# Physical properties of tapioca-starch edible films: Influence of filmmaking and potassium sorbate

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## Abstract

The effect of different gelatinization and drying techniques on physical properties of tapioca starch edible films containing sorbates were studied. Method 1 assayed involved 40 min of gelatinization (rate: 1.6 °C/min and 0.3 °C/min) and drying for a week. In this case, films showed the highest tensile stress, elastic modulus ($E'$) and crystalline degree. When method 2 was applied, film forming solutions were gelatinized using constant heating rate (1.8 °C/min) and dried for a week. This technique, showed a reduced tensile stress and $E'$. Method 3 involved the same gelatinization procedure as method 2 but a faster drying was performed and a more viscous structure, increased moisture content, poorer water vapour barrier properties and less browning were attained. Solubility, in general, was not affected by technique used. The presence of potassium sorbate in the films affected their solubility, colour and mechanical properties. It can be concluded that gelatinization technique and drying method used to obtain edible films affected network characteristics determining changes in physical properties, potentially affecting film performance.
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## 1. Introduction

Interest in edible film and coating development has increased because evidence was obtained about their beneficial effects on fresh and processed foods (Baker, Baldwin, & Nisperos-Carriedo, 1994; Mei, Zhao, Yang, & Furr, 2002). Edible films are capable of providing many functional advantages like modifying vegetable tissue metabolism by affecting respiration; being carriers of antimicrobials, antioxidants and other preservatives; enriching product formulation while acting as carriers of vitamins and minerals; improving structural integrity or handling; controlling location or rate of release of additives, retaining

volatile flavour and they can also reduce packaging waste associated with processed foods (Buonocore et al., 2002; Chung, Papadakis, & Yam, 2001; Franssen, Rumsey, & Krochta, 2002; Greener Donhowe & Fennema, 1994). The marketing of foods is faced with many challenges like producing food of high quality, nutritious, stable and economical and edible films can help to achieve one or more of these functions (Krochta, Baldwin, & Nísperos-Carriedo, 1994).

Cellulose, gums, starches and proteins are basic materials used to elaborate edible films and coatings. Films developed from starch are described as isotropic, odourless, tasteless, colourless, non-toxic and biologically degradable (Krochta et al., 1994). Tapioca starch, naturally or modified, is increasing its utility in food industry because it has some inherent properties that are demanded. The preferred properties of cassava starch include: high transparency, determining suitability for developing sauces for ready-to-eat foods; high resistance to acidity, allowing its

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use for acid-based sauces and jams. It is also applicable for desserts, puddings, soups, fillings and gums due to its high viscosity. As an alternative starch it could replace traditional starches because it is also a lower cost option. Unfortunately it is not easy to replace starches traditionally used because it is difficult to overcome the strong links that exist between producers, starch manufacturers and food industries that utilize this polysaccharide in main importing countries of Europe and North America (FAO, 2004). For these reasons, it is interesting to explore the possibility of developing new products based on tapioca starch, to research about alternative applications and to solve the lack of information about its role as alternative source of starch tending to help to increase its added value.

The formation of starch edible film involves gelatinization of starch granules by heating in excess water. This procedure results in granule swelling and disruption as well as leaching of soluble components (amylose) from the granule. A viscous mass is obtained and it consists of a continuous phase constituted basically by solubilized amylose and a discontinuous phase of remnant granules, mainly based on amylopectin (Zobel, 1994). Cooling of the hot paste, results in a viscoelastic gel. The formation of the junction zones (polymer molecules joined by covalent bonds, hydrogen bonding and/or Van der Waal forces) of a gel can be considered to be the first stage of an attempt by starch molecules to crystallize. The collective processes that take part in the reduction of the solubility of dissolved starch are called retrogradation and involve both the two constituent polymers, amylose and amylopectin, with amylose undergoing retrogradation at a much more rapid rate than does amylopectin. The rate of retrogradation depends on several variables, including the molecular ratio of amylose to amylopectin, structures of the amylose and amylopectin molecules (botanic source of the starch), starch concentration, presence and concentration of other ingredients, such as surfactants, lipids and salts, processing conditions like temperature and shear (BeMiller & Whistler, 1996). Gelation and retrogradation can be interpreted as the result of double helices forming a network of physically cross-linked molecules. As initial juncture points grow into helical segments and then aggregate into A–B-type crystallites, gels or retrograded materials become more rigid and difficult to disperse (Zobel, 1994).

