

Mechanical properties of cassava starch-based nano-biocomposites

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ABSTRACT

In order to reduce the litter problem with regard to the environment, biodegradable materials based on natural polysaccharides, particularly starch, can be produced at low cost and at large scale. Cassava is an abundant and cheap agricultural source of starch and is cultivated throughout Brazilian territory. Starch is not a real thermoplastic material but, in the presence of a plasticizer, high temperatures and shearing, it melts and fluidizes, enabling its use in injection, extrusion and blowing equipments, such as those for synthetic plastics. Plasticizing agents and nanofillers, like montmorillonite clays, can improve mechanical properties of the films, resulting in materials with better flexibility and extensibility. Modifications of the clay surface have been carried to improve interaction between starch molecules and clay platelets.

The aim of the present work was to investigate the mechanical properties of thermoplastic starch reinforced with native and modified clay in order to compare the effect of increasing mineral clay and glycerol contents, stored at different relative humidity.

With the purpose of producing cassava starch nanocomposite films, two concentrations of glycerol (13 and 30 g/100g of starch) as plasticizer and three concentrations of native clay (MMT-Na) and organomodified clay (OMMT-CS) (1.5, 3.0 and 6.0 g/100 g of plasticized starch) were used to prepare films using a melting process, at 70 °C (Rheocord 9000, Haake). Materials without nanoclay particles were used as control. Prior to tests, they were stored for three weeks at 57 % and 75 % RH. Tensile tests were carried out with an Instron tensile testing machine (model 4204, USA), on dumbbell-shaped specimens; at 25 °C with a constant deformation rate of 5 mm·min⁻¹. For each formulation at least five samples were tested.

As expected, increasing glycerol content caused significant decrease in Young's modulus, tensile strength and improved elongation at break. The plasticizer molecules interfered with starch packing, decreasing intermolecular attraction and increasing polymer mobility. As water is a plasticizer, the increase in relative humidity during storage has the same effect as for the rise of glycerol content. Regarding to nanoclay particles, tensile strength and percent elongation at break decreased with increase of MMT-Na content, while Young's modulus was not influenced. On the other hand, tensile strength and Young's modulus raised with increasing content of OMMT-CS. The best combination of mechanical properties was presented by the materials with the highest amounts of glycerol and OMMT-CS, that is: tensile stress of (1.66 ± 0.22) MPa and (0.92 ± 0.12) MPa; percent elongation at break of (14.07 ± 3.28) % and (11.66 ± 1.67) %; and Young's modulus of (20.51 ± 3.28) MPa and (16.84 ± 5.00) MPa, at 57 % and 75 % of RH, respectively.

These results infer that materials based on cassava starch reinforced with nanoclay particles can be considered as an interesting biodegradable alternative for conventional packaging, and also that the two nanofillers tested show different mechanical behavior, being OMMT-CS better than MMT-Na. Further investigation on nanostructure must be carried on in order to verify how are dispersed the nanoclay platelets in the chains of starch.

Keywords: Nanocomposite; Starch; Montmorillonite clay; Mechanical properties.

INTRODUCTION

Food packaging, an important discipline in the area of food technology, concerns preservation and protection of all types of foods and their raw materials, as well from oxidative and microbial spoilage. Petrochemical based plastics such as polyolefins, polyesters, polyamides etc. have been increasingly used as packaging materials, because of their availability in large quantities at low cost and favorable properties such as good mechanical and barrier properties [1].

Because of this, the interest in biodegradable films has been increased and the main researches in biopolymers use polysaccharides like starch [2; 3], chitosan [4], cellulose [5] and pectin [6]. Films based on starch have been focused by many researchers because they are a renewable, cheap and abundant

source [7:10]. Among all kinds of starches, cassava starch is a promising raw material in Brazil as it was the third greatest world producer of cassava in 2007 [11].

The polar character of starch provides low permeability to apolar compounds like oxygen, aromatic compounds and oils, but its permeability to polar substances such as humidity is relatively high [3; 12]. As these films are brittle, it is necessary to use plasticizers to improve their mechanical properties [4; 7:8]. Lately, nanofillers have been used to improve mechanical properties [13].

The most recent researches are focused on layered silicate nanofillers, especially on montmorillonites clays (MMT) due to their availability, versatility, and respectability toward the environment. However, their native structure does not allow a good interaction between the layers and the polymeric matrix. So, to overcome this problem, many authors have been using modified clays, applying surfactants into the clay surface [14].

The isomorphic substitutions that take place inside the clay platelets generate a negative charge naturally counterbalanced by the presence of inorganic cations (Na^+ , Ca^{2+} , ...) into the interlayer spacing leading to a hydrophilic character. To promote the polymer/silicate compatibility, an ion-exchange reaction of these inorganic cations by organic surfactant is often carried out. Depending on the process conditions and on the polymer/nanofiller affinity, the layered silicates dispersed into the polymer matrix can be intercalated by macromolecules and/or exfoliated. Best performances are commonly observed with the exfoliated structures [13].

