CLAUDIA MARCIA GOMES

CATIONIZATION OF CELLULOSE NANOFIBRILS (CNF) FOR APPLICATION AS ADDITIVE TO IMPROVE QUALITY OF EUCALYPTUS KRAFT PULP ON PAPER PRODUCTION

Tese apresentada à Universidade Federal de Viçosa, como parte das exigências do Programa de Pós-Graduação em Ciência Florestal, para obtenção do título de *Doctor Scientiae*.

VIÇOSA
MINAS GERAIS - BRASIL
2015

Ficha catalográfica preparada pela Biblioteca Central da Universidade Federal de Viçosa - Câmpus Viçosa

T

G633c
2015

Gomes, Claudia Marcia, 1975-

Cationization of cellulose nanofibrils (CNF) for application as additive to improve quality of *Eucalyptus* kraft pulp on paper production / Claudia Marcia Gomes. – Viçosa, MG, 2015.

xx, 92f. : il. ; 29 cm.

Inclui apêndices.
Orientador: Rubens Chaves Oliveira.
Tese (doutorado) - Universidade Federal de Viçosa.
Inclui bibliografia.

1. Celulose - Nanofibrila. 2. Papel - Propriedades. I. Universidade Federal de Viçosa. Departamento de Engenharia Florestal. Programa de Pós-graduação em Ciência Florestal. II. Título.

CDD 22. ed. 634.986

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APROVADA: 21 de dezembro de 2015.

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DEDICATÓRIA

Ao meu amado filho Davi.

Uma alegria na minha vida.

A minha amada mãe Carminha.

Um porto seguro na minha vida.

Ao Oldair.

Quanto falta você faz.

Aos alunos.

Um incentivo para busca de conhecimento.

Entender é, no final das contas, o que me motiva.

Claudia Marcia Gomes

AGRADECIMENTOS

A sabedoria de Deus por ter me conduzido até este caminho.

A minha mãe por sempre ter acreditado em mim, me incentivado a estudar e ser para mim um exemplo de ser humano.

Ao professor Rubens Chaves de Oliveira pela orientação, pelos ensinamentos, pela paciência e por estar sempre disponível para auxiliar no que foi necessário durante o desenvolvimento deste trabalho.

Ao professor Jorge Luiz Colodette pelas sugestões, os ensinamentos, além da disponibilidade para contribuir com o desenvolvimento do trabalho.

Ao professor Michael C. K. Tam, por permitir a utilização do seu laboratório e pelas orientações durante o desenvolvimento deste trabalho.

À Prof. Andréia, Prof. Dalton, ao Dr. Diego e ao Prof. Fernando pela disponibilidade em participar da defesa e pelas contribuições para a melhoria do trabalho.

À Dalila Batista Albertassi, pela amizade, contribuição e dedicação durante a condução dos experimentos no LCP/UFV.

À Juliana Sá, pela amizade e contribuição durante a condução dos experimentos no UW e na discussão dos resultados.

À Fernanda Morbeck, ao Edvan, à Renata, ao Mauro Manfredi, à Carla, ao Carlinhos, à Janaína, ao Diego, ao Jesus, pela ajuda nas análises de laboratório.

Aos Drs. Dolores, Wanderly e Fernando, pelo apoio durante esta etapa da minha vida.

Aos colegas do Laboratório de Colóides e Nanomateriais Funcionais/UW, em especial ao Patrick, Dr. Zegqia Shi, Hananim, Rafael e Juliana, pela acolhida, pela amizade e pelo auxílio nas análises laboratoriais.

Aos funcionários, estudante e estagiários do DEF, LCP e UFV, em especial Edinho, Cirinho, D. Conceição, Alexandre e Thiago, pela convivência, por estarem sempre dispostos a ajudar.

Aos colegas do curso de pós-graduação pela amizade, convivência, ajuda no decorrer do curso.

Aos Professores e amigos Ana Márcia, Cassinha e Fernando, por estarem sempre dispostos a ajudar.

Ao Núcleo de Microscopia e Microanálise da UFV pelas análises de imagens.

Ao Leandro, Guilherme, ao Prof. Hélio e ao Pesquisador Ledo, pelo auxílio nas análises estatísticas. À Carolina e ao Alessandro pelas correções do inglês.

A minha família, por estar sempre presente em todos os momentos e sempre dispostos a ajudar. Ao Davi pela paciência durante esta fase em que estive bem menos disponível para ele. Ao Carlos, pelo companheirismo, carinho e paciência durante o desenvolvimento deste trabalho. E, em especial, pela grande ajuda durante o período em que estive no trabalho no Canadá, o que foi imprescindível para a condução dos trabalhos.

A todas as pessoas que ajudaram com os cuidados ao meu filho, Davi, durante o período de desenvolvimento deste trabalho, em especial à minha mãe, à Fátima e ao Carlos.

À Carla, Antônio, Hananim, Sherry McGlynnof, Juliana, Dorothy Tam e Focus group, pela amizade, ajuda e por terem contribuído para que a nossa vida no Canadá fosse mais fácil e agradável.

À Rozimar, pela amizade que construímos na UFRB, e por estar sempre pronta a ajudar e me representar perante UFRB durante a minha ausência.

À UFRB pela licença para a realização do curso de doutorado e aos colegas do curso por cobrir as minhas atividades durante a minha ausência.

À Universidade Federal de Viçosa pela oportunidade oferecida.

Ao CNPq e à CAPES pela concessão do suporte financeiro.

À todos que de alguma maneira contribuíram para a realização deste trabalho.

BIOGRAFIA

CLAUDIA MARCIA GOMES, filha de Jorge Justino Gomes e Maria do Carmo Ladeira Gomes, nasceu em 09 de maio de 1975, em Teixeiras-MG.

Concluiu o segundo grau no COLUNI, Colégio de Aplicação da Universidade Federal de Viçosa- MG.

No período de dezembro de 1995 até fevereiro de 1997 exerceu a função de laboratorista no laboratório de branqueamento de celulose da Universidade Federal de Viçosa.

Em março de 1997, iniciou o Curso de Engenharia Florestal na Universidade Federal de Viçosa-MG, diplomando-se em agosto de 2003. Paralelo ao curso desenvolveu trabalhos de pesquisa na área de branqueamento de celulose, sob a orientação do professor Jorge Luiz Colodette.

Em março de 2004, iniciou o Curso de Mestrado em Ciência Florestal, na Universidade Federal de Viçosa-MG, diplomando-se em fevereiro de 2006.

No período de março de 2006 a fevereiro de 2007 foi bolsista de aperfeiçoamento/DTI-FAPEMIG vinculado ao projeto “Avaliação não destrutiva da madeira visando à produção de polpa celulósica”, sob a orientação do professor Jorge Luiz Colodette.

Em março de 2007 ingressou na Universidade Federal do Recôncavo da Bahia-UFRB como professora assistente do Centro de Ciências Agrárias, Ambientais e Biológicas-CCAAB.

Em março de 2011, iniciou o Curso de Doutorado em Ciência Florestal, na Universidade Federal de Viçosa-MG, diplomando-se em dezembro de 2015.

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LIST OF ACRONYMS, ABBREVIATIONS AND SYMBOLS

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APS: 3-aminopropyltriethoxysilane

BuA: butyl acrylate

CTAB: cetyltrimethylammonium bromide

DDDAB: didodecyldimethylammonium bromide

DHDAB: dihexadecyldimethhylamonium bromide

EA: ethyl acrylate

GMA: glycidyl methacrylate

GPS: 3-glycidoxypropyltrimethoxysilane

HEMA: 2-hydroxyethyl methacrylate

MMA: methyl methacrylate

NMR: nuclear magnetic resonance

PAH: poly(allylamine hydrochlride)

PCL: poly(ε-caprolactone)

PDADMAC: poly(diallyldimethylammonium chloride)

PDDA: poly(diallyldimethylammonium chloride

PEMs: polyelectrolyte multilayers

PEI: polyethyleneimine

PSS: poly(sodium 4-styrenesulfonante)

SEM: scanning electron microscopy

CHAPTER 2

ANOVA: analysis of variance

AgCl: silver chloride

$AgNO_3$: silver nitrate

CI: crystallinity index

CCC: chlorocholine chloride

CMF: cellulose microfibril

CNF: cellulose nanofibril

C-CNF: cationic cellulose nanofibril

C1-CNF: cationic cellulose nanofibril with lower degree of cationization

C2-CNF: cationic cellulose nanofibril with higher degree of cationization

CED: ethylenediamine cupric

DMSO: dimethyl sulfoxide

DP: degree of polymerization

FTIR: Fourier transform infrared spectroscopy

GTMAC: glycidyltrimethyammonium chloride

HPC: hidroxylpropyl cellulose

ISO: International Organization for Standardization

LSC: light scattering coefficient

MFC: microfibrillated cellulose

MW: molecular weight

NaOH: sodium hydroxide

NFC: nanofibrillated cellulose

P-CNF: pristine CNF

REP.: repetitions

R^2: determination coefficient

SEM: scanning electronic microscopy

°SR: Schopper Riegler degree

TAPPI: Technical Association of the Pulp & Paper Industry

TBAH: tetrabutylammonium hydroxide 30-hydrate

TEM: transmission electron microscopy

TEMPO: 2,2,6,6 tetramethylpiperidine-1-oxyl

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RESUMO

GOMES, Claudia Marcia, D.Sc., Universidade Federal de Viçosa, dezembro de 2015. **Cationização de nanofibrilas de celulose (NFC) para aplicação como aditivo na melhoria de qualidade da polpa kraft de eucalipto para produção de papel.** Orientador: Rubens Chaves Oliveira. Coorientadores: Jorge Luiz Colodette e José Lívio Gomide.

Celulose nanofibrila (CNF) refere-se aos aglomerados de fibrilas de celulose com diâmetro na ordem de nanômetros, obtidos a partir de fibras celulósicas, por processamento mecânico. As principais características da CNF são elevadas resistência mecânica e transparência, além do baixo peso específico e coeficiente de expansão térmica. Outro fator de relevância é ser um polímero biodegradável, portanto interessante do ponto de vista ambiental. Adicionalmente, a superfície da CNF apresenta elevada concentração de grupos hidroxilas, o que a torna adequada para a introdução de moléculas ou polímeros, a fim de melhorar o seu desempenho ou desenvolver novas funcionalidades. A CNF tem sido investigada com um substituto aos polímeros sintéticos nas mais diferentes áreas. Este estudo trata da modificação da CNF para utilização como aditivo na produção de papel e foi dividido em três etapas. Na primeira etapa foi realizada uma revisão de literatura sobre modificação superficial de CNF. Na segunda etapa a CNF foi cationizada com o objetivo de tornar a sua distribuição homogênea na estrutura do papel e promover ligações entre as fibras em maior quantidade e mais fortes. As propriedades físico-químicas e ultraestruturais da CNF antes (P-CNF) e após a cationização (C1-CNF e C2-CNF) foram mensuradas com a finalidade de comprovar a cationização e verificar o seu efeito na estrutura da CNF. As CNFs cationizadas apresentaram conteúdos de trimetilamônio de 0.68 (C1-CNF) e 1.21 $mmol \cdot g^{-1}$ (C2-CNF). As reações de cationização diminuíram a espessura e o comprimento das fibrilas, bem como degradaram a cadeia e a estrutura cristalina da celulose, sendo esses efeitos mais pronunciados para a reação que resultou na C2-CNF. Na terceira etapa, as C-CNFs foram utilizadas como aditivo na melhoria de qualidade da polpa kraft de eucalipto para a produção de papel. O efeito da adição das C-CNFs no tempo de drenagem da polpa e nas propriedades físico-mecânicas e ópticas do papel foi avaliado. Após a cationização, a CNF apresentou distribuição homogênea na estrutura do papel. Somente as polpas com elevadas cargas de C-CNFs (3% and 5%) apresentaram tempos de drenagem maiores que aquelas com adição de P-CNF. A adição de C2-CNF resultou em polpas com tempo de drenagem estatisticamente maior que a adição de C1-CNF. Quando comparado com os papéis com adição de P-CNF, aqueles com adição de C-CNFs possuem menores volume específico aparente (VEA) e maiores resistência à passagem de ar (RPA) e lisura. Somente a adição de elevadas cargas de C-CNFs resultou em papéis com índices de rasgo e arrebentamento estatisticamente maiores que aqueles com P-CNF. Uma possível explicação seriam os maiores flóculos presentes durante a formação do papel, o que levou ao maior entrelaçamento entre as fibras. Quando comparada com a P-CNF, a adição de diferentes cargas de C-CNFs não resultou aumento do índice de tração dos papéis. A redução da resistência mecânica para a polpa com baixas cargas de C-CNFs se deve, possivelmente, ao rompimento do papel ter ocorrido na C-CNF, que foi degradada durante a reação de cationização. Os papéis com C-CNFs apresentaram menores coeficientes de dispersão de luz (CDL) e maiores transparências do que aqueles com P-CNF. No geral, o grau de cationização da CNF teve efeito nas propriedades físicas e ópticas do papel, mas não teve efeito nas propriedades mecânicas. Para o uso da CNF cationizada na melhoria das propriedades do papel, a reação de cationização deve ser realizada em meio compatível com a produção de papel e não prejudicar a estrutura da CNF. Adicionalmente, o grau de cationização e a carga de CNF precisa ser otimizada para melhorar as propriedades do papel sem aumentar o tempo de drenagem da polpa.

ABSTRACT

GOMES, Claudia Marcia, D.Sc., Universidade Federal de Viçosa, December, 2015. **Cationization of cellulose nanofibrils (CNF) for application as additive to improve quality of eucalyptus kraft pulp on paper production.** Adviser: Rubens Chaves Oliveira. Co-advisers: Jorge Luiz Colodette and José Lívio Gomide.

Cellulose nanofibril (CNF) refers to cellulose fibril agglomerates with diameter in the nanometer scale, obtained from cellulosic fibers by mechanical processing. Its main characteristics are high mechanical strength and transparency, in addition to the low specific weight and coefficient of thermal expansion. Another relevant factor is to be a biodegradable polymer, therefore attractive from an environmental point of view. Additionally, the surface of the CNF presents high concentration of hydroxyl groups, suitable for introducing molecules or polymers, which can improve its performances or develop new features. The CNF has been studied as a substitute for synthetic polymers in many different areas. In this study, the CNF was modified for use as an additive to produce paper, and consists of three stages. In the first stage, a literature review of surface modification of CNF was conducted. In the second stage, the CNF was cationized in order to make its distribution more homogeneous on paper structure, allowing a large number and strong bounds between the fibers. The physicochemical and ultrastructural properties of CNF before (P-CNF) and after the cationization (C1-CNF and C2-CNF) were evaluated, in order to ensure the modification process and verify its effect on the CNF structure. The CNFs presented trimethylammonium chloride content of 0.68 (C1-CNF) and 1.21 $\text{mmol}\cdot\text{g}^{-1}$ (C2-CNF). The cationization reactions decreased the fibrils thickness and the length, and also degraded the cellulose chain and crystallinity structure, these effects being more pronounced for the reaction that resulted in the C2-CNF. In the third stage, the C-CNFs were used as additive to improve quality of eucalyptus kraft pulp on paper production. The effect of adding C-CNFs on pulp drainage time and on physical-mechanical and optical properties of paper sheets was evaluated. After the cationization, the CNF presented homogeneous distribution on paper structure. Only the pulps with high charges of C-CNFs (3%

and 5%) presented drainage time higher than those with P-CNF. The addition of C2-CNF resulted in pulps with drainage time statistically higher than those with C1-CNF. In general, the papers with addition of C-CNFs presented lower bulk, and higher air resistance and smoothness than those with P-CNF. Only the addition of high charges of C-CNFs resulted in papers with tear index and burst index statistically higher than those with P-CNF. A possible explanation is that larger flocs present during the paper formation can cause a greater entanglement between the fibers. When compared with P-CNF, the addition of different charges of C-CNFs did not increase the tensile index of papers. The reduction of mechanical strength for paper with low charges of C-CNFs may have occurred by rupture of the paper in the C-CNF, which was degraded during the cationic reaction. The papers with addition of different charges of C-CNF presented lower light scattering coefficient and higher transparency than those with P-CNF. In general, the degree of cationization of CNF had effect on the physical and optical properties of paper, however it had no effect on mechanical properties. For the use of cationic CNF as additive to improve quality of *Eucalypt*us kraft pulp on paper production, it is necessary that the cationic reaction be performed in medium compatible with paper production and does not damage the CNF structure. Additionally, the degree of cationization and the charge of CNF have to be optimized to improve the paper properties without increasing the pulp drainage time.

1 GENERAL INTRODUCTION

Cellulose nanofibril (CNF) is originated from cellulose, a material that is renewable, biodegradable and abundant in nature, which makes it attractive from an environmental point of view. Additionally, it has high strength and low specific weight, which makes it attractive for a use as a mechanical reinforcement in polymer matrix, film production and coating (KHALIL *et al*., 2014; WANG and SAIN, 2007; HENRIKSSON *et al*., 2007). These properties, added to the low thermal expansion and high transparency, make the CNF a potential material for electronic devices, such as display and solar cells (JUNG *et al*., 2015; OKAHISA, *et al*., 2009). The elevated barrier properties are useful to food and pharmaceutical packaging applications (LAVOINE *et al*., 2012; MARTINS *et al*., 2012).

Herrick *et al*. (1983) and Turbak *et al*. (1985) were the first to publish papers on mechanical disintegration of cellulose fibers in very inhomogeneous nanofibers, with the width in range of the one hundred nanometers and largest, designated microfibrillated cellulose (MFC). However, the interest of the industry sector began from the development of enzymatic (HENRIKSSON *et al*., 2007, PÄÄKKÖ *et al*., 2007), 2,2,6,6 tetramethylpiperidine-1-oxyl (TEMPO) oxidation (SAITO *et al*., 2007; SAITO and ISOGAI, 2004) pre-treatments, that decreased the energy consumption during production and resulted in very homogeneous nanofibers with smaller width (3.5-20 nm), designated cellulose nanofibril (CNF).

The modifications of CNF have been performed with the objective of reducing the energy consumption in production (EICHHORN *et al*., 2010; MISSOUM *et al*., 2013), improving the dispersion of CNF into polymeric matrix, so as to make it compatible with non-polar solvents and hydrophobic matrices (TINGAUT *et al*., 2009; STENSTAD *et al*., 2008), as well as developing new features, such as removable dyes from wastewater (PEI, *et al*., 2013; QUILAN, *et al*., 2015), drug delivery (KOLAKOVIC *et al*., 2012), electronic device (JUNG *et al*., 2015; OKAHISA, *et al*., 2009), functional package (MARTINS *et al*., 2012), etc.

In the pulp and paper sector, CNF has been investigated as coating (SYVERUD & STENIUS, 2009; AULIN *et al*., 2010) or additive for paper (HII *et al*., 2012; HASSAN *et al.*, 2015), without modification or only with an initial cationic, aiming improving their mechanical and barrier properties.

In the present study, the CNF was previously cationized for use as additive to improve quality of eucalyptus kraft pulp on paper production. The objective was to overcome the difficulty of dispersion of CNF in the paper structure and achieve large number and strong bounds between cationic CNF and fibers.

CHAPTER 1

MODIFICAÇÃO SUPERFICIAL DE CELULOSE NANOFIBRILADA (CNF*)*

RESUMO

O módulo de elasticidade específico da celulose cristalina é superior ao de materiais como alumínio, aço e vidro. Uma maneira de obter fibras com módulos de elasticidades próximos ao da celulose cristalina pura é individualizar as fibras em nanofibras. Quando se faz esta individualização por processo mecânico, obtêm-se a celulose nanofibrilada (CNF). No entanto, algumas características como alto consumo de energia nos processos de produção, a baixa dispersão na matriz polimérica, a incompatibilidade com matriz polimérica apolar, a hidrofilicidade, limitam o seu uso como reforço de polímeros e revestimento de papéis. A superfície da nanofibrila de celulose apresenta elevada concentração de grupos hidroxilas, o que a torna adequada para a introdução de moléculas ou polímeros com o objetivo de superar estas limitações, ou até desenvolver novas funcionalidades para os papéis com a adição de CNF modificada. Esta revisão de literatura apresenta estudos sobre modificações superficial da CNF, incluindo o efeito das modificações nas suas características e na utilização da CNF. Existem poucos estudos sobre este assunto e conclusões definitivas ainda não foram alcançadas. No entanto, as pesquisas caminham no sentido de se utilizar reações que ocorram em solvente não tóxico e que não resultem em redução da resistência mecânica das nanofibrilas.

SURFACE MODIFICATION OF CELLULOSE NANOFIBRILS (CNF)

ABSTRACT

The specific modulus of the crystalline cellulose is greater than other materials such as aluminum, steel and glass. One way to get fiber with values of elastic modulus close to that of pure crystalline cellulose is to individualize the fibers into nanofibers. When this individualization is made by a mechanical process, the nanofibrillated cellulose (NFC) is obtained. However, some features, such as high energy consumption in production processes, low dispersion in the polymer matrix, incompatibility with the non-polar polymer matrix, hydrophilicity, limit the use of NFC as reinforcement of the polymer and paper coating. The surface of the cellulose nanofibrils has a high concentration of hydroxyl groups, suitable for introducing molecules or polymers, in order to overcome these limitations or develop new features for papers with the addition of NFC modified. This review presents studies on modification of NFC surface, including the effect of changes in the characteristics and use of NFC. There are a few studies on this subject and definitive conclusions have not yet been achieved. However, researches point towards the use of reactions in non-toxic solvent, with no reduction of mechanical strength of the fibrils.

1 INTRODUCTION

Nanofibrillated cellulose (NFC), cellulose microfibril (CMF), cellulose nanofibril (CNF) or nanocellulose are terms used for referring to the same material; cellulose fibril agglomerates with diameter between 1 and 100 nm (0,001 and 0,1µm) and length in the micrometer scale, obtained from cellulosic fibers by mechanical processing (CHINGA-CARRASCO, 2011; MISSOUN *et al.*, 2013).

The CNF is characterized by high surface area, in the range of 50-70 m^2/g, about at least 10 times larger than the fibers, with high concentration of hydroxyl groups, forming gels at low concentrations (MISSOUM *et al.*, 2013). Additionally, it has high aspect ratio (greater than 100) and mechanical strength, when compared with the fibers (EICHHORN *et al.*, 2010).

Typical values of the Young´s modulus of fibers are below than crystalline cellulose, aluminum, steel and glass, which are 138, 69, 200 and 69 GPa, respectively. However, when the density of the material is taken into account, the specifc Young´s modulus is obtained, which for crystalline cellulose (92 GPa) is higher than aluminum, steel and glass, which are 92, 26, 28 $GPa \cdot mg^{-1} \cdot m^3$, respectively (EICHHORN *et al.*, 2010).

