



A sustainable approach on the potential use of kale puree in edible wraps

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ARTICLE INFO

Keywords:

Biopolymer
Kale films
Edible wraps
Alginate
Mechanical properties

ABSTRACT

Edible films can be used to prevent food spoilage, and investigations in this regard are paramount. When prepared alongside biopolymers, these materials become totally biodegradable in a short period of time, decreasing the amount of solid residues discarded into the environment. The ingestion of fruits and vegetables has increased in the last decades due to significant health benefits, and their durability comprises an important parameter for their marketing and use. Vegetables come in a variety of colors, sizes and shapes, comprising relevant features for their commercialization and packaging and for final consumers. In this regard, kale leaves are highly consumed in Brazil and new alternatives to improve their physical and organoleptic characteristics for novel applications, such as food wraps and in the replacement of high perishability leaves, are of interest in this scenario. Thus, the aim of the present study was to develop kale puree and sodium alginate films and evaluate their solubility, mechanical and thermal properties and water vapor permeability, focusing on improving their physical and organoleptic properties. The films were prepared by casting sodium alginate solutions with the addition of kale puree employing a film generator. Puree incorporation reduced film water vapor permeability and solubility. Pure alginate films presented a contact angle of $50 \pm 1^\circ$, increasing to $62 \pm 2^\circ$ with the addition of kale puree. The same was noted for the alginate film that, when cross-linked with kale puree displayed an angle increase of $72 \pm 5^\circ$. This behavior may be due to interactions between these components and the hydrophobic phases. Calcium chloride was added for film crosslinking, contributing to biopolymer chain separation and mobility. This study highlights important issues concerning the use of vegetables in the production of edible films, especially biodegradable films, and emphasizes the importance of their development, due to reduced environmental impacts, low costs and the fact that they comprise a renewable resource.

1. Introduction

The type of biopolymer employed in film fabrication influences biodegradable film the composition and functional properties. Proteins and polysaccharides produce films with high mechanical performance, also comprising adequate protection against aromatic compounds and low molar mass gasses, such as oxygen and carbon dioxide, although they are moisture-sensitive due to their hydrophilic nature (Boeira et al., 2022; Saranti, Melo, Cerqueira, Aouada & Moura, 2021).

The use of fruits and vegetables, mainly in pureed form, has been investigated as an alternative source of biopolymers for the development of biodegradable and edible films (Oldoni et al., 2021; Sanchez, Pinzon & Villa, 2022; Wang & Zhao, 2021). Vegetable-based films, for example, display low to moderate oxygen permeability and acceptable mechanical properties, making them a viable alternative for the elaboration of edible packaging and coatings (Jiang et al., 2021; Torres-León et al.,

2018). Furthermore, fruits and vegetables are usually rich in polysaccharides, capable of acting as filmogenic solutions, as well as sugars and organic compounds that can act as plasticizers. Polysaccharides also enhance tensile film properties, making them more suitable for applications such as wraps.

The specific application of fruit purees is more adequate than powder, associated to the presence of film-forming polysaccharides, such as pectin and starch (Kaya & Maskan, 2003), and is an interesting way of combining the mechanical and barrier polysaccharide properties with the sensory and nutritional properties of fruits.

Kale presents the highest antioxidant capacity among *Brassica* vegetables (Fahey, 2015). The health benefits of polyphenols stem from their function as antioxidants and their participation in gene expression, cell adhesion signaling, and cell adhesion by cell receptor and transporter binding. Elderberries, onions, and kale, as well as herbs and spices, comprise some of the highest sources of

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flavonols (Biegańska-Marecik, Radziejewska-Kubzdela & Marecik, 2017; Fernandes, Guedes de Pinho, Valentao, Pereira & Andrade, 2009; Szutowaska, Rybicka, Pawlak-Lemańska & Gwiazdowska, 2020). However, scarce research is available on the effect of these compounds in kale. In this regard, Murtaza et al. (2005) report that antioxidant effects and ascorbic acid, carotenoid, and total phenol contents in kale differ between genotypes, with wild genotypes displaying higher antioxidant activity levels and total phenol contents than cultivated genotypes. In this regard, kale films are particularly interesting for replacing raw kale leaves in preparing stuffed kale rolls, a traditional Eastern-European dish, as they are highly shelf-life stable, display a uniform texture, pronounced tensile properties and tailorable dimensions (Rodríguez, Sibaja, Espitia & Otoni, 2020).

Sodium alginate is a copolymer composed of 1,4-β-D-manuronic (M) and 1,4-α-L-guluronic (G) acid monomeric units distributed in blocks along their chains. This polysaccharide is obtained as alginic acid from the cell walls of brown seaweed, which is subsequently converted into sodium alginate applying chemical processes. Alginate displays antimicrobial activities, and is used as a wound dressing, coating, and additive in medical products and foods, also acting as a selective barrier for moisture regulation while still allowing gas exchanges (Chen et al., 2021; da Silva Fernandes, de Moura, Glenn & Aouada, 2018; Lutfi, Kalim, Shahid & Nawab, 2021). Moreover, alginate is easily cross-linkable with calcium ions, making it more resistant to contact with moist components, which is especially interesting concerning wraps, which are a part of multicomponent foods usually containing moist components, such as meat and sauces.

In this context, this study aims to develop and characterize biodegradable films prepared using kale (*Brassica oleracea L. variety acephala*) and sodium alginate, displaying similar or superior properties to fresh kale, such as a characteristic color, strength, elongation, and thickness. They are also hydrophobic, making them interesting for applications in the food sector, such as kale wraps.

2. Material and methods

2.1. Kale blanching and homogenization

A total of 20 g of kale leaves (*Brassica oleracea L. variety acephala*) (Horta dos Aposentados – Ilha Solteira-SP) were washed under running water to remove coarse dirt and immersed in a 1 (v/v)% hypochlorite solution (Sigma Aldrich) consisting of an active chlorine content equivalent between 2% and 2.5% w/w for 12 min, to reduce microbial loads. A second wash was conducted under running water for 12 min to remove hypochlorite residues and impurities.

The kale leaves were left in deionized water (65 °C) for 5 min for blanching (enzymatic inactivation, to avoid degradation reactions resulting from enzymatic activity) and then placed in an ice bath. After blanching, the leaves were homogenized with distilled water in a high-speed liquefier (Vitamix, Vitamix Corp., Cleveland, OH, USA) at 5000 rpm for 10 min. The obtained kale puree (KP) was filtered (0.1 mm) for better incorporation into the film forming dispersion (FD).

2.2. Film preparation

Four films were prepared in two stages, namely stage I, consisting of pure sodium alginate film (SA) and sodium alginate mixed with the kale puree (SA/KP) and stage II, consisting of cross-linked sodium alginate puree (SA-Ca) and cross-linked sodium alginate mixed with kale puree (SA/KP-Ca).

The FDs were prepared by dissolving sodium alginate (Cromoline, 2% w/v) in water or kale puree (5% w/v in relation to quantified polymer) under mechanical agitation at 1500 rpm and 25 °C ± 2 °C. Thereafter, the FDs were poured onto a polyethylene substrate. For cross-linking, the films were immersed in a calcium chloride 2% w/v solution (Vetec Química Fina) for 1 min.

The dried specimens were left resting for 48 h before analysis at 50% relative humidity (RH).

