

Mechanical properties of tapioca-starch edible films containing sorbates

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Abstract

The effect of sorbate present on mechanical properties of edible films prepared with suspensions of tapioca starch containing glycerol, was studied. Films were prepared by casting the systems after gelatinization. The storage modulus (E') and the tangent of the phase angle ($\tan \delta$) of the film pieces were determined with a Dynamic Mechanical Thermal Analyzer along 8 weeks of storage at a relative humidity (RH) of 57.5% and at 25 °C. Stress–strain behavior along quasi-static tests was also analysed using the same device. Results obtained showed that sorbate incorporation resulted in a decrease ($\cong 75\%$) of E' and an increase ($\cong 200\%$) of $\tan \delta$ after 2 weeks of storage. Antimicrobial presence also affected film performance along storage: it showed a continuous decrease of $\tan \delta$ along 8 weeks storage as well as an increase in the tendency to rupture with time. Films without sorbate showed an increase of $\tan \delta$ along 4 weeks and they presented rupture for all storage periods studied. Aging of starch, characteristics of the network as well as sorbate destruction along storage, are responsible for the changes observed in mechanical properties of the film along 8 weeks. © 2004 Swiss Society of Food Science and Technology. Published by Elsevier Ltd. All rights reserved.

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1. Introduction

Starches are polymers that naturally occur in a variety of botanical sources such as wheat, corn, potatoes and tapioca. It is a renewable resource widely available and can be obtained from different left overs of harvesting and raw material industrialization. They are useful for numerous applications in the food industry and their functional properties depend on the source but are also affected by other factors like chemical modifications, system composition, pH and ionic strength of the media. Grown in tropical areas (Latin America, Asia and Southern Africa) of the world, tapioca is used in Latin

America as a meal, as animal fodder or cooked and eaten as a vegetable. The Food and Agriculture Organization (FAO) highlighted recently that tapioca is a good commercial cash crop and a major source of food security, and that it needs a competitive edge to thrive in the global starch market. Due to shortage or high price of traditional starch sources, such as wheat and soybeans, the tapioca starch is viewed as an alternative source by the food companies for use as an ingredient (Anonymous, 2004).

Starches can interact with many additives or components of the food. As a result of this interaction, different properties of either the additive or the starch might be affected. Starch 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 (Mansour & Guth,

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1968; Duckova & Mandak, 1981) and, 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 the 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) observed that sorbate presence during gelatinization affects sorption isotherms of freeze-dried gelatinized tapioca starch.

Edible films and coatings have long been used to protect food products (Baker, Baldwin, & Nisperos-Carriedo, 1994; García, Martino, & Zartzy, 1998). Cellulose, starch, proteins and lipids can be used to formulate edible films which must be completely neutral with reference to color, taste and odor. The application of edible films is a technological hurdle that can modify vegetable tissue metabolism while affecting respiration; they can be conveyors of antimicrobials, antioxidants and other preservatives; they can enrich product formulation, carrying vitamins and minerals. One important component of edible films is the plasticizer which is required to overcome film brittleness and improve its flexibility and extensibility (McHugh & Krochta, 1994). The most commonly used plasticizers are polyols, mono-, di- or oligosaccharides, fatty acids, lipids and derivatives. According to Donhowe and Fennema (1993) plasticizers improve mechanical properties of starch edible films by decreasing intermolecular attraction and interfering with amylose packing. Sorbic acid, which is a very well known GRAS antimicrobial, behaves as a short chain fatty acid in relation to its reactivity and metabolic pattern (Sofos, 1989). As a consequence, it is possible that it might act as a plasticizer, affecting mechanical properties of the films, when included in their formulation.

The study of mechanical properties of edible films is a subject of great importance due to their influence on product performance and consumer acceptance. In physically cross-linked systems, like edible films based on starches, the density and lifetime of the junction zones will govern the mechanical properties of the network and its responses to applied stress or strain. In this context, it is important to realize that measurements of rheological properties are constrained to certain limited deformation levels and time scales. Consequently, any assessment of the mechanical properties of hydrated gel networks must be carried out under carefully chosen conditions of stress or strain and temperature–time regimes; this is usually accomplished by employing oscillatory (dynamic) tests which are nondestructive to the structure of the specimen tested. Conducting measurements under small deformations

precludes structure breakdown or any interference with the formation of network structure.

