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Cassava Starch-Based Foams Reinforced with Bacterial Cellulose

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ABSTRACT: The objective of this work was to produce composite foams trays based on cassava starch and reinforced with bacterial cellulose using a baking process. Bacterial cellulose (native and modified by a mercerization process) was incorporated into starch composite foams by two methods: direct incorporation of bacterial cellulose powder into the starch matrix during baking process (method 1) or coating the trays surface with bacterial cellulose films (method 2) after they were produced. All formulations resulted in well-shaped trays, and the addition of bacterial cellulose by method 1 improved the foaming ability of starch producing more expanded and thicker trays. The water absorption capacity was reduced by the incorporation of bacterial cellulose, independently of the method of incorporation. The elongation was improved in trays produced by method 2. These results demonstrate that the incorporation of native or modified cellulose was able to improve some properties of cassava starch trays. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 3043–3049, 2013

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INTRODUCTION

Cellulose and starch are the most abundant biopolymers in nature, and among many types of biodegradable polymers, starch is one of the most promising materials for the preparation of biodegradable products[1] with applications in different areas.

In the search for better solutions to the waste management problems associated with petroleum-based synthetic plastics, a new class of biodegradable materials has been studied and developed. Among the most studied biopolymers is cassava starch, which has the advantages of coming from renewable sources and being biodegradable, inexpensive (US$ 0.25–0.60/kg), and widely available.[2–5]

Thermoplastic starch materials have some drawbacks, such as poor water resistance and relatively poor mechanical properties.[6] When natural fibers are mixed with starch materials, the mechanical properties are improved, indicating good adhesion between the reinforcing fibers and the polymeric matrix.[7]

Recently, cellulose from different sources has attracted attention due to its versatility as well as its physical and chemical properties. The inherent biodegradability and renewability of cellulose make it interesting for forming blends with other biopolymers.

Several sources of cellulose such as wood pulp,[8] bleached eucalyptus pulp fibers,[9] flax fibers and ramie fibers[10,11] or crystallites,[12] and tunicin whiskers[13,14] have been tested to obtain biocomposites. The results of these studied demonstrated that the compatibility between cellulose and starch can be observed in the improvement of performance of the biocomposites with regard to mechanical properties[15] and water resistance.[16,17] The performance improvement may be attributed to the occurrence of intermolecular interactions between these different components.

Starch materials can achieve a significant increase in water resistance by adding cellulose, crystallites, or microfibrillated cellulose,[18] and composites prepared with bacterial cellulose displayed better mechanical properties than those prepared with vegetable cellulose fibers.[19]

Despite several groups of researchers analyzing the biocomposite formed between cellulose and starch, few studies have described the preparation and characterization of bacterial cellulose/starch composites.[20,21] Most of the composites use microfibrils of cellulose, nanowhiskers, or vegetal fibers.

The objective of this work was to produce biodegradable foams trays based on cassava starch by baking with the addition of bacterial cellulose as a reinforcement material using two methods: direct incorporation of bacterial cellulose powder into the starch matrix during the baking process (method 1) or coating the surface of the produced trays with bacterial cellulose films (method 2). These biocomposites were characterized in terms of their microstructure, crystallinity, physicochemical, and mechanical properties.

Table I. Description of Trays Samples

Trays samples	Bacterial cellulose type	Method of incorporation of cellulose
Control sample	–	–
NB1	Native	Method 1
MDB1	Modified	Method 1
NB2	Native	Method 2
MDB2	Modified	Method 2

EXPERIMENTAL

Materials

Cassava starch (19% amylose) was provided by Hiraki Industry (São Paulo, Brazil). Glycerol, magnesium stearate, and guar gum were purchased from Synth (Labsynth, São Paulo, Brazil). Native bacterial (NB) cellulose was provided by Bionext Produtos Biotecnológicos (Curitiba, Brazil). The modified bacterial (MDB) cellulose was obtained by the mercerization process. NB cellulose films were soaked in NaOH solutions for 24 h. After this treatment, the films were gradually washed repeatedly with deionized water and then vacuum-dried at 40°C.

