



MARIA LUIZA CAFALCHIO DE OLIVEIRA

**CELLULOSIC NANOFIBRIL AND NANOCCLAY
SPRAY AS COATING ON PAPER SUBSTRATE
FOR PACKAGING**

LAVRAS – MG

2017

MARIA LUIZA CAFALCHIO DE OLIVEIRA

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Dissertação apresentada à Universidade Federal de Lavras, como parte das exigências do Programa de Pós-Graduação em Engenharia de Biomateriais, área de concentração em Compósitos e Nanocompósitos Lignocelulósicos, para a obtenção do título de Mestre.

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LAVRAS - MG

2017

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MARIA LUIZA CAFALCHIO DE OLIVEIRA

**CELLULOSIC NANOFIBRIL AND NANOCLAY AS COATING ON
PAPER SUBSTRATE FOR PACKAGING**

**NANOFIBRILAS CELULÓSICAS E NANOARGILA COMO
REVESTIMENTO POR SPRAY EM PAPEL PARA EMBALAGEM**

Dissertação apresentada à Universidade Federal de Lavras, como parte das exigências do Programa de Pós-Graduação em Engenharia de Biomateriais, área de concentração em Compósitos e Nanocompósitos Lignocelulósicos, para a obtenção do título de Mestre.

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LAVRAS – MG

2017

Aos meus pais Elza e João que sempre me apoiaram nos estudos

DEDICO

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RESUMO

O objetivo deste trabalho foi avaliar os efeitos do revestimento por aspersão de nanofibrilas de celulose (CNF) e nanoargila (NC) na gramatura, espessura, resistência à tração, taxa de transmissão de vapor de água (WVTR) e molhabilidade dos papéis revestidos. As suspensões de CNF e uma mistura de CNF e NC (CNF/NC) foram pulverizadas sobre uma superfície de papel Kraft extensível de 60 g/m². Os papéis revestidos foram secos a 100 ± 5 ° C durante 3 h. Os papéis foram revestidos com 60 g/m² de NFC/NC em 5 camadas (L5), 40 g/m² de NFC/NC em 4 camadas (L4), 30g/m² com NFC/NC em 3 camadas (L3) e 10g/m² de NFC em 1 camada (L2), Os tratamentos foram comparados com os papeis sack kraft de 60 g/m²(C60), 80 g/m²(C80) e 120 g/m²(C120). Imagens de microscopia eletrônica de varredura mostraram que a aplicação de camadas de nanofibrilas celulósicas e nanoargila contribuíram para a redução da taxa de permeabilidade de vapor de água (3,5%; 17%; 14% e 14% da redução de WVTR para L2, L3, L4 e C60, respectivamente), porém os resultados do ângulo de contato mostraram um aumento de 3,5% da molhabilidade da superfície revestida com NFC e de 1% da superfície revestida com NFC/NC em comparação com C60. Os resultados das propriedades mecânicas foram divididos pela gramatura para normalizar a comparação entre tratamentos. Todos os tratamentos apresentam redução da resistência à tração em comparação à C60. No entanto, ao comparar com C120 observou-se aumento de 66% da resistência à tração para L2, 43, 75% para L3, e redução de 18% para L5, já o tratamento L4 apresentou o mesmo valor que C120. Ao analisar o módulo de elasticidade, observou-se que L2 e L3 obtiveram os maiores valores, em comparação com C60, houve aumento de 56% e 38% para L2 e L3, respectivamente, porém houve redução de 7% para L4 e de 30% para L5, comparados com C60. Também foi observado redução do alongamento da ruptura (60%, 50%, 50% e 40% para L2, L3, L4 e L5, respectivamente) em comparação com C60. Assim, os resultados mecânicos e de barreira demonstram o potencial do uso de NFC e NC como revestimento de papel para confecção de embalagens multicamadas.

Palavras-chave: Embalagem multicamada. Nanoargila. Nanofibra de celulose. Papel multicamadas. Propriedades de barreira.

ABSTRACT

The aim of this work was to evaluate the coating effects of cellulose nanofibril (CNF) and nanoclay (NC) spray in the weight, thickness, tensile strength, water vapor transmission rate (WVTR) and wettability in the coated papers. CNF suspensions and a CNF/NC mix were sprayed on a 60 g/m² of kraft paper surface. The coated papers were dried in oven during 3h at 100 ± 5 °C. Were produced coated papers with 60 g/m² and 5 layers (L5), 40 g/m² and 4 layers (4L), 30 g/m² and 3 layers (3L) of NFC/NC mix and papers of 10 g/m² of NFC with 1 layers (L2). These papers were compared with uncoated papers of 60 g/m², 80 g/m² and 120 g/m². Scanning electron images showed that the coating application reduced the permeability rate to water vapor (WVTR reduction of 4%, 17%, 14% in L2, L3, L4 and L5 respectively), however, contact angle results showed a wettability increase with NFC (4%) and NFC/NC (1%) compared to 60 g/m² uncoated paper. Mechanical properties were divide based in the paper weight in order to normalize the comparisons between the treatments. All treatments presented a decrease in the tensile strength compared with the 60 g/m² uncoated paper. However, when the treatments were compared with the 120 g/m² uncoated paper, there was an increasing of 66% in the tensile strength in L2, 44% in L3 and a decrease of 17.9% in L5. The L4 reached the same tensile strength value divided by the weight as the 120 g/m² uncoated paper. The treatments L2 and L3 reached the highest elastic modulus values, with an increase of 56% and 38% respectively when compared with the 60 g/m² uncoated paper. The treatments L4 and L5 showed a decrease in this parameter of 7 and 30% respectively. There were also a decrease in the rupture elongation (60%, 50%, 50% and 40% to L2, L3, L4 and L5 respectively) compared with uncoated paper references. In this way, the mechanical and barrier results showed the potential use of NFC and NC as a paper coating for multilayer package production.

Keywords: Multilayer packaging. Nanoclay. Cellulose nanofiber. Multi- layer paper. Barrier properties.

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PRIMEIRA PARTE

1 INTRODUÇÃO

Tradicionalmente, embalagens têm a função de proteger e conter o produto durante o transporte e armazenamento, ao passo que comunica ao consumidor informações sobre o produto (PAINE; PAINE, 1992; ROBERTSON, 1993).

O papel tem sido amplamente utilizado na fabricação de embalagens, visto que é um material de baixo custo, fácil produção, reciclável e de origem renovável. Porém, alguns fatores como a alta permeabilidade ao vapor de água e a gases, baixa resistência à tração, baixa resistência à punctura e alta higroscopicidade, limitam seu uso e o colocam em desvantagem quando comparado a outros materiais como, por exemplo, metais e polímeros.

Visando a contornar esses desafios, tem sido reportado na literatura o revestimento de papel com diversas substâncias: Ceras (ZHANG et al., 2014), PLA (ZHANG et al., 2015), Nanofibrilas de celulose (AULIN; GÄLLSTEDT; LINDSTRÖM, 2010; LAVOINE et al., 2014) e nanoargilas (GAIKWAD; KO, 2015), desse modo, é possível confeccionar um material com boas propriedades mecânicas e de barreira.

Entre os diversos métodos de revestimento em papel, merece destaque o revestimento por aspensão, que é um processo sem contato, através do qual é possível pulverizar finas camadas do aditivo além de possibilitar também a pulverização sobre superfícies irregulares.

Entre os materiais pesquisados como material de revestimento, merecem destaque as nanofibrilas celulósicas e as nanoargilas. Nanofibrilas celulósicas têm grande potencial para serem aplicadas como aditivos no revestimento de papel, visando à melhoria das propriedades mecânicas e de barreira do papel (AFRA;

MOHAMMADNEJAD; SARAHEYAN, 2016; BENEVENTI et al., 2014; HULT; IOTTI; LENES, 2010; KUMAR et al., 2014). As nanoargilas, por sua vez, oferecem barreira a gases, ao vapor de água e também de propriedades mecânicas (GAIKWAD; KO, 2015; VARTIAINEN; TUOMINEN; NA, 2010). Desse modo, ao aliar as propriedades de cada aditivo sobre um substrato de papel é possível criar um novo material multicamadas com propriedades diferentes.

Neste trabalho, pretende-se contribuir com a melhoria das propriedades mecânicas e de barreira do papel, tornando-o assim um material sustentável e eficiente para ser utilizado na indústria de embalagens. Além disso, sua abordagem consiste em um estudo de embalagem ativa multicamadas, constituídas de nanofibras de celulose e nanoargila com capacidade de adsorver a umidade do interior da embalagem a fim de evitar a proliferação de microorganismos, além de promover uma barreira à umidade do exterior para o interior do local armazenado.

Desse modo, o objetivo deste trabalho é propor uma solução para as limitações quanto às propriedades mecânicas e de barreira do papel na confecção de embalagens que têm como base o papel. Avaliando a gramatura das camadas de nanofibras celulósicas e de nanofibras celulósicas com nanoargila sobre o papel e avaliar seu efeito nas propriedades mecânicas, de barreira e características de superfície do papel.

1.1 Objetivos

1.1.1 Objetivo geral

O objetivo deste trabalho foi avaliar o efeito da aplicação de camadas de nanofibrilas celulósicas e da combinação de nanofibrilas celulósicas com nanoargila nas propriedades mecânicas e de barreira de papéis de embalagem.

1.1.2 Objetivos específicos

- a) Verificar o impacto da gramatura das camadas de nanofibrila celulósica com e sem nanoargilas sobre o papel e avaliar seu efeito nas propriedades de tração (máxima resistência à tração, módulo elástico e alongamento na ruptura);
- b) Verificar o impacto da gramatura da camada de nanofibrila celulósica com e sem nanoargilas sobre o papel e avaliar seu efeito na taxa de transmissão ao vapor de água;
- c) Verificar o impacto da gramatura da camada de nanofibrila celulósica com e sem nanoargilas sobre o papel e avaliar seu efeito na molhabilidade.

2 REVISÃO BIBLIOGRÁFICA

2.1 Celulose e nanofibrilas celulósicas

Dos compostos orgânicos derivados de biomassa, a celulose pode ser considerada a mais abundante (UMMARTYOTIN; MANUSPIYA, 2015). Essa consiste em um biopolímero formado por unidades de monossacarídeos α - D glucose, que se ligam entre si através dos carbonos 1 e 4, dando origem a um polímero linear, conforme pode ser observado na figura 1 (POLETTTO; PISTOR; ZATTERA, 2013).

