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Edible films produced from agrifood by-products and wastes

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ABSTRACT

This study aims to develop edible films using agrifood by-products (pumpkin seeds, broken rice and orange pectin) and wastes (quince peel, potato peel, potato pulp, orange peel, pumpkin peel). The physicochemical characteristics of the films were investigated, including their mechanical and barrier properties. Higher amounts of plasticizer induced poorer mechanical and barrier properties in the films. The most promising ones were obtained with orange pectin, broken rice and pumpkin peel, with water contact angles (WCA) between 48° and 57°, maximum water vapor transmission rate and water vapor permeability of 575 $g.m^{-2}.d^{-1}$ and 108×10^{-12} $g.Pa^{-1}.s^{-1}.m^{-1}$, respectively, Young's modulus between 350 and 800 MPa, maximum tensile strength between 9.0 and 26.25 MPa, and elongation at break between 2.28 and 9.3%. Orange pectin and broken rice are promising raw materials since they led to higher WCA, better barrier and mechanical properties. Broken rice and quince peel can be good substitutes for commercial starch and glycerol, respectively. Agro-industrial by-products and wastes revealed potential for the production of sustainable edible films.

1. Introduction

Worldwide, one third of all food produced for human consumption is lost or wasted, equivalent to 1.3 billion tonnes per year. Annually, 0.50 billion tonnes are the losses of fruits and vegetables during the post-harvest and distribution chain (Andrade, Ferreira, & Gonçalves, 2016). During the processing of fruits and vegetables substantial amounts of pulp, stalks, peels or seeds are generated. These undervalued materials are rich sources of biopolymers such as polysaccharides, proteins, and dietary fibers, as well as other valuable functional molecules such as tannins, flavonoids, polyphenols, and fatty acids (Valdés et al., 2015). Furthermore, food by-products used separately or in combination for biodegradable packaging are mainly decomposed into carbon dioxide and water, being a more sustainable option for food preservation (Flôres et al., 2017; Vargas, Pastor, Chiralt, McClements, & González-Martínez, 2008).

Additionally, plastic pollution from the use of fossil plastics in food packaging that are not properly disposed after use is one of the major issues facing the environment on a global scale. Many efforts are being made to reduce these environmentally hazardous materials (Flôres et al., 2017; Kroll, Warchold, & Pradhan, 2019). Thus, the use of fruits, vegetable and cereals wastes is being investigated to provide more ecological and sustainable alternatives to traditional food packaging. These products can be employed as innovative raw materials to produce food packaging, acting as barrier against moisture and gas exchange between food products and the environment, or as antioxidants or antimicrobials to protect the goods contained therein (Flôres et al., 2017). Food by-products are usually composed of polysaccharides, proteins and lipids, which can produce biodegradable packaging used separately or in combination, and are mainly decomposed into carbon dioxide and water. Thus, their use in the production of biodegradable packaging is seen as a promising alternative, creating more sustainable options for food preservation (Flôres et al., 2017; Vargas et al., 2008).

Much attention has been given to the combination of different types of by-products and wastes from fruits, vegetables and cereals in the production of biodegradable films. As an example, Santos et al. (2016) used avocado pulp obtained from the extraction of avocado oil and produced films from this processing residue. Moreover, the obtained avocado pulp films incorporated with glycerol (as plasticizer) and cassava starch presented the best mechanical properties, exhibiting a tensile strength of 2.70 MPa and an elongation at break of 13.7% (Santos et al., 2016). In Ferreira et al. (2016), the shelf-life of acerolas was

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effectively extended in 50% with the application of biodegradable films made from flours/powders of fruits, vegetable and potato peel wastes. The resulting films proved to be very flexible without the addition of any synthetic plasticizer, showing promising characteristics such as high-water solubility, homogeneous appearance, and mechanical properties (tensile strength and elongation at break of 0.092 MPa and 36%, respectively) (Ferreira et al., 2016). Andrade et al. (2016) produced edible films using 8% and 10% (*w*/w) of a mixed flour obtained from orange, passion fruit, watermelon, lettuce, courgette, carrot, spinach, mint, taro, cucumber and rocket agrifood wastes. Potato peels were also incorporated at 2% and 4% (w/w) in films with 8% mixed flour. The results showed homogeneous and flexible films without the addition of synthetic plasticizers, presenting elongation at break between 31 and 34.5%, which was related to the sugars' content in fruits and vegetables, playing an important role in imparting flexibility to the films (Andrade et al., 2016). The incorporation of potato peel flour enhanced the films' mechanical resistance, resulting in an increase of the tension at break from 27 to 70 KPa, without significant change in the films elongation at break. The higher tension at break was associated with the formation of stronger and more numerous molecular bonds between the polymeric chains of the components used (Andrade et al., 2016). Arquelau, Silva, Garcia, De Araújo, and Fante (2019) developed and characterized films from ripe banana peel flour (4% (*w/v*)), corn starch (33.3–66.6 g of starch/ 100 g of flour) and glycerol (19 g of glycerol/100 g of flour). The increase in corn starch content resulted in greater mechanical resistance due to the ability of this polymer to increase the degree of interaction with the matrix, however, an unwanted increase of the water vapor permeability was also observed due of the intrinsic hydrophilic nature of the starch polymeric chains (Arquelau et al., 2019). Brito, Carrajola, Gonçalves, Martelli-Tosi, and Ferreira (2019) obtained edible films (8% (*w*/w)), based on fruits (sweet orange, passion fruit, watermelon) and vegetables (zucchini, lettuce, carrot, spinach, mint, yams, cucumber, and arugula) with high methoxylated pectin at: 0.25, 0.5 and 1% (w/w). The films were homogeneous, yellowish and malleable, with high solubility in water. Films with pectin showed a 50% decrease in solubility and elongation, as well as an increase in the tensile strength, since pectin can stabilize the polymeric network of the films by hydrophobic interactions between methyl esters or hydrogen bonds between carboxylic and alcohol groups (Brito et al., 2019).

The use of agrifood by-products and wastes in the production of edible films is a big challenge, since plant residues are usually complex materials and their proportion and combination in the formulation of films is crucial to improve the final films' properties (Galus, Arik Kibar, Gniewosz, & Kraśniewska, 2020). This work aims to study the suitability of different agrifood by-products and wastes (of complex composition) in the production of edible films and their combination with starch in order to obtain films with the best mechanical and barrier properties. The composition of the raw materials was evaluated, and the films obtained were physiochemically characterized according to their colour, thickness, water contact angle (WCA), water vapor transmission rate (WVTR) and water vapor permeability (WVP), thermal, mechanical and optical properties, and surface chemical composition (attenuated total reflection - Fourier-transform infrared spectroscopy (ATR-FTIR)). The influence of each type of raw material and its composition on the properties of the produced films was evaluated individually, and not as a mixed flour, as in previous works.

2. Materials and methods

2.1. Raw materials and chemicals

The majority of the raw materials used in this study (agrifood by-products and wastes) were obtained from local food producers (orange peel, pumpkin peel and pumpkin seeds), companies (broken rice and quince peel were provided by the "Agricultural Cooperative of the Municipality of Montemor-o-Velho" and "Casal da vinha" companies, respectively) and restaurants (potato peel was provided by the restaurant "O Convento") in the Centre region of Portugal. Potato pulp was obtained from unfitted potatoes for market.

The agrifood by-products and wastes were sanitized with a diluted sodium hypochlorite solution (1% (*v*/v)) and dried by lyophilization for 48 h, at −80 °C and 20 mbar to preserve the intrinsic properties and composition of the raw materials, and to facilitate their milling. Then, the materials were ground in a commercial blade mill (De'Longhi, Italy) and sieved to the smallest possible fraction. The particles' diameter for both potato peel and pulp were lower than 0.180 mm. Pumpkin peel, pumpkin seed, orange pectin, broken rice and quince peel had particles smaller than 0.250 mm in diameter. Commercial potato starch was obtained from Sigma-Aldrich (USA).

The raw materials were characterized in terms of gross chemical composition, crude fiber, protein, starch, lipids and ash using the AOAC procedures 930.10–997, 978.04–1997, 8.019–1980, 950.54 and 941.12–1975, respectively, with total and reducing sugars being obtained by High-Performance Liquid Chromatography – Refractive Index (HPLC-RI) (Pires et al., 2021). The obtained results are presented in Table 1. As the orange pectin was the same extracted and used in a previous work (Sebastião, Coimbra, Braga, & Gaspar, 2021), it was considered pure and did not follow the same characterization as the other raw materials. Glycerol was used as additive in all formulations.

The solvent used to prepare filmogenic solutions was autoclaved water, to reduce the microbial contamination of the produced films. The glycerol used as plasticizer in the film formulations was purchased from Sigma-Aldrich (USA). All materials were previously washed with water, cleaned with ethanol (70% (*v*/v)) and sterilized in an UV light chamber (Camag, Switzerland). Milli-Q water was used to measure the water contact angle of films.

