



Thermoplastic starch plasticized with alginate–glycerol mixtures: Melt-processing evaluation and film properties



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ABSTRACT

Corn starch melt-processing in the presence of a commonly used plasticizer mixture (water/glycerol) and a non-conventional alternative (alginate/glycerol) was evaluated. All assayed formulations were successfully processed by melt-mixing and injected in circular probes. It was determined that all samples presented a typical viscoelastic behavior, observing a decrease in storage and loss modulus with water and alginate concentration, which facilitated samples processability. Concerning to thermal stability, it was not affected neither for water nor alginate presence. From injected probes, flexible films were obtained by thermo-compression. Films with the highest assayed water content presented a sticky appearance, whereas those containing alginate were non-tacky. Plasticizing action of water and alginate was evidenced by the occurrence of homogeneous fracture surfaces, without the presence of unmelted starch granules. Besides, the shift of glass transition temperature to lower values also corroborated the plasticizing effect of both additives. In conclusion, obtained results demonstrated the well-plasticizing action of sodium alginate on starch matrix, turning this additive into a promissory alternative to replace water during melt-processing of thermoplastic corn-starch.

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1. Introduction

Throughout the years, different alternatives for replacing petroleum-based plastics are being studied in order to face the increasing problem that involves plastic waste disposal and environment contamination. Due to petrochemical-based materials are neither recyclable nor biodegradable, the use of natural polymers in their replacement has been the focus of several investigations (Zhang, Rempel, & Liu, 2014).

Among natural polysaccharides, starch is an abundant low-cost polymer, that offers an interesting alternative in the sustainable development of economical and ecologically attractive materials

(Cai et al., 2014; Schlemmer et al., 2010). In this sense, starch may compete with polymers derived from petroleum for manufacture of packaging materials, being completely biodegradable and obtained from renewable resources such as maize, wheat and potato harvests. Particularly, in food industry is quite important to extend shelf life and enhance food quality while reducing packaging waste. Thus, the exploration of new bio-based packaging materials, such as edible and biodegradable films from renewable resources, found in starch a suitable option that may successfully satisfy this increasing demand (Huq et al., 2012). Starch structure is constituted by two macromolecules, amylose and amylopectin. Amylose is a linear polysaccharide, poly(α -1,4-glucopyranosyl), while amylopectin is poly(α -1,4-glucopyranosyl) with many α -1,6-glucopyranosyl branches. Starch is a semi-crystalline polymer that does not melt in the traditional sense to form a liquid; its melting does mean loss of crystallinity due to disruption of hydrogen bonds. However, to take place starch melting is necessary its processing under high temperature and shear stress in plasticizer presence; the resulting material is commonly called thermoplastic starch (TPS). Traditional equipments employed for thermoplastics

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processing, such as extrusion and thermoforming, can be used by adapting operational parameters to the specific characteristics of starch (Shanks & Kong, 2012). During starch processing, the use of different plasticizers lead to specific properties of the final materials. In this sense, water, glycerol and urea, within others, have been widely studied by several authors (Córdoba, Cuéllar, González, & Medina, 2008; Huang, Yu, & Ma, 2006; Zhang et al., 2014) In the case of water, even though it is considered as a processing aid, two important disadvantages are involved during starch melt-mixing: the formation of water vapor bubbles due to the required high temperatures, and biopolymer adhesion in the equipment (Córdoba et al., 2008).

Within this context, the need of reducing water addition during starch processing promotes to explore other additives as plasticizers. So, a promising alternative could be the use of plasticizing agents derived from biological sources. Recently, sodium alginate has been presented as a possible plasticizer, becoming starch into a thermoplastic material. Accordingly, Córdoba et al. (2008) studied the use of alginate/glycerol mixtures as corn starch plasticizers, in completely absence of water. These authors stressed that the use of alginate allowed improving mechanical properties of TPS films, as well as, their final structure. Despite alginate addition enhanced starch melt-processing, in films fracture surfaces some remaining starch granules were detected. This non-efficient granular disruption is probably due to the complete water absence during starch processing. These results evidenced the important role of water during starch thermo-plasticization. However, as it was aforementioned, the use of this universal plasticizer makes difficult starch melt-processing. Therefore, a midpoint alternative could be taking advantages of alginate as plasticizer and minimizing water content. In this manner, complete starch granular disruption, reduction of polymer adhesion and vapor bubbles formation could be achieved. In this work, starch melt-processing using alginate/glycerol and water/glycerol mixtures as plasticizers was compared. Obtained materials were structural characterized by complementary techniques and their rheological behavior and thermal transitions were also evaluated. Finally, the effect of the different studied formulations on materials final properties was analyzed.

