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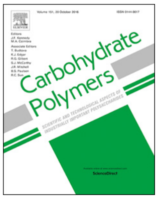

Effects of poly (3-hydroxybutyrate-co-3-hydroxyvalerate) microparticles on morphological, mechanical, thermal, and barrier properties in thermoplastic potato starch films

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ABSTRACT

Biocomposites of potato starch/poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) microparticles were prepared through the solvent casting method. Glycerol was used as a plasticizer. The effects of concentrations of PHBV microparticles as filler and glycerol on crystallinity behavior, surface morphology, dynamic mechanical properties, and thermal stability were studied. Humidity absorption and the water vapor transmission rate (WVTR) were investigated as well. Wide angle X-ray scattering (WAXS) patterns revealed that the plasticizing process occurred successfully. Scanning electron microscopy (SEM) micrographs exhibited good homogeneity of the surfaces for the biocomposites with a lower glycerol concentration. Dynamic mechanical analysis (DMA) results confirmed the reinforcing effect of PHBV microparticles inside the matrix. Thermogravimetric analysis (TGA) indicated that the presence of PHBV microparticles increased the thermal stability of the starch. Results of humidity absorption tests showed that the high hydrophilicity of the starch was reduced once the PHBV microparticles had been incorporated. Also, increasing PHBV microparticles reduced the water vapor transmission rate. However, samples with reduced glycerol content absorbed less humidity and showed a lower water vapor transmission rate.

1. Introduction

In recent decades, bio-based plastics and their related derivatives and biocomposites had been considered as potential alternatives for traditionally employed oil-based non-biodegradable plastics. This is for satisfying environmental concerns such as considerable amount of oily waste production, their contamination effects on the eco-system and also limited fossil sources. In this context, polysaccharides, proteins or biopolyesters are counted as high demanded bio-based materials that can be used as substitutive raw materials in many industries (Siracusa, Rocculi, Romani, & Dalla Rosa, 2008; Tin Sin, Rahmat Rahmat, & Abdul Rahman, 2013; Mohammadi & Ghaffari-Moghaddam, 2015, Chap. 3). Among the natural polymeric materials, starch as a promising potential candidate has been tried widely in the production of edible films, agricultural foils, compostable bags, garbage, and food packaging (BeMiller & Whistler, 2009; Xie, Pollet, Halley, & Avérous, 2013; Shi, Wang, Li, & Adhikari, 2013; Yun & Yoon, 2010). A developmental approach was attempted to incorporate starch into the food packaging industry, a major producer of oil-based plastic wastes all over the world. This is in the light of its unique combination of beneficial properties, such as inherent biocompatible and biodegradable properties, renewability, abundance, non-toxicity, low cost, versatility, purity, and processability (Fabra, Lopez-Rubio, Ambrosio-Martin, & Lagaron, 2016; Angellier, Molina-Boisseau, Dole, & Dufresne, 2006; González, Retegi, González, Eceiza, & Gabilondo, 2015). It has introduced a new window to scientific works and attempts, dominated several investigations and still seeks more studies. By the way, starch is not a thermoplastic material in its pristine state, since its granule internal section is mostly based on lipids while amino acids, enzymes, and proteins are found to be the main constituents of the external parts (Le Corre, Bras, & Dufresne, 2010). Thereby, it undergoes structural changes and modifications by addition of different types of plasticizers, normally water or water soluble plasticizers and polyols, in order to destroy its crystalline structure and convert native semicrystalline starch into thermoplastic starch. Thermoplastic starch could then simply be processed through a variety of process techniques applied to conventional synthetic polymers such as extrusion, molding, thermoforming, electrospinning, and blowing (Xie et al., 2013; Fabra, Perez-

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Masia, Talens, & Chiralt, 2011). Type and amount of plasticizer as well as other process conditions including time, temperature and shear had been demonstrated to be deeply determinative to the final performance of plasticized starch. Hence, it is important to optimize the conditions, which might lead to a flexible product with balanced properties regarding the particular specified application. Glycerol, sorbitol, ethylene glycol, xylitol, urea or maltitol had been proposed in previously reported investigations as plasticizers for various types of starch (González et al., 2015). In a combined act of plasticizer, shear, heat and/or pressure, starch molecular interactions would be destroyed and plasticized mixture of amylose and amylopectin macromolecules would be resulted. Slightly branched amylose, consisting of α-(1-4)-linked D-glucose, and branched amylopectin, comprising both α-(1-4)-linked and α-(1-6)-linked D-glucose units, are known as glycosidic polymers, from which starch is composed (Takeda, Shitaozono, & Hizukuri, 1990). It is also believed that crystalline zones are made up of a double helix formed from an arrangement of the same or different amylopectin branches (Oates, 1997; Gallant, Bouchet, & Baldwin, 1997).

Although starch presents a group of favorable properties, it should be underlined that humidity sensitivity, low mechanical efficiency and poor dimensional stability are identified as some of the most important undesired evident properties of it. Furthermore, crystallization and retrogradation phenomena during aging would diminish its performance. Some solutions to eliminate or improve these critical drawbacks and make starch to furnish more functionality, stability and efficiency might be modifications in the composition, compounding, grafting or introducing fillers and reinforcing agents (Fabra et al., 2016; Angellier et al., 2006; Le Corre et al., 2010).

Fillers such as chitin, kaolin, layer silicates, carbon nanotubes, and cellulose fibers were reported as effective fillers in different starch matrixes (Chang, Jian, Yu, & Ma, 2010; Carvalho, Curvelo, & Agnelli, 2001; Lendvai, Apostolov, & Karger-Kocsis, 2017; Cheng, Zheng, Zhao, & Ma, 2013; Curvelo, Carvalho, & Agnelli, 2001). Obviously, both matrix/filler interphase interactions and the dispersion of filler inside the matrix play an essential role in achieving enhanced properties.

