

RESEARCH ARTICLE

Biofilms based on cassava starch containing extract of *yerba mate* as antioxidant and plasticizer

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Cassava starch based films containing different concentrations of *yerba mate* extract as antioxidant (0, 5, and 20%) were prepared by casting. The effect of the incorporation of the extract on the antioxidant activity, structure, and physicochemical properties of the biofilms was evaluated. Significant antioxidant capacity in the films with *yerba mate* extract was obtained, especially in the materials containing 5% of the additive. The surface roughness and contact angle of the systems containing the extract increased, indicating hydrofobic behavior of the films surface when the additive was used. This was also confirmed by water vapor permeability and water content results. The incorporation of *yerba mate* extract led to an important improvement in the elasticity of the biofilms, as well as to a shift of the relaxations associated with the glycerol-rich and starch-rich phases to lower temperature values, revealing a typical behavior of a plasticized film. The relevant antioxidant and plasticizing effects of *yerba mate* extract on cassava starch films make them promising to be used as coatings or packaging in the food industry.

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1 Introduction

Biopolymers constitute a useful alternative to the development of eco-friendly materials due to advantages such as biodegradability, low cost, and availability [1–3]. Cassava (*Manihot esculenta* Crantz) is a major food and industrial crop in tropical and subtropical Africa, Asia, and Latin America. It could become the raw material for the basis of processed products thereby increasing the demand for cassava and contributing to agricultural transformation and economic growth in developing countries.

In the last years, several investigations have been focused on cassava-starch to develop films to be used as packaging or coating in the food industry [4–10]. Starch plasticized biopolymers have shown great film-forming properties

leading to flexible and extensible materials with homogeneous and smooth surface [11].

The incorporation of antioxidant compounds into biopolymer films constitutes a new strategy to increase the shelf-life of food products and to improve the functionality of conventional packaging materials [12, 13]. The antioxidant active films allow a localized and long effect of the active compounds preventing the development of spoilage reactions [14, 15]. In this sense, the use of antioxidants from natural sources is preferred, taking into account the association of synthetic additives with negative effects for human health.

Yerba mate (*Ilex paraguariensis*) is a plant known by its high polyphenols content, mainly flavonoids and xanthines [16]. Several investigations reported that *yerba mate* have antioxidant, anti-inflammatory, and anti-mutagenic properties [17]. On the other hand, *yerba mate* is considered a potent inhibitor of lipid oxidation reactions.

While *yerba mate* has been a source of research in recent decades for their important healthy characteristics, almost no investigations have been reported in the literature regarding the use of *yerba mate* as additive in a polymer matrix. Machado, Nunes Pereira & Druzian 2012 [18]

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developed films incorporating 20% of *yerba mate* extract into a starch-glycerol-nanocelulose matrix. These authors reported that the incorporation of the antioxidant did not affect the properties of the matrix, concluding that the biocomposite was a viable option for using as a packaging strategy.

It is important to note that, so far, there are very few publications about the use of *yerba mate* extract on plasticized-starch based films, in order to replace synthetic materials for coating or packaging in the food industry. Therefore, the aim of this research was to study the effect of the incorporation of different concentrations of *yerba mate* extract on a cassava starch-glycerol matrix. As the characteristics of a coating when it is in contact with a product and its compatibility with it are very important, the effect of the addition of *yerba mate* extract on the antioxidant activity, and the structural and physicochemical properties of starch films was investigated.

2 Materials and Methods

2.1 Materials

Cassava starch (18 wt% amylose and 82 wt% amylopectin) was provided by Industrias del Maíz S.A, Buenos Aires, Argentina. Analytical grade glycerol (Aldrich) and commercial *yerba mate* (*Ilex paraguariensis*) (Taragüi liviana, Establecimiento Las Marías, Corrientes, Argentina) were used as plasticizer and antioxidant, respectively.

2.2 Preparation of the extract of *yerba mate*

The extract of *yerba mate* was obtained from infusion: 3 g of *yerba mate* and 100 mL of distilled water were heated at 100°C for 40 min. The obtained extract was filtered, cooled at room temperature and kept in dark containers until further use [19, 20].

