



# Elaboration, morphology and properties of starch/polyester nano-biocomposites based on sepiolite clay



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## ABSTRACT

The incorporation of nano-sized sepiolite clays into thermoplastic starch/poly(butylene adipate-co-terephthalate) (TPS/PBAT) blends has been investigated with the goal of improving the matrix properties. TPS/PBAT nano-biocomposites were elaborated with two different proportions of the polymeric phases. The influence of the sepiolite nanoclays on the mechanical, thermal and structural properties of the corresponding blends was evaluated. SEM images confirmed the good dispersion of the sepiolite clay, with a low occurrence of small aggregates in the polymeric matrix. Wide-angle X-ray diffraction showed no significant alteration of the crystalline structures of PBAT and starch induced by the sepiolite clay. The addition of sepiolite slightly affected the thermal degradation of the nano-biocomposites; however, the mechanical tests revealed an increase in some mechanical properties, demonstrating that sepiolite is a promising nanofiller for TPS-based materials.

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## 1. Introduction

The inherent necessity to reduce the environmental pollution caused by plastic wastes has become a global concern, thereby motivating researchers to investigate environmentally friendly materials, with a focus on bio-based polymers as alternatives to the non-biodegradable plastics produced from fossil resources (Chivrac, Pollet, & Avérous, 2009; Avérous & Fringant, 2001). Starch is an inexpensive, biodegradable and abundant raw material, which are all attractive characteristics from commercial and environmental perspectives. To produce thermoplastic starch (TPS), native starch granules are processed under high temperature and shear conditions with the addition of plasticisers such as glycerol and water (Arvanitoyannis, Nakayama, & Aiba, 1998; Altskär et al., 2008; Van Soest, Hulleman, de Wit, & Vliegenthart, 1996).

Despite the great potential of TPS for applications in agricultural and packaging materials, its fragility and high sensitivity to moisture are limiting factors for materials made only of TPS. Hence, TPS is often blended with other polymers, such as PBAT, a biodegradable aliphatic-aromatic copolyester, which combines biodegradability and other desirable physical properties (Olivato et al., 2013; Park

et al., 2002). In addition to improving the biodegradation characteristics, starch can also reduce the cost of the final product compared to synthetics alone (Dean, Yu, & Wu, 2007; Wilhelm, Sierakowski, Souza, & Wypych, 2003).

The morphology of multiphase systems such as blends is influenced by the processing conditions, the miscibility and viscosity of the polymer phases, and by the amounts of each phase in the final mixture. These are the determining characteristics for the performance of starch-based materials (Schwach & Avérous, 2004).

Combining TPS with nanofillers to produce nanocomposites, with the aim of enhancing the mechanical, thermal and barrier properties of the polymeric matrix, is currently the focus of numerous studies (McGlashan & Halley, 2003; Ray & Okamoto, 2003; Bordes, Pollet, & Avérous, 2009; Avérous & Pollet, 2012). Nanofillers based on natural clay minerals are one of the best options to improve the biodegradable polymer matrix properties due to their easy availability, versatility, and their low environmental and health concerns (Chang, Wu, Anderson, & Ma, 2012). The properties of the corresponding multiphase systems (so-called nano-biocomposites) are strongly dependent on the amount of nanofiller and its dispersion state. The improvement in the mechanical properties with the inclusion of nanofillers is primarily a result of good dispersion and strong polymer–filler interactions (Duquesne, Moins, Alexandre, & Dubois, 2007; Chen, Zheng, Sun, & Jia, 2007).

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Taking its many advantages into account, sepiolite nanoclay, a hydrated magnesium silicate with a microfibrillar morphology (needle-like shape) and a particle size ranging between 10 and 5000 nm long, 10 and 30 nm wide, and 5 and 10 nm thick, was considered in this study. Its structure is based on alternating blocks and tunnels (0.36 nm × 1.1 nm) that grow in the fibre direction. The discontinuity of the silica sheets gives rise to the presence of silanol groups (Si–OH) at the edges of the tunnels opened at the surface of the sepiolite particles (Duquesne et al., 2007; Darder et al., 2006; García-Lopez, Fernández, Merino, Santarén, & Pastor, 2010). The sepiolite clay is rather compatible with starch because its silanol groups form hydrogen bonds with the hydroxyl groups of starch (Chivrac, Pollet, Schmutz, & Avérous, 2010). A better clay dispersion can thus be expected, consequently improving the mechanical properties of the polymer nano-biocomposites (García-Lopez et al., 2010; Bilotti et al., 2009).

With the aim of producing efficient starch-based materials, this study investigated the structure/property relationships of TPS/PBAT blends and their corresponding sepiolite-based nano-biocomposites. The mechanical, thermal and structural properties of these materials were evaluated.

