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Influence of citric acid and water on thermoplastic wheat flour/poly(lactic acid) blends. I: Thermal, mechanical and morphological properties

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ABSTRACT

Wheat flour was plasticized with glycerol and compounded with poly(lactic acid) in a one-step twin-screw extrusion process in the presence of citric acid with or without extra water. The influence of these additives on process parameters and thermal, mechanical and morphological properties of injected samples from the prepared blends, was then studied.

Citric acid acted as a compatibilizer by promoting depolymerization of both starch and PLA. For an extrusion without extra water, the amount of citric acid (2 parts for 75 parts of flour, 25 parts of PLA and 15 parts of glycerol) has to be limited to avoid mechanical properties degradation. Water, added during the extrusion, improved the whole process, minimizing PLA depolymerization, favoring starch plasticization by citric acid and thus improving phases repartition.

1. Introduction

Wheat flour is mainly constituted of starch and proteins (Saiah, 2007). Starch, which is a natural renewable polysaccharide, is considered to be a promising raw material for the production of bioplastics. However, it needs intense transformation to disrupt its native structure and to become thermoplastic. It is also possible to plasticize flour to make thermoplastic flour. In low moisture conditions used for thermoplastic processing, the influence of wheat proteins has been shown to be minor, the proteic phase is dispersed in the starch matrix (Chanvrier et al., 2007) and no significant differences were noticed in terms of mechanical and thermal properties between flour and starch (Leblanc et al., 2008). This material shows very similar properties and the same limits as thermoplastic starch. Thermoplastic starch (TPS) is indeed a very interesting product for making non-durable objects. However, its water sensitivity and limited mechanical properties make it only useful for specific applications (Forssell et al., 1999). Citric acid could be a good candidate to increase the range of reachable properties. To our knowledge, there is no study concerning the addition of citric acid in thermoplastic wheat flour. Nevertheless, it has been added to thermoplastic starch in different studies.

Several authors (Shi et al., 2007; Wang et al., 2007a, 2009) have reported that citric acid could form ester bond with starch. The esterification could take place between the carboxyl groups on citric acid and the hydroxyl groups on starch. Nevertheless when glycerol was present, it reacted preferentially with the hydroxyl groups of the glycerol (Wang et al., 2007a). The formation of glycerol citrate esters has been studied by Differential Scanning Calorimetry (DSC) and Fourier Transform Infrared Spectroscopy (FTIR) (Holser, 2008). Even if no ester bond was formed between citric acid and starch, it has been reported that citric acid could form strong hydrogen bond interactions with starch, stronger than glycerol. The thermal and water sensitivity of thermoplastic starch was then improved and retrogradation was inhibited (Holser, 2008; Shi et al., 2007; Yu et al., 2005). Crosslinking of starch films has been performed using citric acid and a catalyst (sodium hypophosphite) (Reddy and Yang, 2010), citric acid bearing three carboxyl groups. Free citric acid, which was not involved in any crosslinking interaction could act as a plasticizer (Shi et al., 2008). Citric acid has also been added to thermoplastic starch to modify its

Abbreviations: DMTA, dynamic mechanical thermal analysis; DSC, differential scanning calorimetry; FTIR, Fourier Transform infrared spectroscopy; PLA, poly(lactic acid); SEM, Scanning Electronic Microscopy; TPS, thermoplastic starch; UTS, ultimate tensile strength.

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physical performance by controlled degradation of starch through an acid-catalyzed hydrolysis of the ether linkages in the polysaccharide chains (Carvalho et al., 2005; Hirashima et al., 2005; Wu et al., 2010). The viscosity of starch was then reduced without relevant changes in water affinity or in dynamic mechanical properties (Da Roz et al., 2011).

Citric acid has been reported to increase the plasticization and melt processing properties of TPS (Ronasi et al., 2010; Shi et al., 2007). It might accelerate the fragmentation and dissolution of starch granules. It could help starch plasticization, even when additives such as montmorillonite are added which normally hinder the plasticization (Wang et al., 2009). The fluidity of TPS was also improved using citric acid. This decrease was explained by some authors by an acid hydrolysis of starch (Ke and Sun, 2003). So, co-plasticizing starch with a mixture of glycerol/citric acid is interesting because it increases starch plasticization, partial esterification can happen, and chains with lower molecular weight are obtained. In wheat flour, addition of citric acid can lead to a decrease in the cross-linking degree of the protein network during extrusion. It has been stated, according to a study of thermo-mechanical behavior of wheat gluten materials (Gomez-Martinez et al., 2009), that an acidic environment might prevent aggregation of gluten protein.

