SEYEDMOHAMMAD MIRMEHDI

PAPER PACKAGING IMPROVEMENT USING CORONA DISCHARGE AND SPRAY COATING OF CELLULOSE NANOFIBRILS AND NANOCLAY

LAVRAS - MG

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A Thesis Submitted to the Federal University of Lavras, in Partial Fulfilment of the Requirements of the Graduate Program in Forest Sciences, area of Wood Science and Technology, for the Degree of Doctor of Philosophy.

Supervisor

Dr. Gustavo Henrique Denzin Tonoli

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APPROVED on the 30th of June 2016.

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2016

This thesis is dedicated to my dear son, Bardiya, who was born during this period and lovely wife, Fatemeh Dabbagh with love and admiration for her love, support, care and encouragement throughout the course of my doctoral research.

DEDICATION

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ABSTRACT

The cellulose nanofibrils (CNF) from wood, non-woody plants and agricultural residues as one of the most abundant natural biopolymer on earth is an interesting new material that has attracted increasing interest due to its renewability, nontoxicity, biodegradability and low cost, which has been used as an important and fundamental materials in various fields such as paper, paper coating, medicines, plastics, cosmetics and etc. A natural use for these nanofibrils can be in the production of paper and paper packaging materials. Actually, the packaging industry has always been using cellulose-based materials, and nowadays, cellulosic packaging is an assorted category, which includes both wrapping materials and containers. In the first phase of this study, CNF water base suspension were coated on kraft writing and printing papers to investigation on the enhancement of the tensile and barrier properties of paper to use in paper packaging. An experimental assembled spray coater was used to coating paper substrate with CNF suspension. The spray variables i.e. concentration of suspension, time, distance and pressure of spray were studied. The coated papers were analyzed in terms of the oxygen transmission rate (OTR) and water vapor transmission rate (WVTR) in order to quantify the barrier effect of the applied coatings. In addition, the tensile strength was determined and image analysis of the structure was performed to examine the coating adhesion. The WVTR and the oxygen permeability of the papers decreased while tensile strength increased with a one-layer coating of CNF. The tensile and morphological properties of the coated papers indicate good adhesion between the coating and the base substrate using spray coater. The properties improved with increasing spray time and pressure and decreasing with concentration and distance. In the second phase, CNF and nanoclay as an aqueous slurry suspension was sprayed on the kraft writing and printing paper surface to achieve a coated sheet. Upon drying, the suspension on the paper surface formed a hybrid nanocomposite layer with CNF (matrix) and nanoclay (mineral filler). The corona discharge was used in order to enhance the wetting of paper surfaces and the resulting in improvement of adherence between paper and hybrid composite. It was observed that by increasing the spray time, all of the properties were improved, while by increasing the nanoclay content, the barrier properties were improved and the tensile strength was decreased. The properties of coated sheets improved with corona discharge. The analysis of tensile strength and morphological properties of the coated sheets indicated good adhesion between the base substrate and the hybrid composite.

Keywords: Cellulose Nanofibrils (CNF). Nanoclay. Spray coating. Corona discharge. Barrier properties.

TABLE OF CONTENTS

FIRST PART..10
1 INTRODUCTION 10
1.1 Objectives 15
1.2 Outline of thesis..16
2 LITERATURE REVIEW 17
2.1 Cellulose: structure, properties, and application....................................17
2.2 Nanocellulose and its preparation..19
2.3 Barrier packaging..20
2.4 Technologies for CNF-based materials production................................20
2.4.1 Layer-by-layer assembly (LBL)..21
2.4.2 Coating..21
2.4.3 Spray coating technique 23
2.5 Nanoclay 25
2.6 Corona Discharge 27
3 CONCLUSION AND FINAL CONSIDERATIONS.................................29
REFERENCES..31
SECOND PART – PAPERS 42
PAPER 1 - SPRAYING CELLULOSE NANOFIBRILS SUSPENSION ON KRAFT PRINTING PAPER SUBSTRATE TO IMPROVEMENT TENSILE AND BARRIER PROPERTIES..42
PAPER 2 - CELLULOSE NANOFIBRILS/NANOCLAY HYBRID COMPOSITE AS A PAPER COATING..65

FIRST PART

1 INTRODUCTION

Cellulose is one of the most abundant renewable organic material in the biosphere which can be found almost everywhere. Global production of cellulose is estimated to be more than 75 billion tons annually (LI et al., 2015). With the initiation and progression of nanotechnology, cellulose, attracts more attention in the new form of “nanocellulose” to be used as advanced material. Nanocellulose is defined as the extracts from native cellulose which in principle can be found in plants and in the next, it can be found in some animals and bacteria (LIN; DUFRESNE, 2014). Nanocellulose is a term that refers to nanosized cellulose. This may be cellulose nanofibrils (CNF), microfibrillated cellulose (MFC), nanocrystalline cellulose (NCC), or bacterial nanocellulose (refers to nano-structured cellulose produced by bacteria) (LI et al., 2015).

The fibrils can be isolated from any sources that contain cellulose, including different kind of wood-based fibers through high pressure, temperature and also high velocity impact grinding, homogenization or microfluidization (BHARIMALLA et al., 2015). Another method for the production of nano-cellulose is acid hydrolysis which causes highly crystalline and rigid nanoparticles often referred to nanowhiskers or NCC which are shorter than the nanofibrils obtained through the mentioned routes (PENG et al., 2011).

CNF that is composed of nanosized cellulose fibrils has high aspect ratio or the ratio of length to width of the fibers is in a wide range, about several micrometers and lateral dimensions are 5–20 nanometers (PANDEY et al., 2015). Water-based suspension of CNF, even in the concentration of below 2% in water, is a pseudo-plastic and exhibits the property of certain gels or fluids that are thick or viscous under normal conditions, but become thin and less viscous over time, when shaken, agitated or otherwise stressed. This property that when the shearing forces are removed, the gel regains much of its original state is known as *Thixotropy* (SALAS et al., 2014).

Nanocellulose as a sustainable biomaterial having exceptional physicochemical properties can be isolated from inexpensive renewable cellulosic biomass (corn stover, sugarcane bagasse, straw and etc.) (PACHUAU, 2015). Nanocellulose has many applications across industrial sectors like packaging industry, information and communication industry, automotive industry, building industry and industries relying on formulations such as the chemical, pharmaceutical, cosmetics, pulp & paper and food industries and allows the development of innovative materials and enhancement of conventional materials properties as well such as strength additives and barrier/coating applications. Nanocellulose can be utilized as fillers in composites, as coating and as thin films, achieving very interesting and promising properties, like improved strength and to provide biodegradable barriers and protection against grease penetration (BHARIMALLA et al., 2015). Most of the studies about nanocellulose focused on the chemistry and the morphology of nanocellulose to the preparation methods and the industrial applications and very few reviews appeared on this topic in the scientific literature, summarized the potential of cellulose in nanoform specifically for the packaging filed (LI et al., 2015). Nanocelluolse has also great potential in various applications, including drug reinforcements, dietary foods, packaging and films and special papers (GUIMARÃES et al., 2015).

Most reviews are focused on using nanocellulose fibers as reinforcement agents in polymer matrices. But, a main use for these fibers is in the production of paper and paper-based packaging materials (LUU et al., 2011). The use of CNF throughout the paper production and specially at the wet-end addition or coating step, has also been reported (TORVINEN et al., 2011), resulting strength benefits.

The morphological properties of nanocelulose depend mainly on the extraction method and the source of the feedstock. In tropical regions, *Eucalyptus* is a fast growing hardwood specie with suitable fiber qualities and relatively low price. In Brazil, bleached *Eucalyptus* kraft pulp (BEKP) is the most abundant and has increasingly become more available among the kraft pulps produced (TONOLI et al., 2013). The other benefit of utilizing *Eucalyptus* is that its higher hemicellulose content than *Pinus* pulp, which facilitates disintegration and can reduce energy input as a key issue for industrial upscaling. The advantages mentioned, indicate a favorable situation for producing nanofibrils using *Eucalyptus* pulp fibers as raw material (TONOLI et al., 2012).

The paper packaging industry has always been using cellulose-based materials in large amount. Cellulosic packaging is an assorted category includes both wrapping materials and containers, primary and secondary packages and flexible and rigid packaging (LEE et al., 2008). The biggest part of the proportions of different packaging materials is accounted for cellulose-based, which figures around 40% of the total (plastics 36%, metals 14%, and glass 8%) (LI et al., 2015). The source of cellulosic fibers, the process of separating and arranging them in the network, the non-fibrous chemical additives used and the various converting processes available caused the large variety of cellulosic packaging materials and their properties. The cellulosic materials in packaging applications are always heterogeneous solids, where cellulose content can be even less than 50% by weight (LI et al., 2015). CNF and NCC have opened wide possibilities of utilizing cellulose based materials in packaging industry (NAIR et al., 2014).

Packaging is the technology of products enclosing and protecting in order to distribution, storage, sale, and use. The main function of food packaging is protecting and preservation of quality. Packaging keeps the food products from surrounding factors and maintains products quality. The levels of chemical migration from the packaging to the product have to be lower than control safe level or otherwise the products might be contaminated and risks the consumer safety. On the other hand, another consideration is the severe problems created by packages to the environment, since most of these products are not normally eco-friendly and are non-biodegradable (LANI et al., 2014). Accordingly, nanocellulose can be used as a sustainable and biodegradable material and may be useful as a barrier in papers and as a wet-end additive to enhance retention, dry and wet strength in common type of paper and paperboard products (MISSOUM et al., 2013).

Research in biopolymers coupled with filler, matrix-filler interaction and new formulation strategies to develop composites have potential applications in food packaging industry. Expected advances and growth in food packaging materials is highly probable with the advent of cheap, renewable and sustainable materials with enhanced barrier and mechanical properties. Generally, nanocellulose have proportionally larger surface area and high aspect ratio than their micro-scale counterparts, and promotes the development of mechanical property like tensile strength and barrier properties like oxygen and water vapor transmission rate (MAJEED et al., 2013).

Nanocellulose and nanoclay blend composites, have emerged as a new type of composite materials offering superior strength like flexural and compressive strengths and gas barrier properties. These organic-inorganic hybrid composites with a nacre-like structure are eco-friendly. They can be an alternative in the near future to several biopolymers or other polymer-inorganic composites and in food packaging industry (GAMELAS; FERRAS, 2015).

Nanoclay hydrophilic bentonite with formula $H_2Al_2O_6Si$ are naturally aluminium silicate, composed of fine-grained minerals having sheet-like geometry referred to as phyllosilicates. The clays are inexpensive, eco-friendly and have found a variety application like in ink formulation, as a thickening agent and in paper industries (RAMIREZ et al., 2010). Currently, nanoclay is the most commercially used nanoparticle. Nanoclay is already used in multilayer film packaging like beer bottles and carbonated drinks. It is reported that nanoclay in plastic bottle, keep juice fresh and make high shelf life up to 30 weeks (SILVESTRE, 2011).

The most common methods to producing packaging materials based on CNF are layer by layer assembly, extrusion, casting evaporation and coating (LI et al., 2015). Coatings are recognized as powerful tools for improving many properties of food and beverage packaging materials (PIERGIOVANNI et al., 2013). It was used the coating method in this study with using gravity feeder spray. Spray coating has many advantages. The coating is applied contactless, and to uneven surfaces while the topography of the substrate has no influence on the coating weight. Tear sensitive web materials can be coated and low coating weights are possible at high web velocities. A closed film can be achieved with a decreased amount of liquid that could result in a reduction of costs and the improvement of quality (CZERWONATIS, 2008).

Interfacial adhesion between the base substrate and the coating layer is the key to progress of multilayer composites production (LANGHE; PONTING, 2016). A variety of methods and surface treatments like electroplating, chemical process, anodic oxidation, thermal spraying and etc. are used to improve functionality of surfaces, mainly to increase wettability and adhesion. Experiences and researches have mostly been made on plastic films and most applications exist in this area (WEBER, 2007). A research has been done to treatment of paper but there is no big picture. All solid and liquid materials have an inherent surface forces which is called surface energy in solid materials, and surface tension in liquids, that it plays an important role in the phenomenon of adhesion. Corona is a visible electrical discharge which occurs when a high voltage, high frequency electrical potential is applied to a surface and increases the surface energy and consequently, the adhesion of the solid material surfaces which is called surface wetting. Although results are invisible to the naked eye, surface treating modifies surfaces to improve adhesion. Corona discharge introduces polar groups into the surfaces, which increases the surface energy and, as a consequence, improves substrate wettability and adhesion. The main chemical mechanism of corona discharge is oxidation. In addition, corona discharge can crosslink surface regions and increase the cohesive strength. A material is wetted, if it's surface energy is higher than the surface tension of the liquid. Corona discharge is widely used in printing, laminating and coating in plastics, cloth, and paper industries (BUTT et al., 2013). Corona discharge is also used to improve the adhesion of the base substrate in the spray coating process and improvement of the barrier properties in packaging materials (PYKÖNEN et al., 2008).

It was not found literature reporting the use of gravity feed spray in paper coating and its efficiency. Therefore, in this study, kraft wrting and printing papers were spray-coated using the laboratory assembled spray system with cellulose nanofibrils water base suspension and also hybrid composite of nanoclay and cellulose nanofibrils as a coating layer on the paper substrate, as a nanotechnology for environmentally compatible food packaging materials. Some of the papers were treated physically using corona treatment to study the adherence and improved features through making a denser layer and also more adhesion.

1.1 Objectives

The overall objective of this thesis was to purpose a new solution for the tensile strength and barrier limitations of paper-based packaging by the application of cellulose nanofibrils coating layer itself and with additive, using spray coating method.

Spray characteristics was a technical challenge. For example, even at low concentrations of CNF, its viscosity increase significantly. So, verifying the concentration of CNF suspension for optimized spraying is important. Also, the resulting properties of papers after coating with CNF are not widely known. The defining key points of this project were:

- To determine the potential of using CNF and CNF/nanoclay hybrid composite as a coating layer and the properties of coated paper.
- To evaluate the effect of the application of CNF and hybrid layer on the tensile and barrier properties of paper packaging.
- To characterize the effect of suspension concentration and the spray variables (time, distance and pressure) on the properties of the coated paper.

