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ORIGINAL ARTICLE

Chemically modified polysaccharides from alternative sources to improve the acerola postharvest quality

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Abstract

The high postharvest losses have affected the profitability of growers worldwide mainly for acerola, a highly perishable fruit. To overcome this, edible coatings with polysaccharides chitosan and galactomannan have been proposed. However, raw polysaccharides are not fully adequate to be used as coatings. In this way, these polysaccharides were chemically modified to get quaternary derivative with improved action on acerola postharvest coating. The chemical modification was confirmed by spectroscopy analyses, showing Infrared peak at 1478 cm^{-1} and ^{1}H-NMR at 3.2 ppm. Modified polysaccharide showed reduction in thermogravimetric T_{max} (~22–40 °C), tensile stress (~6–30 MPa), and elongation (~6%) in comparison with the parent polymers. The water vapor permeability was similar in both cases (~3 g mm kPa^{-1} h^{-1} m^{-2}). The swelling degree (<2% in ethanol and >70%) confirms the hydrophilic character of the modified polymers. Analysis by Scanning Electron Microscopy showed a smoother surface for the modified material. The most affected postharvest physiological parameter for stored acerola (18 days, 12 °C, relative humidity 90%) was the respiration rate (CO_2 mol kg^{-1} h^{-1}) that was lower for uncoated ($1.10\ 10^{-2}\pm1.96\ 10^{-4}$) compared with chitosan derivative ($0.99\ 10^{-2}\pm3.36\ 10^{-4}$) coated fruit. This indicates a post-climacteric peak shift and consequent delayed ripening, improving the acerola postharvest losses.

Keywords Antifungal coating · Edible film · Polysaccharide alkylation · Galactomannan

Abbreviations

CHI	Chitosan
GLM	Galactomannan
GTMAC	Glycidyl trimethyl ammonium chloride
QCHI	Chitosan quaternary salt
QGLM	Galactomannan quaternary salt
NMP	N-methyl-2-pyrrolidone

Introduction

Brazil is the largest producer and consumer of acerola (*Malpighia emarginata*), fruit well known for its high vitamin C content. In the country, acerola is mainly produced in the Northeast region, following crop management practices that allow many harvests along the year (Ribeiro and Freitas 2020). However, the commercialization and consumption of fresh acerola is limited due to its high perishability, presenting high metabolic activity that reduces fruit postharvest life (Alves et al. 1995).

In addition to the cold chain, the use of impermeable polymeric packaging has been shown to reduce fruit metabolic activity and maintain fruit postharvest quality. However, even under these conditions, there are significant fruit losses after harvest. In order to overcome such drawbacks, specific fruit coatings can be developed to effectively reduce metabolic activity, extend postharvest life and reduce losses. Applied directly on the fruit skin, edible coatings make it possible to increase fruit postharvest life, allowing greater flexibility in fruit handling and trading (Galvão et al. 2024).

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Despite its importance, only a few studies have reported the use of polysaccharides as coating materials for acerola fruit. In a first study, it was applied a coating based on cassava starch that reduced the soluble solids and ascorbic acid losses, but other parameters were not evaluated (Maciel et al. 2004). Following, edible films based on vegetable residue flour reduced weight loss of acerola, but with minor influence on pH, titratable acidity and soluble solid content during storage (Ferreira et al. 2016). More recently, an edible film based on pineapple peel flour and yam starch reduced significantly the weight loss and maintained the lightness (L), but had limited influence on total soluble solids, pH, and total titratable acidity (Galvão et al. 2024). In this way, new materials must be studied and evaluated to maintain acerola postharvest quality.

Polysaccharides have been evaluated as economical and efficient edible coatings, especially chitosan (CHI) (Tokatlı and Demirdöven 2020). Other polysaccharides, such as GLM that is mostly obtained from mesquite seeds (*Prosopis juliflora*), have also shown potential for coating formulations (Souza et al. 2023). Such edible coatings act by creating a modified atmosphere inside the fruit, which improves several physiological postharvest changes, such as water loss, decay incidence, mechanical resistance and O_2/CO_2 permeability (Cerqueira et al. 2009). Nevertheless, to achieve such postharvest efficiency, it is necessary a multicomponent system or chemically modified material.

Polysaccharide materials with improved film forming properties can be obtained by chemical modifications to get quaternary salts derivatives (Britto and Assis 2012). This can be achieved with GTMAC, which reacts with chitosan, leading to the formation of QCHI, a chitosan quaternary salt from N-(2-hydroxyl) propyl-3-trimethyl ammonium chloride. This derivative molecule presents better solubility in a wide pH range and enhanced antibacterial activity, mucoadhesiveness, hydrophilicity and hemostatic action, compared to chitosan (Yang et al. 2020).

The objectives of this study were to develop new GLM and CHI modified coatings to maintain quality and reduce postharvest losses of acerola fruit. Our study proposes to carry out the synthesis of quaternary salt of GLM by quaternization with GTMAC to get QGLM. The new coating was characterized regarding its physicochemical properties, as well as its effect on reducing fruit metabolic activity, maintaining quality and reducing postharvest losses of acerola fruit. For comparison, the quaternary chitosan derivative, QCHI, was also evaluated.

Materials and methods

Material

The reagents used in the study were medium molecular weight chitosan (80% deacetylation degree); GTMAC≥97%; NMP≥99.5%; oxalic acid, ≥99%; 2,6 – dichlorophenol indophenol hydrate (sodium salt); glacial acetic acid, 99.7% that were acquired from Sigma-Aldrich®. Dialysis tube was one with an exclusion limit up to 12–14,000 Daltons acquired from Sigma-Aldrich®. GLM was extracted from mesquite seeds *(P. juliflora)*, according to the approach described in previous studies (Souza et al. 2023). The variety 'Junko' acerola (*M. emarginata*) were harvested early in the morning at the 'Bebedouro' experimental station located in the Embrapa Semi-Arid Region, Petrolina, PE, Brazil.

Galactomannan and chitosan quaternization synthesis

The quaternization reaction was carried out based on previous publications (Ruihua et al. 2012; Britto and Assis 2007a), in which the reactional medium consisted of water (3.5 mL), GTMAC (3.0 mL) and NMP (3.5 mL). An amount of 0.5 g of the parent polymer (GLM or CHI) was added to the reaction medium and the system maintained under magnet stirrer at 80 °C for 18 h. Later, the reaction medium was subjected to dialysis for 48 h against distilled water (changed every 12 h) to remove impurities and unreacted reagents. After dialysis, the reacted material was subjected to centrifugation (at 12,857 x g for 10 min and 25 °C, centrifuge Eppendorf, model 5804 R, rotor F-34-6-38) to separate the insoluble fraction of GLM or CHI. Then, the supernatant, containing QGLM or QCHI, was dried by casting on a Petri dish. After the drying, the QGLM and QCHI films were detached from the Petri dish and characterized.

