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Effect of fiber treatments on tensile and thermal properties of starch/ethylene vinyl alcohol copolymers/coir biocomposites

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ABSTRACT

Coir fibers received three treatments, namely washing with water, alkali treatment (mercerization) and bleaching. Treated fibers were incorporated in starch/ethylene vinyl alcohol copolymers (EVOH) blends. Mechanical and thermal properties of starch/EVOH/coir biocomposites were evaluated. Fiber morphology and the fiber/matrix interface were further characterized by scanning electron microscopy (SEM). All treatments produced surface modifications and improved the thermal stability of the fibers and consequently of the composites. The best results were obtained for mercerized fibers where the tensile strength was increased by about 53% as compared to the composites with untreated fibers, and about 33.3% as compared to the composites without fibers. The mercerization improved fiber–matrix adhesion, allowing an efficient stress transfer from the matrix to the fibers. The increased adhesion between fiber and matrix was also observed by SEM. Treatment with water also improved values of Young's modulus which were increased by about 75% as compared to the blends without the fibers. Thus, starch/EVOH blends reinforced with the treated fibers exhibited superior properties than neat starch/EVOH.

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1. Introduction

The potential of biodegradable polymers and more specifically of biocomposites obtained from agro-resources have long been well established (Ashori, 2008; Bilba et al., 2007; Chiellini et al., 2001; Choudhury et al., 2007; Yang et al., 2003). Starch is one of the most studied and promising agro-resources for the production of biodegradable polymers as matrices for biocomposite applications. Starch, derivate from variety of botanical sources (cereals, legumes, and tubers), is widely available raw material for use in bioplastics (Bastioli et al., 1995; Kumar and Singh, 2008). However, due to starch's excessive hydrophilicity and brittleness, blending starch with conventional polymers is a promising approach to improve its drawbacks (Medeiros et al., 2008).

Starch/poly(ethylene vinyl alcohol) copolymer (EVOH) blends provide an interesting polymer system with a wide range of potential mechanical properties; however, the cost is still relatively high. Different kinds of lignocellulosic fibers have been investigated in blends for formulation of biocomposites (Coats et al., 2008; Corradini et al., 2006; Geethamma, 1998; Imam et al., 2005). The incorporation of these fibers as fillers or for reinforcement into blends has received increased attention, particularly for price-driven and high volume applications.

Coir is an abundant, versatile, renewable, cheap, and biodegradable lignocellulosic fiber used for making a wide variety of products (Satyanarayana et al., 1982). Coir has also been tested as a filler or a reinforcement in different composite materials (Choudhury et al., 2007; Corradini et al., 2006; Geethamma, 1998; Owolabi et al., 1985). Furthermore, it represents an additional agroindustrial nonfood feedstock (agroindustrial and food industry waste) that should be considered as feedstock for the formulation of ecocompatible composite materials.

Several factors contribute to the production of fiber-composites with enhanced properties. Fiber–matrix has affected very strongly on the overall performance of the complete composite material (Franco and Valadez-González, 2005). Fiber–matrix interaction can be improved by surface or structural modification of the fibers using various processes such as alkali treatment, bleaching, acetylation and steaming (Corradini et al., 2006; Das et al., 2000; Hill and Abdul Khalil, 2000; Shukla and Pai, 2005).

One of most used modifications is the treatment with an alkali solution (Corradini et al., 2006; Prasad et al., 1983; Ray et al., 2001). The alkaline process, called mercerization, is an effective method that can improve the properties of composites reinforced with lignocellulosic fibers. Bleaching with hydrogen peroxide is

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another chemical treatment widely used in the textile industry that provides surface modification of the fibers (Rout et al., 2001; Salam, 2006).

The incorporation of treated coconut fibers into formulations with starch and EVOH can be a good alternative for producing low cost composites and possibly improving their mechanical properties. Thus, the main objective of the present investigation is to evaluate the influence of different fiber treatments, including washing with water, mercerization and bleaching on mechanical and thermal properties of extruded starch/EVOH blends loaded with the treated coir fibers. Additionally, the fiber/matrix interface was analyzed by using scanning electron microscopy (SEM).

2. Experimental

2.1. Materials

Midsol 50 native wheat starch (12% moisture) was supplied by Midwest Grains, Inc. (Atchinson, KS). Poly(ethylene-co-vinyl alcohol) copolymer (EVOH) was provided by EVAL Company of America (Pasadena, TX) under the trade name EVAL-E105. This particular sample is a random copolymer with roughly 35% ethylene copolymer. Glycerol was obtained from Sigma–Aldrich Corporation (St. Louis, MO). Unripe coconut fiber, from northeast Brazil, was provided by Embrapa Agroindústria Tropical (Fortaleza, CE, Brazil). These coconut fibers had high lignin content (40%) and low cellulose contents (32%).

