http://dx.doi.org/10.21577/0100-4042.20230052 *Quim. Nova,* Vol. 46, No. 8, 778-784, 2023

Artigo

FUNCTIONAL AND TECHNOLOGICAL PROPERTIES OF COFFEE MUCILAGE (*Coffea arabica*) AND ITS APPLICATION IN EDIBLE FILMS

Daiane Bernardi Machado[a,*] **and Rafael Augustus de Oliveira**[a]
[a]Departamento de Processos de Tecnologia, Faculdade de Engenharia Agrícola, Universidade Estadual de Campinas, 13083-875 Campinas – SP, Brasil

Recebido em 07/02/2023; aceito em 29/03/2023; publicado na web 17/05/2023

Brazil is the largest coffee producer in the world, and together with the millions of tons produced, millions of tons of residues are also generated. The generated residues are a source of environmental contamination depending on the chosen processing route. One of the main applications of food industry waste is in the production of raw materials to produce edible films and coatings. Coffee mucilage is a pectin-rich liquid residue from the coffee sector that can be used in the production of value-added products. Given this, the objective of this work was to characterize and evaluate the potential of functional and technological properties of coffee mucilage and your applicability in the production of edible films. The filmogenic mixture was obtained by casting from 10% (w/v) lyophilized coffee mucilage and solvent (water). The films produced from the coffee mucilage presented good homogeneity, continuity (absence of ruptures or fragile regions), flexibility, ease of detachment of the support and handling, without the need to add adjuvant to its formation. In addition, they presented uniformity in thickness, high light barrier and medium water vapor barrier. Thus, it can be concluded that mucilage is a potential product to be used in the cosmetic, pharmaceutical and food industries.

Keywords: characterization; coating; by-products; food.

INTRODUCTION

Countries that stand out as major coffee producers face a serious environmental problem resulted of contamination by residues and by-products generated from the chosen processing route. The main by-products responsible for environmental problems are the coffee husk and pulp, due to the presence of caffeine, polyphenols and tannins and has high concentrations of organic pollutants.[1] For this reason, in recent years, there has been a growing interest in using these residues economically, minimizing their effects on the environment, giving them an alternative destination as a raw material for the generation of new products by efficient biotechnological processes.

One of the main applications of residues in the food industry is the production of raw material for making edible films and coating. Biodegradable and edible films produced from renewable and stable materials are interesting by the scientific and commercial point of view. These biopolymers have the advantage, compared to synthetics, of being biodegradable and coming, mostly, from renewable sources. In addition, they stand out for having multiple uses, being easily discarded, and even for substituting oil-based raw materials.

Edible coatings and films are generally made up of proteins, polysaccharides, lipids or a combination of these.[2] Polysaccharides are very versatile and have aroused great interest due to their functional properties combined with their availability, low cost and low toxicity.[3] Films made from polysaccharides are applied to a wide variety of foods in order to extend the shelf life of these products. Among the various polysaccharides used as polymeric matrices, pectin presents favorable characteristics in making filmogenic solutions, such as great availability, low toxicity and high biocompatibility, allowing water absorption and formation of gels in concentrations below 1% (m/v).[4]

Most of the commercial pectin used by the food industry is obtained from agricultural and food by-products rich in pectic substances (content greater than 15% on dry basis) such as apple pomace, citrus fruit albedo, beet pulp and sunflower heads.[5] In view of the widespread use of pectin in industry, it is necessary new alternative and viable sources for obtaining it, focusing mainly on the use of industrial waste.

The coffee mucilage is a liquid and viscous residue rich in pectin, produced in the coffee industry that is discarded without treatment directly in watercourses, causing serious contamination problems. This residue represents 17% of the mass of cherry coffee fruits[1] and is formed during the maturation of the berry coffee, in which calcium pectate (located in the middle lamella) and protopectin (present in green fruits) of the cell wall are converted into pectins and result in cell wall disintegrating, leaving the cell plasma free.

Despite the negative consequences of coffee debris and its great potential as raw material, there is little information about its use in the generation of products. Thus, the production of films and coatings of coffee mucilage (residues) opens a new way to reuse this product and increases the supply of pectin in the raw materials market. So, the objective of this work was to extract, characterize and evaluate the coffee mucilage as a raw material to produce films, and to characterize them in terms of physical properties (visual aspect, thickness and thermal properties), barrier (water vapor and light permeability) and mechanical (tensile strength and elongation).

MATERIAL AND METHODS

Raw material

The freshly harvested coffee fruits were taken immediately (on the same day) to the peeler, which, by pressing between a rotor surrounded by a separator-peeler grid, peeled (removed the peel or exocarp) of the ripe fruits. Then, the peeled cherries underwent a mechanical process that separated the mucilaginous layer from the grains. At this point, the mucilage was collected and immediately placed in plastic containers and taken to the cooling chamber at a temperature of 10 °C for 24 hours for subsequent drying.

*e-mail: daianebernardi72@gmail.com

Thermogravimetric analysis of fresh coffee mucilage

Thermogravimetric analysis of fresh mucilage and mucilage film was performed on a thermogravimetric analyzer (TGA-50M, Shimadzu, Kyoto, Japan). Samples of approximately 8 mg were placed in platinum crucibles under an inert nitrogen atmosphere of 50 mL min^{-1}, with a heating rate of 10 °C min^{-1} and a temperature range of 25-160 °C, to measure the degradation of the product. Mass loss (TG) and mass loss rate (DTG) at different temperature ranges were determined from thermogravimetric curves.