Quaternary films characterization

^{1}H nuclear magnetic resonance spectroscopy (^{1}H NMR)

The ^{1}H NMR spectrum was obtained on a Bruker AC200 Spectrometer, operating at 200 MHz at a temperature of 80 °C. For analyses, the samples were dissolved in deuterated water/hydrochloric acid (D_2O/HCl) (100/1 v/v) at a concentration of 10 mg/mL. The parameters for acquiring the NMR spectrum were: 90° pulse, corresponding to a pulse width of 8.2 µm; LB = 0.3 Hz; NS = 16. The average degrees of acetylation were determined from the ^{1}H NMR spectrum (Britto and Campana Filho 2004). The degree of acetylation (DA) of CHI was calculated according to Eq. 1:

$$DA\,(\%) = \frac{A_{CH_3}}{3A_{H2}}100 \tag{1}$$

in which, A_{CH3} is the area of the methyl protons from acetamide moiety and A_{H2} is the area of the proton linked to glucosamine carbon 2. The degree of substitution (DS) for QCHI was calculated according to Eq. 2:

$$DS\,(\%) = \frac{A_{3(CH_3)}}{9A_{H1}}100 \tag{2}$$

in which, A_{CH3} is the area of the methyl protons attributed to quaternary ammonium moiety and A_{H2} is the area of the proton linked to glucosamine carbon 1.

Fourier transform infrared spectroscopy (FTIR)

The quaternary materials were analyzed in film form using the ATR technique in a Perkin-Elmer FTIR spectrophotometer, model Spectrum Two, in the range 4000–400 cm^{-1}. For comparison, films of the unmodified GLM and CHI were prepared by casting, using distilled water for GLM and acetic acid (0.5%) for CHI, both at a concentration of 5 mg/mL (Thombare et al. 2023; Britto and Assis 2007a).

Thermogravimetric analysis (TG/DTG)

TG measurements were carried out on a TGA Q500 V20 from TA Instruments. The heating rate was 10 °C/min up to 600 °C under a nitrogen atmosphere at a flow rate of 50 mL/min. The mass used in each experiment was around 10 mg (Britto and Campana Filho 2007).

Morphological analysis by scanning electron microscopy (SEM)

For SEM analysis, the filmogenic solution of CHI, GLM, QCHI and QGLM solutions were deposited on glass slides and dried in a desiccator. Following, the samples were covered with a thin layer of gold and were analyzed in a scanning electron microscope from Tescan, model Vega 3XMU (Nascimento et al. 2019).

Mechanical properties

The mechanical analysis was performed as described before (Souza et al. 2023). The sample film consisted of a rectangular shape, measuring 5 × 10 mm and thickness in the range 0.1–0.2 mm. The stress x strain curve was obtained with a Universal Testing Machine (EMIC, DL 10000, Paraná, Brazil). The cell load was 500 N, with a deformation speed of 5 mm/min. The experiment was repeated at least six times for each sample.

Water vapour permeability

Water vapour permeability (WVP) was determined by gravimetry, according to the ASTM Standard Test Methods (ASTM E96/E95M, 1995), described before (Souza et al. 2023). For this, disc-shaped sample film pieces with a diameter of 30 mm were attached to the measuring cells containing 20 mL of water. The cells were placed in a desiccator containing silica gel at 50% relative humidity. Each cell was weighed on an analytical balance at each 24 h for seven days until the system reaches the steady state. The experiment was performed in triplicate, and permeability was calculated using Eq. 3:

$$WVP = \frac{\Delta M\ E}{T\ A\ S\ (R_1 - R_2)} \tag{3}$$

where WVP is the water vapour permeability (g mm/kPa h m^2); ΔM is the change in mass (g) of the cell; E is the average thickness (mm) of the film; T is the time (hours); A is the permeation area (m^2) of the film; S is the water vapour pressure (3.2 kPa) at testing temperature (25 °C); R_1 is the relative humidity within the cell, expressed as a fraction (1.0); and R_2 is the relative humidity in the desiccator, expressed as a fraction (0.5).

Swelling degree

The degree of swelling in anhydrous ethanol and ethanol/water (1:1 v/v) was measured using an immersion assay as described before (Britto and Assis 2010). Pieces of dried film were weighed (~200 mg) and immersed separately in the liquids for 24 h at room temperature. The samples were removed from the liquids, free surface liquids blotted quickly with filter paper and weighed. The degree of swelling was expressed as a percentage of liquid uptakes after immersion compared to the initial dry weight from Eq. 4:

$$DS = \frac{W_s - W_d}{W_d}(100\%) \tag{4}$$

where DS is the degree of swelling of the film, W_s the weight of swollen sample and W_d is the dried sample. All experiments were conducted in triplicate.

Acerola coating experiment

Coating formulation

Mature green fruits were harvested, washed with chlorinated water (600 µL L^{-1}) and selected to exclude fruit presenting visual defects. Only fruit with density lower than 1 g/mL were used in the study due to the capacity to change skin color from green to red after harvest (Ribeiro and Freitas 2020). Each treatment consisted of 3 replications with 7 fruits per replication that were packed in clamshell boxes with $5 \times 10 \times 17$ cm (height x width x length). The fruits were immersed for 5 s in each filmogenic solution (5.0 mg/mL) of CHI, GLM, QCHI and QGLM. Each solution represents one treatment. The fruits were stored for 18 days at 12 ± 0.5 °C, with relative humidity of $90 \pm 5\%$.

Fruit physiological evaluation

Average mass loss was calculated by subtracting the initial sample weight at harvest by its respective weight after 18 days of cold storage. The weight difference was then multiplied by 100 and divided by its respective weight at harvest. Mass loss was expressed in percentage.

Skin color was analyzed in the equatorial region of each fruit, using a model CR-400 colorimeter (Konica Minolta, Tokyo, Japan). The results were expressed in lightness (L) that corresponds to variations from dark/opaque (0) to white (100), chroma (C) that represents the color intensity, and Hue angle (ºh) that represents the color that ranges from blue (270º), green (180º), yellow (90º) and red (0º).

To determine the respiration rate, the fruit were placed in hermetically sealed glass bottles, with a capacity of 600 mL, and silicone septa on the lids. The bottles were closed for 120 min to collect the headspace gas sample, which was injected into a gas chromatograph (Thermo Finnigan, Thermoquest GC Trace 2000) with a Porapack column, methanator and flame ionization detector (FID). The results were expressed in mol of CO_2 per kg of fruit per hour.

Fruit texture was determined as the maximum force required to press 10% of the fruit diameter using a TA.XT Plus texturometer (Extralab®, São Paulo, Brazil), adapted with a P/75 pressure plate. The results were expressed in Newtons (N).

The soluble solids (SS) content was determined in a juice sample extracted with a domestic centrifuge. About 1 ml of juice was added to a portable digital refractometer PAL-1 (Atago, São Paulo, Brazil) to determine the SS content in each juice sample. The results were expressed in ºBrix. The concentration of ascorbic acid (vitamin C) was determined by titrating 0.5 mL of the juice, diluted in 100 mL of 0.5% oxalic acid, with a solution containing 0.02% of 2,9 dichlorophenol indophenol (DFI) until permanent light pink color (Ribeiro and Freitas, 2020). The results were expressed in mg/100 g of juice.