Plasticizing agents such as glycerol, sorbitol or polyethylene glycol, mono-, di- or oligosaccharides, fatty acids, lipids and derivatives, are usually used to overcome film brittleness and improve its flexibility and extensibility. It is possible to incorporate additives, such as flavours, antimicrobial agents, antioxidants and pigments into edible films to control location or rate of release of these additives in a food (Greener Donhowe & Fennema, 1994; McHugh & Krochta, 1994). 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 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 behaviour of starches during gelatinization. Ofman, Campos, and Gerschenson (2004) reported the effect of sorbates (sorbic acid and it salts) on tapioca starch sorption properties.

Different authors (Arvanitoyannis, Nakayama, & Aiba, 1998a, 1998b; Cha, Cooksey, Chinnan, & Park, 2003; Dawson, Hirt, Rieck, Acton, & Sotthibandhu, 2003; Jangchud & Chinnan, 1999; Le Tien et al., 2000; Menegalli, Sobral, Roques, & Laurent, 1999; Roy, Welle, Gennadios, Zeece, & Testin, 1999) reported that composition, film-forming method and drying process conditions influence film performance when films are based on proteins, chitosan or hydroxypropyl starch. Rindlav, Hulleman, and Gatenholm (1997) reported that crystallinity degree of potato starch edible films is dependent on the temperature, the air humidity and the time that elapses during drying from gel to film. These changes of crystallinity affected amylopectin film mechanical properties but did not influence its oxygen and water vapour permeabilities according to Rindlav-Westling, Stading, Hermansson, and Gatenholm (1998). As a consequence, the study of physical, chemical and mechanical properties of edible films in relation to its composition and processing is a subject of greater importance due to the need of a complete characterization of the film to evaluate advantages and disadvantages of its application in relation to food shelf life.

The objective of this research was to study the physical properties of sorbate-containing tapioca starch-glycerol edible films as affected by gelatinization and drying processes.

## 2. Materials and methods

### 2.1. Materials

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

### 2.2. Preparation of samples

Mixtures of tapioca starch, glycerol and water (5.0:2.5:92.5 in weight) or of starch, glycerol, potassium sorbate and water (5.0:2.5:0.3:92.2 in weight) were prepared.

Films of 2 different formulations were prepared using three methods:

(a) *Method 1.* Heating of 300 g film forming solution on a magnetic stirrer with hot plate at an initial rate of 1.6 °C/min for ≅25 min, moment at which the system

entered in the gelatinization step (gelatinization temperature $\cong 70$ °C). Afterwards, heating was maintained at a lower rate ($\cong 0.3$ °C/min) for an additional period of 40 min (Fig. 1a). After gelatinization, films were casted over glass plates and dried at 50 °C (RH: 22%), for 2 h. Drying was completed in a controlled temperature chamber (Velp, Italy) at 25 °C and RH: 80–90% during a week.

(b) *Method 2.* Heating of 300 g film forming solution on a magnetic stirrer with hot plate at a constant rate of 1.8 °C/min for $\cong 30$ min (Fig. 1b). In this case, it could be visually appreciated that gelatinization began at $\cong 70$ °C. After gelatinization, films were casted over glass plates and dried at 50 °C (RH: 22%) for 2 h. Drying was completed in a chamber (Velp, Italy) at 25 °C and RH: 80–90% during a week.

(c) *Method 3.* Heating of 300 g film forming solution on a magnetic stirrer with hot plate at a constant rate of 1.8 °C/min for $\cong 30$ min (Fig. 1b). After gelatinization, films were casted over glass plates and dried at 50 °C (RH: 22%) for 2 h. Drying was completed over CaCl$_2$ (RH: 0%) at 25 °C during two days.

