shape with dimensions in the  $1 \times 10^{-9}$  to  $1 \times 10^{-7}$  m (1–100 nm) range (<http://en.wikipedia.org/wiki/Nanoparticle>).

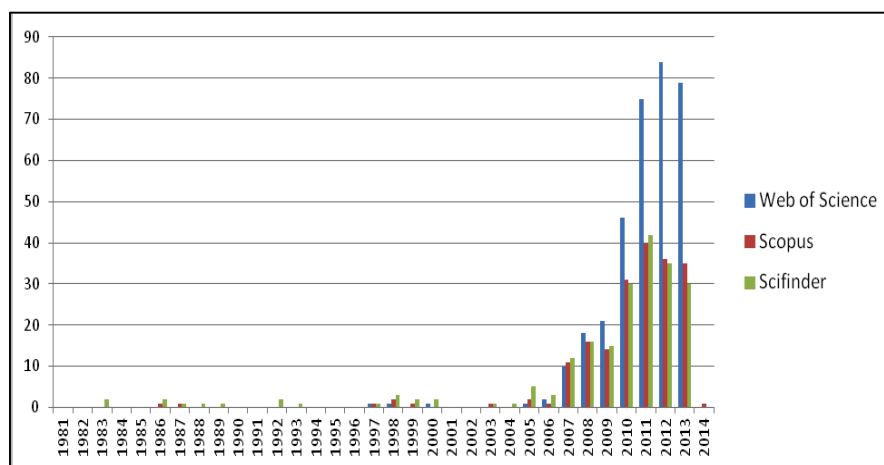
Over the years, several articles have been written concerning MFC and NFC (Herrick et al. 1983, Turbak et al. 1983, Andresen et al. 2006, Henriksson et al. 2007, Pääkkö et al. 2007, Eichhorn et al. 2010, Spence et al. 2010a, 2010b) and NCC (Rånby 1949, Rånby and Ribi 1950, Rånby 1951, Gray 1994, Revol et al. 1994, Xue et al. 1996, Fleming et al. 2001), with the former type said to have a “spaghetti-like” structure and the latter a “rice-like” structure.

There has been an increasing number of publications (both patents and articles) in the research field of nanotechnology for renewable biomaterials, as seen in Figures 9 and 10. This assertion is also clearly seen in Table 2, which lists the most cited patent publications. It can be clearly seen in Figures 8 and 9 that the number of published articles and patents increased from 1981 to 2013, with 2011 being the peak for patent publication and 2012 the peak for article publication. The publication numbers in the table are patents related to MFC (i.e., US4341807A, US4374702A, US4378381A, US4452722A, US4452721A, US4464287A, US4481077A, US4481076A, US4483743A, US4487634A, US4500546A, JP56100801A, and EP120471A2).

**Table 2.** Patents related to microfibrillated cellulose publications (adapted from Charreau et al. 2013)

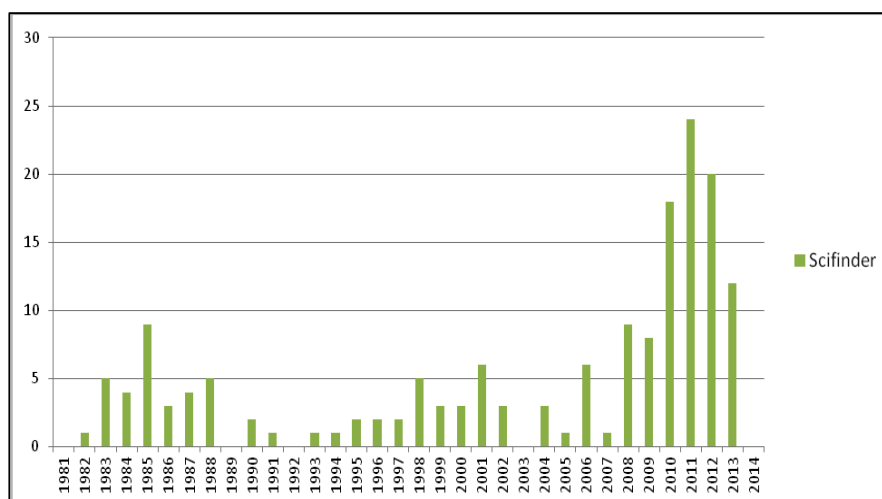
Publication Number	Reference Title	Assignee	Inventors	Publication Year	Citations
US4374702A	Microfibrillated cellulose	Int Telephone & Telegraph Corp	Turbak Albin F, Snyder Fred W, Sandberg Karen R	1983	78
US4500546A	Suspensions containing microfibrillated cellulose	Deut ITT Ind Gmbh, Itt Ind Inc	Turbak Albin F, Snyder Fred W, Sandberg Karen R	1985	59
US4481076A	Redispersible microfibrillated cellulose	Deut ITTInd Gmbh	Herrick Franklin W	1984	50
US5417228A	Smoking article wrapper for controlling burn rate and method for making same	Philip Morris Inc, Philip Morris Prod Inc	Baldwin Sheryl D, Gautam Navin, Houghton Kenneth S, Rogers Robert M, Ryder Judith L	1995	41
US5263999A	Smoking article wrapper for controlling burn rate and method for making same	Philip Morris Inc, Philip Morris Prod Inc	Baldwin Sheryl D, Gautam Navin, Houghton Kenneth S, Rogers Robert M, Ryder Judith L	1993	40
US4481077A	Process for preparing microfibrillated cellulose	Int Telephone & Telegraph Corp	Herrick Franklin W	1984	37
US5964983A	Microfibrillated cellulose and method for preparing a microfibrillated cellulose	Gen Sucriere Sa, Saint-Louis Sucre Sa	Dinand Elisabeth, Chanzy Henri, Vignon Michel R, Maureaux Alain, Vincent Isabelle	1999	37
JP56100801A	Microfibrous Cellulose and Its Manufacture	ITT Ind Inc	Taabaku Arubin F, Sunaidaa Furetsudo U, Sandobaagu Karen R / Sandberg Karen R, Snyder Fred W, Turbak Albin F	1981	36
US4659388A	Additive composition for foods or drugs	Daicel Chem Ind Ltd	Innami Satoshi, Fukui Yoshitaka	1987	36
US4341807A	Food products containing microfibrillated cellulose	Deut ITT Ind Gmbh, ITTInd Inc	Turbak Albin F, Snyder Fred W, Sandberg Karen R	1982	34
WO2000047628 A2	Derivatized Microfibrillar Polysaccharide	Hercules Inc	Cash Mary Jean, Chan Amita N, Conner Herbert Thompson, Cowan Patrick Joseph, Gelman Robert Alan, Lusvardi Kate Marritt, Thompson Samuel Anthony, Tise Frank Peine	2000	33





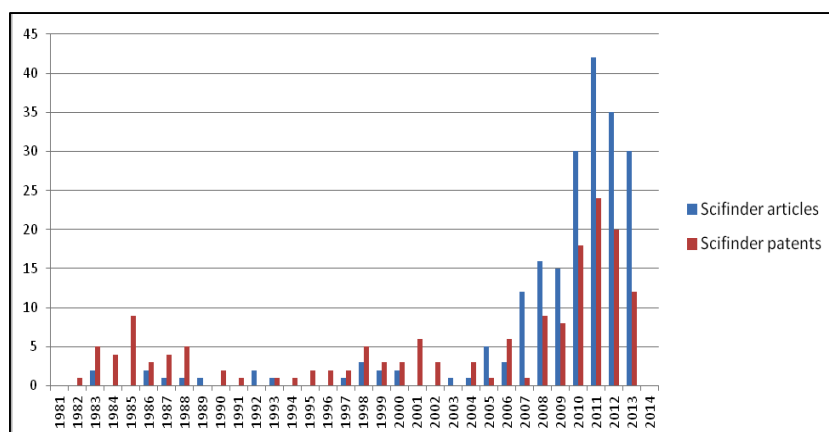
**Figure 8.** Number of journal articles on MFC per publication year, using three databases for the search: Web of Science (WoS), Scopus, and Scifinder

Figure 8 shows the results of a Web of Science search for “microfibrillated cellulose” (refine topic, document type: article; review date: 2013-11-26), a Scopus search for “microfibrillated cellulose” in Title-Abstract-Keywords (refine topic, document type: article; review date: 2013-11-26), and a Scifinder search for “microfibrillated cellulose” (refine topic, document type: include; journal search date: 2013-11-26).

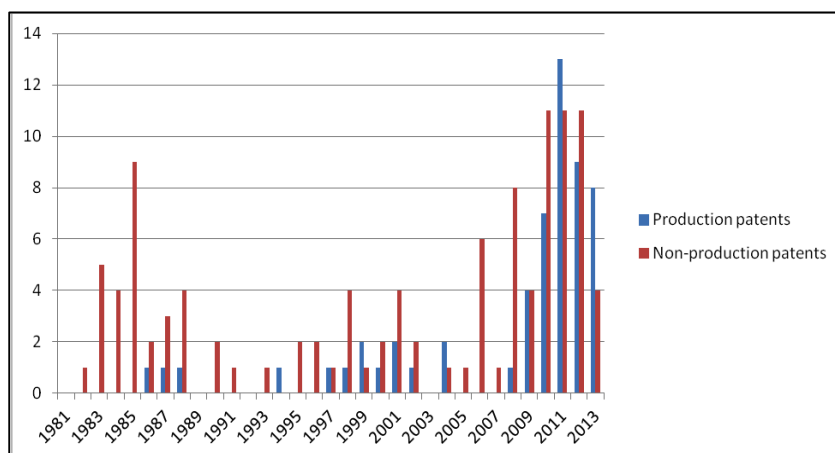


**Figure 9.** Number of MFC-related patents per publication year, using the Scifinder database (journal search date: 2013-11-25)

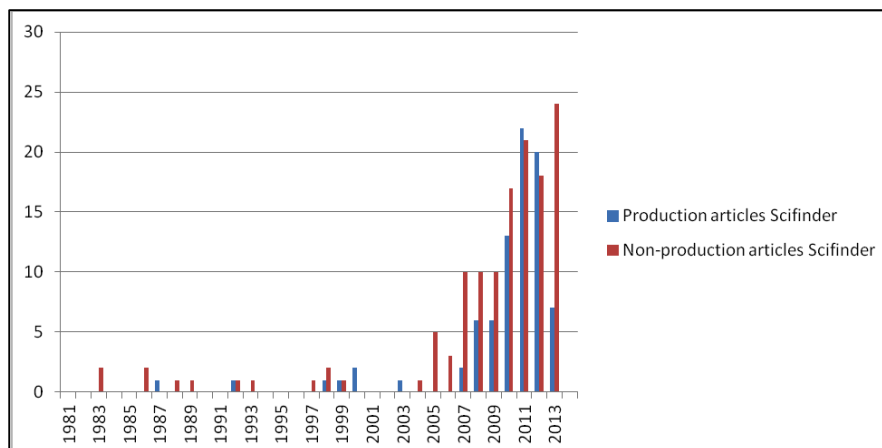
Figure 10 shows comparative data for the number of published journal articles (*y-axis*) and number of published patents as a function of publication year (*x-axis*) obtained using the Scifinder database. The figure shows that the number of patents published from 1982 to 2002 surpasses the number of articles published in the same time frame, but that the number of published articles has increased significantly since 2007 (Figure 10). Figure 11 presents data for the number of production patents and non-production patents as a function of publication year obtained using the Scifinder database.



**Figure 10.** Number of MFC-related journal articles and patents published per year (journal search date: 2013-11-25)



**Figure 11.** Number of MFC-related production and non-production patents published per year (journal search date: 2013-11-25)



**Figure 12.** Number of MFC-related production and non-production articles published per year, using the Scifinder database (2013-11-25)

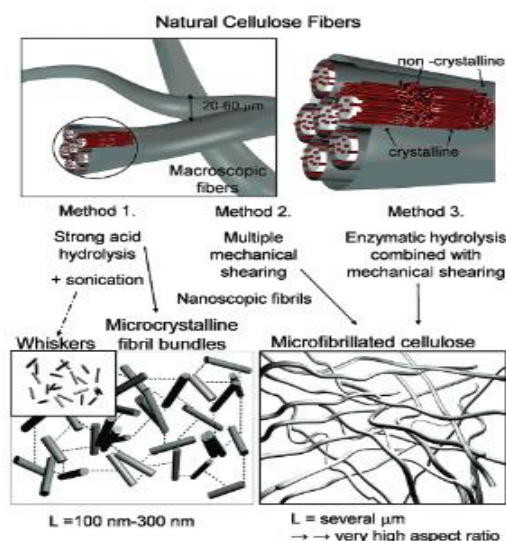
Figure 12 shows the results of a Scifinder search for “microfibrillated cellulose”, as follows: Refine: document type: include: journal production articles: Categorise: category heading: technology: category: processes & apparatus: select all non-production articles: All “microfibrillated cellulose” articles minus production patents (search date: 2013-11-25).

MFC production was conceived in the late 1970s by researchers working at the ITT Rayonier Eastern Research Division Laboratory in Whippany, NJ, USA (Charreau et al. 2013). They used a mechanical high-pressure homogeniser known as a Manton Gaulin-type milk homogeniser to produce thread-like pulp particles, referred to as microfibrillated cellulose or nanocellulose.

For almost thirty years, several approaches have been used to extract fibrils using chemical or enzymatic pretreatment methods combined with mechanical disintegration (Zimmermann et al. 2006, Henriksson et al. 2007, Saito et al. 2007, Stelte and Sanadi 2009, Klemm et al. 2011). MFC is regarded as a newly engineered material obtained from wood, crops, and bacteria. The material is gel-like in appearance at very low concentrations (Turbak et al. 1983, Klemm et al. 2011) and has an extremely high surface area and high aspect ratio (Andresen et al. 2006, Stenstad et al. 2008, Ishii et al. 2011). Some of the special properties of wood-based nanocellulose include: renewability, high strength and stiffness, low density, biodegradability, low thermal expansion, and a high aspect ratio (Charreau et al. 2013). In the early 1980s, it was suggested that MFC could be used in food,

emulsions, cosmetics, medical applications, pharmaceuticals, and as thickeners in paint formulations (US4341807A, US4659388A).

Although many have recently attempted to extract MFC nanomaterials, insufficient knowledge exists regarding how to effectively produce uniform MFC without the MFC being inhomogeneous in fibre composition and containing, for example, fibrillar fines, fibre fragments, fibres, and microfibrils. Pääkkö et al. (2007) used an enzymatic pretreatment method combined with mechanical homogenisation to produce MFC. A more efficient and promising method used to extract fibrils from fibres is the 2, 2, 6, 6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation method, as described by Saito et al. (2006, 2007).



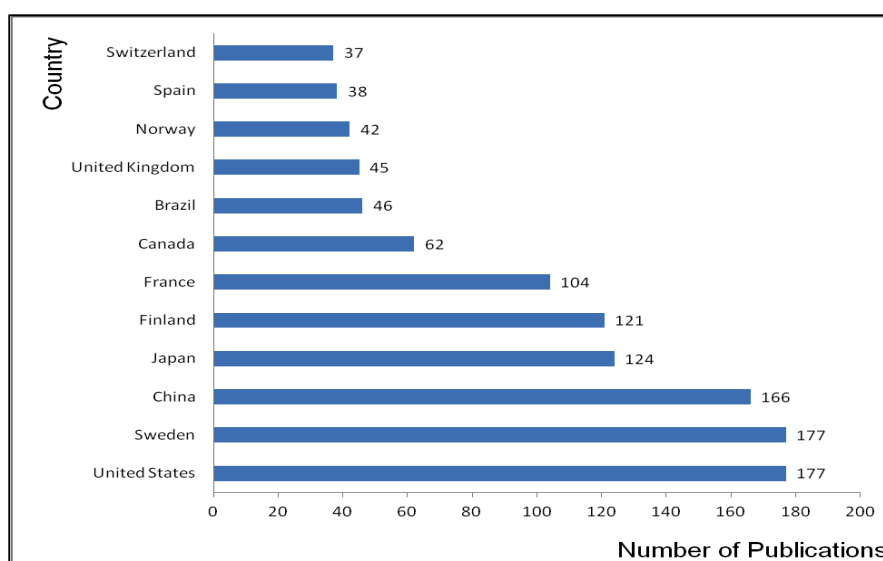
**Figure 13.** Schematic of the major classes of nanocellulose (Courtesy of Pääkkö et al. 2007)

There are two major families of nanocellulose, those of “spaghetti-like” structure, referred to as MFC/NFC, and those of “rice-like” structure, referred to as NCC/CNC (see Figure 13). The birth of NCC/CNC occurred in Uppsala University, Sweden, where Rånby pioneered this work in the late 1940s. He produced NCC by subjecting wood and cotton cellulose to sulphuric acid hydrolysis (Rånby 1949, Rånby and Ribi 1950, Rånby 1951). Rånby’s group called the product cellulose micelles, which are nowadays referred to as NCC/CNC. The NCC/CNC project was later abandoned, and in the 1970s Professor Gray’s group at McGill University in Canada started working on NCC/CNC. Some other important publications about NCC include those by Gray (1994) and Revol et al. (1994). Professor Gray

was awarded the 2013 Marcus Wallenberg Prize “for his contributions to the path-breaking research on NCC/CNC, its fundamental properties and applications. The fundamental discoveries, related to the chiral nematic behaviour of NCC/CNC suspensions, create potential for new wood and other lignocellulosic products for unique value added applications” (<http://mwp.org/>).

As is the case for MFC, the term NCC has also been associated with a number of names such as cellulose nanocrystals, whiskers, monocrystals, microcrystals, microcrystals, crystallites, microcrystallites, nanowhiskers, nanocrystals, nanorods, and nanowires, as well as rod-like cellulose microcrystals and rod-like cellulose crystals (Azizi et al. 2005, Hubbe et al. 2008, Eichhorn et al. 2010, Habibi et al. 2010, Siqueira et al. 2010, Siro and Plackett 2010, Klemm et al. 2011, Moon et al. 2011, Charreau et al. 2013).

The number of publications addressing MFC, broken down by country, is shown in Figure 14, with the United States and Sweden leading with 177 publications each.



**Figure 14.** Number of publications related to microfibrillated cellulose per country (adopted from Scopus database; 2 July 2013)

The main advantage of using chemical pulp as opposed to mechanical pulp is related to the degree of purity of the cellulose moiety in chemical pulp, whereas in mechanical pulp the fibres mainly comprise cellulose, lignin, and hemicellulose, making processability difficult during fibril extraction. The Japanese method, i.e.,

TEMPO-mediated oxidation, presented by Saito et al. (2006) is known to be an excellent method of obtaining well-fibrillated and individualised fibrils with a high aspect ratio (Ishii et al. 2011) and a high specific surface area (Sehaqui et al. 2011).

## **2.2. Mechanical treatment of pulp fibres to form nanocellulose**

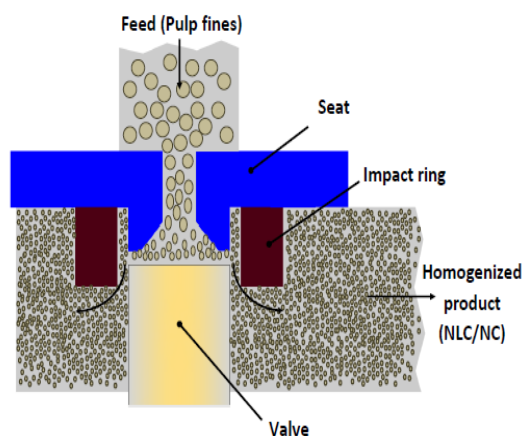
The disintegration of pulp slurries into thread-like materials was first examined by Turbak et al. (1983) and Herrick et al. (1983) using a high-pressure homogeniser. Several new mechanical techniques are now used to produce this material. Some of the novel mechanical techniques used currently are high-pressure homogenisation, micro-fluidisation, super-grinding, micro-grinding, cryo-crushing, and high-intensity ultrasonication. High-pressure homogenisers and micro-fluidisers are the most widely used equipment for extracting MFC from pulp fibres (Ankerfors 2012).

### **2.2.1. Homogeniser**

The homogenisation concept was introduced in the dairy and food industries where the main aim of the technology was to stabilise food emulsions (Paquin 1999). Today, the pharmaceutical, chemical, specialty food, and biotechnology industries all use high-pressure mechanical shearing equipment to emulsify, mix, disperse, and process their products (Floury et al. 2000).

The production of microfibrillated cellulose or nanocellulose is based on the passage of pulp slurries through mechanical equipment, such as high-pressure homogenisers, with, in most cases, chemical or enzymatic pretreatment being performed in such a way so as to lower energy consumption, improve fibrillation, and prevent fibre clogging.

It is well known that the extent of fibrillation is governed by the pressure drop and the number of homogenisation passes. Mechanical pulps are not easy to treat in the homogeniser to form well-fibrillated fibrils. This is because of the cellulose/hemicellulose/lignin interaction, as the lignin in the pulp acts as a “glue” in relation to cellulose, preventing the cellulose molecules from complete individualisation and resulting in the formation of fibril bundles (Osong et al. 2013). The left-hand panel of Figure 15 shows the homogenising equipment at Mid Sweden University, while the right-hand panel presents a schematic of the mechanical treatment process.



**Figure 15.** Photo (left) and schematic (right) of pulp fibre homogenisation (right-hand diagram courtesy of Majid Alimadadi)

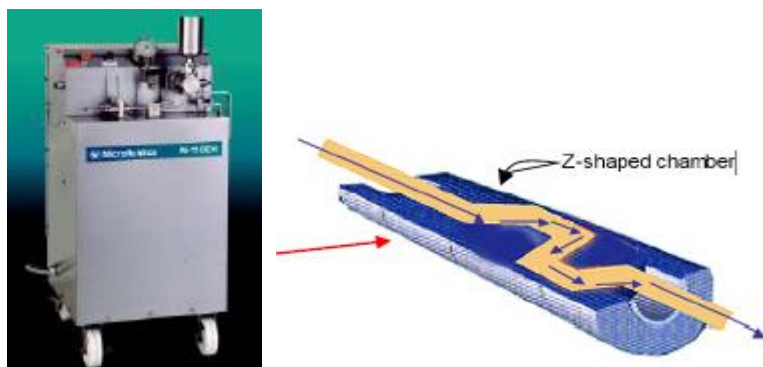
Factors that favour the disintegration of fibres into fibrils in a homogeniser include chemical (or enzymatic) pretreatment, high pressure drop within the valve seat, and multiple passes through the homogeniser. The working principle of the high-pressure homogeniser is that it subjects the fibre suspension to a high impact force and a high shear rate due to the reciprocating action within the valves (see Figure 15). The suspension of cellulose microfibrils is subjected to high-pressure treatment to reduce the fibre size so as to obtain a stable suspension. The valve seats in the homogeniser experience an increase in temperature over time during operation, but the homogeniser continues to function well even at elevated temperatures of up to 140°C.

Most of the energy losses in the homogeniser are due to friction that occurs at the seat, impact ring, and valves of the machine. There is also the issue of clogging at the valve, which leads to a large pressure drop. The major problem that has hindered the commercialisation of nanocellulose is the huge amount of energy consumed in its production and the problem of clogging during homogeniser operation (Herrick et al. 1983, Turbak et al. 1983, Ankerfors 2012). The tendency of the fibres to clog the equipment and block the fibre suspension flow renders the production process unstable, meaning that the whole homogeniser assembly requires dismantling. As the number of passes of pulp slurry through the homogeniser increases, so too does the amount of energy consumed.

### 2.2.2. Micro-fluidiser and micro-grinder

The micro-fluidiser operates at a constant shear rate while the high-pressure homogeniser functions at a constant processing volume; in the micro-grinding process, the fibres are pressed through the stator and rotor disk gap (Spence et al.

2011). Henriksson et al. (2007) and Pääkkö et al. (2007) used the micro-fluidiser method in producing MFC/NFC. The mechanical equipment shown in Figure 16 has a flow rate of 350 mL min<sup>-1</sup>; its first-stage homogenising pressure is 100 bars, with a chamber slit of 400 µm, and second-stage homogenising pressure is 1500 bars, with a chamber slit of 200 µm.



