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Influence of citric acid on thermoplastic wheat flour/poly(lactic acid) blends. II. Barrier properties and water vapor sorption isotherms

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ABSTRACT

The effects of citric acid on wheat flour/glycerol/poly(lactic) acid (PLA) blends prepared by one-step twin-screw extrusion have been studied to improve barrier properties of starch based materials. A series of injected samples were produced from prepared compounds with varying ratio (0–20 part) of citric acid. The effects of citric acid on the water vapor permeability, oxygen permeability and water solubility in the film were then investigated. The barrier properties results proved that citric acid behaves as compatibilizing agent between starch and PLA phases for ratios between 0 and 10 parts. When the added amount exceeds 10 parts, CA acted as a plasticizer and/or promoted the hydrolysis of the starch glycosidic bonds.

1. Introduction

Bioplastics are topical and their use is becoming more abundant in recent years. Researchers focusing their works on the processing of these materials since sustainable policies tend to expand with the decreasing reserve of fossil fuels and the growing concern for the environment. Replacement of conventional plastics by degradable polymers, particularly for short-lived applications such as packaging, catering, surgery is of major interest for different actors of the socio-economical life.

In packaging applications, agro-polymers from agroressources (starch, cellulose, protein, etc.) represent a new alternative to the ubiquitous of synthetic polymers (polyethylene terephtalate, polyvinyl chloride, polystyrene, etc.). These agro-materials represent a strong and emerging answer to develop novel materials labeled “environmentally friendly”.

Therefore, it appears interesting to use raw materials from cereal product for their immense potential, low price and abundant availability, especially wheat flour that mainly contains starch and protein (Chanvrier et al., 2007; Leblanc et al., 2008). Starch is a natural polysaccharide produced by many plants, as a storage polymer. It’s the major carbohydrates reserve in plant tubers and seed endosperm where it’s found as granules (Buléon et al., 1998). It has received considerable attention during the last decades as a biodegradable thermoplastic polymer and is probably the most promising materials among naturally biodegradable polymer using renewable resources. Nevertheless, native starch can not be processed as a thermoplastic material because of the strong intramolecular and intermolecular hydrogen. It can be converted into a continuous polymeric entangled phase by mixing with enough water and nonaqueous plasticizer, generally polyols, such as glycerol (Angellier et al., 2006; Forssell et al., 1997; Ghiasi et al., 1982; Liu et al., 2001).

The starch extraction from wheat flour generates a significant additional cost. Thus, to become fully competitive with conventional plastics, it seemed necessary to use wheat flour as thermoplastic materials. The resulting materials can be manufactured using technology already developed for the production of synthetic plastics. However, its hydrophilic nature makes it very sensitive to moisture attack. Thus, it’s difficult to reach the same characteristics (dimensional stability, barriers and mechanical properties) than polymers derived from fossil resources, most frequently used in food packaging.

Abbreviations: WF, wheat flour; PLA, poly(lactic acid); TPS, thermoplastic starch; WVP, water vapour permeability; β, solubility coefficient (hydrophilicity, adsorptivity); X, equilibrium moisture content; DMTA, dynamic mechanical and thermal analysis; FTIR, Fourier Transform Infrared Spectroscopy; SEM, Scanning Electronic Microscopy.

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To improve barrier properties of plasticized wheat flour, poly(lactic) acid (PLA), known for its good barrier properties was used to obtain thermoplastic wheat flour/PLA blends. Similar values of water vapour permeability (WVP) for PLA and synthetic polymers like PET and PS were reported in the literature (Auras et al., 2005) and WVP of PLA did not vary significantly with changes in RH. The authors also reported a decrease in WVP of PLA with increasing temperature, opposite behavior to that of most petroleum-based polymers that exhibit lower water vapour barrier properties at higher temperatures. The values of permeability for O_2 of PLA have been shown to be comparable to those of equivalent of conventional materials such as PE and PS (Petersen et al., 1999, 2001).

Blending wheat flour (WF) with PLA is one of the most promising and original approaches because WF is an abundant and cheap resource and PLA has good mechanical and barriers properties. To the best of our knowledge, there is no study concerning WF/PLA blends although several authors (Muller et al., 2012; Yew et al., 2009) have reported the barrier properties of thermoplastic starch/PLA blends.

However hydrophilic starch, with plenty of hydroxyl groups and hydrophobic PLA, with hydroxyl and carboxyl end groups present a poor interfacial adhesion (Almenar and Auras, 2010; Martin and Avérous, 2001). Indeed, starch remains in separate conglomerate form in a PLA matrix. Moreover, the great moisture sensitivity of starch is a disadvantage. Ke and Sun (2001) have reported that PLA/starch blends containing gelatinized starch had greater water absorption than the other blends because the gelatinized starch is more sensitive to water than the granular state. To overcome these shortcomings, certain nontoxic functional additives are required to improve the mechanical, barriers properties and water resistibility of the PLA/starch films.

