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Effect of the film-processing conditions, relative humidity and ageing on wheat gluten films coated with electrospun polyhydryalkanoate

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ABSTRACT

In this research, the influence of the processing conditions, the electrospun coating thickness and ageing on the water vapour and oxygen barrier properties and on the mechanical, morphological and optical properties of the materials have been evaluated. The effect of relative humidity on the mechanical properties was also evaluated. When coating the thermoplastic Wheat gluten film with annealed polyhydroxybutyrate electrospun fibres, water permeability dropped up to ca. 88%. Oxygen permeability was also improved and both water vapour and oxygen barrier properties of the multilayer systems remained over the storage time. The applied outer layers seemed to improve the mechanical performance (increasing the Elastic Modulus and Tensile Strength values) of the plasticized WG film. An increase in water content caused a decrease in Tensile Strength and Elastic Modulus values but an increase in EAB of the multilayer WG film due to the plasticization effect of water. The stretchability of these multilayer systems was greatly affected by the thickness of the outer layer and by the relative humidity although no significant variations were observed due to storage time. The appearance of the thermoformed wheat gluten films was brown and translucent and it was slightly diminished over the storage time. This work has demonstrated that it is possible to produce water resistant thermoplastic wheat gluten films by combining an inner layer based on wheat gluten with electrospun PHB outer layers. The use of electrospinning was crucial to guarantee a good adhesion between layers which was, in fact, a key factor for the improved barrier properties attained.

1. Introduction

There is a growing concern around the world over non-degradable petroleum-derived plastics. The renewable and biodegradable nature of agricultural origin polymers renders them appealing for innovative uses in the field of packaging. Among proteins, wheat gluten (WG) is a by-product of the wheat starch that is commercially available at low cost and displays unique viscoelastic properties and low water solubility (Kayserilioglu, Bakir, Yilmaz, & Akkas, 2003; Shewry & Tatham, 1997). WG-based films have been found to be very effective oxygen barriers at low relative humidity conditions.

WG has been widely used to develop films and other bioplastics (Dicharry et al., 2006; Gallestedt, Mattozzi, Johansson, & Hedenqvist, 2004; Zárate-Ramírez, Martínez, Romero, Partal, & Guerrero, 2011). Although WG films are mostly made using the dissolution method (solution casting), films developed by compression – moulding have better properties than solution cast films. Wheat gluten is inherently non-thermoplastic and, therefore, plasticizers, chemical modifications or blending with thermoplastic polymers have been used to develop thermoplastics from wheat gluten (Gallestedt et al., 2004; Sun et al., 2008a, 2008b, Chen, Reddy, Wu, & Yang, 2012). A wide range of conditions have been used to obtain thermoplastics from wheat proteins with varying properties. Since wheat gluten has poor thermoplasticity, plasticizers such as glycerol or chemical modifications are inevitably used to develop thermoplastics from wheat proteins. However, plasticizers such as glycerol, commonly used to plasticize wheat gluten are hydrophilic, absorb large amounts of water and, thus, substantially decrease the mechanical properties and also reduce the water resistance of the thermoplastics (Gallestedt et al., 2004; Kunanopparat, Menut, Morel, & Guilbert, 2008; Pommet, Redl, Guilbert, & Morel, 2005). . Thus, as discussed above, it is necessary to use plasticizers to develop thermoplastics from WG but WG thermoplastics containing plasticizers have poor mechanical properties. In order to overcome this issue and to improve the water resistance of the wheat protein thermoplastics containing plasticizers, different strategies have to be carried out. A strategy to

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avoid the moisture uptake of these hydrophilic materials is to develop multilayer structures in which the hydrophilic WG film is sandwiched between hydrophobic biodegradable materials such as biopolyesters. Nevertheless, the low compatibility of the thermoplastic WG film with hydrophobic materials prevented the use of casting methods to develop multilayer systems or to combine the thermoplastic WG films with hydrophobic layers through compression moulding, since adhesion between the different layers was very poor and partial or even a complete delamination between the different layers took place (Martínez-Sanz, Lopez-Rubio, & Lagaron, 2013). In a previous work, an innovative route based on the electrospinning processing has been recently developed (Fabra, López-Rubio, & Lagaron, 2014a). The use of electrospinning was crucial to attain a good adhesion between the hydrophilic natural polymers such as proteins and the hydrophobic biopolyester layers (both immiscible). Electrospinning makes use of high voltage electric fields to produce electrically charged jets from viscoelastic polymer solutions which on drying, by the evaporation of the solvent, produce ultrathin polymeric structures. To produce fibres, a large number of highly specific conditions including solution properties (polymer concentration, viscosity, electrical conductivity, surface tension and solvent volatility), environmental conditions (temperature, air velocity and humidity) and process conditions (voltage, spinning distance and flow rate) must be met.

