



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 $^1\text{H NMR}$ 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

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).

2.6. 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

Formulations assayed were able to be melt-processed and successfully injected. Obtained probes were translucent and presented a homogenous appearance.

3.1. Probes processing optimizing

Biopolymer processing by industrial methods such as extrusion, injection molding, thermo-compression, calendaring and film blowing is conditioned by the melt rheological behavior and thermal transitions which determine optimal operational conditions, as well as, properties of the final materials. A well-understanding of how different plasticizers and processing parameters affect thermal behavior and viscoelastic properties of thermoplastic starch are relevant features in order to convert this biopolymer into materials with useful and desirable properties.

Thermogravimetric measurements were used to evaluate degradation processes of the obtained materials as a function of temperature. Thermograms of pure alginate, corn starch and glycerol were recorded (figures not shown) and obtained results are in accordance with those reported by several authors (Gómez-Siurana et al., 2013; Işıkkan & Küçükbalcı, 2012; Tonelli, Campos, Mattoso, Franchetti, & Marconcini, 2010). Both polysaccharides presented an initial weight loss, corresponding to samples dehydration, up to 150 °C. According to Wilhelm, Sierakowski, Souza, and Wypych (2003), high humidity content (~15%) of these kind of samples is the

result of the easily diffusion of water molecules within the matrix, through hydrogen bonds with hydroxyl groups of glucosyl units.

Corn starch undergo thermal decomposition in two main steps at around 200–370 °C and 450–550 °C (Perotti et al., 2014). First step is associated to the amylose and amylopectin degradation and the second one is related to "glowing combustion" that occurs in the presence of oxygen, as it was reported by Liu et al. (2013). These authors stressed that during this thermal process, simple gases such as CO, CO₂, and H₂O are released due to reactions of carbonaceous residues with oxygen. Alginate thermogram showed an important mass decrease, approximately 45%, in the temperature range between 200 °C and 300 °C, as a first thermal degradation step. Then, a second weight loss at around 590 °C (~15%) was observed, and finally about 20% of the initial mass remained as a residue (Lencina, Iatridi, Villar, & Tsitsilianis, 2014). The fact that not all alginate initial weight was lost, could be related to the sodium content, as well as, to others inorganic compounds as a consequence of the extraction process from natural sources. Concerning to pure glycerol, its thermogram showed a single weight loss step, at around 245 °C, mainly attributed to the evaporation process (Gómez-Siurana et al., 2013).

TGA and first derivative curves of SG and samples processed with water addition are shown in Fig. 1. Formulations containing water as plasticizer presented the same trend as for SG concerning the thermal degradation steps (Fig. 1a). Two first weight loss events were associated to water evaporation and glycerol leakage, which were not involved in the thermoplastic starch matrix. On the other hand, a slightly shift (<2%) toward higher temperatures was observed for both starch degradation steps located around 320 °C and 500 °C, as it can be appreciated from the first derivatives curves (Fig. 1b and c). Fig. 2 presents TGA and first derivative curves of SG and SGA5/10/15 formulations. Similarly, in SGA thermograms, events related to water and glycerol evaporation, as well as, both starch degradation processes were detected (Fig. 2a). A decrease of ~5% in the temperature associated to first starch degradation was evidenced (Fig. 2b). Particularly, changes observed in the loss weight located between 430 and 550 °C (Fig. 2c) could be attributed to a synergic effect between starch glowing combustion and alginate thermal decomposition.

Thermoplastics materials are able to undergo a reversible process, becoming pliable or moldable above a specific temperature (melting point) and solid upon cooling. Thus, determination of parameters associated to this thermal transition was carried out in order to establish processing temperatures. In this sense, DSC

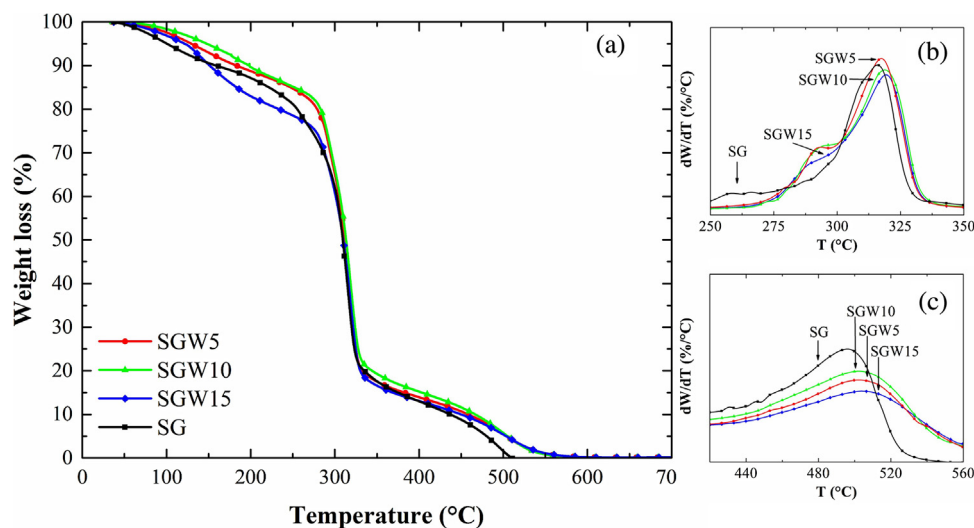


Fig. 1. (a) TGA curves of thermoplastic starch (SG) and SG with 5, 10 and 15% (w/w) water (SGW), (b, c) first derivative TGA curves.