De acordo com Klemm et al. (2011), a partir da celulose podem-se obter 3 tipos de nanoestruturas celulósicas que diferem entre si pelo tamanho, estrutura cristalina, fonte e processo de extração: Celulose nanocristalina (CNC), nanocelulose bacteriana (BC) e nanofibrilas celulósicas (CNF).

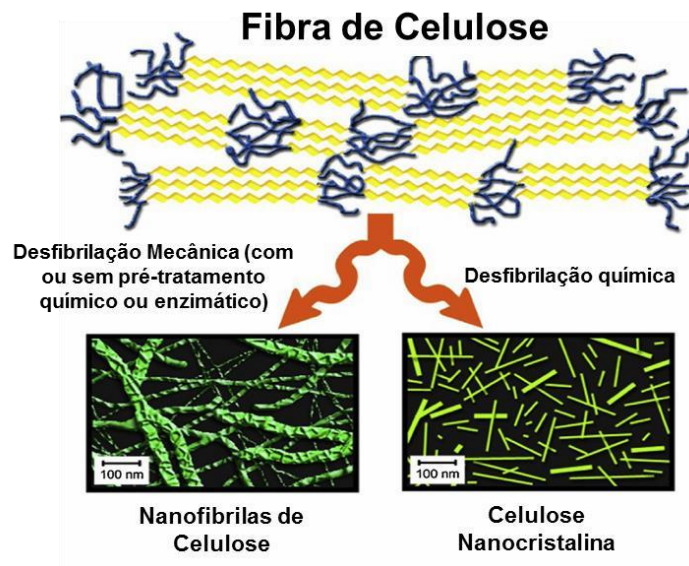
Entretanto, quando se trata a respeito de nomenclaturas, outros termos podem ser utilizados como sinônimo de nanofibrila celulósica. Klem et al. (2011), afirmam que nanofibrila celulósica é sinônimo de celulose microfibrilada, nanofibrila, microfibrila ou ainda de celulose nanofibrilada.

CNC são estruturas que apresentam estrutura totalmente cristalina e alto módulo de Young (EICHHORN, 2011) são obtidas por hidrólise ácida de material celulósico proveniente de diversas fontes tais como, madeira, algodão, cânhamo, linho, tunicados, algas e bactérias, possuem diâmetro variando entre 5 a 70 nm e comprimento de 100 nm a alguns micrômetros (KLEMM et al., 2011), enquanto a BC é produzida por meio da síntese bacteriana de açúcares e álcoois de baixo peso molecular (KLEMM et al., 2011). Por último, as CNF são as unidades resultantes da combinação linear de macromoléculas de celulose contendo região amorfa e região cristalina e têm a capacidade de formar redes entrelaçadas (GUIMARÃES

et al., 2015), o que confere propriedades de barreira e propriedades mecânicas diferentes da celulose em escala macro.

Há divergência entre autores quanto ao diâmetro das nanofibrilas de celulose. Contudo para ser considerada em escala nanométrica, pelo menos, uma de suas dimensões precisa ter menos de 100nm. Desse modo, nanofibrilas celulósicas são estruturas com grande área superficial o que lhes confere alta capacidade de interação entre si ou entre a matriz, quando utilizada como reforço em nanocompósitos (ALUBAIDY; VENKATAKRISHNAN; TAN, 2013).

Figura 1 - Representação de nanofibrilas e nanocristais de celulose.



Fonte: (adaptado de GARCÍA et al., 2016).

As nanofibrilas celulósicas podem ser obtidas após desfibrilação mecânica (com ou sem pré-tratamento químico ou enzimático) de material celulósico de origem vegetal (GARCIA et al., 2016; KLEMM et al., 2011) ou por método

enzimático via hidrólise enzimática com celulases (PÄÄKKÖ et al., 2007). Contudo os métodos mecânicos de isolamento de nanofibrilas são vantajosos por se apresentarem como uma alternativa limpa para obtenção das nanofibrilas, pois não exige o uso de reagentes químicos.

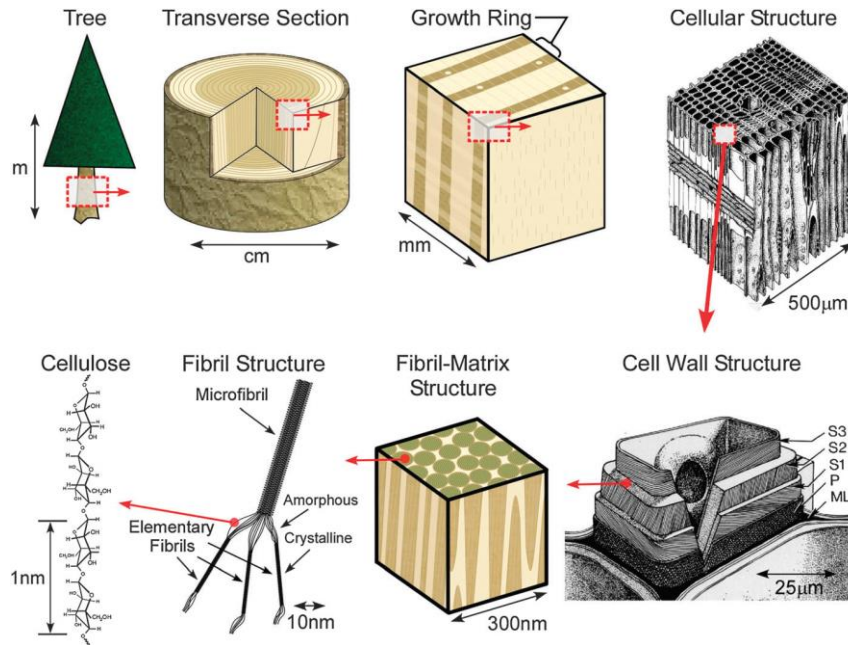
Entre os métodos mecânicos, pode-se citar a refinação e homogeneização de alto cisalhamento, que são realizados na presença de água e consiste em passar a suspensão de fibras celulósicas por uma abertura estreita de um aparelho constituído por duas pedras, uma fixa e outra rotativa. Durante esse processo, ligações químicas entre fibrilas e feixes de fibras ou somente fibras, são quebradas pelas forças de cisalhamento o que promove a liberação das nanofibrilas celulósicas (CHINGA-CARRASCO et al., 2012).

Ainda, entre os métodos mecânicos, há o processo de microfluidização, em que a suspensão é sujeita à alta pressão para passar através de uma câmara de interação de geometria de tipo Y ou Z (ZIMMERMANN et al., 2010). Em contrapartida, no método de sonificação, é realizada uma suspensão de fibras a fim de separar as nanofibrilas de feixes na parede celular da fibra - através de cavitação (PETERSSON; OKSMAN; MATHEW, 2006).

Já a individualização de celulose nanocristalina é feita, exclusivamente, via processos químicos como hidrólise ácida com ácido sulfúrico ou ácido clorídrico (EICHHORN, 2011).

Podem-se obter nanoestruturas celulósicas a partir de diversas fontes, tais como: bactérias (GATENHOLM; KLEMM, 2010), cânhamo (DAI; FAN; COLLINS, 2013), bambu (GUIMARÃES JÚNIOR et al., 2015; ZHANG et al., 2013), madeira (Fig. 2) (BUFALINO et al., 2015; FONSECA et al., 2015; TONOLI et al., 2012), folhas de abacaxi (CHERIAN et al.; 2011), bagaço de cana-de-açúcar (MANDAL; CHAKRABARTY, 2011), sisal (MORÁN et al., 2008) entre outros. As propriedades das nanofibras variam quanto à matéria prima da qual foram obtidas.

Figura 2 - Esquema representativo de nanofibrila de celulose proveniente da madeira.



Fonte: (Adaptado de Postek et al., 2011)

Por ser um material leve (BLEDZKI; REIHMANE; GASSAN, 1996; SIRO; PLACKETT, 2010), de alta rigidez e alta resistência (CHAKRABORTY; SAIN; KORTSCHOT, 2006; SIRO; PLACKETT; 2010), biodegradável e de origem renovável, as nanofibras de celulose têm sido usadas como reforço mecânico em nanocompósitos (LE et al., 2016; LEE et al.; 2014; PETERSSON; OKSMAN; MATHEW, 2006), na produção de filmes de barreira ou revestimentos em embalagens (GUIMARÃES et al., 2015), filmes comestíveis para embalagens (DOGAN; MC HUGH, 2007), na confecção de aerogéis porosos (WANG et al., 2016), na confecção de membranas filtradoras de água (KARIM et al., 2016) em aplicações na medicina (DONG; ROMAN, 2007;

GATENHOLM; KLEMM, 2010; SUNDBERG et al., 2013), na indústria farmacêutica entre outros.

2.2 Nanoargilas

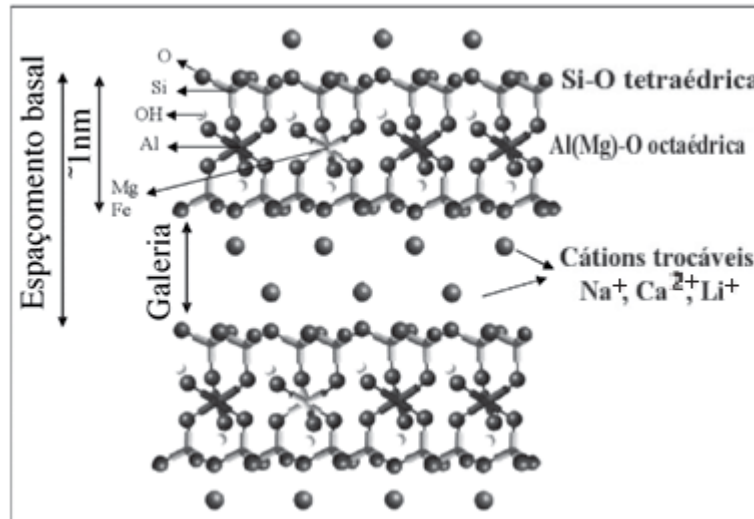
Nanoargilas, ou *nanoclays*, são materiais inorgânicos naturais constituídos por placas as quais apresentam pelo menos uma de suas dimensões em escala nanométrica (FLOODY; THENG; REYES, 2009).

Esses materiais são classificados de acordo com a estrutura laminar em quatro grupos: caolinitas, montmorillonita/esmectita, illitas e chloritas (UDDIN, 2008), são as montmorillonitas (MMT) o argilo mineral mais abundante e mais utilizado para a produção de nanocompósitos (GAIKWAD; KO, 2015).