2.3. Color

Color analyses were performed using a Minolta Colorimeter employing the CIELAB (or CIE L* A* B*) system, which defines three-dimensional coordinates, where L* represents luminosity, with values ranging from 0 (black) to 100 (white), and A* and B* represents color coordinates, which indicate values associated with red/green and yellow/blue, respectively. All analyses were conducted in triplicate (Colucci & Rodrigues, 2022).

2.4. Total solids

Samples measuring 2.5 cm in diameter were weighed and dried in an oven (Lab-Line, Squaroid, USA) at 105 °C for 24 h. The final dry mass was then quantified, and film moisture content (W) was obtained according to Eq. (1):

$$W = (M_o - M_i)/M_o \quad (1)$$

where W comprises the film moisture [%], M_o consists in the initial dry mass [g], and M_i is the final dry mass of the sample [g].

2.5. Film morphology

A cryogenic fracture microscopy analysis was conducted employing an EVO LS15 ZEISS computerized scanning electron microscope (SEM) model operated at 7 kV at a voltage range from 5.00 to 10.00 kV. The films were fixed on a double-faced carbon tape and metalized for 1.5 min using a sputter coater, with the deposit of a thin gold layer on the surface to be analyzed (improved conductivity). The films were placed in a glass desiccator for 24 h to eliminate any film moisture and then cut for subsequent analysis.

2.6. Film thickness determinations

Film thickness was obtained using a micrometer (No. 7326, Mitutoyo Corp., Kanagawa, Japan, with an accuracy of 0.001 mm) at five points around the films and fresh kale leaves. The thickness measurements were used to assess subsequent mechanical test results and water vapor permeability values (WVP) (Saranti et al., 2021)

2.7. Water vapor permeability (WVP) determinations

An adapted ASTM E96-8055 (ASTM, 1980) method detailed by McHugh, Avena-Bustillos and Krochta (1993) was applied. Circular samples 5 cm in diameter were fixed in permeation cells containing 6 mL of distilled water, to promote an increase in RH and provide a moisture difference between the cell and the external environment. This test was conducted in an oven (QUIMIS-Q317M) at 25 °C ± 2 °C and 50% ± 3% RH. The WVP was obtained based on periodic weighing throughout 24 h. All analyses were conducted in triplicate (Saranti et al., 2021)

2.8. Mechanical properties

The mechanical strength of the prepared films was determined according to a stress-strain curve obtained employing the ASTM D882-97 method.

Samples 100 mm long and 13 mm wide were stored at 25 °C and 50 ± 2% RH for 48 h prior to the experiment. The analysis was performed using an Instron equipment (Model 3369, Instron Corp., Canton, Mass., USA) operated with a 100 N load cell and a pulling speed of 10 mm min⁻¹.

Stress (σ) was determined using Eq. (2),

$$\sigma = F \cdot S^{-1} \quad (2)$$

where F is the value of the exerted rupture force, and S is the sectional film area .

Deformation (ϵ) was calculated using Eq. (3), where L and L0 comprise the film elongation length during the experiment and initial film length, respectively.

$$\epsilon = \ln\left(\frac{L}{L_0}\right) * 100 \quad (3)$$

The elastic modulus (E) was calculated using the initial slope of the obtained stress–strain curve (Saranti et al., 2021)

2.9. Contact angle

Film hydrophobicity was analyzed employing a contact angle instrument (KSV Instruments, Helsinki, Finland).

A drop (5–9 μ L) of a standard liquid (deionized water) was deposited onto the film surfaces using a precision syringe. The contact angle value was calculated by averaging the angles measured at the right and left ends of the drop over a 60 s time interval. Each sample was tested six times at 25 °C (Saranti et al., 2021)

2.10. Water solubility

The method described by Pena-Serna and Lopes-Filho (2013) was applied to determine water solubility, defined as the amount of dry matter solubilized after the material remains submerged in water for 4 h. The films were cut into 0.5 g samples and dried in an oven at 105 °C for 24 h to obtain the initial mass (m_i). They were then immersed in 50 mL of deionized water at 25 °C \pm 2 °C for 24 h under agitation at 100 rpm before drying at 105 °C until no further change the weight. The films were then placed in a desiccator for 1 h before final weighing (final mass, m_f). The insoluble matter content is defined as

$$Mi = \frac{m_f}{m_i} * 100 \quad (4)$$

2.11. Swelling degree in water

Swelling values were measured to obtain the water capacity of the insoluble films (stage II). Dry samples (2.5 \times 2.5 cm) were weighed (m_o) and immersed in 20 mL of deionized water under gentle agitation at 25 °C for 24 h. During this timeframe, the samples were withdrawn from the water at 1 h intervals, and excess moisture was removed by sandwiching the film between two filter paper sheets to determine the total mass (m_u). The samples were then submerged in water for subsequent weighing.

The swelling degree was calculated using the ratio between the swollen mass (Mt) and the dry mass (Ms):

The percentage (%) of swelling values were determined using Eq. (5):

$$GI = \frac{Mt}{Ms} \quad (5)$$

where Mt represents the swollen mass after 24 h and Ms represents the dry mass. All tests were performed three times.

2.12. Visual appearance and potential application

Visual and tactile analyses were performed subjectively (Gontard, 1991; Monterrey & Sobral, 1999). The films were evaluated concerning homogeneity (non-observance of insoluble parts or different colors), continuity (absence of breaks or fractures after solvent evaporation), flexibility, detachment ease from the support, and handling ease, as well as the potential application of the new material. Five judges were selected for an analysis of the following subjective facts: were the films homogeneous, continuous, similar to kale and can wraps be prepared with the films.

Table 1

Color parameters - Luminance (L*), green (-a*) and yellow (b*).

Samples	L*	A*	B*
Kale leaf	46.36 \pm 1.4 ^c	-15.00 \pm 0.9 ^b	19.93 \pm 1.0 ^b
SA/KP	54.04 \pm 0.3 ^b	-18.79 \pm 0.5 ^a	47.42 \pm 0.3 ^a
SA/KP-Ca	58.60 \pm 0.3 ^a	-15.25 \pm 0.3 ^b	48.45 \pm 0.5 ^a

*Means followed by the same letter do not differ statistically, by Tukey's test at 5% probability. Sodium alginate with kale puree film (SA/KP); Cross-linked sodium alginate with kale puree film (SA/KP-Ca).

2.13. Statistical analyses

An analysis of variance was performed, and a means comparison was performed applying the Tukey test at 5% probability using the Sisvar® statistical program, at a 95% significance level.

3. Results and discussion

3.1. Color analysis

Sample colors were described using the International Lighting Commission (CIE) system, with the green color of the kale leaves indicating the presence of chlorophyll and intensity directly associated to pigment concentrations. The formed films displayed a homogeneous appearance, with a dark green color and strong leaf odor. In this context, a simple colorimeter measurement provides parameters capable of swiftly and cost-effectively estimating what is being analyzed, as the number of repetitions required and the amount of destroyed product are both reduced. The determined color properties were used to compare the color parameters of the kale films with those of raw kale leaves (the reference application). The obtained color values are depicted in Table 1.

A* values, which indicate a green coloration, were similar between the leaves and the films, with the SA/KP sample displaying a lighter color than the other samples, while leaf B* values varied widely among films due to some yellowish film parts. The reticulated film presented high luminosity values due to its reticulation.

3.2. Moisture and total solids

The most applied drying method in the food industry is oven drying, which is based on water removal using heat. This is an inexpensive and simple method that requires only an oven, an analytical balance, and crucibles to place the samples. However, drying accuracy is affected by several components, such as temperature, sample particle size, sample number and placement in the oven, and crust formation on the sample surface. To evaporate water at atmospheric pressure in a simple oven, the drying temperature must be set at slightly above 100 °C, preserving the sample and preventing the formation of surface crusts, which hinders water evaporation. Table 2 presents the humidity values determined herein.