In the pulp and paper sector, the interest of use of the CNF has been as film, paper coating and pulp additive to improve paper properties.

However, the high concentration of hydroxyl groups on CNF surface leads to strong hydrogen bonds, forming agglomerations of nanofibrils and gel in low concentrations, which makes the dispersion of CNF difficult on cellulose pulp. Additionally, the high capacities of water absorption and oxygen permeability can limit the use of CNF in packaging paper (RADIANOVA *et al.,* 2011).

The surface of the cellulose nanofibrils has a high concentration of hydroxyl groups, suitable for introducing molecules or polymers in order to overcome these limitations or develop new features for papers with the addition of NFC modified. However, researches on CNF modifications are still limited. This review presents studies on surface modification of CNF, including its effects on CNF structure and the use of CNF after the modification.

2 LITERATURE REVIEW

2.1 Surface modification of CNF

The surface modification strategies of the nanofibrils may be divided into: (i) adsorption of molecules or macromolecules on the surface of CNF; (ii) covalent bonds between molecules or polymers and the surface of CNF.

2.1.1 Adsorption on the surface of CNFs

The modification of CNFs by adsorption of surfactants and polyelectrolytes on the surface of the CNFs is performed through electrostatic interactions.

Xhanari *et al.* (2011) used the cetyltrimethylammonium bromide (CTAB), didodecyldimethylammonium bromide (DDDAB) and dihexadecyldimethhylamonium bromide (DHDAB) to modify surfaces of CNFs produced with pre-treatment "TEMPO-oxidation", in order to reduce the adhesion of nanofibers to water or to make them hydrophobic. The cationic surfactants were added directly to the CNF suspension in an aqueous medium at room temperature. Then the suspension was stirred for 15 minutes and films were prepared.

The authors observed that a very low concentration of surfactants is required to give the cationic surfactant adsorption force on TEMPO-mediated oxidized nanofibrils, with the anionic carboxyl groups. The contact angles were larger and adhesion energies with water were lower for the films formed with nanofibrils treated with CTAB in different degrees of substitution as compared to the films with DDDAB, DHDAB and CNFs without treatment. The authors concluded that the CNFs treated with cationic surfactants did not become completely hydrophobic, but increased their water repellency (XHANARI *et al.*, 2011).

In order to increase the barrier property to oil of the carboxymethylated microfibrillated cellulose films, Aulin *et al.* (2008) modified them by coating with perfluorooctadecanoic acid ($C_7F_{15}COOH$), which resulted in reducing the surface energy of 54.5 mN/m to 12 mN/m. According to the author, the surfaces coated with $C_7F_{15}COOH$ have the potential to resist the oil due to their low surface energy. This property is required for paper and paperboard used in food packaging.

Wagberg *et al.* (2008) used CNF carboxymethylated to form polyelectrolyte multilayers (PEMs) with the cationic polyelectrolytes polyethyleneimine (PEI), poly(allylamine hydrochloride) (PAH) and poly(diallyldimethylammonium chloride) (PDADMAC). The method consisted of immersing a silicon substrate in CNF suspension (2%) and solution of polyelectrolyte PEI (2.5 mg/mL) or PDADMAC (1.25 mg/mL) or PHA (1.01 mg/mL) in deionized water, with intermediate water washes "Mili-Q" in order to remove excess and do not contaminate the solutions.

The authors concluded that it is possible to prepare films of cellulose with some cationic polyelectrolyte intercalated between the fibrils (PEMs). In order to determine the interaction between the CNF and the polyelectrolyte of opposite charges, the thickness of the multilayer was measured with elipsometer. The thickness of the layers of the evaluated polyelectrolyte was different, especially the PEI who presented the thickest layer. However, you can control the thickness of the multilayer using NaCl (WAGBERG *et al*., 2008).

Martins *et al*. (2012) produced composites of nanofibrillated cellulose (NFC) and silver (Ag) nanoparticles using polyelectrolytes as binding agent, in order to produce nanopaper antimicrobial to be used in paper coating.

The cationic polyelectrolyte poly(diallyldimethylammonium chloride) (PDDA), PAH, PEI and anionic poly(sodium 4-styrenesulfonate) (PSS) were used. PDDA, PEI and PAH and PSS (0.1% w/v) solutions were prepared in 0.5 M NaCl aqueous. A sample of 5.8 g of the NFC 2% consistency was mixed with 70 mL of cationic polyelectrolyte solution then with 70 mL of anionic polyelectrolyte and again 70 mL of cationic polyelectrolyte. After each step, the nanofibers were separated by filtration and washed with distilled water. Finally, the modified NFC was mixed with 70 mL of colloidal Ag. Photomicrographs confirmed the presence of Ag nanoparticles on the surface of the NFC (Figure 01). The antibacterial activity was observed against *S. aureus* and *K. pneumoniae* for all polyelectrolytes studied and Ag nanoparticles. According to the authors, this technique can be used for the development of papers with bactericidal activity and this property can be adjusted by varying the quantity and characteristics of the NFC/Ag.

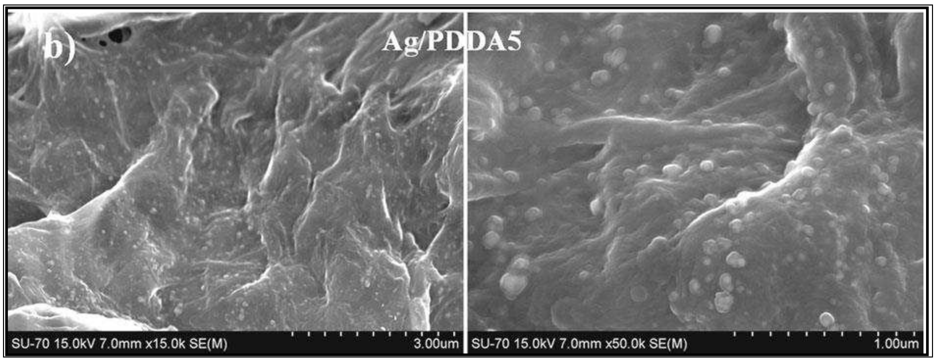

Figure 01- Images of Ag nanoparticles on the surface of nanofibrillated cellulose (NFC) obtained by scanning electron microscopy (SEM) (Source: MARTINS *et al.*, 2012)

2.1.2 Chemical bonds between the molecules and the surface of the CNFs

Despite the efficiency of the methods of molecule adsorption on CNF surface, they are more unstable than the methods based on covalent bonds.

Berlioz *et al.* (2009) modified cellulose microfibrils surface by esterification with palmitoyl chloride in gaseous medium, in order to make it hydrophobic.

The methodology consisted of transferring a sample of 150 mg of cellulose microfibrils (as a support) for a 1 L vessel containing palmitoyl chloride, so that the NFC would not come into contact with the reagent. The vessel was placed in an oven vacuum with temperature control and pressure. As the temperature increased, a fraction of the reaction evaporated and was in contact with the cellulose microfibrils, forming hydrophobic ester bonds (BERLIOZ *et al.*, 2009).

The esterification reaction was confirmed by ^{13}C NMR. It was observed that the acetylation starts in the cellulose surface towards the microfibrils center, so the surface replacement threshold must be optimized in order to maintain the compatibility of the material with apolar matrix, and conserve crystalline cellulose center, or its high mechanical strength (BERLIOZ *et al*., 2009). It is worth mentioning that the absence of solvent is a great advantage, because depending on the type of solvent used, the environmental benefit of using the pulp is reduced.

Kim *et al*. (2002), Nogi *et al*. (2006) and Ifuku *et al*. (2007) introduced acetyl groups in the CNFs from bacterial cellulose. Kim *et al*. (2002) concluded that CNF may be partially acetylated with no change in their morphology, but with a strong reduction of their mechanical properties. According to Nogi *et al*. (2006) and Ifuku *et al*. (2007) acetylation increases transparency and reduces the thermal degradation of the CNF.

Lu *et al*. (2008) modified MFC in order to improve its dispersion in non-polar polymer matrix and increase the connection interfaces with the resulting epoxy composite. The modification of the MFC was performed by grafting 3-aminopropyltriethoxysilane (APS) and 3-glycidoxypropyltrimethoxysilane (GPS) and titanate coupling agent. The modification changed the character of MFC from hydrophilic to hydrophobic After treatment, better and stronger adhesion was obtained between MFC and the epoxy polymer matrix, resulting in improved mechanical properties of the composite.

2.1.3 Chemical bonds between polymers and the surface of the CNFs

Lonnberg *et al.* (2011) used microfibrillated cellulose (MFC) produced from bleached softwood sulfite pulp to enhance the biopolymer matrix of poly(ε-caprolactone) (PCL). MFC was mixed with ε -CL monomer and the reaction by ring-opening polymerization was conducted with catalytic amounts of tin Sn-(Oct) $_2$ at a temperature of 95 °C and reaction time of 18-20 hours. The study investigated the effect of PCL chains with degrees of polymerization of 300, 600 and 1200, the properties of the PCL-CNF composite. The authors concluded that the grafting of PCL improved dispersion of CNF in the nonpolar solvent and in the PCL matrix. The mechanical tests of biocomposites showed improvement mechanical properties for the CNF grafted PCL when compared to untreated

NFC. The size of the PCL chain grafted onto the CNF had a positive effect on the mechanical properties of biocomposites.

Other studies have reported the surface modification of CPF by grafting PCL (BENKADDOUR *et al.*, 2013;. LIN *et al.*, 2009).

Stenstad *et al.* (2008) inserted epoxy functionality on the surface of the MFC by oxidation with cerium (IV) ion, followed by grafting with glycidyl methacrylate (GMA). The advantage of this technique is that the reaction occurs in an aqueous medium, using organic solvents is not necessary.

Figure 02 shows transmission electron micrographs of MFC coated with 20 µmol of GMA and uncoated. It is noted that the modified nanofibrils have thicker and more barbed nature, showing that a thick polymer coating layer is the nanofibers. wider areas along the fibrils indicate that crystalline and amorphous regions have different degrees of substitution during reaction (STENSTAD *et al.*, 2008).

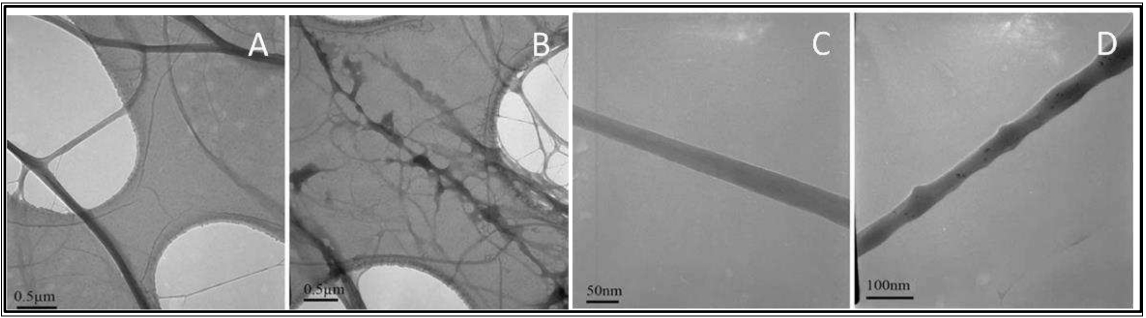

Figure 02- Transmission electron micrograph showing microfibrillated cellulose (MFC) coated with glycidyl methacrylate (GMA) (B and D) and MFC untreated (A and C) (Source: STENSTAD *et al.*, 2008)

Epoxy reactive group used for other applications when associated with ligands which do not react with the hydroxyl groups present on the surface of native MFC. According to the author, an application for this modified MFC would be like stepping into nanocomposites, due to increased interaction between CNFs and the hydrophobic polymer matrix (STENSTAD *et al.*, 2008).

Littunen *et al.* (2011) also used an aqueous medium and nitrate cerium (IV) ammonium $(NH4)_2Ce(NO_3)_6$ for NFC modification by grafting of glycidyl methacrylate (GMA), ethyl acrylate (EA), 2-hydroxyethyl methacrylate (HEMA), methyl methacrylate (MMA) and butyl acrylate (BuA) in order to make the NFC more hydrophobic, and develop new features.

As shown in Figure 03, after dry, well-dispersed products form a fragmented film, a solid mass or granules. The CNFs modified AE and BuA were more hydrophobic. According to the authors, these modification means are ways to overcome the obstacles of using high strength cellulose nanocomposites.

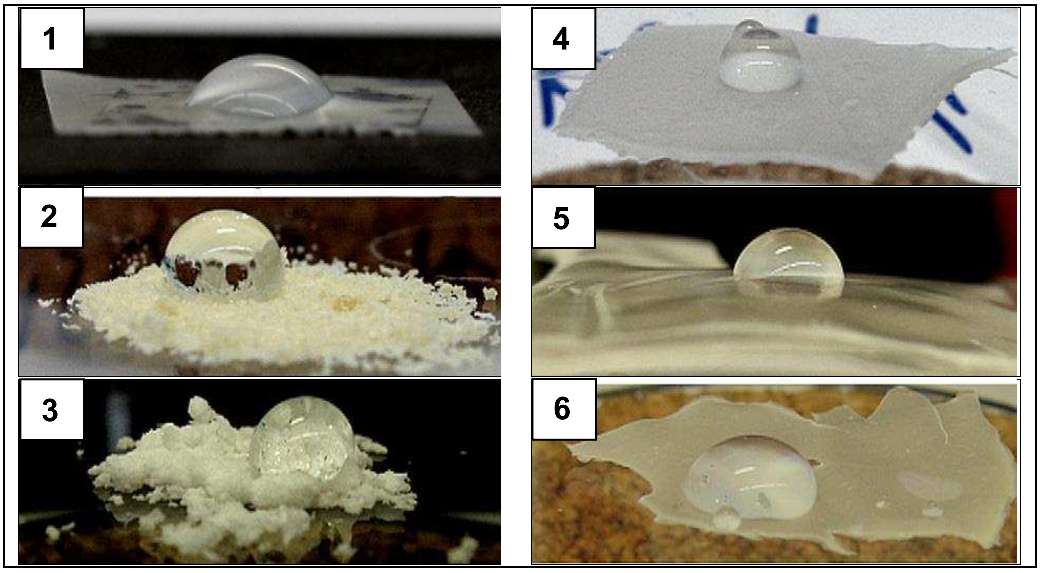

Figure 03 - Water droplets on the surface of the nanofibrillated cellulose (NFC) without modification (1) and the product grafted with glycidyl methacrylate (GMA) (2), ethyl acrylate (AE) (3), methyl methacrylate (MMA) (4), butyl acrylate (BuA) (5) and 2-hydroxyethyl methacrylate (HEMA) (6) (Source: LITTUNEN *et al* ., 2011)

3 CONCLUSIONS

The interest in cellulose nanofibrils has increased in recent years, as a biopolymer with high mechanical properties. However, some features such as their tendency to form agglomerates at low concentrations, incompatibility with non-polar polymer matrix and the hydrophilicity can be obstacles to their use.

To overcome these limitations, modifications of the cellulose nanofibrils have been developed by inserting molecules or polymers on the surface by adsorption or covalent bonding. There are few studies on this subject and definitive conclusions have not yet been achieved. However, research has been towards the use of non-toxic aqueous solvents during the modifying step, in order not to lose the environmental benefit of using a biodegradable raw material and allow the use of this technology on an industrial scale. Additionally, the reaction of modification should not degrade the cellulose structure, in order not to damage their high mechanical strength.

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CHAPTER 2

CATIONIZAÇÃO DE NANOFIBRILAS DE CELULOSE (NFC) PARA APLICAÇÃO COMO ADITIVO NA MELHORIA DE QUALIDADE DA POLPA KRAFT DE EUCALIPTO PARA PRODUÇÃO DE PAPEL

RESUMO

A celulose nanofibrilada (P-CNF) foi cationizada através da reação com cloreto de glicidiltrimetilamônio (GTMAC), na presença de dimetilsulfóxido (DMSO) e hidróxido de tetrabutilamônio (TBAH), visando a sua utilização como aditivo na melhoria da qualidade da polpa kraft de eucalipto para a produção de papel. A modificação catiônica da CNF, seguida de purificação, resultou em dispersões aquosas de C-CNF na forma de gel com elevada viscosidade, transparência e conteúdo de trimetilamônio de 0.68 (C1-CNF) e 1.21 (C2-CNF) $mmol \cdot g^{-1}$. A presença de cloreto de trimetilamônio ligado à CNF foi confirmada por titulação condutimétrica e espectroscopia no infravermelho com transformada de Fourier (FT-IR). As C-CNFs (P-CNF, C1-CNF and C2-CNF) foram caracterizadas pelas análises zeta potencial, viscosidade, difração de raios X e imagens de microscopia eletrônica de transmissão (MET). Na faixa de pH estudada (4-10), os valores de zeta potencial para a P-CNF variaram de -12.1 até -20.0 mV. Após a modificação catiônica, os valores de zeta potencial variaram de +28.5 até +33.7 mV (C1-CNF) e de +33.2 até +54.3 mV (C2-CNF). Esta magnitude do zeta potencial indica uma dispersão instável para P-CNF e estável após a modificação catiônica. As medidas de viscosidade e os espectros de raio X mostraram que a modificação catiônica resultou em forte efeito negativo na ultraestrutura da P-CNF, sendo este efeito mais pronunciado para a C2-CNF. As imagens de MET mostraram que o comprimento e a espessura das C-CNFs são menores quando comparadas com a P-CNF, devido à forte repulsão eletrostática dos grupos amônio quaternários, que é eficiente na individualização das microfibrilas, e devido à degradação das fibrilas pela reação de cationização. P-CNF, C1-CNF e C2-CNF, nas proporções de 0-5% (m/m), foram adicionadas às suspensões de polpas sem

refino e refinada (1000 rev. PFI) e o efeito das CNFs na floculação e no tempo de drenagem da polpa foi analisado. A suspensão de polpa com C2-CNF apresentou uma maior resistência inicial à sedimentação dos flóculos, devido à elevada estabilidade da C2-CNF. No entanto, resultou em uma coluna de sedimento mais densa, devido à forte atração eletrostática entre a carga positiva da C2-CNF e a carga negativa das fibras. A adição de 1% de CNFs não teve efeito significativo na drenagem da polpa. A adição de 3% e 5% de CNFs teve efeito negativo na drenagem da polpa, sendo este efeito mais pronunciado para a C2-CNF. Papéis foram preparados e caracterizados através da medição do conteúdo de nitrogênio, de imagens de microscopia eletrônica de varredura (MEV) e das propriedades físico-mecânicas e óticas. A medição do conteúdo de nitrogênio dos papéis mostrou que os finos tiveram um efeito positivo na retenção da C2-CNF no papel. As imagens de MEV mostraram que as CNFs agem como pontes, aumentando as ligações entre as fibras e reduzindo a porosidade do papel, sendo esses efeitos mais pronunciados para as C-CNFs, devido à sua dispersão homogênea na estrutura do papel. Formação de filmes e redes emaranhadas de nanofibrilas na superfície dos papéis com adição de P-CNF foram observadas. Os papéis com adição de diferentes cargas de C-CNFs apresentaram volume específico aparente (VEA) menor e resistência à passagem de ar (RPA) e lisura maiores que daqueles com adição de P-CNF. Somente a adição de 5% de C-CNFs na polpa sem refino resultou em papéis com índices de tração, de rasgo e de arrebentamento maiores que daqueles com P-CNF. No entanto, a adição de C-CNF pode ser usada como substituição ao refino da polpa somente para o índice de rasgo. Os papéis com adição de diferentes cargas de C-CNFs apresentaram menores coeficientes de dispersão de luz (CDL) e maiores transparências do que aqueles com P-CNF. A adição de P-CNF não teve um efeito claro no CDL e na transparência do papel, devido à aglomeração e distribuição não homogênea das fibrilas na matriz do papel. O grau de cationização da CNF não teve efeito nos índices de tração e arrebentamento do papel. Por outro lado, o efeito da C2-CNF nas propriedades físicas (VEA, RPA e lisura) e no índice de rasgo do papel foi maior que o da C1-CNF. Para as propriedades ópticas, o grau de cationização da CNF não teve efeito nos papéis feitos a partir de polpa não refinada e teve efeito nos papéis feitos a partir de polpa refinada.

CATIONIZATION OF CELLULOSE NANOFIBRILS (CNF) FOR APPLICATION AS ADDITIVE TO IMPROVE QUALITY OF EUCALYPTUS KRAFT PULP ON PAPER PRODUCTION

ABSTRACT

Cellulose nanofibril (P-CNF) was cationized through the reaction with glycidyltrimethyammonium chloride (GTMAC), performed in the presence of dimethyl sulfoxide (DMSO) and tetrabutylammonium hydroxide 30-hydrate (TBAH), for application as additive to improve quality of eucalyptus kraft pulp on paper production. The cationic modification of P-CNF, followed by purification, resulted in highly viscous and transparent like-gel aqueous dispersions of C-CNF, with trimethylammonium chloride content of 0.68 (C1-CNF) and 1.21 (C2-CNF) mmol·g^{-1}. The presence of trimethylammonium chloride attached to the C-CNF was confirmed by conductometric titration and Fourier transform infrared spectroscopy (FTIR). The CNFs (P-CNF, C1-CNF and C2-CNF) were characterized by zeta potential, viscosity, X-ray diffraction and transmission electron microscopy (TEM) images. In the studied pH range (4-10), the zeta potential values for P-CNF varied from -12.1 to -20.0 mV. However, the zeta potential values of C1-CNF and C2-CNF varied from +28.5 to +33.7 mV and from +33.2 to +54.3 mV, respectively. After cationic modification, the values of zeta potential varied from +28.5 to +33.7 mV (C1-CNF) and from +33.2 to +54.3 mV(C2-CNF). This magnitude of zeta potential indicates an unstable dispersion for P-CNF and a stable dispersion after cationic modification. The viscosity measurement and X-ray patterns showed that the cationic modification of CNF resulted in strong negative effects on the ultrastructure of C-CNFs, which were more pronounced on the C2-CNF. The TEM images showed that the fibrils length and thickness of C-CNFs are smaller than the P-CNF, due to the strong electrostatic repulsion of quaternary ammonium groups, which is efficient in separating fibrils from each other, and due to their degradation while the cationization reaction occurred. The P-CNF, C1-CNF and C2-CNF, in weight ratios ranging from 0% to 5% (w/w), were added in the unrefined and refined (1000 rev PFI) pulp suspensions, and the effect of CNFs on the pulp flocculation and pulp drainage time was analyzed. The pulp suspension with

C2-CNF presented the greater initial resistance of flocs to sedimentation, due to the high stability of C2-CNF. However, it resulted in a more dense sediment column, due to the strong electrostatic attraction between the positive charges of C2-CNF and the negative charges of fibers. The addition of 1% of CNFs did not have a significant effect on pulp drainage time. The addition of 3% and 5% of CNFs had a negative effect on the pulp drainage time, this effect being more pronounced for 5% of C2-CNF. Paper sheets were prepared and characterized by nitrogen content measurement, scanning electronic microscopy (SEM) images and physical-mechanical and optical properties. The nitrogen content measurement of paper sheets showed that the fines increased the C2-CNF retention in the paper sheet. The SEM images showed that the CNFs act as a binding agent, increasing the bonds between the fibers and reducing the porous of paper sheets, those effects being more pronounced for C-CNFs, due to its homogeneous dispersion in the paper matrix. Formation of films and networks of nanofibrils in paper sheets surface with addition of P-CNF was observed. The paper sheets with addition of different charges of C-CNFs presented lower bulk and higher air resistance and smoothness than those with P-CNF. The addition of only 5% of C-CNFs in the unrefined pulp resulted in papers with higher tensile index, tear index and burst index than those with P-CNF. However, the addition of C-CNF can be used as a substitute for pulp refining only for the tear index. The paper sheets with addition of different charges of C-CNFs presented lower light scattering coefficient and higher transparency than those with P-CNF. The addition of P-CNF has no clear effect in the light scattering coefficient and transparency of paper sheets. This is due to agglomeration and not homogeneous dispersion of fibrils in the paper sheets. The degree of cationization of CNF did not have any effect in tensile index and burst index of paper sheet. On the other hand, the effect of C2-CNF in physical properties, which includes bulk, air resistance and smoothness, and tear index of paper sheets was higher than that of C1-CNF. For the optical properties, the degree of cationization of CNF did not have any effect in paper sheets made from unrefined pulp, and had an effect in paper sheets made from refined pulp.