**Figure 16.** Microfluidiser equipment

### 2.2.3. Cryo-crushing and super-grinder

Cryo-crushing entails placing refined cellulose fibres under liquid nitrogen to freeze the water content in the fibres, and subsequently subjecting the frozen fibre/nitrogen mixture to high-impact grinding (Chakraborty et al. 2005). Microfibrillated cellulose produced by a super-grinder has been presented by Taniguchi and Okamura (1998). Figure 17 shows laboratory-scale supermass colloidier equipment.



**Figure 17.** Laboratory-scale supermass colloidier equipment



### 2.3. Pretreatment strategies

Production techniques for MFC/NFC have been recently been examined by various researchers (Herrick et al. 1983, Turbak et al. 1983, Taniguchi and Okamura 1998, Chakraborty et al. 2005, Saito et al. 2006, Henriksson et al. 2007, Pääkkö et al. 2007, Saito et al. 2007). In view of the huge amount of energy consumed during MFC/NFC production, scientists have instituted pretreatment methods, such as physical, chemical, or enzymatic pretreatment (Saito et al. 2006, Pääkkö et al. 2007), to reduce the energy consumption.

Ankerfors (2012) confirmed that the major impediment to the successful commercialisation of microfibrillated cellulose was the considerable energy consumed in its production; he claimed that by carefully pretreating the fibres, this problem could be resolved. In addition to energy consumption, homogenisation without pretreatment may produce non-homogeneous fibre mixtures containing microfibrils, fibril fragments, and poorly fibrillated fibres. To produce nanocellulose efficiently, pulp fibres are usually mechanically pre-refined (using valley beating, PFI milling, or refining) to enable the correct treatment in the homogeniser and prevent fibre clogging. This idea was supported a long time ago by Herrick et al. (1983), who claimed that cutting the fibres into smaller pieces facilitated fibre disintegration. Considering the various raw material sources, Spence et al. (2011) argued that it is easier to disintegrate pulp fibres efficiently from softwood bleached kraft pulp from which the lignin has been removed. Pretreatment strategies have been developed to prevent the challenges associated with fibre clogging during homogenisation and to limit the energy consumption.

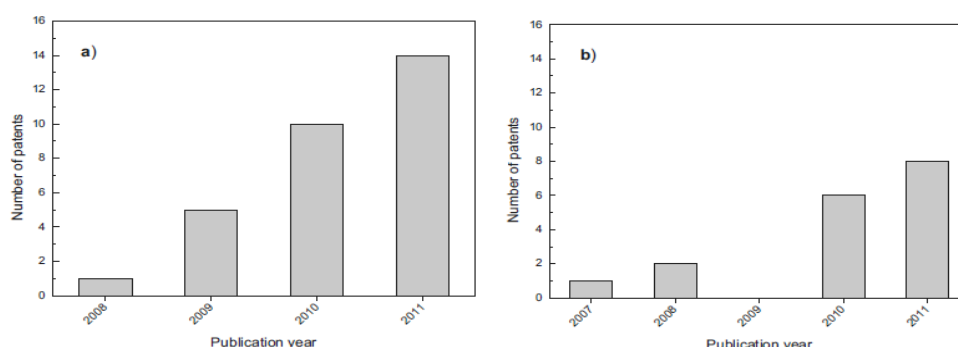
The pioneers of the TEMPO method were Saito et al. (2006), who used this method to introduce charged carboxylate groups into the cellulose material in such a way as to enhance fibrillation. This method is understood to induce repulsion within the fibre matrix, thereby facilitating fibre disintegration during mechanical treatment in the homogeniser. The chemical oxidative pretreatment method seems to have given rise to more publications than has the enzymatic pretreatment method. Table 3 shows various pretreatment strategies, along with the main chemistry involved and their most important effects, that can be used to improve the fibrillation efficiency of nanocellulose.

**Table 3.** Various pretreatment methods with the main chemistry involved and their most important effects, i.e., small diameter of resulting fibrils, reduced energy consumption, and changed surface chemistry

Pretreatment methods	Most important effects	References
TEMPO/NaBr/NaClO	Induce mostly carboxylate groups and some aldehyde groups, improve fibrillation, reduce energy consumption, and produce thinner NFC	Saito et al. (2006), Isogai et al. (2011b)
Periodate-chlorite	Induce mostly aldehyde groups and some carboxylate groups, improve fibrillation, reduce energy consumption, and produce thinner NFC	Liimatainen et al. (2012), Lindh et al. (2014)
Alkaline extraction	Degrade lignin and improve fibrillation	Dufresne et al. (1997)
Carboxymethylation	Increase anionic charge and induce electrostatic repulsion between fibres, improve fibrillation, reduce energy consumption, and produce thinner NFC	Wågberg et al. (2008)
Enzymatic pretreatment	No charges introduced, improve fibrillation, reduce energy consumption, and produce thicker NFC	Pääkkö et al. (2007), Henriksson et al. (2007)
Mechanical pre-refining	No charges introduced, reduce fibre size to avoid clogging, energy-intensive process during refining	Stelte & Sanadi, (2009)

### 2.3.1. Enzymatic pretreatment

Enzymatic pretreatment of wood pulp using endoglucanase has been studied with the aim of facilitating fibre treatment in the homogeniser or micro-fluidiser. Detailed knowledge of how to manufacture MFC/NFC using chemical pulp combined with enzyme treatment is available in Henriksson et al. (2007), who reported that treating fibres with the enzyme endoglucanase enhances fibrillation and prevents the fibres from clogging the homogeniser. Pääkkö et al. (2007) also pretreated the fibre wall of the wood pulp with enzymes and observed that the enzymes assisted the process of pulp disintegration. Figure 18 shows the trends of increasing numbers of publications examining enzymatic and chemical pretreatment methods since 2008.

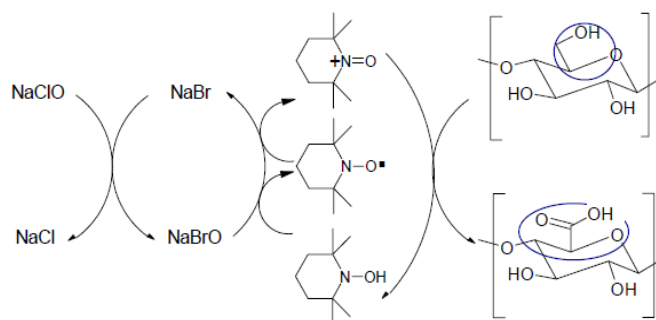


**Figure 18.** Number of MFC-related publications on (a) chemical (i.e., TEMPO: 2,2,6,6-tetramethylpiperidine-1-oxyl) and (b) enzymatic pretreatment strategies (courtesy of Charreau et al. 2013)

### 2.3.2. Chemical pretreatment (TEMPO-mediated oxidation)

According to Saito et al. (2006a, 2006b) and Saito and Isogai (2006), the TEMPO-oxidation pretreatment of pulp is a more efficient means of extracting fibrils from within the fibre walls of most chemical pulps. The TEMPO method offers very good fibrillation efficiency with very small fibre fragments. The method is known for the high aspect ratio and large surface area of its output.

The only disadvantage associated with the TEMPO method concerns the toxicity of the TEMPO radicals, i.e., sodium bromide (NaBr) and sodium hypochlorite (NaClO). Saito et al. (2007) suggested that the TEMPO pretreatment helped loosen the adhesion between the fibrils by preventing the formation of strong interfibrillar hydrogen bonds. The mechanism of the TEMPO-mediated oxidation of cellulose is explained by Bragd et al. (2004). Figure 19 shows the reaction pathway of the TEMPO method; as reported by Saito et al. (2007), the oxidation system associated with the TEMPO radical functions as an oxidising agent and turns the primary alcohols into aldehyde and carboxyl groups. The TEMPO-system oxidation of cellulose affects the hydroxyl group binding to carbon number six (C-6) in the glucose unit.



**Figure 19.** Schematic of the TEMPO-mediated oxidation method: reaction mechanism

## 2.4. Energy consumption during nanocellulose processing

The mechanical processing of nanocellulose is very energy intensive, energy consumption in the range of 6000–30,000 kWh t<sup>-1</sup> being reported. Enzymatic and chemical pretreatment methods combined with mechanical treatment have been introduced to improve the energy efficiency of the overall process.

The demand for NFC and MFC for commercial applications is increasing exponentially in response to the results of research funded by both academia and industry. Progress is still hampered by several factors during the mechanical processing of the pulp fibres. The main challenge has been the huge amount of energy required to produce MFC and NFC. Despite many claims to have developed energy-efficient ways of producing MFC and NFC, it is fair to say that the processes are not economically feasible for low-tech applications such as paper and paperboard products. The homogenising pressure, fibre concentration, and number of passes all affect the amount of energy consumed during processing. Pretreatment strategies such as TEMPO-mediated oxidation, periodate-chlorite oxidation, enzymatic hydrolysis, carboxymethylation, and acetylation have been applied to pulp fibres as ways to reduce the total energy consumption during the main process of mechanically disrupting the fibres to form nanocellulose (Isogai 2013).

The Swedish bio-based research institute Innventia AB was also involved in developing nanocellulose in the late 1980s, and reported high energy consumption of approximately 27,000 kWh t<sup>-1</sup> over the multiple homogenisation cycles required to process pulp fibres into nanocellulose (Ankerfors 2012). The same huge amount of energy is still required for nanocellulose processing, and energy values exceeding 30,000 kWh t<sup>-1</sup> are reported. It has been demonstrated that periodate-chlorite oxidation can be implemented to significantly reduce the overall energy needed for nanocellulose processing. Tejado et al. (2012) studied this approach by

examining how the fibre charge content of bleached softwood kraft pulp chemically pretreated using periodate-chlorite oxidation affected the energy needed to extract cellulose fibres into nanocellulose. The energy consumption values and fibrillation efficiency of nanocellulose have been evaluated using different types of mechanical equipment, such as homogenisers, micro-fluidisers, and micro-grinders (Spence et al. 2011). Energy efficiency during nanocellulose production has been significantly improved by using the TEMPO-oxidation method, reducing the energy consumption by over 95%, i.e., from 700 MJ kg<sup>-1</sup> to approximately 7 MJ kg<sup>-1</sup> (Isogai et al. 2011a). In addition, Syverud et al. (2011) reported energy values of approximately 10,000 kWh t<sup>-1</sup> per pass through the homogenising equipment at an applied pressure of 1000 bars and pulp consistency of approximately 0.5%. They noted that, with the same energy consumption, TEMPO-pretreated pulp fibres were more fibrillated and homogenous than were non-TEMPO pretreated fibres.

High energy consumption during the mechanical treatment of bleached kraft pulp fibre slurries was also studied by Eriksen et al. (2008). They observed an energy demand of approximately 70,000 kWh t<sup>-1</sup> because they did not use any pretreatment, though they stressed that they were not concerned with the energy level during processing. To evaluate the amount of energy consumed when processing the fibre raw materials, Josset et al. (2014) studied the energy consumed when grinding three raw material fibre feedstocks versus the number of grinding cycles. The feedstocks were elemental chlorine-free (ECF) fibre, recycled newspaper fibre, and wheat straw (WS). After two mechanical grinding cycles of the pulp suspension, the energy consumption increased almost linearly with the number of grinding cycles by approximately 0.7 kWh kg<sup>-1</sup> per grinding cycle. After ten grinding passes using a supermass colloidiser with a 15 kW motor, the total energy consumption for processing the different fibre materials was as follows: ECF fibre, 5.25 kWh kg<sup>-1</sup>; recycled newspaper fibre, 6.75 kWh kg<sup>-1</sup>; and WS, 5.75 kWh kg<sup>-1</sup>.

Zhu et al. (2012) and Lindström et al. (2012) have claimed that the nanopulping process could be a favourable way to significantly reduce the overall energy consumption during nanocellulose production, reporting energy consumption of approximately 760 kWh t<sup>-1</sup>. They also state that it is possible to recover some of the energy used in the process, and that the energy consumed if this is done is approximately 446 kWh t<sup>-1</sup>.

Although many have addressed the issue of energy consumption during MFC and NFC production, certain aspects of energy measurement have not been investigated. It is worth noting that some of the key indicators of energy consumption in the pulp and paper sector are: power, motor load of the machine,

motor load of the pump, fibre consistency during treatment, and mass flow. To obtain a clear overview of energy consumption during MFC and NFC processing, we should consider all these factors. Stenius (2014) stated that nanocellulose research still faces some challenges if nanocellulose is to be commercialised. These challenges include high energy consumption during processing, difficulties producing uniform nanocellulosic particles, and dewatering difficulties in papermaking applications.

## **2.5. Nanocellulose characterisation**

Another challenge facing nanocellulose research is learning how to maintain consistent NFC and MFC quality. The current wide variation in quality is attributable to several factors, including particle geometry (i.e., particle size and morphology), NFC and MFC preparation method, raw material sources, and surface chemical pretreatment. NFC and MFC have a tendency to form agglomerates. Rebouillat and Pla (2013) reported that the agglomerating property of nanocellulose is mostly apparent during drying. This variation in quality has made it very difficult to compare the final impacts of NFC and MFC as additives in papermaking and other useful applications. Kangas et al. (2014) stated in their review that there are many different methods to characterise nanocellulose and that it is essential to properly evaluate micro- and nanofibrillated cellulose for use in industrial processing and for safety reasons. They also mentioned that microscopic methods have been the primary methods for evaluating nanocellulose, although these are time-consuming and based on the subjective characterisation of small portions of large cellulosic nanofibrils.

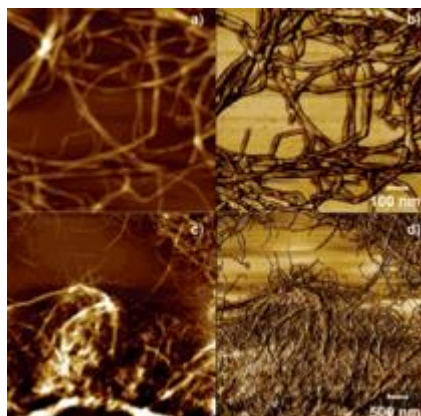
### **2.5.1. Particle morphology**

Chirayil et al. (2014) confirm that MFC and NFC are long and flexible micro- and nanofibrils 1–100 nm wide, several microns long, and composed of alternating crystalline and amorphous regions. Habibi et al. (2010) reported that microscopy techniques are valuable methods for assessing the morphology, structure, and particle size distribution of cellulose nanocellulose. While microscopy methods clearly reveal the fibril structure, they are time consuming, as they sometimes require pretreatment, and are generally expensive.

### **2.5.2. Atomic force microscopy (AFM)**

Pääkkö et al. (2007) and Ahola et al. (2008) used atomic force microscopy (AFM) to gain extensive information for the assessment of MFC and NFC. Andresen et al. (2006) also visualised MFC obtained from the disintegration of bleached softwood sulphite pulp using AFM. Their AFM imaging revealed that the unmodified (i.e., non-silylated) MFC consists of heterogeneous fibril particles, such as thin fibrils and bundles of fibrils. Kaushik and Singh (2011) used AFM to evaluate the

dimensions and homogeneity of wheat straw cellulose nanofibrils produced by steam explosion in an alkaline medium. The AFM micrographs showed that the fibrils were slightly agglomerated. Figure 20 is an AFM image, showing the fibrillar structure of an MFC from sulphite pulp.

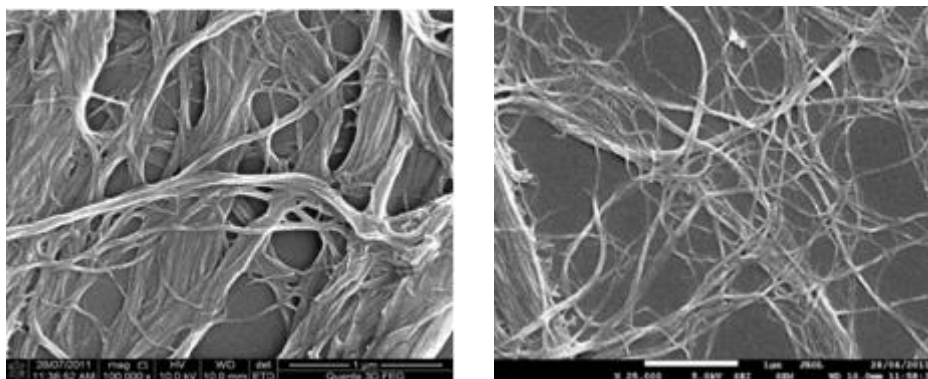


**Figure 20.** AFM images of MFC from bleached sulphite pulp (courtesy of Pääkkö et al. 2007)

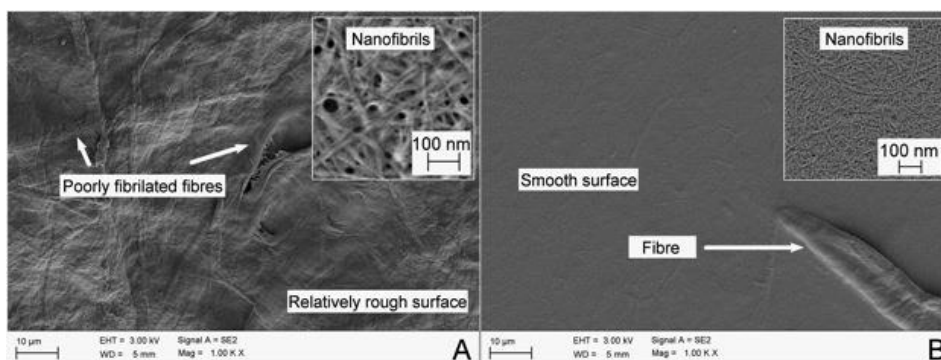
### 2.5.3. Scanning electron microscopy (SEM)

Wood fibres and agricultural fibre residues are hygroscopic, radiation sensitive, thermolabile (i.e., thermally unstable), and poor conductors. Therefore, it is important to prepare samples properly for SEM examination, usually by drying – specifically, freeze-drying, air-drying, or supercritical point drying. However, drying results in certain drawbacks, such as drying artefacts, shrinkage, and structural collapse. SEM has a resolution between that of optical microscopy and that of TEM or AFM, and permits observation of MFC and NFC from the millimetre to true nanometre scale (Kangas et al. 2014). Abe et al. (2007) used field-effect SEM to measure the fibril size of NFC and reported that freeze-dried and oven-dried (o.d.) NFCs had nanofibrils with a uniform diameter of approximately 15 nm. Fall et al. (2014) used AFM and SEM images to characterise the particle size of eucalyptus, acacia, and pine cellulosic nanofibrils in both centrifuged and non-centrifuged samples. Chinga-Carrasco et al. (2013) have demonstrated that it is possible to use laser profilometry together with SEM as complementary tools to evaluate the degree of fibrillation of the microstructure of unbleached MFC, in combination with the qualities of bleached and TEMPO-derived MFC; the method involved staining the unbleached MFC with osmium tetroxide ( $\text{OsO}_4$ ), which is believed to react with the  $\text{C}=\text{C}$  carbon double bonds in lignin. They observed that the qualities of bleached and unbleached MFC are associated with different morphologies and surface chemistries. Figure 21 shows SEM images of MFC (left panel) and NFC (right panel); the fibril structure differs significantly between MFC and NFC, as MFC has many large-scale structures (i.e., fibres) remaining after

mechanical treatment, while NFC has thinner fibrils. Figure 22 clearly shows the highly fibrillated and poorly fibrillated fibrils of a bleached MFC.



**Figure 21.** SEM images of MFC (left) and NFC (right) (courtesy of Varanasi et al. 2013)



**Figure 22.** SEM images of bleached MFC (courtesy of Chinga-Carrasco 2013)

#### 2.5.4. Transmission electron microscopy (TEM)

The true nano-size features of nanocellulose can be evaluated using transmission electron microscopy (TEM) because of its high resolution. TEM has been used for studying “second-generation” MFC (Ankerfors 2012). “Second-generation” indicates that the fibres were carboxymethylated as a pretreatment strategy, followed by high-pressure mechanical treatment using micro-fluidiser equipment. The fibrils produced using this method were 5–15 nm in diameter and over 1  $\mu\text{m}$  long. In addition, Wang et al. (2007) used SEM, TEM, and AFM to assess the dimensions of nanocellulose processed from hemp fibres; they stated that the nanofibrils were approximately 30–100 nm wide and an estimated several micrometres long. Wågberg et al. (2008) used TEM and AFM to characterise MFC



fibrils and reported diameters of approximately 5–15 nm and lengths of approximately 1  $\mu\text{m}$ .

#### **2.5.5. Light microscopy**

Light microscopy is a fast method of characterising the morphological structure of hardwood and softwood cellulose fibres treated in high-pressure homogenising equipment to produce cellulose nanofibres (Stelte and Sanadi 2009). From light microscopy imaging, Stelte and Sanadi (2009) noted that fibrillation occurred solely on the surface of hardwood fibres during refining, more pronounced fibrillation effects on the fibre cell walls being seen after high-pressure homogenisation. Optical microscopy (staining method) has also been used to evaluate the morphology of fibre particles of unbleached high-lignin softwood before and after mechanical treatment, showing that homogenisation considerably reduced the widths of the original pulp fibre particles (Spence et al. 2010a). Evidence for using various optical approaches, such as optical scanning, UV-vis spectrophotometry, and turbidity, to adequately evaluate the fibrillation efficiency of NFC and MFC is presented by Chinga-Carrasco (2013). Importantly, Spence et al. (2010a) and Chinga-Carrasco (2013) confirmed that films from poorly fibrillated nanocellulosic materials are opaque, whereas films from highly fibrillated materials containing larger amounts of nanofibrils are translucent with light transmittance exceeding 90%.

### **2.6. Nanocellulose as a strength additive in papermaking**

The art of papermaking has over 2000 years of history, and the fibrous network of paper is used in our everyday lives in printing, writing, magazine, hygiene, and paperboard paper products. Many scholars have demonstrated that MFC and NFC can be used as strength additives in papermaking applications, to enhance barrier properties in food packaging, to improve paper glossiness, to reduce paper grammage, and to enable smart packaging. This range of applications is partly attributable to their function as wet- and dry-strength additives in paper and paperboard products. MFC and NFC are also used because of their influence on the mechanical strength and barrier properties of end-user products in the pulp and paper industry. A number of researchers have addressed nanocellulose processing and its use in papermaking-related processes (Saito and Isogai 2005, Ahola et al. 2008, Eriksen et al. 2008, Mörseburg and Chinga-Carrasco 2009, Taipale et al. 2010, Yoo and Hsieh 2010, Sehaqui et al. 2011, Bilodeau et al. 2012, Hii et al. 2012, González et al. 2013, Rantanen and Maloney 2013, Su et al. 2013, Djafari Petroudy et al. 2014).

Wet strength is very important for tissue paper, paper towels, paperboard, and other paper grades (Saito and Isogai 2005). Wet-strength additives such as cationic polyelectrolyte and polyamidoamine-epichlorohydrin (PAE) have been used for

many years in papermaking processes. PAE together with cellulose nanofibrils have been used in pulp furnish to improve the mechanical properties of paper sheets (Ahola et al. 2008). An important strengthening technique is to apply polymeric multilayers of cationic and anionic starch to improve the strength properties of paper (Eriksson et al. 2005).

A review of chemical properties affecting both chemically and mechanically processed pulp fibres during papermaking was conducted by Lindström (1992), who found that refining or beating pulp fibres tends to enhance flexibility, increase swelling ability, and thus improve bonding in the sheet during papermaking. Duker et al. (2007) reported paper strength development using a fibre-beating strategy. Details of pulp refining are examined by Lumiainen (2000), who notes that a disadvantage of excess refining is that it makes the paper sheet denser, which is detrimental to bending stiffness. Besides pulp refining or beating, chemical strength additives such as carboxymethyl cellulose (CMC), gums, and starches have been used to increase paper strength (Laine et al. 2002). The relative bonded area (RBA) of fibres is regarded to be important as it contributes significantly to the basic structural properties of paper (Page 1969). Recently, Hirn and Schennach (2015) introduced a new way of quantifying bonding energies between pulp fibres during papermaking. In their work, they considered the effects of mechanical interlocking, capillary bridges, interdiffusion, hydrogen bonding, Van der Waals forces, and coulomb forces on the bonding energy.

