EVALUATION OF A CROSS-LINKING AGENT IN THE PREPARATION OF FILMS BASED ON CHITOSAN AND PECTIN FOR FOOD PACKAGING APPLICATIONS

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The development of edible films applied to fruits and vegetables postharvest have generated recent advances regarding the synergistic effect of components on the shelf life of products. Currently, there are edible films made by combining several biopolymers, including chitosan, starch, pectin, alginate, among others. The application of physical barriers, such as films, on the surface of fruits can regulate the permeability to O_2, CO_2, and water vapor, delaying the natural process of physiological maturity. The use of films also improves the mechanical properties of horticultural products, which are essential in handling them. In the present work, films based on chitosan (antimicrobial agent) and pectin (gelling agent) as a biopolymer matrix, as well as glycerol (plasticizer) and calcium chloride (cross-linking agent), were prepared. The effect of adding the crosslinking agent on the film properties was evaluated by infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and dynamic viscosity testing.

Keywords: edible films, antimicrobial agent, gelling agent, cross-linking agent, biopolymer

INTRODUCTION

Packaging plays a critical role in food conservation, distribution and marketing. Some of its functions are to contain food, and protect it from physical, mechanical, chemical and microbiological action. Food packages are classified as primary (films, bags, bottles or boxes); secondary, which come in direct contact with the food product (containing one or more primary packages) and tertiary (group of primary or secondary packaging containers). Bioplastics used especially in the primary package type could be considered an alternative to synthetic plastics, due to their low environmental impact and biodegradability. The challenges that researchers must face is the development of materials with acceptable mechanical, thermal, gas and water barrier properties for such application. Unfortunately, all these properties cannot be found in individual biopolymers, so a combination of them is the strategy to achieve acceptable food packages.[1]

Chitosan (Q) has received considerable attention from academics and the food industry, due to its particular physicochemical properties, chemical stability, high reactivity and film-forming ability, as well as biodegradability, biocompatibility and non-toxicity. Most research has focused on cellulose and starch as biopolymers for Q compatibilization, and just a few studies have reported on the use of gums, pectin (P) and vegetable or animal proteins with the same objective, through graft copolymerization, surface coating, composite films, casting, extrusion and cross-linking techniques.[1-3] In Q polymer blending, crosslinking has been reported to achieve physical modifications by establishing bonds and electrostatic interaction between two polymer chains, in order to improve the individual performance of the polymer. A limited number of crosslinkers are allowed in food packaging applications, due to safety considerations. Also,

heterogeneous phases are part of the problems to attend and overcome, because of the diverse Q–acid or aqueous and/or organic solvents interactions, which may prevent the dissolution of both polymers to develop the polymer matrix. Unfortunately, to get over the immiscibility phases, it is necessary to add a component that would provide functional bond sites.[3-4]

Edible films have the ability to work synergistically with other packing materials. The use of edible films in food applications and especially in highly perishable products, such as fruits and vegetables, is based on certain characteristics, including cost, availability, functional attributes, mechanical properties (tension and flexibility), optical properties (brightness and opacity), the barrier effect against gas flow, structural resistance to water and microorganisms, and sensory acceptability. Edible films are often made up of a preformed thin matrix that is used as a coating for food or to separate different components. The film-forming solutions can be made up of a polysaccharide, a compound of a protein or lipid nature, or a mixture of these.[5-8] Edible films should have good mechanical properties, generate a barrier effect against gas transport, and can acquire various functional properties, depending on the characteristics of the polymer compounds that form these matrices.[5] Previous reports have recognized the importance of evaluating preformed matrices, with the task of quantifying various parameters, such as mechanical, optical and antimicrobial properties, in order to determine the possibilities of their application in packaging.[9-10] Film characteristics are influenced by parameters, such as the type of material used as structural matrix (conformation, molecular mass, load distribution, among others), conditions of film synthesis (type of solvent, pH, components ratios or temperature) and type and concentration of additives (plasticizers, crosslinking agent, antimicrobial agents or antioxidants).[11-15]

