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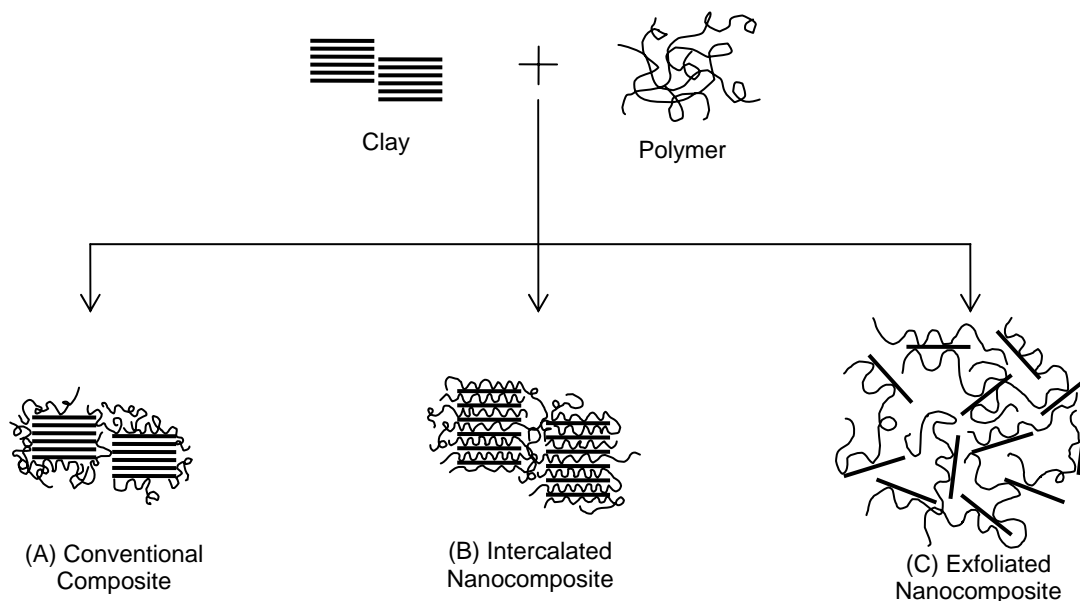
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**Abstract** - In the present work, we report the synthesis and characterization of organic-inorganic hybrid materials based on Cassava starch (biopolymer) and Hectorite clay (a layer silicate). The materials were prepared by solution exfoliation process. In this method, layered clays are exfoliated into single platelets using a solvent in which the polymer is soluble. After the synthesis, the strong interfacial interaction between biopolymer and clay has been evidenced for homogeneous gels formed. When small amounts of clay are added, the PXRD data indicate the formation of exfoliated hybrid materials, in which the individual inorganic layers are separated in the polymer matrix. On the other hand, when great amounts of clay are added, the intercalated hybrid materials are formed, where the insertion of polymer chains into the layered inorganic structure occurs in a regular fashion. The analysis of FTIR confirms the presence of the layered inorganic material and also two major polymeric components of the cassava: amylose and amylopectin. The thermogravimetric data show that the inorganic clay sheets delay the temperature of the biopolymer decomposition.

## Introduction

Organic-inorganic hybrid materials based on the assembly between layered inorganic materials and polymers have received considerable attention in the last years.<sup>1-7</sup> In such materials, the synergistic interaction between the organic and inorganic phases may give rise to materials with new properties that are not present in the individual pristine parts. This emerging class of materials shows enhanced properties such as increased tensile properties, increase thermal stability, gas barrier properties, flame retardancy, and etc.<sup>2</sup>

Particularly, many organic-inorganic hybrid materials can be prepared through the combination of polymers and clays (hydrous layer silicates). Several synthetic routes have been used to prepare these hybrid materials based on clays: (a) exfoliation-adsorption, (b) *in situ* intercalative polymerization, (c) melt intercalation, (d) template synthesis.<sup>2</sup> Depending on the nature of the organic and inorganic components and also of the preparation method, three types of organic-inorganic hybrid materials can be obtained when the clay is associated with a polymer, as shown in Figure 1.