2.2. Edible films formulation and production

A film formulation composed of potato peel, quince peel, glycerol and commercial potato starch (Sigma-Aldrich, USA) was considered from a previous work (Sebastião et al., 2021). In order to improve its properties, the agrifood by-products and wastes (broken rice, orange peel, orange pectin, potato pulp, pumpkin seeds, pumpkin peel and orange peel) were incorporated into the formulation, with the composition of the films shown in Table 2. The new film formulations were obtained by replacing commercial starch, potato peel and quince peel from the initial formulation by the tested raw materials, maintaining the same total mass per volume of water (i.e. the same amount of film-forming materials was added to the same volume for all formulations). The influence of the gross chemical composition of these ingredients on the properties of the final films was then analysed.

The film samples were coded based on the initial letters of the agrifood by-product or waste, as follows: P_PO_{PC} containing Potato peel (P_P) and Orange pectin (O_{PC}); $Q_PP_PB_R$ containing Quince peel (Q_P), Potato pulp (P_{PL}) and Broken Rice (B_R).

To prepare the film solution, the autoclaved water was preheated in a flask and, subsequently, the glycerol and the powders were mixed with an Ultra-turrax® (IKA, T18 basic, Germany). To promote gelatinization of the starchy materials and improve the homogeneity of the mixtures, continuous mechanical stirring was carried out using a rotary evaporator (Büchi, Switzerland) at 60 °C and 100 rpm for 20 min, followed by an increase in temperature to 95 °C at 150 rpm. After one hour at 95 °C, the mixture was filtered with a nylon filter (80 mesh) using a vacuum pump. The filmogenic mixture was filtered to remove any larger particle and possible agglomerates that would increase the roughness and opacity of the produced films, compromising their physicochemical properties. As the average loss of material in the filter was only 15.19 ± 4.69% (*w*/w), it can be assumed that the filtrate has a gross chemical composition and constituent groups similar to the raw materials used for the production of films. Then, 15 mL of the filtrate was added to Petri dishes with 90 mm of diameter and dried in a controlled atmosphere

Table 1
Composition of the raw materials (%, *w*/w in dry basis) used in the production of the films.

Raw materials	Crude fibers (%)	Total Protein (%)	Starch (%)	Total sugars (%)	Reducing sugars (%)	Lipids (%)	Ash (%)
Potato peel (P_P)	3.89 ± 0.02	9.49 ± 0.24	46.30 ± 0.21	11.16 ± 0.18	9.23 ± 0.05	0.56 ± 0.08	11.28 ± 0.25
Potato pulp (P_{PL})	2.31 ± 0.02	11.12 ± 0.32	65.50 ± 0.28	13.99 ± 0.31	12.17 ± 0.24	0.70 ± 0.05	7.03 ± 0.03
Broken rice (B_R)	0.37 ± 0.08	10.90 ± 0.35	60.50 ± 2.76	87.63 ± 0.35	27.13 ± 1.97	0.50 ± 0.11	0.70 ± 0.02
Quince peel (Q_P)	5.79 ± 0.16	1.71 ± 0.09	12.35 ± 0.04	70.93 ± 0.53	67.30 ± 0.5	1.31 ± 0.04	2.66 ± 0.06
Pumpkin peel (PK_P)	32.03 ± 0.30	16.37 ± 0.13	15.75 ± 0.08	38.83 ± 0.41	31.99 ± 0.38	3.09 ± 0.20	10.15 ± 0.17
Orange peel (O_P)	7.80 ± 0.40	4.75 ± 0.04	0.37 ± 0.03	47.09 ± 0.29	39.76 ± 0.16	2.09 ± 0.09	2.41 ± 0.04
Pumpkin seed (PK_S)	25.02 ± 0.25	30.48 ± 0.18	29.20 ± 0.28	7.67 ± 0.16	5.76 ± 0.16	35.17 ± 0.09	3.55 ± 0.06

Table 2
Composition of the film formulations (g/100 mL) according to the amount of each raw material: Quince peel (Q_P), Potato peel (P_P), Pumpkin peel (PK_P), Orange peel (O_P), Broken Rice (B_R), Potato pulp (P_{PL}), Orange pectin (O_{PC}) and Pumpkin seed (PK_S).

Film code	Glycerol	Starch	Peel ($_P$)				Broken rice (B_R)	Pulp ($_{PL}$)	Pectin ($_{PC}$)	Seed ($_S$)
			Quince (Q)	Potato (P)	Pumpkin (PK)	Orange (O)		Potato (P)	Orange (O)	Pumpkin (PK)
P_PO_{PC}	0.4	1.0	–	1.25	–	–	–	–	0.4	–
P_PB_R	0.4	1.0	–	1.25	–	–	0.4	–	–	–
Q_PPK_S	0.4	1.0	0.4	–	–	–	–	–	–	1.25
P_PPK_P	0.4	1.0	–	1.25	0.4	–	–	–	–	–
$Q_PP_PP_{PL}$	0.4	–	0.4	1.25	–	–	–	1.0	–	–
$Q_PP_PB_R$	0.4	–	0.4	1.25	–	–	1.0	–	–	–
Q_PB_R	0.4	1.0	0.4	–	–	–	1.25	–	–	–
P_PO_P	0.4	1.0	–	1.25	–	0.4	–	–	–	–

chamber (Binder, Germany) at 35 °C and 50% RH (Tapia-Blácido, Sobral, & Menegalli, 2005) for 15 to 24 h (depending on the properties/composition of the films).

3. Physicochemical characterization of the films

The films were characterized in terms of thickness, colour, water contact angle (WCA), Young's modulus (E'), maximum tensile strength (Max σ), elongation at break (ETB), water vapor transmission rate (WVTR) and water vapor permeability (WVP). All results are expressed as mean value ± standard deviation.

To measure the films' thickness, a digital micrometer (Tesa Micromaster Electronic Micrometers IP54) with a precision of 0.001 mm was used. Six measurements at random locations were performed for each film. The thickness of the films was used to calculate the respective mechanical properties.

For water contact angle (WCA) measurements, the sessile drop method (Pires et al., 2018) was applied using Dataphysics Instruments GmbH (model OCA20, Germany). Drops of 10 μL of bi-distilled water were placed on the films. At least five measurements were taken for each sample.

The colour of the films was evaluated using a colorimeter (Minolta CR-200b, Japan), employing the CIEL*a*b* colour system and taking at least five random measurements for each film. The films were evaluated for lightness L* (where 0 = black to 100 = white), and the parameters a* (where −60 = green to +60 = red) and b* (where −60 = blue to +60 = yellow). The chroma (C*) and hue angle (h*) of the films were also evaluated.

Each film was also evaluated according to its WVTR and WVP, at least in triplicate, according to the procedure described in ASTM E 95–96 (ASTM E 95-96, 1995). The systems were maintained at a relative humidity (RH) of 98% at 25 °C and weighed periodically for 7 days. Following the standard test procedure and its equations, the WVTR was calculated, being normalized to the test area (A), considering the slope of the water loss vs. time, and calculated according to eq. 1.

$$\mathrm{WVTR}\left(g.m^{-2}.day^{-1}\right) = \frac{\Delta w}{\Delta t \times A} \quad (1)$$

where Δw (g) is the weight difference of the cells; A (m^2) is the area of the film in contact with water vapor; and Δt (day) is the time between measurements.

Since the thickness of the films was previously recorded, the WVP could be also assessed using eq. 2 (ASTM E 95-96, 1995).

$$\mathrm{WVP}\left(g.s^{-1}.m^{-1}.Pa^{-1}\right) = \mathrm{WVTR} \times \frac{l}{P_0(RH_{out} - RH_{in})} \quad (2)$$

where l (mm) is the film thickness; P_0 is the water vapor pressure at 25 °C, RH_{in} and RH_{out} are the relative humidity of the air inside the permeability cell (assumed to be equal to 0%) and in the desiccator outside the permeability cell (98%), respectively and WVTR (g. m^{-2}. day^{-1}) the values of WVTR previously determined for the studied film.

The appearance and morphology of the produced films were evaluated using a stereomicroscope (M80, Leica Microsystems, Germany), and by scanning electron microscopy (SEM) (TESCAN Vega 3 SBH, Czech Republic) at HV 5.0 kV. For SEM analysis, the samples were fixed in stubs with the aid of a double-sided adhesive tape and covered with a mixture of gold and palladium for 30 s in an argon atmosphere, forming a 10 nm layer on the films. The magnification used was 1000× and 5000 × .

The mechanical properties of the films were evaluated using a texturometer (Stable microsystems TA XT Express, UK), at least in triplicate. The films were cut in bone-shape with 60 mm in length, 10 mm in width at the ends, and 5 mm width of narrow portion, according to ISO 527-2 (ISO (1996)., n.d.), and analysed at a tension speed of 1 mm/min. From these tests, it was possible to obtain the values for the maximum tensile strength (Max σ, MPa) and elongation at break (ETB, %) of the produced films, using eqs. 3 and 4, respectively (Hassanzadeh et al., 2017).

$$Max\ \sigma\ (\mathrm{MPa}) = \frac{F}{A} \quad (3)$$

where Max σ (MPa) is the maximum tensile strength the film's sample can endure; F (N) is the measured force applied to the sample; and A (mm^2) is the cross-sectional area of the sample before the test.

$$\text{ETB}\ (\%) = \frac{\Delta L}{L_0} \times 100 \quad (4)$$

where ETB (%) is the elongation at break; ΔL (mm) is the increasing in the sample length between the tensile cell grips when the tensile test is performed; and L_0 (mm) is the initial length of the sample.