Ankerfors et al. (2013) affirmed that fibre properties such as length, specific bond strength, fibre–fibre bonded area, sheet formation, and stress concentration are very important in paper strength development. The use of chemical strength additives has been the primary method of improving paper strength. As an alternative to chemical strength additives, nanocellulose also acts as a strength-enhancing material in the papermaking process, as it has inherently high strength and stiffness. Moreover, nanocellulose has an extremely high specific surface area and could be used to enhance bonding between fibres. It is crucial to begin using nanocellulose as a strength enhancer in paper and paperboard products, particularly to improve the z-strength. Innventia AB, Sweden, one of the leading research actors in NFC and MFC production, has put great effort into developing nanocellulose in papermaking suspensions. One practical and potential use of nanocellulose is in the paper and paperboard industry (Lindström et al. 2014), as this nanomaterial can be used as a strength additive and in barrier/coating applications.

IMERYS FiberLean reports that it can produce low-cost MFC using industrial-scale methods (Svending 2014). The company IMERYS uses its competence in grinding technology to co-grind pulp fibre with a mineral to produce MFC that can be used

in both printing and writing papers. This approach does not require any pretreatment stage. IMERYS has presented evidence that it can produce MFC and mineral composites at 5–6 wt%. This composition can be used in papermaking systems, as it is easy to mix and easy to pump through the pipes in an industrial facility. In 2014, the company claimed to be able to produce 3000 dry tons year<sup>-1</sup> of MFC. It should be noted that the co-grinding methodology used by IMERYS produces relatively coarse MFC. However, the company's researchers have demonstrated that this MFC is optimised for strength in wet-end applications. IMERYS has concluded that the FiberLean processing method offers several advantages, such as maintaining process stability, enhancing the initial strength properties at high filler content, and having little effect on the dewatering property or wet-end chemistry.

Using thermomechanical pulp (TMP) and ground calcium carbonate (GCC) (Hii et al. 2012) examined the effect of MFC on paper strength and dewatering properties. They were convinced that the strength and barrier properties were improved, but noted that the drainage behaviour was negatively affected. However, the press dewatering properties of microfibrillated cellulose added during sheet formation could be optimised without affecting the entire papermaking process. The drainage property-related issue during papermaking has also been examined by Su et al. (2013), who demonstrated that the drainage behaviour during papermaking is influenced by the ionic strength, type of polyelectrolyte, pH, and fibre dimensions. More fibrillated nanocellulose usually experienced poor dewatering, i.e., more time was required for the fibre mat to form during drainage, resulting in poor drainage properties.

Taipale et al. (2010) conducted a comparative study of the papermaking properties resulting from adding different grades of MFCs to the pulp furnish. They examined drainage behaviour as a function of the salt concentration, fixative type, pH, and type of MFC. They found that adding MFC significantly degraded the drainage properties during papermaking. However, when investigating the influence of using cationic polyelectrolytes together with MFC, they became convinced that the drainage properties could be adjusted by altering the processing technology and using a certain dosage and combination of MFC and polyelectrolyte. They found that adding MFC reduced the drainage rate of the pulp suspension while significantly improving the mechanical strength of the paper. Eriksen et al. (2008) presented evidence that MFC could improve the strength properties of TMP paper materials, the only drawback found being poor dewatering.

Mörseburg and Chinga-Carrasco (2009) examined the use of NFC together with clay in layered TMP paper products. They found a significant improvement in both tensile index and z-strength when replacing some bleached softwood kraft pulp fibres with a small amount of NFC and mechanical pulp. Bilodeau et al. (2012) demonstrated the use of MFC in producing new printing and writing paper grades. By mixing MFC with pulp furnish to produce uncoated free sheets using a pilot paper machine, they improved the porosity by 164%, stiffness by 11%, and tensile strength by 30%. However, this was accompanied by a 6% reduction in tear strength and a 6% reduction in bulk.

According to the review by Brodin et al. (2014), MFC and NFC improve the relative bonded area of paper sheets, as the materials are in the nanoscale range and behave similarly to starch. This enhances the molecular contact between pulp fibres, which is the main underlying reason for the strength improvement when using MFC and NFC as strength additives. One drawback of using NFC or MFC directly in the papermaking process is the poor dewatering of the resulting paper. As the materials are in the nanoscale range, they impede water from going through the wire press on the paper machine. According to Torvinen et al. (2014), NFC and MFC could be used to enhance paper strength properties and as a strategy to increase the filler content of super-calendered paper using PCC-MFC/NFC components. They presented evidence that it was possible to reach a high filler content of approximately 35% while reducing the overall cost of processing their intended paper grade.

## **2.7. Nanocellulose in composite films**

The main motive for using NFC and MFC in films is the desire of most companies to use completely renewable packaging materials. Accordingly, nanocellulose is a candidate nanomaterial that could potentially be used in barriers/coatings in bio-based packaging grades. It is also worth noting that the final quality of NFC or MFC intended for barrier or coating application depends greatly on the film-forming process, drying method, and storage conditions, as these parameters will affect the final material properties. Paper materials are usually coated to enhance their surface properties, improve print quality, and – better still – to incorporate new functionalities, such as barrier properties for oxygen, water vapour, and grease/oil (Nygårds 2011). Syverud and Stenius (2009) produced NFC films on Petri dishes and found that the air permeability properties of the films were significantly improved. Their intention was to improve the barrier properties of paper packing products, particularly those used in food packaging.

Furthermore, it is now the case that research into nanocellulose is holistically seeking radical ways to develop new materials with added functionality. There is

growing interest in using nanocellulose together with graphitic materials in making composite films. Andres et al. (2014) described nanographite (NG) as a heterogeneous carbon material comprising a mixture of graphene, multi-layer graphene flakes, and graphite. They demonstrated that a 10% addition of NFC to the NG increased both the wet and dry strength while maintaining the capacitance. NG is also recognised as highly functional and is often tailored to specific applications, such as coating and barrier applications, graphite-based composites, printed electronics, sensors, energy applications, and life-science applications. By using NFC together with 1.25 wt% multi-layered graphene, one can improve the mechanical properties of the nanocomposite, the resulting material having a Young's modulus 16.9 GPa, an ultimate strength of 351 MPa, and a work of fracture of 22.3 MJm<sup>-3</sup> (Malho et al. 2012).

## **2.8. Market potential of nanocellulose and pilot plant facilities**

Some of the unique properties of NFC and MFC include its relative abundance, light weight, dimensional stability, thermal stability, high optical transparency, high thermal conductivity, low oxygen permeability, low toxicity, high strength and modulus, and the fact that NFC and MFC are reusable, recyclable, and biodegradable (Rebouillat and Pla 2013, Nelson 2014, Shatkin et al. 2014, Chirayil et al. 2014). Shatkin et al. (2014) studied market projections for cellulose nanomaterials and made some suggestions regarding its applications (Table 4).

Paper materials can be used as a substrate for flexible electronics and energy devices (Fang et al. 2013). However, paper has the disadvantages of its intrinsic opacity and roughness, and an alternative to paper material could be nanocellulose, as it would be better to use NFC to produce nanopaper with high opacity and excellent smoothness. Fang et al. (2013) developed the first novel transparent and conductive hybrid paper touchscreen with very good anti-glare properties in a bright environment.

Li et al. (2013) suggested that there is need to produce pulp fibre-derived magnetic nanopaper with good magnetic, optical, mechanical, and thermal properties. They claimed that transparent magnetic materials could be used in magneto-optical switches, magneto-optical sensors, bio-analytical applications, optical circulators, modulators, and optical isolators. Zhu et al. (2013) demonstrated that soft and mesoporous wood fibre substrates could be used as a novel platform for low-cost sodium-ion batteries.

**Table 4.** Applications of nanocellulose-enabled products (courtesy of Shatkin et al. 2014)

High volumes	Low volumes	Novel and emerging
Cement: concrete additive	Insulation materials for sound and heat	Sensors: medical, industrial and environmental
Composite materials for the automotive industry: replace glass fibres in auto bodies and interiors	Advanced composite materials: for aerospace structure and interiors	Air and water filtration
Paper coatings and films in packaging products: replace plastic packaging products and films	Aerogels: oil and gas applications	Reinforcement fibre in construction
Packaging composites and fillers	Functional pigments, paint products, and as rheological modifier	Flexible electronics, printed electronics and conducting platforms
Printing papers: to achieve good print quality, high surface smoothness, and enhanced ink adhesion	Construction material and other composites	Cosmetics
Strength additive in paper products and paper composites		Intelligent packaging
Hygiene and absorbent products		Organic LEDs
Textiles		Photovoltaics
		Recyclable electronics
		Photonic films
		3D printing

The production and commercialisation of NFC and MFC, as reported by Miller (2014), are presented in Table 5, which indicates that many universities and companies have made groundbreaking investments in forest-based nanotechnology. In November 2011, the Finnish forest products company UPM claimed to be starting pre-commercial production of MFC at a pilot plant in Espoo, Finland. Stora Enso also started a pre-commercial MFC plant that will deal with customer-driven innovation and product concepts.

In October 2014, Borregaard announced that it had invested approximately NOK 225 million in the production of commercial grades of nanocellulose under the trade name Exilva MFC. Production will reportedly begin in the third quarter of 2016 with a capacity of 1000 tonnes per year, with the potential for expansion. Exilva MFC is expected to be used in several applications ranging from composites to cosmetics, detergents, adhesives, and other industrial formulations.

The German company Rettenmaier produces NCC as an inert filler for pharmaceuticals (Williamson 2012). Daicel in Japan is working on a nanocellulose product known as Nano Celish (trademarked name). The first NCC pilot plant was constructed by CelluForce, and was inaugurated in early 2012 in Windsor, Quebec. Another pilot NCC production facility was created in Edmonton, AB, Canada

through collaboration between the Alberta provincial and Canadian federal governments in partnership with industry.

In the summer of 2012, the US Forest Service Forest Product Laboratory opened an NCC pilot plant in Madison, WI, USA. The Forest Bioproduct Research Institute of the University of Maine has a pilot plant facility for CNF production in Orono, ME, USA (Williamson 2012). More details of the production methods and amounts of pilot-scale facilities around the world can be obtained from Bras et al. (2013).

Recently (2016), MoRe Research AB, a research and development centre in Örnsköldsvik, Sweden, has been collaborating with Holmen, Melodea, and the SP Technical Research Institute of Sweden to invest in a nanocrystalline cellulose (NCC) industrial pilot facility. The NCC pilot plant will be used in developing new materials from cellulosic raw materials and in commercialising nanocrystalline cellulose.

**Table 5.** Nanocellulose pilot plant production facilities (courtesy of Miller 2014)

Industry or university	Country	Announced production amount (dry solids content)
<b>Cellulose nanofibres</b>		
CelluForce	Canada	1 ton day <sup>-1</sup>
Alberta Innovates	Canada	20 kg day <sup>-1</sup>
US Forest Service, Forest Products Laboratory	USA	10 kg day <sup>-1</sup>
Blue Goose Biorefineries	Canada	10 kg day <sup>-1</sup>
FPIInnovations	Canada	3 kg day <sup>-1</sup>
Colorado School of Mines	USA	Lab scale
Melodea Ltd.	Europe (Sweden)	Lab scale
Research universities or private labs	Around the world	<0.1 kg day <sup>-1</sup> (several possible production methods)
<b>Cellulose nanostructured materials</b>		
University of Maine	USA	1 ton day <sup>-1</sup>
Nippon Paper	Japan	150 kg day <sup>-1</sup>
Borregaard	Norway	100 kg day <sup>-1</sup>
Innventia AB	Sweden	100 kg day <sup>-1</sup>
NamiCell	France	100 kg day <sup>-1</sup>
Oji Paper	Japan	100 kg day <sup>-1</sup>
FPIInnovations	Canada	n/a
Stora Enso	Finland	n/a
UPM Kymmene Ltd	Finland	n/a
Daicel	Japan	Lab scale
Luleå University of Technology	Sweden	Lab scale
US Forest Service, Forest Products Laboratory	USA	Lab scale
JRS	Germany	n/a
Omya	Swiss	n/a
BASF/Zelpho	Germany	n/a
CelluComp	UK/Scotland	n/a
InoFib	France	n/a
EMPA	Swiss	15 kg day <sup>-1</sup>
VTT	Finland	15 kg day <sup>-1</sup>
PFI	Norway	15 kg day <sup>-1</sup>
LGP2/Grenoble INP*	France	2 kg day <sup>-1</sup>
Research universities or private labs	Around the world	<0.1 kg day <sup>-1</sup> (several possible production methods)



### **3. MATERIALS AND METHODS**

Several key methodologies were used in this research to address the following two aims:

- To use low-quality fibre materials from a mechanical pulp mill to create value-added products and/or improve the strength properties of existing paper and paperboard products.
- To gain an understanding of nanocellulose production methods and characterisation.

The following methodologies were used in addressing these aims:

- Fractionation techniques employing Bauer-McNett classification and the Britt Dynamic Drainage Jar were used before homogenisation to obtain small fibre particles that could be easily treated in the homogeniser.
- The homogeniser process temperature was adjustable; the main idea was to use an elevated temperature of up to approximately 100°C in the homogenising equipment to influence the lignin softening.
- Chemicals were used to influence the softening and swelling properties of the pulp fibres; conventional chemicals such as hydrogen peroxide were used to develop an easy-to-implement concept.
- Cationic starch and nanocellulose were used as strength additives for paperboard products.
- High-shear homogenisation of pulps.
- TEMPO-mediated oxidation pretreatment strategy.
- Characterisation of MFC and NFC using the crill method.
- Processing of NFC-NG composite film.
- Organic acid (i.e., formic acid) processing of nanocellulose.
- Processing of nanocellulosic foam materials.

### 3.1. Pulps

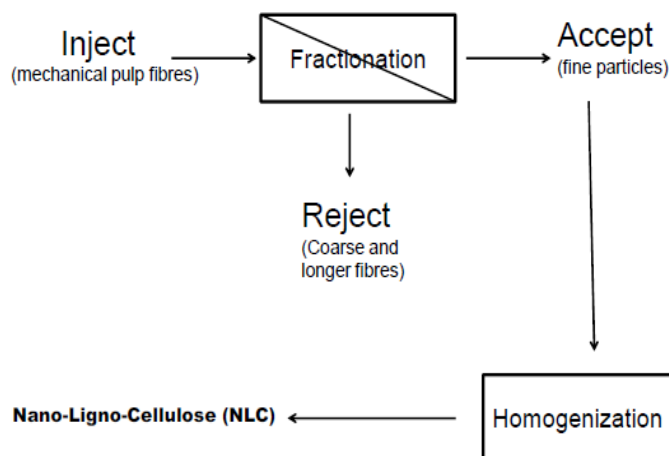
**Thermomechanical pulp (TMP)** – (Papers II and III): The TMP sample used in this investigation had a Canadian standard freeness (CSF) value of approximately 65 mL and a dry solids content of 34%; it was obtained from the SCA pulp mill at Örtviken, Sundsvall, Sweden. The wood type used was fresh Norway spruce (*Picea abies*).

**Chemi-thermomechanical pulp (CTMP)** – (Papers II and III): The CTMP sample used in this investigation was obtained from the SCA Östrand pulp mill, Sundsvall, Sweden. The wood material used was solely never-dried Norway spruce (*Picea abies*) with a high CSF value of approximately 619 mL and an ISO brightness of 76%. The CTMP was used both as the fibre material in the laboratory handsheets and to produce NLC (nanocellulose produced from CTMP is referred to as NLC in this work).

**Bleached kraft pulp (BKP)** – (Papers II and IV): The BKP pulp used in this work was obtained from the SCA Östrand pulp mill, Sundsvall, Sweden. It had a CSF value of approximately 630 mL and was 100% softwood, i.e., 24% spruce (*Picea abies*) and 76% pine (*Pinus sylvestris*). It was a mixture of round wood chips (55%) and sawmill chips (45%) that contained a great deal of sapwood, which is rich in long stiff fibres. The BKP was also used as the fibre material for the laboratory handsheets and to make NC (nanocellulose produced from BKP is referred to as NC in this work).

### 3.2. Homogeniser (papers II–IV)

GEA Niro homogeniser (ARIETE, Model: NS2006H, Serial Number: 8755, 2010, Parma-Italy) was employed to convert the fine particles into the smaller particles referred to as nano-ligno-cellulose (NLC) in this thesis. Pulp fractionation was performed in such a way that the fibres were separated into particular fractions, i.e., fines and longer fibres; this provided the correct fines fraction for mechanical treatment in the homogenising equipment. The pulp slurries were treated in the homogenising equipment at approximately 1% consistency.



**Figure 23.** Schematic of approach to producing nano-ligno-cellulose

The homogenisation pressure was usually set in the 200–300-bar range, but it was sometimes difficult to maintain constant pressure due to the clogging of the fine particles in the homogenising system. An average of approximately 5 L of pulp suspension was used in most of the investigations. The main motor power of the homogeniser is 3 kW while the motor power of the feeding pump is 0.75 kW. The flow rate of the suspension in the homogeniser was 1.4 L min<sup>-1</sup> with an estimated 18 passes per trial.

The homogenising equipment had a maximum working pressure of 600 bars, the pressure being detected by means of the small manometer on the compression head of the machine. Figure 23 is a schematic of our approach to producing nano-ligno-cellulose from mechanical pulp fine materials. A Britt Dynamic Drainage Jar (BDDJ) with a 30-mesh screen and a Bauer-McNett classifier (BMcN) were used as the fractionation equipment. Particles that passed through the fractionation equipment are referred to as fines while those retained on the mesh wire are the coarse and longer fibres. The fines were used as feed material in the homogenising equipment to produce nano-ligno-cellulose.

### 3.3. Pulp fractionation

Two fractionation techniques were implemented: Bauer-McNett (BMcN) classification and Britt Dynamic Drainage Jar (BDDJ) fractionation. It is well known that fibre separation using the BDDJ differs from that using BMcN

classification in terms of effectively having a uniform fibre-size distribution. We starting by using BMcN classification, but found that obtaining the desired fines quality using this process was very time-consuming and tedious. Accordingly, we later decided to switch to using a specially designed 8-L BDDJ, which made it possible to obtain the desired quantity of fines in less time.

### 3.3.1. Bauer-McNett classifier (BMcN) (paper II)

The BMcN classifier was used in the pre-study of this work and the standard mesh screens used were 16-, 30-, 50-, 100-, and 200-mesh screens. The pulp fractions obtained were: R16 (i.e., fibre fraction retained on a 16-mesh screen), P16/R30 (i.e., fibres passing through the 16-mesh screen but retained on the 30-mesh screen), P30/R50, P50/R100, and P100/R200. The fractionation was performed according to the SCAN-CM 66:05 standard and the mesh sizes of the wire screens are presented in Table 6. Fibre fractionation was conducted to obtain small, short fibres that could be easily homogenised. Figure 24 shows the BMcN classifier.



**Figure 24.** Bauer-McNett classifier

**Table 6.** Bauer-McNett classifier screen size

Approximate screen size ( $\mu\text{m}$ )	US standard	Taylor standard
1200	16 mesh	14 mesh
599	30 mesh	28 mesh
297	50 mesh	48 mesh
152	100 mesh	100 mesh
76	200 mesh	200 mesh

### 3.3.2. Britt Dynamic Drainage Jar (BDDJ) fractionation (papers II–V)

The fines fractions were obtained from the pulp samples using the BDDJ fractionation technique. The fractions passing through the 30-mesh screen were considered “fines” and mechanically treated in the homogeniser, while the fractions retained on the 30-mesh screen were discarded. In this thesis, the pulps were fractionated using a specially designed BDDJ (see Figure 25) at the SCA Research Centre in Sundsvall, Sweden. The cut-off or pore size of the BDDJ 30-mesh screen was approximately 600  $\mu\text{m}$ .



**Figure 25.** Specially-designed Britt Dynamic Drainage Jar used in this study, at the SCA Research Centre in Sundsvall, Sweden

### 3.4. FibreLab analyzer (paper II)

The FibreLab optical analyser was used to characterise the fibre length distributions of the various fractions produced using the BMcN and BDDJ devices. FibreLab investigation indicated that the BDDJ 30-mesh screen provided a fibre fraction with an average fibre length under 1.2 mm; the fractions produced using the  $\geq 30$ -mesh screen were much longer and were discarded. One limitation of the FibreLab analyser is its inability to accurately measure very tiny fibrils due to its low resolution; part of the instrument can be seen in Figure 26.



**Figure 26.** FibreLab analyser

### **3.5. Microscopy techniques**

Several microscopy techniques were used in this thesis, namely, light microscopy, AFM, and SEM.

#### **3.5.1. Light microscopy (paper II)**

The light micrographs of TMP, CTMP, and BKP fines were acquired on a DMRX research microscope (Leica, Wetzlar, Germany) using the differential interference contrast (DIC) technique. The samples were diluted to very low concentrations and placed on a mica substrate for imaging.

#### **3.5.2. Atomic force microscopy (AFM) (paper II)**

A silicon wafer was used as an attachment surface for the NLC. P-DADMAC, i.e., poly(diallyldimethylammonium chloride), was used as glue to attach the NLC to the wafer. The wafer was allowed to air dry and images of the NLC materials were acquired using AFM and SEM. More details of the sample preparation method can be found in Henriksson et al. (2007). The surfaces of the specimens were imaged in tapping mode using a Dimension 3100 AFM with a Nanoscope IIIa controller (VeecoInstruments, Santa Barbara, CA, USA). A super-sharpened tip and low frequency were used in the imaging. The height image of the NLC was recorded at 23°C and 50% relative humidity.

#### **3.5.3. Scanning electron microscopy (SEM) (paper II)**

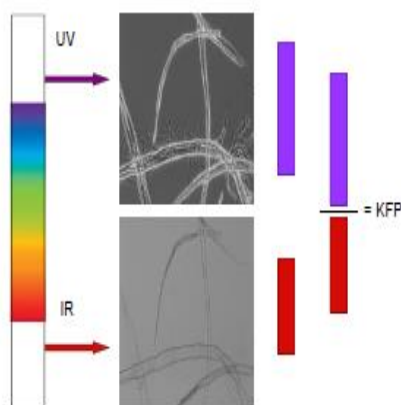
SEM micrographs were acquired using an EVO50 SEM (ZEISS, Oberkochen, Germany) equipped with a backscattered electron detector. The working conditions were as follows: acceleration voltage, 15 kV; pressure in the sample chamber, 0.7 mbar; and working distance, approximately 10 mm. A gold/palladium coating was used for the analysed samples. Sample preparation was performed as described in the light microscopy section.

### **3.6. Rheological properties (paper II)**

The rheological properties of the NLC suspensions were characterised using an MCR-300 rheometer (Physica Messtechnik GmbH, Stuttgart, Germany) with a CC27 concentric-cylinder measuring system adapted to US 200 software. The CC27 concentric cylinder has a diameter of 26.67 mm and a concentricity of 1 µm. The flow curves of the TMP-NLC suspensions were determined using concentrations of 0.66, 0.33, and 0.165% and the samples were homogenised at temperatures of 23 and 140°C. Unless otherwise stated, all the rheological investigations were conducted at a temperature of 23°C.

### 3.7. Crill instrument (papers III and V)

Many nanocellulose researchers have displayed considerable enthusiasm for the latest advances in characterisation techniques. More precisely, the desire is to develop a cheap, fast, and robust method for evaluating particle size distributions. Optical analysing instruments, such as the FibreLab, MorFi, and FibreMaster analysers, are unable to deal with particle size in the sub-micron scale. The main purpose of the crill study was to lay a foundation for developing a rapid and robust method for a continuous online monitoring system for use in process control. The method analyses the interaction between fibres and crill and is based on the optical response of a suspension at two wavelengths of light, UV and IR (see Figure 27). Sample measurements were made at the Dynäs Mondi Mill in Kramfors, Sweden; the measurements were made manually offline, and 1 g of o.d. pulp was used in all investigations. Steenberg et al. (1960) were the pioneers who started developing this technique.



**Figure 27.** Measurement principle of the crill value; KFP = crill value (courtesy of Innventia; Hansen and Sundvall 2012)

Hill and Eriksson (1973) were very clear in their statement concerning particle size evaluation using optical devices, and their measurement approach is based on fibre width distributions. The most critical need is to develop a measurement technique that can determine the width distribution at the sub-micron or nano scale. Hill and Eriksson (1973) provided very reproducible results of measuring fibre widths in the 5–200 micron range and lengths in the 0.2–5 range mm using optical equipment.

