



Biodegradable and non-retrogradable eco-films based on starch–glycerol with citric acid as crosslinking agent



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ABSTRACT

Biodegradable and non-retrogradable starch–glycerol based films were obtained using citric acid (CA) as crosslinking agent at 75 °C. This material allowed decreasing water vapor permeability (WVP) more than 35%, remained amorphous for at least 45 days as a result of the network formed by the CA that avoided starch retrogradation and maintained the degradability in compost, occurring only six days after the films without citric acid. A simulation of the gelatinization process of starch–glycerol with and without CA, using a differential thermal analysis device, showed that the system with CA completed the gelatinization 5 °C before than the other and, CA first reacted with glycerol and then starch–glycerol–CA reaction occurred. The temperature at which the gelatinization process was carried out was critical to obtain the best results. An increase of gelatinization process temperature at 85 °C in system with CA, led to a worsening on WVP and its integrity after a swelling process with dimethylsulphoxide (DMSO), compared to the films processed at 75 °C.

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1. Introduction

In light of the global concern for the accumulation of waste, biodegradable and compostable materials were extensively investigated, in order to partially replace petroleum-based plastics. Among the many polymers used to develop biodegradable films, starch has been focus of investigations because it is a natural polymer from renewable resources, abundant and low cost, that is capable of forming continuous thermoplastic materials (Bertuzzi, Armada, & Gottifredi, 2007; Famá, Bittante, Sobral, Goyanes, & Gerschenson, 2010; Flores, Famá, Rojas, Goyanes, & Gerschenson, 2007; Gutiérrez, Pérez, Guzmán, Tapia, & Famá, 2015; Romero-Bastida et al., 2005). However, its hydrophilic character leads to materials with poor moisture barrier properties and high water sensitivity, being very dependent to ambient humidity, limiting their application as alternative packaging (Averous & Boquillon, 2004).

Another starch problem is its high retrogradation during storage time, causing changes in its crystallinity and thus in its performance such as texture, color, etc. (Farhat, Blanshard, & Mitchell, 2000).

Retrogradation process occurs in two different stages. The first and faster one is due to the amylose retrogradation, while the

second and slower one is due to the formation of an ordered structure of amylopectin (Forsell, Hulleman, Myllärinen, Moates, & Parker, 1999).

Crosslinking reaction appears as a common approach to limit starch retrogradation and to improve its performance for various applications. This process uses multifunctional group reagents (crosslinking agents) to react with the hydroxyl groups of starch (responsible for its hydrophilicity), leading to new chemical bonds between molecular starch chains, getting a different polymer network. By introducing hydrophobic ester groups to substitute hydroxyl groups of thermoplastic starch, its hydrophilic character can be reduced and retrogradation can be prevented (Ghanbarzadeh, Almasi, & Entezami, 2011; Shi et al., 2007; Zhou, Zhang, Ma, & Tong, 2008).

Citric acid (CA) is a natural organic acid with multi-carboxylic structure, reason why it can be used as starch crosslinking agent (Salomão Garcia et al., 2014; Zuraida, Yusliza, Anuar, & Mohd Khairul Muhaimin, 2012). There are several researches showing that the addition of CA to starch base compounds, improves their barrier properties and that the effectiveness of citric acid to crosslink the starch strongly depends on manufacturing conditions (Menzel et al., 2013; Olsson, Hedenqvist, Johansson, & Järnström, 2013a; Olsson et al., 2013b; Reddy & Yang, 2010).

Several works of literature use citric acid as crosslinking agent for starch. In the case of films obtained by casting technique, there is no agreement about the protocol stage in which citric acid must

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be added. Some authors (Reddy & Yang, 2010; Ghanbarzadeh et al., 2011) mix citric acid with water, glycerol and starch before gelatinization process, while others, in order to avoid hydrolysis, first gelatinize starch, cool the mixture, add the CA and finally do the drying stage (Shi et al., 2008; Menzel et al., 2013; Olsson et al., 2013a,b). In particular, the work of Menzel et al. (2013) should be mentioned. In that investigation the authors reported that it was possible to obtain crosslinked starch gelatinizing starch at low temperature from the following protocol: first, the starch was gelatinized in boiling water bath for 45 min; then, the gel was led to room temperature and, at that moment, CA was introduced; finally, starch–CA system was dried at 70 °C for 5 h. In the cases in which it is included after starch gelatinization, the influence of the drying temperature in the crosslinking or hydrolysis of starch is one of the most discussed points in the literature. However, there is agreement in the fact that high drying temperatures lead to a high hydrolysis degree (Menzel et al., 2013; Olsson et al., 2013a,b).

For the crosslinking reaction between starch and CA to occur, temperature is required. The discussion is in which stage of the development of the films this reaction occurs, and what is the order in which the different components of the films react. In the case where CA is added after the gelatinization process, obviously the crosslinking reaction occurs during the drying of the mixture. However, when CA is introduced prior to starch gelatinization, the reactions may occur at any stage of the films obtaining process. To the best of our knowledge there are no researches in the literature discussing this point. Moreover, there have not been reported studies simulating the reactions between CA, starch and glycerol during gelatinization stage or drying of the films, using Differential Scanning Calorimetry (DSC) or Differential Thermal Analysis device (DTA).