The objective of this research was to study the mechanical properties of tapioca-starch edible films containing glycerol as plasticizer with special reference to the influence of sorbate presence on those properties and on the mechanical performance of the film along storage. The results of the study will contribute to understand the effect of film composition on its performance and on food quality along shelf-life.

2. Materials and methods

2.1. Preparation of samples

Mixtures of starch (5.0 g), glycerol (2.5 g) and water (92.5 g) or of starch (5.0 g), glycerol (2.5 g), sorbates (0.3 g) and water (92.2 g) were prepared. Gelatinization was accomplished through heating of 100 g samples at a rate of 2.0 °C/min (Fig. 1) for \cong 18 min, moment at which the system entered in the gelatinization plateau (\cong 70 °C). This process lasted \cong 13 min and afterwards, sample was heated an additional period of 5 min. After gelatinization, the mixtures were casted over glass plates and dried at 50 °C for two hours. Drying was finished at 25 °C (5 days).

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

Pieces of the film for dynamic tests were cut with a scalpel, into strips of 29 × 5 mm. The shape of the specimens for quasi-static tensile tests is shown in Fig. 2 and the 25 × 5 mm samples were obtained from the film, with the help of a scalpel applied to the adequate aluminum pattern specially made for this purpose. The

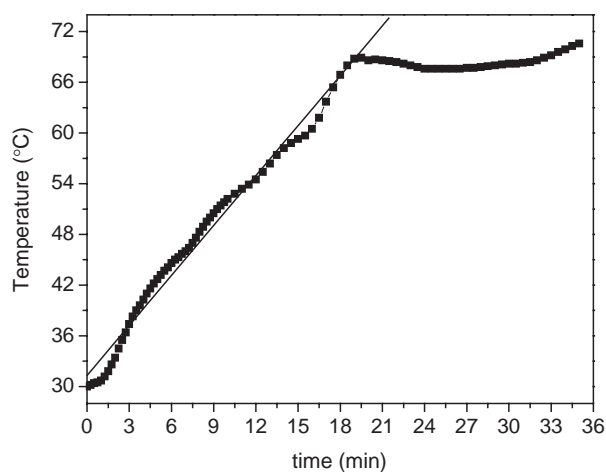


Fig. 1. Sample temperature along the heating applied to perform system gelatinization.

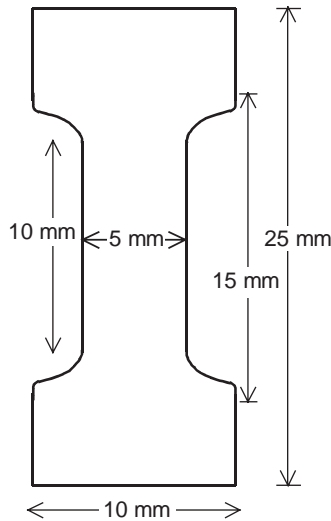


Fig. 2. Shape of the specimens for quasi-static tensile test.

geometry selected minimized the uneven stress distribution and avoided the break in the area of contact with the grips. Microscopic examination of specimens to be tested was performed to detect flaws occurred during preparation.

Before testing, the samples were conditioned at 25 °C, over saturated solution of NaBr (water activity, $a_w \cong 0.575$) during 2–8 weeks and the moisture of those samples was determined.

The thickness of casted films, measured with the help of an optical microscope, was in the range 0.30–0.38 mm.

2.2. Mechanical characterization

The tests for characterizing the visco-elastic properties of the studied material were carried in a DMTA IV Rheometric Scientific equipment (Rheometric Scientific Inc., New Jersey, USA).

The samples were studied in the Rectangular Tension mode with an initial gauge length of 19 mm in the case of dynamic tests and 15 mm, for quasi-static tests.

A constrainer of strain was placed between the molars of the grips to hold the sample firmly without an excessive deformation in that region.

2.2.1. Strain sweep

A strain sweep (up to 1.00% strain) was performed in steps of $5 \times 10^{-3}\%$ strain, initially, to determine the linear visco-elastic range. Assays were performed in triplicate and the average is informed.

2.2.2. Tensile stress–strain behavior

For quasi-static tests, the strain rate was fixed in a value of $5 \times 10^{-4} \text{ s}^{-1}$ and the experiment was performed till rupture, recording the stress (σ)–strain (ε) curves.