The objective of this work was elaborate cassava starch nanocomposite films with, two concentrations of glycerol (13 and 30) g/100g of starch as plasticizer and three concentrations of native clay (MMT-Na) and organomodified clay (OMMT-CS) (1.5, 3.0 and 6.0) g/100 g of plasticized starch. Mechanical tests were applied on materials to observe the influence of MMT organomodification on mechanical behavior of the films.

MATERIALS & METHODS

Cassava starch supplied by Hikari (Brazil); glycerol (99.5 % of purity) supplied by the Société Française des Savons (France); the cationic starch supplied by Roquette (France) with charge density of 944 $\mu\text{equiv}\cdot\text{g}^{-1}$ and cationic functions are quaternary ammonium with chloride as counter anion; the Dellite LVF sodium montmorillonite (MMT-Na) supplied by Laviosa Chimica Mineraria SpA (Italy) with a cationic exchange capacity (CEC) of 1050 $\mu\text{equiv}\cdot\text{g}^{-1}$, were used for films elaboration.

Organomodified Montmorillonite Preparation: the MMT-Na organomodification was carried out with cationic starch by an exfoliation/adsorption technique. Defined amounts of clay and cationic starch were placed in a counter-rotating internal batch mixer Rheocord 9000 (HAAKE, Germany), for 20 min in order to balance their charges.

Starch Dry-Blends Preparation: the proportions used in this study were: 61 g/100g of native starch, 9 g/100g of glycerol, and 30 g/100g of water, corresponding to the formulation with low content of glycerol; and 54 g/100g of native starch, 23 g/100g of glycerol, and 23 g/100g of water, for those with high content of glycerol.

For the preparation of plasticized starch, native cassava starch was first dried overnight at 70 °C in a ventilated oven. Then the starch powder was introduced into a turbomixer, and the glycerol (13 and 30) g/100g of starch was slowly added under stirring. After complete addition of glycerol, the mixture was mixed at high speed to obtain a homogeneous dispersion, and then placed in a ventilated oven at 170 °C for 40 min and occasionally stirred, allowing vaporization of water and diffusion of glycerol into the starch granule. The powder was then stored in polyethylene bags hermetically closed to avoid absorption of humidity from the environment.

Nanobiocomposites Elaboration: to obtain nanobiocomposites, proportions of 1.5 g/100g, 3 g/100g and 6 g/100g of plasticized starch of MMT-Na and OMMT-CS were added to the dry blend. A quantity according to proportion clay-plasticized starch and water was added according to the formulation and the starch nanobiocomposite was prepared by mechanical kneading with a counter-rotating internal batch mixer, Rheocord 9000 (HAAKE, Germany).

The materials were then pressed at 200 MPa and 110 °C. The films were placed in two different controlled relative humidity (57 and 75) % and stored prior to testing, at least for three weeks.

Mechanical Tests: tensile tests were carried out with a tensile testing machine (INSTRON, model 4204, USA), on dumbbell-shaped specimens, at 25 °C with a constant deformation rate of 5 $\text{mm}\cdot\text{min}^{-1}$, according to ASTM D882-09 (2009) [15]. Tensile strength (nominal) was calculated dividing the maximum load by the original minimum cross-sectional area of the specimen (related to minimum

thickness), assuming that the total volume of the sample remained constant. Percent elongation at break (nominal) was calculated by dividing the extension at the moment of rupture of the specimen by its initial gage length and multiplying by 100. Young's modulus was determined and calculated from the slope of the low strain region of the tensile curve. All specimens were evaluated in five replicates, at minimum.

Statistical analysis: analysis of variance (ANOVA) was applied on the results using the statistical program Statgraphics Centurion v.15.0 (StatPoint®, Inc., USA) and the Tukey test was used to evaluate average differences (at a 95 % of confidence interval).

RESULTS & DISCUSSION

As expected, increasing glycerol content caused significant decrease in Young's modulus, tensile strength and improved elongation at break (Table 1). Regarding to the percent elongation at break, there was a great raise (around 200 %) for the materials stored at 57 % RH, when contents of glycerol were increased. However, it was not observed the same behaviour for those stored at 75 % RH, whose increase was only about 20 %, on average. The plasticizer molecules interfered with starch packing, decreasing intermolecular attraction and increasing polymer mobility [7]. As water is a plasticizer, the increase in relative humidity during storage has the same effect as for the rise of glycerol content. Regarding to nanoclay particles, tensile strength and percent elongation at break decreased with increase of MMT-Na content, while Young's modulus was not influenced. On the other hand, tensile strength and Young's modulus raised with increasing content of OMMT-CS.

