

# Processing and Properties of Thermoplastic Starch and Its Blends with Sodium Alginate

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**ABSTRACT:** Viscosity measurements were carried out on corn starch (CS) and CS–sodium alginate (SA) suspensions at low levels of SA [1 to 10% (w/w)], as a function of temperature. The addition of SA caused the granular CS gelatinization process to occur at a lower onset temperature. CS and CS–SA mixtures were extruded in single- and twin-screw extruders, with 15% glycerol and different water contents. Processing of plasticized CS–SA mixtures required lower temperatures, which is consistent with the viscosity results. Homogeneous and flexible extrudates were obtained by processing in a twin-screw extruder. Samples in the composition range between 0 and 10% (w/w) SA were examined using tensile tests as a function of water content. Mechanical properties were dependent on the water content and on the SA composition. A significant increase in the Young's modulus value was observed for the blend containing 1% SA. Dynamic mechanical analysis was carried out for CS and CS–SA blends. Two transitions were detected in the temperature range –80 to 150°C. Scanning electron microscopy was used to examine the morphology of the extruded samples. The surfaces of the films were homogeneous, which demonstrated that the CS granules in all samples were characteristically destructured under the conditions used in processing. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 412–420, 2001

**Key words:** thermoplastic starch; thermoplastic starch–sodium alginate blends; processing; mechanical properties; morphology

## INTRODUCTION

Synthetic polymers have gained credibility in several technological applications because of properties such as low cost and density, thermoplasticity, hydrophobicity, and strength. However, the high amount of plastic waste created each year, associated with the decreasing availability of landfills, has encouraged the development of biodegradable materials that could substitute for synthetic polymers, at least in some of their ap-

plications. Starch is one of the most promising materials to achieve this goal. It is produced worldwide from several crops, and is completely biodegradable in a wide variety of environments.<sup>1,2</sup>

Starch occurs as granules in grains, roots, and tuberous plants. Corn and wheat are its major sources. Starch is composed of a mixture of amylose and amylopectin macromolecules. Both high molecular weight polymers are formed of (1,4)- $\alpha$ -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.<sup>3</sup> The short chains of amylopectin are thought to be arranged as double helices, in clusters of semicrystalline

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character.<sup>4</sup> The native starches differ in water content and in the ratio of amylose to amylopectin.

Most starch granules show Maltese crosses when observed by optical microscopy under polarized light, an indication of crystallinity. The overall crystallinity<sup>5</sup> of the native starches is about 15–45%. To obtain a homogeneous, essentially amorphous polymeric matrix, granular starch should be submitted to thermal and mechanical treatments. As the glass transition of pure starch lies above its decomposition temperature, processing requires the addition of plasticizers. Water and polyols are common plasticizers in these cases. In general, starch films may be homogeneous, but still have poor mechanical properties.

Many studies have dealt with several kinds of starch/synthetic polymer blends, their mechanical properties, and biodegradability characteristics.<sup>6–11</sup> However, in some studies the granular structure of starch was not completely disrupted by processing, as visualized by microscopic techniques.<sup>12–15</sup>

The aims of the present work were to substitute the synthetic polymer in the starch blends by another polysaccharide, to investigate the processing conditions, and to evaluate the properties of the resulting materials. Sodium alginate (SA), a linear polysaccharide obtained from marine algae and composed of (1,4)- $\beta$ -D-mannuronate and (1,3)- $\alpha$ -L-guluronate residues, was chosen because of its structural features, with carboxylic acid groups in every repeating unit that has  $\alpha$  and  $\beta$  configurations. These characteristics were expected to improve compatibility and the mechanical properties of the blends.

## EXPERIMENTAL

### Materials

Corn starch (CS), composed approximately of 20% amylose and 80% amylopectin, was supplied by Refinações de Milho Brasil (São Paulo, Brazil); SA was purchased from Fischer Scientific (Fair Lawn, NJ); glycerol (GL) was purchased from Vetec Química Fina (Rio de Janeiro, Brazil). CS, SA, and GL were used as received.

### Preparation of Plasticized Mixtures

A 60 g/L dispersion of SA in water was prepared at room temperature, under stirring. The re-

quired weight of this dispersion was added to 200-g portions of CS to achieve the desired ratios of 1 : 99 to 10 : 90 (w/w) between SA and CS. To each mixture, 15% glycerol (total weight of solids) was added. After drying in an oven to constant weight, the water content was adjusted to 6 or 15% before processing either in a single- or in a twin-screw extruder, respectively. Plasticized CS was prepared by addition of glycerol and water.

### Determination of the Gelatinization Temperature

To evaluate the effect of SA on CS gelatinization, aqueous suspensions of the plasticized mixtures were prepared at a total concentration of 30 g/L of CS and varying concentrations of SA. The suspensions were analyzed in a Contraves Low Shear 40 rheometer (Uster, Zurich), fitted with concentric-cylinders geometry (MS-DIN 412), as a function of temperature, at a constant shear rate of 100 s<sup>-1</sup>.

