

New Approach to Elaborate Exfoliated Starch-Based Nanobiocomposites

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The present paper reports the successful elaboration of exfoliated plasticized starch-based nanobiocomposites. This was made possible by using cationic starch as a new clay organomodifier to better match the polarity of the matrix and thus to facilitate the clay exfoliation process. To demonstrate the efficiency of this new approach, either natural (MMT-Na) or organomodified (OMMT-CS) montmorillonite were incorporated into the starch nanobiocomposites by a melt blending process. The morphological analyses (SAXD and TEM) showed that MMT-Na leads to the formation of intercalated nanobiocomposites. On the contrary, OMMT-CS allowed the elaboration of well-exfoliated nanobiocomposites. Tensile tests performed on the obtained nanobiocomposites showed that exfoliated nanobiocomposites display enhanced mechanical properties compared to those of the intercalated nanobiocomposites and neat matrix. These results clearly highlight the great interest in using OMMT-CS to obtain starch-based nanobiocomposites with improved properties.

1. Introduction

The use of agro-based products to replace common nondegradable petroleum-based plastics becomes of great interest because of the diminishing fossil resources combined with the increasing environmental concern.¹ Starch, which is an inherently biodegradable and renewable material, is a promising solution to develop new environmentally friendly materials especially for packaging and disposable applications. Several authors have already demonstrated the possibility to transform native starch into thermoplastic resin like products under destructuring and plasticization conditions (water, polyols).^{2,3} Nevertheless, the water sensitivity and the brittleness of these materials have to be overcome to obtain suitable “green” plastics.¹

The classical approach to answer to these weaknesses consists in the preparation of blends or composites.^{4–6} A recent and innovating area of composites called nanobiocomposites, which is a combination of a biodegradable polymer matrix and a nanosized filler, could also be an innovating solution.⁷ Indeed, depending on the geometry and the nature of the nanofiller, new and/or improved properties (gas barrier, mechanical stiffness, transparency, thermal stability, . . .) could be obtained.^{8–11} The main reason for such improvement compared to conventional biocomposites is the large surface area resulting in high interactions between the polymer matrix and the nanofillers when these nanoparticles are well dispersed.

The most intensive researches are focused on layered silicates, and especially on montmorillonites (MMT), as the reinforcing phase due to their availability, versatility, and respectability toward the environment.¹² The isomorphous substitutions that take place inside these clay platelets generate a negative charge naturally counterbalanced by the presence of inorganic cations (Na⁺, Ca²⁺, . . .) into the interlayer spacing leading to a hydro-

philic 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.¹³ Intercalated structures show regularly alternating layered silicates and polymer chains compared to exfoliated structures in which the clay layers are individually delaminated and fully dispersed in the polymer matrix. Best performances are commonly observed with the exfoliated structures.^{12,13}

Many authors have already published on starch-based nanobiocomposites^{14–19} without obtaining a high extent of exfoliation. Because both starch and natural sodium montmorillonite are hydrophilic, they assume that these compounds will have a high affinity, but according to the small-angle X-ray diffraction results presented, it seems that mainly glycerol is intercalated, resulting in a low extent of exfoliation. Other groups have begun to work on the organomodification of the clay platelets to have a better affinity with the plasticized starch matrix but did not obtain a well exfoliated state.^{20–22}

Thus, the aim of this study is the elaboration and the use of a new organomodified montmorillonite to reach the exfoliation state in starch-based nanobiocomposites. To achieve this objective, the MMT is organomodified with cationic starch to match the matrix polarity. To demonstrate the interest of the MMT organomodification, two families of nanobiocomposites are elaborated: one with the organomodified MMT (OMMT-CS), and another one with the natural sodium MMT (MMT-Na). The obtained materials are compared in terms of dispersion, and then the influence of the morphology on the melt viscosity and mechanical properties is investigated.

2. Experimental Section

2.1. Materials. Wheat starch (WS) was kindly supplied by Roquette (France). The amylose and amylopectin contents are, respectively, 23 and 77%. Residual protein content is less than 1%. The glycerol used

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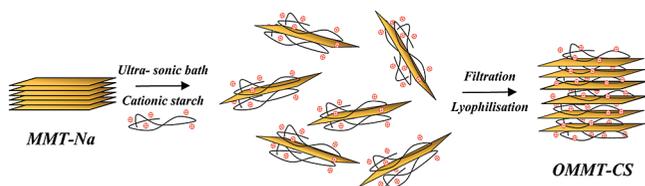


Figure 1. Schematic representation of the MMT-Na organomodification by exfoliation/adsorption technique.

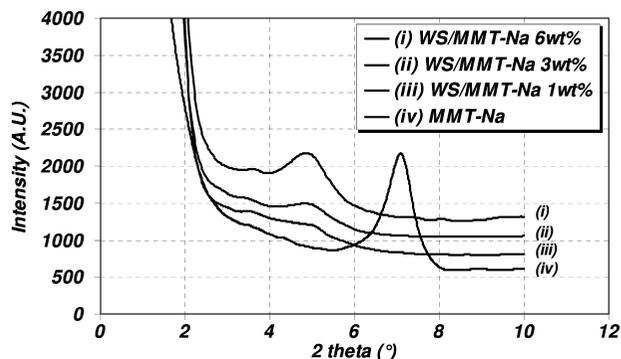


Figure 2. SAXD patterns for MMT-Na and WS/MMT-Na nanobiocomposites with 1, 3, and 6 wt % of clay inorganic fraction.

was kindly supplied by the Société Française des Savons (France) and is a 99.5% purity product. The cationic starch has been kindly supplied by Roquette (France). Its charge density is 944 $\mu\text{equiv/g}$. The cationic functions are quaternary ammonium with chloride as counteranion. The Dellite LVF sodium montmorillonite (MMT-Na) was kindly supplied by Laviosa Chimica Mineraria SpA (Italy) and has a cationic exchange capacity (CEC) of 1050 $\mu\text{equiv/g}$.

