Cassava Starch-Based Films Plasticized with Sucrose and Inverted Sugar and Reinforced with Cellulose Nanocrystals

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Abstract: Bionanocomposites films of cassava starch plasticized with sucrose and inverted sugar and reinforced by cellulose nanocrystals (CNCs) were prepared by solution casting method incorporating 0.1 to 5 wt% of eucalyptus CNCs. The nanocrystals were characterized using transmission electron microscopy, whereas the bionanocomposites properties were studied using Fourier transform infrared spectroscopy, tensile measurements, water solubility, swelling behavior, and water activity (a_w). The water resistance properties (solubility and swelling behavior) of the nanocomposites were enhanced with the addition of cellulose nanofillers. These results were explained in terms of the high crystallinity of the nanocrystals and the formation of a rigid network with the nanofillers, which provide physical barriers to the permeation of water within the hydrophilic cassava matrix. The addition of CNCs in the bionanocomposites decreases a_w linearly, reaching values below 0.5 (for CNCs concentration higher than 4 wt%), a reference value for no microbial proliferation for food product design. The presence of small concentrations of CNCs (0.1–0.3 wt%) also effectively increased the maximum tensile strength (more than 90%) and elastic modulus (more than 400%), indicating the formation of a suitable percolation network in this concentration range. Because the cellulose nanofillers enhanced the mechanical and water stability properties of the nanocomposites, the obtained results in this work may be applied to the development of biodegradable packaging or coatings to enhance shelf life of food products.

Keywords: cellulose nanowhiskers, coatings, nanocomposite, starch, sucrose

Practical Application: The main drawbacks of using starch-based polymers as packaging or coating in the food industry are their low mechanical properties and inherent water sensitivity. This study demonstrates that cellulose nanocrystals can be used to: (i) obtain better mechanical properties (increasing the tensile strength and modulus more than 90% and 400%, respectively; (ii) enhance the water stability and (iii) water activity of starch-based films. These results indicate that the obtained environmentally friendly nanocomposites in this work can be used to the development of films or coatings to enhance the shelf life of food products.

Introduction

Advanced technology in the field of petrochemical-based polymers has resulted in many benefits. However, environmental awareness as a result of nondegradable plastic materials has become a major issue in the last years (Lu and others 2006). In this context, developing entirely biodegradable thermoplastic polymers from agricultural and renewable resources such as starch has received considerable attention (Mathew and Dufresne 2002; Lu and others 2006; Mathew and others 2008; García and others 2011).

The applications of starch-based plastics can include biodegradable packaging in the food industry, particularly as coatings to enhance the shelf life of products. However, the low mechanical properties of starch and its inherent water sensitivity restrict the use of starch films, especially in moist environments. In addition, starch films are relatively brittle. Thus, plasticizers are used to decrease the glass–rubber transition temperature (Tg) below the decomposition temperature of the matrix and also to increase the flexibility of the films. For this matrix, glycerol and water are the most widely used plasticizers (Mathew and Dufresne 2002). Alternatively, Veiga-Santos and others (2007) reported the application of sucrose and inverted sugar as plasticizers in starch films. The authors described that both sucrose and inverted sugar have important effects on the elongation at break of starch films.

An attractive way to increase the mechanical performances of biopolymers is the addition of inorganic nanoparticles (Lu and others 2004; Miyagawa and others 2005; Lu and Larock 2006) or natural organic fillers (Petersson and others 2007; Jiang and others 2008) to prepare different bio-based nanocomposites with improved physical–mechanical properties. However, to produce a

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fully bio-based and biodegradable nanocomposite, both the polymer matrix and the nanoreinforcement have to be derived from renewable resources. In this context, highly crystalline rod-like nanostructures obtained from cellulose, called cellulose nanocrystals (CNCs) or cellulose nanowhiskers (CNWs), are excellent candidates for improving the properties and applications of renewable-based polymers (Habibi and others 2010; Holt and others 2010; Eichhorn 2011). CNCs consisting of highly crystalline rod-shaped nanoparticles can be obtained through a controlled acid hydrolysis (using sulfuric or hydrochloric acid) of different cellulose sources, such as plants or tunicate, a sea animal (Dufresne 2010). The average CNC dimensions obtained from plants are 100–250 nm in length and 5–15 nm in diameter. In addition to their high aspect ratios, the advantages of using CNCs for the design of new bio-based nanocomposites include their renewability, low density, low cost, and high specific mechanical properties (Eichhorn and others 2010; Klemm and others 2011).

