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Effect of Cross-Linking Agent on Mechanical and Permeation Properties of Criolla Orange Pectin

María Guadalupe García and Martin A. Masuelli

Abstract

Pectin from orange peel was extracted and cross-linked, applying different cross-linking agents to visualize any effect on its mechanical and permeation properties. Calcium chloride (II) and iron chloride (III) were the cross-linking agents. Besides, commercial pectin was also used to compare its properties with neat orange pectin. Tensile testing showed mechanical stiffness of the orange pectin matrix in the presence of cross-linking agents. Calcium ions better cross-linked the polymer matrix as shown by their highest tensile strength and elastic modulus, with moderate elongation at break. Iron ions showed a weaker cross-linking effect on the pectin matrix, improving the elastic modulus but retaining almost the same tension strength. Lower elongation at break concerning neat orange pectin was observed for cross-linked samples. Water uptake (WU) and water vapor permeation (WVP) of cross-linked samples had lower values than those of neat orange pectin. However, these results are still high compared with synthetic polymers. Finally, gas permeation assays were performed using N₂, O₂ and CO₂ gases, according to exchangeable gases in fresh fruits and vegetable packaging. Results showed a conveniently modified atmosphere effect by avoiding CO₂ permeation and stabilizing N₂ and O₂ selectivity.

Keywords: polysaccharides, pectins, crosslinking agent, mechanical, permeation properties

1. Introduction

Pectin is a structural heteropolysaccharide present in the primary cell walls of terrestrial plants. It can be obtained from renewable agriculture by-products and food processing industry wastes. These natural sources of pectin make it one of the most abundant biopolymers. It consists of D-galacturonic acid residues which possess carboxylic acid groups, some of which are methyl-esterified. The degree of esterification determines the solubility of pectin and its gelling and film-forming properties. Depending on the origin of pectin, the degree of esterification can vary from high methyl (HMP, up to 50 wt. % of carboxylic acid units are esterified) to low methyl (LMP, lower than 50 wt. % of carboxylic acid units are esterified) [1]. Pectin extracted from criolla orange (*Citrus sinensis*) was first studied and characterized by Masuelli et al. [2]. These authors reviewed the extraction methods and characterization techniques of pectin in solution or film configurations. The intrinsic viscosity of orange pectin from dilute solutions was evaluated to estimate the extracted polymer's molecular weight. Results obtained ranged from 56 to 93 kDa

for basic and acid hydrolysis processes, respectively. Thermal analysis (DSC and TGA) and FTIR spectroscopy were carried out for structure characterization of pectin films. Results showed the presence of T_g (glassy) and T_m (melting) temperatures for pectin, which vary accordingly with the extraction method in the range from 57 to 69°C and 101 to 128°C, respectively. Thermograms (TGA) depicted temperature resistance up to 150°C for all types of extracted pectins. From FTIR analysis, carboxylic acid groups and esterified methyl groups were observed as signals at 1750 cm^{-1} and 1650 cm^{-1} , respectively. Morphological analysis was also carried out by taking SEM images of the film surface. All pectin films showed a homogeneous dense surface without defects. Mechanical, water absorption, and water vapor permeation tests were also performed. All pectin films showed too little resistance to tension and elongation at break compared with commercial pectin. Water absorption was a moderate but fast process, reaching 25% of absorbed water at 60 min of initiating the test. Water vapor permeation was as high as 2.62–5.25 $\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$. Other authors [3], explored the interplay of the degree of methyl esterification (DM), pH, temperature, and concentration on the macromolecular interactions of pectin in solution. They found two levels of organizing pectin structures in solution: (i) chain clusters with a radius of gyration ranging between 100 and 200 nm and (ii) single biopolymer chains with a radius of gyration between ≈ 6 and 42 nm. Besides, they found that chain flexibility increases with DM and acidic pH, whereas hydrogen bonding is the responsible thermodynamic driving force for cluster formation. High methyl pectin creates structures with less efficient packing.

On the contrary, low methyl pectin at pH 7 or higher can turn into more coiled chain conformations in the presence of counterions. Furthermore, the addition of salt to pectin solutions allows the formation of complexes between positively charged ions and negatively charged carboxylic acids, which is facilitated at pH 7 or higher because of deprotonation of carboxylic acid groups. These observations explain the cross-linking effect of positively charged ions on pectin structure and gel formation at higher pH and ion concentration [4].

