UNIVERSIDADE FEDERAL DE LAVRAS

MÁRIO VANOLI SCATOLINO

PARICA CELLULOSE NANOFIBRILS (*Schizolobium parahyba* var. *amazonicum*) FOR FILMS PRODUCTION AND AS AN AGENT FOR PAPER COATING

LAVRAS – MG
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NANOFIBRILAS DE CELULOSE DE PARICÁ (*Schizolobium parahyba* var. *amazonicum*) PARA A PRODUÇÃO DE FILMES E COMO AGENTE PARA RECOBRIMENTO DE PAPÉIS

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

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RESUMO

O objetivo geral do trabalho foi modificar as fibras de *Schizolobium parahyba var. amazonicum* (paricá) por meio de tratamento alcalino (NaOH) e branqueamento ($NaClO_2$ + ác. acético glacial) visando a produção de celulose nanofibrilada (CNFs) e avaliar aplicação delas na produção de filmes e como agente para recobrimento de papéis Writing & Printing (W&P). O trabalho foi dividido em 2 artigos. No primeiro artigo as fibras tratadas e CNFs foram caracterizadas, assim como os filmes produzidos a partir das CNFs geradas. A caracterização das fibras e CNFs foi feita por meio de espectros de FTIR, termogravimetria e microscopia eletrônica de varredura (MEV-FEG). Os filmes gerados a partir das CNFs foram avaliados quanto as suas propriedades mecânicas e de molhabilidade de superfície. O teor de hemiceluloses diminuiu com a sequência de tratamentos. Os espectros de FTIR mostraram que a desfibrilação mecânica causou a ruptura das ligações nas fibras. A temperatura de degradação térmica observada na análise DTG aumentou, ao se comparar as fibras naturais (243°C) com as fibras branqueadas (255°C). O processo de desfibrilação levou a uma maior estabilidade térmica nas CNFs branqueadas em comparação às fibras. As propriedades mecânicas mostraram valores de 6,93 ± 0,18 GPa para módulo de elasticidade (MOE) para os filmes produzidos a partir do material submetido ao branqueamento e 1,65 ± 0,08 GPa para filmes produzidos apenas com CNFs tratadas alcalinamente. Tais resultados mostraram uma superioridade de filmes produzidos a partir das CNFs branqueadas. Uma superfície mais hidrofóbica dos filmes produzidos com CNFs geradas a partir das CNFs branqueadas foi observada. No segundo artigo as CNFs de celulose de paricá foram utilizadas como agente de recobrimento para papéis W&P de gramatura 75g/m² em camadas de 1 a 5. Na segunda etapa do estudo, a fécula de mandioca geleificada foi utilizada em alternância com as camadas de CNFs. As camadas de CNFs e fécula foram depositadas sobre os papéis-base utilizando técnica de revestimento por dip-coating, sendo que a cada camada depositada, o papel era seco a 50 °C por 24h. A deposição de camadas consecutivas resultaram em menor degradação em água para papéis cobertos com CNFs tratadas alcalinamente. A análise termogravimétrica mostrou que o amido começou a degradar em temperatura superior a das nanofibrilas, porém levou menor tempo até atingir a temperatura de máxima degradação. As camadas de amido gelatinizado resultaram em maior aumento de densidade para os papéis. A degradação na água foi baixa para todos os tipos de papéis revestidos. O uso do amido gelatinizado em alternância com as camadas de nanofibrilas com tratamento alcalino resultou em papéis com maior elongação na ruptura. As amostras produzidas com uma camada de nanofibrilas branqueadas e uma camada de amido gelatinizado obtiveram uma resistência à tração de aproximadamente 20% maior que os papéis W&P. A aplicação do amido gelatinizado melhorou as propriedades de superfície dos papéis revestidos com CNFs, porém os papéis W&P apresentaram melhores características superficiais em relação a todos. O sistema de deposição das camadas e secagens em sequência pode ter causado danos à estrutura das fibras do papel, fazendo com que a resistência mecânica dos papéis recobertos ficasse abaixo do papel comercial. Em suma, o presente trabalho envolvendo os 2 artigos contribui com informações importantes sobre filmes e papéis revestidos na superfície utilizando CNFs.

Palavras-chave: Paricá; papéis multicamadas; nanofibrilas branqueadas; molhabilidade; clorito de sódio; ângulo de contato.

ABSTRACT

The main objective of the study was to modify the *Schizolobium parahyba* var. *amazonicum* (paricá) fibers by alkaline treatment (NaOH) and bleaching ($NaClO_2$ + glacial acetic acid) for production of nanofibrillated cellulose (CNFs) and evaluate their application in films production and as agent for coating Writing & Printing (W&P) papers. The work was divided in 2 manuscripts. In the first article the treated fibers and CNFs were characterized, as well as the films produced from the generated CNFs. The characterization of the fibers and CNFs was done by FTIR spectra, thermogravimetry and scanning electron microscopy (SEM-FEG). The films generated from the CNFs were evaluated by the mechanical properties and surface wettability. The hemicelluloses content decreased with the sequence of treatments. The FTIR spectra showed that mechanical defibrillation caused the rupture of the fibers bonds. The thermal degradation temperature observed in the DTG analysis was increased by comparing the natural fibers (243°C) to the bleached fibers (255°C). The defibrillation process led to greater thermal stability for the bleached CNFs when compared to the fibers. The mechanical properties showed values of 6.93 ± 0.18 GPa for modulus of elasticity (MOE) for the films produced from the fibers submitted to the bleaching and 1.65 ± 0.08 GPa for films produced with only alkaline treated CNFs. These results showed a superiority of the films produced from the bleached CNFs. A more hydrophobic surface for the films produced with CNFs generated from the bleached CNFs was observed. In the second article, paricá cellulose CNFs were used as a coating agent for Writing & Printing (W & P) papers with grammage $75g.m^{-2}$ with layers 1 to 5. In the second stage of the study, the gelatinized cassava starch was used in alternation with the layers of CNFs. The layers of CNFs and starch were deposited on the base paper using the dip-coating technique and for each deposited layer, the paper was dried at 50 °C for 24h. The deposition of consecutive layers resulted in less degradation in water for papers covered with alkaline treated CNFs. The thermogravimetric analysis showed that the starch started to degrade in a higher temperature in comparison to the nanofibrils, however, it took less time to reach the maximum degradation temperature. The gelatinized starch layers resulted in a higher density increase to the papers. The degradation in water was low for all types of coated papers. The use of the gelatinized starch in alternation with the layers of nanofibrils with alkaline treatment resulted in papers with greater elongation at break. Samples produced with a layer of bleached nanofibrils and a layer of gelatinized starch obtained a tensile strength of approximately 20% greater than the W&P papers. The application of the gelatinized starch improved the surface properties of CNF coated papers, but the W&P papers showed better surface characteristics than all coated papers. The system of layer deposition and sequential drying may have caused damage to the structure of the paper fibers, causing lower mechanical strength for the coated papers in comparison to the commercial paper. In summary, the present work involving the 2 articles contributes with important information about coated papers using CNFs.

Keywords: Paricá; multilayer papers; bleached nanofibrils; wettability; sodium chlorite; contact angle.

SUMMARY

FIRST PART

1.INTRODUCTION

1.1.General Introduction

Packaging performs a key role in the food industry due to its multiple functions. In addition to containing the product, packaging is very important in maintaining quality, acting as a barrier against factors responsible for chemical, physical and microbiological deterioration. Packaging of food products may be made of metal, plastic, glass, wood or paper (JORGE, 2013).

Even if fast growth in new biopolymers is on the way, it can be said that paper is the only renewable material widely used in packaging applications (HULT et al., 2010). Cellulose derivatives are widely used as packaging materials for food products, being the main paper used in the bags forms, cartridges, cardboard boxes, etc.

Cellulose is the most abundant renewable organic material in the biosphere. Its annual production is estimated to be over 75 billion t (LI et al., 2015). To obtain the pure cellulose from the wood it is necessary to perform some chemical treatments. The most known and industrially used treatments are pulping and bleaching.

The pulping is responsible for the bonds destruction between the fibers of the vegetal, causing their individualization. This process can be done by applying mechanical, thermal, chemical or a combination of these energies. Thus, the plant material is reduced to individual fibers (TONOLI et al., 2011a).

Bleaching is the process of partial or almost complete lignin and extractives removal from the cellulosic fibers. This affects the cell wall chemical composition of the fibers and their surface, the length of the hemicellulose and cellulose chains, as well as the cell wall structure (TONOLI et al., 2011b).

With the development of the nanotechnology, the cellulose attracts more attention in the new form of "nanocellulose" or cellulose nanofibrils (CNFs) to be used as innovative material to obtain new products. CNFs are described as native cellulose product or extract (found in plants and bacteria) (LIN and DUFRESNE, 2014). Most of the works of the literature have developed nanocellulosic films from commercial pulps from species commonly exploited for the paper and cellulose production (SYVERUD et al., 2011; VIANA, 2013) and more recently, reported the production of cellulose nanostructures from non-woody resources such as rice straw, hemp (PACAPHOL and AHT-ONG, 2017), banana steam (XU et al., 2015), jute (LIN et al., 2014), bagasse, bamboo (GUIMARÃES JR et al., 2015a; 2015b), nutshell (JULIE CHANDRA et al., 2016), sisal (KRISHNAN et al., 2015) algae (CHEN et al., 2016) and bacteria (CORRAL et al., 2017).

Given the amount of available vegetal sources, it can be considered that many species still need to have their potentials evaluated in the field of nanotechnology. In this context, the biodiversity of the Amazônia is particularly attractive, since the region is home for around 60,000 vegetal species, which 30,000 of them are considered superior plants (ALBAGLI, 2001).

Considering the Amazonian species in general, one that deserves attention is *Schizolobium parahyba* var. *amazonicum*, which popular name is paricá. Known by being a fast-growing species, paricá stands out mainly in the production of plywood and decorative materials, but little known about the potential of this species for CNFs production.

Today CNFs are mainly used for preparation of nanopapers for both high strength/barrier in packages (LAVOINE et al., 2012; GONZALEZ et al., 2014), electronics applications (ZHENG et al., 2013; JABBOUR et al., 2013) and paper coatings (HULT et al., 2010). The coated paper is a type consisting of a base paper and a coating layer for improvement of certain qualities, including weight, surface brightness, smooth appearance or ink absorption capacity (ZHAO et al., 2014). The CNFs have already been used as coatings for commercial papers Writing & Printing (W&P). Among the investigated points are the effects of CNFs suspension spray time, nanoargyl content and corona discharge on coated paper properties (MIRMEHDI et al., 2018a), the use of CNFs to improve the tensile strength and barrier properties of Writing & Printing (MIRMEHDI et al., 2018b).

In addition to CNFs, other materials have potential for being applied as coatings. Biopolymer films and coatings from polysaccharides, along with other components, are able to control the mass transfer in packages and thus increasing the food shelflife (GARCIA et al. 1999, GARCIA et al. 2000; GONTARD et al. 1993).

1.2.OBJECTIVES

The aim of the work was to evaluate the properties of nanostructured films and coated papers according to a multilayer system, using lignified and delignified paricá CNFs, alternated with cassava gelatinized starch.

The specific objectives are:

- Verify the effect of chemical treatments on the chemical composition and microstructural characteristics of paricá fibers;
- Evaluate the mechanical behavior and the surface wettability properties of nanostructured films from the Amazonian paricá wood;
- Evaluate the mechanical behavior and surface wettability properties of coated papers with CNFs from Amazonian paricá wood;
- Verify the variation in physical and mechanical properties of papers with increasing number of CNFs layers;
- Evaluate the interaction between the layers of CNFs and the cassava starch layers;
- Establish the optimum combination of layers between lignified and delignified CNFs which have the better properties for use in packaging.

1.3. JUSTIFICATIVE

In recent years the number of researches on the development of CNFs has considerably expanded. The interest is related to the possibility of producing optimum materials for several applications, but meeting the sustainability standards required by the current society. However, in order to ensure the viability of large-scale production of cellulose nanomaterials, the supply of the raw material in abundance is fundamental.

In this context, Brazil is in an advantageous position due to its extensive forest and agricultural coverage. The wood from planted or native forests and their wastes composes the picture of the various potential sources of raw material of our country for CNFs production. It is necessary, however, to study in detail the peculiarities of each material in order to make this process viable. This is where the research plays a key role in the development of new materials from non-traditional species.

2.LITERATURE REVIEW

2.1. Cellulosic packaging

As in other materials, substances used for paper production, as various additives, whether of process, or to provide certain characteristics to the papers, printing inks, glues and adhesives, etc. can migrate to the products. Therefore, food packaging papers must be manufactured only with substances approved for this purpose, and must not yield, or allow to migrate, substances that cause a sensory change in the product or which are harmful to human health.

There are regulations and legislation on the roles for packaging in contact with food, indicating which substances are authorized for their production and which must be controlled (ANVISA, 1999).

Cellulose meets the European Union requirements for food contact materials and comply with the US legislation (Food and Drug Administration) regulations for food contact materials. Cellulose-based coatings have the potential to achieve the environmental benefit of recycling or composting as a final destination (GATTI, 2005).

In recent years, CNFs have emerged as a material with excellent properties for packaging applications, being a strong field for research in attempt to improve their properties.

2.2.Cellulose nanofibrils (CNFs)

Turbak et al. (1983) cites that CNF or nanocellulose from wood fibers is a relatively new material, reported in the early 1980s, resulting by the disintegration of cellulose under high shear and impact forces. This process produces a final material which is a network of interconnected microfibrils with dimensions of 10-100 nm if thickness and could show many micrometers in length (CHERIAN et al., 2008; GARDNER et al., 2008). The crystallinity degree of the CNFs is generally lower, since the amorphous part of the cellulose remains (PÄÄKKO et al., 2007).

Even though full commercial scale production of CNF has not yet been achieved, the availability of large amounts of CNFs promoted the development of new materials using them as the main component, often replacing plastic polymer nanocomposites (SIRO and PLACKETT, 2010; SIQUEIRA; BRAS; DUFRESNE et al., 2010) in which the CNFs are used as reinforcement, represents a small fraction of the composite.

CNFs can be obtained by chemical or mechanical procedures. In the first type, partial hydrolysis of the cellulose chains occurs. Initially the cellulose chains placed in the amorphous regions are hydrolyzed due to their greater chemical accessibility. The process results, in most cases, in formation of purely crystalline structures called whiskers or nanocrystals (CORRÊA et al., 2010; SIQUEIRA; BRAS; DUFRESNE, 2009; TONOLI et al., 2012).

Refining and shearing (SYVERUD et al., 2011), microfluidization (ZIMMERMANN et al., 2010), sonification (CHEN et al., 2011), high pressure homogenization (PÄÄKO et al., 2007), mechanical stirring (CHERIAN et al., 2008) and maceration at low temperatures (CHAKRABORTY et al., 2005) can be cited as examples of mechanical methods for CNFs obtaining. These procedures result in obtaining nanocellulose structures containing crystalline and amorphous regions.

The literature reports wood pulp as the main source of the production of CNFs (TONOLI et al., 2012; BUFALINO et al., 2014, BUFALINO et al., 2015), but also some non-woody residues can be exploited as sugarcane bagasse and rice straw (HASSAN et al., 2012), banana rachis (ZULUAGA et al., 2009), bamboo (GUIMARÃES JÚNIOR et al., 2015) and sisal leaves abaca (ALILA et al., 2013).

Several procedures, based on filtration dewatering of diluted MFC suspensions (SYVERUD and STENIUS, 2009; SEHAQUI et al., 2010; ÖSTENBERG et al., 2013), have been proposed to produce MFC nanopaper with excellent mechanical and barrier properties.

In this sense, CNFs may be used for development of cellulosic packaging, including wrapping materials and containers, primary and secondary packages, and flexible and rigid packaging products, or as a coating layer to improve mechanical and/or barrier properties in paper packaging (MISSOUM et al., 2013; BENEVENTI et al., 2014; LI et al., 2015, NAIR et al., 2014).

2.3. Wood chemical treatments

Chemical treatments in natural fibers have been widely researched and used. Among them, mercerization, treatment with acids, with silane, acetyl, isocyanate, permanganate and peroxide groups can be mentioned. These treatments are widely used in order to improve the interface between fiber and matrix in the case of composites (MARINELLI et al., 2008; CORREA et al., 2003; BONELLI et al., 2005).

The mercerization, a type of alkaline treatment, is probably the most popular process for modifying natural fibers. Generally, the chemical treatment begins with an alkaline treatment, referred to in some works as mercerization, basically consisting of immersion of the fiber in alkali solution under heating and strong agitation (ROSA et. al, 2010). Its use presupposes the solubilization of hemicelluloses and lignin, being able to alter the crystallinity of cellulose (ICHAZO et al., 2001; JOSEPH et al., 1996; LI et al., 2007).

A commonly used pretreatment is TEMPO mediated oxidation of cellulose (SIRO and PLACKETT, 2010; LI et al., 2013a, 2013b). This pre-treatment induce certain repulsive charge on the fibers making easy their subsequent fibrillation and significantly decrease the energy input (CHARREAU et al., 2012). Carboxymethylation is other pre-treatment that increases the anionic charges in the formation of carboxyl groups on the surface of the nanofibrils (LAVOINE et al., 2012). Carboxymethylation treatment makes the fibrils highly charged and easier to defibrillate. However, the high cost can limit the use of these pre-treatments.

The removal of lignin from the wood cell wall by delignification processes is cited by authors as one of the important initial stages for fiber separation and CNFs, facilitating the fibrillation and reducing the energy consumed during the mechanical defibrillation process (ABE et al., 2007; IWAMOTO et al., 2008; MORÁN et al., 2008). However, the production of CNFs from lignified fibers for the production of films has already been reported in the literature in the study performed by Viana (2013). The author attributed the higher absorption of delignified treatments to the hydrophobic nature of lignin. The presence of lignin, being less hydrophilic character than the cellulose, resulted in films with lower percentages of water absorption.

