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EUCALYPTUS WOOD NANOFIBRILS AS REINFORCEMENT OF CARRAGEENAN AND STARCH BIOPOLYMERS FOR IMPROVEMENT OF PHYSICAL PROPERTIES

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In tropical countries there are innumerous options of biodegradable polymers and lignocellulosic sources to produce green nanocomposites. The main drawback of carrageenan and starch application for packaging is their poor strength in high moisture conditions. However, blending and addition of cellulose nanofibrils may overcome the limitation. This investigation aimed to compare the physical strength of starch and carrageenan films, and to determine the best blending proportion of these biopolymers. In addition, a recommended load of eucalyptus cellulose nanofibrils, to produce nanocomposites with improved physical strength, was investigated. Carrageenan replaced starch at proportions 100, 80, 50, 20 and 0%. Cellulose nanofibrils were produced from eucalyptus sawdust and added to the films at 10, 20 and 30% loads. Carrageenan is more hydrophilic than starch, hence it should be applied up to 20% in blends. The increase of nanofibrils from 10 to 30% decreased water solubility and absorption, while density increased. A 10% load of nanofibrils was enough to decrease water vapor permeability. The physical strength of carrageenan for packaging may be improved by blending with starch and adding 30% of cellulose nanofibrils.

Keywords: Cellulose nanofibrils, packaging, blends, water barrier properties

INTRODUCTION

Currently, biobased materials are gaining importance due to the need to decrease society's dependency on petroleum based products (Goetz et al. 2009). Biopolymers (biodegradable polymers) may be obtained from renewable resources or synthesised from either petroleum-based chemicals or microbial processes. Through blend of two or more biopolymers a new biopolymer may be designed for specific requirements. Originally, biopolymers were intended to be used in packaging industries, farming and other applications with minor strength requirements. Performance limitations and high production cost are major drawbacks for their widespread acceptance (Mohanty et al. 2002).

Carrageenan is a generic name for a family of polysaccharides obtained by extraction from certain species of red seaweeds (Rhodophyta). It is a water soluble linear biopolymer, increasingly used as natural thickener, formulation stabiliser or gelling agent in applications ranging from food industry (mainly dairy products) to pharmaceutics (De Velde et al. 2002). Carrageenan consists of alternating copolymers of α-(1→3)-D-galactose and β-(1→4)-3,6-anhydro-D- or L-galactose. It is usually classified in three industrially relevant types: λ-carrageenan, which is a highly sulfated galactan with viscosity enhancement properties; ι-carrageenan, which forms thermo reversible soft gels; and κ-carrageenan, which gives strong and brittle gels with water syneresis (Lahaye 2001).

The starch may be extracted from plants such as corn, potato and cassava. It is a semicrystalline polymer composed of a mixture of amylose, a linear polysaccharide, and amylopectin, a highly branched polysaccharide (Avella et al. 2005). Starch is a promising non-wood forestry product due to its high availability and renewable and biodegradable characters (Raabe et al. 2015). Besides, this natural polymer presents interesting properties and characteristics for processing, being an attractive alternative to replace the synthetic polymers in applications that do not require long periods of use (Belhassen et al. 2014).

Even though films made from polysaccharides are expected to be good oxygen and carbon dioxide barriers due to their tightly packed and ordered hydrogen-bonded network structure, they have poor water vapor barrier properties, which result from their hydrophilic nature (Alves et al. 2010). This drawback may be minimised by the addition of cellulose fibres or nanofibrils as reinforcement to produce new biocomposites.

Cellulose is a linear homopolymer composed of anhydroglucose units which are linked together by β-(1→4)-glycosidic bonds. It has fibrillar structure and relatively high elasticity modulus (Fengel & Wegener 1984, Chawla 1998). Plant cellulose occurs in wood, cotton, flax and others, the former being the most important resource for this purpose in the world. Cellulose fibres may be modified into cellulose nanofibrils by the following procedures: shearing forces (refining) ultrasonic fibrillation; high pressure homogenization and steam explosion (Lee et al. 2009, Deepa et al. 2010, Chen et al. 2011, Lee et al. 2011). The diameters of the cellulose nanofibrils usually depend on the source and range from 3 to 20 nm (Sassi & Chanzy 1995). Compared to fibres, nanofibrils have more advantages for reinforcement purposes, including high surface area and aspect ratio (Borges et al. 2010, Lee et al. 2011).

Concerning availability and cost, the high quality nanocomposites are produced with three biodegradable resources which are of high interest to tropical countries with rich biomes. In Brazil, eucalyptus extensive crops provide wood for utility (Bufalino et al. 2012). In cellulose sector, they are the main suppliers of bleached cellulose pulp (Tonoli et al. 2013). In addition, tropical biomes offer many possibilities to obtain starch and carrageenan from various plant and algae species. Although biopolymers allow the production of cohesive and transparent films, there is a gap in their application due to high hydrophilicity (Alves et al. 2010, Prachayawarakorn et al. 2010). This study determined which of the two biopolymers is more resistant at high moisture conditions. The possibility of producing blends that may improve the quality of the less resistant biopolymer was investigated. In addition, the improvement of physical strength of such biopolymers by addition of eucalyptus nanofibrils, was quantified.

