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Mechanical Pulp Based Nano-ligno-cellulose

Production, Characterisation and their Effect on Paper Properties

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ABSTRACT

Almost all research on biorefinery concepts are based on chemical pulping processes and ways of utilising lignin, hemicelluloses and extractives as well as a part of the remaining cellulose for production of nano materials in order to create more valuable products than today. Within the Forest as a Resource (FORE) research program at FSCN we are utilizing the whole chain of unit processes from forestry to final products as paper and board, where the pulping process research focus on high yield processes as TMP and CTMP. As these process solutions are preserving or only slightly changing the properties of the original wood polymers and extractives, the idea is to find high value adding products designed by nature.

From an economic perspective, the production of nanocellulose from a chemical pulp is quite expensive as the pulp has to be either enzymatically (e.g. mono-component endoglucanase) pre-treated or chemically oxidized using the TEMPO (2, 2, 6, 6 –tetramethyl-piperidine-1-oxil)-mediated oxidation method in order to make it possible to disrupt the fibres by means of homogenisation.

In high yield pulping processes such as in TMP and CTMP, the idea with this study was to investigate the possibility to use fractions of low quality materials from fines fractions for the production of nano-ligno-cellulose (NLC). The integration of a NLC 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 board grades. The intention of this research work was that, by using this concept, a knowledge base can be created so that it becomes possible to develop a low-cost production method for its implementation.

In order to study the potential of this concept, treatment of thermo-mechanical pulp (TMP) fines fractions were studied by means of homogenization. It seems possible to homogenize fine particles of thermo-mechanical pulp (1% w/v) to NLC. A corresponding fines fraction from bleached kraft pulp (BKP) was tested as a reference at 0.5% w/v concentration.

The objective presented in this work was to develop a methodology for producing mechanical pulp based NLC from fines fractions and to utilize this material as strength additives in paper and board grades. Laboratory sheets of CTMP and BKP, with the addition of their respective NLC, were made in a Rapid Köthen sheet former. It was found that handsheets of pulp fibres blended with NLC improved the z- strength and other important mechanical properties for similar sheet densities.

The characterization of the particle-size distribution of NLC is both important and challenging and the crill methodology developed at Innventia (former STFI) already during the 1980s was tested to see if it would be both fast and reliable enough. The crill measurement technique is based on the optical responses of a micro/nano particle suspension at two wavelengths of light; UV and IR. The crill values of TMP and CTMP based nano-ligno-celluloses were measured as a function of the homogenization time. Results showed that the crill value of both TMP-NLC and CTMP-NLC correlated with the homogenization time.

Keywords: mechanical pulp, thermo-mechanical pulp, chemi-thermomechanical pulp, fractionation, fines, homogenisation, nanocellulose, nano-ligno-cellulose (NLC), handsheets, strength properties, crill

SAMMANFATTNING

Nästan all forskning kring olika koncept av bioraffinaderier bygger på kemiska processer och sätt att utnyttja lignin, hemicellulosa och extraktivämnen samt en del av den återstående cellulosa för produktion av nanomaterial för att skapa mer värdefulla produkter än vad som finns i dag. Inom Skogen som resurs (FORE) forskningsprogram vid FSCN studeras hela kedjan av enhetsprocesser från skogsbruk till slutprodukter som papper och kartong, där massaprocessernas forskning fokuserar på högutbytes processerna TMP och CTMP. Eftersom att dessa processlösningar bevarar eller endast till liten del ändrar något på egenskaperna för den ursprungliga trä polymeren och extraktivämnena, är tanken att hitta högvärde produkter designade av naturen.

Ur ett ekonomiskt perspektiv är produktion av nanocellulosa från en kemisk massa dyr eftersom massan antingen är enzymatiskt förbehandlad eller kemiskt oxiderad med hjälp av TEMPO.

I mekaniska massaprocesser, såsom i TMP- och CTMP, är det möjligt att tillvarata fraktioner från massan vilken har låg kvalitet och som ej bidrar till goda pappersegenskaper. Dessa fraktioner kan användas som alternativ för produktion av nano-ligno-cellulosa (NLC) . Användning av NLC skulle kunna förbättra kvalitetsnivån på traditionella pappers och kartongprodukter. Således skulle en integrerad NLC produktionsenhet i ett mekaniskt massabruk ha potential att bli ett framtida sätt att använda lämpliga fraktioner av mekanisk massa. Syftet med denna forskning är att utveckla en billig och väl fungerande tillverkningsmetod av NLC.

För att få en fungerande tillverkningsmetod har försök gjorts med olika typer av utgångsmassor samt fraktioneringar av dessa. Tester att framställa NLC från dessa fraktioner har sedan gjorts i en homogenisator. Resultat från dessa försök visar att mekanisk massa är enklare att homogenisera än en kemisk massa vid samma koncentration.

Laboratorie ark av CTMP och BKP, med tillförsel av framtagna NLC från respektive massor, gjordes i en Rapid Köthen arkformare . Resultatet av denna tillförsel gav förbättrad z- styrka samt andra ökade styrkeegenskaper, detta endast med en liten ökning i densitet.

Karakterisering av NLC med avseende på partikelstorleksfördelning är både viktigt och utmanande. Då det i dagsläget inte finns några väl fungerande metoder

framtagna för detta användes och utvärderades Kryll mätningar i studierna . Denna mätningsteknik är baserad på de optiska svaren hos en mikro/nanopartikelsuspension vid två våglängder av ljus, UV och IR. Kryll värden av framtagna TMP och CTMP baserad NLC mättes som en funktion av homogeniseringstiden. Dessa mätningar visade att kryll värdet av både TMP-NLC och CTMP-NLC korrelerade med homogenisering tiden.

Nyckelord: mekanisk massa, termomekanisk massa, kemitermomekanisk massa, fraktionering, homogenisering, nanocellulosa, nano-ligno-cellulosa, NLC, styrkeegenskaper, kryll

ACKNOWLEDGEMENTS

Firstly, I would like to thank **God for God**, and as well thank **man for man**. I must pay special tribute to my supervisors; **Prof. Per Engstrand** and **Dr. Sven Norgren**, their teaching and coaching has been vital to my career development and they, have given me the freedom, confidence and time in relation to all the essentials required in order to grow as a scholar. I should say your valuable criticisms and "nourishable" inputs have enabled me to reach my current level and the dream of becoming a Licentiate would not have been achieved if it had not been for 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 professional conduct, learning from you all has enabled me to achieve the halfway stage to becoming a Ph.D.

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It would have been a "big punch" to my academic career if I was 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 homogenising equipment at T-house, the machine that I use in conducting my research, words alone are unable to state your good work, thanks so much Staffan. **Andrew Butterworth** working with the publishing group at Mid Sweden University library is gratefully acknowledged for the patents and articles search related to microfibrillated cellulose.

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Bryan Dyson – 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. But 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, damage or even shattered. They will never be the same. You must understand that and strive for it". Work efficiently during office hours and also give the required time to your family, friends and have proper rest.

Thanks to **all my friends**, in Sweden, Cameroon and around the globe, for your support and encouragement especially in difficult moments. I would also like to thank **my parents** for providing me with the essential fundamentals; guidance and support to embark upon many years of university education. They have actually helped me to understand the value of hard work, determination and education. Finally, I want to use this medium to say "merci beaucoup (thanks)" to "**ma Cherie (wife)" (Bam Christelle)** and **son (Dylan Sinke Jr.)**; words alone are not enough to 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

LIST OF PAPERS

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

Paper I **An approach to produce nano-ligno-cellulose from mechanical pulp fine materials**
Sinke H. Osong, Sven Norgren and Per Engstrand
Nordic Pulp and Paper Research Journal, 2013, 28(4), 472-479.

Paper II **Crill: A novel technique to characterize nano-ligno-cellulose**
Sinke H. Osong, Sven Norgren, Per Engstrand, Mathias Lundberg and Peter Hansen
Accepted for publication in Nordic Pulp and Paper Research Journal, 2014.

Paper III **Paper strength improvement by inclusion of nano-ligno-cellulose to CTMP**
Sinke H. Osong, Sven Norgren and Per Engstrand
Accepted for publication in Nordic Pulp and Paper Research Journal, 2014.

AUTHOR'S CONTRIBUTION TO THE REPORTS

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

Paper I	Principal author, experimental work, interpretation of results and writing the paper.
Paper II	Principal author, experimental work, interpretation of results and writing 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 III	Principal author, experimental work, interpretation of results and writing the paper.

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
Sinke H. Osong, Sven Norgren and Per Engstrand
Oral Presentation: 3rd International Cellulose Conference (ICC 2012), Sapporo, Japan, October 10, p63, 2012

New products based on mechanical pulps – nano-ligno-cellulose (NLC)
Sinke H. Osong, Sven Norgren and Per Engstrand
Oral Presentation: 8th Fundamental Mechanical Pulp Research Seminar (FMPRS 2013), Åre, Sweden, January 29, p25-26, 2013.

Mechanical properties of high-yield pulp handsheets, as affected by blends of nano-ligno cellulose
Sinke H. Osong, Sven Norgren and Per Engstrand
Poster: 2013 TAPPI International Conference on Nanotechnology for Renewable Materials, 24-27 June, 2013 at KTH Royal Institute of Technology in Stockholm, Sweden.

Nano-ligno-Cellulose as strength enhancer in handsheets
Sinke H. Osong, Sven Norgren and Per Engstrand
Poster: Marcus Wallenberg Prize (MWP) 2013 – Young Researchers, 23-24 September, 2013 Stockholm, Sweden.

ABBREVIATIONS AND ACRONYMS

AFM	Atomic Force Microscopy
BDDJ	Britt Dynamic Drainage Jar
BJ30	Britt Jar 30 mesh wire
BKP	Bleached Kraft pulp
BMcN	Bauer McNett Classifier
CSF	Canadian Standard Freeness
CTMP	Chemi-thermomechanical pulp
FORE	Forest as a resource
IR	Infrared
KFP	Crill value
MFC	Microfibrillated cellulose
NC	Nanocellulose
NCC	Nanocrystalline cellulose
NLC	Nano-ligno-cellulose
P-DADMAC	Poly-diallydimethylammoniumchloride
SEM	Scanning Electron Microscopy
SS	Super sharpened
TEA	Tensile Energy Absorption
TEM	Transmission Electron Microscopy
TEMPO	2,2,6,6 –tetramethyl-piperidine-1-oxil
TMP	Thermo-mechanical pulp
UV	Ultraviolet
WP	Whole Pulp

1. INTRODUCTION

Sweden is covered by approximately 50% of forest. The pulp and paper industry forms part of the forest-based bio-economy, and this sector is of importance to the Swedish economy. The forest-based industry has played an undeniable and pivotal role for ensuring sustainable development as well as one of the major sources of the country's national income with regards to its exports. There are basically two types of pulping process; chemical and mechanical pulping processes.

In the mechanical pulping systems, a great deal of effort is taken with regards to the fractionation in screens and cleaners as well as to optimizing process conditions in order to refine the rejected fractions. The fraction rejected for further treatment can vary from 10 to 50%, depending on the process strategy and the final product (paper/board qualities). In practice, it is common that approximately 10% of the pulp fibres and also a large part of the fines fraction have properties that are unsatisfactory in relation to 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 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 level. The demand for mechanical pulp fibres, especially news grades, coated and uncoated paper products is in a steep and rapid decline based on the electronic media preferences of the present generation of end-users. The industry is now struggling with decelerating profitability, which is affecting the final product performance. This emerging drawback has meant that there is the requirement for a paradigm shift in process technology for the forest-based industry.

An innovation-led and sustainable research for nanotechnology for renewable fibre-based products is the main research topic chosen to connect new ideas in order to improve the strength of the entire forest-based bio-economy. The application of nanocellulose in pulp and paper products is gaining importance with respect to its high strength to weight ratio, renewability and environmental friendliness of the bio-material.

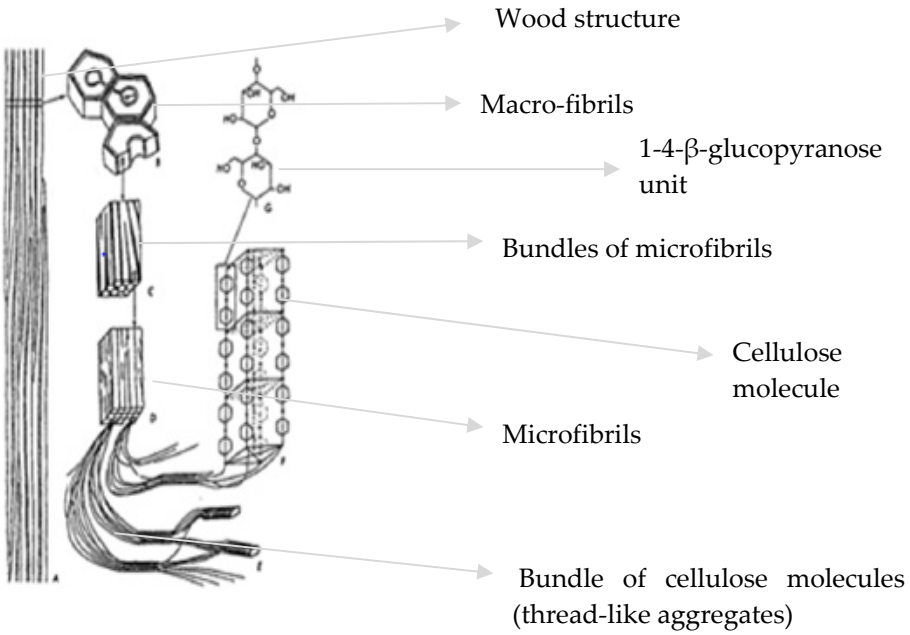

Figure 1. Microscopic model of cellulose in details. The arrows on each section denote the composition of each wood sub-section. (Adapted from Esau 1977).