For both gelatinization techniques assayed, sample final temperature was 82 °C and vacuum was applied to remove air from the systems before casting.
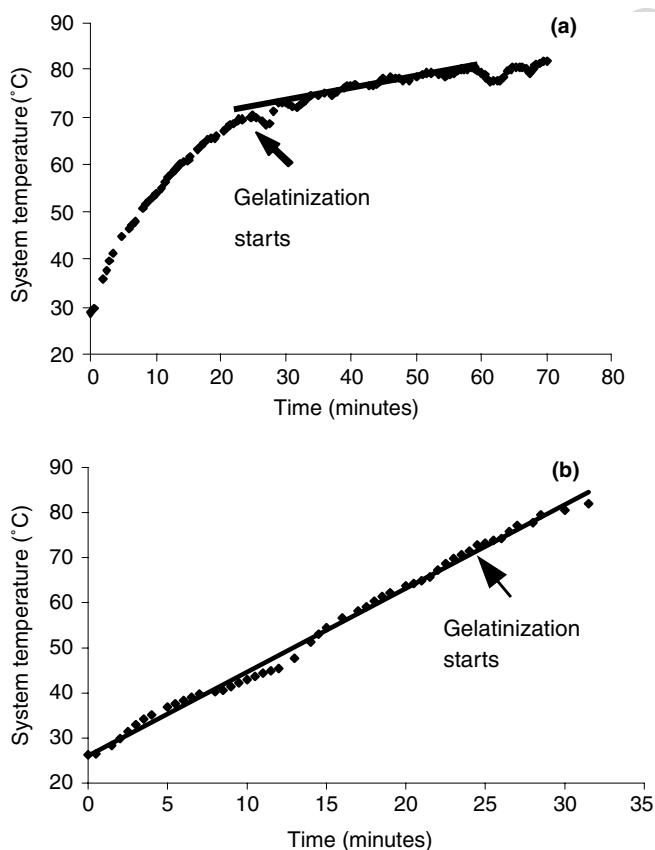


Fig. 1. Film-forming solution temperature along gelatinization. Panel (a): method 1. Panel (b): methods 2 and 3.

Once constituted, films were peeled off from glass plates and before evaluating film properties, samples were conditioned at 25 °C, over saturated solution of NaBr (water activity, $a_W \cong 0.575$) for 7 days. Sample thickness was measured to the nearest 0.01 mm using an optical microscope at three different locations in each specimen.

### 2.3. Moisture determination

Samples were dried in a vacuum oven at 70 °C till constant weight (approximately 30 days). Determination was performed on five film specimens of each formulation and the average is reported.

### 2.4. Potassium sorbate dosage

Potassium sorbate content for films containing the preservative was determined through the oxidation technique which involves distillation and a colorimetric reaction using thiobarbituric acid, as proposed by the AOAC (1990). The average of four determinations is reported.

### 2.5. Mechanical properties

The viscoelastic properties of the studied material were carried out 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 16 mm. Specimens for the tests were obtained from the film according to Famá, Rojas, Goyanes, and Gerschenson (2005), with the help of an scalpel and an adequate aluminium pattern specially made for this purpose. The shape of the specimens was designed according to ASTM D4092 (1996) and considering the maximum elongation permitted by the equipment used. The neck of the film had a length of 10 mm and a width of 5 mm. Above and below the neck, a quarter circle of 2.5-cm radius constituted the border of the films. The necked shape attempt to minimize the uneven stress distribution and to avoid the break in the area of contact with the grips.

The sample was held between the molars of the grips which were covered with constrainers of strain to prevent an excessive deformation of the sample in that region.

Microscopic examination of specimens to be tested was performed and samples with flaws were discarded.

#### 2.5.1. Quasi-static testing

For studying the tensile stress–strain behaviour, the strain rate was fixed in a value of $5 \times 10^{-3}$ s$^{-1}$ and the experiment was performed till rupture, recording the stress ($\sigma$)–strain ($\varepsilon$) curves. The ultimate tensile strength ($\sigma_b$) was evaluated for 70% strain because this is the maximum strain attainable in the equipment for the geometry of sample used. Assays were performed on seven film specimens for each formulation and method.

## 2.5.2. Dynamic testing

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

$$E^* = E' + iE''$$

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 $\delta$ 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 viscoelastic range. The oscillatory tests were carried out at 1 Hz. Data were collected under dynamic temperature ramp test routine at 25 °C. Twelve samples were studied for each condition and type of film.

## 2.6. X-ray diffraction analysis

A Philips X-ray diffractometer with vertical goniometer was used (Cu Kα radiation $\lambda = 1.542$ Å). 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 ($2\theta$) range of 6–33° with a scanning speed of 1 °/min. Distances between the planes of the crystals $d$ (Å) where calculated from the diffraction angles (°) obtained in the X-ray pattern, according to Bragg's law:

$$n\lambda = 2d \sin(\theta)$$

where $\lambda$ 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.