Therefore, the first stage of this investigation aimed to compare the physical strength of starch and carrageenan films, as much as to determine the best proportion to produce blends with these biopolymers. In the second stage, a recommended load of eucalyptus cellulose nanofibrils, to produce nanocomposites with improved physical strength, was investigated.

MATERIALS AND METHODS

Polymer films and blends production

Refined λ-carrageenan was provided by Agar Brasileiro Industria e Commercio Ltda, Brazil. The biopolymer was characterised with average diameter 250 µm, moisture content 18%, pH 6.8 and viscosity 22 cPs. AMISOL® 3408 starch, provided by Corn Products Brasil Company of Brazil, had moisture content 11.48%, 4.8, 10 ppm SO_2, Scott viscosity 89 (12 g 100 ml^{-1}; base 13%), average diameter 17.25 µm (laser measurement) and amylose ± 0.43% (Guimarães et al. 2015). The 100% starch (0_Carr/100_Stch) and 100% carrageenan (100_Carr/0_Stch) films were made with 3% polymer (based on water mass) and 20% glycerol (based on polymer mass). The aqueous solutions were heated until 80 °C, after which glycerol was added and heating was continued for 20 min. Films were produced by the casting method. 40 g of solution were shed in 13 cm-diameter Petri dishes and dried in an acclimatised room at 19 °C and 63% RH for 7 days. In order to produce blends, starch and carrageenan solutions were mixed at the following proportions: 20% carrageenan and 80% starch: (20_Carr/80_Stch); 50% carrageenan and 50% starch (50_Carr/50_Stch) and 80% carrageenan and 20% starch (80_Carr/20_Stch). 100 g of each blend were prepared.

Cellulose nanofibrils production

A *Eucalyptus urophylla* tree was collected from a Brazilian crop and peeled into veneers. Low-quality veneers for plywood production were selected as waste materials, grinded in a hammer mill and processed into sawdust using a disintegrator. The particles were sieved for selection of the fraction that passed through

60 mesh. Pre-treatments of the raw materials were carried out according to Bufalino et al. (2015) by two subsequent procedures. Firstly, the raw sawdust was submitted to alkali treatment in a digester. Parameters were as follows: pressure 0.7 to 1.2 MPa, NaOH solution at 5% (w/w), sawdust to solution proportion of 1000 g 6000 ml$^{-1,}$ reaction time of 0.5 hour and reaction temperature of 150 °C. The fibres were then washed with distilled water until neutral pH. Secondly, alkaline treated fibres were bleached under mechanical stirring using the following parameters: H_2O_2 at 24% + NaOH at 4% solution (v/v), fibre to solution proportion of 50 g 2000 ml^{-1}, reaction time of 2 hours and temperature of 60 °C. The fibres were washed once again with distilled water until neutral pH. The bleached fibres were immersed in distilled water at a proportion of 1% (w/w). The fibres were then submitted to nanofibrillation in a Super Mass Coloider Grinder with an opening between disks of 0.01 mm and rotation 1600 rpm. The suspension was passed through grinder forty times.

Nanocomposite production

The composites were developed with the 0_Carr/100_Stch, 100_Carr/0_Stch and 20_Carr/80_Stch matrices. The 20_Carr/80_Stch composition was selected among other blends of the previous stage of the work due to its higher strength at high moisture conditions. Nanofibril suspensions at 8.5% of consistency were applied to heating at 10, 20 and 30% (w/w) loads based on starch and carrageenan masses, following the same procedures described above. Nine composite samples were developed and tested (Table 1).

Analyses description

Scanning electron microscopy (SEM) photographs of the raw and bleached fibres were taken using a scanning electron microscope, acceleration voltage 10 kV. All samples were previously sputter coated with gold before examination. For transmission electron microscopy (TEM) analysis of nanofibrils, an EM 109 instrument was used. Two droplets of each nanofibril suspensions were diluted in 50 ml of water and sonified for 20 min. One droplet of each homogenised suspension was deposited on a cupper microgrid with Formvar (400 mesh) and allowed to dry. The grids were stained with a 1.5% solution of uranyl acetate and lead citrate, and dried at room temperature. Physical tests were carried out for polymer films, blends and composites with three replicates. The water absorption test followed ASTM E 104-85 (ASTM 1991), performed in a