1 INTRODUCTION

Cellulose nanofibril (CNF) has high strength and low specific weight, which makes it attractive for a use as a mechanical reinforcement in polymer matrix (KHALIL *et al.*, 2014; WANG and SAIN, 2007; HENRIKSSON *et al.*, 2007). Additionally, it is originated from cellulose, a material that is renewable, biodegradable and abundant in nature, which makes it attractive from an environmental point of view.

Bleached kraft pulp (GONZÁLEZ *et al.*, 2013; SAITO *et al.*, 2007; TAIPALE *et al.*, 2010), followed by bleached sulfite pulp (AHOLA *et al.*, 2008; PÄÄKKÖ *et al.*, 2007; ZIMMERMANN *et al.*, 2010) and dissolving pulp (AULIN *et al.*, 2010; HENRIKSSON *et al.*, 2007) from wood have been the most used start materials for CNF production. The pulp industry already produces the cellulosic pulp, which is a competitive advantage. Additionally, the CNF is produced in an aqueous medium which is compatible with paper production.

In the pulp and paper sector, CNF has been investigated as coating (SYVERUD & STENIUS, 2009; AULIN *et al.*, 2010) or additive for paper (HII *et al.*, 2012; HASSAN *et al.*, 2015), without modification or only with an initial cationic, aiming improving their mechanical and barrier properties.

However, the high number of hydroxyl groups lead to strong hydrogen interactions between the nanofibrils, which make the dispersion of CNF in the paper structure difficult, due to its tendency to form agglomerates (MISSOUM *et al.*, 2013). In order to overcome this limitation and achieve large number and strong bounds between cationic CNF and fibers, in the present study, the CNF was previously cationized to be used as additive to improve quality of eucalyptus kraft pulp on paper production. In addition, the ultrastructural and physicochemical properties of unmodified and cationic CNF were carefully evaluated, in order to prove the cationization and verify its effects on CNF.

2 MATERIAL E METHODS

2.1 Materials

Cellulose nanofibrils (CNF) sample was supplied by the Process Development Center, University of Maine, USA and its characteristics are listed in Table 01.

Table 01- Properties of cellulose nanofibrils

Characteristics	CNF
Charge density (mmol·g^{-1})	0.051
Zeta potential-pH 7.0 (mV)	-20.0

Dimethyl sulfoxide (DMSO, ≥99%), tetrabutylammonium hydroxide 30-hydrate (TBAH, ≥98%), glycidyltrimethyammonium chloride (GTMAC, ≥90%), silver nitrate ($AgNO_3$, ≥99%), ethylenediamine cupric (CED, ≥98%), were purchased from Sigma-Aldrich and used without further purification.

For the cationic CNF preparation, ultrapure water (18.2 MΩ cm, Milli-Q water, Millipore) was used.

For the handsheet preparation, distilled water was used. Commercial bleached eucalyptus kraft pulp was supplied by Brazilian pulp and paper industry and its characteristics are listed in Table 02.

Table 02- Properties of bleached eucalyptus kraft pulp

Characteristics	Pulp
Kappa number	0.80
Viscosity, dm^3/kg	661.5
Brightness, % ISO	87.8

2.2 Methods

2.2.1 Cationic modification of cellulose nanofibrils (CNF)

The cationic modification of P-CNF consisted of a nucleophilic reaction between the alkaline activated cellulose hydroxyl groups and epoxy group of GTMAC (ZAMAN *et al.*, 2012), according to the reaction scheme shown in Figure 01.

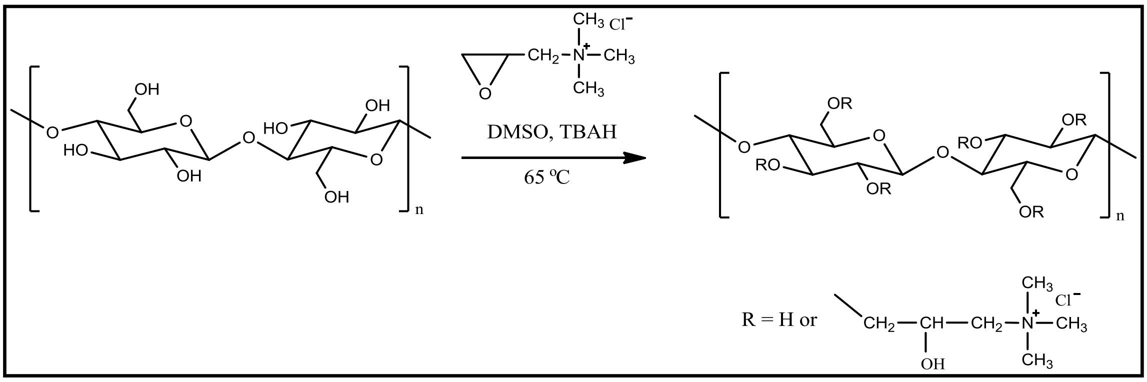

Figure 01 - Reaction schemes for cationic modification of CNF

Briefly, 1.0 g of CNF, 100 mL of dimethyl sulfoxide (DMSO), 2.0 g of tetrabutylammonium hydroxide (TBAH) and 0.3 mL of Millipore water were added in a round-bottom flask. The mixture was stirred at 550 rpm, under N_2 atmosphere for 1 h at 25 °C. Thereafter, the mixture was heated to 65 °C and the GTMAC was added. Two different reaction conditions have been used: (1) GTMAC:hydroxyl molar ratio of 2:1 and reaction time of 3 h, in order to obtain CNF with lower degree of cationization, designated C1-CNF and (2) GTMAC:hydroxyl molar ratio of 3:1 and reaction time of 6 h, in order to obtain CNF with higher degree of cationization, designated C2-CNF. The conditions were defined based on preliminary tests, which has consisted in the removal of mini samples at different reaction times, followed by the determining the degree of cationization. The CNF without cationic modification was designated pristine CNF (P-CNF). The CNFs with cationic modifications were designated C-CNFs (C1-CNF and C2-CNF).

At the end, these final products were cooled down to room temperature, diluted with 100 mL of water and centrifuged at 8500 rpm for 10 min in order to remove the formed by-product during the reactions and unreacted reagents. For each product, the precipitated was washed by acetone and centrifuged at 8500 rpm for 10 min. This procedure was repeated twice. For further purification, the final precipitated was redispersed in water and dialyzed (MW cut-off 10,000-12,400) against deionized water for ten days. To make sure the cationized CNFs were properly purified, the deionized dispersion was filtrated by ultrafiltration. The presence of free GTMAC was monitored by adding a 0.05 M $AgNO_3$ solution to the filtrate. The purification of cationized CNFs were complete when no AgCl precipitate was observed.

2.2.1.1 Potenciometric-conductometric titration

The purpose of potentiometric-conductometric acid-basic titration was to determine the density of carboxyl groups on the P-CNF. While the purpose of conductometric-precipitation titration was to determine the density of quaternary ammonium groups on the C1-CNF and C2-CNF, through the quantification of chloride ions.

The potentiometric-conductometric titrations were performed using a Metrohm 809 Titrando Autotitrator. The measurements were performed at 25 °C in a closed jacketed vessel with a water circulation pump. For the P-CNF, samples of 200 mg were dispersed in 50 mL of water, the pH was adjusted to 2-3, and titrated with 0.1 M NaOH. For the C-CNFs, samples of 30 mg were dispersed in 50 mL of water and titrated with 10 mM $AgNO_3$. The injection volume of titrant was 25 µL, and the interval between injections of 20 s. Each injection, pH and conductivity measurements were recorded at Tiamo software and plotted as a function of the volume of titrant added.

2.2.1.2 Fourier transform infrared spectroscopy (FTIR)

The infrared spectroscopy is a method that detects the frequency of vibration of chemical bonds, allowing the composition of a sample to be identified. FTIR spectra of the CNF, before and after the cationic modification, was measurement to verify the presence of new functional groups after modification.

P-CNF, C1-CNF and C2-CNF films, dried overnight in the vacuum oven at 25 °C, were used for the preparation of KBr pellets. Spectra of CNFs/KBr pellets were recorded using a Vertex 70 FTIR spectrometer (BRUKER), between 400 and 4000 cm^{-1}.

2.2.1.3 Zeta potential

Zeta potential is an important parameter to evaluate the stability of a suspension. Stability prevents particles from attracting one another and, due to that, it prevents the formation of aggregates and precipitates. A suspension is considered unstable if its zeta potential presents values in the range of -30 mV to +30 mV (ASTM, 1985).

The zeta potential of P-CNF, C1-CNF and C2-CNF samples were measured at room temperature over a pH range of 4 to 10 using a Malvern Zetasizer Nano-ZS90. The concentration of the samples was 1 mg/mL. The results presented are the average of four measurements for each sample.

2.2.1.4 Stability of aqueous CNFs dispersion

Aqueous dispersions of P-CNF, C1-CNF and C2-CNF at 0.3% (w/w) were vortexed 30 s in a 15 mL glass jar. Then, sonicated for 10 min at 25% of sonic waves amplitude setting using conventional ultrasonic equipment and allowed to stand at room temperature for 1 month before photographing.

2.2.1.5 Viscosity measurements

Viscosity measurements were used to monitor the cellulose chain degradation after the CNF cationic modification.

The P-CNF, C1-CNF and C2-CNF, previously dried overnight in the vacuum oven at 25°C for 6 hours at 45°C, were dissolved in CED solution. The viscosity was measured by an Automated Pulp Viscosity Analysis (VISCOMAT II, LAGGE TEC, Sweden) using the standard procedure SCAN-CM 15.

2.2.1.6 X-ray diffraction

The objective of this analysis was monitor crystallinity structural changes of cellulose after the cationic modification.

X-ray pattern of P-CNF, C1-CNF and C2-CNF was analyzed using a Rigaku D-M ax X-ray diffractometer with Cobalt Kα radiation (1.79026 Å) generated at 40 kV and 30 mA and velocity of 1.2°/min. The samples were scanned over the range of diffraction angle (2θ) between 10° and 35°. The crystallinity index was calculated using the following equation (SEGAL *et al.*, 1959):

$$CI(\%) = \frac{(I_1 - I_2)}{I_1} \times 100 \tag{1}$$

Where: - CI is crystallinity index

- I_1 is the intensity of the crystalline peak at the maximum between $2\theta \approx 25.5$ and 26.5°
- I_2 is the intensity of diffraction at the minimum between $2\theta \approx 20$ and 21°.

2.2.1.7 Transmission electron microscopy (TEM)

The TEM was used to monitor morphological changes of the CNF after the cationic modification.

The samples of P-CNF, C1-CNF and C2-CNF were prepared by spraying 10 µL of a 0.01% (w/w) dispersion onto a 200-mesh copper grid covered with a holey carbon film and dried overnight. TEM images of CNFs were taken using a Philips CM 10 Transmission Electron Microscope under an acceleration voltage of 60 keV, at 13500x and 34000x magnification. In total, 100 nanofibrils diameter, in each cationic CNF (C1-CNF and C2-CNF), were measured using an image analyzer program, Pro-Image 3.2.

2.2.2 Incorporation of CNFs in the pulp

Unrefined and refined pulps with 1000 revolutions PFI (T248 sp-08) were used. The P-CNF, C1-CNF and C2-CNF aqueous suspensions at 0.05% of consistency, in weight ratios ranging from 0 to 5% (w/w), were added in the pulp suspensions at 0.2% of consistency. The pH was adjusted to 8.5 and the mixture was stirred for 20 min at 500 rpm. Samples of pulp with addition of CNFs suspensions were collected for flocculation and static drainage analysis.

2.2.2.1 Flocculation

Flocculation analyses were performed by adding 5% of P-CNF or 5% of C2-CNF (w/w) in the pulp suspension at 0.2% of consistency. The mixture was transferred to the glass bottle and left to settle in order to precipitate. The height of the column, containing precipitate CNF and pulp, was registered as a function of settling time. The pulp without CNF was used as a reference.

2.2.3 Paper sheets preparation

Paper sheets were prepared from unrefined and refined pulp with 1000 revolutions PFI (T248 sp-08). The P-CNF, C1-CNF and C2-CNF aqueous suspensions at 0.05% of consistency, in weight ratios ranging from 0 to 5% (w/w), were added in the pulp suspensions at 0.2% of consistency. The pH was adjusted to 8.5 and the mixture was stirred for 20 min at 500 rpm. Then, handsheets were prepared (TAPPI 205 om-81) and conditioned at 25 °C and 50% humidity for 48 hours before retention analysis, SEM images acquisition and physical-mechanical tests. The grammage of the sheets was 60 g/m^2.

2.2.3.1 Nitrogen analysis

The C2-CNF retention in paper sheets, prepared from unrefined pulp with and without fines, was determined by measuring the nitrogen content in paper sheets in order to understand the effect of CNF on physical, mechanical and optical properties of paper sheets.

The nitrogen content in paper sheets was determined using a Nitrogen Analyzer TruSpec Micro, LECO (USA). The experiment was conducted in a completely randomized design in a 2x2x2 factorial, which was designed with three replications, totalizing 8 treatments and 24 experimental units. Paper sheets were prepared with addition of 1% and 3% of C2-CNF in the unrefined and refined pulp. Pulps with and without fines were used. The fines of the pulp were removed by Bauer McNett equipped with a 76 µm opening wire cloth.

2.2.3.1.1 Statistical Analysis

The average results of cationic CNF retention in the paper were submitted to F test of analysis of variance (ANOVA), at a significance level of 5%, using the software SISVAR®. The hypotheses tested were: Ho: The averages are statistically equal, i.e., there is no significant difference between treatments; Ha: The averages are statistically different, i.e., there is a significant difference between treatments. To statistically equal averages equal letters were used, whereas for statistically different averages, different letters were used.

2.2.3.2 Scanning electronic microscopy (SEM)

The SEM was used to evaluate the distribution of CNF, before and after the cationic modification, on paper structure.

Samples of 5 mm x 10 mm of paper sheets from unrefined pulp with addition of 0-5% of P-CNF and C1-CNF, and 0-3% of C2-CNF were placed on aluminum plates and coated with a layer of gold. SEM images at 500x and 1500x magnification were taken using an LEO-Zeiss 1430 VP scanning electronic microscopy (Carl Zeiss, Oberkochen, Germany) under an acceleration voltage of 20 kV.

2.2.3.3 Physical-mechanical and optical properties of paper sheets

The following physical-mechanical and optical properties were determined: bulk (T220 sp-06), air resistance (T536 om-96), smoothness (T479 cm-99), tensile index (T494 om-06), tear index (T414 om-98), burst index (T403 om-02), light scattering coefficient (T214 sp-98) and transparency (T522 wd-90), according to TAPPI standard methods, respectively.

2.2.3.3 Statistical Analysis

In order to evaluate the effect of C-CNFs (C1-CNF and C2-CNF) on physical-mechanical, on optical properties and on static drainage time of pulp, optimal mathematical models for the evolution of properties and drainage time were selected, according to the weight ratio of CNFs added in the pulp. The equality between parameters of regressions was tested in pairs, within each degree of pulp refining. Equality between models was defined by F test at 1% significance, according to the methodology described by Regazzi (1993) for linear models. The statistically equal models have been reduced to a single model. Statistically different models were not reduced. The tested hypotheses were: Ho: The models are statistically equal and can be represented by a common format; Ha: The models are statistically different and cannot be reduced to a common format.

2.2.2.2 Static drainage time of pulp

The objective of this analysis was to determine the effect of addition cationized CNF in pulp drainage time.

Samples of pulp suspensions at 0.2% of consistency with addition of 0 to 5% (w/w) of P-CNF, C1-CNF and C2-CNF were used. To measure the static drainage time, the time required for total drainage of pulp suspension during the drainability test (TAPPI T248 om-85) was determined.

3 RESULTS AND DISCUSSION

3.1 Cationic modification of P-CNF

3.1.1 Physicochemical characterizations of CNFs (P-CNF, C1-CNF and C2-CNF)

The cationic modification of P-CNF, followed by purification, resulted in a highly viscous and transparent like-gel aqueous dispersion of C-CNFs (Figure 02).

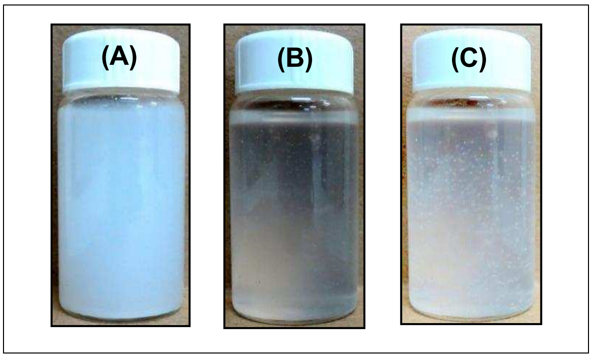

Figure 02 - Aqueous dispersion of P-CNF(A), C1-CNF(B) and C2-CNF(C) at 0.30% (w/w)

3.1.2 Conductometric titration

The density of carboxyl groups on the P-CNF, calculated from the acid-base titration curve (Figure 03), was found to be 0.051 mmol·g^{-1}. The density of quaternary ammonium groups on C1-CNF and C2-CNF, calculated from the precipitation titration curve (Figure 04), were found to be 0.68 mmol·g^{-1} and 1.20 mmol·g^{-1}, respectively. The cationic charge on C-CNFs is due to the ammonium quaternary groups attached to CNFs.

Olszewska *et al*. (2011) modified CNF with GTMAC in aqueous medium in the presence of NaOH and have obtained a quartenary ammonium groups content of 0.35 mmol·g^{-1}. Cationized hemicelluloses with GTMAC in aqueous medium in the presence of NaOH presented a quartenary ammonium content ranging from 0.02 to 0.22 mmol·g^{-1} (LIU *et al.*, 2011). Therefore, the level of cationization of CNF with GTMAC in the present study was found to be higher. This is because the cationization reaction was performed in DMSO and in the presence of an organic base, TBAH. In aqueous medium the epoxide ring is easily hydrolyzed by water (ZAMAN *et al.*, 2012).

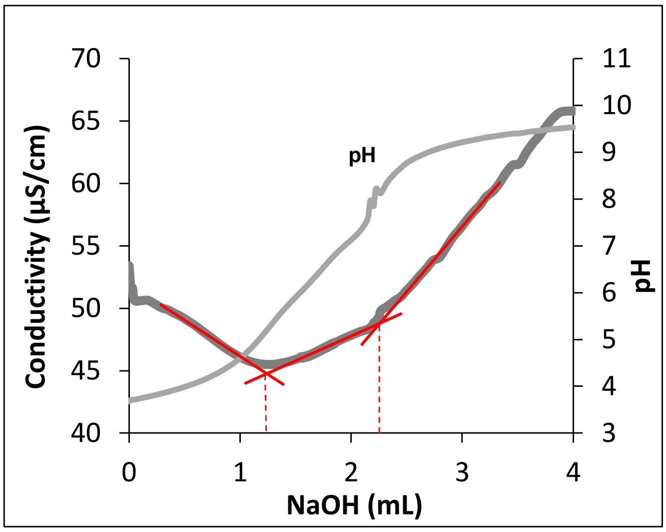

Figure 03 - Conductometric titration of P-CNF

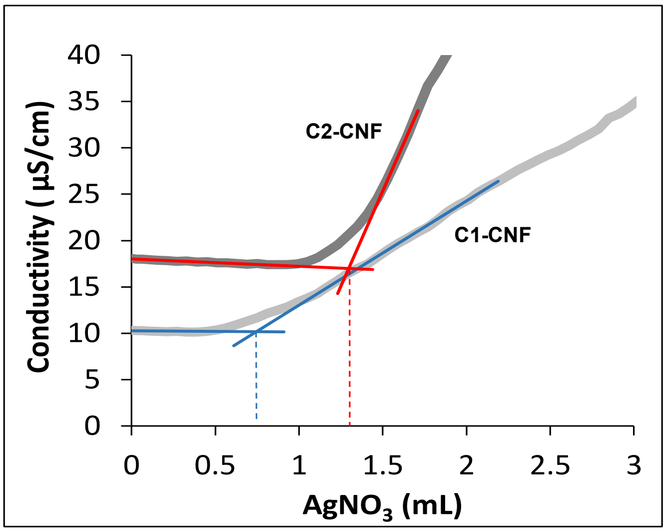

Figure 04 - Conductometric titrations of C1-CNF and C2-CNF

3.1.1.2 Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra for pristine CNF and cationic CNFs (C1-CNF and C2-CNF) are shown in the Figure 05. The absorption bands at 3419 cm^{-1} and 2920 cm^{-1} were due to the stretching of hydroxyl group and the symmetric C-H vibration, respectively (LIU *et al.*, 2011; PENG *et al.*, 2009). The absorption at 897 cm^{-1} can be assigned to the C-H deformation mode of the glycosidic linkage between the glucose units (ZAMAN *et al.*, 2012; REN *et al.*, 2006). The absorbance between 1030 cm^{-1} and 1163 cm^{-1} was attributed to the stretching C-O in C-O-C linkages (ZAMAN *et al.*, 2012; LIU *et al.*, 2011). These same absorption bands were also found by other authors who worked with lignocellulosic materials (LIU *et al.*, 2011; PENG *et al.*, 2009; ZAMAN *et al.*, 2012; REN *et al.*, 2006; LIU *et al.*, 2011).

