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Garlic powder and wheat bran as fillers: Their effect on the physicochemical properties of edible biocomposites

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ABSTRACT

Biocomposites with two different fillers, garlic and wheat bran, were studied. They were based on cassava starch and contained glycerol as a plasticizer and potassium sorbate as an antimicrobial agent and were characterized by scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and infrared spectroscopy (IR). The mechanical performance at room and lower temperatures was also studied.

SEM micrographies of fractured surfaces of the wheat bran composite films showed some ruptured particles of fiber while fibrils of garlic on the order of nanometers were observed when garlic composite films were studied.

Mechanical tests, at room temperature, showed that the addition of wheat bran led to an increment in the storage modulus (E') and hardening and a decrease in Tan δ, while the garlic composite showed a diminishing in the E' and hardening and did not produce significant changes in Tan δ values when compared with systems without fillers (matrix). In the range between −90 °C and 20 °C, all the materials studied presented two peaks in the Tan δ curve. In the case of the wheat bran composite, both relaxation peaks shifted slightly to higher temperatures, broadened and diminished their intensity when compared with those of the matrix; however garlic composite showed a similar behavior to the matrix.

DSC thermograms of aqueous systems showed a slight shift of gelatinization temperature ($T_{\text{gelatinization}}$) to higher values when the fillers were present. Thermograms of films showed that both, garlic and wheat bran composites, had a lower melting point than the matrix.

IR data indicated that interaction between starch and fillers determined an increase in the availability of hydroxyl groups to be involved in a dynamic exchange with water.

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1. Introduction

In the last decades, increasing concern about environmental issues has evolved great interest in the development of biodegradable materials to be used as coatings [1–4].

Among the polymers that can be used for this purpose, starch is an interesting alternative because it is a renewable resource widely available from a range of sources, with a low price and potentially good performance. Starches are extensively used in the food and pharmaceutical industries and can be modified to enhance their functional properties [5]. Due to the increase in the price of starches from traditional sources (i.e.: corn), cassava starch as it is or modified has been recently considered as an economic alternative for the food industry [6].

Starch exists as semi-crystalline granules with complex internal supramolecular packing, being constituted of amylose and amylopectin [7,8]. This packed structure gives rise to the characteristic endothermic first order transition known as gelatinization when the granules are dispersed in water [9] or within glycerol solutions [10] and the system is heated. During gel formation, amylose and amylopectin form inter- and intramolecular physical crosslinks to produce a macromolecular network [11,12]. This phenomenon, followed by water evaporation, gives origin to a film.

Despite the capability of cassava starch to produce films without a plasticizer [13], generally, in the composition of edible films, a plasticizer is used in order to diminish the intermolecular attraction between polymeric chains, increasing the flexibility of the film and favoring its maleability and adherence to the product[9,14]. Glycerol and sorbitol are two plasticizers frequently used in the above mentioned films [15–17]. Antimicrobial agents are sometimes added to prevent spoilage of coated foods [18–20].

Reinforced polymeric matrices are developed to improve the properties of the packaging materials through the partial transmission of the stress to the filler. For example, high modulus fillers can be used to increase the storage modulus and hardness of the material. In the food industry, the addition of fibers to a packaging material can be performed not only to enhance mechanical properties but also to

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change barrier properties or to produce other specific functional effects such as antimicrobial action. In particular, to diminish pollution problems generated by synthetic materials, natural fillers have begun to be used for improving mechanical and barrier properties of packaging materials while helping the biodegradability of the composite [21,22]. Natural materials present great variability as their chemical and physical characteristics are highly influenced by the soil, the weather, the water, in summary, by the environmental characteristics of the region where they are obtained. This determines a lack of reproducibility in the materials developed when using them as a component. Fibers present in vegetal tissues can act as natural fillers. These fillers are mainly composed of cellulose, non-cellulosic carbohydrates and lignin.

A good source of this type of fiber is the bran of wheat [23]. It contains a high percentage of cellulose and offers advantages over the traditional materials of reinforcement, such as its low density, non-abrasive nature, availability, low cost and renewability [24]. Besides the capacity of reinforcing the material and changing the mechanical properties of the coatings [25,26], this natural material has an important nutritional value because of its great concentration of vitamins, minerals and carbohydrates [27,28]. Wheat bran contains 40.2% of dietary fiber and 92% of it is insoluble [29].

