Original Article
Food Science and Technology

ISSN 0101-2061 (Print)
ISSN 1678-457X (Online)

DOI: https://doi.org/10.1590/fst.71421

Pequi mesocarp: a new source of pectin to produce biodegradable film for application as food packaging

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Abstract

This study aimed to develop biodegradable films from pectin extracted from pequi mesocarp and commercial pectin. The films were produced using the casting technique and characterized in terms of their physical, water-related, mechanical, thermal, optical, and microstructural properties. The highest yield of pectin extracted from pequi (26.6%) was obtained using 4% citric acid, a temperature of 80 °C, and an extraction time of 160 min. Commercial-pectin films had a smoother and more regular surface than pequi-pectin films. Pequi-pectin films had higher moisture content (36.25%) and water solubility (76.99%) than commercial pectin films. Pequi-pectin films also showed lower luminosity (55.67*) and higher values of a* (11.56), b*(27.35), opacity (10.67), and Young modulus (82.16 Mpa) than commercial-pectin films. The films exhibited similar thermal behavior, highlighting the presence of exothermic and endothermic peaks for both samples. In the biodegradability tests, both films proved to be 100% biodegradable in four days. The pectin extracted from the pequi mesocarp showed potential for the production of biodegradable films, and this discovery opens up new possibilities for using this byproduct as a raw material for the production of sustainable food packaging.

Keywords: byproduct; *Caryocar brasiliense*; pectin biodegradable films.

Practical Application: The innovation is the use of a natural source for pectin for the production of biodegradable films.

1 Introduction

Environmental pollution caused for the use of synthetic polymers, plastics, and non-degradable packaging materials is one of the greatest challenges that the planet Earth faces (Jouki et al., 2014). Therefore, the demand for biodegradable materials has increased due to their quick degradation process in nature, making the packaging made from these materials ecofriendly (Otoni et al., 2017; Pirsa & Aghbolagh Sharifi, 2020). Different renewable green materials such as carbohydrates, proteins, and lipids have been used as biodegradable materials for smart, active, and bioactive packaging development (Eça et al., 2015; Jacquot et al., 2014; Jouki et al., 2021; Oliveira et al., 2020; Pirsa et al., 2020).

Pectin is a structural polysaccharide extracted from a variety of vegetable tissues of fruits such as pequi mesocarp, which is a byproduct of the food industry. Pectin from vegetable tissues has a high solubility in water, and demonstrates gelling, stabilizing, and thickening properties, which result in excellent film-forming ability (Go & Song, 2020; Nisar et al., 2018; Norcino et al., 2020; Wicker et al., 2014). Pectin films and coatings reveal crystalline or amorphous areas, which can be appropriate for the integration of additives and also for immobilization of water molecules in the film structure, facilitating retention of hydrophilic compounds (Eça et al., 2015).

Pequi (*Caryocar brasiliense*) is a Brazilian Cerrado native fruit belonging to the Cariocaraceas family, which can also be found in Paraguay and Bolivia (Silva Miranda et al., 2020). After industrial processing of pulp in juices, pulps, and jellies, seeds, mesocarp, and exocarp is normally discarded (Araújo et al., 2018). Exocarp and mesocarp contain a high quantity of dietary fibers and pectin, which represent up to 80% of the pequi fruit (Leão et al., 2017; Siqueira et al., 2012) Thus, this material can be a biomass waste source available as a renewable polymer suitable for the production of a bio-based material (Faria-Machado et al., 2015; Ferreira et al., 2018; Leão et al., 2018), which can be used in food packaging. In this context, this work aimed to develop pectin-biodegradable films from the mesocarp of pequi fruit and determine their physical, mechanical, thermal, and biodegradability properties.

2 Methodology

2.1 Material

The pequi mesocarp was purchased at the common market located in Rio Verde (Goiás, Brazil, (S) - 17° 47’ 53”; (W) - 51° 55’ 53”), between October 2017 and February 2018. The raw

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Received 31 Aug., 2021
Accepted 09 Apr., 2022

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material was washed and sanitized. The mesocarps were peeled off, subjected to the bleaching process in boiling water for 6 min, dried in an oven with forced air circulation (60 °C/12 h) (Marconi, MA 035 model, Piracicaba, SP, Brazil), and grounded using a knife mill (Tecnal, Willey TE-650/1, Piracicaba, SP, Brazil) to obtain the pequi flour. The flour was stored at room temperature (~25 °C) in dark containers. All the solvents and reagents used for pequi extraction and films production were PA grade and used as such.

