NANOCELLULOSE MATERIALS FOR PHOTOELECTRONIC DEVICES

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A Thesis Submitted in Partial Fulfillment
of the Requirements for the Degree of

Master of Science in Engineering

in the Graduate Academic Unit of Chemical Engineering

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This thesis is accepted by the Dean of Graduate Studies

THE UNIVERSITY OF NEW BRUNSWICK

March 2017

ABSTRACT

Nanocellulose is an interesting building block for functional materials and has gained considerable interest due to its unique properties. Optical and mechanical properties of nanocellulose films were studied to have a deep understanding of their potential for photoelectronic applications. Photoelectronic device substrates require high mechanical strength and optical transparency. In this work, the impact of production method using mechanical refining and chemical pretreatment (TEMPO) on these properties was evaluated. Bleached softwood kraft wood pulp fibres were used as start material for producing nanocellulose fibres. Mechanical refining using a KRK or a PFI refiner and TEMPO oxidation processing were used. Handsheet paper or films made from the resulting nanocellulose fibres were made and both physical strength and optical properties such as transparency and haze were evaluated. Results show that TEMPO oxidized films had superior mechanical and optical properties than the films produced from mechanical refining method. This high-performance, nanocellulose film is a promising renewable material for a new generation of solar panel and other optoelectronic devices.

DEDICATION

This work is dedicated to Lord God Almighty who gave me light in darkness and who is the reason why I live.

To my Wife Christiana, who has been a constant source of support and encouragement during the challenges of graduate school and life. My children Rejoice, Deborah, Peter and Light for their sacrifice, I am truly thankful to God for having you in my life. This work is also dedicated to my late parents Mr Potoki and Mrs Reginar, who have always loved me unconditionally and whose good examples have taught me to work hard for the things that I aspire to achieve.

ACKNOWLEDGEMENTS

Foremost, I would like to express my sincere gratitude to my advisor Professor Kecheng Li for the continuous support of my Master's study and research, for his patience, assistance, support, motivation, enthusiasm, and immense knowledge. His guidance helped me in all the time of research and writing of this thesis. I could not have imagined having a better advisor and mentor for my Masters study.

Besides my advisor, I would like to thank my co supervisor, Professor Guida Bendrich for encouragement, insightful comments, and motivations.

My sincere thanks also go to my group members in the Department of Chemical Engineering. You made this project a pleasant experience. Thank you for teaching me and sharing you laboratory experience with me and having patience with me.

Finally, thanks to all my friends for their love and encouragement.

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List of Symbols, Nomenclature or Abbreviations

TEMPO: 2,2,6,6-Tetramethylpiperidinyloxy.

KRK: The refiner is one of basic machines used in test and research area of pulp and paper industry and other related industries.

PFI: Pulp beater that subjects pulp to a specific beating schedule to process pulp prior to forming handsheets

FQA: Fiber Quality Analyzer

CSF: Canadian Standard Freeness

CTE: Coefficient of thermal expansion

LM: Light Microscope

Chapter 1: Introduction

1.1 Project Background

Substrate materials play a key role as the foundation for photoelectronic devices [1]. Optoelectronic devices such as mobile phones, organic light-emitting diodes lighting (OLED), and solar cells. They are often used in systems which sense objects or encoded data by a change in transmitted or reflected light. Photoelectric devices which generate a voltage can be used as solar cells to produce useful electric power. The operation of photoelectric devices is based on any of the several photoelectric effects in which the absorption of light quanta liberates electrons in or from the absorbing material. The mechanical strength, optical transparency, and maximum processing temperature are among the critical properties of these substrates that determine its eligibility for various applications [1, 2].

The optoelectronic device industry predominantly utilizes glass substrates and plastic substrates for flexible electronics [3−6]. Recently, many reports demonstrate transparent films based on renewable cellulose fibers that may replace plastic and glass substrates in many optoelectronic devices [7-10]. Solar cells today are made from a wide crocktail of materials, from earth-abundant materials (Silicon and Carbon) to exotic rare earth metals (Indium, Gallium, etc), and polymers to organic materials [1, 5, 7, 9]. Nanopaper or film from cellulose material is entirely more environmentally friendly than plastic substrates due to its composition of natural materials [1, 11−14]. Nanostructure materials from wood that has pore structures from micrometer size down to nanometer sizes are emerging toward novel photonics and optoelectronics, through which photons can be manipulated to achieve desired properties [1, 15].

While traditional transparent substrates such as SiO_2, glass and plastic are solids, transparent paper is a mesoporous network of cellulose micro and nanofiber with controllable pore sizes and pore distributions [1, 2]. This type of paper photonics has tremendous potential; the mesoporous structure of cellulose fiber-based paper allows the density, pore structure, and shape to be tuned dramatically, which is impossible to achieve with traditional plastic substrates [1, 2, 17-25]. The interrelationship between the cellulose raw material is essential for industrial applications, as well as for the processing and the quality of the final fibrillated products and also their capacity for a later industrial upscaling [26]. The geometric properties of the nanocellulose structures (shape, length and diameter) depend mainly on the extraction process and on the origin of the cellulose raw material [27]. Cellulose micro/nanofibres can be obtained from mechanical refining and chemical procedures. Mechanical treatment techniques are currently considered efficient ways to isolate nanofibers from the cell wall of a wood fiber [2, 28]. However, solely mechanical processes consume large amounts of energy and insufficiently liberate the nanofibers while damaging the microfibril structures in the process [28]. Pretreatments, therefore, are conducted before conducting mechanical disintegration in order to effectively separate the fibers and minimize the damage to the nanofiber structures and as well save energy [1]. TEMPO-mediated oxidation is proven to be an efficient way to weaken the interfibrillar hydrogen bonds that facilitate the disintegration of wood fibers into individualized nanofibers [28]. The wood fibers are processed by using a

TEMPO/NaBr/NaClO oxidization system to introduce carboxyl groups into the C_6 positions of the cellulose [1, 2, 16]. This process weakens the bonds between the cellulose fibrils and causes the wood fibers to swell up. The oxidized wood fibers are then fabricated into highly transparent paper [1]. This approach to produce highly transparent paper with high haze using micro-sized wood fibers has the potential to be scaled up to industrial manufacturing levels, which is crucial for commercial applications [1, 2, 4-15]. Solar cell substrates require high optical transparency, but also prefer high optical haze to increase the light scattering and consequently the absorption in the active materials[1]. Common transparent paper substrates generally possess only one of these optical properties [1, 28]. Currently, there is no detailed understanding of the correlation between the morphology of fiber and the optical properties in the literatures. More so, this work intends to give the foundation in developing economic ways to obtain the required properties of films for photoelectronic device application.

1.2 Objectives of the research

The objective of this thesis was to understand the refining process and its influence on fiber and film properties specifically the mechanical and optical properties. The specific objective was to have a detailed understanding of the correlation between fiber morphology and its mechanical and optical properties and to find out which type of cellulose refining or treatment methods that would form more suitable films properties for optoelectronic devices application.

Scope of Study

The scope of this experiment was limited to the use of pilot scale refiner (KRK and PFI Beater) and TEMPO oxidation methods to achieve the above objectives.

1.3 Thesis structure

This research work will be divided into five Chapters. Chapter One will introduce the background, scope, aims and objectives of the thesis structure. Chapter two will review the literature related to this project. The literature will present an overview on refining (KRK and PFI refining techniques), effect of refining on properties of sheet formation, different fiber pretreatment methods etc. Research questions, Nanocellulose, Nanocellulose film, properties of Nanocellulose films, why Nancellulose film is good for optoelectronics devices will be discussed here. The literature will also cover wood chemistry, deep background on the concept of film production to provide some insight into the motivation of this thesis. Past works related to this thesis will be reviewed and any gap will be taken advantage of.

Chapter three outlines the procedures used for nanocellulose production processes. Both mechanical refining and TEMPO mediation oxidation methods will be examined. The refining of pulp will be done with help of KRK and PFI refining procedures. The mechanical refined pulp will be treated with TEMPO/NaBr/NaClO system in order to modify the surface properties of the fibers by selectively oxidizing the C6 hydroxyl groups of glucose in cellulose chain. In the experimental section, the fibers produced by both of these processes will be characterized by using light microscope, Fiber Quality Analyzer (FQA) and Canadian Standard Freeness (CSF). The morphological changes of the refined and chemical treated fibers under different methods used in this work will be compared. Finally, nanocellulose films will be fabricated by different methods mainly Sheet Maker or Former, Vacuum Filtration and Casting methods. The outcome of experimental work will be:

1. Effect of mechanical refining and chemical treatment on fiber morphology, fiber length and freeness
2. Effect of sheet formation techniques on strength and optical properties of the nanocellulose films

The conclusion of this chapter will be drawn from detailed results obtained from the experiments that consist of various studies which includes (1) development of successful nanocellulose production route (2) the morphological changes of wood fibers under different methods used and compared characterization of the fibers using appropriate techniques. Commonly, morphological evidences are given by microscopy and subjective evaluations. Proper characterization requires the quantification of the fibrillated material at several scales. Nanocellulose production methods currently used require too much time and energy consuming to be practical for commercial applications. Some related art techniques are used to liberate nanofibers. These techniques include mechanical treatments and acid hydrolysis. Mechanical treatment techniques are currently considered efficient ways to isolate nanofibers from the cell wall of a wood fiber. However, solely mechanical processes consume large amounts of energy and insufficiently liberate the nanofibers while damaging the microfibril structures in the process. Pretreatments, therefore, are conducted before conducting mechanical disintegration in order to effectively separate the fibers and minimize the damage to the nanofiber structures. TEMPO-mediated oxidation is proven to be an efficient way to weaken the interfibrillar hydrogen bonds that facilitate the disintegration of wood fibers into individualized nanofibers yet maintain a high yield of solid materials. Chapter Four will discuss the nanocellulose processing conditions in relation to the film properties. In this chapter the effect of fiber morphology and fibre length variation on the mechanical and optical properties of the films produced from the refining and TEMPO oxidation processes will be investigated. Mechanical and optical properties are the most significant criteria required for solar panel application. The mechanical strength of films produced in this work will consider the tensile strength, tear strength, thickness and grammage while the optical properties focus is to study the light transmittance and light scattering of films that will be produced as mentioned in the previous chapter. The effect of film thickness on transmittance will be analyzed. This chapter concludes by summarizing the findings of the results obtained from a more detailed analysis of the change in physical and optical properties of the nanocelluose films. Handsheets produced from the fibers obtained from the refining and TEMPO oxidation processes allow understanding how the different pulp samples affect sheet properties. Also, a precise control of the cellulose fiber dimensions enables film substrates with a diverse range of unique properties, experimental investigation of the relationship between the structure and different production techniques which includes the KRK and PFI refining and TEMPO oxidation and their resulting end products properties result is vital in drawing the conclusion. The correlations between different film forming techniques such as solvent casting, filtration, sheet former combined with oven drying and filtration combined with hot pressing are also evaluated to understand their potential for solar panel applications Therefore, it is essential to study these properties in detail, which further opens the gateway to any improvements needed in production processes. Finally, when additional factors are considered, the system becomes more complex and a better understanding of the various relationships is crucial. Desired changes of one fiber parameter might cause undesired changes in other factors because of the presence or control of another third factor. With proper knowledge of the complexity present in the raw material, the various quality requirements could be met with more accuracy. Finally, Chapter five will provide the conclusion and recommendations for future work in this project.

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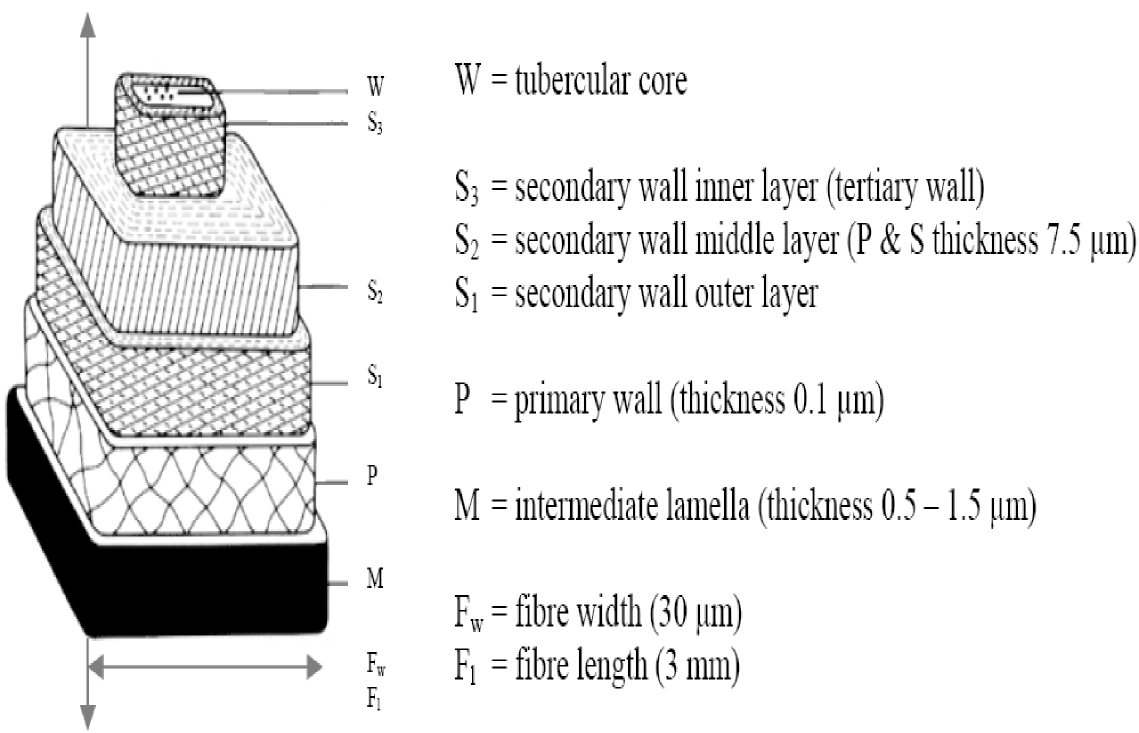
Chapter 2: Literature Review

2.1 Introduction

Currently, there is a widespread research focusing on wood and its derived materials in energy-related materials [1]. For example, cellulose-based substrates have exhibited great promise for solar cells considering the lightweight, abundance, flexibility, and biodegradability of cellulose compared to plastic and glass that are commonly used now [2]. Furthermore, the need to lower the dependence on the fossil fuels that is fast depleting all over the world and reduction of environmental pollution from the emission of greenhouse gases has made the choice of nanocellulose materials very important [1].

2.2 Overview of Wood Structure

Wood fibers are the structure material of paper [2-3]. In order to understand the effects of refining on paper properties the effects of refining on fiber must be clarified. The structure of a tracheid fiber is shown in Fig. 2.1[3]. The fiber is protected by a thin membrane called the primary wall (P). Inside the primary wall is a secondary wall which surrounds the lumen. It consists of a number of concentric layers numbered from the outside to the lumen as S1, S2, and S3. These layers are made up of spirals of fibrils which lie at various angles to the major axis of the fiber [1]. The important points to note are: 1) the primary wall, P, and the S1 secondary wall have very high fibril angles with respect to the fiber axis, and 2) the secondary wall is the predominant layer in the cell wall, which has a very low fibril angle. Therefore, the major tensile stress bearing layer in the axial direction is the S2 layer. The major restraints against swelling are the S1 and P layers [2].The wood pulp fibres have multiscale characteristics [4].



(a)

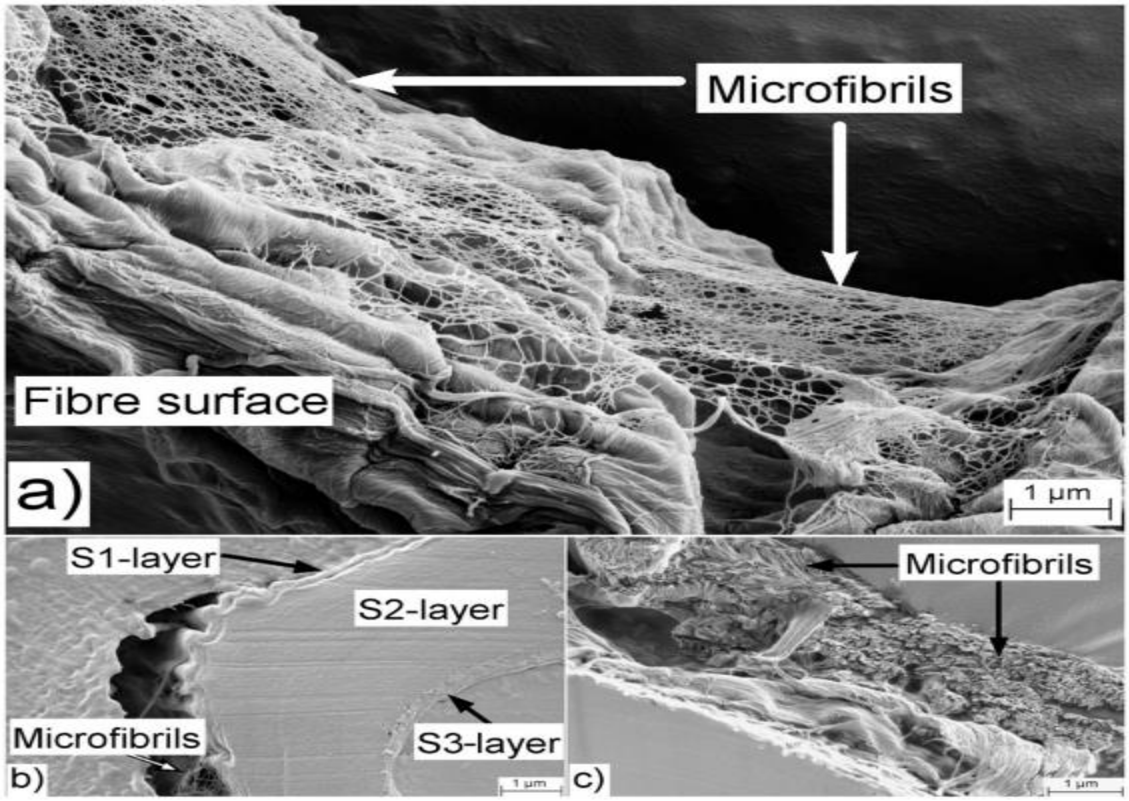


Figure 2.1(a) Structure of Nordic softwood tracheids paper [3] (b) Structure of wood pulp fibres (a) Note the network of microfibrils covering the outer wall layer. (b) Microtomed cross section showing the S1, S2 and S3 layers. (c) Cross-sectional fracture area, showing the microfibrils in the S2 layer[4].

Roughly, typical lengths of fibres are 1 to 3 mm and typical widths are 10 to 50 μm. The fibre wall thickness is roughly between 1 and 5 μm (Figure 2.1). Chemical pulp fibres are produced through chemical pulping where lignin and hemicellulose are extracted. Chemical pulp fibres have a surface, which is characterised by a particular pattern created by wrinkles and microfibrils in the outer layers of the fibre wall structure.

According to Meier [5], the cellulosic components of a wood fibre wall structure are the cellulose molecule, the elementary fibril, the microfibril, the macrofibril and the lamellar membrane. In the work of Maier [5], the term “elementary fibril” was reported to have a diameter of 3.5 nm.

The chemical composition of these layers is primary cellulose, hemicelluloses and lignin. The cellulose and the hemicelluloses molecules are able to form hydrogen bonds with the adjacent molecules. The fibers of paper are bonded to each other by hydrogen bonds, thus giving the fiber network its strength [5, 6]. Under mechanical stress, the layers in the fiber wall can delaminate. When this delamination occurs in the presence of water, the fibers imbibe the water in the separated regions and swell. The water acts as a lubricant between the lamellae, allowing the previously bonded surfaces to slide past one another [6]. Removal of the primary wall and S1 layer can be used to improve strength properties of paper [4, 7].

2.3 Fiber Refining

Wood pulp fibers produced by the pulp mill are generally unsuitable for direct usage [2]. A sheet of paper made from unbeaten fibers is characterized by its low tensile strength; its bulkiness; and open, irregular surface [2]. For most commercial papers, these characteristics are undesirable, but they can, to a large extent, be suitably altered by mechanical processing passing the pulp continuously through a refiner before the stock goes to the paper machine [3]. In this case, the structures of most of the fibers are disrupted in the presence of water. This is accomplished by mechanical treatment between the edges and closely spaced faces of rapidly moving bars, with simultaneous mechanical interaction between the fibers themselves[2]. Refining of fibre causes fibre shorting, internal fibrillation and exterior surface fibrillation in which part of which causes a buildup of small particles called fines [4].

A question of long-standing importance to the process is what is the goal of refining? In this thesis, refining will be carried out to improve the strength properties of paper (particularly tensile strength).

This thesis explores the field of refining by specifically addressing three questions:

1. What mechanical treatment is required to produce internal fibrillation in pulp fibers?
2. What is the relative importance of internal fibrillation compared to external fibrillation and fines in terms of developing sheet strength?
3. How do internally fibrillated fibers influence sheet properties, particularly mechanical and optical properties?

2.3.1 Effect of Refining on Fiber Properties

The main effects of refining on pulp are internal fibrillation, external fibrillation, creation of fines and shortening of fibers as stated above. The details of these effects are described below.

Conventional refining processes have many effects on fibers. In this review, Ebeling's [8] summary is used to categorize the effects as follows:

- Internal structural changes - internal fibrillation; caused by breaking intrafiber hydrogen bonds and replacing the bonds with water molecules.

- External structural changes - external fibrillation, which is defined as pulling fibrils out of the outer walls of the fiber and primary wall removal; fines formation, due to the removal of parts of the outer walls and breaking off of the fibrils.

