



Thermoplastic starch/talc bionanocomposites. Influence of particle morphology on final properties



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ABSTRACT

This work analyzed the effect of talc morphology on structural characteristics and final properties of thermoplastic corn starch (TPS). In this sense, composite films based on TPS containing talc nanoparticles were obtained by melt-mixing and thermo-compression. Talc samples with different morphological characteristics (platy-microcrystalline and blocky-macrocrystalline), derived from their formation process, were used. Platy and blocky morphology was distinguished by Scanning Electron Microscopy performed on composites films. Microcrystalline morphology induced smaller TPS crystallites than macrocrystalline one, indirectly evidenced by X-Ray Diffraction and Differential Scanning Calorimetry. Crystalline character of talc particles also affected visible and UV barrier capacity of TPS films. Blocky morphology of mineral filler led to the highest reduction of TPS water vapor permeation. Both talc samples acted as matrix reinforcement agents. However, macrocrystalline particles induced the major changes on elastic modulus and tensile strength, without affecting films ductility.

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1. Introduction

Nowadays, technological interest is focused on a new generation of composites polymers based on biodegradable matrixes from renewable raw materials with organic or mineral fillers. These biocomposites have several advantages mainly due to their eco-friendly character since they can be naturally degraded plus their renewable origin. Moreover, these materials could be developed from residues or sub-products, as well as, resources derived from agro-industrial activities. In this sense, starch qualifies as a good option because of its world-wide availability, low cost, functionality and biodegradability. In order to evaluate biodegradable character of materials based on these polymers, several techniques were studied being composting, one of the most used (Saiah, Gattin, & Sreekumar, 2012). Naturally, starch is not considered as a

thermoplastic polymer but its processing, in the presence of plasticizers, under high temperature and shear stresses, allows the disruption of its granular structure, becoming into thermoplastic starch (TPS) (Ma, Chang, Yu, & Stumborg, 2009; Pinto, Carbajal, Wypych, Ramos, & Satyanarayana, 2009). TPS-based materials have received considerable attention since their processing is easily scalable, employing the same technology used for synthetic polymers (Parra, Tadini, Ponce, & Lugão, 2004; Tapia Blácido, Sobral, & Menegalli, 2005). In the literature, there are many works related to starch biocomposites development through the incorporation of natural fibers (Narkchamnan & Sakdaronnarong, 2013), nanocrystals (Bodirlau, Teaca, & Spiridon, 2013; Lu, Weng, & Cao, 2005), and clay minerals (Chung et al., 2010; De Melo et al., 2011), among others. Mineral filler presence allows tailoring composites for specific applications by improving their mechanical performance and modifying their barrier and optical properties.

The use of talc particles as filler is a less investigated alternative compared to clay minerals. Talc should be considered a promissory option as polymer reinforcement agent because its world-wide availability, relative low cost, and chemical inertness, as well as,

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its particles have at least one nanometric dimension. This mineral is a naturally occurring magnesium silicate with an ideal chemical formula of $Mg_3Si_4O_{10}(OH)_2$, constituted by stacked platelets, which are formed by thousand of elemental sheets (Steen, 1999). Talc incorporation allows enhancing final properties of starch based materials, without resigning their biodegradable character. Mineral geological origin determines both talc purity, as well as, particle morphology. During talc formation, new mineral phases could be created from preexisting ones. As a consequence, talc ores are also constituted by impurities, including mainly magnesite ($MgCO_3$), calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), and chlorites ($Mg_5(Al,Fe)(Al,Si)_4O_{10}(OH)_8$), among others (Steen, 1999). On the other hand, talc morphology is related to its lamellarity (determined by the individual platelet size) and crystalline character. Thus, long and well-defined platelets are attributed to 'macrocrystalline' talc with high lamellarity. Meanwhile, heterogeneous stack of small and irregular platelets is characteristic of 'microcrystalline' mineral with low lamellarity (Piniakiewicz, McCarthy, & Genco, 1994). Several works reported that these differential characteristics derived from mineral genesis determine final properties of synthetic composites. Thereby, talc purity affects its efficiency by enhancing composite thermal properties since even low levels of impurities (metal ions) catalyze polymer degradation (Flaris, 2005). Moreover, particle characteristics determine their aggregation tendency, affecting filler distribution and dispersion within polymeric matrix (Pukánszky, 1995). Castillo, Barbosa, and Capiati (2013) reported that macrocrystalline talc lead to improved mechanical properties than microcrystalline one on polypropylene based composites. However, concerning to biopolymer matrixes, there is a lack of studies related to the influence of mineral genesis on composite properties. The relevance of knowing geomorphological characteristics of filler particles, associated to its formation process, resides on the possibility to forecast composite performance and to design materials with specific properties depending on their applications.