In addition, the modulus of elasticity (Young's Modulus, E'), expressed in MPa, was also acquired from the previous results, considering the slope between the linear section of the Max σ and the ETB curve.

To investigate the main chemical groups and interactions on the surface of the films and used raw materials, attenuated total reflection - Fourier-transform infrared spectroscopy (ATR-FTIR) was carried out using a Perkin Elmer (FTIR/NIR spectrophotometer, Universal ATR sampling accessory, UK). The experiments were performed at 64 scans with a 4 cm^{-1} resolution, between 550 and 4000 cm^{-1}, with the PerkinElmer spectrum software being used.

The films' chemical components, along with their water content, were analysed using a simultaneous thermal analyser (differential scanning calorimetry/thermogravimetric analysis, DSC/TGA, TA Instruments, model Q600, USA), in duplicate. Small portions of the films (10–15 mg) were heated at 10 °C/min, from 25 °C to 600 °C, under a nitrogen atmosphere (100 mL/min). The presence of the films' components was determined according to their respective melting/boiling points. The water content was obtained based on mass loss up to 100 °C.

The films were stored in controlled atmosphere desiccators with magnesium nitrate ($Mg(NO_3)_2$) (≈ 55% RH at 25 °C) and the raw materials were kept in closed vials after lyophilization, in order to reduce water absorption from the environment.

All results were subjected to analysis of variance (one-way ANOVA) and the mean values compared by Tukey's test (95% confidence) in the statistical software JMP Pro 16 (USA).

4. Results and discussion

Raw materials' composition is detailed in Table 1. Commercial starch was replaced by broken rice and potato pulp, as both raw materials possess >60% of starch in their composition and other compounds that can influence the film properties, such as sugars and proteins. Potato peel was replaced by pumpkin seeds and broken rice, making possible to identify the effect of replacing potato starch with lipids, proteins and fibers (present on pumpkin seeds), and sugars (broken rice). Quince peel was replaced by orange pectin, orange peel, broken rice and pumpkin peel, allowing to identify the impact of decreasing the total amount of sugars on the properties of the films, since all the raw materials used to substitute quince peel have lower sugar's content and higher amounts of other constituents, such as fiber and protein (pumpkin peel and orange peel), and starch and protein (broken rice).

Considering the films' characterization techniques previously detailed, the results for the films, whose film formulation is presented in Table 2, were discussed to evaluate the effect of their composition on the physicochemical properties.

4.1. Colour and thickness

In food packaging the colour of the film can also have a preservative function, reducing photo-oxidation of food. However, the visual appearance of the food packaging can impact consumer's choice (Gaspar et al., 2021; Ren, Yan, Zhou, Tong, & Su, 2017). The colorimetric results obtained for all films are shown in Table 3.

The lightness (L*) of the film's ranged from 83.72 ± 0.24 for the $Q_PP_PP_{PL}$ films to 93.48 ± 0.07 for the Q_PB_R films, confirming the films' good optical properties regarding this parameter (Xu et al., 2019). Films with both quince and potato peel had some of the lowest L* values, with 83.72 ± 0.24 for $Q_PP_PP_{PL}$ and 88.04 ± 0.19 for $Q_PP_PB_R$. Comparing the films with these two raw materials, it is also perceptible that the potato peel is responsible for darker films, so those without this raw material are the lighter ones (Q_PB_R and Q_PPK_S). Furthermore, broken rice (Q_PB_R) produced films with higher L* comparing to pumpkin seeds (Q_PPK_S). According to the film's colour coordinates (a* and b*), those with potato peel tend to have higher a* values, except for P_PO_{PC} which has a* (0.88) lower than Q_PPK_S film (0.93), which indicate that the potato peel also makes the films more reddish. Since both chroma (C*) and hue angle (h*) are calculated using the equations $\sqrt{(a^*)^2 + (b^*)^2}$ and $tan^{-1}\left(\frac{b^*}{a^*}\right)$, respectively, the results show that films with higher and disparate values of the a* and b* coordinates are the ones with higher colour saturation.

Table 3
Colour parameters of the produced films from agrifood by-products and wastes.

Film code	L*	a*	b*	C*	h*
P_PO_{PC}	90.51± 0.31^{b,c}	0.88± 0.08^{c}	9.57± 0.07^{e}	9.61± 0.08^{d}	84.78± 0.50^{b}
P_PB_R	89.81± 0.16^{d}	1.13± 0.05^{c,d}	7.82± 0.13^{f}	7.90± 0.14^{e}	81.77± 0.22^{c}
Q_PPK_S	90.63± 0.22^{b}	0.93± 0.09^{d,e}	11.78± 0.41^{c}	11.82± 0.41^{c}	85.52± 0.25^{a}
P_PPK_P	84.44± 0.48^{f}	4.02± 0.17^{a}	19.40± 0.46^{a}	19.81± 0.49^{a}	78.31± 0.28^{d}
$Q_PP_PP_{PL}$	83.72± 0.24^{f}	3.80± 0.08^{a}	13.32± 0.18^{b}	13.86± 0.20^{b}	74.09± 0.12^{e}
$Q_PP_PB_R$	88.04± 0.19^{e}	2.66± 0.09^{b}	10.71± 0.20^{d}	11.04± 0.22^{c}	76.08± 0.23^{f}
Q_PB_R	93.48± 0.07^{a}	0.83± 0.01^{d,e}	5.84± 0.03^{g}	5.90± 0.03^{f}	81.96± 0.09^{c}
P_PO_P	89.80± 0.14^{c,d}	1.29± 0.07^{c}	13.07± 0.39^{b}	13.13± 0.40^{b}	84.45± 0.16^{b}

* Different letters in the same columns differ significantly (P < 0.05) by Tukey test.

Overall, it can be concluded that potato peel is the raw material with the greatest influence on the colorimetric properties of the films, which is in line with the literature, since the increase in potato peel in film formulations tends to decrease the lightness of the films and increase its chromaticity (Borah, Das, & Badwaik, 2017). It was also observed that broken rice, pumpkin seeds and orange pectin do not seem to considerably reduce the lightness of the films, namely those made of orange pectin, which have the second highest L* value and also have potato peel in their composition. The same trend was previously reported for the use of commercial pectin, not significantly affecting the films' luminosity and the appearance of packaged food products (Brito et al., 2019).

The compared ability of the raw materials to increase the lightness of the films is: orange pectin > broken rice > orange peel > pumpkin peel, for films without quince peel; broken rice > pumpkin seeds, for films without potato peel; broken rice > potato pulp, for commercial starch free films.

The thickness of edible films depends on the type of film casting technique, film solution's physical properties (density, viscosity, surface tension, drying time), and the amount of the constituent polymers used in the casting site (Hatmi, Apriyati, & Cahyaningrum, 2020). It can be observed in Fig. 1.A that the film thickness values varied between 49.95 ± 2.06 and 53.87 ± 1.81 μm. These values are in agreement with several works where similar casting method and concentration of total solids in the solution were used, presenting thickness values from 40 to 65 μm (Chakravartula et al., 2019; Zuo, Song, Chen, & Shen, 2019).

The higher values observed for the $Q_PP_PB_R$, P_PPK_P, $Q_PP_PP_{PL}$ and P_PO_P can be explained considering the total sugars' content of some of the raw materials used in these formulations (Table 1). Indeed, quince peel, orange peel and broken rice, have been previously reported as rich sources of sugars that tend to increase film thickness, acting as plasticizers (Ploypetchara & Gohtani, 2018). In addition, all these formulations have potato peel, concluding that the presence of this raw material improves the thickness films, which may be related to the high starch content in its composition (Fakhouri et al., 2012).

