



# Thermoplastic starch films and thermoplastic starch/polycaprolactone blends with oxygen-scavenging properties: Influence of water content



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## ARTICLE INFO

### Article history:

Received 24 July 2014

Received in revised form 17 October 2014

Accepted 18 November 2014

Available online 4 December 2014

### Keywords:

Biodegradable material  
Oxygen scavenger  
Starch, Polycaprolactone  
Water sorption  
Mechanical properties

## ABSTRACT

A binary oxygen scavenger composed of ascorbic acid (AA) and iron powder (Fe) or copper chloride (CuCl<sub>2</sub>) as catalysts was added in extruded thermoplastic starch (TPS) films. The properties of these films, such as water sorption capacity, oxygen absorption and mechanical properties at different humidity rates are reported. The TPS-AA-Fe film displays interesting oxygen-scavenging properties, which can be triggered by an increase of water content in the film. This material, able to reduce the oxygen rate in the measurement device from 20.9% to 1% in 15 days at 80% relative humidity, could be of interest for the development of short lifetime active food packaging. However, although the hydrophilicity of TPS is an advantage for triggering the oxygen-scavenging activity, its mechanical properties also strongly depend upon relative humidity. In a first attempt at improving the mechanical resistance of the oxygen-scavenging film, TPS-AA-Fe was blended with poly( $\epsilon$ -caprolactone) (PCL), a both biodegradable and hydrophobic polymer. The results show that the addition of 20% PCL only slightly improves mechanical properties, and for relative humidities below 72%.

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## 1. Introduction

Currently, the food packaging industry faces two major issues. Consumers are increasingly demanding food with longer shelf-life and better fresh-like qualities, while they are also asking for food containing fewer preservatives. Therefore, the function of food preservation has been assigned to the packaging, and active packaging has been greatly developed for a few decades. Active packaging can be defined as “a system that changes the condition of the packaging to extend shelf-life or improve safety or sensory properties while maintaining the quality of the food” (de Kruijf et al., 2002). The main active packaging systems involve moisture absorption, oxygen, ethylene or carbon dioxide scavenging, carbon dioxide or ethanol emission, and finally antimicrobial systems (Vermeiren et al., 1999).

Most of the active packaging available in the market is developed from synthetic traditional polymers. They do not take into

account the environmental consideration, which is the second major issue for food packaging industry. Indeed plastic packaging materials are often contaminated by foodstuff, hence recycling is impracticable and most of the times economically not convenient. Biopolymers made of renewable resources and/or biodegradable are thus particularly interesting for food packaging uses. Although lots of researches are dealing with biopolymers suitable for food packaging applications (Tharanathan, 2003; Siracusa et al., 2008; Mensitieri et al., 2011), very few studies concern biomaterials for food packaging which could have an action on food environment to extend its shelf-life. Active edible coating can be considered as bio-based active packaging. The most studied is an edible film based on chitosan, a polysaccharide displaying antimicrobial properties, obtained by deacetylation of chitin (a natural structural component present for instance in crustaceans) (Elsabee and Abdou, 2013). Another way of extending shelf-life of fresh products is the reduction in oxygen rate. Oxidation is indeed one of the major causes of food degradation. Moreover the elimination of oxygen inhibits the development of aerobic microorganism. Oxygen-scavenging packaging is able to eliminate the oxygen initially present within the package headspace and in the food itself, as well as to eliminate low quantity of oxygen that permeates through the polymeric film (Day, 2008). The most common commercially available form of oxygen scavenger is a small permeable sachet containing the active

Abbreviations: TPS, thermoplastic starch; PCL, polycaprolactone; RH, relative humidity; AA, ascorbic acid.

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compound (Miltz and Perry, 2005). This sachet is placed inside the traditional packaging. Iron powder is usually used as oxygen scavenger in these sachets but presents a potential risk of being accidentally ingested. Oxygen scavengers based on organic reducing agents, such as ascorbic acid (AA) have also been developed. Natural and generally recognized as safe; AA has the advantage of being widely used as food ingredient with many functional roles, and is already often added as an oxygen scavenger into liquid food. Its oxygen depletion rate is slow unless it is catalyzed by transition metal ions (Graf, 1994). Copper chloride has been used as a catalyst of AA oxidation in polyethylene based oxygen-scavenging sachets (Graf and Rapids, 1994).

An alternative to the use of sachets is the integration of the active compound directly into the polymeric film structure. Scavengers can be dispersed in the polymeric matrix or introduced into a layer of a multilayered film (Vermeiren et al., 1999). The main difficulties of this approach are the dispersion of the scavenger in the matrix, the accessibility of the scavenger to oxygen and the necessity of an activating system for the oxygen absorption reaction. Without an activating system, the oxygen-scavenging capacity of the active film would be consumed during storage, before packaging use. Most of the studies about oxygen-scavenging films concern petrochemical-based polymers. For example, association of AA and iron has been previously successfully used as oxygen scavenger in a film of ethylene vinyl acetate (Yeh et al., 2008). Until now, only few studies are dealing with the insertion of O<sub>2</sub> scavenger in biopolymers, among them: ascorbic acid in an edible film of glycerol-plasticized lactoserum containing (Janjarasskul et al., 2011); or CuCl<sub>2</sub> and polymeric nanoparticles containing  $\alpha$ -tocopherol incorporated into a gelatin film (Byun et al., 2012).

