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The plasticizing effect of alginate on the thermoplastic starch/glycerin blends

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Abstract

Corn starch and corn starch–alginate (5–15%) blends plasticized with 35% glycerin were prepared, water was intentionally excluded from the formulations. Torque rheometry measurements were carried out during the processing of the blends in a batch counterrotating twin screw mixer. A progressive decrease in the plasticization energy of the blends was observed as the alginate content was increased, with a 5-fold decrease for the blend with the higher alginate content (15%). The steady state torque of the plasticized melted blends also showed a decrease as alginate content was increased; with a drastic drop occurring for the formulation with higher alginate content. After mixing, test specimens for mechanical, thermal and microstructural testing were made by compression molding. A decrease in the elastic properties and an increase in elongation at break and impact resistance was observed when alginate content was increased in the blends. The transition of the materials towards a more viscous behavior, as alginate content was increased, was confirmed by differential scan calorimetric analysis. For the corn starch–alginate blends glass transitions were detected in the temperature range −60 to −90 °C. Scanning electron microscopy was used to examine the morphology of cryofractured surfaces of the molded test specimens. A reduction of the granular crystalline structures typical of corn starch was observed as alginate content was increased in the blends. The experimental evidence presented in this work indicates that, when water is excluded from thermoplastic corn starch preparation, alginate acts synergistically with glycerin increasing the degree and efficiency of the plasticization process.

Keywords: Thermoplastic starch; Thermoplastic starch–alginate blends; Processing; Additives; Mechanical properties; Morphology

1. Introduction

Starch is composed of a mixture of amylase and amylopectin macromolecules. Both high molecular weight polymers are formed of (1,4)-α-D-glucopyranosyl repeating units. Amylose is essentially linear, whereas amylopectin is highly branched with (1,6) glucosidic branching points occurring every 20–25 glucose units. The short chains of amylopectin are thought to be arranged as double helices, in clusters of semicrystalline character. The native starches differ in water content and in the ratio of amylose to amylopectin. As the glass transition of pure starch lies above its decomposition temperature, processing requires the addition of plasticizers (Souza & Andrade, 2001). During processing, starch granules are exposed to high temperature and shear and undergo plasticization, melting and fractionation. Thermoplastic starch can be considered as a homogeneous system composed of a hard elastic network and soft amorphous regions. Amylose complex crystallites, highly entangled starch molecules, poorly plasticized starch-rich sites, or a combination of them could compose the hard elastic network. Soft amorphous regions could be composed of well plasticized regions (Rodriguez-Gonzalez, Ramsay, & Favis, 2004).

Alginates, or salts of alginic acid, are found in all the members of the Phaeophyceae, a class of brown seaweeds, in which alginic acid represents the structural component of intercellular walls, providing both strength and flexibil-

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ity to the algal tissue. It exists in the form of insoluble gel of mixed calcium, magnesium, sodium and potassium salts, and it is extracted from the grounded thallium upon the collapse and subsequent transformation of their tissue in a brown mass (Draget, Smidsrød, & Skjak-Braek, 2002; Fischer & Dorfel, 1955). The alginic acid is a complex mixture of oligomers, polymannuronic acid, polyguluronic acid. The mannuronic acid forms β-(1→4) linkage, so that M-block segments show linear and flexible conformation. The guluronic acid, differently, gives rise to α-(1→4) linkage, introducing in this way a steric hindrance around the carboxyl groups; for this reason the G-block segments provides folded and rigid structural conformations, responsible for a pronounced stiffness of the molecular chains (Avella et al., 2007). In the presence of water, divalent ions form crosslinks in alginate by binding the guluronic residues, inducing a sol–gel transition in the material. The crosslinks are believed to create a stiff egg-box structure, and they impart viscoelastic solid behaviour to the material (Grant, Morris, Rees, Smith, & Thom, 1973).