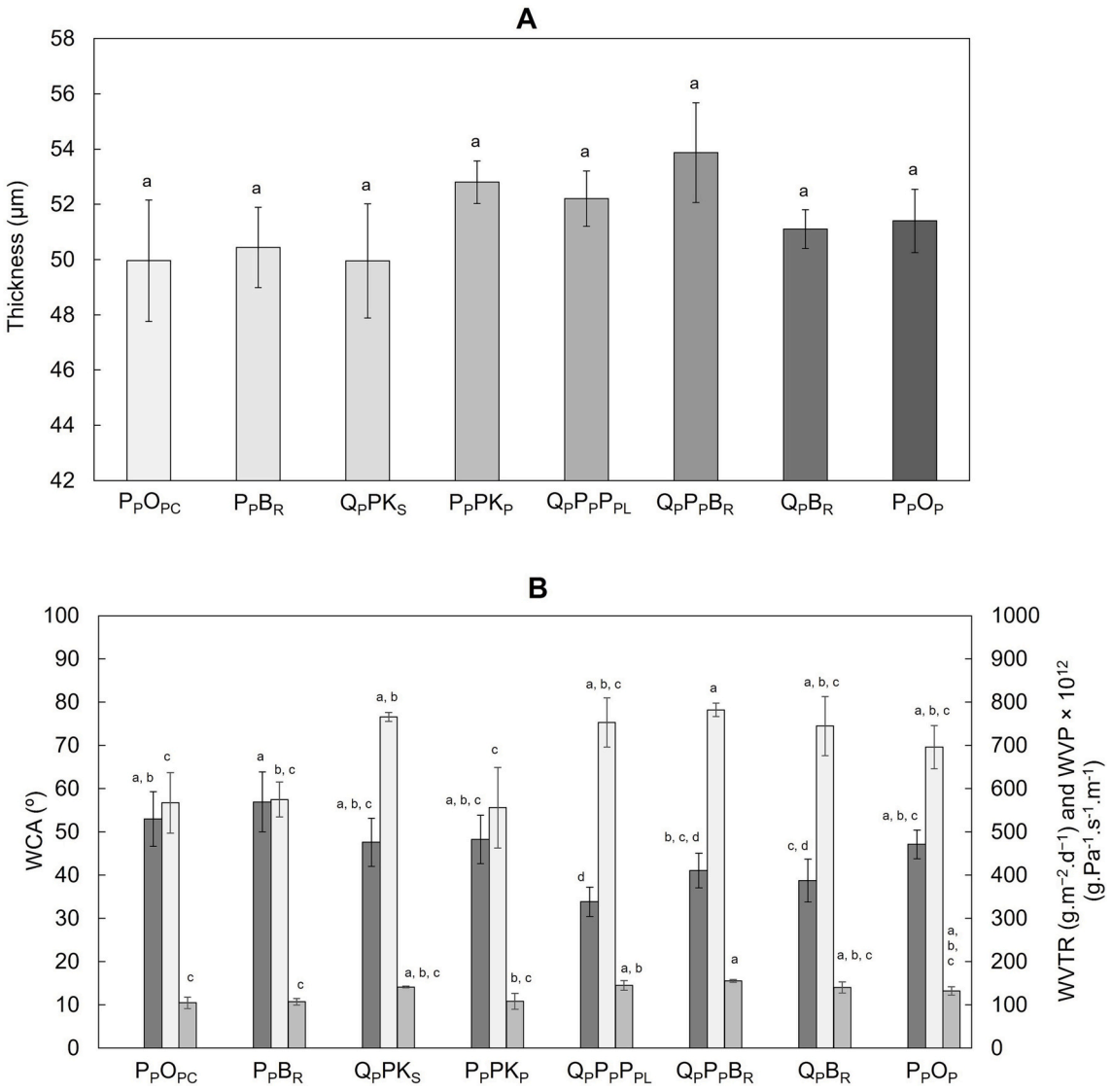

Fig. 1. Thickness (A) and WCA (B, ■), WVTR (B, □) and WVP (B, ■) of the films from agrifood by-products and wastes (mean ± SD). Columns with different letters differ significantly ($P < 0.05$) by Tukey test.

4.2. Water contact angle (WCA), water vapor transmission rate (WVTR) and water vapor permeability (WVP)

The wettability of the films is defined by the contact angle formed between the test liquid and the film itself. As the contact angle increases, the potential interaction between the liquid and the film decreases (Meiron & Saguy, 2007). Fig. 1.B exhibits the results of the water contact angles (WCA) for each film. Values vary between 33.84 ± 3.42° and 56.93 ± 6.92° for $Q_PP_PP_{PL}$ and P_PB_R, respectively, showing that all films produced tend to be hydrophilic as long as their WCA are lower than 90° (Law, 2014). These results are in accordance with the literature, with other authors reporting WCA's for edible films varying between 25° and 100° (Chakravartula et al., 2019; Xu et al., 2019).

The low WCA recorded can be explained by the addition of glycerol and high sugar content in some of the raw materials used, such as quince peel and broken rice, which can increase the hydrophilicity of the films produced (Ghanbarzadeh et al., 2007; Ploypetchara & Gohtani, 2018). Although the addition of glycerol can improve the films' flexibility, it decreases WCA due to its hygroscopic nature and the formation of hydrogen bonds in the film's matrix (Chakravartula et al., 2019; Gaspar et al., 2021). The same argument is applied to sugars, since they have a similar plasticizing effect on films as glycerol and are well known hygroscopic components (Ghanbarzadeh et al., 2007; Ploypetchara & Gohtani, 2018). Plasticizers promote a greater affinity of films with water, as they reduce interactions between polymer molecules and make films more soluble due to their hydrophilic character. Generally, the water affinity of films increases as the number of hydroxyl groups in plasticizers increases (de Freitas, Garcia, Filgueiras, Velasco, & Fakhouri, 2021), with the same trend being observed for the number of hydroxyl, carbonyl and amine groups in proteins (Durell & Ben-Naim, 2017) and aldehyde and ketone groups in sugars (Alén, 2018).

Films containing quince peel have four out of the five lowest WCA, confirming the influence of quince peel and its sugar content on the hydrophilicity of the films (Table 1). When quince peel is replaced by materials with low sugar content (potato peel, orange pectin, broken rice, pumpkin peel or orange peel), the number of water binding sites present in the polymeric matrix, such as hydroxyl, ketone and aldehyde groups, is reduced, which results in films with higher WCA (de Freitas et al., 2021; Ploypetchara & Gohtani, 2018). Quince peel was the raw material that most reduced WCA, along with broken rice, highlighting the importance of the sugars content (Table 1) and its plasticizing effect on the obtained films.

With the obtained data, it is possible to compare the abilities of some raw materials to increase the WCA of the films, where they were

incorporated as a substitute for one of base formulation ingredients. The obtained ranking for the films without quince peel was: orange peel < pumpkin peel < orange pectin < broken rice. For films without potato peel, the use of pumpkin seeds led to WCA values higher than those of broken rice in the respective films. Finally, films without commercial starch and with potato pulp showed lower WCA values than films with broken rice.

As films must act as barriers, reducing moisture variations between the packaged food and the surrounding environment, it is important to evaluate the WVTR and the WVP of the films produced in this study [24]. The mean values of these properties for the films are presented in Fig. 1.B. Values for WVTR ranged from approximately 556 to 782 $g.m^{-2}.d^{-1}$, being significantly lower than those of other biodegradable films produced in previous works (Gaspar et al., 2021; Hatmi et al., 2020; Pires et al., 2018).

Usually, a higher WVTR is related to a lower WCA, due to less favourable surface interactions between water molecules and the polymeric chains of the films [24]. This trend was observed in our results, with, for example, $Q_PP_PB_R$ having the highest WVTR and the lowest WCA. Quince peel seems to be the raw material that most increase WVTR values, as it is present in all four film formulation with the highest values of this property ($Q_PP_PB_R$, followed by Q_PPK_S, $Q_PP_PP_{PL}$ and Q_PB_R) and, when it is replaced by other raw materials, the WVTR of these films decreases. These results can also be explained by the sugar content of this raw material (Table 1), creating a more hydrophilic polymeric matrix, increasing the water absorption rate and producing films with lower barrier properties for food packaging (Fakhouri et al., 2012).

Considering the WVP of the films, the values obtained ranged from 1.04×10^{-10} to 1.55×10^{-10} $g.m^{-1}.s^{-1}.Pa^{-1}$. Similar results were observed for edible films and coatings used as food packaging for fruits and other types of goods, with values of the order of 0.017×10^{-11} and 4.17×10^{-9} $g.m^{-1}.s^{-1}.Pa^{-1}$ (de Freitas et al., 2021; Vargas et al., 2008; Zuo et al., 2019).

Analysing the influence of raw materials on WVP, the main differences are imposed by the presence of quince peel in the formulations. Quince peel films have higher levels of sugar in the polymeric matrix since it is a raw material with a high total sugar content (Table 1), increasing the plasticizing effect, reducing the barrier properties of the films and increasing the WVP (Ploypetchara & Gohtani, 2018). It is also reported that pectin improves the barrier properties of the films when incorporated (Chakravartula et al., 2019), which corroborates the results obtained in this study, since the edible films using orange pectin had lower WVP. WVP mainly depends on the solubility and diffusivity of water vapor through the films' polymeric matrix, with more tortuous paths within the structure of the films leading to more difficult the diffusion of water vapor across the film and lower values of WVP (and vice-versa) (Chakravartula et al., 2019; Dash, Ali, Das, & Mohanta, 2019). Thus, the incorporation of raw materials with high sugar content, such quince peel, can induce an increase in the plasticizing effect in the films, reducing the intermolecular interactions between the film-forming compounds, increasing the mobility of the polymeric chains, reducing the films' tortuosity and increasing their WVP (Rawdkuen, 2019). The opposite can be concluded for pectin, as the presence of this compound has been reported to improve the homogeneity, rigidity and uniform structure of the films, resulting in more tortuous paths for water vapor and reducing WVP (Chakravartula et al., 2019).

