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Physical characterization of cassava starch biofilms with special reference to dynamic mechanical properties at low temperatures

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Abstract

Biofilms based on cassava starch and containing glycerol as a plasticizer were characterized with respect to the effect of potassium sorbate concentration and pH on color, crystallinity and mechanical performance al low temperature.

It could be observed that a lower pH resulted in lower values of yellow index and tan δ and higher crystallinities.

Crystallinity decreased with sorbate addition, which also resulted, in general, an increase in yellow index and moisture content and a decrease of storage modulus for temperatures higher than the glycerol glass transition. Increase in sorbate content displaced the glass transition temperature of a glycerol-rich phase toward lower temperatures and increased the difference between the value that E' took in the glassy region and the value that it took in the rubbery region.

It is concluded that the physical properties of edible films can be affected by the antimicrobial agent, sorbate potentially compromising biofilm performance.

Keywords: Cassava starch; Biofilms; Physical characterization

1. Introduction

Starches are a renewable resource widely available from a range of sources. They are extensively used in the food and pharmaceutical industries and can be modified to enhance their functional properties (Luallen, 1985). Due to the increase in the price of starches from traditional sources (i.e., corn), cassava starch as it or modified has been recently considered as an economic alternative for the food industry (International Fund for Agricultural Development, 2004).

In recent years, starches have been applied alone or as part of a composite for the manufacturing of films and research has been performed concerning the use of these films as a way of improving food shelf life (Baker, Baldwin, & Nisperos-Carriedo, 1994; García, Martino, & Zaritzky, 1998). In particular, the use of edible films as a way of supporting and slowly releasing antimicrobials in food products has been a subject of research. They have been studied as carriers of natamycin and potassium sorbate for antimicrobial surface application (Franssen, Rumsey, & Krochta, 2002), for slow release of lysozyme and nisine (Buonocore, Del Nobile, Panizza, Battaglia, & Nicolais, 2003) and for slow release of propylparaben (Chung, Papadakis, & Yam, 2001). Starches are also used by the pharmaceutical industries. Cross-linked amylose (CLA) obtained through high amylose starch cross-linking with epichlorohydrin was introduced in the early 1990s, as a polymeric material, for drug controlled release. It has been shown that low cross-linked CLA corn starch is more

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resistant to hydration and more appropriate for the control of drug release (Dumoulin, Alex, Szabo, Cartilier, & Mateescu, 1998).

Starches can interact with antimicrobials such as sorbic, benzoic, and *p*-benzoic acids and the nature of this interaction depends on the type of starch as well as on the concentration and the chemical characteristics of the preservative (Duckova & Mandak, 1981; Mansour & Guth, 1968). As a consequence, some properties of the preservative such as its solubility, diffusivity, partition coefficient and the ability to penetrate into a biological membrane can be modified, affecting antimicrobial activity (Kurup, Wan, & Chan, 1995). Functional properties of starch can also be modified. Goodshall and Solms (1992) reported that the addition of sugars, lipids or surfactants can change the behavior of starches during gelatinization. Ofman, Campos, and Gerschenson (2004) reported the effect of sorbate presence on tapioca starch sorption properties and Famá, Rojas, Goyanes, and Gerschenson (2005) showed that mechanical properties of tapioca starch films at ambient temperature are affected by the presence of 3000 μg/g of potassium sorbate.

Sorbic acid and its potassium salt (sorbates, KS), are considered generally recognized as safe (GRAS) additives and have the advantage of having a lower partition coefficient (oil to water) in comparison with other antimicrobials; in this way a significant fraction is available in the aqueous phase to prevent microbial growth (Castro, Garro, Gerschenson, & Campos, 2003). KS activity increases at low pH. However, it is important to take into account that this preservative is unstable in aqueous solution and its oxidative degradation increases with pH decrease. This reaction, depends on the presence of other additives and on the conditions of storage (Binstok, Campos, & Gerschenson, 1998; Gerschenson & Campos, 1995; Gliemmo, Campos, & Gerschenson, 2004). As a consequence of preservative degradation, carbonyl compounds are produced and they can take part in nonenzymatic browning reactions and lead to undesirable changes in quality and acceptability. Moreover, a decrease in the preservative level might affect microbial stability.