Some studies have evaluated the processing of thermoplastic starch using water or water/glycerol mixtures as a plasticizer. Extrusion of low moisture materials at temperatures higher than 130 °C or materials with 30% moisture that are extruded at 100 °C occasionally has resulted in the formation of water vapor bubbles at the exit of the die (Aichholzer & Fritz, 1998; Fletcher, McMaster, Richmond, & Smith, 1985; Willett, Jasberg, & Swanson, 1995; Willett, Millard, & Jasberg, 1998). Also the previous experience in our laboratory indicated that presence of moisture during starch processing causes bubbles in the extrudates and high adhesion of the polymer in the extruder screws. These problems associated with the use of water as plasticizer for thermoplastic starch preparation have been approached in some studies. The use of multi zone extruders where water is evaporated after gelatinization but before plasticization has been suggested (Favis, Rodriguez, & Ramsay, 2003; Rodriguez-Gonzalez et al., 2004).

The blends of starch with several kinds of synthetic polymer and their mechanical properties, and biodegradability characteristics, have been widely studied and reported. The blends of starch with other polymers from biological sources have also been intensely studied, during the last decade (Wang, Yang, & Wang, 2003). The main objective of those studies has been to improve water resistance and strength of thermoplastic starch materials. In particular studies of the blends of corn starch with sodium alginate plasticized with water/glycerin mixtures were reported by Souza and Andrade (2001). They achieved a complete disruption of the granular structure of starch and found a significant increase in Young's Modulus for the blends with 1% alginate. However, the microstructural characteristics and the resulting mechanical properties of thermoplastic starch and its blends are highly dependent on processing conditions and the plasticizers used. In some studies the granular structure of starch has not been completely disrupted by processing, as visualized by microscopic techniques (Psomiadou, Arvanitoyannis, Biliaderis, Ogawa, & Kawasaki, 1997; Ratto, Stenhouse, Auerbach, Mitchell, & Farrell, 1999; Vaidya, Bhattacharya, & Zhang, 1995).

The aim of this study is to evaluate the effect of the alginate content in starch–alginate–glycerin blends, excluding water from the formulations. Plasticization and melt properties are evaluated in a torque rheometer, and mechanical, thermal, and microstructural characteristics of the obtained materials reported. Previous studies have evaluated the blends of corn starch with sodium alginate plasticized with glycerol/water mixtures, however the problems generated by moisture content on processing of thermoplastic carbohydrates have also been widely documented. Although most of the structural elastic properties of alginate are dependent on water content (such as the "egg box" structure formation), its possible beneficial or adverse effects as an additive on glycerin plasticized corn starch thermoplastics have not yet been reported.

2. Experimental

2.1. Materials

The corn starch (CS) used in this work is produced by Industrias del Maìz S.A. Corn Products Andina under the trade name Fécula Saguzena, it is composed of approximately 28% amylose and 72% amylopectin. A commercial alginate (AL) impression material sold under the trade mark Algidenco was used in this work. It is composed of Sodium or Potassium Alginate, and Diatomaceous Earths as particulate filler and has an average molecular weight of $M_W = 2.1 \times 10^5$ Da (Hondrum & Fernandez, 1997). Glycerin USP 99.5% produced by Bell Chem International was used as plasticizer.

2.2. Mixing and mixing properties

Before being used corn starch and alginate powders were dried for 18 h in a convection oven at 105 °C. The dry powders and the glycerin were mixed, in a 1/6 HP blade mixer, for 5 min at 1150 rpm.

The plasticization and melting of the blends were carried out in a Brabender PLE 331 torque rheometer, using the batch mixer (65 g capacity) equipped with counterrotating twin screws. The mixing temperature was set at 140 °C and the screws velocity at 32 rpm, the mixing time was approximately 8 min. Four different formulations were prepared; the glycerin content was 35% by weight in all the formulations. The alginate content in the blends was varied between 0% and 15% by weight. There was no water addition and the blends were plasticized immediately after drying, in order to minimize the amount of water present in the final material. Torque was monitored and recorded trough the whole mixing process.

2.3. Compression molding

After mixing, test specimens for the evaluation of mechanical, thermal and microstructural properties were made by compression molding. The molding temperature was 140 °C. Melt time was 10 min; pressure (21.07 MPa) was progressively applied during 1 min and held during 5 min.

2.4. Tensile test

The tensile test was made according to technical standard method ASTM, D638 (test piece type 1) in a dynamometer Instron Model 4301. All the measurements were carried out at 25 °C and 50% relative humidity, at a cross-head rate of 50 mm min^{-1}; a 50 mm gauge length extensometer was used. For each composition five specimens were tested.