### Extrusion in a Single-Screw Extruder

Plasticized CS and CS-SA mixtures at 99 : 1 to 90 : 10 compositions were extruded into monofilament threads, using a PlastiCorder Bradender model (South Hackensack, NJ) GNF106/2 single-screw extruder, provided with four electrically heated modules, cooled by a refrigeration system, at 20–40 rpm and 70, 80, 95, and 115°C (from feed zone to die end). After processing, the blends were cut into pellets or were ground, and pressed between aluminum sheets at 110°C and 0.92 × 10<sup>2</sup> kPa for 15 min, followed by cooling to 25°C, under pressure. Films of 1 mm thickness were obtained.

### Extrusion in a Twin-Screw Extruder

Plasticized CS and CS-SA mixtures at 99 : 1 to 90 : 10 compositions were extruded into nonexpanded ribbons, using a Haake Rheocord 90 system (Dallas, TX), equipped with a twin-screw extruder fitted with a slit die [25.0 × 1.0 mm (width × thickness)]. The mixtures were manually fed into the extruder and the screw rotation speed was maintained at 40–50 rpm. The extrusion temperature profile varied, depending on the plasticized mixture. For plasticized CS, the temperatures were 90–100, 110–120, 120–130, and 90°C (from feed zone to die end). For the CS-SA mixture, the temperatures were kept constant at 70, 80, 90, and 95°C.

### Conditioning

The extruded samples were dried in an oven at 50°C to constant weight and cooled to room tem-

perature in a desiccator. After being weighed, the samples were stored at 25°C for 96 h, at different relative humidities (RH), provided by glycerol: water solutions and measured by a hygrometer. The water content after conditioning was determined by difference analysis.

### Tensile Tests

Tensile properties were evaluated according to ASTM D882-75b method on rectangular specimens (100 × 8 mm), after equilibration at 5, 9, and 15% water contents, using an Instron Universal Testing Machine (model 4204, Canton, MA), at a rate of 5 mm/min. At least five bars were measured for each sample and the median values were considered.

### Dynamic Mechanical Analysis (DMA)

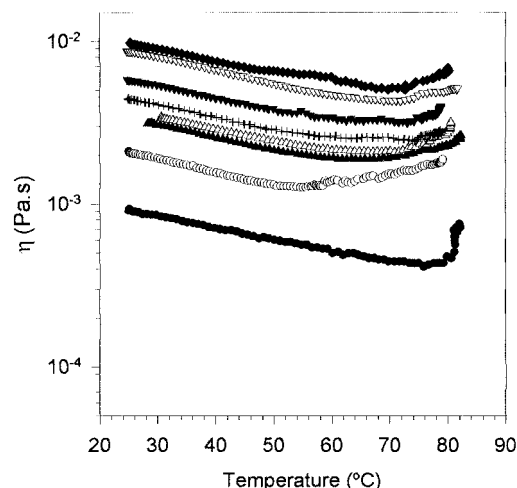
Dynamic mechanical properties were evaluated with a DMTA MkIII unit (Rheometrics) operating in the bending mode. This setup provides the storage ( $E'$ ) and loss ( $E''$ ) moduli and the internal friction ( $\tan \delta = E''/E'$ ) as a function of the temperature, for several frequencies. Samples were compression molded into 150 × 150 × 3 mm sheets at 120°C and 62 kN/m<sup>2</sup> for 10 min. After conditioning, rectangular specimens of 8 × 25 × 3 mm were submitted to a sinusoidal strain of 10%. The temperature was increased at the rate of 2°C/min, from -80 to 150°C, at a frequency of 1 rad s<sup>-1</sup>.

### Scanning Electron Microscopy (SEM)

Thermoplastic CS and CS-SA samples were fractured in liquid nitrogen and stuck to aluminum stubs. The samples were then coated with gold/palladium alloy by vapor deposition and observed under a JEOL model JSM-5300 electron microscope (JEOL, Peabody, MA).

## RESULTS AND DISCUSSION

The viscosity behavior of pure CS and mixed CS-SA suspensions when submitted to increases in temperature at a constant shear rate of 100 s<sup>-1</sup> is shown in Figure 1. As expected, the pure CS suspension presents the lowest viscosities. Viscosity values decrease with temperature. At approximately 82°C, a sharp increase in viscosity takes place, which may be associated with the beginning of the gelatinization process. Mixed