The object of the present research was to study the effect of potassium sorbate concentration and pH on the color, moisture, crystallinity, and dynamic mechanical performance at low temperatures, of biofilms based on cassava starch for the purpose of evaluating its application to food preservation as carriers of antimicrobials.

2. Experimental

2.1. Materials

Mixtures of cassava – starch (5.0 g), glycerol (2.5 g), and water (92.5 g) or of starch (5.0 g), glycerol (2.5 g), potassium sorbate (0.1 or 0.2 or 0.3 g), and water (92.4 or 92.3 or 92.2 g) were prepared.

Citric acid aqueous solution (50.0 g/100 g) was used to adjust system pH to values of 6.7 or 5.0.

Cassava starch was provided by *Industrias del Maíz S.A.* (Argentina). Glycerol, citric acid (Mallickrodt, Argentina) and potassium sorbate (Sigma, St Louis, Missouri) used were of analytical grade.

A quantity of 300 g of the system was gelatinized under constant agitation with a heating rate of 1.6 °C/min until the ~70 °C gelatinization plateau was achieved. The heating continued until the sample acquired a temperature 5% higher than the temperature of the plateau (~73.5 °C). After gelatinization, the gel was degassed for 30 min, with a vacuum mechanical pump.

Portions of the system were distributed in glass dishes and dried at 52 °C for 2 h. Drying was finished at 25 °C. The thickness of casted films, measured with the help of an optical microscope, was 0.35 mm.

Before testing, the samples were conditioned at 25 °C, over saturated solution of NaBr (water activity, $a_W \cong 0.575$).

2.2. Measurements and characterization

2.2.1. Potassium sorbate dosage

Potassium sorbate content, in the films containing the preservative, was determined through the oxidation technique involving distillation and a colorimetric reaction using thiobarbituric acid, as proposed by the AOAC (1990). Determinations were performed in duplicate and the average is reported.

2.2.2. Moisture determination

Samples (≅0.5 g) were dried over calcium chloride, till constant weight, in a vacuum oven at 70 °C as proposed by the AOAC (1990). The reported moisture content represents the average of, at least, three samples.

2.2.3. Color

Color was evaluated with a Minolta CM-508d colorimeter (Minolta, Kyoto, Japan) employing the Hunter and CIE scale.

Circular samples of 2 cm diameter were employed for these tests. Determinations were performed in triplicate and the average is reported.

Color differences were calculated as:

$$\Delta C = \sqrt{\Delta a^2 + \Delta b^2 + \Delta L^2},$$

where L, represents lightness; a, redness; b, yellowness, and $\Delta a = a_i - a$, $\Delta b = b_i - b$, and $\Delta L = L_i - L$. The index i indicates the values taken as references, for each parameter; in our case, we used the film without sorbate as the reference. The color difference (ΔC) is the magnitude of the resultant vector of three component differences: lightness difference, ΔL; red-green chromaticity difference, Δa; yellow-blue chromaticity difference, Δb (Valencia Rodríguez, 2001).

Yellow index, YI, was calculated according to the ASTM D-1925 norm (MacFarlane et al., 1936) using the parameters from the CIE scale:

$$\mathrm{YI} = \frac{100}{Y}(1277X - 1067Z).$$

This equation is intended for determining the degree of yellowness for nearly colorless transparent plastics.

2.2.4. X-ray diffraction analyses

A Philips X-ray diffractometer with vertical goniometer operating at 40 kV and 30 mA was used (Cu Kα radiation $\lambda = 1.542$ Å). Samples mounted on a glass and conditioned at an a_W of 0.575 were attached to the equipment holder and X-ray intensity was recorded with a scintillation counter in a scattering angle (2θ) range of 3–33° with a scanning speed of 1°/min. Distances between the planes of the crystals d (Å) were calculated from the diffraction angles (°) obtained in the X-ray pattern, according to Bragg's law:

$$n\lambda = 2d \sin \theta,$$

where λ is the wavelength of the X-ray beam and n is the order of reflection. For calculation, n was taken as 1.