1.2 Outline of thesis

The thesis was organized into 2 parts, the first part divided in 3 sections and the second in two papers. In the first part, section 2, it is presented a brief literature review of the main topics included in this study, particularly: (I) Cellulose structure, properties, and application and following by nanocellulose and its preparation. (II) reviewing the barrier packaging with emphasis on cellulose based packaging and the technologies for cellulose nanofibrils-based materials production and introducing two more common methods to produce this kind of packaging materials i.e. layer-by-layer assembly and coating, and more common methods of coating, the spray coating technique (III) Two methods to improve the tensile and barrier properties of paper substrate i.e. adding nanoclay as an inorganic filler to CNF matrix and also corona treatment for improving adherence between coating layer and paper substrate and related research in this sector was presented. The evaluation of the information of the topics presented in this section was the basis for definition of the experiments conducted in this study.

Section 3 presents the conclusions and final considerations, and the main findings are presented in two papers in the second part of this thesis.

First paper shows basis weight, thickness and electron microscopy images of coated layer of CNF and also the tensile strength, water vapor transmission rate and oxygen transmission rate of coated papers. Concentrations of cellulose nanofibrils in water with 2 levels (1.4% and 1.7%) were used and the variables of spray system were pressure of spray (4 and 5 bar), distance of spray (distance between the nozzle and paper surface, 15 and 30 cm) and the time of spray (20 and 30 seconds). So, there were 16 treatments for comparison among them and with the control sample or uncoated paper. The effect of these independent variables on the properties mentioned were investigated. In the second paper, there were 3 independent variables, time of spray (30 and 50 seconds), nanoclay content in water based suspension (0, 3 and 5%) and corona treatment in 2 levels (with and without corona treatment). So, there were 12 treatments for comparison among them and with the control sample or uncoated paper. The printing paper were coated according to these treatments and the results showed basis weight, thickness and electron microscopy images of coated hybrid layer of NFC and nanoclay and also the tensile strength, water vapor transmission rate and oxygen transmission rate of the coated papers.

2 LITERATURE REVIEW

The following literature review discusses the main issues on the topic for preparation of this work, as described below.

2.1 Cellulose: structure, properties, and application

Lignocellulosic biomass as renewable resource, has some properties such as widespread, abundant, diverse and inexpensive. It is regarded as a promising and appealing alternative to nonrenewable fossil resources (HU et al., 2015;

JIMÉNEZ-MORALES et al., 2015). Cellulose as a linear long molecule and partially crystalline with β (1→4) linked D-glucose units (Figure 1), is the most abundant biopolymer, representing around 1.5×10^{12} tons of the total annual biomass production (POLETTO et al., 2013).

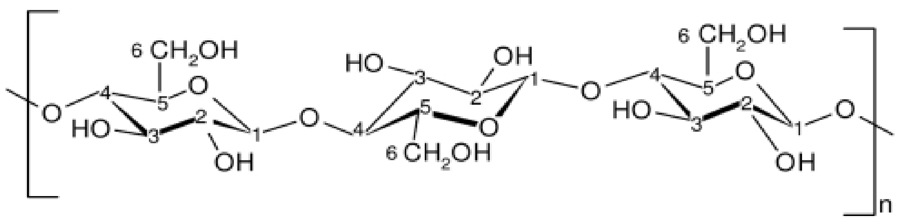

Figure 1- Molecular structure of cellulose

This eco-friendly resource of raw material is one of the main components of plants as in wooden plant is about 50% and in cotton is about 90% (BELGACEM; PIZZI, 2016). Cellulose properties mostly depends on its biological origin and unique hierarchy structure (KIZILTAS et al., 2015).

Cellulose returns to the natural carbon cycle by simple rotting. It is not toxic to living organisms, including humans. Further, as existing quantities of fossil supplies are limited, renewable raw materials, including cellulose, are gaining importance (LABAFZADEH et al., 2014). Cellulose-based materials offer also unique opportunities due to their low cost and global availability (TIMHADJELT et al., 2015).

In 2012, 187 million tons of wood pulp was produced globally. About 90% of it is consumed in the production of paper and cardboard products and only 10% is used for the production of cellulose derivatives (LABAFZADEH et al., 2014). The multiple hydroxyl groups on the glucose bonds with oxygen atoms on the same or on a neighbor chain, holding the chains firmly together side-by-side and forming water-insoluble and highly crystalline structure.

2.2 Nanocellulose and its preparation

Nano- (symbol n) is a unit prefix meaning one billionth. Used primarily with the metric system, this prefix denotes a factor of 10^{-9} m. It is frequently encountered in science for prefixing units of time and dimensions (ABOU EL-NOUR et al., 2010).

Regarding to the European Commission, nanomaterials definition is ″A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm - 100 nm″ (LI et al., 2015).

There are two main procedures to obtain nanocellulose: bottom-up by biosynthesis and top-down by disintegration of plant materials (LEE et al., 2015). Large bundles of natural fibres are treated with strong disintegrate into smaller elementary fibrils whilst retaining the fibrous texture. Herein, it is used the term cellulose nanofibrils (CNF) here for long and semi-flexible fibrils from wood or any other plant pulp.

CNF have diameter in the range of 2–50 nm and lengths up to several micrometers depending on their origin (STELTE; SANDI, 2009; NAIR et al., 2014; HOEGER et al, 2013; SYVERUD, 2009). CNF have some intresting optical and mechanical properties, and therefore can be used as a building block for a variety of high-performance materials (ABRAHAM et al., 2014; KAUSHIK; SINGH, 2011). Intensive mechanical treatment is needed to convert cellulose fiber to nanofibrils (UETANI; YANO, 2011). Several mechanical defibrillation methods have been used for the production of CNF such as microfluidizers (HENRIKSSON, 2008), homogenizers (CHINGA et al., 2012), and grinders (NAIR et al., 2014; WANG et al., 2012).

2.3 Barrier packaging

Barrier packages are those packaging materials that serve as barrier to air, water, grease, microbes, odor and etc. Materials like paper, glass, metal, plastics biopolymer and wax/plastic coated cartoons (ZVONKINA et al., 2014). In relation to non-paper packaging like plastics, metal and glasses, paper packaging has the most favorable properties like sustainable, lightweight, low cost, easily transported and stored and usually is considered as green packaging (MAGNIER; SCHOORMANS, 2015). However, pure cellulose paper does not have barrier properties so it is usually coated by plastic, wax or aluminum. These coating materials limit recyclability of the packaging (HIRVIKORPI et al., 2010). So, there are a new series of packaging materials which are made with putting a dense coating thin layer of nanocellulose on paper or paperboard because of their small size and strong hydrogen bonding characteristics. The nanocellulose coating make a surface smoothening effect on the coated sheets and is a good way for healthy adjacent. These kinds of coating materials are biodegradable, totally recyclable, low density, easily being chemically modified and widely used for nanocomposite applications (RODIONOVA et al., 2011).

2.4 Technologies for CNF-based materials production

There are many different processes applicable which have been presented in the literature, but here it is mentioned only the most promising procedures for manufacturing packaging materials based on cellulose nanofibrils which mentioned before in the introduction. Among these methods, LbL assembly and coating are more common because cellulose nanofibrils have thermostability lower than synthetic polymers and also the poor compatibility with synthetic polymers which lead to serious problems in extrusion processes (REBOUILLAT;

PLA, 2013) On the other hand, easy distribution of the CNFs in water makes it feasible as a water based coating. Even a thin layer of crystalline nanocellulose, applied as a coating or by lamination can provide a substantial improvement in barrier and other properties, that is very useful in packaging applications (LI et al., 2013).

2.4.1 Layer-by-layer assembly (LBL)

For the fabrication of multilayer films, LBL is a basic technique on solid base substrates by controlled adsorption from solutions or dispersions. The enhanced properties are very important for packaging applications, including gas barrier, (JANG et al., 2008; YANG et al., 2011) antimicrobial surfaces (DVORACEK et al., 2009), anti-fog and super hydrophobic (NURAJE et al., 2010; ZHANG; SUN, 2010) and bioactive compounds delivery (KIM et al., 2008). This method has been applied to assemble xyloglucan with cellulose nanocrystals, by using just strong non-electrostatic interactions (JEAN et al., 2009) and this procedure usually builds multilayer sheet of very thin alternating films, mainly relying on electrostatic interactions and hydrogen bonds between a polyanion and a polycation as two or more components are alternately deposited by solution-dipping, spin-coating or spray-coating.

2.4.2 Coating

Coating is known as suitable way to improving many features of food and beverage packaging materials and it should be noted that coatings intrinsically lead to composite structures (LI et al., 2013; FARRIS; PIERGIOVANNI, 2012). In the flexible packaging manufacturing, coatings are thin layers that may be either external or sandwiched between two substrates. Such layers normally have thicknesses ranges from tenths of nanometers to a few micrometers. A great interest is the possibility of using coating technology to increase the sustainability of packaging materials for reducing the thickness of oil-based conventional plastic films by using a thin layer of functional and high performing bio-based material (PIERGIOVANNI; LIMBO, 2015).

A number of cellulose-based materials (hydroxypropyl cellulose and long chain cellulose esters) or cellulose derivatives (nanowhiskers or nanofibrillated cellulose) can be used to surface finish paper and to improve its properties (Havimo et al., 2011; Aulin et al., 2010; Hult et al., 2010; Belbekhouche et al., 2011; Minelli et al., 2010; Syverud; Stenius, 2009; Sothornvit, 2009). Among these, CNF has shown very interesting barrier properties (Hult et al., 2010; Plackett et al., 2010, Syverud; Stenius, 2009; Sothornvit, 2009) and has been used in different studies related to paper coating (Aulin et al., 2011; Hult et al., 2010; Syverud; Stenius, 2009). For example, it was shown that carboxymethylated CNF lead to high barrier properties if it completely covers the paper surface. It seemed that carboxymethylation play an important role in the determination of CNF barrier properties as CNF without such treatment gave discontinuous coatings even at higher coat weights and the final paper showed a decrease in air permeability, and oxygen transmission rate (OTR) values were above those measured for pure NFC films (Aulin et al., 2010; Syverud; Stenius, 2009). However, not only the coat weight but also the interactions between the coating layer and the base paper determine the final barrier properties.

On the contrary, Spence et al. (2011) found that micro fibrillated cellulose lacks water vapor barrier properties in comparison with oil-based plastics and suggested using mineral fillers or waxes coating to improve this property for packaging applications.

Li et al. (2013) addressed the performance of CNC from cotton linters, coated on flexible food packaging films. The 1.5 μm thick coating was applied on polyethylene terephthalate, oriented polypropylene, oriented polyamide and cellophane films. The coated sheets were characterized for their mechanical, optical, antifog and barrier properties. CNC coating reduced the coefficient of friction while maintaining high transparency (~90%) and showed excellent antifog properties and remarkable low oxygen barrier transmission values. The Gelbo Flex test was also used for evaluating the durability of coatings. The results indicated that strong distortions led to some destructions of CNC coating and reduced the oxygen barrier properties of all CNC-coated films. All of the composites films still maintained a significant low O_2 permeability. Compared with others, Gelbo Flex treated coated oriented polypropylene and cellophane films show relatively higher O_2 permeability, probably because of their weak adhesion. In the end, they concluded that, coating technology has a great potential in producing novel packaging materials, starting from conventional plastic films, whose properties can be greatly enhanced by a very thin layer of nanocellulose. A serious issue is the adhesion of hydrophilic cellulose onto the generally hydrophobic plastic substrates, and the research should be focused on surface treatments and possible primers to increase the strength adhesion and the compatibility.

Santarella (2006) applied gelatin coating on a low grammage base paper. Combined with a top coating of barrier latex, both had low water vapor transmission rate values and high grease resistance. However, the oxygen transmission rate value was extremely high.

2.4.3 Spray coating technique

Handheld gravity feeder spray was used in this study as a depositing method to put CNF on the surface of papers as a fiber based substrate. Figure 2 shows coating layer of cellulose nanofibrils deposited on the paper substrate. The results obtained from this investigation can then be easily transferred to a system with better control of the deposition parameters over a large area, such as automated and computer controlled spray coaters.

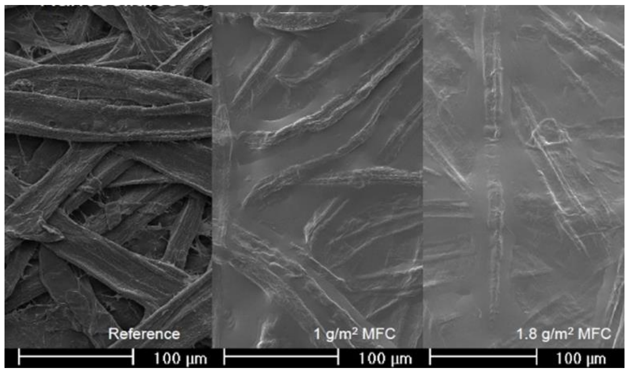

Figure 2- Nanocellulose coatings on paper/ board
Aulin et al., (2010)

This technique is broadly used in industrial coatings and painting. This large area deposition ensures ideal coatings on different surfaces with different morphologies and is often used for in-line production. The fluid waste is reduced to minimal quantities in this technique. Also, the spray coating technique can use broad different fluids with different rheologies, and deposit virtually any kind of solution and obtain the desired film properties (GIROTTO et al., 2009). The other advantages of this method are facility, thickness control at the nano scale and the potential of coating on tridimensional objects, such as small cups and trays.

Hult et al. (2010) investigated on the enhancement of the barrier properties of paper. NFC and shellac were deposited on the fibre based substrates using a spray coating technique. The most significant results obtained were a reduction of air, water vapour and oxygen permeability. It was found that, the NFC coating would not completely cover the surface, while an additional shellac layer would cover the ″pin holes″ leading to a considerably better barrier.