### 3.8. Rapid Köthen Sheet Former (papers IV and VI)

In this work, the process of forming laboratory handsheets involved the use of a Rapid Köthen Sheet Former (see Figure 28). The laboratory sheets had an average grammage of approximately  $65 \text{ g m}^{-2}$  (paper IV) and  $150 \text{ g m}^{-2}$  (paper VI). The following physical properties of the sheets were tested: sheet density, z-strength, tensile index, tear index, burst index, E-modulus, strain at break, tensile stiffness, and air resistance (see Table 7).



**Figure 28.** Rapid Köthen Sheet Former; the handsheets were pressed at 100 kPa and dried under restrained conditions at 93°C for 10 min

**Table 7.** Mechanical properties of laboratory sheets and test methods.

Handsheet properties	Methods	Instruments used
Density (grammage/thickness; $\text{kg m}^{-3}$ )	ISO 5270	Grammage – Mettler Toledo, Switzerland; thickness – L&W Sweden
Tensile index ( $\text{kNm kg}^{-1}$ )	ISO 1924-3	L&W tensile strength tester, Sweden
E-modulus ( $\text{GN m}^{-2}$ )	ISO 1924-3	TH-I L&W, Sweden
Tensile energy absorption (TEA) ( $\text{J kg}^{-1}$ )	ISO 1924-3	TH-I L&W, Sweden
Tear index ( $\text{Nm}^2 \text{kg}^{-1}$ )	ISO 5270	L&W tearing tester, Sweden
Bendtsen porosity ( $\text{mL min}^{-1}$ )	SCAN P85	L&W air permeance tester, Sweden
Z-strength ( $\text{kN m}^{-2}$ )	ISO 15754	L&W ZD tester, Sweden
Burst index ( $\text{kPam}^2 \text{g}^{-1}$ )	ISO 2758	L&W bursting strength tester, Sweden



### 3.9. Pulps for Crill Section (paper V)

**Thermomechanical pulp (TMP):** The TMP sample used here was obtained from the SCA Örtviken pulp mill, Sundsvall, Sweden; it had a CSF value of approximately 65 mL and a dry solids content of 34%. The wood type used was fresh Norway spruce (*Picea abies*).

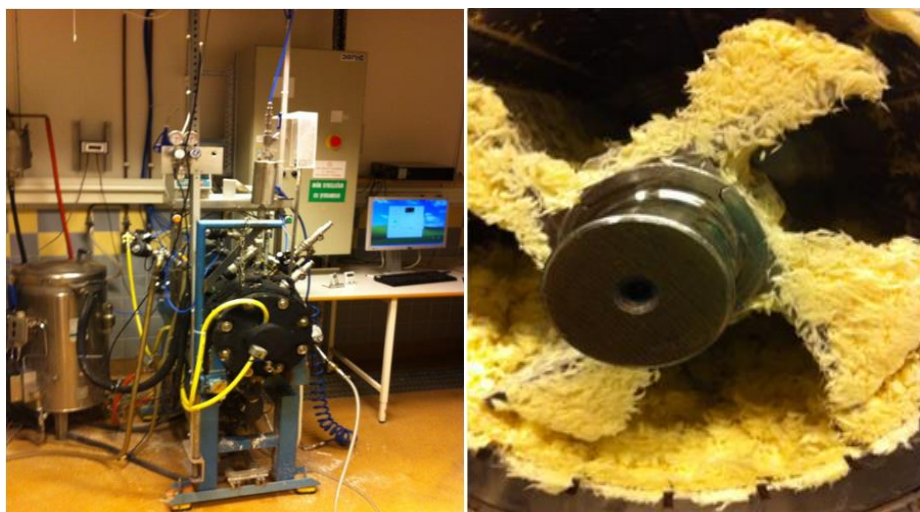
**Chemi-thermomechanical pulp (CTMP):** The CTMP sample used here was obtained from the SCA Östrand pulp mill, Sundsvall, Sweden. The wood material used was solely never-dried Norway spruce (*Picea abies*) with a high CSF value of approximately 619 mL.

### 3.10. Pulp washing (paper V)

A 1% diethylenetriamine pentaacetic acid (DTPA) solution was used to wash 150 g of o.d. pulp of approximately 5% consistency. The pulp slurry was placed in a plastic bag and sealed. The bag was then put into a hot water bath at approximately 70°C for 1 h for the reaction to be effective. After that, the DTPA solution was washed out with distilled water using a Buchner funnel. A pulp dry solids content of approximately 18% was achieved for all the samples, which were stored in a refrigerator at 4°C before further pretreatment in a wing mill refiner.

### 3.11. Wing mill refiner (paper V)

This equipment allows certain process parameters, such as temperature, residence time, and rotor mixing speed (rpm), to be controlled. Although the main purpose of the equipment is to mimic refining conditions, in this work, the wing mill refiner was used solely as a mixer (see Figure 29). Before sodium hydroxide (NaOH) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) pretreatment of the pulp fibres, the temperature of the wing mill refiner was set to 90°C; 150 g of o.d. pulp was placed in the vessel and preheated for 10 min at a rotor speed of 60 rpm. After this, the two chemicals were mixed together and charged via the nozzle at a pressure of 3 bars; immediately after the chemical dosage, the rotor speed was increased to 750 rpm for 1 min to achieve effective mixing. The rotor speed was later reduced to the usual 60 rpm for the rest of the 15-min reaction time. The samples were collected and stored in a refrigerator until further treatment. The chemical reactions were stopped by diluting the mixture with distilled water and then subjecting it to a double fractionation process using a Britt Dynamic Drainage Jar (BDDJ or BJ) using both the 30- and 100-mesh screens.



**Figure 29.** Wing mill refiner, used as mixer in this study

### 3.12. Transmission electron microscopy (TEM) (paper V)

For transmission electron microscopy, a 20- $\mu$ L drop of pulp and MFC dispersion was placed on a QUANTIFOIL 400-mesh copper grid with holey carbon film (EMS, Hatfield, PA, USA). The excess solution was blotted with a filter paper and the dispersion was allowed to dry. Grids with pulp specimens were examined using an FEI Tecnai 12 TEM (FEI, Hillsboro, OR, USA) at an accelerating voltage of 120 kV.

### 3.13. NFC processing using the TEMPO method

Wood pulp-derived NFC was produced using the TEMPO-mediated oxidation method combined with mechanical shearing of the oxidised pulp fibres. The cellulosic raw material used in this work was produced from a commercial sulphite softwood dissolving pulp (Domsjö Fabriker AB, Örnsköldsvik, Sweden), with very low contents of hemicellulose (<5%) and lignin (<1%), and CTMP. A T25 Ultra Turrax high-shear homogeniser (IKA Works, Wilmington, NC, USA; Figure 30) was used in performing the homogenisation trials. The machine was set at 15,000 and 20,000 rpm and the mechanical treatment times for the trials were 30, 60, and 90 min for approximately 2% w/v pretreated and non-pretreated pulp samples.



**Figure 30.** IKA T25 Ultra Turrax high-shear homogeniser

The pulps were subjected to TEMPO oxidation according to the method described by Saito et al. (2006). Chemical oxidations were conducted using NaBr and TEMPO to catalyse the sodium hypochlorite (NaClO) oxidation of primary alcohol groups at C-6 of the cellulose chain to carboxyl and aldehyde groups on the surface of the NFC, so the reaction is called regioselective oxidation. The dosages of NaClO used in these trials were 3, 5, 7, and 10 mmol of NaClO per gram of cellulose. The pH was kept at approximately 9–10 by adjusting it with either NaOH or HCl and the reaction time for the chemical oxidation was approximately 120 min. The reaction was stopped by washing with excess distilled water (more than 100 L) and the samples were stored in the fridge for further use. Figure 31 shows a TEMPO-derived NFC from sulphite pulp at approximately 1.5% concentration.



**Figure 31.** TEMPO-oxidised NFC from sulphite pulp

### **3.14. Preparation of nanographite (paper VII)**

A water dispersion of thermally expanded graphite (SO# 5-44-04; Superior Graphite, Chicago, IL, USA) was prepared. The obtained dispersion had a graphite concentration of 20 g L<sup>-1</sup>. Polyacrylic acid (2 wt% relative to the amount of graphite) was added as a dispersant. To exfoliate the graphite, we let the dispersion pass through the shear zone of a homogeniser for 22 cycles. The resulting NG dispersion has a broad particle size distribution and contains graphene, few-layer graphene, and graphite flakes.

### **3.15. Film casting (paper VII)**

All the NFC and NG suspensions were prepared separately. The desired amounts of NFC and NG were then prepared by efficient manual mixing, and approximately 10 g each of 1 wt% NFC suspension with and without NG suspension were poured (film casting method) into 8-cm-diameter Petri dishes and allowed to dry undisturbed at room temperature for 48 h. The film thickness was approximately  $25 \pm 2$   $\mu\text{m}$ , corresponding to a grammage of 28 g m<sup>-2</sup>.

### **3.16. Sheet resistance measurements (paper VII)**

Before the sheet resistance of the films was measured, the films were first pre-conditioned at 50% relative humidity for 48 h. The four-wire measurements were recorded in ohms, the current setting was 10 mA, and the voltage was 20 V. The sheet resistance in  $\Omega/\text{sq}$  was obtained by multiplying the measured value by 4.532, assuming a film grammage of 28 g m<sup>-2</sup> and a thickness of 25  $\mu\text{m}$ .

### **3.17. NFC-NG mechanical properties (paper VII)**

The mechanical properties were measured using an MTS 4 M/L testing machine (MTS, Eden Prairie, MN, USA) with a 2-kN load cell. The films were pre-loaded at 0.1 N and a test speed of 10 mm min<sup>-1</sup> was used. The nominal gauge length was 50 mm and the grip-to-grip separation was 30 mm. The films were cut into well-defined sections 15 mm wide and approximately  $25 \pm 2$   $\mu\text{m}$  thick.

## **4. RESULTS AND DISCUSSION**

This chapter is organised as follows: 4.1. Summary of appended papers, 4.2. Fibre length distribution, 4.3. Microscopy, 4.4. Rheology, 4.5. Crill, 4.6. Nanocellulose as a strength additive in paper, 4.7. Crill as a qualitative method to characterise nanocellulose, 4.8. NFC-NG composite films, and 4.9. Eco-friendly nanocellulose processing.

### **4.1. Summary of appended papers**

A summary of the appended papers of this thesis is presented in this section.

#### **Paper I: Processing of wood-based microfibrillated cellulose and nanofibrillated cellulose, and applications relating to papermaking: a review**

In paper I, we presented a comprehensive description of nanocellulose in terms of terminology and nomenclature, mechanical processing using different types of equipment, energy consumption during nanocellulose production, chemical and enzymatic pretreatment strategies, characterisation, nanocellulose for papermaking, coating, and films, and, lastly, its applications and market potential. As emerging cellulosic nanomaterials, microfibrillated cellulose (MFC) and nanofibrillated cellulose (NFC) are sources of enormous potential for the forest products industry. The forest products industry and academia are working together to realise the opportunities to commercialise MFC and NFC. However, the processing, characterisation, and material properties of nanocellulose still need improvement if this material is to realise its full potential. Research publications and patents concerning nanocellulose manufacturing, properties, and applications now number in the thousands annually, so it is crucial to review articles treating the “hot topic” of cellulose nanomaterials. This review examines the past and present situation of wood-based MFC and NFC in relation to their processing and papermaking-related applications.

#### **Paper II: An approach to produce nano-ligno-cellulose from mechanical pulp fine materials**

In Paper II, the methodology of producing nano-ligno-cellulose from mechanical pulp was studied. The aim was to produce mechanical pulp-based nanocellulose (i.e., nano-ligno-cellulose) using low-quality fibre fractions. Results indicate that it seems possible to mechanically treat fine particles of thermomechanical pulp (1% w/v) in the homogeniser to produce NLC. BKP fines fractions (0.5% w/v) were also tested as a reference in this study, and it was noticed that these BKP fines fractions

were not that easy to homogenise at a higher concentration (1% w/v). A possible explanation for this could be that the BKP fines have a much higher cellulose content and lower charge than does the fines fraction of the hemicellulose and lignin-rich TMP. Characterisation techniques using, for example, the FibreLab analyser, light microscopy, AFM, SEM, and rheological properties are reported in this paper. The length-weighted fibre length was noted to be a critical property affecting both pressure fluctuations and clogging during high-pressure mechanical shearing in the homogeniser.

### **Paper III: Crill: a novel technique to characterise nano-ligno-cellulose**

In paper III, the crill method was used to evaluate the degree of fibrillation of nano-ligno-cellulose. This measurement technique is based on the optical response of a suspension at two wavelengths of light, UV and IR. The UV light conveys information on both fibres and crill, while IR conveys information only on fibres. Characterising the particle-size distribution of nano-ligno-cellulose is both important and challenging. The objective of this paper was to study the crill values of TMP- and CTMP-based nano-ligno-celluloses as a function of homogenisation time. The results indicated that the crill value of both TMP-NLC and CTMP-NLC correlated fairly well with the homogenisation time.

### **Paper IV: Paper strength improvement by inclusion of nano-ligno-cellulose to CTMP**

In paper IV, the overall aim was to demonstrate the strengthening potential of nano-ligno-cellulose in handsheets of CTMP. For comparison purposes, nanocellulose (NC) was produced from BKP using an approach similar to that used to produce NLC. Both the NLC and NC were blended with their respective pulp fibres and the properties of the resulting handsheets were evaluated relative to sheet density. It was found that making handsheets of pulp fibres blended with NLC/NC improved the mechanical properties of the handsheets while only slightly affecting the sheet density.

### **Paper V: Qualitative evaluation of microfibrillated cellulose using the crill method and some aspects of microscopy**

This work used the crill methodology as a new, simplified technique to characterise the particle size distribution of nanocellulosic material based on CTMP, TMP, and sulphite pulp (SP). In the first part, hydrogen peroxide pretreatment of CTMP and TMP in a wing mill refiner followed by high-pressure homogenisation to produce microfibrillated cellulose (MFC) was evaluated using the crill method. In the second part, the TEMPO oxidation of CTMP and SP

combined with high-shear homogenisation to produce MFC was studied using the crill method. With 4% hydrogen peroxide pretreatment, the crill values of the unhomogenised samples were 218 and 214 for the TMP and CTMP, respectively, improving to 234 and 229 after 18 homogenisation passes. The results of the TEMPO method indicated that, for the 5 mmol NaClO SP-MFC, the crill value was 108 units at 0 min and 355 units after 90 min of treatment – a 228% improvement. The CTMP and TMP fibres and the MFC were freeze dried and the fibrillar structure of the fibres and microfibrils was visualised using scanning electron and transmission electron microscopy.

#### **Paper VI: The use of cationic starch and microfibrillated cellulose to improve strength properties of CTMP-based paperboard**

Regarding paper or paperboard strength development, it is well known that traditional methods such as refining and fibre beating improve flexibility and enhance the swelling ability, thereby improving the bondability and strength properties during paper formation. The main drawback of excess refining is that it could lead to paper densification, which could negatively affect the bending stiffness of paperboard. There is now growing interest in using MFC as an alternative paper strength additive in the papermaking process. However, if one wishes to target extreme strength improvement, particularly for packaging paperboards, then it would be useful to utilise cationic starch (CS) or MFC so as to significantly improve the z-strength property, with only a slight increase in sheet density. The mean grammage of the CTMP handsheets produced in this work was approximately 150g m<sup>-2</sup>, and it was found that handsheets of CTMP blended with CS or MFC had significantly improved z-strength, tensile index, and other strength properties at similar sheet densities. Blending CTMP with 5% TEMPO-based MFC increased the z-strength from 412 to 531 kN m<sup>-2</sup> (a 29% improvement) at a sheet density of 522 kg m<sup>-3</sup>, and increased the tensile index from 38 to 43 kNm kg<sup>-1</sup>.

#### **Paper VII: Nanofibrillated cellulose/nanographite composite films**

Though research into NFC has recently increased, few studies have considered co-utilising NFC and nanographite (NG) in composite films, and it has been a challenge to use high-yield pulp fibres (from mechanical pulps) to produce this nanofibrillar material. It is worth noting that chemical pulp fibres differ significantly from high-yield pulp fibres, as the former are composed mainly of cellulose and have a yield of approximately 50%, while the latter consist of cellulose, hemicellulose, and lignin and have a yield of approximately 90%. NFC was produced by combining TEMPO-mediated oxidation with the mechanical shearing of CTMP and SP; the NG was produced by mechanically exfoliating graphite. The different NaClO dosages used in the TEMPO system differentially

oxidised the fibres, altering their fibrillation efficiency, and this was evaluated using a crill analyser. NFC-NG films were produced by casting in a Petri dish. We examined the effect of NG on the sheet resistance and mechanical properties of NFC films. Adding 10 wt% of NG to 90 wt% of 5 mmol NaClO CTMP-NFC homogenised for 60 min improved the sheet resistance from that of an insulating pure NFC film to 180  $\Omega$ /sq. Further addition of 20 wt% and 25 wt% of NG to 80 wt% and 75 wt%, respectively, lowered the sheet resistance to 17  $\Omega$ /sq and 9  $\Omega$ /sq, respectively. For the mechanical properties, we found that adding 10 wt% of NG to 90 wt% of 5 mmol NaClO SP-NFC homogenised for 60 min improved the tensile index by 28%, tensile stiffness index by 20%, and peak load by 28%. The film's surface morphology was visualised using SEM, revealing the fibrillated structure of NFC and NG. Our methodology yields NFC-NG films that are mechanically stable, bendable, and flexible.

#### **Paper VIII: Eco-friendly design for scalable direct fabrication of nanocellulose**

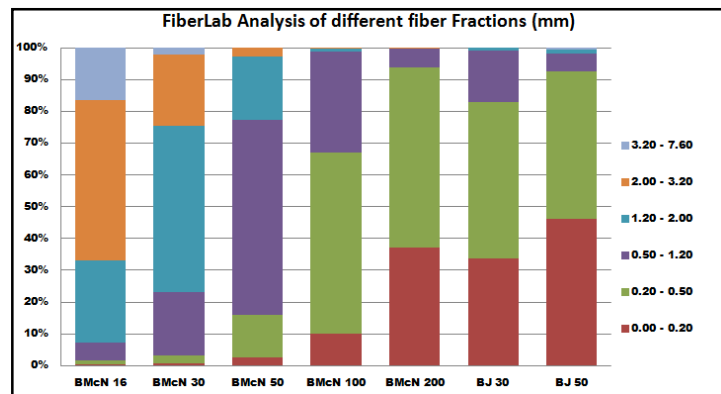
Although remarkable progress has been made in producing nanocellulose using several processing methods, there remain the challenges of reducing the overall energy consumption and of using “green” chemistry and a sustainable approach to make it feasible to produce this novel nanomaterial at industrial scale. We have developed a new eco-friendly and sustainable approach to producing wood-derived nanocellulose using organic acid combined with high-shear homogenisation. We have also made hydrophobic nanocellulose and cross-linked the modified nanocellulosic material. By using an organic acid (i.e., formic acid) at an elevated temperature, we successfully disrupted the fibrillar chain of cellulose into nanocellulose. The fibrillar structure of the nanocellulose suspension was characterised using TEM while the 3D foam structure was analysed using BET. The nanocelluloses were freeze-dried to produce 3D foam materials. We also demonstrated the effects of the chemical cross-linking of nanocellulose modified by UV exposure. This new production approach could be regarded as a direct, simple, inexpensive, and environmentally friendly method of producing nanocellulose.

#### **4.2. Fibre length distribution (paper II)**

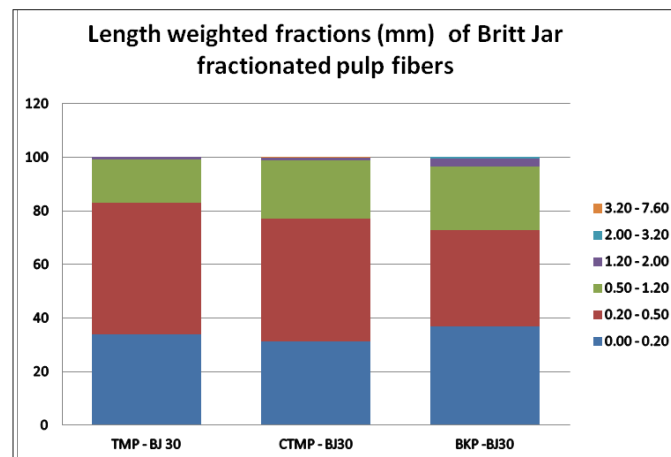
It was noticed that, during the fibre-size distribution measurements, the fibre length was one of the most critical factors affecting system clogging. In the BMcN classifier, the fraction with the most fines was that produced using the 200-mesh screen. Preliminary BMcN experiments indicated that the fibre fractions from the 200-mesh screen were extremely good feed materials for the homogeniser. Fines materials are generally regarded as mechanical pulp fractions able to pass through a 200-mesh (i.e., 76- $\mu$ m) wire screen. In this project, the pulp fractions that passed



through the BDDJ-R30 mesh screen were considered fines. This was the case because, after performing FibreLab analysis, it was clear that the BMcN-R200 fraction is very similar to the BDDJ-R30 fraction in terms of the fibre length distribution (see Figures 32 and 33).



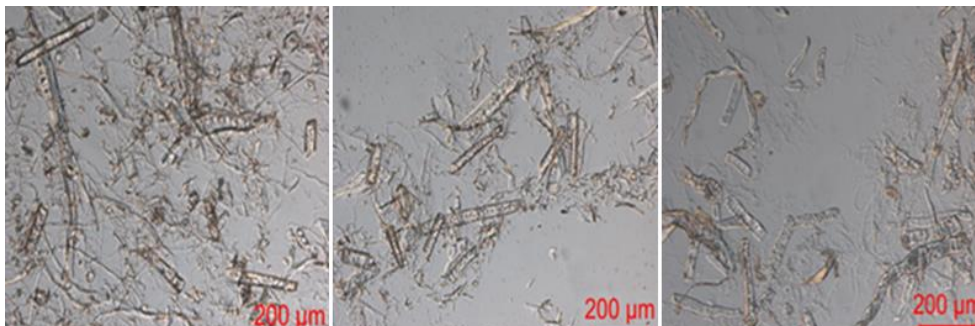
**Figure 32.** Fibre length distribution of the BMcN and BJ fractions (BDDJ = BJ)



**Figure 33.** Fibre length distribution of the BJ fractions using TMP, CTMP and BKP. (BDDJ = BJ)

High-temperature homogenisation had the positive effect of preventing clogging, softening the lignin, and facilitating cellulose extraction. This production method appears to be one that can omit the pre-refining stage (i.e., PFI milling or mild refining), thereby saving energy. It has been reported that both temperature and chemical treatment affect lignin softening (Höglund and Bodin 1976).

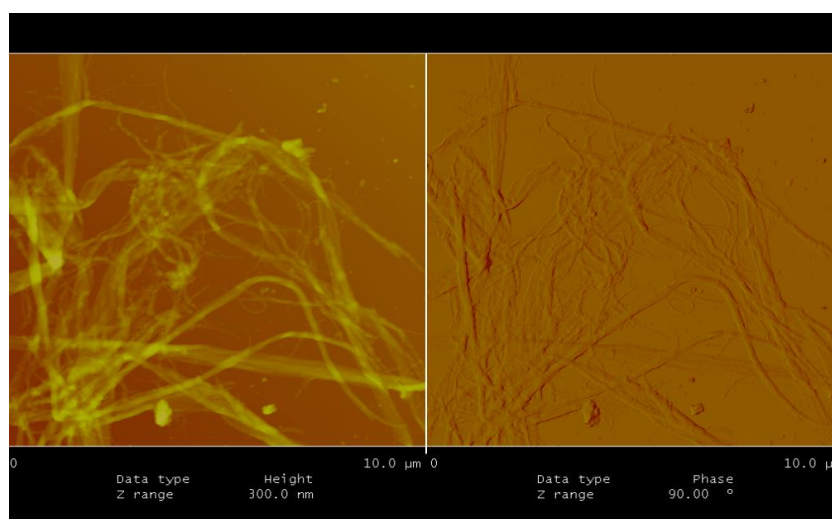
### 4.3. Microscopy (paper II)



**Figure 34.** Light micrographs of fines fractions of TMP (left), CTMP (centre), and BKP (right)

Figure 34 shows light micrographs of TMP fines, CTMP fines, and BKP fines. The rectangular shapes visible in the images represent parenchyma cells. The light micrograph in Figure 34 show how the fines (left-hand image) were disintegrated into tiny particles (centre image) after homogenisation.