Drying

From the result obtained in the thermogravimetric analysis, it was decided to dry the mucilage by freeze drying (lyophilization), because, due to the low degradation temperature (Figure 2), the possibility of enzymatic activity and protein denaturation would be smaller.

Freeze drying

The mucilage was dried in an industrial freeze dryer with a capacity of 80 kg. First, the mucilage was placed in trays of approximately 1 L and taken to freezing process at temperature of −22 °C. After this period, the lyophilization process was started with the vacuum chamber stabilized at 0.75 Torr. In the first 2 hours, the product was kept at −22 °C and, in the third hour, the heating was turned on until all the trays reached a temperature of 38 °C. The lyophilization process lasted 26 hours and the mucilage yield was 14%, that is, in 1 kg of fresh mucilage, 140 grams of powder were obtained.

Centesimal composition

The centesimal composition of the mucilage was determined at the beginning of the experiment to characterize the plant material. The moisture content was determined in an oven with forced air circulation at 60 °C until constant mass. The nitrogen content was defined by the Kjeldahl method described by AOAC[6] and the crude protein was calculated using the conversion factor 6.25 expressed as a percentage.

The determination of the ether extract was performed in a Soxhlet extractor, using petroleum ether as solvent. The ash content was obtained by incineration at 550 °C for five hours, followed by cooling and weighing.[6] The carbohydrate content was determined by difference, subtracting from 100% the sum of the results obtained in previous analyzes. Insoluble fibers (cellulose, lignin and hemicellulose) were determined using the Van Soest method.[7] Water activity was measured by adding a small amount of sample to the water activity meter (AcquaLab, model 4 TEV, USA), which presents the result directly.

Preparation of edible films

The filmogenic solution was obtained by casting methodology[8] from aqueous dispersions of dried coffee mucilage in the proportion of 10% (w/v) with solvent (water). After weighing the solids and adding water, the mixture was stirred on a magnetic stirrer with rotation of 1100 rpm and temperature of 70 °C for 4 min and 30 seconds, so that gelatinization process and formation of gelly solution. The solutions were poured onto acrylic petri dishes, 15 cm in diameter, and taken to the forced air oven, properly leveled, at a temperature of 40 °C for a period of 20 hours, in order to evaporate the solvent and obtain the film. After drying period, the plates were placed in a desiccator with temperature of 25 ºC and 52% of relative humidity, where they remained for 24 hours for later removal of films from the plates and respective characterization.

Characterization of edible film

Visual aspect

The analysis of the visual aspect was subjective and took into account points related to the appearance and formation of the film, especially from the point of view of homogeneity (absence of particles), continuity (absence of breaks or brittle regions), flexibility, ease of detachment of the plate and handling.[9]

Scanning electron microscopy (SEM)

For this analysis, a scanning electron microscope (JEOL, JSM-6390LV, Japan) with backscattered secondary electron sensor was used. The micrographs were performed, evaluating the sample surfaces of the films previously fractured by immersion in liquid nitrogen, in order to avoid distortion of the fracture surface structures. Small samples of the film were fixed on metallic cylindrical supports and covered with a thin layer of gold, using metallizing equipment (Baltec, SCD 0005, Japan) and 15 kV electron beams. The micrograph was observed in a scanning electron microscope, operated at a voltage of 0.3 to 30 kV and current from 1 pA to 1 μA.

Film thickness

The film thickness was measured using a digital micrometer (Mitutoyo, MDC-25P, Japan) with an accuracy of 0.001 mm, taking the arithmetic mean of ten random measurements of the thickness of each sample.

Moisture content

The determination of the moisture content of the film was determined in triplicate by the method of direct drying in an oven.[10] An aliquot (quantity) of 5 g of the film was weighed and dried in an oven at 105 °C until constant weight.

Barrier properties

Transparency/Opacity

The transparency of the mucilage film was determined with a spectrophotometer (BEL, SP-1105, Brazil). The films were cut into 4 cm × 1.5 cm rectangles and placed in a quartz cuvette. An empty cell was used as control. Transparency was measured by transmittance (%) at 500 nm.[11]

Water vapor permeability (WVP)

The water vapor permeability of the film was determined at 25 °C, according to ASTM E 96 / E 96 M-5 method.[12] The diffusion capsules were filled with anhydrous calcium chloride, covered with the film, sealed and placed in a desiccator at 75% relative humidity. The mass gain was determined in each diffusion cell by successive weighing on an analytical balance at intervals of 1 h for 12 hours.

Mechanical properties

The tensile strength (MPa) and deformation (%) parameters of the films were determined using a TA.HDplus texturometer (Texture Analyzer, Stable Micro Systems, United Kingdom) according to the ASTM D882-83 method.[13] Eight repetitions of each film sample were evaluated, with dimensions of 9 cm long and 2.5 cm wide. The thickness of the films was measured before each analysis and taken at four random points using a digital micrometer. The determinations

were performed with an initial distance of the claws of 50 mm and a traction rate of 1 mm s^{-1} under temperature of 25 °C.

Thermal properties

Differential scanning calorimetry

The mucilage film thermogram was performed on a previously calibrated DSC (Differential Scanning Calorimetry) calorimeter. Approximately 5 g of samples were placed in aluminum crucibles, under nitrogen atmosphere at a flow rate of 50 mL min^{-1}, with a heating rate of 10 °C min^{-1}, at temperature range from 0 °C to 180 °C. At the end of the test, the values of fusion heat and melting temperatures were obtained.

RESULTS AND DISCUSSION

Thermogravimetric analyses of fresh mucilage

The thermogravimetric curve of fresh mucilage (Figure 1) shows that two main stages of mass loss occurred: the first stage related to the loss of water molecules bound and adsorbed starting at 61.4 °C, and the second one related to degradation of sugars and pectin occurred at 173 °C.

