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Enhancement of thermoplastic starch final properties by blending with poly(ε-caprolactone)

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ABSTRACT

Final properties of two thermoplastic corn starch matrices were improved by adding poly(ε-caprolactone), PCL, at 2.5, 5, and 10% w/w. One of the thermoplastic starch matrices was processed using water and glycerol as plasticizers (S_G) and the other one was plasticized with a mixture of glycerol and sodium alginate (S_{GA}). Blends were suitably processed by melt mixing and further injected. Films obtained by thermo-compression were flexible and easy to handle. Microstructure studies (SEM and FTIR) revealed a nice distribution of PCL within both matrices and also a good starch–PCL compatibility, attributed to the lower polyester concentration. The crystalline character of PCL was the responsible of the increment in the degree of crystallinity of starch matrices, determined by XRD. Moreover, it was demonstrated by TGA that PCL incorporation did not affect the thermal stability of these starch-based materials. In addition, a shift of T_g values of both glycerol and starch-rich phases to lower values was determined by DSC and DMA tests, attributed to the PCL plasticizing action. Besides, PCL blocking effect to visible and UV radiations was evident by the incremented opacity and the UV-barrier capacity of the starch films. Finally, water vapor permeability and water solubility values were reduced by PCL incorporation.

1. Introduction

Starch is a biodegradable polymer of increasing interest due to its broad usefulness not only in food industry but also as packaging material. It can be obtained mainly from grains and tuberous roots of several botanical sources, representing an abundant and economic raw material. Especially, in Argentina corn starch production is higher than demand including internal consumption as well as exportation. In this sense, the development of value-added products based on corn starch offers a promising alternative to contribute to the national industry (Garzón, 2014; Souza & Andrade, 2001).

Structurally, starch is constituted by two macromolecules: a linear polysaccharide (amylose) and a branched one (amylopectin) responsible of granular aggregates (Wilhelm, Sierakowski, Souza, & Wypych, 2003). This semi-crystalline polymer when is processed under high temperature and shear stress, in the presence of plasticizers, becomes a thermoplastic material (Ma, Chang, Yu, & Stumborg, 2009; Mościcki et al., 2012). This procedure involves the loss of its crystalline character due to the disruption of starch granular structure. Thermoplastic starch materials present attractive properties not only for academic but also for industrial fields, mainly due to their biodegradability and the fact that they are obtained from a renewable low-cost feedstock.

Even though it is feasible to process starch using the technology designed for synthetic polymers, there are some drawbacks associated to the use of water as plasticizer. In this sense, presence of water induces the production of foamy-starch as a consequence of vapour bubbles formation, as well as, the stickiness of the polymer during its processing. Then, the use of sodium alginate as starch plasticizer arises as an alternative to overcome these problems (Córdoba, Cuéllar, González, & Medina, 2008; López et al., 2015). Alginate is a renewable polysaccharide extracted from brown algae with a similar chemical structure to starch, being both highly compatible (Lencina, Iatridi, Villar, & Tsitsilianis, 2014). It is important to highlight that employing alginate as plasticizer not only improves starch thermal processing but also does not compromise neither the biodegradable nor the renewable character of the final materials.

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Industrial applications of starch based materials are limited by the susceptibility of their final properties to certain environment changes. In addition, they present poor mechanical properties and water vapour barrier capacity, compared to synthetic polymers. Thus, blend formation by adding compatible materials represents a promising alternative to improve final properties reducing the sensitivity to environment parameters (humidity, temperature, radiation exposure, etc.), without affecting the biodegradable capacity of starch based materials. Within this context, the use of a hydrophobic biodegradable polymer such as poly(ε-caprolactone) (PCL) for starch-based blends would offer the possibility of enhancing mechanical behaviour and reducing water vapour permeability (Averous, Moro, Dole, & Fringant, 2000; Ortega-Toro, Contreras, Talens, & Chiralt, 2015).

PCL is an aliphatic polyester derived from a ring opening polymerization of the ε-caprolactone monomer, and has a relatively low melting point (~60 °C). Furthermore, its biodegradability and ability to form compatible blends with a wide range of other polymers explain the broad field of PCL applications (Campos et al., 2013; Chiono et al., 2009; De Campos & Martins Franchetti, 2005; Hubackova et al., 2013; Mano, Koniarova, & Reis, 2003; Woodruff & Hutmacher, 2010).

PCL/starch blends have been previously studied mainly based on PCL matrices with starch addition at low concentrations (Cai et al., 2014; Ortega-Toro et al., 2015; Matzinos, Tserki, Kontoyiannis, & Panayiotou, 2002; Li & Favis, 2010; Gáspár, Benko, Dogossy, Réczey, & Czigány, 2005). As it was aforementioned, the main attractive properties of starch lies on its biodegradability and low cost. So, any attempt to improve the final properties of starch based materials must not compromise these relevant positive aspects. In this sense, blends based on starch and PCL should gather the optimal cost–properties combination.

In order to face this challenge, in this work we propose as a novelty, an improvement of the final properties of starch based materials by adding low contents of PCL (up to 10% w/w). This research includes the development of starch-PCL blends using 2.5, 5, and 10% w/w polyester by melt mixing. Two different thermoplastic corn starch matrices were used: one of them was processed using water and glycerol as plasticizers, and the other one was plasticized with a mixture of glycerol and sodium alginate. Films of all formulations were obtained by thermo-compression and they were extensively characterized by studying their microstructure, thermal, and mechanical behaviour, as well as, barrier, solubility, and optical properties. From obtained results, it was evaluated the effect of PCL addition on final properties of starch matrices.