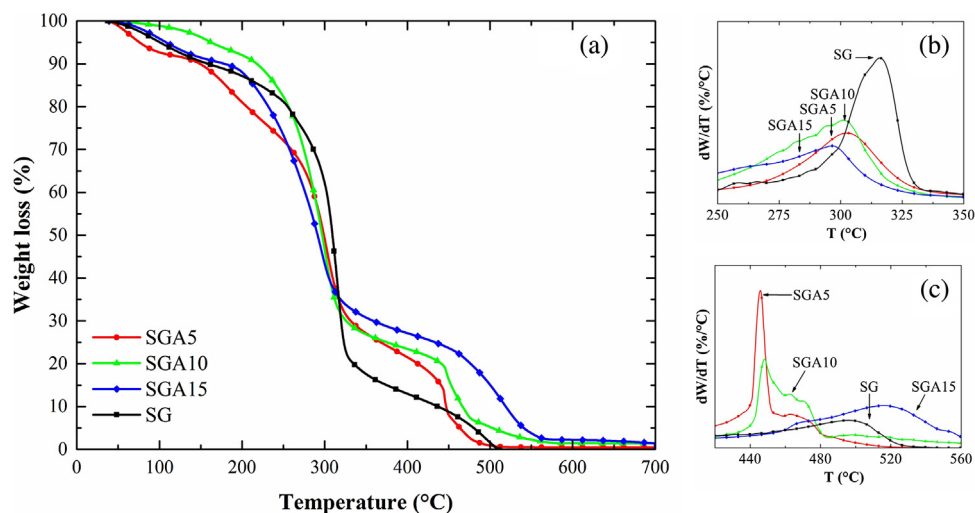


Fig. 2. (a) TGA curves of thermoplastic starch (SG) and SG with 5, 10 and 15% (w/w) sodium alginate (SGA), (b, c) first derivative TGA curves.

assays were performed; showing, for all tested materials an unique endothermic thermal transition related to crystallites starch melting. Estimated parameters from DSC curves are summarized in Table 1. Neither water nor alginate addition led to a significant change in the onset temperature (T_o). Regarding to the peak temperature (T_p), a slight displacement toward higher values was observed. TGA and DSC results suggested that the temperature range of SG processing was not affected by water and alginate addition.

3.1.1. Rheological studies

With the purpose of reducing water evaporation during rheological assays, samples outer edge were coated with silicon grease, as it was previously recommend by Della Valle, Buleon, Carreau, Lavoie, and Vergnes (1998). Before oscillatory assays, linear viscoelastic region was determined by a strain sweep at a fixed frequency of 10 Hz. All studied samples evidenced a typical behavior of viscoelastic materials when storage (G') and loss (G'') modulus remains constant in the linear range and decreases above a critical shear strain (Ghanbarzadeh, Oromiehie, Musavi, Razmi, & Milani, 2006). Then, a dynamic frequency sweep was carried out by applying oscillation amplitude within linear region over a frequency range between 0.1 and 10 Hz. Fig. 3 evidenced the viscoelastic behavior of all studied samples, showing the evolution of G' and G'' as a function of frequency at constant strain amplitude of 3%. Concerning to SG, G' curve resulted larger than G'' one, and both modulus were frequency independent within the evaluated range. This behavior could be explained by a semicrystalline structure as a consequence of the presence of single-helical amylose structures formed after processing. Crystallites are assumed to

Table 1

Thermal properties of thermoplastic starch (SG) and SG with 5, 10 and 15% (w/w) water (SGW) and sodium alginate (SGA).

Sample	T_{g1}^a (°C)	T_o^b (°C)	T_p^c (°C)
SG	-39.1 ± 3	62.8 ± 4.9	115.7 ± 6
SGA5	-42.5 ± 2	63.9 ± 2.0	113.5 ± 9
SGA10	-48.4 ± 4	63.5 ± 2.9	131.7 ± 8
SGA15	-47.9 ± 4	63.1 ± 3.1	124.2 ± 7
SGW5	-49.6 ± 3	63.8 ± 1.8	128.1 ± 13
SGW10	-48.9 ± 4	63.5 ± 2.0	132.7 ± 6
SGW15	-47.1 ± 2	63.9 ± 6	130.3 ± 5

^a Glass transition temperature of glycerol rich-phase (T_{g1}).

^b Onset temperature (T_o).

^c Peak point (T_p).

participate in the formation of an elastic network, embedded in a viscoelastic amorphous phase (Xie, Halley, & Avérous, 2012). The fact that G' was almost frequency independent is an indicative of a transition from liquid- to solid-like viscoelastic behavior and this