**Figure 1**-Schematic illustrations of different types of hybrid materials arising from the clay - polymer interaction.<sup>2</sup>

More recently, some studies have been reported the synthesis and characterization of the organic-inorganic hybrid materials composed of biodegradable polymers from renewable sources and clays.<sup>8</sup> These hybrids containing clays, also called *green nanocomposites*, are considered as a new generation of materials. They are attractive materials to replace the existing petroleum-based plastics. In addition to their enhanced properties in relation to the unmodified biopolymers, these materials exhibit good biocompatibility and degradability. Some examples of biodegradable polymer include Polylactide (PLA), Poly(3-hydroxybutyrate) (PHB), Thermoplastic Starch (TPS), Cellulose, Gelatin, Chitosan, etc. The clays commonly used are classified as 2:1 phyllosilicates of the smectite group (Montmorillonite, Hectorite, and Saponite).<sup>9-14</sup>

In the present work, we report the synthesis and characterization of organic-inorganic hybrid materials based on Cassava starch (biopolymer) and the synthetic Hectorite clay commercialized as Laponite RD<sup>®</sup>. The materials were prepared by solution exfoliation process. In this method, layered clay is exfoliated into single platelets using an appropriated solvent. After exfoliation, the clay is added at the dispersion containing the same solvent and the biopolymer.

Laponite RD<sup>®</sup> is a trioctahedral smectite-type material with some substitutions of Li<sup>+</sup> ions for Mg<sup>2+</sup> ions in the octahedral brucite-like layer and the empirical formula: Na<sup>+</sup><sub>0.7</sub>[(Si<sub>8</sub>Mg<sub>5.5</sub>Li<sub>0.4</sub>)O<sub>20</sub>(OH)<sub>4</sub>]<sup>-0.7</sup>. The negative charge is neutralized by the presence of Na<sup>+</sup> ions.<sup>15</sup> Cassava is a cheap source of starch in Brazil. Studies about blends of cassava starch films have produced materials with interesting properties.<sup>17</sup>

## Experimental

### Synthesis

The materials were prepared by solution exfoliation process. Laponite RD (from Laporte Industries, UK) was exfoliated into single platelets using a solvent in which the polymer is soluble. The Cassava starch/Laponite proportions were 100/0, 95/05, 90/10, 85/15, 70/30 wt%, and the hybrid organic-inorganic materials are noted as Cas-Lap (100/0), Cas-Lap (95/5), Cas-Lap (90/10), Cas-Lap (85/15), and Cas-Lap (70/30), respectively. One dispersion containing Laponite RD in 50 mL of H<sub>2</sub>O (*dispersion 1*) and other containing Cassava powder in 200 mL of H<sub>2</sub>O (*dispersion 2*) were submitted to thermal treatment at 80 °C for 2 hours under vigorous stirring. The amounts of starch and clay in the dispersions are presented in Table I. Dispersion 1 was added slowly on the dispersion 2 and, concomitantly, 1.5 g of inverted sugar cane (from Copersucar) was added. After the addition, the obtained mixture was maintained under thermal treatment at 80 °C for 30 min under vigorous stirring. A volume of 75 mL of the gel obtained was laid in plastic recipients of 12 cm of diameter. The gels were dried at 70 °C for 12 h in an oven. After drying, the films formed were hydrated for 96 h in a closed box containing a saturated solution of KCl.