2. Materials and methods

2.1. Materials

In this work it was employed a 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 2×10^4 gmol^{-1} for amylose and 2×10^5–1×10^6 gmol^{-1} for amylopectin.

Analytical grade glycerol (Anedra, Argentine) and sodium alginate were used as plasticizers. Sodium alginate was purchased by Fluka (Switzerland, No. 71238), with a weight average molar mass of 231,500 gmol^{-1} and a mannuronic/guluronic ratio (M/G) of 0.79 obtained by ^{1}H NMR according to the literature (Gómez, Rinaudo, & Villar, 2007; Salomonsen, Jensen, Larsen, Steuernagel, & Engelsen, 2009).

Solvents and monomers used for the synthesis of PCL were purified according to conventional anionic polymerization standards (Bellas, Iatrou, & Hadjichristidis, 2000; Uhrig & Mays, 2005; Hadjichristidis, Iatrou, Pispas, & Pitsikalis, 2000). ε-Caprolactone monomer(ε-CL, Aldrich) was purified under vacuum prior to use. PCL was synthesized by anionic ring-opening polymerization of ε-CL using the addition product between n-butyllithium (n-Bu$^-$Li$^+$, Sigma Aldrich) and diphenylethylene (DPE, Sigma Aldrich) as initiator. Benzene (Dorwill) and glacial acetic acid (Cicarelli) were used as solvent and terminating agent, respectively. PCL polymerization was performed according to conditions reported in the literature (Balsamo, von Gyldenfeldt, & Stadler, 1996).

Chemical modification of PCL was carried out in solution with sodium hydroxide (NaOH, Cicarelli) with the aim of increasing the compatibility of this polyester with starch matrices. This method is a simple alkaline hydrolysis by immersion of PCL in an aqueous NaOH solution, (5% w/w, 1.25 M) during 4 h at room temperature. Finally, modified PCL was extensively washed with distilled water and vacuum dried at room temperature until constant weight (Oyane et al., 2005).

2.2. Thermoplastic starch

A mixture of native corn starch (S) with 35% w/w glycerol (G) was prepared and named S_G. Besides, a mixture containing 10% w/w sodium alginate (A) was also prepared and it was labeled S_{GA}. Components concentrations were expressed in g per $100 \times g$ of starch. Samples were melt-processed at 140 °C for 30 min employing an Atlas Laboratory Mixing (United States).

2.3. Blends based on thermoplastic starch with chemically modified PCL

Thermoplastic starches S_G and S_{GA} were triturated as fine powder and they were melt-reprocessed with PCL, using different concentrations (2.5, 5, and 10% w/w) of the polyester. Samples so obtained were called $S_GCL_{2.5}$, S_GCL_5, S_GCL_{10}, $S_{GA}CL_{2.5}$, $S_{GA}CL_5$ and $S_{GA}CL_{10}$. They were melt-mixed at 140 °C for 15 minutes employing the aforementioned equipment. After processing, blends were injected using a steel mold attached to the mixing device, obtaining circular samples of 25 mm diameter.

2.4. Film preparation

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

2.5. Film characterization

2.5.1. Structure

Films homogeneity and appearance were examined by Scanning Electronic Microscopy (SEM). Studies were performed in a JEOL JSM-35 CF electron microscope (Japan), with a secondary electron detector. Films were cryo-fractured by immersion in liquid nitrogen, mounted on bronze stubs and coated with a gold layer (~30 Å), using an argon plasma metallizer (sputter coater PELCO 91000).

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 4000–400 cm^{-1} range, using an accumulation of 100 scans and air as background.

Crystal structure identification of studied materials and their degree of crystallinity (C_D) were determined by X-ray diffraction. Films diffractograms were obtained in an X-ray diffractometer Philips PW1710 (Philips, Holland), provided with a tube, a copper anode, and a detector operating at45 kV and 30 mA within 2θ from

3 to 60°. C_D was calculated by the Eq. (1) proposed by Soliman and Furuta (2014):

$$C_D\% = \frac{A_c}{A_c + A_a} \times 100 \quad (1)$$

where A_c and A_a corresponds to the area of crystalline and amorphous phase, respectively.

2.5.2. Thermal degradation

This study was carried out in a thermogravimetric balance TA Instrument Discovery Series (United States). Samples were heated from 30 to 700 °C at 10 °C min^{-1}, under oxidative conditions. Curves of weight loss as a function of temperature were recorded and the maximum decomposition temperature of each component was obtained from first derivative curves.

2.5.3. Thermal properties

Films thermal properties were studied by DSC employing a Pyris 1 Perkin-Elmer® apparatus (United States). All samples were heated from −140 to 100 °C at 10 °C min^{-1} and kept at this temperature for 5 min to eliminate the thermal history. After cooling at 10 °C min^{-1}, samples were heated again from −140 to 100 °C at 10 °C min^{-1} in order to obtain the glass transition temperature (T_g) from the second heating scanning. An empty hermetic pan was used as reference.

