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Properties of baked foams based on cassava starch, sugarcane bagasse fibers and montmorillonite

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A B S T R A C T

The objectives of this work were to develop biodegradable trays from cassava starch, sugarcane fibers and Na-montmorillonite (Na-MMT) using a baking process and to study the effects of these components on the microstructure and physicochemical and mechanical properties of the trays. All formulations resulted in well-shaped trays with densities between 0.1941 and 0.2966 g/cm^3. The addition of fibers and Na-MMT resulted in less dense and less rigid trays. As observed in the water sorption isotherms, the increase in the equilibrium moisture content was more pronounced when the samples were stored at RH (relative humidity) above 75%. The foams had high water absorption capacities (>50%) when immersed in water (1 min). The studied processing conditions resulted in good nanoclay dispersion, leading to the formation of an exfoliated structure. The trays developed in this study represent an alternative for the packaging of foods with low water contents.

1. Introduction

The development of biodegradable packaging based on starch has attracted an increasing amount of attention; however, materials produced from this biopolymer have some problems, including poor mechanical properties and hydrophilicity. Water solubility increases the degradability and the speed of degradation; however, moisture sensitivity also limits the applications of the material. The use of composites and nanocomposites from these materials can also aid in the development of new low-cost products with better performances (Yu, Dean, & Li, 2006).

Fiber-reinforced composites have been studied in various applications and reviewed by many authors because they have excellent specific properties, such as high strength, low weight and good barrier properties. In that respect, natural fibers are generally interesting because they not only have the functional capability to substitute for the widely used glass fibers but also have advantages from the point of view of weight and fiber–matrix adhesion, specifically with polar matrix materials, such as biopolymeric matrices. These agro-based materials are abundant in nature and frequently are wastes from various industrial processes. For example, sugarcane bagasse fiber, which is a poorly valorized waste residue from the sugar and alcohol industries in Brazil, is often used as fuels in households or is sometimes burned in the fields as a means of disposal. Sugarcane bagasse fiber consists of about 40–50% cellulose (Satyanarayana, Arizaga, & Wypych, 2009; Sun, Sun, Zhao, & Sun, 2004).

Nanocomposites are systems that contain fillers with at least one nanosized dimension and represent a new class of materials that exhibit improved mechanical, thermal, barrier and physicochemical properties compared with the starting polymers and conventional (microscale) composites. Although several nanoparticles have been recognized as possible additives to enhance polymer performance, most intensive studies are currently focused on layered silicates, such as montmorillonite (MMT), due to their availability, versatility, low cost and respectability towards the environment and health (Azeredo, 2009).

The montmorillonite crystal lattice consists of 1-nm thin layers with an octahedral alumina sheet sandwiched between two tetrahedral silica sheets. The layers are negatively charged, and this charge is balanced by alkali cations, such as Na^+, Li^+ or Ca^{2+}, in the gallery space between the aluminosilicate layers. Na-montmorillonite (Na-MMT) clay is hydrophilic with a high surface area and is miscible with hydrophilic polymers, such as starch (Ardakani, Mohseni, Beitollahi, Benvidi, & Naeimi, 2010; Ray & Okamoto, 2003). The properties of the resulting

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material are dependent on the state of the nanoclay in the nanocomposite, i.e., if it is exfoliate or intercalate. Intercalation is the state in which polymer chains are present between the clay layers, resulting in a multilayered structure with alternating polymer/inorganic layers. Exfoliation is the state in which the silicate layers are completely separated and dispersed in a continuous polymer matrix (Weiss, Takhistov, & McClements, 2006).

Some patents have reported that the introduction of fibers and/or inorganic fillers is interesting to improve mechanical properties of starch materials (Andersen et al., 1998; Andersen & Hodson, 1995, 2001). Other studies have shown that is possible to obtain food packaging from mixtures of starch, fibers, water and other additives by thermopressing or baking (Carr, Ponce, Parra, Lugao, & Buchler, 2006; Hofmann, Linke, Tsiapouris, & Ziems, 1998; Schmidt & Laurindo, 2010), and these products could be an alternative to the use of expanded polystyrene foams. The foam baking process includes two steps: starch gelatinization and water evaporation, which expands the mixture and forms a foam, and foam dehydration until a final moisture content of 2–4% is obtained (Shogren, Lawton, Doanne, & Tiefenbacher, 1998). Thus, the objectives of this work were to investigate the use of a baking process to prepare composite and nanocomposite trays based on cassava starch, sugarcane bagasse fiber and Na-montmorillonite and then to study the effect of these components on the microstructure and physicochemical and mechanical properties of the trays.

2. Material and methods

2.1. Materials

Cassava starch (19% amylose) was provided by Hiraki Industry (São Paulo, Brazil). Sugarcane bagasse was provided by regional ethanol producers and then was washed, dried and milled to yield particles < 0.70 mm. Na-montmorillonite (Closite® Na^+) was purchased from Southern Clay Products (USA) and was used as received. Glycerol, magnesium stearate and guar gum were purchased from Synth (Labsynth, São Paulo, Brazil).

2.2. Methods

2.2.1. Tray manufacturing by baking

The starch trays were manufactured using different formulations on the basis of previous results (not published). The fiber compositions ranged from 0 to 20 g/100 g of solids, and Na-MMT ranged from 2.5 to 5.0 g/100 g solids. All formulations are shown in Table 1.