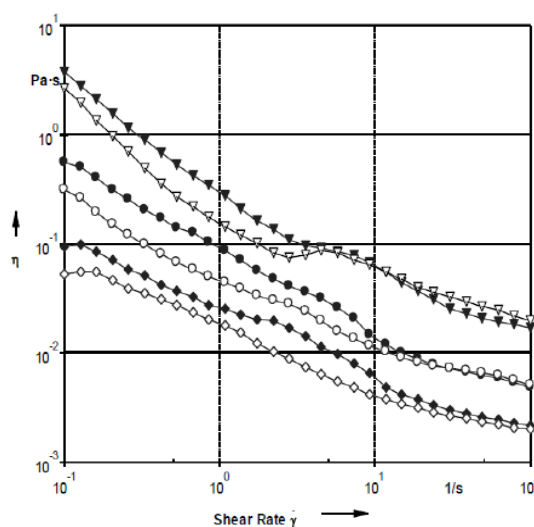
AFM imaging was performed using a super-sharpened tip, and the phase and height images are presented in Figure 35. The diameter of the TMP-NLC fibrils visible in the AFM micrograph is in the range of 90–150 nm. One difficulty encountered when using TMP fines in producing nano-ligno-cellulose was that the fine particles contain a high amount of lignin that “glues” together the cellulose fibrils, preventing complete individualisation of the fines into fibrils (Figure 35).



**Figure 35.** AFM image of TMP-based nano-ligno-cellulose (height and phase image)

#### 4.4. Rheology (paper II)

The flow curve in Figure 36 shows the rheological properties of 0.66, 0.33, and 0.165% TMP-NLC suspensions in a shear rate range of 0.1–100  $\text{s}^{-1}$  and homogenised at 23 and 140°C. From the flow curve presented in Figure 36, it is seen that the shear viscosity (Pa.s) of all the suspensions decreases with increasing shear rate ( $\text{s}^{-1}$ ), meaning that the TMP-NLC exhibits shear thinning behaviour at concentrations as low as 0.165%. Although homogenisation was said to have been conducted at both 23 and 140°C, it was noted that the temperature increased significantly from 23°C to approximately 50°C during homogenisation at room temperature. We expected high-temperature homogenisation to improve the fibrillation efficiency, but as can be seen in Figure 36, the shear thinning behaviour of the 140°C homogenised samples did not correspond to the predictions based on rheological analysis. One explanation for the unexpected behaviour could be the variation in the increase in homogenisation pressure during the treatment of pulp particles.

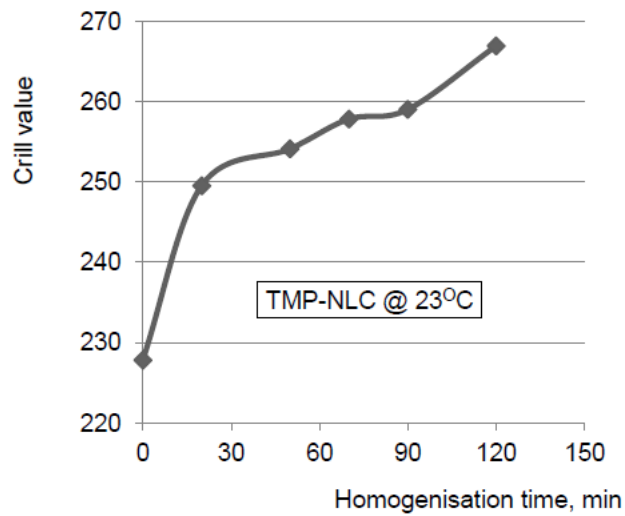


**Figure 36.** Rheological behaviour of nano-ligno-cellulose - (—■— 0.66% TMP-NLC at 23°C, —■— 0.66% TMP-NLC at 140°C —●— 0.33% TMP-NLC at 23°C, —○— 0.33% TMP-NLC at 140°C —◆— 0.165% TMP-NLC at 23°C, —◇— 0.165% TMP-NLC at 140°C).

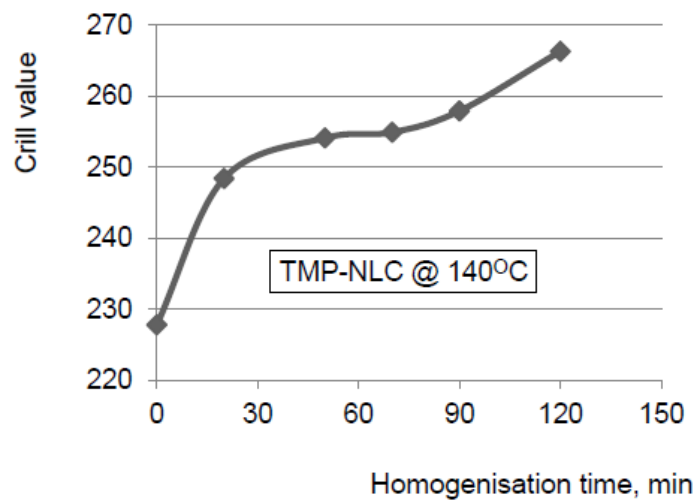
#### **4.5. Crill (paper III)**

In an attempt to circumvent the well-known limitation of optical instruments such as the FibreLab, FibreMaster, and MorFi analysers in characterising tiny fibres or “hyper-fines”, and with the longer-term objective of having a rapid and accurate method for the online characterisation of nano-ligno-cellulose, the crill method is regarded as an alternative to the more conventional techniques currently used in assessing the fibrillar structure of nanofibres. The crill methodology has already been implemented at the mill scale to assess small, thin fibres during refining (Pettersson 2010).

The objective was to highlight the potential of a new technique for characterising the particle size of micro/nanofibres known as crill. The technique provides reliable estimates of the particle size distribution of micro/nanofibres. The crill method is an established technique used at the mill scale for measuring hairy fibres. It is a robust, fast, and reliable method for assessing tiny fibrils. The crill value was plotted relative to homogenisation time, with which it was found to correlate (Figures 37 and 38). The crill value patterns of both TMP and CTMP behave similarly at both 23 and 140°C (results for CTMP-NLC can be seen in paper III). The crill results suggest that the technique requires more development to be considered a tool for mill-scale processing. The crill technique creates opportunities for assessing the particle size distribution of a range of nanocellulose, including TEMPO-oxidised nanocellulose, enzymatically processed nanocellulose, and TMP- and CTMP-based nanocellulose. However, as the technique is still under development, it can only characterise fibrils at the submicron scale, i.e., particles 1000 times smaller than fibres. As shown in Figure 38, high-temperature homogenisation made no significant difference in crill development for spruce TMP.



**Figure 37.** Crill value of TMP-NLC homogenised at 23°C as a function of homogenisation time



**Figure 38.** Crill value of TMP-NLC homogenised at 140°C as a function of homogenisation time

The crill method possesses the inherent ability to assess the particle size of a fibre/crill within a very short time frame (i.e., a few seconds) and without any damage to the pulp suspension under investigation, making it a non-destructive method. It should be noted that using the crill method to characterise NLC makes it possible to reduce the use of time-consuming microscopy techniques in characterising the particle size distribution.

#### 4.6. Nanocellulose as a strength additive in paper

This work explored the use of nanocellulose as a strength additive in paper/board qualities (papers IV and VI), as the development of paper strength is of great importance to paper producers. Handsheets of CTMP blended with sulphate pulp, cationic starch, and MFC were made in a conventional Rapid Köthen Sheet former (paper VI) and their corresponding sheet properties were evaluated relative to sheet density. It was found that the handsheets of CTMP pulp fibres, blended with TEMPO-oxidised MFC, and cationic starch, had improved mechanical properties with only a slightly increased sheet density. Improvements in the strength properties of handsheets, such as z-strength, tensile index, burst index, E-modulus, and strain at break, were observed. Many research teams have studied the use of chemical pulp fibres and their respective MFC and NFC materials as strength enhancers in papermaking. Thorough investigations of the use of MFC as a strength additive have been carried out by many researchers (Eriksen et al. 2008, Taipale et al. 2010, Hii et al. 2012, Sehaqui et al. 2013).

Tensile strength is the strength to withstand deformation or failure in the  $x$ - $y$  direction and it relies on the gradual failure of the interfibre bond (Helle 1962). In this thesis, the following mechanical properties are evaluated: z-strength, burst index, tensile index, strain to break, and tensile energy absorption (TEA). Page (1969) reported that the tensile index increases with the proportion of long fibres. The z-direction tensile strength and the Scott bond energy are both influenced by the bonded area and specific bond strength. The z-direction tensile strength is regarded by Kouba and Koran (1995) as a better strength measure than the Scott bond energy, although both methods correlate acceptably.

Duker (2007) emphasised that the specific bond strength (i.e., strength per unit area) and relative bonded area (RBA) are two parameters that contribute to the strength properties of a fibre network. Hartler and Mohlin (1975) reported that the presence of lignin reduces the fibre joint strength and, in addition, that high hemicellulose content improves the fibre joint strength. The production of high-quality sheets with blends of NLC can provide desirable properties, such as high tensile strength, high burst index, and low density (high bulk), which are useful in end-products such as paperboard and printing paper.

It was found that mixing 80% CTMP with 20% sulphate pulp furnish considerably improved the strength properties of CTMP, though this had a negative effect on the sheet density. In this work, we have used cationic potato starch and anionically highly charged TEMPO-oxidised MFC ( $732 \mu\text{mol g}^{-1}$ ). The rationale for using CS and anionically charged CTMP fibres was that the cations from the CS would have

greater affinity to attract and bind to the fibre surfaces, whereas the TEMPO-based MFC, which is gel-like in texture, would help improve the bonding between the CTMP fibres.

Paper is a fibre network held together by fibre–fibre joints. The strength properties of pulp fibres during handsheet formation are dependent on fibre consolidation during pressing and drying, enabling the laboratory sheets to be continuously compacted in the z-direction. Giertz (1973) emphasised that the strength properties of mechanical pulp sheets depend on the amount of longer fibres in the fibre fraction and the bondability in the fibre network. He stressed that fines play a vital role during laboratory sheet consolidation. Hartler and Mohlin (1975) studied the influence of pulping on interfibre bond strength.

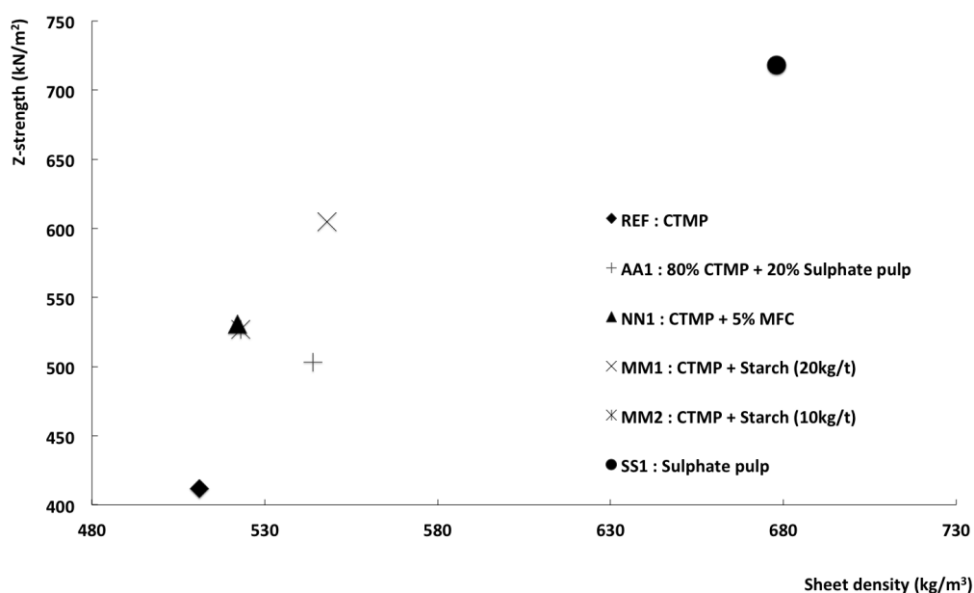
The main effect of the strength improvement was an increase in z-strength (Figure 39) at almost the same sheet densities. The relationship between burst index and sheet density was also affected by the addition of MFC to the CTMP fibre furnish (Figure 41). Sehaqui et al. (2011, 2013) have reported a maximum tensile index at an MFC content of 4%. Addition of cationic starch (20 and 10 kg t<sup>-1</sup>) was seen to significantly improve the paper strength properties, as the starch improved the bonding between the fibres. This is because the positively charged cations from starch are attached to the negatively charged surface of CTMP fibres, and this type of interaction helps improve the paper strength properties during the sheet-forming process.

During pulp disintegration using high-shear homogenisation, it is believed that the interfibrillar bonds on the primary wall and outer lamella of the S1 in the fibre/fines cell wall are shattered, giving rise to tiny hairy-like particles. This loosens the adhesion, freeing individual fibrils and enabling the newly engineered bio-structure to improve fibre–fibre bonding when blended with pulp fibres during handsheet formation. MFC addition improves the strength because it increases both the molecular contact area between the pulp fibres and the fibre–fibre joint strength.

To improve the mechanical strength properties of handsheets, we have tested simply mixing CTMP pulp fibres with MFC, various dosages of cationic starch, and sulphate pulp. In particular, blending cationic starch with CTMP pulp fibres significantly increases the reinforcement of the CTMP sheet, improving the mechanical strength, particularly in terms of the z-strength, tensile index, and other mechanical properties. In this thesis, the z-strength and tensile index properties are examined using cationic starch and MFC (paper VI) as a function of sheet density, as the aim is to improve the strength properties in paperboard for packaging.

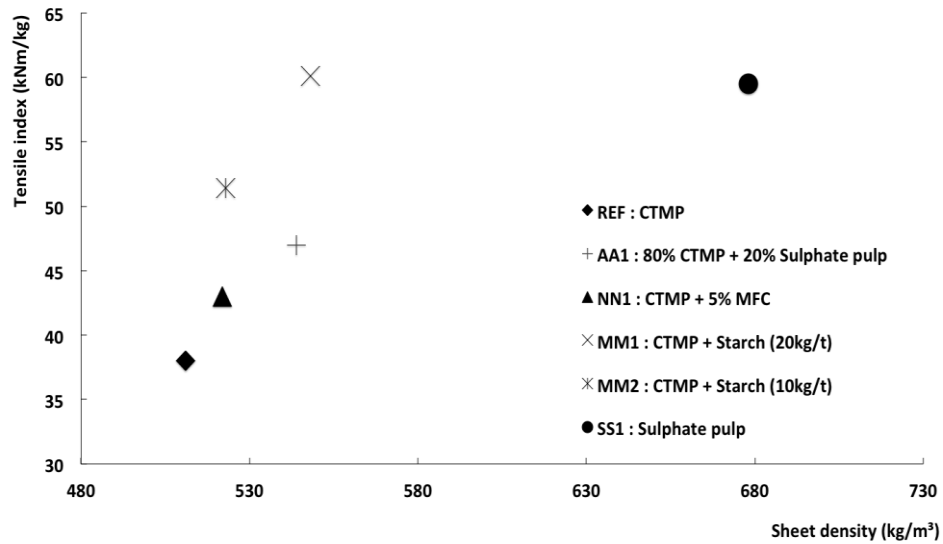
It has been noted that the mechanical strength properties of laboratory sheets differ depending on the sheet-forming methods used (Nygren et al. 2003) due to differences in the experimental set-up and the sheet consolidation mechanism. Our z-strength results could not be compared with any previous results because, to the best of the author's knowledge, no one has published results relating to mechanical pulp-based nano-ligno-cellulose or microfibrillated cellulose. However, a fair comparison is possible using other works, such as that of Eriksen et al. (2008), who used a kraft pulp-based MFC to improve the strength properties of TMP sheets.

Results shown in Figures 39 and 40 indicate that blending CTMP with 5% TEMPO-based MFC increased the z-strength from 412 to 531  $\text{kN m}^{-2}$  (a 29% improvement) at a sheet density of 522  $\text{kg m}^{-3}$  and the tensile index from 38 to 43  $\text{kNm kg}^{-1}$  (a 13% improvement). Blending CTMP with 20 and 10  $\text{kg t}^{-1}$  of CS improved the z-strength to 605  $\text{kN m}^{-2}$  (a 47% improvement) at a sheet density of 548  $\text{kg m}^{-3}$  and to 527  $\text{kN m}^{-2}$  (a 28% improvement) at a sheet density of 523  $\text{kg m}^{-3}$ , respectively, and the tensile index to 60 and 51  $\text{kNm kg}^{-1}$ , respectively. When 80% CTMP was mixed with 20% sulphate pulp, the z-strength (Figure 39) improved from 412 to 503  $\text{kN m}^{-2}$  (a 91-unit improvement) at a sheet density of 544  $\text{kg m}^{-3}$ , an improvement of approximately 22%. In addition, in the 100% sulphate pulp sample, the z-strength was enhanced from 412 to 718  $\text{kN m}^{-2}$ , a 306-unit increase (a 74% improvement), but the drawback was the high sheet density of 678  $\text{kg m}^{-3}$ .



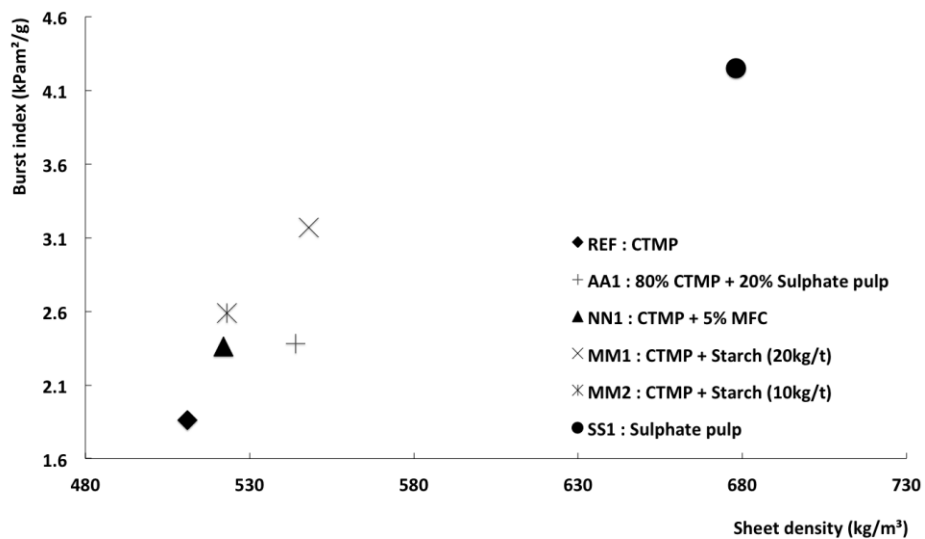
**Figure 39.** Z-strength as a function of sheet density



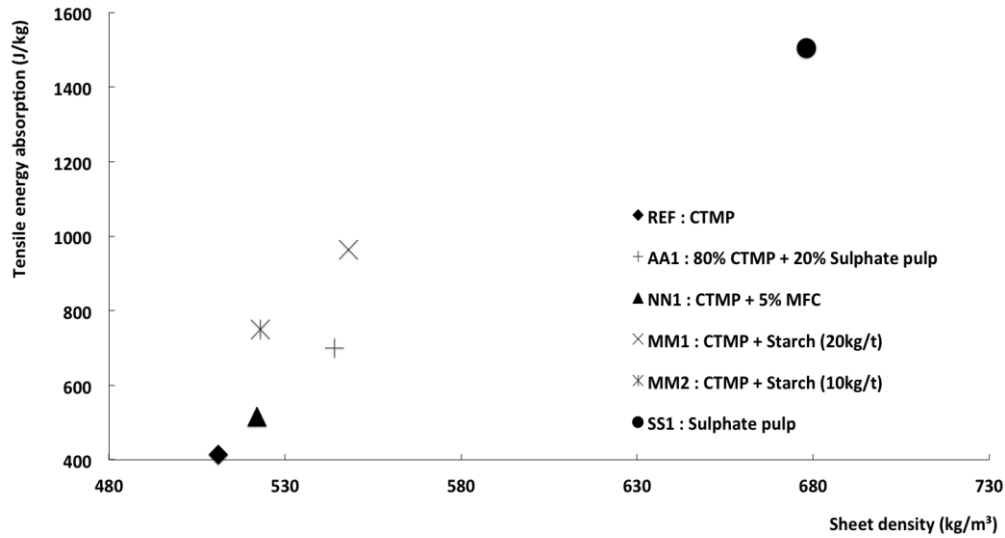


**Figure 40.** Tensile index as a function of sheet density

Figure 41 shows the burst index as a function of sheet density and Figure 42 shows the tensile energy absorption (TEA) as a function of sheet density (this is presented in greater detail in appended paper VI). We can clearly see from Figure 41 that there is a significant improvement with the use of CTMP and cationic starch (20 kg t<sup>-1</sup>).

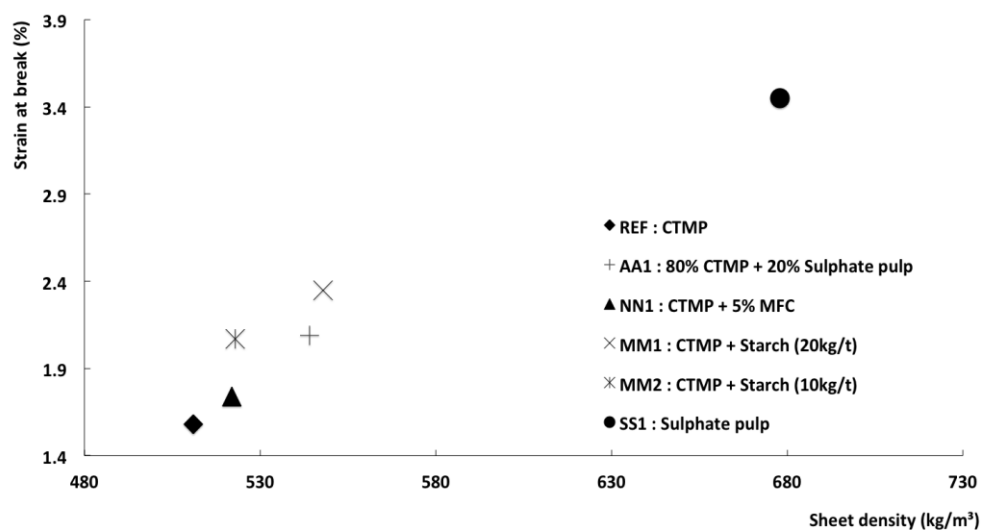


**Figure 41.** Burst index as a function of sheet density

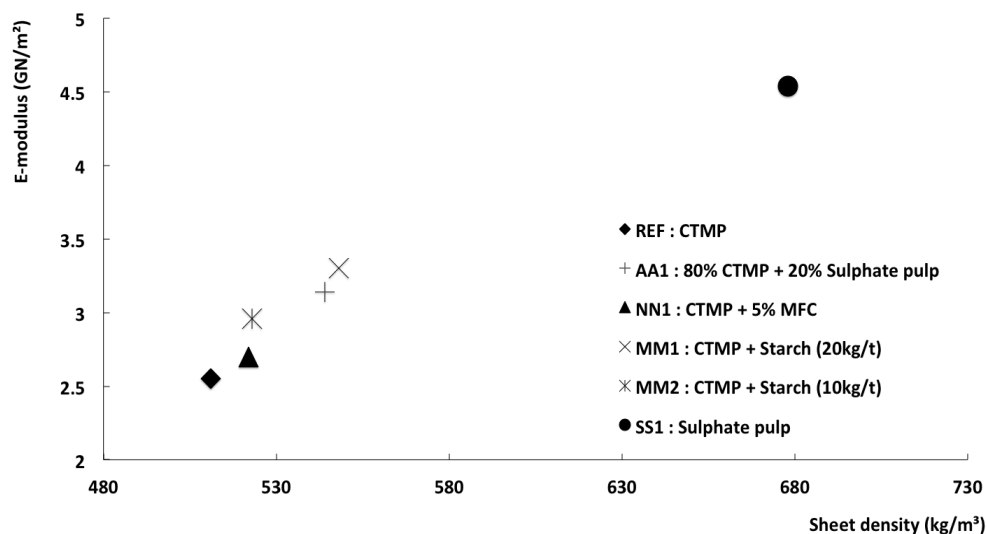


**Figure 42.** Tensile energy absorption as a function of sheet density

Figure 43 shows the strain at break as a function of sheet density and Figure 44 shows the E-modulus as a function of sheet density. We can clearly see from the figures that these properties improve significantly when adding starch (20 kg t<sup>-1</sup>) or 5% MFC. Figure 43 shows a significant increase in strain at break with only a slight increase in sheet density for the CTMP samples blended with CS or MFC. For the tensile energy absorption (TEA; see Figure 42), when the CTMP was blended with 5% TEMPO-based MFC, the TEA increased from 413 to 517 J kg<sup>-1</sup> (a 25% increase) at a sheet density of 522 kg m<sup>-3</sup>. When CTMP is mixed with 20 and 10 kg t<sup>-1</sup> of CS, the TEA increases to 964 J kg<sup>-1</sup> (a 133% improvement) at a sheet density of 548 kg m<sup>-3</sup> and to 750 J kg<sup>-1</sup> (an 82% improvement) at a sheet density of 523 kg m<sup>-3</sup>, respectively. The TEA also improved in 80% CTMP mixed with 20% sulphate pulp, increasing from 413 to 700 J kg<sup>-1</sup> (a 287-unit increase) at a sheet density of 544 kg m<sup>-3</sup>, for an improvement of approximately 69%. In the 100% sulphate pulp sample, TEA increased by 1092 units from 413 to 1505 J kg<sup>-1</sup>, but the drawback was high sheet density. It is also obvious in Figure 44 that CS and MFC have a better effect in terms of strengthening the E-modulus (GN m<sup>-2</sup>).