2.3 Preparation of edible starch based films

Mixture of starch (5.0 g), glycerol (1.5 g), and water (93.5 g) was used for the development of the matrix (TPS). In order to prepare biocomposite films containing the extract of *yerba mate* as an antioxidant, a fraction of distilled water was replaced by the desired concentration of extract (5 and 20 g, namely TPS-Y5 and TPS-Y20, respectively). Each system was homogenized for 40 min and gelatinized under constant stirring and heating rate of 3°C/min until ~96°C to warrant complete gelatinization of the system. The gel was degassed for 7 min with a mechanical vacuum pump and dispensed into polypropylene plates, which were dried at 50°C for 48 h. Films with a thickness of ~0.27 mm were obtained and they were conditioned at room temperature into desiccators

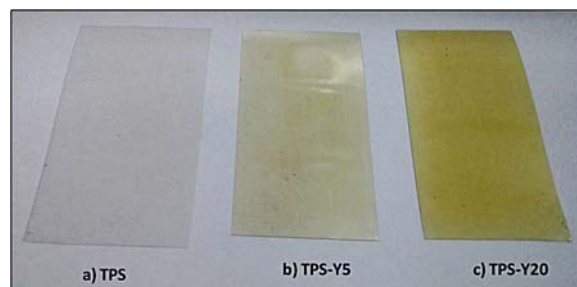


Figure 1. Actual picture of the developed films: (a) TPS, (b) TPS-Y5, and (c) TPS-Y20.

containing saturated NaBr to controlled relative humidity (~56.7%) until use. An actual picture of the three developed films is shown in Fig. 1.

2.4 Characterization

2.4.1 Antioxidant activity

The antioxidant activity of the extract of *yerba mate* was determined using 1,1-diphenyl-2-picrylhydrazyl (DPPH•) as a free radical, according to the method described by Brand-Williams et al. (1995) [21]. The antiradical activity was calculated as the amount of the extract needed to decrease the initial DPPH• concentration by 50%. This value is commonly expressed as Efficient Concentration (EC50), in mg antioxidant per mg of DPPH•. A reaction between 100 µL of each system containing the extract and 3.9 mL of DPPH• ethanol solution (25 mg DPPH•/L of ethanol) was performed for 45 min. The absorbance was determined at 517 nm using a spectrophotometer Shimadzu UV-1800. Chlorogenic acid (AC) was used as standard and the reported results were expressed as mgAC/g of film.

In order to analyze the antioxidant activity of the extract of the films, a known amount of film with an appropriate volume of distilled water was placed in a beaker during 48 h at 25°C. The antioxidant activity of the released extract was determined as previously described and the percent inhibition (%I) of hydroxyl radical DPPH• was calculated as

$$\%I = \left(\frac{\text{Abs}_w - \text{Abs}_s}{\text{Abs}_s} \right) \times 100 \quad (1)$$

where Abs_w is the absorbance of the white and Abs_s is the absorbance of the sample. Similarly, the content of antioxidants of the *yerba mate* in the extract was determined.

2.4.2 Scanning electron microscopy (SEM)

The cryo-fractured surface of the materials was examined using a scanning electron microscope with a Field Emission Gun (FEG) Zeiss DSM982 GEMINI, in order to investigate the morphology of the films.

The samples were cooled in liquid nitrogen, broken and coated with a thin sputtered gold layer before the analysis.

2.4.3 Atomic force microscopy (AFM)

The surface of the films was also analyzed by atomic force microscopy using an AFM-STM (NanoScope IIIa, Digital Instrument, DiVeeco, USA), operating in the tapping mode under the regime of nitrogen atmosphere. A three-dimensional image of a film surface of $5\ \mu\text{m} \times 5\ \mu\text{m}$ was obtained and the surface roughness (RMS) was calculated using the WSxM 4.0 Beta 7.0 Image software Data Acquisition Wizard (Nanotec Electronic S. L., 2014).

2.4.4 Hydrophobicity of the surfaces of the films (contact angle)

The hydrophobicity of the surface of the films was determined by measurements of contact angle θ , using a microscope MicroView (USB Digital Microscope) coupled with an image analysis software (Analysis Software 220 \times 2.0 MP). A drop of distilled water ($2\ \mu\text{L}$) was placed on the surface of each material. The methodology to calculate θ was based on the processing of images by determining the angle formed by the intersection of the liquid-solid interface (drop of water-surface of the film) and the liquid-vapor interface (tangent on the boundary of the drop) [22]. The average of six measurements was reported.

2.4.5 Water vapor permeability (WVP)

Water vapor permeability (WVP) tests were carried out by following ASTM E96-00 (1996) [23] recommendations and using the correction method described by Gennadios, Weller, and Gooding (1994) [24]. Circular acrylic cells containing the films (exposed area of $4.84 \times 10^{-4}\ \text{m}^2$) were located in desiccators at relative humidity (RH) of $\sim 50\%$ at room temperature. WVP values were calculated from the weight gain of the permeation (G) measuring over 24 h for 10 days as:

$$\text{WVP} = \frac{G \times e}{\Delta P \times t \times A} \quad (2)$$

where ΔP is the saturation vapor pressure of water at ambient temperature, t is the time measured in hours, A is the exposed area, and e is the film thickness.