On the other hand, T_g values were also determined in a dynamic-mechanical thermal equipment Q800 (TA Instruments, New Castle, USA) with a liquid nitrogen cooling system, using a clamp tension. Multi-frequency sweeps at a fixed amplitude from −100 to 100 °C at 2 °C/min were carried out. Storage (E') and loss (E'') moduli and tan δ curves as a function of temperature were recorded and analyzed using the software Universal Analysis 2000. T_g values were determined through the inflexion point of the E' curve, as well as, the maximum peak in both the E'' and tan δ curves (Psomiadou, Arvanitoyannis, & Yamamoto, 1996).

2.5.4. Optical properties

Opacity and UV barrier capacity were estimated from absorbance spectrum (200–700 nm) recorded using a PG Instrument T60 UV–vis spectrometer (England) spectrophotometer. Films were cut into rectangles and placed on the internal side of a quartz spectrophotometer cell. Film opacity (AU nm) was defined as the area under the curve (400–700 nm) according to ASTM D1003-00. Films color measurements were performed using a Hunterlab UltraScan XE (United States) colorimeter in the transmittance mode. Color parameters L, a, and b were recorded according to the Hunter scale, in at least ten randomly selected positions for each film sample. Color parameters range from $L = 0$ (black) to $L = 100$ (white), $-a$ (greenness) to $+a$ (redness), and $-b$ (blueness) to $+b$ (yellowness).

2.5.5. Water vapor permeability

Water vapor permeability (WVP) was determined according to ASTM F 1249-89 standard method using a PERMATRAN-W® Model 3/33 (Mocon Inc., United States). Film samples, previously conditioned at 25 °C and 60% RH were placed in a test cell which is divided into two chambers separated by the specimen. The inner chamber is filled with nitrogen (carrier gas) and the outer chamber with water vapor (test gas). Water molecules diffuse through the film to the inside chamber and water vapor transmission rate (WVTR) is registered. Measurements were carried out at 25 °C and films were subjected to a partial water vapor pressure gradient. Masked specimens with precut aluminum foil were used, leaving an uncovered film area of 5 cm^2. From WVTR values, WVP was calculated using equation 2.

$$\mathrm{WVP} = \frac{l\,\mathrm{WVTR}}{\Delta p} \quad (2)$$

where l corresponds to film thickness (μm) and Δp is the partial pressure difference across the film (Pa).

2.5.6. Water solubility

Circular pieces of films (~20 mg) placed into aluminum pans were conditioned in a desiccator containing $CaCl_2$ till constant weight. Then, samples were weighted before adding 5 mL of distilled water and kept at room temperature. These measurements correspond to the initial weight at time 0. Films water solubility was studied by determining their weight loss as a function of immersion time (6, 12, 24 and 48 h). Remaining film was collected by filtration and dried in a vacuum oven (30 °C) until constant weight. Normalized weight loss was calculated as follows:

$$\text{Normalized weight loss} = \frac{(\text{Initial dry weight} - \text{Final dry weight})}{\text{Initial dry weight}} \quad (3)$$

Samples were analyzed in triplicate.

2.6. Statistical analysis

Analysis of variance (ANOVA) was used to compare mean differences on samples properties. Besides, comparison of mean values was performed by Fisher's least significant difference test conducted at a significance level $p = 0.05$.

3. Results and discussion

All formulations were successfully melt-processed and injected. It is important to note that circular mold was fully completed by all molten blends, obtaining materials with homogeneous appearance. Besides, visual observation evidenced a loss of translucence with PCL concentration for both studied matrices. Concerning to film obtaining, studied formulations were easily thermo-compressed from samples without any previous conditioning. Resulting films were flexible and easy to handle, PCL incorporation improved films removal from the contention frames.

3.1. Structure

SEM micrographs and FTIR spectra of S_G and S_{GA}, as well as those blends containing 10% w/w PCL are shown in Fig. 1. As it was reported in a previous work (López et al., 2015), S_G and S_{GA} films presented regular thickness and cross-sections free of cracks, pores and phase separation, as a result of the well-processing (Fig. 1a and c). PCL presence in the blends was evidenced in SEM micrographs and also in FTIR spectra (Fig. 1b, d and e). Regarding to PCL distribution in both matrices, images revealed the presence of reduced polyester aggregates in S_{GA} blends (Fig. 1d). These small agglomerates could be the responsible of the slight irregular surface fracture observed for S_{GA} blends. Otherwise, PCL pull out effect was not detected neither in S_GCL nor in S_{GA}CL materials. Even though several authors reported immiscibility between starch and PCL (Averous et al., 2000; Campos et al., 2013; Ying, Pi-xin, Kun, Hui-yong, & Li-song, 2010), this phenomenon was not evidenced in the studied formulations. This result may be due to the low content of polyester added to the plasticized starch matrices as well as the improved starch–PCL compatibility achieved by the polyester's chemical modification.