In the same year, Sanchez-Garcia et al. (2010) showed improved water barrier property because of embedment of nanocrystalline cellulose in carrageenan matrix. They obtained a novel bionanocomposite and suggested for application in food-packaging and coating applications.

Beneventi et al. (2014) conducted a similar study to Hult et al. (2010). In their study, a laboratory bench for the spray coating of aqueous slurries on wet substrates and the subsequent water removal by vacuum filtration was used to load porous papers with microfibrillated cellulose (MFC). Spray coating presented an accurate control of the coating basis weight. By increasing the MFC basis weight, homogeneous films progressively formed on the substrate with insignificant loss of MFC. Although the base substrate was a porous paper, the MFC coating remained confined on the surface of the substrate, at first forming irregular pots and then, as the MFC basis weight exceeded 6 g/m^2, a continuous film was formed. The formation of MFC film reduced significantly air permeability and led a sharp increase in the tensile properties. Also, after film formation, the further increase of the MFC coating basis weight or putting up another layer led to a linear increase of the tensile properties.

2.5 Nanoclay

Nanocellulose and nanoclay blend films as a new type of composite materials have recently been considered due to offering superior strength and gas barrier properties (GAMELAS; FERRAZ, 2015). The effective dispersion of swelling clays into polymer matrices may offer a unique property profile. The incorporation of this type of additive offers demonstrated enhancement of the modulus of elasticity and barrier properties against oxygen, carbon dioxide and water vapor of the host polymer (Utracki, 2004). Wu et al. (2012) prepared composite films using CNF, with 5 wt.% of montmorillonite (MTM). A composite film with 5% MTM content had Young's modulus 18 GPa, tensile strength 509 MPa, work of fracture of 25.6 MJ m–3, and oxygen permeability 0.006 mL μm m^{-2} day^{-1} kPa^{-1} at 0% relative humidity, respectively, despite having a low density of 1.99 g cm^{-3}. As the MTM content in the CNF/MTM composites was increased to 50%, light transmittance, tensile strength, and elongation at break decreased, while Young's modulus was almost unchanged and oxygen barrier property was further improved to 0.0008 mL μm m^{-2} day^{-1} kPa^{-1}. The resulting composites showed excellent mechanical properties. These results were even better than those of films of neat NFC. In another study of Wu et al. (2014) they prepared composites of CNF and synthetic saponite nanoplatelets (SPN). Mechanical properties of the CNF/SPN composites varied depending on the SPN content. The composite with 10% w/w SPN content (5.6% volume fraction) exhibited characteristic mechanical properties: Young's modulus of 14 GPa, tensile strength of 420 MPa, and strain-to-failure of 10%. This surprising improvement in toughness was interpreted based on a model for fracture of polymer composites reinforced with low-aspect-ratio platelets. They concluded that these composite materials offer a combination of strength, stiffness, and ductility, that is not common in bio-based composites. For instance, composites with other biomaterials such as starch, poly-lactic acid or poly-vinyl alcohol have never approached these values (MULLER et al.; 2012; DARIE et al., 2014; NOORI et al., 2015). In the end, they concluded that since CNF is already stiff and strong, and these properties can be further enhanced in the organic-inorganic composite, thus, the effect of the nanoclay mineral addition is worth being discussed. Aulin et al. (2012) reported similar results. They concluded that the insertion of the nanoclay mineral into the NFC matrix, increased the mechanical property, modulus of elasticity to 17.3 GPa in regard to 14.2 GPa related to neat CNF, when they used CNF/nanoclay, 80/20, while tensile strength decreased from 256 MPa related to neat CNF film to 244 Mpa, when they used 80/20 of CNF/nanoclay ratio. They showed that the insertion of the nanoclay mineral into the NFC matrix also improved the gas barrier properties of the material, namely to oxygen and water vapor permeability. Oxygen transmission rate values of neat CNF films was 454 cm^3 m^{-2} d^{-1} and decreased to 26 cm^3 m^{-2} d^{-1}, when they used 80/20 of CNF/nanoclay proportion. And water vapor transmission rate values of neat CNF films were 70.3 g m^{-2} d^{-1} and decreased to 15.4 g m^{-2} d^{-1}, when they used 80/20 of CNF/nanoclay proportion.

Liu et al. (2011) showed that the composites containing high mineral content (>50 wt. %) can be explored if the transparency of the material is not a final necessity. They showed that nanopaper of enzymatic CNF incorporating with more than 50 wt.% of montmorillonite can be prepared with still some flexibility, high strength and stiffness. Also, the oxygen transmission rate is considerably reduced even at high humidity conditions compared with neat CNF films. As a result, strong composite films with high gas barrier prevention can be produced using larger amounts of the platy clay mineral.

Sun and Joseph (2007) showed that water-based suspension of polymer-clay nanocomposites are expected to provide the coating layer with excellent physical and barrier properties, providing the clay platelets with a high surface area are well dispersed (exfoliated) in the polymer matrix, thereby increasing the diffusion path tortuosity. The surface area and pore volume of Saponite clay /cetyl trimethylammonium bromide prepared in this way was reported to be 1130 m^2/g and 0.92 cm^3/g, respectively.

2.6 Corona Discharge

Paper industry use one sort of atmospheric dielectric barrier discharge (DBD) plasma treatment, which called as corona treatment or corona discharge (ROTH, 2001). This method is usually used to increase adhesion between paper and polymer films. With corona treatment the chemistry properties of surface and surface energy of paper can be modified and it is possible to create new chemical groups mainly, C=O, C-O and COH and deposit thin layers of various polymers on the surfaces. Corona treatment enables dry surface modification only on the substrate surface without altering bulk properties (CERNACOVA et al., 2006; ROTH, 2001).

Cernacova et al. (2006) showed that paper can be coated with aqueous mineral pigment suspension along with starch to improve compatibility with various finishing operations. Such finishing steps including printing and improvement the adhesion between paper and polymer in the extrusion and lamination process, to increase the printability especially with water based inks, and to improve the adhesion in the spray coating process and the barrier properties in packaging materials.

Pykönen et al. (2008) treated paper substrates by using corona treatments. The treatments increased surface energy of papers and they concluded that paper is a multicomponent system, where the constituents that have the lowest surface energy were suggested to transfer to paper surfaces.

Schuman et al. (2005) studied the impact of corona and plasma at atmospheric pressure on the printing and barrier properties of coated paperboard. A fairly intense corona treatment led to an undesirable increase in the WVTR values. A less intense corona treatment preserved the WVTR-value to a great extent, but the printability remained at an unsatisfactory level.

Lahti (2005) has investigated the ageing effect of corona treatment on extrusion coated papers during several months. The surface energy decreased most rapidly immediately after the treatment and then slowed down. The long-time surface energy level still stayed on higher level than that of the samples without corona treatment.

3 CONCLUSION AND FINAL CONSIDERATIONS

Given the above, it became clear the need to test improvement oxygen transmission rate, water vapor transmission rate and tensile properties of paper to use in paper packaging. This improvement is done using cellulose nanofibrils, nanoclay and corona treatment. An experimental assembled spray coater was used to coating paper substrate with CNF aqueous and with CNF/nanoclay hybrid slurry water-based suspension. Corona discharge can be used to improve the adhesion between paper substrate and these suspensions, and finally coating layer after drying. Spray system variables and concentration of CNF and CNF/nanoclay in the suspensions will be investigated. From the results obtained in the two papers presented in the second part of this work, the following conclusions are presented:

Morphology of obtained fibers from Eucalyptus pulp and then obtained cellulose nanofibers showed in Fig. 2 (p. 50) and the diameter distribution of the nanofibers was shown in Fig. 3 (p. 50). The basis weight and thickness of the coated layer (dried CNF layer on paper substrate) in different treatment were achieved and showed in Fig. 4 and 5 (p. 52 and 53). The average and standard deviation values of tensile strength obtained from the paper specimens are shown in Fig. 6 (p. 54) and the correlation between tensile strength of coated papers and basis weight and thickness of NFC layer was shown in Fig. 7 (p. 55). Water vapor transmission rate (WVTR) reduced in all treatments regarding to control sample or uncoated paper and the results is in Fig. 8 (p. 55). Also reduction in WVTR values with increasing basis weight and thickness of NFC layer was shown in Fig. 9 (p. 56). It was found poor oxygen barrier properties in all samples. Fig. 10 and 11 (pp. 58-59) indicated that the CNF layer reduced sheet porosity, i.e., the dense structure formed by the nanofibrils resulted in fewer WVTR.

In the second paper the results are presented in the same manner on first paper, thus, the basis weight and thickness of the coated layer (dried

CNF/nanoclay hybrid composite layer on paper substrate) in different treatment were achieved and showed in Fig.4 and 5 (p. 76). The average and standard deviation values of tensile strength obtained from the paper specimens are shown in Fig. 6 (p. 77) and the correlation between tensile strength of coated papers and basis weight and thickness of hybrid layer was shown in Fig. 7 (p. 78). Water vapor transmission rate (WVTR) reduced in all treatments regarding to control sample or uncoated paper and the results is in Fig. 8 (p. 79). Also reduction in WVTR values with increasing basis weight and thickness of hybrid layer was shown in Fig. 9 (p. 80). It was found here that oxygen barrier properties improved in all samples regarding to uncoated paper and the results were showed in Fig. 10 (p. 82). Regarding to microstructure, Fig. 11 (p. 83) indicated that the hybrid layer reduced sheet porosity, i.e., the dense structure formed by the nanofibrils resulted in improvement barrier properties or less OTR and WVTR values.

Thus, this Ph.D thesis contributes to the better understanding of using spray coating method, CNF, nanoclay and corona discharge in barrier packaging applications. These results indicate potential for ongoing investigations, in the direction of other strategies modification and application of CNF, and to understand the key mechanisms that influence the barrier and mechanical performance of the packaging materials based cellulose and its interaction with different filler and matrices in making composites. Further development of this approach could improve the performance of the papers and for the development of new and engineered cellulose-based materials for diverse packaging applications.

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SECOND PART – PAPERS

PAPER 1 - SPRAYING CELLULOSE NANOFIBRILS SUSPENSION ON KRAFT PRINTING PAPER SUBSTRATE TO IMPROVEMENT TENSILE AND BARRIER PROPERTIES

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ABSTRACT
An experimental assembled spray coater was used to coating kraft printing paper substrate with cellulose nanofibrils (CNF) aqueous slurry suspension. The effects of spraying variables i.e. concentration of suspension, spray pressure, distance and time of spray on the coated sheets were analyzed in terms of the oxygen transmission rate (OTR), water vapor transmission rate (WVTR) and tensile strength. Basis weight and the thickness of coated layer in the different treatments were measured. In addition, image analysis of the structure was performed to examine the coating adhesion. The WVTR of the papers decreased while tensile strength increased with a one-layer coating of CNF. The oxygen transmission rate (OTR) did not show changes. The tensile strength and morphological properties of the coated sheets indicate good adhesion between the coating and the base substrate using spray coater.

KEYWORDS: cellulose nanofibrils (CNF), spray coating, barrier properties, thickness, basis weight, tensile strength

1 INTRODUCTION

Consumers, industries, governments and scientists seek products manufactured from renewable resources with little environmental impact and nominal safety risks. Cellulose nanofibril (CNF), an abundant natural biopolymer, has received heightened interest because it is renewable, nontoxic, biodegradable, stable and inexpensive. CNF is a key, fundamental material in applications such as paper, medicines, plastics and cosmetics. CNF can be extracted from wood, but also can be extracted from other lignocellulosic materials and bacterial cellulose (Miaoa et al. 2016).

Several recent journal review articles illustrate aspects of the production and use of CNF. Much attention has been paid to the application of this material as a reinforcement agent in plastics (Volk et al. 2015; Shao et al. 2015; Chinnama et al. 2016). A natural use for these fibers is the making of paper and packaging materials. The packaging industry has always used cellulose-based materials in sizable amounts. Nowadays, cellulosic packaging includes wrapping materials and containers, primary and secondary packages and flexible and rigid packaging (Missoum et al. 2013). The utilization of packaging materials is about the same worldwide. Cellulosic ranks first, with roughly 40% of the total (Li et al. 2015). Even if fast growth in new green materials and biopolymers is expected, paper and paperboard are now the only renewable materials widely used in packaging. Nevertheless, their application is restricted by poor barrier properties because of the pores in the paper and a low porosity of the base paper is one of the most important requirements to obtain good barrier properties (Hult et al. 2010). Much research has been aimed at improving mechanical properties like tensile strength, elastic modulus, stress at break and scott bond and barrier properties of cellulose packaging materials (Beneventi et al. 2014; Missoum et al. 2013; Li et al. 2015; Johansson et al. 2012; Nair et al. 2014).

The most promising procedures for manufacturing packaging materials based on CNFs are LbL assembly (layer by layer), electrospinning, composite extrusion, casting evaporation, coating and all-cellulose composites (Li et al. 2015). In the present study, a gravity feeder spray was employed to coat paper surfaces. Coatings are powerful tools for enhancing many properties of food and beverage packaging materials (Johansson et al. 2013). In the burgeoning packaging field, coatings incorporate thin layers that may be either external or inserted between two substrates. Coatings intrinsically lead to composite structures. The thickness of such layers normally ranges from tenths of nanometers to a few micrometers. Nowadays, great interest is generated by the possibility of using coating technology to increase the useful life of packaging materials. Thickness of oil-based conventional plastic films can be reduced through a thin layer of functional and high-performing bio-based material. Cellulose on a nanoscale, especially with high crystallinity, is a good contender as a functional layer on various substrates, only recently investigated (Li et al. 2015).

Spray coating has many advantages: The coating is carried out contactless, and a contour coat can be applied to uneven surfaces. Substrate topography does not influence coating weight. Tear-sensitive web material can be coated with a spray; low coating weights are achievable at high velocities. A closed film can be achieved with a decreased amount of liquid, reducing costs and improving quality (Czerwonatis 2008).