- Fiber shortening or cutting.

Internal Structural Changes

The forces of any applied action, whether classified as stressing, pressing, bending, flexing, curling, bruising, kneading, rubbing, twisting, crushing, etc., may be absorbed by the fiber and cause breakage of internal bonds. The bonds in question are between cellulosic fibrils, between fibrils and hemicellulose, between cellulose and lignin, and between hemicellulose and lignin. Mechanical action on the fiber of such intensity that bonds will be broken will usually result in swelling [2].

Swelling of the fiber takes place mainly in the amorphous hydrophilic hemicellulosic interfibrillar material [8]. However, partial crystallization and hydrogen bonds will limit swelling, as will the presence of lignin [9]. The primary wall and the S1 layer of the secondary wall will also restrain the swelling during the earliest stages of refining due to their hydrophobic nature and the high fibril angle of the S1 layer [4, 9-11]

As mentioned previously; desirable papermaking properties result from these internal structural changes.

External Structural Changes

External fibrillation is the delamination of fiber surfaces [3, 4, 12]. This can be defined as a peeling off of fibrils from the fiber surface, while leaving them attached to the fiber surface. Removal of the outer parts of the cell wall will expose the S2 layer. By removing these regions of the fiber, which act as swelling restraints, the fiber becomes more flexible. Steenberg [13] stated that fiber flexibility, both wet and dry, is the second most important item (after fiber length) in strength development. Giertz [9] reported that, at least very early in the beating process, the fraction of fiber surface free from the primary wall can be directly correlated with tensile strength. Therefore, as more hydrophilic hemicelluloses in the S2 layer are brought to the surface, they replace the greater number of hydrophobic lignin molecules in the P and S1 layers, and promote interfiber bonding [1].

Another reason for causing external surface changes is the amount of surface area that is generated for fiber bonding. Throughout his book, Clark [14] emphasizes the importance of external fibrils as the main entity in interfiber bonding. There has never been much denial that the larger fibrils developed from a well-beaten pulp will enhance the cohesiveness of the fibers in a wet sheet [8]

Creation of fines

Fines are produced in refining as a result of fiber shortening or removal of fibrils from fiber walls. In this thesis, fines are defined by the method by which they are made [2]. They are generated by cutting fibers, detachment of large parts of the lamellar structure of the fiber, and breaking off of external fibrils [1].

Generated fines consist mostly of fragments of P and S1 layers of the fiber wall due to the abrasion of fibers against each other or against refiner bars. Fines, meaning loose fibrous material of size less than 0.3 mm, are produced in refining [2, 3].

The presence of fines is detrimental to drainage characteristics of the pulp because of the additional surface area introduced with the suspension [2]. The high water holding capacity of the fines also impedes drainage.

Fiber Shortening

Refining causes fiber shortening which is generally undesirable in refining [2, 3]. If the strain on a fiber is great enough, it will break or be bend and deformed [2]. Fiber cutting which reduce average fiber length and affect paper properties that are related to fiber length, formation and strength. In some rare applications it is a desired effect to improve formation by decreasing the crowding number [4].

2.3.2 Effect of Refining On Paper Properties

Refining causes changes in fibre properties, and this in turn changes paper properties [2-5]. The effects of refining on the paper properties of the final sheet can be classified into four categories: physical properties, strength properties, optical properties, and sheet formation [5].

Effects on Physical Properties

One of the effects of refining on paper physical properties is increasing the density [7-8] . Increased density means the basis weight increases and the thickness decreases. The value of bulk is inversely proportional to the value of density. Thus, refining reduces the bulk of the paper sheet [3].

Fibre length will decrease after refining. The spaces between the fibres and the pores also decrease, and as a result the air permeability increases.

Effects on Sheet Formation

Sheet formation is indicated by the degree of smoothness. The action of refining causes sheet smoothness to increase

Effects on Optical Properties

In general, the optical properties such as brightness, opacity and light scattering coefficient are decreased by refining. Decreasing the light scattering coefficient effectively decreases the opacity. For chemical pulp, by refining the bonded surface increases while opacity decreases. This is in contrast to mechanical pulp, in which the unbounded surface increases and opacity increases by the action of refining [3-4].

Effects on Strength Properties

The main factor that affects strength properties is bonding area. With refining the bonding area increases. Tensile and burst strength will increase after refining. When refining is applied to the fibre, the tear strength decreases after a slight increase at the beginning [2, 8].

2.4 Microfibrillated cellulose

Since the introduction of the transmission electron microscope, it seems that researchers have attempted to disintegrate cellulose fibres into single microfibrils/elementary fibrils for ultrastructural studies [15]. Already in the 1950s, ultrasonic, hydrolysis and oxidation treatments were applied for disintegrating cellulose structures [16,17, 18]. In addition, Ross Colvin and Sowden [20] reported a homogenization process based on beating for opening the structure of cellulose fibres and thus exposing the microfibril structures for transmission electron microscopy (TEM) analysis. The disintegration of cellulose fibres into their structural components (microfibrils) has also found industrial interest. As mentioned above, in 1983, Turbak et al. [19] introduced a homogenisation procedure for fibrillating cellulose fibres with commercial purposes. The MFC terminology, which was originally applied to the fibrillated material, was probably related to the predominant structures encountered in fibre wall structures, i.e. microfibrils [21]. Although microfibrils seem to be the main component of MFC, several studies have shown that fibrillation produces a material which may be inhomogeneous [22, 23], containing, e.g. fibres, fibre fragments, fines and fibrils. Having fibrillated materials with different degree of homogenisation and composed of a variety of structures emphasises the necessity of clarifying the different components encountered in MFC.

Table 1 gives a rough classification of MFC components, including classical terminology that has been applied in plant physiology for decades and terminology related to fibre technology.

The fibril term has been applied for defining structures with a dimension less than 1 μm, although not consequently. Structures with diameters of <1.0 μm have also been observed in the fibre wall structure of pulp fibres. Such structures have been denominated macrofibrils, and diameters of approximately 0.66 μm have been reported [24]. However, according to Meier [5], macrofibrils do not have definite dimensions. A fibril may also be considered an engineered structure as it is produced during mechanical fibrillation. There seems to be no concrete border line between fibrils and fibrillar fines. Fibrillar fines may also be created through refining or beating, from mechanical and chemical pulp fibres, respectively [25]. Subramanian et al. [26] considered fibrillar fines, microfines and microfibrillar cellulose in the same category, i.e. particles that pass a 75-μm diameter round hole or a 200-mesh screen of a fibre length classifier. Such a definition indicates that MFC may also be considered as fines. Both materials are composed of relatively small and fibrillated components. However, according to Turbak et al. [19], no amount of conventional beating yields the microfibrillation obtained with an optimally homogenised product. The microfibrillation mentioned by Turbak et al. [19] does not seem to refer to the creation of micrometre sized particles but to the fibrillation of fibres into individualised microfibrils with diameters less than 100 nm [15]. In this context, it is appropriate to introduce in this review a scale that has been widely emphasised during the last years within modern technology, i.e. “nano”. It seems to be widely accepted that a nanoscale refers to sizes between 0.001 and 0.1 μm (1 to 100 nm). This implies that the nanofibril term refers to fibrils with diameters less than 100 nm. Based on this definition, it seems obvious that microfibrils can be considered nanofibrils, which also are composed of crystalline and amorphous regions. However, the difference between microfibrils and nanofibrils is that the former is a well-defined biological structure found in plant cell walls, whereas the latter can be considered a technological term introduced to describe secondary and engineered structures with diameters less than 100 nm. As mentioned above, conventional MFC production yields materials with inhomogeneous sizes. However, the fibrillation can be facilitated by, e.g. pre-treating the cellulose fibres enzymatically [16, 17, 19] or chemically [16, 18, 20]. Pre-treatments have thus facilitated the production of homogeneous fibril qualities, with fibril diameters less than 100 nm [15,19]. In addition, some authors have reported a filtration procedure to remove poorly fibrillated fibres, thus maintaining mostly the fraction of homogeneous nanofibrils [19].

Table 2.1 Components of micro fibrillated cellulose [15, 17, 24]

Diameter (µm)	**Biological structures**	**Technological terms**
10 to 50	Tracheid	Cellulose fibre
<1	Macrofibrils	Fibrillar fines, fibrils
<0.1		Nanofibril, nanofibres
<0.035	Microfibril	
0.0035	Elementary fibril	

Table 2.1 are the terms and sizes according to terminology and morphology reported in the literature. In general terms, the production of homogeneous fibril qualities may require major costs, including costs related to pre-treatments and to energy consumption during production. The less energy that is utilised, the less is the fibrillation of cellulose fibres and the less the amount of produced nanofibrils [15, 19]. Considering that conventional fibrillation (e.g. homogenisation without pre-treatment) produces a material that is inhomogeneous and may contain a major fraction of poorly fibrillated fibres and fines, can we state that MFC is a nanostructure? MFC per se is not necessarily a nano-material, but contains nano-structures, i.e. the nanofibrils. To define MFC as a nano-structure, it is necessary to give substantial evidence with respect to (1) the fraction of fibrillated fibres, (2) the fraction of nanofibrils and (3) the morphology of the nanofibrils in an MFC material. Provided that a given MFC is composed of an appropriate fraction of individualised nanofibrils, the MFC will have a major influence on the rheological, optical, mechanical and barrier properties of the corresponding materials. Commonly, morphological evidences are given by microscopy and subjective evaluations. Researchers may focus on the visualisation of nano-structures, applying equipment designed for nano-assessment, e.g. SEM, AFM and TEM [19].

2.5 Nanocellulose

Nanocellulose is one of the most promising innovations for the modern forest sector [26, 27]. Nanocellulose fibers possess outstanding properties that include “green” and renewable, high crystallinity varying from 65 to 95% depending on their origin [28, 29]. Natural cellulose fibers with a diameter of 20–50 micrometer are made of thousands of microfibril with a diameter of a few or tens of nanometers that can form smoother films that scatters less light than regular paper. These cellulose fibers can even be dissolved and then used to make transparent films by the same process as plastic industry [30]. In addition, MCF and CNF have extremely high tensile strength of 2-3 GPa [30, 31], and high stiffness with an elastic modulus up to 138 GPa [31, 32, 33]. They also possess a very low coefficient of thermal expansion (CET of 0.1 ppm K^{-1}) [34], which are comparable to quartz [35]. When cellulose nanofibrils are dried from a water suspension, strong interfibril interactions are formed by hydrogen bonds [36]. These interactions prevent the nanofibrils to be redispersed again after drying. This can together with the good mechanical properties of cellulose nanofibrils be utilized in cellulose nanofibril films and composites. In the literature, studies on films based on MFC from wood cells [37-40] and parenchyma cells [41-43] or bacterial cellulose (BC) [44-46] are reported. The MFC films are typically prepared from water suspension by film casting and water evaporation [37, 39, 41, 43]. Films can also be formed by vacuum filtration on a funnel followed by drying [40, 46]. An alternative method is to dewater the suspension by gradual compression in a mould with porous plates [47]. Most of the water is forced to leave the suspension through the porous plates. After compression, the film is dried during hot-pressing. The highest stiffness of 30 GPa is reported from vibration reed testing of a BC nanofibril film [18]. The reported values for MFC nanofibril films are 1-3 GPa, [41] 4.6 GPa, [43] 6 GPa, [37] 7 GPa, [42] 8 GPa, [40] and 16 GPa [38]. Some factors affecting the stiffness of the films are nanofibril orientation and density. There is not much information regarding the film structure in the literature, but it seems as if the films showing the lowest stiffness are prepared by solvent casting [37, 41, 42], while the stiffest films are dried by hot-pressing [38]. The hot-pressing resulted in a film of very high density, 1480 kg/m3 [38]. In general, with a few exceptions, the structural information in the literature is poor for these materials. Proper structural information is necessary for improved understanding of structure-mechanical property relationships. Parameters that are, for example, likely to affect the properties are fibril orientation, density, degree of fibrillation, degree of crystallinity, molecular weight, hemicellulose content and solvents used during film forming [51] . Due to the various unique properties of the films made from CNF and MCF, they are promising potential candidates for oxygen-barrier layers [48, 49] and future electronic devices [50], such as food-packages and flexible displays, respectively. Nanocellulose differs from cellulose in its appearance and form, because nanocellulose is gel-like material in which the fibrils are present in water dispersion. Because of the properties of nanocellulose, it has become a desired raw material, and products containing it would have several uses in industry 52] .

2.6 Properties of Nanocellulose Films

Generally speaking, Nanocellulose film is strong, translucent and easy-to-handle. Films had superb oxygen barrier properties even at high humidity (0.8 $cm^3 \times mm/m^2$ /day; 23°C, 80% RH) [27]. Films had smooth and shiny surface, great visual appearance and excellent printing properties. Films are also impermeable to grease and mechanically very strong

[53] . Table 1 below summarizes the Minimum property requirements for polymer based flexible display substrates.

Table 2.2 Minimum property requirements for polymer based flexible display substrates

Property	**Requirement**
Optical *Total light transmittance over visible wavelength range Haze*	 >85% <0.7%
Thermal *Degradation temperature* *Coefficient of linear thermal expansion (CLTE)*	 >150°C <20ppm/°C
Barrier properties *Water vapor transmission rate per day* *Oxygen transmission rate per day*	 1-10g/m^2 <10-6g/m^2 for OLED 1-10ml/m^2 <10-5ml/m^2 for OLED
Average surface roughness	<5nm
Chemical resistance	Able to resist acid, base and solvent
Flexibility	Able to bend over 0.03m diameter radius 1000 times

2.6.1 Optical properties

One of the amazing properties of transparent paper substrates is their high optical transmittance and tunable optical haze. Regular paper made from common fibers is opaque, but when the fibers go down to nanoscale, the paper becomes transparent due to denser structure [29]. CNF films are expected to be transparent since the diameter of CNF is less than one-tenth of the wavelength of visible light; when the diameter of reinforcing elements is located in this range, they are not expected to cause any appreciable light scattering [50, 54]. Fukuzumi et al. layers [50] found 90% and 78% transmittance at 600 nm of about 20 μm thick CNF films prepared from TEMPO-oxidized softwood and hardwood, respectively [55]. Nogi et al [51] investigated the relationship between surface roughness and transparency of nanofiber films. They found that the surface light scattering caused their films to look like translucent. When the surface of the films was polished by emery paper, the transmittance was increased from around 20% (thickness 60 μm) to 71.6% (55 μm) [55]. Zhu et al [56] modeled the electromagnetic scattering cross section fibers with 25 nm and 50 nm diameters [50]. The result indicates that the light scattering decreases sharply with increases in fiber size, which agrees well with Rayleigh scattering theory [50, 57]. The nanopaper made from 10 nm and 50 nm fibers have a similar diffusive transmittance at 92–93%, but the specular transmittance of nanopaper made from 50 nm fibers is much lower than nanopaper made from 10 nm fibers [50, 57].

The ability to tune the optical haze is critical for various applications. High optical haze is preferred for thin film solar panels and outdoor display applications, while high optical clarity (low haze) is preferred for most indoor displays [52, 57]. The optical haze and transmittance of transparent paper can be tuned by the porosity and the size of fiber. It is critical to design transparent paper with tunable optical properties with low-cost processes [57]. Hu et al. recently investigated highly transparent and hazy paper with hybrid cellulose [53, 57]. The regular wood fibers act as a scaffold of the paper, while NFC fills the voids to decrease the light scattering. Since NFC has a similar light refraction index 1.5 with the regular fiber as opposed to air, the paper may be tuned from opaque to transparent depending on the degree of space filled with NFC [29, 58].

The ability to manage the light scattering effect of transparent paper without sacrificing its original high transmittance is critical for the application in optoelectronics since different devices have different requirements for the optical properties [59]. The ability to modulate the dimension of cellulose fibers in the nanoscale and microsized range by advanced processes enables paper to possess a tailored light scattering effect while maintaining high optical transmittance [60, 54, 59].

Quantitative method to describe the light scattering of transparent substrates is the haze value [54]. Tunable optical haze is a performance-enhancing characteristic of transparent paper compared to plastics used in flexible electronics, because paper is not only a substrate but also a functional component for electronics. This characteristic has great potential to open up new opportunities for transparent paper [54].

The presence of both high transmittance and high haze will be desirable for optoelectronic devices such as thin film solar cells. The efficiency of a thin film solar cell will increase with the enhanced light trapping [61, 29].

2.6.2 Mechanical properties

The mechanical properties of substrates or nanocellulose films play an important role for the comprehensive device [62, 63]. Mechanical properties of CNF films prepared form different cellulose sources by solvent casting or filtration were reported during the past few years. Taniguchi and Okamura [39] prepared microfibrillated cellulose with diameters in the range of 20-90 nm from natural fibers such as wood pulp, cotton, tunicin, chitosan and silk fibers. Translucent films with 3-100 μm thickness were obtained by casting the microfibers suspension on a plastic plate followed by air-drying [53]. Although the exact values of tensile strength were not reported, they have found that the tensile strength of these films formed by wood pulp microfibers was about 2.4 times that of print grade paper and 2.7 times of polyethylene [53]. They suggested that the higher tensile strength was due to the large surface area of microfibers, resulting in stronger hydrogen bonding and enhanced tensile strength of films [53]. Henriksson et al [28] prepared porous cellulose nanopaper films with high toughness from wood nanofibrils by vacuum filtration. The porosity of these films was adjusted by solvent exchange. The structure-property relationships were discussed in their work. The films prepared from water have 28% porosity and show tensile strength and modulus as high as 214 MPa and 13.2 GPa, respectively. When increasing the porosity (from 19% to 40%), the tensile strength and modulus decreased remarkably from 205 MPa to 95 MPa and 14.7 GPa to 7.4 GPa, respectively [63, 64]. Fukuzumi et al [50] prepared transparent films from TEMPO-oxidized cellulose fibers by vacuum filtration. These nanosize cellulose fibers were prepared from TEMPO/NaBr/NaClO oxidation and mechanical disintegration. The films they prepared have tensile strength as high as 233 MPa (softwood cellulose) and 222 MPa (hardwood cellulose); modulus as high as 6.9 GPa (softwood cellulose) and 6.2 GPa (hardwood cellulose) [64, 27]. Saito et al. [30] performed the oxidation step under TEMPO/NaClO2/NaClO system, they found the tensile strength increased remarkably to 312 MPa; based on their knowledge, they thought that the degree of polymerization (DP) is an important factor for the strength and flexibility of individual cellulose fibers and thus directly influence the properties of the films which they formed. The theoretical E-modulus of cellulose fibers as a function of fibril angle was calculated by Page et al [55] and found to be 80 GPa at zero fibril angle. Cox [26] reported that the E-modulus of a well bonded random network of ideal straight and infinite fibers is one third of the E-modulus of the individual fibers. According to the conclusions mentioned above, the maximal theoretical value is about 27 GPa (80/3). As reported in the table 1.1, real fibers are not ideal (they are not straight and not infinite), thus the modulus values are much lower than the theoretical one. Table 2 gives a summary of different mechanical properties of nanocellulose films.

Table 2.3 Mechanical properties of CNF films [53]

Starting material	Preparation method	Tensile strength /MPa	Young's modulus/ GPa	References
Softwood dissolving pulp	Vacuum filtration	104	14.0	65, 67
Bleached sulfite softwood pulp	Casting	180	13.0	66
Never-dried softwood and hardwood bleached kraft pulp	Vacuum filtration	222-233	6.2-6.9	68
Hardwood bleached kraft pulp	Vacuum filtration	312	6.5	69

2.6.3 Thermal properties

Thermal properties of transparent paper are quite important for its application in flexible electronics. Most fabricated devices undergo a heat treatment at a temperature of approximately 150–200^{o}C to obtain the maximum performance of electronic devices [57, 53]. Transparent paper must withstand the processing temperature without wrinkling, tinting, or thermally decomposing. The DP of original cellulose begins to decrease around 250^{o}C, and extensive degradation of cellulose occurs when the temperature is over 300^{o}C

[58-59, 53]. The CTE of crystalline cellulose in the axial direction is around 0.1 ppm K^{-1}, which is more than an order of magnitude lower than plastics, most metals, and ceramics [60, 70]. The optically transparent paper made of cellulose nanofibers has a CTE of 0.1 ppm K^{-1}). This is desirable for displays since it can maintain the dimensional stability under thermal processing condition [57, 61, 53]. Nanopaper fabricated by cellulose nanofibers shows lowest CTE compared to regenerated cellulose fillm and PET, which shows that it has the potential to replace current plastic to fabricate flexible electronics [51].

2.6.4 Oxygen and water vapor barrier properties

Due to the high crystalline content of cellulose and the dense nanofiber network formed by nanofibers, the CNF films are expected to have good barrier properties [53]. Syverud and Stenius [62] reported an oxygen transmission rate of about 17.75 mL m^{-2} day^{-1} Pa^{-1} though CNF films of 21 μm thickness. Fukuzumi et al. [50] reported an unmodified polylactic acid (PLA) film with an oxygen permeability as high as 746 mL m^{-2} day^{-1} Pa^{-1} , which could be decreased to 1 mL m^{-2} day^{-1} Pa^{-1} after casting a thin CNF layer on the PLA film. However, the water vapor transmission rate (WVTR) of CNF films was not investigated till recently. Some results about WVTR were reported on potato starch films and amylopectin films [50, 63, 53]. It was found that cellulose nanofibers and starch composites can decrease the water vapor sorption ability, and the water vapor diffusivity decreases rapidly with increasing the content of cellulose nanofibers.

2.7 Unique Properties of Nanocellulose for Photoelectronic Device Application

Organic Solar Panels have emerged as potential economical alternative to silicon-based solar cells due to their low-cost fabrication by solution processing, lightweight and compatibility with flexible substrates [71, 64].