Several authors have reported improved mechanical properties and good dispersion of CNCs in hydrophilic polymers such as pullulan (Kristo and Biliaderis 2007), chitosan (Li and others 2009; Azeredo and others 2010), polyvinyl alcohol (PVA) (Paralikara and others 2008), and starch (Anglès and Dufresne 2001; Mathew and Dufresne 2002; Lu and others 2006; Mathew and others 2008; García and others 2011). Anglès and Dufresne (2001) described a plasticized waxy maize starch matrix reinforced with tunicin whiskers. In a later study, Mathew and others (2008) evaluated the mechanical behavior of starch nanocomposites plasticized by sorbitol and reinforced by tunicin whiskers with filler contents between 0 and 25 wt%. More recently, García and others (2011) studied the effect of a glycerol plasticizer on the morphology of nanocomposites made from waxy maize starch and starch nanocrystals. Although a number of studies dealing with starch as matrix and polysaccharide as nanofillers can be found in the literature, no study on cassava-starch-based nanocomposites plasticized by sucrose and inverted sugar and reinforced with CNCs has been reported.

In this work, bionanocomposites completely obtained from renewable resources were prepared by combining (in appropriate amounts previously established) (Veiga-Santos and others 2007) the cassava starch matrix, sucrose, and inverted sugar as plasticizers and low contents of CNCs obtained from eucalyptus wood pulp. Because the incorporation of CNCs can enhance the properties of bio-based films, the main goal of this work was to investigate the influence of cellulose nanoparticles on the mechanical, water-resistant properties, and water activity, a_w. The a_w in particular is an important parameter for food product design because it determines the possibility of microorganism proliferation and the shelf life of perishable products. The bionanocomposites were characterized mainly using Fourier transform infrared (FTIR) spectroscopy, tensile test measurements, and water activity testing.

Materials and Methods

Materials

Eucalyptus kraft wood pulp was generously supplied by Bahia Pulp Company (Camaçari, Brazil). Cassava starch was donated by Cargill Agrícola S.A. (Porto Ferreira, Brazil). Commercial sucrose and inverted sugar with 60% inversion were supplied by Açúcar Guarani S.A. (Olímpia, Brazil). Sodium hydroxide, sodium chlorite, sulfuric acid, and acetic acid were purchased from Vetec Química Fina (Duque de Caxias, Brazil).

CNWs preparation

Sulfuric acid hydrolysis of the eucalyptus wood pulp was performed as described previously in the literature and in our previous works, with minor modifications (Beck-Candanedo and others 2005; de Mesquita and others 2010; de Mesquita and others 2011). Briefly, after bleached treatment of the cellulose, using NaOH and NaClO$_2$ (sodium chlorite), the resulting material was ground until a fine particulate was obtained. Then, 10.0 g of cellulose was added to 160.0 mL of 64 wt% sulfuric acid under strong mechanical stirring. Hydrolysis was performed at 50 °C for about 20 min. After hydrolysis, the dispersion was diluted twofold in water, and the suspension was washed using three repeated centrifuge cycles. The last washing was conducted using dialysis against deionized water until the dispersion reached a pH of ∼6. A stable suspension of CNCs was obtained through sonication for approximately 5 min.

Bionanocomposites preparation

Sample films were prepared by casting a mixture of cassava starch (4 g), sucrose (0.7 g), and inverted sugar (1.4 g) in a suspension containing 100 mL of distilled water (Veiga-Santos and others 2007). The bionanocomposites films were prepared by adding the aqueous dispersion of CNCs in the desired quantity. A series of cassava starch bionanocomposites plasticized with sucrose and inverted sugar were prepared with CNC contents of 0, 0.1, 0.2, 0.3, 0.4, 0.5, 1.0, 1.5, 3.0, 4.0, and 5.0 wt% and were coded as F-0.1%, F-0.2%, F-0.3%, F-0.4%, F-0.5%, F-1.0%, F-1.5%, F-3.0%, F-4.0%, and F-5.0%. At least six replicates films of each specific concentration of CNCs were prepared. The samples were heated to 70 °C under constant stirring and with dehydration under renewable circulated air (35 ± 5 °C) in Petri plastic dishes. Samples were stored at 23 °C and 75% relative humidity (RH) for 10 days prior to testing.