Table 1 Composition of the starch and carrageenan in films and composites

Sample	Nanofibril load (%)	Carrageenan/starch proportion (%)
100_Carr/0_Stch + 0% NF	0	100/0
100_Carr/0_Stch + 10% NF	10	
100_Carr/0_Stch + 20% NF	20	
100_Carr/0_Stch + 30% NF	30	
20_Carr/80_Stch + 0% NF	0	20/80
20_Carr/80_Stch + 10% NF	10	
20_Carr/80_Stch + 20% NF	20	
20_Carr/80_Stch + 30% NF	30	
0_Carr/100_Stch + 0% NF	0	0/100
0_Carr/100_Stch + 10% NF	10	
0_Carr/100_Stch + 20% NF	20	
0_Carr/100_Stch + 30% NF	30	

Carr = carrageenan, Stch = starch, NF = nanofibril load controlled environment at 19 °C and 100% RH, in a desiccator. For each film type, two specimens were cut with a 3 cm-diameter circular steel mold. The samples were placed in an oven at 70 °C for 24 hours and subsequently weighed. Samples were weighed after 1, 2, 3, 4, 5, 24, 48, 72 and 96 hours, considering the starting moment they were placed in the desiccator. The amount of water absorbed was estimated for each period by equation 1:

$$WA = \frac{Mc - Mi}{Mi} \times 100 \qquad (1)$$

where WA = water absorption (%), Mc = current mass (g) and Mi = dry mass (g).

The water solubility of the films was determined according to the Gontard et al. (2007) in circular specimens with diameters of 2 cm. Triplicates were evaluated for each film type. The initial dry mass was obtained after drying at 55 ± 2 °C for 24 hours. The specimens were immersed in 40 ml of distilled water for 24 hours at room temperature. The resulting suspensions were filtered, dried at 105 °C for 24 hours and weighed. The solubility of films was expressed as percentage of solubilised mass in relation to the initial mass according to the equation 2:

$$S = \frac{Md - Ms}{Md} * 100 \qquad (2)$$

where S = solubility (%), Ms = nonsolubilised mass (g) and Md = dry mass (g).

The water vapor permeability rate and water vapor permeability of the films were determined in duplicates by gravimetric parameters according to ASTM E 96-00 (ASTM 2000) and literature (Bourtoom & Chinnan 2008, Guimarães et al. 2015). Circular specimen of 10.5 mm of diameter were cut with steel molds and placed in amber glass with 3/4 of its volume containing silica gel (desiccant) with particle size ranging from 1 to 4 mm, previously dried in an oven at 150 °C for 24 hours. Recipient's dimensions were 10 mm of top diameter, 58 mm of length and 26 mm of base diameter. The covers had height and diameter of 18 nm and 20 mm, respectively. They were perforated at the top with the same dimensions of the glass permeation area. The specimens were placed between the glass and cover.

The specimens were kept in an environment with zero water activity. The recipients were placed in sealed desiccators at 18.5 ± 2 °C filled with 800 ml of water, giving 0.1 atmospheric water activity in contact with the upper surface of the specimens. Mass gain measurements were conducted by weighing the specimen at a precision of 0.0001 g, every 24 hours for 7 days. The water vapor permeability rate of the films was estimated using linear regression between weight gain (g) and time (24 hours). The slope of the linear part of the curve represented the amount of water vapor diffusion through the specimen per unit time (g hour^{-1}). The water vapor permeability rate was expressed by equation 3. After determining the saturated vapor pressure of water at test temperature by equation 4, water vapor permeability was determined by equation 5.

$$WVPR = \frac{g}{T \times A} \qquad (3)$$

$$sp = 0.6108e^{\frac{17,27 \times T}{T + 237,3}} \qquad (4)$$

$$WVP = \frac{WVPR \times t}{sp \times \frac{Rh}{100} - sp \times \frac{Rhi}{100}} \qquad (5)$$

where sp = saturated vapor pressure of water at test temperature 18.5 °C (kPa), T = conditioning temperature (18.5 °C) of the desiccator containing cells with biofilms and distilled water, WVPR = water vapor permeability rate (g hour^{-1} m^{-2}), g T^{1} = slope of the line obtained by linear regression of mass gain (g) in relation to conditioning time (h), A = permeation area of each specimen (m^{2}), WVP = water vapor permeability (g mm KPa^{-1} day^{-1} m^{-2}), t = thickness of the specimen (mm), sp = saturated vapor pressure of the water at testing temperature 18.5 °C (kPa), Rhi = relative humidity inside the glass containing silica gel white equals to 0 % and Rh = relative humidity inside the desiccator containing distilled water (100 %). The sp was calculated according to equation 5 (Tetens 1930). Through diameter and thickness, the volume of the samples was calculated and the density was determined in duplicates using equation 6:

$$d = \frac{m}{v} \qquad (6)$$

where d = density (g cm^{-3}), m = is the mass (g) and v = volume (cm^{3}).

RESULTS AND DISCUSSION

Physical properties of carrageenan and starch films and blends

Density of the films varied from 1.11 to 1.44 g cm^{-3}. The films with 80 and 100% starch showed higher average density values (Figure 1). The density of a polymer is related to its chemical composition, molecular weight (single molecules) and the way the molecules are arranged (crystalline structure) (Sarantópoulos et al. 2002). Although lower density was found for 50_Carr/50_Stch blend, intermediate results found for 80_Carr/20_Stch and 20_Carr/80_Stch showed that starch had higher density.