From the scattering spectrum, the effective percent crystallinity of films was determined, according to Hermans and Weidinger (1961), as the ratio of the integrated crystalline intensity to the total intensity. Because of the complexity of the system, the calculated crystallinities are not taken as absolute, but are rather used for comparative purposes. Crystalline area was evaluated on the basis of the area of the main peaks (main d-spacing) which were also used for calculation of relative crystallinity of each d-spacing.

2.2.5. Mechanical characterization

Dynamic mechanical measurements were performed using a Dynamic Mechanical Thermal Analyser (DMTA IV) Rheometric Scientific equipment (Rheometric Scientific Inc., NJ, USA) in the Rectangular Tension mode at 1 Hz, in the temperature range between −90 and 20 °C, at a heating rate of 2 °C/min.

The dimensions of the samples were 15.0 mm × 5.1 mm × 0.35 mm. A constrainer of strain was placed between the grips to hold the sample firmly without an excessive deformation in that region.

The samples were subjected to a cyclic strain lower than 0.4%. These strain values were sufficiently small to assure that the mechanical response of the specimen was within the linear viscoelastic range (Famá et al., 2005).

Storage modulus (E') and loss tangent ($\tan\delta$) were evaluated for each sample. The quantity E', the storage modulus, is a measure of the energy stored elastically, whereas E'', the loss modulus, is a measure of the energy lost as heat. The loss factor is defined as $\tan\delta = E''/E'$, being δ the angle between the in-phase and out-of-phase components of the modulus in the cyclic motion (Chartoff, 1981; Li & Larock, 2001).

Microscopic examination of specimens to be tested was performed and pieces where flaws were detected, were discarded.

No significant differences (level of significance, $\alpha = 0.05$) were observed between determinations of dynamic parameters performed in triplicate.

2.2.6. Differential scanning calorimetry (DSC)

DSC was performed with a Mettler Toledo Schwerzenbach instrument, indium and zinc calibrated. Ten milligram samples contained in aluminum pans were heated in the temperature range −110 to −20 °C, at a scanning rate of 10 °C/min, in nitrogen atmosphere. Two heating scans were performed and the second one is reported.

This determination was used to characterize the behavior of each of the components of the films and to understand trends observed in DMTA results.

2.2.7. Mathematical data treatment and statistical analyses

A two factor (sorbate concentration; pH) experiment was performed. Four levels of sorbate (0, 1000, 2000, and 3000 μg/g) and two levels of pH (5.0 and 6.7) were assayed. Data were analyzed through two-way ANOVA with an $\alpha = 0.05$. Tukey test was the post hoc test applied. Results are quoted on the basis of their average and confidence interval ($\alpha = 0.05$) (Sokal & Rohlf, 1969).

Statgraphics Plus for Windows, version 3.0, 1997 (Manugistics, Inc., Rockville, MD, USA) was used for data treatment and statistical analysis.

3. Results and discussion

Table 1 shows potassium sorbate and moisture content, crystalline fraction and color parameters of the films. It can be observed that the increase in sorbate content was accompanied, in general, by a significant increase in the moisture content, independent of the pH of the system, though, according to the results obtained for the sample containing 2000 μg/g of sorbate, pH seems not to affect significantly the moisture content.

3.1. Color

Table 1 shows that ΔC and YI increased with sorbate concentration: preservative presence promoted color change and increased yellowness of the films. This trend was observed for both pHs studied, but lower values of YI were observed for pH 5.0. Changes in color observed might be ascribed to sorbate browning; it is known that this antimicrobial takes part in browning reactions (Gerschenson & Campos, 1995) and that these reactions decrease with pH (Cheftel, Cheftel, & Besancon, 1983).