2.5. Hardness test

Hardness was determined according to ASTM, D2240 technical standard method, in a Zwick durometer. For each composition three specimens were tested. Measurements were taken, at six different points, for each test piece and were carried out at 25 °C and 50% relative humidity.

2.6. Izod impact test

Izod impact resistance was determined according to the technical standard method ASTM, D256, in a TMI Izod impact instrument with a 2.7 Nm hammer 10.16 ± 0.05 mm indentations were made in the test specimens. All the measurements were carried out at 25 °C and 50% relative humidity.

2.7. DSC measurements

Samples were taken from the compression molded specimens. Thermal analyses were carried out using a Differential Scanning Calorimeter 2910 TA Instruments. Transition temperatures were scanned from −140 to 80 °C, they were calculated from the second heating cycle.

2.8. Scanning electron microscopy (SEM)

Thermoplastic CS and CS–AL samples were fractured in liquid nitrogen and stuck to aluminum stubs. Metallizations were carried out in a Blazers sputter SDC-050, under medium vacuum (<10^{-2} torr) with Argon as attack gas over a gold–palladium plaque. The metalized samples were observed under a FEI QUANTA 200 electron microscope.

3. Results and discussion

The addition of plasticizer allows the carbohydrate molecules to behave in a similar fashion to common thermoplastic synthetic polymers. During plasticization some of the carbohydrate polymer molecules are released from the granular structure. The carbohydrate polymer melts consists of highly plasticized amorphous regions and some remaining granular regions. The amount of each phase present in a given blend will depend on processing time and conditions. The torque measurements for the plasticization and melting process of the prepared formulations are shown in Fig. 1. A decrease in the torque of the melts was observed as the alginate content in the formulations was increased; a particularly drastic drop was observed for the formulation with higher alginate content.

Two characteristic properties, of the plasticization and melting processes, calculated from the torque rheometry data, are shown in Table 1. The plasticization energy was calculated as the integral under the torque–time function, from the time when torque starts to increase, until the time where the maximum torque is reached. This region of the mixing process is where the plasticizer (glycerin) diffuses inside the starch and alginate particles. The particles swell and absorb the plasticizer to form a pseudo solid state (maximum torque) that finally melts (torque decrease) and homogenizes (steady state torque). The diffusion process during the plasticization stage is energetically "fed" by heat flow created by the imposed temperature gradient and by the mechanical energy provided by the rotating screws by means of shear and normal stresses. For that reason the plasticization energy can be taken as an estimate of

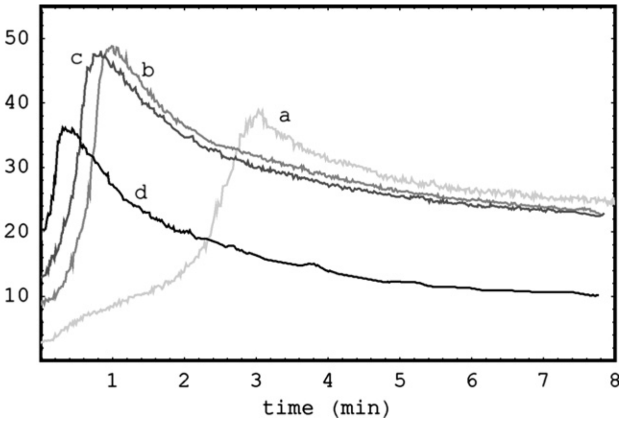

Fig. 1. Torque rheometry measurements for the plasticization and melting processes of starch–alginate–glycerin blends as a function of alginate content. (a) 0% alginate; (b) 5% alginate; (c) 10% alginate; (d) 15% alginate.

Table 1
Characteristic parameters of the plasticization process of the starch–alginate–glycerin blends

Formulation Mixing property	CS	5% AL	10% AL	15% AL
Plasticization energy (Nm min) ± 15%	43.27	22.53	23.89	8.07
Steady torque (Nm) ± 15%	23.08	22.66	22.79	10.20

the thermodynamical favorability of the diffusion process of the plasticizer in the polymer particles, and therefore a measure of the compatibility between the plasticizer and the polymer. The steady state torque is usually used as a comparative estimate of the viscosity of the polymer melts. Although modeling of the flow and deformation phenomena in torque rheometers is highly complex, usually a linear relation between torque and viscosity is assumed for the analysis of torque rheometry data.