No literature reports the use of gravity feed spray in coated paper or its efficiency. Therefore, in this study, kraft printing papers were spray coated with CNF in water base suspension to decrease the oxygen transmission rate and the water vapor transmission rate, and to increase tensile strength. Spraying parameters were investigated for concentration, pressure, distance and time of spray. Thickness changes and basis weight of the coated papers were also studied.

2 MATERIALS AND METHODS

2.1 Materials

The paper substrate was commercial writing & printing paper (W&R) (Suzano Papel e Celulose, Brazil), made of 100 % cellulose of *Eucalyptus* with a nominal basis weight of 75 g/m² and a nominal thickness of 95.5 µm.

To prepare the CNF, bleached dry lap *Eucalyptus* Kraft pulp was obtained from a commercial source (Cellulose Nipo-Brasileira SA, Cenibra, Brazil).

2.2 METHODS

2.2.1 Obtaining the cellulose nanofibrils (CNF)

The pulp was first soaked in deionized water overnight and then disintegrated in a lab mechanical stirrer (Fisatom, model 722). The *Eucalyptus* pulp was fibrillated at suspension solids consistency of 1 % (w/w) using a Supermasscolloider (Model: MKCA6-2J, Masuko Sangyo Co., Ltd., Japan) at 1,500 rpm and the suspension was passed through it 30 times, following suggestions of previous works (Tonoli et al. 2016; Bufalino et al. 2015; Fonseca et al. 2015; Piva et al. 2013).

2.2.2 Morphology of fibers

A Leica DM4000B compound light optical microscope (OM) was used for the initial investigation of the morphology of the pulp fibers and also of obtained cellulose nanofibrils. Suspensions were stained with a drop of ethanol-safranin solution (0.5% v/v) in order to increase the contrast between phases. The obtained cellulose nanofibrils were also viewed in a transmission electron microscope (TEM) FEI Tecnai 12 operated at 120 kV. A drop of the suspension was deposited on a formvar/carbon coated 400 mesh copper grid, and dried before viewing with TEM. The average diameter of the micro/nanofibrils was determined by digital image analyses (Image J 1.48v, National Institutes of Health, USA). A minimum of 500 measurements was collected for data analysis.

2.2.3 Experimental Setup for Spray Coating

CNF water base suspension was deposited onto paper substrates using a laboratory assembled spray coater (see Fig 1). There are seven variables in this kind of spraying that are, concentration of suspension, pressure of spray, distance of spray, time of spray, nozzle type, drops size and spray impact. Since spray nozzles are designed to perform under many different spraying conditions, more than one nozzle may meet the requirements for a given application. Surfaces may be sprayed with any pattern shape. Results are fairly predictable, depending on the type of spray pattern specified. If the surface is immovable, the preferred nozzle is usually some type of full cone nozzle (Fig 1), since its pattern will cover a larger area than the other styles (Lipp 2012), and we used this nozzle for all of the samples. Spray impact and drops size in our study were not important and after study on the other variables, variable parameters in table 1 were selected.

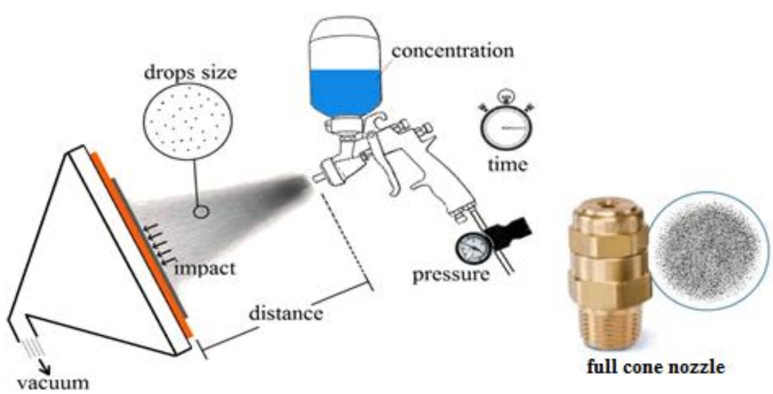


Fig. 1 Scheme of the experimental procedure used for CNF coating on paper substrates

Table 1. Variables of the spray coating in this study

Concentration of CNF (%)	Pressure of spray (bar)	Distance of spray (cm)	Time of spray (s)
1.4	4	15	20
1.7	5	30	30

Because of the high amount of water involved (≈98.5% of the coating dispersion) it was important to paper as base substrate does not get damaged during the coating procedure. All the sample performed very well in the test conditions with no signs of damage. The vacuum dewatering was determined with experimental testing to obtain a consistent removal of the water from the coated papers. No CNF based coating seems to be lost during the process. The drying process was undergone without tension to preserve the superficial profile of the coating deposition.

Before applying CNF on the papers, they were measured for basis weight and thickness for each treatment. Spray was conducted in accordance with the Table 1 and then, the coated papers were placed into the oven for 1 hour in 103 °C, and finally the coated sheet was pressed (1 bar). Each treatment was performed in three replicates. To prepare the control sample, the water was sprayed on the printing paper and then the paper was oven-dried (1 h, ≈103 °C). All samples were conditioned and tested at 23 °C and 50% relative humidity prior to measurements.

3 CHARACTERIZATION

3.1 Thickness and basis weight of samples

The thickness of samples was measured at five positions on each sample, using a Regmed micrometer (model ESP/SA-10, Brazil) according to the standard method ASTM D645-97 (2007). The basis weight or grammage was determined using an electronic analytical balance (JKI, model JK-EAB-2204N, China) according to the standard method ASTM D646-96 (1996). The thickness and basis weight of the papers were measured before and after coating with the NFC suspension on their surfaces and therefore, the coating thickness and basis weight was calculated using subtraction.

3.2 Tensile Strength

The tensile strength was measured on a tensile strength tester, Stable Microsystems (model TATX2i, England) according to ASTM D828-97 (2002). The standard dimension required for performing this test method is 25.4 ± 0.5 mm wide and of such length, usually about 254 mm. The distance between the grip clamping zones is 180 ± 5 mm and the rate of grip separation during test is 25.4 mm/min.

3.3 Water Vapor Transmission Rate (WVTR)

The water vapor transmission rate (WVTR) measurements were performed according to the desiccant method of the ASTM E96 / E96M-16 (2016), at 25 °C with 50% relative humidity (RH; g m^{-2} 24 h^{-1}). Results were averaged over three measurements per sample. The cup method was operated with the desiccant contained inside the cup and the samples sealing the open mouth of the test dishes. Weights were measured every day until constant rate of weight gain was attained.

3.4 Oxygen Transmission Rate (OTR)

The oxygen barrier properties were tested by measuring the OTR of samples according to the ASTM D3985-05 (2010) standard by means of OX-Tran oxygen permeability testing system, model 2/20 (Mocon Inc., USA). At a selected temperature and humidity (23 °C and 1% RH), the coated papers were sealed between a chamber containing oxygen and a chamber void of oxygen. A coulometric sensor measures the oxygen that is transmitted through the material. The commonly used unit is cm^3 m^{-2} 24 h^{-1}. The external side of the samples were put in touch with the permeant gas (100% O_2). The readings were corrected to 1 atm partial pressure gradient of permeant gas. The permeation area was 5 cm^2 and dry conditioning was performed at 23 ° C for 48 to 72 h (dehumidified environment with silica gel).

3.5 Scanning electron microscopy

Cross sectional and surface characterizations were assessed by Scanning Electron Microscopy (SEM, Zeiss LEO EVO 40 XVP, Germany). The accelerating voltage was 20 kV and the magnification between 100 and 1600. The sputter coating technique using gold was used for sample preparation. Secondary electron (SE) detector was selected for analyzing the cross section and surface of the samples.

4 RESULTS AND DISCUSSION

4.1 Morphology of fibers and nanofibrils

The average values of length and diameter of the Eucalyptus raw fiber were around 0.7±0.3 mm and 17±4 µm respectively, which are in the same range found by Belini et al. (2008) and Brisola and Demarco (2011) (Fig 2). Figure 2 shows the eucalyptus fibers before and after defibrillation. Figure 3 depicts the accumulated diameter distribution of nanofibrils determined using the TEM images. Almost 55% of eucalyptus nanofibrils diameters were lower than 40 nm. The average nanofibrils diameter in the suspension was 50±4 nm.

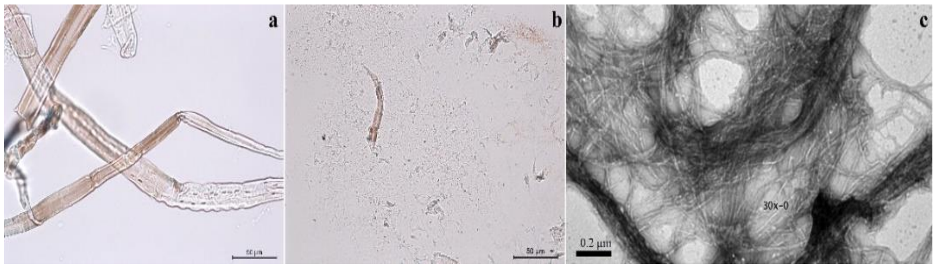


Fig. 2 Typical light microscopy (LM) images of the fibers:(a) before defibrillation; (b) after defibrillation; (c) typical transmission electron microscopy (TEM) micrograph of the nanofibrils derived from the defibrillation process

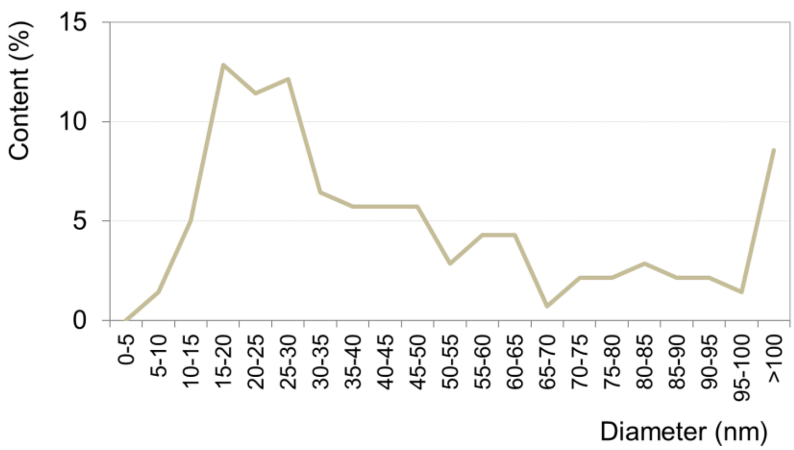


Fig. 3 Accumulated diameter distribution histogram of the nanofibrils

Kraft printing paper base substrate was spray coated with a cellulose nanofibrils water base suspension. Coated papers were measured for basis weight or grammage and studied for tensile strength and barrier properties, WVTR and OTR. Table 2 displays results for coated paper sheets. Statistical significance was set at 0.05.

Table 2. Paper coated samples' characteristics: Average and standard deviation values

Conc. (%)	Pres. (bar)	Dist. (cm)	Time (S)	Thickness (μm)	Basis Weight (g m^{-2})	Tensile Strength (KN m)	WVTR (g m^{-2} 24 h^{-1})
1.4	4	15	20	9.75 ± 0.2	6 ± 0.25	7.2 ± 0.03	25.6 ± 0.2
			30	10.2 ± 0.2	7.1 ± 0.22	7.25 ± 0.03	25 ± 0.15
		30	20	8.7 ± 0.15	5.8 ± 0.2	7 ± 0.025	25.9 ± 0.14
			30	9.6 ± 0.12	6.8 ± 0.23	7.1 ± 0.03	25.6 ± 0.2
	5	15	20	10.7 ± 0.2	8.95 ± 0.3	7.35 ± 0.02	24.4 ± 0.18
			30	11 ± 0.1	9.9 ± 0.1	7.45 ± 0.02	24 ± 0.15
		30	20	9.25 ± 0.2	5.8 ± 0.2	7.15 ± 0.03	25.8 ± 0.18
			30	10 ± 0.15	7 ± 0.15	7.25 ± 0.02	25.5 ± 0.2
1.7	4	15	20	7.75 ±0.14	4.8 ± 0.15	6.95 ± 0.02	27.5 ± 0.2
			30	8.1 ±0.12	5 ± 0.12	7 ± 0.02	27 ± 0.15
		30	20	5.8 ± 0.1	3.7 ± 0.1	6.6 ± 0.03	27.8 ± 0.2
			30	7.2 ± 0.1	4.6 ± 0.14	6.8 ± 0.03	27.3 ± 0.22
	5	15	20	8.1 ± 0.15	5.2 ± 0.16	7 ± 0.02	26.5 ± 0.15
			30	8.6 ± 0.13	5.4 ± 0.1	7.1 ± 0.02	26 ± 0.2
		30	20	6.1 ± 0.12	4 ± 0.1	6.8 ± 0.03	27.65 ± 0.25
			30	7.4 ± 0.1	4.9 ± 0.1	6.9 ± 0.03	27.2 ± 0.2
Control (base paper)				--	--	6.3 ± 0.03	28.55 ± 0.25

4.2 Basis Weight and Sheet Thickness

CNF layer was utilized at a basis weight of 3.7–9.9 g/m^2 in the treatments. Figure 4 shows that maximum basis weight (9.9 g/m^2) occurred at 1.4% concentration, 5 bar pressure, 15 cm distance and time of 30 seconds. The minimum basis weight (3.7 g/m^2) was reached at 1.7% concentration, 4 bar pressure, 30 cm distance and time of 20 seconds. Remaining treatments fell within this range.

Higher amounts of basis weight at the 1.4 % suspension concentration may have resulted from the greater viscosity at 1.7% and the type of nozzle used which caused a smaller amount of CNF to be sprayed. Consequently, a lower volume of CNF suspension was sprayed. CNF suspension is a pseudo plastic, with the properties of certain gels or fluids that are thick (viscous) under normal conditions, but flow becomes thin (less viscous) over time, when shaken, agitated or otherwise stressed. A critical issue that prevents immediate use of CNF as a coating is the rheology of CNF suspensions. Even at a solid level < 2%, the behavior is non-Newtonian with significant viscosities (Haavisto et al. 2011).

