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Study of green nanocomposites based on corn starch and cellulose nanofibrils from *Agave tequilana* Weber

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ABSTRACT

Global environmental pollution issues caused by synthetic materials and the lack of practical utilization of the local industrial lignocellulosic waste, force Mexican researchers to produce new biobased sustainable materials that use industrial waste as a source of components. Herein, we show the preparation and characterization of environmentally friendly starch-based nanocomposites reinforced with cellulose nanofibrils (CNF) extracted from *Agave tequilana* Weber. Tensile, bending and impact mechanical properties of dried and hydrated nanocomposites were studied. Moreover, the water absorption capacity of the nanocomposites were measured and evaluated. The mechanical properties improved because of the presence of a small amount of CNF (1 wt%). This work demonstrates the importance of the addition of a natural biomodifier in a starch matrix to achieve better mechanical properties. Most importantly, this study highlights that lignocellulosic waste from the tequila industry can have a practical application, which is being a source of natural nanoreinforcements for preparation of all-biobased sustainable materials.

1. Introduction

In recent years, researchers and industries all over the world have been searching for new natural-based sustainable materials and processes to tackle the serious and growing environmental issues that affect our planet. In this regard, there is an increasing interest in exploiting plant fibers extracted from agricultural waste in order to produce advanced sustainable materials (Lee, Aitomäki, Berglund, Oksman, & Bismarck, 2014).

In Jalisco, a western state in Mexico, one of the most abundant agricultural waste is the agave bagasse. The agave production is critically important for the economy of Jalisco. The agave is the starting material to produce tequila, which is arguably the most important product of the region because of the considerable revenue generated from its internal consumption and exportation. In 2016, 871.8 thousand tons of agave were used to produce tequila. From that amount, 348.7 thousand tons was agave bagasse ("Regulatory Council of Tequila, Mexico," 2016). Unfortunately, these vast amounts of agave bagasse are being treated as industrial waste with no practical use. This situation opens a unique opportunity for local and international material science researchers to find a useful application of the agave bagasse.

In the context of composite materials, it has been reported that the addition of natural fibers in several polymeric matrices improves the mechanical properties of the composites (Darabi, Gril, Thevenon, Karimi, & Azadfalah, 2012). However, one of the disadvantages of the natural fibers is their hydrophilic character, which affects their compatibility with hydrophobic polymeric matrices, generating a low reinforcement-matrix adhesion. As a consequence, the physical and mechanical properties of the composites and their resistance against natural weathering and biological degradation are negatively affected.

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These negative effects reduce the range of potential applications for these composites (Cao, Chan, Chui, & Xiao, 2012).

In recent years, several investigations regarding composite materials containing *Agave Tequilana (or A. tequilana)* bagasse fibers have been reported. Kestur et al. reported that *A. tequilana* fibers have a thermal stability of approximately 220 °C, making them ideal to act as reinforcements for several polymeric matrices (Kestur et al., 2013). The addition of *A. tequilana* bagasse fibers in polymer matrices improved mechanical and thermal properties of environmentally friendly composites based on polyhydroxybutyrate, poly(hydroxybutyrate-co-hydroxyvalerate) (Torres-Tello et al., 2017). Furthermore, composite materials having polypropylene and polyethylene as their polymeric matrices also showed an increase of mechanical properties when moderated amounts of *A. tequilana* bagasse fibers were added (Cisneros-López et al., 2017; Langhorst et al., 2018; Moscoso-Sánchez et al., 2013).

Cellulose nanoparticles, also known as nanocelluloses, are currently being considered as the next generation of renewable reinforcements for the preparation of advanced and strong nanocomposites with high mechanical performance (Lee et al., 2014). One type of nanocellulose are the cellulose nanofibrils (CNFs), which are extracted from plants (e.g. wood) using enzymatic, chemical and mechanical treatments. Depending on the source and the extraction method, the CNFs have diameters in the range of 2–60 nm and several micrometers of length (Klemm et al., 2011; Torres-Rendon et al., 2016). Because of their unique characteristics and properties, such as their high superficial area and native crystalline domains, the CNFs are ideal candidates to be used as reinforcements in polymeric composites (Hietala, Rollo, Kekäläinen, & Oksman, 2014). So far, only a handful of studies regarding nanocellulosic particles extracted from A. *tequilana* Weber have been reported. Espino et al. demonstrated the feasibility to prepare cellulose nanocrystals (CNCs) from *A. tequilana* bagasse with high aspect ratio and high thermal stability (Espino et al., 2014). Recently, Robles et al. showed that *A. tequilana* byproducts, such as bagasse and leaves, are suitable sources to prepare CNFs and CNCs. High production yields from both types of nanoparticles were obtained (Robles et al., 2018). There are important advantages of using *A. tequilana*-extracted CNFs. For example, environmentally essential plants like trees wouldn´t be needed to obtain such nanoparticles. Furthermore, finding a useful application for thousands of tons of lignocellulosic waste can reduce disposal costs and create green jobs.

It is important to mention that there is a lack of appropriate methods to uniformly distribute CNFs in hydrophobic matrices. This is due to the fact that the CNFs easily form aggregates during drying. These aggregations can not be disassembled because of the strong interaction between the nanofibrils. For this reason, there are only very few successful methods to prepare nanocellulose-based nanocomposites (Hietala et al., 2014).