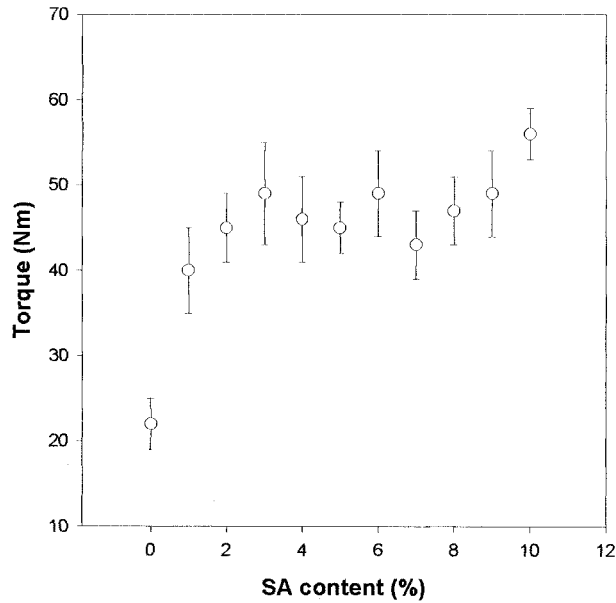


**Figure 1** Effect of the addition of SA on the gelatinization of CS: (●) CS, (○) CS-SA with 1% SA, (▲) CS-SA with 4% SA, (△) CS-SA with 5% SA, (+) CS-SA with 6% SA, (▼) CS-SA with 8% SA, (▽) CS-SA with 9% SA, and (◆) CS-SA with 10% SA.

CS-SA suspensions present a similar viscosity behavior up to a certain temperature, depending on the concentration of SA. The CS-SA dispersion containing the lowest level of SA (at a total polysaccharide concentration of 20.9 g/L and at a SA concentration of 0.21 g/L) presents the lowest threshold temperature. The results indicate that the addition of SA causes the starch gelatinization process to occur at a lower initial temperature, apparently at a slower rate.

The extrudates obtained from processing in the single-screw extruder were clear, flexible, and apparently homogeneous. After pelleting or grinding, the samples were compression molded to obtain 1-mm-thick films. Optical micrographs (not shown) taken from these films showed heterogeneities that resulted either from incomplete melting of the extrudate or from the presence of some intact and fragmented CS granules. The formation of weld lines was also reported for other CS blends obtained from a batch mixer.<sup>16</sup> In the present work, tensile tests were not carried out for CS-SA blends obtained in the single-screw extruder, because failure along the weld lines could be envisaged.

Completely homogeneous, flexible, clear, and transparent extrudates were obtained by processing in the twin-screw extruder. Films of uniform thickness were formed by passing the blends through a calander after exiting from the extruder. As previously detected in diluted suspen-

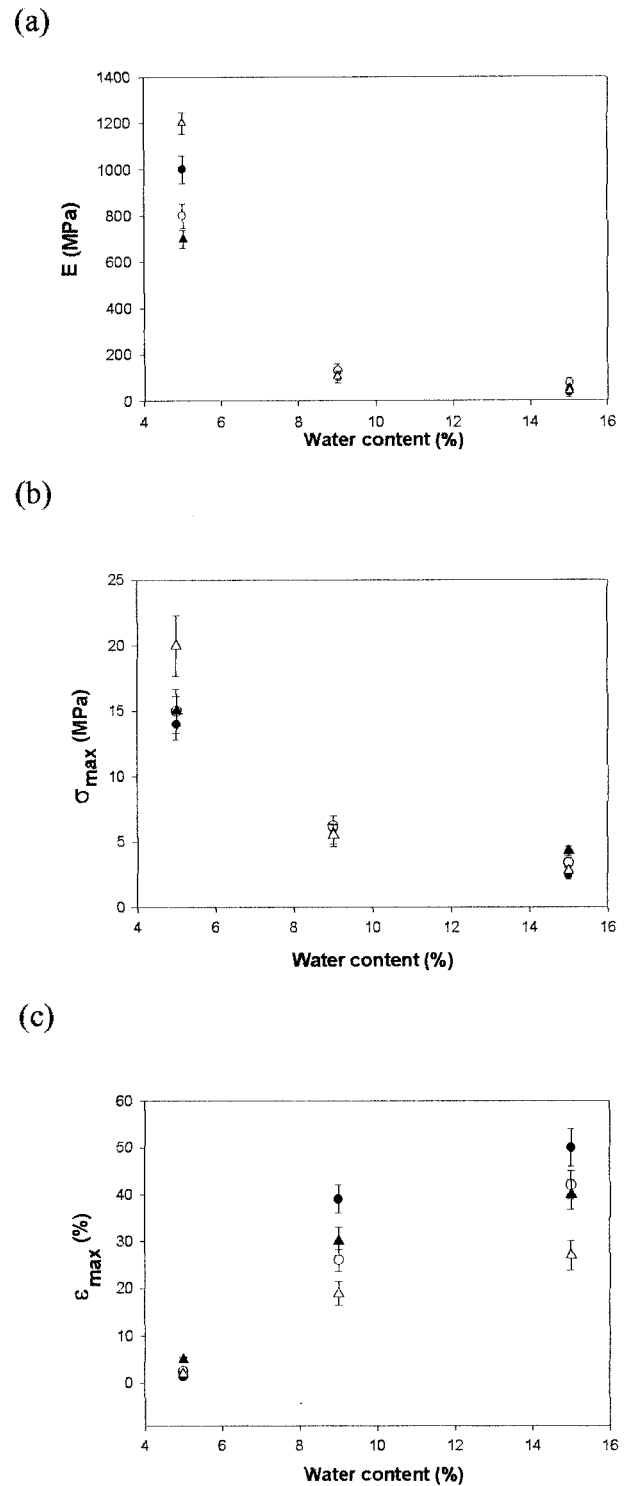


**Figure 2** Torque developed during process of plasticized CS and CS-SA mixtures, in the twin-screw extruder, as a function of SA content.

