

## STARCH AND SYNTHETIC CLAY NANOCOMPOSITES

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### INTRODUCTION

Intercalation compounds are an opened-pore structure class where atomic specimens or molecules could be retained in a reversible manner without loss of structural integrity [1], such as conventional zeolitic systems, mesoporous structures as MCM-41, layered structures as aluminosilicates (cationic clays) and many others. Considering all the host structures and the possible guest specimens that could be matched, the intercalation chemistry offers a really versatile pathway in terms of strategy for synthesis when obtaining well-organized nanoscale structures is desirable [2]. The currently expansion of this field of research is mainly due to the changes made over electronic, magnetic, thermal, catalytical and chemical properties when nanoscale interaction between host and guest is achieved. Simple organic molecules or polymers can be intercalated between the inorganic host layers. Over the last years the development of new materials, especially biodegradable-based nanocomposite, has been increased due to environmental concerns arise from nonbiodegradable petroleum-based plastics [3]. On this route, this work proposes the combination of starch obtained from *Manihot esculenta* (Cassava) and Laponite RD, synthetic cationic clay, in order to improve the biopolymer properties. Cassava starch is mainly constituted of two kinds of polysaccharides, amylose and amylopectin. The first one is a linear macromolecule formed by D-glucose units, while the second one is a branched macromolecule constituted also by D-glucose units [4]. Laponite clay belongs to the group of smectites, trioctahedral group with formula  $\text{Na}_{0.7}[\text{Mg}_{5.5}\text{Li}_{1.4}\text{Si}_8\text{O}_{20}(\text{OH})_4]$ . This clay is well-known by its great capacity of swelling and exfoliation. It has a low layer charge density and the ionic interactions between sodium ions and the clay platelets are not strong enough to hold a stacking structure in the presence of water. The prepared starch-clay nanocomposites in the film form were analyzed by X-ray diffractometry (XRD), thermal analysis (TGA-MS), vibrational spectroscopy (FTIR), scanning electronic microscopy (SEM) and high resolution transmission electron microscopy (HRTEM).

### EXPERIMENT

Cassava starch/clay proportions (wt/wt) utilized were 100/0, 95/05, 90/10, 85/15, 70/30, and the hybrid organic-inorganic materials were 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 for 2 hours under mechanical stirring. The sum of starch and clay amounts was 10 g in each film. Dispersion 1 was added slowly on the dispersion 2 and, concomitantly, 1.2 mL of inverted sugar cane syrup (from Copersucar) was added. After the addition, the obtained mixture was maintained under thermal treatment for 30 min under stirring. A volume of 85mL of the gel obtained was laid in polystyrene plastic recipients. The gels were dried for 12 h in an oven. After drying, the films were hydrated for 96 h in a closed box containing a saturated solution of KCl. XRD patterns were recorded on a Rigaku diffractometer model Miniflex using Cu K $\alpha$  radiation. Mass coupled thermogravimetric analyses (TGA-MS) were recorded on a Netzsch thermoanalyser model TGA/DSC 490 PC Luxx coupled to an Aëolos 403C mass-spectrometer under synthetic air. FTIR spectra were recorded on a Bomem spectrophotometer, model MB-102, with a reflectance accessory. FE-SEM images were obtained in a JEOL microscope, model JSM-7000F, at the Instituto de Química (USP). HRTEM images were recorded on a 300 kV JEM-3010 ARP microscope at Laboratory of Electron Microscopy of the LNLS, Campinas, Brazil. Samples for the TEM images were prepared by dispersing solid samples in ethanol with an ultrasonic bath followed by deposition on a carbon-coated Cu minigrid.

### RESULTS AND DISCUSSION

After starch destructuring and later addition of clay dispersion and the plasticizer, it was observed a great compatibility between the organic and inorganic phases. A homogeneous gel was obtained after the components mixture and a clear and transparent film was formed after solvent evaporation, independent of the starch/clay ratio used. Native starch shows several XRD peaks over the region (2 $\theta$ ) 15-25° due to its hierarchical organization of branched polymer amylopectin along the granule [5]. XRD patterns of the Cas-Lap (100/0) film shows the peaks related to starch but low crystallinity (addition of inverted sugar and the heating process during the films preparation decrease considerably the starch chains organization). Small amounts of clay do not promote structural changes on the resulting film, since XRD profile of Cas-Lap (95/5) film is very similar to Cas-Lap (100/0) sample. Considering that no diffraction peaks related to clay intercala-