An increase in the intensity of the absorption at 1620 cm^{-1} and at 1482 cm^{-1}, originated from the absorbed water in the CNF (LIU *et al.*, 2011) and from the methyl groups of the quaternary ammonium groups (LOUBAKI *et al.*, 1991; SONG *et al.*, 2010; QUINLAN *et al.*, 2015), respectively, can be observed.

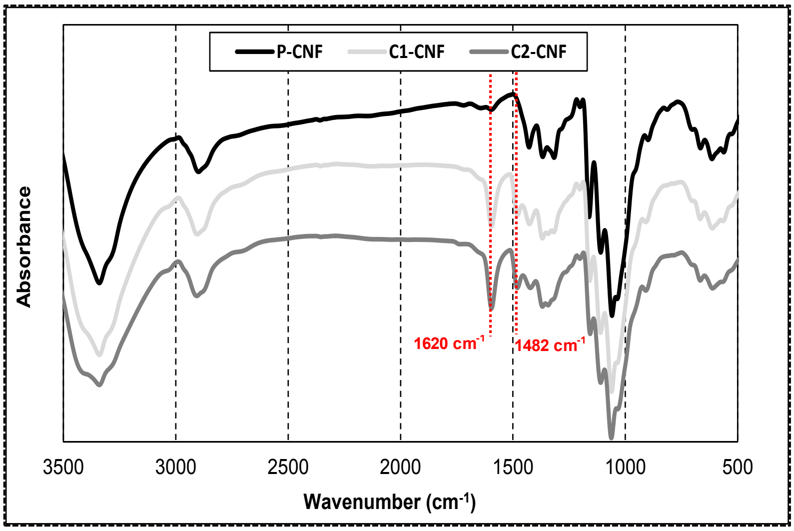

Figure 05 - FTIR spectra for CNF, C1-CNF and C2-CNF

3.1.1.3 Zeta Potential and stability of aqueous CNFs dispersion

Figure 06 shows the zeta potential values of the aqueous dispersions of P-CNF and C-CNFs (C1-CNF and C2-CNF) as a function of pH (4-10). In the pH range studied, the zeta potential values of aqueous dispersion of P-CNF showed negative charge due to the carboxyl groups. After the cationic modification with GTMAC the zeta potential became positive due to the positive charges of the ammonium quaternary groups attached on CNFs. The zeta potential values of the C2-CNF were higher than the C1-CNF in all the pH range studied, due to the greater degree of cationization of C2-CNF. These results are in accordance with the results of conductometric titration and FT-IR spectra.

The charge of the quaternary ammonium groups is pH-independent (TAIPALE *et al.*, 2010). However, the zeta potential values of C-CNFs are influenced by pH (Figure 06) due to the dissociation of the carboxyl groups (Figure 02A) on the CNF with increase of the pH (OLSZEWSKA *et al.*, 2011).

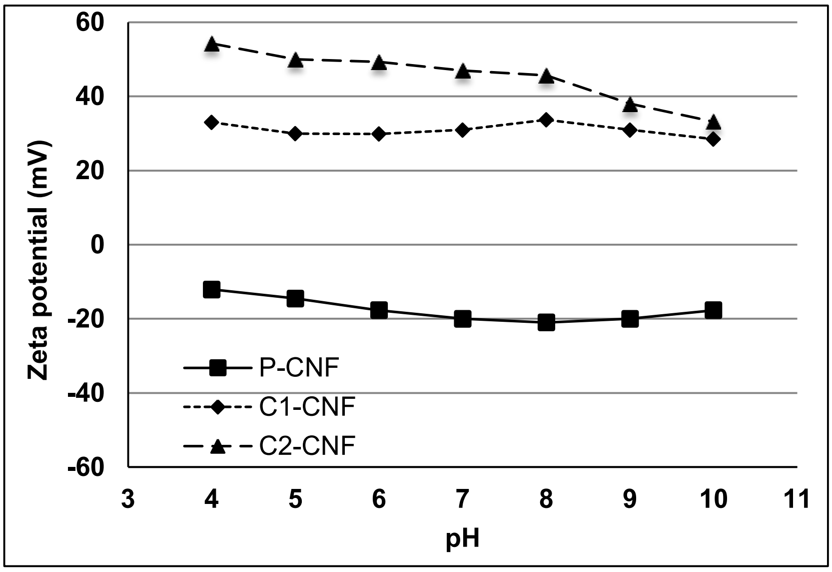

Figure 06 - The zeta potential of aqueous dispersion of CNFs (P-CNF, C1-CNF and C2-CNF) as a function of pH

In the studied pH range, the zeta potential values for P-CNF varied from -12.1 to -20.0 mV. However, the zeta potential values of C1-CNF and C2-CNF varied from +28.5 to +33.7 mV and from +33.2 to +54.3 mV, respectively. This magnitude of zeta potential indicates an unstable dispersion for P-CNF and a stable dispersion after cationization. Clear sedimentation was observed for aqueous dispersion of P-CNF after 1 month (Figure 07.A), so it is not stable. The aqueous dispersion of C-CNFs after 1 month (Figure 07.B and 07.C) was well dispersed, homogeneous and transparent, so it is stable.

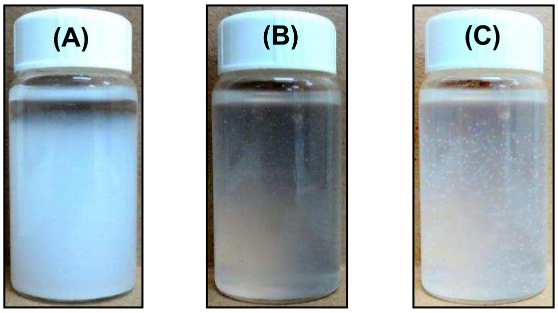

Figure 07 - The stability of aqueous dispersion of P-CNF, C1-CNF and C2-CNF at 0.30% after 1 month

The conductometric titration, FT-IR spectra confirmed that the cationic modification of CNF with GTMAC, in DMSO and in the presence of TBAH, was performed, resulting in C-CNFs with lower (C1-CNF) and higher (C2-CNF) cationization degree, that are stable and homogeneously dispersed in water.

3.1.2 Ultrastructure characterizations of CNFs(P-CNF, C1-CNF and C2-CNF)

3.1.2.1 Viscosity

Table 03 shows the viscosity values for P-CNF and CNF after cationic modification (C1-CNF and C2-CNF).

The C-CNFs showed smaller viscosity than P-CNF. The viscosities of C1-CNF and C2-CNF were reduced in 27.9% and 32.2% respectively, compared to P-CNF (1067 dm^3/kg). Since the reaction of cationic modification degrades the cellulose chain, the higher is the degree of cationization of CNF, the higher is the degradation, due to greater charge of GTMAC and time of reaction required to reach a higher degree of cationization.

According to Lavoine *et al*. (2012), the degree of polymerization and crystallinity are important properties that must not be lost for the elaboration of strong CNF nanocomposites. On the other hand, Zimmermann *et al*. (2010) evaluated how the degree of polymerization of cellulose from different raw material affects the mechanical properties of hidroxylpropyl cellulose (HPC)/CNF films. They found that the highest stiffness was obtained for film of HPC/CNF with the lowest DP (degree of polymerization) and that a slightly lower tensile strength was obtained by film of HPC/CNF with the highest degree of polymerization. Taking into account the SEM images of the different CNFs, the authors conclude that a homogeneous fibrillation of fibers is more important than the degree of polymerization of cellulose for the mechanical performance of HPC/CNF films.

Table 03 - Viscosity for P-CNF, C1-CNF and C2-CNF

CNFs	**Viscosity, dm^3/kg**
P-CNF	1067
C1-CNF	769
C2-CNF	723

3.1.2.2 X-ray diffraction

The X-ray patterns and crystallinity index for P-CNF and C-CNFs (C1-CNF and C2-CNF) are shown in Figure 08 and Figure 09. The peak at 26.5º shows the degree of cellulose crystal structure (HO *et al.*, 2011). The X-ray pattern for C-CNFs (C1-CNF and C2-CNF), when compared with P-CNF, an accentuated decrease in the peak at 26.5^o can be observed. Therefore, the cationic modification of P-CNF resulted in negative effect in the cellulose crystalline structure.

The crystallinity index (CI) is a measure of the amount of crystalline cellulose in relation to the amorphous. After the cationic modification, the crystallinity index for P-CNF (90.8%) decreases for 59.7% (C1-CNF) and 59.5% (C2-CNF). Therefore, the negative effect of the cationic modification on cellulose crystalline structure was similar for C1-CNF and C2-CNF.

Ho *et al*. (2011) attached quaternary ammonium groups by chlorocholine chloride (CCC) to CNF. The cationic modification decreased the degree of polymerization of cellulose, but did not affect significantly the crystal structure of cationic CNF.

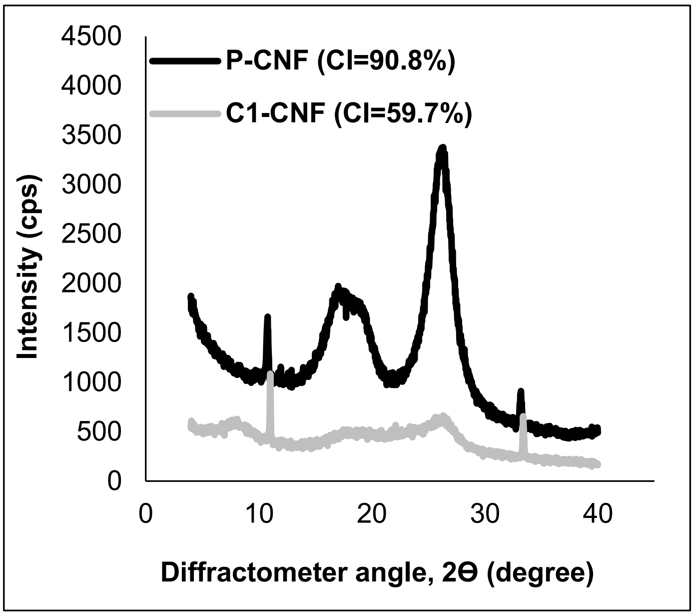

Figure 08 - X-ray pattern of C1-CNF (P-CNF reference)

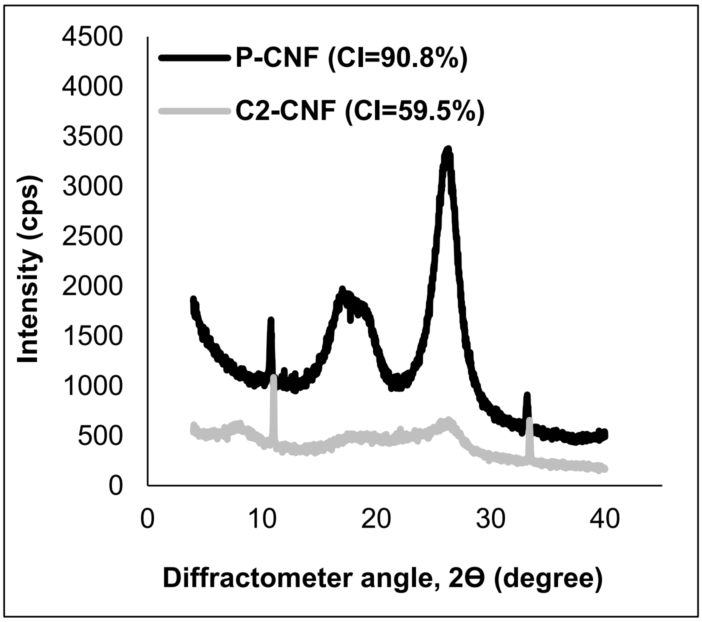

Figure 09 - X-ray pattern of C2-CNF (P-CNF reference)

3.1.2.3 TEM images

The effect of cationization on CNF structure was visualized by TEM images of C1-CNF and C2-CNF under two magnifications (Figure 10B and Figure 10C).

The TEM images of P-CNF were used as a reference (Figure 10A). Due to the hydrogen bonds between the hydroxyl group on the surface of fibrils

(FENGEL and WEGENER, 1989) a network of overlapped loose bundles can be seen. This makes difficult clear measurement of the length of fibrils. However, fibrils with a length up to several micrometers and a diameter at nano-scale (below 100 nm) and above 100 nm can be observed.

Compared to the P-CNF, the fibrils length and thickness of C-CNFs are smaller, due to the strong electrostatic repulsion of quaternary ammonium groups, which is efficient in separate fibrils from each other. Moreover, the C-CNFs are thinner due to their degradation while the cationization reaction occurred.

The diameter distribution of C_1-CNF was between 30-90 nm (Figure 11), with maximum frequency at 40-60 nm, while C2-CNF had diameter distribution between 8-70 nm (Figure 12), with maximum frequency at 10-20 nm. Therefore, when the density of quaternary ammonium was increased from 0.68 to 1.20 $mmol \cdot g^{-1}$, the nanofibrils became thinner and a more homogeneous distribution of diameter occurred.

However, considering that the elementary fibril has a diameter of 3.5 nm (MEIER, 1962), the C-CNFs are nanoaggregates of fibrils. CNF with even smaller diameters (1.6-4 nm) were previously reported (PEI *et al.*, 2013; OLSZEWSKA *et al.*, 2011; SAITO *et al.*, 2007).

According to the new TAPPI Standard WI 3021, CNF (cellulose nanofibrils) and CMF (cellulose microfibrils) have widths in the range between 5-30 nm and 10-100 nm, respectively. However, in this study, all the samples have been designated as CNF.

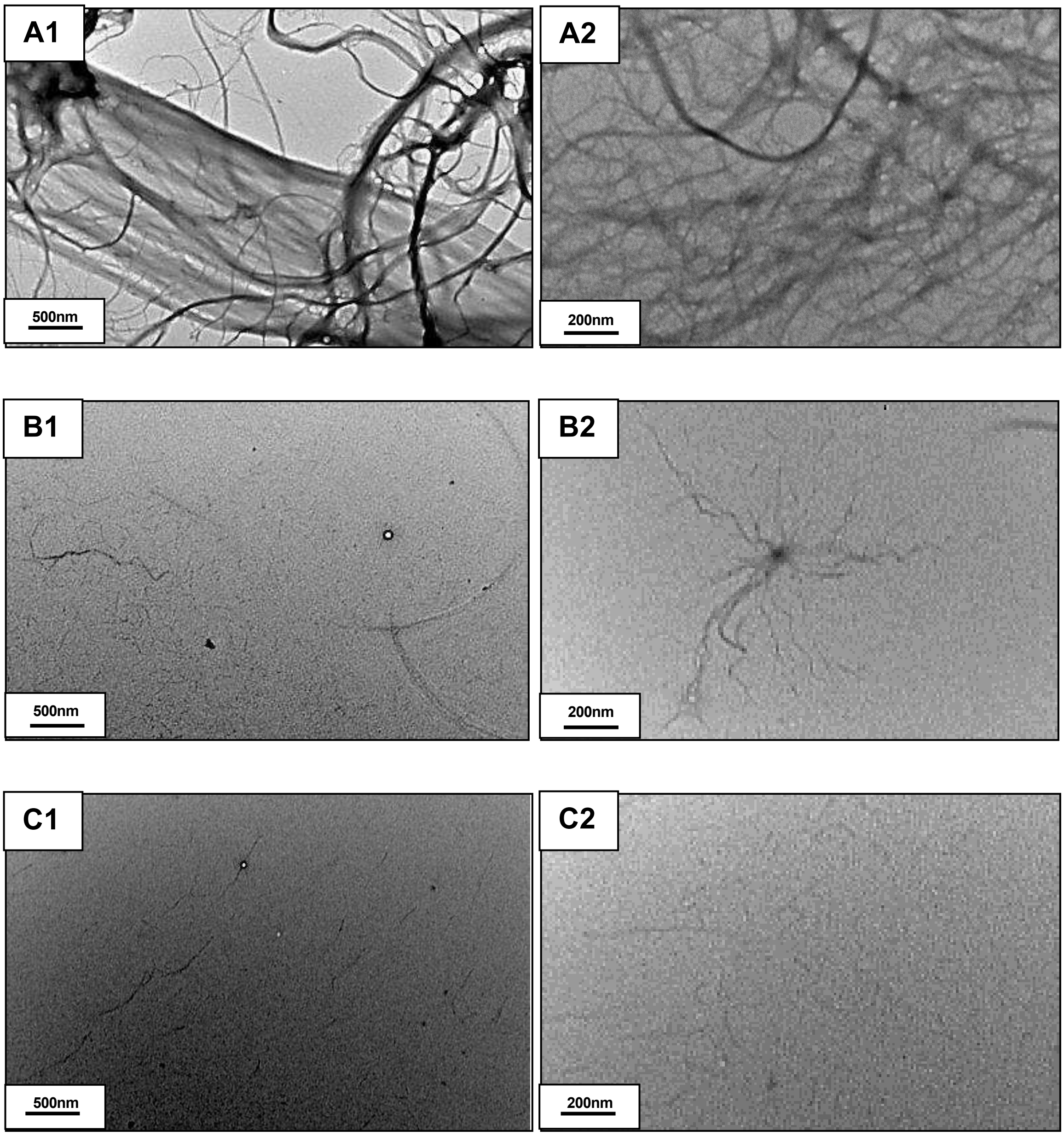

Figure 10 - TEM images of P-CNF(A1 and A2), C1-CNF(B1 and B2) and C2-CNF(C1 and C2) at 13500x and 34000x magnification

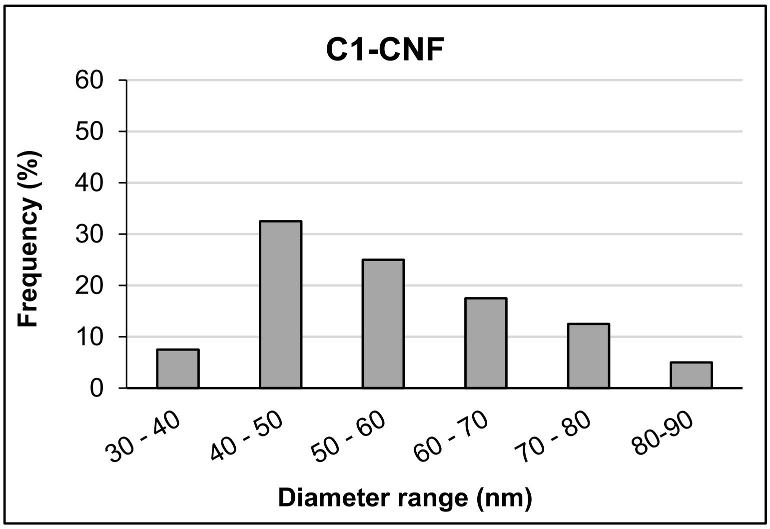

Figure 11 - Diameter distribution of C1-CNF

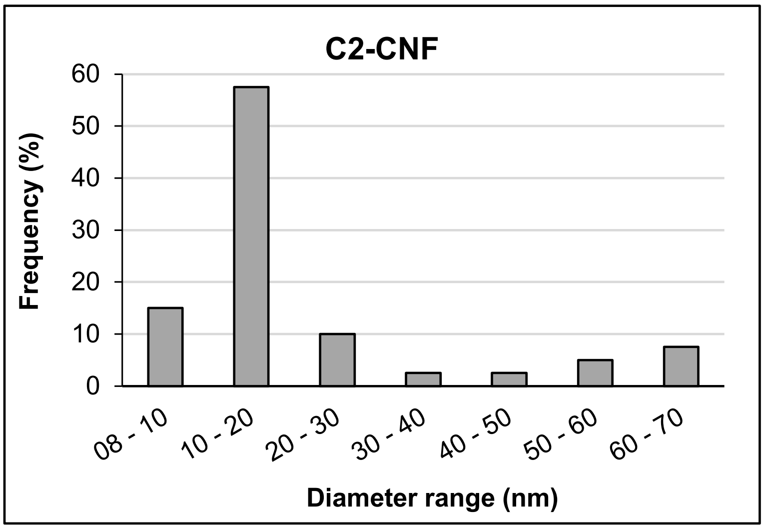

Figure 12 - Diameter distribution of C2-CNF

The modification of CNF that does not damage the cellulose ultrastructure, is desirable for its use as an additive in improving quality of pulps for paper production. In this study, viscosity measurement, X-ray pattern and TEM images showed that cationic modification of P-CNF with GTMAC, performed in DMSO in the presence of TBAH, resulted in strong negative effects on the ultrastructure of C-CNFs, which was more pronounced for the C-CNF with higher cationization degree (C2-CNF). The only exception was for the separation of nanofibrils from each other by the strong electrostatic repulsion of quaternary ammonium groups on surface of fibrils, which is a positive effect of the cationic modification treatment.

3.2 Incorporation of P-CNF, C1-CNF and C2-CNF in the pulp suspension

The P-CNF, C1-CNF and C2-CNF were added in the pulp suspensions and the effect of cationic CNFs on the flocculation (C2-CNF) and drainage time (C1-CNF and C2-CNF) of pulp suspension were determined. The pulp suspensions without CNF and with P-CNF were used as a reference.

3.2.1 Effect of P-CNF and C2-CNF in the pulp flocculation

The effect of P-CNF and C2-CNF in the pulp flocculation was evaluated by measuring the height of the flocculation column as a function of time. The pulp without CNF was used as a reference. Although the heights of the flocculation column of the pulp suspensions were different, they all displayed three flocculation steps: an initial phase of rapid sedimentation of the larger flocs followed by a slow sedimentation of smaller ones and subsequent phase of sediment densification (Figure 13).

Comparing pulps suspensions with CNF (P-CNF and C2-CNF), with the one without CNF, larger flocs with lower initial rate of sedimentation can be observed. However, the flocculation of pulps with CNF has resulted in lower heights of the flocculation column due to the interactions between pulp fibers and CNFs. This behavior was more pronounced for the pulp with C2-CNF due to the strong electrostatic attraction between the positive charge of C2-CNF and the anionic (COOH) charges of pulp fibers, which resulted in large flocs and a more dense sediment column. The greater initial resistance of C2-CNF flocs to sedimentation is due to the high ionic stability of C2-CNF, as indicated by the high positive zeta potential shown in Figure 06. P-CNF has a low negative charge density and the fibrils are strongly linked by hydrogen bonds, which make them difficult to disperse in water and, decrease the flocculation capability. Thus, the flocculation of pulps with P-CNF may have resulted from the hydrogen bonds between the P-CNF and the pulp fibers. These results are in agreement with those found by Korhonen *et al*. (2014) and Eronen *et al*. (2012), who evaluated the effect of different anionic and cationic CNFs on the flocculation.