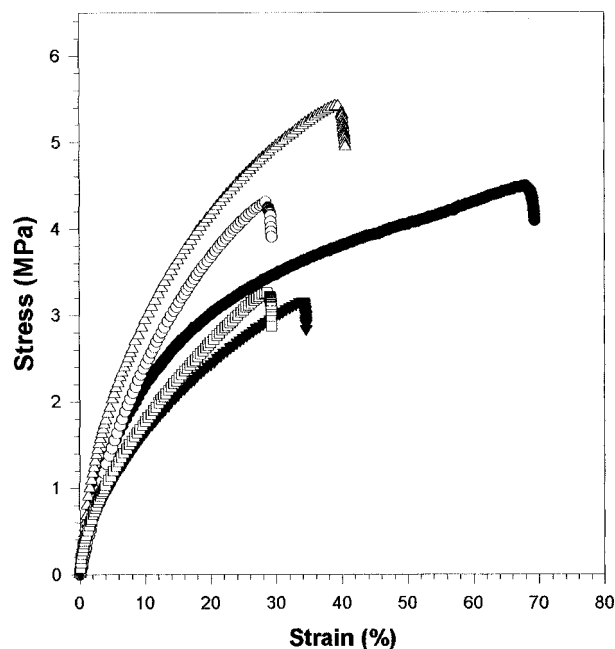
sions by viscosity measurements, the presence of SA in the solid mixtures promoted modifications on the melting of granular CS. Consequently, the conditions used in processing should be different; plasticized CS-SA mixtures were extruded at lower temperatures. The torque generated during extrusion of CS and CS-SA mixtures was monitored continuously and the equilibrium values were plotted as a function of SA content, as shown in Figure 2. The results show that the torque increases significantly when SA is added. A tendency of increasing values of torque as the SA composition is increased may be observed, which reflects the viscosity behavior shown in Figure 1.

To have controlled water contents in the thermoplastic blends, the conditioning of the samples was evaluated. Previous experiments showed the percentage of water that pure thermoplastic CS and CS-SA blends retained after being dried at 50°C, to constant weight. This humidity content was taken into consideration to determine the total water content of the thermoplastics. After drying, the samples were submitted to conditioning at different RH, at 25°C. It was observed that a 96-h period was sufficient to achieve equilibrium.

Figure 3(a)–(c) shows the influence of water content on the tensile properties of thermoplastic CS-SA extrudates with 3–6% (w/w) SA and 15% (w/w) glycerol. No yield point was observed in the



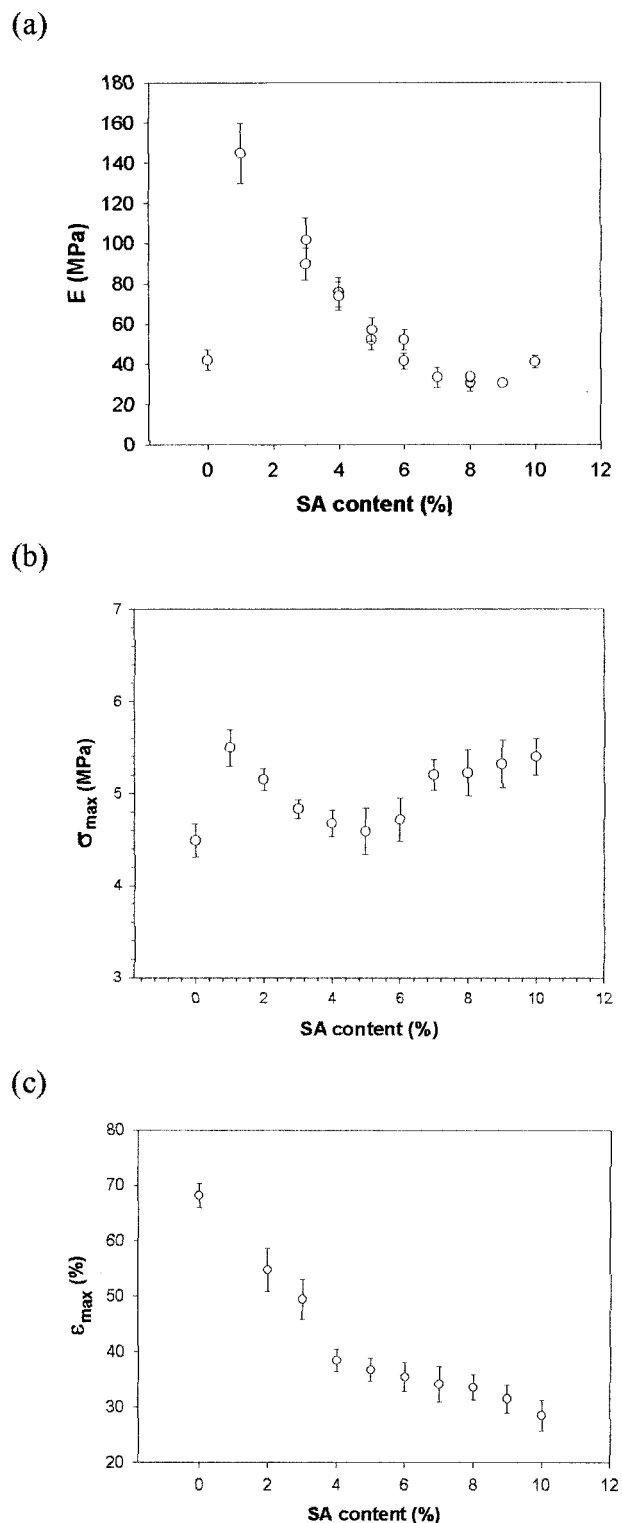
**Figure 3** Influence of water content on (a) Young's modulus ( $E$ ), (b) stress at break ( $\sigma_{max}$ ), and (c) elongation ( $\epsilon_{max}$ ) of thermoplastic CS-SA blends with 15% (w/w) glycerol: (●) 3% SA, (○) 4% SA, (▲) 5% SA, and (△) 6% (w/w) SA.