For the Q_PPK_S film, as its WCA was higher than for other quince peel films, a relatively lower WVTR and WVP was expected. However, this film presented highest values of WVTR and WVP like those observed for the other films with quince peel. Furthermore, the P_PPK_P film, when compared to the Q_PPK_S film, showed a similar WCA but significant differences in WVTR and WVP. These differences may be associated with the considerable amount of protein, lipids and carbohydrates (Table 1) of the pumpkin seeds. Therefore, anomalous results can be obtained by the presence of proteins in pumpkin seeds, since these molecules are known to increase the hydrophilicity of the films (Xu et al., 2019). Lai and Padua (1998), in protein-based films, attributed this increase to the plasticizing effect of water, since water molecules plasticize or swell the polymers, resulting in increased gas permeability due to the reduced tortuosity and diffusion pathways for water vapor from the weaker intermolecular forces within the polymer's structure that are obtained in this scenario (Rawdkuen, 2019). In conclusion, the use of raw materials that contain proteins, sugars and other compounds (glycerol, for instance) in the films formulations, needs to be carefully evaluated, as the excessive amount of these components leads to a decrease in the film's barrier properties (Ghanbarzadeh et al., 2007).

4.3. Films' surface morphology and chemical composition

The surface morphology of the films was inspected using an electronic magnifying stereomicroscope and by SEM. The obtained amplified images and micrographs are presented in Fig. 2. From Fig. 2.A, at a 35× magnification, it is possible to observe that the films presented some material agglomeration on the surface, which was associated with polymer accumulation during drying. In Fig. 2.B the films surfaces micrographs were compared at a resolution of 5000×. In Fig. 2.C, the surfaces and the cross-sections micrographs of the P_PO_{PC} and $Q_PP_PP_{PL}$ films are shown at 1000× and 5000× resolution, respectively. Although, all films surfaces have irregularities, the roughness in some cases is more pronounced than in others, especially in the case of P_PO_P and P_PPK_P films, which present a more prominent lumps on their surfaces at 5000× magnification.

The use of broken rice in the formulation of the film seems to smooth the surface of the films, as is the case of the $Q_PP_PB_R$, Q_PB_R and P_PB_R samples that present more regular surfaces. The replacement of commercial starch by broken rice improves the surface smoothness of the films. The same rougher surfaces were found in the films with higher starch content and lower sugar content in their composition (Table 1), such as those with potato peel and without quince peel or broken rice (Fig. 2). In fact, as already reported in the literature, both the decrease in the total amount of starch and the increase in plasticizer compounds in the films decreased the surface roughness of the films (Abdel-Haleem, 2016; Caicedo, Díaz-Cruz, Jiménez-Regalado, & Aguirre-Loredo, 2022; Ploypetchara & Gohtani, 2018; Xu et al., 2019). This can also be related to the aforementioned WVP values, since the increase in plasticizer compounds reduces molecular interaction, not only increases the smoothness of the films by providing increased mobility of the polymeric chains, but also induces the formation of easier diffusive paths for water vapor to move across the film. This conclusion is confirmed in this work with the films with smoother surfaces and higher WVP, such as $Q_PP_PB_R$, $Q_PP_PP_{PL}$ (as observed in Fig. 2.C) or Q_PB_R, which have higher amounts of plasticizing compounds than film-forming compounds in their composition (Ploypetchara & Gohtani, 2018; Xu et al., 2019).

In the case of $Q_PP_PP_{PL}$, Fig. 2.C presents a smooth structure in the microscopic cross-section. The opposite is observed in the films P_PPK_P or P_PO_P, as they present high roughness (Fig. 2) in relation to the other films, and have some of the lowest WVP values recorded due to the more tortuous and difficult diffusion of water vapor through their structures.

For a better understanding of the structure of the films and some of their intrinsic properties, a FTIR analysis was performed to identify the interactions of the chemical groups as shown in Fig. 3. Although the complex composition of the used wastes and by-products do not allow to identify all the interactions between the phase-forming compounds, the more common peaks of all films and some characteristic bands of the obtained spectra were identified in this section of the work. Table 4 summarizes relevant information about the analysis of characteristic vibrations in FTIR spectra and their correlation with functional groups and interactions between film components, helping to understand the structure of films.

Some films have a peak around 3750 cm^{-1}, which is attributed to hydrogen bonding originated from the moisture in the films and possible protein chains present in some formulations (Ren et al., 2017). The

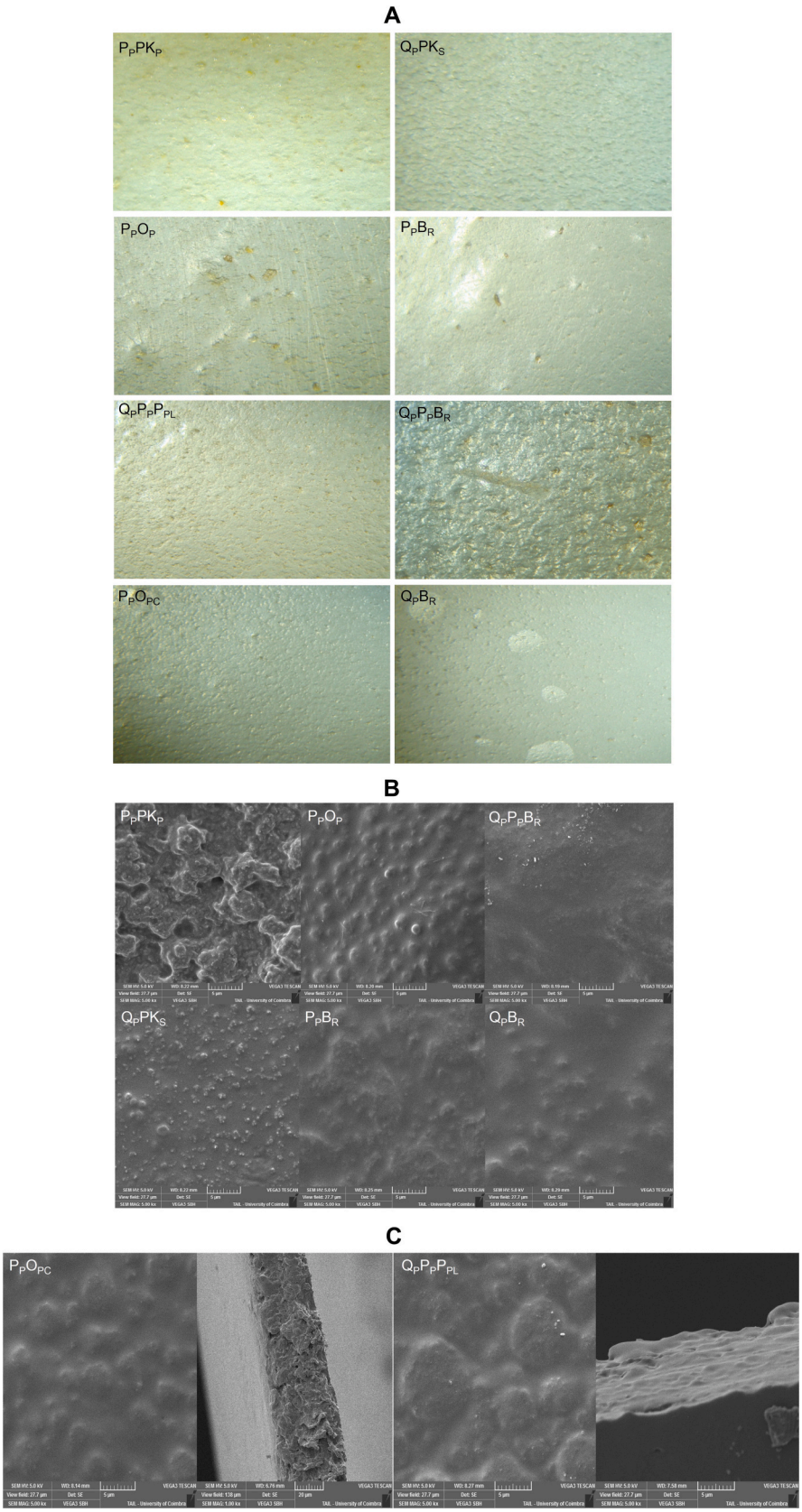

Fig. 2. Stereomicroscope images of the films at 35× magnification (A); SEM micrographs of the films surface at 5000× magnification (B); SEM micrographs of the films surface and cross section (C) at 1000× and 5000× magnification.