2.2. Samples Preparation. *Organomodified Montmorillonite Preparation.* The MMT-Na organomodification was carried out with cationic starch by an exfoliation/adsorption technique (Figure 1). First, 5 g of MMT-Na were introduced into 250 mL of distilled water and dispersed in an ultrasonic bath at 60 °C for 4 h. In parallel, 5.6 g of cationic starch were introduced in 250 mL of distilled water and solubilized in an ultrasonic bath at 60 °C for 1 h. These proportions correspond to the charge equivalence between MMT and cationic starch. Then, the two solutions were pooled together and placed for 1 day at 60 °C in ultrasonic bath. The solution was filtered and washed with 1 L of distilled water at 60 °C to remove the salt formed (NaCl) during the cationic starch adsorption. Then, the filtrate was lyophilized to obtain the cationic starch organomodified clay (OMMT-CS).

Starch Dry-Blends Preparation. The formulation used in this study contained 54 wt % of native starch, 23 wt % of glycerol, and 23 wt % of water. The water was introduced with the clay during the nanobiocomposites elaboration, as described in the next paragraph. Granules of plasticized starch were prepared according to the following procedure. Native wheat starch was first dried overnight at 70 °C in a ventilated oven. Then the starch powder was introduced into a turbomixer, and the glycerol was slowly added under stirring. After complete addition of glycerol, the mixture was mixed at high speed (1700 rpm) to obtain a homogeneous dispersion. The mixture was 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 a polyethylene bag.

Nanobiocomposites Elaboration. To obtain nanobiocomposites, from 1 to 6 wt % of MMT (compared to weight of starch and glycerol) were added into the dry blend. A preweighted amount of MMT (0.46–2.86 g of clay inorganic fraction, depending on the formulation) was first dispersed in 13.5 mL of water to obtain a swollen clay and processed according to the protocol presented hereafter. Then, the dry blend and the swollen clay were introduced together into the mixing chamber. The starch nanobiocomposites were prepared by mechanical kneading with a counter-rotating internal batch mixer, Rheocord 9000

(Haake, USA), at 70 °C for 20 min with a rotor speed of 150 rpm. After melt processing, molded specimens and films were obtained by hot-pressing at 110 °C applying 20 MPa pressure for 15 min. The nanobiocomposite samples were then allowed to equilibrate at 57% RH (relative humidity percentage) for 1 month in a controlled humidity chamber before characterization. Throughout this paper, the obtained samples are designated WS/XXX y% where XXX stands for the type of (organo)clay and y for the weight percentage of clay inorganic fraction.

2.3. Characterization. *SAXD.* The small angle X-ray diffraction (SAXD) morphological analyses were performed on a powder diffractometer Siemens D5000 (Germany) using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at room temperature in the range of $2\theta = 1.5\text{--}10^\circ$ by steps of 0.01° of 4 s each. The clay interlayer spacing values (d_{001}) were calculated from the MMT diffraction peak with the use of the Bragg's law (eq 1).

$$2d_{001}\sin\theta = n\lambda \quad (1)$$

TEM. For transmission electronic microscopy (TEM) observation, the samples were microtomed at low temperature (−80 °C) using a Diatome AG-microtome (Switzerland) equipped with a diamond knife. The ultrathin sections (nominal thickness 60 nm) were examined using a Philips CM 12 (Netherlands) transmission electron microscope using an acceleration voltage of 120 kV.

TGA Characterization. The thermogravimetric analyses (TGA) were performed on a Hi-Res TGA 2950 apparatus from TA Instruments (USA). For all starch/clay nanobiocomposites, the analyses were carried out under “synthetic air”, which is a mixture of 75% N₂ and 25% O₂. The clay content in inorganics (in wt %) of each composite was assessed by the combustion residue left at 600 °C.

Mechanical Tests. Tensile tests were carried out with an Instron tensile testing machine (model 4204, USA) on dumbbell-shaped specimen; at 25 °C with a constant deformation rate of 5 mm/min. For each formulation, five samples were tested. The non linear mechanical behavior of the different samples was determined through different parameters. The true strain (ϵ) is given by eq 2, where L and L_0 are the test piece length during the experiment and at zero time, respectively.

$$\epsilon = \ln\left(\frac{L}{L_0}\right) \quad (2)$$

The nominal stress was determined by eq 3, where F is the applied load and S_0 is the initial cross-sectional area. The true stress (σ) was given by eq 4, where F is the applied load and S is the cross-sectional area. S was estimated by assuming that the total volume of the sample remained constant, according to eq 5.

$$\langle\sigma\rangle = \frac{F}{S_0} \quad (3)$$

$$\sigma = \frac{F}{S} \quad (4)$$

$$S = S_0 \frac{L_0}{L} \quad (5)$$

Young's modulus (E) was determined and calculated from the slope of the low strain region of the tensile curve ($\sigma = \epsilon = 0$). The energy at break values were calculated from the area of the tensile curves obtained for each sample.

3. Results and Discussion

3.1. Morphological Characterization. Figure 2 displays the typical SAXD curves recorded for MMT-Na and the WS/MMT-Na nanobiocomposites elaborated at different clay loading (1, 3, and 6 wt %). The diffraction pattern of MMT-Na displays an intense diffraction peak at low 2θ angles (7.3°) corresponding to a clay interlayer spacing value (d_{001}) of 12 \AA . All the