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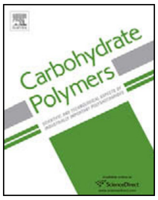

Processing and characterization of polyols plasticized-starch reinforced with microcrystalline cellulose

M. Rico[a,*], S. Rodríguez-Llamazares[b], L. Barral[a], R. Bouza[a], B. Montero[a]

[a] Grupo de Polímeros, Departamento de Física, Universidade da Coruña, Escuela Universitaria Politécnica, Campus de Ferrol, Avda. 19 de Febrero s/n, 15405 Ferrol, Spain
[b] Centro de Investigación de Polímeros Avanzados (CIPA), Edificio Laboratorio CIPA, Av. Collao 1202, Concepción, Chile

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ABSTRACT

Biocomposites suitable for short-life applications such as food packaging were prepared by melt processing and investigated. Biocomposites studied are wheat starch plasticized with two different molecular weight polyols (glycerol and sorbitol) and reinforced with various amounts of microcrystalline cellulose. The effect of the plasticizer type and the filler amount on the processing properties, the crystallization behavior and morphology developed for the materials, and the influence on thermal stability, dynamic mechanical properties and water absorption behavior were investigated. Addition of microcrystalline cellulose led to composites with good filler-matrix adhesion where the stiffness and resistance to humidity absorption were improved. The use of sorbitol as a plasticizer of starch also improved the stiffness and water uptake behavior of the material as well as its thermal stability. Biodegradable starch-based materials with a wide variety of properties can be tailored by varying the polyol plasticizer type and/or by adding microcrystalline cellulose filler.

1. Introduction

The increasing environmental pollution with petroleum-based plastics and the dependency on fossil resources have advanced research on biodegradable polymers, in particular those from renewable sources. However, the development of biopolymers with performance equal to common synthetic polymers is still an open challenge. Starch, a biopolymer of wide availability, stands out for its low cost and biodegradability. The native starch is not a true thermoplastic because of their strong inter- and intramolecular bonds, which cause the melting point is higher than the degradation temperature thereby limiting its processability and applications. Nevertheless, in the presence of a suitable plasticizer, temperature and shear, the starch granules can be fragmented, swelled and melted, and the hydrogen bonds among the starch molecules can be disrupted. As a result a thermoplastic material, known as thermoplastic starch (TPS) can be produced, capable of being processed and with similar applications as conventional thermoplastics (Castillo et al., 2013; Castaño, Rodríguez-Llamazares, Carrasco, & Bouza, 2012; Liu, Xie, Yu, Chen, & Li, 2009).

Plasticizers must be small molecules capable of penetrating the starch molecules and forming hydrogen bonds with the hydroxyl groups of starch. Water, polyols and amides are the most commonly employed plasticizers for TPS (Ma, Chang, & Yu, 2012). Plasticizer plays an important role in the processability and end properties of these materials. By varying the type of plasticizer, the characteristic of TPS can be tailored to specific needs (Ma & Yu, 2004; Mathew & Dufresne, 2002; Schmitt et al., 2015).

TPS still has significant shortcomings that limits its use in industrial applications, such as high water sensitivity and low mechanical properties, which also vary with time and humidity. The incorporation of a ecofriendly biofiller in TPS which act as reinforcement without affecting the biodegradability of the material is one approach to improve the performance of starch based materials (Chivrac, Pollet, & Avérous, 2009; Xie, Pollet, Halley, & Avérous, 2013).

Microcrystalline cellulose (MCC) has been used as ecofriendly filler and reinforcement for biopolymers. MCC is prepared by acid hydrolysis of cellulose, which removes a large part of its amorphous regions resulting in particles essentially formed by crystalline parts that are insoluble in water and resistant to reagents with a few amorphous areas (Azeredo, 2009). MCC has been used for many years in different industries like cosmetics, food stuffs or pharmaceutics because of its low cost, wide availability, renewability,

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* Corresponding author.
E-mail address: mrico@udc.es (M. Rico).

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biodegradability and safety (Das, Ray, Bandyopadhyay, & Sengupta, 2010; Ma, Chang, & Yu, 2008).

The high crystallinity of MCC gives a strong reinforcing ability due to the high modulus. The value of the longitudinal modulus for MCC is close to 150 GPa (Zhang & Zhang, 2016), which improves the mechanical properties of the resulting biocomposites. MCC has been used to reinforce various biopolymer materials such as polylactic acid, PLA (Mathew, Oksman, & Sain, 2005), poly(vinyl alcohol), PVA (Sun, Lu, Liu, Zhang, & Zhang, 2014), and hydroxy propyl methyl cellulose, HPMC (Dogan & McHugh, 2007).

The use of MCC as a reinforcement of thermoplastic starch appears particularly interesting due to the chemical similarities in the polysaccharide structure of starch and cellulose as well as the possibility of formation of hydrogen bonds between both components. It probably leads to a good adhesion of the matrix-filler interface without the addition of a coupling agent or surface modifications. The interfacial adhesion between filler and matrix is crucial to improve the properties of composites. Only a few publications have reported the use of MCC for reinforcing thermoplastic starches (Kumar & Singh, 2008; Ma et al., 2008). Most work studied the reinforcement of starch-based materials with nanofiller of cellulose as nanowhiskers (Babaee, Jonoobi, Hamzeh, & Ashori, 2015; Chang, Jian, Zheng, Yu, & Ma, 2010; García, Ribba, Dufresne, Aranguren, & Goyanes, 2009; González, Retegi, González, Eceiza, & Gabilondo, 2015). According to these studies, materials generally showed improved mechanical properties and moisture resistance with addition of nanocellulose. Such improvements could be expected to occur using MCC as reinforcement of TPS, a filler commercially available and more economical than nanocellulose. Moreover, in these studies the materials were mostly obtained by the casting method instead of conventional melt processing techniques, as it is the purpose of our article. Melt processing has considerable advantages: this method is environmentally friendly due to the absence of solvents, and it is compatible with current industrial processes, such as extrusion and injection molding.