The data were submitted to the analysis of variance and the averages were compared by Tukey's test (5%). The statistical analysis was carried out using the software ExpDes.pt, from the software R, version 3.2.5.

Results and discussion

The quaternization reaction of CHI with GTMAC occurs preferentially at the amino groups, as they are more reactive than the hydroxyl groups. In the GLM molecule, there are no amino groups, so the GTMAC reaction takes place at the hydroxyl groups. After reaction and purification, the casted QGLM and QCHI films were flexible, homogeneous and transparent in appearance. The mass obtained was around 150 mg for QGLM and 220 mg for QCHI, which represents a yield of 30% and 44%, respectively, in relation to the initial mass.

FTIR characteristics of the derivatives

The chemical structure of the GLM polysaccharide was completely elucidated by FTIR, as demonstrated by previous studies (Thombare et al. 2023; Cerqueira et al. 2011; López-Franco et al. 2013). In agreement, the FTIR spectrum for GLM film shows characteristic bands (Fig. 1). The band at 3392 cm^{-1} is related to the vibrational stretching of O–H groups and the band at 2925 cm^{-1} is related to the vibrational stretching of the CH group. The band at 1643 cm^{-1} refers to the stretching of the galactose and mannose rings. The region between 1200 and 1460 cm^{-1} is related to symmetric deformations of the COH and CH_2 groups. The broad band between 1031 cm^{-1} and 1149 cm^{-1} can be attributed to the vibrational stretching related to C–O in the C–O–H bonds. The bands at 813 cm^{-1} and 871 cm^{-1} are attributed to the bonds of the anomeric units of galactose and mannose, respectively. All these bands are also observed in the QGLM spectrum (Fig. 1). However, after the quaternization, a new band is observed at 1478 cm^{-1} that corresponds to the symmetric C–H deformation of the methyl groups of the quaternary ammonium substituent. Furthermore, the presence of a discrete band at 1419 cm^{-1} can also be observed due to the presence of the C–N vibrational stretching mode (Pal et al. 2007), suggesting the modification of the GLM.

Equally for the chitosan, its chemical structure was completely elucidated by FTIR, as demonstrated by previous studies (Britto and Assis 2007; Mourya and Inamdar 2009; Vasconcelos et al. 2011). In agreement, the FTIR spectrum for chitosan film shows the characteristic bands (Fig. 1).

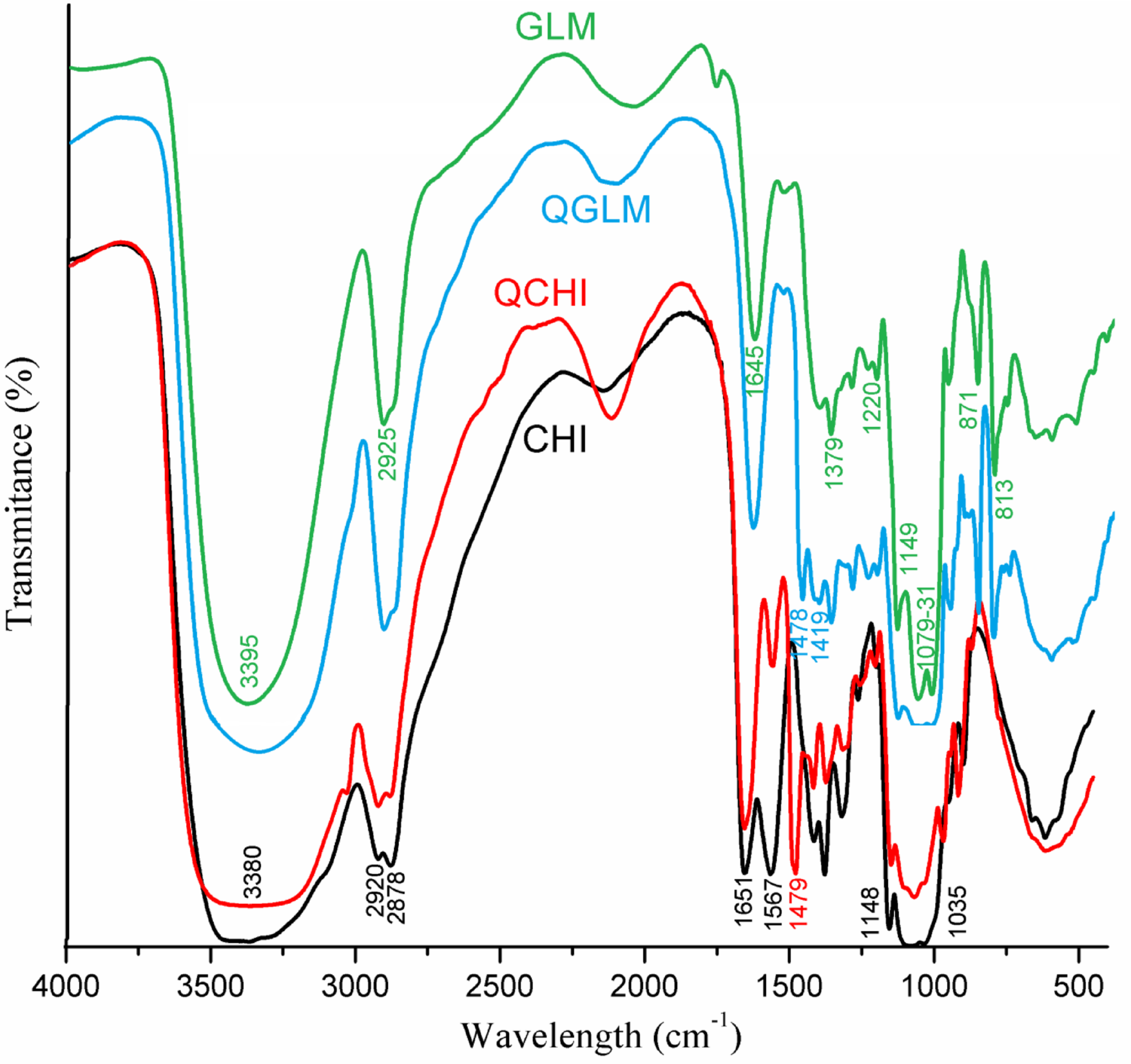

Fig. 1 FTIR spectra for the polysaccharides chitosan, galactomannan and its quaternary derivative

The broad and intense band at 3437 cm^{-1} corresponds to the overlapping of O–H and N–H axial stretching. The band at 2879 cm^{-1} is attributed to axial C–H stretching. The bands at 1653 cm^{-1} and 1567 cm^{-1} correspond to the axial stretching of C=O (amide I band) and angular stretching of N–H$_2$, respectively. The bands at 1156 cm^{-1} and 1037 cm^{-1} correspond to C–O stretching of primary and secondary alcohols, respectively. These main bands are also observed in the QCHI spectrum (Fig. 1). However, after the quaternization a new band is observed at 1479 cm^{-1}, which is attributed to the asymmetric angular deformations of the methyl groups at trimethyl ammonium moiety (Britto and Assis 2007a). Furthermore, there was a reduction in the intensity of the band at 1559 cm^{-1} corresponding to the primary amine and there was also an increase in the intensity of the band at 1655 cm^{-1}, indicating that the primary amines present in chitosan were modified to secondary amine as a result of the reaction with GTMAC (Mourya and Inamdar 2009). On the other hand, the characteristic bands observed between 1148 cm^{-1} and 1035 cm^{-1} remained similar after the reaction of chitosan with GTMAC, indicating that no reaction occurred between the hydroxyl groups linked to carbons C3 and C6, which is in agreement with previous studies (Huang et al. 2014).

