Functional Properties of Extruded Nanocomposites Based on Cassava Starch, Polyvinyl Alcohol and Montmorillonite

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Summary: The objectives of this work were to produce expanded nanocomposites based on cassava starch, polyvinyl alcohol (PVA) and sodium montmorillonite (Na-MMT). The nanocomposites were characterized according to their expansion index (EI), density, water absorption capacity (WAC), mechanical properties and crystallinity. The nanocomposites were prepared in a single-screw extruder using different starch contents (97.6–55.2 g/100 g formulation), PVA (0–40 g/100 g formulation) and Na-MMT (0–4.8 g/100 g formulation). Glycerol (20 g/100 g formulation) was used as plasticizer. The addition of Na-MMT and PVA resulted in an increase of EI and mechanical strength of the foams. Na-MMT and PVA addition resulted in less WAC of the samples. The studied processing conditions resulted in a good nanoclay dispersion, leading to the formation of an intercalated structure.

Keywords: biodegradable; Closite® Na; intercalated nanocomposite; packaging

Introduction

In 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 to come from renewable sources, biodegradability, low cost (US$ 0.25–0.60/kg) and high availability.[1–3]

Starch foams with insulating properties similar to those of polystyrene foam have been industrially produced by the extrusion process, especially for loose fill packaging application these materials have to present low density, good resilience, and compressibility.[4–5] In general, starch foams have promising characteristics; however the materials have some problems, including poor mechanical properties and hydrophilicity. Solubility in water increases the degradability and the speed of degradation, however moisture sensitivity also limits the applications of the material.[5] In this sense, the incorporation of nanosized mineral fillers and the addition of other polymers such as polyvinyl alcohol (PVA) are attractive alternatives to the development of new low cost products with better properties.[6]

Although various materials of nanometer dimensions (lamellar silicates, metal nanoparticles, carbon nanotubes, etc.) can be used for the treatment of polymers, clays have received special attention, such as montmorillonite (MMT) due to their low cost, versatility and simple processing.[7–9]

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

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high surface area and is miscible with hydrophilic polymers, such as starch.[10] When included in the polymeric matrix, the MMT cause changes in the barrier and mechanical properties of nanocomposites, because they create more tortuous paths, thus hindering the diffusion of water vapor and gases, decreasing the permeability of the polymer before them.[11–13]

Some authors have also reported that the resistance of starch foams to the direct contact with water showed an improvement by the addition of a high proportion of polyvinyl alcohol. Polyvinyl alcohol (PVA) is a particularly well suited synthetic polymer for the formulation of blends with natural polymers. PVA is highly polar and can also be manipulated in water solutions or in functional organic solvents depending upon its grad.[4,14]

Thus, the objectives of this work were to evaluate the effects of sodium montmorilonite (Na-MMT) and polyvinyl alcohol on the expansion index, density, water adsorption capacity, mechanical properties and crystallinity of extruded starch foams.

Experimental Part

Cassava starch (19% amylose) was provided by Hiraki Industry (São Paulo, Brazil). Na-MMT (Closite® Na^+) was purchased from Southern Clay Products (USA) and was used as received. PVA was purchased from Reagen (Quimibrás, Rio de Janeiro, Brazil) and glycerol, from Synth (Labsynth, São Paulo, Brazil).

Foam Production by Extrusion

The starch trays were manufactured using different formulations based on previous results.[4,12] To prepare each formulation, the indicated proportions of starch, PVA, Na-MMT (Table 1), glycerol (20%, w/w) and water (sufficient to produce samples with 18% of moisture content before extrusion) were mixed for 5 min with a mixer at 780 rpm (Arno – Brazil). The samples were extruded in a single screw extruder (BGM EL-25, São Paulo, Brazil) with a barrel that was 700 mm long and 25 mm diameter. Temperatures from feeding to die zone were maintained at 120 °C and two 2.8-mm die nozzles were employed to produce cylindrical foam extrudates. The screw speed was maintained at 70 rpm. The extrudates were cut into 100-mm samples with a rotary cutter operating at 20 rpm.

Table 1.
Formulations used to produce cassava starch, PVA and Na-MMT extruded foams.