**Table I** – Amounts of reagents used in the synthesis of the hybrid materials.

Sample	<i>Dispersion 1 (in 50 mL of H<sub>2</sub>O)</i>	<i>Dispersion 2 (in 200 mL of H<sub>2</sub>O)</i>
	Laponite RD (g)	Cassava starch(g)
Cas-Lap (100/0)	0	10
Cas-Lap (95/5)	0.5	9.5
Cas-Lap (90/10)	1.0	9.0
Cas-Lap (85/15)	1.5	8.5
Cas-Lap (70/30)	3.0	7.0

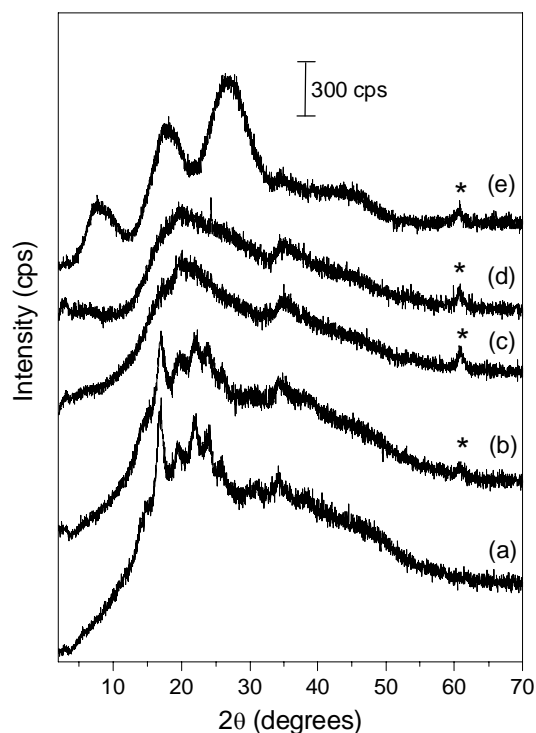
### Characterization

Powder X-ray diffraction (PXRD) patterns were recorded in a Rigaku diffractometer, model Miniflex, using Cu-K<sub>α</sub> radiation (1.541 Å, 30 kV and 15 mA). The step used was 0.02° per second in the angular domain 2-70°. The morphology of the hybrid films was analyzed by Scanning Electron Microscopy (SEM) using a Zeiss DSM 960 - Digital Scanning Microscope. Fourier transform infrared (FTIR) spectra were acquired over the range 4450-450 cm<sup>-1</sup> with 60 scans per sample in an ABB Bomem spectrophotometer, model MB-102, with a coupled diffuse reflectance accessory, using KBr containing 2.5% of the sample. Thermogravimetric analysis (TGA) were performed with a TA Instruments Inc. model Hi-Res<sup>TM</sup> TGA 2950 interfaced to the Thermal Analyst 2000 software, under air, from room temperature to 850 °C at a heating rate of 20 °C min<sup>-1</sup>.

## Results and Discussion

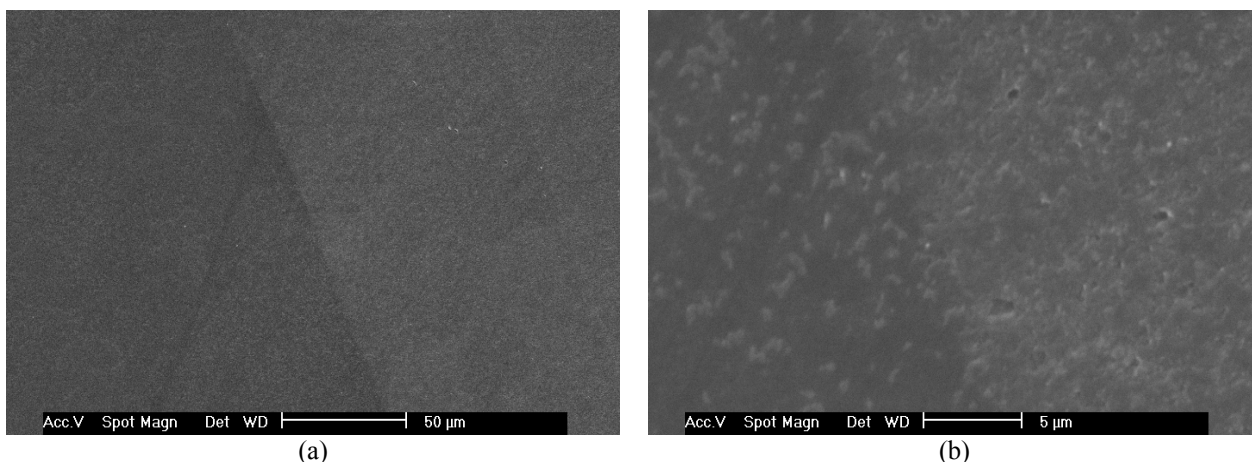
After the synthesis, the strong interfacial interaction between biopolymer and clay has been evidenced for homogeneous gels and films formed. PXRD patterns for the hybrid materials are shown in Figure 2. The diffractogram of the Cas-Lap (100/0) (Figure 2a) shows only the peaks related to starch.<sup>16</sup> The addition of sugar and the heating process during the synthesis of the composites do not change the crystalline structure of the starch. Likewise, the diffraction profile of the Cas-Lap (95/5) (Figure 2b) is very similar to Cas-Lap (100/0). The crystalline structure of the