Assays were performed four times for each sample and condition.

The ultimate tensile strength (σ_b) and elongation at break (ε_b) of the films was evaluated and the energy per unit volume necessary to attain 30% deformation of the sample, was obtained from the area under the corresponding (σ)–(ε) curve.

2.2.3. Oscillatory studies

In this technique, the sample undergoes repeated small-amplitude strains in a cyclic manner. The modulus acquires, in this case, a complex form:

$$E^* = E' + E''.$$

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 (Li & Larock, 2001).

The samples were studied in the tensile mode and were subjected to a cyclic strain of 0.04%. Those strain values were sufficiently small to assure that the mechanical response of the specimen was within the linear visco-elastic range. The oscillatory tests were carried out at 1 Hz. Data were collected under dynamic temperature ramp test routine at 25 °C. Seven samples were studied for each condition and type of film.

2.2.4. Mathematical modeling of stress–strain curves—*theoretical considerations*

The stress–strain relationship, for systems characterized by a single relaxation time, τ , can be written as (Mano & Viana, 2001):

$$\sigma(\varepsilon) = E_0\varepsilon + E_1k\tau(1 - \exp(-\varepsilon/k\tau)), \quad (1)$$

where $k = d\varepsilon/dt$, is the constant strain rate. E_0 is the modulus of the relaxed state and $(E_0 + E_1)$ is the initial modulus.

Real systems are characterized by a broad distribution of relaxation times, each one corresponding to different relaxation process. To represent such a spread in the distribution of relaxation times, the technique of substituting the time by the power of time according to the Kohlrausch–Williams–Watts (KWW) function, is often used. For example, the following expression often used for the relaxation modulus, when systems are characterized by a single relaxation time:

$$E(t) = E_0 + E_1 \exp(-t/\tau) \quad (2)$$

is replaced by:

$$E(t) = E_0 + E_1 \exp(-t/\tau^*)^\beta \quad (3)$$

for real systems. In this expression, β is an empirically determined number that takes values between 0 and 1. It quantifies the extent of deviation from pure

exponentiality. The KWW function implies a spectrum of relaxation times whose breadth is inversely related to the parameter β . The characteristic time τ^* is an adjustable parameter and should not a priori be identified with the average relaxation time (Matsuoka, 1986; Mano & Viana, 2001).

The stress–strain formula for single relaxation time (1) can be modified using a similar criteria to that explained previously for stress relaxation equation (2) to obtain a KWW equivalent of stress–strain formula (Matsuoka, 1986) by substituting $(k\tau)$ by $(k\tau^*)^\beta$ in Eq. (1):

$$\sigma(\varepsilon) = E_0\varepsilon + E_1(k\tau^*)^\beta(1 - \exp(-\varepsilon/k\tau^*))^\beta. \quad (4)$$

The ratio of τ^* and β is called τ_T which, according to Shamblin, Hancock, Dupuis, and Pikal (2000), is an average relaxation time that characterizes molecular motions in amorphous systems.

The curves σ vs. ε experimentally obtained were fitted to Eq. (4) and the parameters β and τ_T were calculated for each system and storage time studied.

2.3. X-ray diffraction analysis

A Philips X-ray diffractometer with vertical goniometer was used (Cu K α radiation $\lambda = 1.542 \text{ \AA}$). Operation was performed at 40 kV and 30 mA. 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 (\AA) were calculated from the diffraction angles (deg) 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.

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. Crystalline area was evaluated on the basis of the area of the main peaks (main d -spacing). Because of the complexity of the system, the calculated crystallinities are not taken as absolute, but are rather used for comparative purposes.

2.4. Moisture determination

Samples were dried over calcium chloride till constant weight, in a vacuum oven, at 70 °C. The moisture determination lasted, approximately, 20 days. Determination was performed in duplicate.

2.5. Potassium sorbate dosage

Potassium sorbate destruction was followed, in the film containing the preservative, through the oxidation technique involving distillation and a colorimetric reaction using thiobarbituric acid, as proposed by the AOAC (1990). Determinations were performed in duplicate.