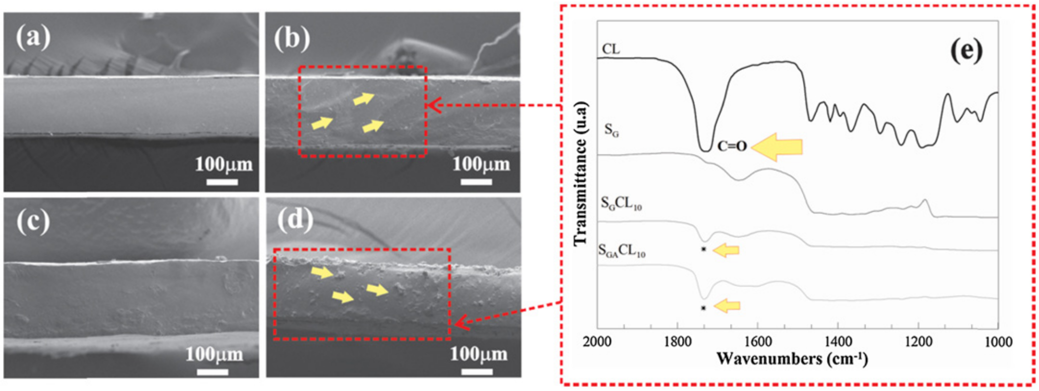


Fig. 1. SEM micrographs of thermoplastic starch matrices: (a) S_G and (c) S_{GA}, as well as, blends containing10% w/w PCL: (b) S_GCL_{10} and (d) $S_{GA}CL_{10}$. (e) FTIR spectra of ε-caprolactone (CL), S_G, S_GCL_{10} and $S_{GA}CL_{10}$.

FTIR analysis allowed to corroborate the presence of PCL in the blends, by detecting the characteristic band of stretching vibration of carbonyl groups at ~1724 cm^{-1} (Fig. 1e) (Ninago, Satti, Ciolino, & Villar, 2013). Even more, a significant shift to higher wavenumbers (~1734 cm^{-1}) of this signal occurred for blends containing 10% w/w PCL. In this sense, Cai et al. (2014) reported similar results for blends based on PCL with thermoplastic corn starch. These authors attributed the effect to a chemical interaction between carbonyl groups of PCL with functional groups of the starch matrix. Similarly, Matzinos et al. (2002) gave analogous arguments about starch–PCL compatibility. This interaction is in accordance with SEM results, concerning to the absence of the pull out effect of PCL, as well as, the non-observed immiscibility between PCL and starch plasticized matrices.

Fig. 2 shows XRD spectra of both matrices, PCL and the blends containing the highest PCL concentration studied. Crystalline structures of S_G and S_{GA} are in accordance with a V-type hydrated (V_h) structure, evidenced by the presence of two sharp peaks at 13.5° and 20.9° (Castillo et al., 2013; Lee & Shin, 2007; Shi et al., 2006). PCL spectrum displayed sharp and strong crystalline peaks at ~21.70° and ~24.07°. The patterns of studied blends were similar to the corresponding matrices, showing the aforementioned characteristic peaks related to PCL diffraction. It is important to note that intensity of PCL peaks in the blends increases with an increase in PCL concentration. Regarding the degree of crystallinity of blends materials, they presented higher values than the corresponding matrices (Fig. 2). This increment was mainly attributed to the PCL crystalline character.

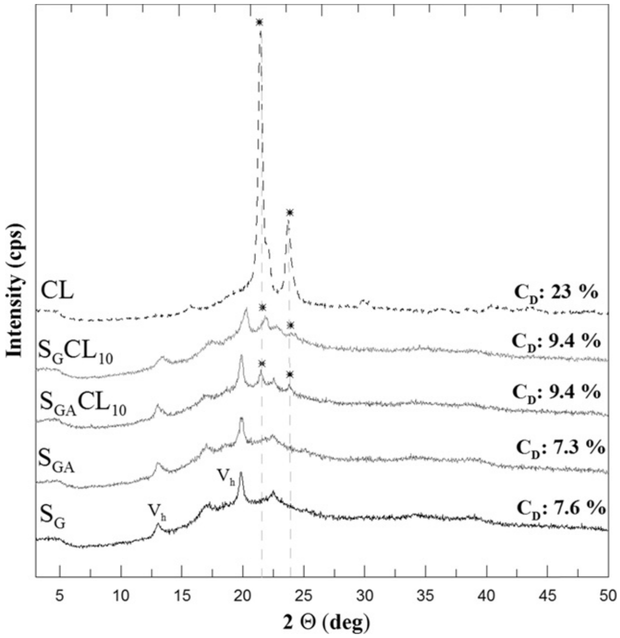


Fig. 2. XRD spectra and degree of crystallinity of thermoplastic starch matrices: S_G and S_{GA}, as well as, blends containing10% w/w PCL: S_GCL_{10} and $S_{GA}CL_{10}$.