## 2.7. Solubility in water

Solubility is defined (Gontard, Guilbert, & Cuq, 1992) as the percentage of film dry matter solubilized after 24 h of immersion in distilled water. The initial percentage of dry matter was determined by drying 2 cm diameter disks in a vacuum oven at 100 °C during 24 h. Disks were cut, weighed and immersed in 50 ml of distilled water, with periodic stirring, during 24 h at 25 °C. Not solubilized films were taken out and dried (100 °C during 24 h) to determine the final weight of dry matter. Solubility is reported as the difference between initial and final dry matter with respect to initial dry matter.

## 2.8. Colour evaluation

Films disks of appropriate diameter were rested on white background standard (Trezza & Krochta, 2000). Measurements were performed in a Minolta colorimeter (Minolta CM-508d, Tokyo, Japan) using an aperture of 1.5 cm-diameter. The exposed area was sufficiently great relative to the illuminated area to avoid any light trapping effect. The Hunter parameters: $L$, $a$ and $b$, and the yellow index (YI) were measured according to a standard test method (ASTM E1925, 1995), in at least five positions randomly selected for each sample. Colour parameters range from $L = 0$ (black) to $L = 100$ (white), $-a$ (greenness) to $+a$ (redness), and $-b$ (blueness) to $+b$ (yellowness). Standard values considered were those of the white background. Calculations were made for D-65 illuminant and 2° observer.

## 2.9. Water vapour permeability

Water vapour permeability (WVP) of films was determined gravimetrically at 25 °C using a modified ASTM E96-00 (2000) procedure.

The permeation cell (acrylic cups) had an internal diameter (ID) of 4.4 cm and an external diameter (ED) of 8.4 cm (exposed area: 15.205 cm$^2$). They were 3.5 cm deep and contained CaCl$_2$ (0% RH; 0 Pa water vapour partial pressure). Film was located between the cell and its acrylic ring shaped cover (4.4 cm ID and 8.4 cm ED) which was adjusted to the cup with four screws located describing a cross. A 7 mm air gap was left between the film and the CaCl$_2$ layer. Rubber o-ring and vacuum grease helped to assure a good seal.

The covered cell was placed in a temperature and RH controlled chamber (Ibertest, España) maintaining a temperature of 25 °C and a RH of 70% ($\cong$2288 Pa water vapour partial pressure). After $\cong$20–24 h a stationary water vapour transmission rate was attained and, from that moment on, changes in weight of the cell (to the nearest 0.1 mg) were recorded daily over a 6 day period. All tests were conducted, at least, in triplicate and WVP values were calculated using the WVP Correction Method described by Gennadios, Weller, and Gooding (1994).

## 2.10. Statistical analysis of data

It was performed a two factor (sorbate concentration; gelatinization/drying technique) experiment with repeated measures on one factor (sorbate content). Two levels of sorbate (0 and 3000 ppm) and three levels of processing (methods 1–3) were assayed. Data were analysed through two-way ANOVA with $\alpha = 0.05$ and Tukey was the post-hoc test applied. Results are informed on the basis of their average and confidence interval for an $\alpha = 0.05$ (Sokal & Rohlf, 2000).

*Statistica* for Windows, version 5.0, 1997 (StatSoft, Inc., Tulsa, OK, USA) was used for data treatment and statistical analysis.

## 3. Results and discussion

### 3.1. Mechanical properties

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. Mechanical properties of starch systems are influenced by the rheological characteristics of the amylose gel matrix, the volume fraction and rigidity of gelatinized granules as well as the interactions between the starch components. Granule size, amylose/amylopectin ratio, physical organization of the granule, minor constituents (lipids, phosphorus, salts, sugars), pH, starch concentration, and shear-temperature–time regimes, are all important contributing factors to viscoelasticity and variability in rheological responses of starch based materials (Biliaredis, 1994). Tapioca starch based edible films studied in the present work, are retrograded starch systems that have been plasticized with glycerol. It is well known that level of retrogradation, directly affects the mechanical properties: recrystallization drastically decreases tensile strain at break while stress and Young modulus increase (Delville, Joly, Dole, & Biliard, 2003).

The deformation nature of the films studied at room temperature, under an applied load, was typical of ductile plastics in terms of the stress and strain (figures not shown). As generally occurs for those materials, the films exhibited two characteristic regions of deformation behaviour 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.