To prepare each formulation (Table 1), the indicated starch, sugarcane fibers, Na-MMT, water and additives (1% w/w magnesium stearate and 1% w/w guar gum) were mixed for 10 min with a mechanic stirrer at 18,000 rpm (Vithory-Brazil), and glycerol (5% w/w for CONTROL films and 10% w/w for all the other formulations) was then added. After further stirring for 10 min, 70–105 g of each formulation was homogeneously layered on a 235-mm long, 180-mm wide and 20-mm deep Teflon mold with a 1.0-mm thick metallic guide. A Teflon lid was placed over the mixture, and thermopressing was applied with a hydraulic press (JOMAQ, São Paulo, Brazil) equipped with an electric heating system, Pt100 temperature sensor and PID (proportional–integral–derivative) controller. One pressing step at 130 °C for 20 min and 100 bar was performed. Finally, the trays were removed from the press, unmolded and stored for 4 days at 25 °C and 58% relative humidity before characterization.

2.2.2. Tray characterization

2.2.2.1. Thickness. The tray thickness was measured with a manual micrometer (Mitutoyo, Japan). For each formulation, the reported value is the average of 3 measurements from 10 tested samples.

2.2.2.2. Density. The density was calculated as the relationship between weight and volume (Shogren et al., 1998). The reported values are the averages of 10 determinations for each formulation.

2.2.2.3. Scanning electron microscopy (SEM). SEM analyses were performed with a FEI Quanta 200 microscope (Oregon, USA). The foam pieces were mounted on bronze stubs using double-sided tape and then coated with a layer of gold (40–50 nm) for surface and cross-section visualization. To obtain the cross-sections, the samples were immersed into liquid nitrogen to prevent deformation during sectioning. All samples were examined using an accelerating voltage of 20 kV.

2.2.2.4. Water absorption capacity. Samples measuring 2.5 cm by 5 cm were weighted and soaked in distilled water for 1, 5, 10, 15, 20, 25 and 30 min. After removing the water excess using tissue paper, the samples were weighed again. The quantity of adsorbed water was calculated as the weight difference and expressed as mass of absorbed water per mass of the original sample (ABNT, 1999). The reported values are the means of five determinations for each formulation.

2.2.2.5. Water sorption isotherms. The starch foam specimens (2.5 × 2.5 cm) were pre-dried for 14 days over anhydrous calcium chloride and then were placed at 25 °C over saturated salt solutions in separate desiccators with the desired levels of relative humidity (32, 43, 58, 75 and 90%) (Rockland, 1960). Each foam specimen was weighed at regular intervals (a minimum of 6 h and a maximum of 12 h), and when two consecutive measurements were equal, it was assumed that equilibrium had been reached. Under the above conditions, an equilibrium period of 14 days was sufficient to establish equilibrium in all samples. The equilibrium moisture content was calculated from the increase in the mass of the dried sample after equilibration at a given RH. All tests were conducted in triplicate.

The sample dimensions (width, length and thickness) were recorded at the initial and final incubation times (14 days) at each RH condition for the water sorption isotherm assays.

2.2.2.6. Crystallinity. The crystallinity of the foams was investigated by X-ray diffraction. The analysis was performed with a Panalytical X'Pert PRO MPD diffractometer (Netherlands), using Kα copper radiation ($\lambda = 1.5418$ Å), at 40 kV voltage and 30 mA current operation. All assays were performed with ramping at 1°/min.

2.2.2.7. Fourier Transform-Infrared Spectroscopy (FT-IR). Foam samples were dried at 70 °C for 3 h in a hot air circulation oven, pulverized with a mortar and pestle, and stored in a desiccator with calcium chloride for 7 days. The pulverized and dried samples were then mixed with potassium bromide and compressed into tablets. The FT-IR analysis was carried out using a Shimadzu FT-IR–8300 (Japan), with a resolution of 4 cm^{-1} and in the range of 4000–400 cm^{-1}.

2.2.2.8. Mechanical properties. A texture analyzer model TA.XT2i (SMS, Surrey, UK) with a 25-N load cell was used to determine the mechanical properties of the foam samples by means of tension tests. Tensile tests were performed using strips measuring 100 mm by 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

Table 1
Compositions of the batters used to prepare the trays based on cassava starch (CS), sugarcane fiber and Na-MMT.

Formulations	CS (g/100 g solids)	Fiber (g/100 g solids)	Na-MMT (g/100 g solids)	Water (mL/100 g solids)	Batter amount (g)
Control	100	–	–	100	80
F10	90	10	–	200	70
F20	80	20	–	200	95
MMT2.5	97.5	–	2.5	150	95
MMT5	95	–	5.0	200	100
F10MMT2.5	87.5	10	2.5	200	100
F10MMT5	85	10	5.0	250	105
F20MMT2.5	77.5	20	2.5	280	100
F20MMT5	75	20	5.0	300	105

was assayed 10 times, and the reported values are the averages of 10 assays.

2.2.3. Statistical analysis

Analysis of variance (ANOVA) and Tukey mean comparison test ($p \leq 0.05$) were performed with the Statistica software version 7.0 (Statsoft, OK, USA).

3. Results and discussion

3.1. Baking process

Limited concentrations of each component (starch, fiber and Na-MMT) (Table 1) were chosen on the basis of previous results. Magnesium stearate was added to prevent the starch foam sticking to the mold, guar gum was added to prevent solid separation (Salgado, Schmidt, Ortiz, Mauri, & Laurindo, 2008; Shogren et al., 1998) and glycerol was added as a plasticizer.

The volume of water added to each formulation was directly related to the fiber and Na-MMT contents. It can be observed that the amount of water added to the mold increased as the fiber and MMT contents increased (Table 1). The values presented in Table 1 correspond to the minimal water volumes that produced homogeneous dispersions and complete trays. Starch pastes must have certain rheological characteristics, which prevent collapse as the water evaporates. Pastes with low water contents were very viscous and result in less expandable and higher density foams, and the presence of fibers and other solids in the formulations are responsible for increasing the viscosity of the mixture, which decreases the foaming ability (Cinelli, Chiellini, Lawton, & Imam, 2006; Shogren et al., 1998).