^{1}H NMR characteristics of the derivatives

The GLM, CHI and derivatives were characterized by ^{1}H NMR to confirm the changes in their chemical structures, as well to calculate the degree of acetylation of CHI, the mannose-galactose ratio for GLM, and the degree of quaternization of the QCHI. The ^{1}H NMR spectrum for GLM shows peaks at 5.02 and 4.73 ppm (Fig. 2a), which are related to the hydrogen atoms linked to the anomeric carbon of the α-D-galactopyranose ring (G1) and to the anomeric carbon of the β-D-mannopyranose ring (M1), respectively.

By integrating the areas associated with the G1 signals at 5.02 ppm and M1 at 4.73 ppm, the mannose: galactose ratio was obtained with a value of 0.3:1. This proportion may vary depending on the source and method used to obtain the GLM. In addition, it affects the film-forming properties of the material, since the higher the D-galactose content, the greater will be its solubility in water (Cerqueira et al. 2011). For the QGLM spectrum, it shows clearly a new intense peak at 3.2 ppm, attributed to the methyl hydrogens of the quaternary ammonium group, indicating the occurrence of chemical modification of GLM by the quaternization reaction.

The ^{1}H NMR spectrum for chitosan (Fig. 2b) shows the following characteristic signals in ppm: (a) $\delta = 4.8$, attributed to hydrogen bonded to the anomeric carbon 1; (b) $\delta = 3.5 < \delta < 4.0$ due to hydrogen bonded to carbon atoms 3, 4, 5 and 6 of the glucopyranose unit; (c) $\delta = 3.2$ attributed to the hydrogen atom linked to carbon 2 of the glucopyranose ring and (d) $\delta = 2$ related to the hydrogen atoms of the methyl moieties of the acetamido groups (Britto and Campana Filho 2004). Using the ratio between the areas of the acetamide methyl protons and the glucosamine carbon 2 proton (Eq. 1), the degree of acetylation (DA) of CHI was 25%.

After the quaternization, the QCHI ^{1}H NMR spectrum showed an intense signal at 3.2 ppm (Fig. 2b), assigned to the hydrogens present in the methyl moieties of the quaternary ammonium group (Britto and Campana Filho 2004). This proves the success of the substitution reaction. Based on the area ratio between the peak attributed to quaternary ammonium and peak of hydrogen bonded to carbon 1 (Eq. 2) the degree of substitution (DS) for QCHI was 33.3%.

Thermogravimetric analysis of the derivatives

The thermal behavior was similar for all the samples, showing initially (25 a 100 °C) a mass loss associated with water evaporation (Fig. 3). This loss of adsorbed water is due to the hydrophilic nature of the polysaccharides, mainly hydroxyl moiety (Britto and Campana Filho 2004; Britto and Campana Filho 2007). The second thermal event refers to the thermal decomposition of the polysaccharides, occurring in the range from 200 to 340 °C. In this thermal decomposition occur depolymerization and breaking of chemical bonds with consequent release of H_2O, CO_2, CH_3HCOH, among other low molar weight components. According to the derivative of the TG curve, the maximum temperature of degradation (T_{max}) was 291 °C for chitosan (Fig. 3), which is in agreement with a previous study and can vary depending on the chitosan source, molecular weight and degree of acetylation (Britto and Campana Filho 2004; Britto and Campana Filho 2007). Particularly for GLM, there is an overlap of two peaks at 292 and 306 °C, indicating the occurrence of two distinct thermal events. This may be related with the thermal decomposition of the two GLM components galactan and mannan. After the chemical modification, there is a clear reduction in the T_{max} for the derivatives. The T_{max} was 273 °C for QGLM and 253, 268 °C for QCHI (overlapping two peaks). This reduction in the T_{max} is common for polysaccharides derivatives such as chitosan (Britto and Campana Filho 2004; Britto and Campana Filho 2007). Even with this reduction in the thermal decomposition temperature, the modified material is stable at room temperature, allowing its use as fruit coating, for example.

Modified polysaccharides morphological analysis by SEM

The morphological analysis showed that non-modified parent polysaccharides, chitosan and GLM, have irregular and rough surfaces typical of formation of agglomeration (Fig. 4). Depending on the solubility, the polysaccharide chain can adopt a coiled conformation, resulting in a colloidal system with agglomeration during the casting film. This is expected to occur manly with GLM, as observed in other studies (Nascimento et al. 2019). After the quaternization reaction, the film morphology changed greatly (Fig. 4). Both QGLM and QCHI showed a smoother surface, without formation of agglomeration. This may be related to the increased solubility of the derivatives, which showed a better filming ability. These results are important from the point of view of commercial applications as fruit coatings. Polymers with low solubility tend to form irregular films, resulting in an irregular coating that reduces its efficiency on maintaining fruit quality (Souza et al. 2023).

Mechanical property

The parent polymers CHI and GLM films showed high tensile strength (TS) values, having the CHI the greatest value (Table 1). On the other hand, the modified polymers showed low tensile strength in comparison with the parent polymers, with the QCHI sample reaching the lowest value. As natural