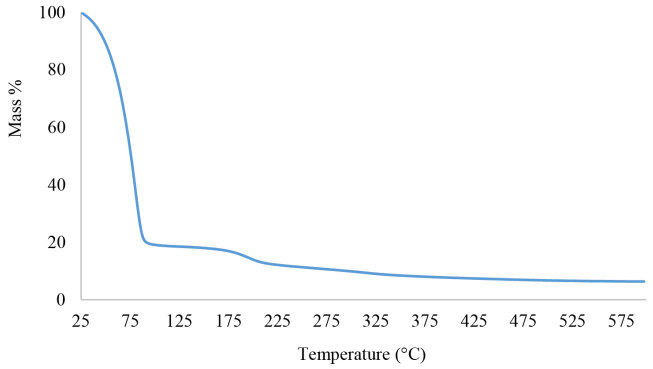

Figure 1. *Thermogravimetric curve (TG) of fresh mucilage*

The first loss started around 30 °C, a relatively low temperature, and may be associated with the loss of volatile solvents, in addition to loss of moisture, since this step extends to a range of 93 °C. This first stage corresponds to a mass reduction of approximately 80% of the sample and can be explained by the high moisture content, 83.8% (Table 1), present in fresh mucilage.

The second stage starts at 173 °C and proceeds to the range of approximately 225 °C. This stage corresponds to the smallest variation in mass of the sample, which is approximately 8%, and can be attributed to the loss of acid groups in the side chain and carbons of the pectin monomers by a process called pyrolytic decomposition.[14]

By the thermogravimetric analysis, it was possible to evaluate the stability of the raw material and its thermal decomposition, serving as parameter for choosing the best method of processing and drying of the material. Thus, it was found that it was not feasible to use the oven drying method, as in this case, there is heat application in temperature conditions generally above 30 °C, subjecting the product to loss of compounds than water. In addition, it was verified, in preliminary tests, that drying in an oven with temperatures above 50 °C causes the start of Mailard reaction due to the high sugar content present in the raw material. The other drying methods, such as infrared, microwave, drum dryer, foam mat, were also considered inadequate for the same reasons presented above.

In view of this, it was decided to dry the mucilage by lyophilization, because it is a process that is carried out at low temperature and allows the chemical and organoleptic properties to remain unchanged. In addition, the product obtained via lyophilization has lower moisture content and, consequently, higher stability during storage.

Mucilage characterization

The characterization of the coffee mucilage obtained from the raw material at the beginning of the process (fresh product) is shown in Table 1.

Table 1. Initial characterization of fresh mucilage

Composition	Fresh Mucilage
Water activity (Aw)	0.993 ± 0.004
Moisture content (%)	83.860 ± 0.087
Ashes (%)	0.713 ± 0.020
Proteins (%)	0.180 ± 0.115
Fibers (%)	4.120 ± 0.145
Lipids (%)	> 0.001
Carbohydrates (%)	11.009
Phenolics compounds (mg/100 g)	118.270 ± 16.852

The initial moisture content was quite high (83.8%), characterizing fresh mucilage as a product with a large amount of water in its composition. In addition, fresh mucilage presented a high Aw, which means that the product is highly perishable. In view of this characteristic, the need for immediate processing of the mucilage is evident, since the product has a shelf life of approximately 10 hours[15] due to its composition.

The phenolic compounds content obtained for fresh mucilage was higher than that obtained for passion fruit pulp (20.0 mg/100 g), guava (83.0 mg/100 g), pineapple (21.7 mg/100 g), but lower than those for mango pulp (544.9 mg/100 g) and acerola (580.1 mg/100 g).[16]

Esquivel and Jimenez[17] characterized the mucilage of Arabica coffee and reported water content of 84.2%, protein content of 8.9%; 4.1% of sugar; 0.91% of pectic substances and 0.7% of ash, values close to those found in this work. Woldesenbet, Woldeyes and Chandravanshi[18] obtained values very similar to this work when evaluating the composition of Arabica coffee mucilage in which the water content was 84.2%, 8% of protein, 2.5% of reducing sugars, 1.6% of non-reducing sugars, 1% of pectin and 0.7% of ash.

The centesimal composition of lyophilized coffee mucilage on wet basis is shown in Table 2.

Table 2. Physico-chemical characterization of freeze-dried coffee mucilage

Composition	Dried mucilage
Water activity (Aw)	0.229 ± 0.014
Moisture content (%)	3.005 ± 0.203
Ashes (%)	4.877 ± 0.050
Proteins (%)	8.813 ± 1.327
Fibers (%)	27.47 ± 0.031
Lipids (%)	0.004 ± 0.003
Carbohydrates (%)	55.398
Phenolics compounds (mg/100 g)	433.054 ± 3.254

After lyophilization process, the moisture content of mucilage dropped to 3.09% (w.b.) and, consequently, the water activity was reduced to 0.229, making possible to store the mucilage for later use. This value is below the recommended limit for water activity of

dehydrated products, which is 0.60, making them microbiologically stable.[19] In addition, the closer the water activity is to 1, the greater the product's susceptibility to chemical, physical, microbiological and enzymatic changes.[20]

Low levels of lipids and high levels of ash and fibers were found in dried mucilage (Table 2). This by-product proves to be a good source of fibers and can be used as a raw material for pectin extraction. Still, the ash content values indicate the product as a good source of minerals when compared to other commercial flours, such as wheat flour (0.68%), yellow corn meal (0.71%),[21] cassava flour (1.2%) and rice flour (0.40%).[22]

The content of phenolic compounds found in dried mucilage (powder) was higher than that of flours obtained from acerola peels (279 mg/100 g), soursop (24.11 mg/100 g) and pineapple (9.11 mg/100 g)[23] and lower than coffee husk (1595 mg/100 g),[24] thus showing its high antioxidant capacity.