On the other hand, it is well known that pectin films are obtained from aqueous solutions after slow solvent evaporation [1]. High molecular weight and low pH are required to facilitate the formation of coil entanglements responsible for film formation. The chain entanglements are supported by H-bonding interactions that give strength and physical resistance to the film. Kontogiorgos et al. [5] found that the strength of interactions and conformational changes on pectin during the transition from a liquid to a glassy state are the main factors influencing the physical properties of the solid-state system. However, in contact with aqueous environments, pectin films can absorb water, first swelling the polymer matrix and then dissolving it. Several authors have probed different methods of preparing water-resistant films. Cruces et al. [6] prepared multilayer films of pectin-beeswax/colophony-pectin varying the ratio between beeswax and colophony. This method reached water vapor permeation values ($56 \times 10^{-13} \text{ g m m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$) almost ten times higher than the WVP value of polyethylene films (LDPE $5.8 \times 10^{-13} \text{ g m m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$). Gharsallaoui et al. [7] prepared composite films of pectin/sodium caseinate to improve the mechanical and water barrier properties of protein-free pectin. These authors found that pectin and protein are negatively charged at neutral pH (pH higher than the isoelectric point of a protein), which favors the formation of macroscopic segregated phases. However, even at high turbidity conditions, which demonstrated phase segregation, some positively charged residues on protein might interact with negatively charged groups on pectin, improving the mechanical and water barrier properties. Other authors have prepared insoluble films by cross-linking the pectin matrix using divalent or trivalent cations [4, 8]. Besides, there exist methods of cross-linking a polymer matrix by reacting it with bifunctional molecules such as glutaraldehyde to

perform covalent cross-linking [9]. Usually, cross-linking of the polymer matrix causes chain stiffness and, consequently, detriment of mechanical properties.

Nevertheless, cross-linking might improve solvent resistance, water vapor, and gas barriers. So, it is interesting to study the proper film formation conditions in the presence of a cross-linking agent to overcome the challenge of obtaining a robust film, easy to manipulate with improved mechanical and barrier properties. In this work, pectin from criolla orange (*C. sinensis*) was cross-linked with divalent calcium ions and trivalent iron ions to improve mechanical and permeation properties. Pectin solutions at pH 3.2 were used to prepare films by the “casting” method. Calcium and iron salts were separately contacted with pectin films by submerging them into ions solutions at 40°C for 24 h. The influence of positively charged ions on film properties was analyzed by uniaxial traction, water uptake, water vapor barrier, and gas permeation experiments. Conclusions about structure-properties relationships were obtained.

2. Materials and methods

2.1 Cross-linked film preparation

Pectin (Pec) from criolla orange was dissolved in distilled water at ambient temperature under mechanical stirring at a concentration of 2 wt.% of solid with 1 vol.% of glycerin (GLY, Biopack Argentina). The pH of the pectin solution measured with a pH meter (Melter Toledo) was 3.2. After the pectin solution was homogeneous, it was spread on a leveled Petri dish and placed in an oven at 40°C for 24 h for slow solvent evaporation. Once a pectin film was formed, it was peeled off and submerged in a 0.1 wt.% CaCl₂ (Merck) solution at 40°C without stirring (stagnant conditions). Diffusion of calcium ions occurred by a driving force of concentration gradient, allowing a moderate cross-linking effect in the polymer matrix. A contact time of 24 h was probed to obtain cross-linked pectin films. After cross-linking time, the pectin film was washed with a hydroalcoholic solution several times to remove excess calcium salt on the film surface. Cross-linked pectin with calcium was named Pec-Ca, and it resulted in a transparent and handling film used for mechanical and barrier characterizations. The same procedure and salt concentration were used in the case of FeCl₃ salt (Merck), and the cross-linked film was called Pec-Fe. This last film was light brown and retained transparency and easy handling. Commercial pectin from citrus peel was supplied by Sigma Aldrich (galacturonic acid ≥74.0%, methoxy groups ≤6.7%), and it was used to prepare uncross-linked films. The same procedure as pectin from criolla orange was used to obtain the commercial pectin film, and it was called Com-Pec.