3.2. X-ray pattern

Fig. 1 shows the X-ray diffraction patterns for films without sorbate (i), with 1000 μg/g (ii), 2000 μg/g (iii) and

Table 1
Composition, crystalline fraction, and color parameters of the cassava starch biofilms

Initial sorbate content (g/100 g, dry basis) of system	pH	Sorbate content of the films (g/100 g, dry basis)[1,2]	Moisture content of the films (g/100 g,dry basis)[1,2]	Glycerol content in the films (g/100 g, dry basis)	Crystalline fraction (%)[2]	Color parameters[1,2]	
						ΔC	YI
0	6.7	–	$25.0 \pm 4.0^{c,d}$	33.00	33.4	0	8.9 ± 0.1^{i}
0.1		1.28 ± 0.33	22.3 ± 0.4^{c}	32.89	24.2	1.3 ± 0.3	10.2 ± 0.1
0.2		$2.19 \pm 0.27^{a,b}$	$38.0 \pm 2.0^{e,f}$	32.46	22.2	$2.9 \pm 0.4^{g,h}$	11.8 ± 0.2
0.3		2.69 ± 0.43^{a}	$44.9 \pm 0.7^{e,f}$	32.05	17.9	4.1 ± 0.6^{g}	12.4 ± 0.2
0	5.0	–	27.2 ± 1.2^{d}	33.00	33.4	0	$8.8 \pm 0.1^{i,j}$
0.2		1.95 ± 0.15^{b}	37.8 ± 1.6^{e}	32.46	25.6	2.5 ± 0.4^{h}	9.8 ± 0.5^{j}

The superscripts a–j, only indicate that the values with the same letter are not significantly (α: 0.05) different.

[1] Data are informed as $x \pm \varepsilon$, being x the average and $\varepsilon = t_{(n-1)}s/n^{1/2}$. t is the Student's parameter ($\alpha = 0.05$); s is the standard deviation and n is the number of samples assayed (three for moisture content or ΔC, two for sorbate content, and six for YI).

[2] Two weeks after gelatinization. Samples were equilibrated at an a_W of 0.575 at 25 °C.

3000 μg/g (iv) of sorbate, at pH 6.7 (a) and 5.0 (b), respectively.

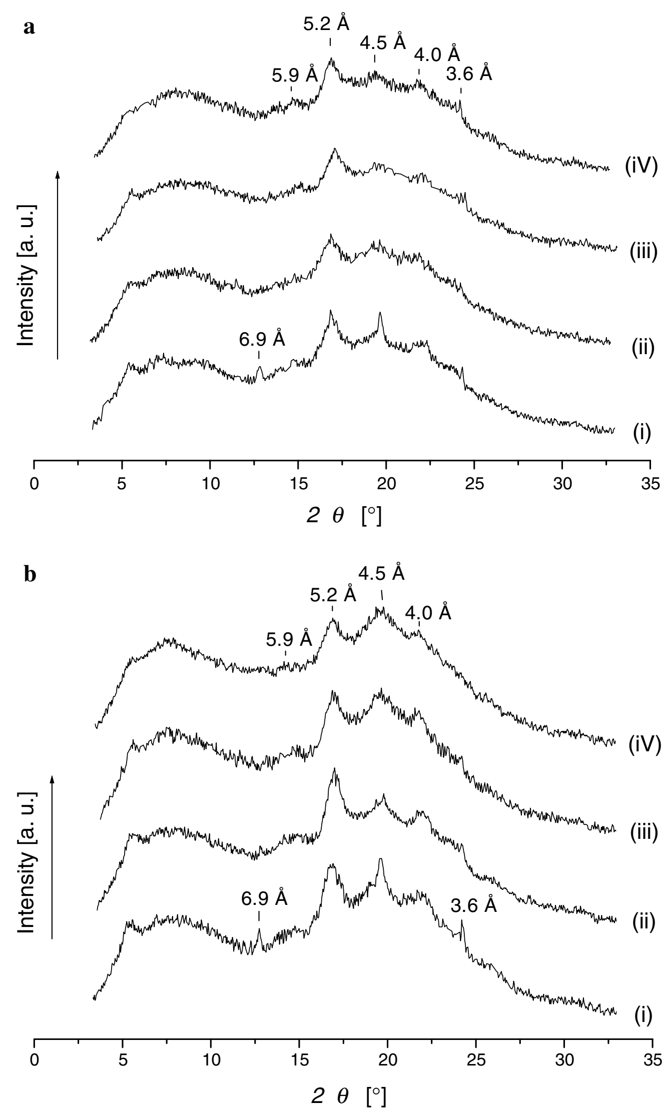

Fig. 1. X-ray diffraction patterns of films without sorbate (i), with 1000 μg/g (ii), 2000 μg/g (iii), and 3000 μg/g (iv) of sorbate. (a) pH 6.7; (b) pH 5.0.