It is important to note that the difference between the phenolic compounds content found between the products (fresh and dried) is due to the fact that the calculation was made based on the total mass of the products. It means, the water content of fresh mucilage, which is 83.8%, directly interferes with the equivalent percentage of phenolic compounds. If the water content of both products was disregarded, the content of phenolic compounds would be 728 mg/100 g for fresh mucilage and 446 mg/100 g for dried one.

Characterization of edible films

Films composed only of mucilage were subjectively analyzed considering the absence of breaks and fractures after drying, the absence of insoluble particles, the ability to manipulate the films and the removal from drying molds without ruptures. The films presented the mentioned characteristics, indicating that no adjuvant adding was necessary to produce them (Figure 2).

Figure 2. *Coffee mucilage films*

The films showed a brownish color. This result is mainly due to the presence of anthocyanins in the coffee husk, which, in the process of mucilage extraction, are pressed and, consequently, release compounds changing their color. In addition to the coloring of the films, the opacity of the films is notorious (Figure 2), which were classified as opaque due to their low transparency value of 6.88%.

In general, the lower the transparency value, the greater the films opacity. Opacity is indicative of the amount of light that can pass over the material surface. Thus, the greater the opacity of a film, the smaller the amount of light that will come into contact with the food product.[25]

As expected, the opacity of mucilage films was greater when compared to pectin-based films that presented an opacity of 7.5%.[26] Lopez-Mata *et al.*,[27] when evaluating films composed of pectin and added with *Aloe vera* gel, observed that the opacity values varied between 9.80 to 10.64%. In other words, when other compounds are added to the pectin film, they directly affect the color and, consequently, its transparency/opacity.

According to Kowalczyk and Baraniak,[28] opacity is desirable to preserve foods that deteriorate in the presence of light, while transparent packaging has the advantage of allowing the consumer to view the food before buying it.

The images obtained by scanning electron micrograph (SEM) were used for evaluating the homogeneity of the film components in the matrix, the film structure and the presence of pores and cracks. The Figure 3 shows SEM images of the surface and fracture of the mucilage films.

There is a dense, cohesive and rough appearance in the morphology of the cross section of the mucilage films. The surface is partially homogeneous with protrusions, without the presence of bubbles/pores and visible defects. The heterogeneity verified on the mucilage film surface is due to the presence of sugars in the pulp and a possible incomplete matrix solubilization. Similar results were found by Espitia *et al.*[29] when compared pectin films and pectin films added from açai pulp, which reported that films containing only pectin presented a more homogeneous surface when compared to films containing pulp. Liu *et al.*[30] analyzed SEM pectin films and revealed that the fractured surface of pectin films had relatively smooth morphology. In addition, Giancone *et al.*[31] stated that pectin films are characterized by highly compacted agglomerates. The presence of irregularities (granules, roughness, holes) in the films may also have contributed to obtain low values of tensile strength for the mechanical tests (Table 3), possibly associated with the discontinuity of the film along the extension, facilitating its rapid breaking.

The films showed homogeneity in thickness and obtained an average of 0.286 mm. The uniformity of the thickness of the films is important, as it serves as a base for calculating several functional

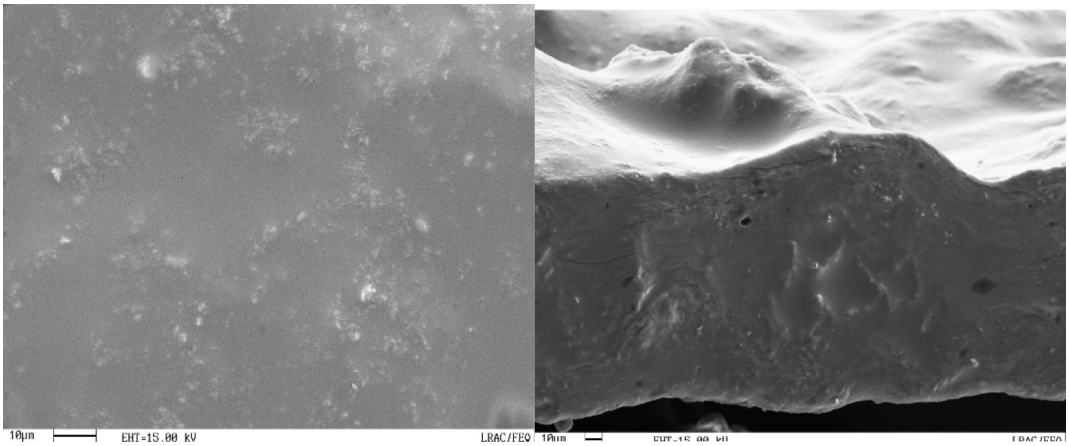

Figure 3. *Micrography obtained by SEM of the mucilage film surface and fracture*

Table 3. Characterization film of the coffee mucilage

Properties	Mucilage films
Moisture content (%, d.b.)	24.5 ± 0.73
Water vapor permeability (g mm kPa^{-1} h^{-1} m^{-2})	0.397 ± 0.05
Tensile strength (MPa)	0.86 ± 0.220
Elongation (%)	24.07 ± 2.81

properties such as opacity, water vapor permeability, rupture stress, among others.[32]

The average thickness of the mucilage films was greater than the values found in the literature for films based on pectin. Melo, Aouanda and Moura,[33] evaluating films composed of pectin in the proportion of 2 and 3%, obtained thickness values of 0.022 and 0.029 mm, respectively. These authors also stated that the thickness can be influenced by the quantity and type of components of the polymeric matrix, preparation technique, type of solvent used, among other factors.