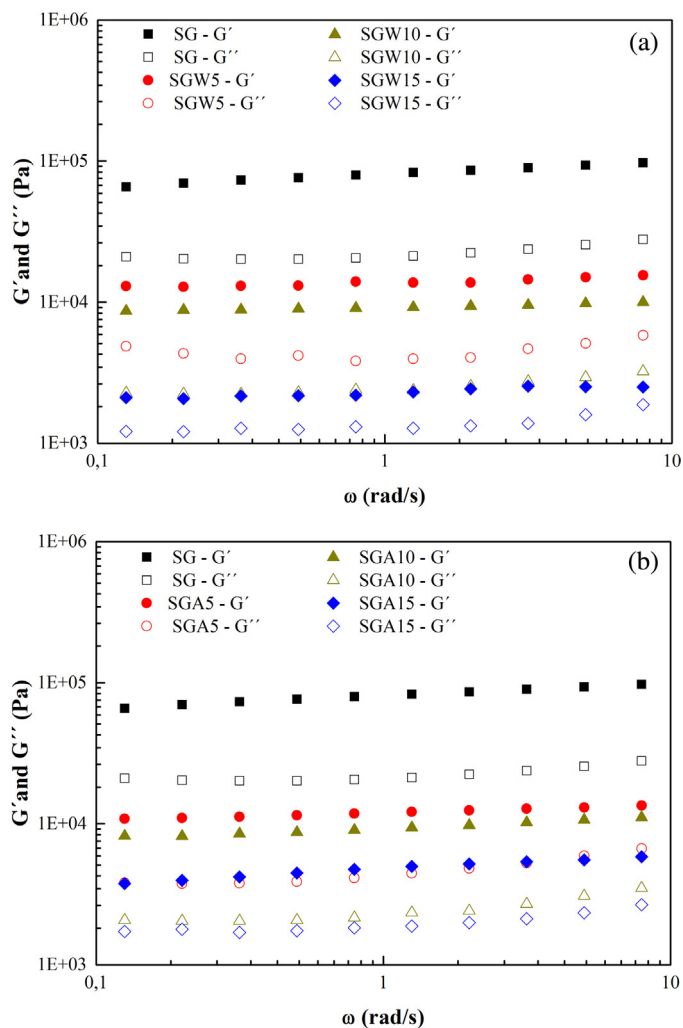


Fig. 3. Storage (G') and loss (G'') modulus as a function of frequency of thermoplastic starch (SG) and SG with 5, 10 and 15% (w/w) (a) water (SGW) and (b) sodium alginate (SGA).

result could be attributed to the restricted long-range motion of starch molecules (Du et al., 2004). Similar results were reported by Rodríguez-González, Ramsay, and Favis (2004) for thermoplastic starch with high glycerol content. Rheological curves of SG samples containing water and alginate presented a similar behavior than those corresponding to SG (Fig. 3a and b). However, a reduction of G' and G'' values of SG with increasing both plasticizers concentration was evidenced. These results are attributed to the increased biopolymer chain mobility and lubrication. It is expected that G' and G'' reduction by alginate and water addition will be in accordance with the effect of these additives on glass-transition temperature of SG. According to Krochta (2002), plasticizers are used to depress the glass-transition temperature of the polymer and to decrease viscoelastic modulus. Plasticizers presence allows separating biopolymer chains from each other, facilitating their movement and increasing matrix flexibility (Lawton, 2004). Comparing both plasticizers, water at 15% (w/w) had the highest plasticizing effect on SG matrix since its incorporation led a greater reduction of G' values than alginate addition at the same concentration.

3.2. Films characterization

3.2.1. Structure

SEM micrographs corresponding to cryofractured surfaces of films based on SG, SGW15 and SGA15 are shown in Fig. 4. Thermo-compression method allowed obtaining films with nearly constant thickness ($132.4 \pm 0.9 \mu\text{m}$), as it can be observed in Fig. 4a for SG films. Films evidenced homogeneous and smooth surfaces, without starch granules. Souza and Andrade (2001) also reported the absence of starch granules within thermoplastic corn starch matrix, mainly attributed to the efficiency of the melt-mixing process. Particularly, in the case of films plasticized with alginate, our results were not in agreement with those reported by Souza and Andrade (2001) since they reported the presence of several undesirable cavities within films structure. On the other hand, it was not detected phase separation neither plasticizer migration from the matrix to the film surfaces. Similar results were reported by López,

Lecot, Zaritzky, and García (2011) for starch films plasticized with glycerol obtained by extrusion and blowing, and by Castillo et al. (2013) for composite films based on thermoplastic corn starch and talc nanoparticles. Concerning to the films surfaces, water and alginate addition allowed obtaining materials with smoother appearance than SG, being this effect more marked for films containing water (Fig. 4b–d). Besides, films containing 15% (w/w) alginate presented higher thickness, $219.9 \pm 5.8 \mu\text{m}$, than SG ones, while addition of water at the same concentration allowed to obtain films with thickness of $165.7 \pm 2.3 \mu\text{m}$. This more pronounced increment by alginate addition could be attributed to the structural modifications caused by plasticizer incorporation (Fig. 4d). In this sense, Zhang and Han (2006) reported that films thickness variation due to plasticizers incorporation depends on its molecular weight. In the particular case of water addition, the effect on SG films thickness was less important, and it could be a consequence of the high humidity absorption by the final material (Fig. 4c). This result is in accordance with the sticky visual appearance of SGW15 films, as well as, their difficulty to handle.

FTIR spectra of SG films and those with 5, 10 and 15% (w/w) alginate are shown in Fig. 5. SG spectrum showed characteristic absorptions bands associated with C–O vibration bonds at 920, 985, 1026, 1074 and 1148 cm^{-1} . Moreover, water content was evidenced by the presence of an acute band at 1640 cm^{-1} . Around 2930 cm^{-1} bands corresponding to symmetric and asymmetric vibration of C–H from CH_2 groups were detected. Besides, a broad band at 3385 cm^{-1} was also detected and it is associated to –OH groups of starch and glycerol structures (Castillo et al., 2013; Yang et al., 2010). Concerning to SGA films, spectra showed typical bands corresponding, not only to starch and glycerol but also sodium alginate. Thus, typical signals at 1690 and 1413 cm^{-1} , attributed to asymmetric and symmetric stretching of alginate carboxyl groups (COO^-) were found. In addition, symmetric and asymmetric vibration bands of C–O–C of polysaccharide rings were observed in the $1200\text{--}1050 \text{ cm}^{-1}$ range (Lencina et al., 2014). Alginate content increase led to a slight shift to higher wavenumbers of band located at 1411 cm^{-1} . These results may be a consequence of bond strength weakening, as well as, stretching frequency reduction (Lencina