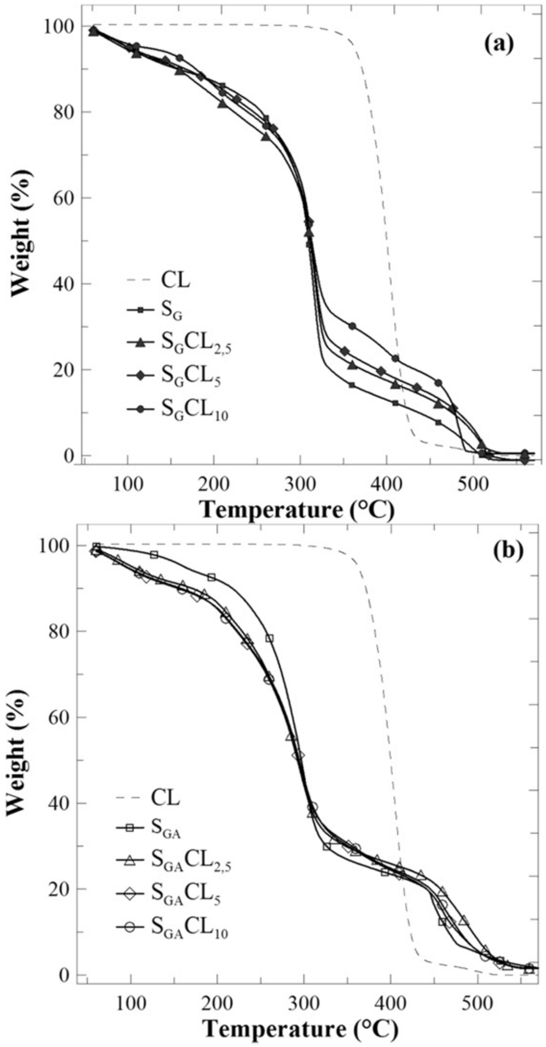


Fig. 3. TGA curves of thermoplastic starch matrices: (a) S_G and (b) S_{GA}, as well as, their corresponding blends with 2.5, 5, and 10% w/w PCL.

3.2. *Thermal degradation*

Thermal stability of polymeric systems is usually studied by thermogravimetric analysis, TGA (Mano et al., 2003). Fig. 3 shows TGA curves corresponding to PCL, S_G, S_{GA} and blends with 2.5, 5 and 10% w/w PCL. As it was expected, S_G and S_{GA} presented mainly three typical weight loss steps. The first one is associated to water and glycerol evaporation, the second one corresponded to starch and alginate degradation and the final event is well known as "glowing combustion" (López et al., 2015; Lencina et al., 2014). Blends containing PCL showed the thermal events corresponding to starch matrices plus PCL decomposition (~400 °C). Previously, other authors have reported similar thermal degradation behavior for blends based on PCL containing different thermoplastic starches (Cai et al., 2014; Hubackova et al., 2013). As it can be clearly observed, polyester incorporation did not affect the thermal stability of these polysaccharide matrices. PCL presence in S_GCL blends was reflected in the temperature range where its degradation takes place. However, in the case of S_{GA}CL blends, the differences among the curves in the region of PCL degradation were not so evident.

3.3. *Thermal properties*

In order to evaluate the influence of PCL incorporation to thermal properties of the studied thermoplastic starch matrices and blends, two complementary techniques were employed: DSC and DMA. The characteristic behavior of the studied blends is shown in Fig. 4 corresponding to DSC thermograms and DMA curves of matrices and blends with 5% w/w PCL. Moreover, thermal parameters of all formulations are summarized in the table included in this figure. Taking into account that these materials are constituted by two phases, one of them rich in starch and the other mainly based on glycerol, it was expected the thermal transition associated to both domains (Liu, Xie, Yu, Chen, & Li, 2009; Pérez, Sandoval, Cova, & Müller, 2014). In this sense, T_g corresponding to the glycerol-rich phase (T_{g1}) and PCL melting point were detected by DSC (Fig. 4a). Meanwhile, DMA supplied T_g values of both glycerol (T_{g1}) and starch (T_{g2}) phases (Fig. 4b). DSC curves revealed that PCL addition slightly shifted T_{g1} to lower values in both matrices (<10%), as a consequence of its plasticizing action. On the other hand, PCL presence was evidenced by detecting its characteristic melting point at around 58 °C (Ninago et al., 2013), being the peak area in accordance to the polyester content in the blends (Fig. 4a).

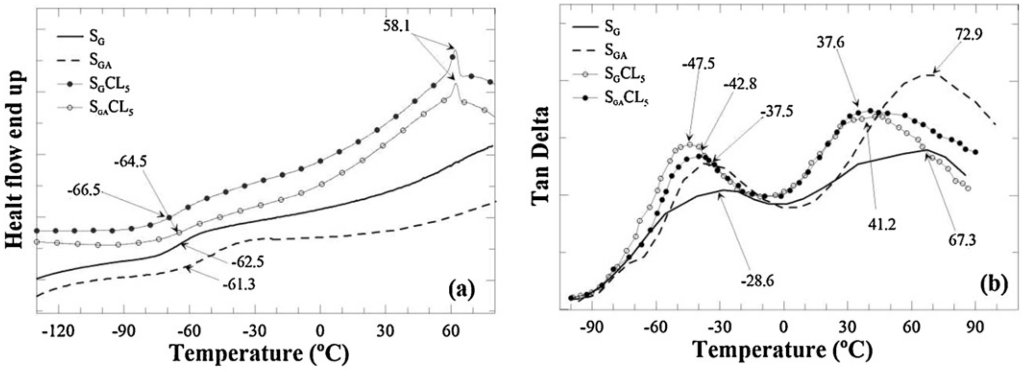
Even though DMA results of T_{g1} were not the same from those obtained by DSC, the plasticizing effect of PCL was also evidenced (Fig. 4b). However, the shift in T_{g1} values detected by DMA was much more pronounced than the corresponding T_g observed by DSC. For S_G and S_{GA}, PCL addition up to 5% w/w considerably reduced glass transitions temperatures of both phases (T_{g1}, T_{g2}). Nevertheless, the use of 10% w/w PCL did not produce the expected reduction in T_g values, being similar to those corresponding to blends with 5% w/w PCL.

Concerning to the plasticizing action of PCL, Shi, Cooper, and Maric (2011) stressed that this polyester is considered a green plasticizer due to several features such as: its biodegradable and innocuous character, its feasibility to be synthesized at large-scale with a relatively low cost and its low glass transition temperature (~60 °C), providing to PCL based materials high flexibility at low temperatures.