The high value of thickness in the mucilage films can be explained by the concentration of dry matter used in the preparation of the films (10% w/v), as due to the mucilage being in its integral form, and the pectin is not extracted, the amount used was greater in relation to films conventionally produced from commercial pectin. In addition, the non-use of plasticizing agents led to an increase in the proportion of solute so that it was possible to remove and handle the films. It is worth mentioning that the comparison with the literature is hindered by the fact that most authors use crosslinking and/or plasticizing agents in the production of pectin films, thus allowing the obtainment of less thick films.

The moisture content of the mucilage films was 24.5%, a value close to that generally observed in works with edible films, which varies from 15 to 30% of moisture content.[34]

The mucilage films showed mean water vapor permeability values of 0.397 g mm kPa^{-1} h^{-1} m^{-2} (Table 3). This value is lower than that recorded for films produced from fruit pulp such as papaya 15% (3.5 g mm kPa^{-1} h^{-1} m^{-2}),[35] banana 7-12% (3.64 at 4.31 g mm kPa^{-1} h^{-1} m^{-2}),[36] guava (5.31 to 7.81 g mm kPa^{-1} h^{-1} m^{-2}) and sleeve (7.49 to 8.97 g mm kPa^{-1} h^{-1} m^{-2}).[37] When compared to pectin films, the results of WVP of the mucilage films are very close to those obtained by Melo *et al.*,[33] when evaluating commercial pectin films at 2 and 3% at temperature of 25 ºC and relative humidity at 75%, with WVP values of 0.415 and 0.333 g mm kPa^{-1} h^{-1} m^{-2}.

Possibly, the lower WVP value of the mucilage film obtained in this study, when compared to biodegradable fruit pulp films, is due to the presence of insoluble fibers in the coffee mucilage (Table 2), causing changes in the structure and reduction of free spaces in the matrix polymeric material, making it difficult for vapor to pass, resulting in a reduction in WVP values.[38] Although the WVP value verified for coffee mucilage films is lower than that of other biodegradable films processed from fruit pulp, it still has a high water vapor permeability when compared, for example, to synthetic films composed by high-density polyethylene and low-density polyethylene and aluminum sheets.[39]

It is also evident that the result presented by the films is satisfactory considering the absence of plasticizers, crosslinkers or blend of compounds, which could interfere in the film barrier characteristics. However, the main objective of this work is not to present combined or elaborated formulations that generate films with optimized properties, but rather to demonstrate that coffee mucilage is suitable to produce biodegradable packaging for multiple uses.

The mucilage films showed a tensile strength of 0.866 MPa (Table 3). These values are lower than those obtained for low and high methoxylation pectin films (3% w/v) in which the tensile strength was 26.07 and 30.81 MPa, respectively.[40] Coffee mucilage contains a high sugar content[18] in its composition, a fact that may explain its reduced resistance, since the composition of the raw material directly interferes with the polymer matrix integration. This hypothesis is attested by Martelli *et al.*,[41] who report that the high content of total sugars presents in fruits and some vegetables can act as plasticizer and, thus, interact with the polymer chains generating "free" volumes between the chains, weakening intermolecular forces and, consequently, reducing the resistance of films.

According to Villadiego *et al.*,[42] the films must be resistant to protect the structure of the food and flexible, so that they can adapt to the possible deformation of the food without breaking. Based on this concept, it is noted that the coffee mucilage film does not reach the first parameter mentioned by the authors, since it presented low breakdown stress, although, it showed high elongation (24%), demonstrating good flexibility. This result may be directly related to the high content of fibers and proteins found in powdered mucilage, giving it greater flexibility.

Guadarrama-Lezara *et al.*,[43] studying the mechanical properties of nopal mucilage films, found that as the concentration increased from 5 to 10%, the elasticity also increased. This result can be attributed to the additional plasticizing effect introduced by sugars contained in nopal mucilage.[44] Lorevice *et al.*[40] reported an elongation capacity of 0.94% for low methoxylation pectin films and 1.79% for high methoxylation films. In general, the thickness of the films directly influences the deformation rate, as observed by Fakhouri *et al.*,[45] who found that films with higher protein concentrations showed higher values of elongation. The mechanical properties of the films are also dependent on the content of plasticizer and additives, thickness and water content used in their production.[46] Melo *et al.*[33] obtained maximum stress values of 53.35 (MPa) for 2% pectin films and 60.32 (MPa) for 3% pectin films. When cocoa pulp was added, the values dropped to 15.09 and 22.91 (MPa), respectively. The same authors, when evaluating films with 2 and 3% of pectin, found values of 1.8 and 2% of elongation, respectively. Still, according to the authors, when adding cocoa pulp to the film formulations, the elongation reached 18 and 12%. It can be inferred, therefore, that when fruit pulp is added, the films tend to be less resistant and more flexible.

Several physical characteristics of polymers, including thermal properties, are determined by the interaction between compounds and the mobility of their chains. Especially for use as packaging, thermal characteristics are relevant considering that they are usually produced on a large scale and at high temperatures.[47] The results of the thermal analysis obtained for the mucilage film are shown in Figure 4.