2.2 Mechanical characterization

CT3 Brookfield texture analyzer with a load cell of 50 kg and a resolution of 5 g was used to perform tensile strength assays at a speed of 5 mm·min⁻¹ according to the ASTM D 882 requirements. For an experiment, samples were cut into rectangular pieces of 40 mm in length and 10 mm wide. Thickness was measured using a Köfer micrometer (precision ±1 μm). To ensure complete relaxation of the polymeric structure once the films were peeled off, they were placed in a humidity chamber for 24 h at a relative humidity of 40% and room temperature (25°C) before they were measured. Then, the experimental procedure was carried out under the same humidity and temperature conditions. Typical curves of tension (σ) versus elongation (ϵ) were built for each sample, and they were used to determine the values of the mechanical parameters, such as young's modulus (E; MPa), tension at break (σ_b ; MPa), elongation

at break (ϵ ; %), and Tenacity (T; $\text{kJ}\cdot\text{m}^{-3}$). Young's modulus was calculated from the slope of the σ - ϵ curves when a linear relationship between them was observed. σ and ϵ were calculated as the final points on the curves; this behavior indicated that rupture of the sample occurred, and tenacity was calculated as the area under the σ - ϵ curves before rupture [10]. The reported results are the average values from at least three film samples. The σ - ϵ relationship is given by the following equation:

$$\sigma = E \times \epsilon \quad (1)$$

where: $\sigma = F/A$ in MPa, F being the force in N and A the transversal area of the specimen in m^2 .

$$\epsilon = \frac{\Delta L}{L_0} \times 100 \quad (2)$$

where: ΔL is the change in length and L_0 is the initial length of the specimen, which was 20 mm.

2.3 Water uptake

Polysaccharides in general and pectin are hydrophilic polymers able to absorb water from the environment to the detriment of the films' physical integrity. It is a matter of science to find ways to prevent water absorption for expanding the field of biopolymers application. Even reducing water uptake under acceptable values would represent a contribution to broadening polysaccharide film applications, for example, for food packaging. In this study, water uptake (WU) was determined gravimetrically. Weights of completely dried samples were measured directly. Film specimens were introduced into bottles containing 20 mL of distilled water and shaken at ambient temperature (25°C). At intervals of 24 h, films were removed from the medium, dried to remove excess water, and immediately weighed. The water uptake of the cross-linked films was calculated according to the following Equation [11]:

$$WU = \frac{W_{24} - W_0}{W_0} \times 100 \quad (3)$$

where: WU is the value of water uptake (%), W_{24} is the weight of swollen film at a time "t = 24 h", W_0 is the weight of dried film at "t = 0".

2.4 Water vapor permeability

Water vapor transmission rate (WVTR) was determined gravimetrically using a modified ASTM Method E 96-95. The film specimen was mounted on an acrylic permeation cell comprised of two chambers. The upper chamber was in contact with water vapor pressure, while the bottom chamber was filled with an adsorbent material. The film specimen was in between both chambers, acting as a barrier. Therefore, the driving force of the global process was the difference in water vapor pressure at both sides of the film specimen. Once the permeation cell was assembled, all systems were placed into a chamber with temperature and relative humidity control. The operational conditions are fixed at $37 \pm 2^\circ\text{C}$ and 98% relative humidity (RH). Water vapor permeability (WVP) ($\text{ng}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$) was calculated from [11]:

$$WVP = \frac{WVTR \times l}{\Delta P} \quad (4)$$

where: WVTR ($\text{ng}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) was measured through a film specimen; l (m) was mean film thickness, ΔP (Pa) was partial water vapor pressure difference across the two sides of the film specimen.

2.5 Gas permeation

Flexible packaging materials must fulfill some specific characteristics according to the food they will pack. Fruits and vegetables are a particular type of food because they continue breathing after harvesting. Fruits and vegetables need oxygen to breathe, converting carbohydrates into carbon dioxide and water vapor. Post-harvest respiration uses stored starch or sugar and will stop when these reserves are exhausted. Therefore, designing a film that can retard fruits and vegetable respiration by controlling oxygen permeability and nitrogen and carbon dioxide exchange is desired. This condition might modify the atmosphere around the fruits and vegetables, altering oxygen levels inside the packaging, retarding the production of ethylene, and, thus, limiting the physiological decay of the product [12, 13]. This modification also reduces ripening-induced quality degradation in texture or loss of bioactive compounds during storage.