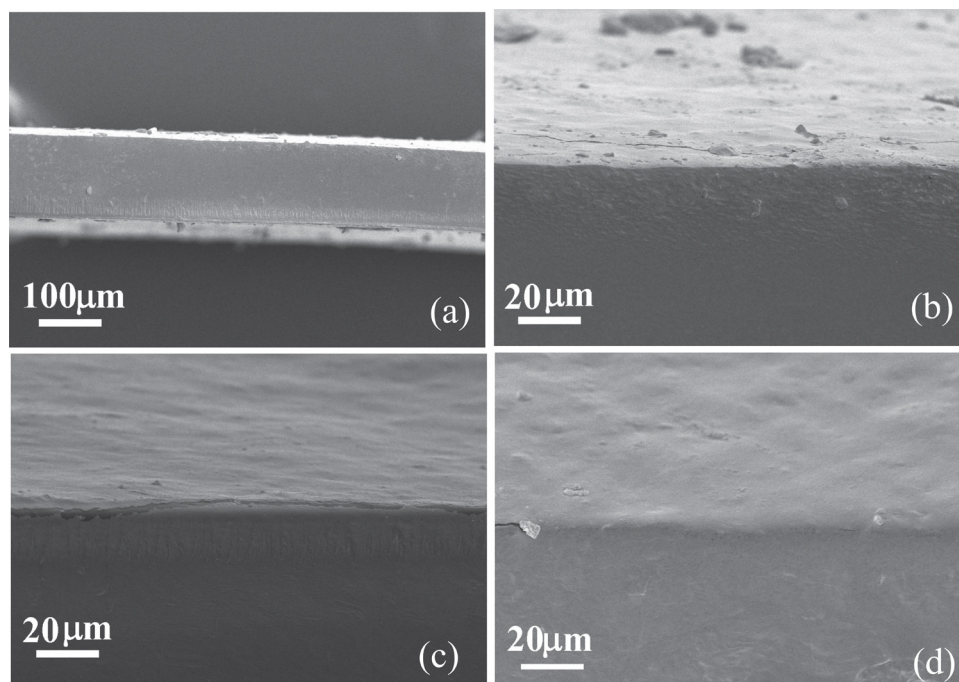


Fig. 4. SEM images of: (a) thermoplastic starch-SG (400 \times), (b) SG (2000 \times), (c) SG with 15% (w/w) water (2000 \times) and (d) SG with 15% (w/w) sodium alginate (2000 \times).

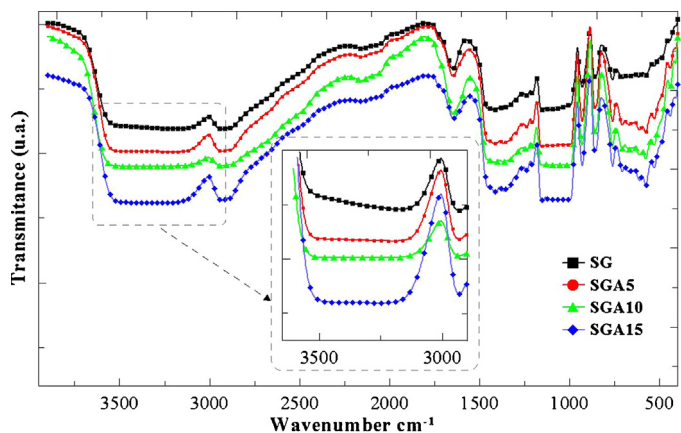


Fig. 5. FTIR spectra of thermoplastic starch (SG) and SG with 5, 10 and 15% (w/w) of sodium alginate (SGA).

et al., 2014). Moreover, absorption band centered at 3300 cm^{-1} was broadened with alginate content. In this sense, Siddaramaiah Swamy, Ramaraj, and Hee Lee (2008) suggested that the broadening region is due to an interaction between alginate (COO^-) and starch ($-\text{OH}$) groups, through hydrogen bonds.

3.2.2. Thermal behavior

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. Native starch is not considered as a thermoplastic polymer mainly due to its chemical structure, and its glass transition temperature (T_g) is located above the decomposition temperature (Souza & Andrade, 2001). In order to transform starch into a thermoplastic material, it is required the disruption of starch granules and their constitutive crystallites into a flowable material (Shanks & Kong, 2012). Granular disruption takes place in the presence of a plasticizer, processed under high shear stress and temperature. In this sense, starch is commonly processed using water and others plasticizers, such as polyalcohols. It is well known that plasticizer presence decreases T_g values, allowing the starch melt processability (Pérez, Sandoval, Cova, & Müller, 2014). An additional function of plasticizers is to prevent starch retrogradation which cause material embrittlement due to gradual polymer recrystallization. This effect derives from the complex formation via hydrogen bonding between plasticizer and polymeric matrix (Shanks & Kong, 2012). In this work the effect of T_g values of starch-based materials by alginate and water addition as plasticizers was studied by DSC. Several authors have established that thermoplastic starch presents two semi-crystalline phases, one of them rich in glycerol and the other one rich in starch (Liu, Xie, Yu, Chen, & Li, 2009; Pérez et al., 2014). Therefore, when thermoplastic starch is heated, two glass transition temperatures are expected to be found. The lower glass transition T_{g1} is associated to the glycerol-rich phase; meanwhile T_{g2} is related to the starch-rich phase and appears at higher temperatures. Fig. 6 shows the heating curves obtained by DSC assays of SG, SGA and SGW, considering all plasticizers concentrations. T_{g1} was well-detected in all studied formulations; however, the second glass transition was only barely noticeable in the case of samples with 5 and 10% (w/w) water and alginate. These results could be attributed to the fact that the change of heat capacity associated to the thermal transition of starch-rich phase is negligible, being difficult to be detected. Similarly, Curvelo, de Carvalho, and Agnelli (2001) by studying composites based on thermoplastic starch with cellulosic fibers, reported only glass transition of plasticizer-rich phase. In the same way, Huang et al. (2006) just detected this T_g by processing starch with urea-formamide as plasticizer. Table 1 summarizes T_g