Garlic is a bulb composed of water, carbohydrates, lectins, prostaglandins, adenosine, vitamins B_1, B_2, B_6, C and E, biotin, nicotinic acid, fatty acids, glycolipids, phospholipids and rich in essential amino acids. It has a high content of organic compounds with sulfur. It has been deeply appreciated from ancient times due to its characteristic flavor as well as its antibacterial action. Nowadays, it is known that it has different medicinal activities: antibacterial, antiseptic, mucolytic and acts as a regulator of the cardiovascular system [30,31]. In comparison with wheat bran, it has a low concentration of dietary fiber and a high percentage of it is soluble in water. Garlic powder contains 1.9% of dietary fiber and 30% of it is water soluble [29].

The objective of this research was to develop biodegradable edible composite films based on cassava starch and wheat bran or garlic as well as to study their physicochemical properties in order to evaluate their potential performance when used in food packaging or coating.

2. Experimental

2.1. Materials

Cassava starch was provided by *Industrias del Maíz S.A.* (Buenos Aires, Argentina). Glycerol (Mallickrodt, Buenos Aires, Argentina) and potassium sorbate (Sigma, St Louis, Missouri) used were of analytical grade. Wheat bran and garlic were bought in the local market (*Dietética Científica S.A.C.I.F.I.*, Buenos Aires, Argentina).

2.2. Film formation

Different types of films were studied in this research: a) cassava starch films and b) two types of composite films involving wheat bran or garlic powders as fillers. The protocol used for their conformation is explained below.

2.2.1. Matrix

Every gram of the aqueous matrix system consisted of 50 mg of tapioca starch, 25 mg of glycerol as a plasticizer, 2 mg of potassium sorbate as an antimicrobial, and 923 mg of distilled water. This system was gelatinized using a heating rate of ~1.7 °C/min until the sample achieved a temperature of 82 °C (~40 min).

After gelatinization, the gel was degassed for 30 min with a vacuum mechanical pump. The gel was distributed in glass dishes and dried at 52 °C (R.H.:22%) for 2 h. Drying was completed in a chamber (Velp, Italy) at 25 °C and R.H.: 80–90% (4 days) giving origin to the matrix films. A complete description of the technique used can be found in Famá et al. [32].

2.2.2. Composites

Composites were conformed by using wheat bran or garlic powder as fillers. Both fillers were milled and sieved through mesh No. 200 and 120 (Zonytest, Buenos Aires, Argentina), obtaining products with a size between 75 µm and 125 µm. The fillers were dried under vacuum at 70 °C and stored under vacuum at room temperature up to the moment of their use. The final moisture of fillers was (10.5 ± 0.3) g/100 g for wheat bran and (15.1 ± 1.3) g/100 g for garlic.

For every gram of the aqueous matrix system, 13.5 mg of filler (garlic or wheat bran) were added, which corresponds to ~15 mg of filler per 100 mg of solids in the films. In this way, aqueous composite systems were obtained.

The protocol for the conformation of the composites was the following: the adequate quantity of filler was hydrated for 24 h in 923 mg of distilled water. Then, the quantities of tapioca starch, glycerol and potassium sorbate described for aqueous matrix system were incorporated [32]. The gelatinization process was performed as described for the matrix system. After gelatinization, the gel was degassed, distributed in glass dishes and dried as previously described giving origin to composite films. To assure system homogeneity, it was necessary to agitate the system during the degasification using an orbital agitator (Vicking, Buenos Aires, Argentina) at 150 rpm.

All materials were equilibrated in NaBr (water activity, a_W ~0.575 at 25 °C) and were characterized 2 weeks after the gelatinization process.

2.3. Scanning electron microscopy (SEM)

The morphology of composite films was studied using a Philips XL series 30, (Philips, Eindhoven, Holland) instrument. The samples were frozen under liquid nitrogen, fractured, glued on a support and sputtered with a thin gold layer. SEM micrographs were carried out using 5 kV secondary electrons. Magnifications used were 1000× and 20,000×.

2.4. Differential scanning calorimetry (DSC)

The heat flow curves of the aqueous systems (matrix and composites) were determined using a differential scanning calorimeter (DSC TA 2010; TA Instruments. New Castle, DE, USA). A sample weight of approximately 10 mg was packed and sealed in a high pressure aluminum pan. The reference was an empty aluminum pan. The heating of the samples was performed in the range of 20 °C–100 °C at a constant heating rate of 2 °C/min. The temperature of gelatinization ($T_{\text{gelatinization}}$) was obtained from the peak of the heating curve; the enthalpy of gelatinization (ΔH_g) was determined as the area below the gelatinization peak. This test was performed in 2 samples of each system.