As can be observed in Table 1, methods 1 and 2 produced films with significantly higher tensile stress than method 3 for both formulations assayed. Arvanitoyannis, Nakayama, and Aiba (1998b), assayed low and high temperature drying methods with hydroxypropyl starch-gelatin films plasticized by polyols, and suggested that at high temperature of drying, polymer chains are trapped in a disordered and entangled state described by a low crystallinity and lower tensile strength. It has been also suggested a more efficient separation of amylose from amylopectin during longer heating times which might promote gelation of the linear starch fraction when gel is cooled (Biliaredis, 1994). Leaching of amylose from granule starts gelatinization process, followed by growth and coarsening associations of chains upon double helix formation and then interlinking of aggregates to form a network with consequently further thickening and rigidity development. Density and lifetime of interactions between continuous matrix of amylose and recrystallized structure of amylopectin also influence the mechanical properties of the films. Slow drying provides a longer time for the occurrence of previously mentioned phenomena and, as a consequence, might contribute to obtain a more elastic film and higher tensile stresses when methods 1 or 2 were applied. It is important to remark that films studied did not show a 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. Table 1 clearly shows that the films without sorbate, showed a higher tensile stress ($\sigma_b$) for the maximum achievable deformation than the films with sorbate and that behaviour was not dependent on the film obtaining method. Method 1 showed the highest tensile stress in films with or without antimicrobial as can be observed in Fig. 2.

As starch based edible films are systems that represent physical gels formed by molecular ordering and subsequent chain aggregation/crystallization, it is very advantageous using small strain mechanical testing to unravel how changes in composition, polymer structure and temperature–time history affects structural changes and interactions of starch macromolecules. Table 1 shows that films obtained with method 1 developed the highest $E'$ value and with method 3, the smallest ones: long time of gelatinization and drying (method 1) resulted in a more elastic network as a consequence of higher molecular order and/or interactions developed during retrogradation, as was explained above. The lower level of organization of polymer chains attained through method 3, could explain the significant ($\alpha = 0.05$) increase of tan $\delta$ values for films containing the antimicrobial and obtained through that technique ($0.78 \pm 0.03$ vs. $0.410 \pm 0.007$–$0.40 \pm 0.01$; method 3 vs. methods 1 and 2). The faster evaporation rate involved in method 3 resulted in a less elastic network. We can also observe in Table 1 that $E'$ values of films without sorbates are always higher than the ones of films with sorbates, for each processing technique assayed, showing a plasticizing effect of sorbates. This plasticizing effect was previously observed by Famá et al. (2005), who reported a decrease of the elasticity in films consisting of tapioca starch, glycerol and sorbates. This was attributed to the structural modification of starch network when sorbates

Table 1
Effect of gelatinization/drying technique on mechanical properties and crystallinity of starch films

|  | $E'$ (MPa) | $E''$ (MPa) | $\sigma_b$ (MPa) at $\varepsilon = 70\%$ | Crystalline fraction |
|---|---|---|---|---|
| *Method 1* | | | | |
| Without sorbate | $29.0 \pm 9.0$ | $7.2 \pm 1.3$ | $2.35 \pm 0.18$ | 30.0 |
| With sorbate | $7.6 \pm 0.7$ | $3.1 \pm 0.4^b$ | $0.74 \pm 0.12^{c,d}$ | 9.4 |
| *Method 2* | | | | |
| Without sorbate | $13 \pm 4$ | $3 \pm 1^b$ | $1.98 \pm 0.26$ | 26.4 |
| With sorbate | $4.3 \pm 0.5^a$ | $1.7 \pm 0.2^b$ | $0.57 \pm 0.08^d$ | 8.4 |
| *Method 3* | | | | |
| Without sorbate | $3.2 \pm 1.1^a$ | $0.9 \pm 0.3^b$ | $1.0 \pm 0.1^c$ | 15.5 |
| With sorbate | $1.3 \pm 0.5^a$ | $1.0 \pm 0.3^b$ | $0.16 \pm 0.04$ | 6.4 |