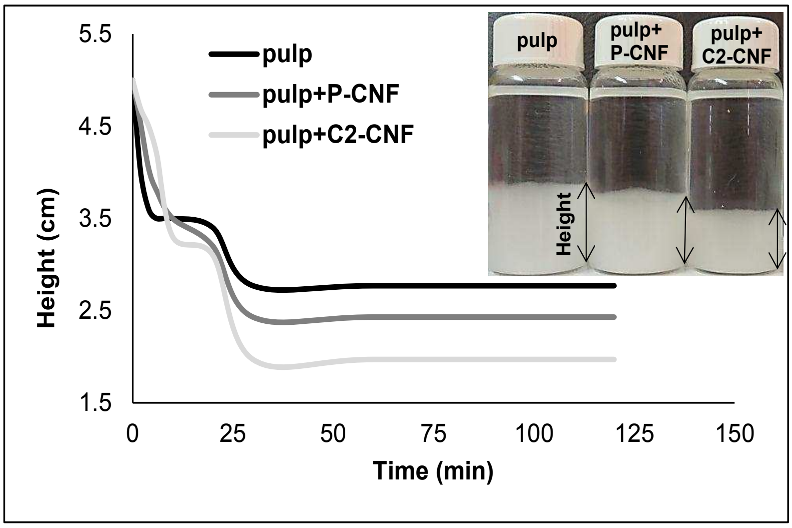

Figure 13 - Height of the flocculation column as a function of time for pulp without CNF, with P-CNF and with C2-CNF

3.2.2 Effect of P-CNF, C1-CNF and C2-CNF on pulp drainage time

Figure 14 shows the effect of the addition of CNFs (P-CNF, C1-CNF or C2-CNF) on the pulp drainage time. The optimal mathematical models for the evolution of drainage time of pulp as a function of charge of added CNFs (P-CNF, C1-CNF and C2-CNF) in the unrefined and refined pulp are showed in Table 04.

To pulp with or without fines, the addition of 1% of CNFs (P-CNF, C1-CNF or C2-CNF) did not have a significant effect on the pulp drainage time. According to Rantanen and Maloney (2013), grammage of paper sheet below 60 g/m^2 and addition of 2% of CNF resulted in very little impact of CNF on pulp drainage time. On the other hand, the addition of 3% of CNFs had a negative effect on the pulp drainage time, and this effect increases as more CNF was added. These findings are in agreement with other authors (TAIPALE *et al*., 2010; HII *et al*., 2012; PETROUDY *et al*., 2014). The CNFs increased the specific surface area of pulp suspension, resulting in higher capillarity force and water retention, and the less connected pores formed a physical barrier, compromising the water flow (SYVERUD and STENIUS, 2009).

Compared with the P-CNF, the negative effect of C-CNFs in the increasing of the pulp drainage time is more pronounced. The higher the degree of cationization (C2-CNF), the higher is this effect. For example, pulp with addition of 3% of C2-CNF resulted in a drainage time 206.7% (unrefined pulp) and 170% (refined pulp) greater than those with 3% of C1-CNF. However, for pulp with addition of 5% of C2-CNF, it was not possible to measure the drainage time, whereas the water was not entirely drained. When compared with P-CNF, the C-CNFs have a smaller diameter (Figure 10) with higher surface area and homogeneous dispersion, besides having a strong hydrophilicity given by the quaternary ammonium groups, which results in higher water retention.

Comparing pulp with and without refine, it can be observed that the refine increases the pulp drainage time, which was expected. However, refine can partially mask the effect of CNFs on drainage time. The addition of 3% of C1-CNF increases the drainage time in 164.7% for unrefined pulp and in 111.5% for refined pulp.

Considering that a longer drainage time of the pulp with CNFs may cause a lower productivity of paper machine, in this study, it was a limiting factor for the use of CNF in industrial-scale production. According to Taipale *et al.* (2010) and Petroudy *et al.* (2014), CNF with a suitable density of charges and retention aid can reduce the drainage time to similar levels to the pulp reference.

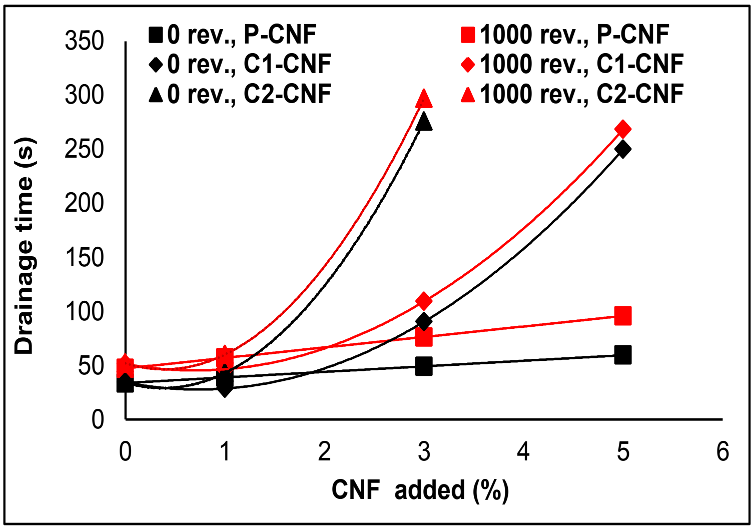

Figure 14 - Drainage time of pulp as a function of charge of P-CNF, C1-CNF and C2-CNF added in the unrefined and refined pulp

Table 04 - Optimal mathematical models for the evolution of drainage time of pulp as a function of charge of CNFs (P-CNF, C1-CNF and C2-CNF) added in the unrefined and refined pulp

Properties	Pulp	CNF	Mathematical models	R^2	Pr>Fc
Drainage time (s)	0 rev.	P-CNF	$\hat{Y} = 33.6949 + 5.1356x$	0.966	0.000
		C1-CNF	$\hat{Y} = 34.2613 - 17.9711x + 12.2198x^2$	0.998	0.0000
		C2-CNF	$\hat{Y} = 34.0000 - 26.8333x + 35.8333x^2$	0.999	0.0000
	1000 rev.	P-CNF	$\hat{Y} = 47.1864 + 9.6949x$	0.918	0.0000
		C1-CNF	$\hat{Y} = 51.2563 - 16.9284x + 12.0665x^2$	0.928	0.0000
		C2-CNF	$\hat{Y} = 52.0000 - 28.8333x + 36.8333x^2$	0.986	0.0000

3.3 Paper sheets preparation

The P-CNF, C1-CNF and C2-CNF were added in the pulp suspensions and paper sheets were prepared. The C2-CNF content, the morphological, physical-mechanical and optical properties of the paper sheets were determined.

3.3.1 Cationic CNF retention in the paper sheets

The C2-CNF retention in paper sheets was determined, by measuring the nitrogen content in paper sheets, in order to understand the effect of fines in the retention of C-CNF on the paper sheets.

The effect of refine in C2-CNF retention in the papers was not significant at 5% of probability using F test (Table 05). However, the used level of refining (1000 rev. PFI) was low. The interaction pulp type (with or without fines) and C2-CNF filler added was significant at the 5% probability, therefore, post analysis was performed (Table 05).

Table 05 - Analysis of variance for the nitrogen content in the paper sheets in a 2x2x2 factorial

FV	SV	SS	MS	Fc	Pr>Fc
Pulp	1	0.126643	0.126643	64.422**	0.0000
Refine	1	0.000133	0.000133	0.067^{ns}	0.7984
C2-CNF	1	0.456394	0.456394	232.162**	0.0000
Pulp x Refine	1	0.000002	0.000002	0.001^{ns}	0.9732
Pulp x C2-CNF	1	0.083851	0.083851	42.654**	0.0000
Refine x C2-CNF	1	0.000027	0.000027	0.014^{ns}	0.9076
Pulp x Refine x C2-CNF	1	0.000004	0.000004	0.002^{ns}	0.9660
Error	16	0.031453	0.001966		
Total	23	0.698508			

** significant at 1% of probability by F test. ^{ns} not significant.
SV= source of variability; GL= degree of freedom; SS= sum of squares; MS= Mean Square; Fc=F calculated; Pr=probability.

Table 06 - Nitrogen content (mg/g) of paper sheets as a function of C2-CNF added in the unrefined and refined pulp with fines

	C2-CNF added (%)	
Pulp	**1**	**3**
with fines	0.030aB	0.422aA
without fines	0.001bB	0.159bA

Average followed by the same lowercase letters in columns do not differ by F test at 5% significance and average followed by the same capital letters on the lines do not differ by F test at 5% significance.

For pulp with fines, the addition of 1% of C2-CNF resulted in 0.030 mg/g of nitrogen content in the paper sheets, and the increase of added C2-CNF of 1% to 3% resulted in 0.422 mg/g of the nitrogen content in the paper sheet. For pulp without fines, the addition of 1% of C2-CNF resulted in 0.001 mg/g of nitrogen content in the paper sheets, and the increase of added C2-CNF of 1% to 3% resulted in 0.159 mg/g of the nitrogen content in the paper sheet. Therefore, for pulp with and without fines, it was observed retention of C2-CNF in the paper sheet, and it was higher with the increase of the charge of C2-CNF added.

It can be observed that the removal of pulp fines decreased the nitrogen content in paper sheets in 96.7% (1% C2-CNF added) and 62.3% (3% C2-CNF added). The fines have a positive effect on CNF retention, because they have a higher specific surface area and mobility than the fibers. Thus, a possible explanation for the removal of pulp fines before the addition of CNF (AHOLA *et al.*, 2008; TAIPALE *et al.*, 2010) is that the fines may mask the effect of CNF on the properties of the paper sheets, which can be more visible using pulp without fines.

3.3.2 Structures of the paper sheets

In Figure 15, Figure 16 and Figure 17, SEM images of the surface of the paper sheets made from unrefined pulp with addition of CNFs (P-CNF, C1-CNF and C2-CNF) are showed. Paper sheets made from unrefined pulp without CNF (Figure 15.A; 0% P-CNF) was used as reference.

When compared with the reference, it can be observed that the CNFs act as a binding agent, increasing the bonds between the fibers and reducing the porous of paper. These effects increase proportionally to the increase of the different types of CNFs added in the pulp. In Figure 15.B-D, formation of P-CNF films at the surface of fibers and networks of nanofibrils between the fibers can be observed. The high amount of P-CNF hydroxyls leads to strong hydrogen bonds between the nanofibrils, which makes the dispersion of fibers more difficult, due to their tendency in forming agglomerations (MISSOUM *et al.*, 2013).

In Figure 16 and Figure 17, a uniform distribution of C1-CNF and C2-CNF, respectively, on the surface of paper sheets can be observed. It is due to the good stability and homogeneous dispersion of nanofibrils with quaternary ammonium groups content, as previously discussed.

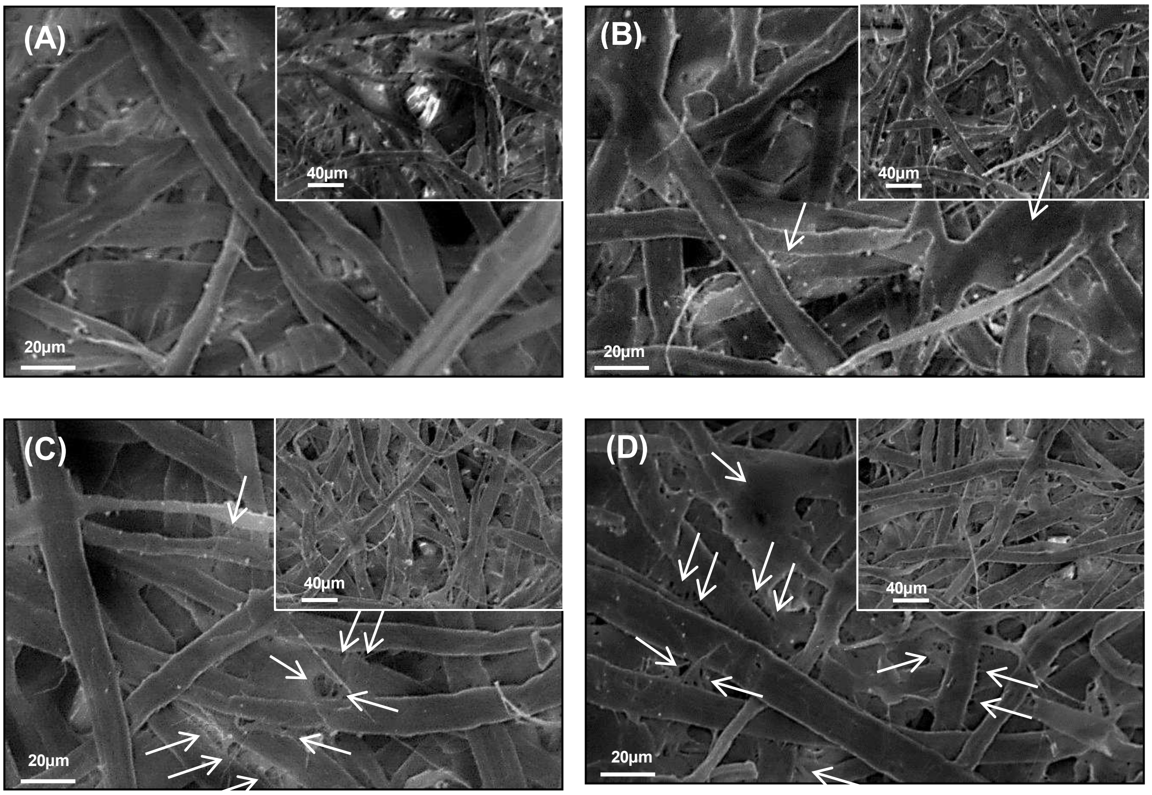

Figure 15 - SEM images of paper sheets made from unrefined pulp with addition of 0%(A), 1%(B), 3%(C) and 5%(D) of P-CNF, at 500x and 1500x magnifications

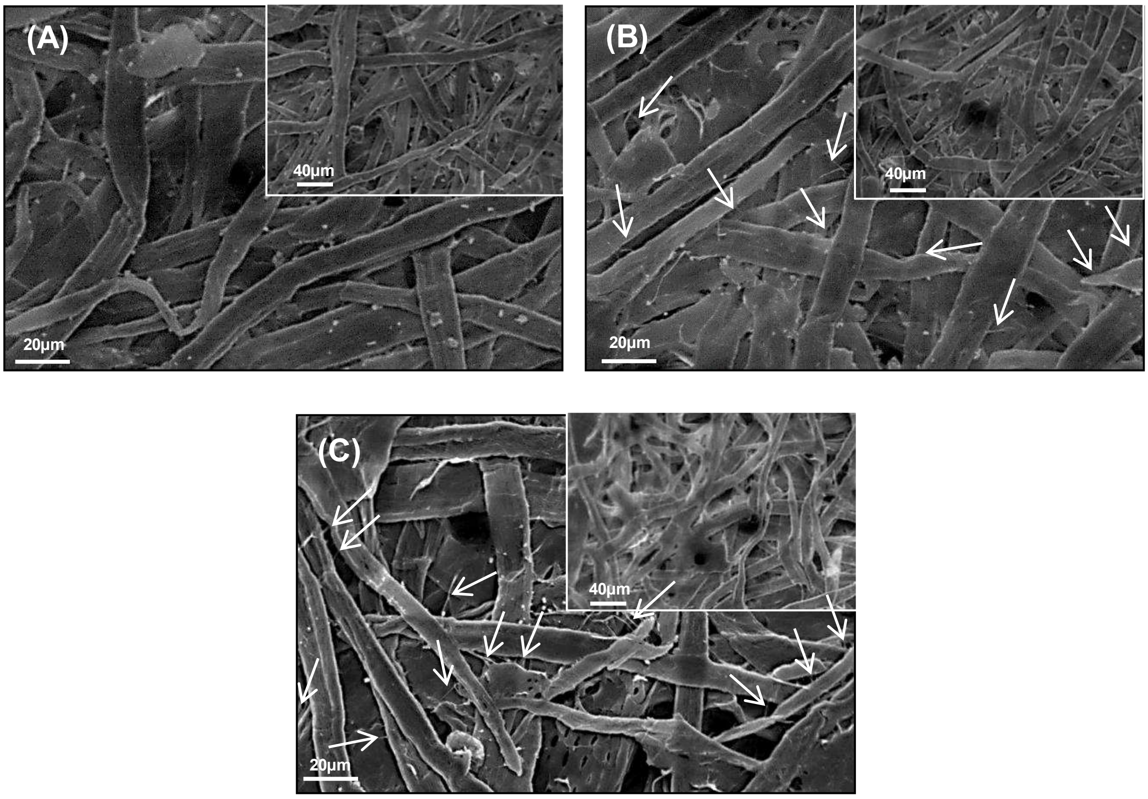

Figure 16 - SEM images of paper sheets made from unrefined pulp with addition of 1%(A), 3%(B) and 5%(C) of C1-CNF, at 500x and 1500x magnifications

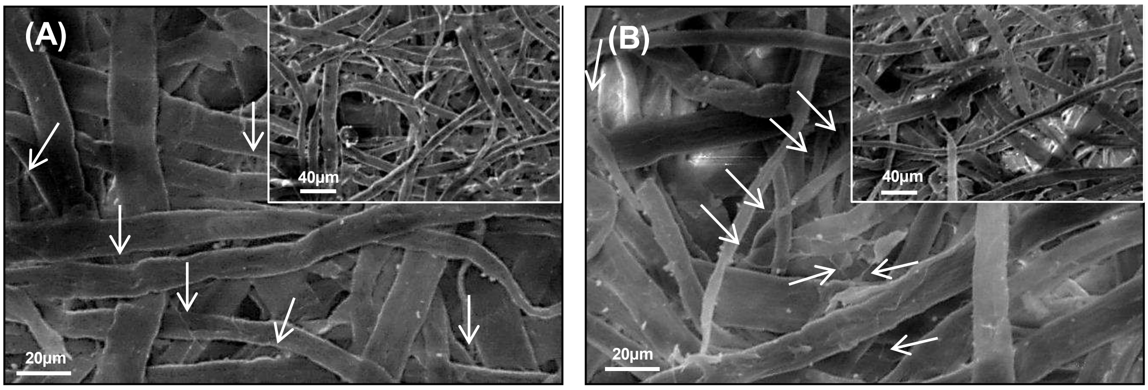

Figure 17 - SEM images of paper sheets made from unrefined pulp with addition of 1%(A) and 3%(B) of C2-CNF, at 500x and 1500x magnifications

3.3.3 Effect of P-CNF, C1-CNF and C2-CNF on the physical-mechanical and optical properties of paper sheets

Physical-mechanical and optical properties of paper sheets made from unrefined and refined pulp with addition of 0-5% of P-CNF and C1-CNF, and 0-3% of C2-CNF were evaluated. Mathematical models for the evolution of properties as a function of charge of CNFs added were statistically selected. These properties of paper sheets, with addition of 5% of C2-CNF, were estimated by optical mathematical models, due to the fact that it was not possible to make an experimental determination. In the Appendix A and B the average (Table 1A) and experimental (Table 1B-7B) results are shown, respectively, of physical-mechanical and optical properties of paper sheets made from unrefined and refined pulp with addition of CNFs (P-CNF, C1-CNF and C2-CNF).

3.3.3.1 Bulk

The bulk contributes for important properties of paper, such as opacity (printing paper), softness and absorbency (tissue paper). The Figure 18 shows the bulk of paper sheets as a function of charge of added CNFs (P-CNF, C1-CNF and C2-CNF) in the unrefined and refined pulp.

For unrefined pulp, the increase of CNFs added from 0% to 5% resulted in decrease in bulk of paper sheets. For refined pulp, the increase of CNFs added from 0% to 1% did not affect significantly the bulk of paper sheets, while increasing from 1% to 5% resulted in decrease in bulk. This trend was also found by Sehaqui *et al*. (2011) and Petroudy *et al*. (2014). The high surface area of CNFs increased the number of bonds between the fibers, however, reducing the bulk of paper sheets.

Comparing unrefined and refined pulp, it can be observed that the negative effect of P-CNF, C2-CNF or C2-CNF on bulk of paper was more pronounced for unrefined pulp. For example, the addition of 3% of C2-CNF in the unrefined and refined pulp resulted in a decrease of 20.7% and 7.89% in bulk of paper sheets, respectively. The refine of pulp also contributes to the decrease in bulk and masks this effect due to the CNFs.

The decrease in bulk of paper sheets, as result of adding CNFs in the pulp, was lower than that of which occurred as a result of pulp refining (23.2%). The only exception was the addition of 5% of C2-CNF, which resulted in a reduction of 26.26% in the bulk of the paper.

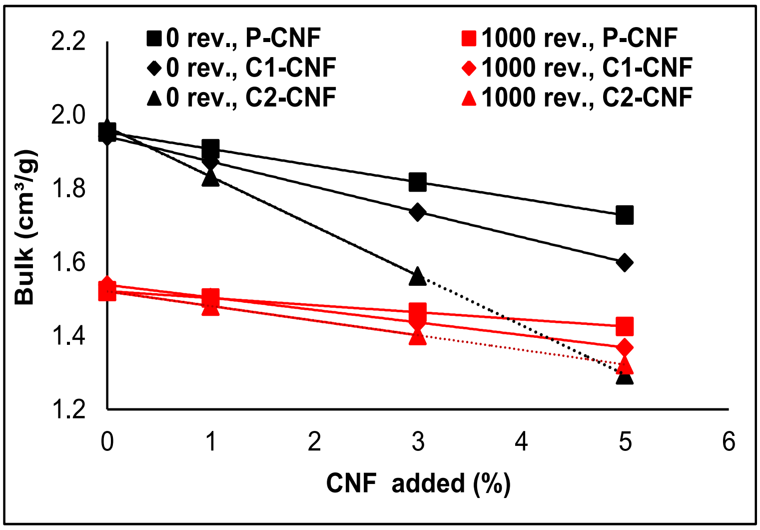

Figure 18 - Bulk of paper sheets as a function of charge of P-CNF, C1-CNF and C2-CNF added in the unrefined and refined pulp

The optimal mathematical models for the evolution of bulk of paper sheets as a function of charge of added CNFs (P-CNF, C1-CNF and C2-CNF) in the unrefined and refined pulp are showed in Table 07.

For unrefined or refined pulp, a significant difference between the curves of bulk as a function of charge of P-CNF and C-CNFs (C1-CNF or C2-CNF) added was observed. Thus, there is a significant difference between the bulk of paper sheets containing at least one same charge of P-CNF and C-CNFs added.

