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Melt processability, characterization, and antibacterial activity of compression-molded green composite sheets made of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) reinforced with coconut fibers impregnated with oregano essential oil

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ABSTRACT

New packaging materials based on green composite sheets consisting of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) and coconut fibers (CFs) were obtained by twin-screw extrusion (TSE) followed by compression molding. The effect of varying the CF weight content, *i.e.* 1, 3, 5, and 10 wt.-%, and the screw speed during melt processing, *i.e.* 75, 150, and 225 rpm, on both the aspect ratio and dispersion of the fibers was analyzed and related to the properties of the compression-molded sheets. Finally, the CFs were impregnated with oregano essential oil (OEO) by an innovative spray coating methodology and then incorporated into PHBV at the optimal processing conditions. The functionalized green composite sheets presented bacteriostatic effect against *Staphylococcus aureus* from fiber contents as low as 3 wt.-%. Therefore, the here-prepared CFs can be successfully applied as natural vehicles to entrap extracts and develop green composites of high interest in active food packaging to provide protection and shelf life extension.

1. Introduction

The use of agro-food residues for the preparation of polymer composites is gaining a significant attention due to their huge availability and low price, being at the same time a highly sustainable strategy for waste valorization. Natural fibers (NFs), particularly those obtained from plants, represent an environmentally friendly and unique choice to reinforce bioplastic matrices due to their relative high strength and stiffness (Yang, Kim, Park, Lee, & Hwang, 2006). The substitution of oil-derived polymers with bio-based polymers as the matrix component results in the term "green composites" (Zini & Scandola, 2011), which indicates that the composite as a whole, *i.e.* both matrix and reinforcement, originates from renewable resources. In this regard, the incorporation of NFs such as jute, sisal, flax, hemp, and bamboo fibers into biopolymers has been recently intensified (Bogoeva-Gaceva et al., 2007). Resultant green composites do not only offer environmental advantages over traditional polymer composites, such as reduced dependence on non-renewable energy/material sources, lower greenhouse gas and pollutant emissions, improved energy recovery, and end-of-life biodegradability of components (Joshi, Drzal, Mohanty, & Arora, 2004), but also a potential reduction of both product density and energy requirements for processing (Faruk, Bledzki, Fink, & Sain, 2014).

Polyhydroxyalkanoates (PHAs) comprise a family of biodegradable aliphatic polyesters produced by microorganisms. PHAs show the highest potential to replace polyolefins in a wide range of applications, including packaging, due to their high mechanical strength and water resistance (Bugnicourt, Cinelli, Lazzeri, & Alvarez, 2014). Among PHAs, poly(3-hydroxybutyrate) (PHB) and its copolymer with 3-hydroxyvalerate (HV), *i.e.* poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV), have so far received the greatest attention in terms of pathway characterization and industrial-scale production. The use of PHA copolymers presents certain advantages since they have a lower melting point and higher flexibility than their homopolymers, which improves melt stability and broadens their processing window (Torres-Giner, Montanes, Boronat, Quiles-Carrillo, & Balart, 2016). Furthermore, the

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introduction of comonomer units induces defects in the crystal lattice, reducing both the degree of crystallinity and crystallization rate (Kunioka, Tamaki, & Doi, 1989).

Several plant-derived NFs, such as regenerated and/or recycled cellulose, pineapple leaf fibers (PALF), wheat straw fibers, wood floor, jute fibers, flax fibers, banana, sisal, and coir fibers, hemp fibers, abaca fibers, bamboo fibers, sugarcane bagasse fibers, kenaf and lyocell fibers, wood powder, and pita (agave) fibers, have been so far studied as sustainable reinforcements to produce PHA-based composite materials (Torres-Giner, Montanes, Fombuena, Boronat, & Sanchez-Nacher, 2016). Recently, cellulose fibers from wheat straw and other by-products have been used in the European Projects ECOBIOCAP and YPACK as a cheap source of fillers to reduce the cost of a PHA matrix for packaging applications, where up to 20% of cellulose fibers were allowed in the final composition. Some previous research studies have also suggested that the incorporation of NFs can definitely strengthen the mechanical performance of both PHB and PHBV and, in some cases, also improve biodegradability (Avella et al., 2000; Barkoula, Garkhail, & Peijs, 2010; Teramoto, Urata, Ozawa, & Shibata, 2004). However, the narrow processing window and the poor melt strength of PHAs are certainly responsible for the rather small number of studies involving extruded composites with potential for being converted into packaging articles such as films and sheets (Cunha et al., 2015). The most promising PHA-based composite manufacturing techniques are extrusion and compression molding, particularly the latter, given the relatively low shear-rates and thermomechanical stresses involved.

Coconut shells represent a good example of agro-industrial non-food feedstock that is still considered as waste, for which relevant industrial new end uses are being currently pursued (Rosa et al., 2009). In particular, it is estimated that around 55 billion coconuts are produced annually worldwide. Most of their husks are abandoned, creating a waste of natural resources and a cause of environmental pollution (Gu, 2009). The coconut fibers (CFs), also referred as coir when completely ground up, are plant-derived NFs of the coconut fruit obtained from the palm tree (*Cocos nucifera* L.). The CFs are present in the mesocarp, which constitutes 30–35 wt.-% of the coconut (Tomczak, Sydenstricker, & Satyanarayana, 2007). Individual CFs show a length of 0.3–1.0 mm and a diameter of 0.01–0.02 mm, resulting in an average aspect ratio of approximately 35 (Hasan, Hoque, Mir, Saba, & Sapuan, 2015). The CFs are also characterized by a high toughness and durability as well as improved thermal stability due to their high lignin content (~40%) and relatively low cellulose content (~32%) (Rosa et al., 2010). These lignocellulosic fibers are not only abundant in tropical countries but also versatile, renewable, cheap, and biodegradable. Therefore, they could become potential substitutes for energy-intensive synthetic fibers in many applications where high strength and modulus are not required (Satyanarayana et al., 1982).