Methods

Tray Manufacturing by Baking. The trays were manufactured using two different methods of incorporation of bacterial cellulose, and the trays samples are described in Table I. In the first method (method 1), the cellulose films (NB or MDB) were dried and milled to yield particles <0.35 mm. The powder obtained was incorporated into the starch matrix as follows: starch (99 g), bacterial cellulose powder (1 g), water (100 mL), and additives (1 g magnesium stearate and 1 g guar gum) were mixed for 10 min with a mechanical stirrer (Vithory-Brazil) at 18,000 rpm; magnesium stearate was added to prevent the starch foam sticking to the mold, and guar gum was added to prevent solid separation.[5] Then, glycerol (5 g) was added, and after further stirring for 10 min, 80 g of each formulation was homogeneously layered on a 235-mm long, 180-mm wide, 20-mm deep Teflon mold with a 1.0-mm-thick metallic guide. A Teflon lid was placed over the mixture, and thermopressure was applied using a hydraulic press (JOMAQ, São Paulo, Brazil) equipped with an electrical heating system, Pt100 temperature sensor, and proportional-integral-derivative controller. One pressing step at 130°C for 20 min at 100 bars was performed. The trays were removed from the press, unmolded, and stored for 4 days at 25°C and 58% relative humidity before characterization.

In the second method (method 2), the surface trays were coated with NB or MDB films. The trays were produced in the same way as described in method 1, without the bacterial cellulose, using 100 g of starch. The NB or MDB films were then soaked in water and placed on the upper surface of the tray to dry (room temperature for 12 h). The weight of the membranes used to coat the trays corresponded to the same weight as the dried membranes incorporated in method 1. The coated trays were conditioned at 25°C and 58% relative humidity before characterization.

A control sample manufactured exclusively with starch was prepared according to method 1, without the addition of bacterial cellulose and using 100 g of starch.

Bacterial Cellulose Characterization. ***Opacity.*** Samples (40 × 40 mm) were analyzed for opacity using a BYK Gardner colorimeter according to Sobral.[22] The colorimeter compared the opacity of the sample to a white (Y_w) and a black (Y_b) standard, according to the equation: $Y = (Y_b/Y_w) \times 100$. The results were given as the percentage of opacity. All the tests were conducted in triplicate.

Water absorption capacity. Native and MDB cellulose films (2.5 cm × 5 cm) were weighed and soaked in distilled water for 5, 15, 30, and 60 min. The samples were weighed after removing the excess water. The quantity of adsorbed water was calculated as the weight difference and expressed as the mass of absorbed water per mass of the original sample.[23] The values are the means of five determinations for each film. The same method was used for the characterization of the trays, which were soaked in water for 1, 15, and 30 min.

X-ray diffraction. X-ray diffraction (XRD) spectra of the bacterial cellulose films were obtained using a Panalytical X'Pert PRO MPD diffractometer (Netherlands), using Kα copper radiation ($\lambda = 1.5418$ Å) at 40 kV and 30 mA. All assays were performed with ramping at 1°/min, analyzing the range of 5°–40° (2θ). The degree of crystallinity was determined for cellulose I as described by Segal et al.[24] and for cellulose II by Hindeleh and Johnson[25] method. The same conditions were used for the characterization of the trays.

Characterization of the Trays. ***Thickness.*** The tray thickness was measured with a manual micrometer (Mitutoyo, Japan). For each formulation, the reported value is the average of three measurements from 10 samples tested.

Density. The density was calculated as the relationship between weight and volume.[26] The reported values are the averages of 10 determinations for each formulation.

Color. The foam color was determined using a colorimeter (CR 10, Minolta Chroma Co., Osaka, Japan). The color parameters range from $L = 0$ (black) to $L = 100$ (white), −a (green) to +a (red) and −b (blue) to +b (yellow).[27] The instrument was calibrated using a set of three Minolta calibration plates. The reported values are averages of five measurements of each formulation.

Scanning electron microscopy. The qualitative assessment of the morphology of the trays was performed using a FEI Quanta 200 microscope (Oregon, USA). Tray pieces were mounted on the bronze stubs using double-sided tape and then coated with a layer of gold (40–50 nm), allowing surface and cross-section visualization. To obtain the cross-section visualization, the samples were prepared by immersion into liquid nitrogen to avoid deformation during the fracture. All the samples were examined using an accelerating voltage of 15–20 kV.