2.2 Pectin extraction

The extraction of pectin from the pequi mesocarp was performed according to Siqueira et al. (2012) with modifications, through heating and acid process. A solution (3.2% w/v) was prepared with distilled water and anhydrous citric acid Synth®), then heated (80 or 100 °C), and homogenized at 1500 rpm using a magnetic stirrer (Splabor, SP-10206/A), for 80 or 160 min. The solution was then cooled at 4 °C, filtered through 150-micron nylon fabric, and washed with 2 volumes of absolute ethyl alcohol (LS Chenicals®). The pectin solution was homogenized for 1 h, filtered in nylon tissue, and washed with 200 mL of 70% ethyl alcohol and 200 mL of 95% ethyl alcohol. The obtained gel, pequi-pectin, was dried in a drying oven (Solab, SL-100/81, Piracicaba, SP, Brazil) at 60 °C until constant weight. The dried pequi-pectin was ground in a knife mill (Fortinox, Star FT51, Piracicaba, SP, Brazil) with 10 mesh granulometry.

The pequi-pectin yield was calculated using the ratio between the final pectin mass obtained and the initial flour mass of the pequi mesocarp used, according to Equation 1.

$$Yield\left(\%\right)=100x\left(\frac{final\ pectin\ weight\left(g\right)}{initial\ pequi\ flour\left(g\right)}\right) \quad (1)$$

The esterification degree (ED) of the obtained pequi-pectin was quantified to determine the amount of free and esterified carboxyl groups according to Fertonani et al. (2009), using Equation 2.

$$ED=\frac{N_2 x V_2}{(N_1 x V_1)+\left(N_2 x V_2\right)} \quad (2)$$

where ED is esterification degree, N_1 is the normality of the NaOH solution (N), and V_i is the spent volume of the NaOH (L).

2.3 Film production

The filmogenic solution was prepared using 1.6% (w/v) of pequi-pectin in distilled water and 1.7% (w/v) of glycerol as described by da Silva et al. (2009), with modifications that were previously tested. The solution was heated and stirred (70 °C/30 min) using a magnetic stirrer (Splabor, SP-10206/A, Presidente Prudente, SP, Brazil). Subsequently, the solution was cross-linked with 50 mL of 5% $CaCl_2$ solution by slow dripping and maintaining constant agitation at 70 °C. After 1 h of precipitation of the residues, 100 mL of filmogenic solution was cast onto an acrylic plate (14 cm diameter), dried in a conventional oven (60 °C/24 h), and stored (52% RH, 25 °C) for 72 h before analysis. The control film was prepared with the same formulation using commercial pectin (Nisar et al., 2018).

2.4 Films characterization

Moisture content

Moisture was determined gravimetrically by drying 2.5 cm film samples at 105 °C until constant weight (Rai et al., 2019).

Film thickness

The average thickness of films was calculated from ten measurements at random positions using a digital micrometer (Qualitylabor MEP/Q, São Paulo, SP, Brazil) with 1 μm of resolution.

Film color and opacity

The color of the films was evaluated using a colorimeter (Hunterlab, ColorFlex EZ, Reston, VA, USA) with CIEL*a*b system, where L* parameter is luminosity varying from 0 (black) to 100 (white), and a* (green to red) and b* (yellow to blue) parameters are tonality. The chromaticity C* and the hue angle (H) indicate the intensity and shade colors, respectively, and were calculated using Equations 3 and 4 (HunterLab, 1996). For color measurement, the surface color of film samples was assessed using a colorimeter against a white color as a standard background (L* = 97.75, a* = –0.49, b* = 1.96). The films were placed in the equipment compartment and five readings were performed on each side of the film.

$$H=\tan^{-1}\left(b^* / a^*\right) \quad (3)$$

$$C=\left[\left(a^*\right)^2+\left(b^*\right)^2\right]^{0.5} \quad (4)$$

The opacity of the films was determined by measuring the absorbance using a spectrophotometer (Metash UV-5100, Shangai, P. R. China) at 600 nm. Each film was cut into a rectangular piece and directly placed into the spectrophotometer test cell against an empty test cell, used as reference. The results were expressed as the ratio between the absorbance and the thickness of the film (600 $nm.mm^{-1}$) (Oliveira-Filho et al., 2020).

Mechanical properties

The mechanical properties of maximum stress (MS), breaking stress (BS), elongation at break (EB), and elasticity module (EM) were determined according to the method ASTM D882-18 (American Society for Testing and Materials, 2018) using an Instron universal testing machine (Model 3367, Grove City, USA) (55% RH, 25 °C). Initially, the films were cut with a width of 25 mm and a length of 120 mm and stored in 55% of humidity and at room temperature prior the analysis. After that, the films were fitted to the equipment with a space between hooks of 100 mm; finally, force and deformation were recorded at a speed of 12 mm per min with a load of 500 N. For each test sample at least three replicates were performed. The abovementioned parameters were calculated according to the ASTM D882 (Jouki et al., 2013).