2.4.6 Moisture content

Moisture content of the different systems was determined using the standard method of analysis of the International Association of Official Analytical Chemistry (AOAC, 1995) [25]. Pieces of films of $\sim 0.4\ \text{g}$ were dried in an oven at 100°C for 24 h.

The percentage moisture content (%H) was calculated as,

$$\%H = \left(\frac{P_i - P_f}{P_i} \right) \times 100 \quad (3)$$

where P_i is the initial weight and P_f is the dry weight of the samples.

2.4.7 Solubility in water

Water solubility values were obtained following the method described by Romero-Bastida et al. (2005) [26] and the correction method described by Hu, Chen, and Gao (2009) [27]. The solubility in water was determined as:

$$\text{Solubility (\%)} = \frac{(m_{\text{si}} - m_{\text{sf}})}{m_{\text{si}}} \times 100 \quad (4)$$

where, m_{si} is the initial dry weight and m_{sf} is the final dry weight.

Initial dry weight values were determined by subjecting disks of 2 cm of diameter in an oven at 100°C for 24 h. Then, the disks were immersed in 50 mL of distilled water for 24 h at 25°C and dried at 100°C for 24 h to obtain the final dry weight values.

2.4.8 Uniaxial tensile tests

Uniaxial tensile tests were carried out in an Instron dynamometer 5982 at 5 mm/min following ASTM D882-02 (2002) [28] standard recommendations. Pieces of films of $50\ \text{mm} \times 5\ \text{mm}$ (length and wide, respectively) were used to perform the tests. Nominal stress (S)–strain (ϵ) curves were obtained and Young's modulus (E), tensile strength (S_u), strain at break (ϵ_b), and tensile toughness values were determined from at least 10 samples of each system.

2.4.9 Dynamic mechanical tests

Dynamic mechanical tests were performed using a Dynamic Mechanical Thermal Analyzer (DMTA IV, Rheometric Scientific) in the rectangular tension mode at 1 Hz, in the range of temperature from -90 – 50°C at a heating rate of $2^\circ\text{C}/\text{min}$. A tensile deformation of 0.04% was used in order to ensure working in the linear viscoelastic range [29]. Sample dimensions used were $15.0\ \text{mm} \times 5.0\ \text{mm}$ (length and width, respectively).

2.4.10 Color and lightness

The color measurements of the films were taken at ten random points on the surface exposed to the atmosphere during the drying step, using a Minolta spectrophotometer, model CR-300. The results were expressed in the CIELab scale (*Commission International de l'Eclairage*), where L denotes the lightness (L: 0 = black and 100 = white) and

a^* and b^* chromaticity: $-a^*$ (greenness) to $+a^*$ (redness) and $-b^*$ (blueness) to $+b^*$ (yellowness).

The color differences between the samples containing the extract and the matrix were calculated as:

$$\Delta E^* = \left[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2 \right]^{1/2} \quad (5)$$

where $\Delta L^* = L_i^* - L^*$ (brightness difference), $\Delta a^* = a_i^* - a^*$ (red-green chromaticity difference) and $\Delta b^* = b_i^* - b^*$ (yellow-blue chromaticity difference). The index i indicates the value of the reference that takes each parameter.

3 Results and discussion

The antioxidant activity of the films containing 5% of extract of *yerba mate* (TPS-Y5) was 3.0 ± 0.1 mg/g of film, while TPS-Y20 showed an activity of 10.4 ± 0.1 mg/g of film; revealing a loss on drying of $\sim 13\%$ y 22% , respectively. This reduction resulted from the migration of some volatile low molecular weight compounds, by the evaporation of water caused by the heating during the gelatinization and drying processes [30]. The effects of the incorporation of the *yerba mate* extract on the microstructure of the starch films were evaluate by SEM (Fig. 2). All systems (TPS, TPS-Y5, TPS-Y20) showed a structure without pores. The incorporation of the extract did not lead to significant differences in the structure of the compounds regardless of the concentration used; indicating that the extract was well dispersed in the starch matrix through hydrogen bonding [31].

The above behavior was expected because the *yerba mate* extract is a hydrosoluble compound where the filmogenic suspension is homogeneous. When films with hydrophobic compounds were investigated, changes in the structure were observed as a function of the nature of the added compounds (basil essential oil, thyme essential oil, and α -tocopherol), due to their low miscibility with the polymers and the different interactions between them and the polymer [32].