The CFs have been tested as reinforcing fillers upon the formulation of different thermoplastic materials, such as low-density polyethylene (LDPE) (Choudhury, Kumar, & Adhikari, 2007; Owolabi & Czvikovszky, 1988) and linear low-density polyethylene (LLDPE) (Choudhury et al., 2007), polypropylene (PP) (Gu, 2009; Hasan et al., 2015; Mir, Nafsin, Hasan, Hasan, & Hassan, 2013; Owolabi & Czvikovszky, 1988; Wambua, Ivens, & Verpoest, 2003), poly(vinyl chloride) (PVC) (Owolabi & Czvikovszky, 1988), starch–gluten (Corradini, Rosa, Mazzetto, Mattoso, & Agnelli, 2006), natural rubber (NR) (Geethamma, Thomas Mathew, Lakshminarayanan, & Thomas, 1998), among others. These previous studies have demonstrated that the incorporation of both untreated and chemically modified CFs into polymer formulations can represent a feasible route to produce low-cost composites with a moderate improvement of the mechanical properties. Interestingly, the CFs are exceptionally hydrophilic as they contain strongly polarized hydroxyl groups on their surface (Westerlind & Berg, 1988). CFs are thus inherently capable to adsorb and hold moisture up to 7–9 times their weight, being proposed as biosorbents for water treatment (Bhatnagar, Vilar, Botelho, & Boaventura, 2010). The outstanding capacity of the CFs to retain water and other polar components certainly opens up new attractive opportunities for potential uses as vehicle of functional and bioactive substances.

The particular chemical and morphological characteristics of the CFs can be explored to adsorb essential oils (EOs), *i.e.* aromatic and volatile oily liquids obtained from herbs and spices. Most EOs and their constituents are categorized as Generally Recognized as Safe (GRAS) by the U.S. Food and Drug Administration (López, Sánchez, Batlle, & Nerín, 2007). Among EOs, oregano essential oil (OEO), extracted from *Origanum vulgare* L., is well-recognized for its antioxidative and antimicrobial action in the food industry (Hosseini, Zandi, Rezaei, & Farahmandghavi, 2013). The biocide performance of OEO has been mainly attributed to its rich composition in phenolic compounds, namely carvacrol (up to 80%), thymol (up to 64%), and the monoterpene hydrocarbons γ-terpinene and p-cymene (both up to 52%) (Burt, 2004). The incorporation of OEO in plastic films to avoid microbial food spoilage currently represents an attractive option for packaging manufacturers. Several studies have demonstrated its efficacy in inhibiting microbial development and synthesis of microbial metabolites, including pathogenic bacteria, yeasts, and molds (Benavides et al., 2012; Hosseini, Rezaei, Zandi, & Farahmandghavi, 2015; Oussalah, Caillet, Salmiéri, Saucier, & Lacroix, 2004; Pelissari, Grossmann, Yamashita, & Pineda, 2009; Seydim & Sarikus, 2006; Zivanovic, Chi, & Draughon, 2005). Besides imparting antimicrobial characteristics to the films, OEO can change flavor, aroma, and odor. Nevertheless, similarly as with other EOs, OEO is volatile and easily evaporates and/or decomposes during processing and preparation of the antimicrobial films. Therefore, its direct exposure to heat, pressure, light or oxygen is a technological challenge.

The objective of the present study was to originally explore the inherent capacity of the CFs to adsorb and hold polar components in order to develop, by conventional melt-processing methodologies, PHBV-based green composite sheets with antimicrobial properties of interest in active packaging applications. To this end, the first part of the study was focused on optimizing the processing conditions of the green composites. In particular, it was analyzed the effect of varying both the CF weight content and the screw speed during melt processing on the aspect ratio and dispersion of the fibers in the PHBV matrices. In the second part, for the optimal processing conditions, the thermal, mechanical, and barrier properties of the compression-molded PHBV sheets were evaluated as a function of the CF content. In the last part, the CFs were impregnated with OEO by an innovative spray coating methodology, incorporated again into PHBV, and the antimicrobial properties of the green composite sheets were evaluated.

2. Experimental

2.1. Materials

Bacterial aliphatic copolyester PHBV was ENMAT™ Y1000 P, produced by Tianan Biologic Materials (Ningbo, China) and distributed by NaturePlast (Ifs, France). The product was delivered as off-white pellets packaged in plastics bags. The biopolymer resin presents a true density of 1.23 g/cm^3 and a bulk density of 0.74 g/cm^3, as determined by ISO 1183 and ISO 60, respectively. The melt flow index (MFI) is 5–10 g/10 min (190 °C, 2.16 kg), as determined by ISO 1133. The molar fraction of HV in the copolymer is 2–3%, whereas the weight-average molecular weight (M_W) is approximately 2.8×10^5 g/mol. According to the manufacturer, this resin is suitable for injection molding, thermoforming, and extrusion.

CFs were kindly supplied by Amorim Isolamentos, S.A. (Mozelos, Portugal) in the form of a liner roll. The fibrous layers were obtained from ripe coconuts, which were manually de-husked from the hard shell by driving the fruit down onto a spike to split it. 100% pure OEO was purchased from Gran Velada S.L. (Zaragoza, Spain) while food-grade paraffinic oil (grade 9578) was obtained from Quimidroga S.A.