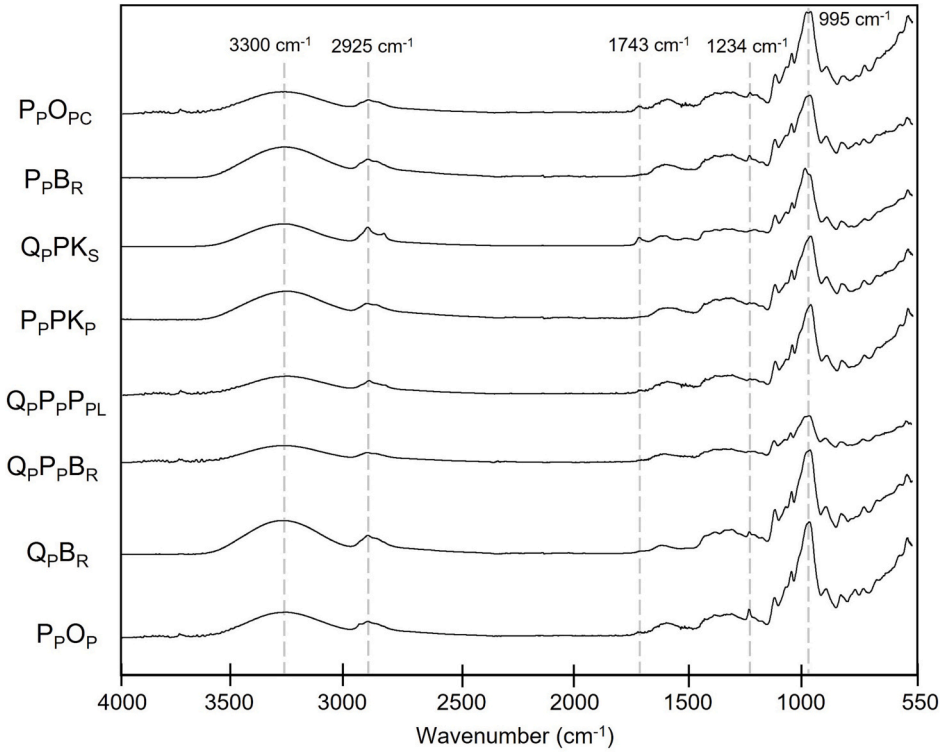

Fig. 3. FTIR spectra of the films.

spectra of all formulations have a peak between 3307 and 3273 cm^{-1}, being related to the free O—H stretching vibrations from glycerol and water, as well as to the -NH stretching vibrations that occur in hydrogen bonds of amides A. The peaks at 2925 cm^{-1} can be seen in all spectra, highlighting some peaks close to 2858 cm^{-1} in some films (Q_PPK_S and Q_PB_R), which show -CH stretching vibrations in the CH_2 and CH_3 groups and stretching of $-NH_3$ (amides B). These peaks are very common in many organic substances (Gaspar et al., 2021) and are seen quite distinctly in Q_PPK_S films. This may be related to the presence of hydrophobic methylene groups in the proteins and the sugars of the raw materials used to produce the film (Ritzoulis et al., 2014).

To better understand the differences between the spectra presented in Fig. 3, the spectrum of each film was compared with the spectrum of its raw material (Supplementary material, Fig. S.1 to Fig. S.8). The peak around 995 cm^{-1} appears in the spectrum of commercial starch, as well as in the case of broken rice and potato pulp (Abdel-Haleem, 2016; Kot et al., 2020) which have starch in their composition. With the except of Q_PPK_S (where this peak is present at 1019.28 cm^{-1}), all films show a peak corresponding to starch, which means that it had a significant influence on the polymeric matrix of the films. According to Table 4, this peak is associated with the stretching of the C-OH and C-O-C bonds, and C—C skeleton stretching vibrations typical of starch functional groups. Some authors observed an increase in the intensity of this peak when the starch content of the films increased (Xu et al., 2019).

As previously indicated, the peak is present at 1019.28 cm^{-1} for the Q_PPK_S film and can be attributed to the influence of pumpkin seeds in the films, being characteristic of the -CH stretching of sugars (Singh et al., 2019). This peak has been previously assigned to a newly formed C-O-C glycosidic bonds in different sugar-protein mixtures, which can indicate favourable interactions between these types of molecules from the respective film-forming compounds (like quince peel and pumpkin seeds) (Fig. S.7) (Rozenberg, Lansky, Shoham, & Shoham, 2019). Furthermore, for Q_PPK_S films, the characteristic bands of pumpkin seeds, between 1743 cm^{-1} and 1234 cm^{-1}, are seen in the Q_PPK_S spectrum. These peaks are associated to adsorbed water or vibrations of the amide bands from proteins (Ritzoulis et al., 2014). Due to the large amount of compounds in the formulation that have a plasticizer effect, along with the presence of proteins in the polymeric matrix, Q_PPK_S films may have been excessively plasticized and present low barrier and mechanical properties (Ghanbarzadeh et al., 2007; Ploypetchara & Gohtani, 2018; Ritzoulis et al., 2014). The presence of proteins and sugars increases the water content of the edible films and explains the anomalous behaviour of the films of this formulation (Basiak, Lenart, & Debeaufort, 2018; Chakravartula et al., 2019; de Freitas et al., 2021).

It should also be noted the presence of a new peak around 1260 cm^{-1} in the films P_PO_P, Q_PR_{PL}, P_PO_{PC} and P_PR_{PL}, that cannot be directly attributed to any raw material or additive used. This new peak can be attributed to the stretching of a newly formed C—N bond, characteristic of a glycosyl-amine moiety and which implies the occurrence of interactions between sugars and proteins present in the filmogenic formulation and that significantly altered the films' polymeric structure (Rozenberg et al., 2019).

4.4. Mechanical properties

The mechanical properties of the films are presented in Fig. 4. Young's modulus (E') ranged from 30 to 800 MPa, maximum tensile strength (Max σ) from 1.37 to 26.25 MPa and elongation at break (ETB) from 2.28 up to 16.80%. These results are in line with other studies that produced edible films with agrifood raw materials as packaging application for the food industry (E' between 0.001 and 418.2 MPa, Max σ between 0.020 and 16.41 MPa, and ETB between 1.4 and 51%), with some of the films from this study presenting higher E' and Max σ, and ETB in the range of those already reported (Brito et al., 2019; de Freitas et al., 2021; Ferreira et al., 2016; Santos et al., 2016; Xu et al., 2019).

The film with the highest maximum tensile strength was P_PO_{PC}, indicating that this film presented the highest resistance to break. Also, it presented the highest E' and the lowest ETB, which shows that this film has greater rigidity, and consequently lower elongation of its structure, than the rest of the films. These values agree with each other, since the higher value for the Young's modulus corresponds to a less flexible film, having a smaller ETB. As this formulation contains pectin, the results can

Table 4
Characteristic vibrations on FTIR analysis and respective vibrations.

Wavelength (cm^{-1})	Vibrations and observations	References
3800–3600	Hydrogen bonding between protein chains and/or moisture content in the films	Ren et al. (2017)
3600–3200	Free O—H stretching vibrations (belonging to glycerol and water), coupled with N—H stretching occurred in hydrogen bonds (amides A)	Chakravartula et al. (2019); Gaspar et al. (2021); Ren et al. (2017); Ritzoulis et al. (2014); Xu et al. (2019)
3000–2800	-CH stretching vibrations in CH_2 and CH_3 groups and are common in many organic substances, as was previously reported by other authors, and stretching of $-NH_3$ (amides B)	Basiak et al. (2018); Gaspar et al. (2021); Ritzoulis et al. (2014); Xu et al. (2019)
1750–1700	Stretching vibration of aldehydes (C═O stretching for acids/esters); it can also be associated to the -NH bending (amide II) since this vibration can produce a peak between 1740 and 1725 cm^{-1}	Gaspar et al. (2021)
1800–1600	Characteristic of carbonyl groups such as carboxylic acids and esters, some authors say; C═N stretch should be present in this range and it has similar conjugation effects to C═O stretch, (present in pectin)	Basiak et al. (2018); Chakravartula et al. (2019); Ren et al. (2017)
1700–1600	Vibration of amide I bands and indicate secondary structure in films containing proteins	Chakravartula et al. (2019); Ren et al. (2017); Ritzoulis et al. (2014); Xu et al. (2019)
1600–1400	Vibrations of amide II bands (-N-H bending) (usually present between, approximately, 1580 and 1490 cm^{-1}); symmetric COO-stretch and to the asymmetrical COO- stretch of carboxyl groups	Gaspar et al. (2021); Ritzoulis et al. (2014); Xu et al. (2019)
1400–1220	Amide III bands with the vibrations in the plane of C—N and N—H groups; the decrease of the intensity of this bands indicates protein denaturation	Chakravartula et al. (2019)
1200–850	Stretching of C-OH and C-O-C bonds, and C—C skeleton stretching vibrations (typical functional groups of starch); some authors observed and the increase of this peak's intensity when the content of starch of the films was also increased; the peaks from 1220 to around 1040 cm^{-1} are also considered as part of amide III band for some authors (C—N stretching vibration).	Basiak et al. (2018); Gaspar et al. (2021); Ritzoulis et al. (2014)
800–650	Attributed to O—H vibrations by other authors; peaks around 670 cm^{-1} also indicate deformation of C—H groups	Gaspar et al. (2021)

be related to the film-forming ability, emulsifying capacity, interchain associations and interactions with other biomolecules of this substance, concluding that pectin reduced the mobility of the polymeric chains and increased the rigidity and mechanical resistance of the structures of the films (Lazaridou & Biliaderis, 2020). The P_PO_{PC} film produced in this study have better mechanical resistance and similar elongations when compared to other edible films produced from agrifood by-products or wastes used as raw materials.