Cellulose is the largest biopolymer on earth, with the feature of excellent biodegradability, biocompatibility, sustainability, versatility, and accessibility, high mechanical strength, and unique optical properties [65, 72].

Cellulose fibers can be used to make transparent films [66], such property is suitable to produce highly transparent and smooth substrates [37, 40, 67, 68]. These properties make these films an interesting alternative for substrates in the electronic industry [65]. Nanocellulose materials are important because of their advanced commercial attributes in energy, but more importantly for their amenability to low cost, large scale, roll-to-roll manufacturing capability [57]. The substrate is one major component of the electronic device. The properties of the substrate will ultimately determine if the device will be flexible or rigid, heavy or light, transparent or opaque, and if it can be applied to roll-to-roll processing [57]. Regular paper and plastic are two common flexible substrates for printed electronics, and nanopaper or nanocellulose films are an emerging transparent and flexible substrate [57, 70, 51]. Table 2.3 is a comparison of nanopaper or nanocellulose film, regular paper, and plastic [45]. Plastic is an unsustainable petroleum-based product that causes ‘white pollution’. Any wood based substrate such as regular paper and nanopaper is renewable, recyclable, and biodegradable, leaving a negligible environmental footprint. Paper also has good shape stability under high temperatures and cellulose has low CTE. Paper also has better printability than plastic[57] . Nanopaper or nanocellulose film possesses high optical transmittance and excellent mechanical properties, including high tensile strength, large Young's modulus, and a small bending radius. Nanopaper meets the requirements for device fabrication, and environmental sustainability [53, 57].

Table 2.4 Comparison of nanopaper or nanocellulose film, traditional paper, and plastic [73-77]

Characteristics	nanopaper	traditional paper	plastic
Surface roughness (nm)	5	5000 - 10000	5
Porosity (%)	20 - 40	50	0
Pore size (nm)	10 - 50	3000	0
Optical transparency at 550 nm (%)	90	20	90
Max loading stress (MPa)	200 - 400	6	50
Coefficient of thermal expansion (CTE) (ppm K^{-1})	12 - 28.5	28 - 40	20 -100
Printability	good	excellent	poor
Young modulus (GPa)	7.4 - 14	0.5	2 - 2.7
Bending radius (mm)	1	1	5
Renewable	high	high	low

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Chapter 3: Production of Nanocellulose by Mechanical Refining and TEMPO Mediation Oxidation Processes

3.1 Introduction

Substrates play a key role as to the foundation for optoelectronic devices [1]. Mechanical strength and optical transparency are among the critical properties of these substrates that determine its eligibility for various applications. The optoelectronic device industry predominantly utilizes glass substrates and plastic substrates for flexible electronics; however, recent reports demonstrate transparent nanopaper based on renewable cellulose nanofibers that may replace plastic substrates in many electronic and optoelectronic devices [1, 2]. Nanopaper is entirely more environmentally friendly than plastic substrates due to its composition of natural materials; meanwhile it introduces new functionalities due to NFCs' fibrous structure [1].

Mechanical refining is widely used prior to homogenization process in order to facilitate defibrillation [1-7, 12]. Disc refiners, PFI mills and Valley beaters were reported prior to the production of NFC [8, 9]. During this process, the dilute fibre suspension is forced through a gap between rotor and stator discs. These discs have surfaces fitted with bars and grooves against which the fibres are subjected to repeated cyclic stresses. This mechanical treatment brings about irreversible changes in morphology and size of fibres [10, 12]. Actually, under the effect of the intense mechanical shearing action in the disc refiner, the cellulose fibres are subjected to repeated loading action of the refiner bars, leading to a progressive peeling off of the external cell wall layers, namely the primary (P) and first secondary (S1), making the thicker secondary cell wall layers [11] more exposed to fibrillation during the homogenization process. However, mechanical refining brings about a damage of the microfibril structure by reducing molar mass and degree of crystallinity [1, 12].

Studies focusing on mechanical properties of neat nanocellulose films are few. Therefore, it is essential to study these properties in detail, which further opens the gateway to any improvements needed in raw materials or production processes [6].
However, solely mechanical processes consume large amounts of energy and insufficiently liberate the nanofibers while damaging the microfibril structures in the process [1].

Currently, TEMPO mediated oxidation is the most common chemical pretreatment and it is worthy of study in nanofiber preparation. It is well known method for modifying selectively the surface of native cellulose under aqueous and mild consideration [9, 10, 21, 22].

Mechanical treatments are currently considered efficient ways to isolate nanofibers from the cell wall of a wood fiber; however, solely mechanical processes consume large amounts of energy and insufficiently liberate the nanofibers while damaging its structures. Pretreatments, therefore, are conducted before mechanical disintegration in order to effectively separate the fibers and minimize the damage to the nanofiber structures [29, 26–28]. TEMPO-mediated oxidation is proven to be an efficient way to weaken the interfibrillar hydrogen bonds that facilitate the disintegration of wood fibers into individualized nanofibers yet maintain a high yield of solid material [19, 23, 24].

In this study, the TEMPO/NaBr/NaClO system was used to modify the surface properties of the regular kraft bleached softwood fibers by selectively oxidizing the C6 hydroxyl groups of glucose. The repulsive force resulting from additional higher negative charges at the surface of the nanofibers loosens the interfibrillar hydrogen bonds between the cellulose nanofibers resulting in the fiber cell walls are significantly open and crush [1, 8, 25]. TEMPO is a highly stable nitroxyl radical which is used extensively in the selective oxidation of primary alcohols to corresponding aldehydes and carboxylic acids. In aqueous environment, TEMPO catalyzed the conversion of carbohydrate primary alcohols to carboxylate (COO^-) functionalities in the presence of a primary oxidizing agent, e.g. sodium hypochlorite (NaOCl) [30, 36, 37].

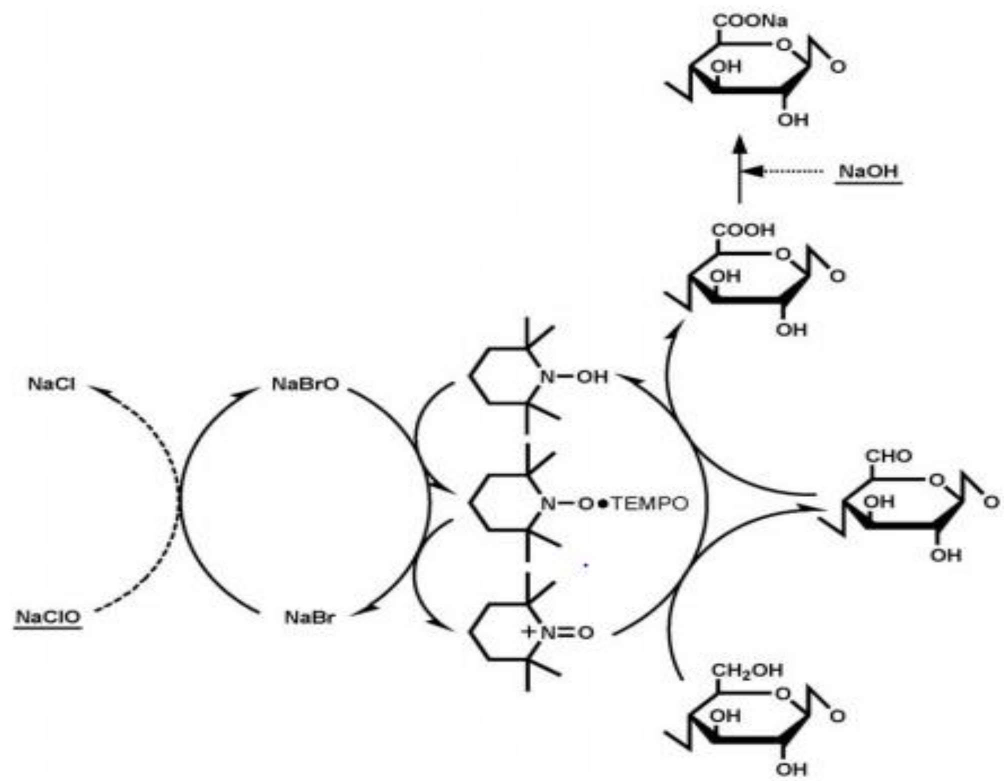


Figure 3.1 Schematic representation of the regioselective oxidation of cellulose by 2,2,6,6 tetramethyl-1-piperidinyloxy (TEMPO) process [37]

As noted above, the basic principle of the process consist of the oxidation of cellulose fibers via the addition of NaClO to aqueous cellulose in the presence of catalyst called 2,2,6,6 tetramethyl -1- piperidinyloxyl (TEMPO) and NaBr at a pH between 10.5 – 11 at room temperature [36]. The C6 primary hydroxyl groups of cellulose are thus selectively converted to carboxylate groups via the C6 groups, and only NaClO and NaOH are consumed as shown in Fig.3.1. In this work we proposed a simple method to manage the mechanical and optical properties of films through mechanical refining and chemical treatment.

3.2 Experimental

3.2.1 Materials

Pulp

Bleached softwood kraft pulp that has already been refined to a certain freeness degree was provided by a local paper mill.

Chemical

TEMPO (2,2,6,6-Tetramethylpiperidin-1-yl) oxyl), sodium bromide (NaBr) and sodium hypochlorite (NaClO) were purchased from Aldrich-Sigma (Stockholm, Sweden).

3.2.2 Nanocellulose production

KRK Refining

This experiment focused on studying the effect of refining intensity on fiber properties. The properties of the pulp were measured before refining. Properties measured were freeness, fiber length, paper strength (tensile, tear, density). The pulp was refined in the pilot KRK refiner at 10% consistency and constant flow rate of 50g/m. The refining temperature was about 20-26 ºC. The refining parameters studied were refining bar gap, energy and number of passes. These measurements were done in order to quantify the refining intensity and the mechanical and optical properties of the fibre. The refining speed was 3,600 rpm. Refining conditions are given in table 3.1. The refining energy was measured with PowerLogic Ion Enterprise energy software.

Table 3.1 Summary of the parameters studied in this experiment.

Parameters	Condition
Consistency	10%
Refiner speed	3600 rpm
Flow rates	50 g/min
Gap	30 and 50 microns

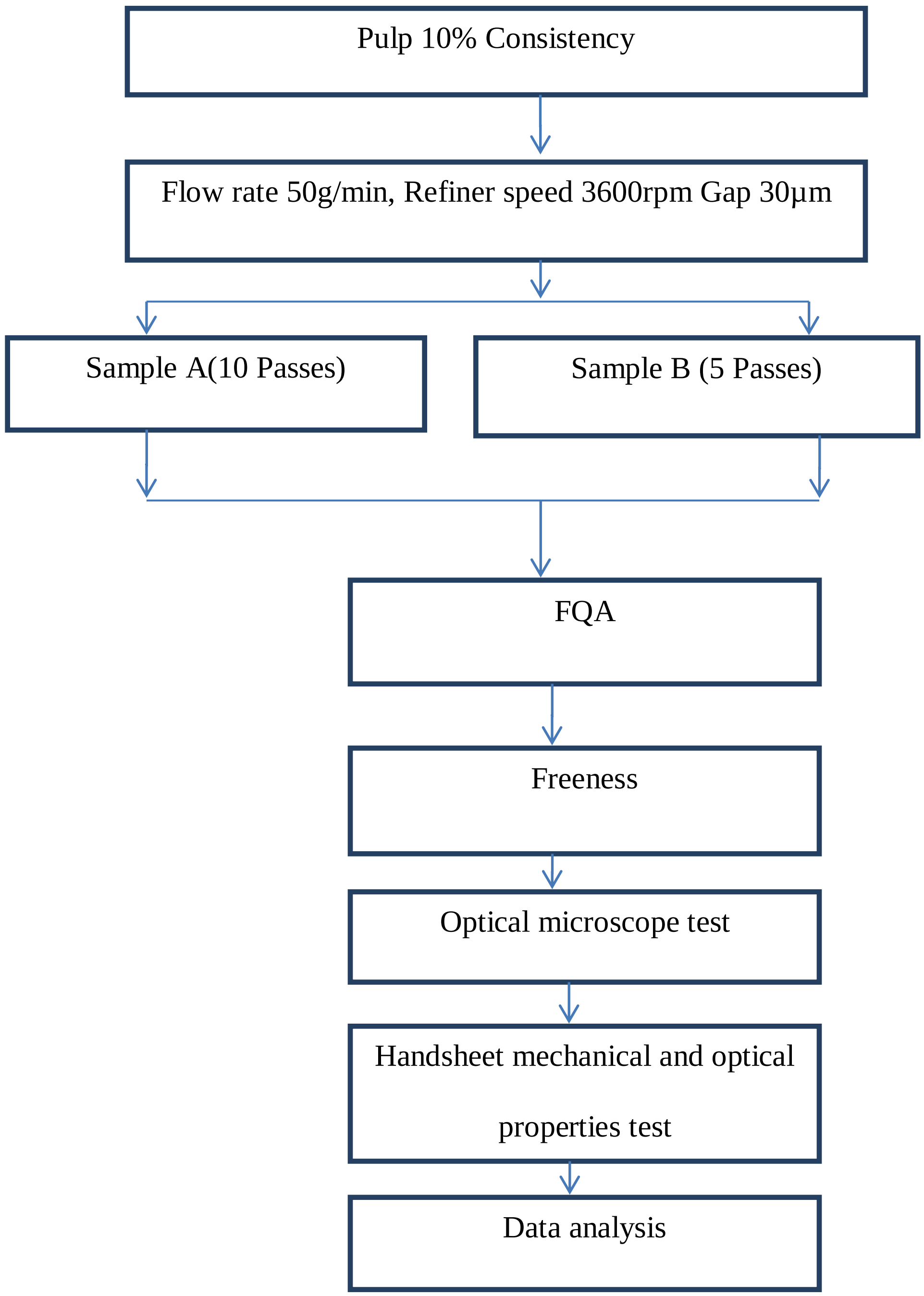


Figure 3.2 Design of experiment for KRK Refining

PFI Beating

For the PFI refining, we transferred the wet pulp and water used for soaking to the disintegrator at a consistency of 10%. The revolution counter was set to 0. Disintegrate was done for different revolutions of 5,000, 8,000 and 10,000rpm and the pulp was completely disintegrated to obtain different freeness levels as per Tappi T 248 sp-00. The pulp freeness was measured on a CSF tester as per Tappi T 227 om-99. The drainage time of the pulp was determined on a Handsheet former as per Tappi T 221 cm-99. The fiber morphology (i.e., the average fiber length, fiber width, fines, and coarseness) was determined on an L&W Fiber tester (Lorentzen &Wettre, Kista, Sweden) as per its operating manual.

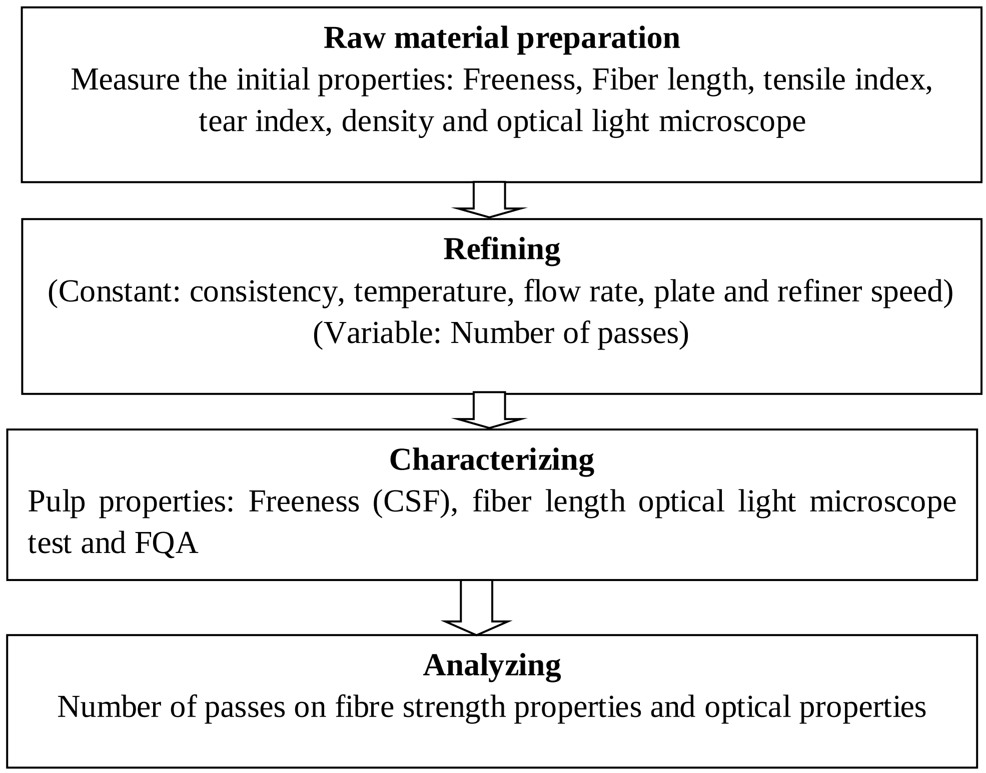


Figure 3.3 Experiment chats for KRK and PFI

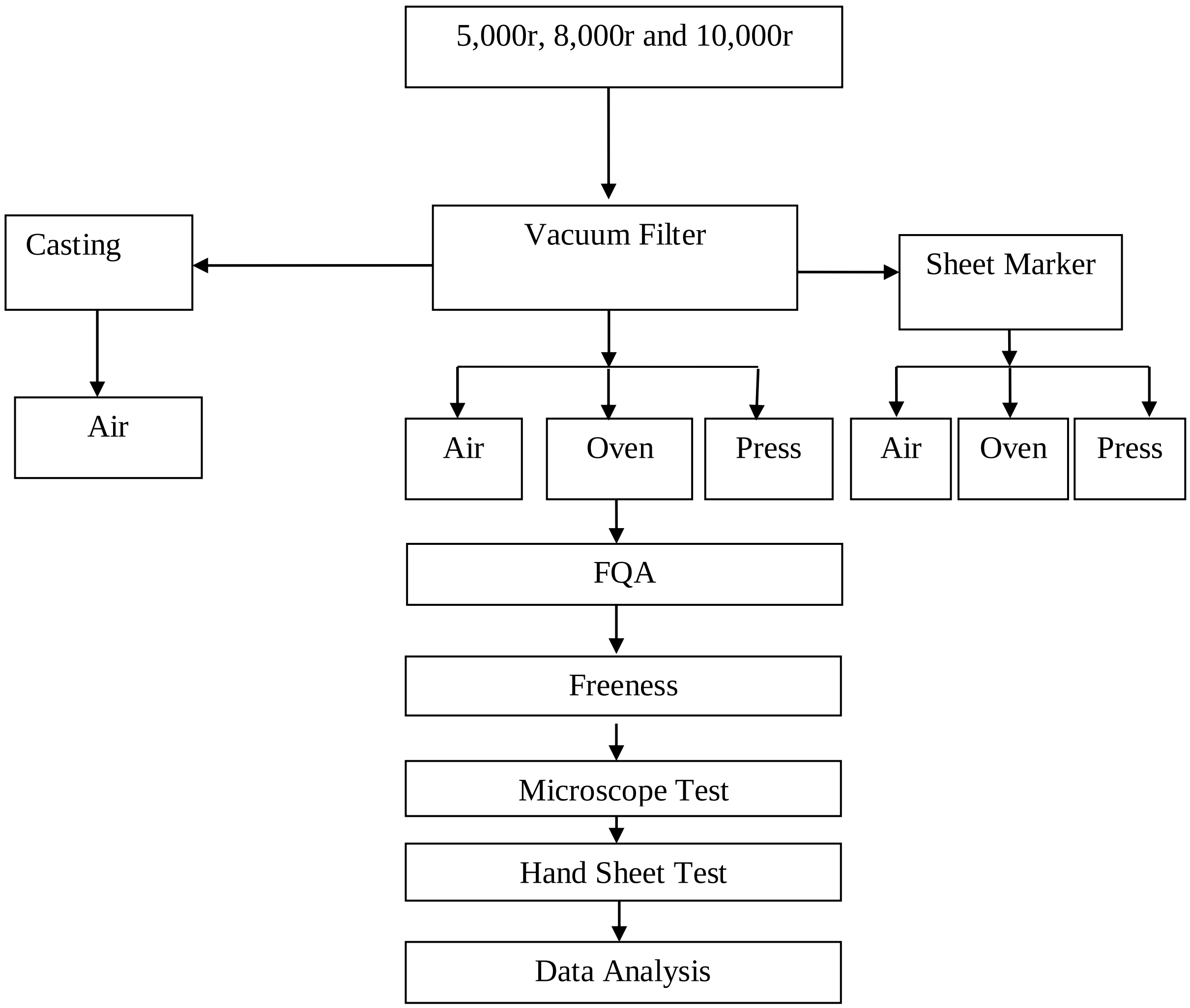


Figure 3.4 Design of experiment for PFI Beating

TEMPO Mediation Oxidation

5 g (dry weight) of wood fibers were dispersed into 450ml of deionized water, 0.11g of TEMPO and 0.64g of sodium bromide (NaBr) were dissolved in 50ml of deionized water and the mixtures were finally stirred continuously for 10 min at 700 rpm to form a uniform suspension. 1.50g of sodium hypochlorite (NaClO) with a concentration of 10 wt % was titrated into the abovementioned suspension at the rate of 0.13ml/min for oxidation process to start. The reaction time was monitored and the pH of the reaction system was kept constant between the ranges of 10.5-11. The reaction lasted approximately 3-4 hours; however, the mixture was continuously stirred at 700 rpm for an additional 4 hours to ensure adequate reaction of the wood fibers. The reaction was terminated by adding 50ml of ethanol. This was followed by filtration and washing of the final product by dialysis. Then ultrasonic treatment of 1% tempo oxidized cellulose suspension by sonicator (energy density was 40w/g for 30-60min).