Film humidity was relatively low when compared to kale leaves, due to the drying process. Kale leaf sample humidity was higher than film humidity, due to the high amount of water found in leaves. The SA/KP-Ca sample (13%), which presented lower hygroscopicity (Fig. 7) due to cross-linking, also presented low moisture content.

3.3. Film morphology

Figure 1 depicts the superficial morphology of the non-cross-linked films. Image A (alginate film) indicates a smooth and homogeneous surface. Image B, which displays the polymeric alginate matrix surface mixed with kale puree, present some surface agglomerates, very similar to those reported by Fernando (2014) & Alexandre (2016) for

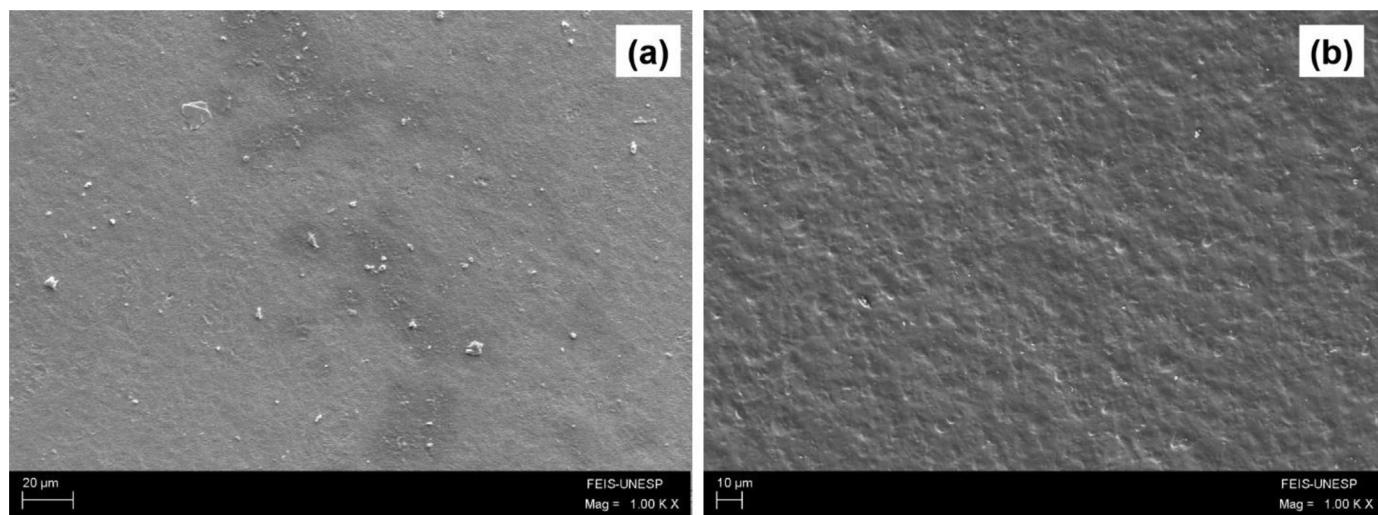


Fig. 1. SEM micrographs with 1000 x magnification for the surface of the films: (a) SA and (b) SA/KP.

Table 2

Percentage of moisture in kale leaf and films: SA, SA/KP, SA-Ca, and SA/KP-Ca.

Samples	Moisture Content (%)
Kale leaf	83 ± 1.2 ^a
SA	21 ± 0.8 ^b
SA/KP	17 ± 0.9 ^b
SA-Ca	18 ± 0.6 ^b
SA/KP-Ca	13 ± 0.9 ^c

*Means followed by the same letter do not differ statistically, by Tukey's test at 5% probability. Sodium alginate film pure (SA); Sodium alginate with kale puree film (SA/KP); Cross-linked sodium alginate pure film (SA-Ca); Cross-linked sodium alginate with kale puree film (SA/KP-Ca).

the alginate-only matrix. Film surface topography changes when kale puree is added are due to varied morphologies, and the formation of agglomerates due to interactions between the polymer and kale fibers.

Figure 2 presents both the surface morphology and cryogenic fractures of the SA/KP-Ca films and fresh kale leaves. A rough surface is noted in image 2A compared to image B in Fig. 1, which represents the non-cross-linked alginate and kale film. Owing to the polar chain approximation in the polymer matrix, a noticeable change in roughness was noted due to surface immersion in 2% (w/v) calcium chloride. However, as depicted in Fig. 2A, calcium chloride immersion also caused film microstructure changes.

As depicted in the cross-sectional micrographs (Fig. 2C and D), the kale puree addition may have disrupted polymeric network interactions, hindering orderly chain alignment and leading to system heterogeneity. Surface roughness can be explained by the contact angle of each surface (*i.e.*, a rougher surface after cross-linking also presented a greater contact angle, resulting in a more hydrophobic surface). The same is noted for non-cross-linked film variations.

3.4. Water permeability value

Figure 3 displays the WVP film results. The pure matrix film presented the highest WVP values, and the addition of kale puree resulted lower WVP values, more pronounced in the films cross-linked with 2% calcium chloride.

Decreasing WVP values is one of the aims of polymeric matrix cross-linking processes (Olivas & Barbosa-Cánovas, 2008; Rhim, 2004). Compared to Pires and Moura (2017), who reported a significant decrease in WVP values, the 2% of the calcium chloride solution employed herein for film cross-linking also hinders water vapor passage. This is due to the fact that a matrix containing a less polar grouping presents chain approximation due to cross-linking and relatively low alginate concentrations, which may not interact with all puree fibers, making water vapor passage difficult. However, the amount of free polar groups is also increased when the matrix is pure and not cross-linked. This interaction causes water vapors to pass freely, increasing WVP values.

The hydrophobic properties of lipids are exploited due to their high water barrier properties, with the efficiency of this property in films determined by the polarity and uniform distribution of lipid particles in the matrix (Bajpai, Baek & Kang, 2012). Thus, to understand the influence of such compounds on film properties, studies focusing on the interaction of added compounds with other components are required (Bonilla, Poloni, Lourenço & Sobral, 2018).

3.5. Mechanical properties

Dietary fibers derived from fruits (squashes) and vegetables (leaves and flowers) contain higher amounts of soluble dietary fibers than other foodstuffs. Plant residues (such as bagasse, stem, and seeds) usually contain relatively high amounts of insoluble dietary fibers, mainly due to their lignin and cellulose content (Hussain, Joudu & Bhat, 2020). The stress at break and deformation at break values of the films developed herein were obtained through tensile tests. Fig. 4 displays tension variations as a function of film composition.

Knowledge on film fibers is also interesting from a technological viewpoint. Fibers can improve certain functional food properties, such as water and vegetable oil absorption rates, emulsification, and potential as a reinforcing component in biodegradable film production. Several studies (Brito, Carrajola, Gonçalves, Martelli-Tosi & Ferreira, 2019; Ma et al., 2022; Wang & Chen, 2014; Zhou et al., 2020) indicate that fiber film incorporation improves mechanical film properties, also significantly improving moisture resistance. In this study, the addition of kale puree and cross-linking resulted in a notable improvement in the tensile strength of the alginate-only film, making this the film with the best mechanical performance in this regard compared to the *in natura* sheet. Previous studies have reported that the incorporation of vegetable flour as a reinforcing agent improves mechanical film resistance (Andrade, Ferreira & Gonçalves, 2016).