starch does not also present significant modifications with the addition of small amounts of clay. PXRD patterns of Cas-Lap (90/10) and Cas-Lap (85/15) show a decrease of the materials crystallinity. For the materials with the proportion Laponite / Starch above 5%, the peak positions in  $2\theta = 61$  degrees (signal marked with \*) indicates the presence of the Laponite clay. This result suggests the presence of the exfoliated inorganic solid in the hybrid materials. On the other hand, the x-ray diffractogram of the sample Cas-Lap (70/30) exhibits several orders of basal reflections ( $00l$ ) indicating ordered layered structure. Taking into account the basal spacing of 1.35 nm (calculated from  $d_{(001)}$  peak) and the clay thickness (0.96 nm), the interlayer distance (about 0.4 nm) suggests the incorporation of monolayers of amylose and amylopectin between Laponite sheets. In this interlayer arrangement, the biomolecules should adopt an orientation with its rings parallel to the inorganic sheets. Similar arrangement was previously observed for other biopolymers intercalated in different clays, such as chitosan and starch in Montmorillonite (MMT).<sup>14</sup>



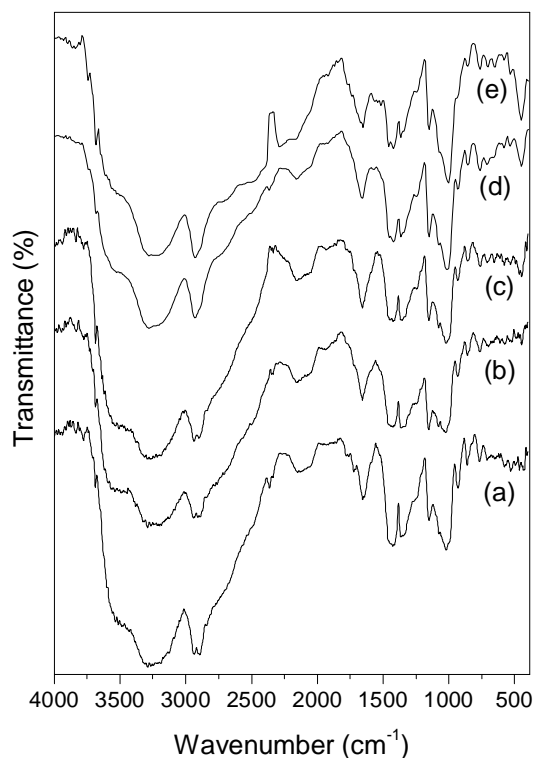
**Figure 2** – PXRD patterns of (a) Cas-Lap (100/0), (b) Cas-Lap (95/5), (c) Cas-Lap (90/10), (d) Cas-Lap (85/15), and (e) Cas-Lap (70/30).

The representative SEM images of the prepared materials are shown in Figure 3. The morphology of the Cas-Lap (90/10) evidences the strong interaction between the clay exfoliated sheets and the cassava starch. Homogeneous films with high transparency are formed.