All the results of tensile strength, percent elongation at break and Young's modulus obtained for the nanocomposite materials are presented in Table 1. It is possible to observe that the content of glycerol strongly influenced all studied properties, for all studied formulations.

Table 1. Tensile strength (TS), percent elongation at break (E_B) and Young's modulus (E) of cassava starch nanobiocomposites formulated with two different glycerol contents and three concentrations of native and organomodified clay, stored for three weeks at (57 and 75) % RH.

Clay (g/100g)	TS (MPa)		E_B (%)		E (MPa)		
	RH (%)		RH (%)		RH (%)		
	57	75	57	75	57	75	
9 g of Gly /100g Starch							
	0.0	11.6±0.54	6.85±0.17	15.41±3.02	26.20±4.98	690.5±118.0	327.7±36.6
MMT-Na	1.5	9.95±1.11	6.02±0.33	7.52±1.24	24.62±3.52	500.6±58.8	226.0±27.8
	3.0	7.12±0.46	6.16±0.39	14.63±3.11	19.56±6.21	391.2±20.2	334.5±47.2
	6.0	6.23±0.50	5.80±0.59	2.21±0.33	3.73±1.26	475.8±48.4	488.6±62.6
OMMT-CS	1.5	8.35±1.13	3.91±0.74	9.34±2.08	14.50±2.93	457.9±63.1	103.9±42.0
	3.0	8.08±0.57	6.70±0.57	7.23±2.00	16.14±2.98	521.3±75.3	314.1±81.8
	6.0	8.60±0.80	7.12±1.05	4.78±0.99	7.74±1.95	541.2±166.5	510.5±109.8
23 g of Gly /100g Starch							
	0.0	2.13±0.22	1.48±0.11	35.76±7.69	28.84±4.34	14.50±1.61	9.35±1.43
MMT-Na	1.5	1.50±0.12	1.06±0.10	19.94±1.61	15.21±2.61	15.67±2.02	11.36±2.24
	3.0	1.30±0.14	0.74±0.05	14.24±2.19	9.50±0.55	18.51±3.31	11.96±1.38
	6.0	1.56±0.19	0.78±0.04	17.01±2.15	10.24±1.19	20.51±3.28	11.90±1.23
OMMT-CS	1.5	1.59±0.31	0.75±0.06	14.05±3.26	11.87±1.55	27.09±5.31	12.70±2.94
	3.0	1.30±0.14	0.78±0.10	9.53±1.04	11.47±1.65	22.66±2.48	12.21±2.89
	6.0	1.66±0.22	0.92±0.12	14.07±3.28	11.66±1.67	20.51±3.28	16.84±5.00

The content and type of clay interfered strongly the mechanical properties of the materials. The use of clay in nanocomposites has the purpose of improve mechanical properties. Even though MMT-Na is a hydrophilic nanofiller with theoretically a good affinity with starch chains, the use of this nanofiller leads to a poor dispersion with a high extent of aggregation into a plasticized starch matrix. In addition, as the molecule of glycerol is much smaller than starch molecules, they intercalate between clay platelets more easily. The use of an organomodified compatibilizer can help the interaction between clay and starch molecules.

The increase of the proportion of MMT-Na in the matrix led to a decrease in tensile strength. For the OMMT-CS, raising the amount of clay contributed to increase tensile strength, as can be seen in Figure 1.

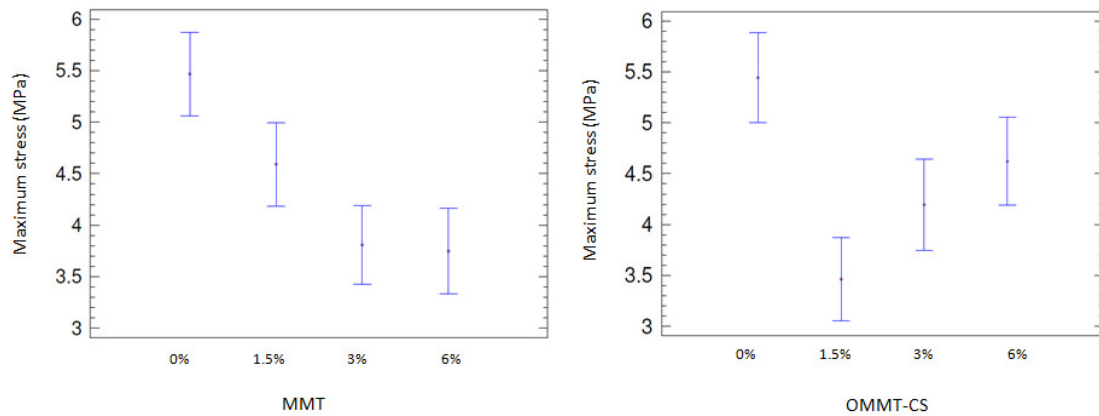


Figure 1 - Variations of tensile strength of nanobiocomposites in relation to the clay content.