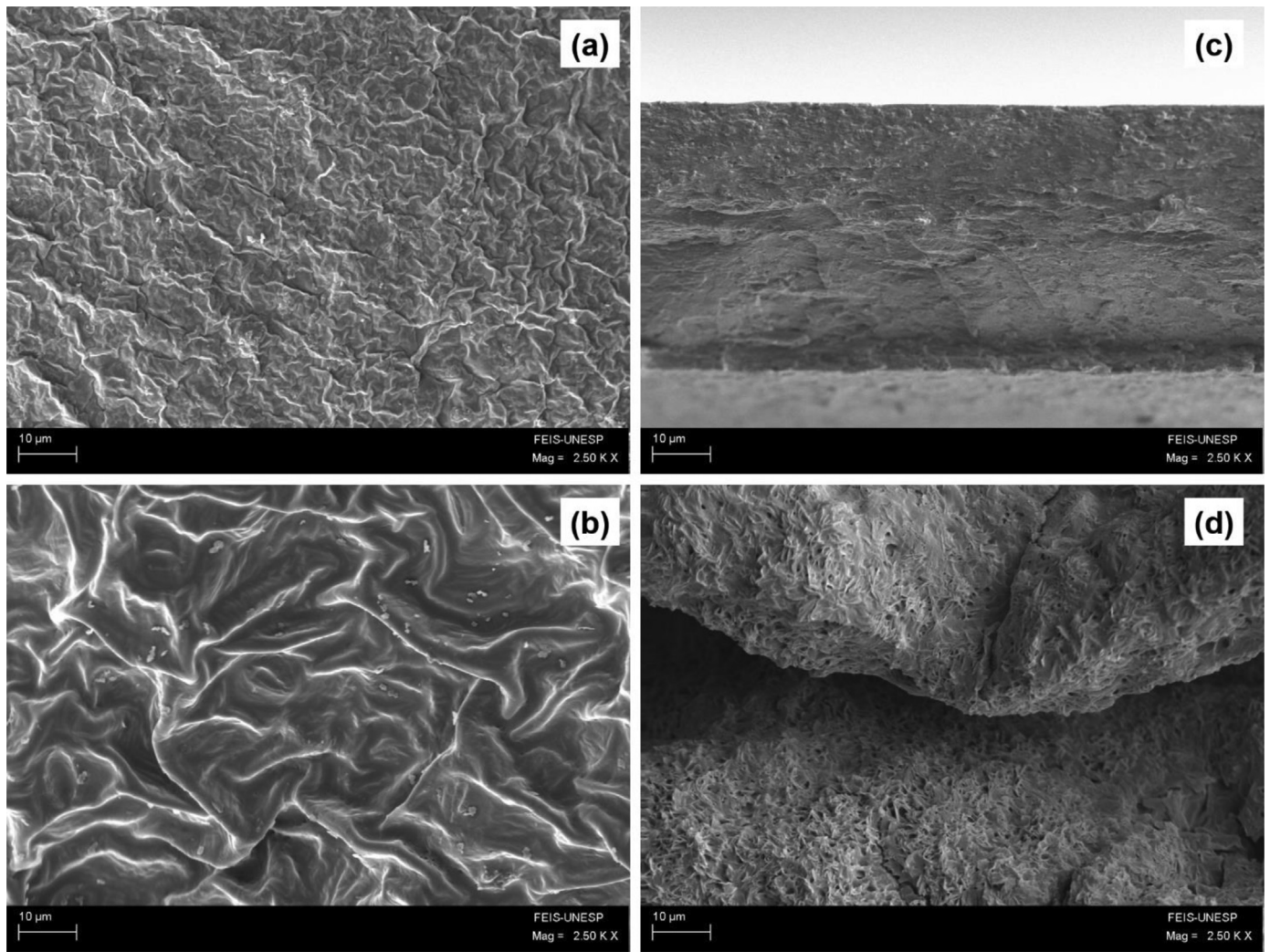


Fig. 2. SEM micrographs with 2500 x magnification for the surface of samples: (a) SA/KP-Ca and (b) Kale leaf, and cryogenic fracture of samples: (c) SA/KP-Ca and (d) Kale leaf.

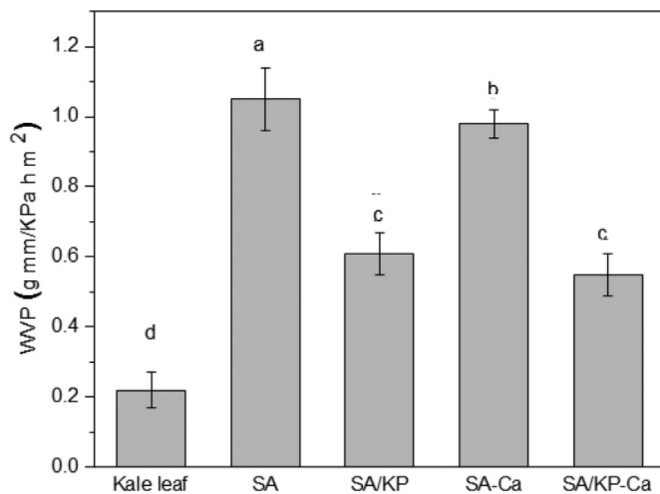


Fig. 3. Water vapor permeability values of kale leaf and SA, SA/KP, SA-Ca, and SA/KP-Ca films.

*The error bar indicates the standard deviation.

*Means followed by the same letter do not differ statistically, by Tukey's test at 5% probability.

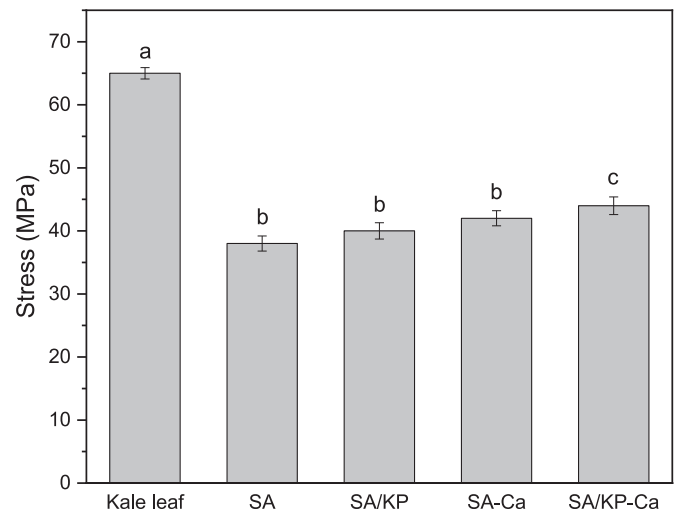


Fig. 4. Average stress values of kale leaf and SA, SA/KP, SA-Ca, and SA/KP-Ca films.

*The error bar indicates the standard deviation.

*Means followed by the same letter do not differ statistically, by Tukey's test at 5% probability.

