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Research paper

Humidity-activated shape memory effect on plasticized starch-based biomaterials

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ABSTRACT

Humidity-activated shape memory behavior of plasticized starch-based films reinforced with the innovative combination of starch nanocrystals (SNCs) and catechin as antioxidant were studied. In a previous work, we reported the processing of gelatinized starch-based films filled with SNCs and catechin as antioxidant agent, and we observed that this novel combination leads to starch-based film with enhanced thermal and mechanical performance. In this work, the humidity-activated shape memory behavior of the previous developed starch-based films was characterized. The moisture loss as well as the moisture absorption were studied since they are essential parameters in humidity-activated shape memory polymers to fix the temporary shape and to recover the original shape, respectively. Therefore, the effect of the incorporation of SNCs and catechin on the humidity-activated shape memory properties of plasticized starch was also studied. Moreover, the effectiveness of catechin to increase the polymer stability under oxidative atmosphere and the thermo-mechanical relaxation of all the starch-based materials were studied. The combination of plasticized starch matrix loaded with both, SNCs and catechin, leads to a multifunctional starch-based films with increased hydrophilicity and with excellent humidity-activated shape memory behavior with interest for potential biomedical applications.

1. Introduction

Shape memory polymers (SMPs) have gained considerable interest during the last years in both academics and industrial sector, focusing the attention on their potential application in the biomedical sector (Peponi, Navarro-Baena, & Kenny, 2014; Yahia, 2015). SMPs have the capacity to memorize their original shape after being deformed in a temporary shape under the application of external stimulus, such as temperature, humidity, pH, light, etc. (Olalla, Sessini, Torres, & Peponi, 2016). These shape changes are achieved throughout the "programming" and the "recovery" stages, regulated by the external stimulus (Peponi, Arrieta, Mujica-Garcia, & López, 2016). In the "programming" stage, the material is deformed and fixed in a "temporary shape". Then, upon the application of an external stimulus, the material recovers its initial shape throughout the "recovery" stage (Chan et al., 2016). One of the most used stimuli is the temperature, therefore, thermally-activated SMPs have to be heated above their characteristic transition temperature (T_{trans}) to induce their shape change (Peponi et al., 2016).

SMPs can be applied in several fields including biomedical applications. However, when SMPs are used for biomedical applications, two key points have to be considered. From one hand, the materials used need to respond to biocompatibility, non-toxicity, biodegradability, sterilizability and specific mechanical properties (Ward Small, Singhal, Wilson, & Maitland, 2010). As example, biodegradable polymeric materials are being investigated in developing medical devices such as temporary biological wound dressing materials, temporary prostheses, three-dimensional porous structures as scaffolds for tissue engineering and for drug delivery in pharmacological applications (Sastry, 2012; Nair & Laurencin, 2007). From the other hand, it is necessary to use a stimulus compatible with the human body (Chan et al., 2016; Lendlein et al., 2010). So, when working with thermally-activated SMPs for biomedical applications, a T_{trans} close to body temperature is required (Lendlein et al., 2010). In order to design SMPs with T_{trans} close to body temperature it is possible playing with their chemical composition or by adding nanofillers able to modify their thermal response (Behrens & Appel, 2016). However, moisture-activation of SMPs can be a good alternative as stimuli-responsive materials for biomedical applications (Chen, Hu, Yuen, & Chan, 2009; Sessini, Raquez et al., 2016). Further investigations showed that the hydrogen bonding is the key player for the humidity activation as well as water absorbed in the polymer plays a main role in the shape recovery process (Zhang, Wang, Zhong, & Du, 2009). Therefore, in order to develop humidity-activated

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SMPs it is possible to use polymers with functional groups able to be involved in hydrogen bonding with water molecules or it is possible to use hydrophilic components.

Thus considering all these properties, biodegradability, hydrophilicity and biocompatibility, starch can be considered as an excellent material for the design of humidity-responsive SMPs for biomedical application. Starch, in fact, is a low cost polysaccharide, abundantly available in nature and one of the cheapest biodegradable polymers. It is produced by agricultural plants in the form of granules, which are hydrophilic (Raquez et al., 2008). Starch is mainly extracted from potatoes, corn, wheat, rice, etc. It is composed of amylose (poly-α-1,4-D-glucopyranoside), a linear polymer and amylopectin (poly-α-1,4-D-glucopyranoside and α-1,6-D-glucopyranoside), a branched polymer (Lourdin et al., 2015). To extend the starch functionalities, several plants have been modified in their starch biosynthesis pathway to modulate the amount of amylose of starch granules (Firouzabadi, F. N. et al., 2007). In other cases starches are modified in their waxy form, for example characterized by a rich content of amylopectin (> 99%) to be used for the synthesis of starch nanocrystals, SNCs. (Bemiller, 1997). Therefore, starch can be used as polymer matrix in form of thermoplastic starch (TPS) by gelatinization of native starch (Averous, 2004) as well as nanofillers in form of starch nanocrystals, SNCs (Angellier, Choisnard, Molina-Boisseau, Ozil, & Dufresne, 2004). The glass transition temperature (T_g) of starch is strongly affected by the relative humidity (RH) at which it is stored showing either a glass-like rigid and fragile mechanical behavior, or a rubber-like behavior (Lourdin, Coignard, Bizot, & Colonna, 1997). However, the brittleness of starches is frequently overcome by the addition of plasticizers to get the flexibility required for film applications (Jiménez, Fabra, Talens, & Chiralt, 2012). Among them, glycerol is a natural plasticizer widely used to develop TPS by reducing intra and intermolecular hydrogen bonds (Arrieta, Peltzer, del Carmen Garrigós, & Jiménez, 2013; Averous, 2004; Jiménez et al., 2012). In the literature there are reports of different biomedical applications of biodegradable starch-based films as SMPs, such as shape-memory resorbable materials (Beilvert et al., 2014), temporary biological wound dressing materials (Arockianathan et al., 2012a, 2012b), scaffolds for bone tissue engineering applications (Martins et al., 2012) and drug delivery systems (Schmitt et al., 2015). However, preliminary studies on shape memory effects on starch-based materials are presented by Chaunier et al. (Chaunier & Lourdin, 2009) in 2009 reporting an example of dual-shape capability of potato starch and by Véchambre et al. (Véchambre, Chaunier, & Lourdin, 2010) in 2010, in which they studied the shape memory response of extruded potato starch triggered by humidity.