The pressing time (20 min) employed during the baking of the trays was higher than those reported in literature, and this probably occurred because the temperature used in this work (130 °C) was lower than those reported by other authors; they reported temperatures of 150–155 °C for 4 min of pre-pressing step and 3 min of pressing step (Salgado et al., 2008) and 200 °C for 3 min of pressing time (Chiellini, Cinelli, Ilieva, Imam, & Lawton, 2009).

Another parameter is the amount of batter used in the mold, which was determined in preliminary studies (not published) as the amount needed (Table 1) to fill the mold and form complete trays. All formulations in this study were able to form well-shaped trays that lacked evident cracks (Fig. 1). According to Chiellini et al. (2009), the batter amount must be adjusted when starch is mixed with fiber or another component that does not promote the foaming process. Lawton, Shogren, and Tiefenbacher (1999) reported that large amounts of batter could increase the quantity of released vapor, producing broken trays.

3.2. Thickness and density

The thickness of the foams ranged from 2.07 to 2.37 mm (Table 2), and the formulation did not affect the thickness (Tukey test, $p \leq 0.05$), which is indicative of the uniformity of the processing conditions.

The foam density ranged from 0.1941 to 0.2966 g/cm^3, and in general, the addition of fiber and Na-MMT decreased the density of the resulting foam (Table 2). According to Nabar, Raquez, Dubois, and Narayan (2005), the processing of starches results in stiff materials, which do not support air cell growth in their foams. It is possible that the fiber and Na-MMT acted as reinforcing fillers that improved the foaming ability of the starch pastes, resulting in more expandable materials. Glenn, Orts, and Nobes (2001) reported a reduction in foam density was achieved with the addition of corn fibers.

The values obtained in this work are higher than the values of expanded polystyrene, which were close to 0.06 g/cm^3 (Glenn et al., 2001; Shey, Imam, Glenn, & Orts, 2006). They are also higher than the values reported by other authors for foams made with high amylose starch (Miladinov & Hanna, 2001) and high amylose maize starch (Guan & Hanna, 2004), which ranged from 0.067 to 0.106 g/cm^3 and from 0.048 to 0.091 g/cm^3, respectively. However, these density values are lower than those reported by Salgado et al. (2008) for foams made of cassava starch, cellulose fibers, and sunflower protein isolate, which ranged from 0.456 to 0.587 g/cm^3.

3.3. Scanning electron microscopy

Scanning electron micrographs of cross-sections of the trays are presented in Fig. 2 and show that the foams have a sandwich-type structure with dense outer skins that contain small cells comprising the surface of the foam. The interior of the foams had large cells with thin walls; this type of structure has been reported by Cinelli et al. (2006) in a study of potato starch–corn fiber foams.

Compared to the control sample (formulated only with starch), all of the formulations showed more expanded structures, with large air cells and lower density structures. The fiber and Na-MMT probably acted as reinforcing fillers, resulting in more expandable materials. In combination with the higher water contents used, these formulations resulted in materials with better expansion properties.

In the samples produced with sugarcane fiber (Fig. 2b, c, f–i), good distribution of these fibers in the foam structure was observed; however, in the samples produced with 20 g fiber/100 g formulation, some fiber-rich regions could be seen (arrows).

3.4. Water absorption capacity

The absorption capacity of the starch foams ranged from 50 to 100 g/100 g of dry matter after 1 min of immersion in water and from 221 to 408 g/100 g of dry matter after 30 min (Fig. 3). These values were similar to those obtained by Cinelli et al. (2006), who worked with potato starch–corn fiber baked foams. According to (Sjöqvist, Boldizar, & Rigdahl, 2010), foaming reduces the weight of structural materials, and the lower density of the porous structure