The crystalline peaks, were analyzed in the interval from 12° to 25° (2θ), identifying the most intense peaks and calculating the distances between the planes of the crystals d (Å) from the diffraction angles (°). It was observed that X-ray pattern showed a B-V structure (García, Martino, & Zaritzky, 2000; Manzocco, Nicoli, & Labuza, 2003; Zobel & Illinois, 1986) which diffracted in the following planes $d \cong 4.0$, 4.5, 5.2, and 6.9 Å (films without sorbate) and $d \cong 4.0$, 4.5, and 5.2 Å (films with sorbate). These peaks are identified in Figs. 1(a) and (b). The 5.2, 4.5, and 4.0 Å peaks coincide with peaks observed for tuber starches. Potassium sorbate also showed peaks at 4.5 and 4.0 Å. Other peaks of lower intensity were observed at 3.6 and 5.9 Å. They can be associated to starch peaks (ICPDS, 1997).

At about 6.9 Å a peak that decreased with sorbate presence can be observed, probably due to the effect of antimicrobial presence on previously existent crystalline characteristics of the system. The intensity of the crystalline peaks decreased with sorbate content increase.

Results concerning crystalline fraction can be observed in Table 1. Sorbate incorporation on starch films diminished the crystalline fraction. It was previously reported (Famá et al., 2005) that sorbate has a plasticizing action on tapioca starch films. It is interesting to observe that the decrease of the pH from 6.7 to 5.0, produced a slight increase in the crystalline fraction, which might be ascribed to a decrease gel strength due to the acidity increase (Donald, 2004, chap. 5).

3.3. Moisture content

The incorporation of potassium sorbate in the films produced an increase in the moisture content of samples (Table 1). It is known that the increase in the crystalline phase of a semicrystalline material is highly linked with the decrease in its moisture content (Chang, Chea, & Seow, 2000). As a consequence, the decrease in crystalline fraction with antimicrobial increase, previously reported, may be the cause of trend observed for moisture content in our samples.

3.4. Mechanical properties

Fig. 2 shows the storage modulus, E' (a), and loss tangent, $\tan\delta$ (b), dependence with temperature for the films with pH 6.7. Two peaks can be observed in $\tan\delta$ curves: a very important one around −62 °C, and other, wide and with low intensity, between −30 and 10 °C. The molecular relaxation around −62 °C, shown in Fig. 2(b) as a peak, also determined an abrupt fall in the storage modulus in that region of temperatures (Fig. 2(a)). This relaxation is generally named as an α-relaxation. The glass transition temperature, T_g is typically identified, in the $\tan\delta$ curve, as the temperature where the maximum of the α relaxation occurs (Lazaridou & Biliaderis, 2000; Ogale, Cunningham, Dawson, & Acton, 2000).

According to Standing, Westling, and Gatenholm (2001), pure glycerol has a glass transition temperature at −78 °C. Other authors (Cherian, Gennadios, & Weller, 1995; Ogale et al., 2000) reported pure glycerol T_g at −93 °C. Wilhelm, Sierakowski, Souza, and Wypych (2003), showed that glycerol-plasticized native cara-root starch films present two relaxations: one at −74 °C and the other, at 188 °C. These peaks can be attributed to two phases originated due to the partial miscibility of starch and glycerol (Forssell, Mikkila, Moates, & Parker, 1997; Wilhelm et al., 2003). The glass transition at −74 °C was attributed to a glycerol-rich phase and the other, to a starch-rich phase.