In order to quantify the impact of the incorporation of the extract of *yerba mate* on the surface topography of the films, AFM analysis was performed. The roughness of the films surfaces that were in contact with the air during the drying step was analyzed through 3D topographical analysis (Fig. 3). Two different behaviors were observed in the biocomposites containing the extract. The micrograph of TPS-Y5 presented a higher number of rounded and homogeneously dispersed peaks, compared to the matrix. On the other hand, the material with the highest concentration of extract presented higher peaks, pointing and not so homogeneously dispersed.

The observations from the topographic images were confirmed with the values of the surface roughness of each system (RMS), resulting 3.7 ± 0.5 , 5.2 ± 0.1 , and 9.7 ± 0.8 nm for TPS, TPS-Y5, and TPS-Y20, respectively.

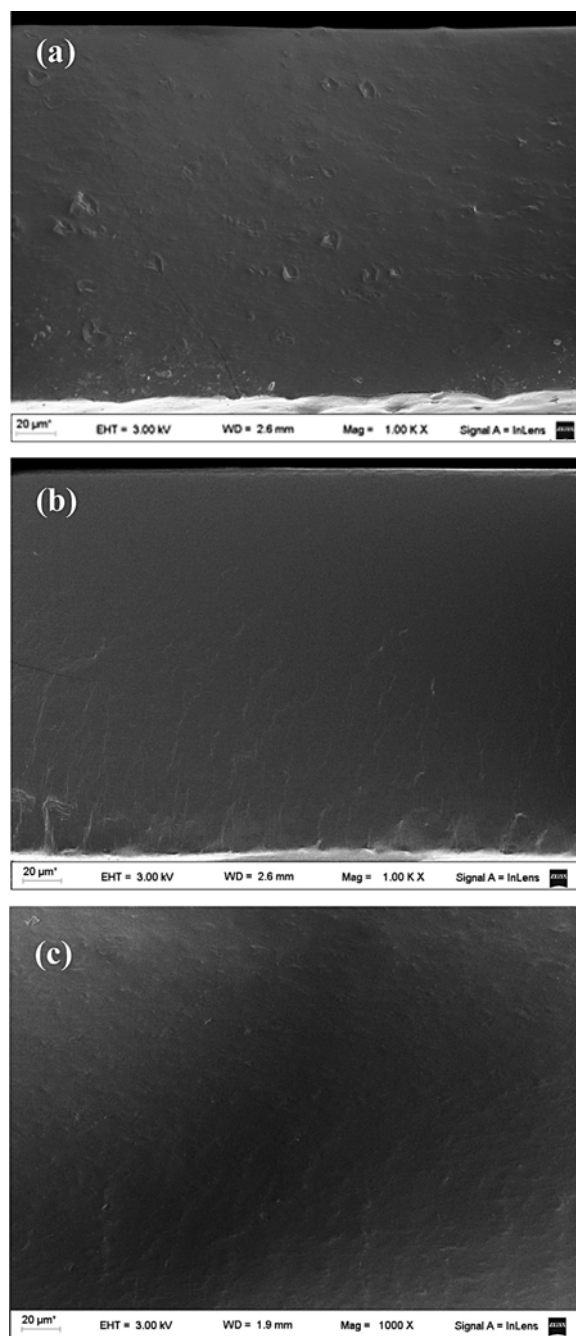


Figure 2. SEM micrograph of the cryogenic fracture surface of: (a) TPS, (b) TPS-Y5, and (c) TPS-Y20.

That is, RMS of the films increased with the concentration of the extract of *yerba mate* from 40 to 260%, approximately.

Erbil, Demirel, Avci, and Mert (2003) [33] related the surface roughness of a material with its hydrophobicity, showing that the larger the roughness, the greater the hydrophobicity. In the same way, these authors involved the contact angle of a material in the relationship between its roughness and hydrophobicity, explaining that a greater