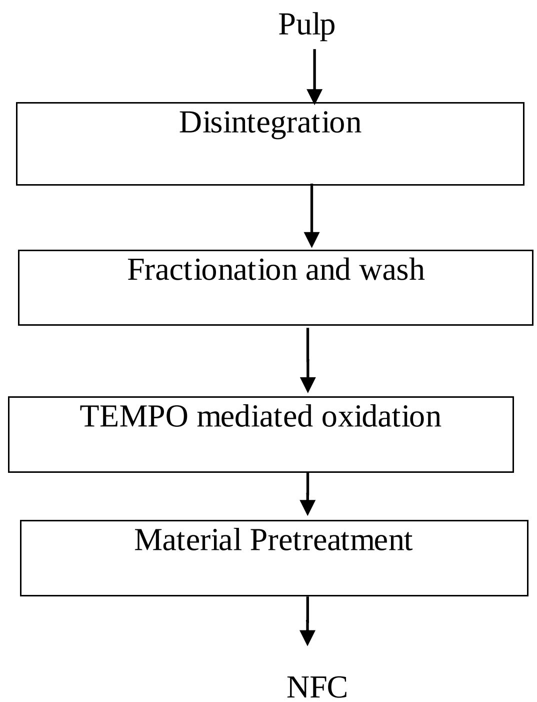


Figure 3.5 Design of experiment for Production of NFC by TEMPO-mediated oxidation and disintegration methods

3.2.3 Characterization

Freeness Test (CSF)

Slurry of approximately 100 mL was taken from the above-mentioned sample, and ion exchange water was added to obtain diluted slurry of 0.3 wt %. This diluted slurry of 1000 mL was accurately measured and taken into a measuring cylinder of 1000 mL capacity to make a test sample. The test sample was measured for temperature with the 0.5° C. accuracy. The freeness of the test sample was measured in accordance with the standard T-227 of TAPPI. Specifically, the quantity of water discharged from the lateral tube was measured with a measuring cylinder, which was corrected to the standard temperature 20° C. in accordance with the temperature of the test sample, which was understood to be the freeness (ml).

Light Microscopy (LM)

The changes in fiber morphology during the mechanical treatment of the pulp fibers were studied using a light microscope (Dialux 20, Leitz, Wetzlar, Germany) at 100-times magnification. Diluted cellulose fiber suspensions after different processing stages were prepared, and one drop of the suspension was placed on a glass slide covered with a coverslip. The images selected were regarded to be representative of the fiber surfaces of the two defibrillated pulp fibers. Fiber Morphology of TEMPO oxidation mediation was also examined using the same procedures.

Fiber Frequency Analysis (FQA)

The dimension and morphology of the wood pulp before and after oxidization was tested using a KajaaniFS300 fiber analyzer and an optical spectroscope (OLYMPUS BX51).

Density Measurements

The weight, area, and thickness of the cellulose fiber films were determined, and the density was calculated. An average of at least five measurements per sample was used for the calculation. The weight of the films was determined on dried films using an analytic balance, and the thickness was determined using a micrometer screw calculating the average of at least three independent measurement at different locations on the film (center, periphery, and between the two).

Determination of Yield in Nanofibrillated Cellulose

A diluted suspension at 0.1-0.2% wt.% was centrifuged at 4500 rpm for 20 min to separate nanofabrillated cellulose (in supernatant) from the non-fibrillated and partially fibrillated residue (in sediment). The supernatant was then removed and the sediment was dried to a constant weight at 100°C in the oven. The yield of CNF was calculated with the following equation below:

$$Yield\,\% = \left(1 - \frac{weight\ of\ dried\ sediment}{weight\ of\ dried\ cellulose\ in\ the\ suspension\ before\ centrifugation}\right) x\ 100 \quad (1)$$

Electron microscopy Test

The morphology of the supernatant and sediment fraction (by centrifuge) was observed by transmission electron microscopy (TEM) and scanning electron microscopy (SEM), respectively. TEM images were obtained by Hitachi HT-7700 with an acceleration voltage 100 kV. A drop of a diluted supernatant (0.01%-0.005%) was deposited on a carbon-coated grid (400 mesh) and allowed to dry at room temperature for 12h. Subsequently, they were negatively stained with 2 % uranyl acetate for 20min in dark place followed by blotting and were used for imaging. The diameter for different CNFs were determined and calculated on the basis of TEM images using an image analyzer program software, Nano measurer. A minimum of 150 measurements were used for evaluating the fiber diameter. For SEM imaging, the sediment was dispersed in deionized water (with solid consistency of about 0.1%) and stirred for 2h to ensure well dispersed solution. The droplet was deposited on a silicon wafer and dried by a Labconco freeze-drying system (Kansas City, MO,USA). In order to improve conductivity, the samples were sputtered with thin gold layer. The images were observed and recorded using a Zeiss EVO40 SEM (Carl Zeiss SMT Inc., Thornwood, NY, USA).

3.3 Results and Discussion

3.3.1 Fiber morphology before and after refining and TEMPO treatment

Fiber Images before and after Refining

The present study evaluated the change in morphology of cellulose fibers during mechanical fibrillation process. The morphological changes of wood fibers were carefully and clearly observed using optical light microscope as shown below. It can be seen that, before fibrillation, pulps consist of fibers with a size of about1.028mm in diameter. After refining to different passes and revolutions, the length of wood fibers becomes short and the cell walls of the fibers were cracked into small fragments. Fig 3.6a-e and Fig. 3.7a-g show the wood fiber unzipped and cleaved in the axial direction that can improve the density of paper. The images show that fibrillation starts at the outer surface of the cellulose fibers and those small-sized fibers are being peeled from the fiber surfaces. Turbak et al. [38] explained two phenomena associated with the refining process of softwood cellulose and termed them external and internal fibrillation. External fibrillation is the raising of fine fibers on the fiber surface through abrasive action, whereas internal fibrillation is related to the breakage of links between the cellulose fibers as a result of mechanical action in the refining processes [38, 39, 41, 42]. It is likely that H-bonds are broken because of the mechanical process, resulting in internal fibrillation. During the mechanical refining process, the cellulose fibers are subjected to repeated loading action of the refiner bars. Hamad [40] reported that, during the refining of cellulose fibers in a disk refiner, the external cell wall layers, the primary (P) and first secondary (S1) layers are gradually peeled off from the fiber surface and expose the inner thicker secondary cell wall layers. On the other hand, the fibers undergo both external and internal fibrillation of the fiber cell walls after about 5 -10 passes and 5,000 – 10,000rev, resulting in a network of micro cellulose fibers. From the microscopy studies, it can be observed that the average fiber diameter decreases with the number of passes. This results in more fibers bridging the network of the film and in increased interaction through both H-bonding and mechanical interaction forces.

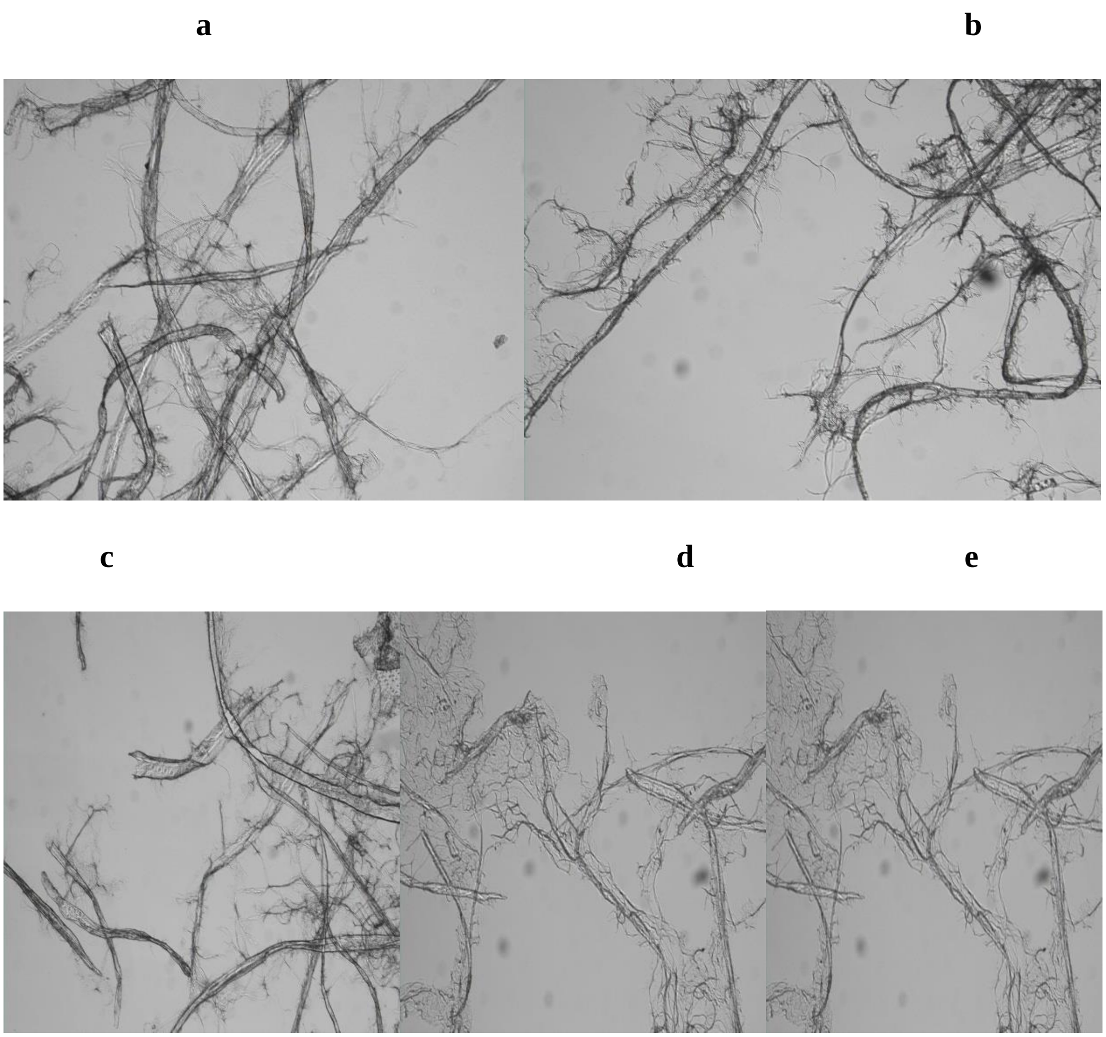
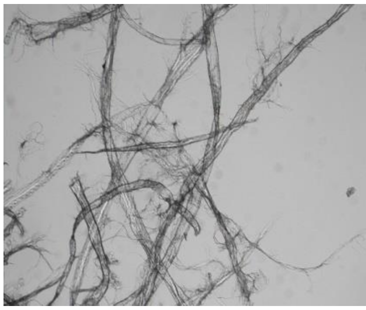
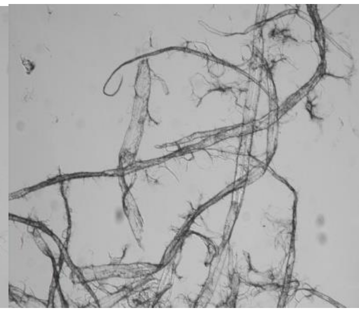
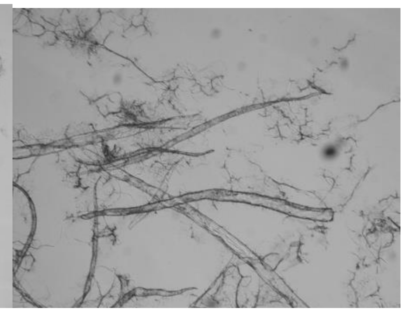


Figure 3.6 Light Microscope Images of KRK Refined Pulp (10X Magnification) (a) Original Fibers (no additional refining) (b) After 5 Passes (c) After 5 Passes + Sonication (c) After 10 Passes (d) After 10 Passes + Sonication (e) 10 Passes + Sonication

a b c

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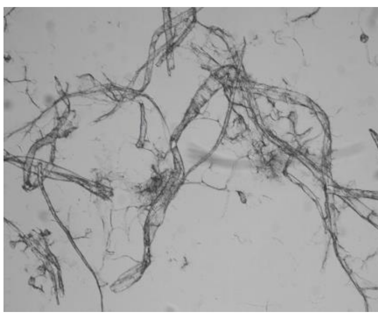  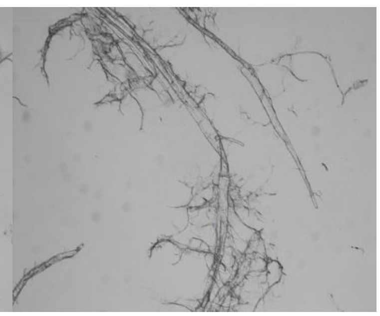

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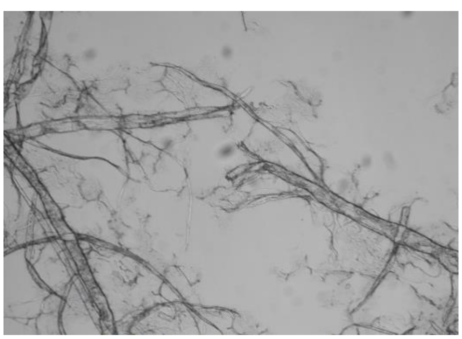

Figure 3.7 Light Microscope Images of PFI Refined Pulp (10X Magnification) (a) Original Fibers (no additional refining) (b) After 5000 r (c) After 5000 r + Sonication (d) After 8000 r (e) After 8000 r + Sonication (f) After 10000 r (g) After 10000 r + Sonication

However, when fibres are ground into nanosize, light microscopy will not be able to observe the morphology of the nanocellulose fibres. Similarly, the FQA is not able to measure the nanosized fibres. Therefore, both LM and FQA results are only from the incompletely fibrillated portion of the fibres, i.e., those much large than nanofibers. In order to observe the nanofibers produced, we have separated the nanofiber portion from the still microfiber portion via a centrifugation process as described in the experimental section. After separation, the yield of nanofiber portion is about 70% and SEM and TEM images of the nanofibers are obtained. Figure 3.7 show a typical image of the nanofibers produced.

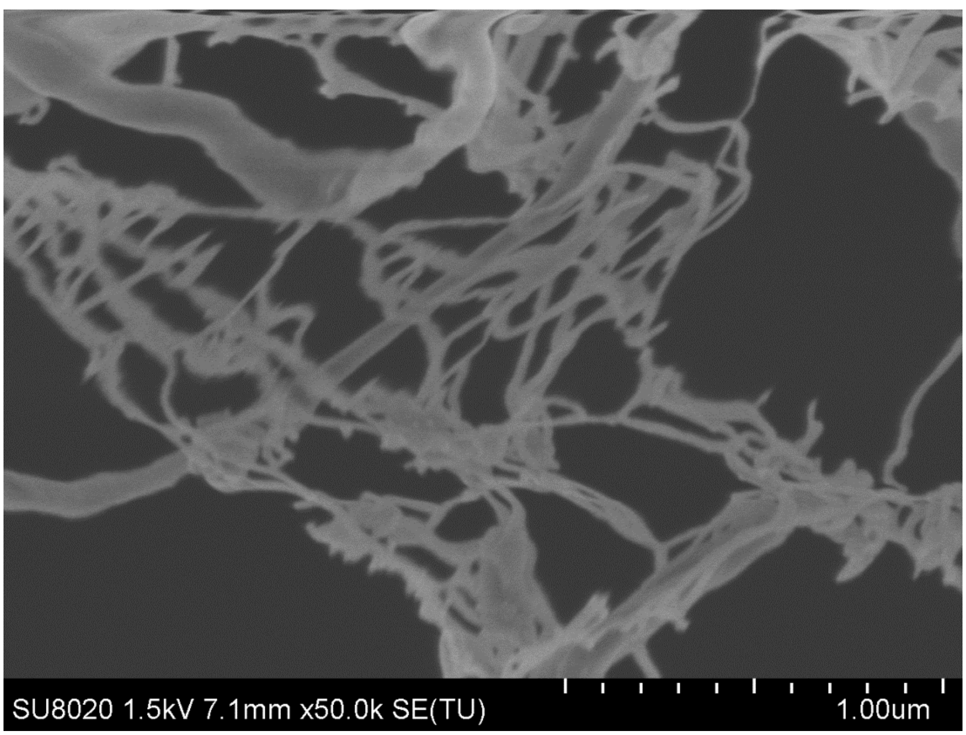

Figure 3.7 SEM Image of Nanocellulose Fibres after 10 Pass Refining and Sonication (Yield ~70%)

Fiber Images before and after TEMPO treatment

The morphological changes of wood fibers images before and after TEMPO treatment were also carefully and clearly observed using Optical light Microscope as shown in the images in Fig. 5.36 below. After TEMPO treatment, the length of wood fibers becomes short and the cell walls of the fibers were cracked into small fragments as seen in fig 3.8b

a **b**

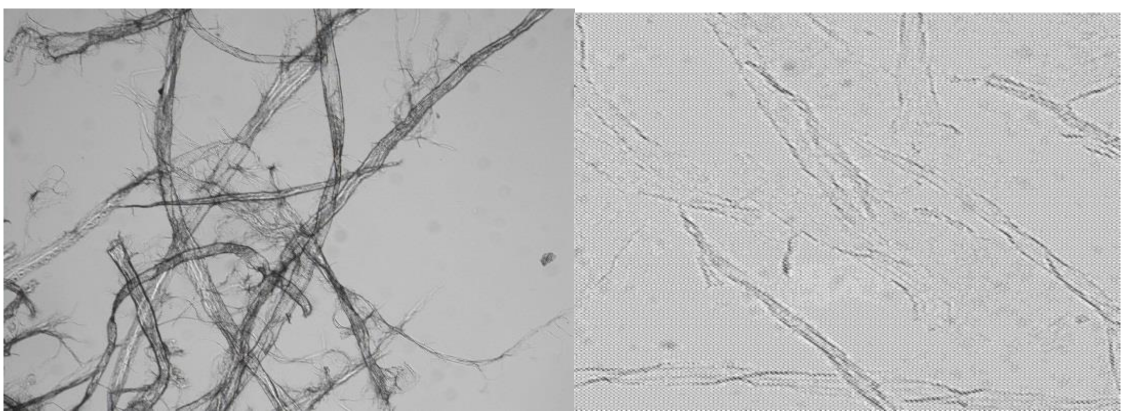

Figure 3.8 Images of Fiber in Light Microscope (a) Before TEMPO Treatment (b) After TEMPO Treatment

However, it must be point out that those observed by LM is much larger than nanofibers produced. In order to observe the nanosized fibres, TEM was used and the results is shown in Figure 3.9.

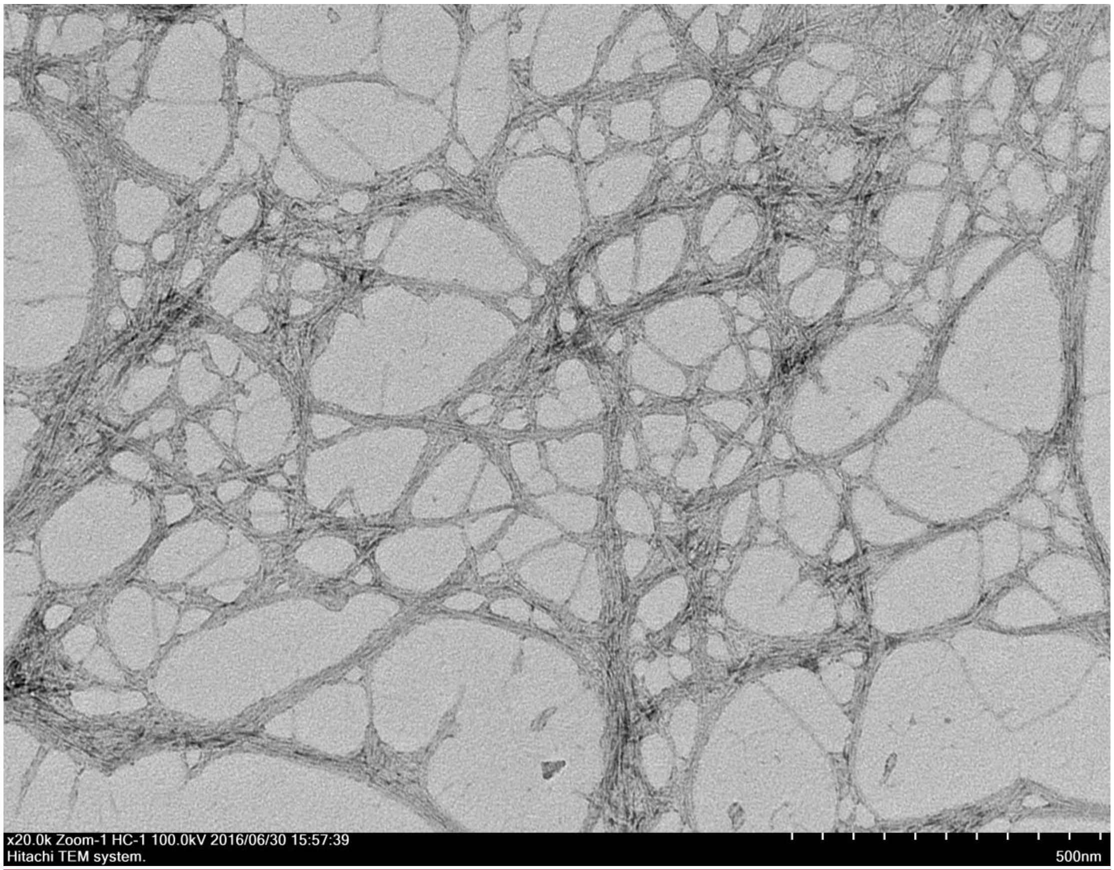

Figure 3.9 TEM Image of Nanocellulose Fibres after TEMPO and Sonication Treatment (Yield ~100%)

Distribution of Wood Fibers before and after Refining

Fiber analyzer FS300 was used to investigate the distribution of fiber length and width before and after refining. The length distribution of original wood fibers is uniform 1.028mm, yet the length distribution after refining the fibers tends to concentrate in the range of 0.7985mm to 0.87733mm, for both KRK and PFI refiners, which indicates wood fibers are cracked into short fibers by refining action or force.