All films with quince peel showed the lowest values of E' and Max σ and the highest values of ETB (excluding Q_PPK_S), suggesting that quince peel increases the flexibility of the polymeric matrices and reduces the mechanical resistance of the obtained films. Agro-industrial by-products, namely broken rice and potato pulp, effectively replaced commercial starch in the produced films, showing lower E' values, but higher flexibility. All these results can be explained considering the amount of sugars present in each formulation and its plasticizing effect. The combination of raw materials with higher amount of sugars in the same formulations, such as quince peel and broken rice, led to an increased in the flexibility of the films, as observed with the low E' values of Q_PB_R and $Q_PP_PB_R$. Those conclusions are in line with information in the literature, where plasticizers, such as glycerol and natural sugars, are added to increase the flexibility of the polymeric chains, making them less brittle and preventing shrinkage during handling and storage (Lai & Padua, 1998; Ploypetchara & Gohtani, 2018; Teixeira, da Róz, Carvalho, & Curvelo, 2007).

It should be noted that, once again, the Q_PPK_S film presented an anomalous profile. These films showed the lowest values of Young's modulus and maximum tensile strength, but also had the second lowest values of elongation at break, which indicates that these films have low flexibility and low mechanical resistance. This can be explained considering the composition of the Q_PPK_S formulation, given the plasticizing effect of the sugars and the low mechanical strength induced by the proteins, both from the quince peel and pumpkin seeds, originating the results obtained (Chakravartula et al., 2019; Ritzoulis et al., 2014).

From this analysis, sugars/plasticizing compounds, proteins and starch appear to be the substances that most influenced the film matrices and respective properties. It has also been proven that the nature and the amount of the added compounds must be fully understood and optimized to improve the final films' properties.

4.5. Thermal events of the edible films

The water content, water evaporation temperature and thermal decomposition temperatures of the films, raw materials and additives were determined by thermogravimetric assays. The results for the raw materials and glycerol are presented in Table 5. The water content of the raw materials ranged from 4.42 ± 0.02% to 13.21 ± 0.27%, for potato peel and commercial starch, respectively, with glycerol presenting a lower water content, since it was laboratory-grade.

Generally, there are four stages of thermal decomposition in biomass that can be identified: at 50–130 °C (dewatering of the films), 130–220 °C (evaporation of volatile compounds due to degradation), 220–460 °C (depolymerisation pyrolysis) and > 460 °C (char formation) (Liang & McDonald, 2014). Moreover, the thermal events of raw materials and films include: decomposition of hemicellulose (220–315 °C), cellulose (315–400 °C), starch (280–350 °C), lignin (> 250 °C), sucrose (130–60 °C), glycerol degradation and simple polysaccharide decomposition (160–230 °C), starch decomposition and degradation (260–450 °C), degradation of low molecular weight proteins' constituents (150–250 °C) and main degradation of proteins and starch (250–400 °C) (Basiak et al., 2018; Liang & McDonald, 2014; Santos et al., 2016; Thomas, 2018; Xu et al., 2019).

Films, raw materials and additives were analysed, taking as an example the analysis of the Q_PPK_S film (Fig. 5.A). The films' initial degradation temperatures were compared with each other by using Fig. 5.B of the films and with the initial degradation temperatures of the respective raw materials and glycerol (Fig. 5.B and Table 5). All films and raw materials presented peaks between 25 °C and 130 °C, which are associated to the evaporation of the free and bounded water present in the films (Liang & McDonald, 2014; Santos et al., 2016; Xu et al., 2019).

Potato peel decreased the initial degradation temperature of the films. When potato peel is present, the main peak of the film occurs at the same temperature as the main peak of this raw material (around 285 °C), in contrast to the other films that have their main peak around 300 °C (Fig. 5.B). These temperatures and peaks related to potato peel

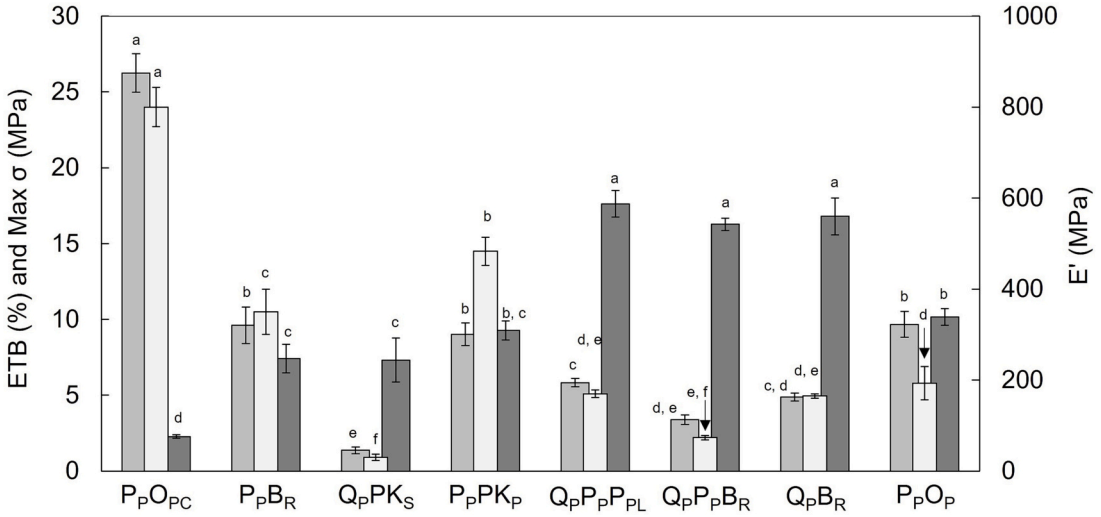

Fig. 4. Films' mechanical properties: Maximum tensile strength (Max σ) (■); Young's modulus (E') (□); Elongation at Break (ETB) (■) (mean values ± standard deviation). Columns with different letters differ significantly ($P < 0.05$) by Tukey test.

Table 5
Water content, water evaporation temperature (T_E) and temperature of thermal decomposition events (T_D) of raw materials and additives used (main peak in bold).

Films' constituents	Water content (%, w/w)	T_E (°C)	T_D (°C)
Glycerol	1.70 ± 0.53	–	**224.95 ± 11.10**
Orange pectin (O_{PC})	12.06 ± 0.38	48.79 ± 1.58	**222.18 ± 11.20**; 301.58 ± 1.18; 402.58 ± 0.96
Potato pulp (P_{PL})	7.37 ± 0.02	54.80 ± 2.36	216.39 ± 0.37; **285.89 ± 0.10;** 311.27 ± 0.98; 421.3 ± 2.52
Broken rice (B_R)	7.27 ± 0.19	55.06 ± 2.82	279.83 ± 2.27; **306.44 ± 3.56**; 373.36 ± 2.48
Commercial starch	13.21 ± 0.27	61.995 ± 4.38	277.92 ± 0.88; **300.80 ± 0.18**; 367.40 ± 5.98
Pumpkin peel (PK_P)	6.28 ± 0.03	54.75 ± 4.34	150.08 ± 1.46; 205.69 ± 0.26; 249.30 ± 1.50; **306.40 ± 0.89**; 378.18 ± 5.80
Potato peel (P_P)	4.42 ± 0.02	75.19 ± 0.12	209.20 ± 2.80; **285.34 ± 0.88**; 426.84 ± 0.50
Orange peel (O_P)	4.55 ± 0.0	63.85 ± 1.54	151.08 ± 4.66; **205.85 ± 0.35;** 257.32 ± 1.96; 334.40 ± 0.35; 456.36 ± 2.78
Quince peel (Q_P)	9.62 ± 0.33	48.28 ± 0.525	143.4 ± 1.51; **202.22 ± 0.12;** 259.15 ± 3.33; 330.44 ± 0.045; 440.94 ± 5.12
Pumpkin seed (PK_S)	5.90 ± 0.29	51.12 ± 0.86	230.97 ± 3.72; **345.58 ± 0.19**; 381.93 ± 1.48

*E – Free and bonded water evaporation; D – thermal decomposition events.

have already been reported in previous studies, being associated with the degradation of hemicellulose, cellulose and lignin from this material (Pardo, Rojas, & Florez, 2021).

Raw materials with peaks between 145 °C and 150 °C, such as orange peel, pumpkin peel and quince peel, induced lower thermal decomposition temperatures of the films. P_PB_R and P_PO_{PC}, films, without these raw materials, have the highest thermal decomposition temperatures, 288.47 °C and 286.91 °C, respectively. Previous works identified the loss of crystalline structure from fructose (around 130 °C), glucose (around 160 °C) and sucrose (around 190 °C), which confirms that the films' peaks in this region can be originated from the decomposition of the sugars present in the raw materials (Lee, Thomas, & Schmidt, 2011). The plasticizing effect of these components, along with the presence of glycerol in all films, shifted the peaks of the raw materials to lower temperatures and reduced the initial temperature degradation of the films. This was previously reported by other authors and it was expected since this type of compounds increase the flexibility of the polymers' chains by decreasing the molecular forces within the polymeric matrix (Basiak et al., 2018; Ploypetchara & Gohtani, 2018).