The melting temperature (T_m) and the heat flow difference (ΔH_m) of the films were determined using the same equipment and heating ~10 mg of sample from 20 °C to 245 °C at a constant heating rate of 10 °C/min. The T_m reported is the peak of the heating curve obtained and the ΔH_m was calculated as the area below the melting peak. The test was performed in 5 samples of each system.

2.5. Infrared spectroscopy (IR)

The infrared absorbance spectra of the films and the fillers were recorded at ambient temperature and atmospheric pressure with a Spectrum One equipment (Perkin Elmer Inc., Shelton, CT, USA) which was equipped with a diamond attenuated total reflectance (ATR) device. The spectra were obtained by recording 16 scans performed with a resolution of 2 cm^{-1} between 700 and 4000 cm^{-1}. The peaks signals were recognized using the software Spectrum V. 5.3.1 (2005. Perkin Elmer Inc., Shelton, CT, USA). Using this software, the background subtraction was performed in the manual mode and the smoothing was performed using the automatic way.

Each sample was scanned three times observing good reproducibility. For comparison between samples, the quotient of intensities at two wavenumbers $[I_{1646\,\mathrm{cm}^{-1}}/I_{2930\,\mathrm{cm}^{-1}}]$ was calculated and results are informed as average ± absolute error. The error was calculated according to Spiridonov and Lopatkin [33].

2.6. Mechanical characterization

Dynamic and quasi static tests were performed using a DMTA IV Rheometric Scientific equipment (USA), in the rectangular tension mode, at 1 Hz.

Dynamics tests of the films were carried out from −90 °C to 20 °C at a heating rate of 2 °C/min and using a fix deformation of 0.04%, to assure working in the linear viscoelastic range [32]. The loss tangent (Tan δ), and storage modulus (E') were obtained as a function of temperature. From these curves, E' and Tan δ at room temperature were obtained.

Quasi static tests of the films were performed at 20 °C and at a constant rate of 5.10^{-3} seg^{-1} and the stress (σ)–strain (ε) curves were obtained.

All the tests were performed in 10 samples of dimensions 5.0 mm × 5.1 mm × 0.35 mm [32]. Reported results are the average of experimental values.

2.7. Mathematical data treatment and statistical analyses

Data were analyzed through the one-way Analysis of Variance (ANOVA) with a probability level, α of 0.05. Tukey's test was the post-hoc test applied. The results are informed on the basis of their average and confidence interval (α: 0.05) unless stated [33].

3. Results and discussion

Fig. 1(A–C) shows the SEM micrographies of cryogenic fractured surfaces of the matrix, wheat bran and garlic biocomposites, at 1000×. In all the films the presence of holes cannot be observed. In the case of wheat bran composites (Fig. 1B), it is possible to observe some ruptured particles of fiber (see highlighted areas). As it is well-known, some components of wheat bran (i.e.: cellulose) are not soluble in water and do not gelatinize [23]. Probably, these characteristics led to the conformation of a material that contained particles of wheat bran distributed in the matrix. In contrast, in Fig. 1C no garlic particles can be distinguished, showing a smoother microstructure for the garlic composite than the one observed for films containing wheat bran. To have more detailed information about the garlic composite, a SEM observation at 20,000× (Fig. 1D) was carried out. Inside the starch matrix, well distributed nano/micro fibers (~275–900 nm) could be observed that can be attributed to the fact that this filler has a high percentage of water soluble components [29], detecting fibrils in the remainder of the solubilization process.