Methods

Transmission electron microscopy (TEM) was used to characterize the CNCs. TEM images were taken using a FEI Tecnai G2-Spirit with a 120-kV acceleration voltage. Diluted water suspensions of the nanowhiskers (0.01% wt/v) were deposited on a carbon–formvar-coated copper grid (300-mesh). The samples were subsequently stained with a 2% uranyl acetate solution.

Mechanical properties were obtained using an Emic Universal Testing Instrument (Model DL2000), operated as specified in the ASTM standard method D882–00 (2000). Film strips of 8 cm × 2.5 cm (length × width) were cut from each preconditioned sample and mounted between the grips of the machine. The initial grip separation and crosshead speed were set to 50 mm and 12.5 mm/min, respectively. At least 10 replicates of each specimen were averaged together.

FTIR spectroscopy was conducted using a Perkin Elmer FTIR spectrophotometer (Model Spectrum 100, Perkin Elmer, Waltham, Mass., USA) in the frequency range of 4000–600 cm^{-1}. The samples were prepared by the KBr-disk method.

Water activity (a_w) was measured with a Decagon, Aqualab Lite. Pure water (a_w of 1.000 ± 0.001%) and LiCl (a_w of 0.500 ± 0.015%) were used as calibration standards. Preconditioned samples (4 cm^2) were cut from the center of the films and evaluated in triplicate.

The degree of weight loss of the samples in distilled water was performed at 37 °C (to increase the solubility of the test films). The samples were submerged in distilled water for 24 h and the weight loss percentage was determined by weight

loss (%) $= (W_b - W_a)/W_a \times 100$, where W_b is the dry weight of the sample before submersion and W_a is the dry weight of the sample after submersion.

For determination of the swelling behavior, the samples were submerged in distilled water for a specific length of time (ranging from 5 to 120 min) at 23 °C. The degree of swelling of each sample was determined by degree of swelling (%) $= (W_a - W_b)/W_b \times 100$, where W_b is the original dry weight of the sample and W_a is the weight after submersion in distilled water.

For statistical analysis purposes, the data were analyzed by ANOVA using a statistical program StatSoft v.7 (StatSoft, Inc., Tulsa, Okla., USA). The Tukey test was used to evaluate average differences (at a 95% confidence interval).

Results and Discussion

Figure 1 shows a typical TEM image of the eucalyptus CNWs. The image shows some isolated rod-shaped nanoparticles and also some laterally aggregated elementary crystallites. These aggregates are often observed (Elazzouzi-Hafraoui and others 2008; de Mesquita and others 2011) in TEM images due to the high specific area of these nanoparticles and the strong hydrogen bonds established between the whiskers (Elazzouzi-Hafraoui and others 2008; de Mesquita and others 2010). The length and width of the CNCs were extracted from several TEM images (about 50 images), and the mean length (L) and diameter (D) of the isolated CNCs were determined to be 145 ± 25 and 6.0 ± 1.5 nm, respectively, resulting in an aspect ratio (L/D) of approximately 24.

Figure 2 shows the FTIR spectra for the neat film (control, without CNCs) and for bionanocomposite films of various CNC concentrations. The main bands that appear in the spectrum of cassava starch are a broad band at 3284 cm^{-1} attributed to -OH stretching and a band at 1647 cm^{-1} due to OH bending vibrations (Zhang and Han 2006; Chen and others 2008; Chen and others 2009). Other important bands that appear in the spectrum of the control film and the nanocomposites are listed in Table 1. Because of the chemical similarities between cassava starch and cellulose and also the relatively low content of nanowhiskers within the cassava starch matrix (up to 5.0 wt%), the FTIR spectra of the control film and the nanocomposite are similar.

Compared to the control film, the broad band at ~3284 cm^{-1} of the nanocomposite with 5 wt% nanocrystals moved from 3284 to 3300 cm^{-1}, suggesting that new hydrogen bonding interactions between CNCs and starch molecules are formed. The formation of hydrogen bonds between CNCs, the cassava starch, and the used plasticizers (sucrose and inverted sugar) is expected considering the chemical structure of these polysaccharides. However, these interactions were difficult to detect in the films with concentrations between 0.1 wt% and 1.5 wt% because of the small amount of nanocrystals in these samples.

The wave number band at 1647 cm^{-1} is strongly influenced by the amount of water molecules bound by the monosaccharides in the films. This peak shifted to 1638 and 1629 cm^{-1} as the nanocrystal concentration increased (Table 1), indicating a different amount of water associated with the matrix. Because a_w is related to the intensity with which water associates with substances, this result is in agreement with the observed changes in the a_w with CNC concentration that will be discussed later in the text.