Water Vapor Permeability (WVP)

The analysis of water vapor permeability was performed according to ASTM E96/E96M-10 (American Society for Testing and Materials, 2011) with modifications at 8 °C of temperature.

The films were sealed with paraffin over an 8 cm diameter technil permeation capsule, containing anhydrous calcium chloride, previously dried in an oven at 200 °C. The capsule was then placed in a desiccator containing a saturated solution of magnesium chloride ($MgCl_2$, 74.8% RH), which was kept in a BOD (Tecnal, TE-371, Piracicaba, SP, Brasil). The capsule weight was monitored through periodic measurements at 30 min intervals during the first 2 hours, every 2 h for the next 8h, and then after 24 h for 7 days (Pagno et al., 2015).

Changes in the weight capsules were recorded as weight gain (g) and were analyzed as a function of time (h). The WVP was calculated using Equation 5.

$$WVP = \frac{g\,x\,t\,x\,\delta}{A\,x\,DPH_2O} \tag{5}$$

where WVP is the water vapor permeability ((g.mm)/(m^2.dia. kPa)), g is the constant rate of weight gain (g/day), t is the time (days), δ is the film thickness (mm), A is the exposed film area (5.02 x 10^{-3} m^2), DPH_2O is the difference in partial pressure of water vapor in the environment near the two sides of the film at the test temperature (kPa).

Water Solubility

The water solubility of the films was carried out using the gravimetric method. The samples were cut (Ø = 2 cm), placed in the oven and dried for 24 hours at 105 °C, and then weighed to obtain the initial weight. After drying, the samples were stirred in 50 mL of distilled water at 25 °C for 24 hours in a magnetic stirrer at 150 rpm (Warmnest, VA, USA). The samples were filtered and the remaining material was dried in an oven at 105 °C/24 h to determine the weight of dry matter not solubilized in water. The solubility calculation was expressed using the initial dry weight (DW_0) and the final dry weight (DW_f) according to ASTM D644-99 (American Society for Testing and Materials, 1999) (Equation 6).

$$Solubility(\%) = \frac{DW_0 - DW_f}{DW_f} x100 \tag{6}$$

FTIR analysis

The spectra of the samples were acquired in the spectral range of 400 and 4000 cm^{-1} with a resolution of 4 cm^{-1} (n = 64) based on a technique of total attenuated reflection (ATR) using a Bruker Vertex 70 coupled infrared absorption spectrometer with a Platinum ATR-unit (Bruker Corporation, Massachusetts, EUA).

Differential Scanning Calorimetry analysis (DSC)

DSC analysis was carried out using Shimadzu DSC-60 PLUS equipment (Santa Clara, CA, USA) in the temperature range from 25 to 300 °C, with a heating rate of 10 °C/min, nitrogen flow at 200 mL/min, and sealed aluminum crucibles.

Scanning Electron Microscopy (SEM)

The microstructural analysis of the films with increments of 2,000x and 3,000x was performed using a JSM-6610 scanning electron microscope (3 kV acceleration voltage; Jeol, Boston, Massachusetts) equipped with Energy dispersive X-ray (EDS) microscopy (Thermo Scientific, Waltham, MA, USA).

Biodegradability test

The biodegradability test was carried out according to the ASTM G160-12 (American Society for Testing and Materials, 2019), with modifications. The soil was prepared by mixing equal parts, bovine manure, fine sand, and fertile soil with low clay content. The soil was sieved and aged for three months and monitored regarding its pH (6.5 to 7.5) and humidity (20 to 30%). The samples were buried in beakers containing the prepared and stored in a BOD incubator (Tecnal, TE 371, Piracicaba-SP, Brazil) with 99% humidity and a temperature of 30 °C, protected from light. The samples were evaluated after 3 days and the soil was carefully removed.

Statistical analysis

The data of the obtained films were treated by analysis of variance (ANOVA), to obtain the means and standard deviation through the SISVAR program (version 5.6) and the means were compared by Tukey test, at the level of 5% significance.

3 Results and discussion

3.1 Yield and degree of esterification of pequi pectin

Table 1 shows the effect of extraction variables on the pequi-pectin yield and on its degree of esterification. The yields of pectin extraction varied between 10.3 and 26.6%, being the lower yield related to the lower citric acid content (1%). Siqueira et al. (2012) also found an increase in yield and a decrease in the degree of esterification with an increase in the temperature of the extraction process. These authors obtained pectin yields varying between 14.89 (1% citric acid) and 55.86% (8% citric acid), while the degree of esterification was 36.9 and 13.78%, respectively. In the present study, the highest pequi-pectin yield (26.6 ± 1.31%) was achieved using citric acid 4%, 80 °C and 160 min of extraction (Table 1). This yield was higher than that obtained by Leão et al. (2018) for pequi-pectin using microwave-assisted extraction (12.75 to 20.79%), as well as for pectin from other sources, such as black mulberry pomace (1.00 to 9.80%) (Khodaiyan & Parastouei, 2020) and apple pomace (commercial pectin main source) (~17%) (Picot-Allain et al., 2020).