Chemical crosslinking involves the formation of covalent bonds between chains and can be achieved using multifunctional monomers at low concentrations by coupling radicals generated by radiation. In contrast, physical crosslinking is due to non-covalent secondary interactions, such as hydrogen bonds, electrostatic interactions, hydrophobic forces, or dipole-dipole interactions.[9] Biopolymer-based packaging films are generally characterized by low resistance. The use of crosslinking agents is an option to improve this specific characteristic, as it increases the mechanical properties on polymer materials in general. Several kinds of crosslinking agents have been evaluated in biopolymer films, where the reaction generates a reticulated structure that provides better resistance. It has been reported that even Q acts as ionic crosslinking agent to other polysaccharides, including P biopolymer, depending on the charge density and solution medium (pH acidic or basic).[16] Several kinds of crosslinking agents for polysaccharides have been evaluated with good results, among them ferric acid[17] for Q. Aldehydes and organic acids also have been reported successfully in crosslinking of polysaccharides.[18-19] Calcium chloride ($CaCl_2$) has been reported as a crosslinker agent for alginate films by addition of divalent Ca^{2+} cations to establish the bonding linkage. Nonetheless, there are few works reporting on the use of calcium chloride as a crosslinking agent for chitosan-pectin films.[7,20]

Based on these considerations, in the present work, the addition of $CaCl_2$ as a crosslinking agent in a blend of Q/P was evaluated. The films were characterized by means of infrared spectroscopy (FTIR); thermal and thermo-mechanical properties of the films were assessed by thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). Dynamic viscosity was determined for solutions before film formation.

EXPERIMENTAL

Materials

Low molecular weight chitosan (Q) (degree of deacetylation of 75%), pectin (P) extracted from apples, $CaCl_2$ with 93% purity and glacial acetic acid were purchased from Sigma-Aldrich. Distilled water was used in the experiments.

For the experimental design, a chitosan-pectin combination was established as the basis of the films, with a concentration of chitosan of 2% (constant) and varying concentrations of pectin. The following codes were used for identifying the materials: Q-Px, where Q stands for chitosan, P – for pectin, and x represents the P content (0.1, 0.35 and 0.5%); and Q-P X-$CaCl_2$ – the films prepared with crosslinking agent, which was added in a fixed content of 1 wt%.

Figure 1 shows the prepared solutions and the appearance of the obtained films. The films were prepared mixing the Q solution in 2M acetic acid, with the P solution in water. Once the solutions were homogeneous, a constant amount of $CaCl_2$ was added under stirring with an IKA mechanical stirrer (model Ministar 20 digital), during 1 h at room temperature.

After that, glycerol (0.5 wt%) was added as plasticizer. The films were dried at room temperature during 2 days.

Characterization

The dynamic viscosity of the solutions was determined before film formation. The principle of operation of a rotational viscometer is to drive a spindle immersed in sample through a calibrated spring. The drag of the fluid against the spindle is measured by the spring deflection, which is measured with a rotary transducer. The measurement range of a rotational viscometer (in centipoise) is determined by the rotational speed of the spindle, the size and shape of the spindle; in the container the spindle is rotating, at the temperature of the fluid (in our case 25 °C and 60 °C), with a speed of 60 rpm, using a R3 spindle and the full-scale torque of the calibrated spring. Each sample was measured 5 times and the average at constant shear was reported. This testing plays a crucial role in research, development, and process control of liquid and semi-liquid products.[2]

The films were characterized by means of Infrared Spectroscopy, with the aim to evaluate the main functional groups and the effect of the addition of the crosslinking agent. For this, Perkin Elmer Spectrum One equipment, with an ATR accessory, with SeZn plate, was used. Spectra were obtained in the wavenumber range from 4000 to 600 cm^{-1}, with 12 scans, with a resolution of 4 cm^{-1}. The thermal stability of the films was evaluated by thermogravimetric analysis (TGA), using TA Instruments Q600 SDT (DSC-TGA) equipment, from room temperature to 600 °C, with a heating rate of 10 °C/min in N_2 atmosphere. The dynamic mechanical analysis (DMA) was carried out using TA Instruments Q800 equipment, in a temperature range from -50 to 200 °C, at a heating rate of 5 °C/min, and a fixed frequency of 1Hz; the samples were fixed with a film type clamp.