The degree of swelling for the control film and bionanocomposite films of various CNC concentrations is shown in Figure 3. In general, we observed a decrease in swelling with the addition of nanowhiskers for all the samples investigated, clearly indicating that nanowhiskers can increase film stability in water. The degree of swelling of both the control film and the nanocomposites increased very abruptly as the submersion time increased up to approximately 10 min, after which the degree of swelling increased gradually, reaching an equilibrium at long submersion times.
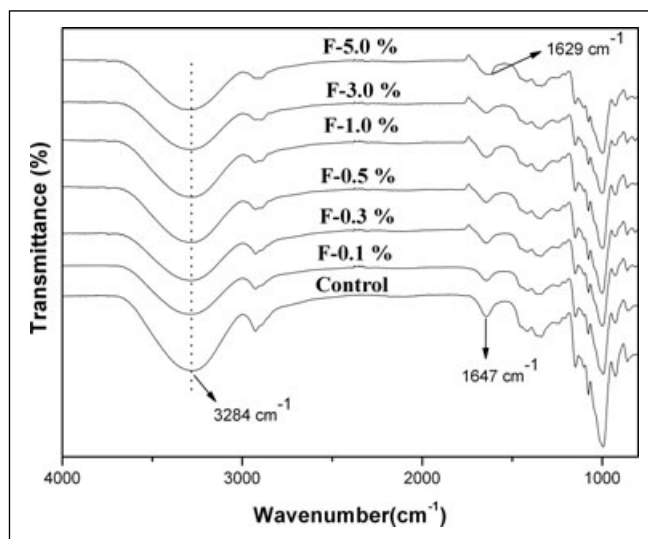

Figure 2–FTIR of the control film and nanocomposites with different CNC concentrations.

Table 1–Location (in cm^{-1}) of the peaks in the FTIR spectra obtained for the control film and the nanocomposites with different nanocrystal concentrations (in parentheses).

Control	Films (0.1; 0.3; 0.5 wt%)	Films (1.0; 3.0; and 5.0 wt%)	Peak assignment
3284	3284; 3284; 3284	3284; 3295; 3300	-OH (st)
1647	1647; 1647; 1647	1647; 1638; 1629	-OH (b)
1150	1147; 1147; 1147	1147; 1156; 1156	C-O (st)
1078	1078; 1078; 1078	1078; 1078; 1087	C-O-H (st)
982	992; 990; 990	990; 990; 990	C-O (st) in C-O-C

The last column (peak assignment) associates the characteristic infrared absorption wave numbers with specific bonds. (st): stretch, (b):bend.
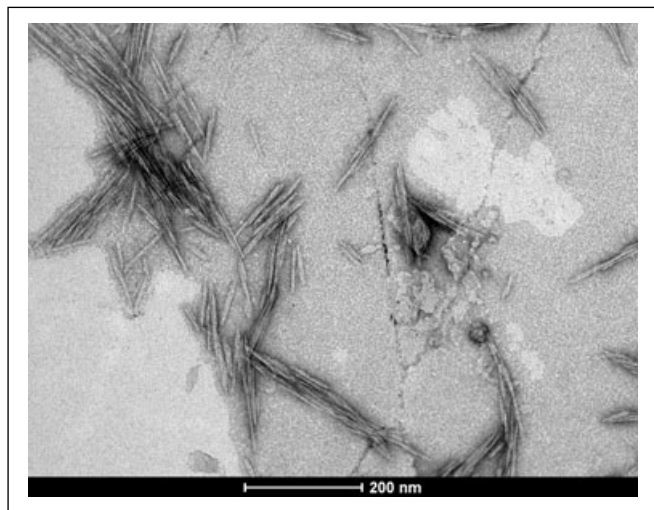

Figure 1–TEM image of eucalyptus CNCs.

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A comparison between film types indicates that the degree of swelling at equilibrium (after a submersion time of 120 min) of pure cassava starch film was the highest (about 200%). For F–0.1% to F–3.0% samples, the degrees of swelling were similar, ranging between 158% and 154%. The F–5.0% sample had the lowest degree of swelling, indicating that the water absorption was lowest when the concentration of nanocrystals was high.