Mechanical properties. A texture analyzer model CT3 (Brookfied, EUA) with a 25-N load cell was used to determine the mechanical properties of the foam samples by tension tests.

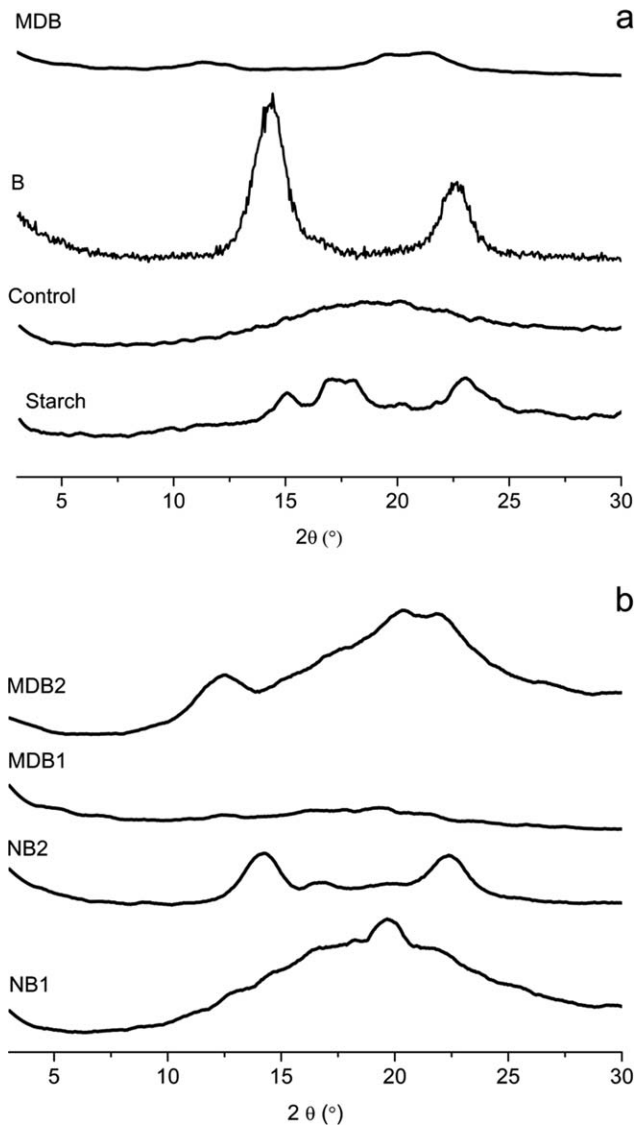

Figure 1. X-ray diffractograms: (a) starch, native bacterial cellulose (B), modified bacterial cellulose (MDB) and control sample; (b) starch-bacterial cellulose trays produced by method 1 (NB1, MDB1), and starch trays produced by method 2 (NB2, MDB2).

Tensile tests were performed using strips measuring 100 mm × 25 mm, an initial grip separation of 80 mm and a crosshead speed of 2 mm/s. Stress–strain curves were recorded during extension, and stress and strain at break were determined. Each formulation was assayed five times, and the reported values are the averages of these assays.

Statistical Analysis. Analysis of variance and Tukey mean comparison tests ($P \leq 0.05$) were performed with Statistica software version 7.0 (Statsoft, OK).

RESULTS AND DISCUSSION

Bacterial Cellulose Characterization

NB and MDB cellulose films were characterized according to their crystallinity, opacity, and water absorption capacity (WAC).

The opacity of the native cellulose film was 64% ± 5%, while the modified cellulose film showed an opacity value of 58% ± 7%. Although the modified films showed a lower opacity value, these values did not differ significantly ($P \leq 0.05$).