Run	Starch (g/100 g)	PVA (g/100 g)	Na-MMT (g/100 g)
1	100.0	–	–
2	97.6	–	2.4
3	95.2	–	4.8
4	77.6	20	2.4
5	75.2	20	4.8
6	57.6	40	2.4
7	55.2	40	4.8

Foams Characterization

Density

Density was obtained by the relationship between mass and volume of the samples, which were cut into specimens of 1 cm and then were placed in a beaker of 25 mL, which was then weighed on an analytical balance. The reported values are averages of 20 determinations of each formulation.[4]

Expansion Index (EI)

The expansion index was calculated dividing the extrudate diameter by the die orifice diameter. The reported values are averages of 20 determinations of each formulation.[15]

Water Absorption Capacity (WAC)

Five sample each fomulation measuring 5 cm were weighted and soaked in distilled water for 1 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.[16]

Mechanical Properties

The compressive strength of the samples was determined in texturometer TA.XT2i

(SMS,Surrey, UK). The extrudates (10 mm long) were placed on a flat plate with the cut surfaces carefully aligned so that the edges were perpendicular to the axis of the sample (direction of extrusion). Then, each piece of foam was compressed once to 80% of its original diameter at a loading rate of 5.0 mm/s using a Knife probe. The force (N) was reported as compression strength. The reported values are averages of 6 determinations of each formulation.[4]

Crystallinity

The crystallinity of the foams was investigated by X-ray diffraction. The analysis was performed with a diffractometer (Panalytical, X'Pert PRO MPD, 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.

Results and Discussion

According to Xu and Hanna,[17] density is an important physical property of extruded foams. Low density is ideal for these products because it reduces production costs. Density of starch foams ranged from 0.30 to 0.44 g/cm^3 and these values signifcantly decreased with addition of Na-MMT (Table 2), but the higher descreases occured when the combination of PVA and Na-MMT was employed. It is possible that the Na-MMT and PVA acted as reinforcing agents that improved the foaming ability of the starch pastes, resulting in more expandable materials. Vercelheze *et al.*[12] reported that addition of Na-MMT on starch baked foams reduce the density of these materials.

Like the density, the expansion index (EI) is an important property to define foam production cost. The EI ranged from 2.21 to 2.91, and Na-MMT and PVA addition signifcantly increased the EI of the foams (Table 2). The effects of the addition of PVA on the properties of potato starch foams were reported[18,19] to improve foaming ability, possibly due to the break of hydrogen bonds of starch, which can then interact with PVA, resulting in flexible materials with greater expansion capacity.

The presence of PVA and Na-MMT also contributed to the significant increase in mechanical strength of materials, which ranged from 70 to 136 N (Table 2). Starch, PVA and Na-MMT are compatible materials, which can interact by hydrogen bonds, resulting in more stiff and brittle foams due to the greater intra e intermolecular interactions.[18,19]

The water absorption capacity (WAC) of the samples ranged from12.48 to 18.15% (Table 2) and the Na-MMT and PVA addition results in less WAC of the samples. The lower result was obtained for the sample produced with the higher levels of PVA (40 g/100 g) and Na-MMT (4.8 g/100 g). Some authors reported that PVA incorporation into starch foams resulted in materials with low capacity to interact with water.[18,19]

Table 2.
Results of expansion index (EI), density, water absorption capacity (WAC) and mechanical strength of extruded foams.

Run	Starch (g/100 g)	PVA (g/100)	Na-MMT (g/100 g)	EI	Density (g/cm^3)	WAC (%)	Strength (N)
1	100.0	–	–	$2.36 \pm 0.31^{b,c}$	0.44 ± 0.01^{a}	18.15 ± 0.61^{a}	70 ± 5^{c}
2	97.6	–	2.4	2.68 ± 0.18^{a}	0.37 ± 0.01^{b}	14.95 ± 0.61^{b}	136 ± 15^{a}
3	95.2	–	4.8	2.91 ± 0.24^{a}	0.37 ± 0.01^{b}	$17.51 \pm 0.82^{a,b}$	99 ± 7^{b}
4	77.6	20	2.4	2.77 ± 0.20^{a}	0.35 ± 0.01^{c}	15.42 ± 1.01^{b}	$102 \pm 12^{a,b}$
5	75.2	20	4.8	2.82 ± 0.30^{a}	0.30 ± 0.01^{d}	14.16 ± 2.68^{b}	$104 \pm 15^{a,b}$
6	57.6	40	2.4	2.21 ± 0.19^{c}	0.34 ± 0.01^{c}	$14.85 \pm 1.14^{b,c}$	93 ± 7^{b}
7	55.2	40	4.8	$2.42 \pm 0.17^{b,c}$	0.33 ± 0.01^{c}	12.48 ± 0.71^{c}	97 ± 9^{b}