One of the most important parameters used in food preservation is the water activity (a_w) control. Thermodynamically, a_w is defined as the ratio of the escaping tendency (fugacity, f) of water in a system (for example, a food product or a film package) to the fugacity of pure water (f_o), $a_w = f / f_o$. For practical purposes, it brings important information about the amount of free (also referred as unbound or active) water present in a sample (Lewicki 2004). Reducing the amount of unbound water minimizes the availability of water to microorganisms, avoiding undesirable chemical changes for storage of products. The shelf life of perishable products is therefore generally longer for systems with low water activity (a_w) values (Mathlouthi 2001). Substrates having a_w values lower than 0.600 are relatively protected from microbial contamination, whereas proliferation of specific microorganisms can occur with a_w values greater than 0.600 (Mathlouthi 2001). Considering that water migrates from areas of high a_w to areas of low a_w, it is important to have low values of a_w for food product design, such as bio-based films that can be used as food products packages.

Comparing the nanocomposites with the control film ($a_w = 0.63$), we can observe that the addition of CNCs decreases a_w values almost linearly (Figure 4). For the nanocomposites with 4.0 and 5.0 wt% of CNCs, the a_w is below 0.5, a reference value for no microbial proliferation for food product design.

Considering that the a_w values are related to the amount of free water in a system, the results above indicates that the presence of the nanocrystals within the matrix decreases the availability of water in the films. It can be due to the high number of hydroxyl groups on the surface of the nanoparticles. These hydroxyl groups can interact with the unbound water molecules present within the matrix via hydrogen bonds (a short-range interaction), decreasing the a_w.

The results described here indicate that a_w can be controlled by incorporating CNCs in the cassava starch films plasticized with sucrose and inverted sugar. Thus, the addition of CNCs can increase the shelf life of the nanocomposites films because they are less susceptible to the growth of microorganisms. Indeed, preliminary short storage test results showed that starch/CNCs film coatings enhanced the shelf life of food products compared to a neat starch matrix (without CNCs). The results of this storage test are currently under investigation and will be described in a next work.

When a biofilm remains in contact with high water activity products or when the material may be in contact with water, water solubility resistance is an important property (Gontard and others 1992; Veiga-Santos and others 2007). The weight loss percentage of the control film and the nanocomposites after submersion in distilled water for 24 h are shown in Figure 4. The addition of CNCs decreased almost linearly the solubility of the films in water up to a concentration of 3 wt% from approximately 56% weight loss for the control film to approximately 38% weight loss for the F–3.0% film. The F–4.0% and F–5.0% films had similar solubilities. These results suggest that the presence of CNCs in the cassava starch matrix increases its stability in water.

The nanocomposite solubility together with the swelling behavior reveals the same influence of CNCs on the water resistance of the films. In a previous work (de Paula and others 2011), we showed that the CNCs can be used to control the hydrolytic degradation of PDLLA polymer because they provide a physical barrier inhibiting the water absorption, the first step of biodegradation in water.

With cassava-starch-based nanocomposites, the matrix is more hydrophilic than the nanocrystals. In addition, the CNCs can provide a physical barrier by creating a tortuous path for water permeation, decreasing water absorption and the interaction of the starch matrix with water molecules. The behavior of CNCs as a physical barrier to water permeation can be explained by the high level of crystallinity of the rigid-rod-shaped nanoparticles (crystallinity index ∼87%, calculated from XRD analysis) and the rigid-hydrogen-bonded network governed by a percolation mechanism established within the matrix. As stated by de Rodriguez and others (2006) in sisal cellulose whiskers reinforced polyvinyl acetate nanocomposites, the three-dimensional network formed by hydrogen bonds between the CNCs significantly inhibits swelling and solubility of the nanocomposites in water, similarly to the
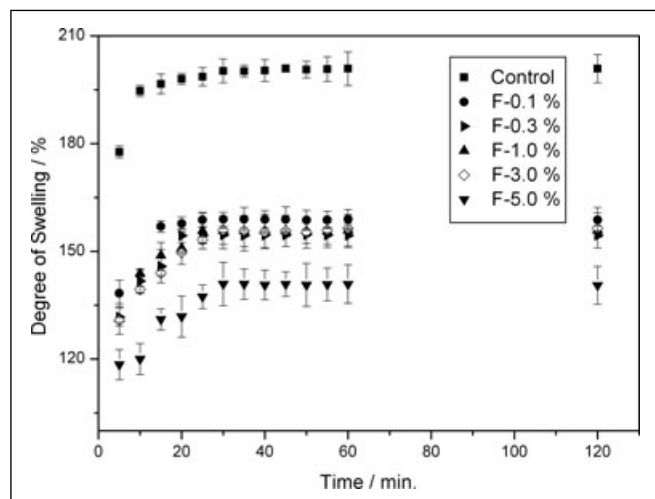
Figure 3–Degree of swelling of the control film (plasticized cassava starch) and the bionanocomposites with different CNC contents.
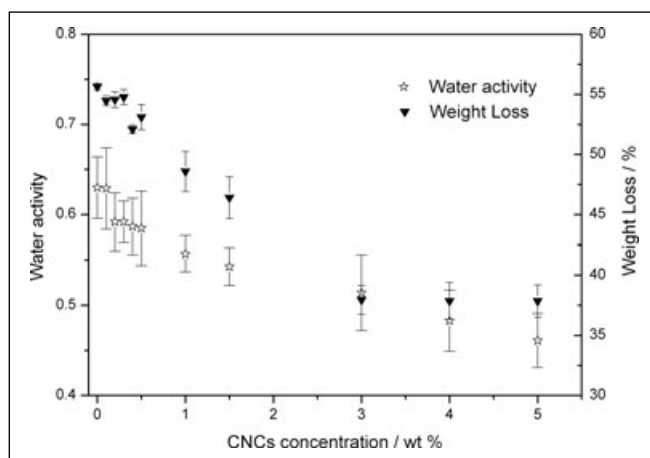