2. Materials and methods

2.1. Materials

In this work it was employed native corn starch provided by Misky-Arcor (Tucumán, Argentine) with an amylose content of $23.9 \pm 0.7\%$, previously characterized by López, García, and Zaritzky (2008) and López, Zaritzky, and García (2010). This polysaccharide presents an average molecular weight of $2 \times 10^4 \text{ g mol}^{-1}$ for amylose and $2 \times 10^5 - 1 \times 10^6 \text{ g mol}^{-1}$ for amylopectin.

Analytical grade Anedra glycerol (Argentine) and sodium alginate were used as plasticizers. Sodium alginate was purchased by Fluka (Switzerland, N°. 71238), with a molecular weight of $231,500 \text{ g mol}^{-1}$ and a mannuronic/guluronic ratio (M/G) estimated in 0.79 by ^1H NMR according to the literature (Gomez, Rinaudo, & Villar, 2007; Salomonsen, Jensen, Larsen, Steuernagel, & Engelsen, 2009).

2.2. Formulation and processing of thermoplastic starch

Mixtures of native corn starch (S), 35% (w/w) glycerol (G) and 5, 10 and 15% (w/w) of distilled water (W) or sodium alginate (A) were prepared. Components concentrations were expressed in g per 100 g of starch. Formulations were named as follows: SG, SGA5, SGA10, SGA15, SGW5, SGW10 and SGW15, in which numbers refers to weight percentages employed for the plasticizer. Samples were

melt-processed at 140°C for 30 min employing an Atlas Laboratory Mixing (United States). Processed mixtures were further injected using a steel mold attached to the mixing equipment, obtaining circular probes of 25 mm diameter.

2.3. Probes processing optimizing

2.3.1. Thermogravimetric analysis (TGA)

Thermal degradation was carried out in a thermogravimetric balance TA Instrument Discovery Series (United States). Samples were heated from 30 to 700°C at $10^\circ\text{C min}^{-1}$, employing air flux (25 mL min^{-1}). Curves of loss weight as function of temperature were recorded and the maximum decomposition temperature of each component was obtained from first derivative curves.

2.3.2. Differential scanning calorimetry (DSC)

DSC was performed on a Pyris 1 Perkin-Elmer® apparatus (United States). Samples were measured under nitrogen atmosphere. Temperature and heat of melting were calibrated by using pure indium metal as a standard reference. Approximately 0.01 g of each sample was employed. All samples were heated from 30 to 250°C at $10^\circ\text{C min}^{-1}$ in order to obtain onset (T_o) and peak temperature (T_p).

2.3.3. Rheological studies

Rheological studies were performed using injected probes. Viscoelastic properties were studied employing a Rheometrics Dynamic Analyzer RDA II (United States) equipped with a plate/plate geometry (diameter 25 mm). Frequency sweeps (0.05–500 Hz) were performed in the linear viscoelastic regime, established by strain sweeps from 0.1 to 5% at a fixed frequency (10 Hz). All experiments were performed at 140°C .

2.4. Films formation

Films were obtained by thermo-compression using a hydraulic press at 140°C and 180 kg cm^{-2} during 6 min.

2.5. Films characterization

2.5.1. Structure

Films homogeneity and appearance were examined by scanning electronic microscopy (SEM). Studies were performed in a JEOLJSM-35 CF electron microscope (Japan), with a secondary electron detector. Films were cryofractured by immersion in liquid nitrogen, mounted on bronze stubs and coated with a gold layer ($\sim 30 \text{ \AA}$), using an argon plasma metallizer (sputter coater PELCO 91000). Thus, film surfaces and their cross-sections were satisfactorily observed.

Fourier Transform Infrared (FTIR) spectra were obtained using a Thermo Nicolet Nexus spectrophotometer (United States). FTIR spectra were recorded at 4 cm^{-1} resolution over the $4000\text{--}400 \text{ cm}^{-1}$ range, using an accumulation of 100 scans and air as background.

2.5.2. Thermal behavior

Films thermal properties were studied by DSC employing the same equipment previously mentioned. All samples were heated from -140 to 100°C at $10^\circ\text{C min}^{-1}$ in order to obtain the glass transition temperature (T_g) from the second heating scanning.

2.5.3. Optical properties

Opacity and UV barrier capacity were estimated from absorbance spectrum (200–700 nm) recorded using a PG Instrument T60 UV-Visible spectrometer (England) spectrophotometer. Films were cut into rectangles and placed on the internal side of a

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