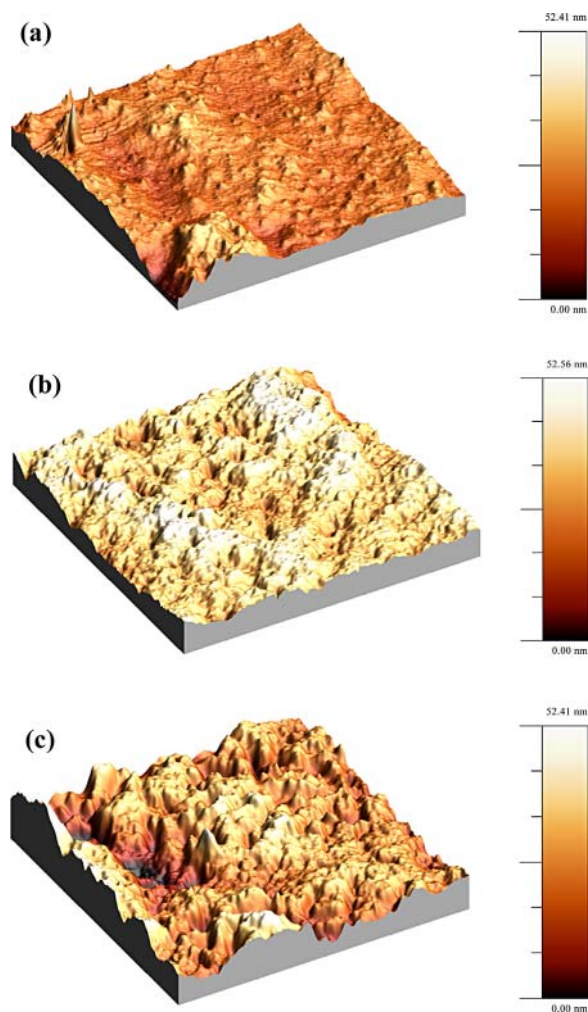


Figure 3. AFM three-dimensional topographic image of the surface of: (a) TPS, (b) TPS-Y5, and (c) TPS-Y20.

roughness increased the contact angle and therefore, the hydrophobicity of the material. The roughness increases the fraction of air entrapped in the surface and thereby increases the water contact angle [34, 35].

In order to evaluate the hydrophobicity of the films, the contact angle (θ) between a drop of water and the surface of each system was measured (Fig. 4). It was found that the contact angle increased when the extract of *yerba mate* was incorporated. In the case of TPS-Y5, this parameter changed from $55 \pm 5^\circ$ (TPS) to $75 \pm 5^\circ$, whereas in TPS-Y20 samples it increased to $66 \pm 4^\circ$. Following the terms “hydrophobic” and “hydrophilic” surfaces, defined for $\theta > 65$ and $\theta < 65^\circ$, respectively [36], the incorporation of the antioxidant led to films with hydrophobic surfaces. Another possible effect of the increase of the contact angle in the biopolymers containing the extract can be related to the higher roughness observed on the surface of these materials respect to the matrix.

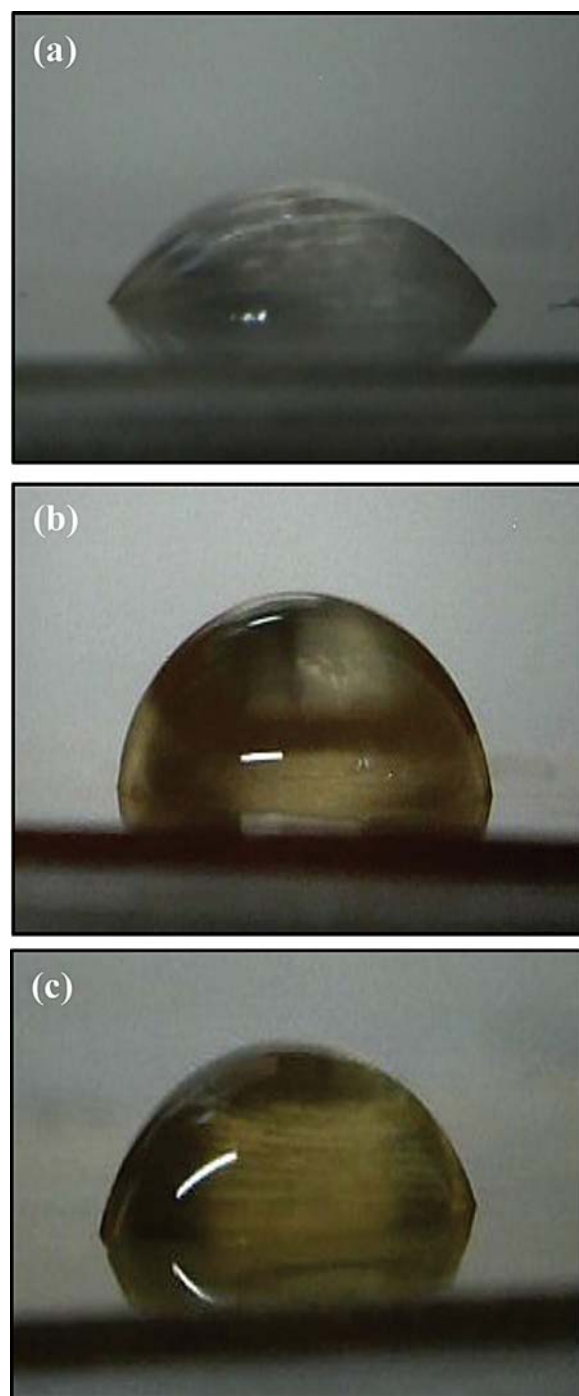


Figure 4. Image of a drop of water deposited on the surface of: (a) TPS, (b) TPS-Y5, and (c) TPS-Y20.