The goal of this work was to evaluate the influence of talc morphological characteristics derived from different geological genesis, on TPS bionanocomposite structure. Besides, the effect of filler presence on optical, thermal, barrier, and mechanical properties of thermo-compressed films was also evaluated through several techniques.

2. Materials and methods

2.1. Materials

Native corn starch was provided by Misky-Arcor (Tucumán, Argentine) with an amylose content of $23.9 \pm 0.7\%$ (López, García, & Zaritzky, 2008). Talc samples from two different ores were used: Australian talc (A10), with a purity degree of 98% w/w, and Argentinean talc (SJ10), containing up to 16% w/w of impurities. Both samples were kindly supplied by Dolomita SAIC (Argentine). Geological origin induces mineral differences such as purity, crystalline character, and morphological aspects.

As it was reported in a previous work, A10 is a platy talc sample, having particles organized in laminar concentric domains like an "onion" structure (Castillo, Barbosa, & Capiati, 2012). Besides, this talc has a microcrystalline morphology, where small platelets are stacked up heterogeneously. On the other hand, SJ10 is a blocky-type talc sample with long and well stacked up platelets which corresponds to a macrocrystalline structure (Castillo, Barbosa, Maiza, & Capiati, 2011). Moreover, these talc particles appear as blocks, with abrupt and well defined borders. Analytical grade glycerol (Anedra, Argentine) was used as plasticizer.

2.2. Thermoplastic starch mixtures

Mixtures of native corn starch, glycerol (30% w/w), distilled water (45% w/w) and talc nanoparticles (0 and 8.7% w/w) were prepared. Component concentrations were expressed in g per 100 g of starch, which implies that 0 and 5% w/w of talc, respect to TPS, were used. Mixtures were prepared using both A10 and SJ10 talc samples and formulations were named TPS, TPS +5% A10 and TPS +5% SJ10, respectively. Talc was premixed with starch to achieve good particle dispersion between both powders. Then, glycerol and distilled water were added and samples were mixed and conditioned at 25 °C during 24 h. Mixtures were processed in a Brabender Plastograph (Brabender, Germany) at 140 °C and 50 rpm for 15 min.

2.3. Films preparation

Thermoplastic starch films were obtained by thermo-compression using a hydraulic press, following the processing conditions reported in a previous work (Castillo, López, et al., 2013). Mixtures were conditioned at 25 °C and 60% relative humidity (RH) and films were prepared at 140 °C and 150 kg cm⁻² during 6 min. Film thickness was measured at least in ten different locations using a micrometer.

2.4. Microstructural characterization

2.4.1. Scanning Electron Microscopy (SEM)

Talc nanoparticles distribution in TPS matrix, as well as, homogeneity and appearance of the developed films, were examined by SEM. This study was performed in a JEOL JSM-35 CF electron microscope (Japan), with a secondary electron detector. Films were cryofractured by immersion in liquid nitrogen, mounted on bronze stubs and coated with a gold layer (~30 Å), using an argon plasma metallizer (sputter coater PELCO 91000). Thus, film surfaces and their cross-sections were satisfactorily observed.

2.4.2. Transmission electron microscopy (TEM)

Dispersion of talc layers was analyzed by TEM. Samples were microtomed at room temperature using an ultramicrotome LKB Ultratome 2088 (KB-Produkter AB., Bromma, Sweden) equipped with a diamond knife. Ultrathin sections (~1000 Å) were picked up using a copper grid. Samples were examined using a JEOL 100 CX (JEOL, Japan) operating at an acceleration voltage of 100 kV.

2.4.3. X-ray diffraction (XRD)

Crystal structure identification of thermoplastic starch, crystallinity degree of TPS and talc intercalation/exfoliation were studied by XRD. Diffractograms were obtained in an X-ray diffractometer Philips PW1710 (Philips, Holland), provided with a tube, a copper anode, and a detector operating at 45 KV and 30 mA within 2θ from 3 to 60°. Crystallinity degree (CD) of TPS matrixes were calculated as the ratio between absorption peaks (without considering those corresponding to talc) and the total diffractogram area, expressed as percentage (%). Besides, according to Bragg's equation, basal spacing (*d*) of talc layers was obtained in order to evaluate the degree of platelets intercalation and exfoliation (Mbey, Hoppe, & Thomas, 2012).

Besides, TPS crystallite size was estimated from XRD spectra, according to the Scherrer equation:

$$L_{hkl} = \frac{K\lambda}{B_{hkl}\cos\theta} \quad (1)$$

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