Figure 4–Water activity (a_w) and weight loss of the films as a function of the CNC concentration.

formation of chemical cross-links within a polymer phase. The high crystallinity of the CNCs has also been used to explain the decrease in the water vapor transmission rate of membranes based on PVA/CNCs (Paralikara and others 2008) and xylan/CNCs (Saxena and Ragauskas 2009).

Figure 5 shows the stress–strain curves for the control film and bionanocomposites with different CNC concentrations. Table 2 shows the influence of the nanocrystals on the mechanical behavior. The modulus (E), tensile strength (σ), and elongation at break (ε) are shown for all the studied nanocomposites.

The presence of CNCs effectively increased the tensile strength (σ) by approximately 90% with the addition of only 0.1 wt% of nanofiller (from 0.87 to 1.61 MPa). The results in tensile strength for the nanocomposites having 0.1 to 0.3 wt% of CNCs are very similar. For example, the nanocomposite with 0.2 wt% of CNCs showed an increase in tensile strength of 92% and an increase in elastic modulus (E) of more than 400% compared to the neat plasticized cassava starch. These results show that the mechanical properties of the nanocomposites were considerably enhanced with only 0.1–0.3 wt% of CNCs, indicating the formation of a suitable percolation network with small amounts of cellulose nanofillers. Moreover, it was observed that this percolation network (in this concentration range) was sufficient to increase the tensile strength and modulus considerably without significantly affecting the elongation at break. These results may be due to good dispersion of the nanocrystals within the matrix and to good interfacial adhesion among the components in this complex system formed by cassava starch, plasticizers (sucrose an inverted sugar), and CNCs. We believe that the large amount of hydroxyl groups present in the plasticizer allows a suitable interface between the components, created by strong hydrogen bond interactions. Above concentrations of 0.3 wt%, we observed a slightly decrease in σ, reaching again similar values of those observed for small concentrations of CNCs in the nanocomposite with 5 wt% of the nanofillers ($\sigma = 1.58$ MPa).

The elastic modulus (E) increased almost linearly with increasing levels of CNWs in the concentration range examined, with an increase of approximately 2500% for the F-5.0% film compared to the control sample.