Unlike the behavior observed in roughness tests, the increase in the concentration of the extract (5–20%) did not influence the value of the contact angle ($p \leq 0.05$). Therefore, the correlation between surface roughness and contact angle can be derived by comparing TPS-Y5 with the matrix. However, this relationship cannot be inferred from the comparison between TPS-Y5 and TPS-Y20.

Table 1. Water vapour permeability (WVP), moisture content, and solubility in water values for the different films investigated

Material	WVP, g/srPa ($\times 10^{-10}$)	Moisture content, %	Solubility, %
TPS	8.8 \pm 0.8	37.9 \pm 0.3	35.2 \pm 3.9 ^{a)}
TPS-Y5	7.3 \pm 0.2	30.8 \pm 1.6	32.0 \pm 3.2 ^{a)}
TPS-Y20	4.5 \pm 0.4	27.8 \pm 1.2	29.8 \pm 1.6 ^{a)}

^{a)} Similar letters in the same column indicate non-significant differences ($p \leq 0.05$).

The hydrophobicity results were also consistent with those obtained from humidity content and water vapor permeability measurements (Table 1).

Water vapor permeability (WVP) is an important property of starch based films. It reflects the capability of films to control the water vapor transmission between a food product and the environment. Generally, starch based films present high WVP values, implying a tendency to increase the phenomenon of water vapor transmission [37].

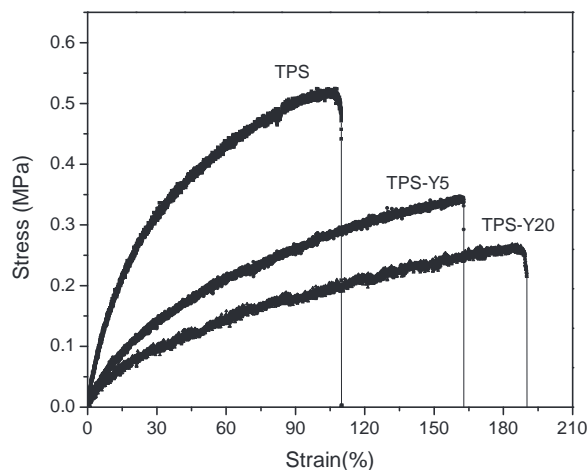
As it is shown in Table 1, WVP values decreased in the biocomposites containing the extract of *yerba mate* compared to that of the matrix, being ~50% lower in TPS-Y20.

Water vapor transfer usually occurs through the pores of a material and, in particular, it is higher in hydrophilic films [24, 38, 39]. Considering that cryo-fractured surfaces of the materials with the extract did not show any pores (Fig. 2) and that they were hydrophobic, lower values of WVP were expected for TPS-Y5 and TPS-Y20 films. The decrease of this property is an important result in terms of the use of the films as coating, because a lower barrier may control better the possible water vapor transference between the product and the environment [40].

On the other hand, Table 1 shows that films with hydrophobic surfaces (TPS-Y5 and TPS-Y20) exhibited lower values of the moisture content. This was probably because the covalent and hydrogen interactions between the polysaccharide network and the polyphenols compounds limited the availability of the hydrogen groups to form hydrophilic bonding with water, subsequently leading to a decrease in the affinity of the films to water [31].

The solubility of biopolymer based films assumes great importance in determining their biodegradability [41]. Water insolubility of films is also important to evaluate them in their potential applications to improve the integrity and safe life of a product [42].

The results of the solubility in water of the different films are shown in Table 1. Although no significant differences in this parameter were obtained, the films containing the extract of *yerba mate* showed a decreasing trend of water solubility with the increase of the antioxidant, possibly due to the miscibility of phenolic compounds with amylose, which

**Figure 5.** Typical nominal stress (s)–strain (e) curves for the different biopolymers investigated.

limited the possibility of forming hydrogen bonds between starch and water [43].

The nominal stress (s) strain (e) curves obtained under quasistatic uniaxial tension at ambient temperature showed the typical behavior of starch-glycerol films, independently of the incorporation of the extract: elastic linear zone followed by a non-linear behavior until failure, which occurs with a precipitous drop of load at the maximum stress with no necking before fracture (Fig. 5). None of the systems exhibited plastic behavior, showing that the films were completely elastic for all the applied forces.