The delignification treatment with sodium chlorite ($NaClO_2$) was used in works to remove lignin, however the researchers concluded that the use of this method may affect the CNFs morphology (YANO et al., 2005; NOGI et al., 2009; OKAHISA et al., 2011).

2.4.Coated papers

The multilayer packaging finds an excellent market in meat industry and meat products, due to its potential to combine properties such as transparency or opacity, mechanical strength, stiffness or flexibility, as well as gas and moisture barrier. The composition of the layers ranges according to the type of the product for being packaged, the need for good barrier properties and low cost of the material, as well as the desired combinations of properties. The growth of the use of multilayers is also a consequence of the possibility of producing efficient packaging with the least material and with the lowest weight possible (JORGE, 2013).

The spray coating technique is widely used in graphic arts, industrial coatings and painting. This deposition technique guarantees optimal coatings on a variety of surfaces with different morphologies and is used for production lines. In addition, the waste is reduced to minimum quantities. Another advantage is the ability to meet a wide spectrum of fluids with different rheologies (GIROTTO et al., 2009). The spray coating method is considered to be effective for these purposes (SASAKI et al., 2002). Spray coating system is originally developed as a resist coating onto non-planar surface; e.g. bonding surface of optical fiber. Spray coating involves ejecting fine liquid particles of smart materials by a jet stream of carrier gas onto the substrate. Spray coating has advantages both in the high-quality formation of chemical solution deposition and also in three-dimensional fabrication including step coverage coating. It is also possible to use spray coating for additional deposition onto deepetched base plates, and coating onto cylindrical non-planar surfaces and micromoldings. Spray coating enables the formation of the structure in both dry and wet conditions by controlling the deposition process conditions (ICHIKI et al., 2004).

Another method used is that of coating by plunging, which in addition to offering advantages such as the homogeneity of layers and low waste of material, dispenses expenses with spray apparatuses. This method provides a coating of the two faces of the paper.

The leading concern in developing and producing multilayer composites for food packaging are suitable barrier and mechanical properties and obviously interfacial adhesion between the coating layer and the base substrate (LANGHE and PONTING, 2016).

Several treatments/barrier coatings have been developed, including surface sizing, extrusion coating, dispersion coating, chemical vapor deposition, etc (MUKHOPADHYAY et al., 2002; KUUSIPALO, 2008).

The bar coating (AULIN et al., 2010) is a simple method which the suspension is applied on the paper by a stick which rolls over the whole base paper surface. However the process requires the use of equipment that can be expensive.

In this case, is necessary to choice a method for deposition onto irregular surfaces, as well as to choose a coating material that could allow a homogeneous coating. A good alternative in this intention is the use of a dip-coating technique, which does not require expensive coating equipment, been simple and cheap (LI et al., 2017).

The homogeneity and uniformity of the layers must be observed, since coatings with heterogeneous characteristics along the same layer may present undesirable characteristics. Factors such as porosity, surface roughness, moisture content and hydrophobicity of the films or papers may influence the resistance of the films to the penetration of liquids (SJÖSTRÖM and ALEN, 1999).

2.5. *Schizolobium parahyba* var. *amazonicum* (paricá)

The paricá, (Figure 1) is a species that occurs in the Amazônia, in primary forest and mainly in secondary forests of solid land and in high plain forests (DUCKE, 1949). It forms a type of monospecific groups (at least as to the composition of the dominant stratum) until the age of six years (JARDIM et al., 1997). It is also known as “pinho cuiabano”.

Figure 1 - *Schizolobium parahyba var. amazonicum* (paricá). Fonte (PROCLIMA, 2018)

Coradin and Muniz (1991), evaluating the native trees woods, the species is describes as belonging to the family Leguminosae and subfamily Caesalpinioideae with a very different background and color, white and with indistinct growth rings. Its grain is considered wavy, medium texture and with accentuated brightness. Its smell is imperceptible and soft when concerning the manual cutting.

According Vidaurre et al. (2010), the paricá is well adapted to the semi-humid equatorial climate, characterized by a dry season and a well defined rainy season, with rainfall predominantly between 1500 and 2000 mm / year. The development of the plants is strongly influenced by the season, where the occurrence of rains impels an explosion of growth, however, the species does not tolerate flooded soils.

The plant has a high regeneration capacity from the stumps of cut trees. Regeneration is closely related to the degree of soil fertility. The more fertile is the soil, greater is the regeneration rate.

The wood of this species has light to moderate density, is easily workable and susceptible to biological attack, and can be used mainly for production of plywood, bins, toys, doors and parquet (CARVALHO, 2007).

Marques et al. (2006) reported that the paricá forestry research and development comes from the decade of 50, and only in the 90's the species came to have business representation, mainly in the production of plywood and laminates, in the Amazon region.

Paricá, an Amazonian species with great economic potential, has become increasingly prominent among reforested species in Brazil, since it has increases in height and diameter that allow its use in a few years (ALMEIDA et al., 2013). One of the main characteristics of the wood, which interferes in its use, is the hygroscopic characteristic, which facilities the moisture content change according to the place where it is used (GALVÃO and JANKOWSKY, 1985). The Fiber Saturation Point (FSP) has a variable value, depending on the type of wood, ranging from 22% for conifers with high resin content up to 35% for hardwoods with high porosity in the sapwood. Below the FSP there are significant changes in the physical-mechanical properties of wood (LOGSDON and CALIL JUNIOR, 2002).

In the cellulose field, paricá stands out as a promising species due to the easy bleaching process and the excellent strength obtained with the bleached paper (PEREIRA et al., 1982). It shows a high content of lignin (34.70%), but can be easily delignified.

In popular medicine, this species is used against dysentery and uterine bleeding. In the region of Barcarena, Pará, the bark tea from the trunk is recommended to cure diarrhea (AMOROZO, 1997). Despite the multiple uses of wood, studies on the use of paricá wood in the CNFs form are still scarce.

2.6.Cassava starch

Starch is one of the most abundant natural materials available for dispersion coating. The challenge with biopolymer materials lies in the operability, the film forming properties, and high affinity for water and water vapor. Therefore, studies on the physico-chemical properties of polymers, starch, and starch mixtures as coating materials are widely carried out (HAN et al., 2010). It is a natural polymer and one of the most promising alternatives, especially due to the attractive combination of low cost and wide availability, high purity, low toxicity and high biodegradability, as well as being environmentally compatible (XU et al., 2005).

Although natural starch is not a thermoplastic material, it can be processed as conventional polymers after some pre-processing. The starch granules have no thermoplastic character in their natural form unless they are completely or partially destroyed and transformed into amylose / amylopectin semi-crystalline matrices under high temperature and / or pressure and in the presence of plasticizers (JIMENEZ et al., 2012; MENDES et al., 2016; VAN SOEST et al., 1996).

The material is composed by amylose and amylopectin with relative amounts of each component varying according to the source. As an example, corn starch has about 28% amylose, while cassava starch has 17%. The ratio of amylose and amylopectin can determine the film-forming properties, barrier properties and mechanical properties, as well as the most suitable processing condition. In general, higher amounts of amylose may improve the mentioned characteristics (FORSSELL et al., 2002; RAQUEZ et al., 2008; RINDLAVA et al., 1997).

Starch particles have already been reported in literature as paper coatings. The modulus of elasticity (MOE) of the coated papers decrease with increasing the content of binders as latex, but increases when using a solid binder as a starch with a basis paper of 58g/m² (GUYOT et al., 1992).

The application of the starch layers alternated with bleached and unbleached CNFs could indicate a positive factor in mechanical terms, justifying the necessity of this study.

3.CONCLUSION

In this work, natural fibers of the Amazonian paricá were alkaline and alkaline + bleached treated to obtain CNFs in both conditions and characterized. The results of the chemical composition demonstrate that the alkali treatment did not remove lignin. However, it decreased considerably the amount of hemicelluloses from paricá. The CNFs were successfully produced from both types of treated fibers. In thermal degradation of alkaline + bleached nanofibrils, higher initial temperature of degradation was observed, while the alkaline treated ones take more time to reach the maximum degradation. SEM analysis confirmed that the diameter of CNFs were mainly in the range of 23 - 31 nm. FTIR measurements support the results of chemical characterization of the fibers, showing the decrease of hemicelluloses and lignin content along the treatments. The mechanical properties showed extreme superiority for films produced with alkaline + bleached CNFs, (MOE about 320% higher). The films from alkaline + bleached CNFs obtained satisfactory mechanical results when compared to films from commercial pulps. In the second article, papers W&P were coated with the same CNFs used for the films production (after alkaline treatment and bleaching) besides layers of gelatinized starch. The gelatinized starch layers resulted in a higher density increase to the papers. The degradation in water was low for all types of covered papers. The deposition of 5 nanofibrils layers, of both types, did not result in expressive gain in terms of maximum force. The use of the gelatinized starch for the fixation of the layers of alkaline treated nanofibrils resulted in papers with greater elongation before the break. The samples produced with one layer of bleached nanofibrils and one layer of gelatinized starch obtained a tensile strength approximately 20% greater than the papers with grammage 75 $g.m^{-2}$. The present work contributes with important information on surface-coated papers using cellulose nanofibrils, as well as the use of new species of raw material for production of CNFs films. Further development of this approach could improve the performance of the films and papers and for the development of new and engineered cellulose-based materials for diverse applications, as packaging.

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SECOND PART – MANUSCRIPTS

MANUSCRIPT 1

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How the surface wettability and modulus of elasticity of the Amazonian paricá nanofibrils films are affected by the chemical changes of the natural fibers

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Abstract: The use of natural resources for the production of nanostructured cellulosic films of high quality could reduce pollution and raw material costs for cellulose industry. This work provides innovative information about the use of Amazonian species not explored in studies involving the production of nanostructured films, as well as the evaluation of important characteristics that may be decisive for the destination of the product. The aim of this study was to modify *Schizolobium parahyba* var. amazonicum (paricá) waste fibers through alkaline (NaOH) and bleaching ($NaClO_2$) treatments for cellulose nanofibrils (CNFs) production and evaluate the characteristics of the nanofibrils and the surface as well as the mechanical resistance of the films obtained. The alkaline treatment was carried out with sodium hydroxide (5% NaOH solution (w/v); 2 h), while the bleaching was performed using sodium chlorite and glacial acetic acid (1.5 g $NaClO_2$; 10 drops of glacial acetic acid; 1 h). The treatments were performed in sequence, producing nanofibrils after alkaline treatment and after the bleaching. Lignin content did not change with the alkaline treatment, but it significantly decreased with bleaching (from 26.1 to 6.8%). Hemicelluloses content decreased with the sequence of treatments. FTIR results showed that the mechanical defibrillation caused disruption of the fiber bonds. The temperature of thermal degradation observed in DTG analysis increased from the natural fibers (243°C) to alkaline + bleached fibers (255°C).

The defibrillation process led to higher thermal stability of the alkaline + bleached nanofibrils in comparison to fibers. Moreover, films were prepared from the obtained CNFs and evaluated by the mechanical properties and surface contact angle. The mechanical properties showed values of 6.93 ± 0.18 GPa for modulus of elasticity (MOE) for the films produced from material which was submitted to the bleaching treatment. The results highlighted a more hydrophobic surface of the film produced with the CNFs generated from the bleached fibers. The results of mechanical properties showed the superiority of the films produced from the alkaline + bleached fibers.

Keywords: Nanostructured films. paricá nanofibrils. mechanical properties. surface properties. cellulose

Introduction

The annual biomass production of cellulose in nature is about 1 trillion tons, making it a virtually inexhaustible source of raw material that can be obtained from woody and non-woody feedstock, since cellulose is the main component of the vegetal cell wall (Ioelovich 2008; Eichhorn et al. 2010). The vegetables fibers are represented by a great diversity of species, since lignocellulosic wastes such as rice husk (Daza Serna et al. 2016), coffee grounds (Huang et al. 2016), hemp stalk (Kim et al. 2016), coconut coir (Subhedar et al. 2017), and bamboo leaves (Huang et al. 2016), up to wood like rubber wood (Khan et al. 2018), eucalyptus (Fonseca et al. 2016), pine (Viana 2013), spruce (Yu et al. 2017), Japanese cedar (Muranaka et al. 2017), among others.

A prior knowledge of the morphology and thermal characteristics of the wood fibers is essential for evaluation of their potential for different applications, such as for panels or pulp and paper industry, or for obtainment of derivative products with new and unique properties, as observed for cellulose nanofibrils (CNFs). The term “micro/nanofibrils” refers to long, flexible micro and nanofibrils consisting of alternating crystalline and amorphous cellulose chains (Siqueira et al. 2009). The films produced from the CNFs can be applied to the production of paper and packaging materials (Mirmehdi et al. 2017). Other applications include flexible organic papers such as electronic papers (*e-papers*) (Zhang et al. 2012), paper coating (Nygårds 2011), and transparent substrates for solar cells (Eichhorn et al. 2010).

Due to the complex chemical composition of wood fibers, chemical treatments have been widely studied and used in order to improve the defibrillation process. Chemical modification can generally be classified as either cell wall modification, or filling of large cell cavities, or a combination of both (Xie et al. 2013). Among these treatments, the most common are alkaline (Bertoti et al. 2009), acid (Mariano et al. 2016), TEMPO oxidation

(Rohaizu and Wanrosli 2017), silane groups (Thakur et al. 2014) and peroxide treatment (Marinelli et al. 2008; Bonelli et al. 2005).

The alkaline treatment is probably the most popular process for modifying natural fibers. This treatment has been used to remove natural impurities, and obtain fibers with low hemicellulose and lignin content (Moubarik et al. 2013). Its application to fibers causes the solubilization of hemicellulose and lignin, and changes the crystal structure of the cellulose fibers (Ichazo et al. 2001; Joseph et al. 1996; Li et al. 2007). It depends on several factors such as fiber origin, treatments and combinations among them, carboxyl contents, yield etc. The biggest hemicellulose content facilitates fibrillation, since this high content inhibits the coalescence between microfibrils. Besides alkali treatment, acid chlorite (acetic acid and sodium chlorite) treatments that employ oxidizing agent chlorine dioxide for bleaching are effective for delignification (Agarwal et al. 2013; Hubbell and Ragauskas 2010; Moubarik et al. 2013). The delignification treatment with sodium chloride ($NaClO_2$) has been studied for removing of lignin (Viana 2013; Bouiri and Amrani 2010). The removal of lignin of the wood cell wall is cited as an important initial step for separation of fibers and obtainment of cellulose nanofibrils (CNFs), which facilitates the fibrillation and reduces the energy spent during the mechanical defibrillation process (Abe et al. 2007; Iwamoto et al. 2008; Morán et al. 2008). The high energy consumption may be due to the complex multilayered structure of the plant fibers and interfibrillar hydrogen bonds.

Previous studies have verified the effect of chemical treatments on several lignocellulosic waste materials for subsequent defibrillation, such as mercerization and bleaching of energycane bagasse (Yue et al. 2015), alkaline and silane treatments of sisal fibers (Orue et al. 2016), alkaline sulfite and methanol treatments of bamboo (*Gigantochloa scortechinii)* (Moradbak et al. 2018), oxidative bleaching of quila (*Chusquea quila*) (Oliveira et al. 2018), TEMPO-mediated oxidation of basts of hemp and flax (Panthapulakkal and Sain 2013; Puangsin et al. 2013), alkaline treatment of banana rachis (Zuluaga et al. 2009; Velásquez-Cock et al. 2016) and alkali treatment + bleaching + mild acid hydrolysis of sunflower stalks (Fortunati et al. 2016). Regarding woody fibers, the literature reports some studies in which alkaline treatments followed by bleaching were performed involving species such as the traditional pine (Viana 2013), eucalyptus (Fonseca et al. 2016) and other non-conventional species like freijó (*Cordia goeldiana*) and amapá (*Brosimum parinarioides*) (Bufalino et al. 2015).

The variety of tree species with potential for CNF production is very huge in Brazilian territory, mainly in Amazonian forest, revealing an extremely diverse fauna and flora. From its wide range of arboreal species, just a small part thereof was deeply characterized and had their potential uses investigated. The knowledge of the chemical treatments of Amazonian wood species that enable the production of CNFs is still limited. Among the Amazonian species, the paricá (*Schizolobium parahyba var. amazonicum*) is one of the most interesting due to its fast growth and high wood productivity per hectare (30 – 35 m^3/year), being planted on large scale in several Brazilian states (Terezo 2010). The wood of this species shows low to moderate density, easy workability and susceptibility to biological attack (Carvalho 2007). The main application of this wood is in the civil construction, which uses the plywood produced from it as a structural element (Almeida et al. 2013). Additionally, this wood is used in lamination industries, generating high quantities of wood wastes that are underexplored.

This study aimed to evaluate the effect of the treatment sequences: alkaline treatment with NaOH and bleaching with $NaClO_2$ and glacial acetic acid on the chemical, morphological and thermal properties of Amazonian paricá wood fibers and, subsequently evaluate the CNFs properties and the surface wettability and mechanical resistance of the films produced from them.

Material and Methods

Harvesting and wood sampling

A certified Amazonian hardwood species was used in this work, namely *Schizolobium parahyba* var. *amazonicum* (paricá). Five year-old trees were harvested from the planted forest area that belongs to Concrem Group, located in the district of Dom Eliseu, PA, Brazil. The logs were reduced to smaller chips, which were subsequently milled in a DPM-4 (Nogueira®) hammer mill, containing a 6.1 mm aperture sieve. For improving the efficiency of the chemical pre-treatments, the particles were sieved for selection of the fraction that passed through 60 mesh (0.250 mm), giving the starting fiber a high surface area.

Sodium chlorite (80%, RT) and acetic acid (glacial, 99.85%) were purchased from Sigma–Aldrich Inc. Sodium hydroxide (98.9%, ACS grade) was obtained from Êxodo Científica Inc. (Hortolândia, SP, Brazil) and it was dissolved in distilled water to prepare 5 wt% solutions. All reagents used were of analytical grade. Distilled water was used for the preparation of the solutions.