Wood Fibers after TEMPO Treatment

The morphological changes of wood fibers were clearly observed in this thesis. After TEMPO treatment, the length of wood fibers becomes short and the cell walls of the fibers were broken down into small fragments. We have to also remember that this is only from the incompletely fibrillated portion. A large portion of the nanosized fibres are not observed by LM, nor detected by FQA.

Compared to the original fibers, the TEMPO-oxidized fibers swell such that the width of the fibers expanded while the length decreased. The average length of the wood fibers dramatically decreased from 1.028mm to 0.61 nm after the TEMPO treatment, and there was a slight reduction in the average width and an enormous increase in fines. The increased fines, reduced fiber length, and the crushed and unzipped TEMPO oxidized fibers tend to form denser fiber network during fabrication that perpetuates high optical transmittance.

a **b** **c**

Figure 3.9 Images of Pulp in Solution (a) before pretreatment (b) after TEMPO oxidization (c) after disintegration

Several hypotheses were postulated to account for this huge change in the delamination process of TEMPO mediation oxidation process, namely (a) the oxidation generates negative charges that bring forth repulsive forces between microfibrils within the cell wall [10], contributing to loosen the microfibrils cohesion held by hydrogen bonding; (b) the oxidation favours the hydration and swelling of the fibres, making them more flexible and crystalline zone more accessible; (c) oxidation loosens the primary and S1 cell wall making S2 layer more accessible and more prone to fibrillation during the homogenization process; (d) finally, the oxidation results in chain scission in amorphous zone, creating defaults within the fibre cell wall, which facilitates the mechanical fibrillation. Level of oxidation is critical in reducing the energy input and improved the yield of nanofibrillation as well as the transparency degree of the cellulose fiber suspension as shown in Fig. 3.9b. Also, in Fig 3.9, highly homogeneous and transparent appearance is observed after TEMPO treatment and homogenization at the same consistency.

3.3.2 Effect of Refining on CSF

As shown in Fig 3.10 – 3.11, freeness content decreased upon the rise in refining revolutions and numbers of passes for the KRK and PFI refiners. Therefore, the highest and lowest freeness values are related to refinement at 5,000rpm and 10,000rpm for PFI and 5 passes and 10 passes for KRK passes refiner respectively.

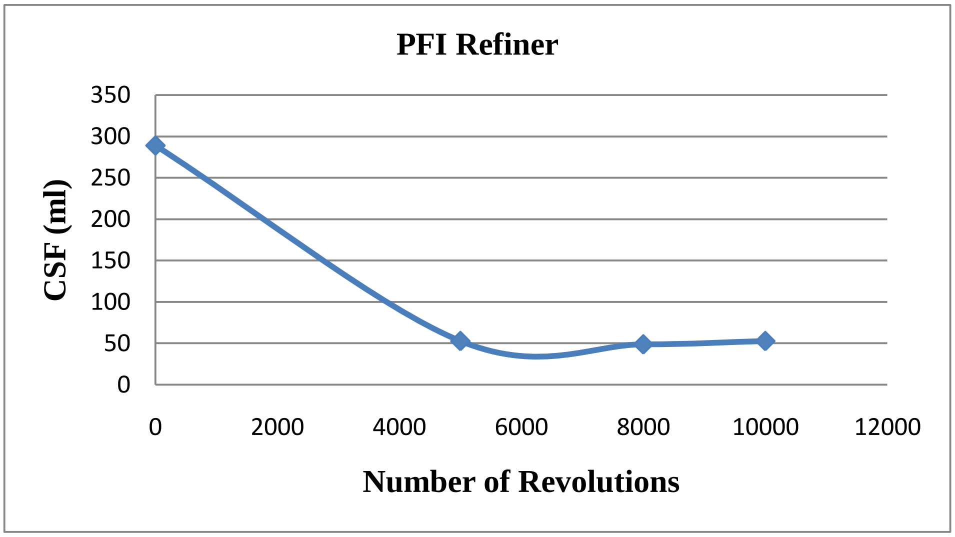

Figure 3.10 Effect of Refining on CSF for PFI refiner

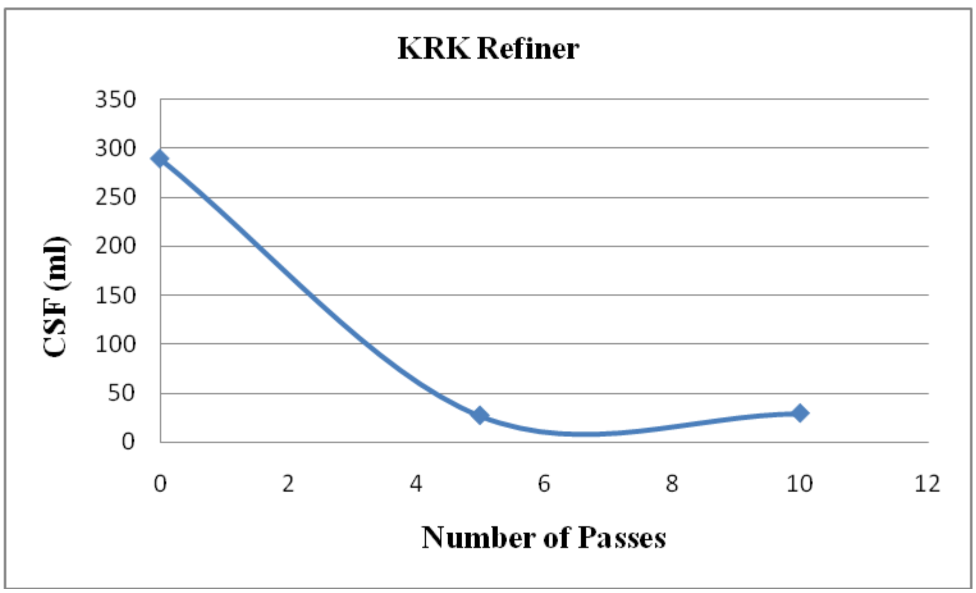

Figure 3.11 Effect of Refining on CSF for KRK refiner

3.3.3 Effect of Refining and TEMPO Oxidation on Fiber Length

The fiber lengths of the pulp samples made at different PFI and KRK refining degrees were tested. Figs. 3.12-3.15 illustrate the effect of PFI and KRK refining on fiber lengths. It can be seen that fiber lengths of both PFI and KRK refining decreased as refining was increased. This can be attributed to the internal fibrillation action of PFI and KRK refiners. Similar trends were noticed for hardwood when Helmer et al. [43] performed beating via valley beater on bleached eucalyptus pulp and observed its effect of fiber length of the pulp. Although, greater fiber shortening was observed in their work than from what was noticed in this work, but it can be attributed to the fact that PFI and KRK refiners apply compressive forces on fibers which leads to an internal fibrillation to the fibers, whereas a valley beater performs fiber cutting. A study on effect of refining performed by industrial refiners on fiber length of softwood and hardwood has been done previously [4, 43]. They all showed fiber shortening as refining was increased. Finally, for the PFI refiner the fiber length was reduced from 0.9595mm to 0.8525mm as we refined from 5,000rev to 10,000rev and for the KRK it decreased from 0.9596mm to 0.877mm at 5 and 10 passes respectively.

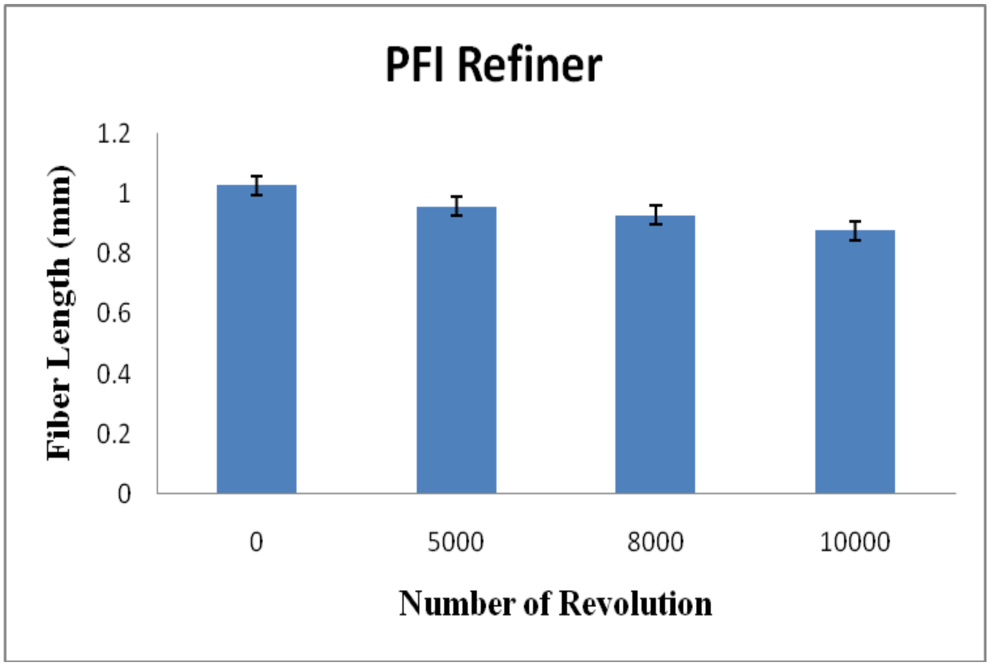

Figure 3.12 Effect of Refining on Fiber Length for PFI Refiner

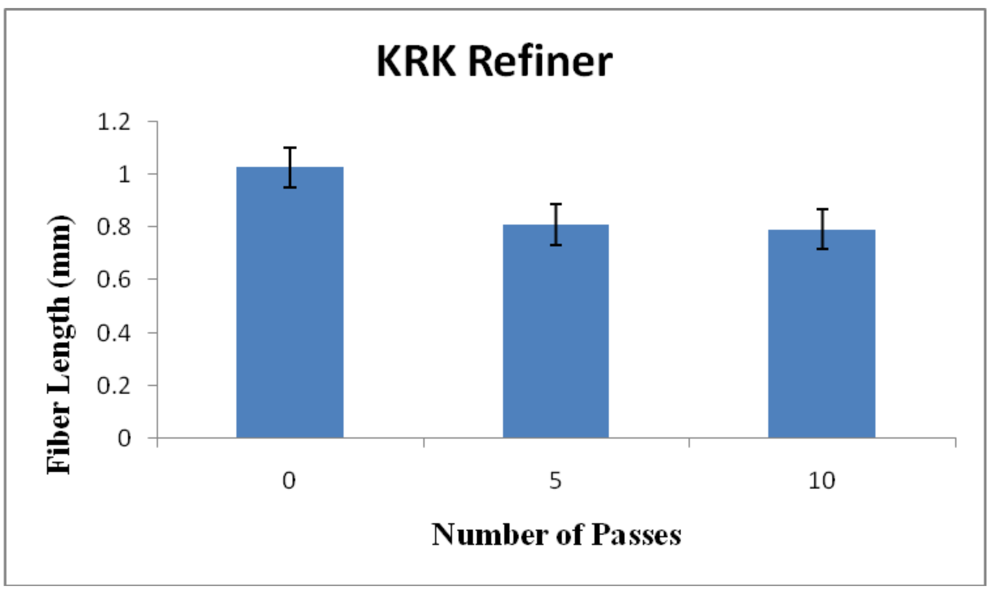

Figure 3.13 Effect of Refining on Fiber Length for KRK Refiner

The fiber length also decreased as CSF increase due to increased refining for both PFI and KRK refiners as shown in Figs 3.14 and 3.15

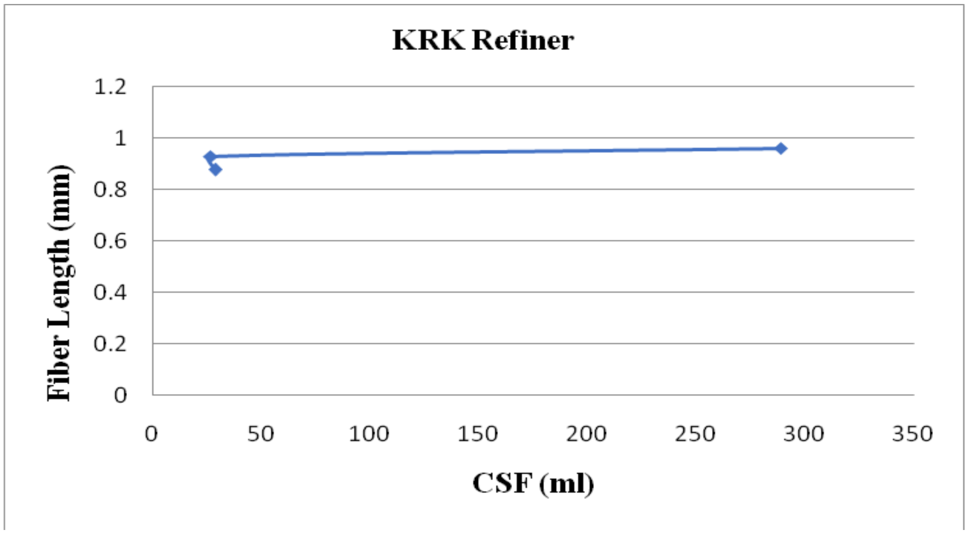

Figure 3.14 Effect of Refining on CSF and Fiber Length for KRK Refiner

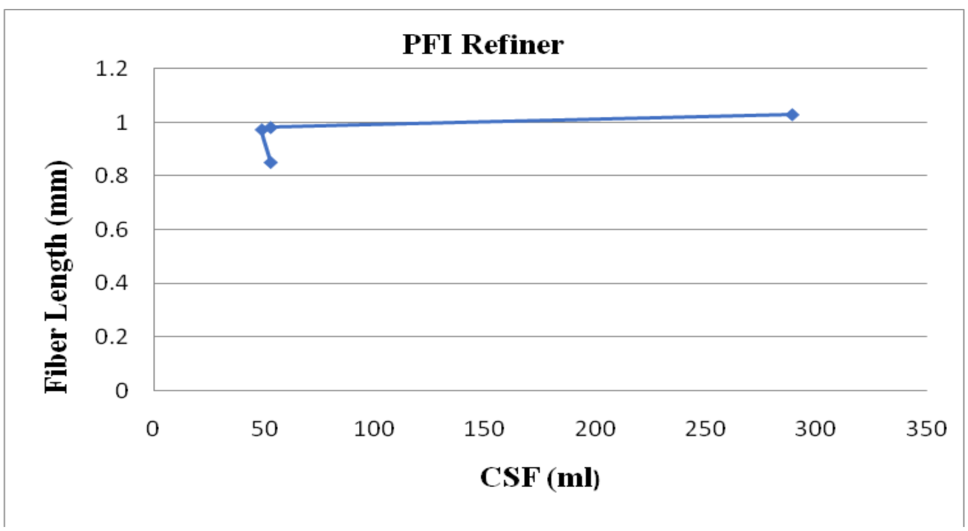

Figure 3.15 Effect of Refining on CSF and Fiber Length for PFI Refiner

3.3.4 Comparison of nanocellulose production techniques from refining and TEMPO oxidation

As noted before, mechanical and optical properties play a major role for nanocellulose films to be suitable for solar panel applications [46]. Films from mechanical and chemical treatment generally have excellent strength properties, which are affected by various factors that include, but are not limited to, cellulose raw material and its composition, production process for nanocellulose, film preparation technique and drying conditions [47].

Traditional ways to produce transparent paper involve fiber-based and sheet processing techniques. Since Herrick at el successfully separated nanofibers from wood pulp using a mechanical process in a high pressure homogenizer in 1983, cellulose nanofibers have attracted great attention because they can be used to manufacture transparent films for electronics, optoelectronic devices, and also for packaging [48]. Various chemical pretreatments and mechanical processing lead to different purification levels and disintegration states of nanocellulose, which contribute to mechanical properties of films prepared from them [49-53, 54]. Mechanical treatment techniques are currently considered efficient ways to isolate nanofibers from the cell wall of a wood fiber. However, solely mechanical processes consume large amounts of energy and insufficiently liberate the nanofibers while damaging the microfibril structures in the process. Pretreatments, therefore, are conducted before conducting mechanical disintegration in order to effectively separate the fibers and minimize the damage to the nanofiber structures.

TEMPO-mediated oxidation is proven to be an efficient way to weaken the interfibrillar hydrogen bonds that facilitate the disintegration of wood fibers into individualized nanofibers yet maintain a high yield.

The morphological difference between refined cellulose nanofibers and TEMPO mediated oxidized cellulose fiber is clear. TEMPO mediated oxidized cellulose fibers are much smaller in size and appear straight, rod-like, while refined cellulose nanofibers fibers are larger and appear more flexible and irregular in shape. Fibrillated portions visible on the refined cellulose nanofibers fibers almost reach the diameter of TEMPO mediated oxidized cellulose fibers. Aspect ratio of refined cellulose nanofibers fibers is higher than that of TEMPO mediated oxidized cellulose fibers. These basic differences in the morphology and size play an important role in the packing of fibers during film formation, and consequently contribute to the final film properties. TEMPO oxidation pretreatment is known to generate very fine scale nanocellulose.

Therefore, the key difference in the methods to produce these fibers is from chemical pretreatment, not from the method to impose mechanical energy.

Density of TEMPO mediated oxidized cellulose fibers films is higher than that of refined cellulose nanofibers films because of the lower aspect ratio of TEMPO mediated oxidized cellulose fibers. Similar density differences between films of cellulose nanofibers obtained by different treatments have been reported by Qing et al. 2013 [54]

The TEMPO mediated oxidized cellulose fibers films have a higher tensile strength compared to refined cellulose nanofibers films but the strain at break is almost double for the refined cellulose nanofibers films. The difference in mechanical properties of refined cellulose nanofibers and TEMPO mediated oxidized cellulose fibers films arise from the difference in their microstructures.

The differences in mechanical properties between refined cellulose nanofibers and TEMPO mediated oxidized cellulose nanofibers reported here is similar to that reported by Qing [54].

3.4 Conclusion

It has been shown that cellulose nanofibers can be isolated using a mechanical fibrillation process from both KRK and PFI refined cellulose pulps used in the present study. Refining processes is effective in converting the original pulp material into microfibers. An increase in processing steps obviously increases the energy required for fibrillation. The results from mechanical testing correlate with the microscopy study and density measurements showing that significant improvements in the mechanical properties first occur after internal fibrillation of the cellulose fibers. However, TEMPO mediation oxidized fibers showed unique properties compared with KRK and PFI refined fibers in terms of small nanofiber diameter, improved yield, high stability in colloidal suspension and the very low energy requirements for successful disintegration. The key findings of this work indicate a promising future for TEMPO and refined fiber cellulose in various applications.

3.5 References

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Chapter 4: Nanopaper Forming and Structure - Properties Relationships

4.1 Introduction

Cellulose nanofibers are one of the most interesting nanoscale biomacromolecular building blocks that are available in nature and have recently gained considerable interest for its unique properties [1]. Films made of nanocellulose can find applications in various areas such as solar panel, printed electronics and sensor. Mechanical, optical and barrier properties play a major role for these films to be suitable for such applications [2]. Therefore, it is essential to study these properties in detail, which further opens the gateway to any improvements needed in raw materials or production processes [3]. Mechanical properties of films made of nanocellulose have been investigated recently by numerous researchers with the focus on the impact of nanocellulose as reinforcement material in composites [4, 5, 6, 7, 8]. Comprehensive literature reviews covering earlier work on the same have come up recently [9, 10, 11, 12, 13]. Studies focusing on mechanical properties of neat nanocellulose films are few. MFC and NFC films generally have excellent strength properties, which are affected by various factors that include, but are not limited to, cellulose raw material and its composition, production process for nanocellulose, film preparation technique and drying conditions. In one of the early works [14], neat films made from MFC produced by super masscolloider grinding method were reported to have superior tensile strength compared to commercial print grade papers. Another early work reported a strong influence of moisture and pectin content on mechanical behavior of films cast from sugar beet cellulose microfibrils [15]. Mechanical properties of nanocellulose films are also reported to be influenced by the pulp type (softwood or hardwood) [16, 17, 18, 19, 20, 21, 22]. Hemicellulose content and lignin content of wood pulp also affect the fibrillation process and mechanical properties of nanocellulose films. Various chemical pretreatments and mechanical processing lead to different purification levels and disintegration states of nanocellulose, which contribute to mechanical properties of films prepared from them [23, 24, 25, 26, 27]. Syverud K, Stenius P (2009) [28] recently compared the strength properties of neat MFC films prepared by filtration and dynamic sheet former, and found the former to create films with higher density and elastic modulus but comparable tensile strength. Sehaqui et al. (2010) [29] developed a new method for a fast preparation of 200 mm diameter MFC films using a semiautomatic sheet former. These MFC films demonstrated better mechanical properties than those prepared using different techniques such as solvent casting, filtration combined with oven drying and filtration combined with hot pressing. Physical and mechanical properties of nanocellulose films depend also on drying conditions as material distortions occur during drying due to the development of moisture gradients within the fiber network [30]. Nanocellulose fibers have much smaller diameters compared to the wavelength of visible light, which allows them either to suppress light scattering due to dense packing [31] or cause it in the forward direction [32] resulting in transparent films unlike conventional paper. High transparency of nanocellulose films make them an interesting choice for various functional applications and therefore light transmission through these films has been an area of interest in some recent studies [33, 34, 35, 36]. Optical properties are affected by surface roughness or the presence of fiber aggregates [37, 38]. Additional homogenization steps increase the optical transparency of films by reducing the number of fiber. Since mechanical strength and optical transparency are among the critical properties of nanocellulose films that determine its eligibility for various applications especially solar panel, hence the need to study the relationship between nanopaper forming and structure-properties relationships.