Pectins are classified as high methoxyl pectin (HM) or low methoxyl pectin (LM) according to their esterification degree or the number of methoxy groups. The esterification degree has an important influence on the pectin properties, such as the gelation mechanism and processing conditions (Sriamornsak, 2011). HM pectin has an esterification degree >42.9% and can form gels at low pH values and high concentration of soluble solids; LM pectin, otherwise, shows less sensitivity to low pH values and requires the presence of Ca^{2+} ions to improve its gel form capacity (Noreen et al., 2017; Voragen et al., 2009). In the present study, the esterification degree of the pequi-pectin ranged from 29.08 to 62.02%, which characterizes pequi-pectin as LM pectin (Table 1). Our result corroborates with those observed by Siqueira et al. (2012), who also extracted pectin from pequi mesocarp with esterification degree ranging from 11.79 to 48.87%. The pectin with the highest yield of extraction presented a degree of esterification of 42.06%, and it was chosen to continue the study and to develop biodegradable films. Thus, it was possible to determine the best conditions of citric acid concentration, time, and temperature of extraction to extract pectin from pequi mesocarp.

3.2 Films characterization

Visual aspect and Scanning Electron Microscopy (SEM) of the pectin films

Figure 1 shows the visual aspect of pequi-pectin and commercial-pectin films (Figure 1A), as well as their surface microstructure and fracture (Figure 1B). The films of commercial-pectin and pequi-pectin were considered homogeneous, flexible, with no brittle areas and no presence of bubbles. The micrographs reveal that the air side surface of the commercial-pectin film was relatively smooth and homogeneous (Figure 1CD), while the pequi-pectin films presented a less regular air side surface. This probably occurred because the extraction process may have been

Table 1. Yield and degree of esterification of pequi-pectin under different extraction conditions.

Citric acid (%)	Temperature (°C)	Time (min)	Yield (%)	Esterification degree (%)
1	80	80	10.3 ± 0.91	62.02
1	80	160	15.2 ± 1.27	56.30
1	100	80	16.6 ± 0.43	53.80
1	100	160	17.1 ± 0.20	36.70
4	80	80	22.9 ± 2.74	51.60
4	80	160	26.6 ± 1.31	42.06
4	100	80	18.1 ± 1.09	38.16
4	100	160	19.9 ± 2.01	33.77
8	80	80	17.4 ± 0.89	35.01
8	80	160	16.2 ± 1.44	42.23
8	100	80	18.2 ± 1.93	33.12
8	100	160	16.5 ± 1.61	29.87