Chemical treatments of the fibers (alkaline treatment and bleaching)

Alkali-treatment was performed following the adapted methodology described by Yue et al. (2015). For each 5 g of paricá fibers, 100 mL of 5% NaOH solution (w/v) was used. The fibers were treated in a water bath at 80°C under agitation of 650 rpm during 2 h. After the treatment, the samples were washed with distilled water and subsequently dried for 24h in a recirculating air oven (50 °C).

The bleaching procedure was adapted from Wise et al. (1946). For each 10 g of fibers, 1.5 g of sodium chlorite ($NaClO_2$) and 10 drops of glacial acetic acid were added to 160 mL of distilled water. The material was kept in a water bath at 80°C for 1 h. Three stages of delignification were performed such that after each stage the material was washed with abundant water for removal of any $NaClO_2$ residue.

Chemical composition of the fibers

The determination of the extractives content and mineral/ash content followed the NBR 14853 (ABNT 2010b) and NBR 13999 (ABNT 2003) standards, respectively. The contents of cellulose, hemicelluloses and lignin of the natural fibers (retained between the 40 and 60 mesh sieve) were obtained using samples after extractives removal. The insoluble lignin content was determined according to the procedures described in NBR 7989 (ABNT 2010a). The holocellulose content (based on extractives-free mass) was determined according to Browning (1963). The cellulose content was obtained following the methodology proposed by Kennedy et al. (1987). The weight difference between the content of holocellulose and cellulose values provide the hemicelluloses content. The mean values of each component were the result of 4 replicates.

Production of the CNFs

120 g of the alkaline and alkaline + bleached fibers were immersed in 6000 mL of distilled water; i.e. at a concentration of 2% (w/w based on dried mass of the fibers). The fibers were then submitted to nanofibrillation through a SuperMasscolloider grinder (Masuko Sangyo MKCA6-3) using an opening between disks of 0.01 mm and grindstone rotation of 1600 rpm, following procedures reported in previous works (Bufalino et al. 2015; Guimarães Júnior et al. 2015; Fonseca et al. 2016). The films were produced from the suspension obtained after 40 passes through the SuperMasscolloider. After 30 and 40 passages, an aliquot was taken for microscopy analyses.

Fibers and nanofibrils measurements

The diameters of the natural fibers and treated fibers, as well as the nanofibrils generated could be obtained by manipulating the software *ImageJ*. The diameters were obtained from the mean value of 20 measurements for each material.

Fourier transformed infrared spectrometry (FTIR)

FTIR spectra of dried samples were measured on a spectrometer Shimadzu (IRAffinity-1) with an attenuated total transmittance mode. The samples were incorporated in KBr at the ratio of 1:100 (w:w) according to the procedures described in Bartz et al. (2012), and crushed and homogenized. The mixture was compressed to form KBr tablets suitable for scanning. Each sample was scanned in the range from 4000 to 500 cm^{-1} with a resolution of 2 cm^{-1}.

Thermal degradation

A representative compound sample of the paricá fibers under various conditions and retained on the 270 mesh (0.037 mm) sieve was prepared for the thermogravimetric analysis (TGA). The thermal degradation of paricá natural fibers, alkaline treated and alkaline + bleached was executed in a TGA Q500 (TA Instruments ®) thermal analyzer. Two replicates were used. Samples of about 4 mg were heated at 10°C/min. The analysis was performed under synthetic air atmosphere (80% N_2 and 20% O_2) from room temperature up to 600°C. The gas flow used was 100 $mL.min^{-1}$. The temperature of initial degradation (T*onset*) was obtained by the projection of the segments before (horizontal) and after (vertical) the deflection point of the TG curves (Figure 1). Similarly, the percentage of residues was obtained by the final point of the curve. The temperature of maximum degradation (T*max*) was obtained through the peaks observed on the DTG curves. According to Zhao et al. (2013), practical processing and application of CNFs are usually performed in synthetic air atmosphere. Therefore, the presented data under such conditions are more reliable for practical purposes.

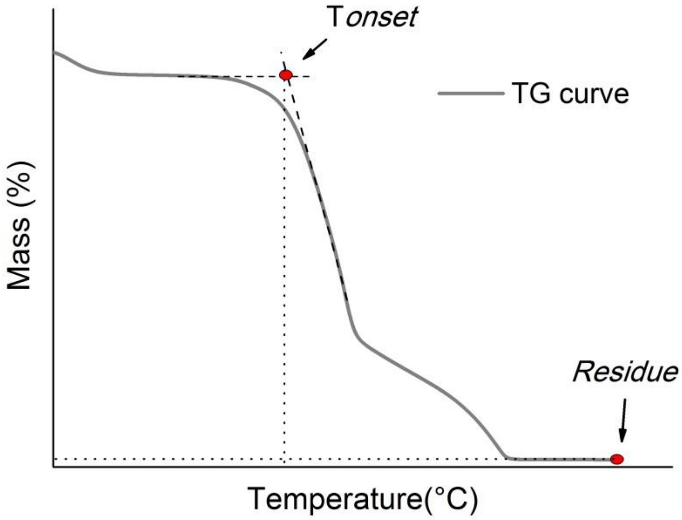

Fig. 1 Scheme for determination of the temperature of initial degradation (T*onset*) and percentage of residues

Scanning electron microscopy (SEM)

The micrographs of natural and treated fibers were obtained from a scanning electron microscope Zeiss Model DMS 940, with tungsten filament operating at 15 kV. The samples were placed in a sample holder (*stubs*) and gold-coated. The micrographs of nanofibrils were performed in a JSM-6701F (JEOL®) Field Emission Guns microscope (FEG), which allows to obtain images with better resolution in comparison to the traditional scanning electron microscope. The handling of the equipment was carried out at 2kV. The nanofibrils were sonicated with ultrasonic tip and deposited in silicon plates.

Preparation of CNF films

The CNF films were prepared by casting, using 40 mL suspensions (1.5% w/v) in acrylic petri dishes with 15 cm diameter. One film of each CNF condition was produced and then they were oven-dried at 50 ± 5°C for around 24 h. A Mitutoyo micrometer was used to obtain the thickness and a digital caliper to obtain the diameter. The mass was obtained at a precision of 0.1 mg. The apparent density of the films was calculated by dividing the mass by the volume of the samples. The thickness obtained for the films produced from the alkaline treated CNF alkaline + bleached CNF (Figure 2) was 105.0 ± 8.0 µm and 50.0 ± 5.0 µm, respectively.

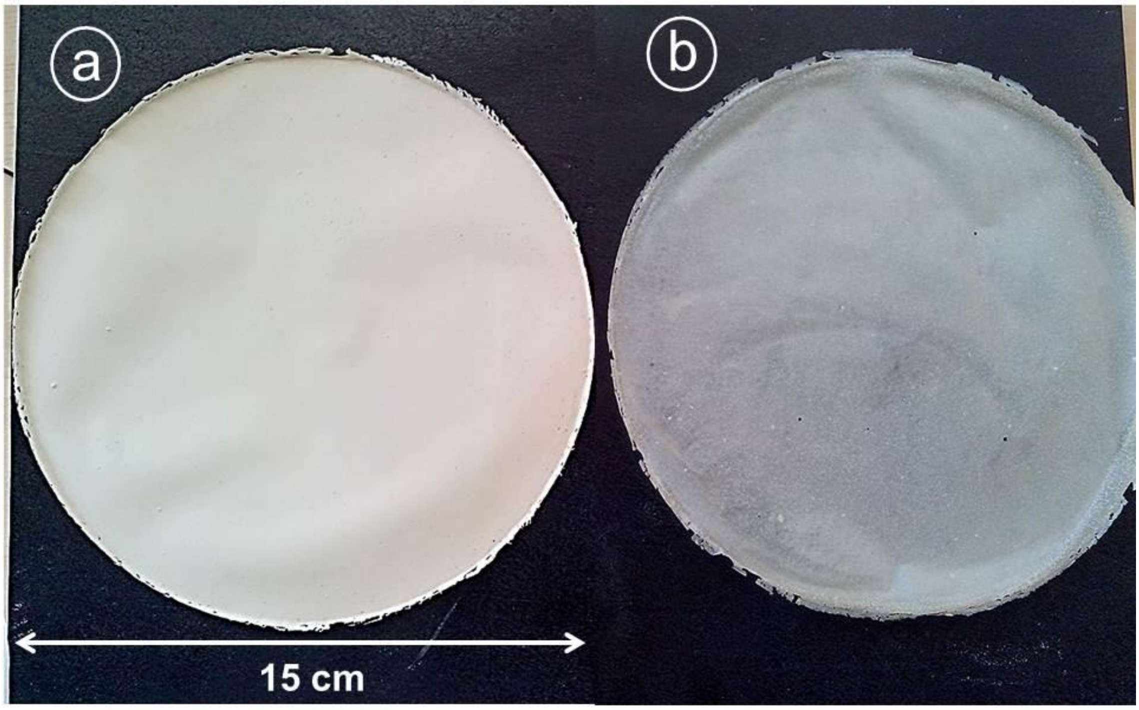

Fig. 2 Films produced from the: **a)** alkaline treated CNF and **b)** alkaline + bleached CNF

Surface wettability

The surface wettability was evaluated using a Kruss Drop Shape Analyzer – DSA25 (Hamburg, Germany). A drop of water was deposited over the sample surface through a syringe. The drop image was captured by a video camera and an image analysis system that determine the contact angle between the water drop and the film surface, which were measured at room temperature (20°C). For each CNFs film, three angle readings were performed after the drop stabilization (2.5 s).

Mechanical strength

The mechanical properties of the dried CNF films were evaluated by the tensile test following the procedures of ASTM D828-16 (2016). The samples were obtained with dimensions of 10.0 x 2.5 cm. Each mean result of the mechanical test was obtained from the average of 5 samples. The modulus of elasticity (MOE) or Young's modulus was calculated by Equation 1:

$$E = \frac{\sigma}{\varepsilon} \quad (1)$$

where E is the MOE (Pa), σ is the applied tensile (Pa), and $\mathcal{E}$ is the longitudinal deformation of the specimen (dimensionless). The tensile modulus was obtained by Equation 2:

$$\sigma_b = \frac{F}{A} \quad (2)$$

where σ_b is the tensile at break (MPa), F is the force applied to the sample break (N); A is the cross-sectional area of the sample (mm²). The test was proceeded using a machine Zwick/Roell - GmbH & Co (Einsingen, Germany) with a tensile speed of 10 mm/min.

Results and discussion

The sequence of treatments with chemical reagents for the alkaline and bleaching treatments caused considerable changes in the contents of chemical components of the natural fibers (Table 1). It is noted that the alkaline treatment considerably reduced the amount of paricá extractives (from 5.5 to 2.2%) and hemicelluloses (from 30.4 to 11.5%). Both are common treatments used in the pulp and paper industries (Leiviskä and Rämö 2008).

Table 1 Average and standard deviation values of the chemical constitution of the fibers in the different conditions.

Component	Natural fibers	Alkali treated	Alkali + bleached
		--------------------------------%--------------------------------	
Extractives*	5.5 ± 0.1***	2.2 ± 0.5	-
Ashes*	0.6 ± 0.1	3.0 ± 0.4	4.7 ± 0.1
Insoluble lignin**	27.5 ± 1.3	26.1 ± 0.5	6.8 ± 0.7
Holocellulose**	73.5 ± 1.8	72.7 ± 2.2	88.3 ± 1.9
Cellulose**	43.1 ± 0.5	61.2 ± 0.4	75.0 ± 0.5
Hemicelluloses**	30.4 ± 0.5	11.5 ± 0.4	13.3 ± 0.5

*Based on total wood mass; ** Based on extractive-free mass of wood; ***Standard deviation

The extractives are colloidal substances that consist of fatty and resin acids, triglycerides and sterols (Featherstone et al. 2006; Qin et al. 2003; Sundberg et al. 2009). Triglycerides are saponified during alkaline treatment, resulting in the release of free fatty acids and glycerol (Leiviskä et al. 2009). The removal of lipophilic extractives during bleaching can be mainly achieved by two mechanisms: (i) the first one includes the dispersion and desorption of pulp lipids; and (ii) the second mechanism includes the chemical degradation/modification of lipids, mainly by oxidative action of bleaching chemicals resulting in more hydrophilic compounds, which may be subsequently removed during washing (Holmbom 2000). The presence of the extractives in the alkaline + bleached fibers was not detected. With the drastic decrease in hemicelluloses content provided by alkaline treatment, consequently a concentration of the cellulose content occurred. The extraction with NaOH reduces the hemicellulose content to about 10–15%, depending on the NaOH concentration and the fiber feedstock (Chaker et al. 2013). Although hemicelluloses are mutually adhered with cellulose nanofibrils by hydrogen bonds and Van der Waals forces, most of them could be dissolved in the alkaline solutions under certain conditions (Wigell et al. 2007).

Low levels of ashes were observed for the natural fibers and alkaline + bleached fibers, while ashes were significantly higher for alkali-treated fibers. This fact may have occurred due to residues of the NaOH used in the alkaline treatment and the extractives removal.

The lignin content practically did not change with the alkaline treatment. It is generally expected that the alkali can penetrate the inter-fibril region and cleave the ether bonds between lignin and hemicellulose (Sun et al. 2000; Mwaikambo and Ansell 2002). However, the low concentration of the alkali solution did not cause lignin removal. Another factor such as the non-application of pressure may have contributed to the non-removal of lignin from the fibers. Chirayil et al. (2014) and Yue et al. (2015) achieved a good quality of delignification when performing alkaline treatment in lignocellulosic fibers. This fact was possible due to the adoption of different parameters such as higher temperature and reagent concentration in relation to this study. Bleaching decreased the lignin content (from 26.1 to 6.8%). Bleaching meant a significant concentration of cellulose content due to the drastic reduction of the lignin. The hemicelluloses content practically did not change. Chlorinated compounds are very selective bleaching reagent, preferentially oxidizing lignin in the presence of carbohydrates (Douglas et al. 2006). Because the different units of lignin are linked by a series of ether and carbon-carbon linkages, lignin presents considerable resistance to chemical degradation (Chen et al. 2001). Although the bleaching removes the amorphous components of the fiber such as hemicellulose and lignin, the amorphous part of the cellulose remains in the fiber, which is removed only by acid hydrolysis, enzymatic, or bacterial processes (Correia et al. 2016).

Figure 3 depicts the FTIR spectroscopy of the fibers and CNFs under various conditions. The peak between 3660 and 3098 cm^{-1} observed in the spectra corresponds to the hydroxyl groups (Sena Neto et al. 2013), which was more intense in the CNFs spectra. This was assumed to be due to the higher surface area of the CNFs than the natural and pre-treated fibers, suggesting that greater amount of free hydroxyl groups was exposed on cellulose (Abraham et al. 2011). A peak at 2900 cm^{-1} was also identified, which is attributed to the asymmetric stretching of C-H and C-H_2 (Sgriccia et al. 2008; Correa, 2010) and is characteristic of organic materials such as cellulose. This peak showed a narrowed aspect for alkaline + bleached fibers as the content of cellulose was higher as also observed for the CNFs. This fact may have occurred due to the higher exposure of the chemical groups, which constitute the cellulose caused by the mechanical defibrillation.

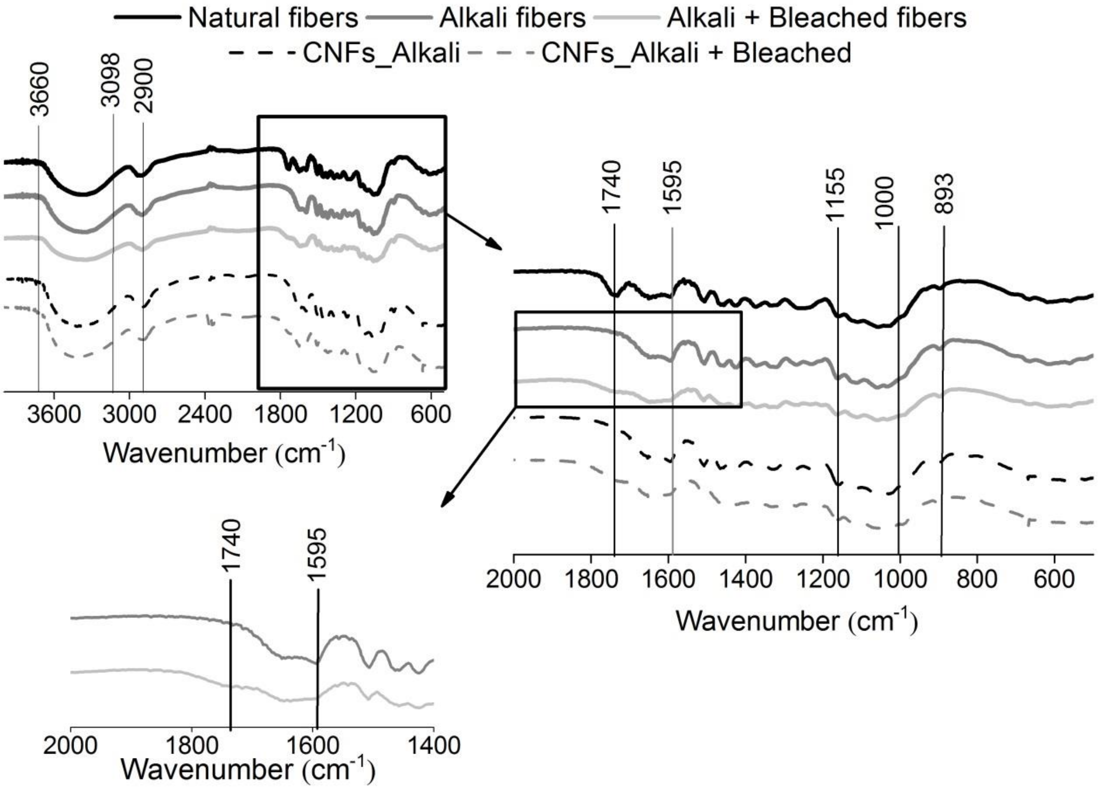

Fig. 3 Typical FTIR spectra of the paricá fibers and CNFs under different conditions

The peak around 1740 cm^{-1} for the natural fibers samples corresponds to the acetyl and uronic ester groups of hemicelluloses and the ester linkage of carboxylic group of the ferulic and p-coumaric acids of lignin (Chirayil et al. 2014). The existence of this peak was also reported by other researchers (Alemdar and Sain, 2008; Sun et al. 2005). This peak was not detected in the alkaline treated fibers, however it appeared in the alkaline + bleached ones, confirming the presence of the ester groups.