As MMT (Fig. 3) têm fórmula química geral dada pela $M_x(Al_4 - Mg_x)Si_8O_{20}-(OH)_4$ e apresentam estrutura laminar de aluminossilicato, pertencentes ao grupo dos fitossilicatos 2:1, ou seja, são constituídas por duas folhas tetraédricas de sílica e uma folha central de octaedro de alumina, unidas entre si por átomos de oxigênio (CALCAGNO, 2007; GAIKWAD; KO, 2015; PAIVA; MORALES; DÍAZ, 2008). Essas placas variam entre 0,1 a 2 μm de diâmetro e 0,5 μm de comprimento e são unidas por forças de Van der Waals e por ligações fracas, e entre elas, existem camadas intermediárias nas quais residem cátions trocáveis como Na^+ , Ca^{2+} (FIG. 3). (PAIVA; MORALES; DÍAZ, 2008).

Já o termo bentonita é usado para definir as argilas constituídas predominantemente pelo argilomineral montmorillonita e apresentam, portanto, as mesmas propriedades das montmorillonitas. Entre essas propriedades, destacam-se: a capacidade de troca de cátions, a resistência à temperatura e a solventes, a capacidade de intercalação com outros materiais entre as placas e a capacidade de inchamento em contato com a água, que pode chegar a até 20 vezes o seu volume inicial (PAIVA; MORALES; DÍAZ, 2008; **SILVA; FERREIRA, 2008**).

Figura 3 - Representação da estrutura da montmorilonita.



Fonte: Paiva, Morales e Díaz (2008).

Tem sido reportado na literatura a incorporação de nanoargilas em matrizes poliméricas visando a melhorar propriedades de barreira (GABR et al., 2013; VARTIAINEN; TUOMINEN; NA, 2009) e de propriedades térmicas e mecânicas (GABR et al., 2013).

Quando dispersos em suspensão polimérica, as nanoplaquetas presentes na estrutura laminar das nanoargilas, se estiverem devidamente exfoliadas, ou seja, separadas, causam um aumento da tortuosidade do caminho de difusão de vapor de água e de gases (GAIKWAD; KO, 2015; VARTIAINEN; TUOMINEN; NA, 2009), o que promove a melhoria das propriedades de barreira.

Porém, as nanoargilas, normalmente, tendem a formar aglomerados quando em contato com a água. Esses aglomerados são mantidos unidos por forças de atração de várias formas físicas e químicas, incluindo forças de *van der Waals*, eletrostática e ligações de hidrogênio. Para quebrar essas ligações e promover a

esfoliação das placas da estrutura da nanoargila, a suspensão de nanoargila e água devem passar por um processo de ultrassonificação. (VARTIAINEN; TUOMINEN; NA, 2009). Essas argilas, então, são exfoliadas em placas de escala nanométricas com razão de aspecto de 10: 1 (LUO; DANIEL, 2003).

Vartiainen, Tuominen e Na (2009) estudaram propriedades de barreira ao vapor de água, ao oxigênio, a óleo e à luz UV em filmes de quitosana com diferentes concentrações de nanoargila bentonita hidrofílica e resultados mostraram melhoria em todas propriedades estudadas.

Por ser um material natural e abundante, tem sido reportado na literatura o uso de nanoargilas em diversos campos, tais como: indústria farmacêutica (CARRETERO; GOMES; TATEO, 2006), em aplicações na medicina (SURESH et al., 2010) na fabricação de cosméticos (PATEL et al., 2006), na confecção de embalagens (MAJEED et al., 2013; GAIKWAD; KO, 2015), indústria têxtil (FLOODY; THENG; REYES, 2009) e na produção de catalizadores (NAGENDRAPPA, 2011).

2.3 Embalagens

2.3.1 Revestimento em embalagens de papel

Devido a sua alta resistência à tração e ao rasgo, o papel *kraft* é largamente utilizado na composição de embalagens multifoliadas (REIS; NOLETTO, 2015).

As embalagens de papel, quando comparadas com embalagens plásticas ou metálicas, apresentam certas vantagens tais como: leveza, baixo custo, facilidade de transporte e armazenamento, além de serem biodegradáveis e de origem renovável (MAGNIER; SCHOORMANS, 2015). Entretanto, tais embalagens apresentam algumas desvantagens em relação aos demais materiais

citados acima, como alta higroscopicidade, baixa resistência mecânica, alta permeabilidade ao vapor de água e a gases (REIS; NOLETTO, 2015).

Visando a contornar os problemas das embalagens de papel, tem-se utilizado o recurso de revestir esse material com outros materiais, a fim de melhorar suas propriedades. Dentre os materiais utilizados podem-se citar: polímeros (REIS; NOLETTO, 2015), ceras (DESPOND et al., 2005), nanoargilas (BUSOLO et al., 2010), nanoestruturas de celulose (EL-WAKIL; KASSEM; HASSAN, 2016; HASSAN et al., 2016; HULT; IOTTI; LENES, 2010; LAVOINE et al., 2016) e amido (TAPARELLI, 2005).

Para a aplicação dos materiais citados acima sobre a superfície do papel, pode-se citar o método de aspersão. Czerwonatis (2008) afirma que esse método, por ser um processo de revestimento sem contato, possibilita a pulverização de finas camadas sobre superfícies homogêneas ou irregulares. É uma técnica que gera pouco resíduo, permite utilização de, praticamente, qualquer tipo de solução com diferentes propriedades reológicas, de modo que as propriedades da película formada possam ser controladas (GIROTTI et al., 2009). Conforme já foi citado, diversos materiais têm sido utilizados como revestimento em papéis, porém nanofibrilas celulósicas e nanoargilas merecem destaque.

Nanoestruturas celulósicas, tais como, nanofibrilas e nanocristais de celulose, podem ser aplicados em embalagens a fim de melhorar suas propriedades (NAIR et al., 2014; TURBAK; SNYDER; SANDBERG, 1983). Segundo Afra, Mohammadnejad e Saraeyan (2016), Beneventi et al. (2014), Hult, Iotti e Lenes (2010) e Kumar et al. (2014), o recobrimento de superfícies de papel com nanofibrilas celulósicas aumentam as propriedades mecânicas e de barreira do papel. Lavoine et al. (2016) estudaram papéis revestidos por aspersão com nanofibrilas celulósicas para fabricação de embalagens com liberação controlada de cafeína e digluconato de clorexidina. Nesse estudo, conseguiram obter uma superfície de nanofibrilas celulósicas homogênea após 5 camadas de aspersão

utilizando 0,9 bar de pressão e velocidade de 5 cm/s. Após cada camada de aspersão, os papéis foram secos à 105°C por 3 min.

Hult, Iotti e Lenes (2010) estudaram as propriedades de barreira em papéis revestidos com nanofibrilas celulósicas e goma laca pelo método de aspersão. Apesar do revestimento de nanofibrilas celulósicas não ter revestido homogeneamente a superfície e ter deixado pequenos buracos, a camada de goma laca cobriu esses buracos e observou-se, então, redução da permeabilidade do oxigênio e da permeabilidade ao vapor de água.

Kumar et al. (2014) concluíram que, ao revestir papéis com nanofibrilas de celulose, houve melhoria tanto de propriedades de barreira ao vapor de água, quanto de propriedades mecânicas. Afra, Mohammadnejad e Saraeyan (2016) avaliaram as propriedades físicas, mecânicas e de barreira de papéis revestidos com suspensões de diferentes concentrações de nanofibrilas de celulose e diferentes números de camadas. Apesar dos resultados mostrarem que houve melhoria em todos papéis revestidos quando comparados com não revestidos nas propriedades de barreira e mecânicas, os autores observaram que os melhores resultados foram alcançados pelos tratamentos nos quais foram aplicadas suspensões de CNF em baixas concentrações, porém em maior número de camadas, o que pode ter promovido o melhor assentamento das nanofibrilas sobre a superfície do papel. Em contrapartida, Lavoine et al. (2014) avaliaram as propriedades de barreira e mecânicas de papéis revestidos com diferentes gramaturas de nanofibrilas celulósicas. Resultados mostraram que a adição de nanofibrilas celulósicas diminuiu o módulo elástico e o índice de tensão de todos tratamentos revestidos, quando comparados com os papéis não revestidos. Os autores associaram tais resultados à possibilidade de que as suspensões de CNF não tenham penetrado na estrutura do papel além de que altos valores de desvio padrão da análise de espessura dos papéis revestidos sugerirem que o revestimento não foi homogêneo.

Klangmuang e Sothornvit, (2006) estudaram a incorporação de nanoargila em filmes de HPMC e de HPMC com cera de abelha. Os autores observaram que os filmes que continham HPMC, cera de abelha e nanoargila apresentaram menor permeabilidade ao vapor de água do que os filmes apenas de HPMC ou de HPMC com cera de abelha. Nesse trabalho, também foram estudadas as propriedades mecânicas dos filmes, e a adição de nanoargila promoveu aumento na resistência à tração e no módulo elástico dos materiais. No trabalho de Mirmedi et al. (2017) entre outras propriedades, foram avaliadas a permeabilidade ao vapor de água e a resistência à tração de papéis revestidos com nanofibrilas celulósicas e com nanofibrilas celulósicas e nanoargila. Os autores observaram que tanto os papéis revestidos apenas com nanofibrilas celulósicas quanto os revestidos com nanofibrilas celulósicas e nanoargila apresentaram aumento da resistência à tração e redução da permeabilidade ao vapor de água, quando comparados com o papel não revestido.

Desse modo, conforme observado nos exemplos já citados, tanto nanofibrilas celulósicas quanto nanoargila têm potencial para promover melhorias de propriedades de barreira e mecânicas quando aplicadas por revestimento em papéis ou quando incorporadas em filmes de matrizes poliméricas, e ao aliar as propriedades de cada material, pode ser possível confeccionar um material multicamadas com propriedades diferentes a de seus constituintes, quando usados isoladamente.

3 CONSIDERAÇÕES FINAIS

O papel é um material de grande importância para a confecção de embalagens por ser um material abundante, de baixo custo, reciclável e de origem renovável, porém devido as limitações do papel quanto as propriedades de barreira

e propriedades mecânicas tem-se buscado soluções para contornar esse problema. Visando a isso, este trabalho buscou avaliar o efeito da adição de nanofibrilas celulósicas e nanoargila nas propriedades de barreira e propriedades mecânicas do papel. Uma vez que trabalhos recentes têm estudado o potencial desses materiais como aprimoradores de tais propriedades.