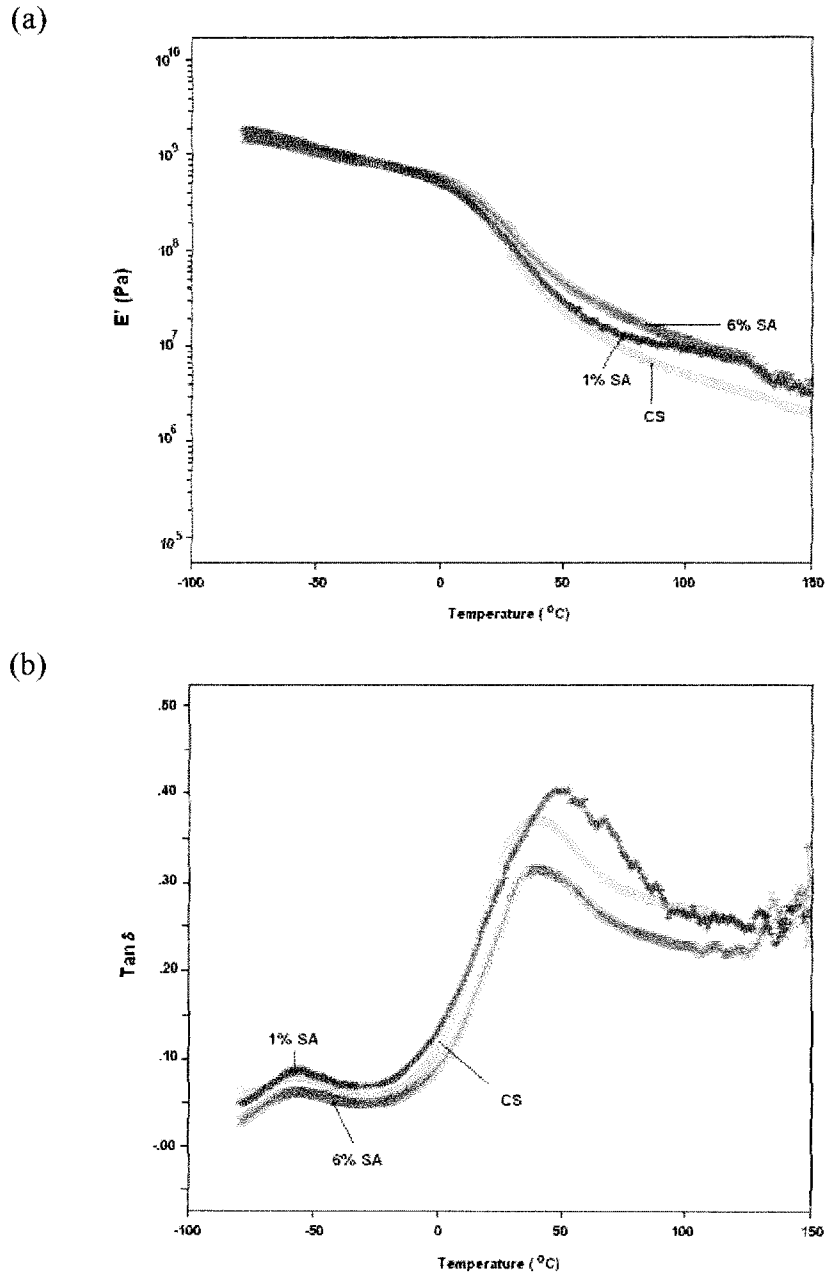
**Figure 4** Stress-strain curves obtained for CS and some CS-SA blends with 15% (w/w) water and 15% (w/w) glycerol contents as a function of SA composition: (●) CS, (○) CS-SA with 1% SA, (△) CS-SA with 5% SA, (▼) CS-SA with 7% SA, and (□) CS-SA with 10% (w/w) SA.