4.2 Experimental

4.2.1 Materials

Microfibrillated and cellulose nanofibers were prepared from regular kraft bleached softwood pulp that has been refined to a certain degree by refining and TEMPO mediation oxidation methods. The pulp suspension was first subjected to mechanical refining steps involving PFI and KRK refiner. The second part was chemically pretreated using TEMPO

4.2.2 Nanopaper formation

Sheet Maker

Three different methods were used for handsheet preparation and drying. For the laboratory sheet former (Tappi T 205 sp-02), a total of 30g of PFI treated pulp was diluted with water, followed by mixing with Ultra Turrax mixer at 1200rpm. The suspension was degassed for 10 min with a water vacuum pump. The filtration was done with a laboratory sheet former under vacuum. The suspension was poured into a hollow cylinder containing a metallic sieve at the bottom with a pore size of 110µm. The top of the sieve has a nitrocellulose ester filter membrane with 0.65µm pore size was placed. The filtration time was recorded. The gel cake formed after filtration is peeled from the membrane and stacked between two filter papers and then two carrier boards. This package was placed in the sheet dryer for about 10 mins at 105^{o}C and vacuum of about 70mbar. Handsheets of 20g/m^2, 40g/m^2 and 60g/m^{2}grammage was produced and dried by oven, press and air methods. Sheet pressing and drying were done according to Tappi T 218 sp-02 at temperature of 107^{o}C for 10mins at pressure of 30 MPa while the air dry was at conditioned in a climate room at 23 ± 1°C and 50 ± 2% relative humidity (RH) for 48 h before testing. The oven drying method was done at 105^{o}C for 4hrs.

Vacuum Filtration

For the filtration method, the above procedure was followed but vacuum filtration on a glass filter funnel of 7.2 cm in diameter was used. After filtration, the wet gel was stacked between filter papers and dried by hot press, air and oven methods. The grammage fabricated was as in sheet former method above.

Cast Method

The casting fabrication method was done as in the above procedure to obtain the fiber solution. The suspension was degassed and poured in a polystyrene Petri dish and air dried for 5 days under controlled atmospheric condition of 24^{o}C.

4.2.3 Mechanical Properties test

Tensile tests of the cellulose nanopaper were performed using universal materials testing Machine (L&W thickness tester, T 411 om-97) equipped with a 500N load cell. Rectangular tensile specimens were 15 mm wide and had an extensometer gauge length of 37 mm and nominal grip length of 60mm. The determination of the paper handsheets density was made according to the Tappi220 sp-01 standard. The apparent film density was calculated from dividing the mass with the sample dimensions. The thickness was measured three times/per sample with a Lorenz Wetter paper thickness meter. The methods and instruments used for measuring various properties of paper are given in Table 4.1.

Table 4.1 Methods and instruments used for the testing of various paper properties

Parameter	Tappi test method	Instrument model (Make)
Grammage	T 410 om-98	-
Thickness	T 411 om-97	L&W thickness tester
Stretch	T 494 om-01	L&W tensile tester
Breaking length	T 494 om-01	L&W tensile tester
Tensile Strength	T 494 om-01	L&W tensile tester
Burst index	T 403 om-97	L&W bursting strength tester
Tear index	T 414 om-98	L&W tearing tester

4.2.4 Optical Properties test

Light Transmittance

The light transmittance of films was measured by a Perkin Elmer Lambda 900 UV/VIS/NIR Spectrometer in the wavelength range of 300–1100 nm. Three parallel measurements were carried out for each film at ambient conditions.

Light scattering

We measured the light scattering by passing a red laser with a diameter of 0.4 cm to strike on the handsheet. The experiment was done for unrefined sheet and refined sheet for 10,000r, 8,000r and 5,000r. The diameters of the scattered light was measured and recorded.

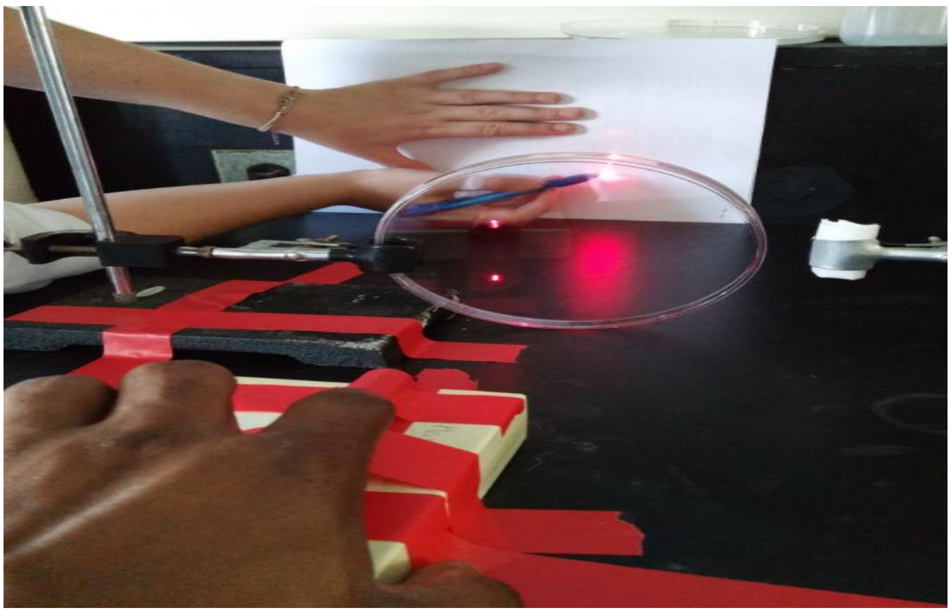

Figure 4.1 Laser Experiment Setup for Light Scatter

4.3 Results and Discussion

4.3.1 Physical strength property

Tensile strength

Refining affects fiber properties and this has an effect on sheet properties. The effects of fiber properties-length of fiber, diameter, strength, specific surface area and fibrillation as well as bonding and flexibility on sheet properties are very important. As the refining for both the PFI and the KRK increases, the tensile strength increases due to fiber surface increase as shown in Fig.4.2 and Fig 4.3 respectively. The tensile strength increased from 23.4108Nm/g at 5,000rev to 37.994Nm/g at 10,000rev for the PFI refiner and from 30.688Nm/g before refining to 44.389Nm/g after 5 passes for the KRK refiner. The tensile strength properties of handsheets were increased by the refining process, which increased the fiber surface areas and fiber flexibility. This result is in agreement with Seth and Bennington [39]; they proved that tensile strength increases as PFI revolution increased. From this result, it can be seen that the tensile strength is strongly dependent upon fiber-to-fiber bonding. For the KRK refiner, fiber with 10 passes has the higher strength and 10,000 rev gave the higher tensile strength for the PFI refiner. This is also in agreement with literature which shows that most strength properties of paper increase with pulp refining, since they rely on fiber-fiber bonding. Fiber length affects sheet formation and the uniformity of fiber distribution. The shorter the fibers, the closer and more uniform the sheet. Fiber length also affects the physical properties of the sheet, such as its strength and rigidity.

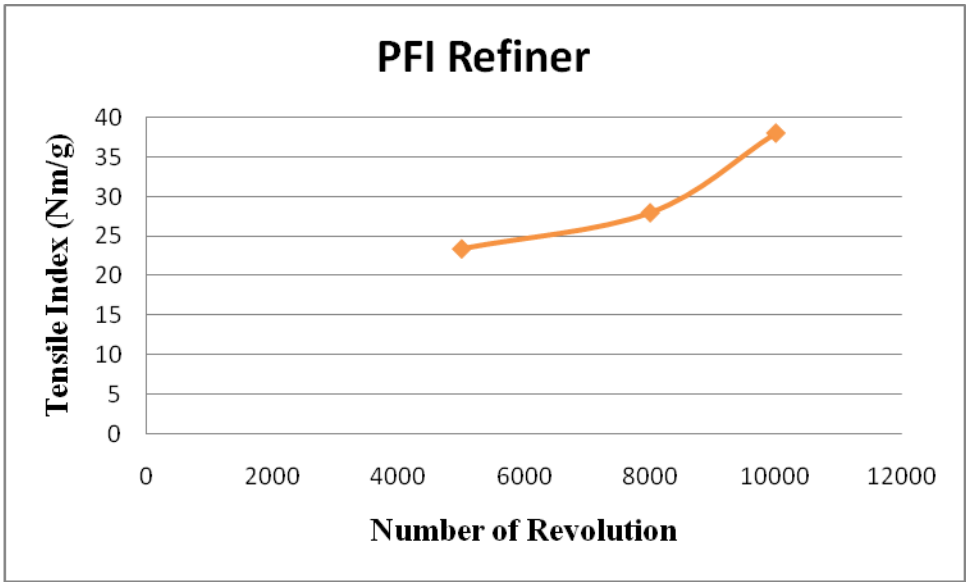

Figure 4.2 Effect of Refining on Tensile Strength for PFI refiner

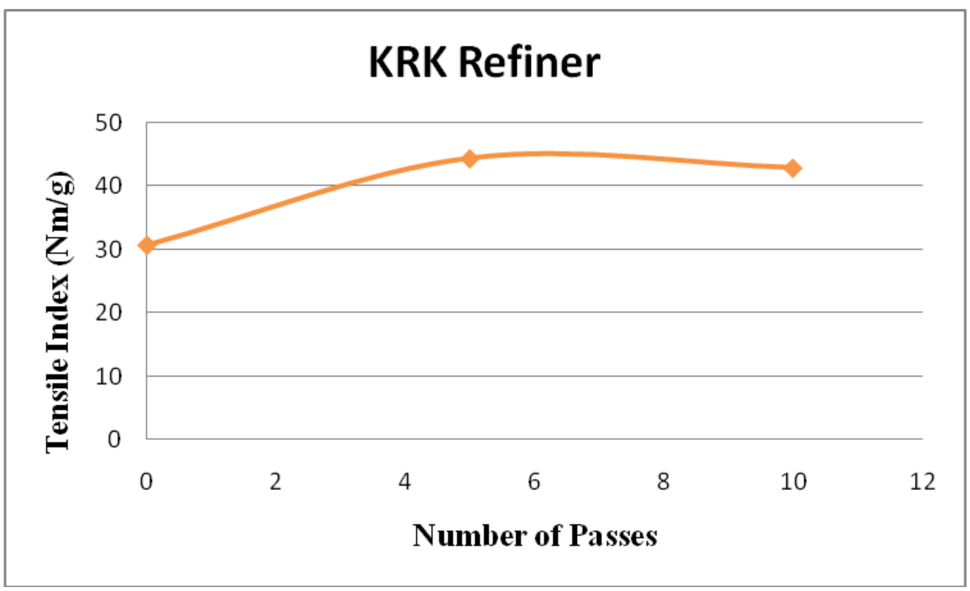

Figure 4.3 Effect of Refining on Tensile Strength for KRK refiner

The higher the tensile strength, the stronger the films will become because tensile strength depends on the intrinsic fiber strength and fiber length but also depend interfiber bonding and therefore refining is a fundamental operation to increase tensile strength [40]

More so, an increase in the handsheet grammage from 20g/m^2 to 60g/m^2 increased the tensile strength from 41.4066Nm/g to 45.7159Nm/g at 10,000rev for the PFI methods as shown in Fig. 4.4 while the KRK values shown in Fig. 4.5 increased in the tensile strength as the grammage increase from 20g/m^2 to 60g/m^2 from 37.5657Nm/g to 42.8906Nm/g for 10 passes. A positive correlation between handsheet grammage and tensile index has been reported in previous studies [41, 42, 43]. This positive correlation can be attributed to the increase in the number of bonding sites in the sheet because of the increasing grammage and increasing number of fibers in the sheet. The tensile strength of paper is significantly affected by the specific bonding strength and by the bonded area [42, 44].

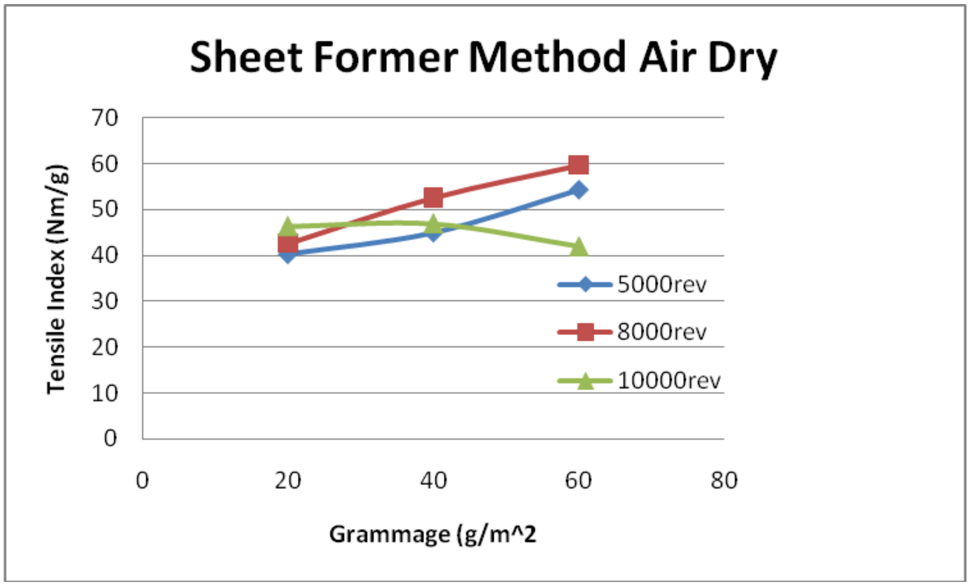

Figure 4.4 Effect of increase in Grammage on Tensile Strength for PFI Refiner

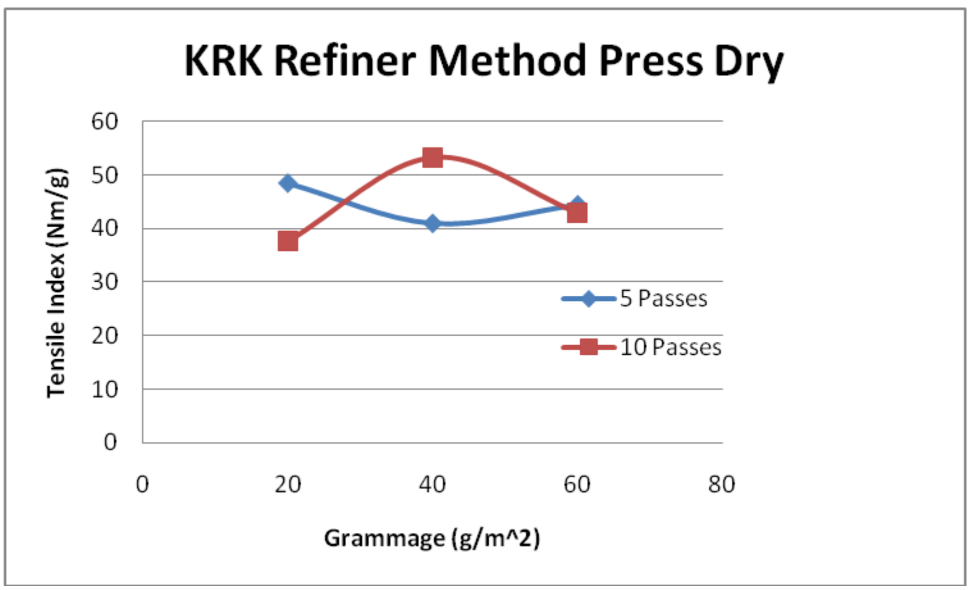

Figure 4.5 Effect of increase in Grammage on Tensile Strength for KRK refiner

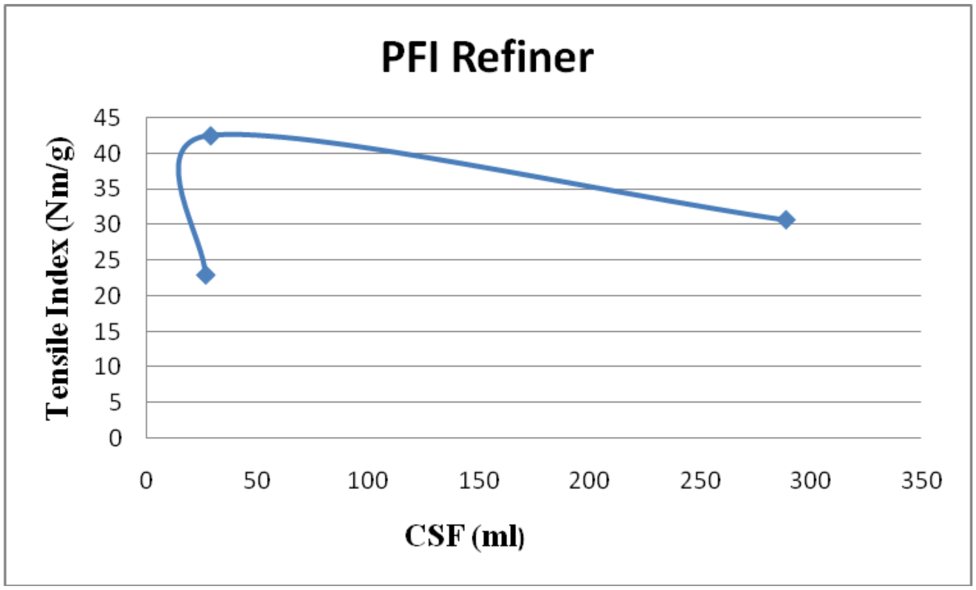

Figure 4.6 Effect of Refining on CSF and Tensile Strength

From Fig. 4.6, it was observed that when freeness decreased, resulting from increasing refining revolution, tensile index also increased until the maximum tensile index was reached and it was 42.25155 Nm/g at 29ml, CFS. Consequently, tensile index decreased if the pulps were continuously refined for a longer period. Finally, the tensile strength is one of the most important mechanical properties of papers that condition to a large extent their suitability for demanding applications.

Tear strength

From Figs 4.7 – 4.10, it was observed that there was a consistent decrease in tear strength as the refining increases, that is, as the number of revolutions of PFI and number of passes for the KRK increases, the tear strength for both cases decreases. Figs. 4.7 and 4.8 indicate the trend of tear strength development against refining for both PFI and KRK refiners. With increase in the number of revolutions from 5,000rev to 10,000rev, the tear index decreased from 3.77295mN/g/m^2 to 2.468519 mN/g/m^2 for the PFI refiner, and 3.2316216 mN/g/m^2 to 2.94094 mN/g/m^2 at 5 and 10 passes for the KRK refiner.

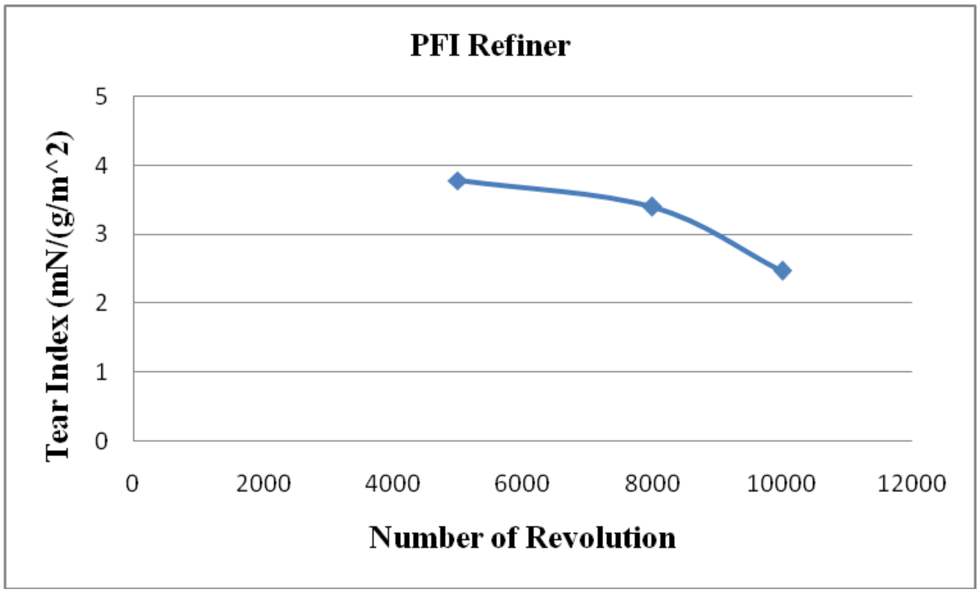

Figure 4.7 Effect of Refining on Tear Index for PFI refiner

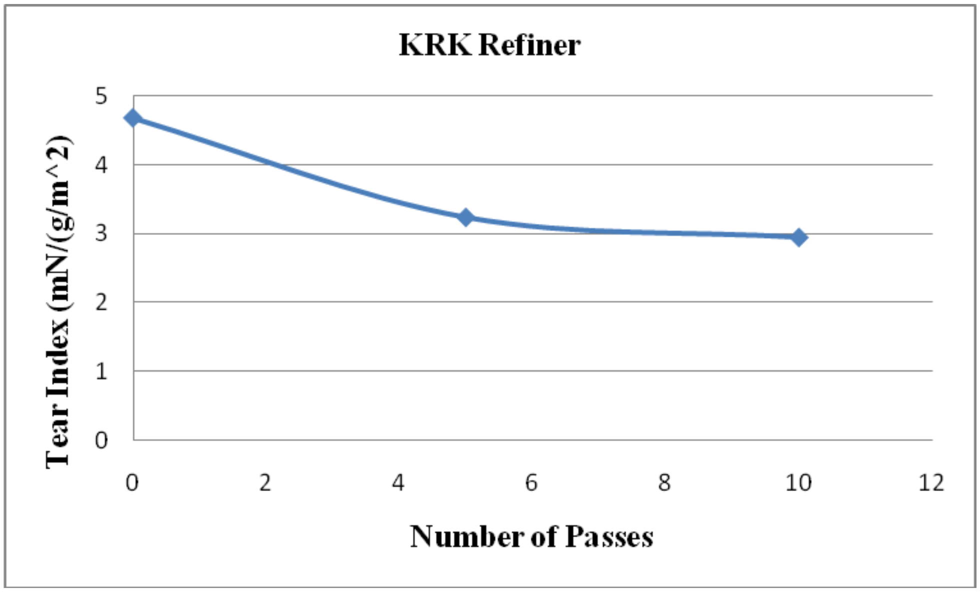

Figure 4.8 Effect of Refining on Tear Index for KRK refiner

Tearing resistance depends on the degree of fiber refining, related to inter fiber bonding, the fiber strength, the fiber length, the quality and quantity of fillers used. Among of them fiber length and fiber bonding are most important factor.