XRD was used to reveal the modification in the supramolecular structure of cellulose after the mercerization process. Native cellulose, namely, cellulose I, is the crystalline cellulose produced naturally by vegetables, bacteria, and algae.[28] Cellulose II, also called regenerated cellulose, refers to cellulose precipitated from solutions, generally alkali solutions,[29,30] as well as the modified cellulose obtained in this work. These two forms of cellulose represent the two main polymorphs of cellulose. The structure of cellulose I is made up of parallel chains,[31,32] whereas the crystalline structure of cellulose II is described as antiparallel.[33]

The XRD profile of NB cellulose is characteristic of cellulose type I as shown in Figure 1, with peaks at $2\theta = 14.3°$ and 22.6°.[34,35] The modified sample (MDB) presented a different profile of diffraction, with peaks at $2\theta = 12.1°$ and 19.8° representative of cellulose II,[36] and the large base of these peaks represents the presence of an increased amount of amorphous cellulose in this sample. The degree of crystallinity of native and MDB cellulose was 63.3% and 51.0%, respectively, demonstrating the increase in the amorphous region in the MDB cellulose (cellulose II). Cellulose fibers are composed of crystalline and amorphous regions, and the conversion of cellulose I into cellulose II implies a different crystalline organization that indicates different properties such as WAC.

The WAC of cellulose has been reported as varying between 100 and 120 times its dry weight.[37] In this work, as demonstrated in Figure 2, after 5 min of soaking in water, the absorption capacity of NB cellulose was observed to be near 300% and that of MDB cellulose was near 400%. After 10 min of soaking in water, both NB and MDB showed an increase in their absorption capacity, but the increase was much higher in the modified cellulose. After 15 min of soaking in water, a slight increase occurred, and the WAC remained stable for both forms of cellulose. The higher values obtained for modified cellulose most

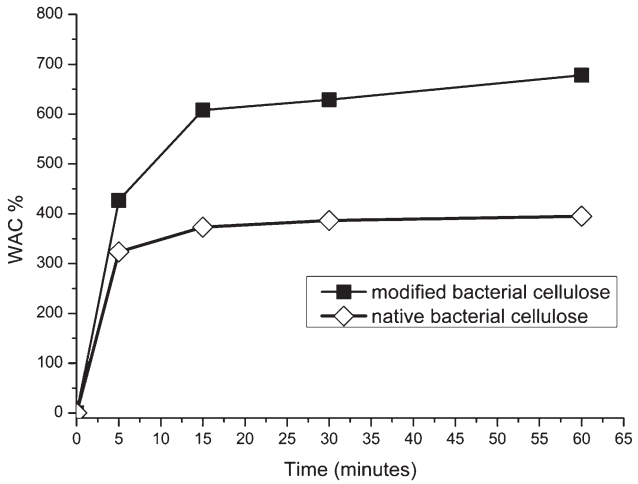

Figure 2. Water absorption capacity of native and modified bacterial cellulose.

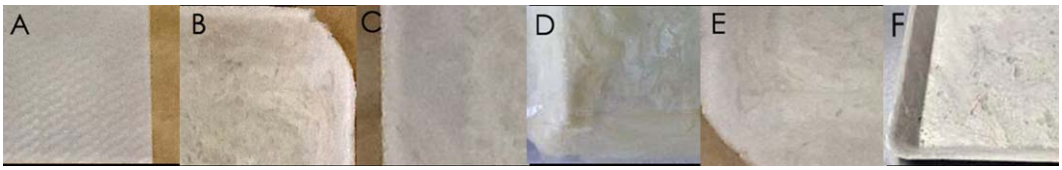

Figure 3. Photographs of bacterial cellulose film and trays: film of bacterial cellulose (A), NB1 (B), MDB1 (C), NB2 (D), MDB2 (E), and control (F) (tray with starch only). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

likely occurred, because, during the process of conversion of cellulose I into cellulose II, part of the crystalline region of cellulose I was converted into amorphous cellulose, into which water penetrates easily.

Composite Foams Trays Characterization

Thickness and Density. All formulations in this study were able to form well-shaped trays, without pores or cracks (Figure 3). The thickness of the trays ranged from 2.12 to 3.02 mm (Table II). The control sample, which was produced without the bacterial cellulose addition, showed the lower thickness value. When this sample was compared to the trays produced by method 1 (NB1 and MDB1 trays), the addition of the filler most likely improved the ability of the starch paste to foam, resulting in more expanded and thicker materials. The NB2 and MDB2 trays showed the higher thickness values (Table II), which occurred, because the trays were coated with the bacterial cellulose films, increasing their thicknesses. The type of bacterial cellulose (native or modified) did not significantly affect the thickness of the trays (Table II; Tukey test, $P \leq 0.05$).