Several authors (Ghanbarzadeh et al., 2011; Ma et al., 2008; Shi et al., 2007; Thiebaud et al., 1997) have reported that citric acid (CA) may improve the water resistance due to reducing available hydroxyl groups of starch. It has also reported that the primary function of films prepared with lipids was blocking moisture transport due to the high hydrophobicity and decrease the water vapor permeability of biopolymeric films (Gontard et al., 1994). It was found that citrate starch does not swell and gelatinize in hot water as a result of cross-linking reaction (Xie and Liu, 2004). Furthermore, citric acid addition to wheat flour caused to significantly decrease the cross-linking degree of the protein network during extrusion (Gómez-Martínez et al., 2009). CA can also act as a plasticizer and has been shown to promote starch hydrolysis by lowering the pH (Hirashima et al., 2004; Shi et al., 2007). Citrate esters can be effective in reducing the glass transition temperature and increase the plasticization of TPS and PLA (Labrecque et al., 1997; Shi et al., 2007).

Plasticizers as polyols can affect the water vapor properties of packaging films (Müller et al., 2008). Study of hydration of plasticized starch has shown that interactions between the components of the system formed by starch, plasticizer and water was significantly dependent on the relative humidity to which theses materials were exposed (Godbillot et al., 2006).

Several authors have investigated the behavior of water vapor permeability and the simultaneous behaviors of water diffusivity and solubility in a polymeric matrix (Miller and Krochta, 1997; Sothornvit and Krochta, 2001; Larotonda et al., 2005; Maria Martelli et al., 2006; Rocha Plácido Moore et al., 2006) and few recent studies were found in the literatures regarding the relative influences of these parameters on the water vapor permeability of starch films (Müller et al., 2009; Muller et al., 2012).

In the present paper, citric acid known as nutritionally harmless compared to other substances used for starch derivatization (Xie and Liu, 2004), was used as an additive on wheat flour/glycerol/PLA blends in an industrial-size-twin-screw extruder. A series of molded samples were produced from prepared compounds to assess their suitability for use as packaging materials. The present paper follows an article already reported by Chabrat et al. (2012) who investigated how the addition of citric acid on wheat flour/PLA blends influences films' thermal, morphological and mechanical properties. In this paper, wheat flour/PLA/citric acid blends have been successfully produced on industrial equipments and citric acid has improved the PLA repartition in the matrix and its effects of both compatibilization and plasticization were seen on the mechanical properties. This second part investigates the barrier properties (WVP and O_2 permeability) and water vapor sorption isotherms of the blends produced without additional water to conclude on the effects of citric acid on WF/PLA interactions and evaluate the possible use of these compounds as packaging materials.

2. Experimental

2.1. Materials

Wheat flour was supplied by Gers Farine (France). It is mainly made up of starch (65%). Secondary components were water (13%), proteins (13%), fibers, essentially hemicelluloses (2%) and lipids (1%). Poly(lactic) acid (PLA) is an extrusion grade and was kindly provided by Natureworks LLC (USA). Its melting temperature was 140 °C. Glycerol (purity 99%) was used as starch plasticizer and was supplied by Gaches Chimie (France). Citric acid was obtained from Sigma–Aldrich (France).

2.2. Thermoplastic starch/PLA blends extrusion

In this study, five different blends were extruded in an industrial-size twin-screw extruder (Evolum HT53, Clextral (France) with L/D = 36). It was equipped with nine modular barrels, each 212.6 mm long. A cylindrical die with 6 holes was fixed at the end of the extruder. The screw rotational speed was fixed at 250 rpm and temperature profile in the nine barrel sections from feed to die were set of 60–140 °C for all the experiments (Fig. 1). The screw profile was divided in two main zones, a plasticization zone composed of kneading elements and reverse screw elements in the first half of the barrel and a mixing zone composed of kneading elements in the second half of the barrel. PLA was introduced at the beginning of the second zone, i.e. after starch plasticization. The compositions of the blends can be understood from their names. First, wheat flour (extruded at its equilibrium humidity (13%)), PLA and glycerol ratio were kept constant at 75 parts, 25 parts and 15 parts respectively. The only variables were citric acid. The generic name for the formulations is CA*x* with *x* indicating the concentration of citric acid, with values between 0 and 20 parts.

2.3. Injection-molding

After stabilization at 60% RH and 25 °C during three weeks, the plastics pellets were injection-molded into disk-shaped specimens using a Negri Bossi VE160-720 injection molding machine (Italy). Molding temperature profile was defined as following: 80/125/130/145 °C and backpressure was 10 bar. The holding pressure was 800 bar during 0.5 s and 600 bar during 0.5 s.

2.4. Moisture, thickness and density

Before any film properties determination, samples were conditioned at 25 °C and 60% RH for at least 20 days to stabilize them. The plastics pellets and injection-molded specimens' moisture were determined in triplicates by gravimetric method, after drying at 105 °C for 24 h and expressed in g water/100 g dry mass. The thickness of the samples was measured (±0.01 mm) using a