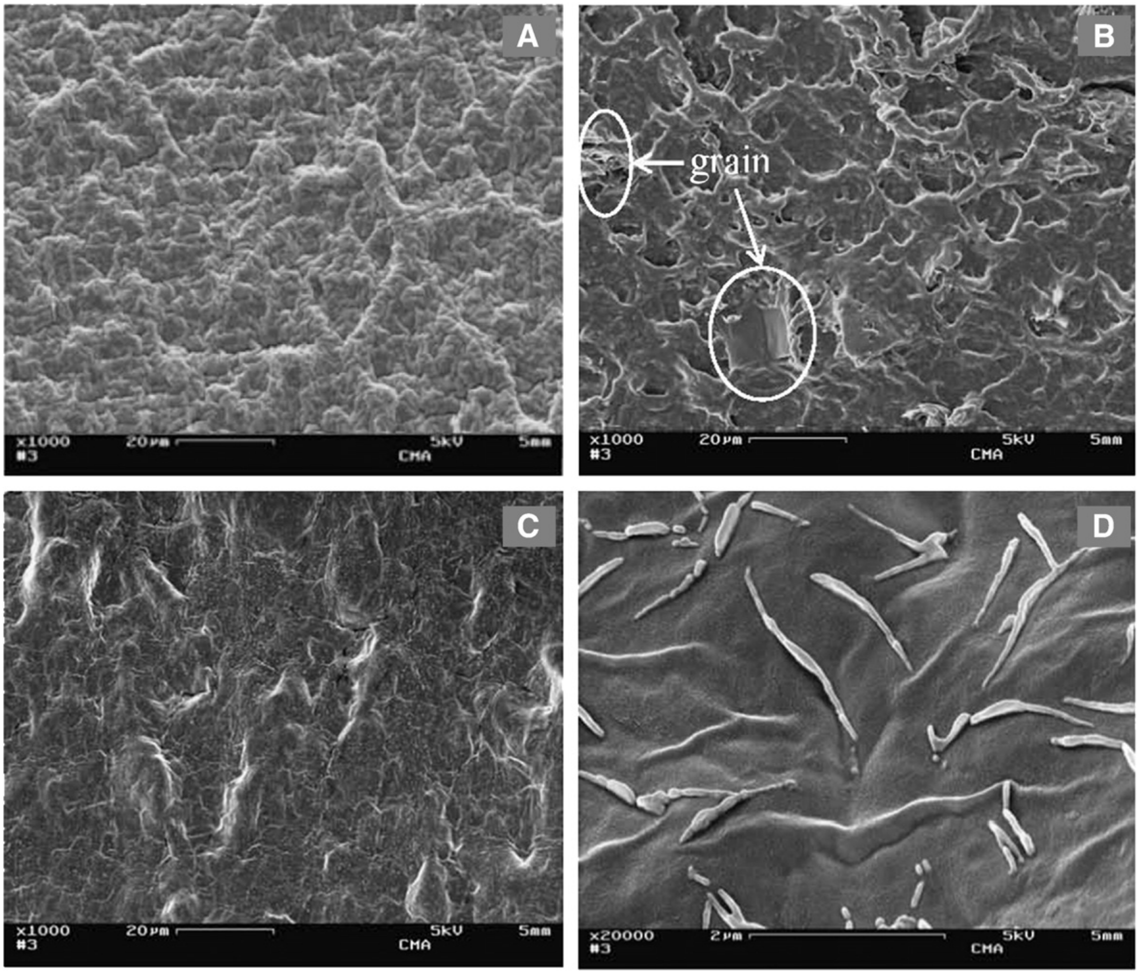

Fig. 1. Micrographies of fractured surface, at 1000×, for (A) matrix film, (B) wheat bran composite film, (C) garlic composite film and (D) micrograph of fractured surface, at 20,000× for garlic composite film.

Fig. 2 shows the DSC thermograms for the matrix and composite aqueous systems. As can be seen, the heat flow curves between 20 °C and 100 °C presented an endothermic peak attributed to the gelatinization of the starch while the systems were heated [8]. The thermograms which present a single peak with no double peak or shoulder are typical of more diluted systems [10]. As can be observed, a slight shift of $T_{\text{gelatinization}}$ to higher temperatures occurred when the filler was present and for both composites. Table 1 shows the values of T_{onset} (temperature at which the gelatinization starts), $T_{\text{gelatinization}}$ (temperature at the peak) and enthalpy value, ΔH_g (the amount of thermal energy involved in gelatinization process). The value of ΔH_g for matrix aqueous system resulted of the order of those reported by Tan et al. [8] and Wongsasulak et al. [34]. In the case of the composite aqueous systems, a decrease of ΔH_g was observed, turning out to be more important when wheat bran composites were studied. Probably, the presence of wheat bran fiber constituted a major barrier to gelatinization occurrence.