The data from the torque rheometry indicates that the plasticization energy of the blends decreases significantly as the alginate content is increased in the formulations. This decrease in plasticization energy can be understood as an enhancement in the thermodynamical favorability of the mixing process when the amount of alginate in the blends is increased. This effect of alginate on the blending properties of starch is very likely related to a higher solubility of alginate in glycerin. The solvated alginate oligomers, increase the plasticizer action of glycerin, these alginate rich regions contribute to increase the highly plasticized, softer domains in the polymer blend, decreasing the viscosity of the melt.

Fig. 2 shows the typical stress–strain curves obtained for the CS–AL blends. The yield point is clearly defined for CS and all CS–AL blends. This is different to what was found by Souza and Andrade (2001), who did not detect a defined yield point for CS–sodium alginate blends plasticized with water/glycerol mixtures. A significant decrease of the elastic region was observed with the increase in the alginate content. The influence of alginate content on the tensile properties of the thermoplastic CS–AL blends is shown in Fig. 3. Again, an evident increase in the plastic behavior of the blends is observed as the alginate content is increased. A 30-fold decrease in Young's Modulus and a 10-fold increase in strain at break were observed when alginate content in the blends was increased from 0% to 15%. In Fig. 4 the results for the hardness test are presented, a significant reduction in hardness is produced with increasing alginate content. This result is in agreement with the plasticizing effect of the alginate already observed in the tensile test. However the greatest change in hardness occurred when alginate content was increased from 5% to 10%, while the largest change in the tensile properties occurred when the alginate content was increased from 10% to 15%. The Izod impact results (Fig. 5) show a significant increase in the capacity of the specimens to absorb energy as the alginate content was increased. As in the hardness test the major change occurred when alginate content is increased from 10% to 15%. The large variances in the results for the 10% and 15% alginate blends are probably due to the unavoidable widening of the v shape cut of test specimens due to the high plasticization of those blends.

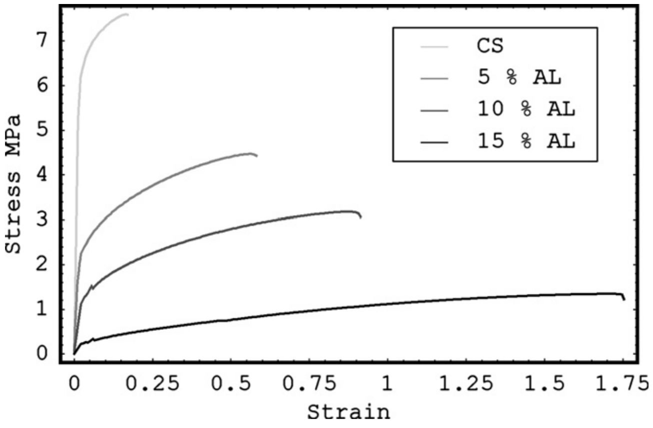

Fig. 2. Strain–stress curves obtained for CS and CS–AL blends plasticized with glycerin, as a function of alginate content.

The impact test results give some insight about the viscoelastic behavior of the CS and CS–AL blends. The small experimental time imposed by the impact test, allows making a relative comparison between the magnitudes of the characteristic time of the materials under study. When the amount of alginate is increased the characteristic time of the material decreases, enhancing its capacity to dissipate energy, in a viscous way. In good agreement with the torque rheometry measurements, the behavior of the mechanical properties indicates a decrease in the hard elastic network typical of thermoplastic CS as the alginate content is increased in the formulations.