Since T_{g2} restricts the final properties of these materials, a reduction in the value of this thermal property may represent an improvement in their versatility, widening the range of potential applications. In this sense, Ortega-Toro, Jiménez, Talens, and Chiralt (2014) concluded that the decrease in T_g values lead to higher blends flowability, as it was observed during injection and thermal compression.

3.4. *Optical properties*

Other relevant issue which determines the final usefulness of polymer materials is related to their optical properties. Thus, the effect of PCL addition to both starch matrices on their opacity



Film formulation	T_{g1} by DSC (° C)	T_{g1} by DMA (° C)	T_{g2} by DMA (° C)
SG	-62.5	-28.6	67.3
$SGPCL_{2.5}$	-63.8	-33.1	58.1
$SGPCL_5$	-66.5	-42.8	37.6
$SGPCL_{10}$	-66.8	-42.5	37.4
SGA	-61.3	-37.5	72.9
$SGAPCL_{2.5}$	-61.8	-40.5	66.7
$SGAPCL_5$	-64.5	-47.5	41.2
$SGAPCL_{10}$	-66.5	-47.2	40.9

T_{g1} : Glass transition temperature of glycerol-rich phase.
T_{g2} : Glass transition temperature of starch-rich phase.

Fig. 4. (a) DSC curves and (b) DMA spectra of thermoplastic starch matrices: S_G and S_{GA}, as well as, their blends with 5% w/w PCL: S_GCL_5 and $S_{GA}CL_5$. Table summarizes T_g values of S_G and S_{GA}, as well as, blends with 2.5, 5, and 10% w/w PCL.

and UV absorption capacity is shown in Fig. 5. An increasing tendency was observed with PCL concentration for S_G and S_{GA} opacity (Fig. 5a). Particularly, for S_GCL blends, this increment was observed above 5% w/w PCL, almost duplicating the initial value with the highest polyester concentration. On the other hand, for S_{GA}CL samples, with the lowest PLC concentration the opacity value was 2.5 times higher than that one corresponding to S_{GA}, reaching an increment of around 4 times for both, 5 and 10% w/w PCL. Opacity development is mainly attributed to the crystalline character of the polyester incorporated to the matrices, as it was evidenced in the values of degree of crystallinity obtained from XRD spectra. Regarding to this effect, Cai et al. (2014) reported the opposite tendency, showing a progressively less crystalline character when thermoplastic starch is added to a PCL matrix.

Results obtained for UV absorption measurements showed that PCL presence lead to an increase of this optical property for both matrices. For S_G and S_{GA} a noticeable increment of ∼30% and ∼40% was observed when 10% w/w PCL was added to each formulation. This result could be attributed to the UV absorption capacity of PCL as it was reported by De Campos and Martins Franchetti (2005). The increment in both optical properties by PCL addition could be associated to a good distribution of the polyester in both matrices, inducing a blocking effect that reduces the transmission of UV–vis radiation across the studied films. On the other hand, the higher irregular structure of S_{GA}CL samples, observed by SEM, could be the responsible of the major dispersion of radiation conducing to a more marked increment of both optical properties compared to S_GCL blends.

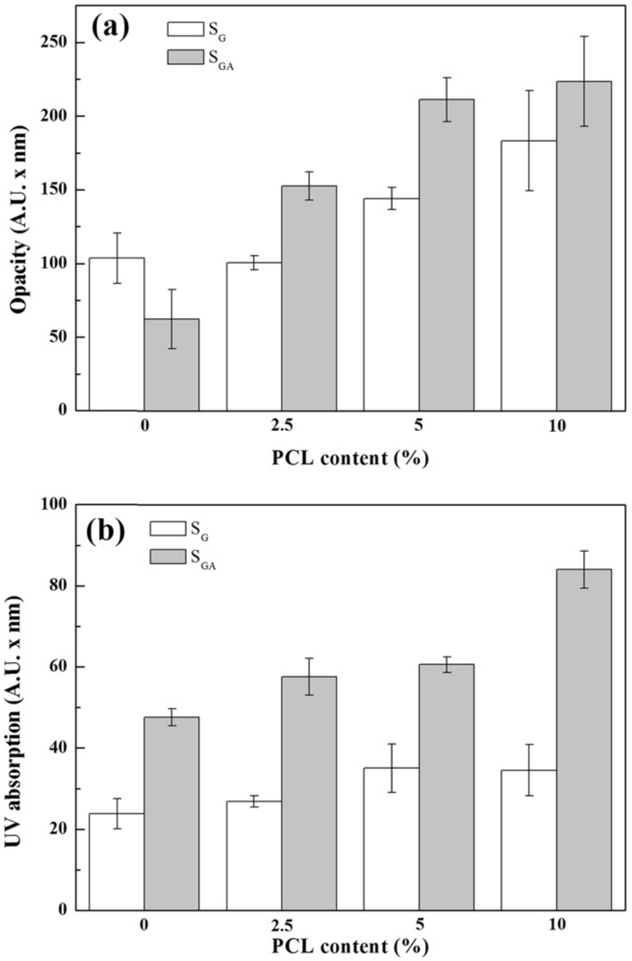


Fig. 5. Effect of PCL addition (2.5, 5, and 10% w/w) on opacity (a) and UV barrier capacity (b) of films based on thermoplastic starch (S_G and S_{GA}).