On the other hand, a minimal amount of oxygen might let anaerobic fermentation process, leading to spoilage [14]. For that reason, studying gas permeation through pectin and cross-linked pectin films is necessary to define the applicability of these films to the packaging of fruits and vegetables. In this study, N_2 , O_2 , and CO_2 permeability were measured at 30°C and 1 bar using a classical time lag apparatus. The effective membrane area was 11.34 cm^2 , and permeate constant volume was 35.37 cm^3 . After the membrane degassing procedure, gas permeation measurements were carried out under high vacuum ($p \approx 10\text{ torr}$) and 30°C for 10 h. The amount of gas transmitted at time “ t ” through the membrane was calculated from the permeate pressure (p_2) readings in the low-pressure side of the permeation cell. Permeability coefficients (P) were obtained from the flow rate into the downstream volume upon reaching the steady-state as:

$$P = \frac{Bl}{T_c p_1} \frac{dp_2}{dt} \quad (5)$$

where: the cell constant $B = 11.53\text{ (cm}^3\text{(STP) K)/(cm}^2\text{ cmHg)}$; high-pressure side p_1 (cmHg); membrane thickness l (cm), the slope of the p_2 versus t plot in steady-state dp_2/dt (cmHg/s), the temperature of the permeation cell T_c (K). Permeability values were obtained in Barrer unit (B), i.e., $1 B = 10^{-10}\text{ cm}^3\text{ (STP) cm}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}\cdot\text{cmHg}^{-1}$ and then converting Barrer to other units for comparison purposes.

Theoretical separation factors (α) were calculated from the relation between the permeation coefficients of pure i and j gases as:

$$\alpha_{i/j} = \frac{P_i}{P_j} \quad (6)$$

3. Results and discussion

3.1 Mechanical properties

Mechanical properties of pectin and cross-linked pectin films were evaluated through strength-strain curves of each sample. Besides, commercial pectin was also analyzed. **Table 1** shows values of young's modulus (E ; MPa), tension at break

Film	E (MPa)	σ (MPa)	ϵ (%)	T (kJ/m ³)
Pec	614 ± 8.9	12.6 ± 0.5	2.7 ± 0.3	15 ± 4
Pec-Ca	989 ± 10.1	21.3 ± 4.0	2.4 ± 1.0	265 ± 8
Pec-Fe	876 ± 9.8	22.0 ± 5.0	4.3 ± 1.0	511 ± 10
Com-Pec	176 ± 3.2	17.2 ± 1.7	30.3 ± 2.4	3330 ± 7

Table 1.
Mechanical properties of films.

(σ ; MPa), elongation at break (ϵ ; %), and tenacity (T ; kJ·m⁻³) of all samples. Results showed an increase in young's modulus and tension at the break with cross-linking, with the modulus being higher in the presence of calcium ions and retaining almost the same tension at break concerning Pec-Fe. An increase in elongation at break was observed in Pec-Fe, additionally with a higher energy absorption during the deformation process. Com-Pec resulted in a more deformable and resilient film reaching 30% of elongation with a tenacity one order of magnitude higher concerning the other samples. Mechanical results depicted a stiffness effect of cross-linking, more pronounced in Pec-Ca. This result might be because calcium ions better accommodate within pectin chains to form a stable egg box conformation regarding Fe ions. Although the ionic radius of calcium ions is higher than for iron ions, their divalent charge better interacts with two adjacent carboxylic acid units negatively charged within two entangled pectin chains. **Figure 1** shows the egg box model for Pec-Ca. Cybulska et al. [15] mentioned that the binding process in chain-to-chain pectin interactions with Ca²⁺ ions required a pronounced shift of one galacturonate chain concerning the other chain. Thus, the interaction of calcium ions with polygalacturonate chains may occur via oxygen atoms in the carboxylate group, in the ring, in the glycosidic bond, and the hydroxyl group of the next residue. Cross-linking formation at pH3.2 may be connected with the binding of calcium ions to pectin, hydrophobic interactions, and the formation of hydrogen bonds [16]. In this case, the interaction of Ca²⁺ with other oxygen atoms in galacturonic acid residues was suggested.

Furthermore, water molecules might also interact with ions, competing with carboxylic acid units to stabilize them. The calcium egg-box model is formed in a two-fold conformation of pectin chains. Remnant water molecules within the pectin matrix might provoke a polymorphic transition from two-fold to three-fold chain conformation, disrupting the egg-box configuration. This fact might explain results obtained by Pec-Fe, which showed lower young's modulus and higher elongations at break correlated with a more hydrated configuration. Regarding the structural possibilities of pectin-Fe, it could be like xanthan gum-Fe studied by Vazquez et al. [17].