At first thermal transitions were scanned from −140 to 240 °C, but mild degradation occurred around 150 °C, possibly due to glycerin evaporation (Rodriguez-Gonzalez et al., 2004). Therefore for the determination of transition temperatures samples were only heated up to 80 °C. DSC analysis of thermoplastic CS and CS–AL blends showed glass transition temperatures below 0 °C. A decreased in T_g was observed as alginate content was increased (Fig. 6, Table 2). CS alone also showed a thermal transition above 0 °C, at 15.52 °C. The T_g for thermoplastic CS found in this work, is in the same range of the one reported by Rodriguez-Gonzalez et al. (2004), who found a T_g of −54 °C for water free thermoplastic CS with 36% glycerol. In the present work, only one thermal transition was observed for the CS–AL blends. Souza and Andrade (2001) found, by DMA analysis, two thermal transitions for glycerol/water plasticized CS–AL blends, one around −55 °C and an upper transition between 0 and 80 °C. Discrepancies in the thermal transitions values can be related to the mixing history of the carbohydrate thermoplastics (Kalichevsky, Jaroszkiewiez, & Blanshard, 1993). Disruption of the crystalline region, such that which occurs during carbohydrate polymer plasticization could lead to the disappearance of thermal transition above T_g. The DSC results are in good agreement with the results obtained in the rheological and mechanical tests. As the T_g of the material decreases the viscous component of its behavior at ambient temperature becomes more important. This is reflected in the mechanical properties with a more rubbery behavior and in the rheological measurements as a decrease in steady state torque.