Neste trabalho foram utilizadas nanofibrilas celulósicas obtidas por defibrilação mecânica de polpa Kraft não branqueada de eucalipto e nanoargila bentonita hidrofílica. Foram preparadas suspensões de 1,4% (m/m) de nanofibrilas celulósicas 1,4% (m/m) de nanofibrilas celulósicas com 1% (m/m) de nanoargila, ambas em água deionizada. As suspensões foram aplicadas sobre papel kraft de 60 g/m² por aspersão, que, então foram secos em estufa à 100 ± 5°C por 3 h.

A primeira parte do trabalho consiste em introdução ao tema e o referencial teórico, no qual foram abordados os materiais utilizados para a realização deste trabalho, já parte 2 é um artigo científico, no qual foi avaliado o efeito da gramatura adicionada de nanofibrilas celulósicas e nanoargila nas propriedades mecânicas e na taxa de transmissão de vapor de água, na microestrutura e na molhabilidade em papéis Kraft de 60 g/m² revestidos e papéis Kraft de 60, 80 e 120 g/m² não revestidos. Resultados mostraram que os papéis revestidos são mais eficientes na barreira ao vapor de água quando comparados com os não revestidos. Ao analisar a microestrutura dos papéis, imagens de Microscópio eletrônico de varredura da superfície dos tratamentos mostraram que a adição das camadas de nanofibrilas celulósicas e nanoargila reduziu consideravelmente a porosidade do papel, uma vez que nanofibrilas celulósicas tendem a formar redes, já as imagens de seção transversal mostraram que a adição de nanoargila e nanofibrilas de celulose causaram uma tortuosidade no caminho de difusão do vapor de água, conforme o trabalho de Gaikwad e Ko (2015) sugere.

A adição de nanofibrilas celulósicas e de nanoargila também aumentaram a molhabilidade do papel revestido, quando comparado com o não revestido de 60 g/m².

Por último, foram comparados a máxima resistência à tração, o alongamento na ruptura e o módulo elástico dos tratamentos. Resultados foram divididos pela gramatura para melhorar a comparação entre os tratamentos. Os tratamentos que mostraram os maiores valores de máxima resistência e de módulo elástico foram os tratamentos com 10 g/m² de adição de nanofibrilas celulósicas (L2) e com 30 g/m² de adição de nanofibrilas celulósicas e nanofibrilas celulósicas/nanoargila (L3).

Esta dissertação de mestrado mostra que a adição de nanofibrilas celulósicas e nanoargila contribui com o entendimento de como a aplicação de CNF e NC agem nas propriedades de barreira e propriedades de tração de papéis multicamadas obtidas pelo método de aspersão, além de confirmar a viabilidade de tais matérias como potenciais aditivos para melhorar propriedades de barreira e de tração em papéis. Este trabalho visa a explicar os mecanismos e as modificações que ocorrem na estrutura do papel após o revestimento, e visa a contribuir para futuros trabalhos na área de embalagens multicamadas.

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PARTE II - Artigo científico

**EFFECT OF SPRAYING CELLULOSE NANOFIBRILS AND
NANOCLAY ON MECHANICAL AND BARRIER PROPERTIES
OF MULTILAYER PAPERS**

Artigo formatado segundo as normas da revista *Journal of Wood Chemistry and Technology*

**Running Title: SPRAYING CNFs AND NC FOR PAPER
PROPERTIES ENHANCEMENT**

**EFFECT OF SPRAYING CELLULOSE NANOFIBRILS AND
NANOCLAY ON MECHANICAL AND BARRIER PROPERTIES
OF MULTILAYER PAPERS**

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ABSTRACT

The objective of this paper was to evaluate the effects of cellulose

nanofibrils (CNF) and nanoclay (NC) spray coating on basis weight, thickness, tensile strength, water vapor transmission rate (WVTR), and wettability of the coated papers. Suspensions of CNF and a mixture of CNF and NC (CNF/NC) were sprayed on a 60 g/m² extensible kraft paper surface as base substrate. Coated papers were oven dried at 100±5°C for 3 h. Coated papers with addition of 60g/m² of CNF/NC with 5 layers (L5), 40 g/m² of CNF/NC with 4 layers (L4), 30g/m² with CNF/NC in 3 layers (L3) and 10g/m² of CNF with 1 Layer (L2) was produced and compared with uncoated 60 g/m² (C60), 80 g/m² (C80) and 120 g/m² (C120) papers. Scanning electron microscopy images showed that the application of layers of cellulosic nanofibrils and nanoaclyay contributed to the reduction of the WVTR (3.5%; 17%; 14% and 14% of WVTR decrease to L2, L3, L4 and C60, respectably), however contact angle results showed a wettability increase of CNF (3.5%) and CNF/NC (1%) coated surface with uncoated 60g/m² paper. Mechanical properties results were divided by basis weight to Normalize comparison between treatments. When compared to 60 g/m² uncoated paper, all treatments present decrease of tensile strength. However, when compared with 120 g/m², uncoated paper, it was observed an increase of 66% of tensile strength for L2,

43.75% for L3, a decrease of 17.9 for L5. L4 reached the same value of tensile strength divided by basis weight than 120g/m² uncoated paper. L2 and L3 achieved highest values of elastic modulus, was observed an increase of 56% and 38%, when compared with 60g/m² uncoated paper, for L2 and L3 respectively, while it was observed 7% of decrease for L4 and 30% for L5. Also, was observed an elongation at break decrease (60%; 50%; 50% and 40% to L2, L3, L4 and L5, respectively) in comparison with uncoated paper references. Thus, mechanical and barrier results demonstrate the effectiveness of CNF and NC use as coating for paper to confection of multilayer package.

KEYWORDS: Cellulose nanofibrils (CNF), Nanoclay, Spray coating, Barrier properties, nanocellulose.

1. INTRODUCTION

Traditionally, the function of packaging is to protect and to contain products over transport, storage and commercialization, besides to communicate the consumer with information about the product (PAINE 1991; ROBERTSON 1993). Nowadays, paper is the most important

material of packaging industry, due to low price, recyclability, abundance (AFRA et al., 2016; LAVOINE et al., 2014) and mechanical characteristics such as high strength and flexibility (AFRA et al., 2016).

However, the use of paper in packages is limited due to poor barrier properties of paper. The coating of paper with different materials has been reported in literature: polymers and biopolymers (ZHANG et al., 2015), waxes (DESPOND et al., 2004), clays (KK & KO; 2015), starch (LI et al., 2016), nanoscale materials such as nanoclay (BUSOLO et al., 2010) and nanocellulosic structures (HULT et al., 2009; BENEVENTI et al., 2014; KUMAR et al., 2016; LAVOINE et al., 2014).

Due to large surface area, nanoscale materials promote different properties than the same material in macro scale. For example, cellulosic nanofibrils have a high ratio aspect that gives it the capacity to form interlaced nets.

Notably/particularly nanoclays (NC) and Cellulosic nanofibrils (CNF) have great potential to be applied in multilayer paper based package.

Barrier properties of nanoclays and mechanical and barrier properties of cellulosic nanofibrils could overcome paper based packages challenges.

Cellulose fibers can be processed to obtain nanostructures with different

properties that depend on extraction method and of the cellulose source.

There are two different types of cellulosic nanostructures: cellulose nanofibrils (CNF) that can be extracted by delamination of cellulosic material (wood or non-wood fibers) by mechanical pressure and/or after chemical or enzymatic treatment. These structures are constituted by amorphous and crystalline regions and have average diameter between 20 and 50 nm and several micrometers of length (GARCÍA et al., 2016).

Cellulose nanocrystals (CNCs) are crystalline structures that may be obtained by acid hydrolysis with average size of 5 – 70 nm diameters, and 100 – 250 nm length. Recent studies reported the production of cellulose nanostructures from wood (BIAN, 2017; TONOLI et al., 2012; BUFALINO et al., 2015) and some non-wood resources such as agricultural waste (PETROUDY, 2017; HASSAN et al., 2012), hemp (PACAPHOL & AHT-ONG, 2017; PULIKKALPARAMBIL et al., 2017), jute (LIN et al., 2014), bamboo (GUIMARÃES et al., 2015a), sisal (KRISHNAN et al., 2015), algae (CHEN et al., 2016) and bacteria (CORRAL et al., 2017).

Several applications have been reported in literature for the use of CNF's, such as improvement of paper properties (AFRA et al., 2016; HERRERA

et al., 2016; AULIN et al., 2010; BRODIN et al., 2014; SEHAQUI et al., 2013; LAVOINE et al., 2016), in biomedical and medical applications (GATENHOLM & KLEMM, 2010; DONG & ROMAN, 2007; SUNDBERG et al., 2013; KOWALSKA-LUDWICKA et al., 2013), electronics device (JUNG et al., 2015, NOGI et al., 2009), as reinforcement for polymeric matrices (CHO & PARK, 2011; VOLK et al., 2015; SHAO et al., 2015; CHINNAMA et al., 2016), in fiber-ciment (Fonseca et al., 2016) and in packaging industry (MISSOUM et al., 2013; HULT et al., 2009; DOGAN & MCHUGH; 2007). The use of nanoscale materials may be justified by the capacity of improving mechanical and barrier properties due to their high surface area. CNFs can form a large network structure, and consequently, increase mechanical resistance and decrease water vapor and gas permeability of paper sheets.

Nanoclays are mineral particles whose are structured in plates that can be exfoliated in nanometer layered structures (PAIVA et al., 2008). The best-Know nanoclay is montmorillonite that is a hydrophilic clay formed by layers of silica tetrahedral sheets and alumina octahedral sheets at 2:1 ratio (FLOODY et al., 2009). Due low cost, abundance and ecofriendly, nanoclays has been show interesting to be used in many applications such

as cosmetics industry (PATEL et al., 2006), medicine applications (SURESH et al., 2010), pharmacy (CARRETERO et al., 2006), and as coating papers to improve barrier properties (MAJEED et al., 2013; VARTIAINEN et al., 2009). In this sense, nanoclays are an interesting material to be used in based package industry.

This work aims to evaluate the effect of CNF and CNF/NC basis weight addition on tensile strength, wettability and water vapor transmission rate (WVTR) of coated papers.

2. MATERIALS AND METHODS

2.1 Material

The paper substrate used in this research was commercial sack kraft paper with nominal basis weight of 60 g/m² sack kraft paper of 60, 80 and 120 g/m² were used as reference that were also provide by Klabin.

