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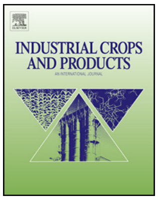

Effect of agave fiber content in the thermal and mechanical properties of green composites based on polyhydroxybutyrate or poly(hydroxybutyrate-co-hydroxyvalerate)

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ABSTRACT

In this study, agave fibers which are an important waste product of the Tequila industry are evaluated for the production of green biocomposites prepared with two biopolymers: polyhydroxybutyrate (PHB) and its copolymer with hydroxyvalerate P(HB-HV). The biocomposites were produced by compression molding with two main objectives: (1) to reduce the amount of biopolymer (due to its high cost) in the final piece and (2) to improve the mechanical properties of the material. In order to evaluate the effect of fiber content over both biopolymers, three agave fiber contents were used (10, 20 and 30 wt%) to prepare them. Afterwards, a comprehensive thermo-mechanical characterization was performed. The results showed that the addition of agave fiber (30 wt%) to both matrices enhances their tensile modulus by 80 and 50% in comparison with PHB and P(HB-HV) respectively, while for their flexural modulus the increase was 36 and 41% respectively. Additionally, tensile and flexural strength were not affected negatively while a significant increase in impact strength was obtained (44 and 66% respectively for biocomposites containing 30 wt% of agave fiber in comparison to PHB and P(HB-HV) matrices). The results show a significant positive role of agave fibers on behalf of moduli reinforcement and toughening for these brittle biopolymers.

1. Introduction

The growing problem of contamination caused by synthetic polymers as well as the future exhaustion of oil has led to the search of alternative materials that can replace those synthetic polymers. In this sense, biopolymers have drawn the attention because they can be produced from renewable resources such as glucose, xylose or sucrose among others, as well as from renewable waste feedstocks with the advantage that the biopolymers can be completely biodegradable (Bourque et al., 1995; Brämer et al., 2001; Lenz and Marchessault 2005; Babu et al., 2013; Cesário et al., 2014). However, the biopolymers market is still relatively small compared to traditional oil based polymers.

Biopolymers can be classified into three groups: 1) natural polymers, such as starch and cellulose-based polymers, 2) synthetic polymers obtained from natural monomers, like polylactic acid (PLA) and 3) polymers from microbial fermentation which are intracellularly synthesized and accumulated as energy and carbon storage by a wide range of bacteria, known as polyhydroxyalkanoates (PHAs) such as polyhydroxyburyte (PHB) (Wong et al., 2002; Barkoula et al., 2010a; Lopes et al., 2011; Cesário et al., 2014). PHB is a medium-crystalline polymer comparable to polypropylene in characteristics like melting point, strength and modulus, that make it an attractive material to substitute synthetic polymers in some applications (Barkoula et al., 2010a; Hossain et al., 2011). However, PHB is brittle and thermally unstable just above its melting point which needs in its processing stage a very careful temperature control to keep its molecular weight and properties (Wong et al., 2002; Barkoula et al., 2010a; Hossain et al., 2011). To overcome these drawbacks, the hydroxybutyrate (HB) has been copolymerized with hydroxyvalerate (HV). The P(HB-HV) copolymer has a lower melting point than the PHB and higher flexibility that allows melt stability. Furthermore, HV in the copolymer influences

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properties such as crystallinity and crystallization rate (Bhardwaj et al., 2006).

The production of composite materials by the addition of natural or synthetic fibers to polymer matrices allows the improvement of mechanical and thermal properties. Natural fibers like flax, hemp, jute, kenaf, abaca, sisal and agave as reinforcements offer some advantages compared to synthetic fibers such as low density, renewability, biodegradability and low cost; in addition they are non-toxic and have good physical and mechanical properties (Barkoula et al., 2010b; Shahzad, 2012; Bledzki et al., 2015; Santos et al., 2015). Specifically, the agave fiber (agave bagasse) used in this work is a waste of the tequila industry and represents a serious environmental issue in the state of Jalisco (Mexico). In 2015, the tequila regulatory council reported that over 303,000 tons of bagasse was obtained as a side product. Kestur et al. (2013) showed by means of scanning electron microscopy images that agave fibers have thick-walled cells that are closely packed; they have an irregular lumen with longitudinal arrangement and contain a large number of fibrils with the binding and pith material in between, and an internal structure that shows the helical winding of microfibrils. Also in their study, they reported a crystallinity of 70% obtained by X-ray diffraction. By thermogravimetric analysis, the agave fibers show thermal stability up to 220 °C which makes them suitable to reinforce many polymers (Kestur et al., 2013; Cisneros-López et al., 2015). The chemical composition of agave fibers (extractives 6–7, cellulose 58–63, lignin 21–24 and hemicellulose 10–13 wt.%) was reported by Pérez-Fonseca et al. (2014); in that study they reported an increase in several mechanical properties of polyethylene (impact strength and tensile and flexural modulus) by reinforcement with agave fiber. Several studies have been reported on agave fiber (*A. tequilana* Weber var. Azul) composites having good mechanical properties (Leduc et al., 2008; López-Bañuelos et al., 2012; Pérez-Fonseca et al., 2014; Cisneros-López et al., 2016). Nevertheless, the combination of agave fibers with biopolymers as matrices to produce green-composites has not been fully studied. These green-composites, which are a combination of natural fibers and biopolymers, have surged as an environmental-friendly and attractive alternative to conventional composites which are difficult to be recycled or substantial cost is required for their disposal (Mohanty et al., 2001; Mohamed et al., 2008; Nyambo et al., 2010). Also, the lack of compatibility between hydrophilic natural fibers and the hydrophobic conventional polymer matrices (e.g. polyolefins) is reduced when biopolymers such as PLA or PHB are used as matrices due to their partial polar character resulting in better adhesion and dispersion that allows the attainment of better mechanical properties. Furthermore, because biopolymers are still more expensive than polyolefins, a reduction in costs can be achieved by the addition of waste fibers.