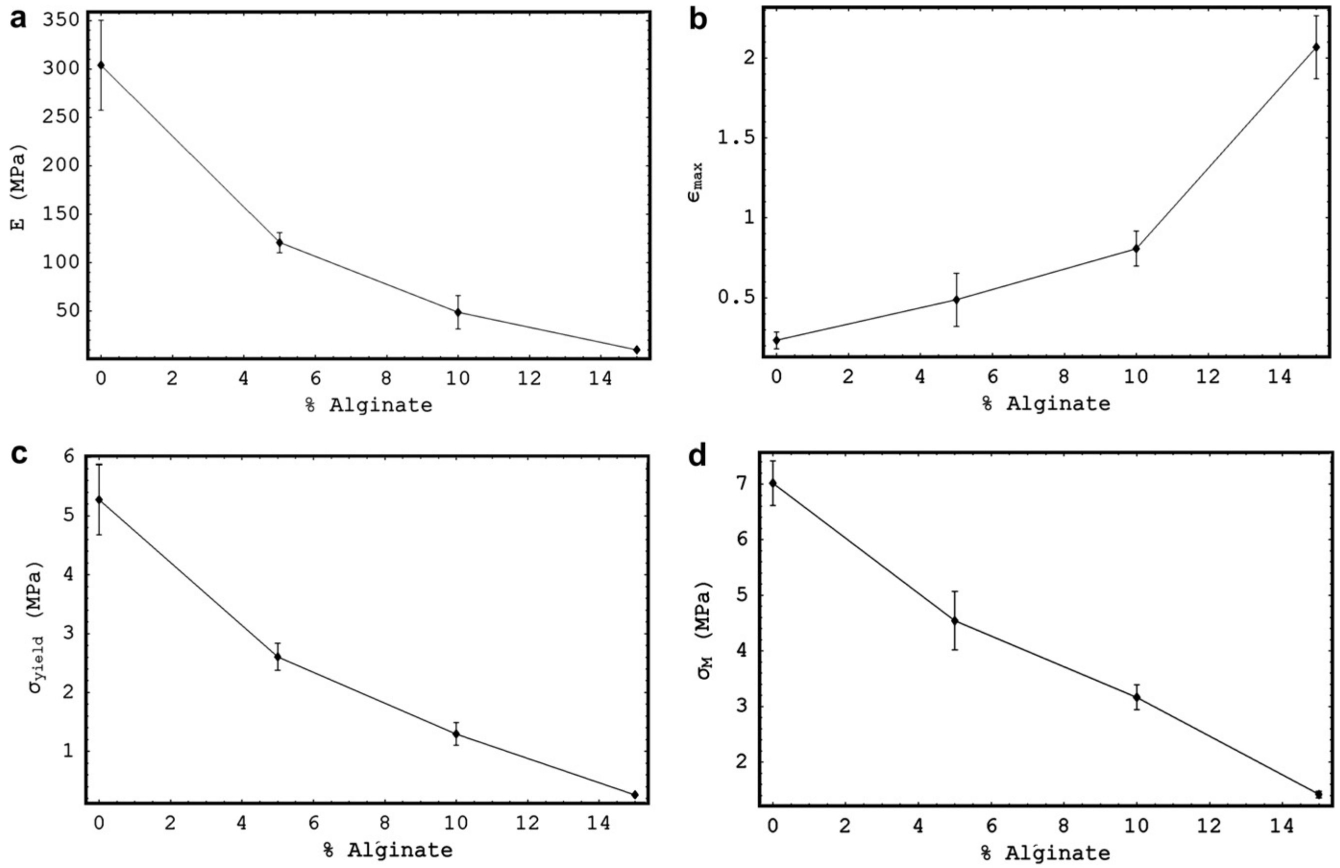

Fig. 3. Tensile properties of CS and CS–AL blends plasticized with glycerin, as a function of AL content. (a) Young's Modulus. (b) Elongation at break. (c) Yield stress. (d) Maximum stress.

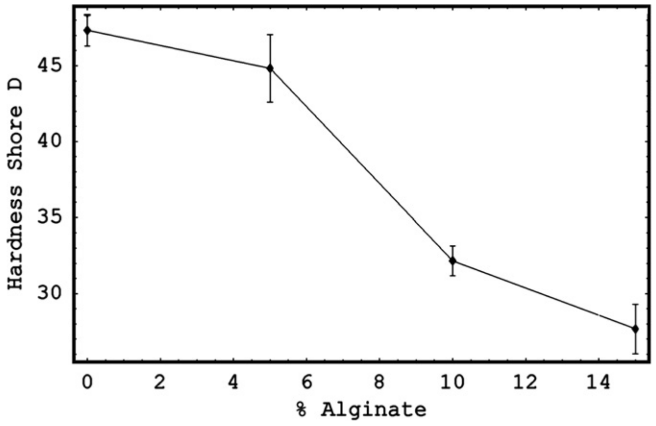

Fig. 4. Shore D hardness of CS and CS–AL blends plasticized with glycerin, as a function of AL content.

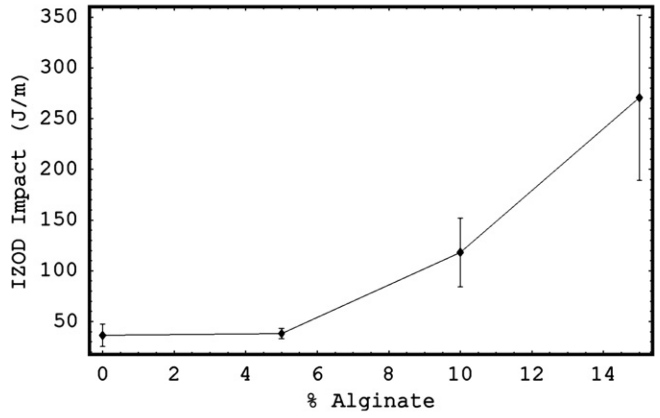

Fig. 5. IZOD Impact results for CS and CS–AL blends plasticized with glycerin, as a function of AL content.

SEM micrographs of cryofractured surfaces of the test specimens of CS and CS–AL thermoplastic blends are shown in Fig. 7 (400×) and 8 (1600×). For the CS alone an amorphous homogeneous matrix surrounds well defined predominant granular domains. This indicates that with the processing conditions applied in this work, and with glycerin as sole plasticizer the CS granular structure was not completely disrupted. However as alginate content is increased in the blends, the granular domains become smaller and scarcer. Once again the alginate effect is evident; it contributes to increase the highly plasticized regions in the CS–AL thermoplastic, making the material more homogeneous. The disappearance of the thermal transition above 0 °C in the DSC

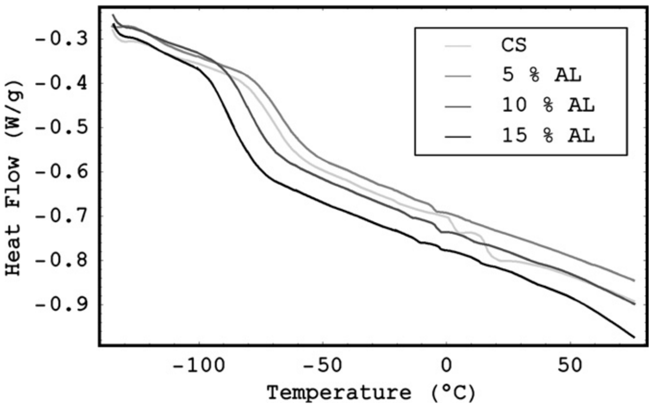

Fig. 6. DSC scans for CS and CS–AL blends plasticized with glycerin. For CS two thermal transitions were detected in the scanned range. For the CS–AL blends only one transition was detected in the scanned range, the upper temperature transition fades out. Exothermic heat flow up.