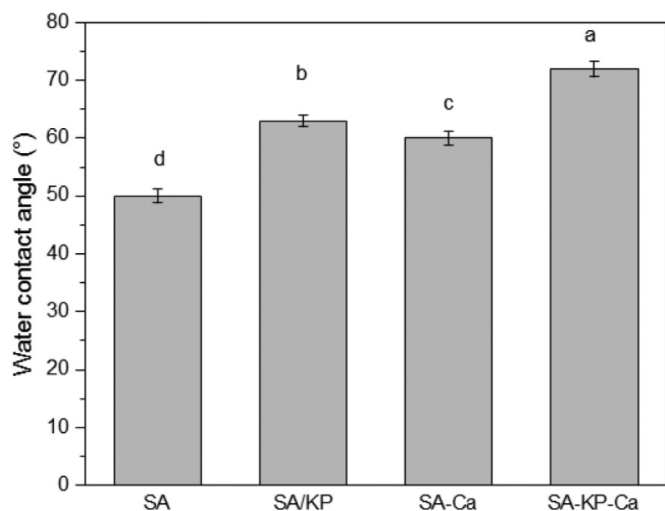


Fig. 5. Water contact angle on films surface: SA, SA/KP, SA-Ca, and SA/KP-Ca. *The error bar indicates the standard deviation. *Means followed by the same letter do not differ statistically, by Tukey's test at 5% probability.

Melquiades (2014) reported that maximum stress values at rupture in isolated films increased when mixed with potato peel flour. The addition of fruit and vegetable residues increases the starch film content of films, leading to high tensile strength (σ). Low stress at break values can be elucidated by the diversity of chemical compounds in the raw material, which can interfere with polymer matrix integration. Furthermore, high total sugar contents present in fruits and some vegetables can act as plasticizers, directly influencing the mechanical behavior of films. These compounds are generally low molecular weight polymers miscible in polymeric matrices, filling the spaces between chains when added to polymeric matrices, decreasing chain-chain interactions via intermolecular forces (Mallick, Pal, Soni & Shankar, 2021; Malm, Nar-simhan & Kokini, 2019; Vattanagijyingyong, Yonemochi & Chatchawal-saisin, 2021).

Thus, the final material may display a lower elastic modulus, resulting in a more rigid polymer with better impact resistance, leading to more versatile applications in the packaging area.

3.6. Contact angle

The phenomenon of liquid scattering on a solid surface, as noted in contact angle measurements, is determined by the relative magnitude of the cohesive and adhesive molecular forces that exist between liquids and between a liquid and solid (Fig. 5). A contact angle is less than 90° when the adhesive forces on the solid surface are greater than the cohesive forces, resulting in a more hydrophilic surface. Conversely, when contact angle is greater than 90° , the surface is more hydrophobic. In composites, fibers absorb part of the glycerol, resulting in a less hydrophilic matrix (Angles & Dufrene, 2000; Curvelo, De Carvalho & Agnelli, 2001).

Crosslinked films display higher contact angle values when compared to their respective non-crosslinked films, probably associated with the reorientation of the side chains of the crosslinked polymer molecules, with a preferred orientation of the hydrophobic residues at the film-air interface (Farris et al., 2011).

According to Angles and Dufresne (2000), amylopectin molecules display a strong affinity for cellulosic fiber surfaces, due to the high density of their hydroxyl groups, which reduces the general mobility of the amylopectin domains. Thus, the crystalline glycerol and amylopectin coating in starch-cellulose composites can lead to restricted mobility on the cellulosic fiber surface. The increased tensile strength and decreased elongation at break confirm this regarding mechanical film properties.

Thus, moisture content in starch composites is always higher than in starch-cellulose composites.

3.7. Water solubility

Water solubilization is a significant film parameter, as some applications require the films to be insoluble and resistant to water, while others demand a high solubility percentage. Edible film solubility indicates integrity in aqueous environments, and high solubility may indicate that low water resistance. Furthermore, film solubility is an important biodegradability factor when used as packaging (Maizura, Fazilah, Norziah & Karim, 2007). In addition, the use of a cross-linking agent, such as kale puree, can lead to new edible film properties, as film preparation and composition directly influence material solubility.

The water solubility of the developed films ranged from 16.8% to 62.9%. The addition of kale puree and the cross-linking process led to a significant ($P < 0.05$) reduction in water solubility for the SA/KP-Ca sample. Some studies have indicated that glycerol concentrations up to 30% result in increased solubility, identified in the stage I samples without no cross-linking investigated herein, containing only the polymer and glycerol.

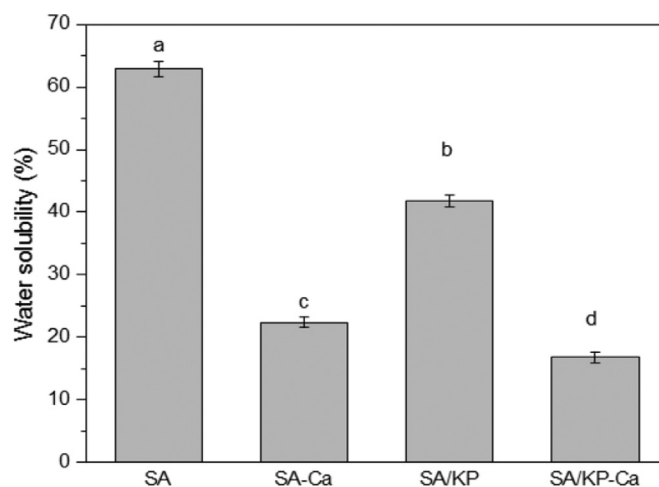


Fig. 6. Water solubility of films for stages I and II.

*The error bar indicates the standard deviation.

*Means followed by the same letter do not differ statistically, by Tukey's test at 5% probability.

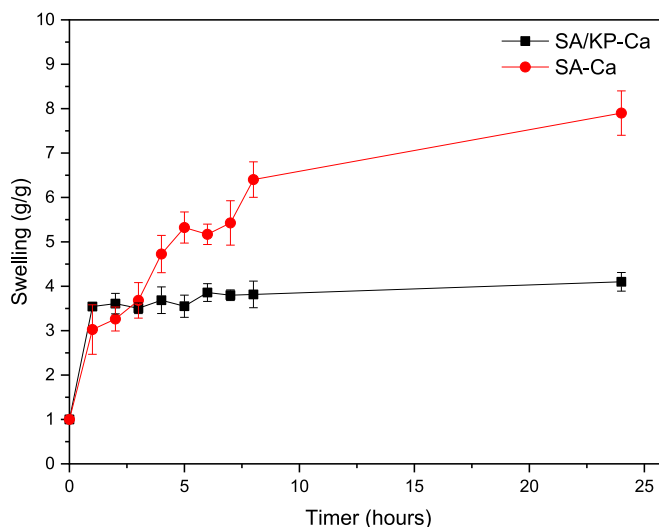


Fig. 7. Swelling of edible films cross-linked with calcium chloride.

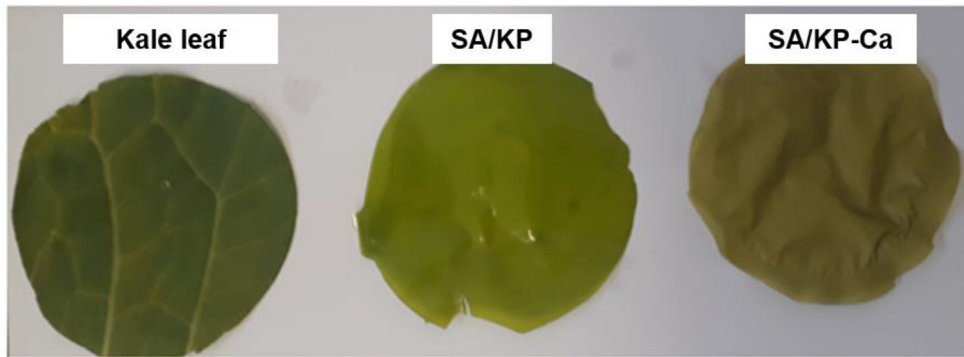


Fig. 8. Samples of kale leaf and films prepared with sodium alginate and kale puree.