The deformation of C=C lignin groups are represented by peaks at 1595 cm^{-1} (Garside and Wyeth 2003). For paricá alkaline + bleached fibers, this peak was less intense in comparison to the natural fibers and alkaline treated fibers. Those results agree with the chemical analysis, which still detected the presence of residual lignin in the alkaline + bleached fibers. CNFs also presented this peak. The peaks at around 1155 cm^{-1}, which refers to C–O vibration and 1000 cm^{-1}, which corresponds to C–O valence vibration at C(6) (Tonoli et al. 2016), increased for alkaline treated and alkaline + bleached fibers and was observed in the same form for both types of CNFs. The peak near to 893 cm^{-1} is due to the β-glycosidic linkages of glucose ring of cellulose (Chirayil et al. 2014). The content of hemicelluloses in alkaline treated fibers and alkaline + bleached fibers could be a factor that provides better mechanical defibrillation. According to Chaker et al. (2013), removing hemicelluloses, the microfibrils tend to approach, favoring their strong interaction through hydrogen bonding, thus rendering the fibers harder to defibrillate. The treated fibers exhibited a higher temperature of initial degradation (T*onset*) in comparison to the natural fibers (Figure 4).

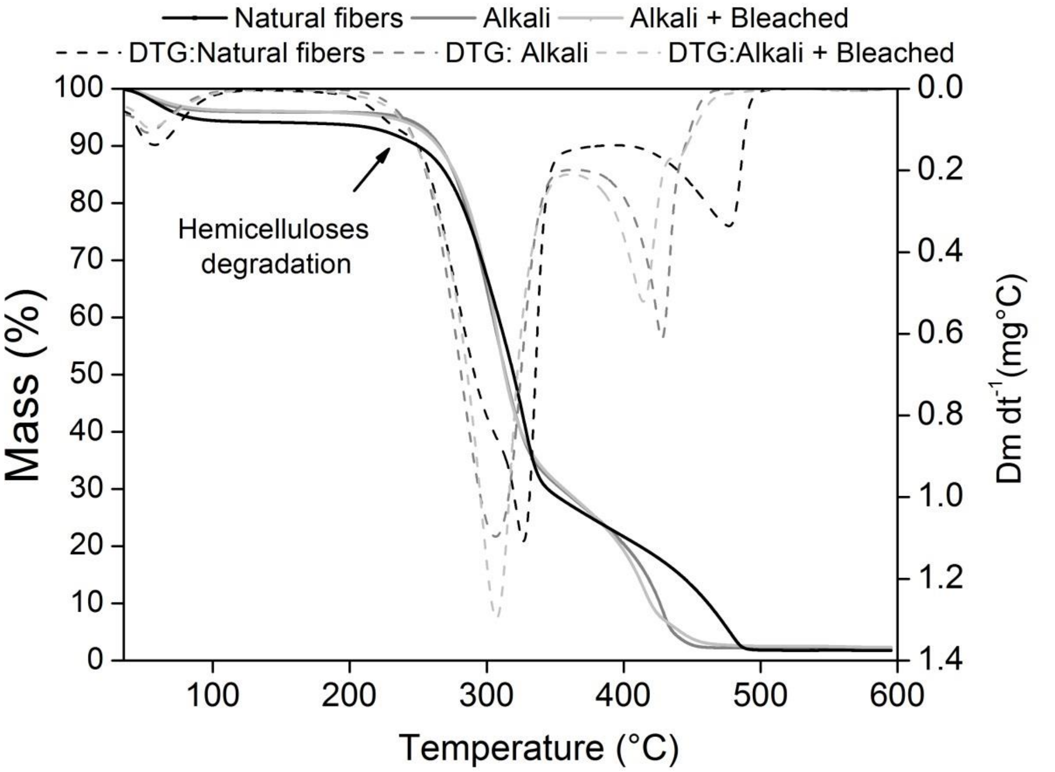

Fig. 4 Typical TGA and DTG curves of the natural fibers, alkaline treated and alkaline + bleached fibers

This fact may be due to the content decrease of non-cellulosic components, mainly hemicelluloses, provided by the treatments (see Table 1). In the alkaline pre-extraction process, the ester linkages between polysaccharides and lignin were hydrolyzed (Lehto and Alén 2013), resulting in the dissolution of hemicelluloses. Hemicelluloses are partially or completely pre-extracted under alkaline conditions prior to the pulping stages (Bai et al. 2012; Hamzeh et al. 2013; Liu et al. 2013). The degradation of the hemicelluloses can be noticed due to the formation of a slight peak at around 230°C in the derivative curves of natural fibers. The literature reports that the thermal degradation behavior of lignocellulosic materials is related to the chemical composition (Fisher et al. 2002).

The first peak occurs due to the release of volatiles and the sample ignition by pyrolysis, while the second peak means the carbonization of formed charcoal (López-González et al. 2013). The partial removal of lignin caused by bleaching resulted in an anticipation of the second peak of degradation (413°C) observed for alkaline + bleached fibers. In addition, the residue content observed was higher in the treated fibers, which possibly occurred due to the adsorption of chemical products by the fibers. The thermal analysis of CNFs showed a higher T*onset* when compared to the respective original fibers (Figure 5).

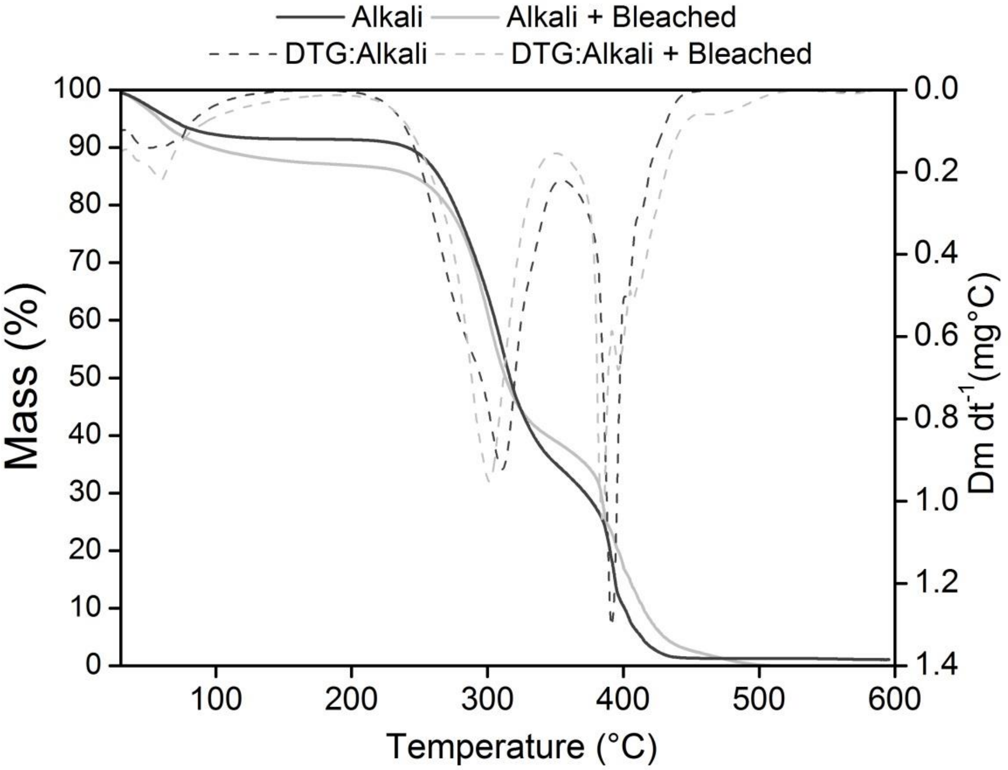

Fig. 5 Typical TGA and DTG curves for the CNFs obtained after alkaline and alkaline + bleaching treatments of the fibers

The alkaline CNFs had an initial degradation at 266°C, reaching the maximum point at 311°C, while the bleached material showed a lower interval of temperature until the maximum degradation (274 – 300°C) (Table 2). The result indicates that alkaline CNFs showed a slower degradation in comparison to the bleached ones, which was assumed to be due to the lowest amount of lignin in the bleached CNFs. Lignin presents higher thermal stability, because it presents a predominantly aromatic and three-dimensional matrix, consisting of phenylpropane units that give the molecule high resistance to thermal degradation (Sharma et al. 2004; Gani and Naruse, 2007; Yang et al. 2007; Nakamura et al. 2008; Burhenne et al. 2013).

Table 2 Thermal characteristics of the paricá fibers and resultant CNFs.

	Material	T*onset* (°C)	T*max* (°C)	Residue (%)
Fibers	Natural	243	327	1.8
	Alkali-treated	255	306	2.1
	Alkali + Bleached	255	307	2.3

CNFs from	Alkali-treated fibers	266	311	1.2
	Alkali + Bleached fibers	274	300	0.0

T*onset* = Temperature of initial degradation; T*max* = Temperature of maximum degradation

The removal of non-cellulosic components may have led to a closer approximation of cellulose nanofibrils. Therefore, when one nanofibril starts to degrade, it can induce the thermal degradation of the surrounding nanofibrils (Quiévy et al. 2010). Abraham et al. (2011) reported a higher thermal stability for the extracted CNFs when compared with the natural fibers. Acordingly, Zhao et al. (2013) cited that the utilization of raw plant fibers as starting materials which contained a considerable amount of matrix substances with lower thermal stability, such as hemicelluloses, may generate CNFs with higher thermal stability. It is possible to observe the difference between the defibrillation levels from 20 to 40 cycles (Figure 6).

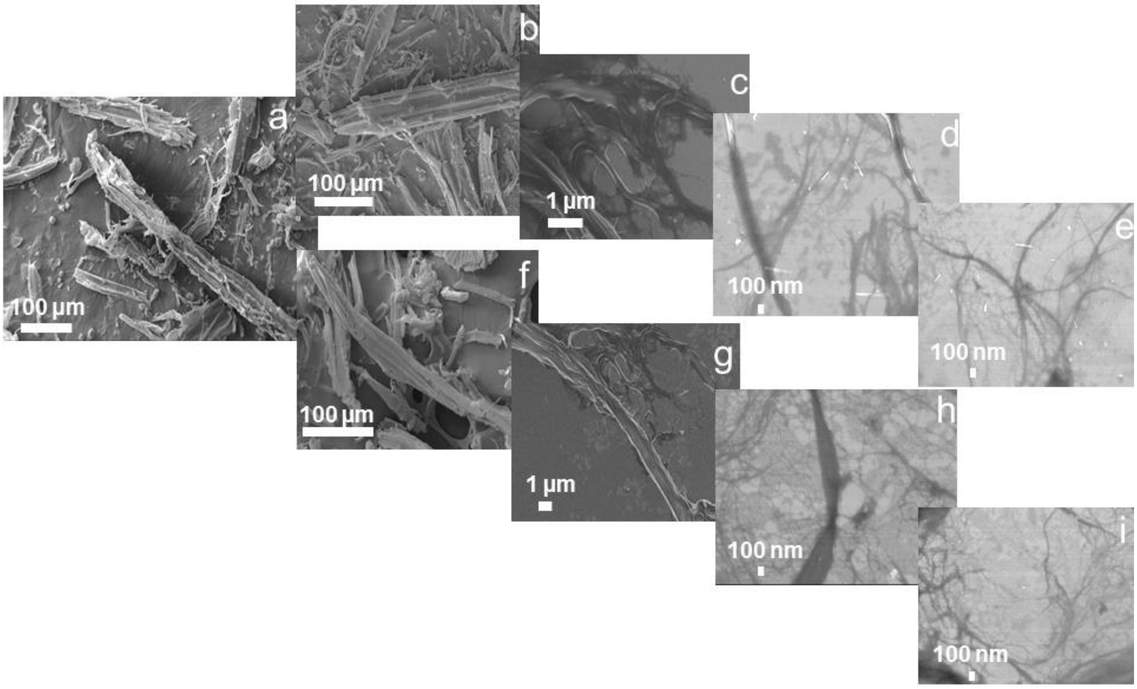

Fig. 6 Typical scanning electron microscopy (SEM) micrographs of paricá fibers and CNFs: **a)** corresponds to the natural fibers; **b)** corresponds to the alkaline treated fiber; **c)**, **d)** and **e)** correspond to the CNFs obtained from alkaline treated fibers after 20, 30 and 40 passages through the SuperMasscolloider, respectively; **f)** corresponds to alkaline + bleached fiber; **g)**, **h)** and **i)** correspond to CNFs obtained from alkaline + bleached fibers after 20, 30 and 40 passages through the SuperMasscolloider, respectively

The micrographs showed that after 20 passages through the SuperMasscolloider, the structures were still in microscale (Fig. 6c and 6g). However, after 30 passages through the defibrillator, structures were mostly in nanoscale, which clearly supports the isolation of CNFs. After 40 passages, all the structures showed nanoscale dimensions (Fig. 6e and 6i). The literature reports on nanofibrils production from bleached rice straw and bagasse pulps by mechanical defibrillation where 30 passages were enough for their generation (Hassan et al. 2012). The diameter of the structures indicates that the mechanical defibrillation generated materials in nanoscale (Figure 7).

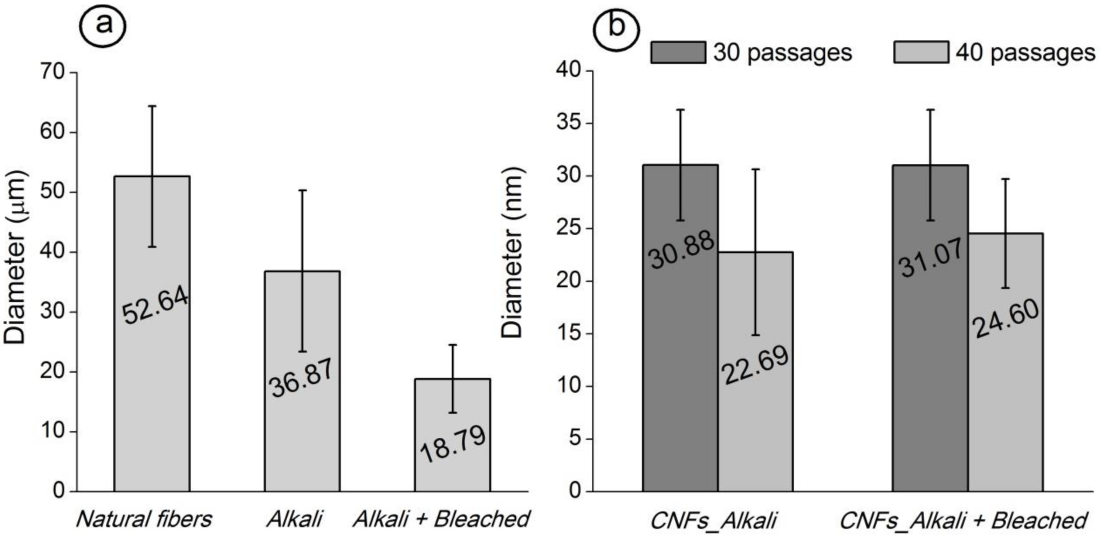

Fig. 7 Average of the diameters obtained; **a)** diameters of natural and treated fibers; **b)** diameters of the CNFs at different conditions

It is possible to notice that the alkaline and bleaching reactions changed the fibers morphology. After bleaching treatment, fiber bundles became defibrillated and the fiber diameter decreased. This decrease is due to the removal of binding material by chemical treatment, thus enabling the fibers to separate into an individual form (Chirayil et al. 2014). Diameter reduction may be due to the separation of the primary cell wall of the fiber due to the removal of cementing materials like hemicellulose and lignin (Hornsby et al. 1997). The reduction of the fiber diameter after alkaline treatment and bleaching has been similarly reported in literature by Gassan and Bledzki (1999) and Bufalino et al. (2015). Both types of CNFs showed the same range of nanofibril diameter from 30 to 40 passages, which indicates that, when in nanoscale, the chemical composition of the structures has no significant effect on the defibrillation process. The films obtained from both treated CNFs suspension were used for the determination of their surface wettability (Figures 8 and 9).