For unrefined pulp, the addition of different charges of C-CNFs (C1-CNF or C2-CNF) resulted in paper with lower bulk, as compared to that containing P-CNF. On the other hand, for refined pulp, only higher charges of C-CNF (5% of C1-CNF; 3% and 5% of C2-CNF) resulted in paper with lower bulk, as compared to that with addition of P-CNF. The strong electrostatic attraction between the positives charges of C-CNFs and anionic charge of fibers reduces the bulk and increase density of the paper. Similar bulks were found for papers sheets made from refined pulp containing low charges of P-CNF or C-CNFs (C1-CNF and C2-CNF).

For unrefined or refined pulp, a significant difference between the curves of bulk as a function of charge of C1-CNF and C2-CNF added was observed. Thus, there is a significant difference between bulk of paper sheets containing at least one same charge of C1-CNF or C2-CNF added. For unrefined and refined pulp, the bulk of paper sheets containing C2-CNF was lower than those containing C1-CNF, due to the higher surface area and cationic charge of C2-CNF if compared to C1-CNF.

Table 07 - Optimal mathematical models for the evolution of bulk of paper sheets as a function of CNFs (P-CNF, C1-CNF and C2-CNF) added in the unrefined and refined pulp

Properties	Pulp	CNF	Mathematical models	R^2	Pr>Fc
Bulk (cm^3/g)	0 rev.	P-CNF	$\hat{Y} = 1.9524 - 0.04509x$	0.946	0.0000
		C1-CNF	$\hat{Y} = 1.9415 - 0.0684x$	0.918	0.0000
		C2-CNF	$\hat{Y} = 1.9665 - 0.1345x$	0.993	0.0000
	1000 rev.	P-CNF	$\hat{Y} = 1.5213 - 0.0192x$	0.0850	0.0000
		C1-CNF	$\hat{Y} = 1.5380 - 0.0340x$	0.9404	0.0000
		C2-CNF	$\hat{Y} = 1.5203 - 0.0397x$	0.999	0.0000

3.3.3.2 Air resistance

The Figure 19 shows the air resistance of paper sheets as a function of charge of added CNFs (P-CNF, C1-CNF and C2-CNF) in the unrefined and refined pulp.

For unrefined and refined pulp, the increase of CNFs added from 0% to 1% did not significantly affect the air resistance of paper sheets, while the increase from 1% to 5% resulted in an increase in air resistance of paper sheets. A similar result was found by Petroudy *et al*. (2014), who also added low charges of CNF to the pulp. The increase of air resistance in paper containing CNFs is due to the decrease of the microporous originated from entangled of fibers in paper structure, as can be seen in SEM images (Figure 15, Figure 16 and Figure 17).

Comparing unrefined with refined pulp, it can be observed that the positive effect of P-CNF, C1-CNF or C2-CNF on air resistance of paper sheets was more pronounced for unrefined pulp with the addition of 3% of CNFs, and for refined pulp with 5% of CNFs. The maximum increase in air resistance of paper sheets was of 5120% in relation to the reference (3.20s/100cm^3), obtained with addition of 5% of C1-CNF/C2-CNF on the refined pulp. The fibrillation of fibers and generation of fines during the refining increase the air resistance of paper and mask this effect partially due to the addition of CNFs.

The increase in air resistance of paper sheets as result of addition of 3% and 5% of C1-CNF or C2-CNF to the pulp was higher than that one which occurred as a result of pulp refining (410%). The increase in air resistance of paper sheets because of addition of 1% of C1-CNF or C2-CNF to the pulp was lower than that one which occurred as a result of pulp refining (410%).

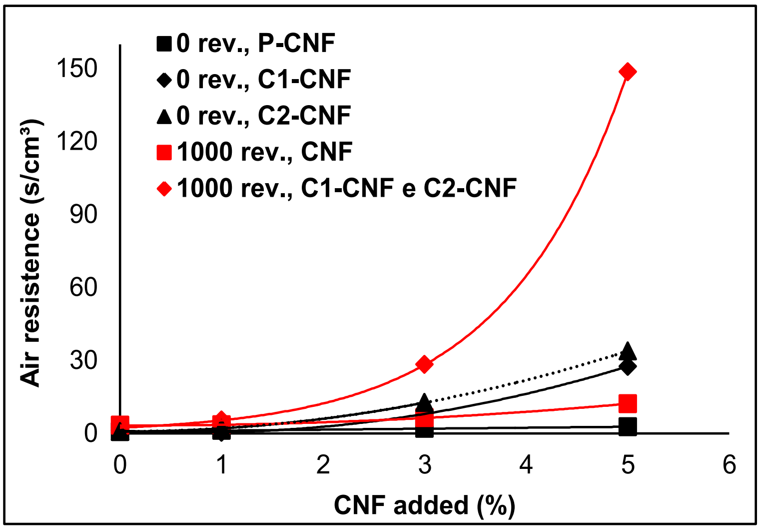

Figure 19 - Air resistance of paper sheets as a function of charge of P-CNF, C1-CNF and C2-CNF added in the unrefined and refined pulp

The optimal mathematical models for the evolution of air resistance of paper sheets as a function of charge of added CNFs (P-CNF, C1-CNF and C2-CNF) in the unrefined and refined pulp are showed in Table 08.

For unrefined or refined pulp, a significant difference between the curves of air resistance as a function of charge of added P-CNF and C-CNFs (C1-CNF or C2-CNF) was observed. Thus, there is a significant difference between the air resistance of paper sheets containing at least one of same charge of P-CNF and C-CNFs added.

For unrefined and refined pulp, the addition of different charges of C-CNFs (C1-CNF or C2-CNF) resulted in a paper with higher air resistance, as compared to those containing P-CNF. The only exception was for paper with addition of 1% of C1-CNF (2.99 s/cm^3), which presented lower air resistance than that containing P-CNF.

For unrefined pulp the positive effect of C2-CNF was higher than of C1-CNF. For refined pulp no significant difference between the curves of air resistance for paper as a function of C1-CNF and C2-CNF added in the pulp was observed.

The increase of air resistance in paper containing C-CNFs, as compared to that containing P-CNF, was higher because the C-CNFs have more homogeneous dispersion in the paper structure, this effect being more pronounced for C2-CNF as compared to C1-CNF.

Table 08 - Optimal mathematical models for the evolution of air resistance of paper sheets as a function of CNFs (P-CNF, C1-CNF and C2-CNF) added in the unrefined and refined pulp

Properties	Pulp	CNF	Mathematical models	R^2	Pr>Fc
Air resistance (s/cm^3)	0 rev.	P-CNF	$\hat{Y} = 0.7462 + 0.3983x$	0.998	0.0000
		C1-CNF	$\hat{Y} = 1.1672 - 2.1975x + 1.4944x^2$	0.984	0.0000
		C2-CNF	$\hat{Y} = 0.7800 - 0.0300x + 1.3300x^2$	0.998	0.0000
	1000 rev.	P-CNF	$\hat{Y} = 3.2927 - 0.1187x + 0.3796x^2$	0.984	0.0000
		C1-CNF and C2-CNF	$\hat{Y} = 2.3448e^{0.8299x}$	0.901	0.0000

3.3.3.3. Smoothness

In both printing and barrier applications, surface smoothness is a desirable property (BRODIN *et al*., 2014). The Figure 20 shows the smoothness of paper sheets as a function of charge of added CNFs (P-CNF, C1-CNF and C2-CNF) in the unrefined and refined pulp.

For unrefined and refined pulp, the increase of CNFs added from 0% to 1% did not significantly affect the smoothness of paper sheets, however, with a subsequent increase when the charge of CNFs increases from 1% to 5%. The CNF fills empty spaces between the fibers in the paper structure, making a smooth paper surface. The only exception was for the addition of different charges of P-CNF in refined pulp, which has no effect in smoothness of paper sheets.

Comparing unrefined with refined pulp, it can be observed that the positive effect of P-CNF, C1-CNF or C2-CNF on smoothness of paper sheets was more pronounced for unrefined pulp. The maximum increase in smoothness of paper sheets was of 93.9% for unrefined pulp and of 89.5% for refined pulp, obtained with addition of 5% of C2-CNF, respectively.

The increase in smoothness of paper sheets, as a result of adding CNFs in the pulp was lower than the one that occurred as a result of pulp refining (57.2%). The only exception was for paper with addition of 5% of C2-CNF (18.5 s), which presented higher increase (93.9%) in smoothness than the refined pulp.

Refine also has positive effect in smoothness, and masks partially this effect due to the addition of CNFs.

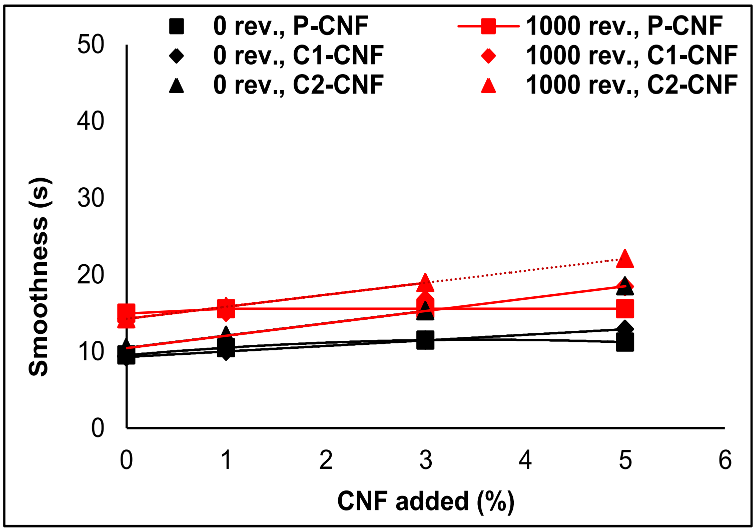

Figure 20 - Smoothness of paper sheets as a function of charge of P-CNF, C1-CNF and C2-CNF added in the unrefined and refined pulp

The optimal mathematical models for the evolution of smoothness of paper sheets as a function of charge of added CNFs (P-CNF, C1-CNF and C2-CNF) in the unrefined and refined pulp are showed in Table 09.

For unrefined or refined pulp, a significant difference between the curves of smoothness as a function of charge of P-CNF and C-CNFs (C1-CNF or C2-CNF) added was observed. Thus, there is a significant difference between smoothness of paper sheets containing at least one of the same charge of P-CNF and C-CNF added.

Paper sheets made from unrefined and refined pulp with addition of 3% or 5% of C-CNFs, and made from unrefined pulp with addition of 1% of C2-CNF presented higher smoothness than those with P-CNF. With exception of the unrefined pulp with addition of 1% of C2-CNF, the pulp with addition of 1% of C-CNFs resulted in paper with smoothness similar to that containing P-CNF. C-

CNFs have lower and more homogeneous dimensions, when compared with the P-CNF.

For unrefined or refined pulp, a significant difference between the curves of smoothness as a function of charge of C1-CNF and C2-CNF added was observed. Thus, there is a significant difference between smoothness of paper sheets containing at least one of the same charge of C1-CNF or C2-CNF added. For unrefined and refined pulp, the smoothness of paper sheets containing C2-CNF was higher than those containing C1-CNF, due to the lower and more homogeneous dimensions of C1-CNF when compared with C2-CNF.

To the best of our knowledge, there are studies on effect of CNF in smoothness of paper sheets only when CNF was applied as coating of paper. The CNF applied as a coating of paper increase the surface smoothness and the increase number of passes through homogenizer resulted in an increase on the surface smoothness of the coated sheet (SYVERUD and STENIUS *et al.*, 2009).

Table 09 - Optimal mathematical models for the evolution of smoothness of paper sheets as a function of charge of CNFs (P-CNF, C1-CNF and C2-CNF) added in the unrefined and refined pulp

Properties	**Pulp**	**CNF**	**Mathematical models**	**R^2**	**Pr>Fc**
Smoothness (s)	0 rev.	P-CNF	$\hat{Y} = 9.5036 + 1.1344x - 0.1593x^2$	0.997	0.0020
		C1-CNF	$\hat{Y} = 9.2263 + 0.7239x$	0.806	0.0000
		C2-CNF	$\hat{Y} = 19.5360 + 4.9540x - 1.0640x^2$	1.000	0.0001
	1000 rev.	P-CNF	$\hat{Y} = 14.2325 + 0.8382x$	0.878	0.0000
		C1-CNF	no model adjusted to data	-	-
		C2-CNF	$\hat{Y} = 14.2477 + 1.5667x$	0.864	0.0000

3.3.3.4. Tensile index

The Figure 21 shows the tensile index of paper sheets as a function of charge of CNFs (P-CNF, C1-CNF and C2-CNF) added in the unrefined and refined pulp. Pp

For unrefined and refined pulp, the increase of charge of P-CNF added from 0% to 5% resulted in an increase in tensile index of paper sheets. Similar results have been reported previously (GONZÁLEZ *et al.*, 2012;. HII *et al.*, 2012; TAIPALE *et al.*, 2010). The explanation is the high surface area of CNFs increased the number of bonds between the fibers increasing the tensile index of paper sheets. On the other hand, the increase of C-CNFs (C1-CNF or C2-CNF) added from 0% to 1% resulted in a reduction of tensile index of paper sheets, with a subsequent and unexpected increase when the charge of C-CNFs increase from 3% to 5%. These results are in agreement with Ahola *et al.* (2008), who added a mix of cationic polyelectrolyte (PAE) and nanofibrils in the pulp and measured the dry and wet tensile of paper.

Comparing unrefined with refined pulps, it can be observed that the positive effect of P-CNF, C1-CNF or C2-CNF on tensile index of paper sheets was more pronounced for unrefined pulp. For example, the addition of 5% of C1-CNF in the unrefined and refined pulp resulted in an increase of 65.64% and 10.2% in tensile index of paper sheets, respectively. Refining pulp also contributes to the increase in tensile index and partially masks this effect due to the addition of CNFs.

For paper sheets made from unrefined pulp with addition of CNFs, the maximum increase in tensile index was 65.6%, obtained with addition of 5% of C1-CNF or C2-CNF. The increase in tensile index of paper sheets as a result of pulp refining was 175.5%. The refining of pulp is a mechanical process that exposes more hydroxyl groups on surface of fibers, thus increase the number of links sites between the fibers and result in improved mechanical properties of paper sheets.

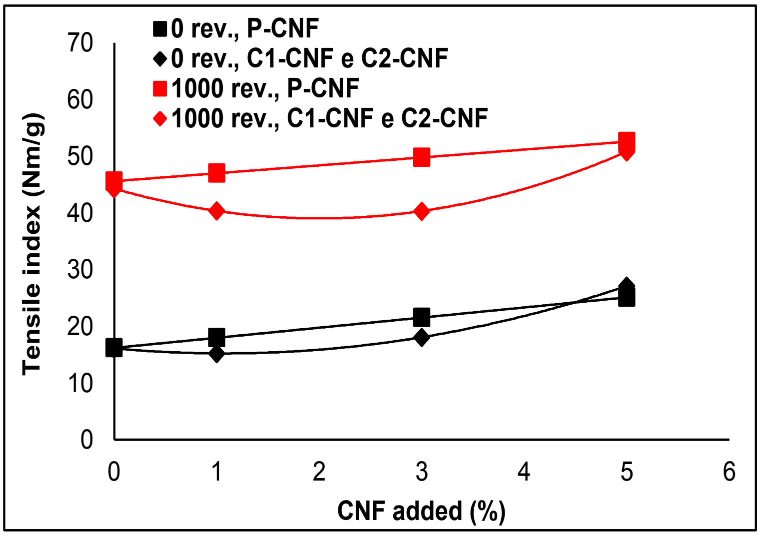

Figure 21 - Tensile index of paper sheets as a function of charge of P-CNF, C1-CNF and C2-CNF added in the unrefined and refined pulp

The optimal mathematical models for the evolution of tensile index of paper sheets as a function of charge of added CNFs (P-CNF, C1-CNF and C2-CNF) in the unrefined and refined pulp are shown in Table 10.

For unrefined or refined pulp, a significant difference between the curves of tensile index as a function of charge of added P-CNF and C-CNFs (C1-CNF or C2-CNF) was observed. Thus, there is a significant difference between tensile index of paper sheets containing at least one of the charge of P-CNF and C-CNF added.

Paper sheets made from unrefined and refined pulp with addition of 1% and 3% of C-CNFs (C1-CNF or C2-CNF) presented a lower tensile index in comparison to those with P-CNF. Paper sheets made from pulps with addition of 5% of C-CNFs presented higher (unrefined pulp) or similar (refined pulp) tensile index than those with P-CNF. The cationic modification of P-CNF decreased the degree of polymerization and crystallinity index of cellulose (item 3.1.2), and therefore, despite strong electrostatic bonds between the negative charges of fibers and positive charges of C-CNFs, the C-CNFs are weaker and break more easily than the P-CNF. On the other hand, according to Ahola *et al.* (2008), the increase in tensile index at the highest fibrils addition may occur due to precipitation or mechanical attachment of large aggregate flocs of fibers during sheet formation. According to Demuner *et al.* (1990), with the increase of the volume of eucalyptus pulp flocs greater is the entanglement between the fibers capacity and the tensile index.

For unrefined and refined pulp no significant difference was observed for curves of tensile index of paper sheets as a function of C1-CNF and C2-CNF added in the pulp.

Table 10 - Optimal mathematical models for the evolution of tensile index of paper sheets as a function of CNFs (P-CNF, C1-CNF and C2-CNF) added in the unrefined and refined pulp

Properties	Pulp	CNF	Mathematical models	R^2	Pr>Fc
Tensile index (Nm/g)	0 rev.	P-CNF	$\hat{Y} = 16.2007 + 1.7830x$	0.999	0.0000
		C1-CNF and C2-CNF	$\hat{Y} = 15.975 - 1.1589x + 0.6815x^2$	0.930	0.0000
	1000 rev.	P-CNF	$\hat{Y} = 45.6152 + 1.3937x$	0.916	0.0000
		C1-CNF and C2-CNF	$\hat{Y} = 44.302 - 5.2479x + 1.3098x^2$	0.864	0.0000

3.3.3.5. Tear index

The Figure 22 shows the tear index of paper sheets as a function of charge of CNFs (P-CNF, C1-CNF and C2-CNF) added in the unrefined and refined pulp.

For unrefined and refined pulp, the increase of CNFs added from 0% to 3% did not significantly affect the tear index of paper sheet, however, with subsequent increase when the charge of CNFs increase from 3% to 5%. The explanation is that the paper sheets with addition of CNFs have more bonds between the fibers than those without CNF. According to Brandon (1981), tear resistance of paper sheets depends on the total number of fibers participating in the sheet rupture, the length of the fibers, and the number and strength of bonds between the fibers (BRANDON, 1981). Hassan *et al*. (2015) have found that the increase of added microfibrillated cellulose from 0% to 10% resulted in an increase in tear index of paper sheets made from softwood pulp, which is in agreement with the results obtained in this study. On the other hand, Petroudy *et al*. (2014) have found that the addition of 5% of CNF to the bagasse pulp resulted in a decrease in the tear index of paper sheet. Gonzáles *et al*. (2012) reported that the addition of up to 9% and 6% of nanofibrillated cellulose in unrefined and in refined eucalyptus pulp, respectively, resulted in little variation in tear index of paper sheets.

Comparing unrefined and refined pulp, it can be observed that the positive effect of CNFs (P-CNF, C1-CNF or C2-CNF) in tear index of paper sheets was more pronounced for unrefined pulp. For example, the addition of 5% of C1-CNF in the unrefined and refined pulp resulted in an increase of 141.5% and 72.9% in tear index of paper sheets, respectively. Refining pulp also contributes to the increase in the tear index and partially masks this effect due to the addition of CNFs.

The increase in tear index of paper sheets as a result of pulp refining was 154%. The maximum increase in tear index of paper sheets as a result of addition of CNF in the pulp was 178%, for addition of 5% of C1-CNF or 5% of C2-CNF. These results indicate that the addition of 5% of C1-CNF or C2-CNF can be used as a substitute for pulp refining. The addition of CNFs promotes the increase of bounds between the fibers without damaging the fibers structure. Whereas, the refining of the pulp is a mechanical process that increases the bounds between the fibers, it damages, however, the structure of the fibers. According to Hassan *et al*. (2010) ruptures of fibers and pulling fibers out of the paper sheet are involved in tearing, and the latter occurs more than the first.

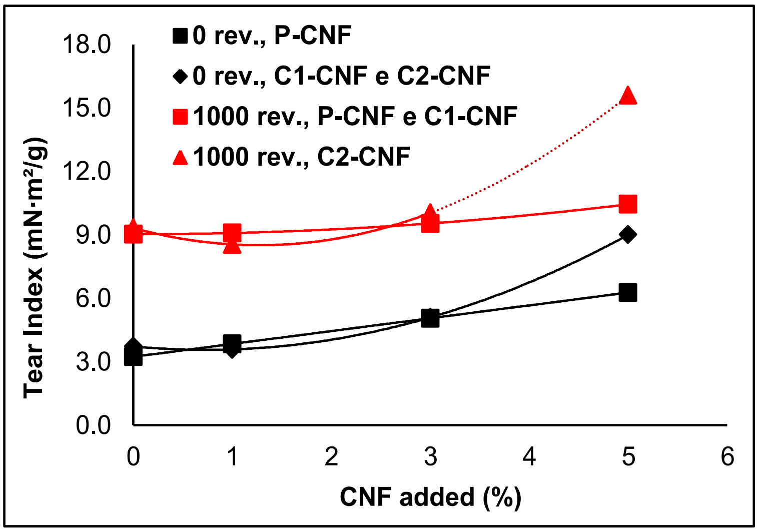

Figure 22 - Tear index of paper sheets as a function of charge of P-CNF, C1-CNF and C2-CNF added in the unrefined and refined pulp

The optimal mathematical models for the evolution of tear index of paper sheets as a function of charge of added CNFs (P-CNF, C1-CNF and C2-CNF) in the unrefined and refined pulp are shown in Table 11.

For unrefined pulp, a significant difference between the curves of tear index as a function of charge of added P-CNF and C-CNFs (C1-CNF and C2-CNF) was observed. Thus, there is a significant difference between the tear index of paper sheets containing at least one of the same charge of P-CNF and C-CNFs added. The pulps with addition of C1-CNF and C2-CNF presented performance statistically equal throughout the range of addition of CNFs. The addition of only 5% of C-CNFs resulted in paper sheets with tear index higher, as compared to that containing P-CNF. The addition of 1% and 3% of C-CNFs resulted in paper sheets with tear index similar, if compared to that containing P-CNF.

For refined pulp, no significant difference between the curves of tear index as a function of charge of added P-CNF and C1-CNF was observed. On the other hand, a significant difference between the curves of tear index as a function of charge of P-CNF and C2-CNF added was observed. Thus, there is a significant difference between tear index of paper sheets containing at least one of the charge of P-CNF and C2-CNF added. The addition of only 5% of C2-CNF resulted in paper sheets with tear index higher than that with P-CNF. The addition of lower charges of C2-CNF resulted in paper sheets with tear index similar to that with P-CNF.