Wood is a biodegradable biopolymer and consists mainly of three chemical components: cellulose, hemicelluloses and lignin. Several articles have been published that have described findings with regards to the wood components in greater detail; including Sjöström (1993), Fengel and Wegener (1989), and Levin and Goldstein (1991). The hierarchical structure of wood presented in Figure 1, shows both the macroscopical and microscopical structure of wood from the fibre level to the 1-4-β-glucopyranose unit. As shown in Figure 1, the idea in this project is to extract the thread-like aggregate from mechanical pulp fibres. In this thesis the name nano-lignocellulose (NLC) is used and which of course could be questioned. The reason for the choice of name is motivated by our aim to utilize the knowledge regarding wood polymers related research in the mechanical pulping area. In addition, to understand how to extract fibre materials into micro or nano-fibrils with width lower than 200 nm. More specifically we chose to utilize the ionic polymer and softening aspect of the amorphous wood polymer, hemicellulose and lignin so as to enhance delamination of the fibrillar structure during homogenisation.

1.1. Motivation

It is now the case that the pulp and paper industry is now attempting to emulate an already existing concept of the petro-chemical industry, in which power and

petroleum chemicals have been co-produced for hundreds of years. In the pulp and paper industry, the term biorefinery has gained significant importance during the past few years and now, traditional pulp fibres, newly engineered fibres (nanocellulose), dissolved lignin, hemicelluloses and energy are also co-produced within the same industry. One difference between the petro-chemical industry and the pulp and paper industry is that pulp and paper industry can produce large amounts of physical and biodegradable products which are linked to "green" legislation in support of bio-renewable materials and bio-economy policies.

Based on the declining growth in relation to news grades and for both, coated and uncoated paper qualities, as shown in Figure 2 (Johnsson 2013), the research interest of the majority of mills has shifted towards the newly engineered fibres (nanocellulose). Nanocellulose has been shown to be a potential candidate for renewable nanotechnological applications in the forest-based industry.

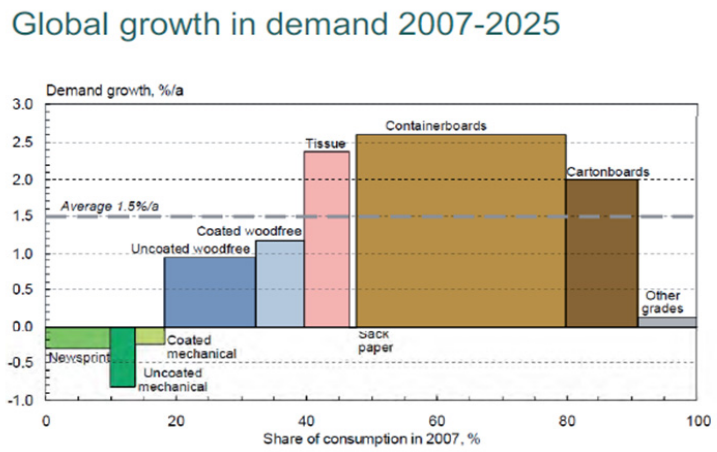

Figure 2. The use of printing papers is declining High Yield Pulp developments focus more on board grades (Johnsson 2013).

The world's population today is estimated to be 7.12 billion people, with China and India having 36.9% (2.63 billion people as of 2013) (http://en.wikipedia.org/wiki/List_of_countries_by_population) of the world's population. The population of China is around 1.36 billion and India has almost 1.27 billion people. It is strongly believed by many that the Asian market is becoming an emergent market for paper and paperboard products. Although there is decline regarding news grades, coated and uncoated papers in the western world, there is a strong belief that there will shortly be a rise in demand for these in the Asian markets as their industrialisation increases.

The idea of having a miniature nano-ligno-cellulose (NLC) plant in the same mechanical or chemi-mechanical pulp mill in order to improve existing paper quality should prove to be an asset as, the market for low grade paper products is still expected to rise as well as the steady global growth demand for board and carton board products.

1.2. Background

Mid Sweden University (FSCN) is currently performing research in a project known as "FORE", which refers to the forest as a resource, financed by the European Regional Development Fund, 2011-2014. The overall aim of the project is to show the synergetic possibilities and to investigate opportunities related to the forest industry through the production systems, with improved efficiency to a large range of sustainable bio-material-based new and existing products (Björkqvist et al. 2010), see Figure 3. One of the sub-objectives of the FORE project (this work) was to utilize low quality fibres in a mechanical pulp and paper mill in order to produce new products and/or improve the product quality of traditional products within these industries.

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" involves a number of pulps, which include: stone groundwood, pressure groundwood, super pressure groundwood, thermo-groundwood, refiner mechanical pulp, pressure refiner mechanical pulp, thermo-mechanical pulp, chemi-mechanical and chemi-thermomechanical pulp (Sundholm 1999).

Thermomechanical pulp (TMP) and chemi-thermomechanical pulping (CTMP) are the two main pulps of interest in this study. The stone groundwood is noted for its even proportion of fines and fibre fraction (50/50) whereas the thermo-mechanical and chemi-thermomechanical pulps have somewhat higher amounts of fibre fractions, with the fines content being in the range of 30% (Giertz 1973). There is a significant difference between chemical pulps (sulfite and sulfate) and mechanical pulps (TMP and CTMP) both in terms of the manufacturing processes and the yield (the yield for chemical pulp is about 45-50% and that for mechanical pulp is about 90-95%). Figure 4 shows the structural and morphological appearance of the fibre wall of a TMP.

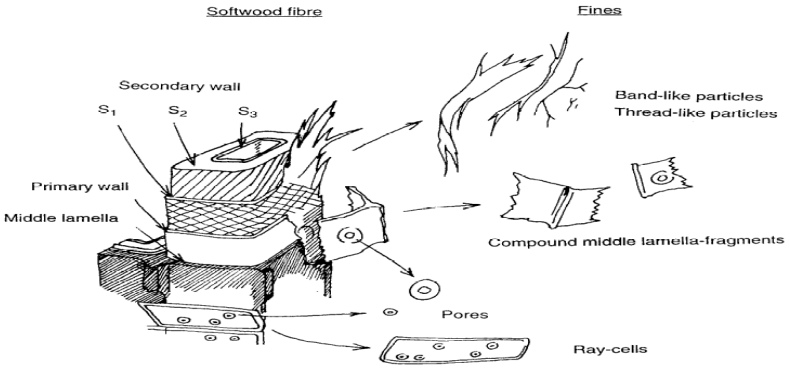

Figure 4. Structural appearance of Thermo-mechanical pulp fines (Rundlöf 2002).

Fines are known to have higher anionic groups than fibres, due to the significantly higher amounts of pectin in fines than in fibres. Fines are said to be more charged than fibres because the fines contain more fatty acid and extractive content and these extractives are also a source of carboxyl groups. It is worth noting that fines consist of a wide range of particles; 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 provide the strengthening effect. Dillen et al. (1973) also commented on the fact that the geometrical dimensions of mechanical pulp fibres (fines, fibres, fibre aggregate, fibre fragments) are vital in relation to the concept of papermaking.

1.4. Research Objectives

The chemical pulping process has been a dominant driver in the pulp and paper industry with respect to the concept of biorefinery. From an economic perspective, the production of nanocellulose from a chemical pulp is, however, quite expensive as the pulp is either enzymatically (e.g. mono-component endoglucanase) pre-treated or chemically oxidised using the TEMPO (2, 2, 6, 6 –tetramethyl-piperidine-1-oxil)-mediated oxidation method.

In mechanical pulping processes such as in TMP and CTMP, it is possible to use fractions of low quality material as alternatives for the production of nano-ligno-cellulose (NLC). The integration of a nano-ligno-cellulose production unit in mechanical pulping production has the potential to become a future means of utilizing suitable fractions of mechanical pulp, as this nano-ligno-cellulose could improve the quality level of traditional products such as paper and board grades. The intention of this research work is that, by using this concept, a knowledge base can be created so that it becomes possible to develop a low-cost production method for its implementation.

The objective presented in this work was to develop a methodology for producing mechanical pulp based nano-ligno-cellulose from fines fractions and to optimize the usage of NLC in order to improve the strength properties of paper and board products. However, to produce nano-ligno-cellulose from mechanical pulp feedstock and to characterize its particle-size distribution in a broader mapping from the evolutionary development of this unique product has been always a challenging task. Another sub-aim of the research is to contribute to the knowledge associated with mechanical pulp based nano-ligno-cellulose by supporting the development of new production method and/or the improvement of current state-of-the-art method for particle-size characterisation.

1.5. Research Hypothesis

The main hypothesis of this work was that we can utilize the softening and swelling properties of lignin and hemicellulose to enhance delamination of fibrils during homogenisation of mechanical pulps. And the technical idea was to produce nano-ligno-cellulose from a mechanical pulp fine fraction by means of homogenisation and also to utilize the produced NLC as strength additive in paper-making process.

1.6. Thesis Outline

The outline of this thesis is divided into following chapters: chapter 1 provides a brief introduction to the study, motivation, background, mechanical pulping, research objectives and, research hypothesis. Chapter 2 describes the literature review related to microfibrillated cellulose (MFC), types of MFC, mechanical treatment of pulp (homogeniser, microfluidizer, micro-grinder, cryo-crushing and super grinder), pre-treatment strategies (enzymatic and chemical (TEMPO-radical)), and microscopical analyses (TEM and AFM) of MFC. Chapter 3 presents the material and methods. Chapter 4 highlights the main results achieved during the work, as well as an interpretation and discussions of the results obtained in the work. Finally, a conclusion is presented in Chapter 5. Chapter 6 and 7 represent future work and references, respectively.

2. LITERATURE REVIEW

A survey of literature is given in order to gain an understanding of what has occurred within the field of forest nanotechnology for renewable biomaterials.

2.1. Microfibrillated Cellulose (MFC)/Nanocellulose (NC)

There are three kinds of nanocellulose namely, microfibrillated cellulose (MFC), nanocrystalline cellulose (NCC) and bacteria 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, with very little being mentioned with regards to NCC and BNC. The IUPAC definition of nanoparticles or nanomaterials refer to it as any shape with dimensions in the 1×10^{-9} to 1×10^{-7} m (1-100 nm) range (http://en.wikipedia.org/wiki/Nanoparticle).

Over the years, several articles have been written concerning microfibrillated cellulose (MFC) (Turbak et al. 1983, Herrick et al. 1983, Andresen et al. 2006, Henriksson et al. 2007, Pääkkö et al. 2007, Eichhorn et al. 2010, Spence et al. 2010a, Spence et al. 2010b) and nanocrystalline cellulose (NCC) (Rånby 1949, Ranby and Ribi 1950, Rånby 1951, Revol et al. 1994, Gray 1994, Xue et al. 1996, Fleming et al. 2001), with the former type being referred to as "spaghetti-like" structure, while the latter is referred to as "rice-like" structure.

There have been an increasing number of publications (both patents and articles) in the research field of nanotechnology for renewable biomaterials, as seen in Figure 6 and Figure 7. This assertion is also clearly seen in Table 1 where the most cited patents publications are listed. It can be clearly seen in Figure 5 and Figure 6 that the number of published articles and patents increased from 1981 -2013, with 2011 being the peak for patent publication and 2012 the peak for article publication. The publication numbers are patents related to microfibrillated cellulose (MFC) (US4341807A, US4374702A, US4378381A, US4452722A, US4452721A, US4464287A, US4481077A, US4481076A, US4483743A, US4487634A, US4500546A, JP56100801A, and EP120471A2).

Table 1. 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 Anita N, Conner Herbert Thompson, Cowan Patrick Joseph, Gelman Robert Alan, Lusvardi Kate Marritt, Thompson Samuel Anthony, Tise Frank Peine	2000	33

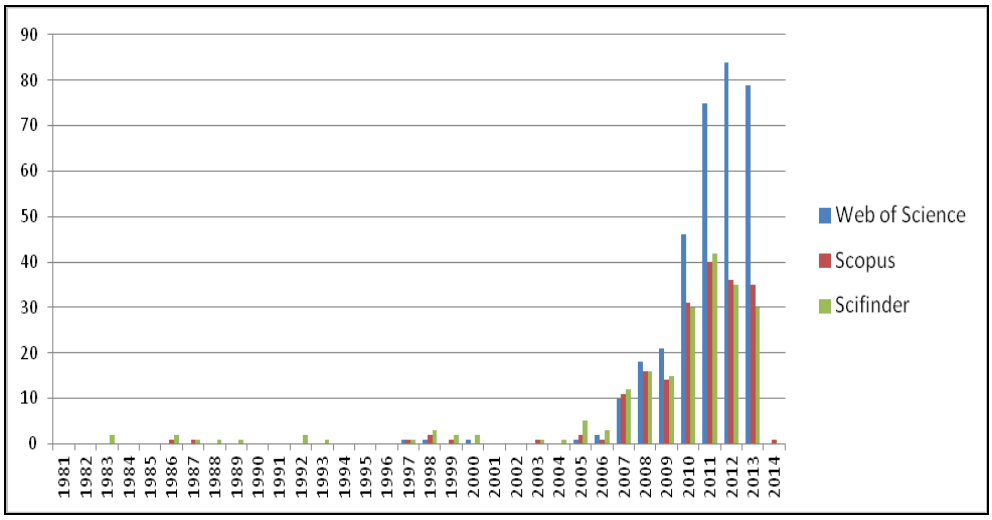

Figure 5. Number of journal articles of MFC as a function of publication year, using three databases for the search: Web of science (WoS), Scopus and Scifinder.

Figure 5: ***Web of Science Search***: "microfibrillated cellulose" in Topic Refine: document types: Article; Review Date: 2013-11-26 ***Scopus Search***: "microfibrillated cellulose" in Title-Abstract-Keywords Refine: document type: Article; Review Date: 2013-11-26, ***Scifinder Search***: microfibrillated cellulose as entered Refine: document type: include: (journal search date: 2013-11-26).