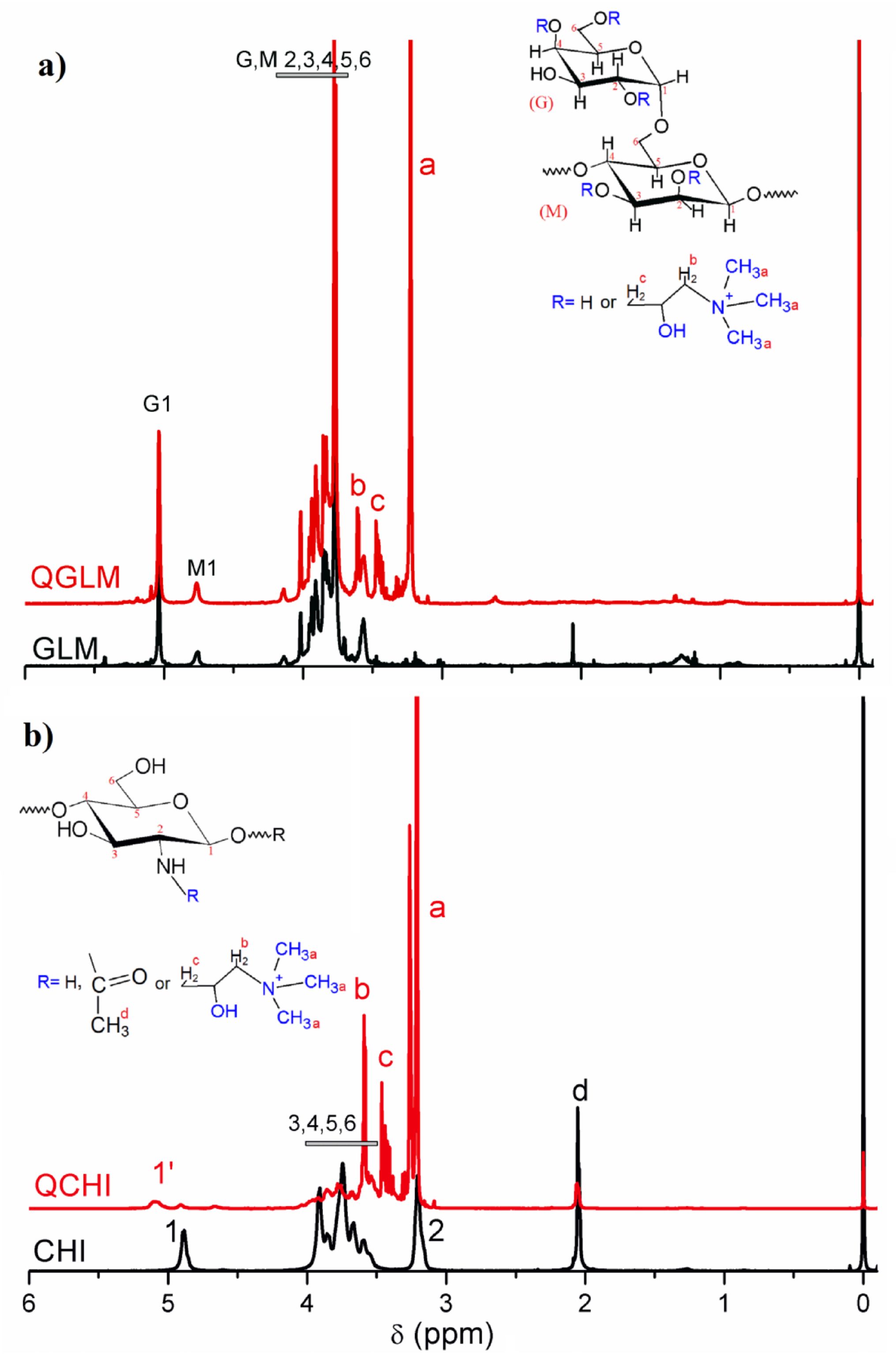

Fig. 2 ^{1}H NMR spectra for the polysaccharide (**a**) galactomannan and its quaternary derivative; and (**b**) chitosan and its quaternary derivative

polymers, several factors can affect the mechanical performance of chitosan and galactomannan, mainly the material source (Dos Santos et al. 2015). Further, physical chemistry characteristics influence greatly the mechanical property as interchain interactions, molecular weight, chain structure and conformation, water and plasticizer contents. Evidently, the chemical modification affects greatly the interchain interaction, mainly for polyelectrolyte, influencing the

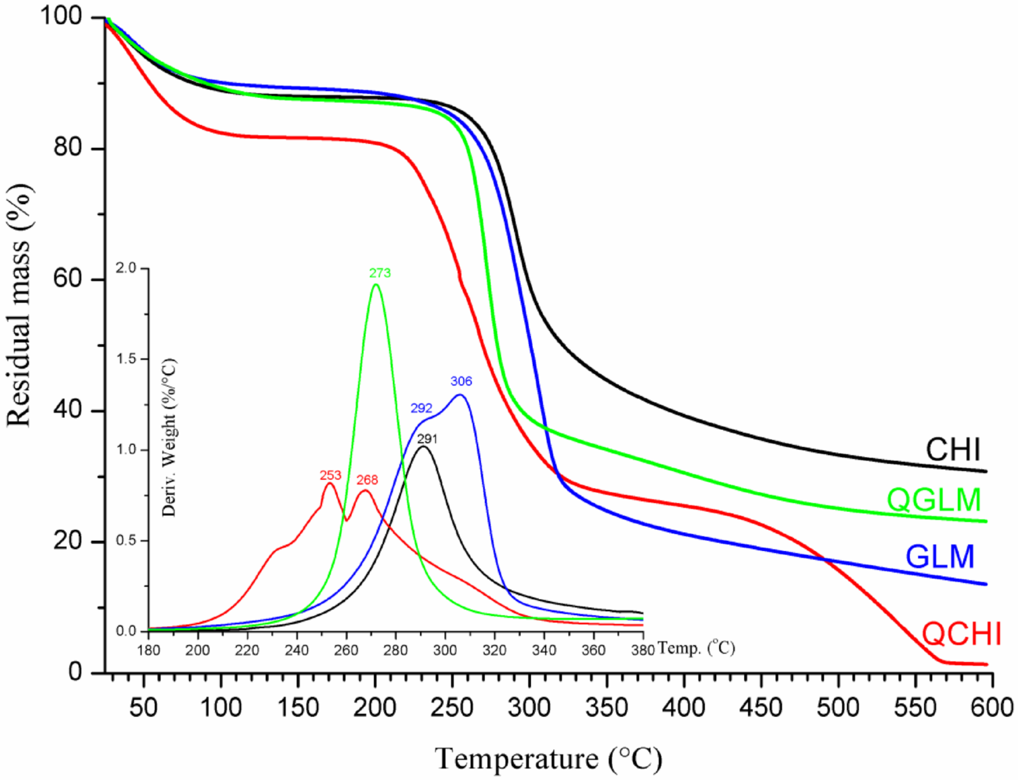

Fig. 3 Thermogravimetric curve for the polysaccharides chitosan, galactomannan and quaternary derivatives in N_2 atmosphere and heating rate of 10.0 °C min^{-1}. Insert: Corresponding DTG curves in the range 180–380 °C

tensile strength. In a previous study with different chitosan derivative, the quaternization process decreased the tensile strength for the parent chitosan film but increased for the alkylated ones (Britto and Assis 2007b). In general, all polysaccharide material exhibits a non-linear viscoelastic behavior, with a stress versus strain curve typical of brittle material. The elongation, or maximum strain, reflects the same behavior, with the parent polymers having higher values in comparison with the modified polymers (Table 1). Despite the specific TS and elongation values for each material, all of them showed good ability to form film suitable to edible coating.

Film water vapor permeability

The WVP, calculated according to Eq. 3, was shown in Table 1. The analysis shows that the WVP for the chemically modified GLM is similar to that non-modified one. Generally, the introduction of a quaternary moiety in the polysaccharide chain results in a more hydrophilic material due to the cationic character of the generated polyelectrolyte. However, depending on the degree of substitution such change is not imparted, which may be occurring with GLM. Although the WVP can vary depending on the GLM source (Dos Santos et al. 2015), the values found are similar to observed in other studies (Almeida et al. 2021).

Regarding the polysaccharide CHI, a different aspect was found, in which the chemical modification had a deep impact on the WVP. The WVP increased greatly for the derivative QCHI, indicating that the chitosan chain was deeply modified by the introduction of quaternary moiety, which resulted in a more hydrophilic polyelectrolyte (Britto and Assis 2007a). In agreement, WVP values for CHI is similar to observed in other studies (Kołodziejska and Piotrowska 2007).