Figure 1: Chitosan-pectin solutions and appearance of the films

RESULTS AND DISCUSSION

Dynamic viscosity

Table 1 reports the dynamic viscosity values of individual solutions of Q and P, at the specified concentrations. It is worth mentioning that the dynamic viscosity was measured prior to the formation of the films. The data show that Q at 2% has a high viscosity at 25 °C, which decreased when the measurement was made at 60 °C. This variation makes sense, since the increase in temperature favors the flow of solutions, which is reflected in a decrease of this value with approximately 80%. The values found are within the ranges reported in previous works, which indicated that the value of viscosity depends on the concentration of Q, its degree of deacetylation and obviously the pH of the solution.[21] On the other hand, P solutions have low viscosity values, similar to that of regular water, and as the concentration increases, an increase in viscosity is observed. This behavior is associated with the fact that P is a material that has a stabilizing and thickening capacity.[22] As pointed out by other authors, it is important to know the flow behavior of P solutions, since gel formation depends on a critical concentration, which may affect compatibility with other solutions, when a combination with other polysaccharides in intended.[23]

The dynamic viscosity values of combined Q-P showed an increase as the P content increased; this observation remained true at both temperature levels studied. This behavior is attributed to the thickening effect caused by P, when it is combined with Q, presenting much higher values than that of individual P solutions, but lower than that of Q solutions.[23]

On the other hand, when adding the crosslinking agent ($CaCl_2$) to the Q-P solutions, it can be observed that, with a concentration of 0.1P, the value of dynamic viscosity showed an increase of approximately 10%. However, when increasing the concentration of P solution, the opposite effect is observed, as the dynamic viscosity decreased by 28% and 36% at 25 °C, and by 11% and 7% at 60 °C. A slight gelling behaviour was observed in the appearance of the solution, making it slightly less fluid. This is evidence of a kind of crosslinking in the polysaccharide structure of the films, where the

content of P seems to be a limiting key factor that improves the structure of the films.

Table 1
Dynamic viscosity results

Film	Dynamic viscosity (cP)	
	25 °C	60 °C
Q	1083	212
P 0.1	7.67	—-
P 0.35	8.81	—-
P-0.5	15.0	—-
Q-P 0.1	132.8	36.52
Q-P 0.1 $CaCl_2$	146.5	45.33
Q-P 0.35	261.8	65.8
Q-P 0.35 $CaCl_2$	188.2	58.2
Q-P 0.5	314.9	86.88
Q-P 0.5 $CaCl_2$	200.6	80.2