In Fig. 2(b) it can be observed that an increase in antimicrobial content produced a displacement, to lower temperatures, of the maximum of $\tan\delta$ peak. This trend agrees with the very well-known effect of plasticizer incorporation to a system: it moves their T_g to lower temperatures (Chartoff, 1981).

Fig. 3 shows the heating thermograms obtained in this work for glycerol solution (a) which showed a T_g value of −95 °C. The glycerol–starch films showed, in the range of temperatures studied, only one relaxation around −68 °C when studied by DSC, which according to previously cited authors might be associated with the T_g of a glycerol-rich phase. As a consequence, it can be concluded that the peak observed at −62 °C through DMTA (Fig. 2(a)) might be associated with the glycerol-rich phase of the system under study, taking into account that $\tan\delta$ peaks at a frequency of 1 Hz are shifted upwards in temperature compared with the T_g measured by DSC (Chartoff, 1981).

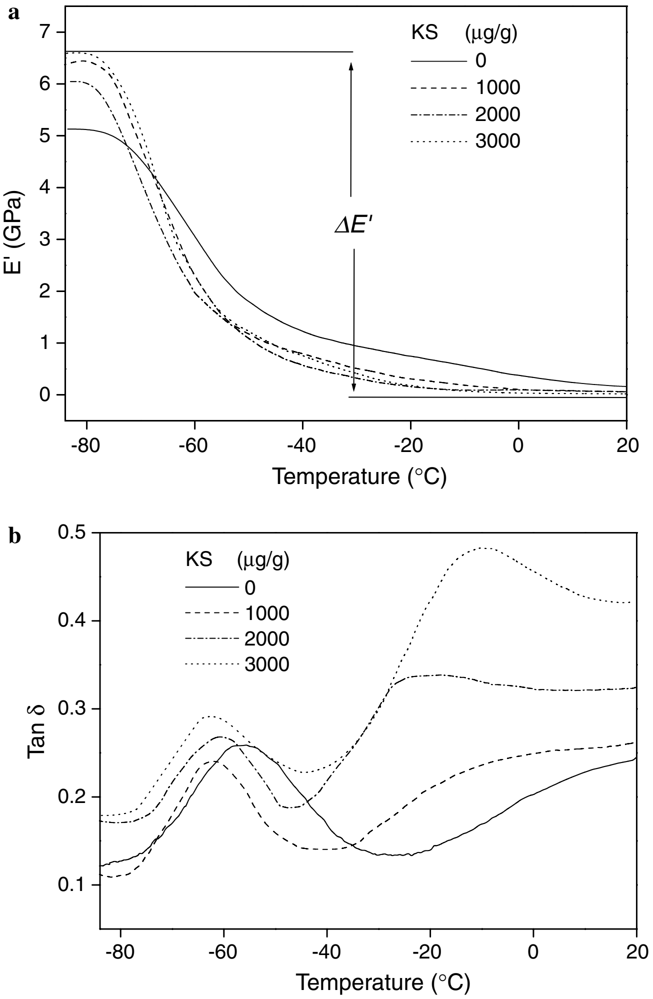

Fig. 2. Change with temperature of the storage modulus (a) and loss tangent (b) for films of pH 6.7.