stress versus strain curves. At water contents lower than 5%, the materials became easily broken and difficult to be tested. Increasing water contents caused a decrease in the Young's modulus ( $E$ ) and stress at break ( $\sigma_{\max}$ ) for all samples. The decrease in  $E$  with increasing water content is characteristic of a polymeric material being plasticized through its glass-to-rubber transition.<sup>17</sup> At a water content of 5%, the blends are glassy and  $E$  and  $\sigma_{\max}$  reach the maximum values of 1200 and 20 MPa, respectively, for the CS-SA blend with 6% SA. At 9 and 15% water contents, the materials are rubbery, with  $E$  values in the range 0–200 MPa. Moreover, the effect of SA composition on the  $E$  and  $\sigma_{\max}$  values seems to diminish. On the contrary, the effect of SA composition on the elongation at break ( $\epsilon_{\max}$ ) is enhanced, when the water content is increased from 5 to 9 and 15%. This result is consistent with the idea that, at higher water contents, the macromolecules composing the system can form a stronger entangled network. At 9 and 15% water contents, maximum values of  $\epsilon_{\max}$  reach 40 and 50%, respectively, for the CS-SA blend with 3% SA.

Figure 4 shows stress-strain curves obtained for CS and some CS-SA blends with 15% water



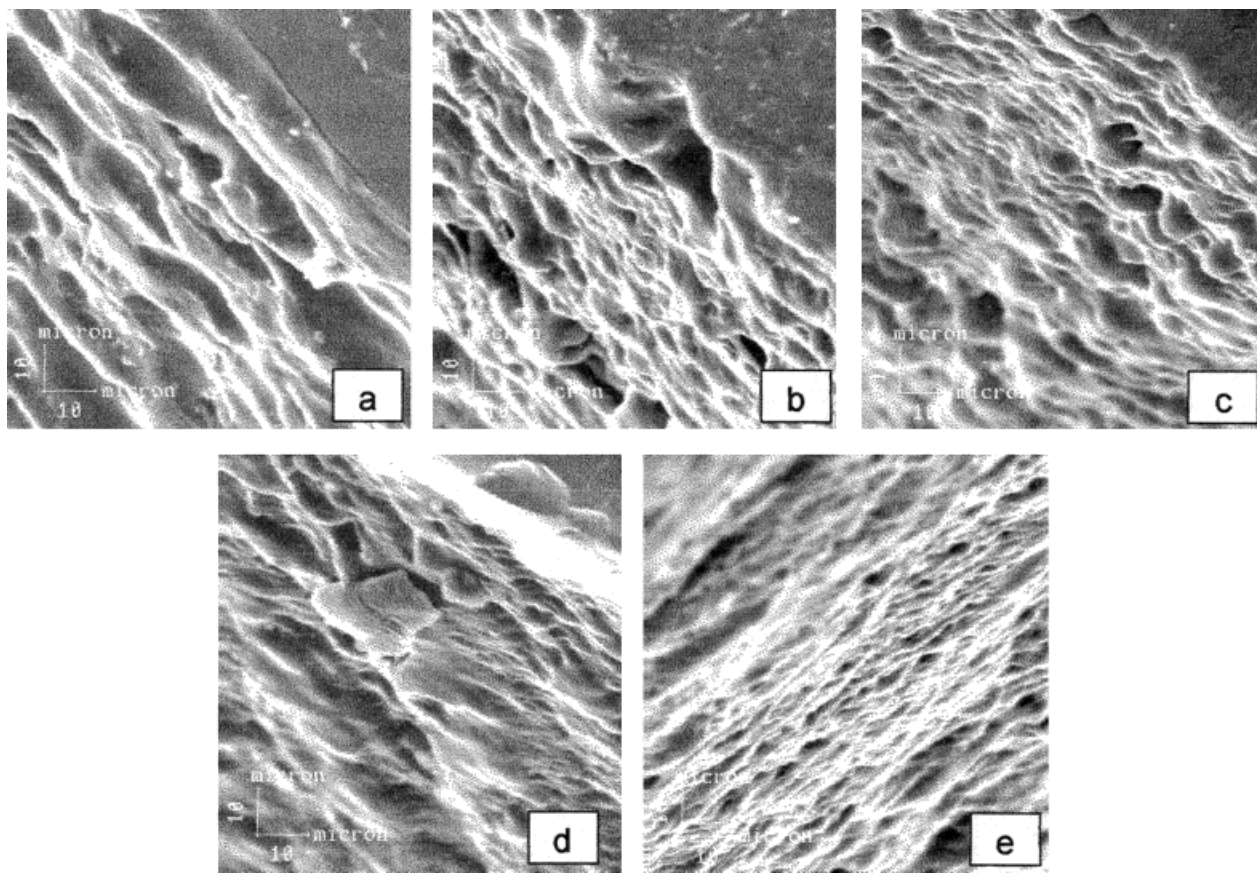
**Figure 5** Tensile properties of CS and CS-SA blends as a function of SA composition: (a) Young's modulus ( $E$ ), (b) stress at break ( $\sigma_{\max}$ ), and (c) elongation ( $\epsilon_{\max}$ ).