In this sense, Shibata et al. (2004) studied the effect of adding lyocell to different polymer matrices such as P(HB-HV), PLA and polybutylene succinate (PBS). They observed that the composites exhibited better mechanical properties (impact resistance, tensile strength and modulus); and that under the right conditions they were easily degraded. Barkoula et al. (2010a) reported an improvement in impact strength with the fiber content for composites based on PHB/flax and P(HB-HV)/flax. Similar results were presented by Kuciel and Liber-Kneć (2011) using PHB and kenaf fibers, and Graupner and Müssig (2011) for PHB with lyocell and kenaf fibers, achieving increments up to 130% in impact strength when lyocell was used as reinforcement. However, Singh et al. (2008) reported a decrease in impact strength (47–20 J/m) for composites based on P(HB-HV) and recycled cellulose fiber; they attributed that decrease to the reduced plastic deformation of P(HB-HV) due to the presence of stiff cellulose fibers.

To the best of our knowledge, composites prepared with the systems PHB and P(HB-HV) have not been fully characterized and there are not any literature reports on agave composites with such systems, offering in addition an alternative to use waste fibers and also the possibility to decrease the amount of biopolymer and consequently a cost reduction for the production of biocomposite materials with enhanced properties. In this sense, the effect of agave fiber content (0, 10, 20 and 30 wt%) in the final properties of green composites based on PHB or P(HB-HV) is presented here by means of morphological, mechanical (static and dynamic) and thermal characterization.

2. Materials and methods

2.1. Materials

The biopolymer matrices used in this study were PHB and P(HB-HV) containing 12% of HV supplied by Goodfellow (UK). Their molecular weights (557,000 and 509,000 Da respectively) were determined by gel permeation chromatography using a Waters HPLC chromatograph equipped with a controller model 600, refractive index detector model 2414, autosampler model 717 plus and a quaternary pumps module model 60f. As reinforcement, agave fibers (*A. tequilana* Weber var. Azul) were obtained from an agave bagasse deposit from industrial waste of a local tequila company (Jalisco, México).

2.2. Composites preparation

The agave fibers were treated before being used. The fibers were soaked in water for 24 h and then passed through a Sprout-Waldron refiner (D2A509NH) with two 30 cm diameter discs, one fixed and the other rotating at 1770 rpm to separate the pith from the fibers. Afterwards, the fibers were placed in a centrifuge to remove excess water and finally dried outdoors. Then, the agave fibers were milled and sieved. Fibers between 40 and 50 mesh (400–297 μm) and an aspect ratio (L/D) of 10 were used.

Prior to the blending process, polymers and fibers were dried at 60 °C for 24 h to remove humidity. Then, the blends were prepared with different fiber contents (0, 10, 20 and 30% wt) in a mixer Haake Rheomix 254, with a mixing time of 6 min at 180 °C and 50 rpm. The obtained blends were dried in an oven during 48 h at 60 °C and later molded by compression to obtain sheets of 0.2 × 12.7 × 12.7 cm in a hydraulic press (Schwabenthan model Polystat 200 T) at 180 °C in two stages: (1) a pre-heating for 4 min without pressure and (2) 6 min at a pressure of 200 bar. The composite samples were cut with a laser machine (Guian model GN-600LS) into different geometries to perform all the characterizations.

2.3. Morphology

Composite samples were immersed in liquid nitrogen to be cryogenically fractured. Then, the exposed surfaces were coated with Au/Pd under vacuum during 120 s using a SPI Module Sputter Coater. The fractured surface of the composites was observed using a scanning electron microscope (SEM) TESCAN MIRA3 LMU to characterize the state of fiber adhesion/dispersion in the matrix.

2.4. Thermal characterization

Thermogravimetric analysis (TGA) was conducted to evaluate the thermal stability of the fiber, polymer matrices and composites. The tests were performed on a TA Instruments TGA DISCOVERY using samples of 5–10 mg at a heating rate of 10 °C/min from 40 to 600 °C under nitrogen atmosphere. Thermal behavior of the samples was studied via differential scanning calorimetry (DSC) using a TA Instruments DSC DISCOVERY. Each sample (2–5 mg) was heated at 10° C/min from −20 to 200° C (to eliminate any thermal history).