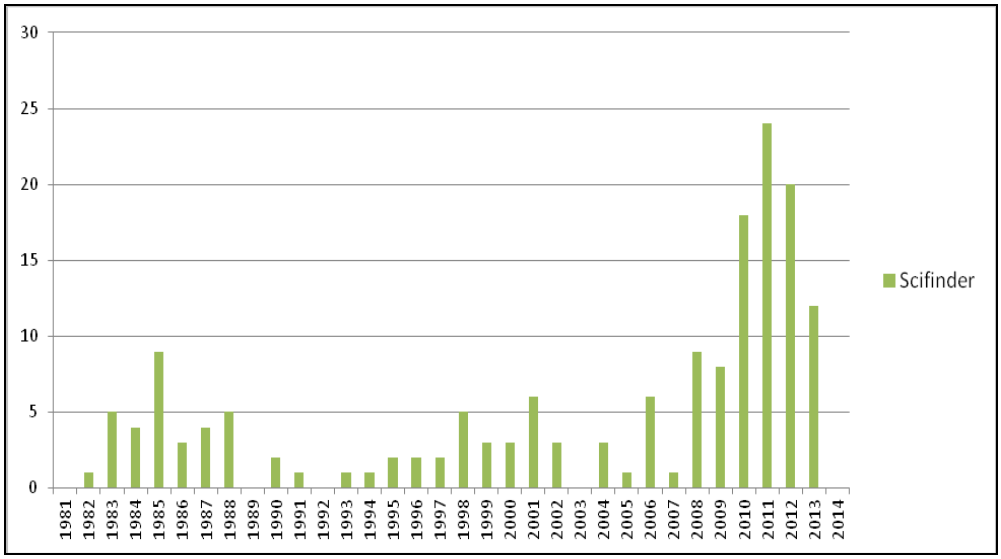

Figure 6. Number of patents of MFC with respect to publication year, using the Scifinder database (journal search date: 2013-11-25).

Figure 7 shows a comparative data of number of published journal articles (y-axis) and number of published patents as a function of publication year (x-axis) using Scifinder database. It is seen from the Figure that the number of patents published from 1982-2002 surpasses the number of articles published in the same time frame but as from the year 2007 the number of published articles increases significantly (Figure 7). Figure 8 presents the number of production patents and non-production patents as a function of publication year using Scifinder search.

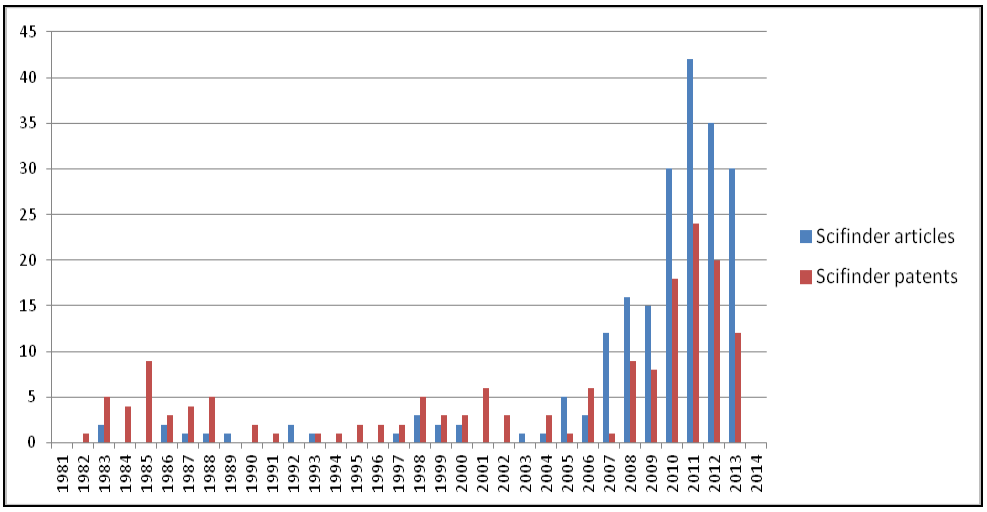

Figure 7. Number of published journal articles of MFC and number of published patents as a function of publication year (journal search date: 2013-11-25).

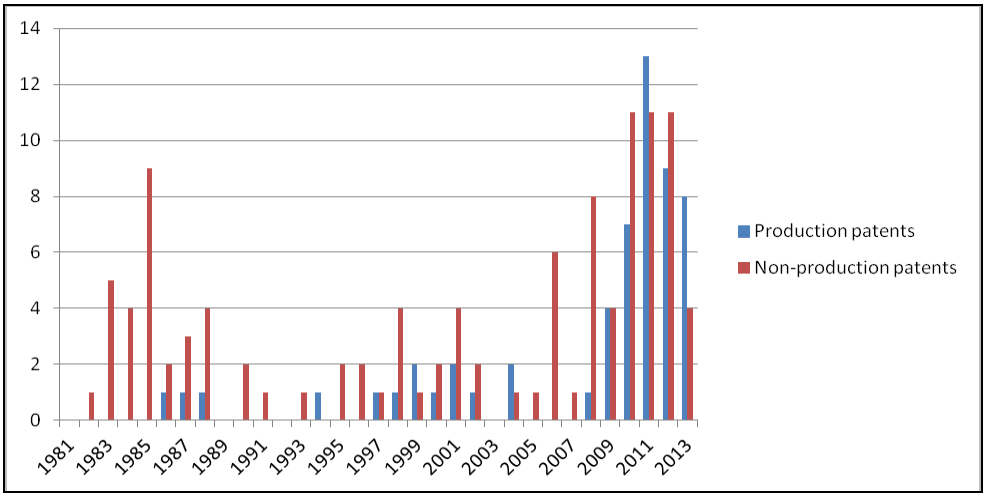

Figure 8. Number of production patents and non-production patents of MFC as a function of publication year (journal search date: 2013-11-25).

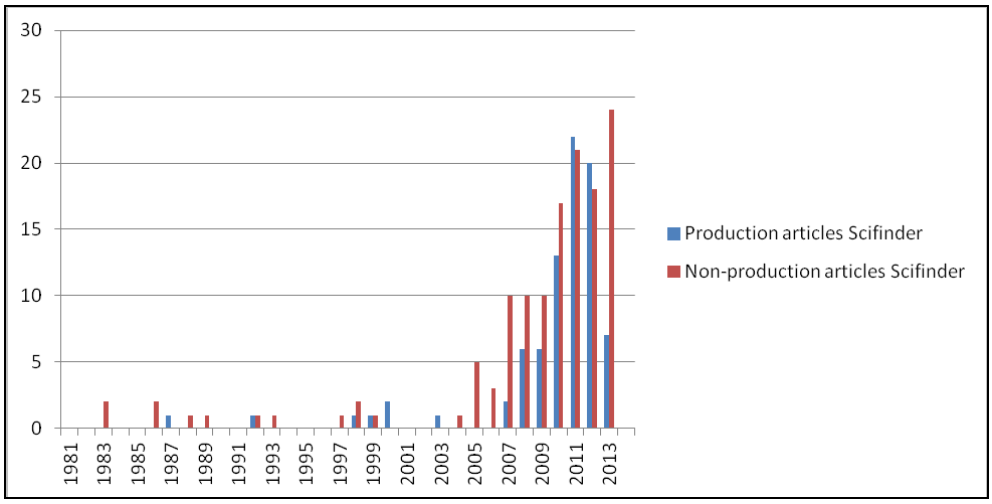

Figure 9. Number of production articles and non-production articles of MFC as a function of publication year, using the Scifinder database (2013-11-25).

Figure 9 is a **Scifinder Search**: "microfibrillated cellulose" as entered Refine: document type: include: journal production articles: Categorize: category heading: technology: category: processes & apparatus: select all non-production articles: All "microfibrillated cellulose" articles minus production patents Date: 2013-11-25.

The production concept of nanocellulose or microfibrillated cellulose began in the late 1970s by researchers working at ITT Rayonier Eastern Research Division Laboratory in Whippany, New Jersey, 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. Until this point, there had been no specific nomenclature of this type of nano-biomaterial produced by high shear forces in a high pressure homogeniser. Several schools of thought have referred to microfibrillated cellulose or nanocellulose as: microfibrillated cellulose, nanocellulose, microfibrillar cellulose, microfibrillized cellulose, nanofibrillated cellulose, nanofibrillar cellulose, nanoscale fibrillar cellulose and cellulosic fibrillar fines (Hubbe et al. 2008, Siro and Plackett 2010, Siqueira et al. 2010, Eichhorn et al. 2010, Klemm et al. 2011, Moon et al. 2011, Charreau et al. 2013).

For almost thirty years, several approaches have been used to extract fibrils using chemical (or enzymatic) pre-treatment methods combined with mechanical disintegration (Zimmermann et al. 2006, Saito et al. 2007, Henriksson et al. 2007, Stelte and Sanadi, 2009, Klemm et al. 2011). MFC is regarded as a newly engineered material obtained from woods, crops and bacteria. The term

microfibrillated cellulose means engineered materials with a diameter less than 100 nm. The material is gel-like in appearance at very low concentrations (Turbak et al. 1983, Klemm et al. 2011), and also has an extremely high surface area and high aspect ratio (Ishii et al. 2011, Andresen et al. 2006, Stenstad et al. 2008). Some of the special properties of wood based nanocellulose include: ***renewability, high strength and stiffness, low density, biodegradability, low thermal expansion and high aspect ratio*** (Charreau et al. 2013). It was suggested, in the early 1980s, that microfibrillated cellulose (MFC) could be used in food, emulsion, cosmetics, medical, pharmaceutical, as thickeners in paint formulations (Turbak et al. 1983, *US4341807A, US4659388A*). The interest in this case, is to utilize MFC in paper and paperboard applications, specifically as a strength enhancing agent for mechanical pulp fibres (TMP and CTMP).

Although many have attempted to extract fibre-based materials in recent times, insufficient knowledge exists regarding how to effectively produce uniform MFC without there being inhomogeneous fibre composition, such as fibrillar fines, fibre fragments, fibres and microfibrils. Pääkkö et al. (2007) used an enzymatic pre-treatment method combined with mechanical homogenisation to produce MFC. A more efficient and promising method applied to extract fibrils from fibres is the 2, 2, 6, 6-tetra methyl piperidinyl-1-oxy (TEMPO) -mediated oxidation method, as described by Saito et al. (2006, 2007).

Some pilot plant facilities for MFC/NCC production has been taken from the literature of Williamson (2012), the forest-based industry in Finland UPM in November 2011 claimed to be starting pre-commercial production of MFC at a Pilot plant in Espoo, Finland. Stora Enso also started a MFC pre-commercial plant that will deal with customer-driven innovation and product concepts. Borregaard is also known as a dealer with MFC. Rettenmaier, a company in Germany produces NCC as inert filler for pharmaceuticals (Williamson 2012).

Daicel in Japan works with nanocellulose product known as the Nano Celish product (trademarked name). The first NCC pilot plant was constructed by CelluForce, and was inaugurated in early 2012 in Windsor, Quebec. There is another pilot facility created through a collaboration of the Alberta and Canadian federal government in partnership with the industry, in Edmonton, Canada, that will produce NCC. In the summer of 2012, the U.S. Forest Service Forest Product Laboratory opened an NCC Pilot Plant in Madison, Wisconsin, USA. Presently, in the University of Maine, the Forest Bioproduct Research Institute has a pilot plant facility for cellulose nano-fibril (CNF) in Orono, Maine, USA (Williamson 2012). More details of World pilot scale facilities with respect to methods of production and production amount could be read from the literature of Bras et al. (2013).

2.2. Types of microfibrillated Cellulose or Nanocellulose

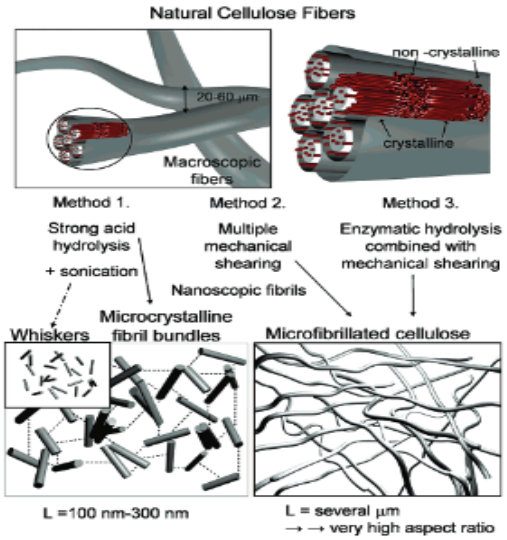

Figure 10. Schematic representation of the major classes of nanocellulose (Courtesy of Pääkkö et al. 2007).

There are basically two major families of nanocellulose, the "spaghetti-like" structure, referred to microfibrillated cellulose (MFC) and the "rice-like" structure, referred to as nanocrystalline cellulose (NCC), see Figure 10. The birth of nano-crystalline-cellulose (NCC) occurred in Uppsala, Sweden. This work was pioneered by Rånby in the late 1940s. He produced NCC by using sulphuric acid hydrolysis of wood and cotton cellulose (Ranby 1949, Ranby and Ribi 1950, Ranby 1951). Rånby's group called the product cellulose micelles, which is nowadays referred to as NCC. The NCC project was later abandoned, and in the 1970s Professor Derek Gray's group at McGill University in Canada started working on NCC. Some other important publications of NCC include Gray (1994) and Revol et al. (1994). "The Marcus Wallenberg Prize (2013) was awarded to Professor Derek Gray, McGill University, Canada, for his contributions to the path breaking research on nanocrystalline cellulose (NCC), its fundamental properties and applications. The fundamental discoveries, related to the chiral nematic behaviour of NCC suspensions, create potential for new wood and other lignocellulosic products for unique value added applications" (http://mwp.org/).

As is the case for microfibrillated cellulose, the term nanocrystalline cellulose (NCC) has also been associated with a number of names such as: cellulose nanocrystals, cellulose whickers, monocrystals, microcrystals, microcrystals crystallites, microcrystallites, nanowhiskers, nanocrystals, nanorods, rod-like cellulose microcrystals, rod-like cellulose crystals and nanowires (Azizi et al. 2005,

Hubbe et al. 2008, Siro and Plackett 2010, Siqueira et al. 2010, Eichhorn et al. 2010, Habibi et al. 2010, Klemm et al. 2011, Moon et al. 2011, Charreau et al. 2013).

