Journal of Colloid and Interface Science 483 (2016) 84–92

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Regular Article

Tailoring barrier properties of thermoplastic corn starch-based films (TPCS) by means of a multilayer design

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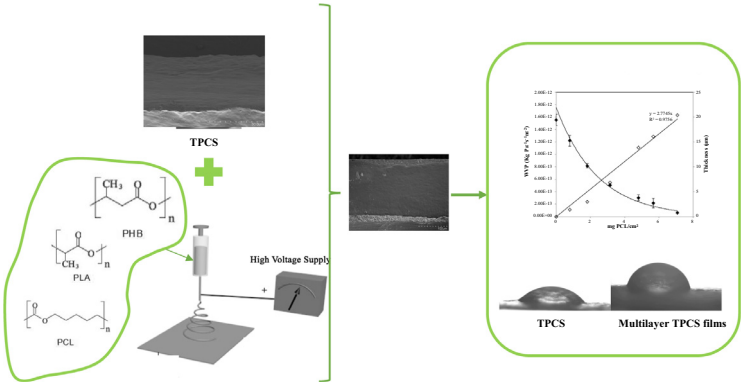
GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 May 2016
Revised 8 August 2016
Accepted 10 August 2016
Available online 11 August 2016

Keywords:
TPCS
Electrospinning
Multilayer
Barrier properties
Biopolyesters

ABSTRACT

This work compares the effect of adding different biopolyester electrospun coatings made of polycaprolactone (PCL), polylactic acid (PLA) and polyhydroxybutyrate (PHB) on oxygen and water vapour barrier properties of a thermoplastic corn starch (TPCS) film. The morphology of the developed multilayer structures was also examined by Scanning Electron Microscopy (SEM). Results showed a positive linear relationship between the amount of the electrospun coatings deposited onto both sides of the TPCS film and the thickness of the coating. Interestingly, the addition of electrospun biopolyester coatings led to an exponential oxygen and water vapour permeability drop as the amount of the electrospun coating increased. This study demonstrated the versatility of the technology here proposed to tailor the barrier properties of food packaging materials according to the final intended use.

1. Introduction

The use of biopolymers has received increased attention in the last decades as potential substitutes for conventional polymers in a broad range of applications. Among biopolymers, polysaccharides, like starch, are interesting renewable resources that have different applications. Indeed, the introduction of starch in the plastic sector has been motivated by its low cost and biodegradability and by the fact that it is available in large quantities [30]. However, starch cannot be processed through conventional plastic equipment without further modification because its degradation begins at a temperature lower than its melting point [4]. By the addition of water or other plasticizers such as glycerol or sorbitol, the native

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http://dx.doi.org/10.1016/j.jcis.2016.08.021
0021-9797/

crystalline structure of starch is irreversibly disrupted (the so-called gelatinization phenomenon) and thus, the granular starch is transformed into a thermoplastic starch (TPS) which vary from a soft material (high plasticizer level) to a brittle material (low plasticizer level) depending on the moisture and plasticizer level [19].

The barrier to water vapour and oxygen are two essential properties to consider in starch-based materials because oxygen and water molecules can deteriorate food properties. Indeed, one of the main problems of starch-based films is their high water sensitivity arising from their hydrophilic character, which leads to strong plasticization [31]. This effect negatively affects some characteristics such as the oxygen barrier properties, which are excellent at low hydration levels and plasticizer content but decrease as water sorption increases [20,31]. Therefore, many research works have focused on improving starch performance either by blending it with other moisture resistant biodegradable polymers such as polylactic acid (PLA) and polycaprolactone (PCL) [1,5,8,21,23] or through the addition of dispersed nanoreinforcing agents to generate nanobiocomposites [12]. However, from an industrial implementation point of view, it is important to highlight that complex multilayer structures are suggested as an alternative to improve the performance of biopolymers, being the most efficient form to constitute barrier materials [14,15]. Whilst this multilayer design has been widely used for synthetic materials, it has been scarcely developed for biodegradable food packaging systems due to technological problems associated to the scaling-up process and multilayer assembly. Nowadays, this methodology is being successfully exploited by means of electrohydrodynamic processing, also known as electrospinning, to improve the barrier and functional performance of biodegradable polymers thermodynamically immiscible with the additional advantages of forming electrospun coatings [15] or bioadhesives [16,17] which show excellent adhesion between layers, avoiding the use of synthetic adhesives.