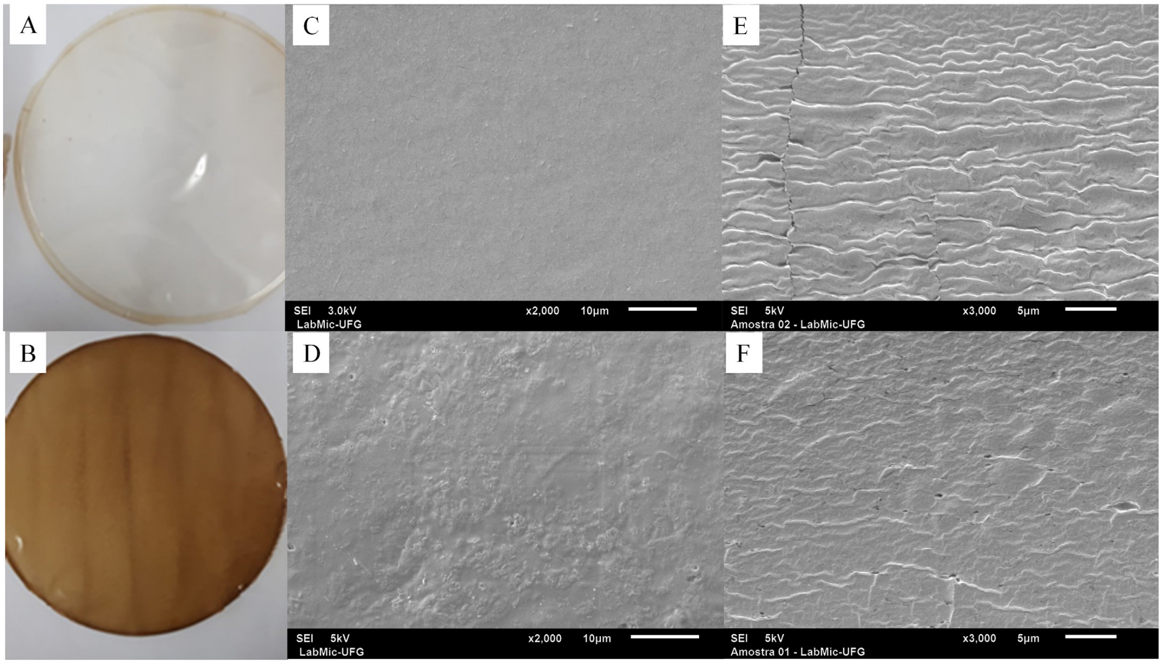

Figure 1. Visual aspect of the commercial-pectin (A) and of the pequi-pectin films (B). Scanning electron microscopy (SEM) micrographs of the surface 2000x (C and D) and of the fracture of the films 3000x (E and F).

responsible for dragging out other secondary organic compounds such as fibers, what will be elucidated in the subsequent FTIR analysis. In addition, the commercial-pectin also undergoes compound purification processes that were not carried out in the present study. Micropores and cracks were observed in the fracture micrographs of both films, however, they were present in greater amounts in the commercial-pectin film (Figure 1EF), suggesting that these fibers extracted with pectin could cause some disruption of the film structure, reflected by a less regular surface. Similar behavior has been reported for films of pectin with mango pulp (Oldoni et al., 2021).

FTIR spectra of the pectin films

The FTIR spectra of the pequi-pectin and commercial-pectin films are shown in Figure 2. The intensity correlation between the peaks at 1713 cm^{-1} for pequi-pectin and 1715 cm^{-1} for commercial-pectin, which is representative of the stretching of the C=O bond, stands out as a direct indication of the low degree of esterification of the pectin extracted from the pequi mesocarp.

Furthermore, between 1750-1350 cm^{-1} some bands of lower intensity were identified for the commercial-pectin film, among them one of the characteristic pectin peaks, at 1742 cm^{-1}, which represents the stretching of the C=O bond from non-ionized carboxylic groups (methylated or protonated). This band has already been demonstrated for commercial-pectin with a low degree of esterification (Ciriminna et al., 2017).

Another notable difference in the FTIR spectra of the films concerns the "fingerprint zone" between 1350 and 900 cm^{-1}. The pequi-pectin film showed a higher number of peaks in this region (1019, 1146, and 1345 cm^{-1}), is probably attributed to C–C and C–O bonds in secondary organic compounds (Akinalan Balik et al., 2019). This may be explained by the fact that the pectin produced from the pequi mesocarp has not undergone a purification process, therefore presenting a greater number of organic compounds than the commercial-pectin.

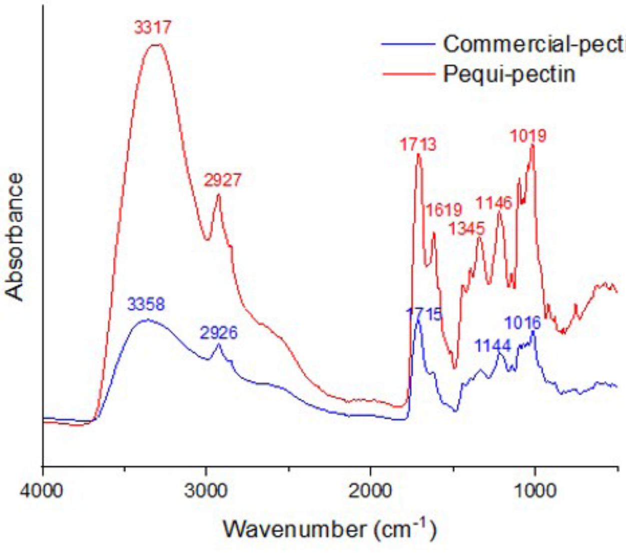

Figure 2. Infrared spectra of the pequi-pectin and commercial-pectin films.

Both films showed a small peak of similar intensity at 2927 cm^{-1} and 2933 cm^{-1} (pequi-pectin and commercial-pectin, respectively). This peak represents the O-H elongation in the carboxylic groups and indicates the typical behavior of glycerol (Cerqueira et al., 2012; Oliveira et al., 2021), which was used in the same amount in both film formulations. Finally, at 3317 cm^{-1} is located a broad band with a much higher intensity for the pequi-pectin film, related to the stretching of the O-H bond and the water content of the film (36.25% of moisture content compared with 19.97% for the commercial-pectin films).