Values followed by the same letter are not significantly different ($p > 0.05$). $\sigma_b$: ultimate tensile strength; $E'$: storage modulus; $E''$: loss modulus.
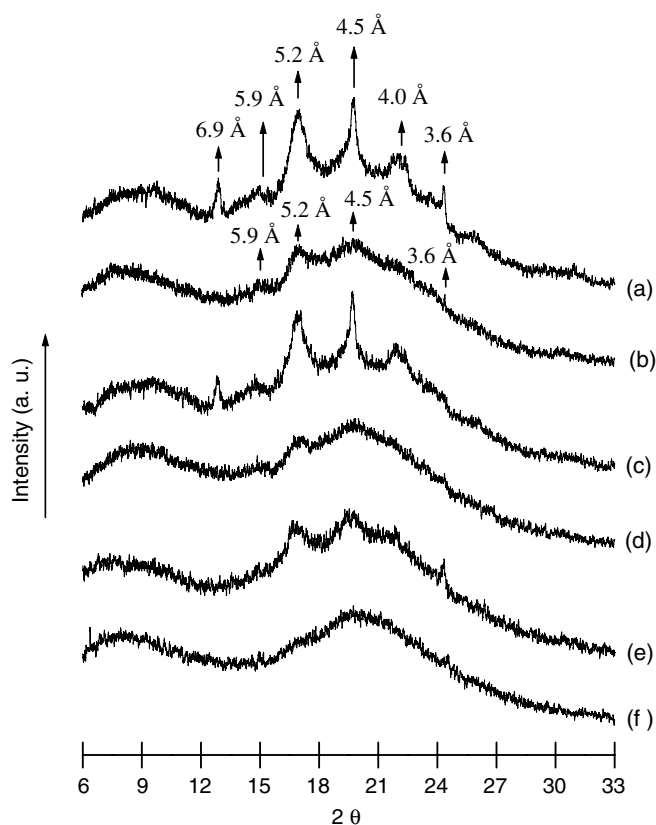
Fig. 2. X-ray diffraction pattern of different films studied. (a): M1 without sorbates. (b): M1 with sorbates. (c): M2 without sorbates. (d): M2 with sorbates. (e): M3 without sorbates; (f): M3 with sorbates.

were incorporated, which determined that under stress, movements of polymer chains were facilitated. For films without sorbate no significant difference was observed in $\tan\delta$ for different methods applied ($\tan\delta = 0.254 \pm 0.004$, $0.244 \pm 0.005$ and $0.280 \pm 0.030$ for methods 1, 2 and 3, respectively).

It is interesting to remark that two way ANOVA showed a significant influence of sorbate concentration and casting method on $E'$, $\tan\delta$ and $\sigma_b$ as well as a significant interaction between those factors in relation to these mechanical parameters.

### 3.2. X-ray diffraction pattern

Starch helices that are packed in regular arrays determining crystallinity, can be evaluated by X-ray diffraction. 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).

Fig. 2 shows the X-ray diffraction patterns of films without and with sorbate for all techniques assayed. For these

samples, the most intense peaks were identified and distances (*d*) between the planes of the crystallites (Å) were calculated from the diffraction angle. Crystallinity fraction can be observed in Table 1. Films with sorbate showed a B–V pattern and a crystallinity of 9.4%, 8.4% and 6.4% for methods 1–3 respectively, and it could be observed spatial-d of ≅3.6, 4.5, 5.2 and 5.9.

Water in the crystalline fraction is limited to the amount held in the crystal lattice; amorphous fraction is available to sorption of relatively high levels of water (Zobel, 1994). As can be observed in Table 2 and, as a consequence of smaller crystallinity, samples obtained by method 3 showed a significantly ($\alpha$: 0.05) greater moisture content two weeks after gelatinization. It is well-known that water is a plasticizer and, as a consequence, it might affect mechanical behaviour of starch films. This could also contribute to the smaller stiffness observed for samples obtained through method 3: lower $E'$ and $\sigma_b$ values. Slow drying could promote ordering of chains, causing a similar crystallinity level for methods 1 and 2 and, therefore, no significant changes in moisture content. Arvanitoyannis et al. (1998a) reported that edible films obtained by evaporation of hydroxypropyl starch-gelatine solutions at 20 °C during a week, resulted in films with more densely packed polymer chains, increased molecular ordering, higher percentage crystallinity and higher tensile strength than films obtained by high temperature drying. Low or high rate of gelatinization, combined with slow drying rate, applied in methods 1 and 2, probably caused a greater crystalline fraction, lower moisture content, higher tensile stress and $E'$ values. Method 3 resulted in an increased amorphous phase due to faster water evaporation.