The explanation for the higher tear index of paper sheets with addition of C-CNF is that the strength of the ionic bounds between C-CNF and fibers is greater than that of the hydrogen bonds between the P-CNF and fibers.

For unrefined and refined pulp, a significant difference between the curves of tear index as a function of charge of C1-CNF and C2-CNF added was observed. Thus, there is a significant difference between tear index of paper sheet containing at least one of the same charge of C1-CNF and C2-CNF added. For unrefined and refined pulp, the tear index of paper sheets with addition of 5% of C2-CNF was higher than those with addition of 5% of C1-CNF, because the number of bonds between the fibers is higher for paper sheets with C2-CNF than those with C1-CNF.

Table 11 - Optimal mathematical models for the evolution of tear index of paper sheets as a function of charge of CNFs (P-CNF, C1-CNF and C2-CNF) added in the unrefined and refined pulp

Properties	**Pulp**	**CNF**	**Mathematical models**	**R^2**	**Pr>F**
Tear index ($mN \cdot m^2/g$)	0 rev.	P-CNF	$\hat{Y} = 3.2406 + 0.6075x$	0.935	0.0001
		C1-CNF and C2-CNF	$\hat{Y} = 3.7311 +0.4406x +0.2992x^2$	0.999	0.0000
	1000 rev.	P-CNF and C1-CNF	$\hat{Y} = 9.0334 + 0.0021x + 0.0562x^2$	0.908	0.0000
		C2-CNF	$\hat{Y} = 9.3329 - 1.2904x + 0.5091x^2$	0.947	0.0000

3.3.3.6. Burst index

The Figure 23 shows the burst index of paper sheets as a function of charge of added CNFs (P-CNF, C1-CNF and C2-CNF) in the unrefined and refined pulp. According to Brandon (1981), paper sheet burst strength depends on fiber length, on the bounds between the fibers and on the stretch of the sheet.

The burst index showed a similar tendency to the tensile index. For unrefined pulp with addition of CNFs (P-CNF, C1-CNF and C2-CNF) and for refined pulp with addition of P-CNF, the increase on the charge of CNFs added from 0% to 5% resulted in an increase of burst index of paper sheets. On the other hand, the refined pulp with addition of C-CNFs (C1-CNF and C2-CNF) from 0% to 1% shown a decrease of burst index of paper sheets, with a subsequent and unexpected increase when the charge of C-CNFs increases from 3% to 5%. Hassan *et al*. (2010) found that the addition of up to about 50% of microfibrillated cellulose in the bagasse pulp did not affect the burst strength of paper sheets. Charini *et al*. (2013) added microfibrillated cellulose in the hardwood kraft pulp and found that the addition of up to 6% resulted in a small increase on the burst index of paper sheets, while the addition of 10% increased the burst index of paper by about 30%. Gonzáles *et al*. (2013) added 3% of nanofibrillated cellulose in the eucalyptus kraft pulp and found the burst index 3 times greater than the reference (without CNF).

Comparing unrefined and refined pulp, it can be observed that the positive effect of CNFs (P-CNF, C1-CNF or C2-CNF) in burst index of paper sheet was more pronounced for unrefined pulp. For example, the addition of 5% of P-CNF resulted in an increase in the burst index of paper sheets of 118% for unrefined pulp and 34.9% for refined pulp. The refining of pulp also contributes to the increase in the burst index of paper sheets and partially masks this effect due to the addition of CNFs.

For paper sheets made from pulp with addition of CNFs, the maximum increase in burst index was 198%, obtained with addition of 5% of C1-CNF or C2-CNF. The increase in burst index of paper sheets as a result of pulp refining was of 323%.

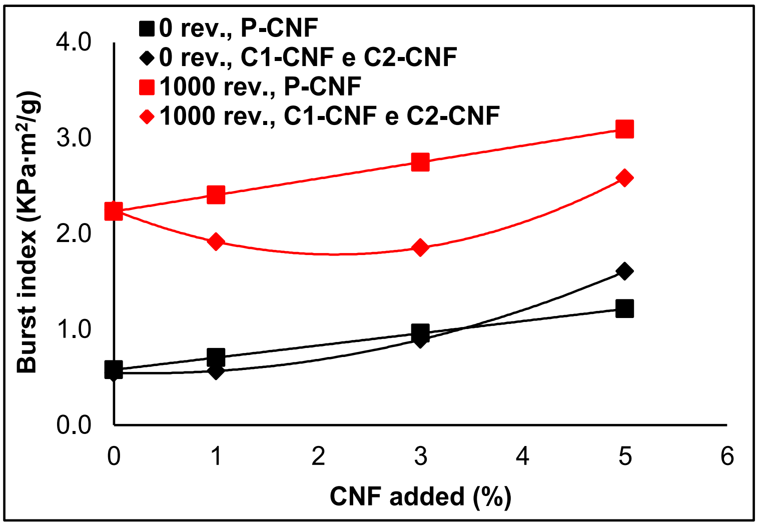

Figure 23 - Burst index of paper sheets as a function of P-CNF, C1-CNF and C2-CNF added in the unrefined and refined pulp

The optimal mathematical models for the evolution of burst index of paper sheets as a function of charge of added CNFs (P-CNF, C1-CNF and C2-CNF) in the unrefined and refined pulp are shown in Table 12.

For unrefined or refined pulp, a significant difference between the curves of burst index as a function of charge of added P-CNF and C-CNFs (C1-CNF or C2-CNF) was observed. Thus, there is a significant difference between burst index of paper sheets containing at least one of the charge of P-CNF and C-CNF added.

For unrefined pulp, paper sheets with addition of small charges of C-CNFs (1% and 3%) presented burst index lower by about 15% in comparison to those with P-CNF. However, the addition of 5% of C-CNFs resulted in a burst index 36% higher in comparison to that with 5% of P-CNF. For refined pulp, paper sheets with addition of different charges of C-CNF (C1-CNF or C2-CNF) presented burst index lower by about 20-30% in comparison to those with P-CNF. Thus, the positive effect of higher charge of C-CNFs did not appear on refined pulp, due to the fact that the refining pulp partially masks the effect of C-CNF. However, this tendency was clearly observed.

For unrefined and refined pulp no significant difference was observed for curves of burst index of paper sheets as a function of C1-CNF and C2-CNF added in the pulp.

Table 12 - Optimal mathematical models for the evolution of burst index of paper sheets as a function of charge of CNFs (P-CNF, C1-CNF and C2-CNF) added in the unrefined and refined pulp

Properties	Pulp	CNF	Mathematical models	R^2	Pr>Fc
Burst index ($KPa{\cdot}m^2/g$)	0 rev.	P-CNF	$\hat{Y} = 0.5792 + 0.1272x$	0.976	0.0000
		C1-CNF and C2-CNF	$\hat{Y} = 0.547 - 0.0282x + 0.048x^2$	0.965	0.0000
	1000 rev.	P-CNF	$\hat{Y} = 2.2334 + 0.1718x$	0.976	0.0000
		C1-CNF and C2-CNF	$\hat{Y} = 2.2474 - 0.4283x + 0.099x^2$	0.808	0.0000

3.3.3.7. Light scattering coefficient and transparency

Figure 24 and Figure 25 show the light scattering coefficient and transparency and of paper sheets as a function of charge of added CNFs (P-CNF, C1-CNF and C2-CNF) in the unrefined and refined pulp, respectively.

For unrefined and refined pulp, the increase of the addition of C-CNFs (C1-CNF or C2-CNF) from 1% to 5% resulted in a decrease in the light scattering coefficient and an increase in transparency of paper sheets. The addition of 1% of C-CNFs has not effect in light scattering coefficient and transparency of paper sheets, due to its low retention. According to Yano *et al.* (2005), reinforcing elements with diameters less than one-tenth of visible light wavelengths (70.5 nm) are not expected to cause light scattering. The TEM images showed that the C-CNFs (C1-CNF and C2-CNF) are in range required to not cause light scattering and, consequently, contribute to increase the transparency of paper sheets.

For unrefined and refined pulp, the addition of different charges of P-CNF has no clear effect in the light scattering coefficient and transparency of paper sheets. This is due to agglomeration and not homogeneous dispersion of fibrils in the paper sheets. Gonzáles *et al.* (2012) added different charges of unmodified cellulose nanofibrillated in the eucalyptus pulp and Hassan *et al.* (2010) in the bagasse pulp and no significant effect in opacity of paper sheets was found.

The increasing transparency of printing and writing paper is not desirable, due to the fact that printing may appear on the reverse side of the paper sheet. The increase in transparency of paper sheets as a result of pulp refining was 16.5%. However, the addition of P-CNF improves the mechanical properties of paper sheets without affecting their transparency significantly.

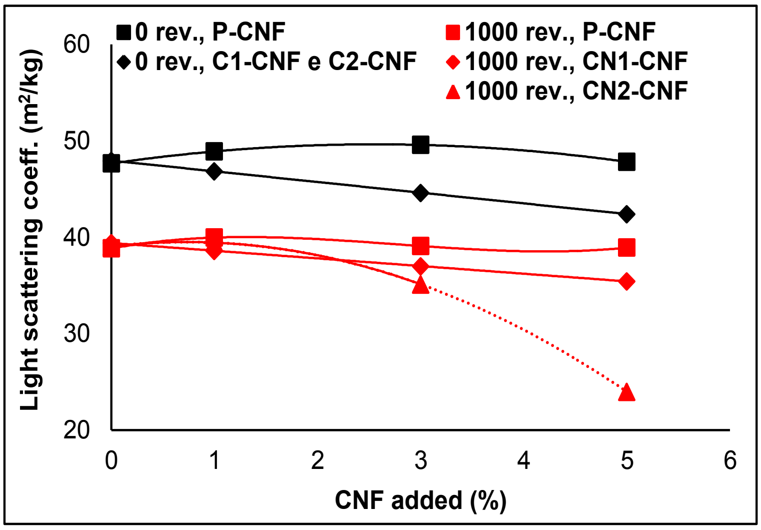

Figure 24 - Light scattering coefficient of paper sheets as a function of P-CNF, C1-CNF and C2-CNF added in the unrefined and refined pulp

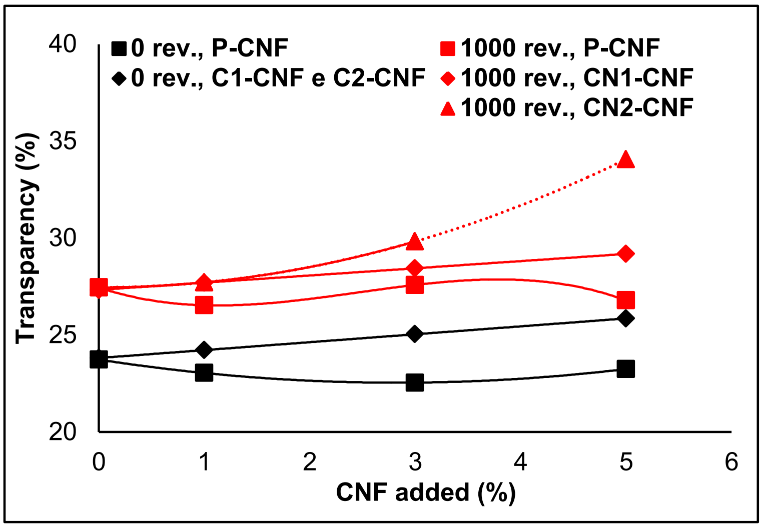

Figure 25 - Transparency of paper sheets as a function of P-CNF, C1-CNF and C2-CNF added in the unrefined and refined pulp

The optimal mathematical models for the evolution of light scattering coefficient and transparency of paper sheets as a function of charge of added CNFs (P-CNF, C1-CNF and C2-CNF) in the unrefined and refined pulp are shown in Table 13.

Table 13 - Optimal mathematical models for the evolution of burst index of paper sheets as a function of charge of CNFs (P-CNF, C1-CNF and C2-CNF) added in the unrefined and refined pulp

Properties	Pulp	CNF	Mathematical models	R^2	Pr>Fc
[1]LSC (m^2/kg)	0 rev.	P-CNF	$\hat{Y} = 47.641 + 1.558x - 0.3048x^2$	0.935	0.0000
		C1-CNF and C2-CNF	$\hat{Y} = 47.9404 - 1.1093x$	0.956	0.0000
	1000 rev.	P-CNF	$\hat{Y} = 38.818 + 2.031x - 1.016x^2 + 0.123x^3$	0.981	0.0000
		C1-CNF	$\hat{Y} = 39.3891 - 0.7954x$	0.968	0.0000
		C2-CNF	$\hat{Y} = 39.038 + 1.2467x - 0.8527x^2$	0.924	0.0000
[2]Transp. (%)	0 rev.	CNF	$\hat{Y} = 23.738 - 0.8417x + 0.1488x^2$	0.896	0.0000
		C1-CNF and C2-CNF	$\hat{Y} = 23.8198 + 0.4082x$	0.960	0.0000
	1000 rev.	P-CNF	$\hat{Y} = 27.462 - 1.8275x + 1.0496x^2 - 0.1422x^3$	0.914	0.0000
		C1-CNF	$\hat{Y} = 27.3362 + 0.3706x$	0.975	0.0000
		C2-CNF	$\hat{Y} = 27.462 - 0.0053x + 0.2653x^2$	0.958	0.0010

[1] Light scattering coefficient; [2] Transparency.

For unrefined and refined pulp, a significant difference between the curves of light scattering coefficient as a function of charge of added P-CNF and C-CNFs (C1-CNF or C2-CNF) was observed. Thus, there is a significant difference between light scattering coefficient of paper sheets containing at least one of the charge of P-CNF and C-CNF added.

For unrefined and refined pulp, paper sheets with addition of different charges of C-CNFs presented a lower light scattering coefficient, if compared to that containing P-CNF, as expected.

For unrefined pulp, no significant difference was observed for curves of light scattering coefficient of paper sheets as a function of C1-CNF and C2-CNF added. However, for refined pulp, the addition of 3% and 5% of C2-CNF resulted in paper sheets with lower light scattering coefficient than those with C1-CNF.

The light scattering coefficient had the opposite behavior to the transparency, which is in agreement with Kubelka and Munk equation (DENCE and REEVE, 1996).

4 CONCLUSIONS

The C-CNFs presented trimethylammonium chloride content of 0.68 (C1-CNF) and 1.21 mmol·g^{-1} (C2-CNF). The cationization reactions decreased the fibrils thickness and the length, and also degraded the cellulose chain and crystallinity structure. The C-CNFs were used as additive to improve quality of eucalyptus kraft pulp on paper production and to the following conclusions were drawn:

- The fines increased the C2-CNF retention in the paper sheet.
- The refine did not have effect in the retention of C2-CNF in the paper sheet. However, the used level of refining (1000 rev.) was low.
- Only the pulps with high charges of C-CNFs (3% and 5%) presented drainage time higher than those with P-CNF. The addition of C2-CNF resulted in pulps with drainage time statistically higher than those with C1-CNF.
- After the cationization, the CNF presented homogeneous distribution on paper structure, allowing a large number and strong bonds between the fibers.
- In general, the papers with addition of C-CNF presented lower bulk and higher air resistance and smoothness than those with P-CNF.
- Only the addition of high charges of C-CNFs resulted in papers with tear index and burst index statistically higher than those with P-CNF. A possible explanation is that larger flocs present during the paper formation can cause a greater entanglement between the fibers.
- When compared with P-CNF, the addition of different charges of C-CNFs did not increase the tensile index of papers.
- The reduction of mechanical strength for paper with low charges of C-CNFs may have occurred by rupture of the paper in the C-CNF, which was degraded during the cationic reaction.

- The papers with addition of different charges of C-CNFs presented lower light scattering coefficient and higher transparency than those with P-CNF.
- In general, the degree of cationizarion of CNF had effect on the physical and optical properties of paper sheets, however it had no effect on mechanical properties.
- Refining pulp also contributes to the physical-mechanical and optical properties of paper sheets, it partially masks this effect due to the addition of CNFs.
- The advantage of P-CNF, when compared with the C-CNF, is that it increases the mechanical properties of paper sheets, even with low charges, without a significant reduction in optical properties.

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2 GENERAL CONCLUSIONS

After the cationization, the CNF presented homogeneous distribution on paper structure, allowing a large number and strong bonds between the fibers, which reflected significantly on the paper properties. However, for the use of cationic CNF as additive to improve quality of *Eucalypt*us kraft pulp on paper production, it is necessary that the cationic reaction be performed in medium compatible with paper production and does not damage the CNF structure. Additionally, the degree of cationization and the charge of CNF have to be optimized to improve the paper properties without increasing the pulp drainage time.

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APPENDIX A

Table 1A - Experimental results of physical-mechanical and optical properties of paper sheets made from unrefined pulp, with addition 0%, 1%, 3% and 5% of P-CNF

Energy[1] (Wh)	P-CNF (%)	°SR[1]	Rep.[1]	Grammage (g/m^2)	Thickness (µm)	Bulk (cm^3/g)	Smoothness (s)	Air resistance (s/100cm^3)	Tensile index (N·m/g)	Tear index (mN·m^2/g)	Burst index (KPa·m^2/g)	LSC[1] (m^2/kg)	Transparency (%)
0	0	20.0	A	66.3	131	1.98	9.15	0.780	16.5	3.50	0.519	47.8	23.6
			B	66.1	131	1.98	8.72	0.780	16.6	3.59	0.580	47.7	23.6
			C	66.2	131	1.98	9.82	0.750	16.2	3.64	0.519	47.9	23.7
			D	66.1	131	1.98	10.2	0.780	16.5	3.65	0.550	49.2	23.6
			E	66.4	131	1.97	9.78	0.810	15.9	3.69	0.535	48.4	23.7
0	1	22.0	A	66.1	125	1.89	9.90	1.00	17.8	3.55	0.796	48.7	23.3
			B	66.4	124	1.87	10.3	1.23	17.8	3.16	0.719	48.5	23.3
			C	65.2	124	1.90	10.6	1.06	17.9	3.18	0.735	48.8	23.2
			D	66.3	125	1.89	10.8	1.17	18.7	3.50	0.735	48.8	23.2
			E	66.4	124	1.87	10.5	1.02	17.4	3.45	0.673	48.8	23.2
0	3	26.0	A	65.9	119	1.81	11.9	2.03	20.0	5.22	0.99	49.5	22.4
			B	65.3	118	1.81	10.9	1.89	22.0	5.24	1.03	50.0	22.4
			C	65.5	118	1.80	11.2	1.95	22.9	4.87	1.02	49.9	22.4
			D	65.1	117	1.79	12.0	1.81	20.1	5.28	0.94	49.5	22.4
			E	66.0	118	1.79	11.5	2.09	22.0	4.84	1.08	49.7	22.5
0	5	28.5	A	67.4	117	1.74	10.7	2.92	25.4	6.57	1.17	47.7	23.3
			B	67.1	117	1.74	10.7	2.61	24.9	6.56	1.29	47.9	23.2
			C	67.4	117	1.74	11.6	2.77	24.9	6.13	1.20	47.6	23.3
			D	67.3	118	1.75	11.0	2.77	25.7	6.30	1.13	47.9	23.3
			E	67.4	117	1.74	11.9	2.63	25.2	6.23	1.11	47.7	23.3

[1] Rep.=Repetitions; Energy= specific energy consumption; °SR=degrees Schopper Riegler; LSC=Light scattering coefficient.

Table 2A - Experimental results of physical-mechanical and optical properties of paper sheets made from unrefined pulp, with addition of 0%, 1%, 3% and 5% of C1-CNF

Energy[1] (Wh)	C1-CNF (%)	°SR[1]	Rep.[1]	Grammage (g/m^2)	Thickness (µm)	Bulk (cm^3/g)	Smoothness (s)	Air resistance (s/100cm^3)	Tensile index (N·m/g)	Tear index (mN·m^2/g)	Burst index (KPa·m^2/g)	LSC[1] (m^2/kg)	Transparency (%)
0	0	20.0	A	66.3	131	1.98	9.15	0.780	16.5	3.50	0.519	47.8	23.6
			B	66.1	131	1.98	8.72	0.780	16.6	3.59	0.580	47.7	23.6
			C	66.2	131	1.98	9.82	0.750	16.2	3.64	0.519	47.9	23.9
			D	66.1	130	1.98	10.2	0.780	16.5	3.65	0.550	49.2	23.4
			E	66.4	132	1.97	9.78	0.810	15.9	3.69	0.535	48.4	23.7
0	1	18.0	A	63.9	129	1.85	9.68	1.25	14.9	3.55	0.506	47.9	24.1
			B	64.0	128	1.85	10.1	1.13	14.2	3.67	0.538	47.5	24.2
			C	63.9	127	1.85	9.28	1.19	14.5	3.93	0.712	46.9	24.5
			D	63.9	129	1.86	9.12	1.15	14.2	3.71	0.759	47.4	24.3
			E	64.0	128	1.85	9.00	1.23	15.8	3.41	0.633	47.2	24.3
0	3	43.0	A	64.9	109	1.68	11.3	7.80	18.5	4.24	0.802	43.1	26.0
			B	63.9	108	1.69	11.0	7.94	19.5	4.15	0.882	45.2	25.1
			C	64.2	108	1.68	12.3	7.36	17.1	4.27	0.882	43.2	25.4
			D	64.4	108	1.68	13.0	7.33	18.5	4.27	0.835	44.5	24.9
			E	64.2	108	1.68	11.8	7.27	17.1	4.13	0.837	45.9	24.8
0	5	72.0	A	64.2	105	1.63	12.4	29.3	27.8	9.50	1.60	42.1	26.2
			B	64.0	104	1.63	13.0	25.4	28.2	9.25	1.78	43.0	25.4
			C	65.9	108	1.64	12.4	30.0	26.1	8.61	1.53	43.5	25.0
			D	64.0	105	1.64	13.0	25.5	26.1	9.25	1.54	43.3	25.6
			E	65.9	108	1.64	13.0	28.2	26.7	8.50	1.61	42.2	26.1

[1] Energy= specific energy consumption; °SR=degrees Schopper Riegler; Rep.=Repetitions; LSC=Light scattering coefficient.