The water uptake of polymers during exposure to distilled water versus time was analysed (Figure 2). Higher water uptakes are usually related to higher susceptibility to biodegradation of biopolymers (Chiu et al. 2009). The increase in the starch content clearly reduces water absorption by films, hence starch is less hydrophilic than carrageenan. In starch films, the solubilised amylose molecules, due to their linearity, are parallel and get close enough to form hydrogen bonds between hydroxyl groups of adjacent polymers. As a result, the affinity with water is reduced in comparison to powder starch (Wurzburg 1986). The carrageenan high hydrophilic character is attributed to sulfate groups with high ionisation tendency (Pourjavadi et al. 2004).

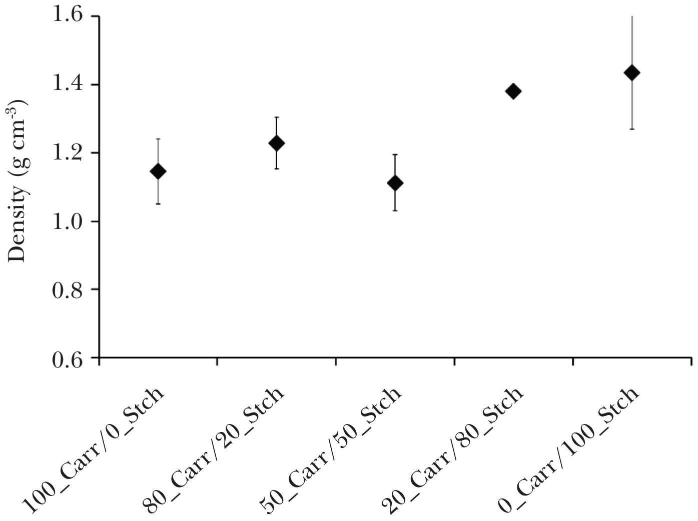

Figure 1 Density of the starch and carrageenan films and blends; Carr = carrageenan, Stch = starch

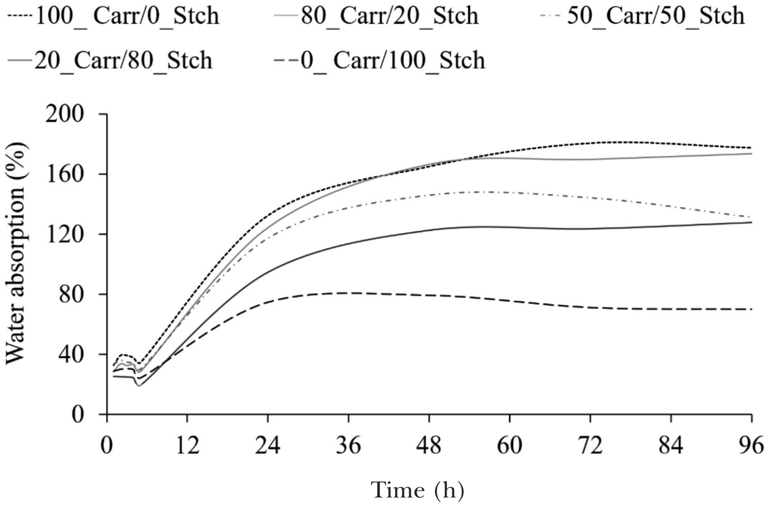

Figure 2 Patterns of water absorption rate of the starch and carrageenan films and blends; Carr = carrageenan, Stch = starch

Starch films (0_Carr/100_Stch) absorbed up to 80% of water and stabilisation was achieved around 30 hours. Oppositely, carrageenan (100_Carr/0_Stch) had absorption values above 160% and stabilisation was not reached before 70 hours. Intermediate results of absorption may be observed for all blends and stabilisation was reached around 50 hours. The water vapor permeability of starch films (0_Carr/100_Stch) was much lower than that found for carrageenan films (100_Carr/0_Stch) as depicted in Figure 3. Differences in water vapor permeability may be related to the difference in water molecule diffusion and hydrophilic to hydrophobic ratio (Garcia et al. 2000). The greatest affinity of biopolymers for water molecules results in higher water diffusion, giving films higher water vapor permeability, as found for 100_Carr/0_Stch samples.

Similar water vapor permeability values were found for 80_Carr/20_Stch and 50_Carr/50_Stch samples. However, 20_Carr/80_Stch blend showed much lower water vapor permeability than the other blends. In comparison to starch films (0_Carr/100_Stch), the addition of another biopolymer leads to interaction with starch chains, breaking their intact network of inter chain hydrogen-bonding. Therefore, blends are a possibility to improve the performance of carrageenan films with poor water vapor permeability.