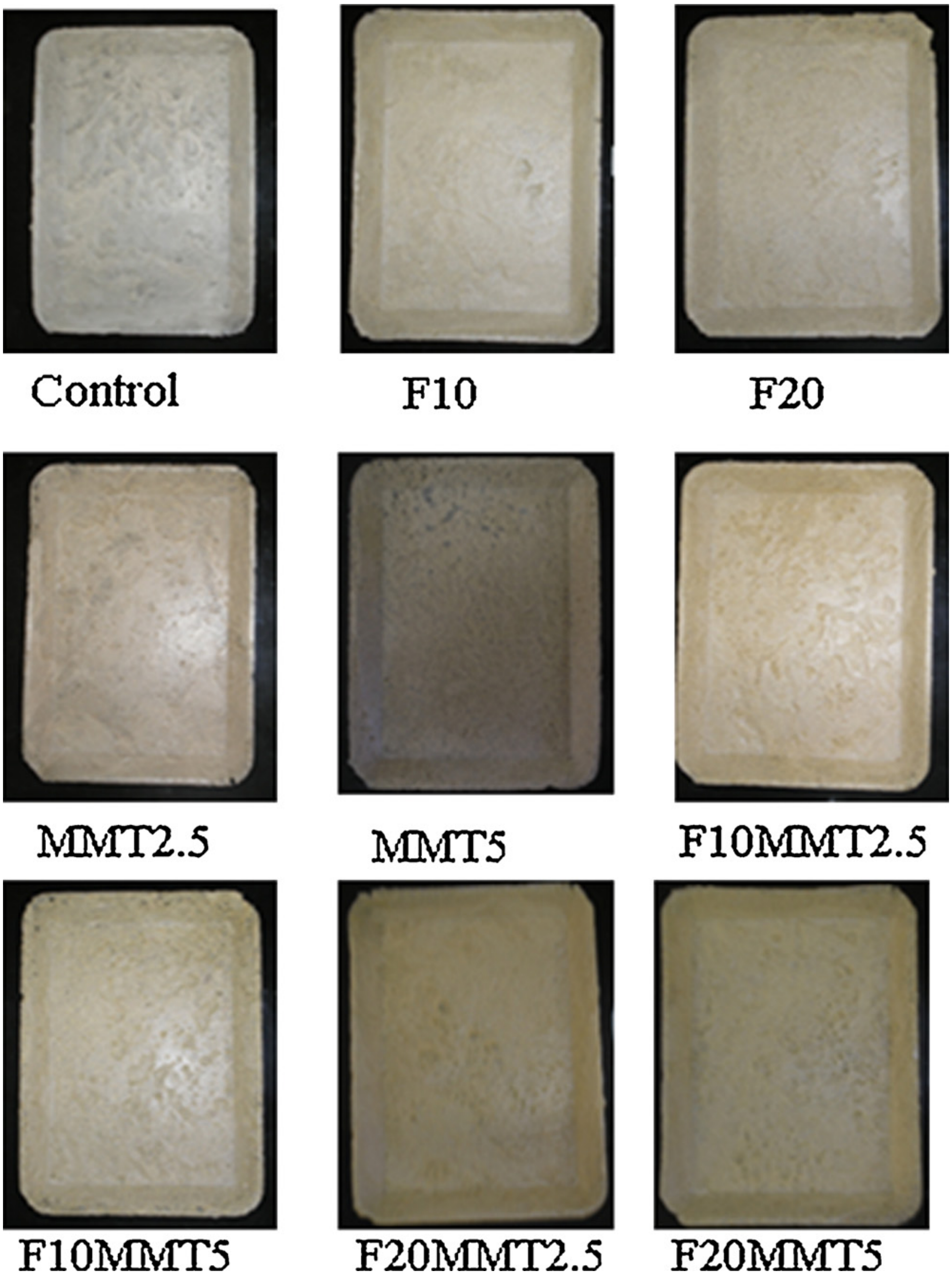

Fig. 1. The appearances of trays based on cassava starch, sugarcane fiber and Na-MMT.

Table 2
Thickness, density and mechanical properties of the trays based on cassava starch, sugarcane bagasse fiber and Na-MMT.

Formulations	Thickness (mm)	Density (g/cm^3)	Stress at break (MPa)			Strain at break (%)		
			33% RH	60% RH	90% RH	33% RH	60% RH	90% RH
Control	2.12 ± 0.04^{a}	0.2809 ± 0.0264^{a}	13.26^{b,A}	11.39^{c,d,A}	10.54^{c,A}	1.79^{b,B}	1.69^{b,B}	4.76^{b,A}
F10	2.34 ± 0.05^{a}	0.2123 ± 0.0216^{c,d}	7.95^{a,A}	4.37^{a,B}	3.65^{a,B}	2.49^{a,B}	2.19^{a,B}	6.45^{a,A}
F20	2.37 ± 0.06^{a}	0.2500 ± 0.0124^{b}	7.47^{a,A}	5.74^{a,b,A}	4.58^{a,A}	2.43^{a,B}	2.35^{a,B}	6.85^{a,A}
MMT2.5	2.26 ± 0.04^{a}	0.2788 ± 0.0261^{a}	12.64^{b,A}	13.76^{d,A}	6.78^{a,b,c,B}	2.99^{a,B}	2.76^{a,B}	6.94^{a,A}
MMT5	2.12 ± 0.10^{a}	0.2359 ± 0.0147^{c,b}	7.40^{a,A}	5.77^{a,b,A}	6.52^{a,b,A}	2.37^{a,B}	2.14^{a,B}	6.27^{a,A}
F10MMT2.5	2.07 ± 0.38^{a}	0.2181 ± 0.0111^{c,d}	11.36^{b,A}	6.91^{a,b,B}	8.71^{b,c,B}	2.50^{a,B}	2.45^{a,B}	5.94^{a,A}
F10MMT5	2.20 ± 0.62^{a}	0.2966 ± 0.0213^{a}	7.00^{a,A}	8.86^{b,c,A}	6.83^{a,b,c,A}	2.55^{a,B}	2.54^{a,B}	5.99^{a,A}
F20MMT2.5	2.10 ± 0.06^{a}	0.1941 ± 0.0081^{d}	6.29^{a,A}	6.95^{a,b,A}	6.02^{a,b,A}	2.37^{a,B}	2.34^{a,B}	6.27^{a,A}
F20MMT5	2.20 ± 0.10^{a}	0.1985 ± 0.0009^{d}	5.37^{a,A}	6.70^{a,b,A}	3.63^{a,A}	2.34^{a,B}	2.24^{a,B}	5.93^{a,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).