The development of MFC started in the late 1970s, in which pulp fibres were mechanically treated in a high-pressure homogeniser to produce thread-like particles, referred to as microfibrillated cellulose or nanocellulose and this work was initiated by Turbak and co-workers at ITT Rayonier. Their research group stated that MFC could be used in several applications, such salad dressing, thickeners, rheological modifiers and food dessert sauces. Today, pulp fibres are usually pre-treated (chemical/ enzymatic or combine) in such a way as to reduce the number of homogenisation passes and also to enhance fibrillation.

The number of publications related to microfibrillated cellulose in relation to the various countries involved is shown in Figure 11, with the United States and Sweden being at the top with a total of 177 publications each.

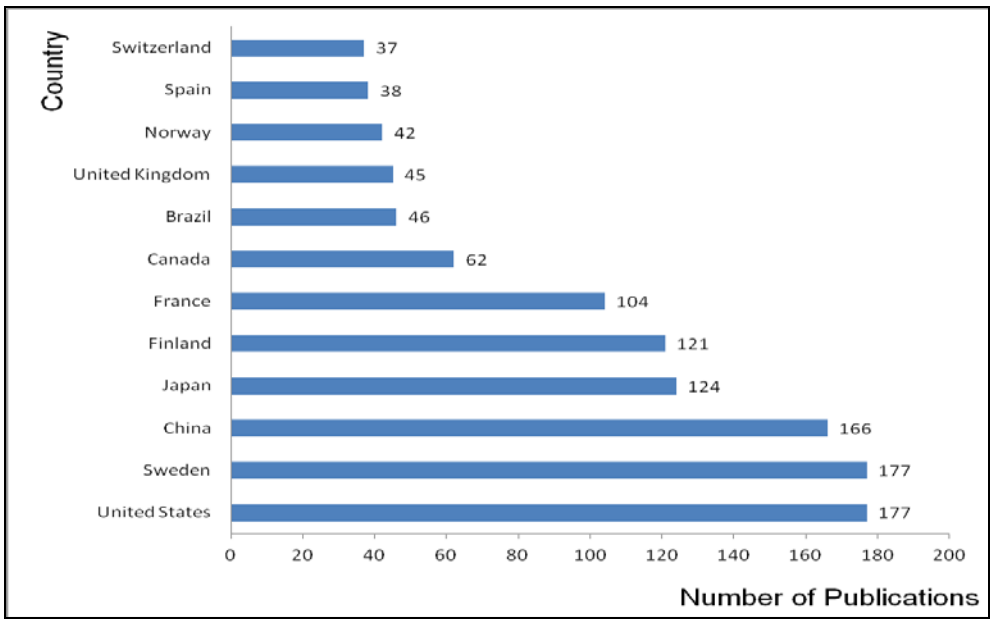

Figure 11. Country in relation to number of publications related to microfibrillated cellulose (adopted from Scopus database, July 2, 2013 at 15:00 local time)

The main advantage of using chemical pulp as opposed to mechanical pulp is the referral to the degree of purity of the cellulose moiety in chemical pulp, whereas in mechanical pulp the fibres are composed mainly of cellulose, lignin and hemicellulose, thus making processability difficult during fibril extraction. The Japanese method (TEMPO-mediated oxidation process) invented by Saito and co-

workers (2006) is known to be an excellent method of obtaining well fibrillated and individualized fibrils with a high aspect ratio (Ishii et al 2011) and a high specific surface area (Sehaqui et al 2011).

2.3. Mechanical Treatment of pulp fibres to MFC

The disintegration of pulp slurries into thread-like materials were first examined by Turbak et al. (1983) and Herrick et al. (1983) using a high pressure homogeniser. Today, several new equipment/techniques have been used to produce this material. Some of the novel physical/mechanical techniques used nowadays include: high pressure homogenisation, micro-fluidization, super-grinding, micro-grinding, cryo-crushing and high-intensity ultrasonification. High pressure homogeniser and micro-fluidizer are the mostly used equipments in extracting microfibrillated cellulose from pulp fibres (Ankerfors 2012).

2.3.1. Homogeniser

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

The production route for the microfibrillated cellulose or nanocellulose is based on the passage of pulp slurries into mechanical equipment such as a high pressure homogeniser, with, for the majority; chemical or enzymatic pre-treatment being performed in such a way so as to; lower energy consumption, improve fibrillation and also avoid 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 regarding the formation of well fibrillated fibrils. This is because of the cellulose/hemicellulose/lignin interaction, as the lignin in the pulp acts as a gluing substance in relation to cellulose, thus preventing the cellulose molecule from complete individualization, thereby forming fibril bundles due to the presence of lignin (Osong et al. 2013). Figure 12 shows the homogenising equipment (first) at Mid Sweden University, and the second sketch in the Figure 12 is the schematic representation of the mechanical treatment process.

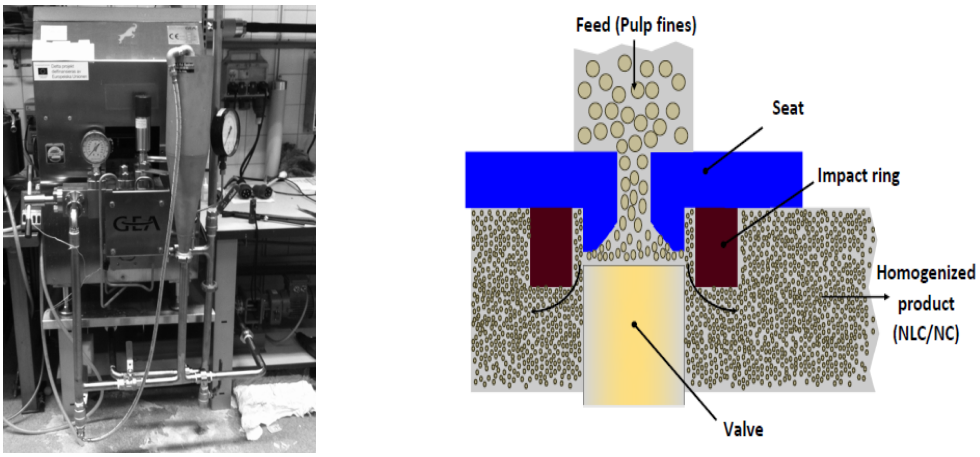

Figure 12. Picture (left) and schematic diagram (right) of pulp fibres homogenisation action (illustration courtesy of Majid Alimadadi for the right diagram).

Factors that favour the disintegration of fibres into fibrils in a homogeniser include: chemical (or enzymatic) pre-treatment, high pressure drop within the valve seat and multiple numbers of 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 12. The suspension of cellulose microfibrils undergoes the process of high pressure treatment in order to reduce the size of the fibres so as to obtain a stable suspension. The valve seats in the homogeniser experience an increase in temperature over time during the operation; the homogeniser works in a convenient manner at elevated temperatures (0-140^{o}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 an extensive pressure drop. The major problem that has hindered the commercialization of nanocellulose is the huge amount regarding the energy consumption, and the issue of clogging during the operation (Herrick et al. 1983, Turbak et al. 1983, Ankerfors 2012). The clogging tendency of the fibres blocks the flow of the fibre suspension and renders the production process unstable, and, hence, the whole assembly requires dismantling. As the number of passes of the pulp slurry through the homogeniser increases, so the amount of energy also increases.

2.3.2. Micro-fluidizer and Micro-grinder

The micro- fluidizer operates at a constant shear rate whilst the high pressure homogeniser functions at a constant processing volume, but, 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 microfluidizer method in relation to producing MFC. The mechanical instrument in Figure 13 has a flow rate of 350 ml/min, and, the first stage homogenising pressure is 100 bars, with the chamber slit of 400 μm and the second stage homogenising pressure is 1500 bars, with the chamber slit of 200 μm.

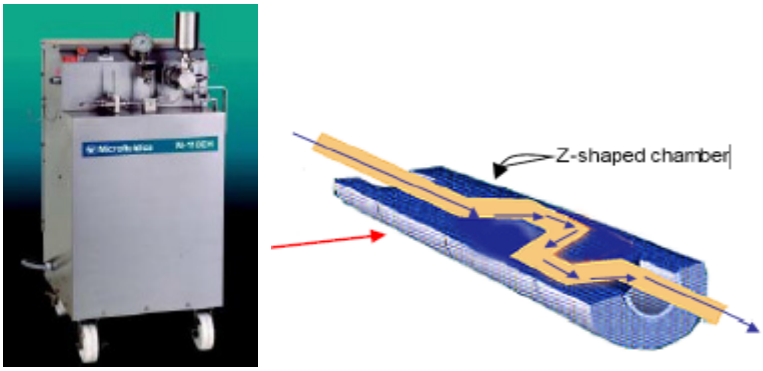

Figure 13. Microfluidizer equipment.

2.3.3. Cryo-crushing and super-grinder

Cryo-crushing means placing refined cellulose fibres under liquid nitrogen to freeze the water content in the fibres, and subsequently exert high impact grinding on the frozen fibre/nitrogen mixture (Chakraborty et al. 2005). Microfibrillated cellulose produced by a super-grinder has been elucidated on Taniguchi and Okamura (1998). Figure 14 represents Laboratory Scale Supermass Colloider Equipment.

Figure 14. Laboratory Scale Supermass Colloider Equipment MKCA 6-2 Masuko Sangyo Ltd.

2.4. Pre-treatment strategies

Production techniques of microfibrillated cellulose have been elucidated in recent times (Herrick et al. 1983, Turbak et al. 1983, Taniguchi and Okamura 1998, Chakraborty et al. 2005, Saito et al. 2006, Saito et al. 2007 , Henriksson et al. 2007, Pääkkö et al. 2007). By taking into account the huge amount of energy consumption during MFC production, scientists have instituted pre-treatment methods such as physical, chemical or enzymatic (Saito et al. 2006, Pääkkö et al. 2008) to curtail the energy consumption.

Ankerfors (2012) confirmed that the major drawback to a successful commercialization of microfibrillated cellulose was the high energy consumption, and, by carefully pre-treating the fibres, this problem can be resolved. In addition to the energy consumption, homogenisation without pre-treatment may produce non-homogeneous fibre mixtures containing microfibrils, fibril fragments and poorly fibrillated fibres. To produce nanocellulose efficiently, pulp fibres are usually mechanical pre-refined (valley beater, PFI milling or refining) in order to enable the correct treatment in the homogeniser as well as avoiding fibre clogging. This idea was supported by Herrick et al. long time ago (1983) and, they attested that by cutting fibres into reduced sizes eases the fibre disintegration. In view of the 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. Pre-treatment strategies have been developed to prevent the challenge associated with fibre clogging during homogenisation and as well to curtail the energy consumption. Extensive pulp pre-treatment studies have been performed by several research groups using either the enzyme-assisted method or the chemical (TEMPO-mediated oxidation) method.

The pioneers in the TEMPO method were Saito and co-workers. They used this method to introduce charged carboxylate groups into the cellulose material, in such a way as to enhance fibrillation (Saito et al. 2006). This method is understood to induce repulsion between the fibres and thereby facilitate fibre disintegration during mechanical treatment in the homogeniser. Figure 15 shows the increasing trend of both enzymatic and chemical pre-treatment methods from 2008. It appears that the chemical oxidative pre-treatment method tends to have a great number of publications than is the case for the enzymatic method.

2.4.1. Enzymatic pre-treatment

Enzymatic pre-treatment of wood pulp using endoglucanase has been studied with the aim of facilitating fibre treatment in the homogeniser or microfluidizer. Detailed knowledge regarding how to manufacture microfibrillated cellulose using chemical pulp combined with enzyme treatment is available in the paper

Henriksson et al. (2008). Henriksson et al. (2008) reported that the treatment of fibres with the enzyme endoglucanase enhances fibrillation and prevents the fibres from clogging in the homogeniser. Pääkkö et al. (2007) also pre-treated the fibre wall of the wood pulp with enzymes and observed that the enzymes assisted with the process of pulp disintegration.

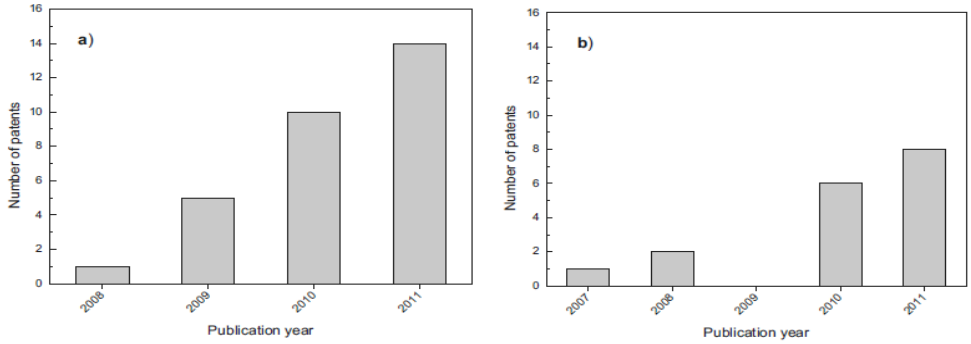

Figure 15. Number of publications of MFC with respect to both Chemical (a) TEMPO: 2, 2, 6, 6 –tetramethyl-piperidine-1-oxil and (b) Enzymatic pre-treatment strategies. (Courtesy of Charreau et al. 2013).

2.4.2. Chemical pre-treatment (TEMPO- mediated oxidation)

According to Saito et al. (2006a, 2006b) and Saito and Isogai (2006) the TEMPO (2, 2, 6, 6 –tetramethyl-piperidine-1-oxil)-mediated oxidation pre-treatment 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 and with very small fibre fragments. The TEMPO-method is known for its high aspect ratio and large surface area.