All samples showed poor resistance to water solubility with values above 98% (Figure 4). This is attributed to the hygroscopic nature of the biopolymers. Starch films (0_Carr/100_Stch) and blends containing higher amount of biopolymer (20_Carr/80_Stch) showed lower solubility possibly due to their higher density. For packaging applications, high water solubility of starch is a disadvantage (Carvalho et al. 2001, Prachayawarakorn et al. 2010). On the other hand, for drug release applications, high water solubility is desirable (Monterrey-Quintero & Sobral 2000). Considering packaging applications, 20_Carr/80_Stch was selected among blends for the production of nanofibrils reinforced composites.

Morphological quality of raw fibres, bleached fibres and nanofibrils

Morphological analysis by scanning electron microscopy revealed that raw sawdust consisted of fibre bundles, and the presence of amorphous non-cellulosic components may be attested in fibre surface (Figure 5a). Alkaline pretreatment with NaOH dissolves lignin, and the bleached fibres provide whiter products with lower amounts of impurities and improved resistance to yellowing (He et al. 2010). Therefore, individualised and free-from-impurities of bleached fibres were obtained after pre-treatments, as observed by the scanning electron microscopy (Figure 5b).

Eucalyptus nanofibrils were successfully produced, as observed by transmission electron microscopy (Figure 5c). Nanofibrils usually exhibit diameters of less than 100 nm and lengths of several micrometers, thus having a large aspect ratio that increases hydrogen bonding capacity (Syverud et al. 2011, Tonoli et al. 2013).

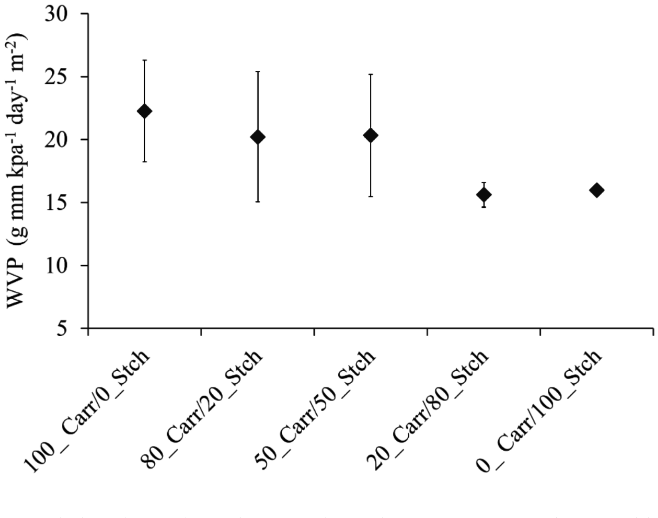

Figure 3 Water vapor permeability (WVP) of the starch and carrageenan films and blends; Carr = carrageenan, Stch = starch

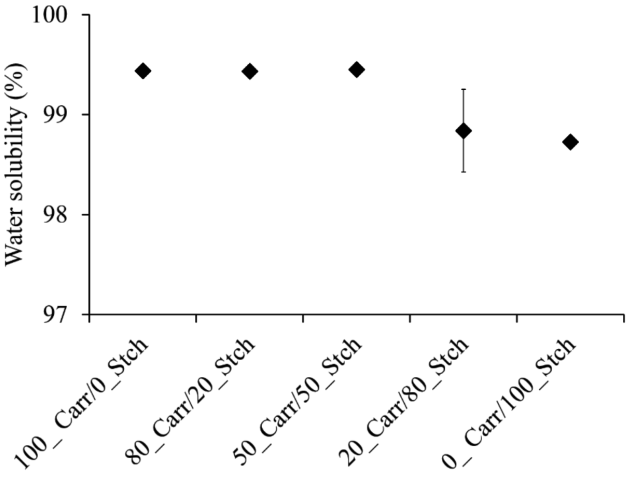

Figure 4 Water solubility of the starch and carrageenan films and blends; Carr = carrageenan, Stch = starch