This work focuses on the development and research of starch biocomposites reinforced with microcrystalline cellulose and plasticized with two different molecular weight polyols (glycerol, sorbitol, and a mixture of both (1:1)). Biocomposites will be prepared by melt processing. The effect of the plasticizer and the filler amount on processing properties, developed morphology, crystallization and thermal, dynamic mechanical and water resistance properties of the TPS material will be evaluated.

2. Experimental

2.1. Materials

Wheat starch with a purity of 87% and composed of 25% amylose according to the manufacturer data was kindly supplied by Roquette, with an original moisture content of 12 wt.% determined by gravimetric method.

The polyols plasticizers used were glycerol ($C_3H_8O_3$, molar mass of 92.09 $gmol^{-1}$) and D-sorbitol in solid state ($C_6H_{14}O_6$, molar mass of 182.17 $gmol^{-1}$) supplied by Sigma-Aldrich and Scharlau respectively. Microcrystalline cellulose (MCC) with a particle size of 10 – 100 μm, determined by light scattering particle size analyzer (Saturn Digisizer II from Micromeritics, Georgia, USA), was supplied by Sigma-Aldrich and used as the reinforcement.

2.2. Preparation of TPS and TPS/MCC composites

Mixtures of wheat starch, plasticizer and microcrystalline cellulose particles were prepared maintaining the plasticizer/starch ratio at 40:60 in all mixtures. Three different plasticizers were examined (glycerol, sorbitol and sorbitol:glycerol (1:1) mixture). The MCC filler contents were 0, 5 and 10 wt.%. All amounts were based on the dry weight. The samples were coded specifying the type of plasticizer and wt.% of MCC filler, as shown in Table 1.

Neat TPS and TPS/MCC composites were prepared by melt processing using an internal mixer (Brabender W50-E, 3 zones PL-type 2000-3, Duisburg, Germany). The respective components of the samples were first premixed at room temperature and then introduced into internal mixer. The materials were processed at a temperature of 120 °C with a rotor speed of 60 rpm for 10 min. The processed samples were compression-molded by using a hot press (IQAP LAP PL-15, Cataluña, Spain) at 120 °C and 100 bar of pressure. From the molded sheets, pieces were cut for the different tests.

2.3. Characterization of TPS and TPS/MCC composites

2.3.1. Scanning electron microscopy (SEM)

Morphologies of the fracture surfaces of neat TPS and TPS/MCC composites were observed in a scanning electron microscope (JEOL-JSM 6400, Tokyo, Japan) operated at 20 kV. Prior to analysis, samples were cooled in liquid nitrogen and fractured. The fracture surfaces were coated with a gold thin film.

2.3.2. X-ray diffraction (XRD)

The crystalline structures of neat TPS and TPS/MCC composites as well as native wheat starch and cellulose microcrystalline were analyzed by X-ray diffraction (XRD) using a Siemens D5000 diffractometer (Karlsruhe, Germany). The equipment operated at a current of 30 mA and voltage of 40 kV. The wavelength of the copper anode is λ $(K\alpha) = 1.54$ Å. Scans were performed from $2\theta = 1.15°$ to 40° at scanning step rate of 0.005° in step time of 4s. Crystallinity index of neat TPS was calculated as the ratio between the crystalline area under the absorption peaks and the total diffractogram area. The amorphous region was estimated using an iterative smoothing curve (Frost, Kaminski, Kirwan, Lascaris, & Shanks, 2009).

2.3.3. Thermal stability

Thermal stability of TPS materials was evaluated by using a thermogravimetric analyzer Perkin Elmer TGA 7 (Massachusetts, USA) in a temperature range between 50 °C and 800 °C at a heating rate of 10 $°C.min^{-1}$ under inert argon atmosphere.

2.3.4. Dynamic mechanical properties

Dynamic mechanical behavior of TPS materials was determined by means of a Perkin Elmer DMA7 (Massachusetts, USA) device using a three-point bending geometry. Specimens with dimensions of approximately $20 \times 5 \times 3$ mm^3 were cut from molded parts and tested. The dynamic storage modulus (E') and loss factor ($tan\ \delta$) were measured as a function of temperature from −70 °C to 80 °C with a constant heating rate of 5 °C min^{-1} and a frequency of 1 Hz.

2.3.5. Water absorption

Water absorption tests were conducted to all materials on samples with dimensions of $8 \times 8 \times 3$ mm^3. The rate of water absorption depends largely on the surface/volume ratio of the piece, and therefore, it is necessary that dimensions of all samples to be tested are identical.

Prior to the water absorption measurements, the samples were dried at 70 °C during 72 h, cooled and then weighted. Immediately after, the samples were placed in hermetic containers conditioned at 20 °C ± 2 °C and four different relative humidity (RH) environments. Saturated solutions of potassium hydroxide (KOH), magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$), sodium chloride (NaCl) and potassium nitrate (KNO3) were used to create environments of 9%, 33%, 75% and 95% RH respectively, as is stipulated in UNE-EN ISO 1998:483. At specific time intervals, samples were