The only disadvantage associated with the TEMPO method is in relation to the toxicity of the TEMPO-radicals, i.e. sodium bromide (NaBr) and sodium hypochlorite (NaClO). Saito et al. (2007) suggested that the pre-treatment assisted in loosening the adhesion between the fibrils by preventing the formation of strong interfibrillar hydrogen bonds. The mechanism regarding the TEMPO-mediated oxidation of cellulose is explained in Bragd et al. (2004). Figure 16 shows the reaction pathway of the TEMPO-method, and, as reported by Saito et al. (2007), the oxidation system associated with the TEMPO- radical, functions as an oxidizing agent and turns the primary alcohols into aldehyde and carboxyl groups. The TEMPO-system oxidation of cellulose occurs with regards to the hydroxyl group binding to carbon number six (C-6) in the glucose unit.

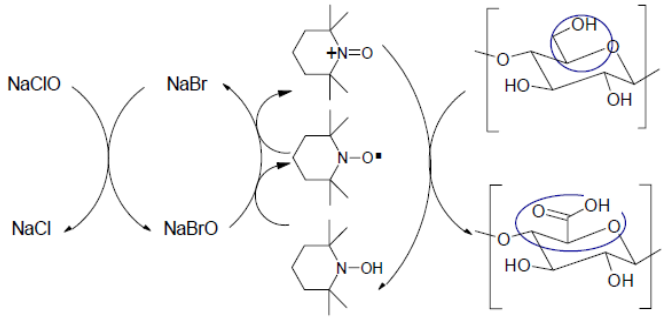

Figure 16. Schematic representation of the TEMPO-mediated oxidation method – reaction mechanism.

2.5. Microscopical Techniques

Several scholars have used microscopy techniques such as TEM and AFM to analyze the nanofibrils produced from pulp fibres. In this section, the TEM image is taken from Klemm et al. (2011) and AFM height and phase image is taken from Pääkkö et al. (2007), see Figures 17 and 18.

2.5.1. Transmission electron microscopy (TEM)

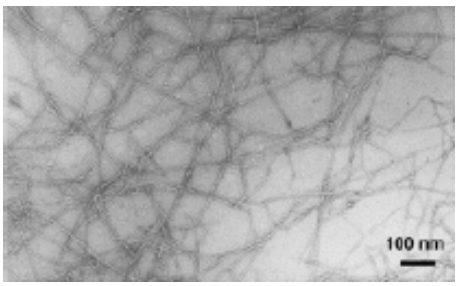

Figure 17. TEM Image of nanocellulose (Klemm et al 2011).

2.5.2. Atomic Force Microscopy (AFM)

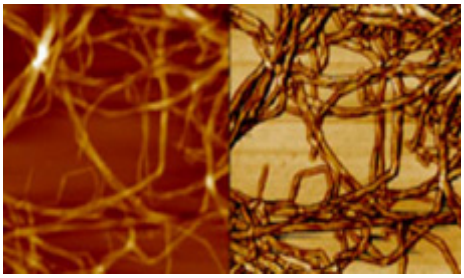

Figure 18. AFM micrograph of nanocellulose (Pääkkö et al. 2007).

3. MATERIALS AND METHODS

The key methodologies for this research were as follows:

- Fractionation techniques (Bauer McNett Classification and Britt Dynamic Drainage Jar) were implemented prior to homogenisation in order to obtain tiny fibre particles that can be easily treated in the homogeniser.

- Homogeniser process temperature was adjustable; the main idea was to use an elevated temperature of up to approximately 140^{o}C in the homogenising equipment so as to affect the lignin softening.

- *The use of chemicals to affect the softening and swelling properties of the pulp fibres; using conventional chemicals such as sodium sulphite, sodium hydroxide and hydrogen peroxide to develop an easy to implement concept.*

- *To improve the energy efficiency during homogenisation to the corresponding quality levels of the final product.*

The last two concepts are still to be investigated, and are thus written in *italic form*. This forms part of the ongoing work, which is not reported in this thesis.

3.1. Pulps

Thermo-mechanical pulp (TMP) – (Paper I, II) **:** The TMP sample used in this investigation was of Canadian Standard Freeness (CSF) value of about 65 ml and with a dry solid content of 34%, which 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) - (Paper II, 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 Canadian Standard Freeness (CSF) of about 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 paper).

Bleached Kraft Pulp (BKP) - (Paper I, III): The BKP pulp used in this work was collected from the SCA Östrand pulp mill, Sundsvall, Sweden. It is of Canadian Standard Freeness (CSF) of about 630 ml and is 100% softwood and a mix of 24% spruce (Picea abies) and 76% pine (Pinus sylvestris), with a mixture of round wood chips (55%) and saw mill chips (45%) that contained a great deal of sapwood,

which is rich in long stiff fibres. The BKP was also used both as the fibre material in the laboratory handsheets and to make NC (nanocellulose produced from BKP is referred to NC in this work).

3.2. Homogeniser (paper I, II, III)

A GEA Niro high pressure homogeniser was employed to treat the fine particles to smaller particles which would be referred to as nano-ligno-cellulose in this thesis. Pulp fractionation was performed in such a way so that the fibres were separated into a particular fraction (fines and longer fibres); this will eventually provide the correct fines fraction for mechanical treatment in the homogenising equipment. The pulp slurries were treated in the homogenising equipment at approximately 1% consistency.

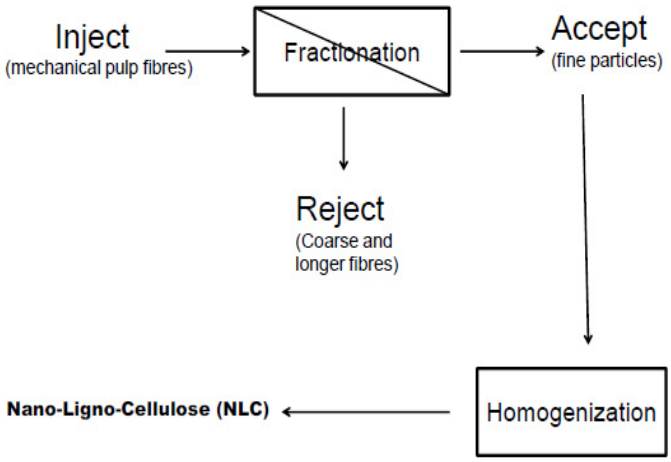

Figure 19. Schematic approach to produce nano-ligno-cellulose

The homogenisation pressure was usually set within the 200-300 bars range, but it was sometimes difficult to maintain a constant pressure due to the clogging of the fine particles in the homogenising system. An average of approximately 5 litres of pulp suspension was used almost in the majority 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 is 1.4 l/min with an estimated 18 passes per trial.

The homogenising equipment has a maximum working pressure of 600 bars; and the pressure is detected by means of the small manometer on the compression head of the machine. Figure 19 shows a schematic view of our approach to producing nano-ligno-cellulose from mechanical pulp fine materials. A Britt Dynamic Drainage Jar 30-mesh screen and a Bauer McNett Classifier were used as the fractionation equipments. Fractionation was achieved using BMcN and BDDJ; particles that passed the fractionation equipment are referred to as fines while those retained on the mesh wire are regarded as coarse and longer fibres. The fines are used as feed material in the homogenising equipment to produce nano-ligno-cellulose.

3.3. Pulp Fractionation

Two fractionation techniques were implemented: the Bauer McNett classification and the Britt Dynamic Drainage Jar fractionation.

3.3.1. Bauer McNett classifier (BMcN) (Paper I)

The Bauer McNett classifier (BMcN) was used in the pre-study of this work and the standard mesh screens used were: 16, 30, 50, 100, and 200. And the pulp fractions obtained were: R16 (i.e. retained fibre fraction of a 16 mesh wire), P16/R30 (i.e. fibres that passed through the 16 mesh screen and were retained on the 30 mesh), P30/R50, P50/R100, and P100/R200. The fractionation was performed according to SCAN-CM 66:05 Standard and the sieve sizes of the wire screens are presented in Table 2. The reason for the fibre fractionation is to obtain short and tiny fibres that could be easily homogenized in the machine. Figure 20 shows a picture of the BMcN classifier.

Figure 20. Bauer McNett Classifier

Table 2. Bauer McNett Classifier sieve size

Approximate Sieve size (μm)	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 (Paper I, II, III)

The fine fractions were obtained from the pulp samples by means of the BDDJ fractionation technique. The fractions passing through the 30 mesh screen were considered as "fines" and used for mechanical treatment in the homogeniser while the retained fractions on the 30 mesh wire are discarded. In this thesis, the pulps were fractionated using a specially designed BDDJ (see Figure 21) at the SCA Research Centre in Sundsvall, Sweden. The cut-off or pore size of the BDDJ 30mesh screen was approximately 600 μm.

Figure 21. Diagram of a specially-designed Britt Dynamic Drainage Jar at the SCA Research Centre in Sundsvall, Sweden (used in this study).

3.4. FibreLab Analyzer (Paper I)

An optical instrument, FibreLab, was used to characterize the fibre length distributions of the various fractions of the BMcN and BDDJ devices. The FibreLab

investigation showed that the BDDJ-30 wire mesh provided a fibre fraction with an average fibre length, which was shorter than 1.2mm, while the fractions for the ≥ 30 mesh were much longer, and these were discarded. One of the limitations of FibreLab is with regards to not being able to accurately measure very tiny fibrils, due to its lower resolution; part of the instrument can be seen in Figure 22.

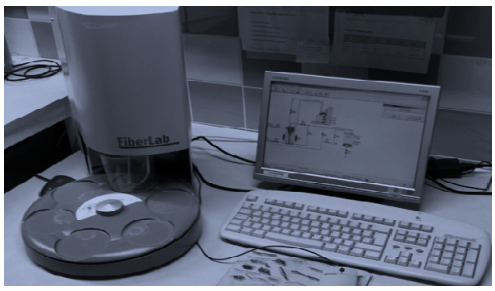

Figure 22. FibreLab Analyzer

3.5. Microscopical techniques

Three microscopical techniques were used in this thesis namely, Light microscopy, AFM and SEM.

3.5.1. Light Microscopy

The micrographs of TMP, CTMP and BKP fines were recorded on a Leica DMRX Research Microscope using Differential Interference Contrast Technique (DIC).
The samples were diluted to very low concentrations and placed on a mica substrate for imaging.

3.5.2. Atomic Force Microscopy (AFM) (Paper I)

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

3.5.3. Scanning Electron Microscopy (SEM) (Paper I)

SEM micrographs were taken using a ZEISS EVO50 equipped with a Backscattered Electrons (BSE) detector. The working conditions were as follows: acceleration

voltage was 15 kV; pressure in the sample chamber was 0.7 mbar and working distance approximately 10 mm. Au/Pd (Gold/Palladium) coating was used for the analyzed samples. Sample preparation was performed as explained in the light microscopy section.

3.6. Rheological Property (Paper I)

The rheological properties of the NLC suspensions were characterised on a Physica MCR-300 (Physica Messtechnik GmbH, Stuttgart, Germany) with a concentric-cylinder (CC27) rheometer series adapted to a US 200 software. The concentric cylinder (CC27) has a diameter of 26.67 mm and a concentricity of 1 μm. The flow curves of the TMP-NLC were determined using the following concentration: 0.66%, 0.33%, and 0.165% and the samples were homogenized at temperatures of both 23 and 140^{O}C. unless otherwise stated and, all the rheological investigations were conducted at a temperature of 23^{O}C.

3.7. Crill Instrument (Paper II)

There has been a great deal of enthusiasm shown by many researchers in the nanocellulose literature in relation to working on the latest advances in characterisation techniques. More precisely, the desire is to determine a cheap, fast and robust method for evaluating a particle size distribution. Optical analyzing instruments such as Kajaani FibreLab, MorFi and FibreMaster are not able to deal with the particle size distribution in the sub-micron scale. The main purpose of the crill study has been to lay a foundation stone for the development of a rapid and robust method for a continuous online monitoring system regarding process control. The method views the interaction of fibres and crill between UV and IR, see Figure 23. Sample measurements were conducted at the Dynäs Mondi Mill in Kramfors, Sweden, and the measurements were conducted manually offline. 1g of oven dried pulp was used in all investigations. Steenberg et al. (1960) were the pioneers who started the development of this technique.

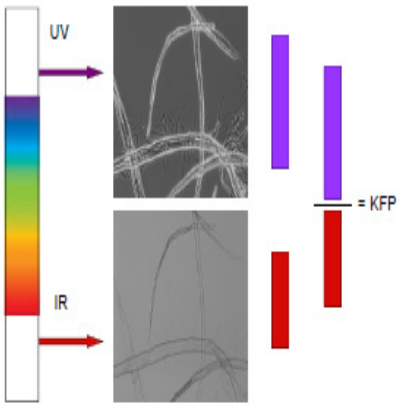

Figure 23. An illustration of the measurement principle of crill value, KFP = "crill value" (by courtesy of Innventia – Hansen and Sundvall 2012).

Hill and Eriksson (1973) were very clear in their statement concerning particle size evaluation using optical devices and their measurement approach has been based in terms of fibre width distributions. This adds to the information many have highlighted fibril dimension in terms of length and width for MFC. The most critical parameter for many is to develop a measurement technique which is able to provide a width distribution within the sub-micron or nano-scale. Hill and Eriksson (1973) provided very reproducible results that can be obtained for measuring fibre width within the 5-200 micron range and length within of 0.2-5 range mm using optical equipment.

3.8. Rapid Köthen Sheet Former (Paper III)

For the process involving the formation of a laboratory handsheet, this involved the use of a Rapid Köthen Sheet Former, see Figure 24. The laboratory sheets made had an average grammage of about 65 g/m$^{2.}$ The following physical properties were tested on the sheets: sheet density, z-strength, tensile index, tear index, burst index, E-modulus, strain at break, tensile stiffness and, air resistance were observed (Table 3, n = number of test pieces).

Figure 24. Rapid Köthen Sheet Former, the handsheets were pressed at 100kPa and dried under restrained conditions at 93^{o}C for 10 mins.