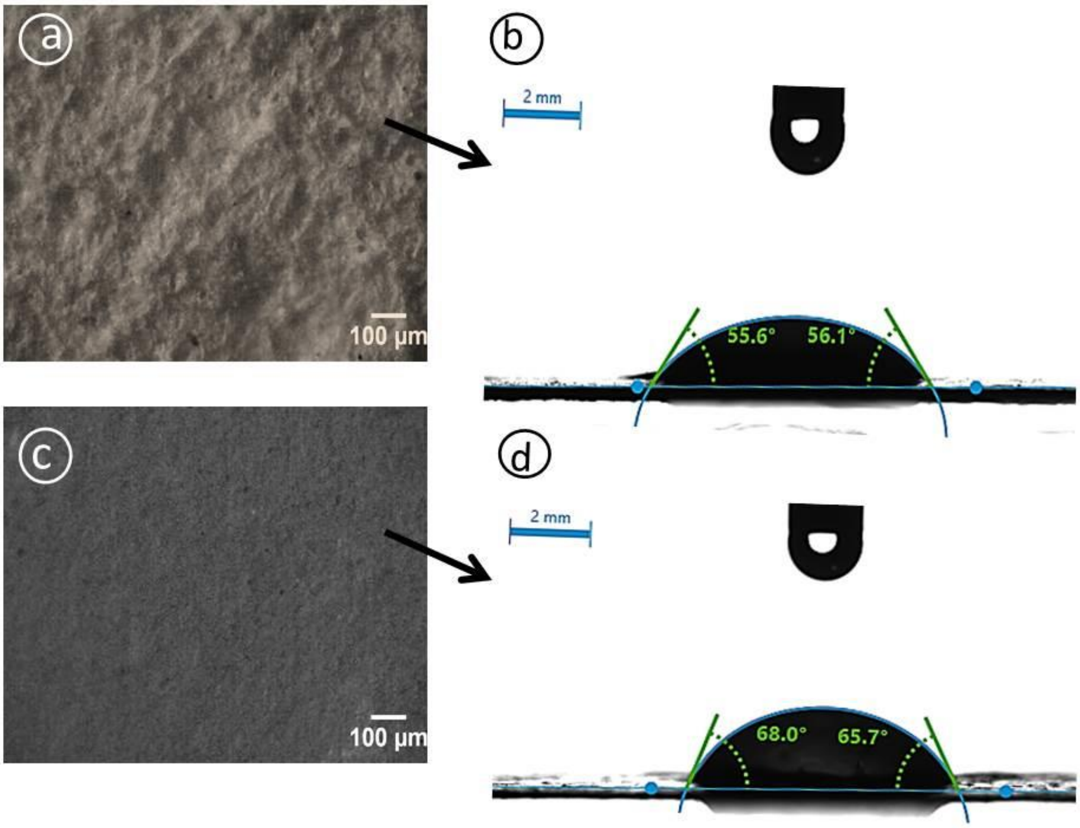

Fig. 8 Surface wettability of the CNF films: **a)** light microscopy image of the CNF film surface produced from alkaline treated fibers; **b)** contact angle of a water drop on the CNF film produced with alkaline treated fibers; **c)** light microscopy image of the CNF film surface produced from alkaline + bleached fibers; **d)** contact angle for the CNF film produced from alkaline + bleached fibers

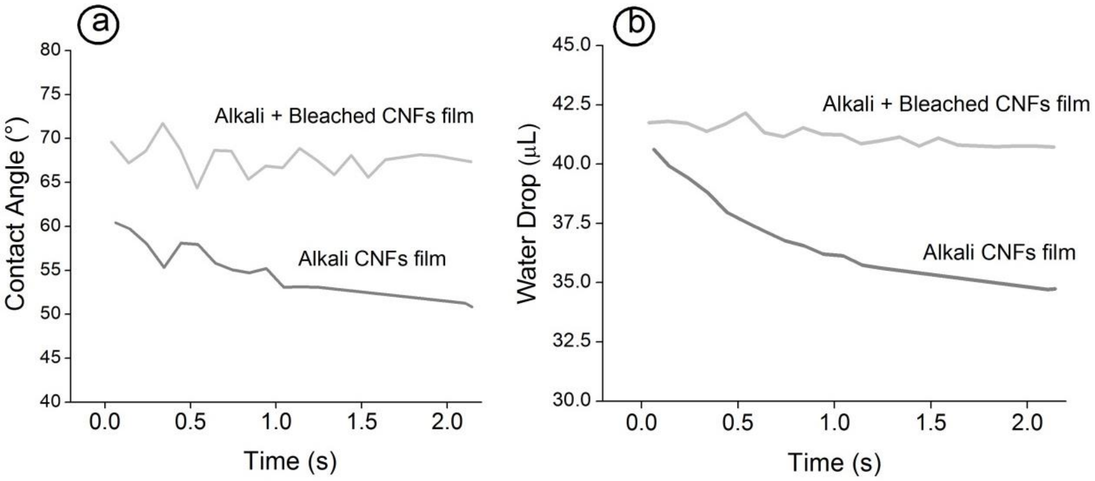

Fig. 9 Parameters of surface wettability of CNF films: **a)** variation of contact angle until drop stabilization; **b)** variation of volume until drop stabilization

It is evident in Fig. 8a that films produced from alkaline treated material showed a grainy surface aspect in comparison to those produced from the alkaline + bleached one. This was assumed to be due to the high amounts of amorphous components as lignin in the origin fibers. The tendency of the amorphous structure to form agglomerates after defibrillation has been reported in literature for films containing lignin. The agglomerates formed by the lignin may hinder the bonds between the chain structures during the formation of the film (Nevárez et al. 2011). This fact provides less cohesion of the structure of the film. As a result, the CFNs films led to lower mean contact angles (55.6 – 56.1°) (Fig. 8b). On the other hand, the films produced from alkaline + bleached fibers and CNFs showed a tightly compacted surface, probably due to the better arrangement of the nanostructures. The parameters of surface wettability support the results obtained for mean contact angle. It can be noted a decrease in contact angle values and in water drop volume for alkali CNFs film, while these parameters for alkali + bleached CNFs film showing an oscillation, however practically did not decrease. After 2.5 s, the contact angle and water drop volume showed a tendency of stabilization for both types of film. The typical tensile-elongation curves of these films highlight the superiority in tensile strength of the alkali + bleached films when compared to the alkali CNFs ones (Figure 10).

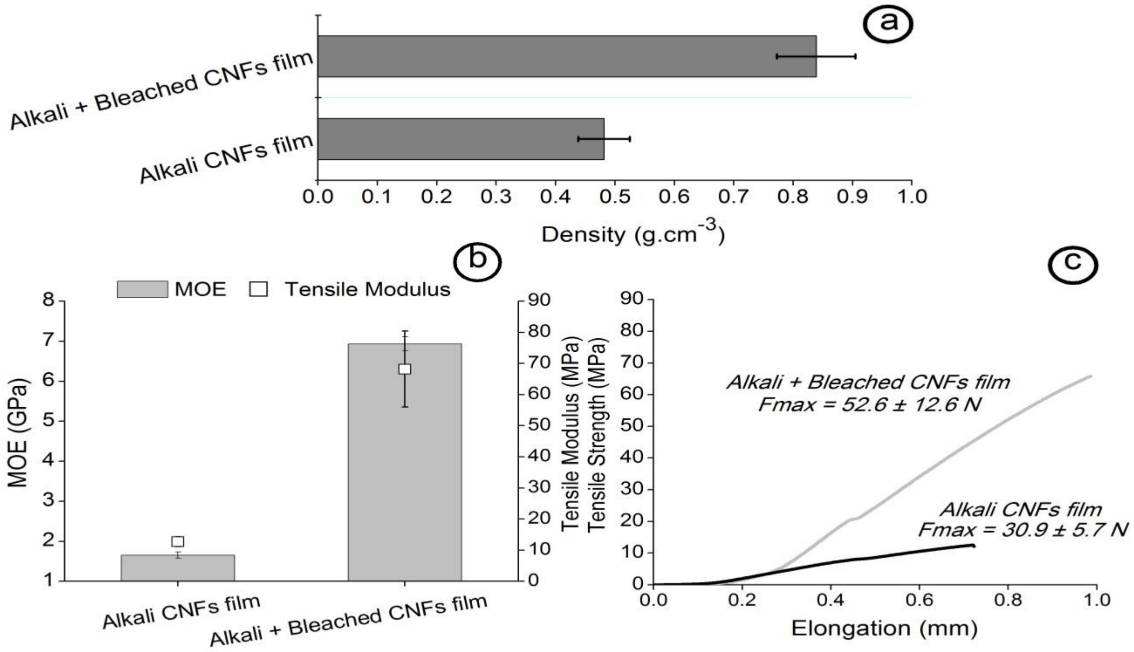

Fig. 10 Density and mechanical properties of the CNFs film: **a)** Density of the CNFs film; **b)** MOE and Tensile Modulus of the CNFs film; **c)** elongation behavior with increasing force

Notably, the increase in tensile strength with chemical yield is consistent with the increased compaction (increased density) of alkaline + bleached CNFs due to the increased collapsibility and bonding capacity of the fibers. The numerous hydroxyl groups on the nanofibrils surface allow facile formation of strong hydrogen bonds that contribute improvements in both strength and toughness to these films. Scatolino et al. (2017a) found better physical and permeability properties for films with higher density, produced with wastes of Amazonian woods. Ferrer et al. (2012) and Scatolino et al. (2017b) cited that the presence of residual lignin does not cause a negative effect on the film properties. It was shown that the presence of residual lignin could benefit some properties of the resulting nanocomposites. However, Nogi et al. (2009) reported that films made from lower lignin contents are more densely packed with much finer fibrils, which could contribute to the higher mechanical properties of the films produced from alkaline + bleached fibers. The results of the mechanical tests showed that the films produced from the material exposed to bleaching obtained higher MOE (6.93 ± 0.18 GPa) and tensile modulus (68.20 ± 12.18 MPa) in comparison to the films produced with material which was submitted only to the alkaline treatment (1.65 ± 0.08 GPa and 12.95 ± 1.66 MPa, respectively). The values obtained in this study can be compared to those found in literature (Table 3).

Table 3 Mechanical properties obtained for the nanocellulose films of this study and presented in literature.

Raw material	MOE (GPa)	Tensile Modulus (MPa)
Alkaline treated CNF from paricá	1.65 ± 0.08	12.75 ± 1.62
Alkaline + bleached CNF from paricá	6.96 ± 0.17	68.20 ± 12.18
Commercial pulp from *Pinus radiata* [a]	7-8	60 to 95
Waste paper pulp [b]	7	140
Commercial pulp from *Spruce* sp. [c]	15.7 – 17.5	100 to 154

[a] Iwamoto et al. (2007)
[b] Wang et al. (2013)
[c] Syverud and Stenius (2009)

The values reached for MOE and tensile modulus in this study, considering the alkaline + bleached CNFs, were close to those obtained for films produced with industrial pine cellulosic pulp. Commercial pulps from *Spruce* sp. produced films with much higher mechanical properties compared to the films of this study and the other commercial pulps. When evaluating nanocellulose films, special attention is required in regards to the raw material. In general, commercial pulps come from a process where there is an effective control to maintain the integrity of the fibers, which are obtained from a pre-selected and homogeneous material. On the other hand, with the use of waste material this level of control becomes difficult, especially with regard to the integrity of the fibers and obtainment of high purity cellulose from the pre-treatments, which implies a challenge for the production of high performance CNF films.

Conclusion

Natural fibers of the Amazonian paricá were alkaline and alkaline + bleached treated to obtain CNFs in both conditions and characterized. The results of the chemical composition demonstrate that the alkali treatment did not remove lignin. However, it decreased considerably the amount of hemicelluloses from paricá. The CNFs were successfully produced from both types of treated fibers. In thermal degradation of alkaline + bleached nanofibrils, higher initial temperature of degradation was observed, while the alkaline treated ones take more time to reach the maximum degradation. SEM analysis confirmed that the diameter of CNFs were mainly in the range of 23 - 31 nm. FTIR measurements support the results of chemical characterization of the fibers, showing the decrease of hemicelluloses and lignin content along the treatments. The mechanical properties showed extreme superiority for films produced with alkaline + bleached nanofibrils, (MOE about 320% higher). The films from alkaline + bleached CNFs obtained satisfactory mechanical results when compared to films from commercial pulps. Further studies on pre-treatments for lignocellulosics may improve the defibrillation efficiency and optimize the process of obtaining the CNFs.

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MANUSCRIPT 2

To be submitted to Cellulose

Alternating of layers of Amazonian paricá cellulose nanofibrils and cassava starch as a coating for Writing & Printing papers: effect on mechanical properties

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Abstract: The study of nanostructured materials from renewable sources can be the "development key" of products which, in addition to good quality, reduce the pollution and costs with raw materials for the industries, such as pulp and paper. The aim of this study was to evaluate the alternation of layers between cassava starch and paricá nanofibrils as coating on the common paper surface and its mechanical characteristics in relation to uncoated Writing & Printing (W&P) papers. The alkaline and bleaching treatments occurred in sequence before the nanofibrils (CNFs) production. The papers were coated by the "dip coating" method, in which one of the faces is passed over the surface of the CNFs suspension. Hemicelluloses content decreased with treatments, mainly due to alkaline treatment. Residual lignin and hemicelluloses were still detected in the alkaline + bleached fibers. The CNFs and the starch presented practically the same temperature of maximum degradation (first peak of the TG analysis). None of the papers was degraded in significant amounts after water immersion. The mechanical properties of the papers coated with the alkaline CNFs showed a declining trend with more layers of coating (from 47.07 to 31.05 MPa). The papers coated with the starch layer were highlighted in mechanical tests for alkaline and alkaline + bleached CNFs. The system of sequential drying of the layers may have caused damage to the structure of the paper fibers bonding, resulting in lower mechanical strength for the coated papers in comparison to the commercial paper. The water degradation of the papers coated was strongly low for all treatments, being the highest degradation value of 4%, obtained for 1 layer of nanofibrils with alkaline treatment. There was significant improvement in the surface wettability properties of the papers in which the gelatinized starch was applied for both types of CNFs, since the drop was kept stabilized for a long time. The use of the gelatinized starch alternating layers with CNFs may be promising for improving the properties of W&P papers.

Keywords: Coated papers. bleaching. hemicelluloses. surface properties. cellulose

Introduction

Paper is the simplest and cheapest way to conserve and transport a product from the place of acquisition to the place of consumption. However, this conservation is limited due to the low moisture resistance and poor mechanical properties. The packaging for food, for example, involves a delicate balance between the need to provide sufficient protection to secure food quality and safety. Thus, the alternative of coatings development on the paper surface appears as a possible alternative for reinforcement and improvement of mechanical properties. Various treatments/barrier coatings have been developed, including surface sizing, extrusion coating, dispersion coating, chemical vapor deposition, etc (Mukhopadhyay et al. 2002; Kuusipalo 2008). In this case, is necessary to choice a method for deposition onto irregular surfaces, as well as to choose a coating material that could allow a homogeneous coating. A good alternative in this intention is the use of a dip-coating technique, which does not require expensive coating equipment, been simple and cheap (Li et al. 2017). Various materials have already been studied and applied as coatings with satisfactory results, such as resins (Hult et al. 2010), waxes (Pereira et al. 2014), clay (Morsy and El-Sherbiny, 2004), varnishes (Hernández and Cool, 2008), eucalyptus nanofibrils (Mirmehdi et al. 2018) and natural polymers such as starch (Koivula et al. 2016; Fabra et al. 2016). In opposition to synthetic polymers, the starch is obtained from renewable sources, being biosynthesized and stored by plants in the form of granules of varying sizes which depend of the source (Reis et al. 1997). The selection of nanofibrillated cellulose and starch as a coating factor in common papers may be a good alternative to reinforce conventional papers. In general, the production of CNFs from raw wood requires the realization of pre-treatments such as alkaline treatment and bleaching. The alkaline treatment causes alteration in the network structures of hydrogen bond due to reaction with alkaline based solution, such as sodium hydroxide (NaOH), especially on the internal and external structure of fibers. This also caused changes in the surface roughness and in the color of the natural fibers (Bakri et al. 2017). In addition, previous work reports the potential of alkaline treatment in the removal of hemicelluloses from hardwood kraft pulps (Hutterer et al. 2016). On the other hand, the bleaching treatment is responsible for strongly lignin removal. The common laboratory method for bleaching fiber is an acid-chlorite delignification treatment that utilizes acetic acid and sodium chlorite as reagents. This method bleaches and solubilizes lignin at moderate temperatures, around 70 °C (Hubbel and Ragauskas, 2010). Lignin, which acts as barrier for the modification of cellulosic fibers, should be removed in the pretreatment process (He et al. 2009). Starch-based films can be produced with good mechanical properties of tensile strength and elongation at break compared to films made with synthetic polymers (Lourdin et al. 1997; Parra et al. 2004; Yan et al. 2012). In addition, the increased use of recycled fibers in packaging materials has been strongly encouraged. Polysaccharide-based films generally have good mechanical properties and are good barriers to gases (Otoni et al. 2016). However, when the film consists exclusively of native starches, the tendency is the obtainment of poor adhesion due to the extensive stress cracking (Li et al. 2018). Several studies have investigated the association of starch with other polymers due to the relative ease of obtaining materials with satisfactory properties without the requirement of significant investments. These studies investigated: properties of films produced with CNFs associated with PVA and starch (Guimarães Júnior et al. 2015), starch-carboxy methyl cellulose film with essential oils (Mohsenabadi et al. 2018), blueberry waste and starch films (Luchese et al. 2018), starch films containing silver nanoparticles (Ortega et al. 2017) and bentonite clay in cassava starch films for the reduction of permeability (Monteiro et al. 2018). However, the literature is still deficient of researches showing about the coating in terms of quantity of material deposited as layers over the papers, as well the use of the gelatinized starch with other coating materials on surfaces such as cellulose nanofibrils and the interaction between them. In this context, the purpose of this paper is to investigate the potential of gelatinized cassava starch alternating with nanocellulose on the common paper surface and to compare its behavior in terms of wettability and mechanical properties in relation to uncoated commercial papers.

Materials and Methods

Obtainment of the raw materials

A certified Amazonian hardwood specie around 5 years of age was used in this work, namely *Schizolobium parahyba* var. amazonicum. The wood was provided by Concrem, which is a Brazilian company which works in the production of (*Medium density fiberboard*) MDF and plywood from paricá species. The collected logs were milled for production of particles. The resulting particles were sieved for selection of the fraction that passed through 60 mesh (0.250 mm). The alkali-treatment was performed following the adapted methodology described by Yue et al. (2015), while the bleaching procedure was adapted from Wise et al. (1946). Alkali scouring was performed before bleaching operations in order to improve the bleaching effect. According to Nasri-Nasrabadi et al. (2014), the molecular bonds between lignin-hemicellulose are more likely to exist than lignin-cellulose, by dissolving hemicellulose, the structure of lignin is more accessible to $NaClO_2$ bleaching stage. The two types of treated fibers (alkaline and alkaline + bleached) were immersed in distilled water in a concentration of 2% (w/w based on dried mass of the fibers) (Figure 1). The fibers were then submitted to nanofibrillation through a SuperMasscolloider grinder (Masuko Sangyo MKCA6-3) using opening between disks of 0.01 mm and stones rotation of 1600 rpm. The CNFs suspensions were obtained after 40 passes of the fibers through the SuperMasscolloider (Figure 2).