**Figure 6** Dynamic mechanical properties at 1 Hz for CS and CS-SA blends as a function of SA composition: (CS) thermoplastic CS alone, (1% SA) CS-SA blend with 1% SA, (6% SA) CS-SA blend with 6% SA; (a) storage modulus ( $E'$ ), (b)  $\text{tan } \delta$ .

and 15% glycerol contents as a function of SA composition, from 0 to 10%. The variation of  $E$  for CS and CS-SA blends may be visualized in Figure 5(a). Blends with low SA compositions, up to 5% (w/w) show improved values of  $E$ , compared to that of thermoplastic CS. In particular, a three-fold increase in  $E$  is observed when 1% SA is added, and gives rise to a maximum. The effect of SA addition on  $\sigma_{\text{max}}$  is shown in Figure 5(b).

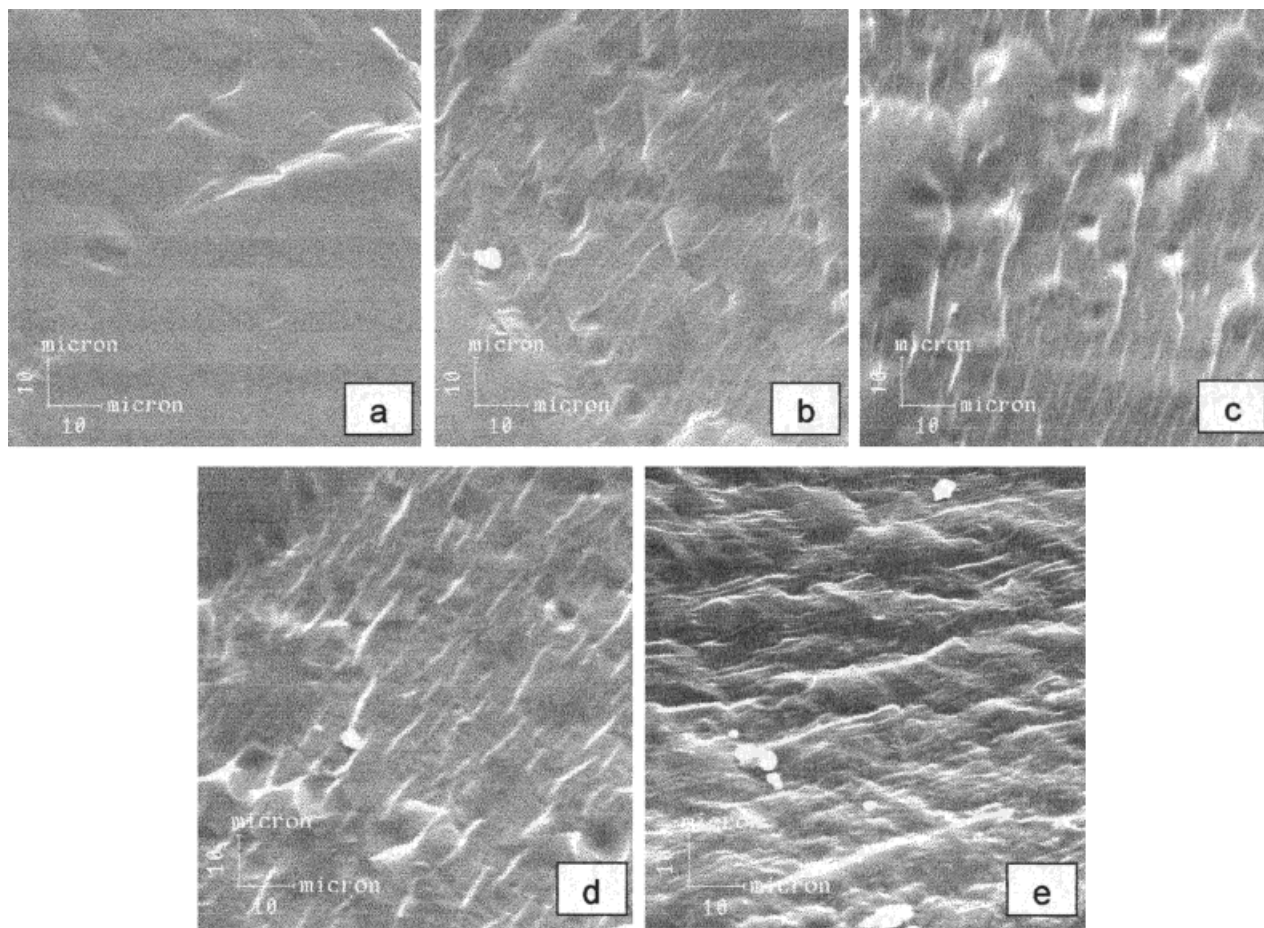
Higher values of  $\sigma_{\text{max}}$  are observed for the blends in relation to CS alone. A significant decrease in  $\epsilon_{\text{max}}$  is observed for CS-SA blends with the increase in the SA composition [Fig. 5(c)]. The  $\epsilon_{\text{max}}$  values are generally considered to be highly sensitive to the state of the interface.<sup>18</sup> According to the results shown in Figure 5(c), a better adhesion between the different polymers is achieved for lower SA composites.