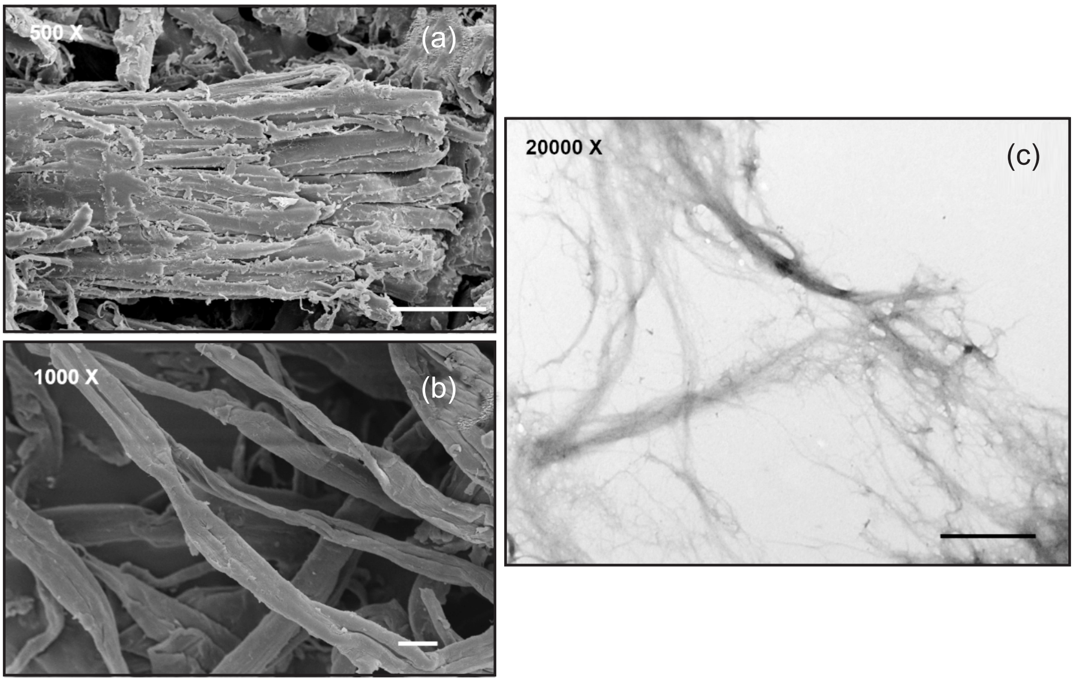

Figure 5 SEM micrographs of the raw fibres (a) and bleached fibres (b) and TEM micrographs of de nanofibrils (c)

Physical properties of carrageenan and starch nanocomposites

Higher loads of nanofibrils resulted in a remarkable increase of density (Figure 6). Moreover, nanocomposites reinforced with 10, 20 or 30% of nanofibrils showed greater strength than non-reinforced films and blends. The denser structure and reduced porosity of nanocomposite films are due to the rigid hydrogen-bonded network among cellulose nanofibrils and the combination between nanofibrils and matrix (Samir et al. 2005, Saxena et al. 2010). Overall analysis showed that higher proportions of starch combined with lower proportions of carrageenan and higher proportions of nanofibrils resulted in lower water absorption of the films (Figure 7). Although it is known that cellulose is highly hydrophilic, it is less hydrophilic than starch (Bodîrlău et al. 2013). Besides, cellulose semi-crystalline structure decreases water absorbency in nanocomposites (Ghanbarzadeh & Almasi 2011).

The water absorption curves showed two distinct phases. Before 24 hours absorption, kinetics was very fast. However, after 48 hours, the

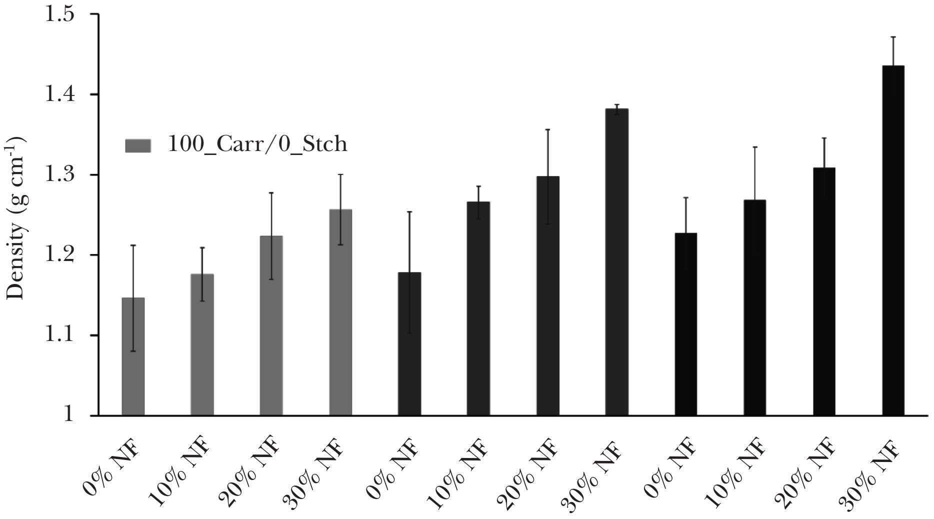

Figure 6 Density of the non-reinforced films and blends (0% NF) and nanocomposites reinforced with different loads cellulose nanofibrils (10% NF, 20% NF and 30% NF); Carr = carrageenan, Stch = starch, NF = nanofibril load

pattern was of slow kinetic absorption followed by equilibrium moisture content. Despite nanofibril addition, carrageenan matrices showed higher water absorption (100_Carr/0_Stch). Composites reinforced with nanofibrils may be applied as packaging mostly due to adequate barrier properties against oxygen and fat, unlike synthetic plastics. However, they are unlikely to resist high humidity due to their hydrophilic nature (Aulin et al. 2010). This effect possibly may be minimised by chemical modification of the material surface or coatings formed by the use of multiple layers of coupled nanocelulose with resins (Spence et al. 2010, Chun et al. 2012).