The elastic response over the whole range of deformation observed reveals that when these materials deform, more elastic potential energy is stored, increasing their internal energy without occurring irreversible thermodynamic transformations.

This characteristic is important when a film is intended to be used in food products as coating, because if irreversible thermodynamic transformation happens for an occasional force, the film would not be trustworthy.

Tensile parameter values are presented in Table 2.

The addition of the extract of *yerba mate* led to a decrease in both Young's modulus and tensile strength values, as well as to a significant increase in the strain at break values.

The results of tensile parameters of these films showed values of stiffness one order smaller and a decrease of s_u around 50% compared to the matrix material. Strain at break values significantly increased with increasing the concentration of the extract of *yerba mate*, resulting ~60% higher in the case of the film containing 5 and ~80% for TPS-Y20 film. A decrease in E and s_u values and an increase in deformation at break values were also observed in starch-based films containing other antioxidants such as garlic acid [44], basil essential oil, thyme essential oil, citric acid and α -tocopherol [32], oleic acid [45], and essential oils: *Zataria*

Table 2. Young's modulus (E), tensile strength (s_u), strain at break (e_b), tensile toughness, and relaxation temperatures (T_1 , T_2) values

Material	E , MPa	s_m , MPa	e_b , %	Tensile toughness, $J/m^2 (\times 10^6)$	T_1 , °C (± 1)	T_2 , °C (± 1)
TPS	1.9 ± 0.2	0.51 ± 0.04	107 ± 3	$3.8 \pm 0.4a$	-58	26
TPS-Y5	0.69 ± 0.07	$0.31 \pm 0.03^{a)}$	156 ± 5	$3.2 \pm 0.7a),b)$	-62 ^{a)}	-9
TPS-Y20	0.42 ± 0.05	$0.28 \pm 0.04^{a)}$	183 ± 7	$3.1 \pm 0.2^{b)}$	-63 ^{a)}	-13

a),b) Similar letters in the same column indicate non-significant differences ($p \leq 0.05$).

multiflora Boiss, pennyroyal, or cinnamon [46, 47]. The general behavior observed in the mechanical properties from the addition of the antioxidant was attributed to a reduction in cohesive forces of the network of starch, leading to a decrease in the tensile strength and resulting in a more deformable material. This behavior is commonly found in the literature when a low molecular weight additive such as a plasticizer is incorporated into polymeric materials.

Based on this idea, the decrease in the modulus and maximum stress with increasing extract concentration could be due to the presence of low molecular weight molecules from the majority of the components of the extract, which are inserted between the starch chains. By introducing small molecules through the network of the formulations, the matrix becomes less dense enhancing the movement of the molecules under the application of a stress [48]. Finally, the tensile toughness defined as the work done to break a sample (which is determined by integrating the stress-strain curve), was not affected by the addition of the extract. Contrary to our mechanical results, when Machado, Nunes Pereira, and Druzian 2012 [18], investigated the addition of 20% of *yerba mate* extract in starch-glycerol-nanocellulose-based films, they did not show any significant difference in tensile parameters (modulus, strength, and deformation at break), respect to the matrix (Table 2).

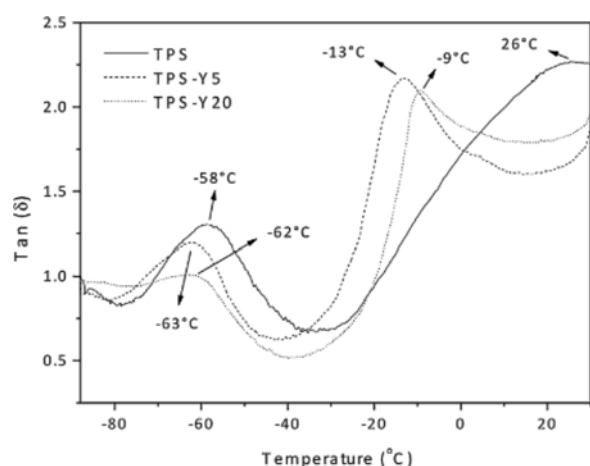


Figure 6. Loss tangent ($\tan \delta$) values as a function of temperature for the different biopolymers investigated.

Taking into account the potential uses of the films in the food industry, a more flexible material would be more efficient as a coating in direct contact with food because the improvement of extensibility might help to avoid chipping or cracking of the film during subsequent handling. The strength values for the films containing the extract appear rather low for food packaging; however, these films would be effective as direct coating of food. Previous works showed the effectiveness of edible films with similar strength values when they were applied to different food such as fruit, meat, or cheese [49–51].