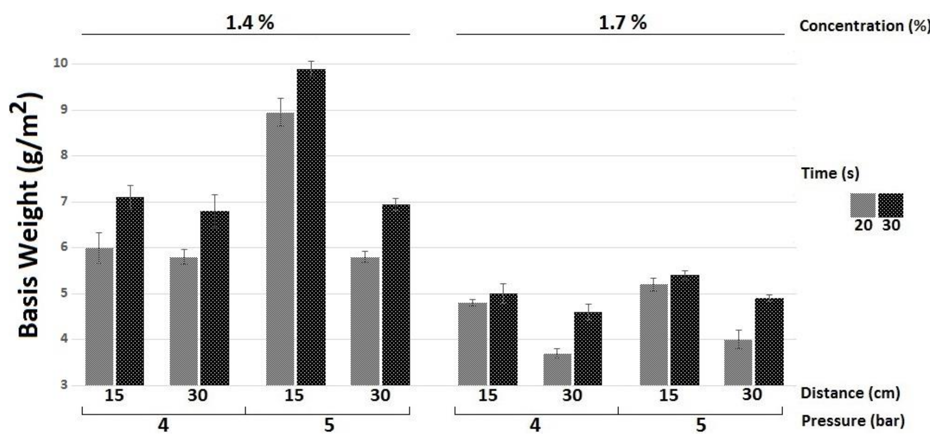


Fig. 4 Concentration, pressure, distance and time of spray impacts on basis weight of coated papers.

Thickness of CNF layer was in the range of 5.8–11 microns across treatments. Figure 5 presents maximum and minimum thickness. Trend was similar for basis weight. Figure 5 demonstrates that coated layer thickness and coated layer basis weight (Fig. 4) were directly correlated.

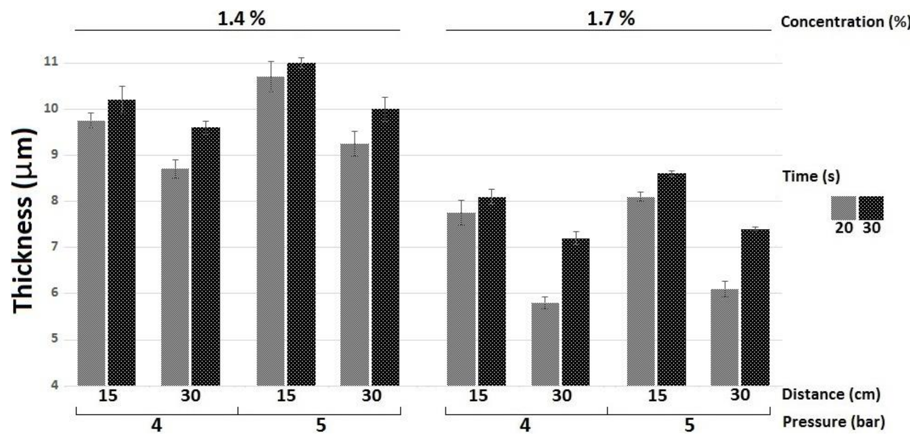


Fig. 5 Thickness of the coated papers as a function of concentration, pressure, distance and time of spray

The maximum basis weight and thickness valuse were obtained with 1.4% concentration of water base suspension of CNF, spray pressure of 5 bar, distance between nozzle and paper surface of 15 cm and 30 seconds of spraying time. Obviously, greater amount on CNF was deposited on the sheet surfaces regard to these treatments. It seems that the spraying was less effective at a concentration of 1.7% and this is justified due to higher viscosity than 1.4%. Increasing spray pressure from 4 to 5 bar increased the output of the suspension. Over a distance of 15 cm it provides greater amount of suspension sprayed in a smaller application area, while at the 30 cm, suspension can spread more easily because the air layer between the spray gun and the sheet surface, thus suspension can be thrown out of the application area, which may have contributed to lower deposition of CNF on the surface of the sheets.

4.3 Tensile Strength

Figure 6 shows average and standard deviation values of tensile strength obtained from the paper specimens. Statistical results disclosed significant differences between coated papers at all spray variables. All paper samples were cut in machine direction.

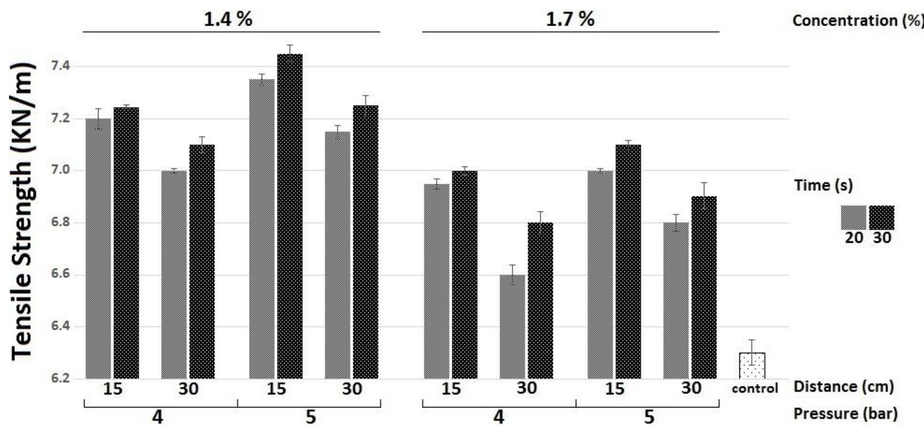


Fig. 6 Tensile strength of the coated papers as a function of concentration, pressure, distance and time of spray

In Fig. 6, tensile strength is increased for all coated paper, contrasted with untreated paper or control sample. The tensile strengths correlate directly with the basis weight and sheet thickness. Comparing tensile strength results with the sheets' basis weight and thickness confirms. Coated papers with superior basis weight and thickness showed better strength. In the best treatment, tensile strength increased about 18% over uncoated paper. These values also agree with the measurements of Rodionova et al. (2012). Their investigation focused on the impact of thickness and basis weight on the tensile strength of layered films prepared by bar coating. Figure 7 shows that coated papers' tensile strength increased with the basis weight and thickness of the NFC layer deposited on the paper base substrates.

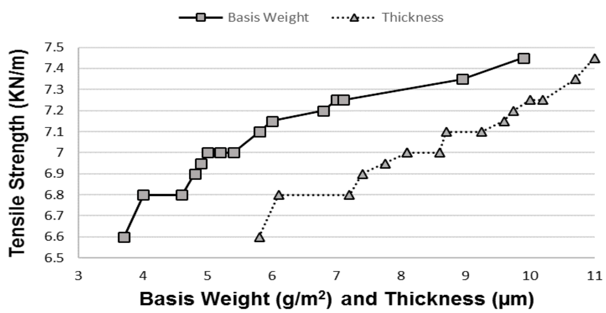


Fig. 7 Correlation between tensile strength of coated papers and basis weight and thickness of CNF layer

4.4 Water Vapor Transmission Rate

Generally, water vapor transport can occur under mechanisms including diffusion through inter-fiber void space, Fickian diffusion, Knudsen diffusion, surface diffusion, bulk solid diffusion within fibers and capillary transport. Diffusion through inter-fiber void space is the dominant transport mechanism in sheet paper (Spence et al. 2011).

Obviously, vapor molecules encounter resistance in passing through thicker sheets. It was confirmed that water vapor transmission rate was negatively correlated to sheet thickness (Fig. 9).

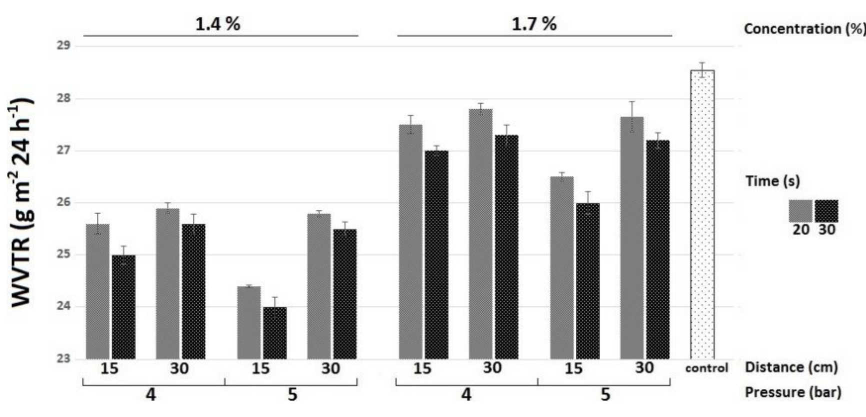


Fig. 8 Water vapor transmission rate of coated papers as a function of concentration, pressure, distance and time of spray

Water vapor transmission rate was analyzed on coated paper. Results are presented in Fig. 8. As can be seen in Fig. 8, the uncoated paper (control) has higher value of water vapor transfer at around 28.5 g m^{-2} 24 h^{-1}, and WVTR decreased to 24 g m^{-2} 24 h^{-1}, with a roughly 16% reduction at the 11 µm additional CNF layer on the paper (106.5 µm for coated paper).

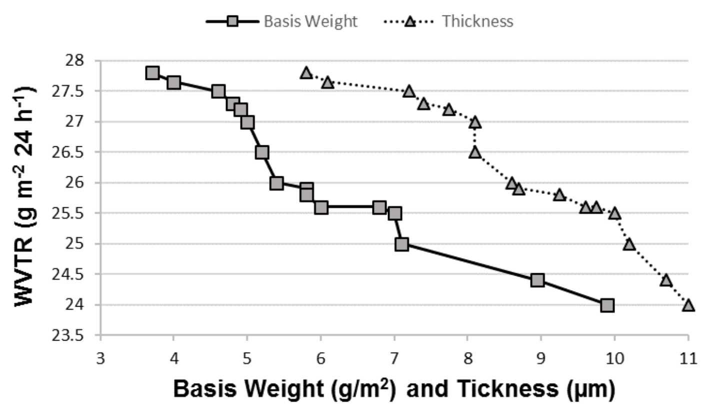


Fig. 9 Reduction in WVTR values with increasing basis weight and thickness of NFC layer

These values trends agree with the measurements of Hult et al. (2012). Their results showed that this technique can be an effective way to extend the application of paper based materials in the food packaging area, and avoiding using of oil derived products.

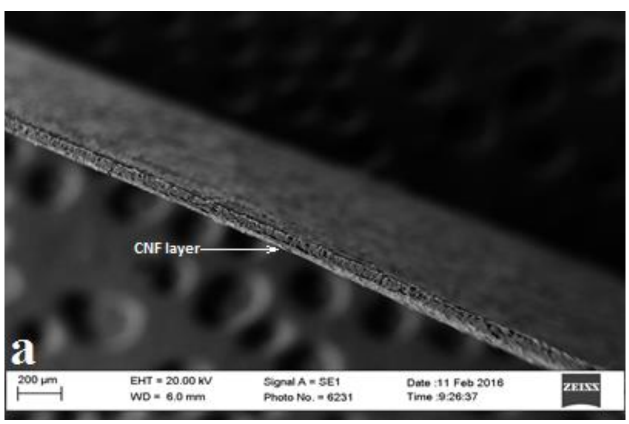
4.5 Oxygen Transmission Rate

OTR values of coated papers could not be analyzed because values were too high (OTR > 155000 cm^3 m^{-2} 24 h^{-1}). The obtained results are usual for cellulose behavior (Corte 1982), and the samples do not display a high barrier for oxygen. CNF coating with the spray deposition technique did not permit reaching the barrier values achieved by Syverud and Stenius (2009) with 30 µm NFC film.

Material is defined as a "high oxygen barrier" if OTR is less than 3 cm^3 m^{-2} 24 h^{-1} (at 25 °C, 50% RH) for a 25 µm–thick film (Fang et al. 2005; Tuil 2000). The acquired barrier properties, which are not as high as expected, are probably caused by the incomplete closure of the base paper surface pores by the NFC coating, due to the coating's formation of inhomogeneity. Even if the dimensions of those inhomogeneities are 5 µm and lower, they permit oxygen molecules to pass. The Van der Waals diameter of an O_2 molecule is 0.29 nm (Hult et al. 2010). With such minute dimensions, oxygen molecules breach the nanopores and influence the final OTR. Thomas et al. (1998) measured OTR on corn zein–coated paper and found poor oxygen barrier properties.

4.6 Microstructure

The influence of crystallinity and the CNF network's ability to form hydrogen bonds led to a dense microstructure in CNF film, which plays a considerable role in increasing tensile strength and decreasing WVTR in coated papers and in the CNF layer. Figure 10 displays the paper sample with the best results, clarifying the matter.



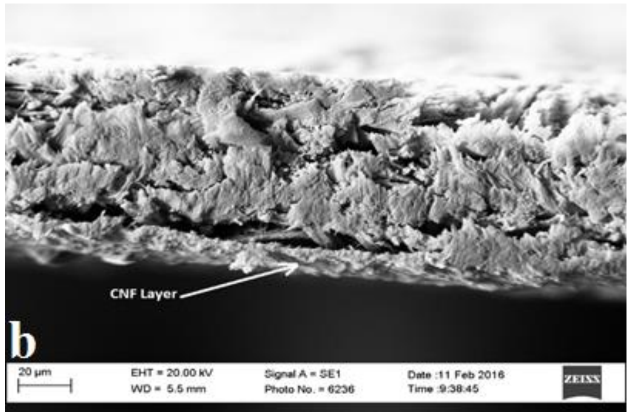
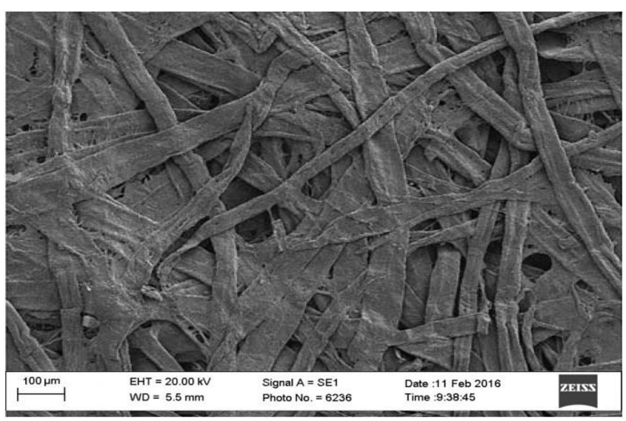


Fig. 10 Scanning electron microscopy images of coated paper with 11 µm CNF layer. (a) cross section; (b) detail of the cross section

SEM micrographs demonstrated that the CNF layer reduced sheet porosity as it mentioned before, i.e. the dense structure formed by the nanofibrils resulted in satisfactory barrier properties (Fig. 11). Modifying the structure of the pore network by reducing pore size or increasing sample crystallinity should drive down WVTR. Previous studies indicated a role for NFC coat layer density, pore structure and size in reducing WVTR through the surface coating method (Spence et al. 2011; Chinnan and Park 1995; Hu et al. 2000; Shorgen 1997).