The increase of nanofibril content substantially decreased water solubility. Unlike non-reinforced films and blends, nanocomposites reinforced with 10, 20 and 30% nanofibrils did not solubilise (Figure 8). This is mainly attributed to the character of cellulose, a relatively stable polymer that does not readily dissolve in water (Lan et al. 2011). Moreover, starch is able to form hydrogen bonds with the hydroxyl and carboxyl groups of cellulose, and this strong structure could reduce the diffusion of water molecules into the materials (Ghanbarzadeh et al. 2010), hence reduce solubility. This may be associated with the good interaction between matrix and nanofibrils which prevented the polymers from being dissolved. The increased solubility with addition of coconut fibre in corn gluten polymers and polyhydroxybutyrate-co-valerate was attributed to poor adhesion of fibres and matrix (Corradini et al. 2014). As a consequence of low solubility of cellulose and good adhesion between nanofibrils and matrix, the lowest value was observed for 0_Carr/100_Stch + 30% NF composites.

Water vapor permeability of nanocomposites remarkably decreased with higher additions of nanofibrils, mainly compared to non-reinforced films as showed in Table 2. The reduction of water vapor permeability is due to strong hydrogen bonds between nanofibrils and hydrophilic matrix. Hence, nanofibrils increase bulk density and decrease voids in polymeric matrix, resulting in tortuosity and hinder transmission of fluids (Beck-Candanedo et al. 2005, Müller et al. 2008, Saxena et al. 2010).

The water vapor permeability of plasticised hydroxypropylmethyl cellulose (HPMC)-coated films was 1.7 g mm m^{-2} day^{-1} kpa^{-1} at 40 °C and 75% RH (Laboulfie et al. 2013), which is much higher than those found in this study. The LDPE polymer, often used in the production of plastic bags and agricultural sector, have water vapor permeability of only 0.11 g mm m^{-2} day^{-1} kpa^{-1} (40 °C, 75% RH), but is not biodegradable and has poor mechanical strength (Laboufie et al. 2013, Guimarães Junior et al. 2015).

CONCLUSIONS

Both carrageenan and starch are environmentally friendly alternatives to petroleum-based polymers