In order to improve its properties starch can be modified by adding nanofillers obtaining nanocomposites. In general, the addition of nanofillers to a polymer matrix increases its mechanical strength and stiffness and sometimes can generate functional properties, originating from the synergetic effect between both components (Peponi, Puglia, Torre, Valentini, & Kenny, 2014). Among bionanofillers, special attention has been paid to SNCs (Lin, Huang, Chang, Anderson, & Yu, 2011).

Green tea polyphenols, in particularly catechin (Cat), have gain interest owing to their multiple biological effects due to their strong antioxidant capacity (Castro López et al., 2012). Catechin is also interesting from a processing point of view since their antioxidant activity protects the polymer matrices during thermal and thermomechanical processing (Arrieta, Castro-López et al., 2014; Arrieta, Peltzer et al., 2014). Moreover, catechin can be used to improve shape memory response of polymeric matrices (Arrieta, Sessini, & Peponi, 2017).

In our previous work (Sessini, Arrieta, Kenny, & Peponi, 2016) we reported the processing of gelatinized starch-based films filled with SNCs and catechin as antioxidant agent for edible films. It was observed that for film manufacturing the inherent brittleness of starch can be overcome by the addition of 35 wt% of glycerol as plasticizer (S-Gly35). Additionally, we observed that the novel combination of plasticized starch compounded with both SNCs and Cat leads to materials with enhanced thermal and mechanical performance.

Based on these previous results, the main objective of the present work is to design high performance humidity-activated shape memory starch-based films, for potential biomedical applications. With this purpose, the humidity-activated shape memory behavior was characterized for neat starch plasticized with 35% of glycerol and its filled counterparts. In order to know the parameters to fix the temporary shape and to recover the original shape, the moisture loss as well as the moisture absorption was studied evaluating also the effect of the incorporation of both SNCs and catechin on the humidity-activated shape memory properties of plasticized starch-based films.

2. Materials and methods

2.1. Materials

Native potato starch (moisture content of 12% and amylose content of 18–21%) was kindly supplied by Novamont. Glycerol and catechin dehydrate were purchased from Panreac Quimica (PRS) and Sigma-Aldrich, respectively. Waxy maize starch (N200) used to synthesize the SNCs, was supplied by Roquette Laisa (Spain). Sulfuric acid (H_2SO_4) was purchased from Sigma-Aldrich. SNCs were synthesized by acid hydrolysis as reported in our previous work (Sessini, Raquez et al., 2016). In brief, waxy maize starch was dispersed in an aqueous solution of H_2SO_4 and heated at 40 °C under continuous mechanical stirring (100 rpm) for 5 days. The final suspensions were washed by successive centrifugations in distilled water (10,000 rpm for 10 min) until reaching neutral pH and then, it was filtered and stored at 4 °C.

2.2. Film preparation

The starch-based films were obtained by gelatinization of starch/water/glycerol dispersion (Sessini, Raquez et al., 2016). Briefly, TPS was successfully obtained by gelatinization of an aqueous dispersion of 1 wt% of potato starch and 35 wt% of glycerol relative to the mass of starch. The dispersion was gelatinized at 80 °C during 15 min under continuous stirring. Starch solution, was cast over polystyrene petri dish in a ventilated oven at 35 °C for 24 h to obtain films with a thickness of about 100 μm. The obtained unfilled film was named S-Gly35. The polymeric matrix was reinforced by adding 1 wt% (relative to the mass of starch) of catechin (S-Gly35-Cat) and SNCs (S-Gly35-SNC), respectively. Moreover, the synergetic effect of both catechin and SNCs was evaluated in the starch-based films by adding together catechin and SNCs, both at 1 wt% relative to the mass of starch, obtaining the sample named S-Gly35-Cat-SNC.

2.3. Characterization techniques

Before characterization, all the starch-based films were stored for one week at 50% RH.

The SNCs dispersion into the polymer matrix was studied by Field Emission Scanning Electron Microscope (FE-SEM, Hitachi S8000). The cryo-fracture surfaces of the starch-based films filled with SNCs were observed. The films were previously frozen using liquid N_2 and then cryo-fractured. All the samples were chrome coated by an automatic sputter coater Quorum Tech Q 150T ES previously to be observed by FE-SEM.

Dynamic Mechanical Thermal Analysis (DMTA) of the samples was carried out using a DMA Q800 from TA Instrument in film tension mode with an amplitude of 5 μm, a frequency of 1 Hz, a force track of 125% and a heating rate of 2 °C min^{-1}. The samples were cut from casted films into rectangular specimens of approximately 20 mm x 6 mm x 0.10 mm.

Surface wettability of the starch-based films was studied through static water contact angle (WCA) measurements using a KSV Theta goniometer. The volume of the droplets was controlled to be about