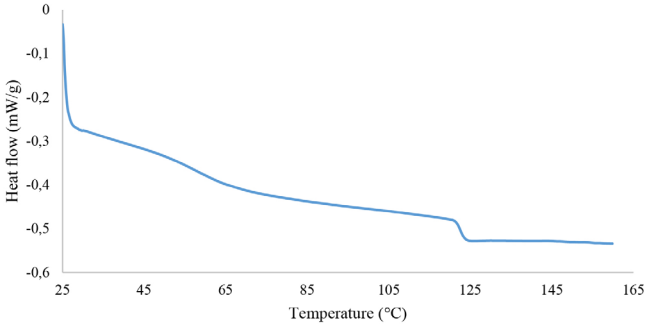

Figure 4. *DSC curve of the mucilage film*

The glass transition temperature (Tg) found for the coffee mucilage films was 121 ºC (Figure 4). This means that, at temperatures below this value, the film will appear rigid, like a fragile glass, but

at temperatures above Tg, it will be in a rubbery, more elastic and flexible state.

Mishra, Datt and Banthia,[48] studying molar mass pectin films (30,000-100,000 g mol^{-1}), determined Tg = 95 °C Tg for the pectin. Lai, Sung and Chien,[49] evaluating the Tg of different samples of pectin with low (22%) and intermediate (64%) degree of esterification, obtained values of 75.2 ºC and 96.2 ºC, respectively.

The melting temperatures of the cellulosic structures present in the mucilage are above the tested range. Such temperatures are around 174 to 400 ºC, as in the case of fruit pulp films,[41] confirmed by the thermogravimetric curves (Figures 5 and 6).

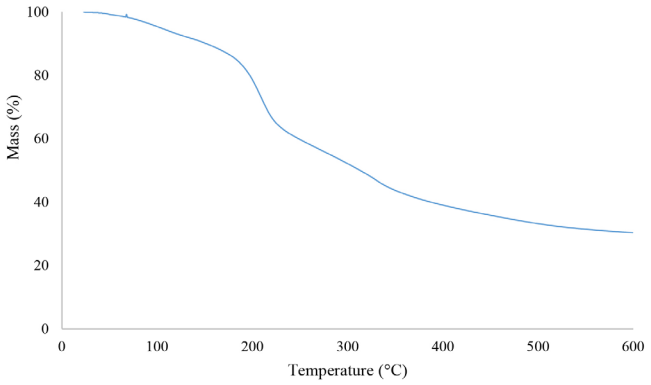

Figure 5. *Thermogravimetric curve (TG) of the mucilage films*

The mucilage film thermogram showed that the films present a multi-degradation process in an inert atmosphere (Figure 5). It is possible to observe in the TGA curve that there is a first event characterizing the loss of mass relative to the loss of moisture and then, the onset of degradation. Regarding the final residual mass (%) obtained after heating to 600 ºC, the value was 30%. Giancone *et al.*[31] studied the thermal stability of edible high-methoxylation pectin films with different surface densities by means of TGA and reported two main losses of mass: the first between 30 and 150 °C, and the second at 250 °C, caused by the thermal degradation of the samples.

It is observed by the DTG curve (Figure 6) that the mucilage films showed four mass loss events; the first at 49 °C, the second at 103 °C, the third at 209 °C and the fourth at 329 °C. However, it can be subdivided into two main stages of degradation: the first, which occurs below 160 °C, is due to the dehydration of the film, mainly associated with the evaporation of water from the polymeric structure; and the second, which comprises two distinct peaks, as evidenced by the DTG curves (Figure 6), is related to the decomposition and depolymerization of the film components.

According to Lacerda *et al.*,[50] the first stage corresponds to the loss of water from the material, it means, the greater the loss in the first stage, the more wet the sample is. The data obtained in this step corroborate with the results found in the analysis of the water content (Table 2), in which the mucilage film presented about 24% (d.b.) water in its composition.

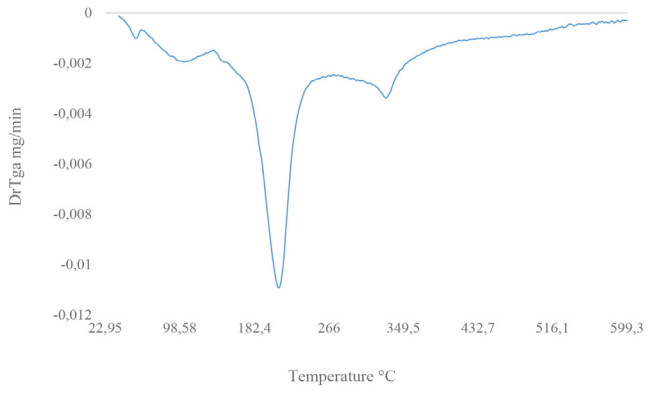

Figure 6. *Derivative of the thermogravimetric curve (DTG) of mucilage films*

In particular, the most evident loss of mass, which started at 174 °C and peaked at 209 °C, can be attributed to the degradation of pectin. Mendes *et al.*,[51] when evaluating films of pure pectin and blends of pectin and coffee grounds, verified four stages of mass loss with more pronounced degradation in the range of 200 to 237 °C, results close to those found in this present work. The mucilage films of coffee showed good thermal stability up to 200 °C, so the pectin molecules present in the films will be partially destroyed and the initial structure of the films will be disordered only when subjected to temperatures above this. This disorder occurs after the breaking of the inter and intramolecular hydrogen bonds between the hydroxyl groups which are responsible for maintaining the ordering of the polymer matrix in the films.[52]

CONCLUSIONS

Coffee mucilage has a high content of fibers, proteins, minerals, and phenolic compounds, making it a product with multiple uses in the food industry. Furthermore, proved to be a suitable material to produce edible films, in addition to have environmentally favorable aspects for its production, since it proposes a completely non-toxic and biodegradable plastic packaging, whose production chain uses material from a renewable source.