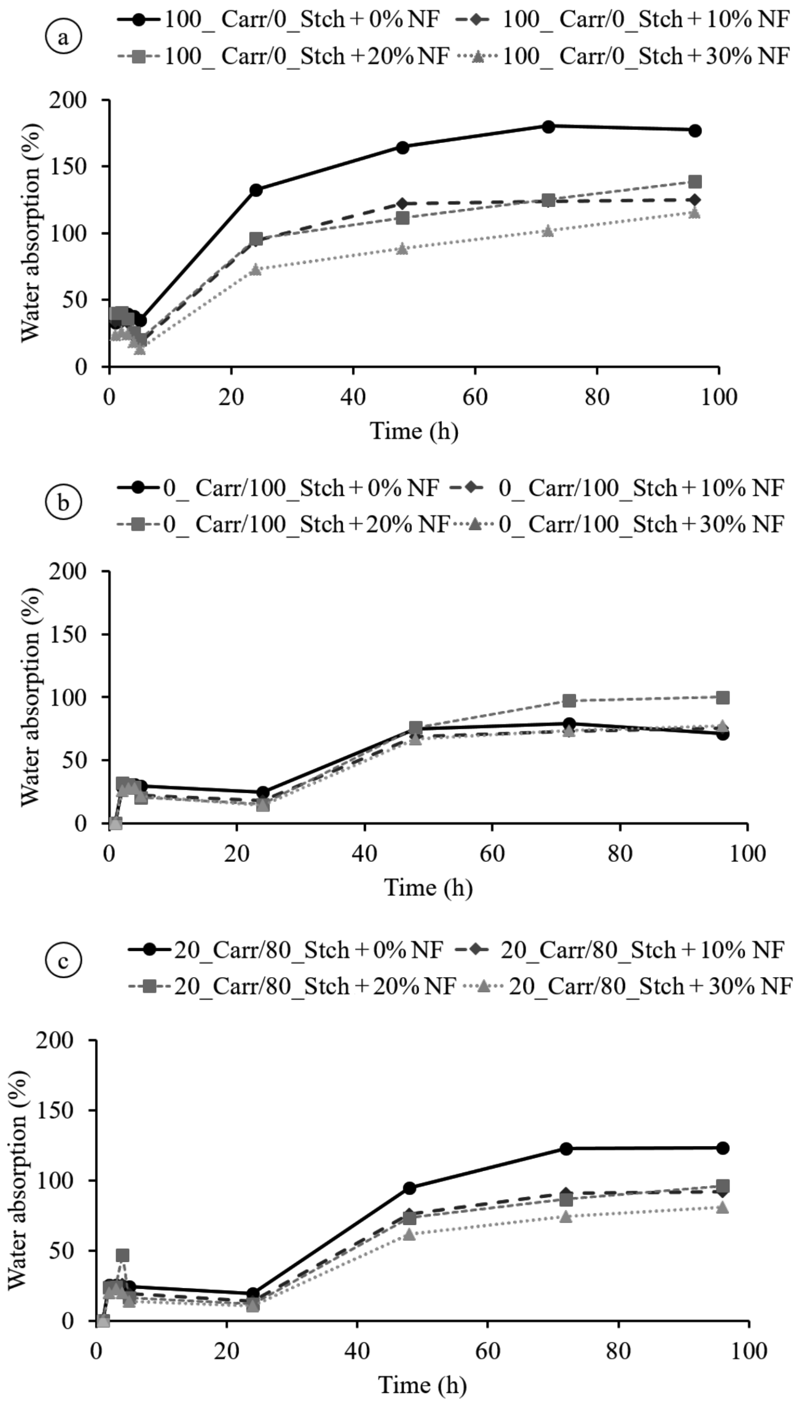

Figure 7 Patterns of water absorption of the non-reinforced films and blends (0% NF) and nanocomposites reinforced with different loads of cellulose nanofibrils (10, 20 and 30% NF); Carr = carrageenan, Stch = starch, NF = nanofibril load

that allow to produce thin films by the casting method. Nevertheless, their hydrophilic nature decrease physical strength which may hinder application possibilities. This work proved that carrageenan is far more hydrophilic than starch, hence the addition of carrageenan to starch should be up to 20%, if better physical strength for packaging purpose is required.

The addition of cellulose nanofibrils provided a substantial improvement of all physical properties in nanocomposites. The increase of nanofibrils from 10 to 30% decreased water solubility and absorption, while density increased. However, this trend was not observed for water vapor permeability. A 10% load of nanofibrils was enough to remarkably decrease water vapor

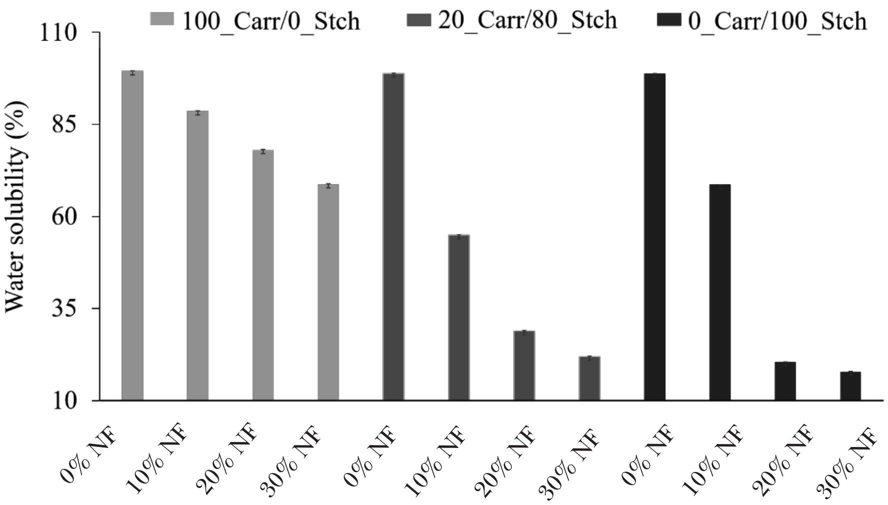

Figure 8 Water solubility of non-reinforced films and blends (0% NF), and nanocomposites reinforced with different loads of cellulose nanofibrils (10, 20 and 30% NF); Carr = carrageenan, Stch = starch, NF = nanofibril load

Table 2 Water vapor permeability of starch and carrageenan films and composites

Samples	WVP (g mm kpa^{-1} day^{-1} m^{-2})
100_Carr/0_Stch + 0% NF	22.26 ± 0.534*
100_Carr/0_Stch + 10% NF	0.02 ± 0.0020
100_Carr/0_Stch + 20% NF	0.01 ± 0.0013
100_Carr/0_Stch + 30% NF	0.01 ± 0.0030
20_Carr/80_Stch + 0% NF	15.62 ± 0.9374
20_Carr/80_Stch + 10% NF	0.01 ±0.0010
20_Carr/80_Stch + 20% NF	0.02 ± 0.0017
20_Carr/80_Stch + 30% NF	0.01 ± 0.0030
0_Carr/100_Stch + 0% NF	15.97 ± 0.389
0_Carr/100_Stch + 10% NF	0.01 ± 0.0013
0_Carr/100_Stch + 20% NF	0.02 ± 0.0015
0_Carr/100_Stch + 30% NF	0.02 ± 0.0030

Carr = carrageenan, Stch = starch, NF = nanofibril load, WVP = water vapor permeability, * = standard deviation values

permeability in relation to non-reinforced films and blends. The composites developed with a matrix of starch/carrageenan added at a proportion of 20 to 80% reinforced with 30% cellulose nanofibrils showed the highest strength in high moisture conditions among samples that combined the three bioresources.

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