Films without sorbate showed greater crystallinity: 30.0%, 26.4% and 15.5% for methods 1–3 respectively. It is also observed a B–V-type crystal structure (Fanta, Shogren, & Salch, 1999; Manzocco, Nicoli, & Labuza, 2003), probably due to plasticizer presence (glycerol), that diffracts for the following main spatial-d (arranged in an ascending order) ≅3.6, 4.0, 4.5, 5.2, 5.9, 6.9 (methods 1

Table 2
Effect of gelatinization/drying technique on sorbate content, moisture content and water vapour permeability (WVP) of tapioca starch edible films (averages and confidence intervals are reported)

|  | Sorbate content (g/100 g, d.b.)[A] | Moisture (g/100 g, d.b.)[A] | WVP[B] (×10^10 g/s m Pa) |
|---|---|---|---|
| *Method 1* |  |  |  |
| Without sorbate |  | 42.7 ± 1.6[b] | 6.3 ± 0.9[d,e] |
| With sorbate | 4.00 ± 0.28[a] | 43.6 ± 1.3[b] | 6.1 ± 0.8[e] |
| *Method 2* |  |  |  |
| Without sorbate |  | 41.3 ± 3.6[b] | 8.1 ± 1.9[d,e] |
| With sorbate | 4.51 ± 0.89[a] | 41.7 ± 0.8[b] | 8.1 ± 1.0[d] |
| *Method 3* |  |  |  |
| Without sorbate |  | 49.0 ± 1.4[c] | 14.4 ± 1.5[f] |
| With sorbate | 5.98 ± 0.71 | 49.5 ± 3.6[c] | 16.1 ± 1.3[f] |

Values followed by the same letter are not significantly different ($p > 0.05$).
[A] d.b.: dry basis.
[B] Film thickness was ≅0.30 mm.

and 2) or 4.0, 4.5, 5.2, 6.9 (method 3). The higher crystalline degree for the films without sorbate explains their higher stress at break, $E'$ and its lower $\tan\delta$ values. The plasticizing action exerted by sorbate partially prevented crystallization development because it could interact with polymeric chains hindering their alignment and/or because it might interfere with amylose packing (Famá et al., 2005). It was observed that for the different techniques of fabrication assayed, moisture content of tapioca starch films did not change in the absence or presence of sorbate although the crystalline degree diminished when the antimicrobial was present (Table 2). Che and Rhee (2002) reported a slight increase in humidity at different RH of soy protein films when they were plasticized using 0.3, 0.5 and 0.7 g plasticizer/g protein. On the other hand, Rindlav et al. (1997) reported that the water content of potato starch films increased with increasing B-type crystallinity, which was partly explained by the higher water content of the B-type crystalline areas as compared with amorphous areas. Probably the moisture contents observed in this work are reflecting that the sorbate might interfere with amylose packing through the development of polymer–sorbate hydrogen bonds which replaced polymer–polymer interactions (Yang & Paulson, 2000) and inhibited the formation of polymer–water hydrogen bonds in the amorphous areas. It is also possible that the water incorporated in the B-type crystalline structure present in a higher proportion in films without sorbate has compensated the diminishing of water sorbed in the decreased amorphous structure. Godbillot, Dole, Joly, Roge, and Mathlouthi (2005) observed that below 44% equilibrium relative humidity, glycerol-plasticized wheat starch films were less hygroscopic than unplasticized starch films.

### 3.3. Sorbate content

Table 2 shows the sorbate concentration two weeks after gelatinization. Method 3 showed the highest sorbate content which can be attributed to the shorter gelatinization and drying process applied for its development. Gerschenson and Campos (1995) showed that heat abuse can result in sorbate destruction.

### 3.4. Solubility

As can be seen in Fig. 3, film solubility was the same ($\cong 22\%$) for all processing techniques applied but increased significantly when sorbate was present in films based on tapioca-starch. The presence of antimicrobial produced less organized networks, as has been seen in X-ray diffractograms, that showed a solubility of $\cong 31\%$ for all gelatinization/drying methods assayed.

### 3.5. Water vapour permeability

Corrected WVP values can be observed in Table 2. Method 3 resulted in significantly higher WVP value as
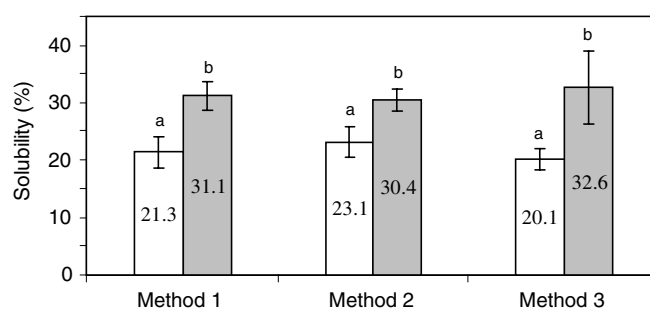


Fig. 3. Effect of gelatinization/drying technique on solubility of tapioca-starch edible films. ▪ with sorbates; □ without sorbates. Averages and confidence intervals are reported. Bars with the same letter are not significantly different ($p > 0.05$).

the result of a less tight starch network. It is important to remark that this gelatinization/drying technique practically doubled the WVP value when compared with method 1. Sorbate presence did not affect WVP. Similar results were reported by Cagri, Ustunol, and Ryser (2001), for a protein based film containing 0.50% and 0.75% sorbic acid. It is well-known that edible films tend to be poor moisture barriers due to abundant hydrophilic groups in biopolymer matrix; however, technique applied to prepare films can help to improve moisture barrier properties. In our case, method 1 proved to give origin to films with the lowest WVP values.

