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Active pseudo-multilayered films from polycaprolactone and starch based matrix for food-packaging applications

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ABSTRACT

Within the recent years, researches dealing with the applications of intelligent and active packaging for food applications have taken a great importance. Intelligent packaging-systems are used to inform and advertise the consumers by giving information on the food quality during transport and storage. Active packaging-systems have also acquired new functions as antimicrobials and/or oxygen or water scavenging activities by incorporating active molecules. The aim of these packaging is to maintain or extend the quality and shelf-life of the food element. The application of this strategy, concerning bio-sourced packaging, is recent. In this work, polycaprolactones were blended in a starch based matrix to improve the suitability for contact with food of the packaging and to obtain a modulated water-scavenger effect. The migration of PCL in the pseudo-multilayered and multilayered films was investigated by FT-IR. Moreover, chitosan was included in the formulation to reduce the bacterial adhesion potential on the packaging.

1. Introduction

To preserve the environment and reduce the pollution due to oil derived plastics, researches focused on renewable resources to perform biodegradable materials [1]. These materials have a great diversity of industrial applications including packaging [2], agricultural films or construction. Among renewable resources, starch is one of the most important polysaccharides obtained from plants. Biodegradable thermoplastic films can be tailored from starch with additives such as plasticizers to improve the processability by conventional plastic-forming equipments. Some authors have already published on this subject [3,4] and different plasticizers have been considered. The more usually used plasticizers include water [5], glycerol [6] or sorbitol [7].

However in all cases, a purification step is necessary to obtain starch from plants, and this step increases the time and cost required to develop bio-based materials. In this work, starch based blends were compared to thermoplastic materials produced from flour without any treatment. To avoid problems of food applications, a by-product flour, containing a poor protein ratio (<7%), was chosen. This flour obtained from wheat is generally composed by a large part of starch with few traces of lipids and minerals.

Within the last years, different technologies have been used to improve the quality and to extend the shelf-life of food products. Active packaging is one of these technologies and consists of active molecules included into the packaging which could interact with the food or its environment by several mechanisms [8]. Active agents are

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scavengers for absorption of oxygen [9,10], ethylene [11,12], carbon dioxide [9], water [13], odors, etc. or even antimicrobial compounds [14,15] or anti-oxidant particles [16].

In order to adapt the properties of a starch based matrix, it is possible to blend it with another polymer in order to increase the mechanical properties, adjust the transport properties and/or improve the suitability for contact with food of the film. Plasticized starch can be mixed with polyamide to reduce water absorption [17] and/or to increase the mechanical properties of the film [18]. To improve their mechanical properties, thermoplasticized starches (TPSs) are blended with polycaprolactone (PCL) supplemented [19] or not with polyethylene [20,21].

Several authors have studied blends between thermoplasticized starch and biopolyesters. Martin and Avérous [22] had obtained a reduction of the water sorption with an addition of polylactic acid (PLA) in a TPS matrix but tensile strain and impact properties were reduced. These drawbacks were attributed to a low miscibility between TPS and PLA and caused by the phase separation. In another case, Avérous and Fringant [23] reduced the water sorption of TPS by an addition of polybutylene succinate adipate (PBSA) or polybutylene adipate-co-terephtalate (PBAT). The elastic modulus of these blends was in accordance with theoretical modulus calculated by the law of mixtures, but it is not the case about strains at break of blends which could be lower than strain at break of pure polymers. Tensile strain was decreased with an addition of PBSA whereas it was increased with an addition of PBAT. Usually, biopolyester incorporation in a TPS matrix induced an improvement of water barrier properties and the blends stay biodegradable. Nevertheless, the biopolyesters are weakly compatible with TPS and induced a phase separation in the blends. These phase separations led to different morphologies. Schwach and Avérous [24] have studied some TPS/biopolyester blends and have shown different morphologies, especially a core–shell morphology with a rich in starch core phase and a rich biopolyester surface phase. Averous et al. [20] have obtained this morphology with TPS/PCL blends where the surface corresponds to a PCL layer with a thickness of several microns. This specific morphology is due to the difference in viscosity between the TPS and the biopolyester. In fact, the biopolyester is usually less viscous than the TPS and migrates towards the surface during the extrusion process. This migration could be promoted by a high incompatibility of TPS and the biopolyester. For a packaging application, it is important to know and understand the morphology of the blend.

The role of active packaging is to improve the quality and to extend the shelf-life of food products but the main risk of these packaging is the migration of substances from the packaging. It is then essential to obtain non-migratory active packaging [25]. Plasticized starch or plasticized flour are known to lead to migration in the food matrix and need the use of multilayered structure with external layer composed of a safety component acting as a diffusion barrier. Different polyesters such as polylactic acid (PLA) [26] or PCL [2] are used.

In active packaging, some additives can be incorporated in the formulation to induce an antimicrobial of bacterial adhesion inhibitory effect [8]. Chitosan (CS) is a good candidate because of its biocompatibility, biodegradability, low toxicity and antimicrobial potential [27]. The antibacterial mechanisms of chitosan are still unknown. Chitosan's antimicrobial activity is influenced by the pH, its deacetylation degree and its molecular weight [28]. Tripathi et al. [29] have formulated a chitosan-starch film that shows potential applications in food packaging.

In this work, different wheat starch or wheat flour based blends with PLC have been formulated and processed by extrusion or co-extrusion. An antimicrobial agent, namely chitosan (CS), was added to the formulation. PCL, starch and CS were selected because they can be extruded without degradation within the same range of temperature (80–110 °C). After processing, the structure of the films was characterized by Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). The mechanical properties of the films were investigated by VideoTraction® tests and the water behavior by sorption measurements. The antimicrobial activity of the films was evaluated by direct counting of adherent bacteria at the surface.

2. Materials and methods

2.1. Materials

The wheat starch was provided by Sigma–Aldrich and the wheat flour was provided by Grands Moulins de Paris (France). To avoid any competition with food industry, the flour selected in this study contained a low protein ratio (7% w/w).

PCL were provided by Perstorp (United Kingdom) with three different molecular masses: 37 kg/mol (PCL37), 50 kg/mol (PCL50) and 80 kg/mol (PCL80).

CS powder 652 was provided by France-Chitine (France) with a deacetylation degree equal or superior to 90%. Amounts of CS in formulations are 5% or 20% w/w.

Pseudo-multilayered films were performed by a 3-steps extrusion processing: (1) starch or flour powder were plasticized with glycerol (20% w/w) and water (10 wt.%) by twin-screw extrusion (Scamex, France) after to blending in a turbomixer (2000 rpm, 5 min), (2) TPS or thermoplasticized flour (TPF) granulates were blended with PCL granules and extruded by a single-screw extruder, and (3) the blend compounds were cast-extruded to obtain films. Extrusion temperature-profiles were comprised between 90 and 115 °C. The screw speed was fixed to 40 rpm. CS could be added in Step 1 in the starch or flour powder.

Multilayered films were performed by co-extrusion processing. Steps 1 and 2 are similar to pseudo-multilayered film-processing. Step 3 consists in two single-screw extruders connected through a co-extrusion block (Fig. 1) with PCL/CS granulates in extruder 1, which corresponds to the external layers of the film, and TPS/PCL or TPF/PCL blends compounds in extruder 2, which corresponds to the internal layer of the film.