The melting points for matrix and composite films as well as for fillers can be observed in Fig. 3. The values related to this process (onset, T_0; melting peak temperatures, T_m and melting enthalpy, ΔH_m) are reported in Table 1. Both garlic and wheat bran composite films showed a lower melting point than the matrix (Fig. 3A). The melting point of the filler occurred at 141.5 °C for garlic powder and at 126.5 °C for wheat bran (Fig. 3B), these temperatures being lower than T_m of the matrix film, a fact that might explain the shift observed for T_m of composites. The ΔH_m for composite films resulted higher than that of the matrix, showing greater energy consumption for composite films that could be ascribed to a greater crystallinization degree for these films due to a more incomplete gelatinization during its conformation.

In Fig. 4A, the IR spectra of matrix, wheat bran composite and garlic composite films can be observed. The spectra are dominated by a broad band assigned to the stretching vibration modes of OH-groups from the absorbed water and from the polymer itself, at ca. 3300 cm^{-1}[35], and bands can be identified corresponding to: CH_2 modes at ~2925 cm^{-1}, OH bending at ~1645 cm^{-1} and C O modes at ~1741 cm^{-1} [13,35]. Slight differences in OH bending and C O modes were observed with the filler addition. Fig. 4B shows an amplification of the IR spectra of previously cited films as well as the IR spectrum of fillers, all in the range of 1755 cm^{-1}–1580 cm^{-1}. As can be observed, the peak around 1741 cm^{-1} was not observed for the garlic powder (Fig. 4B, line b) and it diminished its intensity and shifted to lower wavenumber for garlic composite film (Fig. 4B, line c). The absorbance band at 1645 cm^{-1} is sensitive to H-bonding and amount of hydroxyl interactions. In that range, the garlic addition produced an important change in the spectrum with respect to that of the matrix film. In the range of 1610–1650 cm^{-1}, two peaks, one at ~1649 cm^{-1} and other at ~1614 cm^{-1}, were observed in the matrix film (Fig. 4A, line a); while, the spectra of the garlic and composite film showed one at ~1633 cm^{-1} and ~1645 cm^{-1}, respectively. Following Dumoulin et al. [36], the ratios between the intensity of the peak at 1646 cm^{-1} (I_{1645}) to the one at 2930 cm^{-1} (I_{2925}) were calculated, to compare the free water retention for the different systems. The results showed that the matrix film exhibited a ratio $[I_{1646\,\text{cm}-1}/I_{2930\,\text{cm}-1}]$ of 0.11 ± 0.01; for the garlic composite film, $[I_{1646\,\text{cm}-1}/I_{2930\,\text{cm}-1}]$ took a value of 0.57 ± 0.04.

Data showing low free water retention when the filler was absent is consistent with the hypothesis that when amylose chains were involved in a double helix conformation (interchain bonds are favored) the structure was more resistant to hydration; thus, the water retention was lower. The presence of garlic increased the availability of hydroxyl groups to be involved in a dynamic exchange with water; this trend was expectable due to the high number of OH-groups present in the garlic

Table 1
Parameters of gelatinization for aqueous systems and parameters of melting for matrix and composite films. Results are informed on the basis of their average and confidence interval (α: 0.05).

Materials	Gelatinization			Melting		
	T_{onset} (°C)	$T_{\text{gelatinization}}$ (°C)	ΔH_g (J/g)	T_0 (°C)	T_m (°C)	ΔH_m (J/g)
Matrix	68.3 ± 0.1	75.2 ± 0.1	3.44 ± 0.09	195 ± 1	204 ± 1	191 ± 3
Garlic composite	69.2 ± 0.1	77.1 ± 0.1	3.2 ± 0.1	118 ± 1	143 ± 1	233 ± 4
Wheat bran composite	68.2 ± 0.1	76.2 ± 0.1	3.0 ± 0.1	118 ± 1	146 ± 1	225 ± 3

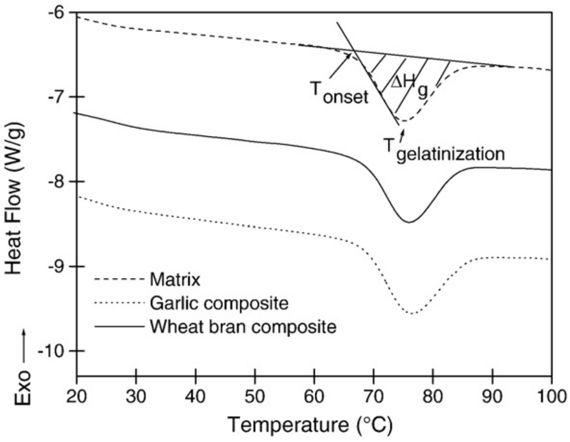

Fig. 2. Differential scanning calorimetry thermograms for aqueous matrix system and both aqueous composite systems.