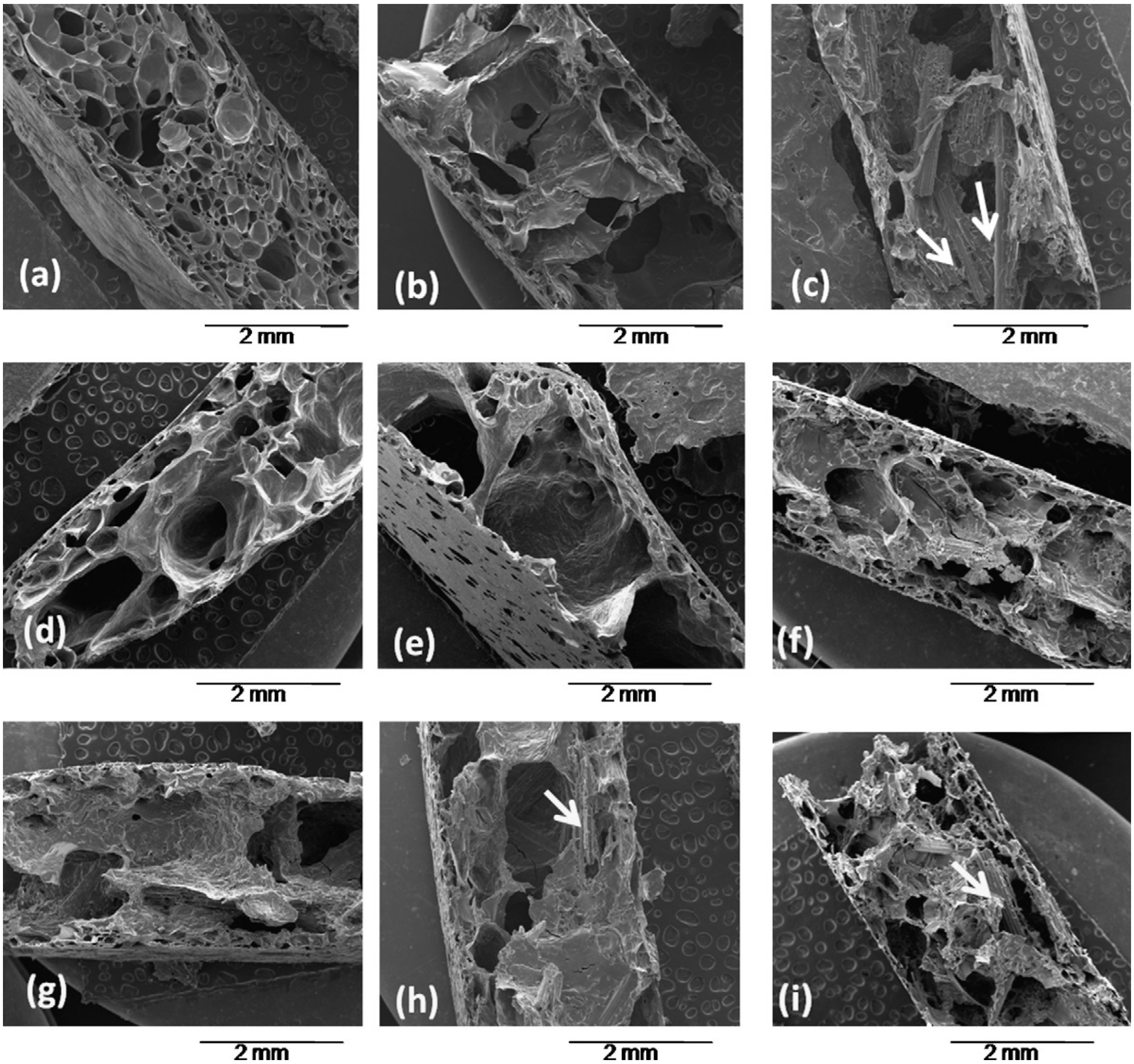

Fig. 2. SEM of cross-sections of the trays: (a) control; (b) F10; (c) F20; (d) MMT2.5; (e) MMT5; (f) F10MMT2.5; (g) F10MMT5; (h) F20MMT2.5; and (i) F20MMT5.

provides a greater absorption capability, similar to that observed in this work.

At initial times (until 10 min), the control foams absorbed less water than the other samples, and after 30 min of immersion in water, the formulations F10MMT2.5 and F20MMT5.0 resulted in foams with lower absorption capacities than the control samples (Fig. 3). (Sjöqvist et al., 2010) reported that the increase in the amount of absorbed water at 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 absorption by the starch itself. This idea was supported by the observations in this work, as the control foams (only starch) had higher density and less porosity and absorbed less water than the other foams at initial times. Then, after 30 min, the addition of fiber and Na-MMT decreased the water absorption of the foams.

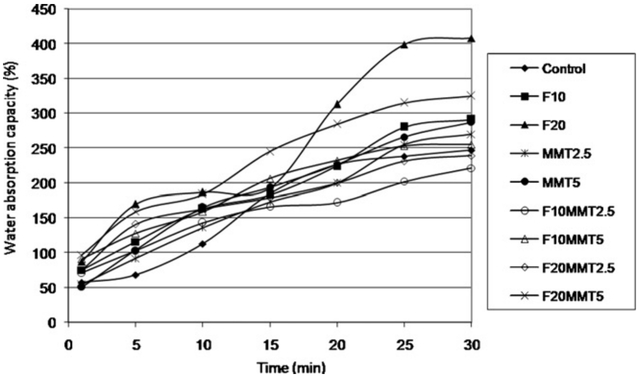

Fig. 3. Water absorption capacity of the trays.

In important to point out that 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 probably at high rates, as observed by the absorption capacity measured in this work (Fig. 3).

3.5. *Water sorption isotherms*

The moisture sorption isotherms of the starch foams are displayed in Fig. 4. As observed in Fig. 4, the foams manufactured with fiber and Na-MMT presented similar sigmoidal isotherm patterns; the equilibrium moisture content of the samples increased with increasing water activity, but the increase in the equilibrium moisture was more pronounced when the samples had a_w above 0.75. This behavior is interesting because the main problem with these materials is their sensitivity to moisture (Mali,