The films produced from coffee mucilage showed good homogeneity (absence of particles), continuity (absence of breaks or fragile regions), flexibility, ease of detachment from the support and handling, without the need to add adjuvant to its formation. In addition, they presented uniformity in thickness, high barrier to light and weak barrier to water vapor.

ACKNOWLEDGMENTS

This work was financed by the National Council for Scientific and Technological Development (14833/2017-7).

REFERENCES

1. Murthy, P. S.; Naidu, M. M.; *Resour., Conserv. Recycl.* **2012**, *66*, 45. [Crossref]
2. Liu, F.; Chiou, B. S.; Avena-Bustillos, R. J.; Zhang, Y.; Li, Y.; Mchugh, T. H.; Zhong, F.; *Food Hydrocolloids* **2017**, *65*, 1. [Crossref]
3. Soliva-Fortuny, R.; Rojas-Grau, M. A.; Martín-Belloso, O. In *Edible Coatings and Films to Improve Food Quality*; Bai, J., ed.; CRC Press: Boca Raton, 2011, p. 103-136.
4. Abid, M.; Cheikhrouhou, S.; Renard, C. M. G.; Bureau, S.; Cuvelier, G.; Attia, H.; Ayadi, M. A.; *Food Chem.* **2016**, *215*, 318. [Crossref]
5. Ciriminna, R.; Hernández, N. C.; Hernández, A. I. R.; Pagliaro, M.; *Biofuels, Bioprod. Biorefin.* **2015**, *4*, 368. [Crossref]
6. AOAC; *Official Methods of Analysis of AOAC International*, 18th ed.; AOAC International: Gaithersburg, 2006.
7. Silva, D. J.; *Análise de Alimentos: Métodos Químicos e Biológicos*, 1ª ed.; UFV: Viçosa, 1990.
8. Fakhouri, F. M.: *Bioplásticos Flexíveis e Biodegradáveis à Base de Amido e Gelatina*; Tese de Doutorado, Universidade Estadual de Campinas, São Paulo, Brasil, 2009. [Link] accessed in May 2023
9. Sarantópoulos, C. I. G. L.; Oliveira, L. M.; Padula, M.; Coltro, L.; Alves, R. M. V.; Garcia, E. E. C.; *Embalagens Plásticas Flexíveis - Principais Polímeros e Avaliação de Propriedades*; CETEA/ITAL: Campinas, 2002.