Cellulose nanofibrils was obtained from commercial eucalyptus bleached kraft pulp (Jacarei/SP, Brazil), composed of approximately 99 wt% of holocellulose (cellulose + hemicellulose). The cellulose fraction was composed of 92.2 wt% α -cellulose, 6.9 wt% β -cellulose and 0.9 wt% of γ -cellulose, according to TAPPI T 203 cm-99 (2009) standard.

Nanoclay hydrophilic bentonite ($H_2Al_2O_6Si$) provided by *Sigma-Aldrich* was used in association with cellulose nanofibrils in the nanofibrils/nanoclay suspension.

2.2 Obtention of cellulose nanofibrils (CNFs)

Eucalyptus bleached kraft pulp was soaked for 72 h in deionized water in proportion of 2%(w/w) and disintegrated under mechanical stirring (Fisatom, model 722) at 900 rpm. Then, this suspension was submitted to 30 passages through the defibrillator, SuperMasscolloider (Model: MKCA6-2J, Masuko Sangyo Co., Ltd., Japan) at 1500 rpm, following suggestions of previous works (TONOLI et al., 2016; GUIMARÃES JR. et al., 2015a; BUFALINO et al., 2015; FONSECA et al., 2016).

SuperMasscolloider mechanical defibrillator is constituted by a fixed stone and a rotative stone (Fig. 1) that by shear forces promote cellulose defibrillation, resulting on a gelatinous suspension. According to Chinga-Carrasco (2012), during defibrillation, bonds between elementary fibrils, bundles of fibers and fibers are disrupted by shear forces, resulting on liberation of the CNFs.

2.3. Nanoclay exfoliation

A fraction of 3% of bentonite hydrophilic nanoclay was added in deionized water (w/w) and submitted for 24h in magnetic stirrer. Thus, this suspension was sonicated for 10 min in sonicator according to Bardet et al. (2015) methodology.

This step is important to promote exfoliation of the nanoclay plates and to facilitate the incorporation of nanoclay in the polymeric matrix in addition to promote a better adhesion to the substrate.

2.4. CNF and CFN/NC solutions

It was prepared CNF and CNF/NC solutions that was sprayed on paper. 1,4%(w/w) CNF was solubized on deionized water, and, thus it was stirred at 900 rpm for 30 min. To CNF/NC suspension, was preparete a suspension with CNF suspension and NC exfoliated solution so that the final concentration was 1,4% of CNF and 1% NC. This suspension was stirred at 900 rpm for 30 min in order to intercalate the nanoclay plates in the nanocellulosic matrix. Researches has shown a good interaction of polymer with inorganic clays (GABR et al., 2013; VARNATIAINEM). A good exfoliated nanoclay can be intercalated in nanocellulosic matrix,

keeping a close interaction with the nanocellulosic nets (GABR et al., 2013; VARNATIAIEN et al., 2009; KK & KO, 2015).

2.5. Experimental setup for the spray coating

Cellulosic nanofibril (CNF) and cellulosic nanofibril with nanoclay (CNF/NC) suspensions were sprayed onto paper substrates using a laboratory assembled spray coater. Variables and parameters used in this process was pressure of 0.4MPa, 30 s of spraying time and 30 cm of distance between spray nozzle and substrate (Table 1). According to Shanmugam et al. (2017), the operational range of CNF suspension concentration for spraying coating is between 1% and 2%. Below 1% wt, the suspension was too dilute and it is not sufficient to form a continuous and homogenous layer over substrate, however, high concentrations of CNF suspension (above 2% wt) is very viscous to be applied by spray technique. Based on that, it was prepared CNF suspension with 1.4% wt and CNF/NC suspension with 1.4% wt of cellulose nanofibrils and 1% of nanoclay.

The papers sheets were coated over a vacuum dewatering with function to obtain a consistent removal of the water from the coated papers before

oven drying, as can be seen in Fig 2. After each coating step, papers were oven drying at 100 ± 5 °C without pressure for 3h..The treatments are represented in Fig 3.

All samples were conditioned and tested at 23°C and 50% of relative humidity (RH) prior to characterizations.

2.6. Production of nanofibril and nanofibril/nanoclay films

It was produced films of nanofibril and nanofibril/nanoclay with similar basis weight of addition layers of coating papers. Both films were produced by casting method. 40 g of suspensions of nanofibril (22.2% w/w) and nanofibril/nanoclay (58.9% w/w) was deposited on petri dishes and oven dried at 60°C for 48 h. This concentration of suspension was calculated aiming to produce films of basis weight similar of addition layer of papers (thereabout 20 g/m² nanofibril/nanoclay films and 10 g/m² cellulosic nanofibril films).

2.7. Thickness and basis weight of the papers and films

It was measured the thickness of the paper before and after coating of each treatment and CNF and CNF/NC films using a Regmed micrometer

(model ESP/SA-10, Brazil) according to the ASTM D645- 97 (2007) standard method.

To determinate basis weight, samples of 16 mm of diameter was oven dried at $100 \pm 3^{\circ}\text{C}$ and weighted in electronic analytical balance (JKI, model JK-EAB-2204N, China) according to the standard method ASTM D646-96 (1996). Results were calculated according to eq. 1 and were made five measurements per sample. The basis weight (Bw) of the papers were measured before and after spray coating process.

$$\mathbf{Bw} = \frac{M}{A} \text{ (g/m}^2\text{)} \text{ (1)}$$

Where Bw: Basis weight (g/m^2); M= mass of sample (g); A=Area of the sample (m^2).

2.8. Tensile properties of the papers and films

Tensile test was performed on a universal testing machine MTS Landmark- servohydraulic test system, according to ASTM D828-97 (2002). All specimens were cut in the machine direction. Data were acquired by Station Manager software.

The standard dimension of the specimens required for performing this test is 20 ± 0.5 mm wide and around 100 mm length. The distance between

the grip clamping zones was 50 mm and the rate of dislocation of 14.1 mm/min. Tensile strength, elastic modulus and elongation at break results of coated paper was divided by basis weight. Results are the average of five samples per treatment.

2.9. Water vapor transmission rate (WVTR) of the papers

The water vapor transmission rate (WVTR) measurements were performed according to the desiccant method of the ASTM E96 / E96M-16 (2016) standard, as used by Guimarães Jr. et al. (2015a, b) at 20°C and 75% RH. Results are the average of three samples per treatment. The changes of mass were monitored every day for eight days.

2.10. Scanning electron microscopy (SEM) of the papers

Surface and cross sectional of the papers were assessed by scanning electron microscopy (SEM) using a Zeiss LEO EVO 40 XVP (Germany) with secondary electron (SE) detector and accelerating voltage of 20 kV. Samples were gold coated with a sputter coating technique.

2.11. Wettability

To check the wettability of papers and films, contact angle measurements were carried out by depositing calibrated droplets of water on coated papers, uncoated papers and films using Kruss Advance equipment. The apparatus used was a dynamic contact angle Data-Physics OCA absorption tester, equipped with a CCD camera working at up to 200 images per second. Was used 3 samples of each treatment. Results are an average of six first experimental data.

3. RESULTS AND DISCUSSION

3.1. Scanning electron microscopy (SEM) of the surface of the papers

SEM surface images show presence of porous on uncoated 60 g/m² paper (Fig 4), although it is possible to observe a reduction of porous with the coating layers (Fig 5; Fig 6 and Fig 7). 10 g/m² of CNF (L2) (Fig 5) and 30 g/m² of CNF/NC (L3) (Fig. 6) coatings promoted a smooth and uniform layer over the paper substrate, on the other hand, with of 60 g/m² CNF/NC addition (L5) it was not so efficient. SEM surfaces images of L5 (Fig 7) show porous and roughness of the paper coated surface.

3.2. Scanning electron microscopy (SEM) of the crossectionof the

papers

Cross-section SEM images show that the addition of CNF and CNF/NC (Fig. 8) on paper surfaces promoted increase in thickness while created a tortuosity between both sides of paper. It's can be observed also, that L5 aspersion was not efficient, Fig. 8 (d) show roles on the microstructure of coated paper. Whereas C60 (Fig 8e) was correctly coated with CNF and CNF/NC layers in both sides of paper.

3.3. Thickness and basis weight of the papers and films

Thickness and basis weight are important factors for paper coating properties. Thin CNF layers are sufficient to change surface properties, however, to change barrier properties is required thicker and uniform layers (Brodin, 2014).

It was deposited CNF and CNF/NC layers on 55.2 ± 0.5 g/m² sack kraft papers. The increase of thickness and basis weight was proportional to the number of layers deposited. It can be observed (table 2) that each nanofibril layer and nanofibril/nanoclay layer addiction increased around 10 g/m² and 20 g/m² of basis weight respectively.

3.4. Tensile strength of the papers

Coated papers achieved different basis weight values, thus to normalize comparison inter treatments, every mechanical result was divided by basis weight value of correspondent treatment.

Due to inter-fibril bonds, CNF usually form a network. Although a similar process occurs with cellulose pulp fibers, in the nanoscale cellulosic fibrils they have more fibrils per gram of material when compared to pulp scale fibers, and consequently, can be form more bonds inter-fibrils (BRODIN et al., 2014).

When compared to C60 (control), all treatments present decrease of tensile strength. Lavoine et al. (2014) studied mechanical properties on CNF coated papers by two different methods of coating (bar coating and size press), and was showed higher tensile index for uncoated paper than CNF coated papers. In their study, they associated this behavior with four factors: (1) non-uniformity of coating layers; (2) insufficient coat weight of CNF to promote improvements on mechanical properties and (3) CNF can be not penetrate into paper structure; (4) the amount of water that penetrate on paper structure was higher than the quantify of CNF.

120g/m² Kraft paper is usually used to grains and seeds 60kg packages,

wherefore, the results were compared with 120g/m² uncoated paper. It was observed increase of around 66% of tensile strength for L2 (15%wt of CNF and 85% wt of paper) and 43.75% for L3 (65% of paper; 24% of CNF/NC and 12% of CNF) when compared with C120 (100% paper). On the other hand, tensile strength of L5 (18% of CNF; 36% of CNFNC and 56% of paper) was 19% lower than C120, and L4 (21% of CNF; 21% of CNF/NC and 59% of paper) achieved same value of tensile strength that C120. According to Brodin et al. (2014), tensile strength of the paper sheet is determined by weak links in the structure, and when first cracks are created, forces on other parts increases that causes further cracks and break of paper. High value basis weight standard deviation (± 7.96 g/m²) of L5 suggests a heterogeneous coating that can be prejudice tensile strength of the paper (Fig 7) moreover; crossection SEM images of L5 (Fig 8 e) show roles into structure of this coated paper, that can be contributed with creation of weak links inter CNF, CN and paper fibers.