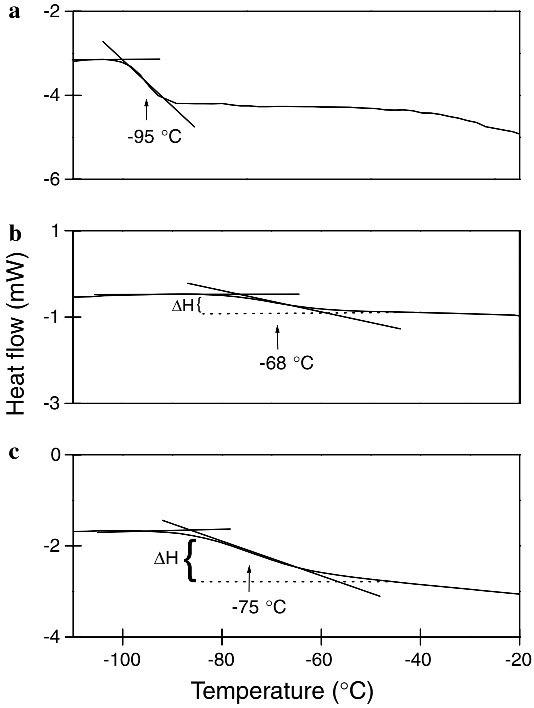

Fig. 3. Heating thermograms of glycerol solution (25 g/100 g) (a); tapioca starch–glycerol (2:1) films (b); starch–glycerol–sorbate (2:1:0.08) films (c).

On the other hand, Figs. 3(b) and (c), show that the addition of sorbate increased the change in the enthalpy (ΔH) during relaxation and the temperature range of the transition for the films. According to Bair (1981, Chapter, 10) the magnitude of ΔH can aid in estimating the fraction of material participating in a particular phase of a multi-component systems. In Fig. 2 it can be observed that a higher concentration of sorbate produced a greater difference between the values of E' in the glassy region and in the rubbery region ($\Delta E'$). For the film without sorbate (Fig. 2(a)) $\Delta E'$ showed a value of 5.2×10^3 MPa, while in the film with 2000 µg/g KS, $\Delta E'$ showed a value of 6.4×10^3 MPa, indicating that sorbate increased the fraction of material relaxing; it behaved as a plasticizer. It must be remembered that films with sorbate also have higher moisture content and that water acts as a plasticizer.

Figs. 4(a) and (b) show the change of E' and $\tan\delta$ with temperature, for films without sorbate and with 2000 µg/g of sorbate, both systems at pH 5.0. It can be observed the same trend for $\Delta E'$ change with antimicrobial concentration, previously stated for pH 6.7. Comparison between Figs. 4 and 2 show that pH seemed not to affect glycerol-rich phase behavior.

Figs. 2(b) and 4 (b) show that the width of the peaks observed between −30 and 10 °C was strongly affected by sorbate content at both pHs studied. As it increased, the peak was better defined. In Fig. 5 it is shown the change of $\tan\delta$ in the temperature range −50 to 20 °C, for films of pH 6.7 (a) and 5.0 (b), respectively. It can be observed that behavior was strongly influenced by sorbate content, as it increased, the peak between −30 and 10 °C was better defined. As previously stated, an increase in sorbate content is related with a decrease in the crystalline fraction. Comparing (a) and (b) it can be concluded that the peak between −30 and 10 °C was less notorious when the pH decreased for films containing 2000 µg/g of sorbate. It is well known that relaxation can be suppressed or can appear as a relatively minor event difficult to detect in polymers that develop a high degree of crystallinity (Chartoff, 1981). As a consequence, the behavior observed in this research might be ascribed to changes in crystalline fraction: X-ray studies showed that the crystalline fraction was slightly greater for films with pH 5.0 than for the ones with pH 6.7 and that it decreased with sorbate content.

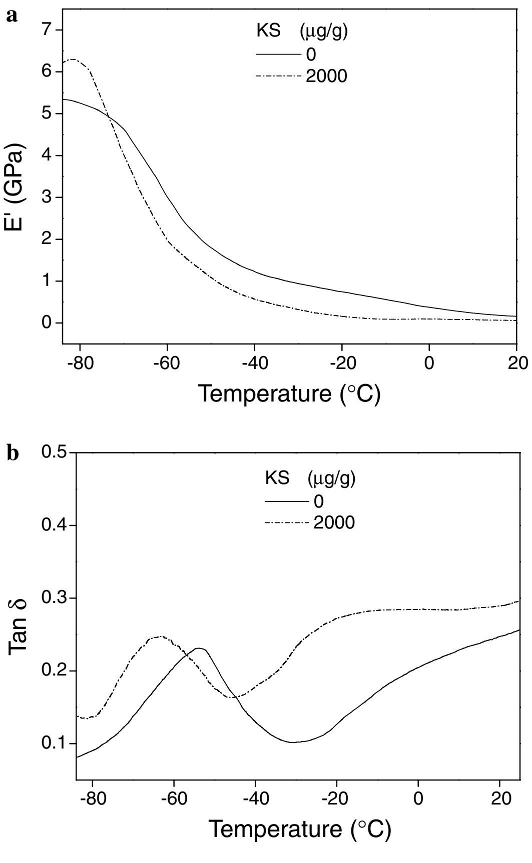

Fig. 4. Change with temperature of the storage modulus (a) and loss tangent (b) for films of pH 5.