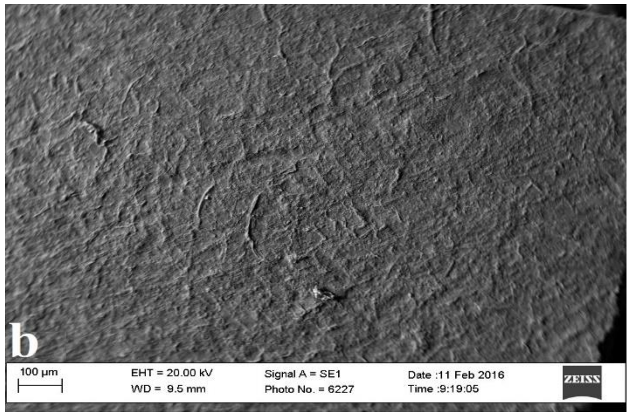


Fig. 11 Scanning electron microscopy images of the (a) uncoated paper and (b) CNF-coated layer

5 CONCLUSIONS

Cellulose nanofibrils were successfully obtained from Eucalyptus by mechanical defibrillation, presenting average diameters of 50±4 nm, with around 55% of the nanofibrils with diameter lower than 40 nm. The greater the nanofibrils content, the higher the thickness of the films, which interfere on strength and barrier properties. At the best treatment, tensile strength increased about 18% in comparison to uncoated paper and the WVTR decreased to about 16%, while basis weight and the thickness of added CNF layer were 9.9 g/m^2 and 11 µm respectively. The maximum valuse were obtained with 1.4% concentration of CNF suspension, spray pressure of 5 bar, spraying distance of 15 cm and 30 seconds of spraying time. The present work contributes with information on surface-coated papers with CNF and using spray coating method. Further development of this approach could improve the performance of the papers and for the development of new and engineered cellulose-based materials for paper-based packaging applications.

6 ACKNOWLEDGEMENTS

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PAPER 2 - CELLULOSE NANOFIBRILS/NANOCLAY HYBRID COMPOSITE AS A PAPER COATING

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ABSTRACT

The objective of this paper was evaluate the effects of spray time, nanoclay content and corona discharge on oxygen transmission rate (OTR), water vapor transmission rate (WVTR), basis weight, thickness and tensile strength of the coated papers. An aqueous slurry base, a mixture of cellulose nanofibrils (CNF) and nanoclay particles, was sprayed on a kraft writing & printing paper surface as base substrate. Upon drying, the suspension on the paper surface formed a hybrid nanocomposite layer with CNF (matrix) and nanoclay (mineral filler). Paper substrate was coated by a laboratory-assembled spray coater. Corona discharge enhanced the wetting of paper surfaces, improving adherence between paper and hybrid composite. Increased spray time improved tensile strength and barrier properties i.e. OTR and WVTR. Higher nanoclay content in coated paper enhanced its barrier properties but reduced its tensile strength. Tensile strength and morphological properties demonstrated effective adhesion between base substrate and hybrid composite.

KEYWORDS: Cellulose nanofibrils (CNF), Nanoclay, Spray coating, Barrier properties, Corona discharge

1 INTRODUCTION

Nanomaterials science has been propelled by rising demand for new food packaging substances that meet the public’s expectations. Biopolymers possess intrinsic permeability to vapors and gases, with poor mechanical properties, boosting interest in discovering new strategies to improve such properties (Majeed et al. 2013). Recent biopolymer research and development has addressed fillers, matrix-filler interaction and new formulation strategies in composites' expansion (Dhar et al. 2015). With cheap, renewable and sustainable materials featuring enhanced barrier and mechanical properties, food packaging materials are expected to expand (Ghaderi et al. 2014).

Cellulose nanofibrils (CNFs) are aggregations of rudimentary nanofibrils (composed of crystalline and amorphous parts) with micrometer length, 10–100 nm in diameter (Jonoobi et al. 2015). CNFs are ordinarily isolated by mechanical processes, including homogenization, high pressure, grinding and refining (Wang et al. 2007). In low concentrations (of around 2%), CNFs form a gel-like substance, useable in producing biodegradable, homogenous and dense films (Vartiainen and Vikman 2013; Vartiainen et al. 2011).

Recent review articles describe aspects of production and use of CNF. Significant consideration has been garnered by their use as reinforcement agents in plastics (Volk et al. 2015; Chinnama et al. 2016; Follain et al. 2013; George et al. 2014; Li et al. 2015). The primary application for these fibers is the production of paper and packaging materials. Perhaps an explosion in new green materials and biopolymers is about to occur, but at the time of this writing, paper and paperboard are the sole renewable materials extensively employed in packaging applications. Numerous studies (Chinnama et al. 2016; Hult et al. 2010; Beneventi et al. 2014; Missoum et al. 2013; Li et al. 2015) have been conducted with the objective of creating cellulose packaging materials with enhanced mechanical and barrier properties, and promising results have been realized. Testing the combination of new materials is vital, to find suitable solutions.

Nanoclay hydrophilic bentonite with formula $H_2Al_2O_6Si$ are naturally aluminium silicate, composed of fine-grained minerals having sheet-like geometry referred to as phyllosilicates. These hydrous silicates are known as phyllosilicates (Wu et al. 2014). The clays are naturally-occurring, low-priced and eco-friendly, and have found diverse applications (Garrido-Ramírez et al. 2010). Industrial applications for nanoclays include multilayer film packaging, beer bottles, carbonated drinks, and thermoform containers. In plastic bottles, nanoclays reduce gas permeability and keep oxygen-sensitive foods fresher and thus increase the shelf life of the foods (Silvestre et al. 2011).

Nanoclay-nanocellulose composites have emerged lately as a new type of composite material, with intresting strength and gas barrier properties (Kalia 2016). These organic-inorganic hybrid composites are environmentally friendly, and obtainable from renewable resources (Wu et al. 2014). In food packaging applications, these composites will soon pose a meaningful alternative to biopolymers or polymer-inorganic composites (Gamelas and Ferraz 2015).

Among the several coating methods, spray coating has many advantages. Since the coating is carried out contactless, a contour coat maybe applied to uneven surfaces. The substrate's topography has no bearing on coating weight. Tear-sensitive web material can be coated. Low coating weights are achievable at high web velocities. Closed film can be attained with less liquid, leading to improved cost and higher quality (Czerwonatis 2008).

The leading concern in developing and producing multilayer composites is interfacial adhesion between the coating layer and the base substrate (Langhe and Ponting 2016). A variety of methods and surface treatments like electroplating, chemical process, anodic oxidation, thermal spraying and etc. are used to improve functionality of surfaces, mainly to increase wettability and adhesion. Most experience has been achieved with plastic films, and most applications have occurred in this area. Limited research has been accomplished in paper discharges, but without breakthroughs to date (Weber 2007). All materials have an integral surface force, which in solid materials, surface energy, liquids, and surface tension play important roles in adhesion. Corona is a visible electrical discharge which occurs when a high voltage, high frequency electrical potential is applied to a surface and increases the surface energy and consequently, the adhesion of the solid material surfaces which is called surface wetting. The term for this is increased surface wetting. A material is considered wetted if its surface energy is greater than the liquid's surface tension. Corona discharge is often found in coating, printing and laminating of plastics, cloth, and paper (Butt et al. 2013). Corona discharge improves adhesion in spray coating and in barrier properties in packaging materials (Pykönen et al. 2008). In this research, a coating layer of a hybrid composite of nanoclay and cellulose nanofibrils on paper substrate is proposed as a nanotechnology for environmentally compatible food packaging materials. An aqueous slurry water base suspension of CNF/nanoclay was sprayed on the paper's surface using a laboratory-assembled spray system. Some papers were treated using corona discharge to evaluate adherence and improved features by generating both a denser layer and more adhesion. The barrier properties (oxygen transmission rate and water vapor transmission rate), tensile strength, and physical properties (thickness and basis weight of the coated paper) were examined.

2 MATERIALS AND METHODS

2.1 Materials

Paper substrate was a commercial printing & writing (P&W) paper supplied by Suzano Papel e Celulose, Brazil, made of 100 % cellulose of Eucalyptus with a basis weight of 75 g/m² and a thickness of 95.5 µm. To prepare the CNF, bleached dry lap *Eucalyptus* Kraft pulp was obtained from a commercial source (Cellulose Nipo-brasileira - Cenibra, Brazil). Nanoclay hydrophilic bentonite

(Sigma-Aldrich) with formula $H_2Al_2O_6Si$ with average particle size ≤ 25 μm, was used as a filer in the matrix of cellulose nanofibrils.

2.2 Methods

2.2.1 Obtaining the cellulose nanofibrils (CNF)

The pulp was first soaked in deionized water overnight and then disintegrated in a lab mechanical stirrer (Fisatom, model 722). The Eucalyptus pulp was fibrillated at suspension solids consistency of 1 % (w/w) using a Supermasscolloider (Model: MKCA6-2J, Masuko Sangyo Co., Ltd, Japan) at 1500 rpm and the suspension was passed through it 30 times following suggestions of previous works (Tonoli et al. 2016; Bufalino et al. 2015; Fonseca et al. 2015; Piva et al. 2013).

2.2.2 Morphology of fibers and nanofibrils

A Leica DM4000B compound light optical microscope (OM) was used for the initial investigation of the morphology of the pulp fibers and also of obtained cellulose nanofibrils. Suspensions were stained with a drop of ethanol–safranin solution (0.5% v/v) in order to increase the contrast between phases. The obtained cellulose nanofibrils were also viewed in a transmission electron microscope (TEM) FEI Tecnai 12 operated at 120 kV. A drop of the suspension was deposited on a formvar/carbon coated 400 mesh copper grid, and dried before viewing with TEM. The average diameter of the micro/nanofibrils was determined by digital image analyses (Image J 1.48v, National Institutes of Health, USA). A minimum of 500 measurements was collected for data analysis.

2.2.3 Corona discharge

The treatment with corona discharge was done using of a continuous electrical discharger (Corona Brasil Ind., model Pt-1) of high voltage, i.e. 10 kV, frequency of 60 Hz, potential of 0.5 kW and electric current of 0.06 A, which increases the surface wettability of paper before coating, and allowing the improved adherence of other materials. Paper sheets were passed with 1 cm distance under the tip of the stationary electrode at a speed of 450 mm/min.

2.2.4 Spray coating of paper

CNF/nanoclay suspension was spray coated onto P&W paper substrates using a lab spray coater (see Fig. 1). Variable parameters of spray were selected regarding to the best treatment of our previous study (concentration of CNF 1.4%, pressure of spray 5 bar, and distance of spray 15 cm). In the present study, we examined the effect of nanoclay content, Corona discharge and the spray time (Table 1).

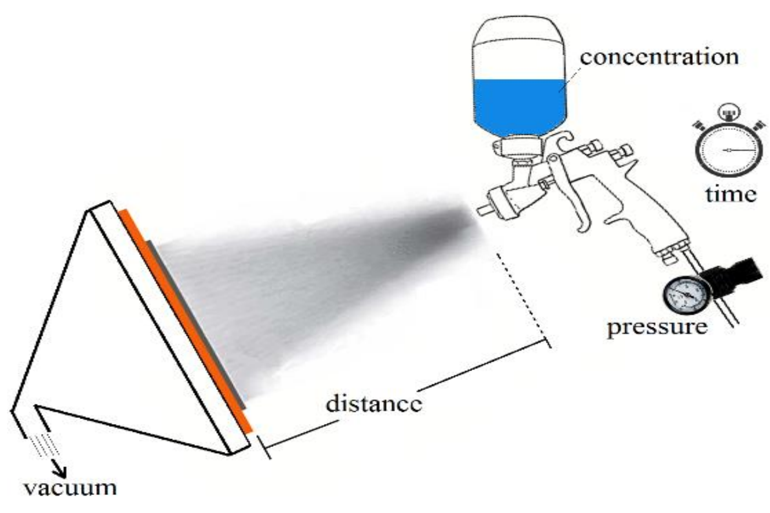

Fig. 1 Scheme of the experimental procedure used to coat the P&W paper substrates

All samples prepared, presented no signs of damage. The vacuum dewatering was determined with experimental testing to obtain a consistent removal of the water from the coated papers. No CNF based coating seems to be lost during the process. The drying process was undergone without tension to preserve the superficial profile of the coating deposition.

Before applying the CNF/nanoclay suspension on the substrates, the papers were measured for basis weight and thickness for each treatment. Spray was conducted and then, the coated papers were placed into the oven for 1 h at 103 °C, and finally the coated sheet was pressed (1 bar). Each treatment was performed in three replicates. To prepare the control sample, the water was sprayed on paper and then the paper was dried in the oven (1 h, ≈103 °C). All samples were conditioned and tested at 23 °C and 50% relative humidity (RH) prior to measurements.

3 CHARACTERIZATION

3.1 Thickness and basis weight

The thickness of samples was measured at five positions on each sample, using a Regmed micrometer (model ESP/SA-10, Brazil) according to the standard method ASTM D645/D645-97 (2007). The basis weight was determined using an electronic analytical balance (JKI, model JK-EAB-2204N, China) according to the standard method ASTM D646-96 (1996). The thickness and basis weight of the papers were measured before and after coating with the suspension on their surfaces and therefore, the coating thickness and basis weight was calculated using subtraction.