Table 2
Thermal transitions temperatures and transitions width for CS and CS–AL blends as a function of alginate content

% AL	T_g (°C)	Transition width (°C)	Upper transition (°C)	Transition width (°C)
0.00	−69.48	25.00	15.52	3
5.00	−66.61	18.00	–	–
10.00	−79.34	22.00	–	–
15.00	−86.98	20.00	–	–

scans of the CS–AL blends could be related to the reduction of the granular starch-rich domains. The disruption of the granular structures is naturally related to plasticization, because the undisrupted starch granules usually act as filler that harden the thermoplastic starch materials (Wang et al., 2003).

The results presented in this work show the addition of alginate to the starch/glycerin blends substantially increase the capacity of the plasticizer to disrupt the starch granules, which results in a significant plasticization of the blends. The observed effects in mechanical, thermal and processing properties indicate that highly solvated alginate oligomers are acting as a secondary plasticizer. This new plasticizer system (glycerin solvated alginate) should be more efficient in disrupting the bonds holding together the starch granules. The glycerin provides the mobility to the plasticizer system, giving it the capacity to penetrate and diffuse through the starch granules. On the other hand solvated oligomers provide higher steric hindrance capacity to disrupt and spread apart the bonds in the starch granules, producing this way a higher increase in the free volume of the blend. Therefore besides increasing the highly plasticized domains, the plasticized alginate oligomers act synergistically with the plasticizer to accomplish the dissolution of the crystalline structures of starch granules.

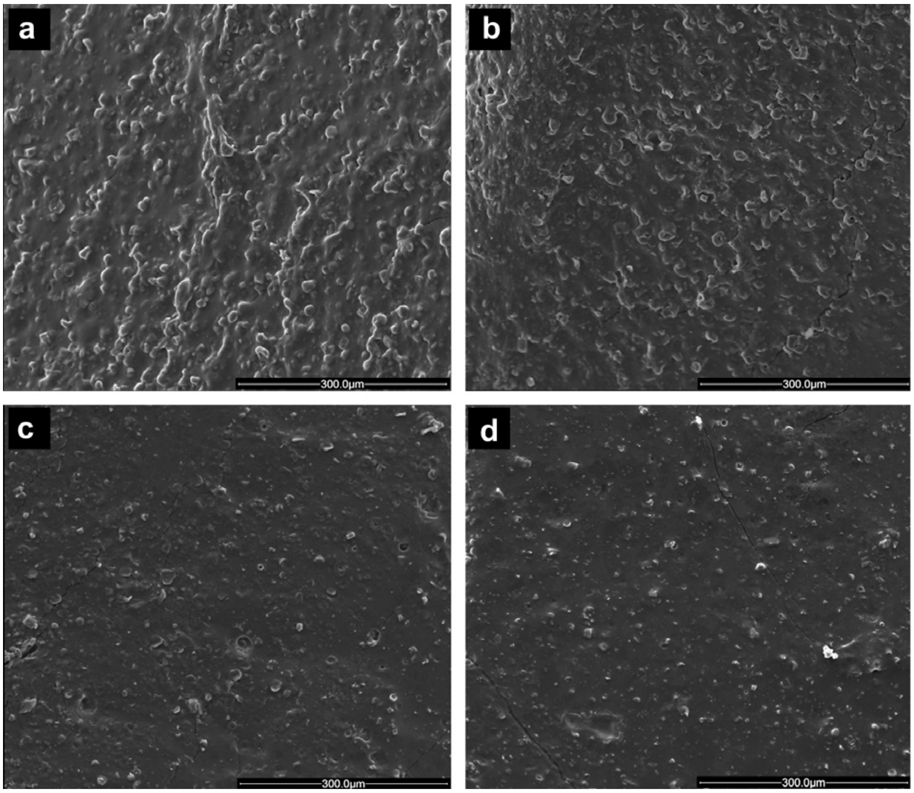

Fig. 7. SEM micrographs at 400× of cryofractured surfaces of CS and CS–AL blends plasticized with glycerin. (a) CS Alone; (b) 5% AL; (c) 10% AL; (d) 15% AL.