2.6. Mathematical data treatment and statistical analysis

It was performed a two factor (sorbate concentration; time) experiment with repeated measures on one factor (time). Two levels of sorbate (0 and 3000 ppm) and three levels of time (2, 4 and 8 weeks) were assayed. Data were analysed through two-way ANOVA with an $\alpha = 0.05$. Tukey test was the post hoc test applied. Results were informed on the basis of their average and confidence interval ($\alpha = 0.05$). A “ t ” test for the difference of medias was applied to study the influence on different parameters of: (a) sorbate presence for each time studied and (b) storage time for each kind of film (Sokal and Rohlf, 1969).

Nonlinear regression analysis was applied to model stress–strain curves and integration was performed for work calculation.

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

3. Results and discussion

The stress–strain experiments are one of the most used tests to characterize the mechanical behavior of visco-elastic polymeric materials. The initial slope of these stress–strain curves defined as the Young modulus, is found to depend on the temperature and the strain rate (Mano & Viana, 2001).

Assays performed showed that deformation values up to 0.30–0.38% were in the linear visco-elastic range for films studied. Fig. 3(a) and (b) shows the tensile stress (σ)–strain (ε) behavior of the films. It can be observed that the deformation nature of the polymers at room temperature, under an applied load, was typical of ductile plastics in terms of the stress and strain. As generally for those materials, the films exhibited two characteristic regions of deformation behavior in their tensile stress–strain curves. At low strains (lower than 10%) the stress increased rapidly with an increase in the strain and the initial slopes were steep in the elastic region, indicating the high elastic modulus of the materials. At higher strain (higher than 10%) the films showed a slow increase in stress with strain, until failure occurred. Curves obtained showed that the behavior of both type of films is different and that storage time

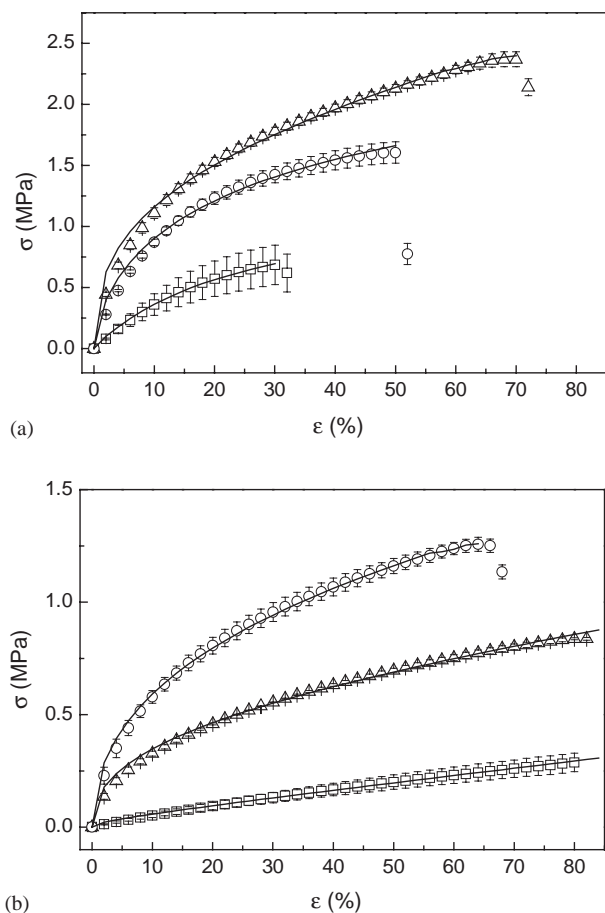


Fig. 3. Stress–strain relationship for films. (a) Films without sorbates; (b) films with sorbates. \square , 2 weeks of storage; \triangle , 4 weeks of storage; \circ , 8 weeks of storage.

affects that behavior. ANOVA showed that sorbate, time or the interaction between sorbate and time exerted significant effects ($P < 0.05$) on the parameters evaluated (E' , $\tan \delta$, σ_b , ε_b), confirming the trend previously stated.