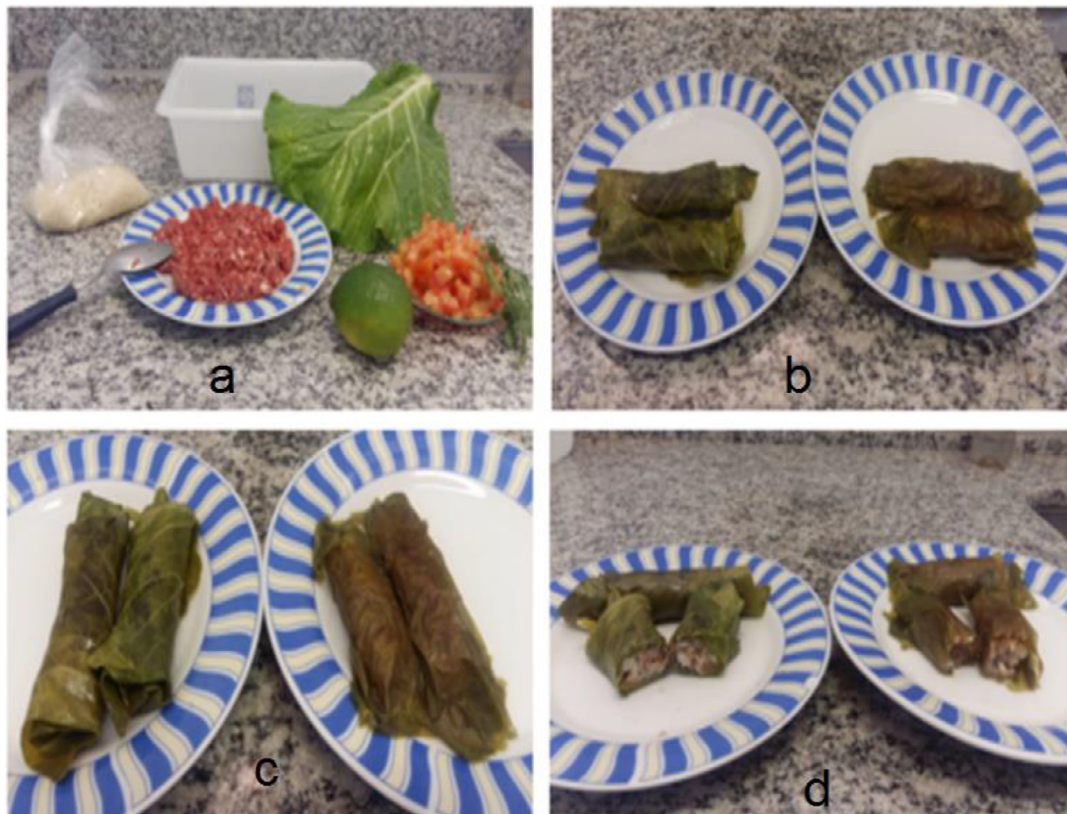


Fig. 9. Potential application of edible films as Wraps: a) ingredients for wraps prepared; b) wraps with kale; c) wraps with kale film; d) wraps with kale films and inner part.

The solubility responses of the studied films were obtained through a factor interaction analysis. The interaction was significant at a $P < 0.05$ probability level between stages I and II (Fig. 6). This is due to the hydrophobic characteristics caused by the sheet fibers in stage I and the cross-linking agent in stage II, which may then interact with the hydrophobic domains of calcium chloride, separating the polymer chains and facilitating water passage. Based on these factors, SA and SA/KP solubilization was proven inefficient, although partial solubilization was observed in stage I samples. Considering the hydrophobicity of kale leaves, stage II film characteristics were improved, adding value to the final product.

High solubility does not make films unfeasible, as this may be necessary in cases where the films must be exposed to water during dehydrated packaged food processing. Edible packaging has been used in this case to package portions of food ingredients or additives to be dispersed in food mixtures (individual soup, tea, sugar, and spice portions),

where high solubility is desirable (*i.e.*, instant dissolution in the applied medium).

3.8. Swelling degree in water

Factors that affect the swelling of edible films range from the concentrations of the applied reagents (monomer, cross-linking agent, and reinforcing agent) to preparation methods (Fisher & Phillips, 2008). The swelling behavior of the samples herein was studied with regard to swelling values (g/g) and time (min), and stage II films containing 2% calcium chloride CaCl_2 (Fig. 7).

The swelling values were compared to the films cross-linked with 2% CaCl_2 . SA-Ca film exhibiting slightly higher swelling values than the SA/KP-Ca film. This is due to the fact that increasing kale fibers concentrations lead to more entangled chains, making water absorption more difficult. The fact that alginate contains more anionic groups (–

COO- and OH-free), that can interact with water molecules, explains the fact that the SA/KP-Ca film stabilizes within 2 h and does not absorb water like the SA-Ca film.

3.9. Visual appearance and potential application

In addition to the characteristic fresh kale color, good continuity, homogeneity, and manageability results were observed herein (Fig. 8). The color of SA/KP films and SA/KP-Ca films were similar to fresh kale leaves. This study aimed to develop a polymeric material with natural polymers and vegetables that may be used to replace traditional gastronomy wraps in different countries.

As the produced films were visually homogeneous in color and displayed a characteristic odor, a laboratory test for potential applications was conducted as a subjective test. Similarities between the fresh kale and kale puree films are noted in Fig. 9. Traditional ingredients were used herein for film development, allowing for wrap preparations.

4. Conclusion

The results reported herein demonstrate that the produced films present the potential to be used as edible films. Kale puree was incorporated into a sodium alginate matrix, which underwent a cross-linking process, conferring satisfactory film properties in terms of strength, color, aroma, homogeneity, continuity, and manageability. The solubility of the SA/KP film decreased compared to the SA film without the need for cross-linking, due to hydrophobic characteristic of kale. The solubilization of the alginate films in water increased without the use of the cross-linking agent. The degree of swelling decreased with increasing kale concentrations due to the hydrophobic characteristic of this material, hindering water absorption. The value of the prepared material stems from the use of sustainable raw materials and their ability to improve the nutraceutical potential of foodstuffs. Edible films employing kale puree display high potential for use in food packaging, aiming at the reuse of this agricultural residue in added value -applications.

Ethical statement - Studies in humans and animals

It does not present studies with humans or animals.

Declaration of Competing Interest

There is no conflict of interest.

Data Availability

No data was used for the research described in the article.

Acknowledgments

Fauze. A. Aouada would like to thank the Brazilian National Council for Scientific and Technological Development (CNPq; Grant No. 312414/2018-8). M. R. de Moura thanks the São Paulo Research Foundation (FAPESP) (Grants No. 2019/06170-1 and No. 2013/07296-2 CEPID) and Brazilian National Council for Scientific and Technological Development (CNPQ) (Grant No. 315513/2021-7). The Physics and Chemistry Department of the São Paulo State University (UNESP) and the PROPG are acknowledged for financial support. This study was partially funded in by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES; Finance Code 001.2019) and Capes-Print, Funding code: 001 Process:88887.194785/2018-00.

Reference

AMERICAN SOCIETY FOR TESTING AND MATERIALS - ASTM. (1980). Standard test method for water vapor transmission of materials (1980). E96 - 80. *ASTM. Annual Book of American Standard Testing Methods* Philadelphia, PA.