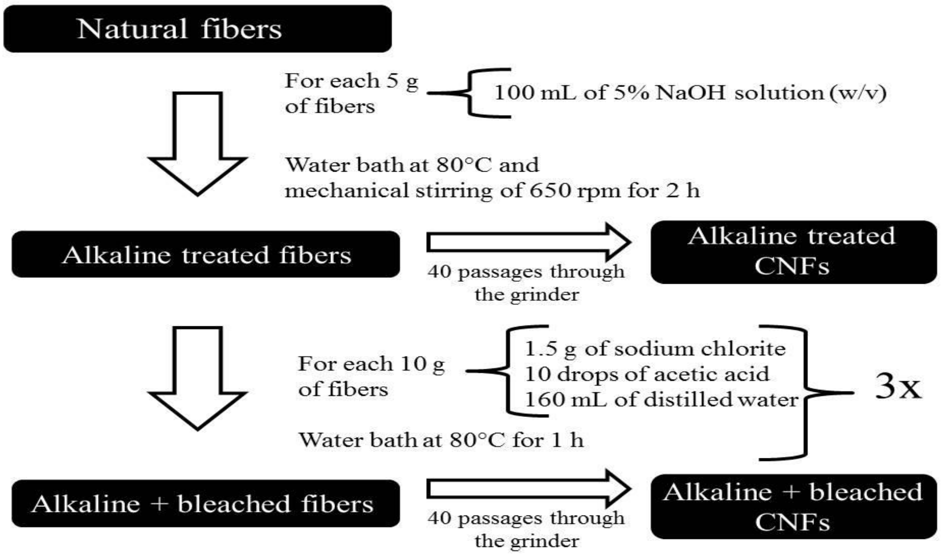


Figure 1. Scheme of the treatments from the natural fibers to the alkaline + bleached fibers and generation of the CNFs.

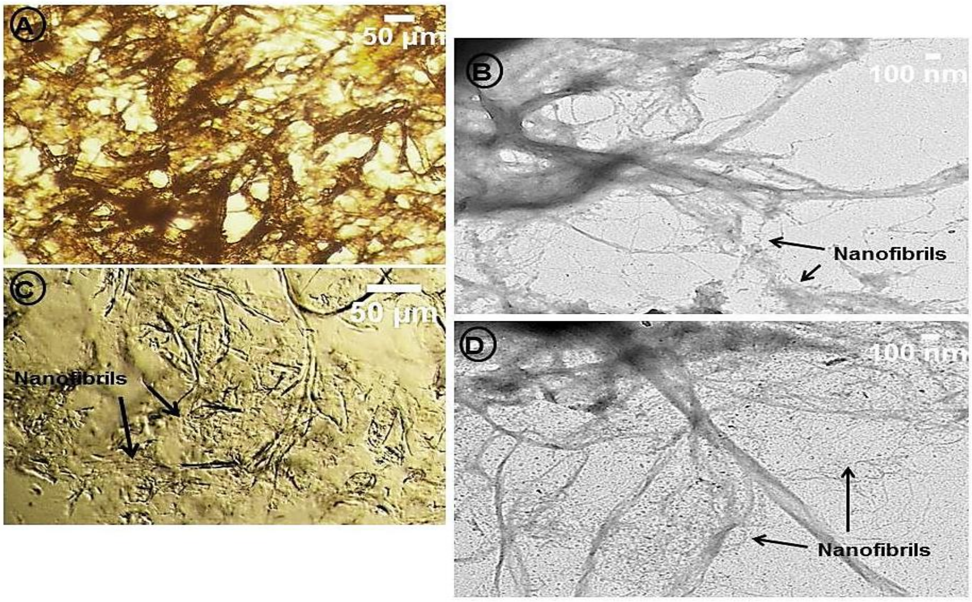


Figure 2. Typical images of paricá CNFs suspensions; A) polarized light microscopy image of the alkaline treated CNFs suspension; B) transmission electron microscopy image of the alkaline treated CNFs suspension; C) polarized light microscopy image of the bleached CNFs suspension; D) transmission electron microscopy image of the bleached CNFs suspension.

Coating the papers

The paper used for the production of the coatings was a commercial Copimax paper – 75 g.m^{-2}, provided by Suzano Papel & Celulose S.A. (Suzano, SP - Brazil). The suspension of CNFs used for the coating was prepared in a concentration of 2% (m:m). The cassava starch used for production of the gelatinized layer was donated by Cargill Company (MG, Brazil), amylopectin content 85%. It was prepared in a concentration of 2% (m:m) under heating and constant stirring to avoid the formation of "agglomerates". About 70% of the starch granules are broken at a temperature of 70 °C (Souza and Andrade, 2000), therefore this point was defined as the point of starch gelatinization. The suspension of CNFs was transferred into a tray and the 75 g.m^{-2} papers had one of the sides passed over the suspension surface, leaving a coating layer. The layers were made from 1 to 5 with the alkaline and alkaline + bleached CNFs suspensions (Figures 3, 4 and 5). The gelatinized starch layer was deposited by the same way, over the CNFs layer of over the paper. After the coatings, the papers were dried at 50 °C for 24 h.

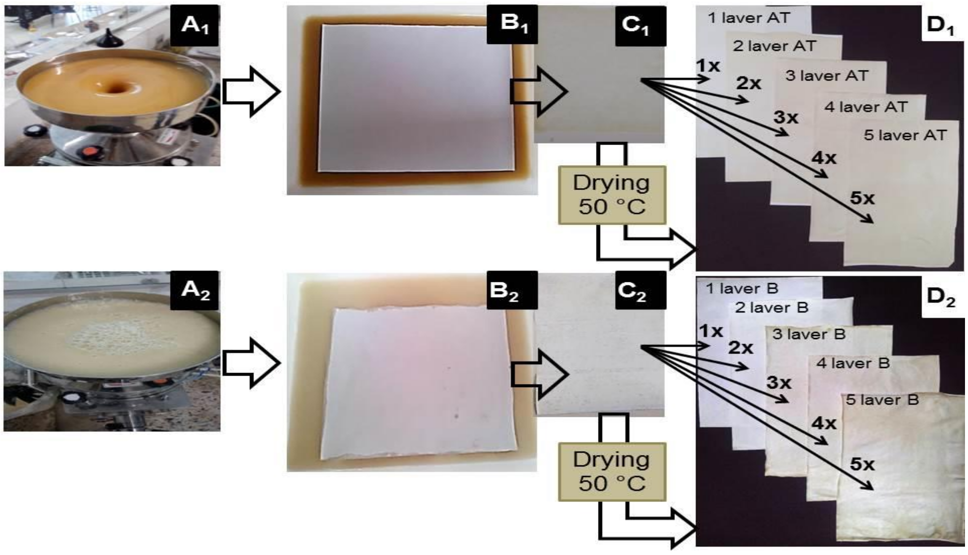
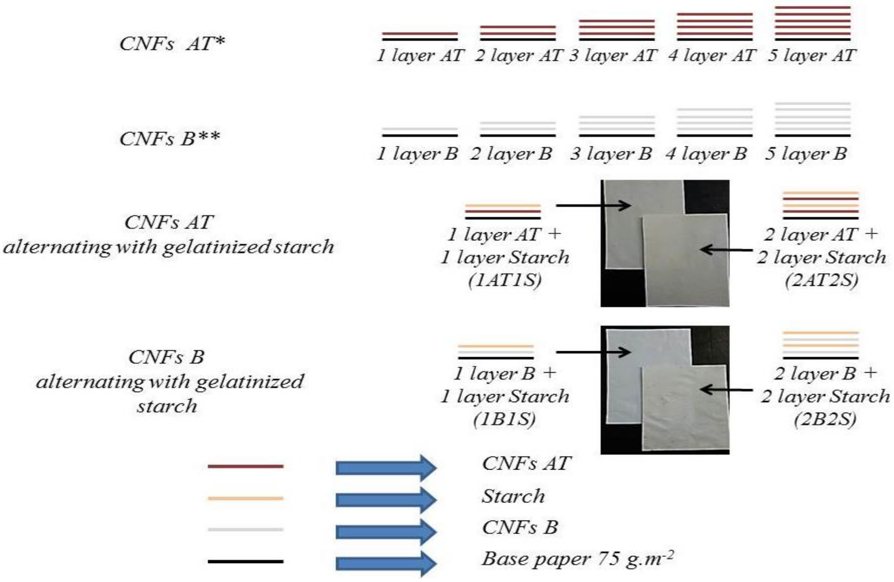


Figure 3. Scheme of W&P paper coatings; A_1) and A_2) production of CNFs alkaline treated and alkaline treated + bleached, respectively; B_1) and B_2) process of paper coating with the CNFs suspensions; C_1) and C_2) coated papers with one layer of CNFs suspension; D_1) and D_2) coated papers with 1 to 5 layers of CNFs suspensions after drying.



*AT: Alkaline treated; ** B: Bleached

Figure 4. Structure of the layers deposited over the papers.

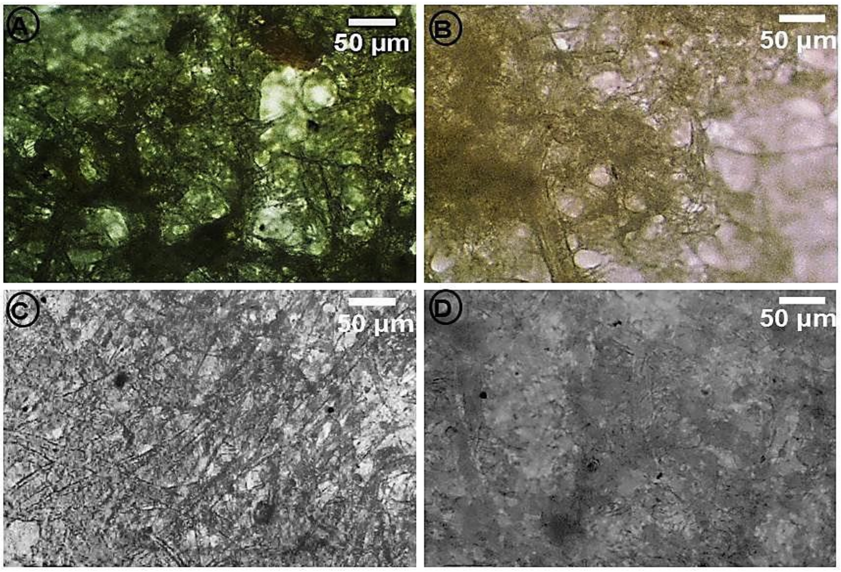


Figure 5. Polarized light microscopy images of the papers structure covered with paricá CNFs; A) and B) sample of coated paper covered with one and five layers of alkaline treated CNFs, respectively; C) and D) sample of coated paper with one and five layers of alkaline + bleached CNFs, respectively.

Mechanical strength

The mechanical properties of the coated papers were evaluated by the analysis of tensile strength curves following the procedures of ASTM D828-16 (2016). The samples were cut with the dimensions of 10 x 2.5 cm (Figures 6a and d). Each curve was generated by the mean result of the mechanical test was obtained from the average of 5 samples. The test was proceeded using a machine Zwick/Roell – D-89079 (Einsingen, Germany) with tensile speed of 10 mm/min. Maximum force measurements at break were also provided by the machine.

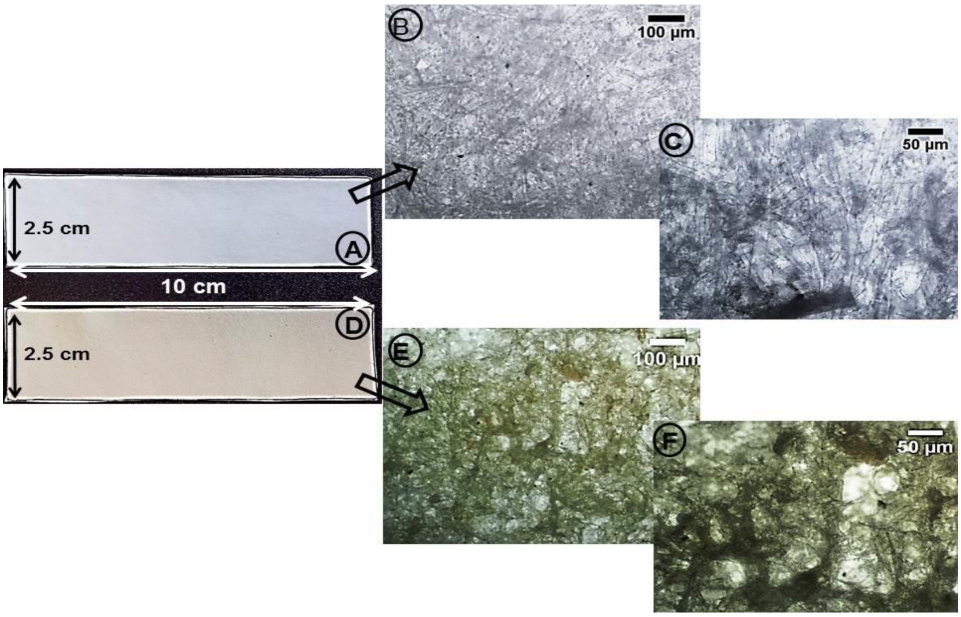


Figure 6. Structure of the papers covered with one layer of paricá CNFs; A) sample of coated paper with one layer of bleached CNFs; B) and C) polarized light microscopy image of paper samples coated with one layer of bleached CNFs; D) sample of coated paper with one layer of alkaline treated CNFs; E) and F) polarized light microscopy image of paper samples coated with one layer of alkaline treated CNFs.

Densities and grammage of the papers

A Mitutoyo micrometer was used to obtain the thickness and a digital caliper to obtain the diameter. The samples mass were obtained with a precision of 0.1 mg. The grammage expresses the mass (g) per area (m^2). The density of the commercial and coated papers ($g.cm^{-3}$) was calculated by dividing the mass by the volume of the samples. A film of each type of nanofibril, as well as a gelatinized starch film was produced in order to calculate the density of the layer deposited on the paper.

Chemical composition of the treated fibers

The contents of cellulose, hemicelluloses and lignin of the natural fibers (retained between the 40 and 60 mesh sieve) were obtained using samples after extractives removal. The determination of the extractives content and mineral/ash content were carried out according to the NBR 14853 (ABNT, 2010) and NBR 13999 (ABNT, 2003) standards, respectively. The insoluble lignin content was determined according to the procedures described in NBR 7989 (ABNT, 2010a). The holocellulose content was determined according to Browning (1963). The cellulose content was obtained following the procedures described in Keneddy et al. (1987). The hemicelluloses content was obtained by difference between the content of holocellulose and cellulose values. The mean values of each component were the result of 4 replicates.

Nanofibrils measurements

The diameters of the nanofibrils generated were obtained by manipulating the software *ImageJ*. The diameters were obtained from the mean value of 20 measurements for each material. The mean diameter obtained for the alkaline nanofibrils and the alkaline + bleached nanofibrils were 22.69 ± 7.88 and 24.60 ± 5.19 nm respectively.

X-ray diffraction (XRD)

Crystalline structures of the fibers and CNFs were analyzed by a XRD 600 (Rigaku®) difractometer with CuKα radiation ($\lambda = 1.540$ Å) at 30 kV and 30 mA over the angular range $2\theta = 5 – 37.5°$ at a rate of 2θ/min. The fibers were compressed in an aluminum sample holder furrows. The crystallinity index (CI) was calculated from the ratio between the area below all the crystalline peaks and the total area below the whole curve, determined after deconvolution (including non-crystalline fraction) following the Eq. (1).

$$CI(\%) = \frac{\Sigma Acrystalline\ peaks}{\Sigma Acrystalline\ peaks + \Sigma Aamorphous\ halo} \text{ x } 100 \quad (1)$$

Thermal degradation

A representative compound sample of the paricá CNFs and starch was prepared for the thermogravimetric analysis (TGA). The thermal degradation was executed in a TGA Q500 (TA Instruments ®) thermal analyzer. The samples were heated at 10°C/min from room temperature up to 600 °C. The analysis was performed under synthetic air atmosphere (80% N_2 and 20% O_2). According to Zhao et al. (2013), the practical processing and application of

CNFs are usually performed in synthetic air atmosphere. Therefore, the presented data here may be more reliable in such conditions.

Degradation in water

The samples were previously dried at 105° C and immersed in water for 24 h. After the immersion, the coated papers were dried at the same temperature and weighted again. The degradation was expressed in percentage.

Morphological Analysis

The structure of the coated and uncoated papers was visualized by light optical microscopy in order to identify the layers morphology obtained. A Nikon LV100 POL compound polarized light microscope was used for the initial investigation of the morphology of the particles. Scanning electron microscopy (SEM) photographs of the samples were taken using a JMS 6510 model scanning electron microscope developed by JEOL Company (Tokyo, Japan) with an acceleration voltage of 10 kV. All samples were previously sputter coated with gold prior to examination.

Surface wettability

The surface wettability was evaluated using a Kruss Drop Shape Analyzer – DSA25 (Hamburg, Germany). A drop of water was deposited over the sample surface through a syringe. The drop image was captured by a video camera and an image analysis system that determine the contact angle between the water drop and the paper surface, which were measured at room temperature (20°C). The contact angles were measured during 40 s while the camera captured the drop images.