Table 3A - Experimental results of physical-mechanical and optical properties of paper sheets made from unrefined pulp, with addition of 0%, 1% and 3% of C2-CNF

Energy[1] (Wh)	C2-CNF (%)	°SR[1]	Rep.[1]	Grammage (g/m^2)	Thickness (µm)	Bulk (cm^3/g)	Smoothness (s)	Air esistance (s/100cm^3)	Tensile index (N·m/g)	Tear index (mN·m^2/g)	Burst index (KPa·m^2/g)	LSC[1] (m^2/kg)	Transparency (%)
0	0	20.0	A	66.3	130	1.98	9.15	0.780	16.5	3.50	0.519	47.8	23.6
			B	66.1	130	1.98	8.72	0.780	16.6	3.59	0.580	47.7	23.6
			C	66.2	130	1.98	9.82	0.750	16.2	3.64	0.519	47.9	23.9
			D	66.1	130	1.98	10.2	0.780	16.5	3.65	0.550	49.2	23.4
			E	66.4	130	1.97	9.78	0.810	15.9	3.69	0.535	48.4	23.7
0	1	23.3	A	66.5	121	1.82	13.0	2.13	14.9	3.55	0.548	46.2	24.1
			B	66.4	120	1.81	12.7	2.14	14.9	3.64	0.503	45.7	24.4
			C	65.5	119	1.81	13.7	2.02	15.3	3.89	0.533	46.5	24.5
			D	67.0	121	1.81	14.9	2.22	14.9	3.86	0.542	46.2	24.4
			E	66.4	120	1.81	12.9	1.89	15.0	3.42	0.512	47.1	24.3
0	3	27.0	A	65.8	103	1.57	14.7	12.6	19.4	5.75	0.922	43.5	25.7
			B	65.4	103	1.57	14.4	12.0	21.1	5.90	1.02	43.2	25.5
			C	65.3	103	1.58	13.8	12.8	22.1	5.32	0.907	43.5	25.5
			D	66.4	104	1.56	14.9	13.1	17.9	6.27	0.861	43.4	25.3
			E	66.0	104	1.57	16.3	12.8	19.4	6.23	0.923	43.5	25.5

[1] Energy= specific energy consumption; °SR=degrees Schopper Riegler; Rep.=Repetitions; LSC=Light scattering coefficient.

Table 4A - Experimental results of physical-mechanical and optical properties of paper sheets made from refined pulp (1000 rev. PFI), with addition of 0%, 1%, 3% and 5% of P-CNF

Energy[1] (Wh)	P-CNF (%)	°SR[1]	Rep.[1]	Grammage (g/m^2)	Thickness (µm)	Bulk (cm^3/g)	Smoothness (s)	Air resistance (s/100cm^3)	Tensile index (N·m/g)	Tear index (mN·m^2/g)	Burst index (KPa·m^2/g)	LSC[1] (m^2/kg)	Transparency (%)
13	0	25.0	A	66.2	101	1.53	15.5	3.05	45.2	8.69	2.30	38.7	27.3
			B	65.7	100	1.52	15.0	3.42	44.3	9.06	2.36	39.0	27.5
			C	65.8	100	1.52	14.1	3.25	45.4	9.64	2.30	38.8	27.8
			D	65.6	100	1.53	14.7	3.27	44.6	8.95	2.22	38.8	27.2
			E	66.3	100	1.51	15.4	3.03	45.0	9.48	2.27	38.8	27.5
13	1	27.5	A	66.4	100	1.51	17.2	3.81	45.8	9.25	2.44	39.9	26.4
			B	67.2	102	1.52	16.4	3.78	48.5	8.87	2.38	39.9	26.6
			C	65.8	100	1.52	11.3	3.86	47.0	8.71	2.22	39.9	26.6
			D	66.7	101	1.51	16.0	3.56	48.7	8.75	2.32	40.0	26.5
			E	67.0	101	1.51	14.6	3.59	46.6	9.00	2.25	39.9	26.6
13	3	32.5	A	66.8	96.0	1.44	14.9	5.66	52.9	9.25	2.89	39.1	27.5
			B	67.5	97.0	1.44	14.0	6.55	51.8	9.26	2.69	39.0	27.7
			C	66.6	96.0	1.44	16.5	5.78	49.4	9.52	2.59	39.1	27.5
			D	66.5	96.0	1.44	16.0	6.61	48.9	9.77	2.75	39.0	27.7
			E	67.0	96.0	1.43	16.4	6.61	51.9	9.70	2.95	39.1	27.5
13	5	40.5	A	69.5	100	1.44	14.3	12.6	52.1	10.5	3.19	39.0	26.7
			B	69.2	99.0	1.43	15.1	11.8	51.0	10.6	2.92	38.9	26.8
			C	69.4	100	1.44	14.7	11.8	53.9	10.6	3.00	38.9	26.7
			D	69.5	100	1.44	15.0	11.5	49.8	10.5	3.26	38.8	26.8
			E	69.3	100	1.44	15.9	13.4	52.2	10.4	3.10	38.9	27.0

[1] Energy= specific energy consumption; °SR=degrees Schopper Riegler; Rep.=Repetitions; LSC=Light scattering coefficient.

Table 5A - Experimental results of physical-mechanical and optical properties of paper sheets made from refined pulp (1000 rev. PFI), with addition of 0%, 1%, 3% and 5% of C1-CNF

Energy[1] (Wh)	C1-CNF (%)	°SR[1]	Rep.[1]	Grammage (g/m^2)	Thickness (µm)	Bulk (cm^3/g)	Smoothness (s)	Air resistance ($s/100cm^3$)	Tensile index (N·m/g)	Tear index ($mN·m^2/g$)	Burst index ($KPa·m^2/g$)	LSC[1] (m^2/kg)	Transparency (%)
13	0	25.0	A	66.2	101	1.53	15.5	3.05	45.2	8.69	2.30	39.5	27.3
			B	65.7	100	1.52	15.0	3.42	44.3	9.06	2.36	39.0	27.5
			C	65.8	100	1.52	14.1	3.25	45.4	9.64	2.30	38.4	27.5
			D	65.6	100	1.53	14.7	3.27	44.6	8.95	2.22	39.5	27.4
			E	66.3	100	1.51	15.4	3.03	45.0	9.48	2.27	38.8	27.5
13	1	21.0	A	66.4	102	1.54	13.9	2.98	37.0	8.21	1.67	38.7	27.8
			B	64.8	99.0	1.53	13.3	2.92	34.7	10.00	1.67	38.4	27.8
			C	65.5	100	1.53	12.6	3.06	39.2	8.94	1.72	39.0	27.6
			D	64.4	98.0	1.52	15.8	2.97	36.0	10.06	1.61	39.0	27.6
			E	64.8	99.0	1.53	15.1	3.00	37.0	9.04	1.77	39.4	27.5
13	3	42.0	A	67.4	96.0	1.43	16.5	23.0	39.1	9.62	1.98	37.5	28.0
			B	67.6	96.0	1.42	16.0	23.1	45.9	9.59	1.95	36.1	28.7
			C	67.2	96.0	1.43	17.4	24.5	40.4	9.90	1.86	37.1	28.3
			D	67.6	96.0	1.42	17.4	24.5	39.6	9.85	1.95	37.8	28.5
			E	67.5	96.0	1.42	16.6	25.2	41.3	9.61	1.84	37.4	28.1
13	5	70.0	A	69.9	96.0	1.37	15.4	169	51.2	10.3	2.59	36.6	29.1
			B	69.1	95.0	1.37	21.7	169	49.7	10.2	2.45	34.4	29.7
			C	67.8	93.0	1.37	17.3	169	45.7	10.4	2.59	34.5	29.6
			D	66.9	92.0	1.37	20.1	164	51.2	10.4	2.45	35.0	29.3
			E	68.5	94.0	1.37	18.5	169	49.7	10.3	2.59	35.7	28.8

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[1] Energy= specific energy consumption; °SR=degrees Schopper Riegler; Rep.=Repetitions; LSC=Light scattering coefficient.

Table 6A - Experimental results of physical-mechanical and optical properties of paper sheets made from refined pulp (1000 rev. PFI), with addition of 0%, 1% and 3% of C2-CNF

Energy[1] (Wh)	C2-CNF (%)	°SR[1]	Rep.[1]	Grammage (g/m^2)	Thickness (µm)	Bulk (cm^3/g)	Smoothness (s)	Air resistance (s/100cm^3)	Tensile index (N·m/g)	Tear index (mN·m^2/g)	Burst index (KPa·m^2/g)	LSC[1] (m^2/kg)	Transparency (%)
13	0	25.0	A	66.2	101	1.53	15.5	3.05	45.2	8.69	2.30	39.5	27.3
			B	65.7	100	1.52	15.0	3.42	44.3	9.06	2.36	39.0	27.5
			C	65.8	100	1.52	14.1	3.25	45.4	9.64	2.30	38.4	27.8
			D	65.6	100	1.53	14.7	3.27	44.6	8.95	2.22	39.5	27.2
			E	66.3	100	1.51	15.4	3.03	45.0	9.48	2.27	38.8	27.5
13	1	24.5	A	65.8	96.6	1.47	15,5	5.33	37.6	8.50	1.94	40.4	27.6
			B	65.5	97.0	1.48	14,5	4.73	40.3	8.67	1.88	39.3	28.2
			C	64.3	95.0	1.48	14,5	4.84	42.0	8.46	1.82	40.0	27.6
			D	66.0	98.0	1.48	14,5	4.11	41.3	8.71	1.94	39.5	27.5
			E	66.4	98.0	1.48	14,7	5.42	40.3	8.42	1.91	38.1	27.7
13	3	69.0	A	67.4	94.0	1.40	18.6	26.4	41.7	9.88	1.83	35.0	30.1
			B	65.9	92.0	1.40	18.1	27.6	42.2	9.85	1.97	35.1	29.9
			C	62.9	88.0	1.40	19.1	29.8	43.4	10.1	1.97	34.9	29.7
			D	63.7	89.0	1.40	21.5	27.8	42.6	10.1	2.05	35.0	29.7
			E	63.2	89.0	1.41	19.3	27.5	41.0	10.2	1.97	35.5	29.8

[1] Energy= specific energy consumption; °SR=degrees Schopper Riegler; Rep.=Repetitions; LSC=Light scattering coefficient.

APPENDIX B

Table 1B - Summary results of identity test models for drainage time, bulk, air resistance and smoothness of paper sheets

Variables	Pulp	CNF added	Pr>Fc
Drainage time (s)	0 rev.	P-CNF/C1-CNF	0.0000
		P-CNF/C2-CNF	0.0000
		C1-CNF/C2-CNF	0.0000
	1000 rev.	P-CNF/C1-CNF	0.0000
		P-CNF/C2-CNF	0.0000
		C1-CNF/C2-CNF	0.0000
Bulk (cm^3/g)	0 rev.	P-CNF/C1-CNF	0.0000
		P-CNF/C2-CNF	0.0000
		C1-CNF/C2-CNF	0.0000
	1000 rev.	P-CNF/C1-CNF	0.0000
		P-CNF/C2-CNF	0.0000
		C1-CNF/C2-CNF	0.0001
Air resistance (s/cm^3)	0 rev.	P-CNF/C1-CNF	0.0000
		P-CNF/C2-CNF	0.0000
		C1-CNF/C2-CNF	0.0000
	1000 rev.	P-CNF/C1-CNF	0.0000
		P-CNF/C2-CNF	0.0000
		C1-CNF/C2-CNF	0.3676
Smoothness (s)	0 rev.	P-CNF/C1-CNF	0.0008
		P-CNF/C2-CNF	0.0000
		C1-CNF/C2-CNF	0.0000
	1000 rev.	P-CNF/C1-CNF	0.0018
		P-CNF/C2-CNF	0.0000
		C1-CNF/C2-CNF	0.0000

Table 2B - Summary results of identity test models for tensile index, tear index, burst index, light scattering coefficient and transparency of paper

Variables	Pulp	CNF added	Pr>Fc
Tensile index (Nm/g)	0 rev.	P-CNF/C1-CNF	0.0000
		P-CNF/C2-CNF	0.0000
		C1-CNF/C2-CNF	0.0190
	1000 rev.	P-CNF/C1-CNF	0.0000
		P-CNF/C2-CNF	0.0000
		C1-CNF/C2-CNF	0.1352
Tear index ($mN{\cdot}m^2/g$)	0 rev.	P-CNF/C1-CNF	0.0052
		P-CNF/C2-CNF	0.0072
		C1-CNF/C2-CNF	0.5078
	1000 rev.	P-CNF/C1-CNF	0.0158
		P-CNF/C2-CNF	0.0000
		C1-CNF/C2-CNF	0.0000
Burst index ($KPa{\cdot}m^2/g$)	0 rev.	P-CNF/C1-CNF	0.0000
		P-CNF/C2-CNF	0.0000
		C1-CNF/C2-CNF	0.3494
	1000 rev.	P-CNF/C1-CNF	0.0000
		P-CNF/C2-CNF	0.0000
		C1-CNF/C2-CNF	0.0270
Light scattering coefficient (m^2/kg)	0 rev.	P-CNF/C1-CNF	0.0000
		P-CNF/C2-CNF	0.0000
		C1-CNF/C2-CNF	0.0291
	1000 rev.	P-CNF/C1-CNF	0.0000
		P-CNF/C2-CNF	0.0000
		C1-CNF/C2-CNF	0.0000
Transparency (%)	0 rev.	P-CNF/C1-CNF	0.0000
		P-CNF/C2-CNF	0.0000
		C1-CNF/C2-CNF	0.4672
	1000 rev.	P-CNF/C1-CNF	0.0000
		P-CNF/C2-CNF	0.0000
		C1-CNF/C2-CNF	0.0000

APPENDIX C

Table 1C - Parameter estimation, R^2 e P-value of models to estimate the static drainage time of the pulps

Variable	Refine (rev.)	CNF	Models	β_0	β_1	β_2	R^2	Pr>Fc
Drainage time (s)	0	P-CNF	Linear	33.6949	5.1356	-	0.966	0.0000
			Quadrático	32.7336	32.7336	0.3731	0.981	0.0310
		C1-CNF	Linear	2.7797	43.5424	-	0.874	0.0000
			Quadratic	34.2613	17.9711	12.2198	0.998	0.0000
		C2-CNF	Linear	3.2857	85.7857	-	0.912	0.0000
			Quadratic	34.0000	26.8333	35.8333	0.999	0.0000
	1000	P-CNF	Linear	47.1864	9.6949	-	0.918	0.0000
			Quadratic	52.6432	- 0.9673	2.1181	0.881	0.0000
		C1-CNF	Linear	20.1695	43.8136	-	0.878	0.0000
			Quadratic	51.2563	16.9284	12.0665	0.928	0.0000
		C2-CNF	Linear	20.4286	86.9286	-	0.910	0.0000
			Quadratic	52.0000	28.8333	36.8333	0.986	0.0000

Table 2C - Parameter estimation, R^2 e P-value of models to estimate the bulk of the paper sheets

Variable	Refine (rev.)	CNF	Models	β_0	β_1	β_2	R^2	Pr>Fc
Bulk (cm^3/g)	0	P-CNF	Linear	1.9524	- 0.0451	-	0.946	0.0000
			Quadratic	1.9724	- 0.0812	0.0071	0.983	0.0000
		C1-CNF	Linear	1.9415	-0.0684	-	0.918	0.0000
			Quadratic	1.9806	- 0.1434	0.0149	0.998	0.0000
		C2-CNF	Linear	1.9665	-0.1345	-	0.993	0.0000
			Quadratic	1.9792	- 0.1861	0.0166	0.998	0.0000
	1000	P-CNF	Linear	1.5213	- 0.0192	-	0.850	0.0000
			Quadratic	1.5314	- 0.0389	0.0039	0.914	0.0000
		C1-CNF	Linear	1.5380	- 0.0340	-	0.940	0.0000
			Quadratic	1.5349	- 0.0280	- 0.0012	0.942	0.0390
		C2-CNF	Linear	1.5203	- 0.0397	-	0.999	0.0000
			Quadratic	1.5220	- 0.0460	0.0020	1.000	0.2590

Table 3C - Parameter estimation, R^2 e P-value of models to estimate the air resistance of the paper sheets

Variable	Refine (rev.)	CNF	Models	β_0	β_1	β_2	R^2	Pr>Fc
Air resistance (s/cm^3)	0	P-CNF	Linear	0.7462	0.3983	-	0.998	0.0000
			Quadratic	0.7575	0.3763	0.0044	0.999	0.6120
		C1-CNF	Linear	- 2.6827	5.3249	-	-	0.0000
			Quadratic	1.1672	- 2.1975	- 2.1975	0.984	0.0000
		C2-CNF	Linear	- 0.3600	4.1500	-	0946	0.0000
			Quadratic	0.7800	- 0.0300	1.3300	0.998	0.0000
	1000	P-CNF	Linear	2.3148	1.7921	-	0.923	0.0000
			Quadratic	3.2927	- 0.1187	0.3796	0.999	0.0000
		C1-CNF and C2-CNF	Exponential	2.4099	0.8133	-	0.901	0.0000

Table 4C - Parameter estimation, R^2 e P-value of models to estimate the smoothness of the paper sheets

Variable	Refine (rev.)	CNF	Models	β_0	β_1	β_2	R^2	Pr>Fc
Smoothness (s)	0	P-CNF	Linear	9.9138	0.3327	-	0.703	0.0000
			Quadratic	9.5036	1.1344	- 0.1593	0.997	0.0020
		C1-CNF	Linear	9.2263	0.7239	-	0.806	0.0000
			Quadratic	9.2292	0.7962	- 0.0144	0.929	0.7730
		C2-CNF	Linear	10.448	1.6100	-	0.705	0.0000
			Quadratic	9.5360	4.9540	-1.0640	1.00	0.0001
	1000	P-CNF	Linear	15.1102	0.0223	-	0.324	0.8880
			Quadratic	14.8942	0.4443	-0.0838	0.866	0.4780
		C1-CNF	Linear	14.2325	0.8382	-	0.878	0.0000
			Quadratic	14.5676	0.1834	0.1301	0.917	0.3130
		C2-CNF	Linear	14.2477	1.5667	-	0.864	0.0000
			Quadratic	14.0870	0.0786	0.5573	0.817	0.0050

Table 5C - Parameter estimation, R^2 e P-value of models to estimate the tensile index of the paper sheets

Variable	Refine (rev.)	CNF	Models	β_0	β_1	β_2	R^2	Pr>Fc
Tensile index (Nm/g)	0	P-CNF	Linear	16.2007	1.7830	-	0.999	0.0000
			Quadratic	16.3158	1.5581	0.0446	1.000	0.4850
		C1-CNF and C2-CNF	Linear	14.2411	2.2479	-	0.852	0.0000
			Quadratic	15.9750	- 1.1589	0.6815	0.930	0.0000
	1000	P-CNF	Linear	45.6152	1.3937	-	0.916	0.0000
			Quadratic	44.8159	2.9553	-0.3102	0.999	0.0160
		C1-CNF and C2-CNF	Linear	40.8780	1.2370	-	0.343	0.0000
			Quadratic	44.3020	- 5.2479	1.3098	0.864	0.0000

Table 6C - Parameter estimation, R^2 e P-value of models to estimate the tear index of the paper sheets

Variable	Refine (rev.)	CNF	Models	β_0	β_1	β_2	R^2	Pr>Fc
Tear index (mN·m^2/g)	0	P-CNF	Linear	3.2406	0.6074	-	0.935	0.0000
			Quadratic	3.4091	0.2782	0.0654	0.932	0.0001
		C1-CNF and C2-CNF	Linear	2.9603	1.0654	-	0.873	0.0000
			Quadratic	3.7311	0.4406	0.2992	0.999	0.0000
	1000	P-CNF and C1-CNF	Linear	3.3745	0.7855	-	0.886	0.0000
			Quadratic	9.0334	0.0021	0.0562	0.908	0.0000
		C2-CNF	Linear	8.8960	0.3100	-	0.402	0.0000
			Quadratic	9.3329	1.2904	0.5091	0.947	0.0000

Table 7C - Parameter estimation, R^2 e P-value of models to estimate the burst index of the paper sheets

Variable	Refine (rev.)	CNF	Models	β_0	β_1	β_2	R^2	Pr>Fc
Burst index ($KPa \cdot m^2/g$)	0	P-CNF	Linear	0.5792	0.1272	-	0.976	0.0000
			Quadratic	0.5410	0.2019	-0.0148	1.000	0.0004
		C1-CNF and C2-CNF	Linear	0.4219	0.2142	-	0.914	0.0000
			Quadratic	0.5470	- 0.0282	0.0480	0.965	0.0000
	1000	P-CNF and C1-CNF	Linear	2.2334	0.1718	-	0.976	0.0000
			Quadratic	2.2508	0.1378	0.0067	0.978	0.4999
		C2-CNF	Linear	1.9956	0.06613	-	0.187	0.0000
			Quadratic	2.2474	- 0.4283	0.0990	0.808	0.0000

Table 8C - Parameter estimation, R^2 e P-value of models to estimate the light scattering coefficient of the paper sheets

Variable	Refine (rev.)	CNF	Models	β_0	β_1	β_2	β_3	R^2	Pr>Fc
Light scattering coefficient (m^2/kg)	0	P-CNF	Linear	48.4263	0.0236	-	-	0.320	0.2200
			Quadratic	47.6410	1.5580	- 0.3048	-	0.935	0.0000
		C1-CNF and C2-CNF	Linear	47.9404	-1.1093	-	-	0.959	0.0000
			Quadratic	48.3380	- 1.8792	0.1511	-	0.994	0.0050
	1000	P-CNF	Linear	39.4695	-0.0986	-	-	0.209	0.0020
			Quadratic	39.2984	0.2356	- 0.0663	-	0.383	0.0040
			Cubic	38.8180	2.0310	- 1.0160	0.1230	0.981	0.0000
		C1-CNF	Linear	39.3891	- 0.7954	-	-	0.968	0.0000
			Quadratic	39.1508	- 0.3298	-0.0924	-	0.992	0.1090
		C2-CNF	Linear	39.7688	- 1.4331	-	-	0.836	0.0000
			Quadratic	39.0380	1.2467	- 0.8527	-	0.924	0.0000

Table 9C - Parameter estimation, R^2 e P-value of models to estimate the transparency of the paper sheets

Variable	Refine (rev.)	CNF	Models	β_0	β_1	β_2	β_3	R^2	Pr>Fc
Transparency (%)	0	P-CNF	Linear	23.3546	- 0.0927	-	-	0.160	0.0000
			Quadratic	23.7380	- 0.8417	0.1488	-	0.896	0.0000
		C1-CNF and C2-CNF	Linear	23.8198	0.4082	-	-	0.932	0.0000
			Quadratic	23.6150	0.8076	- 0.0790	-	0.998	0.0000
	1000	P-CNF	Linear	27.1865	- 0.0397	-	-	0.302	0.0370
			Quadratic	27.1191	0.0919	- 0.0261	-	5.41	0.0600
			Cubic	27.4620	- 1.8275	1.0496	- 0.1422	0.914	0.0000
		C1-CNF	Linear	27.3362	0.3706	-	-	0.975	0.0000
			Quadratic	27.4483	0.1514	0.04353	-	1.000	0.0570
		C2-CNF	Linear	27.2345	0.8285	-	-	0.946	0.0000
			Quadratic	27.4620	- 0.0053	0.2653	-	0.958	0.0010