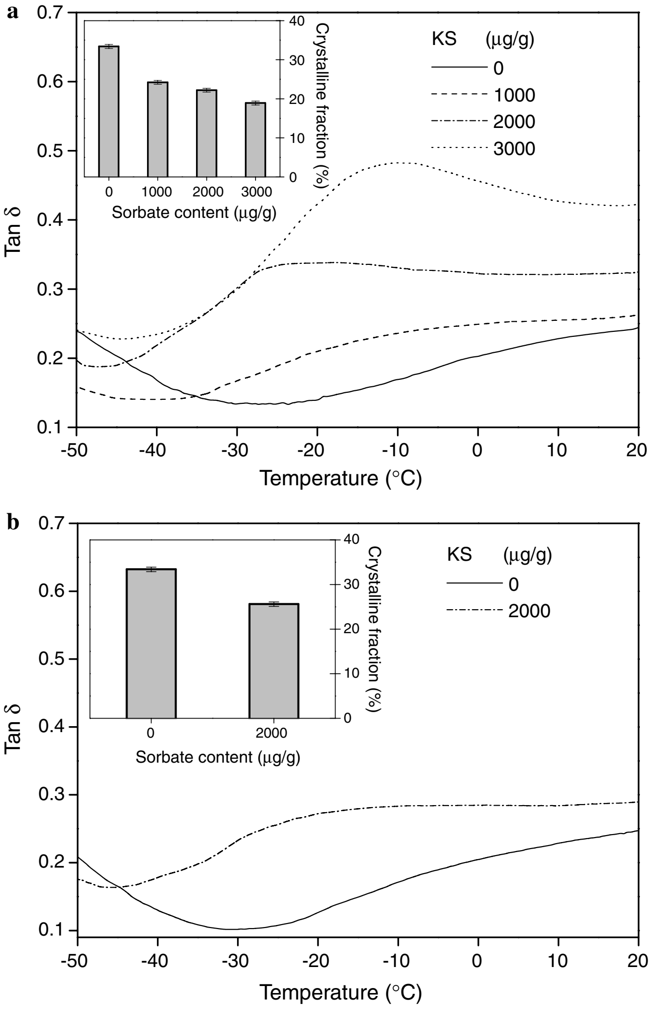

Fig. 5. Crystalline fraction and loss tangent change with temperature. Films with different concentrations of potassium sorbate and pH 6.7 (a); films with different concentrations of potassium sorbate and pH 5.0 (b).

It can be seen an excellent agreement between the results obtained concerning the effect of sorbate on dynamic parameters and on moisture and crystalline fraction.

4. Conclusions

Biofilms based on cassava starch and containing 32.5% (w/w, dry basis) of glycerol as plasticizer showed two mechanical relaxations between −90 and 20 °C. The peak observed at −62 °C was associated with the glass transition temperature of a glycerol-rich phase and the other, wide and with low intensity, observed between −30 and 10 °C, was dependent on acid level and sorbate content. An increase in the acidity or a decrease of the antimicrobial led to crystallinity increase as well as to a decrease of moisture content, loss tangent and of the difference among the value that E' took in the glassy region and the value that it showed in the rubbery region ($\Delta E'$).

Results of this work showed that the mechanical behavior of the biofilms can be explained on the basis of X-ray and moisture content results.

The increase in antimicrobial content produced a greater yellow index potentially affecting food product quality.

It is concluded that changes in mechanical and physicochemical properties of films due to antimicrobial presence must be considered during film formulation and processing to assure their efficiency as antimicrobial carriers without impairment of overall product quality.

Acknowledgments

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