Results and discussion

Properties of the coated papers

A decreasing trend for tensile modulus was noted according to the increase of the number of layers when the curves of tensile strength were evaluated, for the papers coated with alkaline treated and alkaline + bleached treated CNFs (Figures 7 and 8).

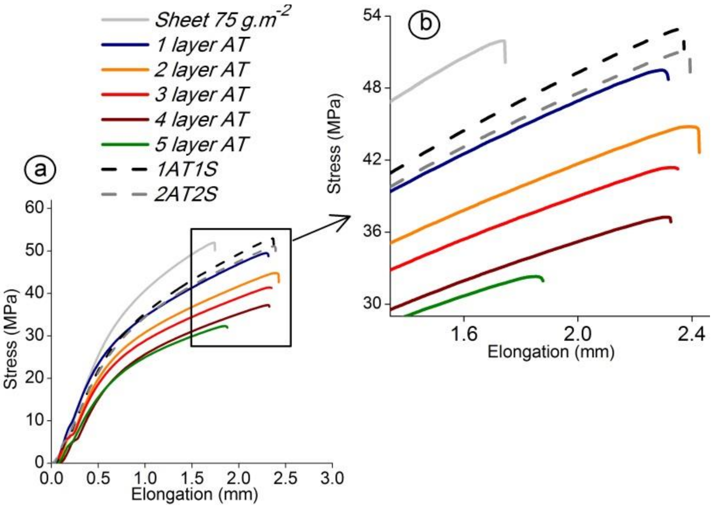


Figure 7. Mechanical properties of the commercial and coated papers with the alkaline treated CNFs; a) and b) mechanical behavior of the commercial and coated papers with the alkaline treated CNFs; c) maximum force of the commercial and coated papers with the alkaline treated CNFs.

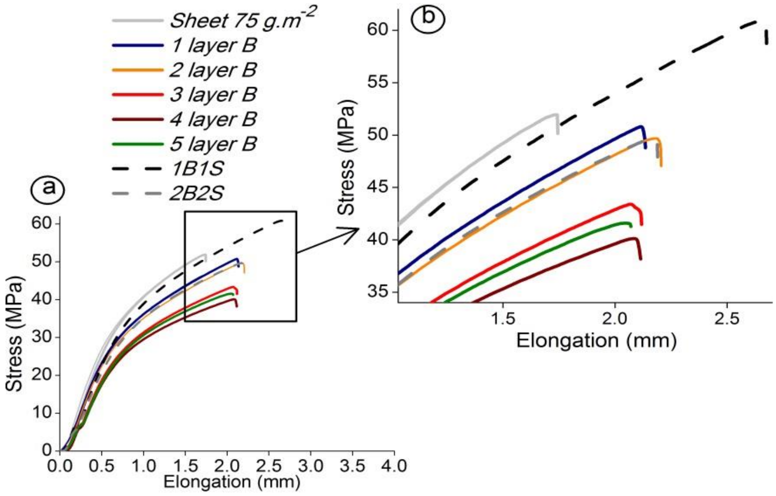


Figure 8. Mechanical properties of the commercial and coated papers with the alkaline + bleached CNFs; a) and b) mechanical behavior of the commercial and coated papers with the alkaline + bleached CNFs; c) maximum force for the commercial and coated papers with the alkaline + bleached CNFs.

The increase in thickness was evident according to the increase in the number of layers on commercial paper (Table 1). This decrease in the tensile modulus was according to the decreasing values for density of the samples of both CNFs types used for the coatings (Figure 9). This decline in density values occurred due to the low values observed for the layers of nanofibrils. The density of the bleached CNFs layers was higher in comparison to alkaline treated nanofibrils (Table 2). For the starch layer, the density value obtained was higher than the observed for the nanofibrils layers.

Table 1. Thickness of the commercial and coated papers.

Paper	***Thickness (µm)***	***Paper***	***Thickness (µm)***
Commercial sheet 75 g.m^{-2}	*108 ± 3*	*Commercial sheet 75 g.m^{-2}*	*108 ± 3*
1 layer AT	*127 ± 0.5*	*1 layer B*	*116 ± 1*
2 layer AT	*140 ± 2*	*2 layer B*	*122 ± 5*
3 layer AT	*155 ± 4*	*3 layer B*	*130 ± 5*
4 layer AT	*165 ± 9*	*4 layer B*	*140 ± 0.6*
5 layer AT	*180 ± 15*	*5 layer B*	*150 ± 9*
1AT1S	*135 ± 3*	*1B1S*	*125 ± 3*
2AT2S	*145 ± 4*	*2B2S*	*137 ± 7*

*Standard deviation

Considering the total of 5 layers deposited on the paper surface, for both types of nanofibrils, it is estimated that the mean thickness of each layer of alkaline CNFs was 14.4 ± 3.3 µm, while the layers of bleached CNFs showed mean thickness of 8.4 ± 1.7 µm. In both cases the CNF coatings generated extremely thin layers.

Table 2. Mean density of the layers deposited on the commercial paper surface.

Layer	***Mean density (g.m^{-3})***
Alkaline treated CNFs	0.482 ± 0.043*
Bleached CNFs	0.839 ± 0.066
Starch	1.007 ± 0.073

*Standard deviation

Mechanical properties mainly depend on single fibril and interfibril bonding, which can be affected by aspect ratio, chemical composition (cellulose, hemicellulose, lignin, etc) or processing approach (Qing et al. 2013; Wang et al. 2013). It is noted a large difference between the insoluble lignin and cellulose contents when comparing the alkaline treated and alkaline + bleached fibers (Figure 10). Different studies have shown that a higher amount of lignin in cellulose fibers reduces the rate of fibrillation or microfibrillation of cellulose fibers to finer fibrils (Nair and Yan. 2015; Spence et al. 2010). In addition, these results implied that lignin in films might interfere in hydrogen bonding between fibrils, thus weakening the interfibril bonds and resulting in low mechanical property, as previously related by Bian et al.

(2018). It is noted that the maximum force shows a tendency to increase during the promotion of successive layers, both for the alkaline treated and the alkaline + bleached CNFs. Considering the papers in which the alkaline treated CNFs, the gelatinized starch applied did not overcome the mechanical resistance of the commercial paper of 75 g.m^{-2}. On the other hand, when the gelatinized starch was deposited over the layer of the bleached CNFs, a slight increase in the mean value of tensile modulus at rupture has occurred in comparison to commercial papers and other coated papers. The affinity between starch and cellulose due to their structural similarity can be exploited not only to enhance the mechanical properties of composites but also to produce biodegradable materials (Dufresne et al. 2010; Avérous 2004; Zhao et al. 2008).

In general, good adhesion to fibers is believed essential for all kinds of starch-based size materials (Li et al. 2016a). The adhesion exhibits the function of increasing the strength of fibrous goods such as papers and sized warps by bonding the fibers in the goods together (Li and Zhu. 2016). Bleaching treatment helps to eliminate components as lignin and increase the exposure of the uniform microfibrils in secondary wall (Feng et al. 2018). Greater exposure of them may imply in a better adhesion between CNFs after the fibers defibrillation, both in the same layer and in the better adhesion between overlapping layers, which gave greater mechanical strength to the paper coated with bleached CNFs.

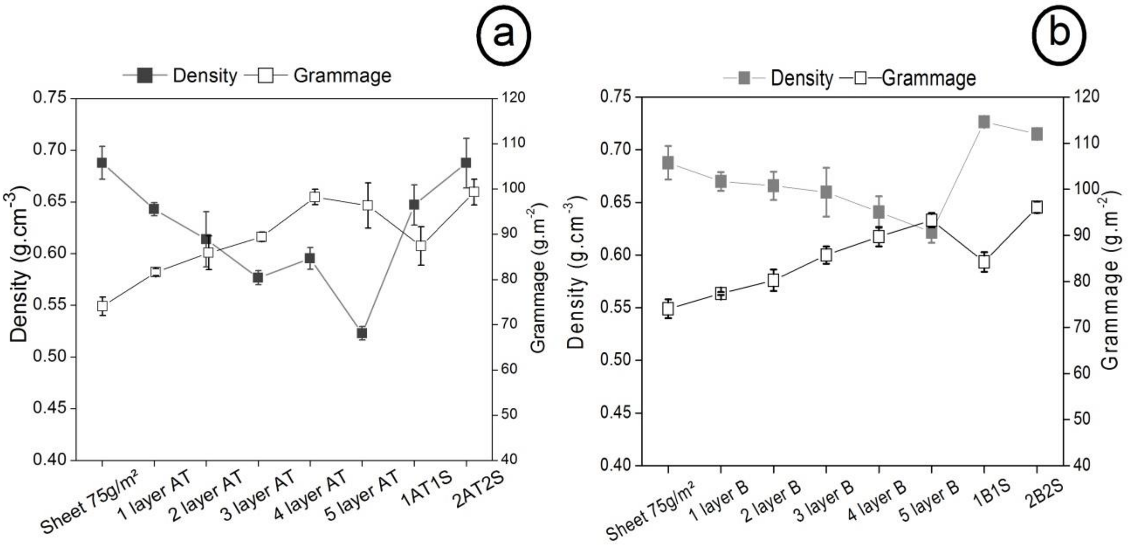


Figure 9. Density and grammage for the W&P and coated papers; a) commercial and coated papers with the alkaline treated CNFs; b) commercial and coated papers with the alkaline + bleached CNFs.

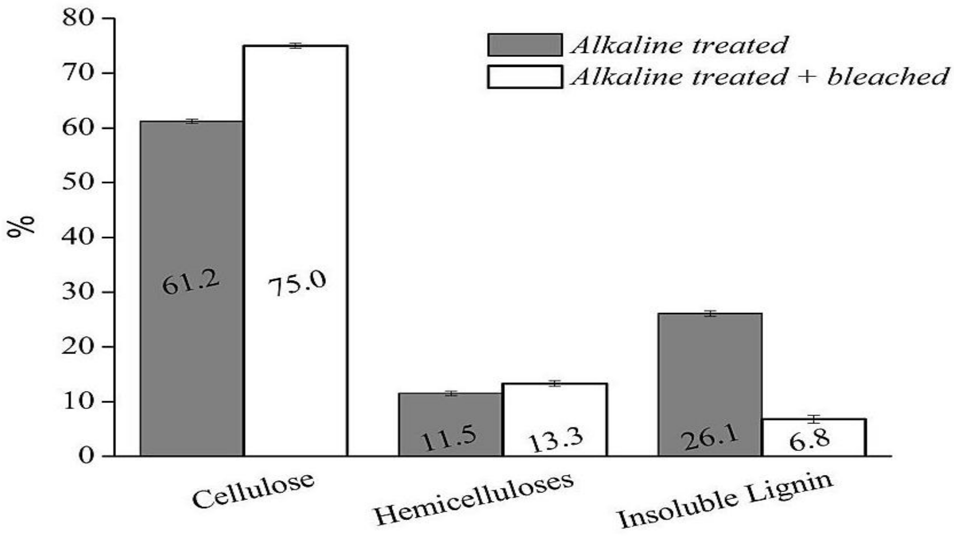


Figure 10. Chemical analysis of the paricá treated fibers.

Even after the alkaline treatment, the paricá fibers showed a high lignin content. Bleaching resulted in a significant decrease of the fibers lignin content. However, there was still a little residual lignin content. Owing to the existing complex network bonds between lignin and polysaccharides, lignin cannot easily be removed from plant cell wall (Shahbazi et al. 2017a). The $NaClO_2$ bleaching stage, additionally, provides a high-quality bleached pulp by eliminating the residual phenolic molecules, such as lignin, polyphenol, and proteins (Dufresne, 2012; Heidarian et al. 2016). The cellulose of the paricá was also influenced by the treatment. It was noted a concentration of cellulose in the bleached material from 61.2 to 75%. Previous studies reported the cellulose content of hemp fibers increased up to 92.3 % when treated by solutions of NaOH and $NaClO_2$ for 1hr (Kang et al. 2013).

It is noted a little difference between the starch degradation temperature peak and the two types of CNFs when the first peak of degradation is focused (Figure 11).

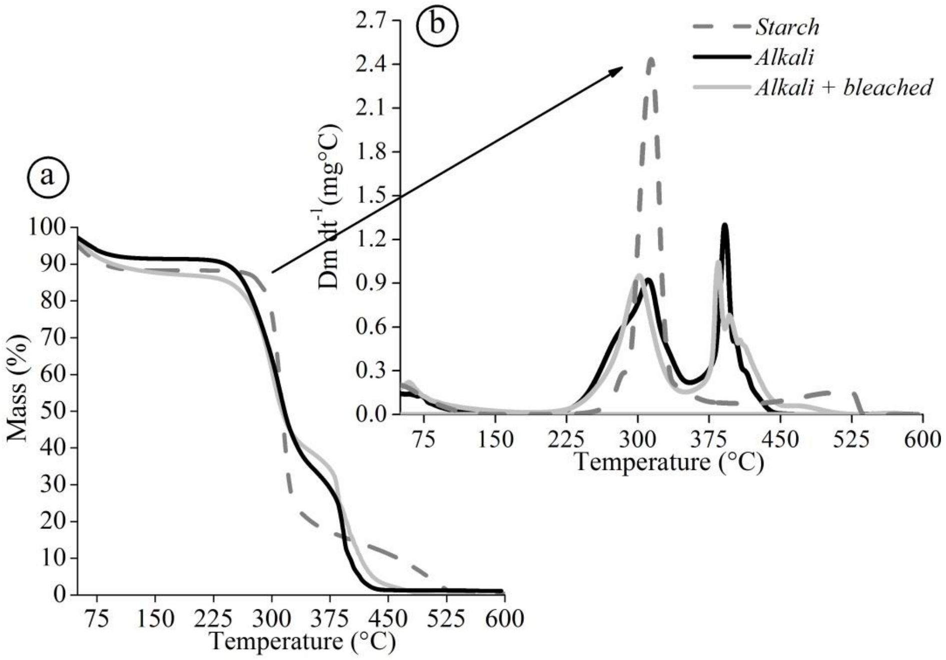


Figure 11. a) TGA and b) DTG curves obtained for the CNFs and starch samples in oxygen atmosphere.

The maximum thermal degradation temperature found for alkaline treated CNFs was 311 °C, while for alkaline + bleached CNFs it was 300 °C. For cassava starch, the degradation temperature was also 311 °C. Saelee et al. (2016) reported CNFs obtained by sodium chlorite bleaching combined with high pressure homogenization treatment and the T*max* 336 °C. Similarly, Feng et al. (2018) obtained T*max* value for sugarcane bagasse CNFs bleached with H_2O_2 close to 352 °C. Such good thermal stability of CNFs is mainly due to the low damage to the cellulose fibers. A previous study (Nair et al. 2017) reports the T*max* of 335 °C for lignocellulosic nanofibrils (LNFCs), which is much higher than most reported data for pure cellulose nanofibrils (Jiang and Hsieh, 2013; Nair and Yan, 2015; Quiévy et al. 2010). The high thermal stability was attributed to the high amount of residual lignin on the nanofibrils compared to other studies. It is noted that the cassava starch obtained a lower value of crystallinity index in relation to all paricá alkaline treated and alkaline treated + bleached CNFs (Figure 12).

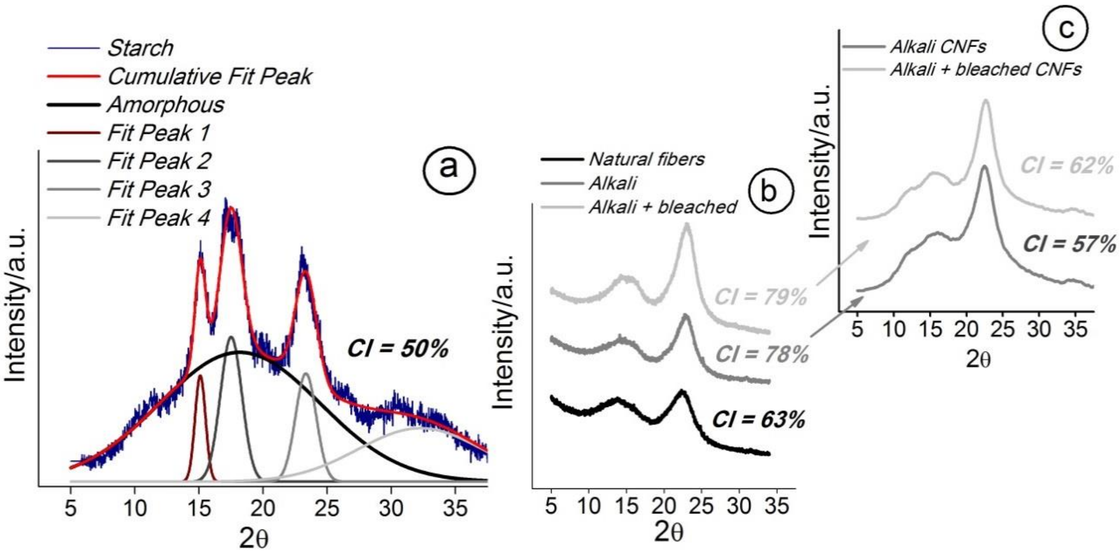


Figure 12. Typical x-ray diffraction of starch and paricá treated CNFs; a) typical example of deconvolution made for the starch sample; b) typical diffractogram designed for samples of natural and treated fibers; c) typical diffractogram designed for samples of both types of CNFs.

Starch consists of amorphous and crystalline domains. The amorphous regions are highly susceptible to hydrolysis and, under controlled conditions, may be dissolved leaving the rigid crystalline regions intact (Dufresne, 2014). The alkaline treatment considerably affected the CI of the fibers. After the bleaching treatment, the CI increased as the hemicelluloses and lignin contents decreased. The increase in crystallinity after chemical treatments has been reported by several authors (Alemdar and Sain, 2008; Li et al. 2009; Fonseca et al. 2019). This was expected due to the removal of the amorphous structure of lignin and hemicellulose. However, the pulp after bleaching still consists of amorphous cellulose (less ordered) and crystalline cellulose (more ordered) (Pääkko et al. 2007; Dufresne 2006; Klemm et al. 2005; Beck-Candanedo et al. 2005).