Figure 6 shows the loss tangent ($\tan \delta$) dependence with temperature for the three studied systems. The behavior of the curves was similar to that previously reported in starch-glycerol films [4, 52, 53]. Two peaks corresponding to relaxations of the studied materials were observed: one around -60°C (T_1) and another between -10 and 30°C (T_2). The transition around -60°C is associated with the molecular relaxation corresponding to the glycerol-rich phase and is accompanied by an abrupt fall in storage modulus [52, 54]. This relaxation is generally identified as a glass transition relaxation [55, 56]. The peak observed at temperatures in the range of -10 to 30°C corresponds to the relaxation of the starch-rich phase [29, 57]. Both relaxations shifted towards lower temperatures when the extract was added. It is known that a shift in the relaxations of a starch-glycerol-based material to lower temperatures may be associated with the effect produced by the addition of a plasticizer component [47, 52]. According to the results obtained in quasi-static uniaxial tensile tests, the dynamic mechanical results would indicate that the incorporation of the extract of *yerba mate* into starch films behave similarly to a plasticizer.

The color of the films can also influence the consumer acceptability of a product [58]. Table 3 shows the most relevant parameters color of the studied systems. Slight changes in the color of the films with the incorporation of the extract of *yerba mate* were observed. Chromaticity parameters, a^* and b^* , presented very slight changes from the incorporation of the antioxidant (decreases in a^* , showing a tendency to green and increases in b^* , tending to yellow), while brightness showed a tendency to decrease, which was more notorious for TPS-Y20 films. The brightness of the films is related with the surface morphology reached during

Table 3. Color parameter values for the different systems investigated

Material	Color parameters			
	a*	b*	L	ΔE
TPS	-0.92 ± 0.02	5.94 ± 0.07	89.2 ± 0.6	–
TPS-Y5	-1.95 ± 0.03	13.9 ± 0.3	87.3 ± 0.4	8.0 ± 0.4
TPS-Y20	-2.1 ± 0.1	30.2 ± 0.3	79.9 ± 1.2	26 ± 1

film drying [59] and in general, the smoother the surface, the greater the brightness. The results observed for the parameter *L* of the developed films agreed with those reported in AFM.

Consequently, the color difference (ΔE^*) of the biocomposites containing the extract rose with increasing the antioxidant concentration (~ 8 for TPS-Y5 and ~ 26 for TPS-Y20).

4 Conclusions

The influence of the incorporation of different concentrations of extract of *yerba mate* as antioxidant on cassava starch-glycerol-based biofilms, in order to develop a new material that can be used as functional food packaging or coatings, was investigated. The antioxidant activity of the biofilms with the extract was very effective, being better in the system with only 5% of *yerba mate* due to the less migration of some low molecular weight volatile compounds during the gelatinization and drying process. The films containing the extract presented a homogeneous structure without pores and exhibited higher values of surface roughness and contact angle, indicating hydrophobic behavior of their surface. The hydrophobic nature of these systems reverberated on the water vapor permeability and water content, showing decreases in both parameters. Hence, these new biofilms seem to be very promising as coating of food products because they may control the possible transfer of the food humidity to the environment or vice versa.

The addition of the extract of *yerba mate* also led to important increases in the strain at break, showing a material with more flexibility, as a typical behavior of a plasticized film. The idea of a plasticizing effect of the *yerba* when it is added to starch-glycerol films was confirmed from the shift of the relaxations associated with the glycerol- and starch-rich phases to lower temperatures for the films containing the extract. Taking into account the potential uses of these kind of materials in the food industry, a higher flexibility would make them very promising as a coating in direct contact with food, helping to avoid chipping, or cracking during handling.

The antioxidant and plasticizer effect observed on cassava starch based films, derived from the incorporation of the

extract of *yerba mate*, makes us to think about their potential use as coating of food products in order to retard their oxidation, avoid chipping, or cracking during handling and increase their shelf life.

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The authors declare that no financial/commercial conflicts of interest with the preparation of this study conducted.

5 Novelty statement

In recent years the interest on biodegradable materials as an alternative to their synthetic counterparts, especially in industries such as food, has greatly increased. The originality of this work relies on the use of *yerba mate* as an antioxidant, in the formation of coatings of food in direct contact with them.

While *yerba mate* has been a source of research over the past decades for its important healthy features, no studies about the characteristics of starch-*yerba mate* films were found in the literature. The possibility of incorporating cassava starch films containing antioxidants of *yerba mate* into nutritional health appear promising due to their great properties to retard the oxidation and consequently increase the shelf life of food products.

6 References

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