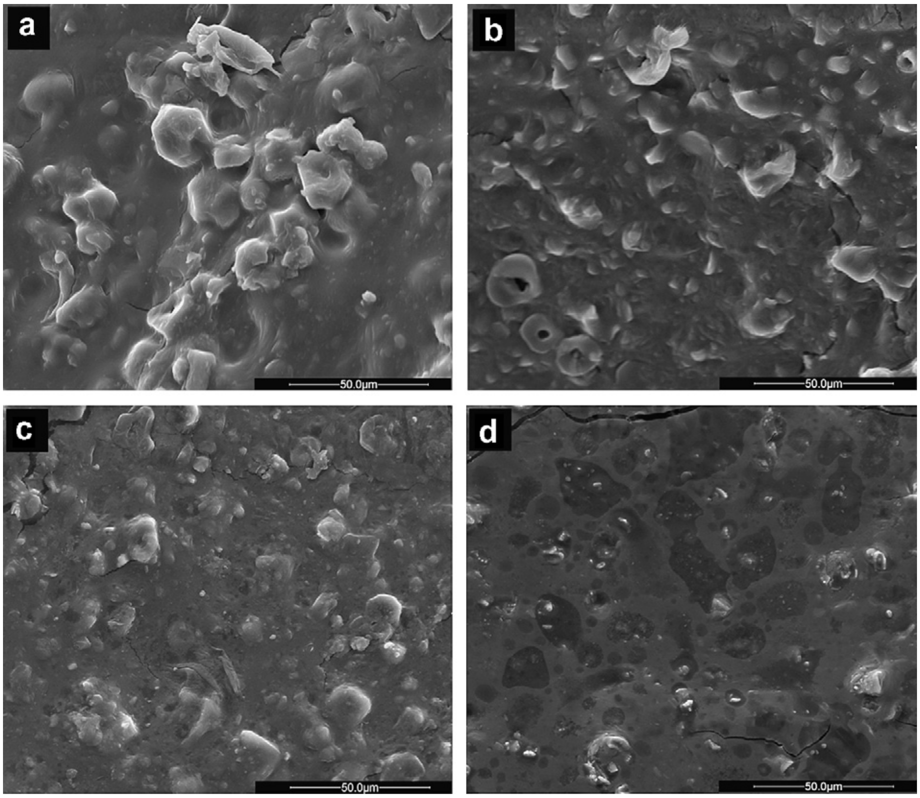

Fig. 8. SEM micrographs at 1600× of cryofractured surfaces of CS and CS–AL blends plasticized with glycerin. (a) CS alone; (b) 5% AL; (c) 10% AL; (d) 15% AL.

4. Conclusions

The effect of the addition of alginate in the processing of glycerin plasticized CS, when water is excluded from the blends, was investigated using torque rheometry. A significant decrease in plasticization energy and in steady state torque was observed when alginate content was increased from 0% to 15%. Test specimens for mechanical testing were made by compression molding. Elastic properties of the CS–AL blends decreased while elongation at break and impact resistance increased as the alginate content was increased. The tendency of the blends to become more rubbery as AL content was increased was confirmed by DSC. The glass transition temperature decreased 20 °C when alginate content was increased from 0% to 15%. SEM micrographs of cryofractured surfaces showed a progressive decrease of the granular starch structures as alginate content was increase in the blends.

The experimental evidence presented in this work, indicates that the addition of alginate to CS thermoplastics causes an evident plasticizing effect. With out the presence of water alginate does not seem to form "egg-box" structures that could lead to a stiffening of the material. For the contrary alginate acts synergistically with the plasticizer and the granular structures, typical of starch, are disrupted significantly more than with the plasticizer alone. The effect of alginate on processing and in the mechanical and microstructural properties of thermoplastic CS is so significant that it could be proposed as a secondary plasticizer for thermoplastic CS, when water has been excluded from the formulation. The threshold alginate content on thermoplastic CS for specific needs and applications should be determined.

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