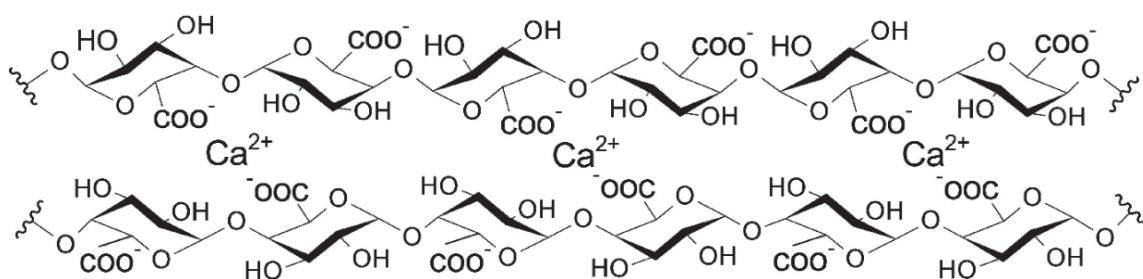


Figure 1.
Calcium "egg-box" model for pectin, based on [15].

3.2 Water uptake analysis

The hydrophilic nature of polysaccharides is a known characteristic that prevents some of these biopolymers' applications. Some strategies to reduce water uptake in films are cross-linking, blending, and mixing with other materials such as hydrophobic polymers [18], waxes [19], inorganic components [20], among others. In this study, cross-linking of the pectin matrix with calcium and iron ions was used to reduce the water uptake ability of film samples. **Table 2** shows WU results. A reduction in absorption capacity was observed in the presence of cross-linking concerning criolla orange pectin. Even when all values were significantly high, they depicted a weak cross-linking effect on water uptake. This result might be a consequence of the method used to cross-link the samples, which was ion diffusion from slightly concentrated solutions toward the matrix of the submerged film. Furthermore, this result might be evidence of superficial instead of full matrix cross-linking. It is well known that diffusion is a mass transport mechanism driven by concentration gradients and facilitated by temperature and stirring. The cross-linking procedure was performed under ambient temperature in stagnant conditions. Besides, Pec-Ca showed lower water absorption than Pec-Fe following its tighter egg-box cross-linking conformation mentioned in the previous section. On the other hand, Com-Pec showed complete solubility in water after a contact time of 24 h. This result might be explained considering the low methoxyl content of commercial pectin (galacturonic acid $\geq 74.0\%$, methoxy groups $\leq 6.7\%$) compared to criolla orange pectin [2]. Methoxy groups confer hydrophobic characteristics to the pectin backbone, which explains Pec's lower solubility in the water regarding Com-Pec.

3.3 Water vapor permeability

Permeability depends on the solubility and diffusivity of water vapor molecules within the polymeric matrix [11]. When the polymer is hydrophilic, water molecules find many interacting sites and hopping by the polymer matrix through the formation of hydrogen bonds [21]. Hence, water vapor permeation is facilitated within hydrophilic polymers such as pectin. Despite this disadvantage, cross-linking reduces these interactions by blocking polar groups on pectin such as carboxylate and hydroxyl groups through interactions with divalent and trivalent ions such as Ca^{2+} and Fe^{3+} . In order to study the effect of cross-linking on water vapor permeation, measurements were made gravimetrically using a modified ASTM Method E 96–95 (ASTM 96). Results are shown in **Figure 2**. A slight decrease in WVP of Pec-Ca concerning Pec was observed.

On the contrary, Pec-Fe showed an increase regarding orange pectin. This last result might be explained by an increased solubility of water vapor molecules through the polymer matrix favored by interactions with trivalent iron ions in the three folded chain conformation. Com-Pec showed the highest permeation value

Film	WU(%)
Pec	372 ± 38
Pec-Ca	326 ± 20
Pec-Fe	338 ± 25
Com-Pec	—

Table 2.
Water uptake values.