Observing Fig. 5.B, it is possible to conclude that the lowest temperature of thermal decomposition events occurred around 145 °C, with the highest degradation rate for all the films occurring between 283 °C and 301 °C. This demonstrates that the films have good resistance to thermal decomposition, with high degradation temperatures. Those good thermal properties are very important for the application of the films in the food industry, since edible films can be submitted to thermal processes during their preparation, processing and consumption (Soares, Lima, Oliveira, Pires, & Soldi, 2005). Another interesting observation is that broken rice has peaks and thermal events similar to commercial starch, which means that it can replace partially or totally the commercial starch in film formulations.

To confirm the observed trends between the physicochemical properties of the films and their composition, the composition of the filtrate that originates each film was calculated considering the data reported in Tables 1 and 2, with the obtained results being exhibited in Fig. 6.

Considering the composition of each edible film's filtrate presented in Fig. 6, it is possible to observe that starch (whether commercial or obtained from the used food by-products and wastes) is the main constituent of the produced films. Furthermore, films with quince peel possess higher amounts of sugar and Q_PPK_S presents the highest amount of protein and lipids of all formulations. These trends correlate well with the data from the FTIR (Fig. 3) and thermogravimetric measurements (Fig. 5), confirming the influence of each raw material and their respective composition in the obtained physicochemical properties of the produced films.

5. Conclusions

The distinct compositions of the agrifood by-products and wastes used in this study were determinant in the properties of the produced films. The use of raw materials with significant amounts of compounds that act as plasticizers must be carefully evaluated, as their over-addition compromises the films' properties. Thus, films with high sugar content showed low mechanical resistance, increased flexibility and lower initial degradation temperatures. Orange pectin and broken rice seem to be good raw materials to produce biodegradable films since they induced higher WCA and better optical, barrier and mechanical properties. Quince peel induced higher flexibility in the films and can possibly replace other plasticizers, such as glycerol. Broken rice showed

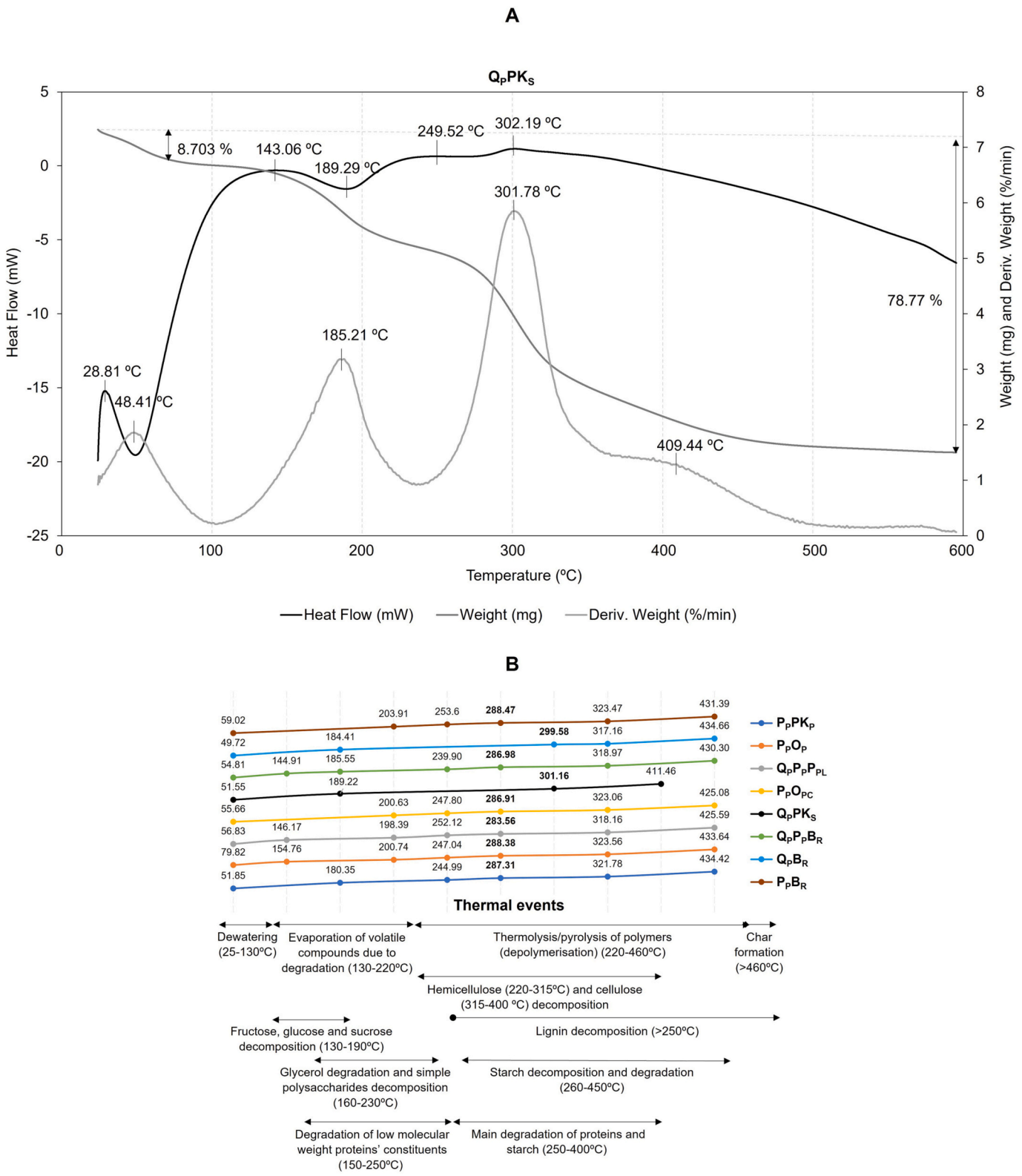

Fig. 5. Q_PPK_S film thermogram (A); temperatures of the peaks present in all film thermograms, and related possible thermal events (main decomposition temperature in bold) (B).

similar thermal events when compared to commercial starch and can possibly be used as its substitute. The most promising films were P_PO_{PC}, P_PB_R e P_PPK_P, with orange pectin, broken rice and pumpkin peel replacing quince peel. These formulations have higher WCA, lower WVP and WVTR, higher E' and Max σ, being in accordance with the values found in literature for other edible films made from fruits, vegetables and cereals' residues. The produced edible films can be used as stand-alone protective barriers for a wide variety of food products, including fruits and vegetables, snacks, bakery and confectionery products, and even meat and poultry. Consumers can also safely consume these goods

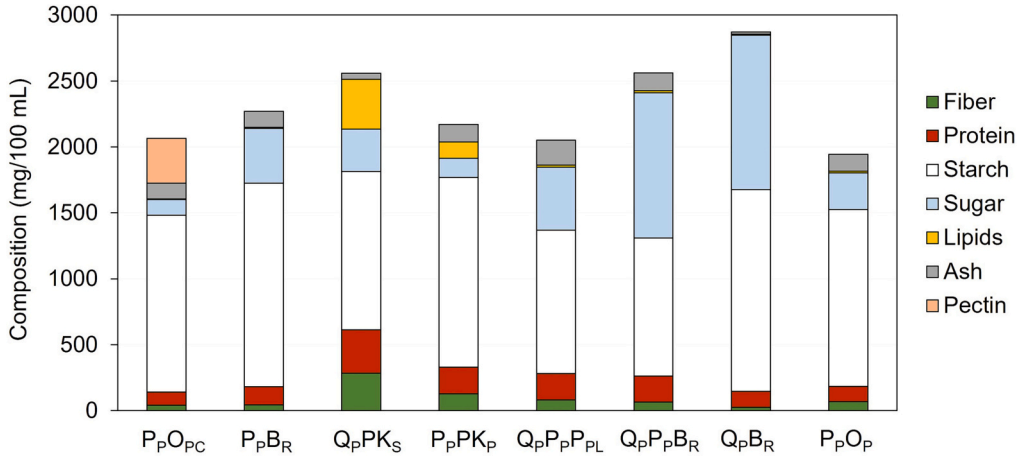

Fig. 6. Composition of each film's filtrate per 100 mL of initial filmogenic solution.

with the edible film still intact, if they choose to.

Overall, the use of agro-industrial by-products and wastes to produce edible films presented good results, being necessary further investigation to produce edible films with better properties than the non-sustainable packaging alternatives currently available.

CRediT authorship contribution statement

Alexandre M.S. Jorge: Data curation, Formal analysis, Investigation, Software, Validation, Visualization, Writing – original draft. **Marisa C. Gaspar:** Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Supervision, Validation, Visualization, Writing – review & editing. **Marta H.F. Henriques:** Investigation, Resources, Writing – review & editing. **Mara E.M. Braga:** Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Supervision, Validation, Visualization, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no conflict of interest.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ifset.2023.103442.

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