Table 3. Mechanical Properties of laboratory sheets and test methods.

Handsheet properties	**Methods**	**Name of instruments**
Density (grammage/thickness) (kg/m^3)	ISO 5270 (n=8)	Grammage – Mettler Toledo, Switzerland. Thickness – L&W Sweden
Tensile index (kNm/kg)	ISO 1924-3 (n=8)	L&W tensile strength tester, Sweden
E-modulus (GN/m^2)	ISO 1924-3 (n=8)	TH-I L&W, Sweden
Tensile energy absorption(TEA) (J/kg)	ISO 1924-3 (n=8)	TH-I L&W, Sweden
Tear index (Nm^2/kg)	ISO 5270 (n=3)	L&W tearing tester, Sweden
Porosity Bendtsen(ml/min)	SCAN P85 (n=2)	L&W air permeance tester, Sweden
Z-strength (kN/m^2)	ISO 15754 (n=5)	L&W ZD tester, Sweden
Burst index (kPam^2/g)	ISO 2758 (n=8)	L&W bursting strength tester, Sweden

4. RESULTS AND DISCUSSION

This chapter starts with; 4.1. Summary of scientific publication, 4.2. Fibre length distribution (paper I), 4.3. Microscopy (paper I), 4.4. Rheology (paper I), 4.5. Crill (paper II), 4.6. Strength properties (Paper III).

4.1. Summary of appended papers

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

Paper I : An approach to produce nano-ligno-cellulose from mechanical pulp fine materials

In Paper I, the methodology of producing nano-ligno-cellulose from mechanical pulp is studied. The aim was to produce mechanical pulp based nanocellulose (nano-ligno-cellulose) using low quality fibre fractions. Results indicate that it seems possible to mechanically treat fine particles of thermo-mechanical pulp (1% w/v) in the homogeniser in order to produce NLC. Bleached kraft pulp (BKP) fine fractions (0.5% w/v) were also tested as a reference in this study, and it was noticed that this fines (BKP) fractions were not that easy to homogenize at a higher concentration (1% w/v). A possible explanation for this could be that the BKP fines have much higher cellulose content and lower charge level compared to the fines fraction of the hemicellulose and lignin-rich TMP. Characterisation techniques such as FibreLab, light microscope, AFM, SEM and rheological properties are reported in this paper. Fibre length-weighted was noted to be a critical property in relation to both pressure fluctuations and clogging during high pressure mechanical shearing in the homogeniser.

Paper II: Crill: A novel technique to characterize nano-ligno-cellulose

In paper II, the crill method is used to evaluate the degree of fibrillation of nano-ligno-cellulose and the measurement technique is based on optical response of a suspension at two wavelengths of light; UV and IR. The UV light contains information on both fibres and crill, while IR only contains information on fibres. As the characterisation of 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. Results showed that the crill value of both TMP-NLC and CTMP-NLC correlated fairly well with the homogenisation time.

Paper III: Paper strength improvement by inclusion of nano-ligno-cellulose to CTMP

In paper III, the overall aim was to show the strengthening potential of nano-ligno-cellulose on handsheets of chemi-thermomechanical pulp (CTMP). For comparison reasons, nanocellulose (NC) from bleached kraft pulp (BKP) was produced in a similar approach as NLC. Both the NLC and the NC were blended with their respective pulp fibres and their corresponding handsheets properties were evaluated with respect to sheet density. It was found that the handsheets of pulp fibres blended with NLC/NC improved the mechanical properties of handsheets with only a slight effect in relation to the sheet density.

4.2. Fibre length distribution (paper I)

This section **(paper I)** presents the production methodology used in the work. This new concept is vital for understanding fibre fractionation techniques that were used before mechanical treatment. It was also noted in this section that during the fibre-size distribution measurements, the fibre length was one of the most critical factors that affects clogging in the system. In the BMcN classifier, the fraction with the highest amount of fines was with the 200 mesh wire. Preliminary BMcN experiments indicated that the fibre fractions from the 200 mesh were extremely good feed materials for the homogeniser. Fines materials are generally regarded as mechanical pulp fractions that have the ability to pass through the 200 mesh (76 µm) wire screen. In this project fines are also considered as pulp fractions that passed through the BDDJ-R30 mesh wire. This was the case because, after performing FibreLab, it could be clearly seen the BMcN-R200 is very similar to the BDDJ-R30 mesh screen in terms of the fibre length distribution, see Figure 25 and Figure 26.

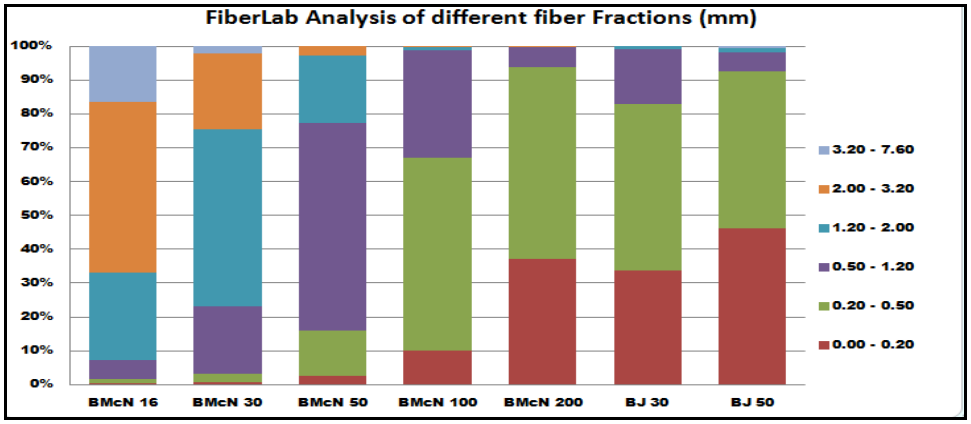

Figure 25. Fibre length distribution of both BMcN and BJ fractions (BDDJ = BJ).

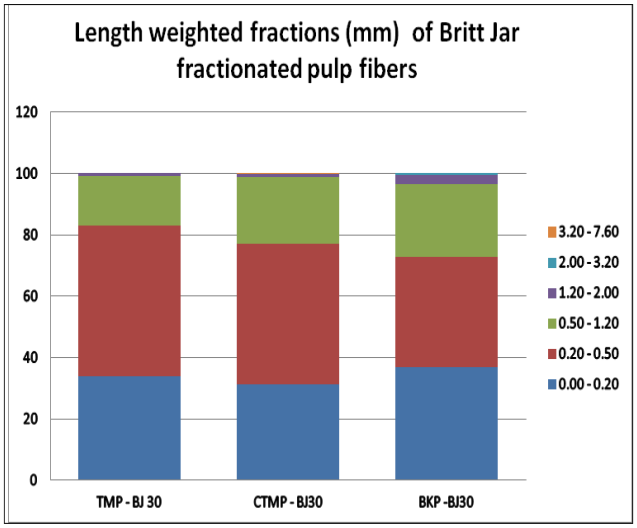

Figure 26. Fibre length distribution with respect to BJ fraction using TMP, CTMP and BKP. (BDDJ = BJ).

A positive influence of high temperature homogenisation was in order to avoid clogging and to soften the lignin and ease cellulose extraction. This production method appears to be one of the methods that misses out the pre-refining stage (PFI milling, mild refining), thereby saving energy. It has been reported that both temperature and chemical treatment affect lignin softening (Höglund, Bodin 1976).

4.3. Microscopy (paper I)

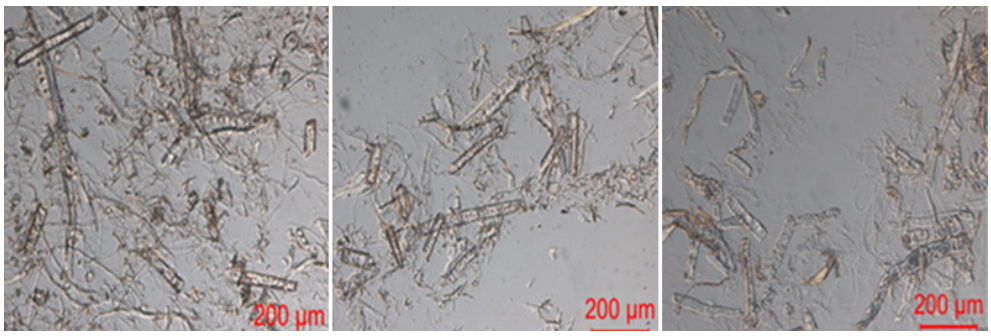

Figure 27. Light micrograph of fines fraction of TMP (1st), CTMP (2nd) and BKP (3rd) respectively.

Figure 27 shows the light microscope images of TMP fines, CTMP fines and BKP fines. The rectangular shapes represent parenchyma cells. The SEM micrographs in

Figure 28 show how the fines (1st image) have been disintegrated into tiny particles (2nd image) after homogenisation. The SEM image in Figure 28 reveals the fibril dimension before homogenisation, with fibril diameter of approximately 19 μm. The SEM micrograph also reveals the fibril dimension after homogenisation, with fibril diameter of approximately 110 nm (Fig 28).

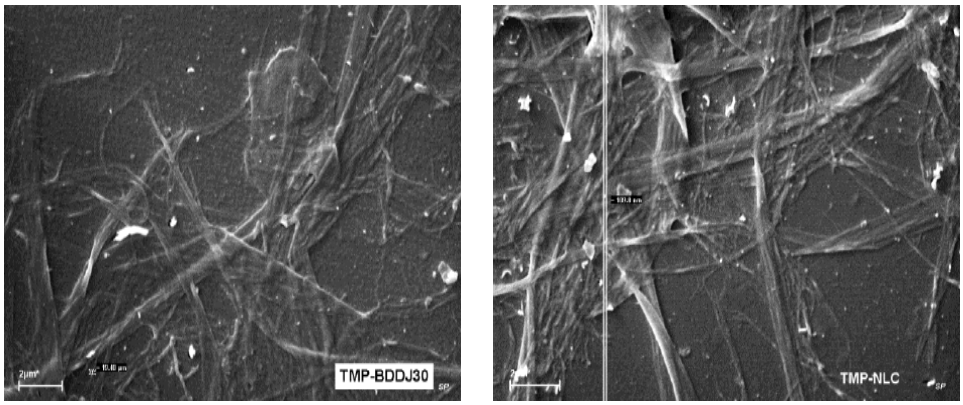

Figure 28. SEM micrograph of TMP fine (1st) and TMP-NLC (2nd)

The AFM imaging technique was performed using a super sharpen tip, and the phase and height images are presented in Figure 29. The diameter of TMP-NLC fibril as viewed on AFM is in the range of 90-150 nm. One of the difficulties faced when using thermo-mechanical pulp fines in producing nano-ligno-cellulose was that the fine particles contain a high amount of lignin, which acts as a gluing substance to the cellulose fibrils, thus preventing complete individualization of the fines into fibrils (Figure 29).

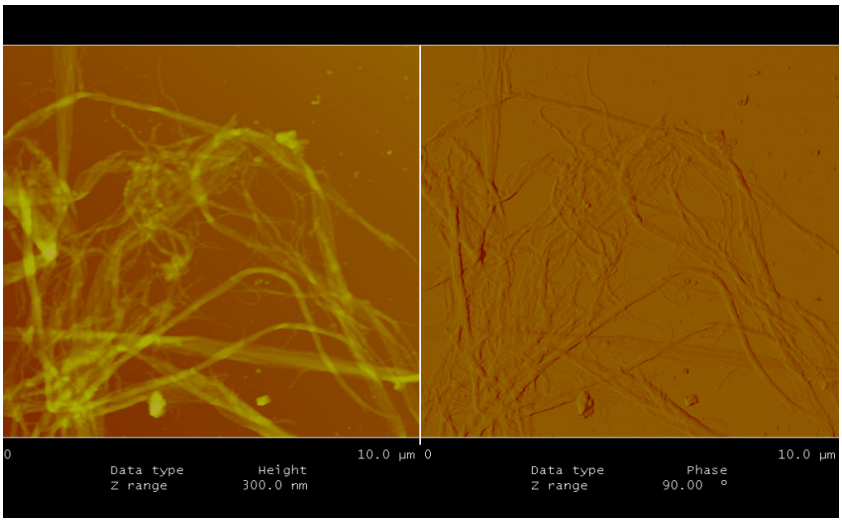

Figure 29. AFM image of TMP-based nano-ligno-cellulose (Height and Phase image)

4.4. Rheology (paper I)

The flow curve in Figure 30 shows the rheological behaviour of TMP – NLC at shear rate range between 0.1 and 100 s^{-1}. The rheological properties of TMP-NLC suspension (0.66%, 0.33%, and 0.165%) homogenized at both 23^{O}C and 140^{O}C. From the flow curve presented in Figure 30, it is seen that the shear viscosity (Pa.s) of all the suspensions decreases with an increasing shear rate (s^{-1}), thus the TMP-NLC exhibits a shear thinning behaviour at a concentration as low as 0.165%. Although homogenisation was said to be conducted both at both 23^{O}C and 140^{O}C in this section however, it was noticed that there was a significant increase in temperature from 23^{O}C to about 50^{O}C during homogenisation at room temperature. We expected high temperature homogenisation to improve the fibrillation efficiency but as can be seen in Figure 30, the shear thinning behaviour of the 140^{O}C homogenized samples did not correspond to the predicted hypothesis using rheological analysis. One explanation for the unexpected behaviour could be the variation in the increment of homogenisation pressure during treatment of pulp particles.