It has been reported in literature, the use of cellulosic nanofibril as strength enhancer (Iwamoto et al. 2007; Eriksen et al. 2008). Afra et al. (2016) showed increase tensile index in CNF coated paper when compared with uncoated paper. The tensile index increase was

proportional with CNF basis weight addition. Syverud & Stenius (2009) studied mechanical properties of CNF coated paper and was observed a 6% decrease on tensile index with 2g/m² of CNF addition when compared with uncoated paper, however, thicker layers addition (4 g/m² and 8 g/m²) promoted 6% and 14% of tensile index increase, respectively. Indeed Afra et al. (2016) studied CNFs coating layers on papers sheets, and they also observed that stiffness is proportional of CNF basis weight addition. Lavoine et al. (2014), also observed a decrease of elastic modulus with CNF addition. In their work was observed a range of decrease of 20 at 45% of elastic modulus for 3 until 14 g/m² basis weight of CNF addition. Elastic modulus results were divided by basis weight (table 5) to normalize the comparison inter treatments.

With 10 g/m² of CNF (L2) spray coating and with around 19 g/m² CNF/NC (L3) addition, it was observed a high increase of elastic modulus (56% for L2 and 28% for L3). On other hand, with higher basis weight of CNF/NC addition (57 g/m² for L5 and 42 g/m² for L4) was observed a considerable decrease of elastic modulus (30% and 7% for L5 and L4, respectably) when compared with uncoated paper. The elongation of break of all treatment decrease after layers coating (60%; 50%; 50%

and 40% to L2, L3, L4 and L5, respectively) when compared with uncoated papers. Sack extensible kraft paper is constituted by many micro wrinkling that confers extensibility properties of paper. CNF and CNF/NC addition formed a layer over papers that prejudice the extensibility. According to Gabr et al., 2013, agglomerated nanoclay is responsible to create stress concentrations in polymer that can cause decrease of elongation at break.

3.5. Wettability

Wettability can be defined as the tendency for a water drop to spread on a substrate surface and can be evaluated by contact angle of a water drop with the surface.

Low values of contact angle indicate that material is hydrophilic and the water drop spread on surface. According to Oliveira (2011), hydrophilic materials are those that have contact angle lower than 90° and hydrophobic material are those have contact angle higher than 90° . It was observed that both CNF and CNF/NC coatings layers decreased contact angle of coated papers when compared with control paper (C60), and CNF layer led to a hydrophobic character to the paper surface.

10g/m² CNF (L2) coating above 60g/m² paper substrate showed around 22% contact angle decrease when compared with control (C60).

A similar behavior was observed on CNF/NC coatings, L3 showed 1% of contact angle decrease Due CNF capacity to form networks (Pääkkö et al., 2007), coating layers probably facilitate the water drop spread.

Furthermore, the nanoclay used in this work is a hydrophilic nanoclay that confirm the wettability increase in all coated papers.

However, CNF/CN coated paper was more hydrophobic than CNF coater paper. CN are formed by layers of silica tetrahedral sheets and alumina octahedral sheets that contains Ca²⁺ or Na⁺ that have the capacity of adsorbed water (PAIVA et al., 2008; SILVA e Ferreira et al., 2008), whereas when rightly dispersed on polymeric matrices, nanoclays presents goods barrier properties (Gabr et al., 2013; KK & KO et al, 2015).

In addition, it was also evaluated the contact angle of 10g/m² CNF film and 20g/m² CNF/NC films, that showed values of 79° and 94° for contact angle of CNF and CNF/NC film respectively. Andrade et al., (2014) studied effect of CNF coating on wettability of gelatin- based edible coatings on banana end eggplant epicarps, and was showed that enhance

wettability of coated surface.

3.6. Water vapor transmission rate (WVTR) of the papers

The reduction of WVTR was observed for all treatments when compared to uncoated references. SEM micrographs (Fig. 4; Fig. 5; Fig 6; Fig. 7) demonstrated that the CNF and CNF/NC layers reduced sheet porosity that can be contributed with WVTR reduction. However, wettability results that CNF and CNF/NC addition showed that these layers facilitate water drop spread on surface when compared to uncoated paper, suggesting that the coated papers may adsorbed a percent of water.

10 g CNF coating over 60 g/m² paper (L2) promoted a 3.5% WVTR decrease when compared with uncoated paper. CNFs are hydrophilic material, whatever, due high ratio aspect and amorphous and crystalline structure, CNFs have the capacity to form networks (Dufresne et al., 2013) that may promote the decrease of WVTR (Fig. 5 and Fig. 6).

CNF/NC coating layers on paper promoted lower water vapor permeability than just CNF coating layer. Results showed that (L3) 30 g/m² CNF/NC (10 g of CNF and 20g of NC) promote a higher water vapor barrier (17%) than uncoated 60 g/m² paper. L5, that was coated

with 57 g/m² (20 g/m² of CNF and approximately 37 g/m² of CNF/NC) promote a reduction of around 14% while 42 g/m² (L4) of CNF/NC (20 g of CNF and 22 g/m² of NC) promote a reduction of around 14% of WVTR in comparison to 60 g/m². According to KK et al., (2015) and Mohan & Kanny (2011ab), nanoclay successfully dispersed on polymeric matrix can be difficult the diffusion through the matrix properties due tortoise path created by exfoliated plates that can be improve barrier properties. According to Vartiainen et al. (2009), the plates of nanoclay adsorbed water and, thus, expand and form single individual barrier layers against vapor transmission.

4. CONCLUSIONS

Coated papers were more efficient in the water vapor barrier when compared to the uncoated ones. SEM surface images of film surface and cross-sections showed that the addition of CNF and CNF/CN reduced paper porosity and cellulose nanofibrils tend to form networks, the cross-section images showed that the addition of nanoclay and cellulose nanofibrils caused a tortuosity in the way in which water vapor runs. The addition of cellulose nanofibrils and nanoclay/nanofibrils also increased

the wettability of the coated paper as compared to the uncoated 60g m².

Finally, the tensile strength, the elongation at break and the elastic modulus of the treatments were compared. Results were divided by weight of papers to normalize comparison between treatments. The treatments with the highest values of tensile strength and elastic modulus were treatments with 10 g / m² of cellulosic nanofibrils (L2) and 30 g / m² of cellulosic naofibrils and nanofibrils / nanoclay (L3) added.

Therefore, this work shows the high potential of CNF and NC as coating of paper for improvement of mechanical and barrier properties in multilayer packages.

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test system.

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Table 1: Variables and parameters of the spray coating tested in this study.

	N° of CNF	N° of CNF/NC	N° of Paper	Total
Treatments	Layers	Layers	Layers	Layers
L5	2	2	1	5
L4	2	1	1	4
L3	1	1	1	3
L2	1	0	1	2
Control	0	0	1	1

Where L2: 10g/m² CNF coated paper; L3: 30 g/m² CNF and CNF/NC coated paper; L4: 40 g/m² CNF and CNF/NC coated paper (10g/m² of CNF on one face of paper and 30g/m² of CNF and CNF/NC on other face of paper); L5: 60 g/m² CNF and CNF/NC coated paper (30g/m² of CNF and CNF/NC on each face of paper); Control: 60g/m² uncoated paper.

Table 2: Treatments, number of layers, average and deviation values of thickness (mm) and of basis weight (g/m²).

Treatment	Number of Layers	Thickness (mm)	Basis weight (g/m ²)
L2	2	0.107 ± 0.002	65.5 ± 0.8
L3	3	0.126 ± 0.004	85.2 ± 2.7
L4	4	0.141 ± 0.006	97.2 ± 2.5
L5	5	0.189 ± 0.006	112.4 ± 8.0
c60	1	0.097 ± 0.002	55.2 ± 0.5
c80	1	0.124 ± 0.002	73.6 ± 1.0
c120	1	0.182 ± 0.002	112.6 ± 1.8

Where L2: 10g/m² CNF coated paper; L3: 30 g/m² CNF and CNF/NC coated paper; L4: 40 g/m² CNF and CNF/NC coated paper (10g/m² of CNF on one face of paper and 30g/m² of CNF and CNF/NC on other face of paper); L5: 60 g/m² CNF and CNF/NC coated paper (30g/m² of CNF and CNF/NC on each face of paper); C60: 60g/m² uncoated paper; C80: 80 g/m² uncoated paper and C120: 120 g/m² uncoated paper.

Table 3: Thickness and basis weight average and deviation values of CNF and CNF/NC films.

Film	Thickness (mm)	Basis weight (g/m²)
CNF	0.015 ±0.001	9.57 ± 0.27
CNF/NC	0.037±0.002	19.41 ± 0.34

Table 4: Tensile Strength (MPa), basis weight (g/m²) and tensile divided for basis weight (RM/BW) for coated and uncoated papers.

Treatment	Tensile strength (Mpa)	Basis weight (g/m²)	TS/BW (MPa*m²/g)
L2	34.5 ± 7.3	65.5 ± 0.8	0.53 ± 0.11
L3	39.2 ± 5.5	85.2 ± 2.7	0.46 ± 0.06
L4	31.2 ± 2.3	112.4 ± 8.0	0.32 ± 0.02
L5	29.6 ± 2.1	97.2 ± 2.5	0.26 ± 0.02
C60	30.2 ± 4.1	55.2 ± 0.5	0.55 ± 0.07
C80	34.7 ± 3.8	73.6 ± 1.0	0.47 ± 0.05
C120	35.6 ± 1.6	112.6 ± 1.8	0.32 ± 0.01

Where L2: 10 g/m² CNF coated paper; L3: 30 g/m² CNF and CNF/NC coated paper; L4: 40 g/m² CNF and CNF/NC coated paper (10g/m² of CNF on one face of paper and 30 g/m² of CNF and CNF/NC on other face of paper); L5: 60 g/m² CNF and CNF/NC coated paper (30 g/m² of CNF and CNF/NC on each face of paper); C60: 60 g/m² uncoated paper; C80: 80 g/m² uncoated paper and C120: 120 g/m² uncoated paper.

Table 5: Average and standart deviation of elastic modulus (MOE), basis weight and elastic modulus divided for basis weight (MOE/BW) for coated and uncoated papers.