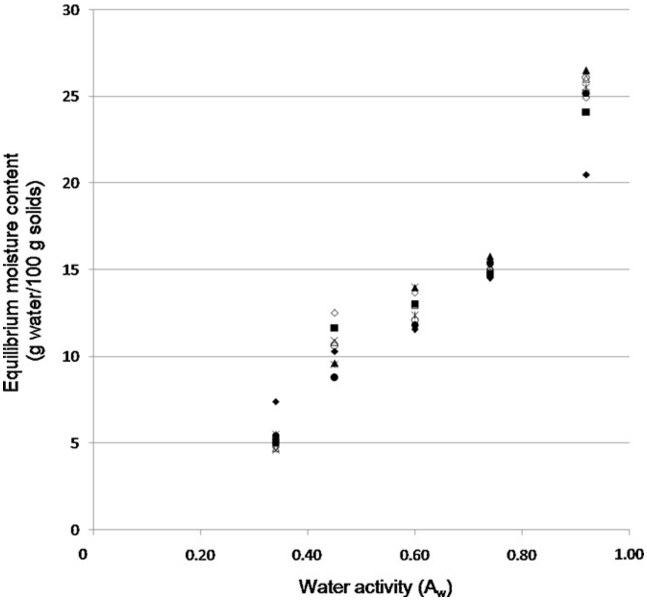

Fig. 4. Water sorption isotherms of the trays: Control (♦), F10 (■), F20 (▲), MMT2.5 (✳), MMT5 (•), F10MMT2.5 (O), F10MMT5 (△), F20MMT2.5 (◊) and F20MMT5 (×).

Grossmann, García, Martino, & Zaritzky, 2006; Salgado et al., 2008). The foams produced in this work were relatively stable to moisture increases with increasing water activity (relative humidity/100 g), and showed moisture equilibrium content ranging from 4.58 to 15.75 g water/100 g solids in a_w between 0.32 and 0.75.

The foams manufactured exclusively with starch (control samples) showed higher water uptake at lower RH (32%) and lower uptake at higher RH (90%) than the ones produced with fiber and Na-MMT (Fig. 4). The presence of fiber in these materials was probably responsible for the equilibrium moisture content increase at 90% RH ($a_w = 0.90$). Sugarcane fiber is basically composed of cellulose, hemicelluloses and lignin, and during the baking process (130 °C/20 min/100 bar), cassava starch probably forms linkages with cellulose, which melts at low temperatures (136.24 °C) (Guan & Hanna, 2003). According to Guan and Hanna (2004), lignin and hemicelluloses tend to maintain the matrix in starch–fiber foams manufactured at temperatures above the melting point of cellulose, and as the moisture increased, the hydrophilic lignin–hemicellulose matrix absorbed water more readily than starch matrices.

It is important to highlight that none of the samples showed dimensional changes during storage at all RH conditions, which is an interesting characteristic. According to Nabar et al. (2005), starch-based foams tend to gain weight upon moisture sorption in a humid environment due to their hygroscopic nature, and this is also accompanied by shrinkage of the foam dimensions, which was not observed in this work.

3.6. Crystallinity

Fig. 5 shows the XRD patterns of the starch foams. According to data in the literature (Camargo, Colonna, Buléon, & Molar, 1988; Huang et al., 2007; Zobel, 1988), cassava starch has a C-type crystallinity with peaks at $2\theta = 15.3^\circ$, 17.3°, 18.3°, 22 and 23.5°, which can be seen in Fig. 5 in the diffractogram of cassava starch, and these peaks disappeared in the foams as a consequence of gelatinization during the foam processing.

According to Van Soest and Vliegenthart (1997), during the thermal processing of native starch, the granular structure is completely or partially destroyed, resulting in an amorphous matrix, and two types of crystallinity can be distinguished after processing: residual crystallinity and process-induced crystallinity. The residual crystallinity is caused by the incomplete melting of starch during the processing and can be A-, B- or C-type, which occur in native starches. The induced crystallinity is associated with the crystallization of amylose that appears as V_H-, V_A- or E_H-type crystallinity. The peaks at $2\theta = 12.9^\circ$ and $2\theta = 20^\circ$ (Fig. 5b–d) probably resulted from foam processing, and they are typically V_H-type crystallinity, which is found in materials processed at temperatures below 180 °C and water contents above 10%, such as the foams produced in this study.

In the diffractogram of sugarcane fiber (Fig. 5a), a more important peak was observed at $2\theta = 22$ °C, and in foams containing fibers (Fig. 5b and d), the same peak was found but with a lower intensity. The peak probably resulted from residual crystallinity of cellulose, which melts at 136.4 °C and was not completed melted during the baking process. Mulinari, Voorwald, Cioffi, Silva, & Luz (2009) reported that this peak ($2\theta = 22$ °C) was found in cellulose samples.

Na-MMT (Closite®-Na) showed a characteristic peak at $2\theta = 7.1^\circ$ (Fig. 5e), which is very close to that reported by other authors between 7.3 and 7.96° (Chaudhary, 2008; Chung et al., 2010; Majdzadeh-Ardakani, Navarchian, & Sadeghi, 2010). In all foams produced with Na-MMT (Fig. 5c and d), there were no diffraction peaks between $2\theta = 4^\circ$ and $2\theta = 10^\circ$. The loss of the peak from the clay is due to the good clay dispersion, which leads to disordered clay tactoids with a low concentration of clay agglomerates and suggests the formation of an exfoliated structure. In addition, in the diffractogram of the MMT5 tray, no diffraction peaks were observed in the range of $2\theta = 2^\circ$ and $2\theta = 10^\circ$ (Fig. 5e), confirming the loss of the Na-MMT peak.

Is it likely that the production process favored the exfoliation of Na-MMT. The raw materials were mixed for 20 min at 18,000 rpm. In the first 10 min, water, starch and other solids were mixed; glycerol was then added, and the paste was mixed for 10 more min. According to Chung et al. (2010), good dispersion of clays in a starch matrix can be achieved by first preparing the nanocomposites in diluted aqueous solutions followed by plasticization.