Nor are there studies in the literature that discuss the influence of the maximum temperature at which the mixture is brought during gelatinization process. However, this step could be critical in the crosslinking process. For example Ghanbarzadeh et al. (2011) obtained films of starch crosslinked with CA, heating the mix of all components at 90 °C for 30 min and drying at 60 °C in oven. Marques et al. (2006) report crosslinked starch films with tetraethylene glycol diacrylate, heating the mix of all components at 90 °C and drying at room temperature.

On the other hand, low field nuclear magnetic resonance (¹H NMR) is a technique used to characterize the water mobility of polymers and polymer composites (Mendes, Silva, & Lino, 2012; Preto, Tavares, & Da Silva, 2007), rarely used in natural polymers such as chitosan and starch (Fundo et al., 2014; Gaudín, Lourdin, Le Botlan, Ilari, & Colonna, 1999) and there is no precedent of its application in crosslinked starch.

Finally, one of the most important points to be evaluated in films to be used as packaging is their biodegradability. Starch can be readily metabolized by a range of microorganisms to fermentation products such as ethanol and methane (Tang & Alavi, 2011). It is quickly attacked by microorganisms when it is buried in soil. Prakash Marana, Sivakumara, Thirugnanasambandhama, and Sridharba (2014) showed, using tapioca starch based composites that the increase of water sorption promotes the entry of soil microorganisms, which use the starch films as a source of energy for their growth. There is agreement in the literature that crosslinking starch with citric acid modifies water sorption. Moreover, Maiti, Ray, Mitra, and Mukhopadhyay (2013) and Imam, Cinelli, Gordon, and Chiellini (2005) showed in starch–poly(vinyl alcohol) blends crosslinked with different crosslinking agents that the starch degradation rate buried in soil is slowed when the system is crosslinked. While it is expected that the esterified or citric acid crosslinked starch do not degrade too slow, no studies in the literature reported this point.

Therefore, the purpose of this report was to provide a complete characterization of cassava starch crosslinked with citric acid. The focus was to show the influence that has the maximum temperature reached during starch gelatinization process on the film properties when this process is performed in presence of citric acid. Besides, the goal was to demonstrate that heating the mixture up to 75 °C is enough to obtain a completely gelatinized crosslinked material, whereas if the final temperature is 85 °C, signs of incipient hydrolysis are obtained. The manuscript also aimed to improve knowledge about the reactions between the different components (starch, CA and glycerol) during the gelatinization stage. To achieve this, the reactions between different components were simulated using a DTA. After characterization by means of Fourier transform infrared spectroscopy (FTIR) the possible esterification or crosslink reaction were identified. Furthermore, the influence of the final temperature of the gelatinization process and the presence citric acid on the mobility of water contained in the formed films were analysed by low field nuclear magnetic resonance (¹H NMR). The efficiency of CA as crosslinking agent was determined by studies of swelling in dimethylsulphoxide (DMSO) and XRD, through the evaluation of the material retrogradation. Moisture content, moisture absorption and water vapor permeability were also studied. Finally biodegradability studies were performed to evaluate the effect of crosslinking in the films degradation. The combination of all these determinations allowed proposing a model that describes the interactions present in the developed materials, helping to design new materials with improved properties.

2. Experimental

2.1. Materials

Cassava starch (18 wt.% amylose and 82 wt.% amylopectin) was provided by *Industrias del Maíz S.A, Buenos Aires Argentina*. Citric acid (Biopack) and glycerol (J. T. Baker) were of analytical grade.

2.2. Preparation of plasticized starch films

Thermoplastic starch was processed by casting as previously reported (García, Famá, Dufresne, Aranguren, & Goyanes, 2009; Medina Jaramillo, González Seligra, Goyanes, Bernal, & Famá, 2015). Four different systems using the same manufacturing protocol were developed. Table 1 provides the composition of the samples on dry basis. Two of the systems were constituted by aqueous suspensions containing cassava starch (5.0 g/100 g of system), glycerol (1.5 g/100 g of system) and distillate water (93.5 g/100 g of system). The mixture was smoothly stirred during 45 min at room temperature and constant agitation of 250 rpm. After that, the mixture was heated at 3 °C/min under the same rpm. The heating process was completed at 75 °C (TPS75) or at 85 °C (TPS85). Then, the stirring was continued for 5 min at the same final temperature in each case (75 °C or 85 °C). The resulted gel was degassed with a vacuum pump for 10 min, cast in glass petri dishes and dried at 50 °C during 24 h. Other two systems were prepared incorporating 0.5 g of citric acid into a similar aqueous suspension previously described, using the same processing methodology (TPS75–CA y TPS85–CA). This CA was

Table 1
Samples composition of the different developed systems, on dry basis.

Components	Dry basis (wt.%)	
	TPS75//TPS85	TPS75-CA//TPS85-CA
Starch	76.9	71.4
Glycerol	23.1	21.4
Citric acid	0	7.2

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