Longer fibers increase the tear strength because it is able to distribute the stress over more fibers and more bonds, whereas short fibers concentrated the stress in a smaller region. As observed in tensile strength result, most of the strength properties of film increased with pulp refining, since they depend on the fiber-fiber bonding. However, the tear strength, which depends highly on the strength of individual fibers, decreases with refining. This is in total agreement with literature that attributed the effect of refining on tear strength due to the attrition in strength of the individual fibers [45, 46, 47, 48]. The highest and lowest amounts of tear strength occurred at 5000rpm and 10,000rpm for PFI refiner for the KRK and 5 passes and10 passes for the PFI refiner.

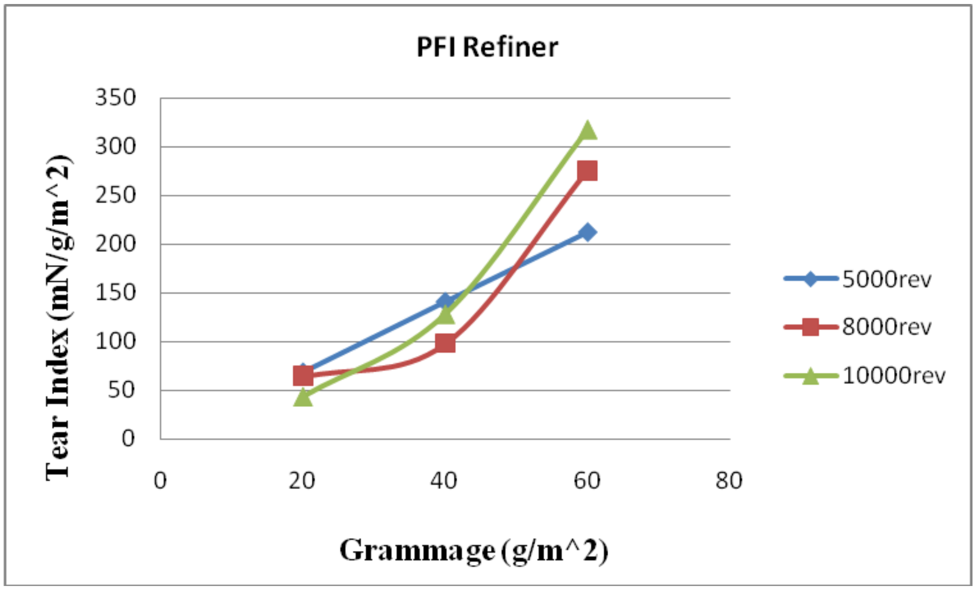

Figure 4.9 Effect of Grammage on Tear Strength for PFI refiner

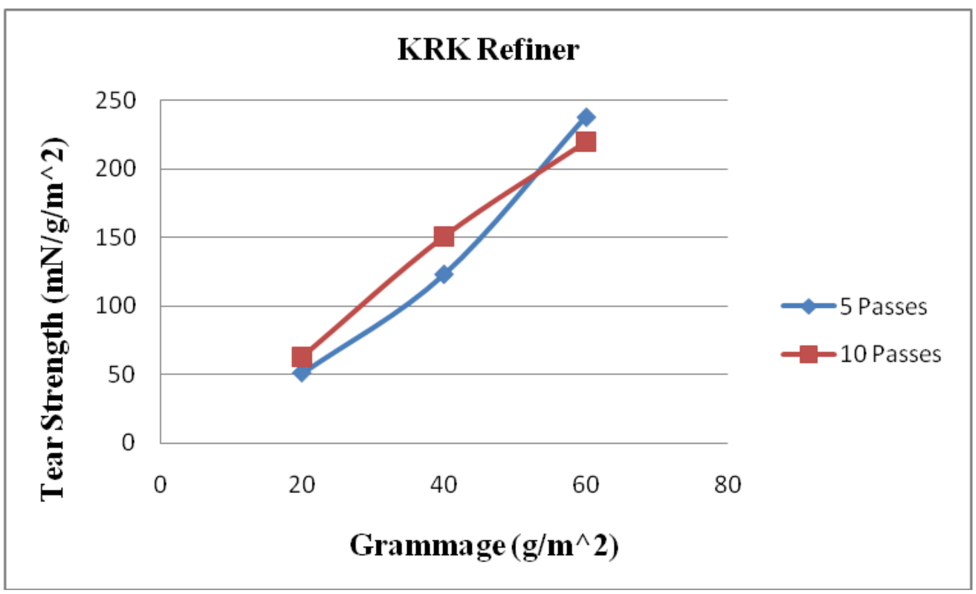

Figure 4.10 Effect of Grammage on Tear Strength for KRK refiner

The tear index of the handsheets gradually decreased with decreasing grammage (Figure 4.9–4.10). Winters et al. (2002) [49] also noted that tear index decreased with decreasing grammage. Tear index depends on individual fiber strength, while tensile and burst indices of handsheets depend on bonding ability of fibers. On the other hand, tear index increase usually reaches a peak value before falling off gradually despite tensile and burst indices increments. This result may be attributed to fiber strength losses during refining. Thus, possible fiber failure increases during tearing test [50].

4.3.2 Optical property

The optical properties of films are quite important in the context of their applications. The light transmittance was measured in the 300-1100nm wavelength range. Figure 4.11 shows the UV-Visible light spectra (300-800nm). The transmittance in the UV region drops significantly as it depends on wavelength and decreases due to higher light scattering as the wavelength of the light approaches the diameter of fiber [51].

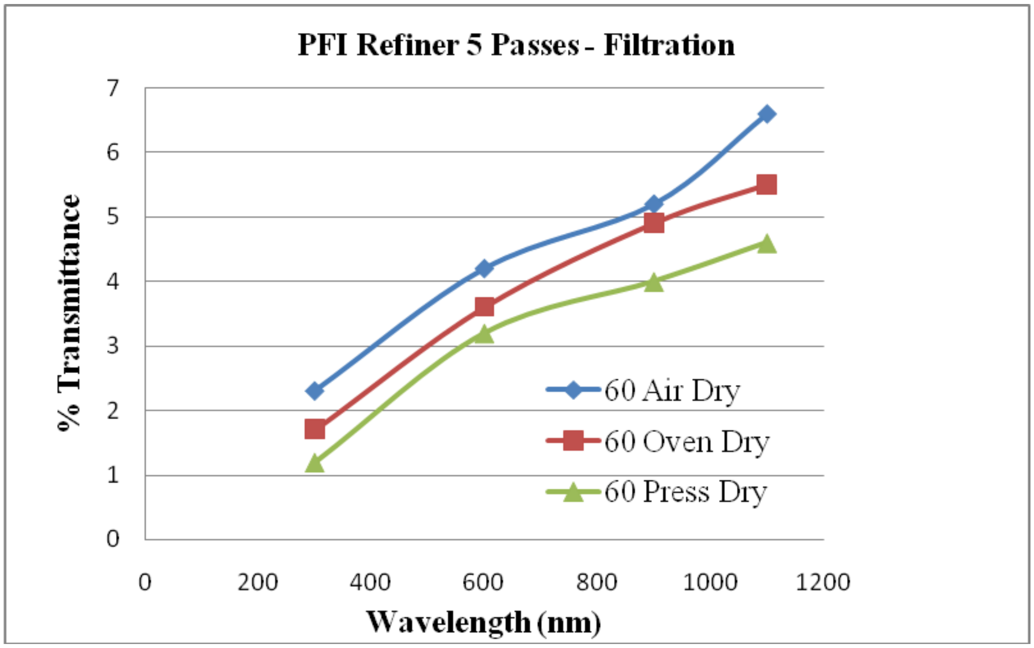

Figure 4.11 Effect of Wavelength on Transmittance

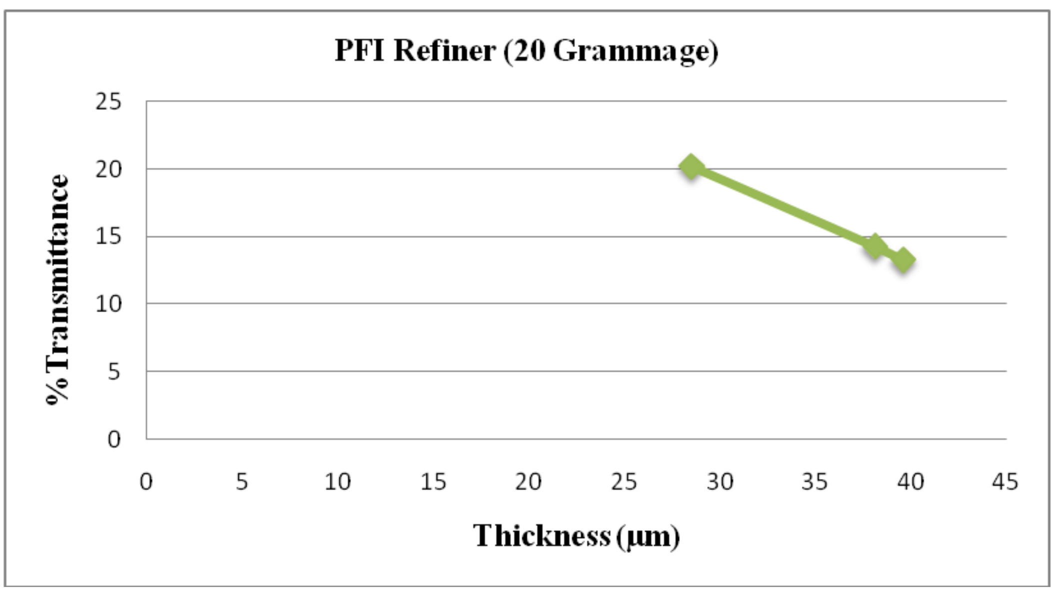

Figure 4.12 Effect of Thickness on Transmittance

Thickness had a slightly more pronounced impact on light transmittance. Thickness of the film affects the transmittance of our films. We discovered that as the thickness increased from 28.5µm to 39.625µm the percentage transmittance decreased from 20.2 to 13.3. This is due to an increase in light scattering within the film as shown in Fig 4.12. Here, we noticed that transparency is a function of light scattering elements since the fibers we obtained from both refining processes still have micron size fragments of fibers that scatter light.

4.3.3 Grammage/thickness

More so, the lower light transmittance in micro sized films from refined fibers from PFI and KRK is due to the presence of large fiber fragments or fiber aggregates. The packing density also decreases for larger fibers as is the case for the refined films reported here. Large fibers and large pores significantly increase back scattering of light [51].

From the results obtained, the highest transparency of about 21% at a wavelength of 1100nm was achieved from both the KRK and PFI refining methods. Sheet former films fabrication method gave the highest transparency with press method given the least transparency. From the drying method, press drying was most transparent and oven dry was least in transparency as shown in Fig. 4.12.

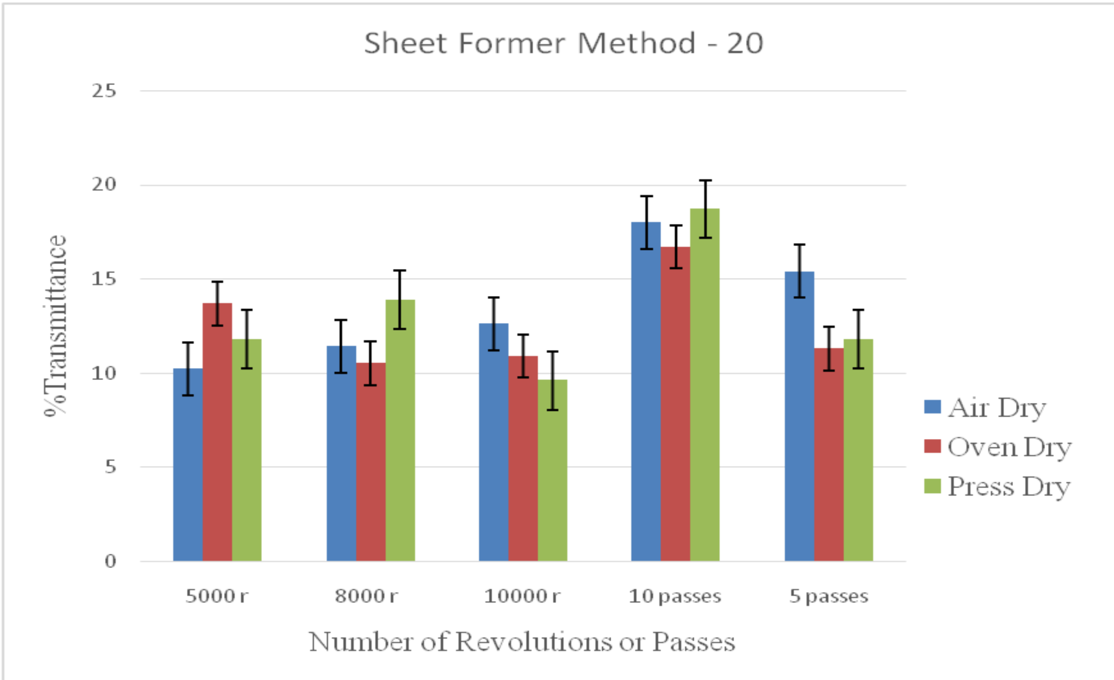

Figure 4.13 Effect of Refining Method on Transmittance

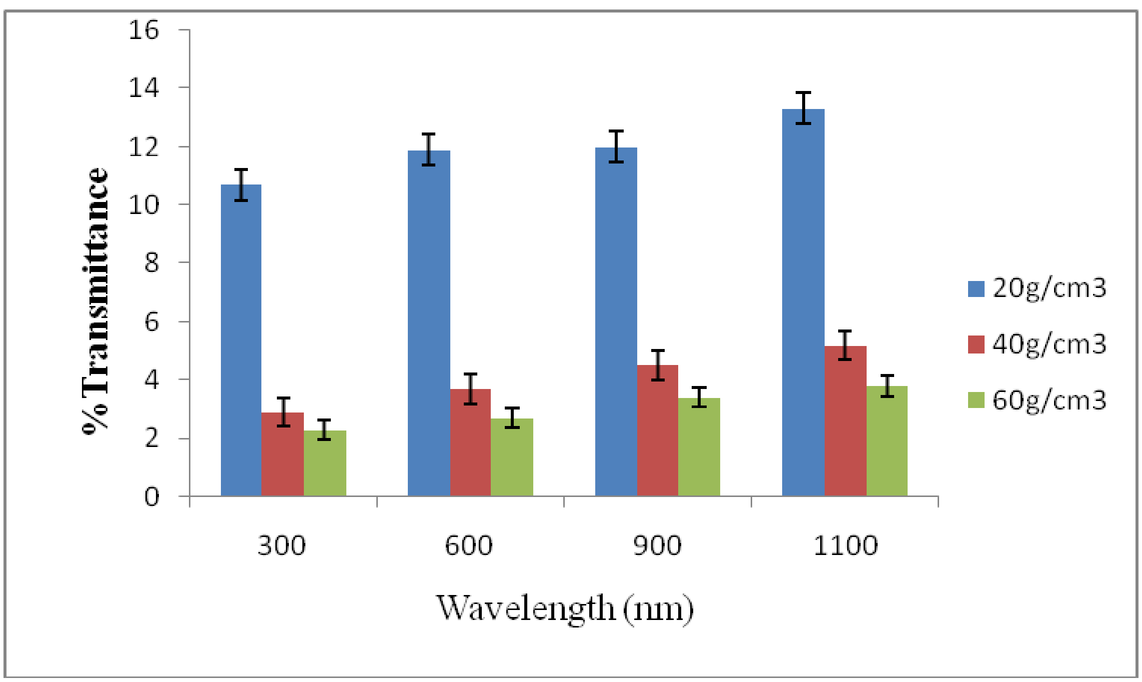

Figure 4.14 Effect of Wavelength on Transmittance at Different Grammages

Also, it was noticed that the film grammage affects the transmittance. Generally, 20g/m^2 gave the highest transparency while 60g/m^2 gave least in transparency for all the cases considered.

a. **b.**

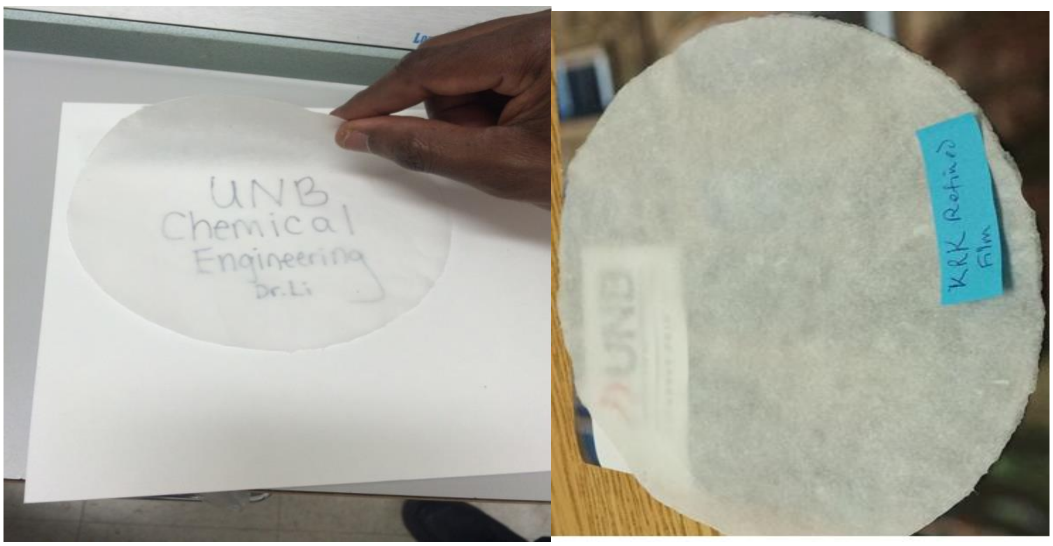

Figure 4.15 Samples of Films from (a) PFI and (b) KRK Refiners

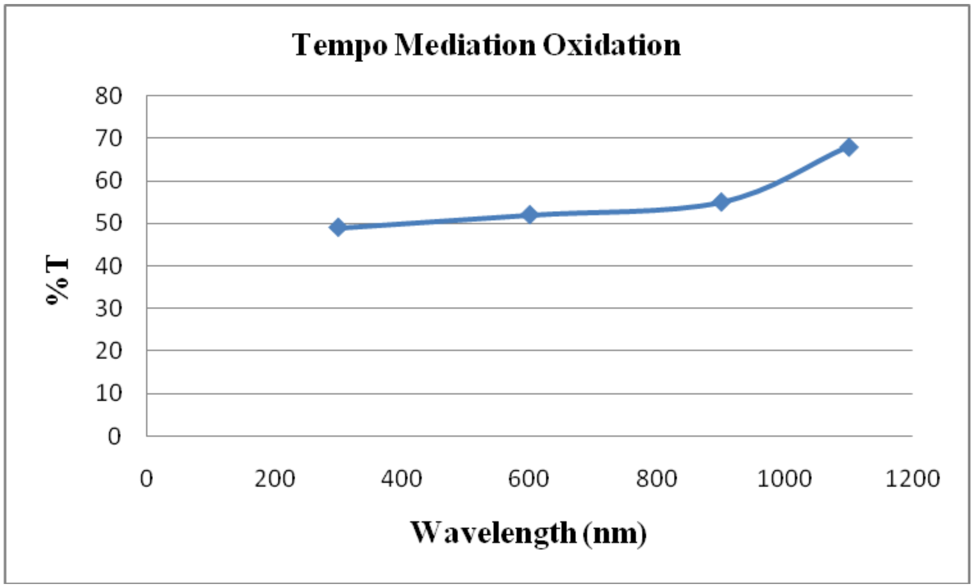

Figure 4.16 Effect of Wavelength on Transmittance

Light scattering

From the Laser light experiment, it was observed that similar trend was followed for all the films fabricated and dried from different methods. For the PFI refining, the 5,000rev has the most light scattering and the 10,000rev has the least, while 5 passes has more light scattered than the 10 passes for the KRK refining.