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 1 shows the X-ray diffraction patterns of the starch foams. According to data in the literature,[20–22] cassava starch has a C-type crystallinity with peaks at $2\theta = 15.3°$, $17.3°$, $18.3°$, $22°$ and $23.5°$, which can be seen in Figure 1 in the diffractogram of cassava starch and these peaks disappeared in the foams as a consequence of gelatinization during the foam processing. Na-MMT (Closite®-Na) showed a characteristic peak at $2\theta = 7.1°$ (Figure 1), which is very close to that reported by other authors between 7.3 and 7.96°.[23,24]

It can be observed that the characteristic peak of Na-MMT ($2\theta = 7.1°$) was shifted to a smaller angle ($2\theta = 5.07°$) in all foam samples (Figure 1), which was consequence of an increase in the interplanar spacing (d_{001}) of the Na-MMT incorporated in the extruded foams ($d_{001} = 17.41$ Å) compared to pure Na-MMT ($d_{001} = 11.70$ Å), strongly indicating that there was an intercalation of the nanoclay in the polymeric matrix of the foams. When the polymer molecules penetrate into the interlayer space of Na-MMT by increasing the distance between the lamellae of the nanoclay, while maintaining the ordering of the same, there is an intercalated nanocomposite.[9] Some authors[25] reported that in starch-Na-MMT based nanocomposites plasticized with glycerol, when glycerol is present in concentrations above 10% (w/w) is favored the formation of intercalated structures, as observed in this work.

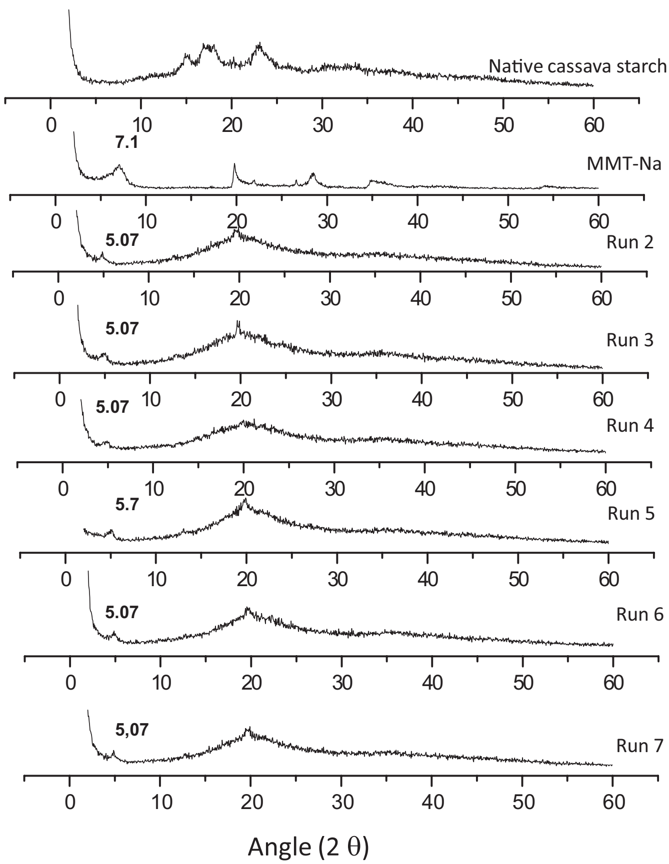

Figure 1.
Difractograms of native cassava starch and extrueded starch foams.

Conclusion

It was possible to produce biodegradable cassava starch nanocomposites by extrusion with the addition of polyvinyl alcohol and sodium montmorillonite. The studied processing conditions generated a good nanoclay dispersion, leading to the formation of an intercalated structure. The addition of Na-MMT and PVA resulted in an increase of EI and mechanical strength. The water absorption capacity of the foams decreased with the incorporation of Na-MMT and PVA. The sample formulated with 75.2% starch, 20% PVA and 4.8% Na-MMT showed the best combination of mechanical, WAC and expansion properties.

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