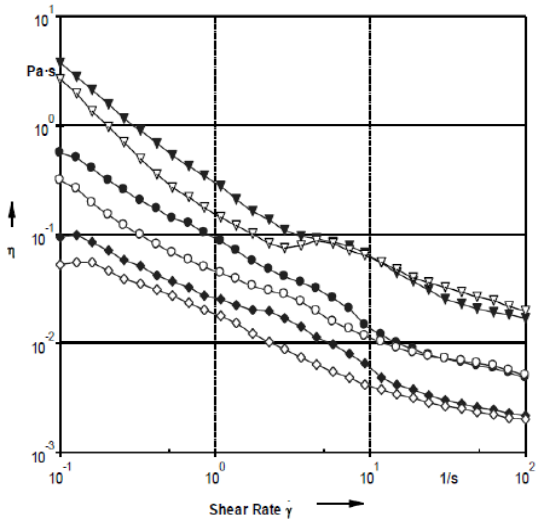

Figure 30. Rheological behaviour of nano-ligno-cellulose - (0.66% TMP-NLC at 23°C, 0.66% TMP-NLC at 140°C 0.33% TMP-NLC at 23°C, 0.33% TMP-NLC at 140°C 0.165% TMP-NLC at 23°C, 0.165% TMP-NLC at 140°C).

4.5. Crill (paper II)

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

The objective was to highlight the potential of a new particle size characterisation technique of micro/nano fibres, known as the crill. The technique provided indications of a reliable estimate with regards to analyzing a particle size distribution of micro/nano fibres. The crill method is an already established technique used at the mill-scale for measuring hairy fibres. It is a robust, fast and reliable method of assessing tiny fibrils. The crill value was plotted in relation to homogenisation time, and, it was found that the crill value correlated with the homogenisation time (Figure 31 and Figure 32). The pattern for both TMP and CTMP behave in a similar manner, both at 23 and 140°C (results for CTMP-NLC could be seen in paper II). The crill results suggested that the technique requires more development in order to be considered as a tool for process at the mill-scale.

The crill technique opens up opportunities for a range of nanocellulose, including TEMPO-oxidised nanocellulose, enzymatic processed nanocellulose, thermo-mechanical, and chemi-thermomechanical based nanocellulose to be assessed in terms of particle size distribution. However, since the technique is still in the development stage, the method can only characterize fibrils in the submicron scale, i.e. a particle 1000 times smaller than fibres. As shown in Figure 32 high temperature homogenisation did not show any significant difference in crill development for spruce thermo-mechanical pulp (TMP).

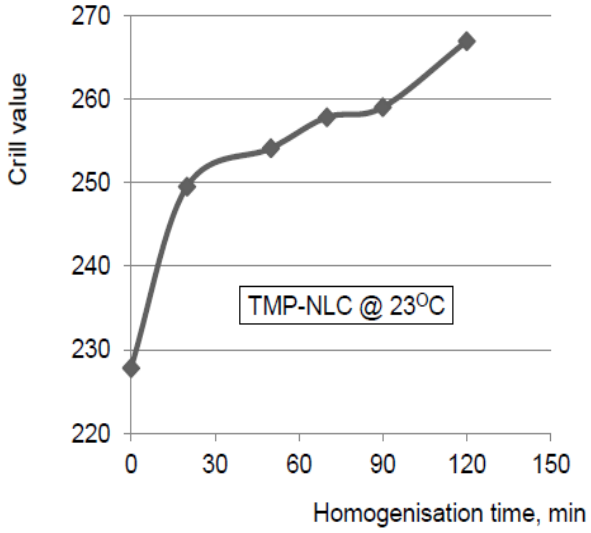

Figure 31. Crill value of TMP-NLC homogenized at 23°C as a function of homogenisation time.

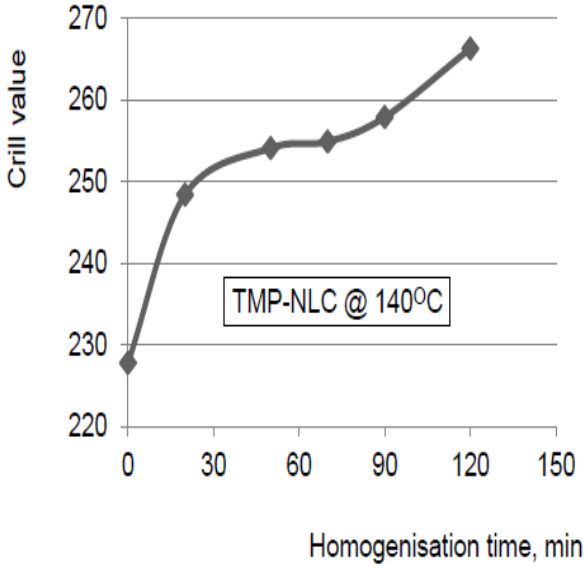

Figure 32. Crill value of TMP-NLC homogenized at 140°C as a function of homogenisation time.

The crill method possesses the inherent ability of assessing the particle size of a fibre/crill in a very short time-frame (few seconds) and without any damaging effect on the pulp suspension under investigation (non-destructive method). It can be noted that by using crill in characterising NLC, it becomes possible to reduce the time-consuming microscopy technique in characterising particle size distribution.

4.6. NLC as a strength additive in paper (Paper III)

This work was to utilize NLC as a strength additive in paper/board qualities, since the development of paper strength is of great importance for paper producers. Handsheets of CTMP and BKP, with the addition of their respective NLCs, were made in a conventional Rapid Köthen Sheet former and their corresponding properties were evaluated with respect to sheet density. It was found that the handsheets of pulp fibres, blended with NLC, improved the mechanical properties, with only a slight effect in relation to the sheet density. Improvements in strength properties of handsheets such as z-strength, tensile index, tear index, burst index, E-modulus, strain at break, tensile stiffness and, air resistance were observed. Many research teams have studied the use of chemical based MFC as a strength enhancer and some of these researches are, briefly reported in this thesis. Thorough investigations of the use of MFC as strength additives have been carried

out by many (Eriksen et al. 2008, Taipale et al. 2010, Hii et al. 2012, Ahola et al. 2008, Sehaqui et al. 2013).

The tensile strength is regarded as the strength that can withstand deformation or failure in the x-y direction and it relies on the gradual failure in the inter-fibre bond (Helle 1962). In this thesis, the following mechanical properties are evaluated: Z-strength, tear index, burst index, tensile index, tensile stiffness, stretch to break and tensile energy absorption (TEA). Page (1969) reported that the tensile index increases with long fibres. The z-directional tensile strength and the Scott Bond energy are both influenced by the bonded area and specific bond strength. The Z-directional tensile strength is regarded by Kouba and Koran (1995) as the best option when compared with the Scott bond, though both methods do correlate-acceptably.

Duker (2007) highlighted that the specific bond strength (strength per unit area) and relative bonded area (RBA) are the two parameters that contribute to the strength property in a fibre network. Hartler and Mohlin (1975) reported that the presence of lignin decreases the fibre joint strength and, additionally, high hemicellulose content improved the fibre joint strength. Production of high-quality sheets by blends of NLC can provide desirable properties such as high tensile strength and burst index as well as low density (high bulk), which can be used in end-products such as paperboard and printing paper.

It was found that a blend of NLC with pulp fibre handsheets improved the z-strength and other important mechanical properties at almost the same density. This acts as confirmation regarding the unique properties of NLC, which include; ***high strength and stiffness, low density, biodegradability and, renewability.*** The air resistance properties of all the samples investigated was considerably improved by the addition of NLC.

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

The most prominent effect of strength improvement was an increase in z-strength (Figure 33) at almost the same sheet densities. The relationship between burst

index and sheet density was also affected by the addition of NLC to the fibre furnish of both pulps (Figure 35). The highest amount of NLC added (i.e. 15% NLC), improved the tensile index of BKP to about 30% as compared to the non-blended BKP fibres (see Figure 34). Sehaqui et al. (2011 and 2013) have reported a maximum in tensile index at NLC content of 4%.

The low strengthening effect of NLC can be attributed to the amorphous (hemicellulose and lignin) part of the pulp. In mechanical pulps (TMP and CTMP) the fines contribute significantly during sheet consolidation. The behaviour of lignin and hemicellulose during homogenisation might have an influence on the strength properties of the handsheets. In the chemical pulp based nanocellulose (NC), however, it is noted that the BKP fibres are longer and have very low amounts of fines, and long fibre quality corresponds to a better strengthening effect. The strength properties of pulp fibres blended with NLC or NC were better than those which were not mixed with NLC/NC.

During pulp disintegration, using high pressure and high shear forces in the homogenising equipment, 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 into tiny and hairy-like particles. This loosens up into individual fibrils and thus enables the newly engineered bio-structure to improve fibre-fibre bonding when blended with pulp fibres during handsheet formation. An explanation for the strength improvement using NLC is because it increases both the molecular contact area between the pulp fibres and the fibre-fibre joint strength.

In relation to an improvement of the mechanical strength properties of handsheets, an attempt has been made by simply mixing pulp fibres with NLC/NC. Blending NLC/NC with pulp fibres, and in particular NC, increases the reinforcement of the fibres, and thus improves the mechanical strength, particularly in relation to the z-strength. In this thesis, the z-strength effect is studied using NLC blended with pulp fibres as a function of sheet density, as shown in Figure 33. The 15% NLC content in the pulp furnish very slightly affected the sheet density for the CTMP and as well provided an improved z-strength. The plots in Figure 33 shows that addition of NLC or NC to pulp furnishes (CTMP and BKP) change the relationship between the z-strength and sheet density.

It has been noted that the mechanical strength properties of laboratory sheets differ with respect to the type of sheet forming methods (Nygren et al. 2003) used due to differences in the experimental set-up and the mechanism regarding sheet consolidation. These z-strength results could not be compared to any previous work 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 by using other works such as that of Eriksen et al. (2008) in which they used a kraft pulp based MFC to improve the strength properties of TMP sheets.

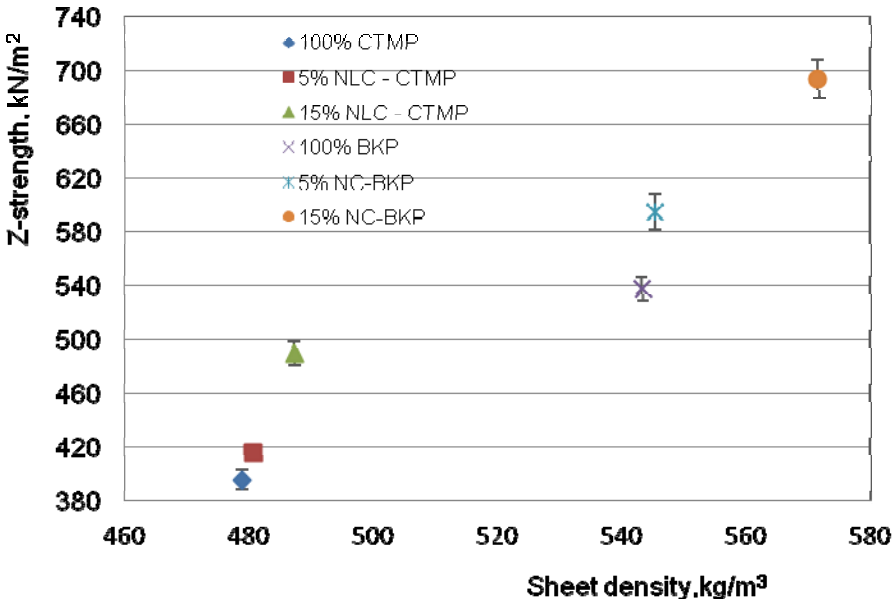

Figure 33. Z-strength as a function of sheet density

Tensile strength is regarded as the maximum tensile force per unit width that a test sample can endure (Brännvall 2007). The tensile measurement can be read from the appended publication section, paper 3. In this thesis, the tensile index is plotted as a function of sheet density. It appeared that the tensile index for the NLC-CTMP blend shows a marginal strength improvement as compared to the tensile index of the non-blended sample. The tensile index of the BKP increased by 36% when 15% of BKP-NLC is added to the fibres (Figure 34). It is not appropriate to compare the tear strength of BKP to that of CTMP as the BKP is an unrefined pulp. Figure 36 and 37 show both the tear index as a function of sheet density and TEA as a function of sheet density (More of this could be read in appended paper 3).

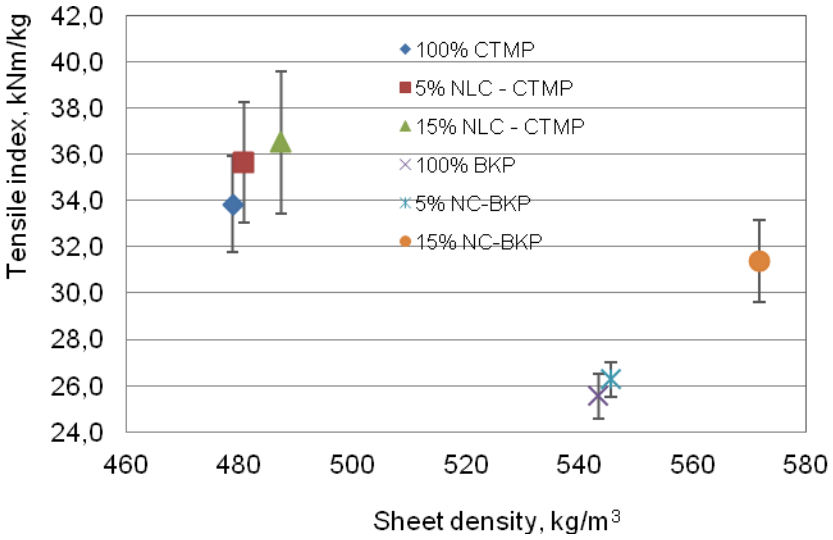

Figure 34. Tensile index as a function of sheet density.