The effect of PCL addition on luminosity (*L*) and chromaticity parameters (*a*, *b*) of S_G and S_{GA} is shown in Fig. 6. As it can be observed in Fig. 6a, luminosity of S_G slightly decreased with PCL content; meanwhile for S_{GA} matrix, a more pronounced *L* decrease was detected with the highest polyester concentration. In Fig. 6b no significant changes by PCL addition were evidenced neither in *a* nor *b* parameters in any of the studied samples. However, values of parameter *b* for S_{GA} based materials were higher than those of S_G ones, attributed to the yellowness of alginate (López et al., 2015).

3.5. Water vapor permeability

Fig. 7 shows the effect of PCL addition to the WVP of S_G and S_{GA} matrices. As it can be observed, the presence of the polyester in S_G films lead to a significant reduction in this barrier property, achieving a reduction of 25% for blends with the highest PCL concentration. This result could be attributed to the hydrophobic character of the polyester, representing an obstacle to water vapor transmission across the film. On the other hand, S_{GA} films presented a significant lower WVP value (1.4 times) than S_G matrices. This result could be mainly attributed to two factors. First, the

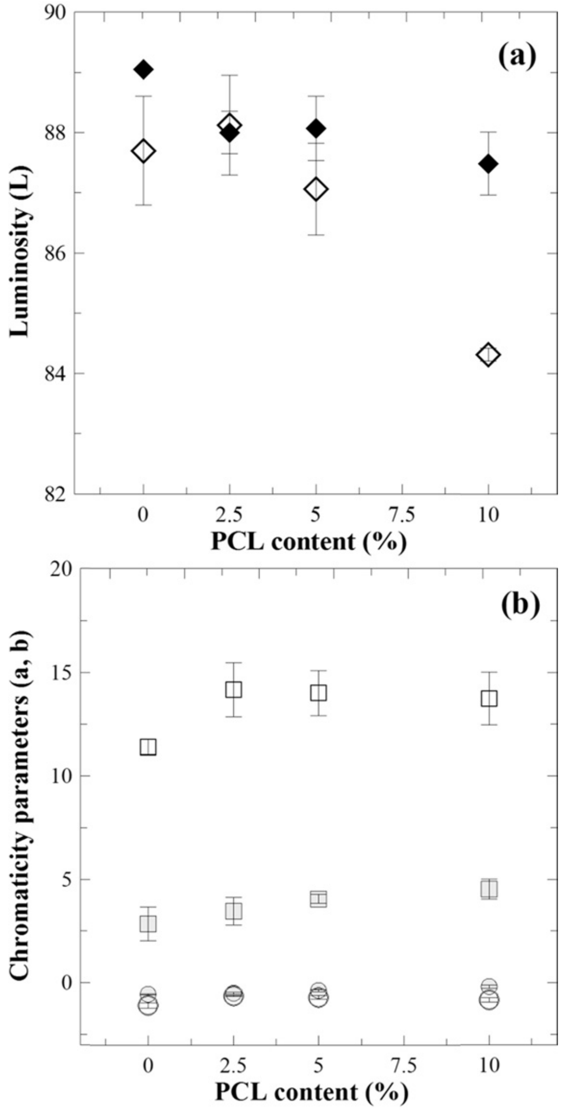


Fig. 6. Effect of PCL addition (2.5, 5, and 10% w/w) on luminosity (a) and chromaticity parameters (b) of films based on thermoplastic starch (S_G and S_{GA}). Symbols: ♦ L_1 (S_GCL), ◊ L_2 (S_{GA}CL), ● a_1 (S_GCL), ○ a_2 (S_{GA}CL), □ b_1 (S_GCL), ■ b_2 (S_{GA}CL).

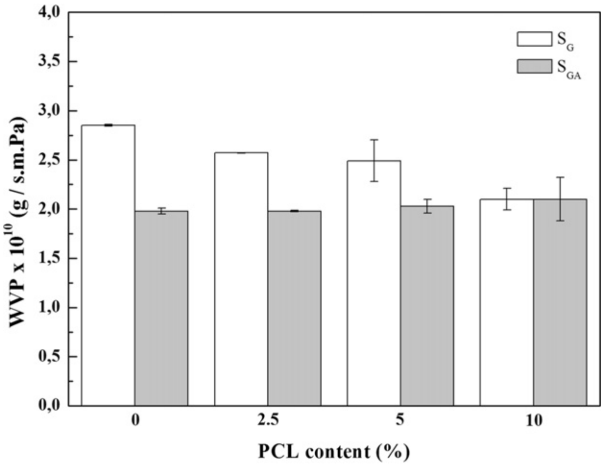


Fig. 7. Effect of PCL addition (2.5, 5, and 10% w/w) on water vapor permeability (WVP) of films based on thermoplastic starch (S_G and S_{GA}).