Comparing the WVP for the two modified polysaccharides, QGLM may be more appropriated to reduce weight loss by water transpiration due to its low hydrophilic character in comparison with QCHI. However, for edible coating several parameters must evaluated to get most adequate.

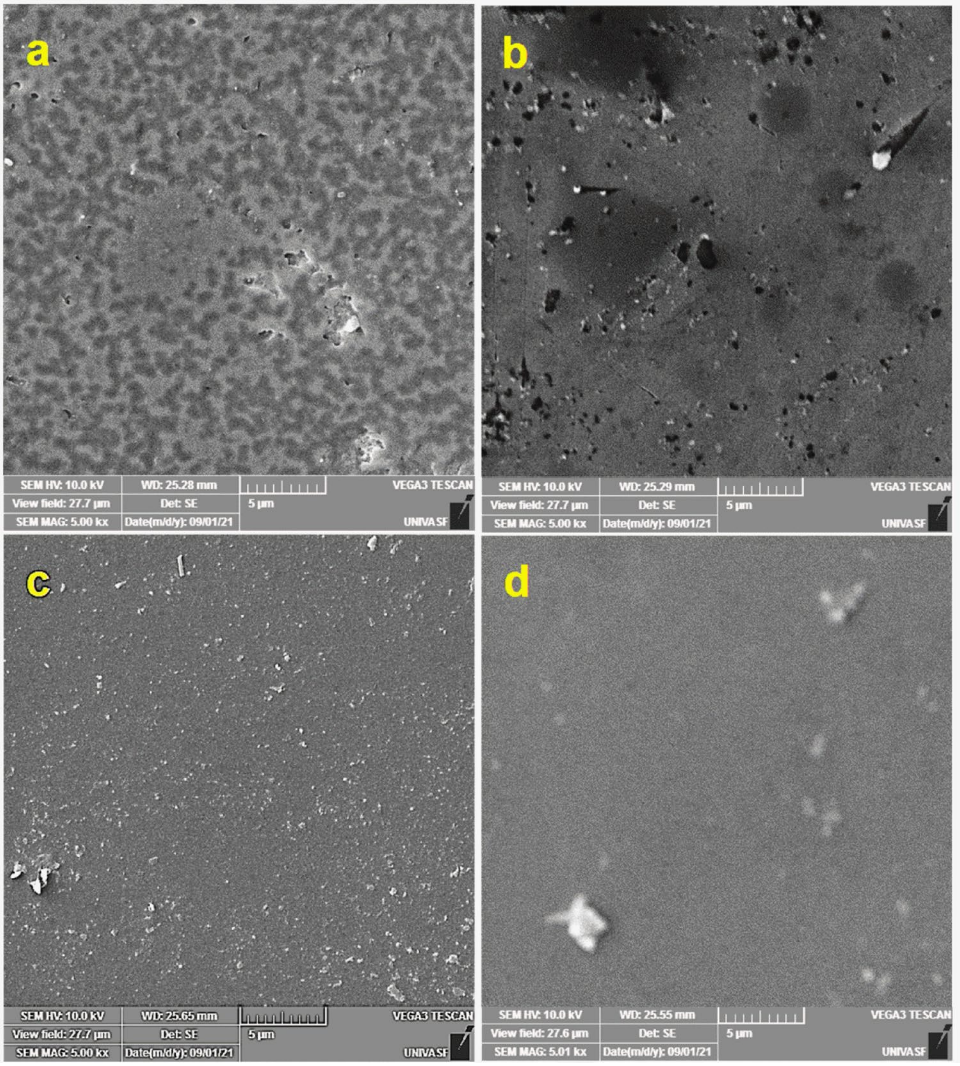

Fig. 4 SEM images for the polysaccharides chitosan, galactomannan and quaternary derivatives deposited on glass slides

Table 1 Average values ± standard deviation of mechanical stress x strain parameters (tensile strength and maximum deformation yield), Water Vapor Permeability (WVP) and Swelling degree for galactomannan (GLM), chitosan (CHI) and its respective quaternary salts (QGLM) and (QCHI).

Film	Tensile Stress* (MPa)	Elongation (%)	WVP (g mm kPa^{-1} h^{-1} m^{-2})	Swelling degree (%)	
				DS_{eth}	$DS_{e/w}$
GLM	24.1 ± 4.3^b	8.3 ± 2.1^b	2.09 ± 0.52^b	5.6 ± 1.1^a	19.3 ± 2.9^b
QGLM	18.7 ± 1.5^b	2.3 ± 1.0^c	1.89 ± 0.24^b	0.6 ± 0.1^c	72.4 ± 3.2^a
CHI	39.3 ± 9.0^a	14.8 ± 1.0^a	3.24 ± 0.30^a	4.5 ± 0.4^a	80.2 ± 8.0^a
QCHI	7.4 ± 2.3^c	8.8 ± 2.2^b	4.04 ± 0.44^a	2.3 ± 0.4^b	–

*Averages followed by the same letter are statistically equal according to Tukey test (5%)

Swelling degree

The degree of swelling, determined in anhydrous ethanol (DS_{eth}) and ethanol/water ($DS_{e/w}$), provides additional information about the hydrophilic characteristics of chitosan and its derivatives (Table 1). The analysis shows that the relative amount of absorbed anhydrous ethanol decreases for the derivatives in comparison with the parent polymers. The introduction of quaternary moiety increases the hydrophilic character of the polysaccharides, resulting in charged polyelectrolyte with low affinity to more apolar species as ethanol. However, the presence of methyl group also influences the hydrophobic character, contributing to ethanol absorption. This fashion and values were reported before (Britto and Assis 2010). For the $DS_{e/w}$ analysis, it is observed that absorbed amount is greatly superior that found for DS_{eth}, indicating the hydrophilic character of these materials. In agreement, QCHI become soluble in the mixture ethanol/water, having the greatest hydrophilic character. This confirms that CHI and its derivatives are more hydrophilic materials in comparison with GLM in accordance with discussed for WVP values.