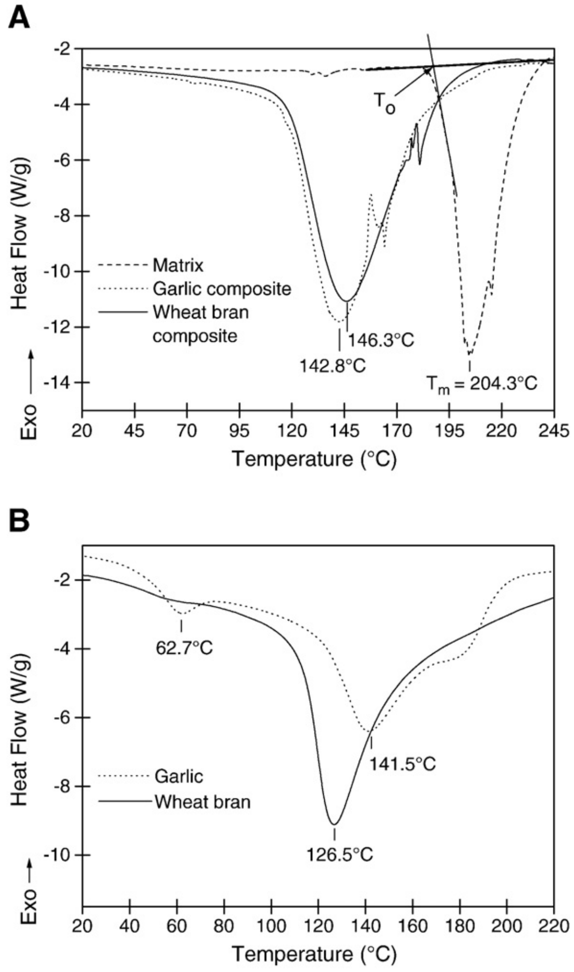

Fig. 3. Differential scanning calorimetry thermograms for matrix and composite films (A) and for the fillers used (B).

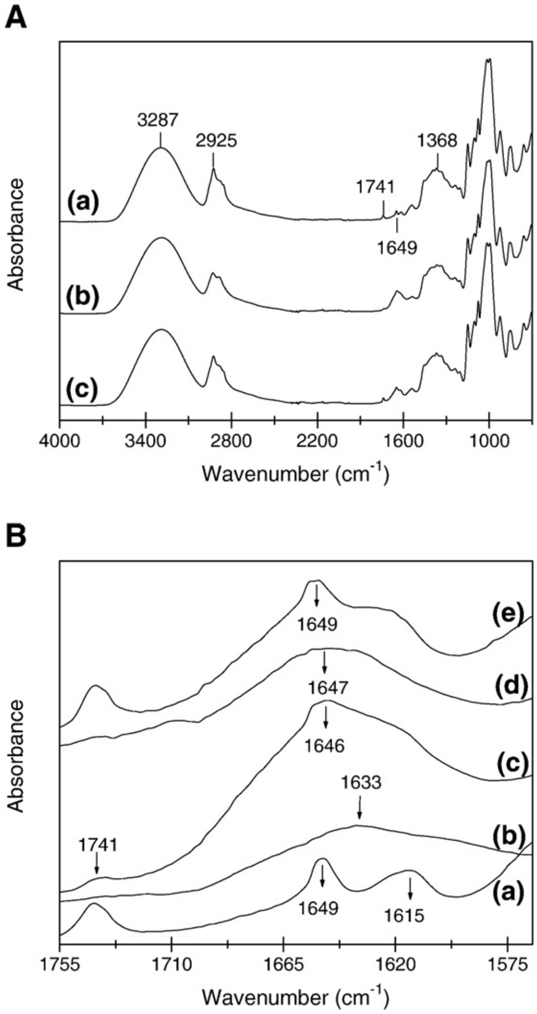

Fig. 4. Infrared absorption spectra. Panel A: (a) matrix film, (b) wheat bran composite film and (c) garlic composite film. Panel B: (a) matrix film, (b) garlic, (c) garlic composite film, (d) wheat bran and (e) wheat bran composite film.