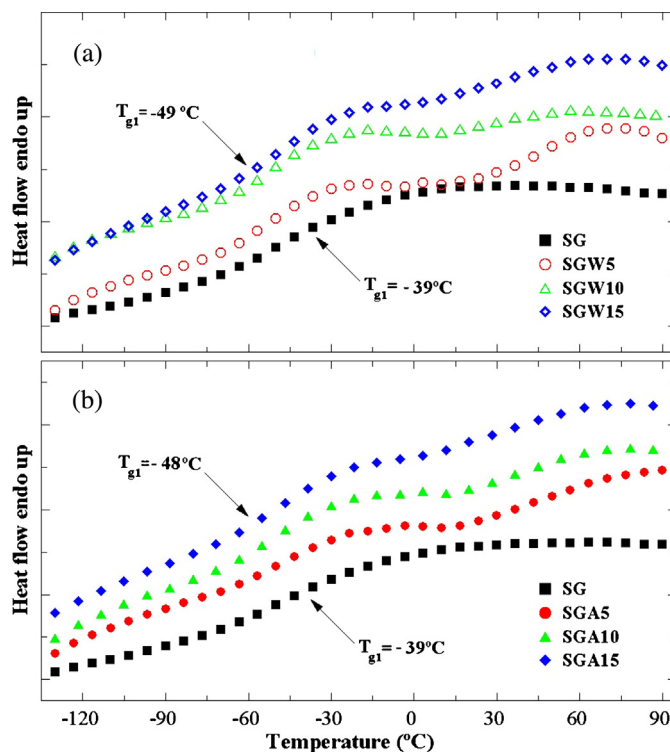


Fig. 6. DSC curves of thermoplastic starch (SG) and SG with 5, 10 and 15% (w/w) (a) water (SGW) and (b) sodium alginate (SGA). Glass transition temperature of glycerol-rich phase (T_{g1}).

values obtained from DSC curves. Water and alginate addition shifted SG T_{g1} to lower temperatures, as expected. T_{g1} obtained for SGA5 was slight lower ($\sim 3.5^\circ\text{C}$) than the corresponding to SG (Fig. 6b and Table 1). However, addition of 10 and 15% (w/w) alginate produced a significant T_{g1} reduction of around 10°C . Our results were in accordance with those obtained by Córdoba et al. (2008) working with plasticized starch materials; since they reported a reduction in T_g values of glycerol-rich phase by alginate addition. On the other hand, samples processed with water as plasticizer showed values of T_{g1} in the range of -49 to -47°C , representing a reduction of $\sim 10^\circ\text{C}$ (Fig. 6a and Table 1).

3.2.3. Optical properties

Study of films optical properties is relevant since they condition the potential applications of these materials, especially in food packaging field. In this sense, absorption and transmission of ultraviolet (UV) and visible (VIS) light by polymers is important where the products are sensitive to these radiations. Thus, to adequately preserve food quality, packaging materials have to provide an efficient barrier against UV and/or VIS light, preventing product photodegradation. In this regard, light may promote adverse reactions, such as oxidation processes, bond scission, formation of unpleasant volatile compounds and vitamins losses, among others (Goncalves, Coutinho, & Marrucho, 2010). On the other hand, another significant issue in fresh food is the effect of UV light on the package since this kind of radiation is a common method used to minimize food initial microbial charge (Joshi, Pawar, Kevadiya, & Bajaj, 2011). So, the transmission of both radiations are important parameters in designing the right packaging to preserve and protect products until they reach the consumer.

Fig. 7 presents results from UV-vis spectrometric measurements. Plots reveal that addition of 5% (w/w) of both plasticizers did not affect significantly ($p > 0.05$) SG films opacity. However, higher amounts of water or alginate produced a proportional decrement of