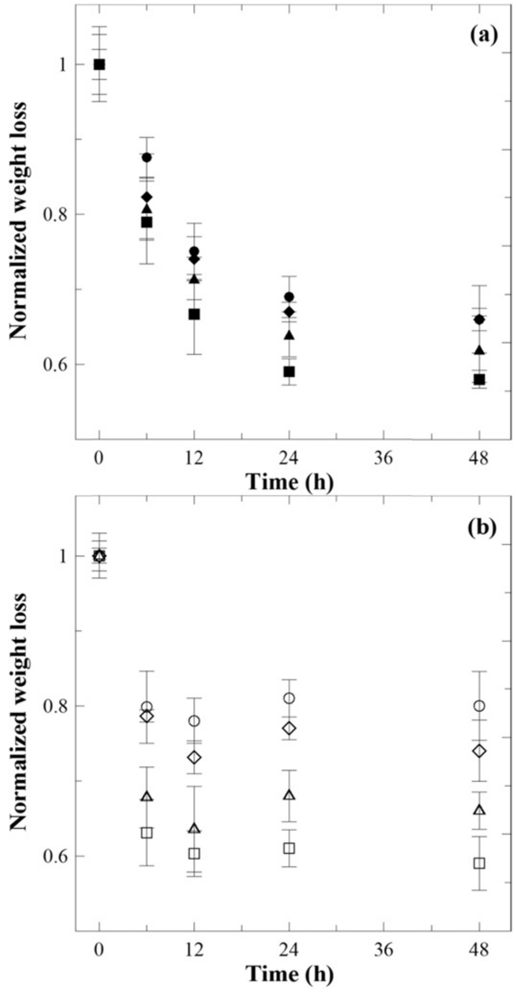


Fig. 8. Normalized weight loss as a function of water immersion time of thermoplastic starch matrices: (a) S_G and (b) S_{GA}, as well as, their corresponding blends with 2.5, 5, and 10% w/w PCL. Symbols: ■ (S_G), ▲ ($S_GCL_{2.5}$), ♦ (S_GCL_5), ● (S_GCL_{10}), □ (S_{GA}), △ ($S_{GA}CL_{2.5}$), □ ($S_{GA}CL_5$), ○ ($S_{GA}CL_{10}$).

fact that the alginate used in this study has a relatively low mannuronic/guluronic, *M*/*G* ratio (0.79) could be the responsible that S_{GA} matrices showed low WVP values. In this sense, Olivas and Barbosa-Cánovas (2008) stressed that alginate films with a high proportion of G proved to be good moisture barriers. These authors reported that films with a 0.45 *M*/*G* ratio showed WVPs two or three times lower than 1.5 *M*/*G* films. On the other hand, the amount of water vapor which crosses S_{GA} matrices was reduced due to the high water absorption and retention capacity of the sodium alginate (Davidovich-Pinhas & Bianco-Peled, 2010). As it can be observed in Fig. 7, PCL addition did not affect WVP values of S_{GA} matrices. The heterogeneous PCL distribution and the presence of some agglomerates in S_{GA} films, evidenced by SEM, could be the responsible of the no effect of polyester addition on WVP values.

3.6. *Water solubility*

Taking into account that starch based materials are highly susceptible to humidity, their water solubility it is an important parameter which limits the final applications. Within this context, PCL hydrophobic character may represent a good alternative to reduce water sensitivity of starch matrices. Results of water solubility assays are presented in Fig. 8.

As it was expected, a decrease of samples weight was achieved with increasing immersion time. Even more, for all samples, the major weight loss was reached within the first 12 h and then an asymptotic tendency was observed. The main effect of PCL addition to starch matrices was the reduction of their weight loss, being more marked with the highest polyester concentration. Moreover, S_{GA}CL blends resulted less hydrophilic than S_GCL ones. In this sense, after 48 h of immersion, for S_G and S_{GA} the addition of 10% w/w PCL reduced 17% and 33% their weight loss, respectively.

4. Conclusions

In this work, the addition of PCL (2.5, 5.0 and 10.0% w/w) to two thermoplastic corn starch matrices (SG and SGA) was studied. All formulations were well processed by melt-mixing and able to be injected, achieving homogeneous materials. Besides, flexible and manipulable films were obtained by thermo-compression, without any previous conditioning. SEM micrograph evidenced a homogenous PCL distribution in both matrices. The slight irregular surface fracture observed for S_{GA} blends was attributed to the occurrence of small polyester aggregates. A well matrix–PCL adhesion was corroborated by the absence of PCL pull out phenomenon. In addition, the compatibility between starch and polyester was also evidenced by FTIR due to a significant shift for the PCL carbonyl signal to higher wavenumbers. XRD analysis revealed that PCL incorporation did not modify the crystalline structure of starch matrices; however, an increment in the degree of crystallinity was detected. Concerning to thermal degradation, the stability of these starch matrices was not affected by PCL presence.

DSC and DMA results evidenced the plasticizing effect of PCL by a shifting of T_g values of both glycerol and starch-rich phases to lower values in both matrices. It is important to note that a reduction in T_g of starch rich-phase implies an enhancement of the blends flowability, facilitating their processability. Regarding to PCL effect on opacity and UV absorption capacity of S_G and S_{GA} matrices, it was detected an increment in both properties induced by polyester blocking effect. On the other hand, PCL incorporation to starch matrices improved their water vapor barrier capacity, since WVP values of blends were significantly lower than the corresponding to S_G and S_{GA}. Even though, water solubility of both starch matrices was reduced by PCL addition, S_{GA}CL blends showed lower values of weight loss than S_GCL ones. In conclusion, PCL addition to thermoplastic starch matrices, at low concentrations, favored their processability, as well as, improved their final properties (mainly water vapor barrier capacity and water solubility), without compromising their thermal stability.

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