- Andrade, R. M., Ferreira, M. S., & Gonçalves, É. C. (2016). Development and characterization of edible films based on fruit and vegetable residues. *Journal of Food Science*, 81(2), E412–E418 doi. [10.1111/1750-3841.13192](https://doi.org/10.1111/1750-3841.13192).
- Angles, M. N., & Dufresne, A. (2000). Plasticized starch/tunicin whiskers nanocomposites. 1. Structural analysis. *Macromolecules*, 33(22), 8344–8353 doi. [10.1021/ma0008701](https://doi.org/10.1021/ma0008701).
- Bajpai, V. K., Baek, K. H., & Kang, S. C. (2012). Control of Salmonella in foods by using essential oils: A review. *Food Research International*, 45(2), 722–734 doi. [10.1016/j.foodres.2011.04.052](https://doi.org/10.1016/j.foodres.2011.04.052).
- Biegańska-Marecik, R., Radziejewska-Kubzdela, E., & Marecik, R. (2017). Characterization of phenolics, glucosinolates and antioxidant activity of beverages based on apple juice with addition of frozen and freeze-dried curly kale leaves (*Brassica oleracea* L. var. *acephala* L.). *Food Chemistry*, 230, 271–280 doi. [10.1016/j.foodchem.2017.03.047](https://doi.org/10.1016/j.foodchem.2017.03.047).
- Boeira, C. P., Flores, D. C. B., Alves, J. S., Moura, M. R. de, Melo, P. T. S., Rolim, C. M. B., et al., (2022). Effect of corn stigma extract on physical and antioxidant properties of biodegradable and edible gelatin and corn starch films. *International Journal of Biological Macromolecules*, 31, 698–706 doi. [10.1016/j.ijbiomac.2022.03.164](https://doi.org/10.1016/j.ijbiomac.2022.03.164).
- Bonilla, J., Poloni, T., Lourenço, R. V., & Sobral, P. J. (2018). Antioxidant potential of eugenol and ginger essential oils with gelatin/chitosan films. *Food Bioscience*, 23, 107–114 doi. [10.1016/j.fbio.2018.03.007](https://doi.org/10.1016/j.fbio.2018.03.007).
- Brito, T. B., Carrajola, J. F., Gonçalves, E. C. B. A., Martelli-Tosi, M., & Ferreira, M. S. L. (2019). Fruit and vegetable residues flours with different granulometry range as raw material for pectin-enriched biodegradable film preparation. *Food Research International*, 121, 412–421 doi. [10.1016/j.foodres.2019.03.058](https://doi.org/10.1016/j.foodres.2019.03.058).
- Chen, J., Wu, A., Yang, M., Ge, Y., Pristijono, P., Li, J., et al., (2021). Characterization of sodium alginate-based films incorporated with thymol for fresh-cut apple packaging. *Food Control*, 126, Article 108063 doi. [10.1016/j.foodcont.2021.108063](https://doi.org/10.1016/j.foodcont.2021.108063).
- Colucci, L. A., & Rodrigues, L. N. C. (2022). Development of orally disintegrating films HPMC-based containing captopril: Mechanical, optical and physicochemical studies. *Brazilian Archives of Biology and Technology*, 65 doi. [10.1590/1678-4324-2022220073](https://doi.org/10.1590/1678-4324-2022220073).
- Curvelo, A. A. S., De Carvalho, A. J. F., & Agnelli, J. A. M. (2001). Thermoplastic starch-cellulosic fibers composites: Preliminary results. *Carbohydrate polymers*, 45(2), 183–188 doi. [10.1016/S0144-8617\(00\)00314-3](https://doi.org/10.1016/S0144-8617(00)00314-3).
- da Silva Fernandes, R., de Moura, M. R., Glenn, G. M., & Aouada, F. A. (2018). Thermal, microstructural, and spectroscopic analysis of Ca2+ alginate/clay nanocomposite hydrogel beads. *Journal of Molecular Liquids*, 265, 327–336 doi. [10.1016/j.molliq.2018.06.005](https://doi.org/10.1016/j.molliq.2018.06.005).
- Fahey, J. W. (2015). Brassica: Characteristics and properties. In *Encyclopedia of food and health* (pp. 469–477). Elsevier Inc. doi. [10.1016/B978-0-12-384947-2.00083-0](https://doi.org/10.1016/B978-0-12-384947-2.00083-0).
- Farris, S., Introzzi, L., Biagioni, P., Holz, T., Schiraldi, A., & Piergiovanni, L. (2011). Wetting of biopolymer coatings: Contact angle kinetics and image analysis investigation. *Langmuir*, 27(12), 7563–7574 doi. [10.1021/la2017006](https://doi.org/10.1021/la2017006).
- Fernandes, F., Guedes de Pinho, P., Valentao, P., Pereira, J. A., & Andrade, P. B. (2009). Volatile constituents throughout *Brassica oleracea* L. var. *acephala* germination. *Journal of Agricultural and Food Chemistry*, 57(15), 6795–6802 doi. [10.1021/jf901532m](https://doi.org/10.1021/jf901532m).
- Fisher, K., & Phillips, C. (2008). Potential antimicrobial uses of essential oils in food: Is citrus the answer. *Trends in Food Science & Technology*, 19, 156–164 doi. [10.1016/J.TIFS.2007.11.006](https://doi.org/10.1016/J.TIFS.2007.11.006).
- Gontard, N. (1991). *Films et enrobages comestibles: étude et amélioration des propriétés filmogènes du gluten montpellier, tèse (Doutor em "Biochimie, biologie cellulaire et moleculaire science des aliments")*. Université Montpellier II.
- Hussain, S., Jöudu, I., & Bhat, R. (2020). Dietary fiber from underutilized plant resources—A positive approach for valorization of fruit and vegetable wastes. *Sustainability*, 12, 5401 doi. [10.3390/su12135401](https://doi.org/10.3390/su12135401).
- Jiang, G., Zhang, Z., Li, F., Rui, X., & Aisa, H. A. (2021). A comprehensive review on the research progress of vegetable edible films. *Arabian Journal of Chemistry*, 14(4), Article 103049 doi. [10.1016/j.arabjc.2021.103049](https://doi.org/10.1016/j.arabjc.2021.103049).
- Kaya, S., & Maskan, A. (2003). Water vapour permeability of pestil (a fruit leather) made from boiled grape juice with starch. *Journal of Food Engineering*, 57(3), 295–299 doi. [10.1016/S0260-8774\(02\)00326-6](https://doi.org/10.1016/S0260-8774(02)00326-6).
- Lutfi, Z., Kalim, Q., Shahid, A., & Nawab, A. (2021). Water chestnut, rice, corn starches and sodium alginate. A comparative study on the physicochemical, thermal and morphological characteristics of starches after dry heating. *International Journal of Biological Macromolecules*, 184, 476–482 doi. [10.1016/j.ijbiomac.2021.06.128](https://doi.org/10.1016/j.ijbiomac.2021.06.128).
- Ma, Y., Ma, Y., Yu, Z., Chiou, B. S., Liu, F., & Zhong, F. (2022). Calcium spraying for fabricating collagen-alginate composite films with excellent wet mechanical properties. *Food Hydrocolloids*, 124, Article 107340 doi. [10.1016/j.foodhyd.2021.107340](https://doi.org/10.1016/j.foodhyd.2021.107340).
- Maizura, M., Fazilah, A., Norziah, M. H., & Karim, A. A. (2007). Antibacterial activity and mechanical properties of partially hydrolyzed sago starch-alginate edible film containing lemongrass oil. *Journal of Food Science*, 72(6), 324–330 AugdoiPMID: 17995673. [10.1111/j.1750-3841.2007.00427.x](https://doi.org/10.1111/j.1750-3841.2007.00427.x).
- Mallick, N., Pal, D., Soni, A. B., & Shankar, R. (2021). Effect of drying temperature and addition of plasticizer & cross-linker on the properties and stability of corn starch/polyvinyl alcohol/rice husk based bio-composite films. *Materials Today: Proceedings*, 44, 3106–3109 doi. [10.1016/j.matpr.2021.02.797](https://doi.org/10.1016/j.matpr.2021.02.797).
- Malm, M. J., Narsimhan, G., & Kokini, J. L. (2019). Effect of contact surface, plasticized and crosslinked zein films are cast on, on the distribution of dispersive and polar surface energy using the Van Oss method of deconvolution. *Journal of Food Engineering*, 263, 262–271 doi. [10.1016/j.jfoodeng.2019.07.001](https://doi.org/10.1016/j.jfoodeng.2019.07.001).
- McHugh, T. H., Avena-Bustillos, R., & Krochta, J. M. (1993). Hydrophilic edible films: Proffided procedure for water vapor permeability and explanation of thickness effects. *Journal of Food Science*, 58(4), 899–903 doi. [10.1111/j.1365-2621.1993.tb09387.x](https://doi.org/10.1111/j.1365-2621.1993.tb09387.x).
- Monterrey, E. S., & Sobral, P. J. D. A. (1999). Caracterização de propriedades mecânicas e óticas de biofilmes a base de proteínas miofibrilares de tilápia do Nilo usando uma metodologia de superfície-resposta. *Food Science and Technology*, 19(2), 294–301 doi. [10.1590/S0101-20611999000200025](https://doi.org/10.1590/S0101-20611999000200025).