tion were observed, Cas-Lap (95/5) film can be classified as a nanocomposite preferentially exfoliated. The increase of clay content in the nanocomposite causes a significant decrease in materials crystallinity. On the other hand, XRD pattern of Cas-Lap (70/30) film exhibits several orders of basal reflections (001) indicating an ordered layered structure. The presence of a basal spacing ( $d_{001}$ ) of 1.35 nm suggests the formation of a nanocomposite preferentially intercalated. The FTIR spectra of hybrid films are characteristic of polysaccharides. The bands in the region around  $1455 - 1362 \text{ cm}^{-1}$  are attributed to  $\text{CH}_2$  bending in plane. For the hybrid materials, band assigned to Si - O bending is observed at around  $465 \text{ cm}^{-1}$  and its intensity increases in the hybrid films with large amount of clay. It is also observed an increase of absorption in the  $1000 - 1040 \text{ cm}^{-1}$  range when the clay content is increased, probably related to the strong band associated with Si - O stretching. The profile of TGA curves for native starch and Cas-Lap (100/0) sample are very similar; both materials present three main steps of thermal decomposition. The first step corresponds to the release of adsorbed water molecules and occurs from room temperature to  $135 \text{ }^\circ\text{C}$  for native starch and until  $250 \text{ }^\circ\text{C}$  for Cas-Lap as confirmed by DTG-MS curves. For the Cas-Lap (100/0) sample, the second and third steps of biomolecule decomposition occur between  $250 \text{ }^\circ\text{C}$  and  $580 \text{ }^\circ\text{C}$  with water vapor,  $\text{CO}_2$  and mainly  $\text{CO}$  release. The final residue content also varies with the clay loading, ranging from about 6.7 - 23 (wt/wt). In the clay composite materials, in addition to the biopolymer decomposition, in the third step takes also place the partial dehydroxylation of clay sheets, around  $700 \text{ }^\circ\text{C}$ . In the case of Cas-Lap (70/30), host inorganic structure increases the thermal stability of the biomolecule in relation to the unmodified biopolymer.

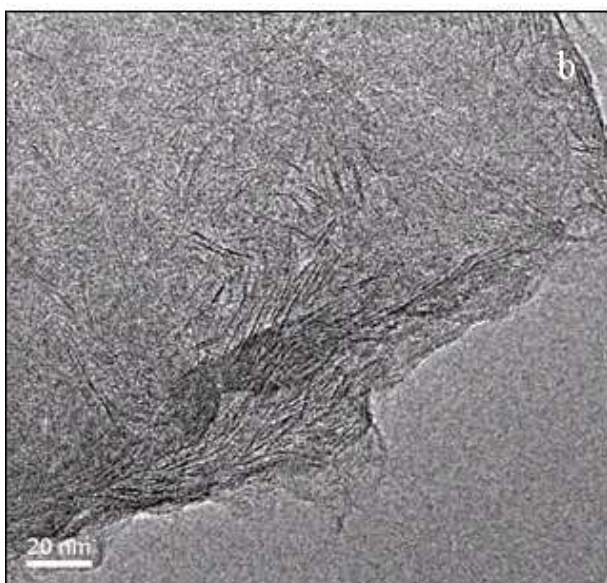


FIG. 1: TEM image of Cas-Lap (70/30) film

SEM images of the native starch reveals its granular nature, while all the films obtained lose this morphology due to starch destructuring process. All the resulting films show high homogeneity and transparency, even those with high content of clay, evidencing strong interaction between clay and starch. HRTEM image of Cas-Lap (70/30) film (figure 1) shows the inorganic sheets (black straight lines) inserted over the polymeric matrix with some degree of organization. The clay length ranges from 20 to 30 nm. It is also observed that clay particles tend to agglomerate over certain regions of the sample due to high clay loading. These agglomerates also show a certain level of organization due to polymer intercalation, compatible with the results obtained from XRD where several basal reflections were observed for this sample.

## CONCLUSION

Homogeneous organic-inorganic hybrids were successfully prepared through previous exfoliation of clay and starch destructuring in order to maximize the hydrophilic interactions between them. XRD patterns show that in lower concentrations of clay, the exfoliated form of clay is dominant while increasing the clay loading, a well-organized nanocomposite is formed. SEM images show the disruption of granular starch structure to obtain homogeneous nanocomposites for all starch/clay ratio. HRTEM images confirmed the development of intercalated nanocomposites when clay content is high corroborating XRD data.

## ACKNOWLEDGEMENTS

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