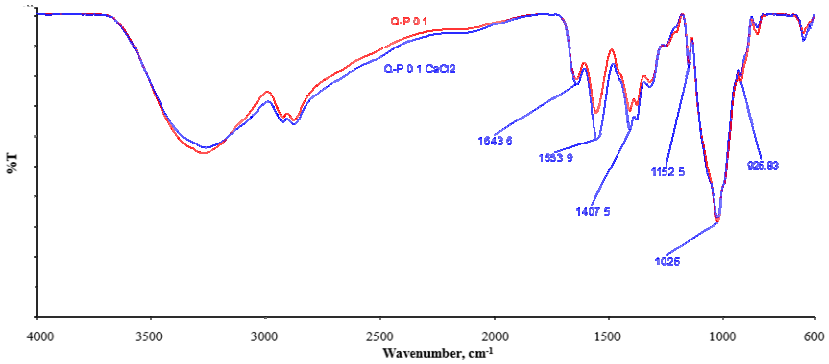

Figure 2: FTIR spectra of Q-P 0.1 and Q-P 0.1 $CaCl_2$

FTIR characterization

FTIR analysis was performed to identify the main functional groups and the interactions of compounds in the different film formulations, in addition to the formation of new functional groups as a consequence of the resulting bonds due to crosslinking. Figure 2 shows the FTIR spectra of the films Q-P 0.1 and Q-P 0.1 $CaCl_2$. The main functional groups of Q are present at 3263, 1590, 1405 and 1026 cm^{-1}, attributed to OH stretching, bending of N-H, angular vibration of -(CH2)- and C-O groups of the glycoside ring.[18,24,25] This shows that Q is participating as a crosslinking polymer with $CaCl_2$ at low P concentration, mainly in the amino group, which is present at 1552 cm^{-1} (N-H) and a higher intensity of the peak is observed. On the other hand, P interacts with alkyl groups in the Q-P polymer blend, which corresponds to the signals at 2875 and 1408 cm^{-1}.

Figure 3 depicts the IR spectra of Q-P 0.35 $CaCl_2$ and Q-P 0.35. A generalized increase in the band intensities can be observed in these spectra; mostly, in the crosslinked Q-P film, due to a contribution of hydroxyl, carbonyl, carboxylate and glycosidic groups at 3263, 1749-1640, 1408 and 1152 cm^{-1}, respectively, attributed to the P structure, which allow an improved bonding process through the divalent cation (Ca^{+2}). Concurrently, the contribution of Q is noted through the functional groups at 2870 cm^{-1} representing C-H and the amine group at 1554 cm^{-1} from the amide II group; the latter to a higher degree, noted during the crosslinking process.[26-27] This behavior suggests non-covalent crosslinking in the Q-P blend, especially in P functional groups, in both cases with $CaCl_2$.

All the spectra show the characteristic peaks for each functional group of Q and P, it is possible to observe differences in the intensity of the signals (decreasing) at 3263 and 1026 cm^{-1}, especially when increasing the concentration of P, which suggests that ionic crosslinking occurred between P and $CaCl_2$, the Q-P bonding was realized through the amino groups, and there were no changes in the characteristic functional groups of Q and P. Similar behavior was reported by Li *et al.*,[17] who indicated that crosslinking of Q is

carried out by non-covalent bonds. On the other hand, Hamdi *et al*. reported that Q interacts with the plasticizer through hydrogen bonds in the OH groups.[24]

The shift of OH groups to a higher wavenumber is attributable to the presence of ionic crosslinking at higher concentrations of P (Fig. 4). On the other hand, a decrease in the intensity of the peaks is observed, this is caused by a lower availability of active binding sites, since these were occupied by the bonding of Q and P. This phenomenon is noted primarily in the double band at 1753-1643 cm^{-1} (COO^-), 1408 (CH_3), and 1027 cm^{-1} (C-O-C), corresponding to carboxylate, alkyl and glucoside groups of P, respectively. The strong peak at 1620 cm^{-1} (amide I) is indicative of interchain intermolecular hydrogen bonding and the shift of the peak at 1560 cm^{-1} (NH) to a lower wavenumber is associated with hydrogen bonding. It is important to point out that the band at 1656 cm^{-1} corrasponding to the acetyl group (amide I) of Q overlaps with that at 1643 cm^{-1} of the carboxylate group of P, which corroborates the crosslinking process between Q and P. This behavior is attributed to intermolecular salt-type bonds.[24,28,30] It has been reported that the crosslinking generates an increase in intensity of the peaks attributed to glycosidic bonds and better intermolecular interaction, increasing the hydrogen bonds.[20]