**Figure 43.** Strain at break as a function of sheet density

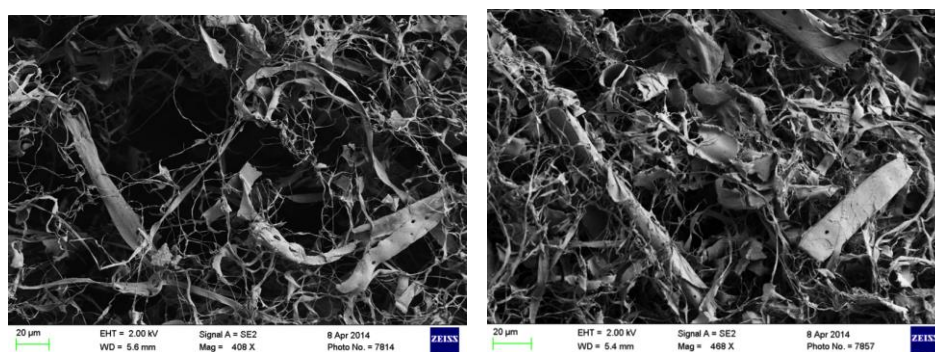


**Figure 44.** E-modulus as a function of sheet density

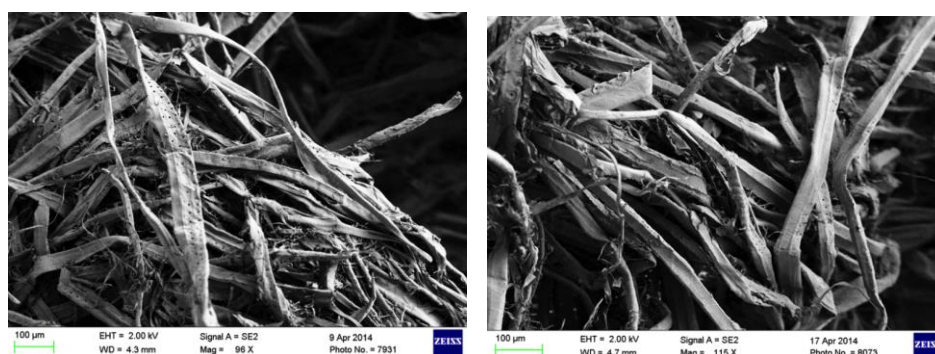
#### 4.7. Crill as a qualitative method to characterise nanocellulose

The SEM and TEM images (Figures 45–51) show the improved fibrillation of the fibres after BDDJ fractionation and the homogenisation process. Figure 51 shows how the fibrils have become “glued” into fibrillar bundles due to the presence of lignin. One reason for using hydrogen peroxide on TMP and CTMP was to induce

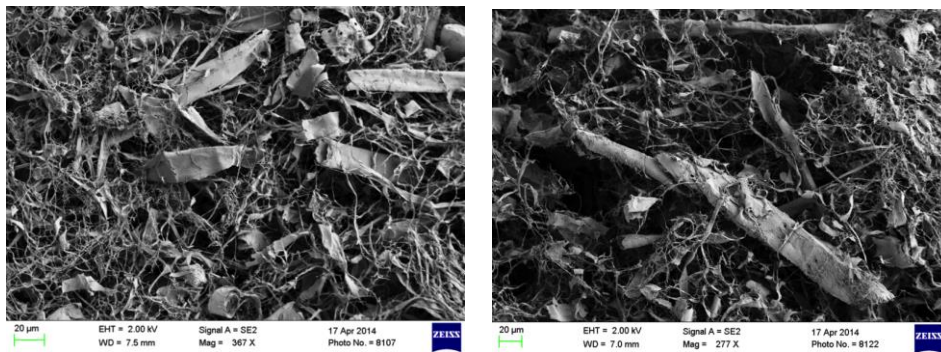
delignification and improve fibrillation efficiency: the lignin content will decrease after peroxide treatment, thereby reducing the gluing effect during homogenisation. It was first necessary to wash the pulp using diethylenetriamine pentaacetic acid (DTPA) before treatment in the wing mill refiner, as the DTPA helps stabilise the hydrogen peroxide decomposition and improve the brightness of the pulp (Karlsson 2013). Figures 45–51 show the SEM images of hydrogen peroxide-pretreated TMP and CTMP samples, as well as their resulting MFCs. It can be seen from the SEM images that the fibre size decreases with fractionation, and decreases still further with homogenisation. It should be noted that because of the presence of lignin in the TMP and CTMP sample, it was almost impossible to completely individualise the fibres into nanofibrils.



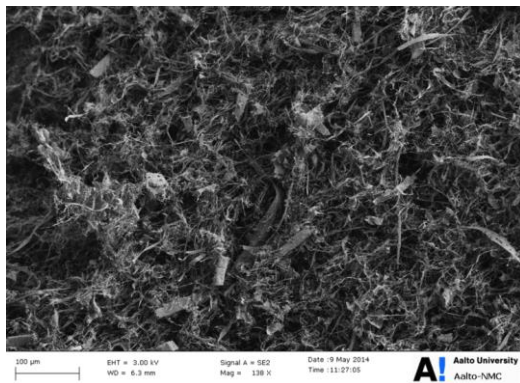
**Figure 45.** SEM images of accepted TMP-BJ100 samples: first image is of sample AA8 (4% peroxide treated) and the second is of sample AA9 (1% peroxide treated)



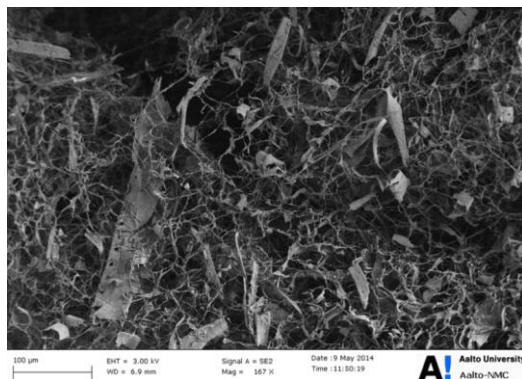
**Figure 46.** SEM images of rejected CTMP-BJ30 samples: first image is of sample BB21 (untreated coarse, longer fibres) and the second is of sample BB24 (1% peroxide treated)



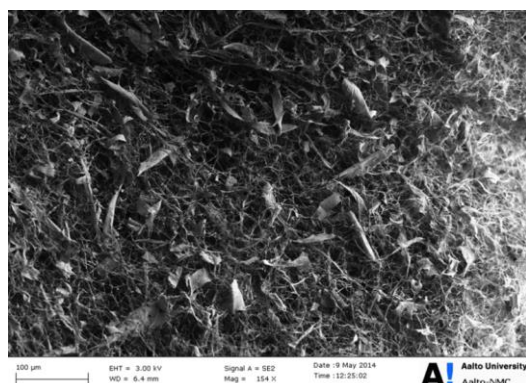
**Figure 47.** SEM images of accepted CTMP-BJ100 samples: first image is of sample BB27 (4% peroxide treated) and the second is of sample BB28 (1% peroxide treated)



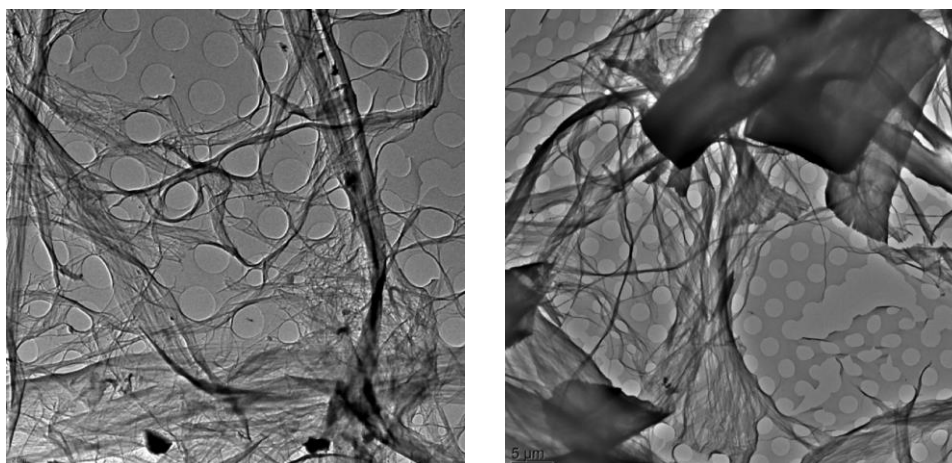
**Figure 48.** SEM image of TMP-based MFC sample C18 (4% peroxide treated)



**Figure 49.** SEM image of TMP-based MFC sample F18 (untreated)



**Figure 50.** SEM image of CTMP-based MFC sample H18 (1% peroxide treated)



**Figure 51.** TEM images of TMP-based MFC and CTMP-based MFC samples, respectively: the first image is of sample D18 (1% peroxide treated TMP-MFC) and the second is of sample F18 (untreated CTMP-MFC)

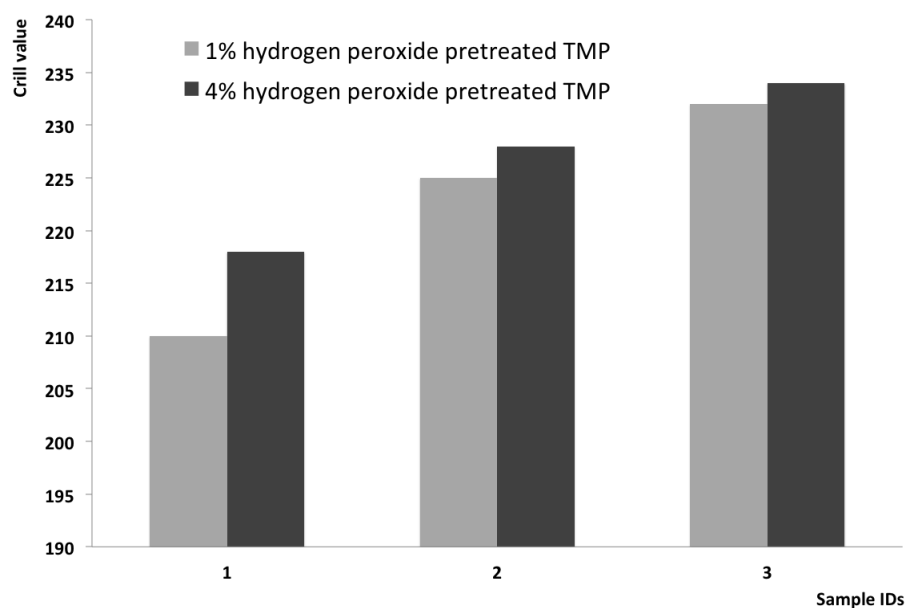
One reason for using TEMPO oxidation in the second part of paper V was to induce fibre swelling and facilitate the mechanical disruption of the fibres during high-shear homogenisation. TEMPO oxidation helps loosen the adhesion in the fibre wall and make it easier to reduce the fibre particle size from the microfibril to nanofibril scale. The high fibrillation efficiency is a well-known advantage of the TEMPO-based nanocellulose production process; accordingly, in this work we compare the crill values with the homogenisation times and chemical treatment dosages. Such comparisons clearly indicate that the crill values improve with higher NaClO dosages and longer mechanical treatment times. It is well known that the TEMPO method converts the hydroxyl group of cellulose into

corresponding carboxylate groups and some aldehyde groups, thereby introducing negatively charged groups on the surface of the cellulose chain (Saito et al. 2006). Okita et al. (2009) reported that the TEMPO oxidation of lignin-rich pulps (e.g., TMP) requires the addition of more NaClO to obtain the same level of oxidation for fibres with cellulose contents exceeding 90%. In addition, De Nooy et al. (1995) explained that TEMPO oxidation is selective for primary alcohols and that the isolation of individual MFCs is enabled by the electrostatic repulsion between fibrils. Ma and Zhai (2013) also attested that lignin is dissolved during TEMPO-mediated oxidation, affecting NaClO consumption and thereby the degree of fibrillation.

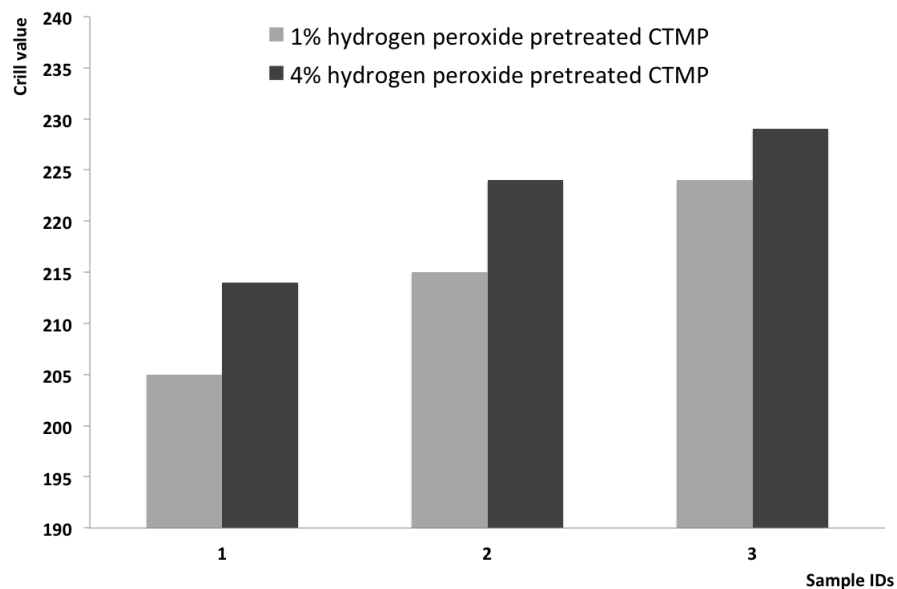
Our results indicate that it is possible to use hydrogen peroxide acid pretreatment and TEMPO oxidation combined with mechanical homogenisation to strategically produce nanocellulose, and that the method can easily be upscaled. It was obvious from the SEM images that mechanical treatment had reduced the fibre size. We have previously reported that TMP can easily be softened at elevated temperatures due to the presence of lignin in the fibres. The softening of the lignin alone, however, does not seem to improve the fibrillation efficiency; it could be that the lignin serves to “glue” together the cellulose and hemicellulose, hindering proper fibrillation (Osong et al. 2013).

When considering the number of homogenisation passes versus the non-homogenised reference samples, we noticed that with 1% hydrogen peroxide pretreatment, the crill values for the untreated samples were 210 and 205 units for the TMP and CTMP samples, respectively, and that after 18 homogenisation passes, the crill values increased to 232 and 224 units, respectively, for a 22-unit improvement for the TMP and a 19-unit improvement for the CTMP samples (Figures 52 and 53). With 4% hydrogen peroxide pretreatment (see Figures 52 and 53), the crill values for the untreated samples were 218 and 214 units for the TMP and CTMP samples, respectively, increasing after 18 homogenisation passes to 234 and 229 units, respectively, for a 16-unit improvement for the TMP and a 15-unit improvement for the CTMP samples.





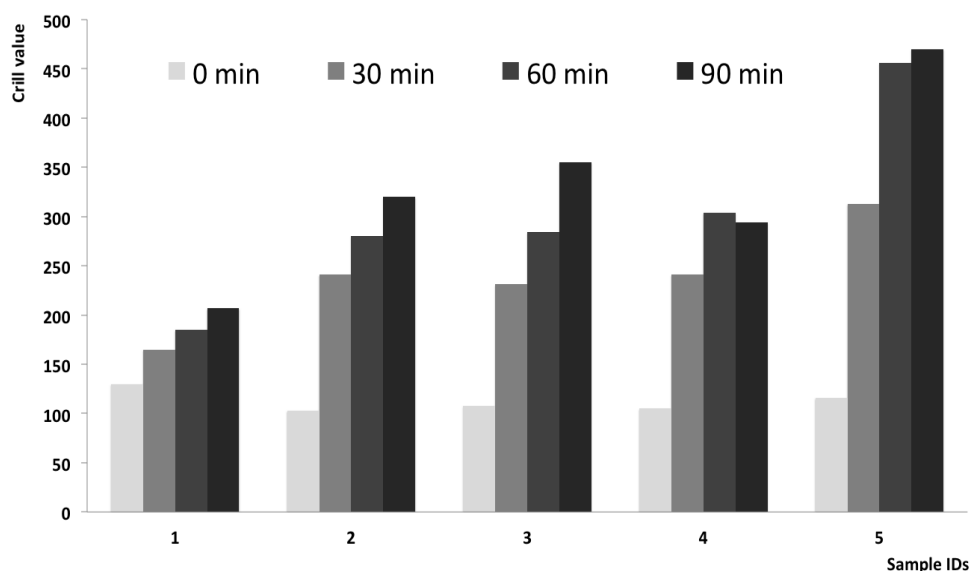
**Figure 52.** Crill values for TMP-based MFC relative to chemical (i.e., hydrogen peroxide) treatment and number of homogenisation cycles. Note: “sample 1” is non-homogenised, “sample 2” is homogenised for 9 cycles, and “sample 3” for 18 cycles



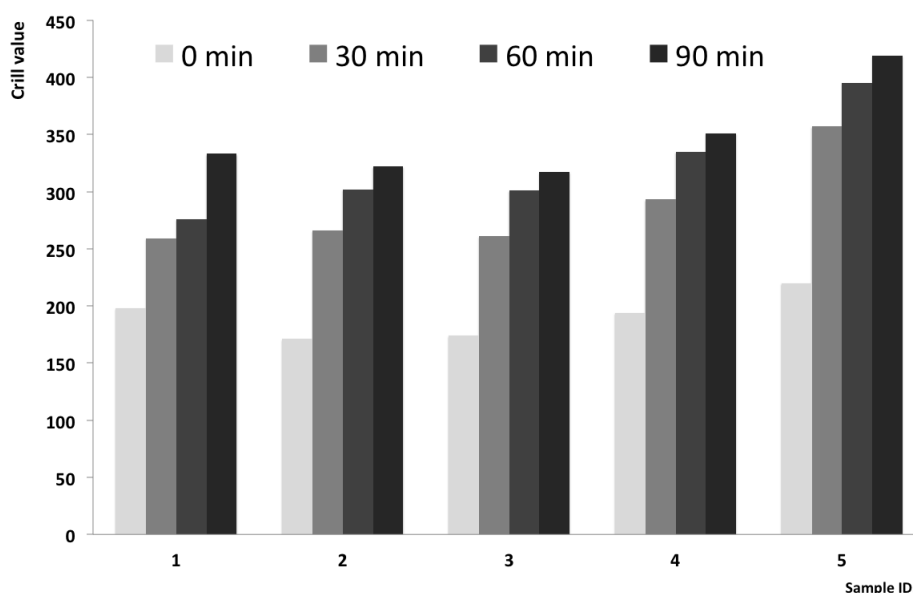
**Figure 53.** Crill values for CTMP-based MFC relative to chemical (i.e., hydrogen peroxide) pretreatment and number of homogenisation cycles. Note: “sample 1” is non-homogenised, “sample 2” is homogenised for 9 cycles, and “sample 3” for 18 cycles



Enormous challenges are still encountered when using mechanical pulps (i.e., CTMP and TMP) because the lignin serves to “glue” together cellulose and hemicellulose, hindering effective fibrillation during mechanical shearing. To broaden the applications of CTMP and TMP, it is crucial to use these materials in producing nanocellulose. In addition, the TEMPO-oxidation reaction is usually conducted at a high pH of 9–10; during the reaction, we noticed a reduction in brightness (i.e., a pulp-yellowing effect) in the lignin-rich CTMP fibres. It is possible that the NaClO added to the pulp as a bleaching agent also generates chromophore groups on the lignin in alkaline media, leading to a change in colour. However, the crill results shown in Figures 54 and 55 indicate that it was relatively easier to produce nanocellulose from the oxidised pretreated pulp samples than from the non-pretreated samples.



**Figure 54.** Crill values of SP-based MFC relative to chemical (TEMPO) treatment and high-shear homogenisation time. Note: “sample 1” is non-chemical pretreated, “sample 2” is 3 mmol NaClO TEMPO pretreated, “sample 3” is 5 mmol NaClO TEMPO pretreated, “sample 4” is 7 mmol NaClO TEMPO pretreated, and “sample 5” is 10 mmol NaClO TEMPO pretreated



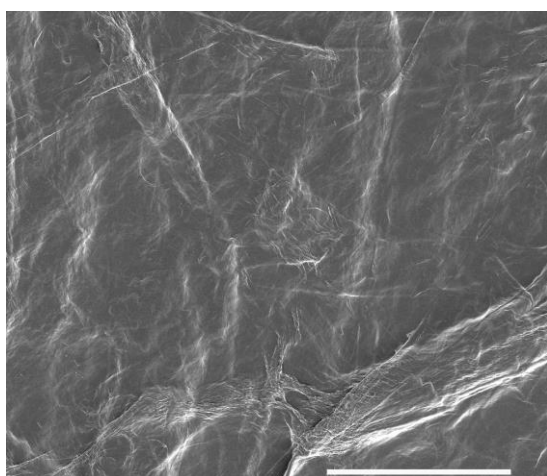
**Figure 55.** Crill values of CTMP-based MFC relative to chemical (i.e., TEMPO) treatment and high-shear homogenisation time. Note: “sample 1” is non-chemical pretreated, “sample 2” is 3 mmol NaClO TEMPO pretreated, “sample 3” is 5 mmol NaClO TEMPO pretreated, “sample 4” is 7 mmol NaClO TEMPO pretreated, and “sample 5” is 10 mmol NaClO TEMPO pretreated

#### 4.8. NFC-NG composite film (paper VII)

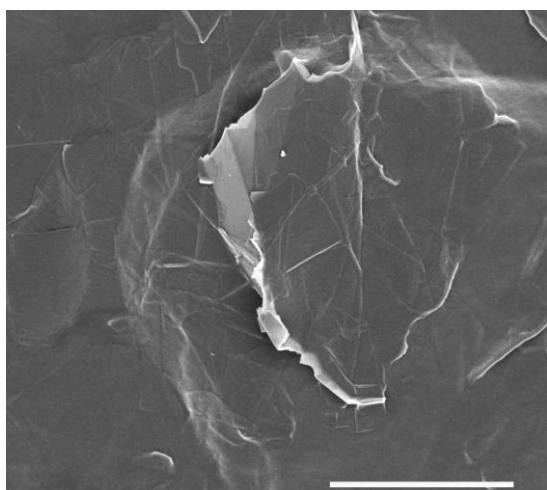
Research into cellulosic nanomaterials, such as nanofibrillated cellulose (NFC), has increased dramatically over the years. FSCN at Mid Sweden University has recently studied the possibilities of using these materials in sustainable nanocomposites with good electrical and mechanical properties. The electrical properties are of utmost importance, as pure NFC is non-conducting. Very few published scientific articles have addressed improving the electrical and mechanical properties of various types of NFC-nanographite composite materials. Most of these studies have solely used chemical pulp-based nanomaterials. In this work, we have used both chemical pulp- and CTMP-based NFC and processed it with exfoliated graphite to produce NFC-nanographite composite films. The exfoliated graphite is referred to as nanographite (NG) throughout this paper. The objective of this study is to explore NFC-NG composite material to improve our fundamental knowledge and to gain a better understanding of this new composite material.