One of the main challenges is to preserve the eco-friendly properties of the generated product; bio-based fillers stand out when options are considered and selected. PHBV is a natural bacterial derivative polyester with marked biodegradability and biocompatibility activities. It exhibits an acceptable broad range of adjustable processability, ductility, and crystallinity in correlation with the number of hydroxybutyrate and hydroxyvalerate units in its backbone (Chodak, 2008, Chap. 22). While it was used in several scientific reports as a bio-based matrix in polymeric biocomposites and/or blends, its application as the reinforcing agent for polymeric matrices has barely been tested (Wang et al., 2013; Yu, Qin, & Zhou, 2011; Yu et al., 2012; Yu et al., 2013).

The main objectives of the present research consisted of, firstly, analyze the role of PHBV microparticles as filler in the final properties of potato starch plasticized by glycerol and secondly, investigate the influence of glycerol concentration on the impact of PHBV microparticles in the starch. Obtained biocomposites were examined and discussed in the terms of crystalline structure, dynamic mechanical behavior, surface morphology and thermal stability as well as their humidity absorption and water vapor transmission rate. The biocomposites obtained could thus be considered for food packaging applications.

2. Experimental

2.1. Materials and processing

Potato starch with an amylose content of 20% was purchased from Roquette Feres S. A. (France). Glycerol (99.5% purity, 92.09 g mol^{-1} molar mass) was supplied by Sigma-Aldrich S. A. (Spain), and used as received. Dichloromethane solvent with 99.9% of purity and sodium dodecyl sulfate (SDS) were supplied by the Scharlau Company (Spain). PHBV microparticles were produced in our laboratory with the emulsification/solvent evaporation method (Farrag, Montero, Rico, Barral, & Bouza, 2018). In this regard, PHBV was dissolved in dichloromethane, the concentration of which was 1% w/v, using sonication. To prepare the aqueous phase, SDS was dissolved in water, the concentration of which was 15% w/v. PHBV solution was poured on the aqueous solution. The ratio between both phases was 1:2 organic to aqueous phase. The emulsion was formed by stirring for 1 h using mechanical stirrer followed by sonication in an ice bath for 3 min using a conventional sonication bath. The organic solvent was evaporated by stirring overnight at 40 °C. The particles were collected in the aqueous solution, washed with deionized water for several times and then lyophilized. Lyophilisation was performed with a Lyoquest-85 (Azbil Telstar Technologies, S. L. U., Spain) at 0.2 mbar for five days.

In order to perform the humidity absorption tests, three types of salts with analytical grade were used to provide test mediums with different relative humidity of 95% (potassium nitrate, KNO_3), 75% (sodium chloride, NaCl) and 54% (magnesium nitrate hexahydrate, Mg$(NO_3).6H_2O$). The salts were supplied from Scharlab S. L. (Spain).

Biocomposites of potato starch/PHBV microparticles with two different concentrations (3 wt.% and 6 wt.% based on total dry mass) were prepared through the solution casting method. The starch was kept at room temperature in a desiccator for one week before it was used. Then 2.1 g of starch was mixed with two different amounts of glycerol (0.90 g and 0.45 g) as plasticizer. Table 1 lists the sample codes and compositions. In the case of biocomposites, PHBV microparticles were dry mixed with starch with specific concentration as indicated above. Meanwhile stirring with a glass bar, distilled water was introduced to the solution until reach the completely homogenous dispersion with the final volume of 60 mL. Then the mixture was heated in a microwave oven with manual stirring in order to complete the plasticizing process. Then it was poured onto a Teflon® sheet lined petri dish and was left for drying in an oven for 24 h at 30 °C. For the equilibration of the water content, all films were kept in a humidity chamber with 40% RH at room temperature for 72 h prior to do any experiments. Films thicknesses were 0.10 mm–0.12 mm after the drying was complete.

2.2. Characterization techniques

Wide angle X-ray scattering (WAXS) patterns were performed using a Siemens D5000 (Siemens AG, Germany) diffractometer with a wavelength of the copper anode λ $(K_\alpha) = 1.5418$ Å. The device was operating at a voltage of 40 kV and a current of 30 mA. Scanning was performed in the range of 2θ between 5° and 40° at a rate of 0.02° min^{-1}.

Scanning electron microscopy (SEM) images were taken by a FESEM Ultra Plus microscope (ZEISS, Germany) in a very high vacuum condition. The samples had previously been sputter – coated with Iridium (Ir) using QUORUM Q150T-S Turbo – Pumped Sputter coated (QUORUM Technologies Ltd., UK).

A dynamic mechanical analyzer (DMA 7, PerkinElmer, USA) was used in order to carry out the dynamic mechanical measurements in film extension mode in the temperature range of −70 °C to 60 °C at a heating rate of 2 °C min^{-1} in inert gas medium with a flow rate of 40 mL min$^{-1.}$ Test samples had rectangular shape with dimensions of

Table 1
Sample codes and compositions.

Sample	Starch (g)	Glycerol (g)	PHBV microparticles (wt.%)
PoS/Gly0.90	2.1	0.90	0
PoS/Gly0.90/PHBV3	2.1	0.90	3
PoS/Gly0.90/PHBV6	2.1	0.90	6
PoS/Gly0.45	2.1	0.45	0
PoS/Gly0.45/PHBV3	2.1	0.45	3
PoS/Gly0.45/PHBV6	2.1	0.45	6