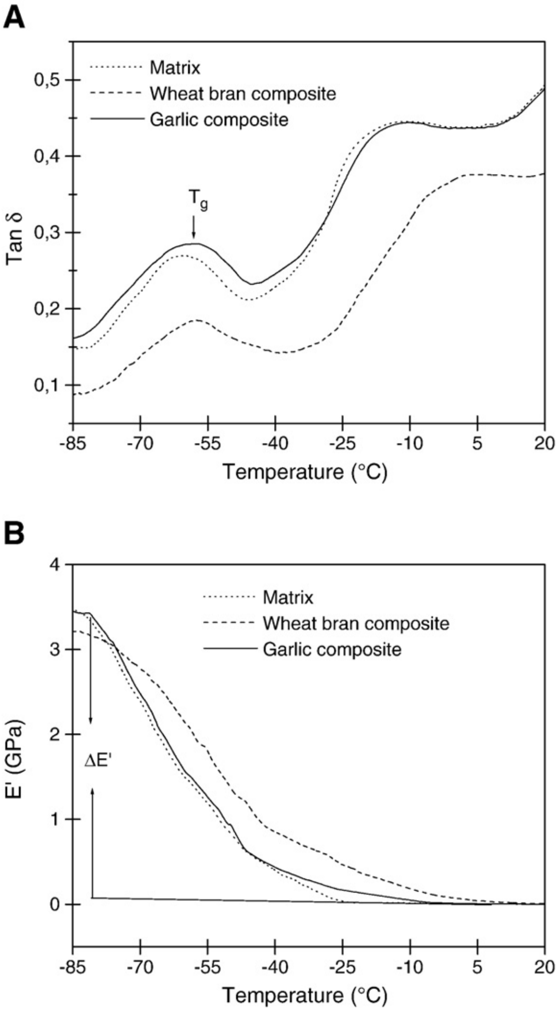

Fig. 5. Tan δ (A) and E' (B), as a function of the temperature for matrix, wheat bran composite and garlic composite films.

powder [31,37]. The interaction between starch and fillers created a network that might promote water penetration, enhanced by the availability of free hydroxyl groups to hydrate and to swell.

In the case of wheat bran composites (Fig. 4B, line e), the samples presented a peak at ~1649 cm^{-1} and a shoulder around ~1620 cm^{-1}. The ratio between the intensity of the peak at ~1649 cm^{-1} and the one at ~2925 cm^{-1} resulted in a value of 0.32 ± 0.03 which is higher than the ratio observed for the matrix film (0.11 ± 0.01). Again, the presence of the filler led to the constitution of a network that might promote water penetration, enhanced by the availability of free hydroxyl groups to hydrate and to swell. On the other hand, the peak at ~1615 cm^{-1} observed for the matrix film disappeared for both biocomposites; this peak lies in the deformation region for molecular water [38] and its disappearance can be attributed to changes in the material structure that inhibit water from deformation and/or to a change in the water status when fillers are present.

Fig. 5 shows the loss Tangent, Tan δ (A), and storage modulus, E' (B), as a function of the temperature for the matrix, garlic composite and wheat bran composite films. It can be observed that all materials studied presented two peaks in the Tan δ curve (Fig. 5A): one around −60 °C and the other one, wide with low intensity between −30 °C and room temperature, as was reported by Famá et al. [32]. The first peak is associated with the phase rich in glycerol from the starch–glycerol partially miscible system [39,40]. The peak around 0 °C is related with a rearrangement of amorphous starch chains in the presence of moisture [41]. Both relaxation peaks shifted slightly to higher temperatures, broadened and diminished their intensity with the wheat bran fiber addition, trends that are usually observed in particulate composites [42–44]. As it is well-known, the shift of one relaxation to higher temperatures is associated with the decreased mobility of the polymer chain. These results can be attributed to the interactions between the polymeric matrix and the added filler as previously stated. The garlic composite seems to behave in a similar manner to that shown by the matrix; however, the peak around −60 °C is slightly wider than the matrix's. This trend could be ascribed to the occurrence of two opposite effects: 1) it is well-known that the addition of a filler shifts to higher temperatures [45,46] and broadens, peaks associated with relaxation and 2) garlic powder contains chemical moieties that possess OH and NH$_2$ groups [31,37] capable of forming hydrogen bonds. As a consequence, garlic powder can affect the polymeric network formation, developing a plasticizing action [47] and the composite might behave as a material with a higher concentration of plasticizer. This plasticizing effect produces a shift of glass transition temperature (T_g) of the glycerol rich peak (~−60 °C) to lower temperatures. The compensation of both effects might have determined the null shift in the T_g temperature for this system.