The trays density ranged from 0.1905 to 0.3231 g/cm^3 (Table II). The addition of bacterial cellulose by method 1 resulted in less-dense materials compared to control samples. The production of the less-dense materials most likely occurred, because the addition of filler generated more expandable materials, with lower density values. The processing of starches results in stiff materials,[38] which do not support air cell growth in their foams. The fiber may have acted as reinforcing filler that improved the foaming ability of the starch pastes, resulting in more expandable materials. The same trend was observed by Vercelheze et al.,[5] and these authors reported a reduction in foam density achieved with the addition of sugarcane bagasse fibers.

The NB2 and MDB2 trays had higher density values compared to trays produced by method 1 (NB1 and NB2), but when these trays were compared to control sample, the density values were not significantly (Tukey test, $P \leq 0.05$) affected by the coating (Table II), and certainly this occurred because the increase in weight resulted from the coating was very low when compared with the total weight of the trays. The type of bacterial cellulose (native or modified) did not significantly affect the density of the trays prepared by method 2 (Tukey test, $P \leq 0.05$; Table II).

The density values obtained in this work are higher than the values of expanded polystyrene alone, which are close to 0.06 g/cm^3.[39,40] The density values of these foam specimens are also similar to the values obtained by Vercelheze et al.,[5] who studied foams based on cassava starch, sodium montmorillonite (Cloisite®Na$^+$), and sugarcane bagasse fibers.

Color Parameters of the Trays. The color parameters of samples are shown in Table II. The luminosity (L^*) of the trays ranged from 72.76 to 78.29, indicative of the whiteness of these samples. The incorporation of bacterial cellulose by method 1 did not significantly affect the luminosity of the trays (Tukey test, $P \leq 0.05$) when these samples were compared to control one (Table II). The samples produced by method 2 (NB2 and MDB2) had the lower L^* values between the two groups of trays because of the presence of the films on tray surfaces. The type of bacterial cellulose (native or modified) did not significantly affect the luminosity of the trays (Tukey test, $P \leq 0.05$; Table II).

The increase in a^* and b^* color parameters was related to the redness and yellowness of the samples, respectively, and in this work, these color parameters were not affected by the type of bacterial cellulose or by the method of incorporation (Table II), which is an interesting result, and an advantage once several authors reported that the addition of vegetal fibers to starch materials resulted in an increase in the color parameters, limiting the use of these reinforcing agents in food applications.[2,5,41]

Table II. Thickness, Density, and Color of the Trays Samples

			Color parameters		
Trays samples	Thickness (mm)	Density (g/cm^3)	L^*	a^*	b*
Control sample	2.12 ± 0.04 c	0.2809 ± 0.0264 a	76.12 ± 2.31 a	1.06 ± 0.32 a	6.52 ±0.72 a
NB1	2.26 ± 0.04 b	0.1920 ± 0.0212 b	78.29 ± 2.12 a	1.54 ± 0.33 a	6.49 ±0.56 a
MDB1	2.30 ± 0.08 b	0.1905 ± 0.0227 b	79.04 ± 2.15 a	1.49 ± 0.25 a	5.74 ±0.75 a
NB2	3.02 ± 0.10 a	0.3111 ± 0.0400 a	72.76 ± 2.23 b	1.18 ± 0.12 a	5.18 ±1.12 a
MDB2	3.01± 0.07 a	0.3231 ± 0.0312 a	72.48 ± 3.10 b	1.17 ± 0.15 a	4.18 ±1.15 a

The data are the means of replicate determinations ± standard deviation. Different letters in the same column indicate significant differences ($P \leq 0.05$) between means (Tukey test).