Table 1 shows that the film without sorbate, after 2 weeks of storage, showed a higher storage modulus, a lower loss tangent and a lower strain at break than the films with sorbate ($P < 0.05$). It is important to remark that the films containing sorbate did not show a necking phenomenon, presenting no discernible maximum (rupture) in the force–displacement curve till 80% strain which is the maximum strain attainable in the equipment for the geometry of sample used. As stress–strain tests give an indication of the strength of a material, it can be concluded that sorbate presence seemed to increase the flexibility of the polymer chains. As a result, the elongation at break for the resulting polymer increased and it was obtained a higher ductility at the expense of stiffness. It can also be observed (Table 1) that the work *per unit* of volume, necessary for attaining a strain of 0.3, was greater for films without sorbates after 2 weeks of storage. This fact confirms the greater

Table 1
Sorbate effect on the mechanical properties of the starch films^{a,b}

	Films without sorbates	Films with sorbate
Lineal range (ε , %)	$0.38 \pm 0.03a$	$0.30 \pm 0.05a$
Storage modulus (E' , MPa)	5.20 ± 1.20	1.33 ± 0.23
Loss tangent ($\tan \delta$)	0.163 ± 0.022	0.460 ± 0.030
Stress at break (σ_b , MPa)	0.69 ± 0.15	0.30 ± 0.06
Strain at break (ε_b , %)	30.5 ± 0.5	$> 80\%$
Work ^c 3×10^{-5} (W_{30} , J/m ³)	1.3 ± 0.3	0.2 ± 0.0

Values followed by the same letter are not significantly different ($P > 0.05$).

^aAt two weeks of storage over 57.5% RH.

^bAverage and confidence interval ($\alpha = 0.05$) for each parameter are reported.

^cWork to attain a strain = 0.3.

stiffness of these films while the greater $\tan \delta$ values obtained for films containing sorbates, implied a more viscous (or less elastic) network.

Fig. 4 shows the X-ray diffraction patterns of films without (a) and with (b) sorbate after two weeks of storage. For these samples, the most intense peaks were identified and distances (d) between the planes of the crystallites (\AA) were calculated from the diffraction angle. Results can be observed in Table 2. The film without sorbate showed greater crystallinity: 36%. It is observed a B–V-type crystal structure (Fanta, Shogren, & Salch, 1999; Manzocco, Nicoli, & Labuza, 2003) that diffracts for the following spatial- $d \cong 3.6, 4.0, 4.5, 5.2, 5.9, 6.9$. Films with sorbate showed a crystallinity of 12% and spatial- d of $\cong 4.0, 4.6, 5.2$. The higher crystalline degree for the films without sorbate, might explain their higher E' value (Table 1). It is well-known that mechanical behavior of starch films is affected by the water content and the presence of crystalline phases. In our case, the film without sorbate showed a lower moisture content for 2 week storage (Table 3) fact that is related to its higher crystallinity and could also contribute to the higher E' observed.

In general, tuber starches show B-type crystal structure. Introduction of complexing agents into starch preparations disrupts double helix conformations by forming stable single chain V-conformation helices. The V-conformation is a result of amylose being complexed with substances such as aliphatic fatty acids, surfactants, emulsifiers, *n*-alcohols, glycerol, dimethyl sulfoxide. When amylose and polar lipids are present, V-structures can result from gelatinization, both during heating and upon cooling (Zobel, 1994).

A major component of edible films is the plasticizer. The addition of plasticizing agent to edible films is required to overcome film brittleness caused by extensive intermolecular forces. Plasticizers reduce these forces and increase the mobility of polymer chains,

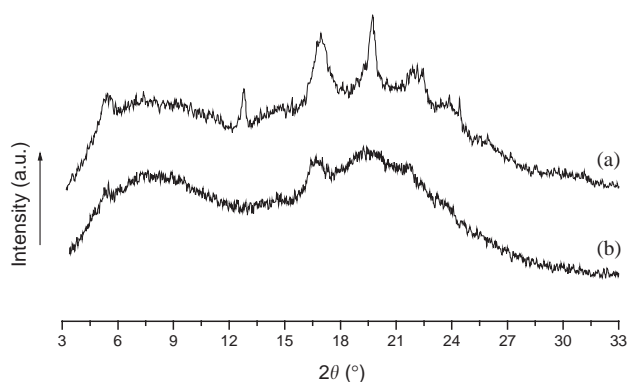


Fig. 4. X-ray diffraction of films (a) without sorbate and (b) with 3000 ppm sorbate, after two weeks. Intensity in arbitrary units (a.u.).