Physical, optical, and water-related properties of the pectin films

The thicknesses, weight, moisture content, and water activity of pequi-pectin and commercial-pectin films are shown in Table 2. Both pequi- and commercial-pectin films showed similar thicknesses of 0.08 and 0.07 mm, respectively, with no significant difference ($p > 0.05$). The pequi-pectin film also presented higher moisture content (36.25%) and water solubility (76.99%), which may suggest that films from pequi-pectin have more carboxyl and hydroxyl groups available for hydrogen bonding to bond with water as previously discussed in the FTIR analysis (Figure 2).

Although pequi-pectin films had higher WVP due to their hydrophilic nature, this did not significantly influence WVP. The lack of significant variation in WVP may be due to a concomitant increase in water molecule diffusivity and solubility (Santos et al., 2014), resulting in discontinuities present in higher proportions in the commercial-pectin film matrix as shown in the fracture micrographs (Figure 1).

Due to the influence caused by the consumer acceptance and the commercial success of the final product, the polymer color used in the production of films plays an important role in the manufacturing and marketing of food packaging (Dash et al., 2019). In the present work, the pequi-pectin film showed a darker color with significantly lower L* values (55.67) than

Table 2. Physical, optical, and water-related properties of the pequi-pectin and commercial-pectin films.

Property	Commercial-pectin film	Pequi-pectin film
Thickness (mm)	0.07 ± 0.04^a	0.08 ± 0.02^a
Moisture content (%)	19.97 ± 1.04^b	36.25 ± 0.55^a
Water solubility (%)	45.53 ± 9.31^b	76.99 ± 4.27^a
WVP (g.mm)/(m^2.dia.kPa)	14.78 ± 0.05^a	15.07 ± 0.08^a
Opacity	0.92 ± 0.02^b	10.67 ± 0.01^a
L*	90.69 ± 0.78^a	55.67 ± 0.90^b
a*	-0.51 ± 0.04^b	11.56 ± 0.78^a
b*	8.96 ± 1.29^b	27.35 ± 0.94^a
Chroma	8.71 ± 1.269^b	29.71 ± 0.62^a
hue	93.44 ± 0.63^a	67.06 ± 1.97^b

WVP is Water Vapor Permeability. Different superscript letters on the same line represent significantly different samples in relation to that parameter at a level of 5% significance by Tukey's test.

the commercial-pectin film (Table 2). The pequi-pectin film also showed a more reddish and yellowish coloration based on the positive values of a* and b* (11.56 and 37.55, respectively), which were significantly higher than the commercial-pectin film. The yellow color is characteristic of pequi mesocarp and has already been demonstrated by Leão et al. (2017). The dark, reddish, and yellow colors can be the result of non-enzymatic browning reactions, such as Maillard reactions during drying of extracted pectin and filmogenic solution processing (Galvis-Sánchez et al., 2016; Gouveia et al., 2019).

The values found in the present study for commercial-pectin film correlate with results reported by Eça et al. (2015) for pectin based-films from different sources (90.6, 0.80, and 14.4 for L*, a*, b*, respectively). Despite a visual yellowish color, the film containing pequi-pectin showed a higher a* value (11.56), meaning a slightly red tendency similar to that obtained for strawberry pectin film (11.3) by Eça et al. (2015).

In terms of opacity, pequi-pectin film showed the highest opacity (10.67 ± 0.01 A_{600}/mm) in comparison with commercial-pectin film (0.92 ± 0.02 A_{600}/mm), which can be justified by the presence of insoluble fibers (cellulose and hemicellulose) from the pequi mesocarp that were not separated during the pectin extraction process. Similar behavior was reported by Oldoni et al. (2021) in pectin films and mango pulp with higher insoluble fiber contents.

Mechanical properties of the pectin films

Table 3 shows the mechanical properties of pectin-based films. The only significant parameter ($p < 0.05$) affected by pectin source was Young's modulus. This parameter was about three times higher for pequi-pectin than for commercial-pectin films. Thus, pequi-pectin films were more resistant to elastic deformation than commercial-pectin films, which reflects in their stiffness and strength (Jantrawut et al., 2017). One of the factors of influence for the Young's modulus of the pequi-pectin films being higher than that for the commercial-pectin film may have been the concentration of glycerol used (which acts together with the water to provide greater flexibility).

Another factor that may have affected the higher Young's modulus value for pequi-pectin film is the possible presence of secondary organic compounds, which were confirmed in FTIR and physicochemical tests; compounds such as starch may have come from the pectin extraction process, bonded with it in a compact polymeric network. When films are subjected to stress, the polymer chains formed absorb part of this energy before the breakage; thus, the polymeric network was more resistant to applied deformation (Lorevice et al., 2016). Another evidence of that is the presence of more polar groups (such as the OH, evidenced by the broad band at 3317 cm^{-1} in the FTIR spectra) in the pequi-pectin films, which allow a greater number of pectin hydrogen bonds with other components, leading to a more compact and resistant network (Lorevice et al., 2016; Rodsamran & Sothornvit (2019).