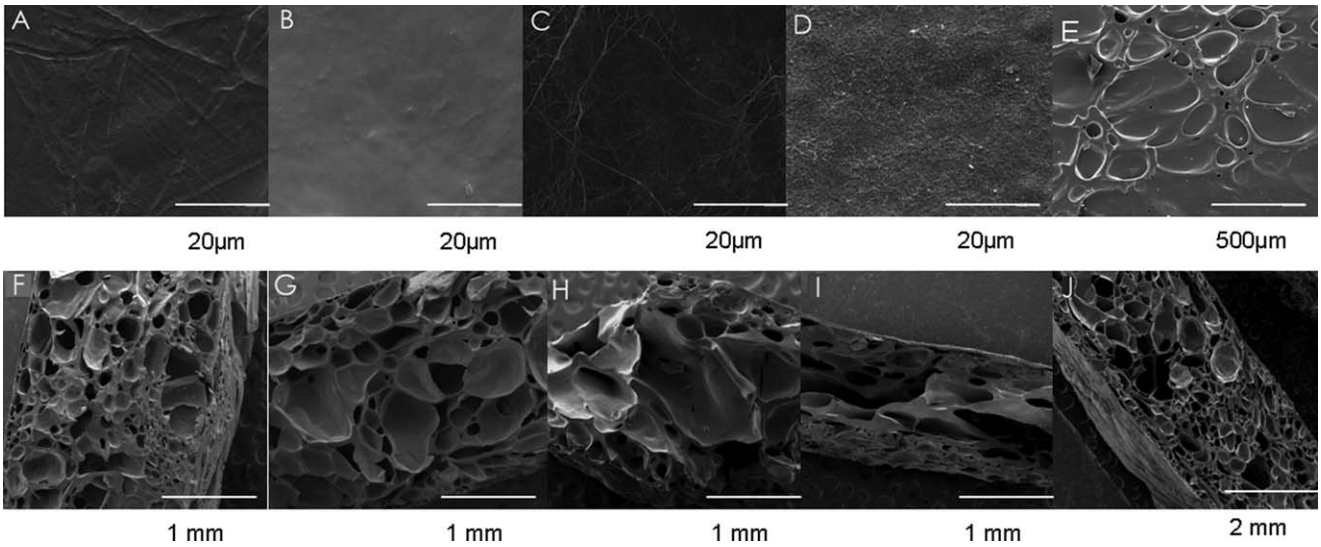

Figure 4. SEM micrographs of surface of trays: NB1 (A), NB2 (B), MDB1 (C), MDB2 (D), control (E); and cross-sections of trays: NB1 (F), NB2 (G), MDB1 (H), MDB2 (I), and control (J).

X-ray Diffraction. According to literature data,[42,43] cassava starch has a C-type crystallinity with peaks at $2\theta = 15.3°$, 17.3°, 18.3°, 22.0°, and 23.5°, seen in Figure 1 in the diffractogram of cassava starch. These peaks disappeared in the control trays as a consequence of starch gelatinization during the baking process. As expected, in the trays produced by method 1, the diffraction profiles of NB1 and MDB1 trays were different, and the peaks of the crystalline structure of bacterial cellulose disappeared during the baking process, and this occurred because of the crystalline melting of bacterial cellulose submitted at this thermal processing (baking). George et al.[44] reported an endothermic peak at 120.47°C observed by differential scanning calorimetry, which was related to the crystalline melting temperature of the NB cellulose, and these authors also reported that the NaOH-treated membranes showed lower melting temperatures when compared with native cellulose ones.

In the samples produced by method 2, the diffractograms of NB2 and MDB2 trays were similar to the diffractograms of pure NB cellulose and MDB cellulose, respectively, once the films were used to coat the trays.

Scanning Electron Microscopy. In the trays produced by method 1 [Figure 4(B,D)], the SEM micrographs of the surface provided evidence of the strong interfacial adhesion between the bacterial cellulose and the starch matrix, shown by the excellent dispersion of cellulose within the matrix, without aggregates or small fragments or isolated fibrils. The incorporation of bacterial cellulose resulted in trays with a more uniform surface when compared with the control sample [Figure 4(E)]. Obviously, in the case of the samples prepared by method 2, the fibrils of bacterial cellulose were clearly observed in the surface of the trays [Figure 4(A,C)].

All the formulations showed expanded structures with large air cells, and the incorporation of bacterial cellulose by either method 1 or method 2 did not change this morphology. As observed in the scanning electron micrographs of cross-sections of the trays [Figure 4(F–J)], the baked starch foams have a sandwich-type structure with dense outer skins that contain small cells comprising the surface of the foam.

Water Absorption Capacity. The WAC of the starch trays increased significantly with the increase of immersion time for all samples (Table III). Following 1 min of immersion in water, the WAC ranged from 30 to 57%, and following 30 min of immersion, the absorption capacities ranged from 113 to 247%. According to Sjöqvist et al.,[45] foaming reduces the overall weight of the structural materials, and the lower-density and porous structure possess a greater absorption capacity. A similar phenomenon was observed in this work.