3.7. Fourier Transform-Infrared Spectroscopy (FT-IR)

All of the spectra (Fig. 6) showed a wide absorption band corresponding to O–H stretching around 3448–3413 cm^{-1}, which could indicate the occurrence of H-bonding interactions between components of the foams during the manufacturing process.

As observed in the FT-IR spectra of the trays (Fig. 6), the shift of the band at 3627 cm^{-1} from the free OH group of the MMT surface to a lower frequency (around 3400 cm^{-1}) indicates an interaction between the starch and MMT, and similar findings have been reported by other authors (Field, Sternhell, & Kalman, 2002; Liu, Chaudhary, Yusa, & Tadé, 2011).

For all formulations, bands around 1656–1640 cm^{-1}, which are associated with angular O–H bending of water molecules, were observed, suggesting that intermolecular hydrogen interactions may be also due to starch, fiber, nanoclay and glycerol interactions with water (Fig. 6). According to Dean, Yu, and Wu (2007), the key interaction between unmodified layered silicates and water is the ion–dipole interaction between the sodium ion (located in the intergallery space of the clay) and the dipole of the water molecule. Starch hydroxyl groups could also interact directly with the sodium ion of the clay (similarly to the water molecules) or with its hydroxyl groups, making a very compatible system (Huang, Yu, & Ma, 2004).

The peaks observed at 2900 cm^{-1} correspond to –C–H stretching; H–C–H and –C–O–H conjugated bending vibrations appeared in all spectra (Fig. 6), except in the Na-MMT spectra. All of the foams produced with Na-MMT and fiber showed peaks at 1035 cm^{-1}, which correspond to –C–O bond stretching of starch and fibers, and

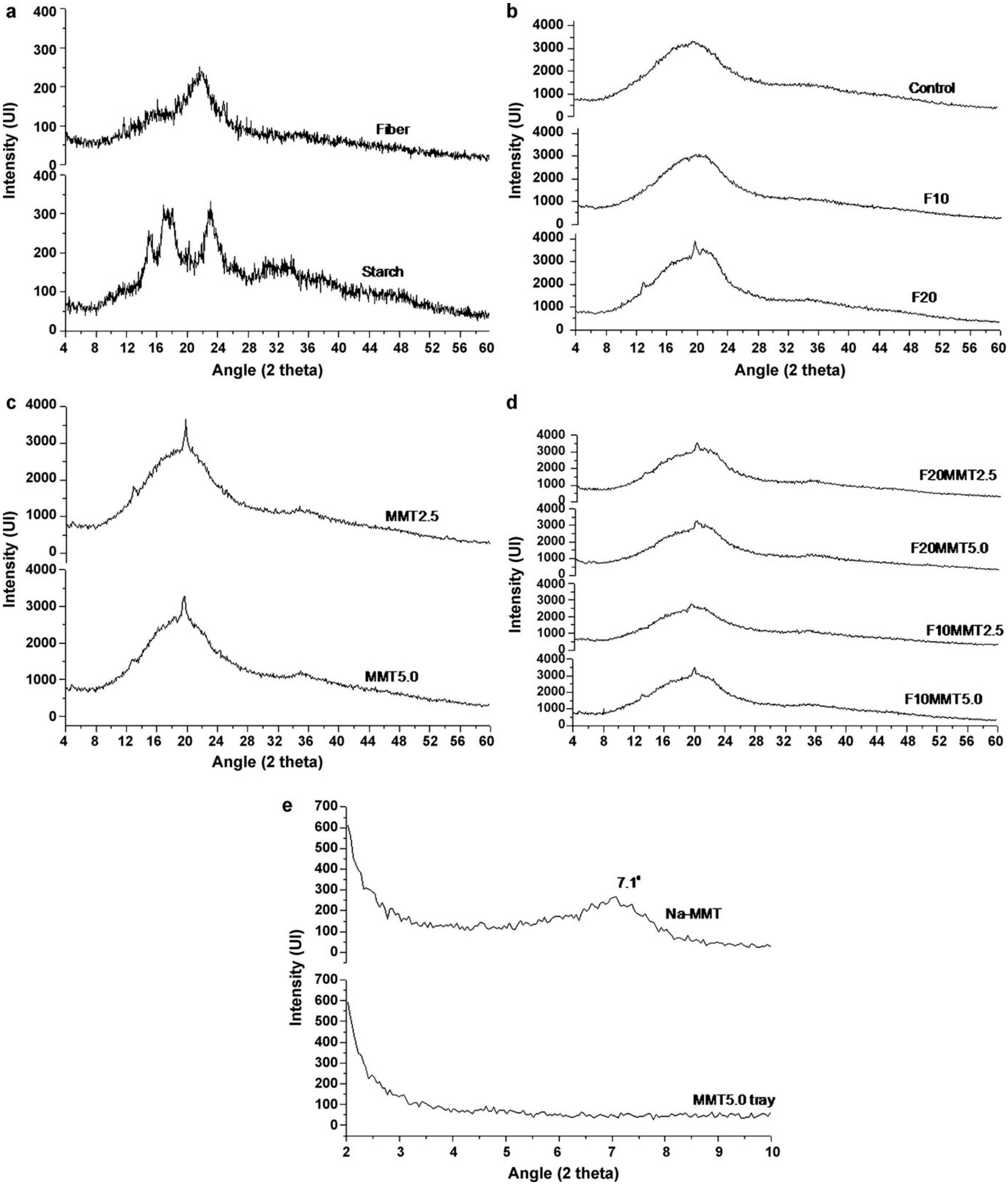

Fig. 5. X-ray diffraction patterns of cassava starch, sugarcane fiber and Na-MMT and trays based on cassava starch, sugarcane fiber and Na-MMT.