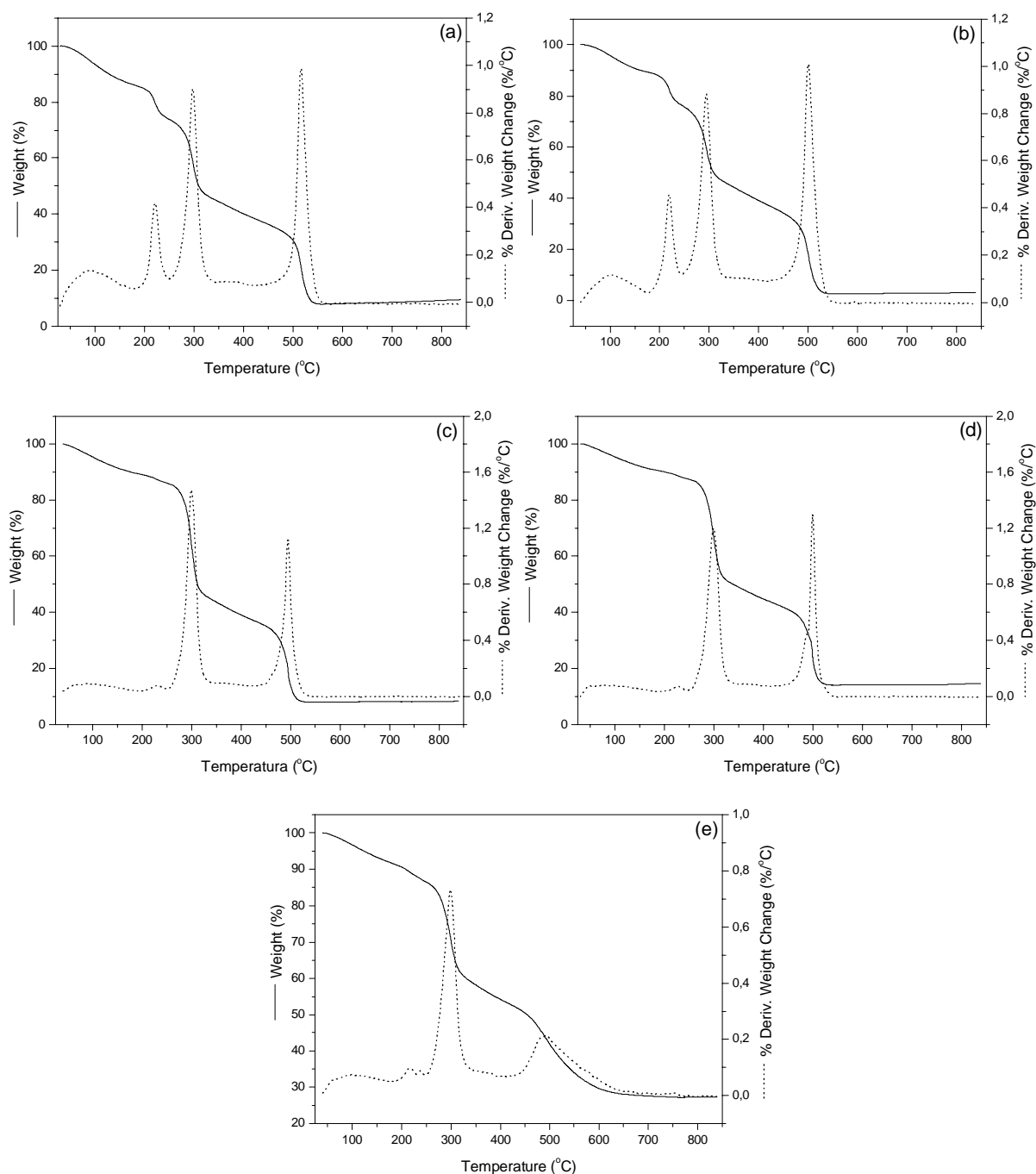
**Figure 3** – SEM of Cas-Lap (90/10) with magnification of (a) 500x and (b) 4000x.