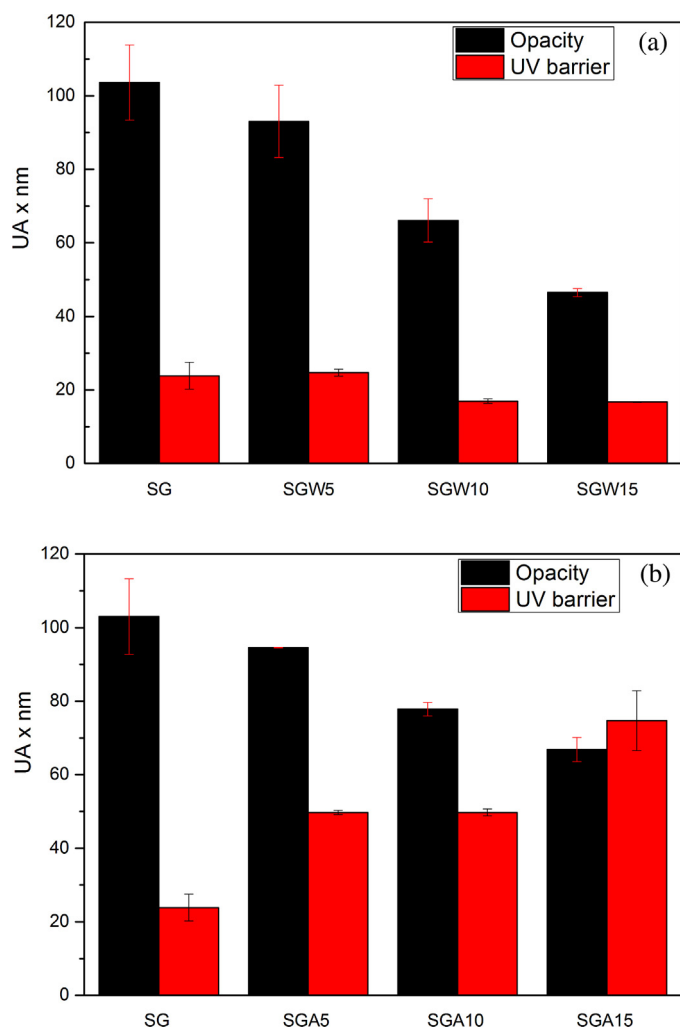


Fig. 7. Opacity and UV barrier capacity of films based on thermoplastic starch (SG) and SG with 5, 10 and 15% (w/w) (a) water (SGW) and (b) sodium alginate (SGA).

this optical property with plasticizers concentration. Besides, SGW films resulted less opaque than SGA ones.

Regarding UV barrier property, it is important to notice that SG presented the ability to absorb UV radiation, since a peak in the range of 270–300 nm was found in the UV–vis spectra. Furthermore, this property was practically not affected by 5% (w/w) water incorporation, although 10 and 15% (w/w) water content decreased significantly SG UV absorption (~30%) (Fig. 7a). In contrast, alginate addition increased noticeable this optical property. Obtained values for SGA5 and SGA10 were two times higher than the corresponding to SG films. Moreover, with 15% (w/w) alginate addition, the UV barrier capacity of SG films was increased in 300% (Fig. 7b). This result could be attributed to the absorption of chromophore functional groups of both alginate and SG matrix.

Other relevant characteristics of these films, associated to potential applications, are their color attributes. It is important to highlight that in food packaging these features condition the product acceptability by consumer. Chromaticity parameters (a , b) and luminosity (L) of studied samples are summarized in Table 2. SG films showed a yellowish color, presenting positive b values. Use of water as plasticizer did not affect significantly L , a and b values of SG films. However, alginate incorporation modified chromaticity parameters of SG films, meanwhile luminosity was not affected. Thus, a values decreased while b values increased, both

Table 2

Optical properties of films based on thermoplastic starch (SG) and SG with 5, 10 and 15% (w/w) water (SGW) and sodium alginate (SGA).

Sample	L^a	a^a	b^a	UVB ^b	OP ^c
SG	89.6 ± 0.6	-0.5 ± 0.08	2.8 ± 0.90	23.8 ± 3.7	103.6 ± 17
SGA5	87.2 ± 1.0	-0.9 ± 0.05	5.8 ± 0.81	59.8 ± 2.7	80.6 ± 19
SGA10	88.7 ± 0.9	-1.1 ± 0.13	11.4 ± 0.40	47.6 ± 2.1	62.3 ± 20
SGA15	88.1 ± 0.7	-1.6 ± 0.09	15.6 ± 0.45	74.7 ± 8.1	66.8 ± 3
SGW5	88.5 ± 0.3	-0.7 ± 0.07	2.1 ± 0.16	24.7 ± 0.9	71.2 ± 30
SGW10	88.9 ± 0.4	-0.6 ± 0.08	2.0 ± 0.27	16.1 ± 0.6	57.7 ± 11
SGW15	89.1 ± 0.2	-0.6 ± 0.03	1.8 ± 0.07	16.0 ± 0.8	43.0 ± 4

^a Hunter color parameters: Luminosity (L), $-a$ (greenness) to $+a$ (redness), and $-b$ (blueness) to $+b$ (yellowness).

^b Hunter color parameters: UV barrier (UVB).

^c Opacity (OP).

proportionally with alginate concentration (Table 2). Resulting color of SGA films were yellow-greenish to soft orange.

Thus, it is possible to trigger materials with specific functional properties like optical properties, by exploring the uses of non-conventional plasticizers, such as sodium alginate.

4. Conclusions

The effect of adding different plasticizers during corn starch processing was evaluated. Thus, water/glycerol and sodium alginate/glycerol mixtures were used, considering the first combination a typical starch plasticizer; meanwhile the second one represents a non-conventional alternative. All studied formulations were able to be melt-processed and successfully injected. Obtained probes were translucent with homogenous appearance. Alginate and water presence led to a reduction in both, storage and loss modulus of SG samples. Furthermore, neither water nor alginate affected thermal stability of SG-based materials. Injected samples were able to be thermo-compressed in order to obtain flexible films, confirming the thermoplastic character of all studied materials. Even though, all formulations allowed to obtain films with good appearance, those containing the highest assayed water content were sticky and difficult to handle; in contrast to SGA films.