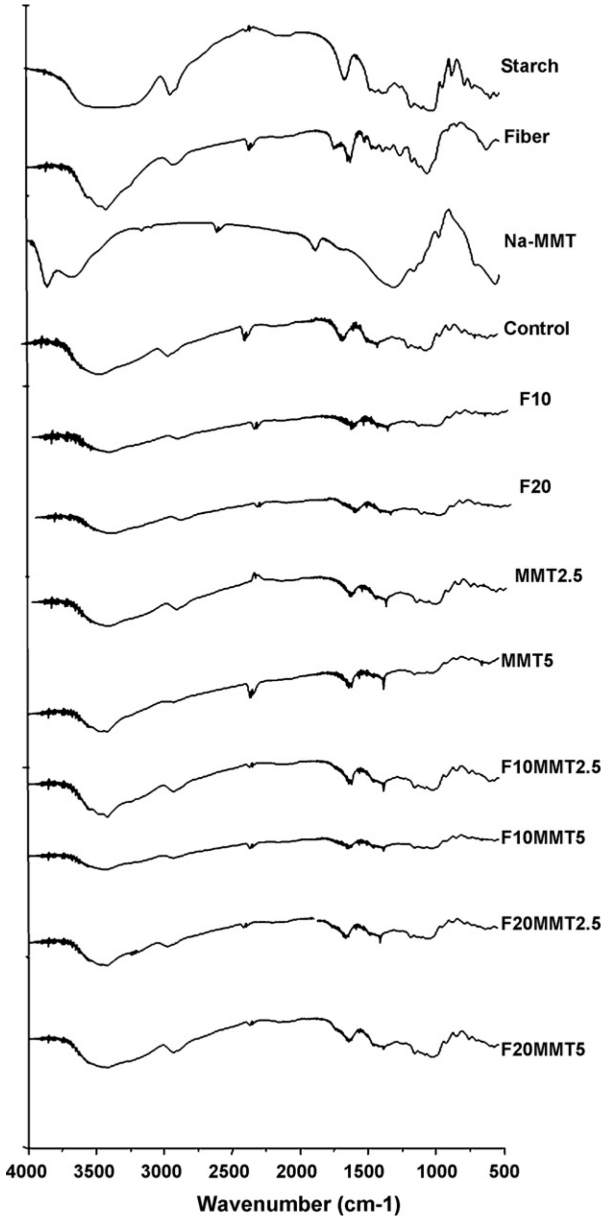

Fig. 6. FT-IR spectra of cassava starch, sugarcane fiber and Na-MMT and trays based on cassava starch, sugarcane fiber and Na-MMT.

at 1200–1220 cm^{-1}, which correspond to C–O–C bond stretching of the starch and fiber. These bands occurred at lower frequencies than those observed in the control foams (1024 and 1200 cm^{-1}), indicating that the hydrogen bonding interaction between the starch molecules was weakened, and interaction with the other components were favored. According to Huang et al. (2004), a lower peak frequency is consistent with a stronger interaction.

3.8. Mechanical properties

The stress at break of foams stored at 33% RH ranged from 5.37 to 13.26 MPa (Table 2), and in general, the control foams had significantly higher values (Tukey test, $p \leq 0.05$) compared with other foams. However, the MMT2.5 and F10MMT2.5 foams had values similar to the control samples and presented the highest stress at break values when stored at 60 and 90% RH (Table 2).

The variation in the RH during conditioning did not significantly affect (Tukey test, $p \leq 0.05$) the stress at break of the produced foams (Table 2). For the F10, MMT2.5 and F10MMT2.5 foams, the stress at break values decreased when the samples were stored at 90% RH. These results agree with the isotherm data, which showed that the increase in the equilibrium moisture was more pronounced at RH above 75%. In these cases, water exerts a plasticizing effect and acts as a mobility enhancer, which makes these materials less resistant and more flexible at high RH conditions (Mali et al., 2006).

The control foams showed the lowest strain at break values at all RH conditions; the additions of fiber and Na-MMT increased the strain at break values of all samples (Table 2). According to Nabar et al. (2005), starch foams are stiff and brittle due to the greater intermolecular interactions between starch molecules. Some authors reported that the presence of other components in the starch matrix, which decrease the high cohesion forces of this polymeric matrix, also decrease the brittle characteristics and consequently decrease the stress and increase the strain at break of these materials (Cinelli et al., 2006; Lawton, Shogren, & Tiefenbacher, 2004). These results agreed with the FT-IR results, which indicated that some interactions between the starch molecules were weakened in foams produced with fiber and Na-MMT.

The strain at break values were stable when the samples were stored at 33 and 60% RH (Table 2), and these values only increased when the samples were stored at 90% RH, confirming the plasticizing effect of water.

4. Conclusions

In this study, baking raw materials that are economically important in South America, such as cassava starch and sugarcane bagasse fiber, produced well-shaped biodegradable trays. The fiber and Na-MMT interfere with foaming, so additional amounts of water and batter are needed to form complete trays.

The addition of fiber and Na-MMT decreased the density and stress at break and increased the strain at break values of the starch foams. The foams manufactured with fiber and Na-MMT presented more pronounced increases in the water equilibrium moisture levels when the samples were stored in RH above 75%, which resulted in materials with stable mechanical properties despite variations in the RH between 33 and 60%. This behavior is interesting because the main problem with these materials is their sensitivity to moisture.

The studied processing conditions resulted in good nanoclay dispersion in the polymeric matrix, which led to the formation of an exfoliated structure.

All of the produced foams had high water absorption capacities (>50%) when immersed in water (1 min), which is related to their porosity and lower density. The produced materials need further development to improve the expansion, water sorption capacity, processing times, as well, the use of hydrophobic additives and the study of the possibility to microwave these foams; however, this study is a key first step in the production of composites on an industrial scale.

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