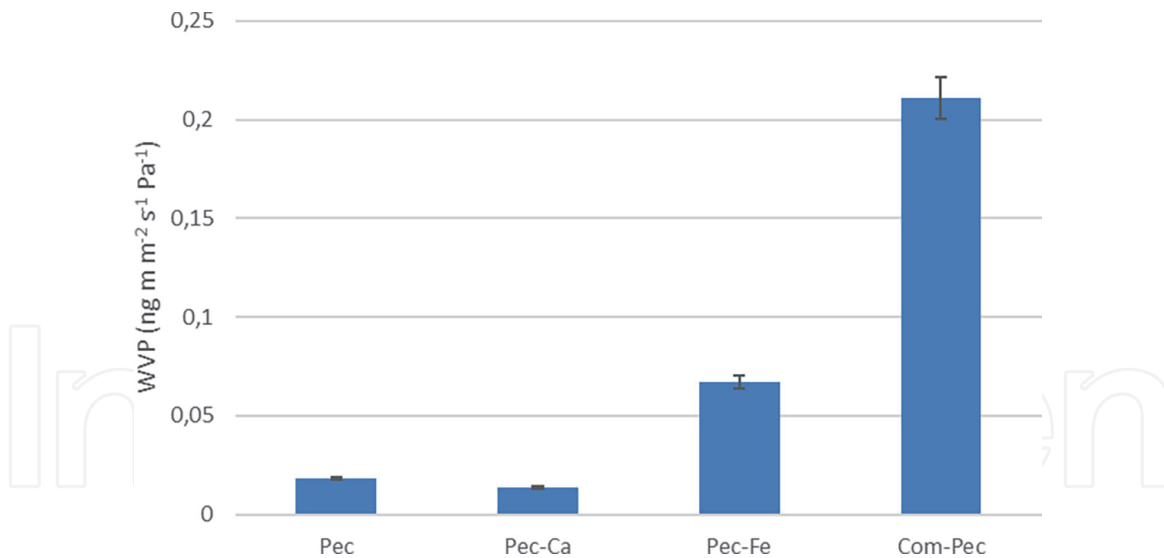


Figure 2.
Water vapor permeation of pectin films.

according to the hopping mechanism of water vapor molecules proposed by Cruces et al. [21].

As mentioned before, Com-Pec has $\geq 74.0\%$ of de-esterified carboxylic acid groups; hence the polymeric matrix is full of polar groups able to interact with water vapor molecules to hop through. WVP result of commercial pectin agreed with that reported by Cruces et al. ($0.0361 \text{ ng}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$) [21]. Other authors have studied water vapor permeation properties in polysaccharides and cross-linked polysaccharides. Values in the range from 1.5 to $0.6 \text{ ng}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$ were reported for alginate-calcium cross-linked films [22], starch-based biopolymer with rye flour, cellulose, and citric acid as additives showed a WVP value of $0.87\cdot\text{ng}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$ [23], xylan-alginate films containing bentonite, or halloysite clays showed a reduction in WVP from 0.394 for control film to 0.210 for 5 wt% for either clay [24]. Considering the reported WVP values for a variety of biopolymers, it is concluded that sensitivity to water vapor of hydrophilic polymers is still a matter of study.

3.4 Gas permeation

Gas permeation was measured in pectin films to analyze their ability to control gas exchange between internal and external sides of the packaging. According to our knowledge, O_2 and CO_2 are among the most important gases that take part in fruits and vegetable respiration. N_2 is an inert gas representing about 78% of atmosphere content, and it might show preservation effects [25]. The three main gases used in modified atmosphere packaging (MAP) are N_2 , O_2 , and CO_2 . Decreasing the respiratory rate of fruits and vegetables in food packaging retards their deterioration. This effect occurs by reducing at least 5% of O_2 permeability, heightening CO_2 concentration, and regulating N_2 exchange inside the packaging. Oxygen promotes several deteriorative reactions in food, such as fat oxidation, browning reactions, and pigment oxidation. Besides, oxygen is necessary for bacteria and fungi growth. Carbon dioxide dissolves readily in water, increasing the acidity of food surroundings which can cause pack collapse due to the reduction of headspace volume. Nitrogen does not support the growth of aerobic microbes, and it is used to balance the volume decrease caused by CO_2 solubilization in water [26]. Gas permeation results and gas selectivity are shown in **Tables 3** and **4**, respectively.

Film	Thickness (μm)	P_{N_2}	P_{O_2}	P_{CO_2}
Pec	152	3.87	1.44	0.33
Pec-Ca	90	3.34	2.84	0.40
Pec-Fe	258	5.16	1.45	0.59
Com-Pec	254	3.06	0.49	2.04

$P = (\text{cm}^3 \cdot \mu\text{m} \cdot \text{m}^{-2} \cdot \text{d}^{-1} \cdot \text{atm}^{-1})$.