The SEM micrographs in Figures 56 and 57 show the morphological structure of the pure CTMP NFC and sulphite-based NFC-NG composite films, respectively.

The SEM micrograph in Figure 56 shows that the sample contains many large-scale fibres and that the nanofibrils are not easily detected, while Figure 57 shows that the sample contains nanographite platelets embedded in the NFC network. The NFC from the SP consisted mainly of cellulose, providing a good surface for chemical modification using the TEMPO-mediated method. In contrast, the NFC from CTMP comprised three substances, i.e., cellulose, hemicellulose, and lignin, and thus was poorly fibrillated when treated with TEMPO, as the NaClO reacted with lignin, reducing the amount of NaClO originally intended to react with the pulp cellulose.



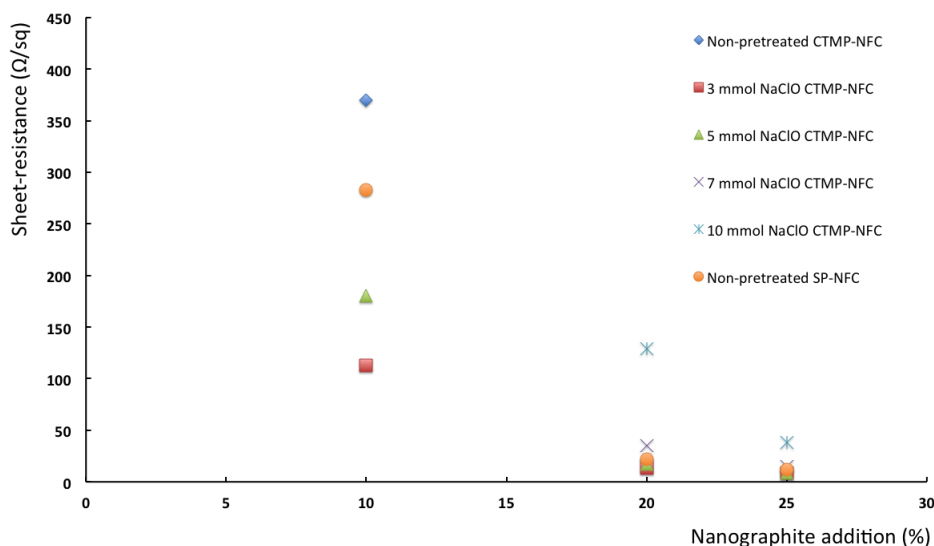
**Figure 56.** SEM surface micrograph of pure CTMP-NFC at 500 $\times$  magnification (bar is 100  $\mu$ m)



**Figure 57.** SEM surface micrograph of sulphite pulp-derived NFC-NG at 10,000 $\times$  magnification (bar is 5  $\mu$ m)

The electrical and mechanical properties of the NFC-NG films were evaluated and it was observed that adding NG improved the electrical and mechanical properties of the composite films. Unfortunately, owing to the high dewatering resistance of the NFC-NG suspension, the composite films could not be produced by vacuum filtration but instead using a casting method in which the films had to be allowed to dry at room temperature for approximately 48 h.

For the 3 mmol NaClO CTMP-NFC sample, the same addition level of NG (i.e. 25 wt%) resulted in a sheet resistance of 10  $\Omega/\text{sq}$  for the 90-min sample and 9  $\Omega/\text{sq}$  for the 60-min sample, i.e., almost the same improvement, see paper VII. For the 5 mmol NaClO CTMP-NFC sample, the same addition level of NG (i.e. 25 wt%) resulted in a sheet resistance of 11  $\Omega/\text{sq}$  for the 90-min sample and 9  $\Omega/\text{sq}$  for the 60-min sample – again, almost the same improvement (see Figure 58). For the 7 mmol NaClO CTMP-NFC sample, the same addition level of NG resulted in a sheet resistance of 25  $\Omega/\text{sq}$  for the 90-min sample and 15  $\Omega/\text{sq}$  for the 60-min sample. For the 10 mmol NaClO CTMP-NFC sample, the same addition level of NG resulted in a sheet resistance of 61  $\Omega/\text{sq}$  for the 90-min sample and 38  $\Omega/\text{sq}$  for the 60-min sample. Finally, for the non-pretreated SP-NFC, adding 25 wt% of NG reduced the high sheet resistance from that of an insulating material to a sheet resistance of 18  $\Omega/\text{sq}$  for the 90-min sample and 12  $\Omega/\text{sq}$  for the 60-min sample.



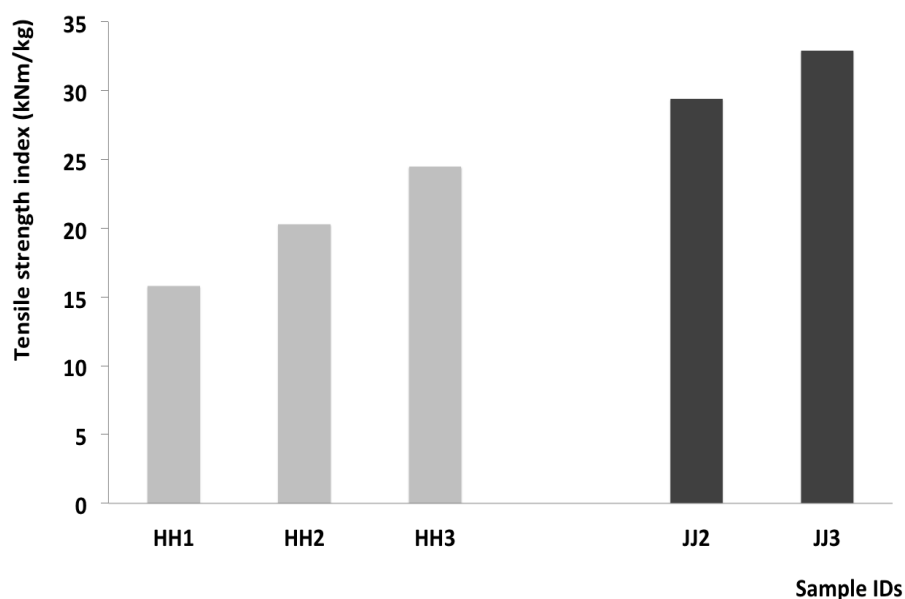
**Figure 58.** NFC-NG homogenised for 60 min

As seen in Figure 58, increasing the amount of NG from 10 wt% to 25 wt% in 3 mmol NaClO CTMP-NFC homogenised for 60 min significantly reduced the sheet

resistance. There was a remarkable improvement, as the 25 wt% NG addition reduced the film's previously very high sheet resistance to nearly zero. This resulted in a somewhat electrically conductive composite film (though no further electrical testing was conducted), as sheet resistance is related to the electrical conductivity of most materials.

Figure 58 shows the measured sheet resistances of the composite films as a function of the amount of NG added to the NFC. A slight deviation in the measurement trend should be noted, probably attributable to non-uniformity in sheet thickness and to poor homogeneity of the composite films. Both the SP- and CTMP-blended NG composites exhibit similar trends, though the sheet resistance of SP-derived NFC-NG was somewhat higher, exceeding the considered range (i.e., above 400  $\Omega/\text{sq}$ , which is why Figure 58 mainly features CTMP-based NFC-NG films), possibly attributable to the high surface-charge system of the NFC of the SP-based composite film. Considering the different dosages of TEMPO oxidation, one can clearly see from the graph that the higher the oxidation level, the higher the sheet resistance. This suggests that, as expected, as the films become more oxidised and plastic in texture, the sheet resistance increases. Also as expected, the more NG in the sample, the lower the sheet resistance and the more electrically conductive the composite film.

The improved strength properties of the NFC-NG composite films could be attributed to better fibre network consolidation between the thread-like particles of NFC and NG. Figure 59 clearly indicates that a 25 wt% NG content provides a film stronger than neat NFC film, possibly because of the high-strength properties of NG and because its high specific surface area facilitates good mixing in the NFC matrix. However, the mechanical and electrical properties of the composite films are not regarded as exactly reflecting the amount of added NG, as the consistency of the slurries was considered the same in order to facilitate calculation of the mixtures' compositions. The 10, 20, and 25 wt% NG contents were used to give a qualitative indication of whether adding NG improves the material properties of the films. It is also important to note that the mixing efficiency of NG in the NFC matrix is critical, as poor mixing could affect the results in terms of both the electrical and mechanical properties. In this work, the composite films were produce by stirring both suspensions manually.



**Figure 59.** Tensile index relative to added nanographite

In this work, we have demonstrated that the mechanical properties of NFC films (see Figure 59) can be enhanced by adding NG. This strength improvement was explained by Malho et al. (2012) and Yan et al. (2014) as due to the molecular interaction that physically binds NFC and NG; this binding greatly depends on the degree of mixing of both suspensions, as could clearly be seen after casting and drying the composite film. As seen in Figure 59, samples JJ2 and JJ3 have tensile indices of approximately 29 and 33  $\text{kNm kg}^{-1}$ , respectively – approximately a 12% improvement. It is worth mentioning that adding 10 wt% of NG, i.e., the change between samples HH1 and HH2, significantly increased the tensile index of the composite film from 15.8 to 20.3  $\text{kNm kg}^{-1}$  (a 28.5% enhancement), and that adding 20 wt% of NG, i.e., the level in HH3, produced a 21% improvement in tensile strength from that of the HH2 sample (i.e., from 20.3 to 24.5  $\text{kNm kg}^{-1}$ ).

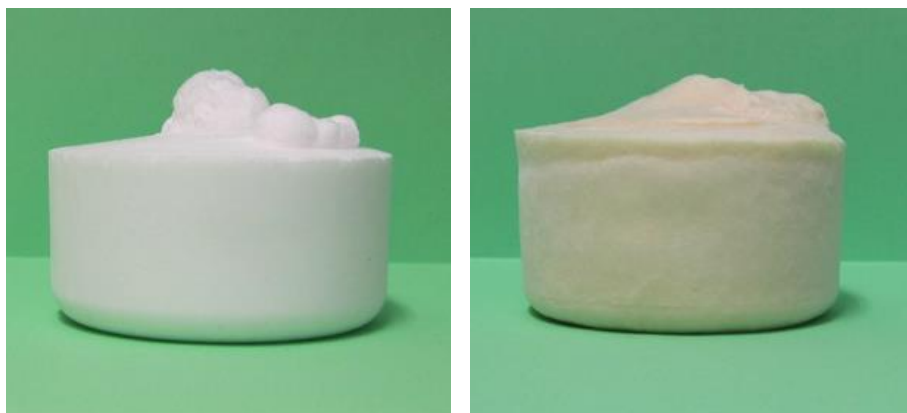
#### 4.9. Eco-friendly nanocellulose processing (paper VIII)

Our results indicate that it is possible to use organic acid as a pretreatment that, when combined with high-shear homogenisation, can strategically produce nanocellulose, and that the method can be upscaled. The results obtained so far indicate that we can successfully process nanocellulose and that, in addition, we can chemically functionalise the cellulosic materials. It was obvious from our visual assessment that we had converted hydrophilic cellulose nanomaterials into hydrophobic materials. The nanocellulose cross-linking results indicate that we can improve the material properties by simply irradiating the nanocellulosic material

with UV light. The hydrophilic nature of cellulosic materials means that they easily absorb water from the atmosphere, which negatively influences their physical and mechanical strength properties. Cellulose has several hydroxyl groups on its chain, meaning that the cellulosic materials have very poor humidity-resistance properties. This disadvantageous hydrophilicity of the material can be improved by chemical modification. In this work, nanocellulosic foam materials are made and then post-modified. Overall, such formic acid chemistry seems very promising in nanocellulose processing.

Also in this work, TEMPO-oxidised nanocellulose was produced so that it could be compared with the nanocellulose produced via the new organic acid pretreatment method. High fibrillation efficiency is a well-known advantage of TEMPO-based nanocellulose processing. In making such a comparison, the degree of fibrillation was not considered a priority, but the chemistry and sustainability of the process were of utmost importance. Many have described the TEMPO/NaClO/NaBr system as an unsustainable and toxic processing method, as it involves chlorine and bromine chemistry. Furthermore, it is well known that the TEMPO method converts the hydroxyl group of cellulose into corresponding carboxylate groups and some aldehyde groups, thereby introducing negatively charged groups on the surface of the cellulose chain.

In the formic acid process, no charge groups are introduced on the surface of the cellulosic material. Moreover, the organic acid hydrolysis process is very mild under our experimental condition and avoids hydrolysing the cellulose chains to sugars. Figure 60 shows the freeze-dried 3D structure of TEMPO-derived nanocellulose foam materials made from bleached sulphite pulp and CTMP, respectively. However, in this paper VIII, the focus is on sulphite pulp-based nanocellulose NFC. CTMP-NFC foam is presented here just to show that it is possible to use ligno-cellulosic pulp fibres to produce NFC foam materials too.



**Figure 60.** 3D structure of TEMPO-derived sulphite pulp-based NFC foam (left) and TEMPO-based CTMP-NFC foam (right)

After successfully producing nanocellulosic materials via two different processing routes, i.e., the formic acid approach and the TEMPO-mediated oxidation approach, we conclude that there is good potential to produce nanocellulose using the formic acid method, as the process is new and sustainable with the following advantages:

- Formic acid is a “green”, non-toxic chemical.
- Formic acid is very cheap.
- No “purification step” is involved in the method, as in sulphuric acid hydrolysis, thereby reducing the overall processing time and cost.
- The process is simple and can easily be upscaled, it does not require any pressurised systems as the temperature used is under 90°C.
- It is possible to process high consistencies of pulp fibres.
- It can be considered a low-energy fibrillation process.
- The method is environmentally friendly and sustainable.

It can be concluded that the TEMPO-mediated oxidation method enables the fibres to swell. This results in a high proportion of well-individualised nanofibrils with a very high aspect ratio. This is not the case in the formic acid method, as there is no change in the charge of the materials and, as such, the cellulose fibres do not swell.



## 5. CONCLUSIONS

This thesis focuses on the processing of nanocellulose originating from pulp fibres, specifically, mechanical pulp fibres. In this work, we have developed a methodology for producing mechanical pulp-based nanocellulose from fibres and fines fractions and for optimising the usage of nanocellulose in order to improve the strength properties of paper and paperboard products. Another sub-aim of the research was to build new knowledge of mechanical pulp-based nanocellulose by supporting the development of a new production method and/or improving the current state-of-the-art method for microfibril characterisation. In addition, while striving to develop completely new products, in order to widen the application of mechanical pulp fibres, we have studied the possibility of co-utilising nanofibrillated cellulose (NFC) and nanographite (NG) in composite film applications. We have also designed an eco-friendly nanocellulose processing method using organic acid, and produced a foam structure of freeze-dried nanocellulose.

It was found that blending the pulp fibres with nanocellulose improved the mechanical properties of the resulting handsheets, with only a slight effect on the sheet density. The results presented here indicate significant strength improvement with the use of different levels of starch (i.e., 20 and 10 kg t<sup>-1</sup>) and 5% TEMPO-based MFC. We noticed that the strengthening impact of 5% TEMPO-based MFC was approximately equal to that of 10 kg t<sup>-1</sup> of CS. It is therefore possible to use CS or MFC to improve the strength properties of paperboard products.

The results of crill measurements indicate an increase in crill values as the homogenisation time increases. Although further development of the crill method is required before it can be used for online quality control in a future nanocellulose plant, the robustness and speed of the technique suggests that the crill method has a bright future. We successfully produced nanocellulose through two different processing routes, i.e., hydrogen peroxide pretreatment and TEMPO-mediated oxidation. We conclude from the improvement in crill values that there is better potential to produce nanocellulose using the TEMPO method than using hydrogen peroxide pretreatment, as the process yields a uniform size distribution of nanocellulose microfibrils under 100 nm in size.

We conclude that it is also possible to produce NFC-NG composite films with enhanced sheet-resistance and mechanical properties, the films produced being quite stable, flexible, and bendable. We believe that realising this idea would create new possibilities for technological advancement in the area of high-yield pulp technology, potentially giving rise to new value-added products. SEM

micrographs reveal the morphological structures of pure CTMP-NFC, pure SP-based NFC, and of those NFCs blended with NG.

Lastly, we introduce the use of “green” and sustainable chemistry for nanocellulose processing. An organic acid (i.e., formic acid) was used at an elevated temperature to mildly hydrolyse the sulphite pulp fibres before high-shearing homogenisation. The resulting nanocellulose was subsequently freeze-dried and some chemical functionalisation and click reactions were performed. It was possible to produce a 3D structure of freeze-dried nanocellulose foam.

## **6. RECOMMENDATIONS**

Nanocellulose is actually a “hot” research field at the moment, and there are still many opportunities to work with and explore cellulose nanomaterials. The aim of this research was to create a knowledge base supporting the development of a low-cost method of producing nanocellulose, with applications in paper and paperboard products, composite films, and foams. There is a need for an environmentally responsible and sustainable method for producing nanocellulose with barrier properties that enable its use in packaging to replace petroleum-based polymers. Research into using organic acids and chemical functionalization via organic-click chemistry is one option for sustainable nanocellulose processing. As recently reported by a Japanese company producing nanocellulose using phosphorus chemicals. It would be interesting to study this type of phosphorus-based chemical processing of nanocellulose and to explore possible methods for the post-modification of nanocellulose. Lastly, it would be interesting to study the processing of nanocrystalline cellulose using mechanical pulp fibres and to search for new types of applications.

## 7. REFERENCES

- Abdul Khalil, H.P.S., Davoudpour, Y., Islam, Md. N., Mustapha, A., Sudesh, K., Dungani, R., & Jawaid, M.** (2014): Production and modification of nanofibrillated cellulose using various mechanical processes: a review. *Carbohydrate Polymers*, 99, 649–665.
- Abe, K., Iwamoto, S., and Yano, H.** (2007): Obtaining cellulose nanofibers with a uniform width of 15 nm from wood. *Biomacromolecules*, 8(10), 3276–3278.
- Ahola, S., Österberg, M., Laine, J.** (2008): Cellulose nanofibrils—adsorption with poly (amideamine) epichlorohydrin studied by QCM-D and application as a paper strength additive, *Cellulose*, 15(2), 303–314.
- Andres, B., Forsberg, S., Dahlström, C., Blomquist, N., and Olin, H.** (2014): Enhanced electrical and mechanical properties of nanographite electrodes for supercapacitors by addition of nanofibrillated cellulose. *Physica Status Solidi B*, 251(12), 2581–2586.
- Andresen, M., Johansson L.S., Tanem, B.S., Stenius, P.** (2006): Properties and characterization of hydrophobized microfibrillated cellulose. *Cellulose*, 13(6), 665–677.
- Ankerfors, M.** (2012): Microfibrillated cellulose: Energy-efficient preparation techniques and key properties. Licentiate Thesis, Department of Fibre and Polymer Technology, Royal Institute of Technology, Stockholm, Sweden.
- Ankerfors, M., Duker, E., and Lindström, T.** (2013): Topo-chemical modification of fibres by grafting of carboxymethyl cellulose in pilot scale. *Nordic Pulp and Paper Research Journal*, 28(1), 6–14.
- Azizi Samir MAS, Alloin F, Dufresne A.** (2005): Review of recent research into cellulose whiskers: their properties and their application in nanocomposite field. *Biomacromolecules*; (6), 612–26.
- Baldwin SD, Gautam N, Houghton KS, Rogers RM, Ryder JL.** (1993): Smoking article wrapper for controlling burn rate and method for making same. US5263999A.
- Baldwin SD, Gautam N, Houghton KS, Rogers RM, Ryder JL.** (1995): Smoking article wrapper for controlling burn rate and method for making same. US5417228A.
- Bilodeau, M., Bousfield, D., Luu, W., Richmond, F., and Paradis, M.** (2012): Potential applications of nanofibrillated cellulose in printing and writing papers. TAPPI International Conference on Nanotechnology for Renewable Materials, June 5-7, Montreal, Quebec, Canada.

**Björkqvist, O., Engstrand, P., Htun, M., Norgren, M.** (2010): "FORE". SPCI/Svensk Pappertidning, Sweden. pp. Nr. 2 (2010):pp. 24–25.

**Bragd, P.L., Bekkumand, H.van., Besemer, A.C.** (2004): TEMPO-mediated oxidation of polysaccharides: survey of methods and applications, *Topics in Catalysis* 27(1–4), 49–66.

**Brännvall, E.** (2007): Aspect on strength delivery and higher utilisation of the strength potential of softwood kraft pulp fibres, Doctoral thesis 2007, Royal Institute of Technology, Stockholm.

**Bras, J., Missoum, K., Belgacem, M., N.** (2013): Water re-dispersible dried Nanofibrillated Cellulose, 2013 TAPPI INTERNATIONAL CONFERENCE ON NANOTECHNOLOGY FOR RENEWABLE MATERIALS, 24-27 June 2013, Stockholm, Sweden.

**Brodin, F.W., Gregersen, Ø.W., Syverud, K.** (2014): Cellulose nanofibrils: Challenges and possibilities as a paper additive or coating material – A review. *Nordic Pulp and Paper Research Journal*, 29(1), 156–166.

**Cash MJ, Chan AN, Conner HT, Cowan PJ, Gelman RA, Lusvardi KM, Thompson SA, Tise FP.** (2000): Derivatized microfibrillar polysaccharide. O2000047628A2.

**Chakraborty, A., Sain, M., Kortschot, M.** (2005): Cellulose microfibrils: A novel method of preparation using high shear refining and cryocrushing, *Holzforschung*, 59(1), 102–107.

**Charreau, H., Foresti, M., L., Vazquez, A.** (2013): Nanocellulose Patents Trends: A Comprehensive Review on Patents on Cellulose Nanocrystals, Microfibrillated and Bacterial Cellulose, *Recent Patents on Nanotechnology*, 7, 56–80.

**Chinga-Carrasco, G.** (2013): Optical methods for the quantification of the fibrillation degree of bleached MFC materials. *Micron* 48: 42–48.

**Chinga-Carrasco, G., Averianova, N., Gibadullin, M., Petrov, V., Leirset, I., Syverud, K.** (2013): Micro-structural characterisation of homogeneous and layered MFC nano-composites. *Micron* 44, 331–338.

**Chirayil, C.J., Mathew, L., and Thomas, S.** (2014): Review of recent research in nanocellulose preparation from different lignocellulosic fibers, *Rev. Adv. Mater. Sci.*, 37, 20–28.

**De Nooy, A. E. J., Besemer, A. C., & Van Bekkum, H.** (1995): Highly selective nitroxyl radical-mediated oxidation of primary alcohol groups in water-soluble glucans. *Carbohydrate Research*, 269(1), 89–98.

**Dillen, S., Forsberg, E., Marklund, K., Minge, S.** (1973): Groundwood fractionation in a conventional screening system and its influence on quality,

International Mechanical Pulping Conference, June 18-21, Stockholm, Sweden, 26:1–26:26.

**Dinand E, Chanzy H, Vignon MR, Maureaux A, Vincent I.**(1999): Microfibrillated cellulose and method for preparing a microfibrillated cellulose. US5964983A.

**Dufresne, A., Cavailé, J.Y., & Vignon, M.R.** (1997): Mechanical behavior of sheets prepared from sugar beet cellulose microfibrils. *Journal of Applied Polymer Science* 64(6): 1185–1194.

**Duker, E.** (2007): The use of Carboxymethyl cellulose in papermaking; aspect on process integration and strength-enhancing mechanisms, Lic thesis, Royal Institute of Technology, Stockholm Sweden.

**Duker, E., Brännvall, E., and Lindström, T.** (2007): The effects of CMC attachment onto industrial and laboratory-cooked pulps. *Nordic Pulp & Paper Research Journal*, 22(3), 356–363.