Blending poly(lactic acid) (PLA) with thermoplastic starch has become widespread in the bioplastics community in the last 10 years, in order to reach different properties and decrease the price of bioplastics. But PLA and TPS are known to be non-miscible, and non-compatibilized blends exhibit weak properties (Martin and Avérous, 2001).

The influence of citric acid on TPS/PLA blends has thus been reported in different studies (Ke and Sun, 2003; Wang et al., 2007b, 2010). It has been established that even without water, plasticization of starch with glycerol was possible when citric acid (0–4%) was present. When water was present, the blend was more homogeneous but thermal stability was decreased. In both cases, a better interaction between PLA and TPS has been found (Wang et al., 2010).

Citric acid has also been used as an additive to starch-PVA (poly(vinyl alcohol)) films (Park et al., 2005). It was reported that adding citric acid decreased the strength of the films but provided better strength than glycerol-added films. This was attributed to the better hydrogen bonding between citric acid and starch-PVA molecules than with glycerol. Citric acid is composed of carboxyl and hydroxyl groups which increase the different interactions between the components of the blend (Yoon et al., 2006; Yun et al., 2006). When added to thermoplastic starch/LDPE blends, citric acid improved starch plasticization and increased the mechanical properties of the blend (Wang et al., 2007b).

Citrate esters are known to plasticize PLA (Ke and Sun, 2003; Labrecque et al., 1997). Moreover, citric acid is inexpensive, nontoxic and considered nutritionally harmless as approved by FDA. Indeed, it is a metabolic product of the body (Krebs cycle). Citric acid, when concentration is less than 20%, shows no significant toxicity effect on the cell proliferation (Shi et al., 2008).

In order to improve thermoplastic wheat flour properties, and so to reach new application fields, it was chosen to be blended with a small amount of poly(lactic acid). Three additives were used for the compounding in an industrial-size twin-screw extruder: water, glycerol and citric acid. Water is the most known starch plasticizer. Glycerol is commonly used as a plasticizer to obtain thermoplastic starch. Citric acid, which is a natural occurring organic acid, was chosen to improve starch plasticization and the phases miscibility. The obtained compounds have then been molded in dumbbell-shape specimens to assess their mechanical, thermal and morphological properties. The influence of water and citric acid, in a wide range, on material properties has been studied.

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) is an extrusion grade. 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, ten different blends were extruded in an industrial-size twin-screw extruder (Evolum HT53, Clextral (France) with L/D = 36) at a temperature of 60–140 °C and screw rotational speed of 250 rpm. The screw profile was divided into 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. Poly(lactic acid) was introduced at the beginning of the second zone, i.e. after starch plasticization. A cylindrical die with 6 holes was fixed at the end of the extruder. The compositions of the blends can be understood from their names. First, wheat flour (extruded at its equilibrium humidity (13%)), poly(lactic acid) and glycerol ratio were kept constant at 75 parts, 25 parts and 15 parts respectively. The only variables were water and citric acid ratios. The generic name for the formulations is CA*x*. When a *W* is present before this name, it means that 10 parts of extra water was present in the formulation during the extrusion. This water was added to help processing and to study the behavior between water and citric acid. *x* indicates the concentration of citric acid, with values between 0 and 20 parts. The formulation WCA5 contained thus 10 parts of water and 5 parts of citric acid.

2.3. Injection-molding

After stabilization at 60% RH and 25 °C, the plastics pellets were injection-molded into dumbbell-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 300 bar during 1 s. For experimental reasons, WCA2 was not injected; no results from injection-molded specimens are available for this formulation.

2.4. Tensile testing

A Tinius Olsen H5kT (UK) universal testing machine was operated at a crosshead speed of 5 mm/min and used for tensile testing. Young's modulus, ultimate tensile strength, elongation at break and toughness were recorded for each specimen. Toughness represents the energy by volume unit necessary to break the dumbbell specimen. It was calculated from the area under the force–displacement curve. Injection dumbbell specimens were conditioned at 60% RH and 25 °C for 3 weeks prior testing. Each mechanical parameter was averaged from 5 to 10 specimens.

2.5. Dynamic mechanical and thermal analysis

Dynamic mechanical and thermal analyses (DMTA) of the samples were performed with a Tritec 2000 DMA (Triton Technology, UK) in a multi-frequency mode over the temperature range −80 to 180 °C with a scanning rate of 2 °C/min. The amplitude and frequencies were kept constant at 25 μm and 1 and 10 Hz, respectively. The geometry used was the single cantilever bending mode with one extremity of the bar fixed, while the other one was