The FTIR spectra are showed in Figure 3. The spectra are characteristic of polysaccharides. They exhibits broad bands at around 3800-3000  $\text{cm}^{-1}$  due to O–H stretching vibrations of water and hydroxyl groups and also the bands at around 1650-1630  $\text{cm}^{-1}$  attributed to  $\text{H}_2\text{O}$  bending.<sup>18</sup> The bands in the region of 2925  $\text{cm}^{-1}$  are due to C–H stretching while the bands in the region at around 1455-1362  $\text{cm}^{-1}$  are attributed to  $\text{CH}_2$  bending in plane. For the C–O–C stretching, it is observed one triplet with bands at 1156  $\text{cm}^{-1}$ , 1071  $\text{cm}^{-1}$ , and 1020  $\text{cm}^{-1}$ .<sup>18</sup> The OH bending can be recognized at 655  $\text{cm}^{-1}$ . For the hybrid materials, the Si-O bending band is observed at around 465  $\text{cm}^{-1}$  and its intensity increases in the hybrid materials with larger amount of clay.<sup>19,20</sup> It is also observed an increase of absorption in the 1000-1040  $\text{cm}^{-1}$  range from Figure 3c to 3e that can be related to the strong band associated with Si-O stretching.<sup>20</sup>



**Figure 3** - FTIR spectra of (a) Cas-Lap (100/0), (b) Cas-Lap (95/5), (c) Cas-Lap (90/10), (d) Cas-Lap (85/15), and (e) Cas-Lap (70/30).

The thermogravimetric curves are presented in Figure 5. The profile of the curves for the Cas-Lap (100/0) and Cas-Lap (95/5) are very similar (Figures 4a and 4b); both materials present three main steps of thermal decomposition. The first step corresponds to the release of water molecules and the event occurs from room temperature up to 250 °C. The mass loss in this region was 25.7% for the material without clay, and 23.2% for the Cas-Lap (95/5). For the hybrid materials Cas-Lap (90/10), Cas-Lap (85/15), and Cas-Lap (70/30), the weight loss associated with the water molecules is around 13%. For the Cas-Lap (100/0), the second and third steps of decomposition occur between 250 °C and 580 °C, the mass loss is about 65.1% and the event corresponds to the **organic components** decomposition. The percentage of the residue was about 9.3%. In the clay composite materials, in addition to the biopolymer decomposition, in the second and third steps take also place the partial dehydroxylation of Laponite clay sheets. According to Yariv et al.<sup>21</sup>, for the Laponite pristine, above 600 °C the exchangeable cations migrate into the silicate layer and the clay structure collapses. In the case of Cas-Lap (70/30) composite (Figure 4e), host inorganic structure increases the thermal stability of the organic biomolecule guest in relation to the unmodified biopolymer. The thermal decomposition of the organic biomolecules in Cas-Lap (70/30) sample seems to extend above 500°C which can be interesting to retard the starch decomposition.



**Figure 4** – TGA curves of (a) Cas-Lap (100/0), (b) Cas-Lap (95/5), (c) Cas-Lap (90/10), (d) Cas-Lap (85/15), and (e) Cas-Lap (70/30).

## Conclusion

Organic-inorganic materials based on synthetic hectorite clay and cassava starch were synthesized. The materials were prepared by solution exfoliation process. In this method, layered clays are exfoliated into single platelets in water, a solvent in which the polymer is soluble. After the synthesis, the strong interfacial interaction between biopolymer and clay has been evidenced for homogeneous gels and films formed. When small amounts of clay are added, the PXRD data indicate the formation of exfoliated hybrid materials, in which the individual inorganic layers are separated in the polymer matrix. On the other hand, when great amounts of clay are added the intercalated hybrid materials are formed in a regular fashion, as a result of the polymer chains insertion into the layered inorganic structure. The analysis of FTIR spectra confirms the presence of both forms: the biopolymers and the layered inorganic material. According to TGA analysis, the different steps of thermal decomposition are dependent of the amount of clay in the hybrid material. In general, the thermal protection occurs when the biomolecule is incorporated into the clay interlayer region. In a

subsequent work, we will demonstrate the tensile and gas barrier properties of these organic-inorganic hybrid materials.

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