Table 2
X-ray parameters for tapioca starch edible films

Film	Sample crystallinity (%)	<i>d</i> -spacing (Å)
Without sorbate	35.87	3.66–3.74
		3.97–4.03–4.10
		4.52
		5.24–5.31
		5.92
		6.92
With 3000 ppm of sorbate	11.62	4.08
		4.62
		5.2–5.4

thereby improving flexibility and extensibility of the film. This avoids chipping or cracking of the film during subsequent handling and storage, which could impair barrier properties. On the other hand, plasticizers generally increase gas, water vapor and solute permeability of the film and could decrease elasticity and cohesion. The most commonly used plasticizers are polyols, mono-, di- or oligosaccharides, lipids and derivatives. Because of its ability to affect the texture of many polymers, water is the most ubiquitous and uncontrollable plasticizer during storage of food products. According to Gontard, Guilbert, and Cuq (1993), glycerol improves film extensibility but reduces film puncture strength, elasticity and water vapor barrier properties. Puncture strength also decreases with hydration. Glycerol is compatible with amylose and improves mechanical properties of films by decreasing intermolecular attraction and interfering with the amylose packing (Donhowe & Fennema, 1993). Plasticizers such as glycerol, sorbitol or polyethylene glycol are often used to modify the mechanical properties of hydrophilic films. They limit crystal growth and recrystallization along storage because they interact with the polymeric chains hindering their alignment and, thus, crystal formation (García, Martino, & Zaritzky,

Table 3
Effect of storage along 8 weeks on moisture, sorbate content and mechanical parameters^{a,b}

Film without sorbates	σ_b^c (MPa)	ϵ_b^d (%)	$W_{30}^e \times 10^{-5}$ (J/m ³)	τ^{*f} (s)	β^f	τ_T^f (s)	Moisture (g/100 g, db) ^g	Sorbate content (g/100 g)
2 weeks	0.69±0.15	30.5±0.5	1.3±0.3	36,000±720	0.924±0.012	37,350±720	36.3±3.0	4.00±0.36h
4 weeks	2.32±0.09	71.3±4.7	3.7±0.1	74,400±1488	0.430±0.080a,i	205,000±1500	28.1±4.1b	3.25±0.48h
8 weeks	1.61±0.08	49.5±0.5	2.9±0.1	40,800±816	0.610±0.060a,j	60,100±820	26.2±4.5b	2.13±0.30
Film with sorbates	σ_b^c (MPa)	ϵ_b^d (%)	$W_{30}^e \times 10^{-5}$ (J/m ³)	τ^{*f} (s)	β^f	τ_T^f (s)	Moisture (g/100 g, db) ^g	Sorbate content (g/100 g)
2 weeks	0.30±0.06	> 80	0.2±0.0	110,000±2200	0.410±0.060d,e	342,000±2200	48.0±3.1f	4.00±0.36h
4 weeks	0.84±0.01	> 80	1.1±0.0	100,000±2000c	0.450±0.005d,i	248,000±2000	41.0±3.9f,g	3.25±0.48h
8 weeks	1.26±0.09	65.0±9.0	1.9±0.1	96,000±1920c	0.501±0.015e,j	191,300±1900	39.6±4.0g	2.13±0.30

Values followed by the same letter are not significantly different ($P > 0.05$).

^aStorage was performed at 25 °C over 57.5% RH.

^bAverage and confidence interval ($\alpha = 0.05$) for each parameter are reported.

^c σ_b : Stress at break.

^d ϵ_b : Strain at break.

^e W_{30} : Work to attain a strain = 0.3.

^f τ^* and β : Parameters of the KWW equation. $\tau^*/\beta = \tau_T$.

^gdb: dry basis.

2000). According to trends observed in this work and to previously mentioned results of other researchers, sorbate developed a plasticizing action on studied films because it limited crystal growth and produced a decrease in film elasticity probably due to its interference with the amylose packing, its effect on chain attraction or due to its effect on the increase in moisture content at constant water activity. Ofman et al. (2004) studied the effect of different levels of potassium sorbate on the water sorption behavior of freeze-dried tapioca starch gel. They observed that the addition of potassium sorbate to starch before the gelatinization process increased the amount of water sorbed by the system, but experimental moisture content of the mixture was lower than the one predicted by the mass balance, revealing the existence of an interaction between starch and the preservative.