Table 3. Mechanical properties of pequi-pectin and commercial-pectin films.

Property	Commercial-pectin film	Pequi-pectin film
Max. Tension (MPa)	7.07 ± 3.21^{a}	6.12 ± 4.10^{a}
Tension at break (MPa)	2.48 ± 1.58^{a}	2.67 ± 2.58^{a}
Elongation at break (%)	18.20 ± 8.34^{a}	11.97 ± 5.95^{a}
Young modulus (MPa)	28.57 ± 8.25^{b}	82.16 ± 8.09^{a}

Different superscript letters on the same line represent significantly different samples in relation to that parameter at a level of 5% significance by Tukey's test.

The elongation at break values of the obtained films in our study (11.97 and 18.12% for pequi-pectin and commercial-pectin films, respectively) were higher than those obtained by Gouveia et al. (2019) (1.29%) and by Rodsamran & Sothornvit (2019) (~1.77%) for commercial HM pectin film and lime pectin-based film, respectively, both also plasticized with glycerol. The elongation at break values obtained were satisfactory since they reflect greater flexibility of the material in being deformed before the final breaking (Bharkatiya et al., 2010; Jantrawut et al., 2017).

The amount of plasticizer used may have been the main cause of the lower values of maximum tension reported for the pequi-pectin and commercial-pectin films (6.125 and 7.075 MPa, respectively) when compared to the values obtained Gouveia et al. (2019) (14.19 MPa) and by Rodsamran & Sothornvit (2019) (around 17 MPa). Several authors already reported the effects of decreasing the tensile strength of pectin-based films with increasing glycerol concentration (Hiorth et al., 2003; Hoagland & Parris, 1996; Jantrawut et al., 2017; Perez et al., 2009)

Differential Scanning Calorimetry (DSC) of the pectin films

DSC curves provide information on the thermal stability of biodegradable films produced from pequi-pectin and commercial-pectin (Figure 3). The films exhibited similar thermal behavior, highlighting the presence of exothermic and endothermic peaks for both samples.

The broad endothermic peaks observed at 132.36 and 114.85 °C for the pequi-pectin and commercial-pectin films, respectively,

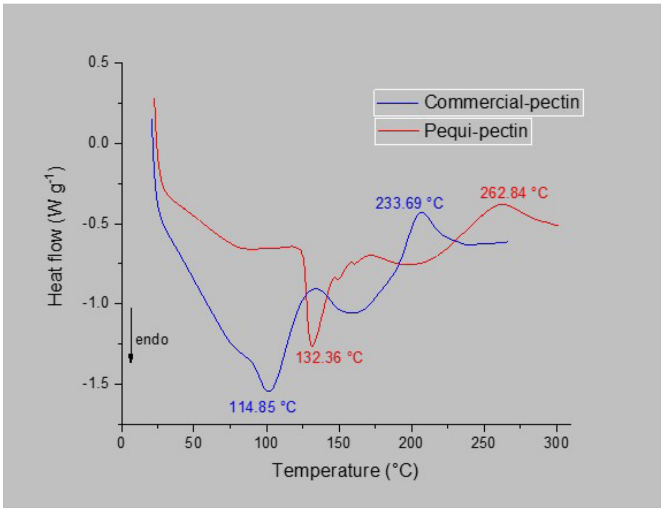

Figure 3. Differential Scanning Calorimetry thermograms of the pequi-pectin and commercial-pectin films.