10. Instituto Adolfo Lutz; *Métodos Físico-Químicos para Análise de Alimentos*, 4ª ed.; IAL: São Paulo, 2008.
11. Tang, C. H.; Jiang, Y.; Wen, Q. B.; Yang, X. Q.; *J. Biotechnol.* **2005**, *120*, 296. [Crossref]
12. Fadini, A. L.; Rocha, F. S.; Alvim, I. D.; Sadahira, M. S.; Queiroz, M. B.; Alves, R. M. V.; Silva, L. B.; *Food Hydrocolloids* **2013**, *30*, 626. [Crossref]
13. American Society for Testing and Materials (ASTM); *Method D882-83: Standard Test Methods for Tensile Properties of Thin Plastic Sheeting*, 1980.
14. Monfregola, L.; Bugatti, V.; Amodeo, P.; Luca, E.; Vittoria, V.; *Biomacromolecules* **2011**, *12*, 2311. [Crossref]
15. Velez, A. R.; Lopez, J. C. J.; WO2013088203A1, (CA2564595 A), **2011**.
16. Kuskoski, E. M.; Asuero, A. G.; Orales, M. Y.; Fett, R.; *Cienc. Rural* **2006**, *36*, 1283. [Crossref]
17. Esquivel, P.; Jiménez, V. M.; *Food Res. Int.* **2012**, *46*, 488. [Crossref]
18. Woldesenbet, A. G.; Woldeyes, B.; Chandravanshi, B. S.; *Asian J. Sci. Technol*. **2015**, *6*, 1467. [Link] accessed in April 2023
19. Chisté, R. C.; Cohen, K. O.; Mathias, E. A.; Ramoa Júnior, A. G. A.; *Cienc. Tecnol. Aliment. (Campinas, Braz.)* **2007**, *27*, 265. [Crossref]
20. Cunha, H. V. F.; *A Diferença entre Atividade de Água (Aw) e o Teor de Umidade nos Alimentos*, 2016. [Link] accessed in April 2023
21. Guilherme, F. F. P.; Jokl, L.; *Cienc. Tecnol. Aliment. (Campinas, Braz.)* **2005**, *25*, 63. [Crossref]
22. Becker, F. S.; Eifert, E. C.; Soares Junior, M. S.; Tavares, J. A. S.; Carvalho, A. V.; *Cienc. Rural* **2013**, *43*, 1911. [Crossref]
23. Souza, M. S. B.; Vieira, L. M.; *Braz. J. Food Technol*. **2011**, *14*, 202. [Crossref]
24. Garcia, L. R. P.; Del Bianchi, V. L.; *Braz. J. Food Technol*. **2015**, *18*, 307. [Crossref]
25. Marcondes, P. D. G.; Darby, D. O. In *The Wiley Encyclopedia of Packaging Technology*; Yam, K. L., ed.; Hoboken: John Wiley & Sons, 2009, p. 1202-1207.
26. Nisar, T.; Wang, Z. C.; Yang, X.; Tian, Y.; Iqbal, M.; Guo, Y.; *Int. J. Biol. Macromol*. **2018**, *106*, 670. [Crossref]
27. López-Mata, M. A.; Cabrera, M. G.; Gregorio, E. V.; Flores, P. P. Z.; Ibarra, S. E. B.; Figueroa, G. G. M.; Cota, L. Q.; Onofre, J. E. J.; *Iran. Polym. J*. **2018**, *27*, 545. [Crossref]
28. Kowalczyk, D.; Baraniak, B.; *J. Food Eng*. **2011**, *105*, 295. [Crossref]
29. Espitia, P. J. P.; Avena-Bustillos, R. J.; Du, W.; Teófilo, R. F.; Soares, N. F. F.; Mchugh, T. H.; *Food Packag. Shelf Life* **2014**, *2*, 38. [Crossref]
30. Liu, L.; Liu, C. K.; Fishman, M. M.; Hicks, K. B.; *J. Agric. Food Chem.* **2007**, *55*, 2349. [Crossref]
31. Giancone, T.; Torrieri, E.; Di Pierro, P.; Cavella, S.; Giosafatto, S. L.; Masi, P.; *Food Bioprocess Technol*. **2011**, *4*, 1228. [Crossref]
32. Xie, L.; Hettiarachchy, N. S.; Ju, Z. Y.; Meullenet, J.; Wang, H.; Slavik, M. F.; Janes, M. E.; *J. Food Sci*. **2002**, *67*, 280. [Crossref]
33. Melo, P. T. M.; Aouanda, F. A.; Moura, M. R.; *Quim. Nova* **2017**, *40*, 247. [Crossref]
34. Bierhalz, A. C. K.; Kieckbusck, T. G.; *Anais do 10° Congresso Brasileiro de Polímeros*, Foz do Iguaçu, Brasil, 2009. [Link] accessed in April 2023
35. Barros, T. T. A.; Tosi, M. M.; Assis, O. B. G.; *Polym. Eng. Sci*. **2018**, *59*, 287. [Crossref]
36. Martelli, M. R.; Barros, T. T.; Assis, O. B. G.; *Revista Brasileira de Produtos Agroindustriais* **2015**, *17*, 301. [Link] accessed in April 2023
37. Viana, R. M.; Sá, N. M. S. M.; Barros, M. O.; Borges, M. F.; Azeredo, H. M. C.; *Carbohydr. Polym.* **2018**, *196*, 27. [Crossref]
38. Muller, C. M. O.; Laurindo, J. B.; Yamashita, F.; *Food Hydrocolloids* **2009**, *23*, 1328. [Crossref]
39. Cuq, B.; Gontard, N.; Cuq, J. L.; Guilbert, S.; *J. Food Sci*. **1996**, *61*, 580. [Crossref]
40. Lorevice, M. V.; Otoni, C. G.; Moura, M. R.; Mattoso, L. H. C.; *Food Hydrocolloids* **2016**, *52*, 732. [Crossref]
41. Martelli, M. R.; Barros, T. T.; De Moura, M. R.; Mattoso, L. C. H.; Assis, O. B. G.; *J. Food Sci*. **2013**, *78*, 98. [Crossref]
42. Villadiego, A. M. D.; Soares, N. F. F.; Andrade, N. J.; Puschmann, R.; Minim, V. P. R.; Cruz, R.; *Rev. Ceres* **2005**, *52*, 221. [Link] accessed in April 2023
43. Guadarrama-Lezama, A. Y.; Castaño, J.; Velázquez, G.; Carrillo, H.; Ramírez-Alvarez, J.; *J. Food Sci. Technol.* **2018**, *55*, 3739. [Crossref]
44. Saberi, B.; Chockchaisawasdee, S.; Golding, J. B.; Scarlett, C. J.; Stathopoulos, C. E.; *Int. J. Biol. Macromol*. **2017**, *10*, 345. [Crossref]
45. Fakhouri, F. M.; Martelli, S. M.; Caon, T.; Velasco, J. I.; Mei, L. H. I.; *Postharvest Biol. Technol*. **2015**, *109*, 57. [Crossref]
46. Basiak, E.; Lenart, A.; Debeaufort, F.; *Int. J. Biol. Macromol*. **2017**, *98*, 348. [Crossref]
47. Lorevice, M. V.; Moura, M. R.; Mattoso, L. H.; *Quim. Nova* **2014**, *37*, 931. [Crossref]
48. Mishra, R. K.; Datt, M.; Banthia, A. K.; *AAPS PharmSciTech* **2008**, *9*, 395. [Crossref]
49. Lai, Y. C.; Sung, P. H.; Chien, J. T.; *Cereal Chem*. **2000**, *77*, 544. [Crossref]
50. Lacerda, L. G.; Demiate, I. M.; Fogueroa, A. M.; Schnitzler, E.; *Brazilian Journal of Thermal Analysis* **2015**, *4*, 12. [Link] accessed in April 2023
51. Mendes, J. F.; Martins, J. T.; Manrich, A.; Sena Neto, A. C.; Mattoso, L. H. C.; Martins, M. A.; *Carbohydr. Polym*. **2019**, *210*, 92. [Crossref]
52. Teixeira, P. R. S.; Teixeira, A. S. N. M.; Farias, E. A. O.; da Silva, D. A.; Nunes, L. C. C.; Leite, C. M. S.; da Silva Filho, E. C.; Eiras, C.; *J. Polym. Res*. **2018**, *25*, 127. [Crossref]