It is important to remark that two-way ANOVA showed that there was a significant interaction between casting technique and sorbate concentration in WVP results: sorbate depressed WVP for method 1 and increased permeability for method 3.

### 3.6. Colour

Table 3 shows colour parameters for studied films. It can be observed that method applied affected them: films containing antimicrobial and obtained through method 1 showed the lowest "$a$" values. It can be also observed that the parameter "$a$" was negative for all films studied but its value was significantly smaller when sorbate was present. Two-way ANOVA of results obtained for parameter "$a$", showed that there were significant interactions between sorbate concentration and gelatinization/drying method applied.

The "$L$" and "$b$" values of films with sorbate were not significantly affected by the preparation method. In general, sorbate presence produced a significant decrease in "$L$", increase in "$b$" and in the yellow index (YI), showing that the film containing the antimicrobial browned more intensively. ANOVA analysis showed that sorbate presence and method used significantly affected YI and there were also detected significant interactions between these two factors.

It can be seen in Table 3 that films containing the antimicrobial and obtained through method 1 showed the highest YI, while method 3 developed the lowest YI values. As was mentioned above, the latter method seemed to

Table 3
Effect of gelatinization/drying technique on colour parameters of tapioca-starch edible films (averages and confidence intervals are reported)

| | $a^A$ | $b^A$ | $L^A$ | $YI^B$ |
|---|---|---|---|---|
| *Method 1* | | | | |
| Without sorbate | $-1.08 \pm 0.02^a$ | $5.02 \pm 0.01^b$ | $85.42 \pm 0.04^d$ | $10.10 \pm 0.03^g$ |
| With sorbate | $-0.57 \pm 0.07$ | $5.95 \pm 0.07^c$ | $82.40 \pm 0.30^{e,f}$ | $13.02 \pm 0.26^h$ |
| *Method 2* | | | | |
| Without sorbate | $-1.14 \pm 0.03^a$ | $5.11 \pm 0.14^b$ | $84.45 \pm 0.43^{d,e}$ | $10.36 \pm 0.38^g$ |
| With sorbate | $-0.82 \pm 0.03$ | $5.64 \pm 0.17^c$ | $82.20 \pm 1.80^f$ | $12.02 \pm 0.46^{h,i}$ |
| *Method 3* | | | | |
| Without sorbate | $-1.17 \pm 0.02^a$ | $4.75 \pm 0.11^b$ | $85.63 \pm 0.13^d$ | $9.44 \pm 0.26^g$ |
| With sorbate | $-0.69 \pm 0.04$ | $5.56 \pm 0.08^c$ | $83.24 \pm 0.33^{d,f}$ | $11.87 \pm 0.20^i$ |

Values followed by the same letter are not significantly different ($p > 0.05$).
[A] Hunter parameters.
[B] YI: yellow index.

prevent more effectively sorbate degradation and therefore, browning development.

## 4. Conclusion

Different processing methods applied to obtain tapioca starch-glycerol edible films, affected their physical properties with the exception of solubility. In general, sorbate presence increased yellow index and reduced crystalline degree and Young modulus. It could be observed that long time of gelatinization and slow drying rate (method 1) resulted in a more solid network, higher crystallinity degree and smaller WVP. When starch systems were gelatinized using fast heating rate and slow drying (method 2), films obtained showed reduced elastic characteristics and slightly increased permeability. Fast water evaporation (method 3) produced a less organized and more amorphous matrix, higher moisture content and poorer water barrier properties. This latter method seemed to prevent more effectively sorbate degradation and browning development. Therefore, it is more optimal to apply short gelatinization and drying times to produce films of better antimicrobial stability and consumer appeal. However, method 3 also produced films with poorer mechanical characteristics that may affect the film performance. The characteristics of the product to which the edible film will be applied and the goal of film application will determine the method of obtention that is convenient to be used.

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