Table 2 Average values ± standard deviation of physiological quality of uncoated (CTL) and coated 'Junko' acerolas stored for 18 days at 12 °C. *Averages followed by the same letter are statistically equal according to Tukey test (5%)

Coat	Mass loss* (%)	Skin color			Respiration rate (mol of CO_2 /kg h)	Force (*N*)	Vit. C (mg/100 g)	Brix (º)
		L	C	ºh				
CTL	-12.3 ± 1.9^{a}	38 ± 4^{a}	21 ± 4^{a}	45 ± 10^{a}	$0.99\ 10^{-2} \pm 3.36\ 10^{-4b}$	42.7 ± 0.4^{b}	1232 ± 80^{a}	7.60 ± 0.14^{a}
GLM	-11.0 ± 4.3^{a}	38 ± 3^{a}	22 ± 0.3^{a}	51 ± 3^{a}	$1.01\ 10^{-2} \pm 3.73\ 10^{-4b}$	42.9 ± 0.5^{ab}	1261 ± 22^{a}	7.34 ± 0.11^{b}
QGLM	$- -10.5 \pm 3.0^{a}$	40 ± 3^{a}	23 ± 3^{a}	62 ± 9^{a}	$1.06\ 10^{-2} \pm 1.38\ 10^{-4ab}$	43.2 ± 0.5^{ab}	1275 ± 21^{a}	7.14 ± 0.07^{c}
CHI	-9.8 ± 6.3^{a}	38 ± 2^{a}	22 ± 2^{a}	50 ± 14^{a}	$1.02\ 10^{-2} \pm 6.92\ 10^{-4b}$	42.6 ± 0.5^{b}	1247 ± 17^{a}	7.35 ± 0.07^{b}
QCHI	-7.8 ± 4.2^{a}	40 ± 3^{a}	23 ± 3^{a}	60 ± 14^{a}	$1.10\ 10^{-2} \pm 1.96\ 10^{-4a}$	43.7 ± 0.3^{a}	1258 ± 48^{a}	7.20 ± 0.06^{bc}
CV (%)	32.50	6.56	10.44	16.46	3.38	0.87	6.49	1.04

Physiological evaluation of coated acerola

Some acerola physiological parameters showed significant changes in response to fruit coatings, while other parameters were not affected by coating treatments. Fruit mass loss and skin color (luminosity, L; chroma, C and Hue angle, h) were not affected by coating treatments (Table 2). However, both parameters showed a trend of lower mass loss and red color (Hue angle) development in response to coating, mainly in response to QGLM and QCHI coating, compared to control uncoated fruit. Although there are only a few studies on the application of edible coatings on acerola fruit, statistical differences between coated and uncoated fruit quality have been reported (Maciel et al. 2004; Abreu 2019). Indeed, these studies have reported fruit mass loss of 18.6% for uncoated and 12.4% for coated acerola fruit after 15 days of storage at 5 °C. In other study, a nanocomposite edible film developed with acerola puree, alginate, cellulose whiskers or montmorillonite resulted in a weight loss of 7.2–4.4%, compared to 11.1% weight loss in uncoated acerola stored for 7 days at 6 °C (Azeredo et al. 2012). Therefore, coatings can have a great effect on reducing acerola weight loss, which has been reported to reach values as high as 20% during 14 days of storage at 10 °C (Ribeiro and Freitas 2020). Considering the results observed in our study, coated acerola fruit reached about 10% weight loss, suggesting that improvements in the coating composition can add beneficial effects on reducing fruit weight loss during storage by reducing fruit mass loss in response to transpiration and respiration (Ribeiro and Freitas 2020; Britto and Assis 2012; Galvão et al. 2024).

Acerola respiration rate was lower in uncoated, GLM and CHI coated fruit, compared to QCHI coated fruit after 18 days of storage at 12 °C (Table 2). Acerola is a climacteric fruit, characterized by an increase in respiration rate after harvest, reaching a peak and decreasing afterwards during storage and senescence (Ribeiro and Freitas 2020). Therefore, the lower respiration rate observed in uncoated acerolas is possibly the result of the post-climacteric peak decrease in respiration rate that leads to fruit senescence (Ribeiro and Freitas 2020). On the other hand, the higher respiration rate observed in the QCHI coated acerola suggests that the fruit were at the developmental stage that precedes the climacteric peak, showing that QCHI effectively delayed fruit ripening and senescence, compared to control uncoated fruit. Indeed, previous studies have reported similar behavior for uncoated and coated fruits during storage (Tokatlı and Demirdöven 2020). Efficient coatings reduce the internal O_2 concentration in the fruit, inhibiting respiration and delaying ripening and senescence, which extends fruit postharvest life (Alves et al. 1995).

Acerola texture was lower in uncoated and CHI coated fruit, intermediate in GLM and QGLM coated fruit, and higher in QCHI coated fruit (Table 2). Similar to the result observed for the respiration rate, fruit texture also shows that QCHI coating effectively delayed fruit ripening, maintaining higher flesh firmness, than uncoated fruit during 18 days of storage at 12 °C (Table 2). In addition, QCHI coated acerola had a firmer texture that is highly desirable to reduce mechanical damage during handling and transportation (Ribeiro and Freitas 2020).

Acerola vitamin C content was not affected by coating treatments during 18 days of storage at 12 °C (Table 2). Usually, vitamin C content decreases during fruit ripening (Maciel et al. 2004; Minh et al. 2019) due to biochemical oxidation (Ribeiro and Freitas 2020), which was not observed in our study.

The soluble solids content (°Brix) was higher in uncoated, intermediate in non-modified coated (CHI and GLM), and lower in quaternary derivative coated (QGLM and QCHI) acerola fruit (Table 2). Soluble solids content has been reported to increase during acerola fruit ripening characterized from changes in skin color from green to red (Ribeiro and Freitas 2020). Indeed, considering that soluble solid content is expected to increase during acerola fruit ripening, these results, together with respiration rate and flesh firmness, suggest that QGLM and QCHI coatings had a positive effect on inhibiting acerola ripening and senescence, extending fruit postharvest life (Ribeiro and Freitas 2020).

Conclusion

It was possible to obtain films from chemically modified GLM and CHI by quaternization reaction with GTMAC, which was confirmed by spectroscopy analyses. The new material has good thermal, mechanical, morphological and hydrophilic characteristics, allowing its use as edible fruit coatings. The shifting in the post-climacteric peak pattern for respiration rate indicated clearly that the coated acerola fruit with quaternary modified materials restrained the ripening and senescence compared to uncoated and non-modified GLM or chitosan coated fruit. Modified polysaccharide has potential to reduce postharvest losses and even reduce the fungal contamination; an issue to be explored in future studies.

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Data availability The data that support the findings of this study are available from the corresponding author, Dr. de Britto, upon reasonable request.

Code availability Not applicable.

Declarations

Conflict of interest The authors declare no conflict of interest, financial or otherwise.

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References

Abreu CTA (2019) Development of edible biofilm enriched with red propolis applied to the coating of acerola (*Malpighia emarginata*). RIUFAL Repositório Institucional da UFAL. http://www.repositorio.ufal.br/handle/riufal/5217. Accessed 19 May 2025

Almeida LBS, Figueiredo EAT, Dias FGB, Santos FMS, Fernandes BD, Vicente AA, Cerqueira MA, Silva ALC, Vale DA, Souza BWS (2021) Antimicrobial properties of chitosan and galactomannan composite coatings and physical properties of films made thereof. Future Foods 3:100028. https://doi.org/10.1016/j.fufo.2021.100028

Alves RE, Chitarra AB, Chitarra MIF (1995) Postharvest physiology of acerola (Malpighia emarginata DC.) fruits: Maturation changes, respiratory activity and refrigerated storage at ambient and modified atmospheres. Acta Hortic 370:223–229. https://doi.org/10.17660/ActaHortic.1995.370.35

Azeredo HMC, Miranda KWE, Ribeiro HL, Rosa MF, Nascimento D (2012) Nanoreinforced alginate–acerola puree coatings on acerola fruits. J Food Eng 113:505–510. https://doi.org/10.1016/j.jfoodeng.2012.08.006