Transmittance of paper with different thickness

Thickness of paper affects the transmittance of our transparent paper. As the thickness increases from 43.5µm to 74.37µm the transmittance decreases due to an increase in to light scattering within the film occurred. The grammage of the nanopaper also has effect on the transparency of the films, see figure 4.16a and b. Film sample with 20g/m^2 grammage appears more transparent than that of 60 g/m^2.

a **b**

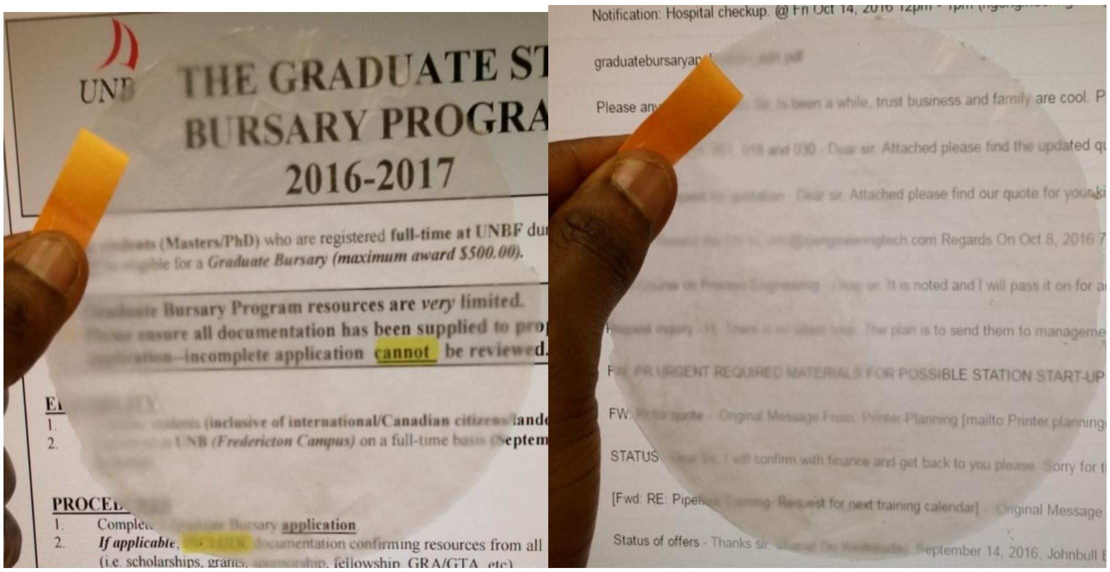

Figure 4.17 Film Samples from TEMPO Oxidation Method with different thickness (a) 22 g/m^2 and (b) 60 g/m^2.

4.3.4 Comparison of transmittance from refining and TEMPO nanocellulose films

One can observe from Fig. 4.17a and 4.17b, that TEMPO oxidation method films are more transparent than refined films of similar thickness. However, there is no significant difference in transparency among refined films, that is the KRK and PFI refined fibers fabricated into films.

Thickness of the TEMPO oxidation method films has a minimal impact on light transmittance as shown in Fig. 4.16a and b. However, thickness had slightly more pronounced impact on light transmittance in refined films.

The lower light transmittance in refined films is due to presence of large fiber fragments or fiber aggregates.

The packing density also decreases for large fibers as is the case for refined films reported here. Large fibers and large pores significantly increase back scattering of light [58]. The refined and TEMPO oxidized films reported here show similar light transmittance in visible region as those reported by Sehaqui et al [59] and Qing et al. 2013 [60]. TEMPO oxidized fibers have much smaller diameters compared to the wavelength of visible light, which allows them either to suppress light scattering due to dense packing [61] or cause it in the forward direction [58] resulting in transparent films unlike those from KRK and PFI refined pulps. High transparency of TEMPO oxidized nanocellulose films make them an interesting choice for various functional applications and therefore light transmission through these films has been an area of interest in some recent studies [60, 62, 63] Optical properties are affected by surface roughness or the presence of fiber aggregates [61]. Transparency is a function of light scattering elements and refined pulp still has micron size fragments of fibers that scatter light. As the fiber size decreases, the film becomes more and more transparent [64].

4.3.5 Forming methods and nanopaper properties

Four different nanopaper preparation methods and three drying techniques were used in this thesis. The preparation methods include casting, vacuum filtration and sheet press, while the drying methods include air, oven and press methods respectively.

Table 4.2: Comparison of Nanopaper forming methods

Preparation Method	Film Thickness (µm)	Drying Time (hr)	Density (g/cm^3)	Tensile Strength (N/m)	%T
Casting					
(Air Dry)	40.0	144	0.47	566	13.3
Vacuum Filtration					
(Air Dry)	50.0	12-24	0.50	571	7.2
(Oven Dry)	60.0	≈ 1	0.38	924	9.7
(Press Dry)	40.0	≈ 0.33	0.52	827	7.1
Sheet Former					
(Air Dry)	40.0	12-24	0.35	719	10.2
(Oven Dry)	30.0	≈ 1	0.62	819	13.7
(Press Dry)	40.0	≈ 0.33	0.54	974	11.8
TEMPO Oxidation					
(Air Dry)	65.0	12-24	1.34	98E6	68

The differences between the different preparation and drying methods and properties of the resulting nanopapers are compared and summarized in Table 4.2. Casting is the most time-consuming method, requiring about 144 hours and results in nanopaper with low mechanical properties of about 566N/m.

For the Vacuum filtration, the oven drying method has a tensile strength of about 924N/m. The mechanical properties are much improved, and preparation time about 1 hour which is shorter compared to casting method. Vacuum Filtration and pressing dry method significantly reduces preparation time to about 20 minutes (0.33hr) due to the fast drying. Hot-pressing requires substantial pressure and well-aligned plates.The tensile strength and tear strength of the air dry nanopaper are in the same range with cast nanopaper (tensile strength 571 N/m, 566N/m and tear strength 64N/m, 69N/m). Syverud and Stenius (2009) [65] recently compared the strength properties of neat MFC films prepared by filtration and dynamic sheet former, and found the former to create films with higher density and elastic modulus but comparable tensile strength. Sehaqui et al. (2010) [29] developed a new method for a fast preparation of 200 mm diameter MFC films using a semiautomatic sheet former. These MFC films demonstrated better mechanical properties than those prepared using different techniques such as solvent casting, filtration combined with oven drying and filtration combined with hot pressing. Physical and mechanical properties of nanocellulose films depend also on drying conditions as material distortions occur during drying due to the development of moisture gradients within the fiber network [30]. Films produced from TEMPO oxidation method have superior mechanical strength than refined films, having tensile strength of 98MPa.

Vacuum filtration and drying can conveniently performed in a single piece of equipment. Furthermore, the nanopaper specimens prepared by this procedure, have the best mechanical properties, see Table 4.2.

The mechanical properties of nanopaper are very sensitive to orientation distribution of the nanofibers.

The high ultimate strength indicates that the constrained drying leads to good in-plane orientation of the nanofibers and possibly also higher density. Furthermore, the cast sample suffers from wrinkling. Even slower drying would provide less severe moisture concentration gradients and may reduce the wrinkling problem.

FromTable 4.2,the percentage transmittance of sheet former + oven dry and casting + air dry at wavelength of 110nm are 13.7 and 13.3 respectively, which are much higher than those from the vacuum filtration method. TEMPO oxidized films demonstrates a higher optical transmittance percentage of about 68 at 1100nm, which is higher than that from the refined method.

As discussed above, in refined pulp, there are plenty of cavities that form throughout the network of microsized fibers causing enhanced light scattering behavior due to the refractive index mismatch between cellulose (1.5) and air (1.0). Homogeneous and more conformal surface is observed due to the collapse of the TEMPO-oxidized wood fibers and there is a significant amount of small fragments in the pulp that fill in the voids within the film. This causes less light scattering to occur within the TEMPO-treated films and allow more light to pass through it.

Effect of Density

Densities were estimated from the weight and volume of the sample determined from measurements of thicknesses and widths.

The relationships between density and refining level of pulp are shown in Figure 4.18 and 4.19. Both graphs demonstrate that when refining revolution and number of passes continues to raise, then the density increase which is in contrast with bulk properties as shown in Fig 4.20. Density of films is usually a converse of bulk of paper. Hence, when bulk decreased, density should be increased. Fiber surface of unbeaten pulp isn't destroyed and break fiber to fibril (fine fiber). When unrefined pulp forms a handsheet it is bulky and compare to refined pulp that can form dense handsheet. The fibrillations of refined fibers are increase fiber-to-fiber bonding and fine fibers plug holes in bonding area. Hence, paper having high density is the result from refining influence.

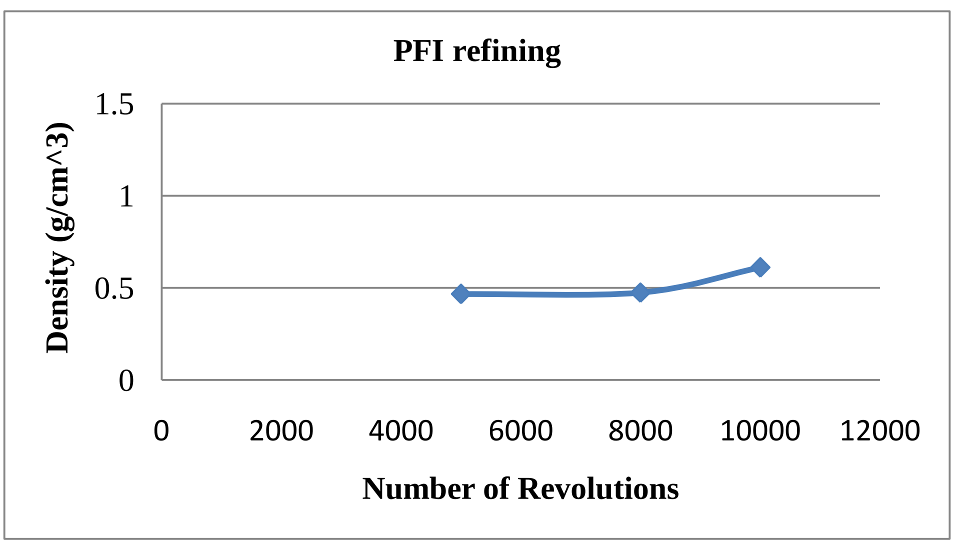

Figure 4.18 Effect of Refining on Density for PFI Refiner

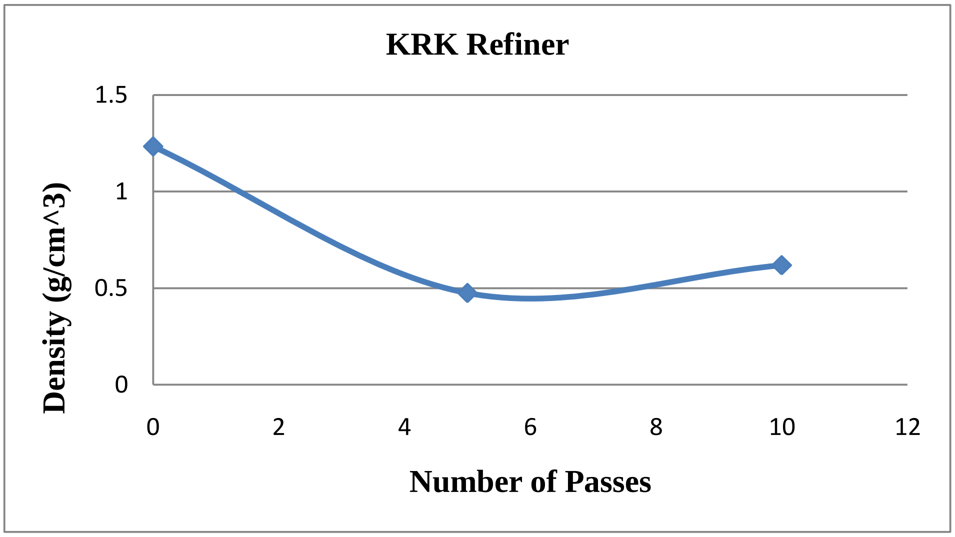

Figure 4.19 Effect of Refining on Density for KRK Refiner

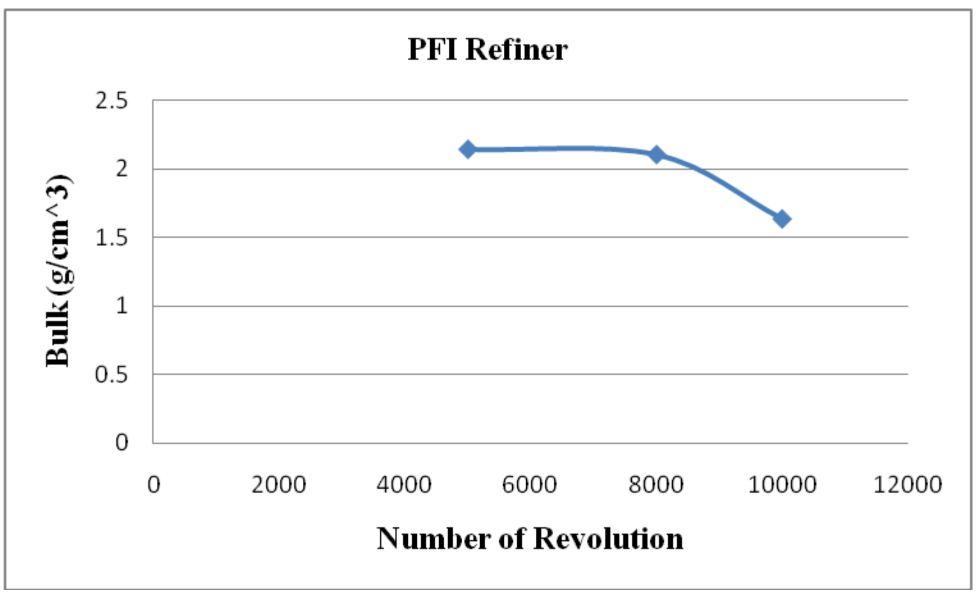

Figure 4.20 Effect of Refining on Bulk Density for KRK Refiner

The sheet density (kg/m^3) is one of the most important structural properties of paper, and it has an important effect on other properties. Higher density indicates better inter-fiber bonding in the sheet. Therefore, sheet density can be used as a measure of the degree of inter-fiber bonding [40]. The relationship between handsheet grammage and density of the handsheets of both PFI and KRK refiners were observed in this study (Figure 4.18 and 4.20). This finding is in agreement with previous studies [49]. The increases in density that occurred with increasing grammage were evident in handsheets from both refining methods.

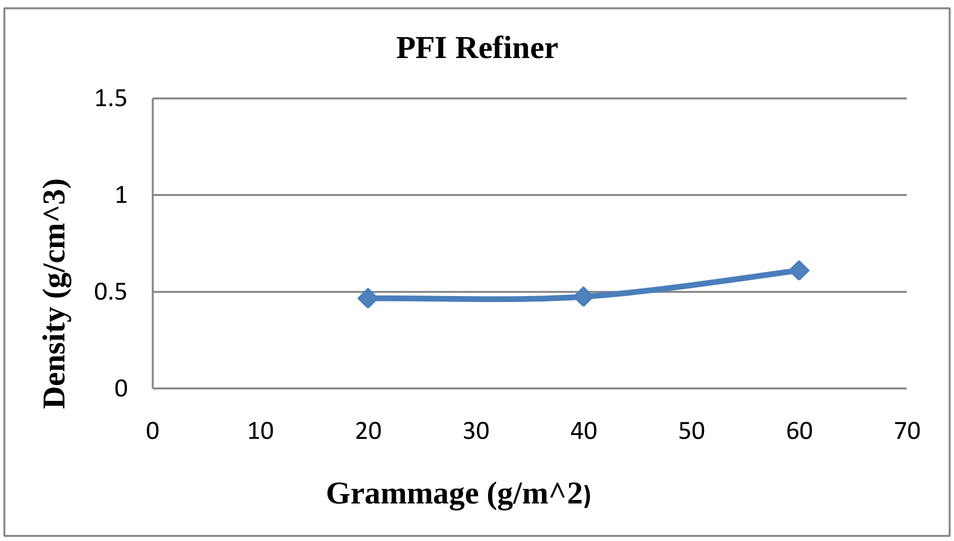

Figure 4.21 Effect of Grammage on Density for PFI Refining

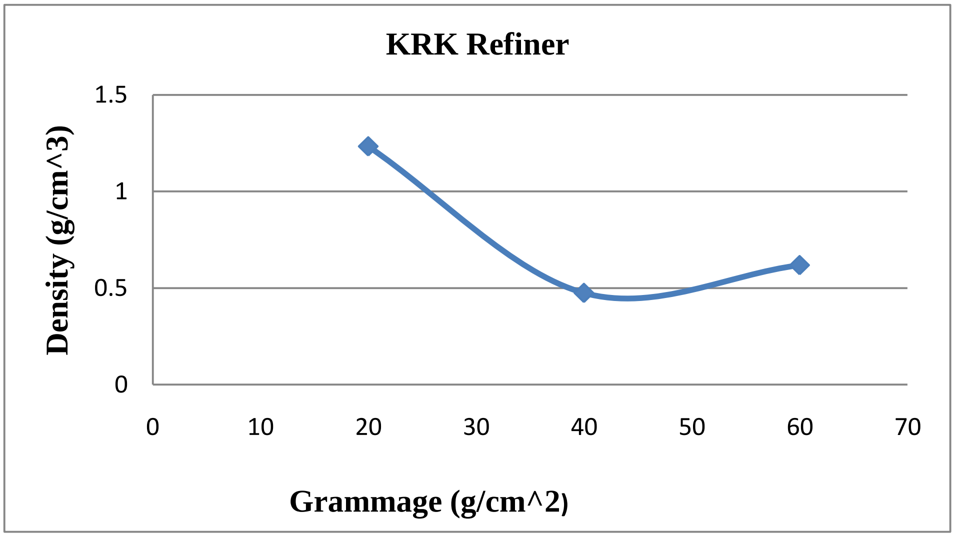

Figure 4.22 Effect of Grammage on Density for KRK Refining

There is a continuous increase in density (smaller diameter resulting in better packing) throughout the refining and homogenizing process for the cellulose fiber films (Figure 4.21 – 4.22). The density increases films by a factor of about 4 during the fibrillation process. The increase in density of the films is directly related to the increasing tensile strength and modulus of the films. Similar trends are observed for films of both KRK and PFI refined fibers. The porosity decreases with increasing density, and the contact surface between adjacent cellulose fibers within the network increases, resulting in higher strength and stiffness.

Nevertheless, the surfaces of the cellulose films are porous and rather inhomogeneous in their morphology, which explains the relatively low mechanical properties when compared to those used in other studies that are based on cellulose fiber films obtained by suction filtration on a membrane, [66, 67, 68] because this process compact the films.

4.4 Conclusion

Processing conditions for producing cellulose nanofibrils films significantly impact the mechanical and physical properties of the films. TEMPO films had better tensile strength and higher transparency than films made from mechanically treated films. Also, Cast TEMPO films had the highest transparency than any of the mechanical films, but cast films from mechanical treated films had lower transparency than filtered and air- or oven-dried films.

4.5 References

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Chapter 5: Conclusions and Recommendations

5.1 Summary

Two major studies were done and reported in this thesis. The first study examined refining and the effect of change of fiber morphology on the mechanical and optical properties of cellulose film, while the second part explored the impact of chemical treatment using TEMPO mediated oxidation process to achieve a desirable mechanical and optical properties of films that can be applied to solar panel technology.

The following conclusions may be drawn from the results of this thesis:

1. The primary effect on pulp fibers of the repeated compressive action of the roll refiner is internal fibrillation and major paper strength development is possible with internally fibrillated fibers.
2. As expected, PFI and KRK refining methods together improved tensile and burst strength, increased paper density and improved drainability by decreasing the freeness. Refining also reduced tear strength and sheet thickness.
3. Processing conditions for producing cellulose nanofibrils, as well as the process conditions for producing films significantly impact the mechanical and physical properties of the films.
4. TEMPO oxidized films had better tensile strength and higher transparency than films made from refining process and mechanically treated films
5. Extremely very short fiber (fines) significantly develops tensile strength, stiffness and tends to have smoother surface and denser structure.

6. The small lateral size of the cellulose nanofibers prepared from TEMPO oxidized method makes it possible to provide almost transparent and highly viscous dispersions. TEMPO oxidized films obtained in this work have percentage transmittance of about 68 at 1100nm; this showed that the fibers exhibit optical properties directly related to the fiber size, which is better than that of refining that gave percentage transmittance of 21 due to large fibers.

In conclusion, this study provides the demonstration that precise control of the cellulose fiber dimensions enables paper substrates with a diverse range of unique mechanical and optical properties. These results provide a promising platform for future development of green, disposable optoelectronic devices.

5.2 Recommendations for Future Work

Based on the results from this study, the following recommendations will help future studies:

1. Transmission haze is an important requirement for solar panel application. However, the measurement was not successfully done because of the unreadiness of the measuring tools.
2. Additional morphological study of the fibers may be done using AFM

Appendix

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Publications:

Shuangxi Nie, Shuangfei Wang, Chengrong Qin, Shuangquan Yao, Johnbull Friday Ebonka,Xueping Song, Kecheng Li, Removal of hexenuronic acid by xylanase to reduce adsorbable organic halides formation in chlorine dioxide bleaching of bagasse pulp, Bioresource Technology 196 (2015) 413–417.

Conference Presentations:

Johnbull Friday Ebonka, Kecheng Li, Guida Bendrich, Kelechi Margaret Oyoh, Nanocellulose for Recyclable Solar Panel Application, Renewable & Alternative Energy of Nigeria, Federal University of Technology, Akure, April 26, 2017. Accepted