## 2. Experimental

### 2.1. Materials

Nano-biocomposites were produced with native cassava starch (amylose  $20.8 \pm 0.6$  wt%; protein  $0.28 \pm 0.1$  wt%; lipids  $0.11 \pm 0.6$  wt%; ash  $0.22 \pm 0.6$  wt%, db) obtained from Indemil (Paranavaí, Brazil), glycerol (99.5% purity) kindly supplied by Novance (Paris, France) and PBAT (poly(butylene adipate-co-terephthalate)) supplied by BASF (Ludwigshafen, Germany) under the commercial name Ecoflex®. Neat sepiolite, also known as natural or sodium sepiolite (S), is a commercial clay with a cation-exchange capacity (CEC) of 150  $\mu$ equiv/g, and it was supplied by Tolsa (Madri, Spain) under the trade name Pangel® S9.

### 2.2. Thermoplastic starch (TPS) preparation

As the first step, starch/glycerol dry-blends were prepared. In this process, native cassava starch was dried overnight at 70 °C in a ventilated oven. The dried starch was then introduced in a turbo-mixer, and glycerol was slowly added while stirring at 1700 rpm until a homogenous mixture was obtained. The mixture was dried at 170 °C in a ventilated oven for 40 min, and then the dry-blend was recovered and stored in a sealed plastic bag. To obtain TPS, the dry-blend was processed, with the addition of water, in a Rheomix OS (Haake, USA) counter-rotating internal batch mixer at 70 °C for 20 min with a rotor speed of 150 rpm, resulting in a formulation containing 54 wt% cassava starch, 23 wt% glycerol and 23 wt% water. TPS/sepiolite nano-biocomposites and a master-batch (TPS + 10 wt% sepiolite) were also produced using the same processing conditions with the incorporation of the appropriate amount of sepiolite clay into the TPS.

### 2.3. Production of blends and nano-biocomposites

The different blends (TPS/PBAT) and nano-biocomposites were produced by mixing in a Rheomix OS (Haake, USA) counter-rotating internal batch mixer at 130 °C for 20 min and 150 rpm. The mixtures were then compression moulded (Labtech Engineering Company, Muang, Thailand) at 130 °C for 12 min with a pressure of 20 MPa. Two TPS/PBAT proportions were tested, 50:50 and 80:20, with 0, 1, 3 or 5 wt% of sepiolite clay. The corresponding samples were designated as XX/YY/Z, where X is the proportion of TPS, Y is the proportion of PBAT in the blend, and Z is the wt% of sepiolite clay.

Reference materials based on neat TPS or PBAT with 3 wt% sepiolite were also produced. All of the samples were conditioned at a  $53 \pm 2\%$  relative humidity and  $25 \pm 2$  °C for 20 days to obtain stabilised samples before the analysis and to take into account the post-processing aging of these materials.

### 2.4. Characterisation

#### 2.4.1. Mechanical properties

The tensile strength, elongation-at-break and Young's moduli were determined according to ASTM D638-03 using a Universal Testing Machine MTS 2/M (Minnesota, USA) at a strain rate of 50 mm/min at 20 °C.

#### 2.4.2. Scanning electron microscopy (SEM)

A FEI Quanta 200 scanning electron microscope (FEI Company, Tokyo, Japan) was used to observe the cryogenic fractured surfaces of the samples. The materials were stored at 25 °C in a desiccator with CaCl<sub>2</sub> ( $\approx 0\%$  RH) for 3 days and then coated with a gold layer using a sputter coater (BAL-TEC SCD 050). The images were taken at magnifications of 2000 $\times$  and 4000 $\times$ .

To observe the morphologies of the samples by SEM, the 50/50/0 and 80/20/0 systems were subjected to solvent extraction. For the 50/50/0 sample, the TPS phase was selectively extracted by stirring the sample at room temperature for 4 h in a solution of DMSO/HCl (8 M). For the 80/20/0 sample, the PBAT phase was extracted with chloroform using similar conditions. After drying, the samples were subjected to the previously described treatments before performing the SEM imaging.

#### 2.4.3. Thermogravimetric analysis (TGA)

The thermal stability of the different materials was determined by TGA using a Q5000 instrument (TA Instruments, New Castle, USA); samples of approximately 5 mg were heated from 25 °C to 700 °C at 20 °C/min under an air atmosphere (flow rate of 10 ml/min).

#### 2.4.4. X-ray diffraction (XRD)

X-ray diffraction (XRD) analysis was conducted using a D8 Advance (Bruker, Massachusetts, USA) diffractometer with a CuK $\alpha$  radiation source ( $\lambda = 0.1546$  nm) operating at 40 kV and 40 mA. The samples were scanned over a  $2\theta$  range from 5 to 50° at a scan rate of 0.9°/min.

#### 2.4.5. Melt viscosity analysis

The data recorded during the mixing (torque values vs residence time) in the internal batch mixer were used to evaluate the melt viscosity of the multiphase systems under thermo-mechanical treatment.

#### 2.4.6. Statistical analysis

The data were analysed using STATISTICA 7.0 software (Statsoft, Oklahoma), with analysis of variance (ANOVA) and Tukey's test at a 5% significance level.

## 3. Results and discussion

### 3.1. Melt viscosity analysis

The torque vs residence time curves were recorded during the processing of TPS/PBAT blends and are shown in Fig. 1. All the nano-biocomposites showed an increase in the torque value at the beginning of the process, which corresponds to the melting of PBAT and TPS. The addition of sepiolite altered the viscosity of the samples, leading to higher torque values with increased

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