Britto D, Assis OBG (2007a) A novel method for obtaining a quaternary salt of chitosan. Carbohyd Polym 69:305–310. https://doi.org/10.1016/j.carbpol.2006.10.007

Britto D, Assis OBG (2007b) Synthesis and mechanical properties of quaternary salts of chitosan-based films for food application. Int J Biol Macromol 41:198–203. https://doi.org/10.1016/j.ijbiomac.2007.02.005

Britto D, Assis OBG (2010) Hydrophilic and morphological aspects of films based on quaternary salts of chitosan for edible applications. Packag Technol Sci 23:111–119. https://doi.org/10.1002/pts.884

Britto D, Assis OBG (2012) Chemical, biochemical, and microbiological aspects of chitosan quaternary salt as active coating on sliced apples. Food Sci Technol 32:599–605. https://doi.org/10.1590/S0101-20612012005000089

Britto D, Campana Filho SP (2004) A kinetic study on the thermal degradation of N,N,N-trimethyl chitosan. Polym Degrad Stab 84:353–361. https://doi.org/10.1016/j.polymdegradstab.2004.02.005

Britto D, Campana Filho SP (2007) Kinetics of the thermal degradation of chitosan. Thermochim Acta 465:73–82. https://doi.org/10.1016/j.tca.2007.09.008

Cerqueira MA, Souza BWS, Simões J, Teixeira JA, Domingues RM, Coimbra MA, Vicente AA (2011) Structural and thermal characterization of galactomannans from non-conventional sources. Carbohyd Polym 83:179–185. https://doi.org/10.1016/j.carbpol.2010.07.036

Cerqueira MA, Lima AM, Teixeira JA, Moreira RA, Vicente AA (2009) Suitability of novel galactomannans as edible coatings for tropical fruits. J Food Eng 94:372–378. https://doi.org/10.1016/j.jfoodeng.2009.04.003

Dos Santos VR, Souza BW, Teixeira JA, Vicente AA, Cerqueira MA (2015) Relationship between galactomannan structure and physicochemical properties of films produced thereof. J Food Sci Technol 52(12):8292–8299. https://doi.org/10.1007/s13197-015-1961-6

Ferreira MS, Fai AEC, Andrade CT, Picciani PH, Azero EG, Gonçalves ÉC (2016) Edible films and coatings based on biodegradable residues applied to acerolas (Malpighia punicifolia L.). J Sci Food Agric 96:1634–1642. https://doi.org/10.1002/jsfa.7265

Galvão MBF, Stamford TCM, de Melo FABR, de Lima GS, de Oliveira CEV, de Oliveira ILN, Bidô RCA, Pintado MME, de Oliveira MEG, Stamford TLM (2024) Development of edible coatings based on pineapple peel (Ananas comosus L.) and yam starch (Dioscorea alata) for application in acerola (Malpighia emarginata DC). Foods 13:2873. https://doi.org/10.3390/foods13182873

Huang J, Cheng Z-H, Xie H-H, Gong J-Y, Lou J, Ge Q, Wang Y-J, Wu Y-F, Liu S-W, Sun P-L, Mao J-W (2014) Effect of quaternization degree on physio chemical and biological activities of chitosan from squid pens. Int J Biol Macromol 70:545–550. https://doi.org/10.1016/j.ijbiomac.2014.07.017

Kołodziejska I, Piotrowska B (2007) The water vapour permeability, mechanical properties and solubility of fish gelatin–chitosan films modified with transglutaminase or 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) and plasticized with glycerol. Food Chem 103:295–300. https://doi.org/10.1016/j.foodchem.2006.07.049

López-Franco YL, Cervantes-Montaño CI, Martínez-Robinson KG, Lizardi-Mendoza J, Robles-Ozuna LE (2013) Physico chemical characterization and functional properties of galactomannans from mesquite seeds (Prosopis spp.). Food Hydrocol 30:656–660. https://doi.org/10.1016/j.foodhyd.2012.08.012

Maciel MIS, Lima VLAG, Santos ES, Lima MS (2004) Effects of biofilm and refrigeration on acerola postharvest conservation. Rev Bras Frutic 26:168–170. https://doi.org/10.1590/S0100-29452004000100044

Minh NP, Trang NTT, Mai PX, Pha PTL, Son DT (2019) Synergistic combination of chitosan and cinnamid acid as edible coating to extend self-life of acelora cherry (Malpighia emarginata) fruit. J Global Pharma Technol 11:210–215

Mourya VK, Inamdar NN (2009) Trimethyl chitosan and its applications in drug delivery. J Mater Sci-Mater Med 20:1057–1079. https://doi.org/10.1007/s10856-008-3659-z

Nascimento JADA, Gomes LKS, Duarte DS, Lima MACD, Britto D (2019) Stability of nanocomposite edible films based on polysaccharides and vitamin C from agro-industrial residue. Mater Res 22:1–10. https://doi.org/10.1590/1980-5373-mr-2019-0057

Pal S, Mal D, Singh RP (2007) Synthesis and characterization of cationic guar gum: a high-performance flocculating agent. J Appl Polym Sci 105:3240–3245. https://doi.org/10.1002/app.26440

Ribeiro BS, Freitas ST (2020) Maturity stage at harvest and storage temperature to maintain postharvest quality of acerola fruit. Sci Hortic-Amsterdam 260:108901. https://doi.org/10.1016/j.scienta.2019.108901

Ruihua H, Bingchao Y, Zheng D, Wang B (2012) Preparation and characterization of a quaternized chitosan. J Mater Sci 47:845–851. https://doi.org/10.1007/s10853-011-5862-4

Souza GPG, Duarte DS, Souza AVV, Ribeiro Júnior PM, Lima MAC, Britto D (2023) Active antifungal edible coating based on nanocomposite cast films from galactomannan. Int J Postharvest Technol Innov 9:1–19. https://doi.org/10.1504/IJPTI.2022.10051231

Thombare N, Mahto A, Singh D, Chowdhury AR, Ansari MF (2023) Comparative FTIR characterization of various natural gums: a criterion for their identification. J Polym Environ 31:3372–3380. https://doi.org/10.1007/s10924-023-02821-1

Tokatlı K, Demirdöven A (2020) Effects of chitosan edible film coatings on the physicochemical and microbiological qualities of sweet cherry (Prunus avium L). Sci Hortic-Amsterdam 259:108656. https://doi.org/10.1016/j.scienta.2019.108656

Vasconcelos CL, Bezerril PM, Pereira MR, Ginani MF, Fonseca JLC (2011) Viscosity-temperature behavior of chitin solutions using lithium chloride/DMA as solvent. Carbohydr Res 346:614–618. https://doi.org/10.1016/j.carres.2010.12.016

Yang X, Wang B, Qiao C, Li Z, Li Y, Xu C, Li T (2020) Molecular interactions in N-[(2-hydroxyl)-propyl-3-trimethyl ammonium] chitosan chloride-sodium alginate polyelectrolyte complexes. Food Hydrocol 100:105400. https://doi.org/10.1016/j.foodhyd.2019.105400