Treatment	Elastic modulus (MPa)	Basis weigth (g/m²)	MOE/BW (MPa*m²/g)
L2	3222.6 ± 150.4	65.5 ± 0.8	49.27 ± 2.3
L3	3436.4 ± 525.9	85.2 ± 2.7	40.33 ± 6.17
L5	2519.4 ± 199.5	97.2 ± 2.5	22.41 ± 1.77
L4	2834.3 ± 358.6	112.4 ± 8.0	29.17 ± 3.69
C60	1739.8 ± 108	55.2 ± 0.5	31.51 ± 1.96
C80	1937.4 ± 192.1	73.6 ± 1.0	26.32 ± 2.61
C120	1201.8 ± 328.5	112.6 ± 1.8	10.68 ± 2.92

Where L2: 10 g/m² CNF coated paper; L3: 30 g/m² CNF and CNF/NC coated paper; L4: 40 g/m² CNF and CNF/NC coated paper (10g/m² of CNF on one face of paper and 30 g/m² of CNF and CNF/NC on other face of paper); L5: 60 g/m² CNF and CNF/NC coated paper (30 g/m² of CNF and CNF/NC on each face of paper); C60: 60 g/m² uncoated paper; C80: 80 g/m² uncoated paper and C120: 120 g/m² uncoated paper.

Table 6: Average and standart deviation of elongation at break, basis weight and elongation at break divided for basis weight (EB/BW) for coated and uncoated papers.

Treatment	Elongation at break (mm)	Basis weighth (g/m²)	EB/BW (mm*m²/g)
L2	0.04 ± 0,01	65.5 ± 0.8	0.0006 ± 0.0001
L3	0.05 ± 0.006	85.2 ± 2.7	0.0005 ± 0.0001
L5	0.05 ± 0.009	97.2 ± 2.5	0.0004 ± 0.0001
L4	0.06 ± 0.015	112.4 ± 8.0	0.0006 ± 0.0002
C60	0.1 ± 0.01	55.2 ± 0.5	0.0017 ± 0.0002
C80	0.1 ± 0.011	73.6 ± 1.0	0.0017 ± 0.0001
C120	0.2 ± 0.019	112.6 ± 1.8	0.0014 ± 0.0002

Where L2: 10 g/m² CNF coated paper; L3: 30 g/m² CNF and CNF/NC coated paper; L4: 40 g/m² CNF and CNF/NC coated paper (10g/m² of CNF on one face of paper and 30 g/m² of CNF and CNF/NC on other face of paper); L5: 60 g/m² CNF and CNF/NC coated paper (30 g/m² of CNF and CNF/NC on each face of paper); C60: 60 g/m² uncoated paper; C80: 80 g/m² uncoated paper and C120: 120 g/m² uncoated paper.

Table 7: Average and standard deviation of tensile strength, Elongation at break and elastic modulus (MPa) for CNF and CNF/NC films.

Treatment	Tensile Strength	Elongation at break (mm)	Elastic Modulus (MPa)
CNF film	24.1 ± 3.3	0.03 ± 0.02	1870.7 ± 14.3
CNF/NC film	11.9 ± 0	0.01 ± 0	1893.2 ± 237.6

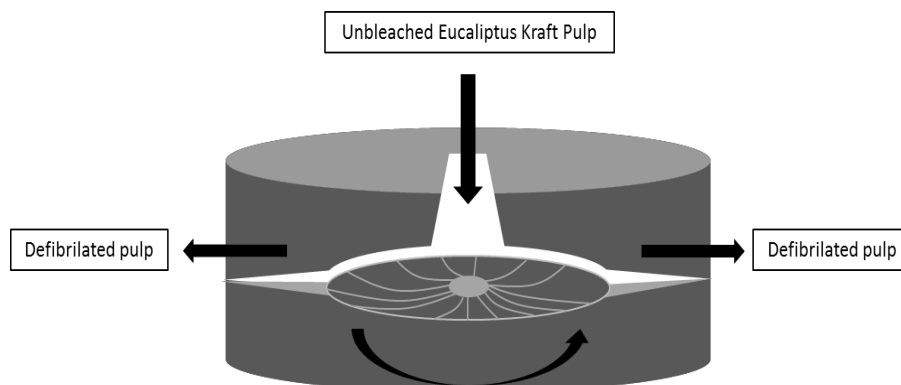


Fig 1: Representative scheme of grinder interior.

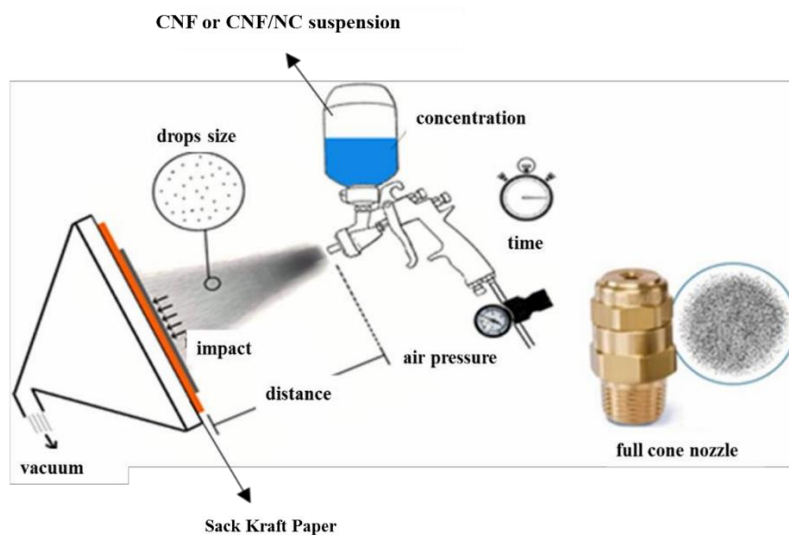


Fig. 2: Scheme of the experimental procedure used for spray coating the writing & printing paper with cellulose nanofibrils (Adapted of Mirmehdi, 2017).

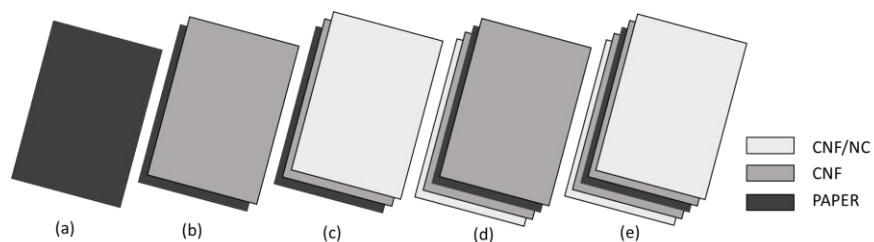


Fig. 3: Representative scheme of uncoated and coated paper. (a) uncoated 60g/m² paper (C60); (b) CNF layer over paper (L2); (c) CNF/NC over CNF layer over paper (L3); (d) CNF layer over paper over CNF layer over CNF/CN layer (L4) and (e) CNF layer over paper over CNF layer over

paper over CNF layer over CNF/CN layer (L5).