- Murtaza, I., Beigha, G. M., Shah, T. A., Hussain, A., Khan, A. A., & Kaur, C. (2005). Antioxidant activity and total phenolic content of kale genotypes grown in Kashmir valley. *Journal of Plant Biochemistry and Biotechnology*, 14(2), 215–217 doi: [10.1007/BF03263250](https://doi.org/10.1007/BF03263250).
- Oldoni, F. C., Bernardo, M. P., Oliveira Filho, J. G., de Aguiar, A. C., Moreira, F. K., Matoso, L. H., et al., (2021). Valorization of mangoes with internal breakdown through the production of edible films by continuous solution casting. *LWT*, 145, Article 111339 doi: [10.1016/j.lwt.2021.111339](https://doi.org/10.1016/j.lwt.2021.111339).
- Olivas, G. I., & Barbosa-Cánovas, G. V. (2008). Alginate–calcium films: Water vapor permeability and mechanical properties as affected by plasticizer and relative humidity. *LWT-Food Science and Technology*, 41(2), 359–366 doi: [10.1016/j.lwt.2007.02.015](https://doi.org/10.1016/j.lwt.2007.02.015).
- Pena-Serna, C., & Lopes-Filho, J. F. (2013). Influence of ethanol and glycerol concentration over functional and structural properties of zein–oleic acid films. *Materials Chemistry and Physics*, 142(2–3), 580–585 doi: [10.1016/j.matchemphys.2013.07.056](https://doi.org/10.1016/j.matchemphys.2013.07.056).
- Pires, V. G., & Moura, M. R. D. (2017). Preparação de novos filmes poliméricos contendo nanoemulsões do óleo de melaleuca, copaíba e limão para aplicação como biomaterial. *Química Nova*, 40, 1–5 doi: [10.21577/0100-4042.20160130](https://doi.org/10.21577/0100-4042.20160130).
- Rhim, J. W. (2004). Physical and mechanical properties of water resistant sodium alginate films. *LWT-Food Science and Technology*, 37(3), 323–330 doi: [10.1016/j.lwt.2003.09.008](https://doi.org/10.1016/j.lwt.2003.09.008).
- Rodríguez, G. M., Sibaja, J. C., Espitia, P. J., & Otoni, C. G. (2020). Antioxidant active packaging based on papaya edible films incorporated with Moringa oleifera and ascorbic acid for food preservation. *Food Hydrocolloids*, 103, Article 105630 doi: [10.1016/j.foodhyd.2019.105630](https://doi.org/10.1016/j.foodhyd.2019.105630).
- Sanchez, L. T., Pinzon, M. I., & Villa, C. C. (2022). Development of active edible films made from banana starch and curcumin-loaded nanoemulsions. *Food Chemistry*, 371, Article 131121 doi: [10.1016/j.foodchem.2021.131121](https://doi.org/10.1016/j.foodchem.2021.131121).
- Saranti, T. F. S., Melo, P. T. S., Cerqueira, M. A., Aouada, F. A., & Moura, M. R. de (2021). Performance of gelatin films reinforced with cloisite Na+ and black pepper essential oil loaded nanoemulsion. *Polymers*, 13, 4298 doi: [10.3390/polym13244298](https://doi.org/10.3390/polym13244298).
- Szutowska, J., Rybicka, I., Pawlak-Lemańska, K., & Gwiazdowska, D. (2020). Spontaneously fermented curly kale juice: Microbiological quality, nutritional composition, antioxidant, and antimicrobial properties. *Journal of Food Science*, 85(4), 1248–1255 doi: [10.1111/1750-3841.15080](https://doi.org/10.1111/1750-3841.15080).
- Torres-León, C., Vicente, A. A., Flores-López, M. L., Rojas, R., Serna-Cock, L., Alvarez-Pérez, O. B., et al., (2018). Edible films and coatings based on mango (var. Ataulfo) by-products to improve gas transfer rate of peach. *LWT*, 97, 624–631 doi: [10.1016/j.lwt.2018.07.057](https://doi.org/10.1016/j.lwt.2018.07.057).
- Vattana jiyong, Y., Yonemochi, E., & Chatchawalsaisin, J. (2021). Miscibility characterization of zein/methacrylic acid copolymer composite films and plasticization effects. *International Journal of Pharmaceutics*, 601, Article 120498 doi: [10.1016/j.ijpharm.2021.120498](https://doi.org/10.1016/j.ijpharm.2021.120498).
- Wang, T., & Zhao, Y. (2021). Optimization of bleaching process for cellulose extraction from apple and kale pomace and evaluation of their potentials as film forming materials. *Carbohydrate Polymers*, 253, Article 117225 doi: [10.1016/j.carbpol.2020.117225](https://doi.org/10.1016/j.carbpol.2020.117225).
- Wang, Y., & Chen, L. (2014). Cellulose nanowhiskers and fiber alignment greatly improve mechanical properties of electrospun prolamin protein fibers. *ACS Applied Materials & Interfaces*, 6(3), 1709–1718 doi: [10.1021/am404624z](https://doi.org/10.1021/am404624z).
- Zhou, W., Zha, D., Zhang, X., Xu, J., Guo, B., & Huang, Y. (2020). Ordered long polyvinyl alcohol fiber-reinforced thermoplastic starch composite having comparable mechanical properties with polyethylene and polypropylene. *Carbohydrate Polymers*, 250, Article 116913 doi: [10.1016/j.carbpol.2020.116913](https://doi.org/10.1016/j.carbpol.2020.116913).