To replace petrochemical-based polymers by renewable ones, starch has attracted considerable attention due to its natural abundance, and its ability to transform into thermoplastic resin-like products under destructuring and plasticizing conditions (Liu et al., 2009; Averous, 2004). Thermoplastic starch (TPS) has several advantages such as total compostability and renewability of the resource. Besides, TPS shows a wide range of properties according to the plasticizer level and the forming process used. One interesting property for packaging application is that oxygen permeability of starch-based films is found low when they contain a low amount of plasticizers (Dole et al., 2004). However, TPS is a very hydrophilic material. Its gas permeability increases in high humidity environments (Follain et al., 2005) and its mechanical properties are very variable as a function of humidity rate. To overcome these issues while maintaining its biodegradability, one strategy consists in associating TPS with another biodegradable polymer (Yu et al., 2006). Blends of TPS with polycaprolactone (PCL), a hydrophobic and biodegradable polyester, can be an interesting way of improving mechanical and water barrier properties of starch-based films (Myllymäki et al., 1998; Li and Favis, 2010). In previous work (Mahieu et al., 2013), we have shown that blending 30% PCL (50 000 g mol<sup>-1</sup>) with TPS leads to a homogeneous material. The surface affinity for water of blend films is reduced, as well as the variability of mechanical properties with humidity rate, even if the effect of the blend on water sorption of the film is low.

In this work, TPS and TPS-PCL blend are used as matrixes for the elaboration of a biodegradable and oxygen-scavenging material. To give oxygen-scavenging capacity to the matrix, reducing compounds were added: ascorbic acid, and iron powder (Fe) or copper chloride (CuCl<sub>2</sub>) as catalysts. The main objective of this study is to investigate the oxygen absorption capacity of the starch-based films including AA and Fe or CuCl<sub>2</sub> at different humidity rates, and the active compound influence on the mechanical properties of the film as a function of humidity.

**Table 1**  
Initial composition of the samples.

	Formulations (% w/w)					
	Starch	Glycerol	PCL	AA	Fe	CuCl <sub>2</sub>
TPS	80	20				
TPS-AA	68	17		15		
TPS-AA-Fe	66.8	16.7		15	1.5	
TPS-AA-CuCl <sub>2</sub>	66.8	16.7		15		1.5
TPS-PCL	64	16	20			
TPS-PCL-AA	52	13	20	15		
TPS-PCL-AA-Fe	50.8	12.7	20	15	1.5	

## 2. Experimental

### 2.1. Materials

Unmodified wheat starch, ascorbic acid, iron powder, copper chloride and glycerol were obtained from Sigma–Aldrich (France). Wheat starch contains 26% amylose ( $M_w \sim 1.5 \times 10^6$  g mol<sup>-1</sup>; Lee, 2007) and 74% amylopectin.  $M_w$  of amylopectin was estimated around  $1 \times 10^9$  g mol<sup>-1</sup> (Stevenson et al., 2007). The iron powder purity is more than 99% and its diameter is  $100 \pm 20$   $\mu$ m. PCL CAPA 6500 was purchased from Perstorp (UK). Its average molecular weight is 50 000 g mol<sup>-1</sup>.

### 2.2. Sample preparation

In a first step starch was blended with glycerol in a thermo-regulated turbo-mixer and heated in an oven at 170 °C for 1 h, allowing diffusion of glycerol into the starch granules. Then active compounds and/or PCL powder were added in the starch–glycerol blend and the humidity rate was adjusted at 10% w/w. The resulting mixture was extruded and granulated in a single screw extruder (SCAMEX, France) equipped with two heating zones regulated at 100 °C, then 110 °C around the screw and 90 °C for the die, at a screw speed of 50 rpm.

In a second step, these granules were extruded through a slit die and calendered to obtain films (about 1 mm thickness). Temperatures used on the extruder were 110 °C, 120 °C and 100 °C, at a screw speed of 50 rpm. Films were stored in controlled chambers at different relative humidities.

The various formulations studied are presented in Table 1. Glycerol/starch ratio was always 20/80 w/w. 20% glycerol has been shown to be the maximum rate leading to starch plasticization without phase separation between starch and glycerol (Lourdin et al., 1997; Godbillot et al., 2006). The amount of ascorbic acid introduced corresponds to the theoretical quantity needed to react with all the oxygen present in the experimental device. Iron powder or copper chloride was added at the rate of 10% w/w of the AA quantity. PCL was blended at a level of 20% w/w.

### 2.3. Water sorption measurements

Water vapor sorption-isotherms of each sample were deduced from the static-gravimetric technique of water vapor sorption by using saturated salt solutions at 23 °C. These solutions were prepared to generate an environment with controlled humidity in a closed chamber. Square samples of 2 cm<sup>2</sup> of each material were cut and dried in a desiccator under vacuum and in the presence of P<sub>2</sub>O<sub>5</sub>. Then samples were placed in triplicate in chambers with different water activities obtained with above-saturated salt solutions of LiBr ( $a_w = 0.06$ ), LiCl (0.11), CH<sub>3</sub>COOK (0.23), MgCl<sub>2</sub> (0.33), Mg(NO<sub>3</sub>)<sub>2</sub> (0.53), CoCl<sub>2</sub> (0.65), NaCl (0.75), KCl (0.85) and KNO<sub>3</sub> (0.94) respectively (Greenspan, 1977). Samples were weighted until equilibrium for 1 month. Water sorption isotherms were

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