3.2 Tensile Strength

The tensile strength was measured on a tensile strength tester, Stable Microsystems, (model TATX2i, England) according to ASTM D828-97 (2009). The standard dimension required for performing this test method is 25.4 ± 0.5 mm wide and of such length, usually about 254 mm. The distance between the grip clamping zones is 180 ± 5 mm and the rate of grip separation during test is 25.4 mm/min.

3.3 Water vapor transmission rate (WVTR)

The water vapor transmission rate (WVTR) measurements were performed according to the desiccant method of the ASTM E96 / E96M-16 (2016), at 25 °C with 50% relative humidity (RH; g m^{-2} 24 h^{-1}). Results were averaged over three measurements per sample. The cup method was operated with the desiccant contained inside the cup and the samples sealing the open mouth of the test dishes. Weights were measured every day until constant rate of weight gain was attained.

3.4 Scanning electron microscopy (SEM)

Cross section and surface characterizations were assessed by scanning electron microscopy (SEM, Zeiss LEO EVO 40 XVP, Germany). The accelerating voltage was 20 kV and the magnification between 100 and 1600. The sputter coating technique was used for gold coating on the samples. A secondary electron (SE) detector was selected for analyzing the cross section and surface of the samples.

3.5 Oxygen transmission rate (OTR)

The oxygen barrier properties were tested by measuring the OTR of samples according to the ASTM D3985-05 (2010) standard by means of OX-Tran oxygen permeability testing system, model 2/20 (Mocon Inc., USA). At a selected temperature and humidity (23 °C and 1% RH), the coated papers were sealed between a chamber containing oxygen and a chamber void of oxygen. A coulometric sensor measures the oxygen that is transmitted through the material. Oxygen transmission rates are expressed in $cm^3\ m^{-2}\ 24\ h^{-1}$. The external side of the samples were put in touch with the permeant gas (100% O_2). The readings were corrected to 1 atm partial pressure gradient of permeant gas. The permeation area was 5 cm^2 and dry conditioning was performed at 23 ° C for 48 to 72 h (dehumidified environment with silica gel).

4 RESULTS AND DISCUSSION

4.1 Morphology of fibers

The average values of length and diameter of the eucalyptus fibers were around 0.7±0.3 mm and 17±4 µm respectively, which are in the same range found by Belini et al. (2008) and Brisola and Demarco (2011) (Fig 2). Figure 2 shows the eucalyptus fibers before and after defibrillation.

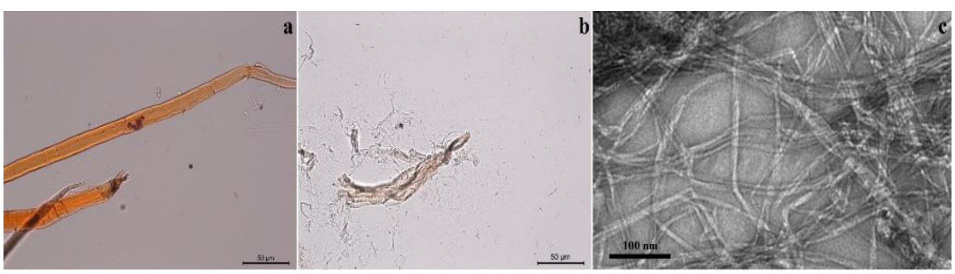

Fig. 2 Light microscopy (LM) images of the fibers:(a) before defibrillation; (b) after defibrillation; (c) Transmission electron microscopy (TEM) micrograph of the nanofibrils from the defibrillation process

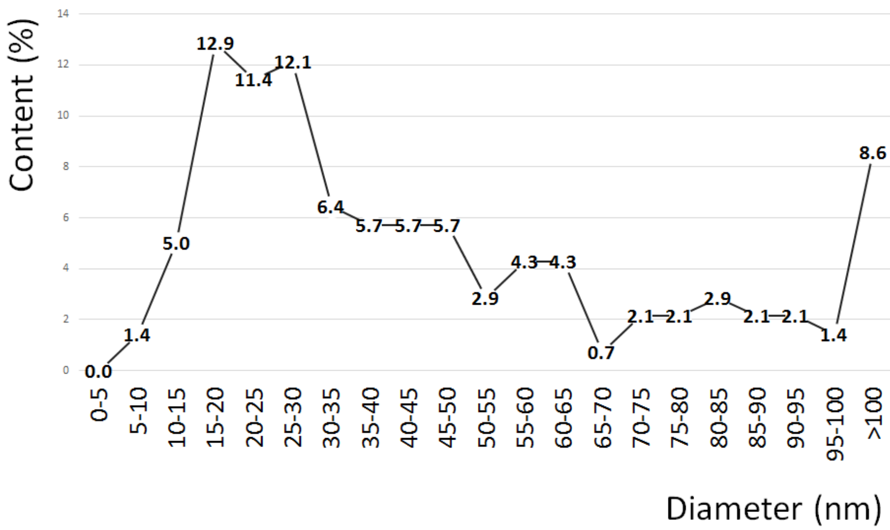

Fig. 3 Accumulated diameter distribution graph of the nanofibrils

Figure 3 depicts the accumulated diameter distribution of nanofibrils determined using the TEM images. Almost 55% of Eucalyptus nanofibrils diameters were lower than 40 nm. The average nanofibrils diameter in the suspension of eucalyptus was 50±4 nm.

After drying and forming a hybrid composite layer, the coated papers were evaluated through basis weight and thickness. Then, tensile strength and the barrier properties were also examined. Table 1 shows the results obtained from paper sheets. An alpha level of 0.05 was selected to judge the data and determine the statistical significance of differences. The values of the thickness and basis weight are linked solely to the hybrid layer.

Table 1 Average and standard deviation values of characteristics of the coated paper samples studied

Time (S)	Clay (%)	Corona	Thick. (μm)	Basis Weight (g m^{-2})	Tensile Strength (KN m)	WVTR (g m^{-2} day)	OTR (cm^3 m^{-2} day)
30	0	--	11 ± 0.3	9.9 ± 0.2	7.4 ± 0.06	24 ± 0.7	Out of range
		Corona	9 ± 0.15	10 ± 0.2	8.2 ± 0.07	22 ± 0.8	Out of range
	3	--	19 ± 0.4	22 ± 0.4	6.8 ± 0.05	14 ± 0.4	88600 ± 2000
		Corona	17 ± 0.3	22.5 ± 0.3	7.6 ± 0.06	12 ± 0.4	62800 ± 2200
	5	--	22 ± 0.5	29 ± 0.5	6.5 ± 0.05	8 ± 0.3	36400 ± 1100
		Corona	19 ± 0.35	29.5 ± 0.4	7.1 ± 0.05	7 ± 0.3	25200 ± 1200
50	0	--	19 ±0.35	17.7 ± 0.4	7.8 ± 0.06	22.7 ± 0.5	Out of range
		Corona	16 ±0.2	17.7 ± 0.3	8.9 ± 0.07	20 ± 0.9	Out of range
	3	--	28 ± 0.5	36 ± 0.5	7 ± 0.06	12 ± 0.3	32000 ± 1000
		Corona	26 ± 0.35	36.5 ± 0.4	8.2 ± 0.06	11 ± 0.3	21200 ± 1000
	5	--	32 ± 0.5	43 ± 0.5	6.7 ± 0.05	5 ± 0.2	12600 ± 400
		Corona	29 ± 0.4	43 ± 0.4	7.4 ± 0.06	4 ± 0.2	8800 ± 500
		Control (base paper)			6.3 ± 0.04	28.55 ± 0.7	Out of range

4.2 Basis Weight and Sheet Thickness

The hybrid layer's basis weight ranged from 9.9–43 g/m^2 among the treatments. Figure 4 shows that maximum basis weight (43 g/m^2) was achieved with spray time of 50 s and nanoclay content of 5%. Corona discharge had no effect on values of basis weights. Minimum basis weight (9.9 g/m^2) was achieved with spraying time of 30 s and no nanoclay.

Figure 4 demonstrates that by escalating spray time and nanoclay content, the basis weight of the sheets was augmented. Increasing the quantity of nanoclay had superior impact on basis weight of sheets, rather than expanding the amount of CNF by rising spray time. This can be driven by the higher density of nanoclay, which achieved bulk density of 600–1100 kg/m^3, while the nanocellulose fibers' density is much lower (Salas et al. 2014).

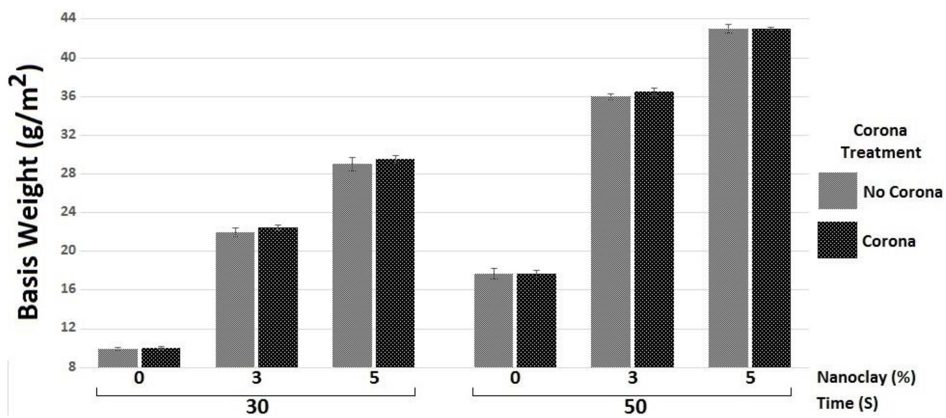

Fig. 4 Basis weight of the coated papers as a function of corona discharge, nanoclay content and spray time

Hybrid layer thickness in the treatments ranged from 9–32 µm. Figure 5 shows that maximum and minimum thickness and the trend were similar to basis weight, although the corona discharges had no effect on basis weight, while the effect of corona discharge on thickness was observable.

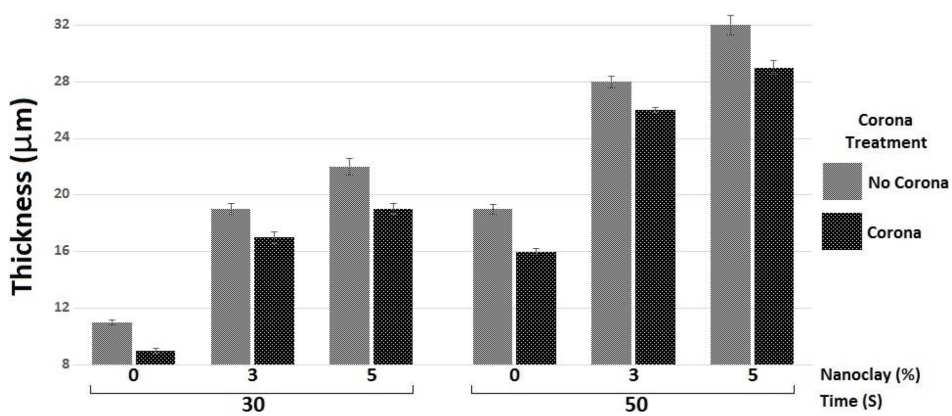

Fig. 5 Coated paper thickness as a function of corona discharge, nanoclay content and spray time

Figure 5 shows that while corona discharge had no impact on basis weight of the hybrid layer, its thickness had been reduced. The papers' increased surface tension force resulting from corona discharge could be a factor. Consequently, nanocellulose fibers and nanoclay became denser under the tension force from the paper surface.

4.3 Tensile Strength

Average and standard deviation values of tensile strength acquired from paper specimens are shown in Fig. 6. Statistical results uncovered significant differences among papers at all spray variables. All paper samples were cut in machine direction (MD).

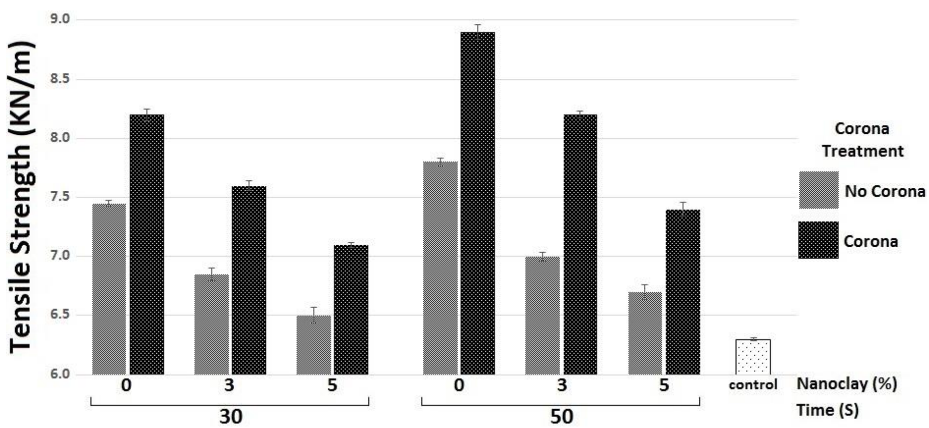

Fig. 6 Tensile strength of coated papers as a function of corona discharge, nanoclay content and spray time

Figure 6 makes evident that tensile strength rises for all coated paper compared to untreated paper or the control sample. Basis weight and sheet thickness are directly correlated with tensile strength. This was confirmed by comparing tensile strength results with basis weight and thickness of the sheets (Fig. 7). Coated papers with higher basis weight displayed better strength and elongation, in agreement with measurements of Rodionova et al. (2012). They investigated the thickness and basis weight of the tensile strength of the layered films prepared through bar coating. Figure 6 also shows that the tensile strength of the coated papers decreased when nanoclay content rose, and grew with corona discharge. The paper strength properties typically decline with increased filler content, largely because of the low physico-chemical compatibility of the filler and cellulosic fibers (low adhesion) and dispersion problems (Gamelas and Ferraz 2015). The best treatment was found to occur when tensile strength increased about 41%, compared with uncoated paper.