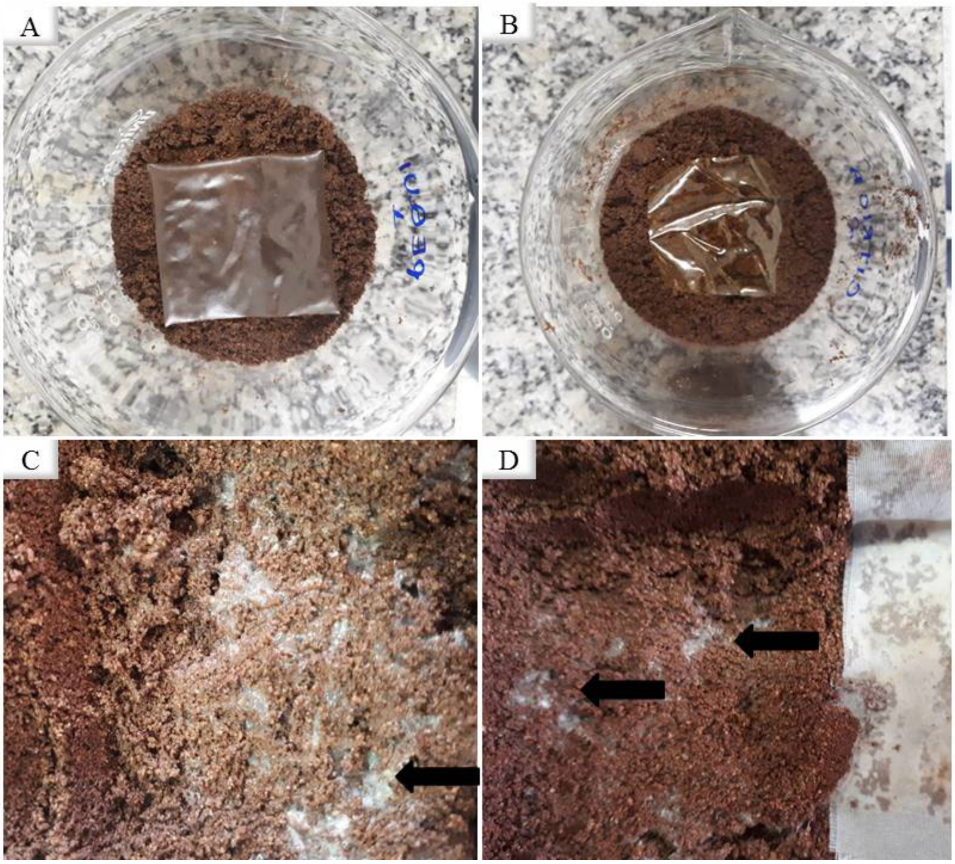

Figure 4. (A) and (B) Preparation of the pequi-pectin and commercial-pectin films. (C) and (D) Biodegradation process of the films over three days.

indicate weight loss for vaporization of the water and the glycerol. Jantrawut et al. (2017) observed an endothermic peak at 115 °C for low methoxyl pectin films. The methoxylation degree may also influence the appearance of the peak, being proportional to the temperature of pectin's degradation (Einhorn-Stoll & Kunzek, 2009).

The exothermic peaks of the films were observed at temperatures of 262.84 and 233.63 °C for the pequi-pectin and commercial-pectin films, respectively. These peaks indicate the degradation by decomposition, which may be related to the breakdown of pectin chains. The higher temperature of degradation of the pequi-pectin film may be associated with the cross-linking with calcium chloride, which promotes the strengthening of the three-dimensional network of pectin. Nisar et al. (2018) found values of exothermic decomposition between 231.53-234.88 °C for citrus pectin films incorporated with clove essential oil. Cervera et al. (2004) and Chaudhari & Singhal (2015) showed peaks at temperatures from 200 to 300 °C, which they also associated with the characteristic polymeric decomposition. Manrich et al. (2017), in turn, found temperature values higher (390-546 °C) for the maximum loss rates of cutin and tomato pectin films, which was attributed to the presence of a strongly reticulated three-dimensional network.

Biodegradability of the pectin films

Figure 4 shows the results of the biodegradability tests of pequi-pectin and commercial-pectin films. All films had biodegradation characteristics, where a small part of the films can be observed (Figure 4AB), with the remainder already biodegraded. After four days, it was not possible to separate the film from the soil to follow the weight loss. The high biodegradability of the films can be associated with their high-water solubility, since they disintegrate in the presence of moisture (Oliveira et al., 2019) (Table 2). Similar results were reported by other authors for films also based on polysaccharides such as cassava starch with clove essential oil (Sousa et al., 2019), alginate and hydrolyzed cotton proteins (Oliveira et al., 2019), and pectin with pulp mango (Oldoni et al., 2021).

4 Conclusion

The pequi mesocarp is an important source for pectin extraction with good characteristics for the production of biodegradable films. Pequi-pectin films had higher moisture content, solubility, values of a*, b*, opacity, and Young's modulus, and lower luminosity than commercial-pectin films. The films exhibited similar thermal behavior, highlighting the presence of exothermic and endothermic peaks for both samples and 100% biodegradability over four days. The pectin extracted from the pequi mesocarp showed potential for the production of biodegradable films, and this discovery opens up new possibilities for using this byproduct as a raw material for the production of sustainable food packaging.

Acknowledgements

The authors were supported by funding from Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES – Finance Code 001), Fundação de Amparo à Pesquisa do Estado de Goiás (FAPEG), IF Goiano, and Laboratório Multiusuário de Microscopia de Alta Resolução (LabMic/UFG).

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