The content of hemicelluloses in alkaline treated fibers and bleached fibers could be a factor that provides better mechanical defibrillation. According to Chaker et al. (2013), removing hemicelluloses, the microfibrils will be into a close contact, favoring their strong interaction through hydrogen bonding, thus rendering the fibers harder to defibrillate. In addition, some content of hemicelluloses presents an important role in mechanical nanofibrillation process since they act as inhibitors of micro/nanofibrils coalescence, which may facilitate their delamination (Zhang and Tong, 2007; Klemm et al., 2011).

The CNFs from treated fibers presented a decrease of CI values in comparison to the original fibers. A reduction in crystallinity index was observed by Tonoli et al. (2012) when comparing milled fibers with nanofibrils. The defibrillation may cause damage to the crystalline structure underwent during the high shearing action suffered by the fibers. Chen et al. (2011) also reported some damage to the crystalline domain of nanofibrils when defibrillation treatment was applied. Furthermore, the amorphous structures probably have been reorganized during their oven drying, when fibril samples were prepared for the analysis (Tonoli et al. 2016). Pacaphol and Aht-Ong (2017) found a decrease of the CI after defibrillation of the bleached fibers (microscale), probably due to the damage and imperfection of crystals after high shear and impact force attack on mechanical treatment. Accordingly, Uetani and Yano (2011) found that mechanical treatment forces from grinder could damage crystalline structure of cellulose in Japanese cedar pulps and decrease de CI in 10% compared with the original pulp. Dai et al. (2018) found a decrease of relative crystallinity when evaluating the XRD patterns from starch with an increase of ball milling time, which indicated that the starch structures were significantly damaged and might not be appropriate for starch nanocrystals production. In addition, the increase in mobility of the nanofibrils in water during the defibrillation may cause damage to the ordered part of the cellulose molecules (Jonoobi et al., 2011) and increase the proportion of the disordered part, resulting in a lower CI for nanofibrils. Furthermore, adding the cellulose with crystalline nature to starch could increase the interactions between OH groups of both the polysaccharide structures. These interactions increased the crystalline regions and consequently decreased the hydrophilic nature of the interface (Tabassi et al. 2016).

The coated papers showed no clear tendency for values of degradation in water when comparing to the commercial papers with the grammage 75 g.m^{-2} (Figure 13). For the papers coated with alkaline treated CNFs, there was a tendency of decrease for degradation from the first layer to the following. Such tendency was not observed for bleached CNFs.

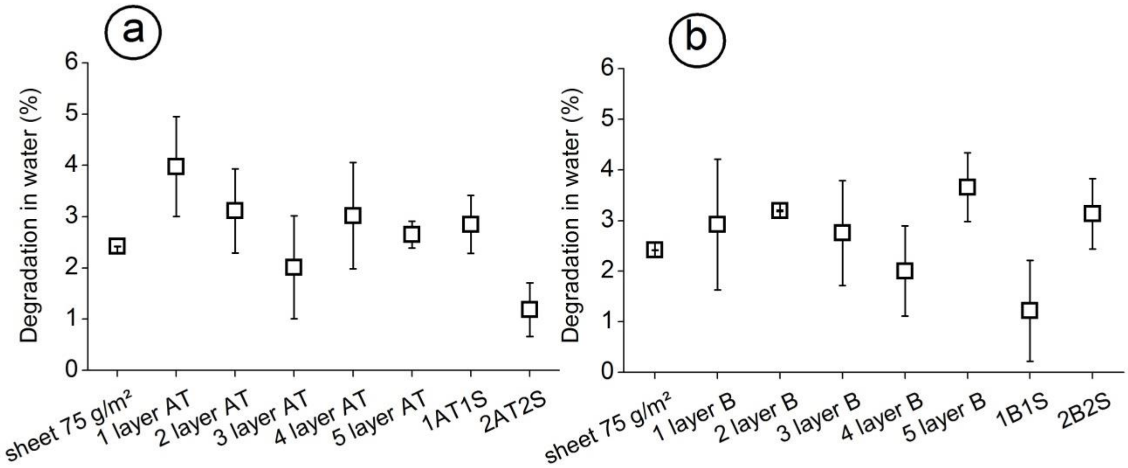


Figure 13. Degradation in water for the commercial and coated papers; A) samples of commercial and coated papers with alkaline CNFs; B) samples of commercial and coated papers with alkaline + bleached CNFs.

Overall, the degradation of all the types of papers was low. Even as a hydrophilic polymer, cellulose is insoluble in water due to the dense structure arrangement and due to strong intermolecular hydrogen bonds between molecules (Onoda-Yamamuro et al. 2007). Therefore, their water degradation is above all related to leaching out of the aggregates than to the solubility of the fiber components. Scatolino et al. (2017) evaluating sheets of bleached fibers composed by wastes of Amazonian woods, found values extremely high (close to 100%) for degradation in water. This result was probably found due to the use of the *casting* method for the sheets production. This method is based on the production of sheets or films by evaporation of the solvent contained in the suspension. However, this method may not provide a satisfactory cohesion between the fibers when in microscale. On the other hand, sheets produced by industrial processes undergo pressing and drying which provide good adhesion between the fibers. However, when food exudes liquid or is commercialized in aqueous solution, low solubility of the package material is desired (Fakhouri et al. 2007). The values for degradation in water found in this study were lower in comparison with other biopolymers used for film production. Vicentino et al. (2011) evaluated films produced with native cassava starch finding degradation values of 55%. Similarly, the literature reports values of 100% for water degradation in films produced with pectin (Batista et al. 2005).

Surface wettability

The commercial papers of both grammage studied obtained excellent surface wettability properties, since the water drop remained practically intact during the first 40 seconds of testing (Figure 14). These papers, before their production, pass by a process called "internal gluing", which chemicals are added to the pulp during the preparation. These products are deposited on the fibers with the purpose of controlling the liquids penetration after the manufacture of the paper. These are rosin based adhesives, silicones, polyethylenes, perfluorocarbons and synthetic glues. It can be seen that the paper coated with only one layer of alkaline treated CNFs showed no relevant resistance to drop penetration, since instantaneously (3 s) the drop penetrated in the layer structure (from 46° to 25°). The same occurred to the papers covered with 5 layers of alkaline treated nanofibrils. Five layers of bleached nanofibrils provided a contact angle of 50° after 20 s. Better quality of surface wettability may be due to the fact that these layers show higher density in relation to the layers with alkaline treated nanofibrils (see Table 2). The addition of the gelatinized starch layer provided an improvement in the surface wettability properties over papers coated only with CNFs (Figures 15 and 16).

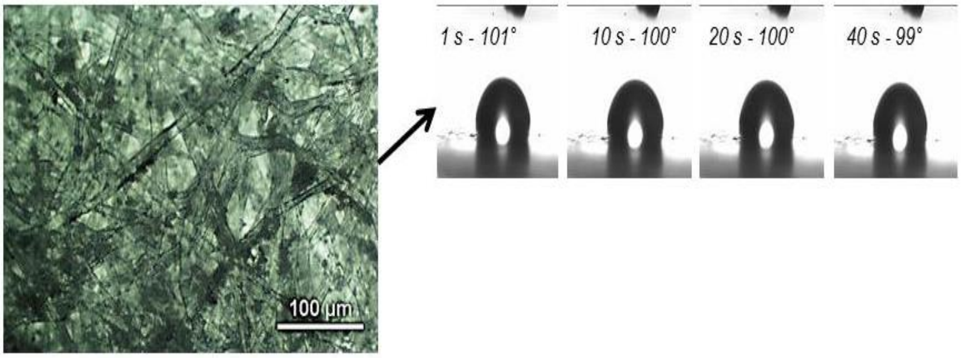


Figure 14. Polarized light microscopy of a W&P paper sample.

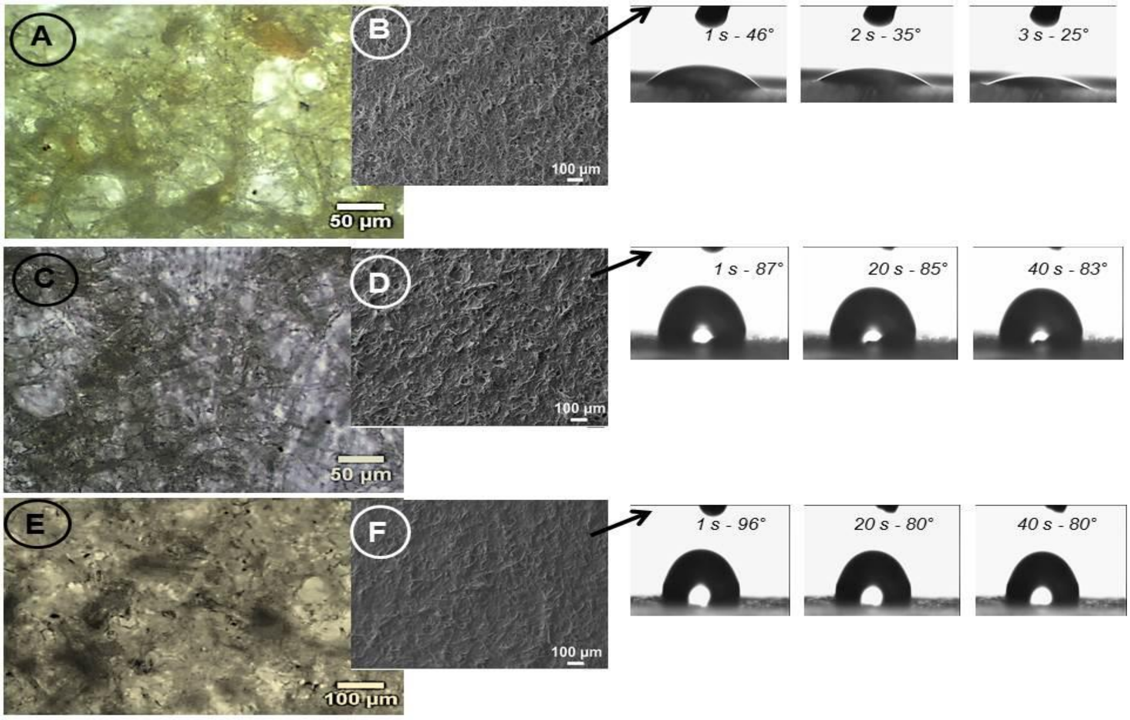


Figure 15. Polarized light microscopy and SEM micrographs of: A and B) sample of coated papers covered with one layer of alkaline treated CNFs; C and D) sample of coated papers covered with one layer of alkaline treated CNFs alternating with gelatinized starch; E and F) sample of coated paper with two layers of alkaline + bleached CNFs alternating with two layers of gelatinized starch.

When the gelatinized starch was added over the nanofibrils layer there was a significant increase in the drop penetration strength. During 40 s of measurements, the contact angle ranged from 92° to 80°. The polarized light microscopy image (Figure 15 C) shows that the paper surface coated with gelatinized starch presented smaller amount of interstitial zones compared to the layer of only nanofibrils alkaline treated (Figure 15 A). In addition, the presence of lignin in the CNFs may form agglomerates and result in irregular surface of the layer (Figures 15B, D and F). This interaction among the nanofibrils and the gelatinized starch strengthened the intermolecular forces and resulted into physical crosslinking. Starch is a polymer of D-glucose with each glucose unit having three free hydroxyl groups. This entanglement of polymer chains allowed more surface strength to the layer. The availability of hydroxyl groups of the CNFs and the starch facilitated their participation in hydrogen bonds when they came in close proximity (Guan et al. 2004). In addition starch is also applied to the dry sheet in an attempt to increase the water penetration resistance into paper (sizing)

(Guan et al. 2008a). For unmodified starches, the driving force of adsorption is mainly of hydrogen bonds and Van der Waals interaction (Guan et al. 2008b).

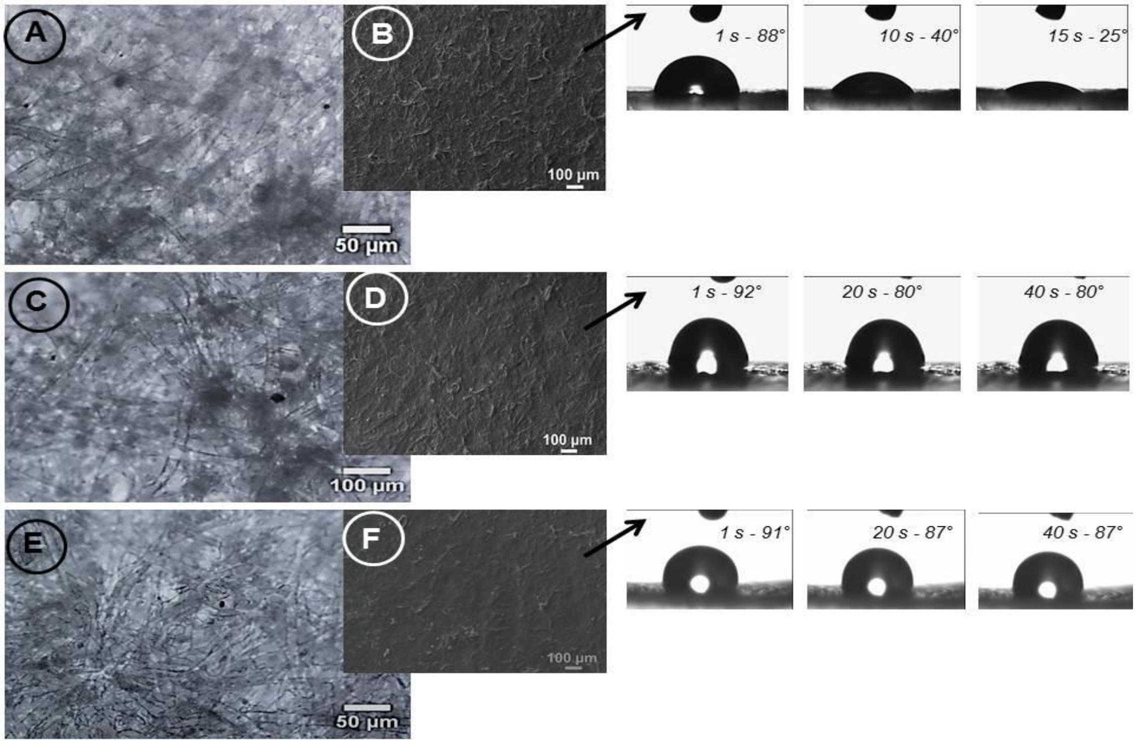


Figure 16. Polarized light microscopy and SEM micrographs of A and B) sample of coated paper with one layer of alkaline + bleached CNFs; C and D) sample of coated papers covered with one layer of alkaline + bleached CNFs with one layer of gelatinized starch; E and F) sample of coated paper with two layers of alkaline + bleached CNFs with two layers of gelatinized starch.

The literature reports that starch is a water-soluble polymer and when a water droplet coming into contact with its surface, it is rapidly absorbed into the starch matrix. Moreover, the hydrophilic character of water can cause to a strong interaction with the surface of starch film (Shahbazi et al. 2017b).

The SEM micrographs showed that the gelatinized starch layer promoted a more homogeneous appearance and provided lower granularity to the surface of coated papers. The more compact surface, the cohesiveness, the homogeneity, the absence of phase separation and minimum presence of bubbles, clusters and fissures are good evidences of the improved microstructure of these nanocomposites (Mali et al. 2004). The use of this type of cellulosic nanoreinforcement in polysaccharides matrices has increased because of their great affinity. Large specific surface area, high aspect ratio and high capacity to form structured nets make cellulosic nanofibrils excellent low-cost and non-toxic reinforcement agents (Chang et al.

2010). Therefore, films made from lower lignin contents are more densely packed with much finer fibrils and interstices between these fibrils (Nogi et al. 2009). The surface is considered hydrophobic when its contact angle, measured using pure water, is higher than 90° (ASTM, 2013). In the case of this work, the addition of the gelatinized starch layer contributed to the surface "hydrophobization" of both types of nanofibrils used. According to Dufresne (1998), the water resistance of starch-based composites can be improved with the addition of a small amount of cellulose fibers. Intermolecular interaction between starch and CMC resulted in more compact molecule structure of starch-CMC mixture, and tensile strength was therefore increased (Li et al. 2008).

Conclusion

Papers were coated with CNFs after alkaline treatment and bleaching besides layers of gelatinized starch. Cellulose nanofibrils were successfully obtained from the Amazonian paricá by mechanical defibrillation from both types of treated fibers. The mean diameter obtained were close to 22.69 ± 7.88 and 24.60 ± 5.19 nm for the alkaline nanofibrils and the alkaline + bleached nanofibrils, respectively. The results of chemical composition demonstrate that the alkali treatment was not enough to remove lignin. However, the treatments decreased considerably the amount of hemicelluloses from paricá. In thermal degradation of alkaline + bleached nanofibrils, higher initial temperature of degradation was observed, while the alkaline treated ones take more time to reach the maximum degradation. The gelatinized starch layers resulted in a higher density increase to the papers. The degradation in water was low for all types of covered papers. The deposition of 5 nanofibrils layers, of both types, did not result in expressive gain in terms of maximum force. The use of the gelatinized starch alternated with layers of alkaline treated nanofibrils resulted in papers with greater elongation before the break. The system of sequential drying of the layers may have caused damage to the paper structure. The samples produced with one layer of bleached nanofibrils and one layer of gelatinized starch obtained a tensile strength approximately 20% greater than the papers with grammage 75 g.m^{-2}. The present work contributes with important information on surface-coated papers using cellulose nanofibrils and encourages the study of new methods of coating the papers, as well as drying the deposited layers. 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 applications, as packaging

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