The percent elongation at break naturally decreases when clay is added to the material because part of its stiffness is transferred to starch matrix. MMT-Na and OMMT-CS composites presented different behaviours. There was a gradual decrease in percent elongation at break when MMT-Na was used, while the presence of OMMT-CS into starch matrix did not influence this property, as shown in Figure 2:

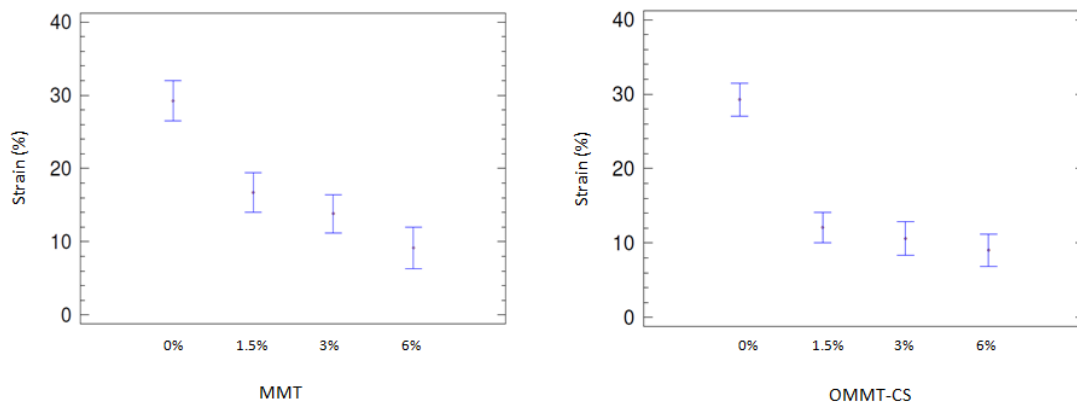


Figure 2 - Variations of percent elongation at break (strain %) of nanobiocomposites in relation to clay content.

It can be observed in Figure 3, that there was not a clear tendency in Young's modulus, that is the presence of MMT-Na diminished this property up to 3 g/100g in relation to cassava starch nanocomposite formulated without clay. Nevertheless, the presence of OMM-CS differently modifies this property, as lower content of clay lower was the value of Young's modulus. Comparing with the film formulated without clay, only that produced with 1.5 g/100g of OMMT-CS presented a Young's modulus significantly different ($P>0.05$).

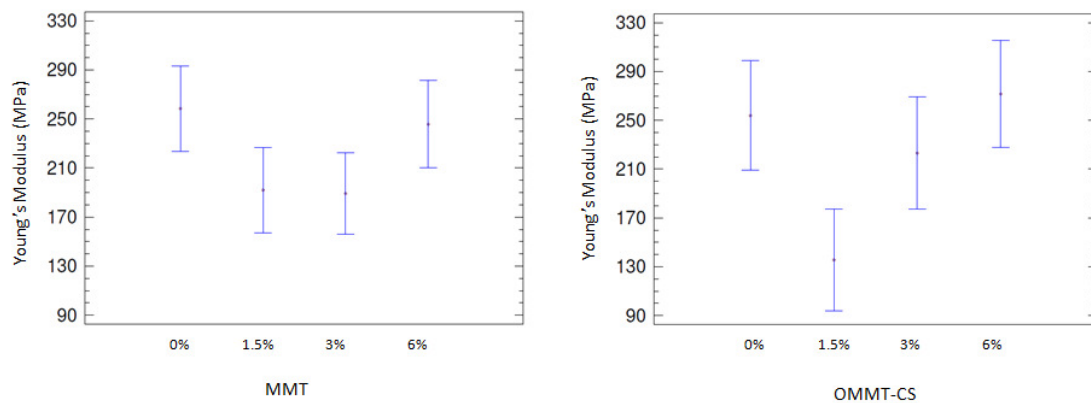


Figure 3 - Variations of Young's modulus of nanobiocomposites in relation to clay content.

CONCLUSION

As the elongation at break decreased with larger amounts of native clay added to the starch matrix, it is possible to infer that the dispersion of clay platelets depends on the proportion of clay, since the presence of clay stacks weakens the material. In contrast, the addition of organomodified clay caused a drop at elongation at break, but it kept constant regardless the amount of OMMT-CS added, which implies that the platelets were well exfoliated. This loss of elongation is due to the transference of the stiffness of the clay platelets to the starch matrix, when they have a good interaction.

All the parameters studied have great influence on mechanical properties of the nanocomposite. Because of this, the best proportion of compounds depends directly on the conditions of storage after the production of the material.

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