The relaxation associated with the glycerol rich phase, observed in the loss tangent curves, is in good agreement with the abrupt fall in the storage modulus (Fig. 5B). The filler addition produced a marked decrease in the intensity of the main relaxation, generating a greater difference ($\Delta E'$) between the E' value in the glassy zone and the E'

value in the rubbery zone, for the wheat composite film, while the incorporation of garlic did not change these values significantly (Table 2).

As can be observed in Table 2, the wheat bran fiber addition led to a significant increment in the E' and a decrease in the Tan δ at 20 °C, while garlic composite films showed a significant decrease of E' (~40%) and no significant change in the Tan δ value at 20 °C. The increment in the E' with the fiber addition is expectable taking into account that the E' of wheat bran is higher than the modulus of the matrix material, and this fiber is not soluble in water; therefore, the E' of wheat bran composites should be higher. As previously stated, garlic powder can affect the polymeric network formation, developing a plasticizing action and the composite might behave as a material with a higher concentration of the plasticizer, determining trends observed in Table 2.

The stress (σ)–strain (ε) curves of edible films are shown in Fig. 6. As can be observed, they showed a non-linear behavior from 5% of deformation and on, arriving to a plastic deformation region. The wheat bran composite film curve shows a significant increase of the hardening (defined as the tension to achieve the same deformation) with respect to the matrix film; while the addition of garlic led to a significant decrease in this parameter. These results are expectable taking into account the dynamic mechanic results obtained for studied samples.

4. Conclusions

Composite films developed revealed that wheat bran maintained its micrometric characteristics while garlic powder, due to the solubility in water of a great part of its components, changed to a nanometric filler.

The addition of both fillers lowered the melting point of the conformed materials. This trend can be attributed to the lower melting point of the fillers.

The presence of the filler led to the constitution of a network that might promote water penetration, enhanced by the availability of free hydroxyl groups to hydrate and to swell. The composite conformed based on garlic, showed a decrease in the E' and stress at a fixed deformation, probably associated with a plasticization of the material generated by the components of garlic that are soluble in water. In contrast, for the composite conformed with wheat bran as a filler, important improvements in mechanical properties were obtained: the E' and the stress at 70% of strain were higher than the one of matrix film. In addition, all the materials presented deformations higher than 70% without break.

It is concluded that edible biocomposite films can be developed based on cassava starch and using garlic powder or wheat bran as fillers. Their physical properties are highly influenced by the type of filler present, potentially affecting their performance as food packaging or coating. It must be stated that due to the influence of water, soil and weather on the characteristics of natural components used, trends herein reported can be affected when using components from another origin.

Table 2
Parameters of glass transition (T_g, $\Delta E'$), storage modulus (E') and loss tangent (Tan δ) at 20 °C for matrix and composite films. Results are informed on the basis of their average and confidence interval (α: 0.05).

Materials	Glass transition		E' (MPa) at 20 °C	Tan δ at 20 °C
	T_g (°C)	$\Delta E'$ (MPa)		
Matrix	−60.3 ± 0.5	2.7 ± 0.1	1.2 ± 0.3	0.53 ± 0.01
Garlic composite film	−58.6 ± 0.5	2.6 ± 0.1	0.72 ± 0.13	0.52 ± 0.02
Wheat bran composite film	−57.0 ± 0.5	3.1 ± 0.1	8.1 ± 0.9	0.41 ± 0.01

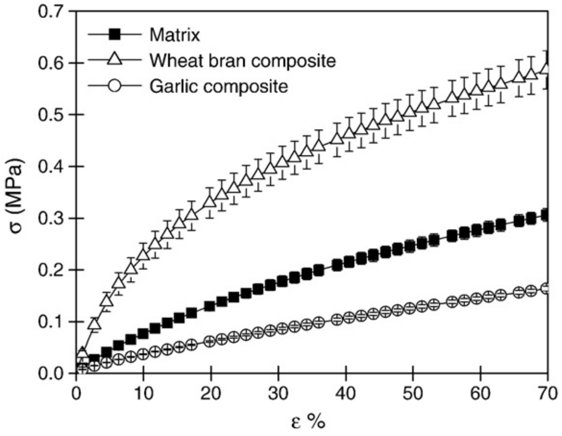

Fig. 6. σ–ε curves for matrix (■), wheat bran composite (△) and garlic composite (○) films.

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