**Eichhorn SJ, Dufresne A, Aranguren M, et al.** (2010): Review: current international research into cellulose nanofibres and nanocomposites. *J Mater Sci* 2010; 45: 1–33.

**Eriksen, Ø., Syverud, K., Gregersen, Ø.** (2008): The use of microfibrillated cellulose produced from kraft pulp as strength enhancer in TMP paper, *Nordic Pulp and Paper Research Journal*, 23(3), 299–304.

**Eriksson, M., Pettersson, G., and Wågberg, L.** (2005): Application of polymeric multilayers of starch onto wood fibres to enhance strength properties of paper. *Nordic Pulp and Paper Research Journal*, 20(3), 270–275.

**Esau** (1977): *Anatomy of seed plants*, Wiley, NY.

**Fall, A. B., Burman, A., and Wågberg, L.** (2014): Cellulosic nanofibrils from eucalyptus, acacia and pine fibers. *Nordic Pulp and Paper Research Journal*, 29 (1), 176–184.

**Fang, Z., Zhu, H., Preston, C., Han, X., Li, Y., Lee, S., Chai, X., Chen, G., and Hu, L.** (2013): Highly transparent and writable wood all-cellulose hybrid nanostructured paper. *Journal of Materials Chemistry*, 1(39), 6191–6197.

**Fengel, D. and Wegener, G.** (1989): *Wood Chemistry, Ultrastructure, Reactions*, Walter de Gruyter, New York, NY, USA.

**Fleming, K., Gray, D.G., Matthews, S.** (2001): Cellulose crystallites, *Chemistry - A European Journal*, 7(9), 1831–1835.

**Floury, P., Desrumaux, A., Lardieres, J.** (2000): Effect of high-pressure homogenisation on droplet size distribution and rheological properties of model

oil-in-water emulsions, *Innovative Food Science and Emerging Technologies* 1, 127–134.

**Giertz, H. W.** (1973): Basic Difference between Mechanical and Chemical Pulp. Int. Mech. Pulping Conf., Stockholm, Sweden, June 18-21, 1973, Sweden, pp.6:1– 6:11.

**Gonzalez, I., Vilaseca, F., Alcala, M., Pelach, M. A., Boufi, S., and Mutje, P.** (2013): Effect of the combination of biobeating and NFC on the physico-mechanical properties of paper. *Cellulose*, 20(3), 1425–1435.

**Gray, D.G.** (1994): Chiral nematic ordering of polysaccharides, *Carbohydrate Polymers* 25(4), 277–284.

**Habibi Y, Lucia L, Rojas OJ.** (2010): Cellulose nanocrystals: chemistry, self-assembly, and applications. *Chem Rev*; 110: 3479–500.

**Hansen, P., Sundvall, Ö.** (2012): On-line crill sensor commercially available 2012, International Paper Physics and 8th International Paper and Coating Chemistry Conference Stockholm Sweden, June 10–14 2012, poster.

**Hartler, N. and Mohlin, U-B.** (1975): Cellulose fibre bonding. Part 2. Influence of pulping on interfibre bond strength, *Svensk Papperstidning* 78(8), 295.

**Helle T.** (1962): “Sammenliknende studier over sulfat-og sulfitpapir” licentiate dissertation NTU.

**Henriksson, M., Henriksson, G., Berglund, L., Lindström, T.** (2007): An environmentally friendly method for enzyme-assisted preparation of microfibrillated cellulose (MFC) nanofibres. *European Polymer Journal.*, 43(8), 3434–3441.

**Herrick FW.** (1984): Process for preparing microfibrillated cellulose.US4481077A.

**Herrick FW.** (1984): Redispersable microfibrillated cellulose – Cellulose microfibrillée redispersable, Redispergierbare mikrofibrillierte cellulose. EP120471A2.

**Herrick FW.** (1984): Redispersible microfibrillated cellulose.US4481076A.

**Herrick, F., Casebier, R., Sandberg, K.** (1983): Microfibrillated cellulose: morphology and accessibility. *J. Appl. Polym. Sci.: Appl. Polym. Symp* 37: 797-813.

**Hii, C., Gregersen, Ø. W., Chinga-Carrasco, and Eriksen, Ø.** (2012): The effect of MFC on the pressability and paper properties of TMP and GCC based sheets. *Nordic Pulp and Paper Research Journal*, 27(2), 388–396.

**Hill, J and Eriksson, L.** (1973): Mechanical pulping processes evaluated by an optical device, International Mechanical Pulping Conference, June 18-21, Stockholm, Sweden,10:1–10:13.

- Hirn, U., and Schennach, R.** (2015): Comprehensive analysis of individual pulp fiber bonds quantifies the mechanisms of fiber bonding in paper. *Scientific Reports*, 5:10503, 1–9.
- Höglund, H., Bodin, O.** (1976): Modified thermo-mechanical pulp, *Svensk Papperstidning*, Sweden, 79(11), 343–347.
- Hubbe MA, Rojas OJ, Lucia LA, Sain M.** (2008): Cellulosic nanocomposites: a review. *BioResources*; 3: 929–80.
- Innami S, Fukui Y.** (1987): Additive composition for foods or drugs. US4659388A, 1987.
- Ishii, D., Saito, T., Isogai, A.** (2011): Viscoelastic evaluation of average length of cellulose nanofibres prepared by TEMPO-Mediated Oxidation. *Biomacromolecules*, 12, 548–550.
- Isogai, A.** (2013): Wood nanocelluloses: fundamentals and applications as new bio-based nanomaterials. *Journal of wood science*, 59(6), 449–459.
- Isogai, A., Saito, T., & Fukuzumi, H.** (2011a): TEMPO-oxidized cellulose nanofibers. *Nanoscale* 3(1), 71–85.
- Isogai, T., Saito, T., & Isogai, A.** (2011b): Wood cellulose nanofibrils prepared by TEMPO electro-mediated oxidation, *Cellulose*, 18(2), 421–431.
- Johnsson, M.** (2013) : Mechanical pulping market challenges, 8th International Fundamental Mechanical Pulp Research Seminar, 29-31 Jan 2013, Åre, Sweden, pp128–137.
- Josset, S., Orsolini, P., Siqueira, G., Tejado, A., Tingaut, P., Zimmermann, T.** (2014): Energy consumption of the nanofibrillation of bleached pulp, wheat straw and recycled newspaper through a grinding process. *Nordic Pulp & Paper Research Journal*, 29(1), 167–175.
- Kangas, H., Lahtinen, P., Sneek, A., Saariaho, A-M., Laitinen, O. and Hellén, E.** (2014): Characterization of fibrillated celluloses. A short review and evaluation of characteristics with a combination of methods. *Nordic Pulp & Paper Research Journal*, 29(1), 129–143.
- Karlsson, A.** (2013) : Improved hydrogen peroxide bleaching of mechanical pulps through fundamental understanding of the influence of heat, iron, fines and chemical treatment on chromophore content, University. Mid Sweden University doctoral thesis, ISSN 1652-893X ; 170.
- Kaushik, A. and Singh, M.** (2011): Isolation and characterization of cellulose nanofibrils from wheat straw using steam explosion coupled with high shear homogenization. *Carbohydrate research*, 346(1), 76–85.



- Klemm, D., Kramer, F., Moritz, S., Lindström, T., Ankerfors, M., Gray, D., et al.** (2011): Nanocelluloses: A New Family of Nature-Based Materials. *Angewandte Chemie Int. Edition*, 50(24), 5438–5466.
- Koubba A. And Koran Z.** (1995): "Measure of the internal bond strength of paper/board" *TAPPI J.*, 78(3), 103–111.
- Laine, J., Lindström, T., Nordmark, G.G., and Risinger, G.** (2002): Studies on topochemical modification of cellulosic fibres-Part 2. The effect of carboxymethyl cellulose attachment on fibre swelling and paper strength. *Nordic Pulp & Paper Research Journal*, 17(1), 50–56.
- Lewin, M. and Goldstein, I.S.** (1991): *Wood Structure and Composition*, Marcel Dekker Inc., New York, NY, USA.
- Li, Y., Zhu, H., Gu, H., Dai, H., & Fang, Z.** (2013). Strong transparent magnetic nanopaper prepared by immobilization of Fe<sub>3</sub>O<sub>4</sub> nanoparticles in a nanofibrillated cellulose network. *Journal of Materials Chemistry A*, 1(48), 15278–15283.
- Liimatainen, H., Visanko, M., Sirviö, J.A., Hormi, O.E., Niinimäki, J.** (2012): Enhancement of the nanofibrillation of wood cellulose through sequential periodate-chlorite oxidation. *Biomacromolecules*, 13, 1592–1597.
- Lindh, J., Carlsson, Daniel O., Strømme, M., Mihranyan, A.** (2014): Convenient One-Pot Formation of 2,3-Dialdehyde Cellulose Beads via Periodate Oxidation of Cellulose in Water. *Biomacromolecules*, 15, 1928–1932.
- Lindström, M. E., Söderberg, D., & Henriksson, G.** (2012): Single-step method for production of nano pulp by acceleration and disintegration of raw material, World Patent No. WO2012/115590.
- Lindström, T.** (1992): Chemical factors affecting the behaviour of fibres during papermaking. *Nordic Pulp and Paper Research Journal*, 4, 181–192.
- Lindström, T., Aulin, C., Gimäker, M., & Persson, T.** (2014): The emergence of practical nanocellulose applications for a more sustainable paper/board industry, *Indian Pulp and Paper Technical Association (IPPTA)*, Vol. 26, 53–61.
- Lumiainen, J.** (2000): Refining of chemical pulp. *Papermaking part*, 1, 86–122.
- Ma, P., and Zhai, H.** (2013): Selective TEMPO-mediated oxidation of thermomechanical pulp. *BioRes.* 8(3), 4396–4405.
- Malho, J-M., Laaksonen, P., Walther, A., Ikkala, O., Linder, M. B.** (2012): Facile Method for Stiff, Tough, and Strong Nanocomposites by Direct Exfoliation of Multilayered Graphene into Native Nanocellulose Matrix. *Biomacromolecules*, 13, 1093–1099.

**Miller, J.** (2014): Nanocellulose: Technology Applications, and Markets. TAPPI International Conference on Nanotechnology for Renewable Materials, 23-26 June, Vancouver, British Columbia Canada.

**Moon RJ, Martini A, Nairn J, Simonsen J, Youngblood J.** (2011): Cellulose nanomaterials review: structure, properties and nanocomposites. *Chem Soc Rev*; 40: 3941–94.

**Mörseburg, K. and Chinga-Carrasco, G. (2009):** Assessing the combined benefits of clay and nanofibrillated cellulose in layered TMP-based sheets. *Cellulose*, 16(5), 795–806.

**Nelson, K.** (2014): Low cost production of nanocellulose with the AVAP biorefinery technology. TAPPI International Conference on Nanotechnology for Renewable Materials, 23-26 June, Vancouver, British Columbia Canada.

**Nygårds, S.** (2011): Nanocellulose in pigment coatings – Aspects of barrier properties and printability in offset. Sweden: Linköping University, Department of Physics, Chemistry and Biology and Innventia AB (Master's Thesis).

**Nygren O., Bäck R. and Höglund, H.** (2003): On characterisation of mechanical and chemimechanical pulps, International Mechanical Pulping Conference, Quebec City, Canada, 97–103.

**Okita, Y., Saito, T., Isogai, A.** (2009): TEMPO-mediated oxidation of softwood thermomechanical pulp. *Holzforschung*, 63, 529–535.

**Osong S., H., Norgren, S., Engstrand, P.** (2013): An approach to produce nanoligno-cellulose from mechanical pulp fine materials, *Nordic Pulp and Paper Research Journal*, 2013 28(4), 472–479.

**Pääkkö, M., Ankerfors, M., Kosonen, H., Nykänen, A., Ahola, S., Österberg, M., Ruokolainen, J., Laine, J., Larsson, P.T., Ikkala, O. and Lindström, T.** (2007): Enzymatic hydrolysis combined with mechanical shearing and high-pressure homogenisation for nanoscale cellulose fibrils and strong gels. *Biomacromolecules*, 8(6), 1934–1941.

**Page, D., Seth. R.S., El-Hosseiny, F.** (1985): "Strength and chemical composition of wood pulp fibres. "8<sup>th</sup> fundamental research symposium, Cambridge 1: 77–91.

**Page, D.H.** (1969): A theory for the tensile strength of paper, *TAPPI*, 52(4), 674–681.

**Paquin, P.** (1999): Technological properties of high pressure homogenisers: the effect of fat globules, milk proteins, and polysaccharides, *International Dairy Journal* 9, 329–335.

**Pettersson, T.** (2010): On-line crill measurements for improved control of refining, Control Systems 2010, SPCI, Stockholm.

- Rånby BG, Ribí E.** (1950): Über den feinaufbau der zellulose. *Experimentia*; 6: 12-4.
- Rånby BG.** (1949): Aqueous colloidal solutions of cellulose micelles. *Acta Chem Scand*; 3: 649–50.
- Rånby BG.** (1951): Fibrous macromolecular systems. Cellulose and muscle. The colloidal properties of cellulose micelles. *Discuss Faraday Soc*; 11: 158–64.
- Rantanen, J. and Maloney, T. C.** (2013): Press dewatering and nip rewetting of paper containing nano- and microfibril cellulose. *Nordic Pulp and Paper Research Journal*, 28(4), 582–587.
- Rebouillat, S., and Pla, F.** (2013): State of the Art Manufacturing and Engineering of Nanocellulose: A Review of Available Data and Industrial Applications, *Journal of Biomaterials and Nanobiotechnology*, 4, 165–188.
- Revol, J. F., Godbout, L., Dong, X-M., Gray, D. G., Chanzy, H. and Maret, G.** (1994): Chiral nematic suspension of cellulose crystallites, Phase separation and magnetic field orientation. *Liquid Crystals* 16(1): 1271–34.
- Rundlöf, M.** (2002): Interaction of dissolved and colloidal substances with fines of mechanical pulp-Influence on sheet properties and basic aspects of adhesion, Doctoral Thesis, Department of Wood Chemistry, Royal Institute of Technology, Stockholm, Sweden.
- Saito T, Nishiyama Y, Putaux JL, Vignon M, Isogai A.** (2006a): Homogeneous suspensions of individualized microfibrils from tempocatalyzed oxidation of native cellulose. *Biomacromolecules*; 7: 1687–91.
- Saito, T. and Isogai, A.** (2006): Introduction of aldehyde groups on surfaces of native cellulose fibres by TEMPO-mediated oxidation, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 289(1–3), 219–225.
- Saito, T. and Isogai, A.** (2005): A novel method to improve wet strength of paper. *Tappi journal*, 4(3), 3–8.
- Saito, T., Kimura, S., Nishiyama, Y., Isogai, A.** (2007): Cellulose nanofibres prepared by TEMPO-mediated oxidation of native cellulose. *Biomacromolecules*, 8(8), 2485–2491.
- Saito, T., Okita, Y., T.T. Nge, T.T., Sugiyama, J., A. Isogai, A.** (2006b): TEMPO-mediated oxidation of native cellulose: Microscopic analysis of fibrous fractions in the oxidised products, *Carbohydrate Polymers*, 65(4), 435–440.
- Sandberg KR, Synder FW, Turbak AF.** (1981): Microfibrillated cellulose. GB2066145A.

- Sehaqui, H., Zhou, Q., and Berglund, L. A.** (2013): Nanofibrillated cellulose for enhancement of strength in high-density paper structures, *Nordic Pulp and Paper Research Journal*, 28(2), 182–189.
- Sehaqui, H., Zhou, Q., Berglund, L. A.** (2011): High-porosity aerogels of high specific surface area prepared from nanofibrillated cellulose (NFC), *Composites Science and Technology*, 71(13), 1593–1599.
- Seth R.S. and Page D. H** (1988): “Fibre properties and tearing resistance” *TAPPI J.*, 71(2), 103–107.
- Shatkin, J. A., Wegner, T.H., Bilek, E., Cowie, J.** (2014): Market projections of cellulose nanomaterial-enabled products– Part 1: Applications. *Tappi journal*, 13(5), 9–16.
- Siqueira G, Bras J, Dufresne A.** (2010): Cellulosic Bionanocomposites: a review of preparation, properties and applications. *Polymers*; 2: 728–65.
- Siro I. and Plackett D.** (2010): Microfibrillated cellulose and new composite materials: a review. *Cellulose*; 17: 459–94.
- Sjöström, E.** (1993): *Wood Chemistry, Fundamentals and Applications*, Academic Press Inc., San Diego, CA, USA.
- Spence, K. L., Venditti R. A., Rojas, O.J., Habibi, Y., Pawlak, J.J.** (2011): A comparative study of energy consumption and physical properties of microfibrillated cellulose produced by different processing methods. *Cellulose*, 18(4), 1097–1111.
- Spence, K. L., Venditti, R. A., Habibi, Y., Rojas, O. J., Pawlak, J. J.** (2010a): The effect of chemical composition on microfibrillar cellulose films from wood pulp: Mechanical processing and physical properties. *Bioresource Technology* 101, 5961–5968.
- Spence, K. L., Venditti, R. A., Rojas, O.J., Habibi, Y., Pawlak, J. J.** (2010b): The effect of chemical composition on microfibrillar cellulose films from wood pulps: water interactions and physical properties for packaging applications. *Cellulose* 17: 835–848.
- Steenberg, B., Sandgren, B., Wahren, D.** (1960): Studies on Pulp Crill, Part 1. Suspended fibrils in paper pulp fines, *Svensk Papperstidning* Nr 12, pp 395–397.
- Stelte, W. and Sanadi, A. R.** (2009): Preparation and characterization of cellulose nanofibres from two commercial hardwood and softwood pulps. *Industrial & engineering chemistry research*, 48(24), 11211–11219.
- Stenius, P.** (2014): Nanocellulose technology – Conclusions and perspectives 2006 – 2014. 5th Recent advances in cellulose nanotechnology research seminar, October 28-29, Trondheim, Norway.

- Stenstad, P., Andresen, M., Tanem, B. S., and Stenius, P.** (2008): Chemical surface modifications of microfibrillated cellulose. *Cellulose*, 15(1), 35–45.
- Su, J., Mosse, W.K.J., Sharman, S., Batchelor, W.J., Garnier, G.** (2013): Effect of tethered and free microfibrillated cellulose (MFC) on the properties of paper composites. *Cellulose* 20(4), 1925–1935.
- Sundholm J.** (1999): Papermaking Science and Technology Vol.5; Mechanical Pulping, ISBN 952-5216-05-5, Fapet Oy, P.O. Box 146, FIN-00171 Helsinki, Finland.
- Svending, P.** (2014): Commercial break-through in MFC processing. TAPPI International Conference on Nanotechnology for Renewable Materials, 23-26 June, Vancouver, British Columbia Canada.
- Syverud, K. and Stenius, P.** (2009): Strength and barrier properties of MFC films. *Cellulose*, 16(1), 75–85.
- Syverud, K., Chinga-Carrasco, G., Toledo, J., Toledo, P.G.** (2011): A comparative study of Eucalyptus and Pinus radiata pulp fibres as raw materials for production of cellulose nanofibrils. *Carbohydrate Polymers*, 84(3), 1033–1038.
- Taabaku AF, Sunaidaa FU, Sandobaagu KR** (1981) (original inventor) - **Sandberg KR, Synder FW, Turbak AF** (inventor DWPI): Microfibrous cellulose and its manufacture. JP56100801A.
- Taipale, T., Österberg, M., Nykänen, A., Ruokolainen, J., Laine, J.** (2010): Effect of microfibrillated cellulose and fines on the drainage of kraft pulp suspension and paper strength, *Cellulose* 17: pp1005–1020.
- Taniguchi, T., Okamura, K.** (1998): New films produced from microfibrillated natural fibres, *Polymer International* 47, 291–294.
- TAPPI.** Proposed New TAPPI Standard: Standard Terms and Their Definition for Cellulose Nanomaterial. Draft for Review, WI 3021.
- Tejado, A., Alam, M.N., Antal, M., Yang, H., van de Ven, T.G.M.** (2012): Energy requirements for the disintegration of cellulose fibers into cellulose nanofibers. *Cellulose* 19(3), 831–842.
- Torvinen, K., Kouko, J., Passoja, S., Keränen, J.T., Hellén, E.** (2014): Cellulose micro and nanofibrils as a binding material for high filler content papers, TAPPI Papercon, 733–746.
- Turbak AF, Snyder FW, Sandberg KR** (1983): Microfibrillated cellulose. US4374702A.
- Turbak AF, Snyder FW, Sandberg KR** (1983): Suspensions containing microfibrillated cellulose. US4378381A.

- Turbak AF, Snyder FW, Sandberg KR.** (1982): Food products containing microfibrillated cellulose. US4341807A.
- Turbak AF, Snyder FW, Sandberg KR.** (1984): Microfibrillated cellulose. US4483743A.
- Turbak AF, Snyder FW, Sandberg KR.** (1984): Suspensions containing microfibrillated cellulose. US4452722A.
- Turbak AF, Snyder FW, Sandberg KR.** (1984): Suspensions containing microfibrillated cellulose. US4452721A.
- Turbak AF, Snyder FW, Sandberg KR.** (1984): Suspensions containing microfibrillated cellulose. US4464287A.
- Turbak AF, Snyder FW, Sandberg KR.** (1984): Suspensions containing microfibrillated cellulose. US4487634A.
- Turbak AF, Snyder FW, Sandberg KR.** (1985): Suspensions containing microfibrillated cellulose. US4500546A.
- Turbak, A., Snyder, F., Sandberg, K.** (1983): Microfibrillated cellulose, a new cellulose product: properties, uses, and commercial potential. J. Appl. Polym. Sci.: Appl. Polym. Symp. 37: 815–827 (United States) ITT Rayonier Inc., Shelton, WA.
- Varanasi, S., He, R., Batchelor, W.** (2013): Estimation of cellulose nanofibre aspect ratio from measurements of fibre suspension gel point, Cellulose 20:1885–1896.
- Wågberg L, Decher G, Norgren M, Lindström T, Ankerfors M, Axnas K.** (2008): The build-up of polyelectrolyte multilayers of microfibrillated cellulose and cationic polyelectrolytes. Langmuir 24(3): 784–795.
- Wang, B., Sain, M., and Oksman, K.** (2007): Study of structural morphology of hemp fiber from the micro to the nanoscale. Applied Composite Materials, 14(2), 89–103.
- Williamson, M. (Journalist Engineer)** (2012): Nanocellulose: On the cusp of commercialization, Focus on Nanotechnology, pp31-36, ipw 10-11/2012, www.ipwonline.de.
- Xue, M.D., Kimura, T., Revol, J.-F., Gray, D.G.** (1996): Effects of ionic strength on the isotropic-chiral nematic phase transition of suspensions of cellulose crystallites, Langmuir 12 (8), 2076–2082.
- Yan, C., Wang, J., Kang, W., Cui, M., Wang, X., Foo, C. Y., Chee, K., J., Lee, P., S.** (2014): Highly Stretchable Piezoresistive Graphene-Nanocellulose Nanopaper for Strain Sensors. Adv. Mater., 26, 2022–2027.

**Yoo, S. & Hsieh, J. S.** (2010): Enzyme-assisted preparation of fibrillated cellulose fibers and its effect on physical and mechanical properties of paper sheet composites. *Industrial and Engineering Chemistry Research*, 49(5), 2161–2168.

**Zhu, H., Helander, M., Moser, C., Stahlkranz, A., Söderberg, D., Henriksson, G., and Lindström, M.** (2012): A novel nano cellulose preparation method and size fraction by cross flow ultra-filtration. *Current organic chemistry*, 16(16), 1871–1875.

**Zhu, H., Jia, Z., Chen, Y., Weadock, N., Wan, J., Vaaland, O., Han, X., Li, T., Hu, L.** (2013): Tin anode for sodium-ion batteries using natural wood fiber as a mechanical buffer and electrolyte reservoir. *Nano letters* 13(7), 3093–3100.

#### **Internet References**

<http://en.wikipedia.org/wiki/Nanoparticle> (February 27, 2014).

[http://en.wikipedia.org/wiki/List\\_of\\_countries\\_by\\_population](http://en.wikipedia.org/wiki/List_of_countries_by_population) (October 28, 2013).

<http://mwp.org/> (October 28, 2013).

<http://mwp.org/symposium/symposium-1995/> (October 28, 2013).