The E' vs. time profile observed along film storage (Fig. 5a) revealed an initial rapid rise in modulus with storage time, followed by a phase of slower E' development constituting a biphasic gelation process. According to studies performed by Biliaredis (1994) along aging, the first phase corresponds to amylose gelation, while the later has been attributed to amylopectin crystallization. Recrystallization of amylopectin within the gelatinized granules enhances their rigidity, thereby reinforcing the composite network.

As it can be seen in Table 3, the film without the antimicrobial showed, for each storage time studied, a significantly ($P < 0.05$) greater stress at break and work

per unit volume than the film with sorbate; the storage modulus was also greater for 2 and 4 weeks (Fig. 5a). Conversely, the film with sorbates showed significantly ($P < 0.05$) higher elongation at break for each storage time studied.

When aqueous starch suspensions are heated above the gelatinization temperature, irreversible swelling of the granules occurs along with a concomitant loss of structural order but granules still maintain their identity. As granules continue to expand, amylose leaches out into the aqueous intergranular phase; these processes bring about a substantial increase in viscosity. If the starch concentration is high enough (usually higher than 6% w/w), the mixture of swollen granules and exuded amylose behaves as a visco-elastic paste. On cooling and aging of the gelatinized starch, the reorganization of starch polymers leads to gelation and crystallization of amylose and amylopectin; thickening and rigidity development occur during storage as a result of chain aggregation (retrogradation). From this description, starch gels can be regarded as a polymer composite in which swollen granules (particles) are embedded in and reinforce a continuous matrix of entangled amylose molecules. Starch gels are composite networks where it is important the crosslink density in the continuous phase, the rigidity, volume fraction and spatial distribution of swollen granules as well as the interactions between the starch components and all these factors determine the mechanical properties of starch gels (Biliaredis, 1994; Hug-Iten, Escher, & Conde-Petit, 2001).

The significant ($P < 0.05$) increase of stress at break and work per unit volume (Table 3) with storage time, for the film containing the antimicrobial and for the film without sorbate for storage times shorter than 8 weeks and the increase in E' for both films (Fig. 5) up to 4 weeks, might be attributed to the increase in crystalline state with time. However, for longer storage, the tensile strength of the film without sorbates, decreased. The drop was previously reported for rubbery materials by Li and Larock (2001). In our case, the decrease in tensile strength may be attributed to the nonuniform network structure present when the degree of retrogradation is high. The interfaces between amorphous and crystalline regions might be relatively weak in strength, determining the decrease in tensile strength and E' observed, for 8 weeks of storage, for the film without sorbate (Fig. 5a). The increase of elongation at break observed from 2 to 4 weeks of storage for the film without sorbates (Table 3) can be ascribed, according to Nielsen and Landel (1994), to the increase in the spatial regularity of the crosslinked network. The decrease between 4 and 8 weeks of storage is probably linked to system segregation.

For the film containing the antimicrobial, rupture observed for 8 weeks of storage (Fig. 3) might be linked to the lower sorbate content as a consequence of its destruction. As can be seen in Table 3, sorbate

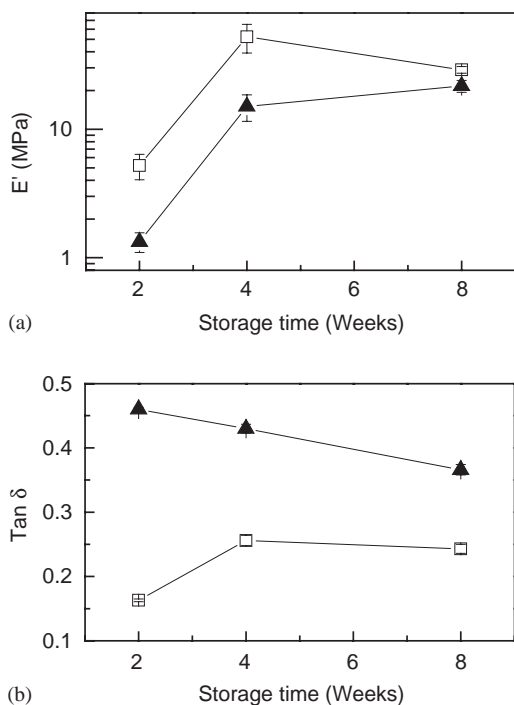


Fig. 5. Storage modulus (a) and loss tangent (b) change along storage. ▲, films with sorbates; □, films without sorbates.

concentration decreased with time due to its oxidation (Campos & Gerschenson, 1996); the decrease of its plasticizing effect might also contribute to the monotonous increase in E' and decrease in $\tan \delta$ observed for this system along storage (Fig. 5).