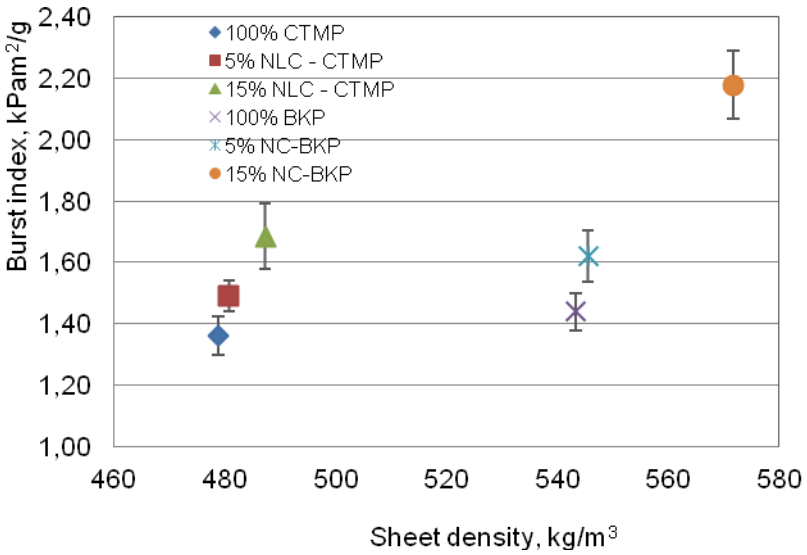

Figure 35. Burst index as a function of sheet density.

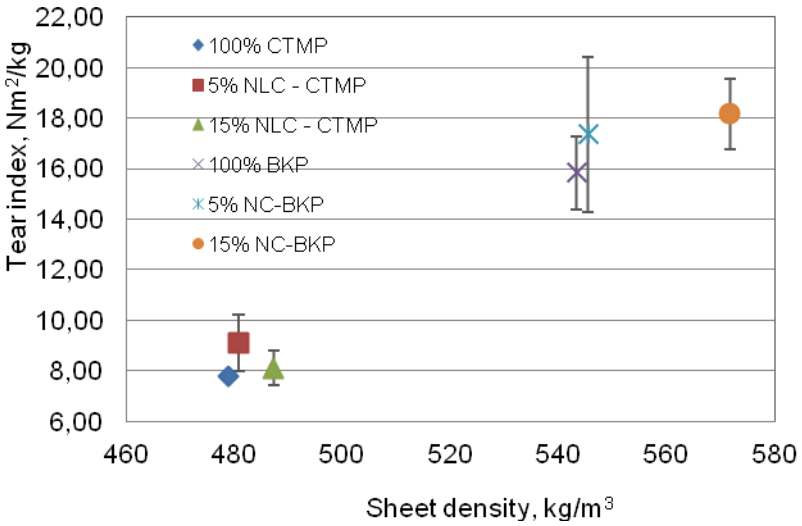

Figure 36. Tear index as a function of sheet density.

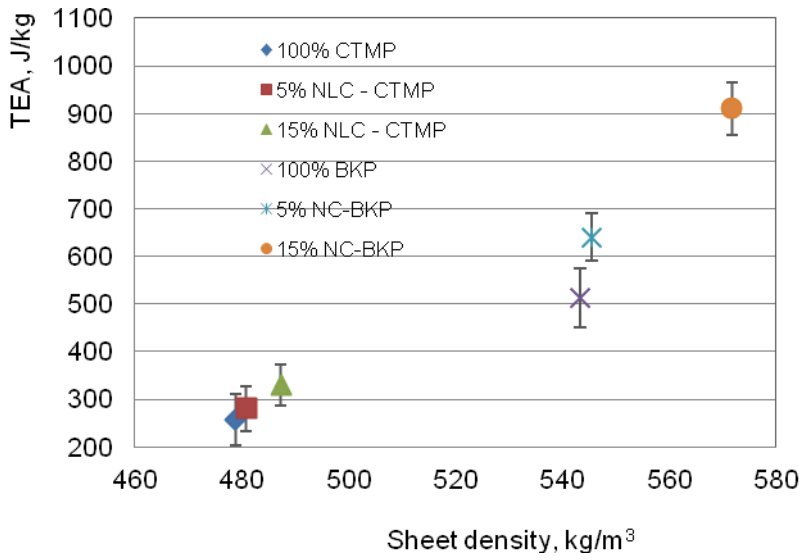

Figure 37. TEA as a function of sheet density.

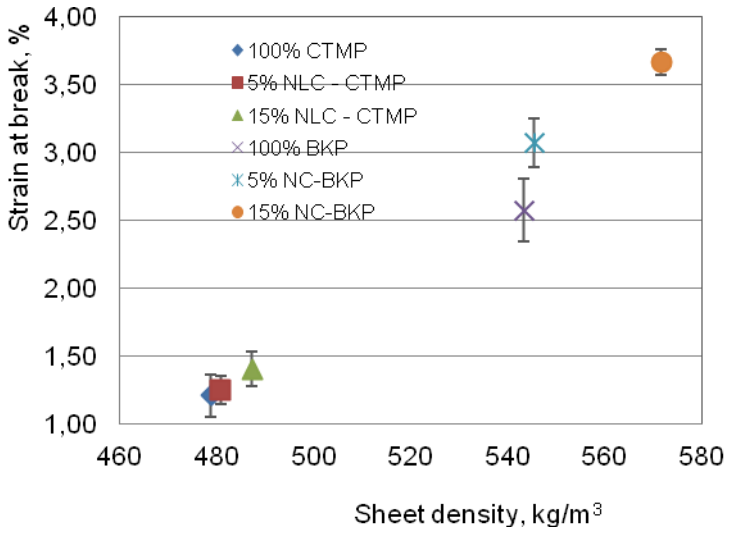

Figure 38. Strain at break as a function of sheet density.

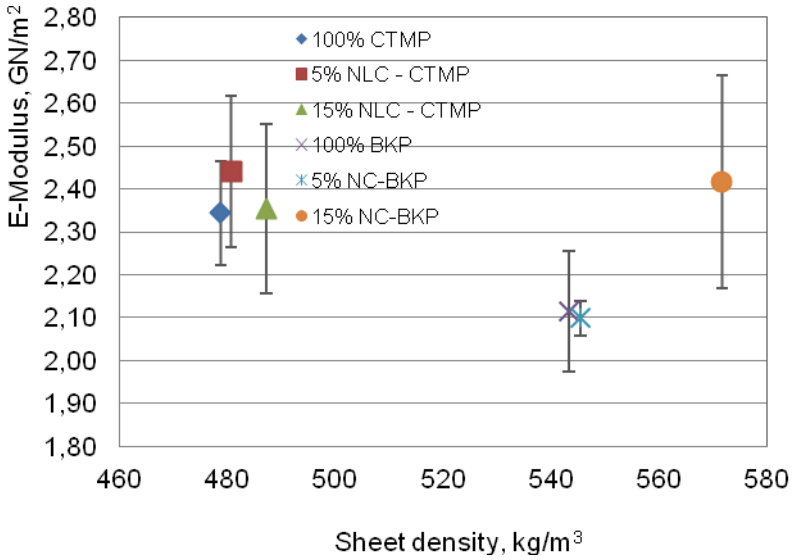

Figure 39. E-modulus as a function of sheet density.

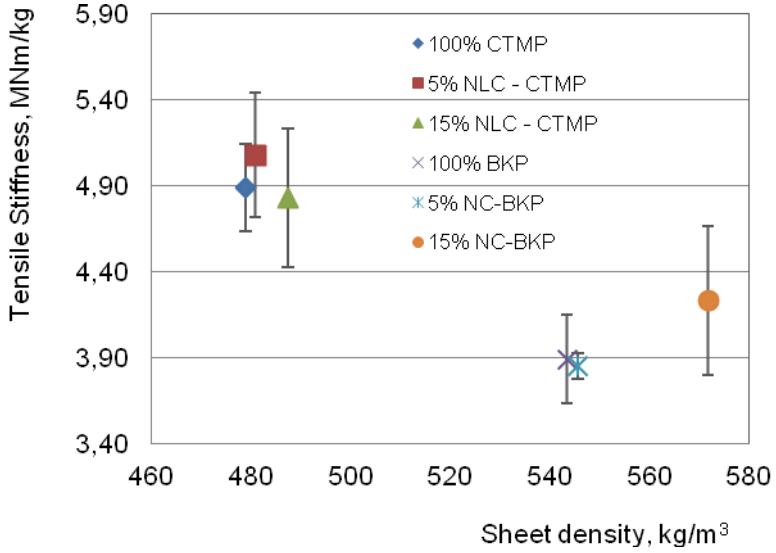

Figure 40. Tensile Stiffness as a function of sheet density.

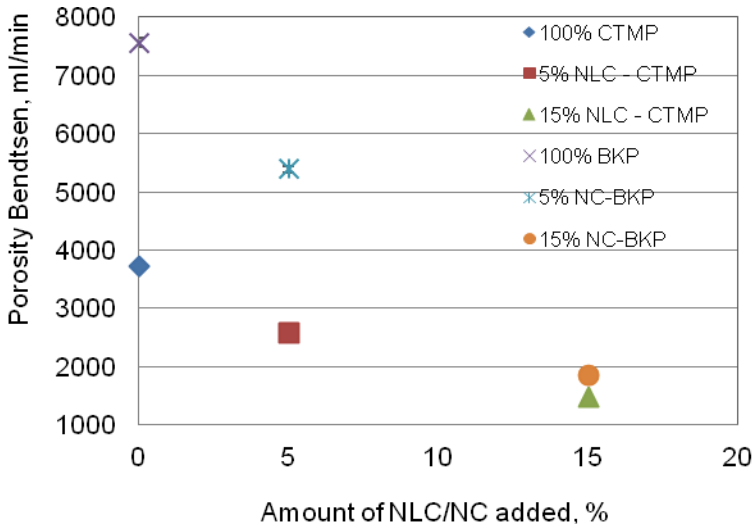

Figure 41. Air resistance permeability (Porosity Bendtsen) as a function of NLC/NC content.

The tear index is an indication of the out-of-plane tearing of laboratory sheets. The tear index is improved by using longer fibres and thus providing increasing fibre strength (Seth and Page 1988). It is clearly evident from the plot in Figure 37 that a 15% addition of NLC to the pulp fibres did not significantly improve the TEA of CTMP, and did not provide any large impact on the sheet density. The strain at

break as a function of sheet density, E-modulus as a function of sheet density, Tensile Stiffness as a function of sheet density, Air resistance property (Porosity Bendtsen) as a function of amount of NLC/NC added can be respectively seen in Figures 38, 39, 40, 41. In most paper mills, the strength properties are under continuous development using several options as highlighted in the literature of Duker et al. (2007), and includes, pulp beating, refining and the use of strength additives. Chemical pulp based MFC has been used as a strength enhancer in most research work. The reasoning for this research was to further this assertion using mechanical based pulp fibres. The combination of a CTMP fibres furnish with a CTMP-based NLC proved to offer a good indication of the z-strength enhancement potential for production for paperboards. For CTMP without any addition of NLC, the z-strength is around 396 kN/m^2 but after the addition of 15% CTMP-NLC, the z-strength is increased to 490 kN/m^2, showing an approximate 20% increment in the z-direction sheet strength.

In this study, a high burst index was achieved for a 15% NLC blended CTMP. It is believed that by increasing the dosage to about 30%, it would be possible to considerably improve the burst index, however, in terms of economics , using a high dosage of NLC is not acceptable. A CTMP –NLC blend could be regarded as a good candidate for a paperboard application in which light weight and high bulk are the most interesting properties. As can be observed in Figure 35 the burst index did not significantly change for all the pulp samples despite their added amounts of NLC. These results are in agreement with those reported by Eriksen and co-workers (2008), who also noticed that the addition of 4% kraft MFC could be used to improve the strength properties of TMP laboratory sheets. The TEA data show that all the pulp had a similar pattern of increase, the exception being the 10%NLC-TMP.

As shown in Figure 37, there is a slight increase in the TEA with the addition of NLC to both pulp samples (CTPM and BKP). With regards to the CTMP furnish, the TEA for CTMP fibres was improved by adding 15% NLC into the CTMP and increase from about 257 to 330 J/kg was noticed. The BKP blended sample (15% NC-BKP) showed the most remarkable improvement, with a 78% TEA increment using the 15% NC-BKP blend. The TEA for the CTMP fibres improved significantly by adding 15% of CTMP into the CTMP fibre furnishes. The Bendtsen air-leak method has been routinely used in pulp and paper mills as a reliable characterisation method for measuring air permeability for paper and paperboard. A decrease in air permeability is observed with the addition of NLC/NC for both CTMP and BKP laboratory sheets, the reduction being more pronounced for BKP, see Figure 41. It is known that air permeability is directly related to the amount of fines fractions in a pulp fibre furnish. This is evident in the plot in Figure 41, where the CTMP has smaller air permeability due to the large amount of fines in the CTMP as compared to that for the BKP.

5. CONCLUSIONS

The preliminary investigation of the BMcN fractionation enabled the correct fibre length to be used for mechanical treatment in the high pressure homogeniser. The research work presented is of interest to those working with forest-based nanotechnology for renewable materials and of, significant interest to the pulp and paper industry. The overall scope of this work is to present a production method for NLC using mechanical pulp fines, and to characterise the NLC qualities with application prospects focused on the paper and paperboard industry. As previously discussed, the main objective of producing NLC was to use as a strength additive in paper/board products. It was found that the handsheets of pulp fibres, blended with NLC, improved the mechanical properties, with only a slight effect in relation to the sheet density.

Results from crill measurements show an increase in crill values as the homogenisation time increases. Although further development of the crill method is required before it can be fully 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 and could be seen as potential tool for characterising particle size distribution in both the micro and nano scale in a microfibrillated cellulose (or nano-ligno-cellulose) plant.

6. FUTURE WORK

The intention of this research work was to create a knowledge base for a low-cost production method using only conventional chemicals such as sodium sulphite, sodium hydroxide and hydrogen peroxide so as to develop an easy to implement concept. The continuation of this work will aim to utilize NLC as a cost-effective substitute for CMC in multi-layer fibre applications e.g. paperboard. It would also be a good idea to study the influence of charge groups with respect to fibrillation as well as the swelling of fibre walls. Furthermore, a thorough study of fibre wall structure should be performed using Raman microscopy and also a strategy to improve energy efficiency with respect to efficient pulp fibrillated will be tested.

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