Table 3.
 Gas permeation in pectin films.

Film	$\alpha_{\text{N}_2/\text{O}_2}$	$\alpha_{\text{O}_2/\text{CO}_2}$	$\alpha_{\text{N}_2/\text{CO}_2}$
Pec	2.68	4.40	11.78
Pec-Ca	1.17	7.09	8.33
Pec-Fe	3.56	2.46	8.73
Com-Pec	6.21	0.24	1.50

Table 4.
 Gas selectivity.

Results shown in **Table 3** depict a modified atmosphere by pectin and cross-linked pectin films. Considering fruit or vegetable packed in these films, it would be possible to see that normal atmosphere content (78% N_2 , 21% O_2 , and 0.01% CO_2) and its gas ratios have been modified. These results are better observed from **Table 4**, which we analyzed forwards. From **Table 3**, a reduction in N_2 permeability can be observed in the case of Pec-Ca and Com-Pec regarding orange pectin. On the contrary, an increase in P_{N_2} was observed for Pec-Fe. Oxygen permeability increased for Pec-Ca, demonstrating a detriment in its ability to reduce oxygen content inside the packaging.

On the other hand, P_{CO_2} was lower in the case of Pec, Pec-Ca, and Pec-Fe than Com-Pec. The barrier to CO_2 might represent a promising property for MAP. Differences in gas permeability between calcium and iron cross-linked films might be related to the polarity of ions concerning gases. Besides, the availability of ions within the less hydrated two-folded chains in the case of Ca^{2+} or more hydrated three-folded chains conformation in Fe^{3+} could also influence the interactions with permeate gases. These molecular conformations can also explain the increment in P_{CO_2} for Pec-Fe. **Table 4** shows gas selectivity for selected gas pairs taking into account their abundance and gas ratio in the usual atmosphere. N_2/O_2 ratio in a usual atmosphere is around 3.71. From **Table 4**, it is observed that Pec-Fe has the closest value to that of the familiar atmosphere, while Pec and Pec-Ca have lower ratios and Com-Pec has the highest one. These results indicate that all films act as selective gas barriers favoring the permeance of N_2 more than O_2 , except for Pec-Ca, in which N_2/O_2 selectivity is almost 1, i.e., no selectivity for N_2 nor O_2 .

On the other hand, selectivity to O_2 against CO_2 was pronounced in the Pec-Ca film, followed by Pec and Pec-Fe. These results prove that an excellent barrier to CO_2 is reached in cross-linked films. Furthermore, Com-Pec showed an opposite behavior concerning O_2/CO_2 selectivity being more permeable to CO_2 . Finally, N_2/CO_2 selectivity was excellent for Pec, and it was similar in the case of Pec-Ca and Pec-Fe. Values shown in **Table 4** indicate that N_2 permeability can balance the volume decrease caused by CO_2 solubilization in water as respiration and transpiration occur in fruits and vegetables. Commercial pectin showed less selective films for N_2/CO_2 gas pair according to its lower barrier to CO_2 .

According to Sandhya [26], there has been much commercial interest in developing films with high gas transmission rates. High gas transmission films are obtained by modifying the film manufacturing process so that gases such as O₂, CO₂, and water vapor exit or enter the package in a controlled manner such that aerobic respiration needs are met, and desirable CO₂ and moisture levels are maintained. This work successfully controlled gas permeation and selectivity to obtain a modifying atmosphere inside packaging were achieved.

4. Conclusions

An exhaustive analysis of the effect of cross-linking of the pectin matrix with calcium and iron ions was carried out. Mechanical and permeation properties were studied and discussed to find new insights about structure–property relationships of modified films. Mechanical stiffness was observed when pectin was cross-linked with Ca²⁺ and Fe³⁺ showing higher Young's modulus and tension at break than orange and commercial pectin. Reduced water uptake was observed for Pec-Ca and Pec-Fe. However, values still being high concerning synthetic polymers. Similar results were obtained for water vapor permeation being Pec-Ca which depicted the lowest value. Finally, gas permeation assays were performed, demonstrating a good ability of cross-linked films to modify the atmosphere inside a packaging destined for fruits and vegetables packaging.


As a general conclusion, the conformation of two-folded chains in Pec-Ca concerning the three-folded chains in Pec-Fe was responsible for obtaining stronger mechanical properties, lower water uptake and water vapor permeation, and promising O₂/CO₂ selectivity in this cross-linked film.

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