On the other hand, it is well-known that packaging materials must have time stable properties in order to protect the food stuff and give a long shelf-life. However, biopolymers, including WG films, suffer from ageing. So, one of the challenges for the successful use of biodegradable polymer products is to achieve controlled lifetime. Products must remain stable and function properly during storage and intended use, but after that they should biodegrade efficiently. Only a limited amount of studies have been reported on this topic despite that it is perhaps the most important problem that has to be solved before WG films can be of commercial interest for food packaging applications (Mojumdar, Moresoli, Simon, & Legge, 2011).

In the previous study, Fabra et al., 2014a reported the effect of the PHA nature on the barrier and tensile properties of thermoplastic wheat gluten films prepared with 28 %-wt. of glycerol. In this work, water resistant WG multilayer films with improved mechanical and barrier properties have been developed by electrospinning polyhydroxyalkanoates (PHAs) fibres onto both sides of a thermoplastic WG film. In the present work, the effect of ageing and relative humidity on the physicochemical (barrier and water sorption, tensile and optical) properties and thus, on the stability of the thermoplastic wheat gluten films containing higher amount of glycerol have been evaluated.

Thus, the aim of this work was, on the one hand, to develop thermoplastic WG films with good strength and water stability using PHAs fibre coatings as outer layers and, on the other hand, to evaluate the stability of the developed multilayer systems over a three months period.

2. Materials and methods

2.1. Materials

Polyhydroxybutyrate (PHB) pellets were supplied by Biomer (Krailling, Germany). PHB was reported to have 0–40 wt% of plasticizers and an unreported amount of non-toxic nucleating agents to improve melt processing (Hänggi, 2011). Wheat gluten (WG) was purchased from Sigma–Aldrich (Madrid, Spain). Glycerol (Panreac Quimica, S.A. Castellar Del Vallés, Barcelona, Spain) was used as plasticizer. 2,2,2-Trifuoroethanol (TFE) with 99% purity were purchased from Sigma–Aldrich (Spain) and it was used as a solvent for the PHB. All products were used as received without further purification.

2.2. Preparation of films

2.2.1. Preparation of plasticized wheat gluten films

Plasticized wheat gluten films were obtained following the methodology previously described by Chen et al. (2012). Wheat gluten was thoroughly mixed with 35% (w/w) glycerol and the mixture was then spread evenly on Teflon and placed in a compression mould (Carver 4122, USA) at a pressure of 40,000 lbs. Preliminary trials were firstly conducted to select the time and temperature for compression-moulding and it was found that a compression time of 12 min at 100 °C provided optimum handling properties.

2.2.2. Preparation of wheat gluten films coated with electrospun polyhydryalkanoate

Thermoplastic WG films were coated with PHA mats produced by means of the electrospinning technique. PHB solutions in 2,2,2-trifluorethanol having a total solids content of 10 wt% were used to generate the electrospun fibres. PHB fibre mats were directly electrospun onto both sides of the plasticized wheat films by means of a Fluidnatek® electrospinning pilot plant equipment from Bioinicia S.L. (Valencia, Spain) equipped with a variable high-voltage 0–60 kV power supply. PHB solutions were electrospun under a steady flow-rate using a motorized high throughput multinozzle injector, scanning vertically towards a metallic grid used as collector, in which the thermoplastic WG film was attached. The distance between the needle and the collector was 20 cm and experiments were carried out at ambient temperature. The voltage of the collector and injector were set at 24 kV and 19 kV, respectively.

Three different deposition times (2, 5 or 10 min for each film side) were evaluated in the thermoplastic WG film to see how deposition time affected physical properties.

Electrospun PHB coatings presented an opaque and whitish appearance. With the aim of obtaining transparent and continuous pellicles, an additional heating step was applied. Coated films were placed in between hot plates at 145 °C or 160 °C during 1 min (without pressing) to melt and homogenize the PHB phase. Both temperatures were chosen according to the transparency of the multilayer and the melting point of the PHB. As it has been previously reported, 145 °C was the minimum temperature necessary to turn the PHB fibres transparent and 160 °C was near to the melting point of the PHB which greatly contribute to obtain a more uniform and homogeneous layer (Fabra et al., 2014a).

2.2.3. Film conditioning and storage

Before the mechanical test, samples were equilibrated in desiccators at two different relative humidity conditions (0 and 75%) at 25 °C by using silica gel and an oversaturated solution of NaCl, respectively, for one week (non-stored samples) when the first series of analyses were carried out and for three months (stored samples) in order to perform the second series of analyses. For barrier, contact angle, optical and microstructural analysis, samples were stored at 0% RH.

2.3. Characterization of films

2.3.1. Scanning Electron Microscopy (SEM)

SEM was conducted on a Hitachi microscope (Hitachi S-4800) at an accelerating voltage of 5 kV and a working distance of 12–16 mm. Thermoplastic WG films as well as the nanostructured multilayer systems were cryo-fractured after immersion in liquid