Glass transition temperature associated to the glycerol-rich phase was shifted to lower values by alginate and water addition, evidencing their plasticizing effect. This action was also evidenced in SEM micrographs. In fact, homogeneous and smooth surfaces, without unmelted starch granules confirmed the melt-mixing and thermo-compression efficiency. SG films opacity decreased with increasing both plasticizers concentration; meanwhile UV barrier capacity was enhanced with alginate but decreased with water incorporation.

Thus, it was demonstrated the feasibility of using sodium alginate as starch plasticizer instead of water. This non-conventional plasticizer allows to maintain plasticizing effect avoiding, at the same time, the main disadvantages associated to the use of water during starch melting process.

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References

- Cai, J., Xiong, Z., Zhou, M., Tan, J., Zeng, F., Meihuma, et al. (2014). Thermal properties and crystallization behavior of thermoplastic starch/poly(ϵ -caprolactone) composites. *Carbohydrate Polymers*, 102, 746–754. <http://dx.doi.org/10.1016/j.carbpol.2013.10.095>

- Castillo, L., López, O., López, C., Zaritzky, N., García, M. A., Barbosa, S., et al. (2013). Thermoplastic starch films reinforced with talc nanoparticles. *Carbohydrate Polymers*, 95(2), 664–674. <http://dx.doi.org/10.1016/j.carbpol.2013.03.026>
- Córdoba, A., Cuéllar, N., González, M., & Medina, J. (2008). The plasticizing effect of alginate on the thermoplastic starch/glycerin blends. *Carbohydrate Polymers*, 73(3), 409–416. <http://dx.doi.org/10.1016/j.carbpol.2007.12.007>
- Curvelo, A. A. S., de Carvalho, A. J. F., & Agnelli, J. A. M. (2001). Thermoplastic starch ± cellulosic fibers composites: Preliminary results. *Carbohydrate Polymers*, 45, 183–188.
- Della Valle, G., Buleon, A., Carreau, P. J., Lavoie, P. a., & Vergnes, -B. (1998). Relationship between structure and viscoelastic behavior of plasticized starch. *Journal of Rheology*, 42(3), 507–525. <http://dx.doi.org/10.1122/1.550900>
- Du, F., Scogna, R. C., Zhou, W., Brand, S., Fischer, J. E., & Winey, K. I. (2004). Nanotube networks in polymer nanocomposites: Rheology and electrical conductivity. *Macromolecules*, 37, 9048–9055.
- Ghanbarzadeh, B., Oromiehie, A., Musavi, M., Razmi, E., & Milani, J. (2006). Effect of polyolic plasticizers on rheological. *Iranian Polymer Journal*, 15(10), 779–787.
- Gomez, C. G., Rinaudo, M., & Villar, M. A. (2007). Oxidation of sodium alginate and characterization of the oxidized derivatives. *Carbohydrate Polymers*, 67(3), 296–304. <http://dx.doi.org/10.1016/j.carbpol.2006.05.025>
- Gómez-Siurana, A., Marcilla, A., Beltrán, M., Berenguer, D., Martínez-Castellanos, I., & Menargues, S. (2013). TGA/FTIR study of tobacco and glycerol–tobacco mixtures. *Thermochimica Acta*, 573, 146–157. <http://dx.doi.org/10.1016/j.tca.2013.09.007>
- Goncalves, C. M. B., Coutinho, J. A. P., & Marrucho, I. M. (2010). Optical properties. In R. Auras, L.-T. Lim, S. E. M. Selke, & H. Tsuji (Eds.), *Poly(lactic acid): Synthesis, structures, properties, processing, and applications* (pp. 97–113). Hoboken, NJ, USA: John Wiley & Sons, Inc. <http://dx.doi.org/10.1002/9780470649848>
- Huang, M., Yu, J., & Ma, X. (2006). High mechanical performance MMT-urea and formamide-plasticized thermoplastic cornstarch biodegradable nanocomposites. *Carbohydrate Polymers*, 63(3), 393–399. <http://dx.doi.org/10.1016/j.carbpol.2005.09.006>
- Huq, T., Khan, A., Dussault, D., Salmieri, S., Khan, R. A., & Lacroix, M. (2012). Effect of gamma radiation on the physico-chemical properties of alginate-based films and beads. *Radiation Physics and Chemistry*, 81(8), 945–948. <http://dx.doi.org/10.1016/j.radphyschem.2011.11.055>
- Işıklan, N., & Küçükbalcı, G. (2012). Microwave-induced synthesis of alginate-graft-poly(N-isopropylacrylamide) and drug release properties of dual pH- and temperature-responsive beads. *European Journal of Pharmaceutics and Biopharmaceutics*, 82(2), 316–331. <http://dx.doi.org/10.1016/j.ejpb.2012.07.015>
- Joshi, G. V., Pawar, R. R., Kevadiya, B. D., & Bajaj, H. C. (2011). Microporous and mesoporous materials mesoporous synthetic hectorites: A versatile layered host with drug delivery application. *Microporous and Mesoporous Materials*, 142(2–3), 542–548. <http://dx.doi.org/10.1016/j.micromeso.2010.12.040>
- Krochta, J. M. (2002). Proteins as raw materials for films and coatings: Definitions, current status, and opportunities. In *Protein-based films and coatings*. Boca Raton, FL: CRC Press LLC.
- Lawton, J. W. (2004). Plasticizers for zein: Their effect on tensile properties and water absorption of zein films. *Cereal Chemistry*, 81, 1–5.