In general, moisture content decreased along storage for both films (Table 3). This trend is in accordance with the increase in crystalline state that occurs during retrogradation and, probably, contributed to the change observed in mechanical parameters along storage. According to Dumoulin, Alex, Szabo, Cartilier, and Mateescu (1998), water retention is relatively low when the polysaccharide chains are involved in a double helix formation. It is important to remark that along the period studied, moisture content was always higher for the film containing the antimicrobial and that sorbate destruction with storage time might also contribute to moisture decrease for this film.

As can be observed in Table 3, the β parameter calculated for σ – ε curves showed, in general, lower β values and higher values of τ_r when sorbate was present, confirming the plasticizing action exerted by this antimicrobial on tapioca starch films. A value of $\cong 0.4$ – 0.5 was calculated for the film containing the antimicrobial, indicating a broad distribution of relaxation times and it tended to increase slightly with storage time, while sorbates degraded due to oxidation and moisture content decreased. As it is known that samples containing plasticizers show an increase in flexibility (Gontard et al., 1993), it is expectable that the reduction in sorbate and moisture content with time, might produce a decrease in the number of chain segments that cooperate in relaxation and an increase in β value. Retrogradation occurring along storage may also contribute to trends observed. The decrease of τ_r with storage time, might be ascribed to the antimicrobial destruction and/or to the increase in crystalline degree with its concomitant moisture decrease. The β parameter, decreased significantly ($P < 0.05$) between 2 and 4 weeks of storage for the system without sorbates and, according to the coupling theory, a decrease in the beta parameter can be interpreted as a strengthening of the coupling between the relaxing species and the medium. The increase in τ_r along the same period might indicate that the average of the new relaxation times is higher for 4 weeks. Cortés and Montserrat (1998) mentioned that some researchers interpreted the β parameter as a measure of the degree of cooperativity in the relaxation process or as a measure of the number of chain segments involved in a particular relaxation event: low values of β correspond to a high degree of cooperativity and/or a large number of chain segments involved in the relaxation. For 8 weeks of storage, β tended to increase slightly and τ_r decreased significantly ($P < 0.05$) for the films without sorbate and this trend might be ascribed to the segregation, previously explained.

4. Conclusions

Sorbate presence in edible films formulated with tapioca starch and glycerol resulted, in general, in a marked increase in strain at break, a decrease of storage modulus and a more limited degree of crystallinity, behavior characteristic of plasticizers. After two weeks of storage, strain increased more than two times and tensile strength dropped to less than 50% of the values observed when sorbate was not present. It is important to remark that this behavior might improve starch film performance along food shelf-life because it might delay film mechanical aging which eventually can impair food acceptance by consumers.

The mechanical properties of the films, at room temperature, were intimately related to their degree of crystalline state, degree that conditioned moisture content. Increased crystallinity, generally increased the elastic modulus of the films and the ultimate tensile strength.

Higher values of $\tan \delta$ and a decrease in friction factor with storage was observed for films containing the antimicrobial while films without sorbate showed an increase of $\tan \delta$ up to 4 weeks of storage. The increase in elongation at break observed between 2 and 4 weeks of storage for films without sorbates may be attributed to an increase in the spatial regularity of the crosslinked network while the decrease between 4 and 8 weeks of storage was probably linked to system segregation.

It can be concluded that mechanical properties of tapioca starch-based films were affected by sorbate addition with antimicrobial purposes, being also affected their behavior along storage. Aging of starch which affect moisture content, characteristics of the network and sorbate destruction, seemed to be responsible for the changes observed in mechanical properties of the edible films along 8 weeks storage. The decrease of elasticity and improvement of extensibility due to sorbate presence, might help to avoid chipping or cracking of the film during subsequent handling and storage which could impair barrier properties. Anyhow, it must be remembered that the plasticizing effect exerted by sorbate might increase gas, water vapor and solute permeability of films and could decrease cohesion, possibilities that will be evaluated in future research. All this trends might affect film performance in food products in relation to product quality and consumer acceptance.

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