Taking advantage of the methodology already described, this paper reports, for the first time, a comparative study in which the effect of different amounts of electrospun biopolyesters coatings (polylactic acid –PLA-, polycaprolactone –PCL- and polyhydroxybutyrate –PHB-) has been analyzed and compared in terms of barrier efficiency.

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 [18]. The semicrystalline polylactide (PLA) used was a film extrusion grade produced by Natureworks (with a D-isomer content of approximately 2%). The molecular weight had a number-average molecular weight (Mn) of ca. 130,000 g/mol, and the weight average molecular weight (Mw) was ca. 150,000 g/mol as reported by the manufacturer. The polycaprolactone (PCL) grade FB100 was supplied by Solvay Chemicals (Belgium).

Corn starch (CS) was kindly supplied by Roquette (Roquette Laisa España, Benifaio, Spain) and glycerol (Panreac Quimica, S.A. Castellar Del Vallés, Barcelona, Spain) was used as plasticizer.

N,N-dimethylformamide (DMF) with 99% purity and trichloromethane (99% purity) were purchased from Panreac Quimica S.A. (Barcelona, Spain). 2,2,2-Trifuoroethanol (TFE) with 99% purity were purchased from Sigma-Aldrich (Spain). All products were used as received without further purification.

2.2. Preparation of films

2.2.1. Preparation of thermoplastic corn starch films (TPCS)

Corn starch and glycerol, as plasticizer, were dispersed in water using a polymer:glycerol:water ratio of 1:0.3:0.5 (w/w/w) and the dispersion was melt-mixed in a Brabender Plastograph internal mixer at 130 °C and 60 rpm for 4 min. The mixture was then spread evenly on Teflon and placed in a compression mould (Carver 4122, USA) at a pressure of 30,000 lbs and 130 °C for 5 min.

2.2.2. Preparation of multilayers TPCS systems

TPCS films were coated with PHB, PLA or PCL 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. The PLA and PCL electrospinning solutions were prepared by dissolving the required amount of the biopolymer, under magnetic stirring, in a solvent prepared with a mixture of trichloromethane (TCM):N,N-dimethylformamide (DMF) in order to reach a 5 or 12% in weight (wt%) of PLA and PCL, respectively. The TCM:DMF ratio used for PLA and PCL was 85:15 and 65:35, respectively.

PHB, PLA or PCL fibre mats were directly electrospun onto both sides of the TPCS 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. Biopolyester 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 neat TPCS film was attached. The distance between the needle and the collector was 20, 24 and 31 cm for PHB, PLA and PCL, respectively, and the experiments were carried out at ambient temperature. The voltage of the collector and injector were set at 24 kV and 19 kV, respectively.

Different deposition times (0, 2, 10, 20, 40, 60 and 90 min), were evaluated in the TPCS film to see how deposition time affected barrier properties. The total amount of electrospun material ($mg\ cm^{-1}$) was estimated by weighing the TPCS film before and after collection of the electrospun material.

With the aim of obtaining transparent and continuous outer layers based on PHB, PLA or PCL, an additional heating step was applied. Coated TPCS films were placed between hot plates at 160 °C to melt and homogenize the PHB or PLA phase and 60 °C to melt the PCL layer.

2.3. Characterization of films

2.3.1. Scanning Electron Microscopy (SEM)

A Hitachi S-4800 microscope (Hitachi High Technology Corp., Tokyo, Japan) was used to observe the morphology of films cross-sections. Cross-sections of the samples were prepared by cryo-fracture of the films using liquid N_2. The samples were mounted on bevel sample holders with double-sided adhesive tape, and sputtered with Au/Pd under vacuum. Samples were observed using an accelerating voltage of 10 kV and a working distance of 12–16 mm. Layer thicknesses were measured by means of the Adobe Photoshop CS3 extended software from the SEM micrographs in their original magnification.

2.3.2. Barrier properties

2.3.2.1. Water Vapour Permeability (WVP). The WVP of TPCS and multilayer structures was determined by using the ASTM [3] gravimetric method using Payne permeability cups (Elcometer SPRL, Hermelle/s Argenteau, Belgium) of 3.5 cm diameter. For each type of samples, measurements were done in triplicate and water vapour permeability was carried out at 25 °C and 0–100% relative humidity gradient, which was generated by using dry silica gel