In this study, nanocomposites containing thermoplastic starch as the matrix and CNFs as reinforcements (TPS/CNF nanocomposites) were prepared and characterized. The incorporation of CNFs improves mechanical properties and do not affect water absorption. The resulting TPS/CNF nanocomposites are first examples of starch-based composites using *A. tequilana* bagasse waste-extracted CNFs as reinforcements.

2. Experimental

2.1. Materials

Fibers (bagasse) of *Agave tequilana* Weber Blue variety were obtained from the company Mundo Agave in Jalisco, Mexico. The thermoplastic starch (TPS), extracted from corn, was bought from the Mexican company IMSA. Glycerin, hydrochloric acid (HCl, 37%), hydrogen peroxide (H_2O_2, 30%) and sodium hypochlorite (NaOCl, 13%) were purchased from Golden Bell. Sodium bromide (NaBr, 97%) was purchased from Products Chemical Monterrey. Sulfuric acid (H_2SO_4, 95%) and sodium hydroxide (NaOH, 97%) were acquired from Karal company. Anthraquinone (AQ, 97%), Sodium chlorite ($NaClO_2$, 90%) and 2, 2, 6, -tetramethylpiperidine-1-oxyl radical (TEMPO, 98%) were bought from Sigma-Aldrich.

2.2. Methods

2.2.1. Preparation of bleached cellulosic fibers

Before bleaching, the agave bagasse was subjected to an acid hydrolysis using a 0.5% sulfuric acid solution with a hydromodule of 8:1. The hydrolysis was made in a rotary digester at 160 °C for 30 min. Subsequently, the hydrolyzed bagasse was cooked in the presence of a solution of sodium hydroxide (23.2%) and anthraquinone (0.1%), with a hydromodule of 5:1, in a rotary digester at 170 °C for 2.5 h. The resulting pulp was washed and purified. The bleaching process was carried out by performing four sequential chemical treatments. The first treatment was done using a solution of chlorine dioxide (D_o). The components were a 10 wt% pulp, 1.7 wt% ClO_2 and 0.15 wt% HCl 1.0 N. The treatment was performed at 60 °C for 0.5 h, having a final pH between 2 and 3. The second step consisted in performing an alkaline extraction (E) on the same 10 wt% pulp used in the previous treatment. A 5 wt% of NaOH 1.0 N was used and the extraction was performed at 70 °C for 1 h, with a final pH of ≥ 10.5. In the third step, chlorine dioxide (D_l) was added to the system (1.0 wt% ClO_2) with 0.15 wt% of NaOH 1.0 N. The process was performed at 80 °C for 3 h. In the fourth step using hydrogen peroxide (P) (1.5 wt%), 1.0 wt% NaOH 1.0 N was added to get an initial pH between 11.5 and 11.8. This step was carried out at 80 °C for 3 h. Finally, a alkaline treatment to eliminate hemicelluloses was performed under the following conditions: 0.5 g of NaOH for each 100 g of pulp (dry based), at room temperature (25 °C), for 0.5 h.

2.2.1.1. Characterization of the bleached cellulose. The quantity of the remaining hemicelluloses in the pulp was determined according to the TAPPI UM 236 method. The contents of alpha, beta and gamma celluloses in the pulp were obtained by applying the TAPPI T 203 om-93 standard. The degree of polymerization was determined by viscosimetry.

2.2.1.2. Preparation of cellulose nanofibril (CNFs) aqueous suspensions. First, a TEMPO mediated oxidation, using the TEMPO/NaOCl/NaBr system, was performed under alkaline conditions (pH 10.5) on the bleached cellulose according to the method reported by Tsuguyuki and Isogai (2004) and Isogai, Saito, and Fukuzumi (2011). Afterwards, the oxidized pulp (4 wt%) was subjected to mechanical treatments using first a blender (Oster) with a speed of 15,000 rpm for 2 h. Then, an ultra-turrax (JANKE & KUNKEL) was used at 20,000 rpm for 5 min. Finally, a sonic treatment (sonication bath, Branson) was carried out for 30 min until the pulp became a gel-like suspension.

2.2.1.3. Fourier transform infrared spectroscopy (FTIR). For this characterization, a spectrophotometer Perkin-Elmer (model Spectrum GX) was used. The attenuated total reflectance (ATR) technique was used and all spectra were obtained from 64 scans, with a resolution of 4 cm^{-1}, in the frequency range of 4000 to700 cm^{-1}.

2.2.1.4. X-ray diffraction (XRD) and atomic force microscopy (AFM). XRD profiles were obtained using a Panalytical diffractometer (model Empyream, α = 1.54184 Å, Cu Kα radiation). The used step was 0.026 and the collection time was 60 s per step. The degree of crystallinity was calculated using the MAUD (Materials Analysis Using Diffraction) program in the Rietveld method. For AFM, an atomic force adsorption microscope (Park SYSTEMS, model NX10) was employed to analyze the CNFs. In order to prepare the samples, CNF suspensions were diluted in water until a ratio of 1:100 was reached and then sonicated for 3 h. The samples were deposited in