The incorporation of bacterial cellulose was effective in decreasing the WAC of starch trays (Table III). All samples that included this filler, independently of the method of addition used, showed lower WAC values when compared with the control sample. The samples prepared by method 2 showed lower WAC than samples prepared by method 1 (Table III). According to Martins et al.,[19] starch is more hydrophilic than bacterial or vegetal cellulose, and when the cellulosic films were used as coating on a surface of the tray in our work, this resulted in decreasing of WAC values.

When method 1 was used to prepare the trays, the WAC values were significantly lower when the native cellulose was used (NB1; Table III). During mercerization, the alkali penetrates the cellulose fiber and causes a rearrangement of the crystal packing of chains from native cellulose I,[46] with chains aligned in parallel, to cellulose II, where the chains are antiparallel, and increases the specific surface area of the fiber, making the hydroxyl groups of the cellulose macromolecules more easily accessible to interact with water, as observed in our work. During the process of conversion of cellulose I into cellulose II, part of the crystalline region of cellulose I was converted into

Table III. Water Absorption Capacity and Mechanical Properties of Trays Samples

	WAC (%)			Mechanical properties	
Trays samples	1 min	15 min	30 min	Tensile strength (MPa)	Elongation (%)
Control sample	57 ± 4 aC	185 ± 13 aB	247 ± 22 aA	11.39 ± 0.89 a	1.69 ± 0.02 b
NB1	39 ± 7 cC	86 ± 6 dB	143 ± 9 cA	12.15 ± 0.92 a	1.57 ± 0.55 b
MDB1	46 ± 4 bC	125 ± 6 bB	185 ± 13 bA	10.97 ± 1.05 a	1.99 ± 0.27 b
NB2	30 ± 4 dC	104± 14 cB	140 ± 7 cA	11.07 ± 1.21 a	30.35 ± 3.97 a
MDB2	30 ± 3 dC	77 ± 9 dB	136 ± 7 cA	13.05 ± 1.38 a	37.58 ± 4.35 a

The data are the means of replicate determinations ± standard deviation. Different small letters in the same column and capital letters in the same line indicate significant differences ($P \leq 0.05$) between mean (Tukey test).

amorphous regions where water penetrated easily. This conversion could explain the water absorption behavior of native and modified films, where the modified cellulose film showed higher values than native cellulose film (Figure 2).

When method 2 was used, the cellulose type did not affect the WAC (Table III). Sjöqvist et al.[45] reported that the increase in the amount of absorbed water at the initial times is related to the porosity of the foam, but the increase in the amount of absorbed water with increasing time might be related to water absorption by the starch itself. In this work, when method 2 was used, the cellulose films most likely acted as a barrier, slowing the contact of the water with the porous structure of the trays, independently of the cellulose type.

The absorption test used in this work does not distinguish between pore absorption and absorption by the starch-based material itself. Both processes occur simultaneously and most likely at high rates, as observed from the absorption capacity measured in this work.

Mechanical Properties. The tensile strength of samples was not affected by bacterial cellulose incorporation (Table III), but elongation values of NB2 and MDB2 were higher than those of control samples. The coating most likely acts as a support for the trays, preventing their disruption under a tensile force, which is an interesting characteristic for these materials. Starch foams are stiff and brittle due to the greater intermolecular interactions between starch molecules,[36] and so any alternative that improves the elongation of these materials is promising.

CONCLUSIONS

This study demonstrated that the incorporation of bacterial cellulose type I and cellulose type II, even at a low concentration (1%), was able to improve some of the properties of cassava starch trays. The trays produced with bacterial cellulose produced biocomposites that were more expanded, thicker, and without changes in color parameters. The trays produced by method 1 were less dense and had lower WAC, and the scanning electron microscopy demonstrated an excellent dispersion of cellulose within the matrix, which was shown in the uniform surface of the trays. Method 2 is useful to produce trays with lower water absorption capacities and higher elongation. The main difference related to bacterial cellulose type (native or modified) was the WAC, which was higher for MDB cellulose and for the trays produced with this cellulose type. These results provided an initial insight into the use and characteristics of bacterial cellulose in starch-based composites as a function of the method of formation of the biocomposites.

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