- Lencina, M. M. S., Iatridi, Z., Villar, M. A., & Tsitsilianis, C. (2014). Thermoresponsive hydrogels from alginate-based graft copolymers. *European Polymer Journal*, 61, 33–44. <http://dx.doi.org/10.1016/j.eurpolymj.2014.09.011>
- Liu, H., Xie, F., Yu, L., Chen, L., & Li, L. (2009). Thermal processing of starch-based polymers. *Progress in Polymer Science*, 34(12), 1348–1368. <http://dx.doi.org/10.1016/j.progpolymsci.2009.07.001>
- Liu, X., Wang, Y., Yu, L., Tong, Z., Chen, L., Liu, H., et al. (2013). Thermal degradation and stability of starch under different processing conditions. *Starch – Stärke*, 65(1–2), 48–60. <http://dx.doi.org/10.1002/star.201200198>
- López, O. V., García, M. A., & Zaritzky, N. E. (2008). Film forming capacity of chemically modified corn starches. *Carbohydrate Polymers*, 73(4), 573–581.
- López, O. V., Lecot, C. J., Zaritzky, N. E., & García, M. A. (2011). Biodegradable packages development from starch based heat sealable films. *Journal of Food Engineering*, 105(2), 254–263. <http://dx.doi.org/10.1016/j.jfoodeng.2011.02.029>
- López, O. V., Zaritzky, N. E., & García, M. A. (2010). Physicochemical characterization of chemically modified corn starches related to rheological behavior, retrogradation and film forming capacity. *Journal of Food Engineering*, 100(1), 160–168. <http://dx.doi.org/10.1016/j.jfoodeng.2010.03.041>
- Pérez, A., Sandoval, A. J., Cova, A., & Müller, A. J. (2014). Glass transitions and physical aging of cassava starch – Corn oil blends. *Carbohydrate Polymers*, 105, 244–252. <http://dx.doi.org/10.1016/j.carbpol.2014.01.032>
- Perotti, G., Tronto, J., Bizeto, M., Izumi, C., Temperini, M., Lugão, A., et al. (2014). Biopolymer–clay nanocomposites: Cassava starch and synthetic clay cast films. *Journal of the Brazilian Chemical Society*, 25(2), 320–330.
- Rodríguez-González, F. J., Ramsay, B. A., & Favis, B. D. (2004). Rheological and thermal properties of thermoplastic starch with high glycerol content. *Carbohydrate Polymers*, 58(2), 139–147. <http://dx.doi.org/10.1016/j.carbpol.2004.06.002>
- Salomonsen, T., Jensen, H. M., Larsen, F. H., Steuernagel, S., & Engelsen, S. B. (2009). Alginate monomer composition studied by solution- and solid-state NMR – A comparative chemometric study. *Food Hydrocolloids*, 23(6), 1579–1586. <http://dx.doi.org/10.1016/j.foodhyd.2008.11.009>
- Schlemmer, D., Rodrigues, T. C. A. F., Cunha, S. M., Macedo, J. L., Angélica, R. S., & Sales, J. A. (2010). Biodegradable thermoplastic starch/clay nanocomposite films analysed by XRD and FTIR. In *7th International Symposium on Natural Polymers and Composites* (pp. 296–299).
- Shanks, R., & Kong, I. (2012). Thermoplastic starch. In A. Z. El-Sonbati (Ed.), *Thermoplastic elastomers* (pp. 95–116). Melbourne, Australia: InTech. <http://dx.doi.org/10.5772/2038>
- Siddaramaiah Swamy, M. T. M., Ramaraj, B., & Hee Lee, J. (2008). Sodium alginate and its blends with starch: Thermal and morphological properties. *Journal of Applied Polymer Science*, 109(6), 4075–4081. <http://dx.doi.org/10.1002/app.28625>
- Souza, R. C. R., & Andrade, C. T. (2001). Processing and properties of thermoplastic starch and its blends with sodium alginate. *Journal of Applied Polymer Science*, 81(2), 412–420. <http://dx.doi.org/10.1002/app.1453>
- Tonelli, R., Campos, A., De Mattoso, L. H. C., Franchetti, S. M. M., & Marconcini, J. M. (2010). Biodegradation, mechanical and thermogravimetric characterization of thermoplastic starch (TPS). In *7th International Symposium on Natural Polymers and Composites* (pp. 1139–1141).
- Wilhelm, H.-M., Sierakowski, M.-R., Souza, G. P., & Wypych, F. (2003). Starch films reinforced with mineral clay. *Carbohydrate Polymers*, 52(2), 101–110. [http://dx.doi.org/10.1016/S0144-8617\(02\)00239-4](http://dx.doi.org/10.1016/S0144-8617(02)00239-4)
- Xie, F., Halley, P. J., & Avérous, L. (2012). Rheology to understand and optimize processibility, structures and properties of starch polymeric materials. *Progress in Polymer Science*, 37(4), 595–623. <http://dx.doi.org/10.1016/j.progpolymsci.2011.07.002>
- Yang, C., Xu, L., Zhou, Y., Zhang, X., Huang, X., Wang, M., et al. (2010). A green fabrication approach of gelatin/CM-chitosan hybrid hydrogel for wound healing. *Carbohydrate Polymers*, 82(4), 1297–1305. <http://dx.doi.org/10.1016/j.carbpol.2010.07.013>
- Zhang, Y., & Han, J. (2006). Mechanical and thermal characteristics of pea starch films plasticized with monosaccharides and polyols. *Journal of Food Science*, 71, 109–111.
- Zhang, Y., Rempel, C., & Liu, Q. (2014). Thermoplastic starch processing and characteristics – A review. *Critical Reviews in Food Science and Nutrition*, 54(10), 1353–1370. <http://dx.doi.org/10.1080/10408398.2011.636156>