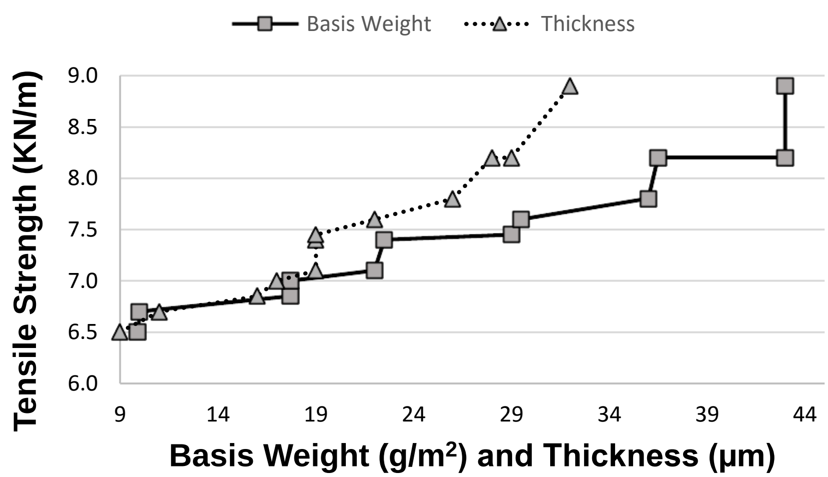

Fig. 7 Correlation between tensile strength of coated papers, and basis weight and thickness of hybrid layer

Studies on composite materials have shown that bonding between elements has a significant influence on the composite's mechanical properties. Corona discharges produced molecular groups chemically bonded to hydrocarbon or polymer chains, mirroring the polar group attachment model (Roth 2001). Consequently, it seems that the tensile strength of coated papers improved through corona discharge, enhancing adhesion between the base paper and hybrid layer.

4.4 Water Vapor Transmission Rate

Moisture reduces the shelf life of foods through many undesirable reactions, including autoxidation, vitamin degradation, enzymatic reactions and microbial reaction. Texture and crispness of some food products are also affected by moisture. Hence, low WVTR through packaging material is desirable (Robertson 1993).

Introducing the nanoclay mineral into the CNF matrix improves the material's gas barrier properties to oxygen and water vapor (Aulin et al. 2012; Wu et al. 2014). Gas barrier capability is mostly the result of the inherent highly-ordered nanoplatelet-like structure of the mineral, which is preserved in the composite with CNF. This structure offers a tortuous path for the dispersion of the gas molecules, thus hampering permeability. Beyond high strength and gas barrier properties, high transparency can also be attained for composites of NFC with low incorporated quantities of layered silicate mineral (Gamelas and Ferraz 2015).

However, it is clearly more problematic for water vapor molecules to pass through thicker sheets (Piergiovanni et al. 2013).

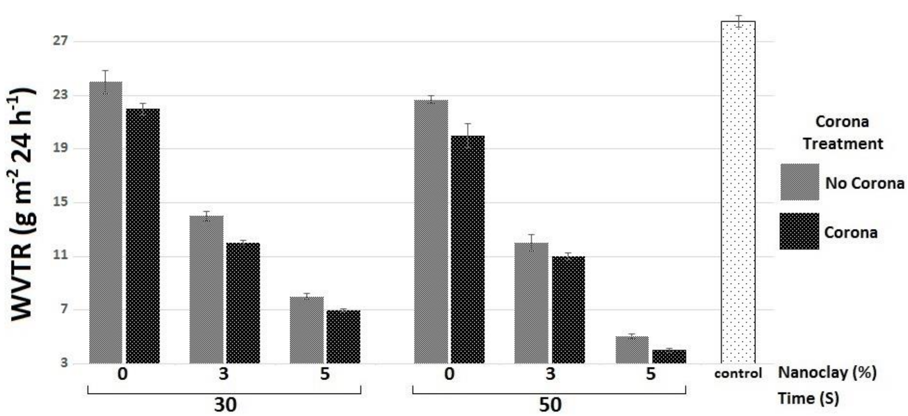

Fig. 8 Water vapor transmission rate of coated papers as a function of corona discharge, nanoclay content and spray time

Figure 8 shows that increased coating weight resulted in a significant decrease in WVTR. Uncoated paper (control) has a higher value of water vapor transfer at roughly 28.5 g m^{-2} 24 h^{-1}, and WVTR decreased to 4 g m^{-2} 24 h^{-1} with roughly an 86% reduction with 29 µm thickness of added hybrid layer (124.5 µm for coated paper). Water vapor transmission rate was confirmed as negatively correlated to the sheets' basis weight and thickness, except for those sheets that had received corona discharge, in which cases thickness decreased and WVTR declined (Fig. 9).

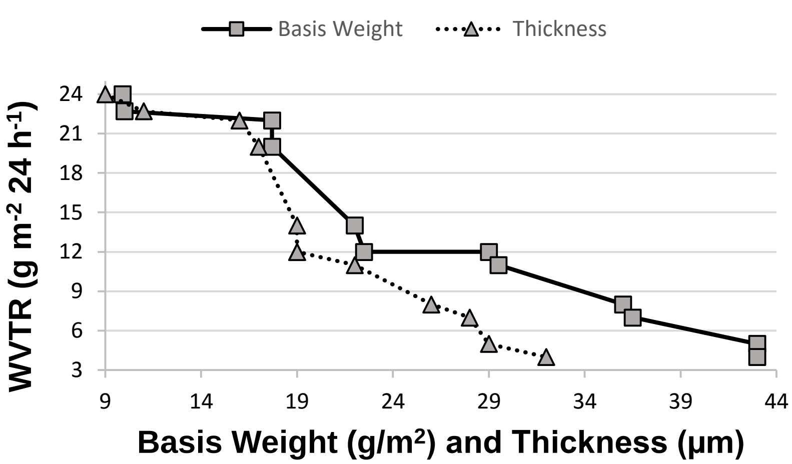

Fig. 9 Reduction in WVTR values with increasing basis weight and thickness of hybrid layer

These data are consistent with earlier studies, which showed that CNCs reduced WVTR of composite films (Abdollahi et al. 2013; George et al. 2014; Follain et al. 2013; Dhar et al. 2015; Li et al. 2013). Regarding to Hult et al. (2010), a material can be considered ''high moisture barrier'' if values are between 1-10 g m^{-2} 24 h^{-1} (at 25° C, 50% RH), for a 25 µm thick film, and as can be seen in Fig. 8, two of treatments fall in this range.

4.5 Oxygen Transmission Rate (OTR)

Low oxygen permeability is a key requirement for food packaging materials (Thomas et al. 1998). With excessive oxygen permeability in packaging material, oxidative reactions can develop, in which proteins and lipids degrade and result in food spoilage (Robertson 1993). In addition, microorganisms present in food can begin to grow at certain levels of oxygen.

Because values were too high, the OTR values of the coated papers without nanoclay filler could not be analyzed (OTR >155000 cm^3 m^{-2} 24 h^{-1}). In fact, obtained results are typical for cellulose performance (Corte 1982), and the samples do not exhibit a high barrier for oxygen. CNF coating with spray deposition technique did not allow reaching barrier values, as had been accomplished by Syverud and Stenius (2009) with 30 µm CNF film. Obtained barrier properties, lower than expected, are probably caused by incomplete closure of base paper surface pores by the CNF coating, after inhomogeneity formed in the coating. Even if inhomogeneity dimensions range from 5 µm and lower, they permit passage of oxygen molecules. The Van der Waals diameter of an O_2 molecule is 0.29 nm (Hult et al. 2010). Due to this very small dimension, oxygen molecules can penetrate through the nanopores and influence the final OTR. Thomas et al. (1998) performed OTR measurement on corn zein–coated paper and discovered poor oxygen barrier properties. Measured values were approximately 95,000, 35,000, and 16,000 cm^3 100 $in.^2$ day, for coating levels of 5, 10, and 15 Ib/ream, respectively. The average and standard deviation values of WVTR obtained from the paper specimens with nanoclay filler appear in Fig. 10.

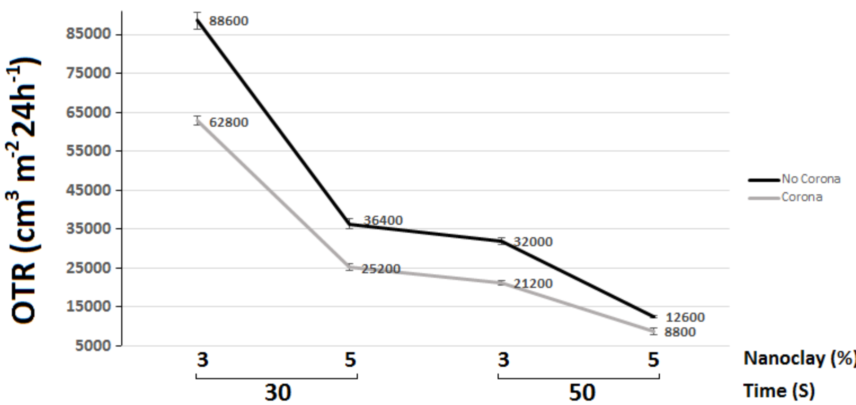

Fig. 10 Oxygen transmission rate (OTR) of the coated papers as a function of corona discharge, nanoclay content and spray time

As with WVTR, corona discharge reduced pores and thus OTR values. OTR can occur by diffusion through inter-fiber void space, and is the leading mechanism of transport in paper sheets (Spence et al. 2011). Efforts to improve adhesion between base paper and hybrid layer through corona discharge have been effective. Through use and increase in the amount of nanoclay, OTR values were lowered. This can result from the nanoplatelet-like structure of the nanoclay (preserved in the composite with CNF) and increasing its thickness. Since CNF is present in strong hydrogen bonding, by achieving an appropriate percolation network (Dufresne 2010) with the presence of nanoclay and the effect of corona discharge, a more impermeable network is formed. A film that is considered to have a high barrier has an oxygen transmission rate range of approximately 1-10 $cm^3\ m^{-2}\ 24\ h^{-1}$. A moderate transmitter film will have a rate of approximately 1000-10000 $cm^3\ m^{-2}\ 24\ h^{-1}$, and a high transmitter film will have an oxygen transmission rate more than 10000 $cm^3\ m^{-2}\ 24\ h^{-1}$ (Ebnesajjad 2013).

4.6 Microstructure

Creating a dense microstructure in CNF film depends on the influence of crystallinity and the CNF network's ability to form hydrogen bonds. Figure 11 shows that this plays a significant role in increasing tensile strength and barrier properties in coated papers and in the hybrid layer.

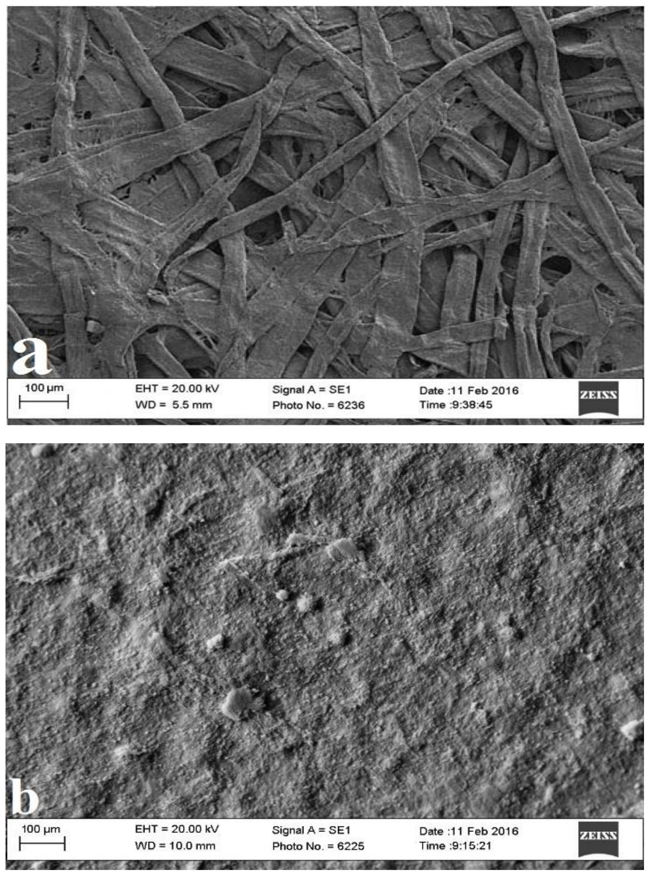

Fig. 11 Scanning electron microscopy images of the (a) uncoated paper (control) and (b) hybrid coating layer

SEM micrographs imply that the hybrid layer reduced sheet porosity. In other words, the dense structure formed by the hybeid layer led to superior barrier properties. Modifying the structure of the pore network (decreasing pore size or increasing sample crystallinity) would be expected to reduce the barrier properties. These results are consistent with previous studies pointing to a role for NFC coat layer density, pore structure and size in reducing WVTR through a surface coating method (Spence et al. 2011; Chinnan and Park 1995; Hu et al. 2000; Shorgen 1997).

5 CONCLUSIONS

Tensile and permeability of food packaging materials are important properties to assure that the packaged products are reasonably protected from external factors, and that the deteriorating changes are kept at low rates. When a material is intended for food contact, there are also safety issues involved, since there is the possibility of migration of components to the food. Here, cellulose nanofibrils were successfully obtained from eucalyptus by mechanical defibrillation, presenting average diameters of 50±4 nm, with around 55% of the nanofibrils with diameter lower than 40 nm. The greater the nanofibrils content, the higher the thickness of the films, which interfere on strength and barrier properties. At the best treatment, tensile strength increased about 41% in comparison to uncoated paper and the WVTR decreased to about 86%. Also, at the best treatment, OTR decreased about 90% compared to the highest value obtained. The present work contributes with important information on surface-coated writing and printing papers using cellulose nanofibrils. Further development of this approach could improve the performance of the papers and for the development of new and engineered cellulose-based materials for diverse packaging applications.

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