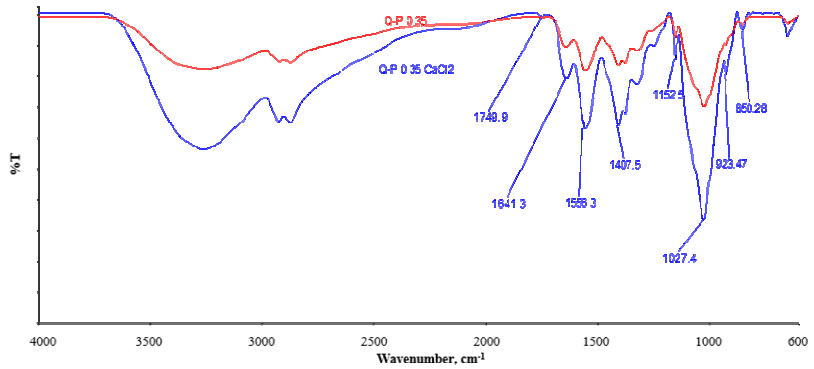

Figure 3: FTIR spectra of Q-P 0.35 and Q-P 0.35 $CaCl_2$

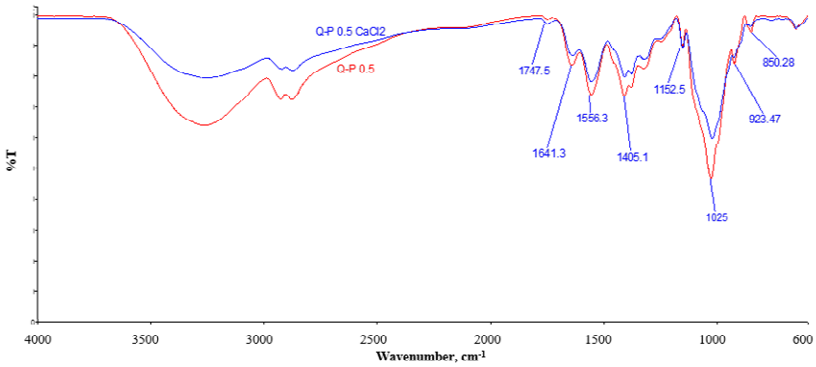

Figure 4: FTIR spectra of Q-P 0.5 and Q-P 0.5 $CaCl_2$

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was used to determine the thermal stability of films and evaluate the effect of addition of $CaCl_2$ as crosslinking agent on this property. Figure 5 shows the TGA thermogram (5a) and the derivative weight loss curve (5b) for Q-P 0.1 and Q-P 0.1 $CaCl_2$. In Figure 5a, it is possible to identify three main weight loss stages: the first occurs between 40-150 °C, corresponding to 18% weight loss and it is associated with the evaporation of water and solvents; the second stage, occurring between 150-360 °C, corresponds to the polysaccharides decomposition and plasticizer degradation, besides the cleavage of the OH bonds (41% weight loss),[25,30,31] with a maximum degradation temperature of 252 °C. There is a third minimal weight loss (6%) after

360 °C and up to 590 °C.[33] At 600 °C, a residue of 29% remains. It is evident that the film comprising the crosslinking agent has a better thermal stability, which suggests that this film has a more complex structure that delays the thermal decomposition of polysaccharides, resulting in a high residual content at the end of the analysis.

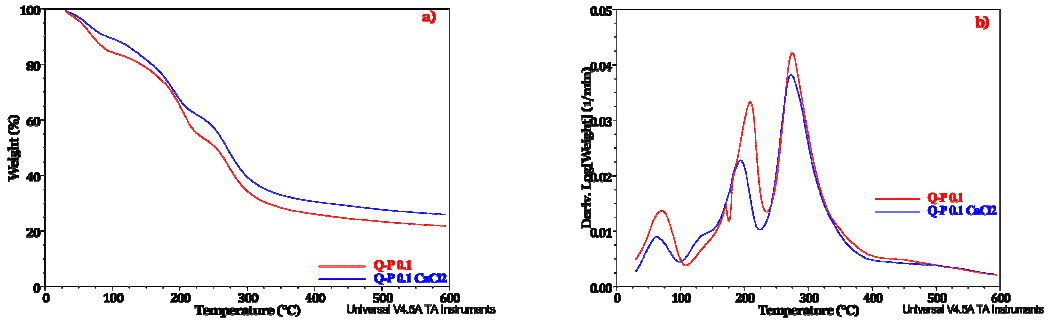

Figure 5: TGA thermogram (a) and DTG thermogram (b) for films Q-P 0.1 and Q-P 0.1 $CaCl_2$