**Figure 7** SEM micrographs of external surfaces of CS and CS-SA blends: (a) CS alone, (b) CS-SA blend with 3% SA, (c) CS-SA blend with 5% SA, (d) CS-SA blend with 7% SA, and (e) CS-SA blend with 10% SA.

Dynamic mechanical properties are reported in Figure 6(a) and (b), in terms of the temperature dependence of the storage modulus ( $E'$ ) and  $\tan \delta$ , respectively, for CS and CS-SA blends, with 1 and 6% (w/w) SA. In Figure 6(a),  $E'$  remains almost the same for the three samples, with a slow decrease in the temperature range  $-80$  to  $0^\circ\text{C}$ . A differentiated stiffening effect may be observed in the range  $\sim 10$  to  $90^\circ\text{C}$ , when  $E'$  is higher for the blend containing 6% SA. At this temperature, in the rubbery region,  $E'$  values for the two CS-SA blends are equal, probably affected by recrystallization of one of the components of the CS-SA blend with 1% SA. No such tendency was detected for the other samples. In Figure 6(b), two distinct transitions are observed for each of the CS-SA blends and for CS alone. Previous studies based on the glass-transition temperatures and the corresponding heat capacity increments determined for barley starch-glycerol-water mixtures characterized the system as either monophasic or bi-

phasic, depending on the total content of plasticizers.<sup>19</sup> At intermediate plasticizer levels (between 20 and 35% total contents of water and glycerol), two glass transitions were observed and phase separation was suggested to occur. DMA carried out for such mixtures showed two loss peaks, attributed to the transitions of a starch-poor phase (lower temperatures) and of a starch-rich phase (higher temperatures). In the present work, the first transition is observed in the same temperature range for the three samples, with the maximum at around  $-55^\circ\text{C}$ , and may be related to a polymer-poor phase. The upper transition, between  $0$  and  $80^\circ\text{C}$ , may be attributed to the glass transition of a CS-rich phase.<sup>12,13,19</sup> The maximum  $\tan \delta$  value occurs at a higher temperature for the blend with 1% SA. The peak for the blend with 6% SA occurs at the same temperature as that for CS alone and shows the lowest magnitude. Because the water content is the same for the samples, the result obtained for the blend



**Figure 8** SEM micrographs of cryofractured surfaces of CS and CS-SA blends: (a) CS alone, (b) CS-SA blend with 3% SA, (c) CS-SA blend with 5% SA, (d) CS-SA blend with 7% SA, and (e) CS-SA blend with 10% SA.

with 1% SA, observed for this  $\tan \delta$ , may reflect the recrystallization process previously detected for the  $E'$  behavior.

SEM micrographs taken from the surfaces of the extruded CS and CS-SA films are shown in Figure 7. Native CS granules are typically spherical in shape, with a diameter of approximately  $10 \mu\text{m}$ . No such image is seen and thus CS was completely melted during extrusion. Moreover, a homogeneous phase distribution may be observed at all CS-SA compositions. Because CS-SA blends were extruded at temperatures lower than that of CS alone, partial melting could have been observed for the blends. However, at least in the surfaces observed by SEM, no CS granules were visualized.

In Figure 8, cryofractured surfaces of extruded CS and CS-SA blends are shown. For the CS-SA blends [Fig. 8(b)–8(d)], the presence of cavities is clearly observed. These cavities are always in the

form of valleys, in both corresponding fracture surfaces. Moreover, these cavities have approximately the same diameter ( $\sim 4 \mu\text{m}$ ) and their distribution seems not to depend on SA composition. They are present even in thermoplastic CS. Thus, their presence cannot be attributed to phase separation.

## CONCLUSIONS

The effect of the addition of SA to plasticized CS suspensions and to plasticized CS in the solid state was investigated by viscosimetric measurements and extrusion processing. The onset of the gelatinization temperature was shown to occur at lower temperatures for CS-SA suspensions. Plasticized CS-SA mixtures with low levels of SA [1 to 10% (w/w)] were extruded at temperatures lower



than that of plasticized CS alone. These results indicated that some kind of interaction exists between both polysaccharides. Homogeneous, transparent, and flexible films were obtained by extrusion in a twin-screw extruder. The mechanical properties of CS-SA blends varied with the SA composition and with the water content. A three-fold increase in Young's modulus, relative to CS alone, was detected for the blend with 1% SA. Two transitions were observed by DMA for both plasticized CS and CS-SA blends. Cavities in the form of valleys were visualized in cryofractured surfaces of CS and CS-SA blends. Further studies on the dynamic mechanical properties and morphology of blends extruded with lower glycerol contents could give additional information to clarify the phase behavior of CS-SA systems.

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