A considerable decrease in the elongation at break was observed for concentrations greater than 1.0 wt% (Table 2). Sufficiently high concentrations of CNCs increase the possibility of the formation of a stiff and continuous network of cellulose nanofillers linked together through hydrogen bonding that would hinder chain stretching (Lu and others 2006; Azeredo and others 2009; Siqueira and others 2010). The decrease in the elongation at break with increased CNC loading has been described by other authors as an indication of good interaction between the starch and the nanowhiskers (Azeredo and others 2009).
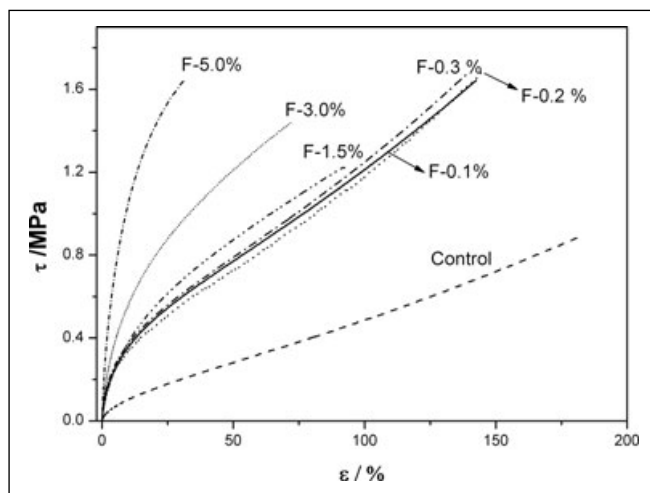
Conclusions

Bionanocomposites obtained entirely from renewable resources were prepared with cassava starch plasticized with sucrose and inverted sugar and reinforced by CNCs. The length and diameter of the CNCs obtained from eucalyptus were determined to be 145 ± 25 and 6 ± 1.5 nm, respectively. The addition of cellulose nanofillers clearly decreases the swelling of the films, indicating that the nanocrystals increased the film stability in water. Moreover, the solubility of the films in water linearly decreased as the concentration of CNCs increased. The results on swelling behavior together with the solubility in water were explained mainly in terms of the high crystallinity of the CNCs and the formation of a rigid network with the nanofillers that provide physical barriers inhibiting the permeation of water in the films. The a_w linearly decreased with the concentration of the CNCs in the bionanocomposites. The a_w for the nanocomposites with 4.0 and 5.0 wt% of CNCs is below 0.5, a reference value for no microbial proliferation for food product design. The decrease in a_w was explained due to the presence of high amount of hydroxyl groups on the surface of the nanocrystals that can interact with unbounded water molecules present inside the matrix through hydrogen bonds interactions. The mechanical properties of the bionanocomposites were also considerably enhanced by small concentrations of CNCs. The nanocomposite with 0.2 wt% CNCs showed an increase in tensile strength of 92% and an increase in elastic modulus of more than 400% compared to the neat film, indicating the formation of a suitable percolation network with small amounts of cellulose nanofillers. Finally, since the incorporation of CNCs into the studied bio-based films could enhance not only the mechanical and water stability properties but also decreased the a_w of the nanocomposites, the obtained results in this work may be applied to the development of environmentally friend films or coatings to enhance shelf life of food products. Storage test of food products using these films is currently under investigation and will be described in a next work.

Figure 5–Stress–strain curves for the control film and the nanocomposites with different CNC concentrations.

Table 2–Values of elastic modulus, stress at break, and strain at break for the control film and the bionanocomposites with different contents of CNCs.

	Modulus (GPa)	Stress at break (MPa)	Elongation at break (%)
Control	1.00 ± 0.24[c]	0.87 ± 0.22[b]	180.44 ± 4.05[a]
F-0.1%	4.97 ± 1.11[a]	1.61 ± 0.16[a]	140.21 ± 6.01[b]
F-0.2%	5.34 ± 0.88[b]	1.68 ± 0.21[c]	135.10 ± 12.75[c]
F-0.3%	4.82 ± 1.32[d]	1.63 ± 0.27[a]	137.33 ± 19.49[d]
F-0.4%	3.04 ± 1.23[e]	1.54 ± 0.14[d]	146.61 ± 14.32[e]
F-0.5%	2.39 ± 0.52[f]	1.36 ± 0.21[e]	154.51 ± 25.54[f]
F-1.0%	5.01 ± 1.20[a]	1.30 ± 0.36[f]	132.81 ± 26.11[g]
F-1.5%	5.33 ± 0.82[b]	1.20 ± 0.18[g]	89.94 ± 23.04[h]
F-3.0%	9.81 ± 1.46[g]	1.39 ± 0.36[h]	67.22 ± 21.99[i]
F-4.0%	9.38 ± 1.79[h]	1.23 ± 0.16[i]	71.02 ± 24.74[j]
F-5.0%	25.65 ± 2.13[i]	1.58 ± 0.21[j]	27.29 ± 10.24[k]

Experimental values with the same letter and in the same column (in parentheses) mean that they are not significantly different ($P > 0.05$).
The $\pm$ values are deviation from the average values.

Acknowledgments

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