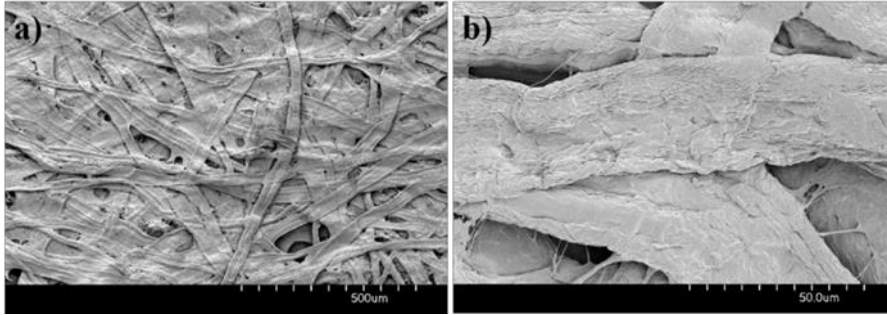


Fig 4: Typical Sem surface images of control sack kraft paper

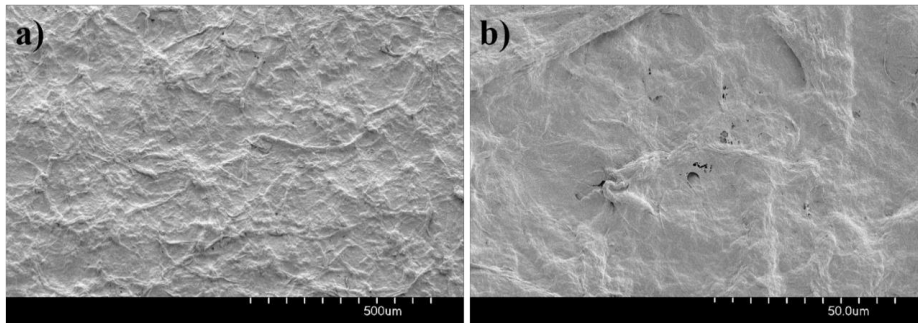


Fig 5: SEM surface images of L2

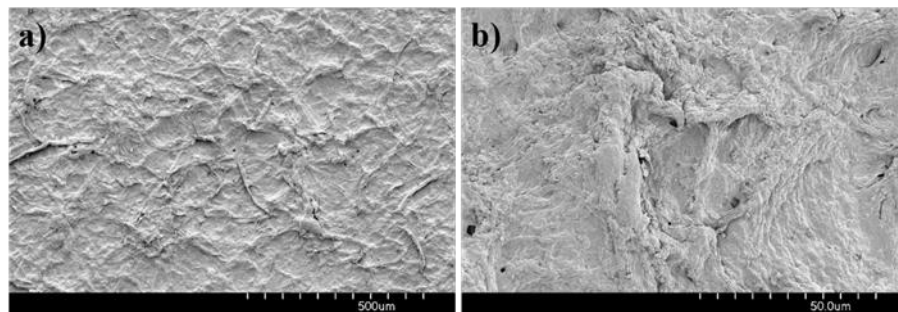


Fig 6: Sem surface images of L3

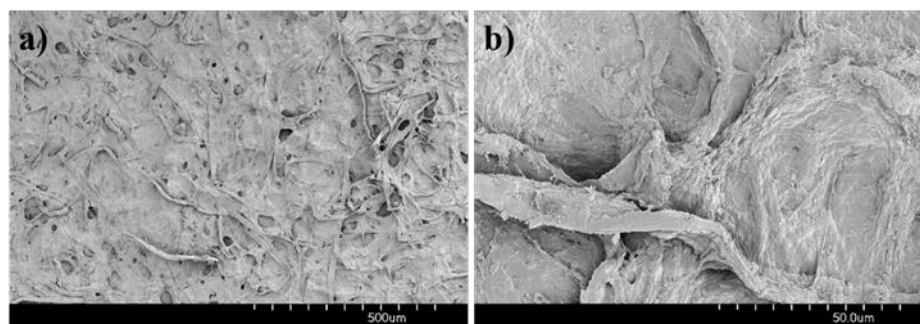


Fig 7: Typical SEM surface images of L5

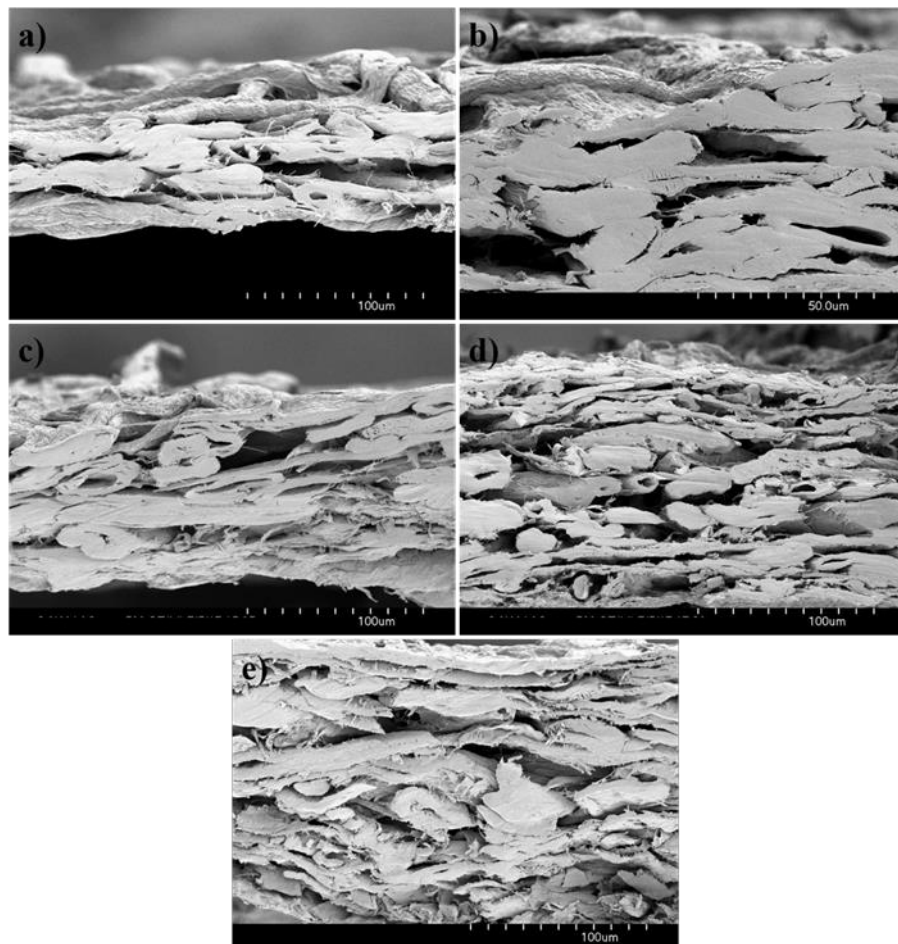


Fig 8: Typical SEM image of cross section of papers, where (a) is uncoated paper (C60); (b) 10g/m² CNF coated paper; 30 g/m² CNF and CNF/NC coated paper (L3); (d) 30g/m² CNF and CNF/NC applied in each face of paper (L5); 10g/m² CNF applied in one face of paper and 30g/m² CNF and CNF/NC applied in the other face (L4)

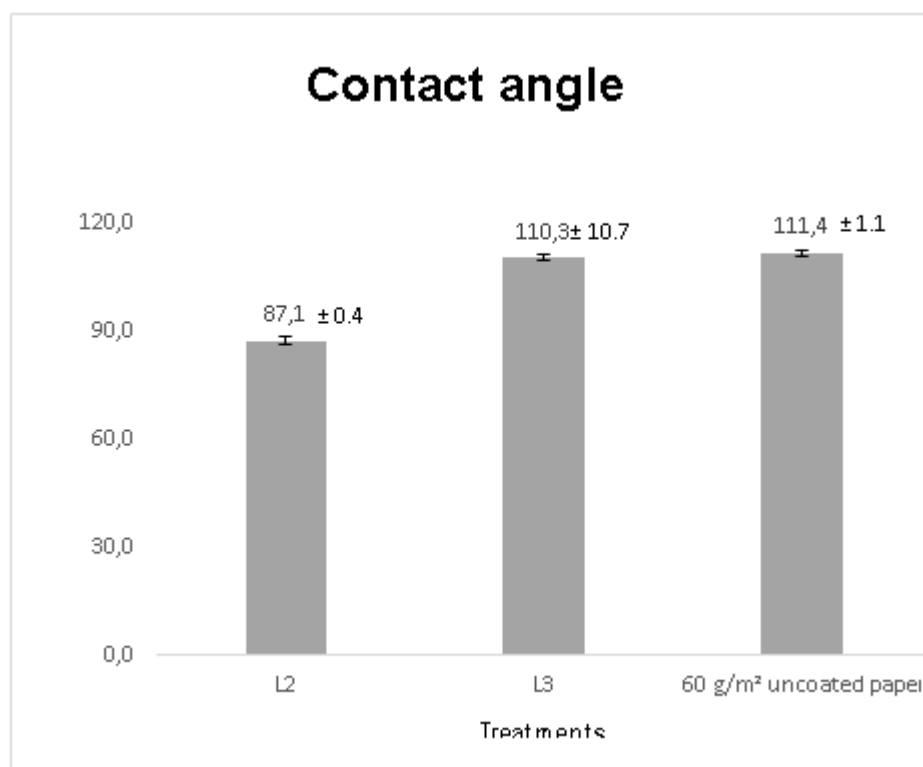


Fig. 9: Contact angle average of 60 g/m² uncoated paper; CNF layer over 60g/m² paper (L2) and CNF/NC layer over CNF layer over 60g/m² paper (L3).

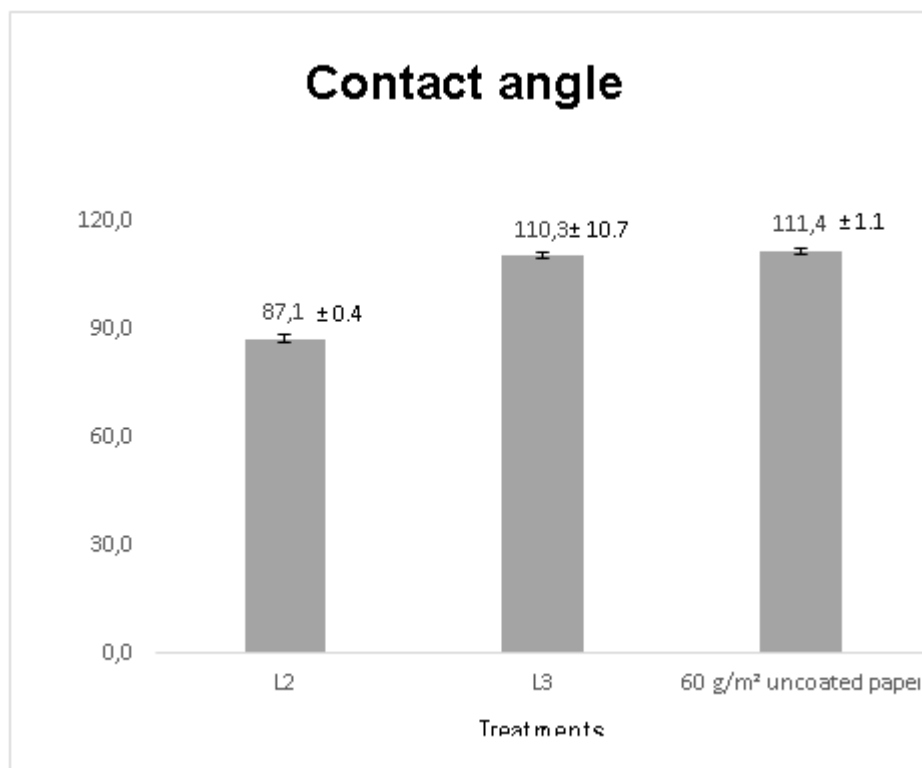


Fig. 10: Contact angle average of 11g/m² CNF films and 19 g/m² CNF/NC films.

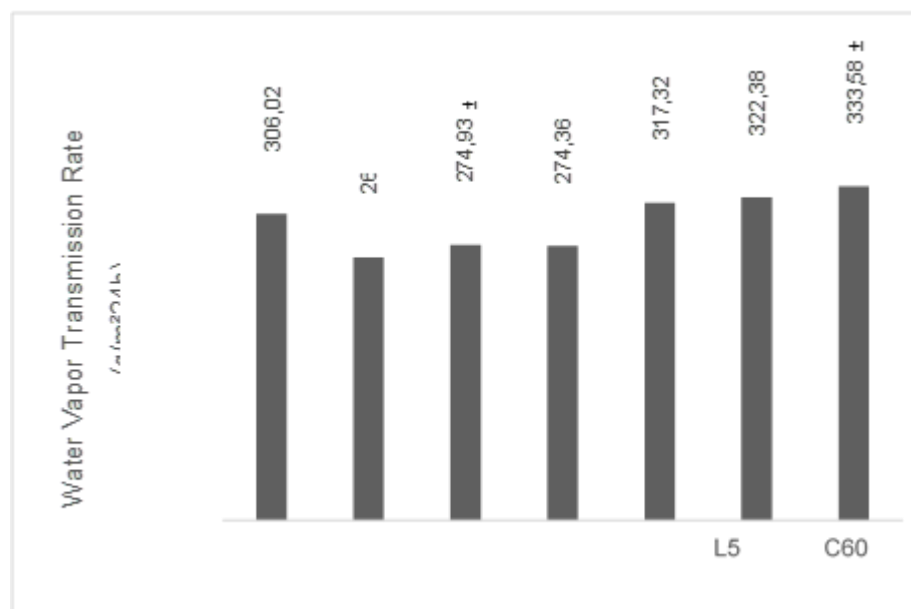


Fig. 11: WVTR average values for uncoated and coated papers.