2.2. Coconut fiber treatments and mercerization

All fibers were pre-washed with large amount of distilled water and dried at 50 °C until constant weigh, prior to treatment. The mercerization process consisted of immersing coir fibers (200 g) in a 10% (w/v) sodium hydroxide aqueous solution (2 L) for 3 h at 70 °C with occasional shaking followed by washing with distilled water several times to remove any absorbed alkali (Corradini et al., 2006).

2.3. Bleaching

Coconut fibers (200 g) were added to a 2 L solution containing 320 mL (30%; w/w) hydrogen peroxide and 1 g sodium hydroxide at 85 °C and stirred for 1 h. Subsequently, the material was washed thoroughly with water and dried in an oven at 50 °C until it has reached a constant weight (Katz, 1977; Rout et al., 2001; Shukla and Pai, 2005).

2.4. Sample preparation

Blends of thermoplastic starch (50%; w/w), EVOH (30%; w/w), water (10%; w/w) and glycerol (10%; w/w) as plasticizer were melting extruded with unripe coconut fibers. The weight of fibers in the composites was 15% of total weight of polymers (starch and EVOH). The fibers were chopped in a knife mill and sieved through a 40-mesh sieve. Before extrusion, starch, EVOH and coconut fiber were premixed in a sealed ziplock bag and stored for 24 h.

This mixture was introduced into a co-rotating twin-screw extruder (Leistritz Micro 18) with six heating zones whose temperatures were set at 85, 95, 105, 115, 110, and 105 °C from feed to die. The screws have a diameter of 18 mm and the barrel has a length to diameter ratio of 30:1. A K-Tron Soder T-20 loss-in-weight feeder was used to control the solids (starch–EVOH–fiber) feed rate. A Bran + Luebbe N-P31 metering pump was used to control the liquid (glycerol–deionized water) feed rate. Following extrusion, the blended material was pelletized and injected into an injection molding machine (BOY 15S, screw diameter = 22 mm, injection time = 7 s, cooling time = 20 s, mold dimensions: 73.5 × 49 × 1.5 mm) at 150 ± 1 °C.

2.5. Tensile properties

Tensile strength (TS), tensile modulus (E) and elongation at break (ε) were determined according to ASTM D3039, under ambient conditions, using an Instron 5500R Universal Testing Machine (Instron Corp., Canton, MA). Prior to testing, samples were equilibrated at 50% relative humidity in a chamber containing saturated solutions of calcium nitrate. The testing conditions used were: cross head speed of 5 mm/min and load cell of 0.1 kN. Dumbbell samples (1.5 mm thick) were tested with a gauge length of 20 mm. The reported values are the average of at least 10 measurements.

2.6. Thermal properties

Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere. The samples were heated from room temperature to 800 °C at a heating rate of 10 °C/min and a nitrogen gas flow rate of 60 mL/min. The derivative of TGA curves (DTG) was obtained using TA analysis software.

2.7. Scanning electron microscopy (SEM) morphological characterization

Coconut fiber was mounted onto aluminum specimen stubs using double-sided adhesive carbon tabs (Ted Pella, Redding, CA). In addition to the Instron-fractured surfaces, composite materials were also fractured in liquid nitrogen to observe the interior of the unstressed composite. A composite sample was dropped directly into liquid nitrogen and fractured with a pre-chilled razor blade held in a vice-grip. The fractured pieces were picked out of the liquid nitrogen using a pre-chilled forceps and placed in a desiccator to thaw to reduce the condensation of water on the surface of the material. All composite materials, fractured by the Instron Testing Machine and in liquid nitrogen, were mounted with the fractured surfaces facing up. All specimens were coated with Gold–Palladium for 45 s in a Denton Desk II sputter coating unit (Denton Vacuum USA, Moorestown, NJ). Specimens were viewed in a Hitachi S4700 field emission scanning electron microscope (Hitachi HTA, Japan) at 2 kV.

2.8. Statistical analysis

Statistical analysis included statistical hypothesis test (Student's t-test) to verify the existence of significant differences among the data at 95% confidence level using Microsoft Office Excel 2003 software.

3. Results

The alkali treatment changed the color of the fibers from brown to dark brown and the bleaching with H_2O_2 produced yellowish brown fibers, indicating that the expected modification (removal of wax, fatty substances and lignin) might have been achieved, as demonstrated in works of other research groups (Katz, 1977; Rout et al., 2001).