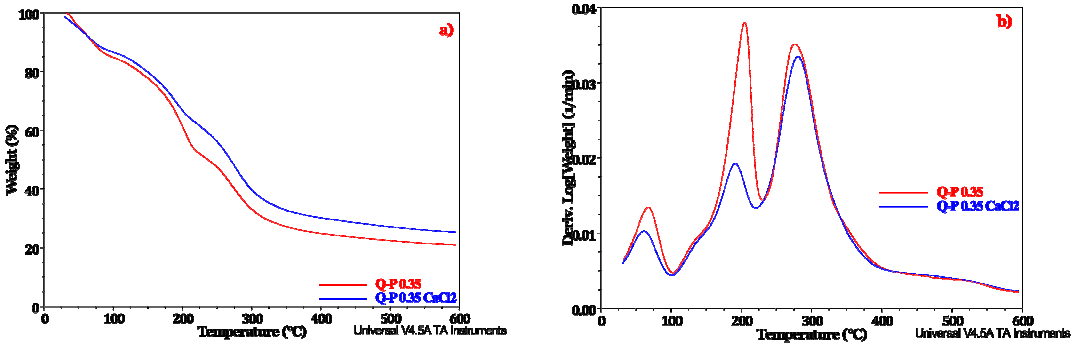

Figure 6: TGA thermogram (a) and DTG thermogram (b) for films Q-P 0.35 and Q-P 0.35 $CaCl_2$

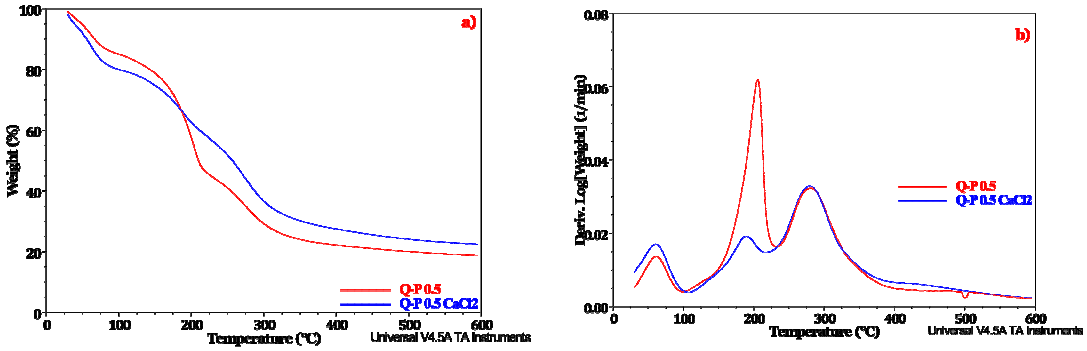

Figure 7: TGA thermogram (a) and DTG thermogram (b) for films Q-P 0.5 and Q-P 0.5 $CaCl_2$

These three decomposition steps are more evident in Figure 5b (derivative DTG curve): the first, around 100 °C, the second one around 200 °C and the third one – below 300 °C. Also, an interesting finding is that the derivative weight quotient is lower in the stages attributed to polysaccharides decomposition, which can be associated with the ionic crosslinking that occurred in this structure. Also, it is evident that the second stage derivative peak is lower for film Q-P $CaCl_2$ than for the film without crosslinker, which confirms the occurrence of crosslinking in the polysaccharide structure,[31] corroborating the findings of FTIR analysis. Some reports have suggested that this increase in thermal stability is due high intermolecular interaction between Q and P, which intensifies the hydrogen bonds, generating a more compact structure.[21,30] Other reports indicated only two main decomposition stages for polysaccharides in Q/(polyvinyl

alcohol/P), the first from 50 to 150 °C, and the second one from 250 to 350 °C.[5]

The Q-P 0.35 and Q-P 0.35 $CaCl_2$ films (Fig. 6a and 6b) have a similar behavior to that of films Q-P 0.1, with and without $CaCl_2$, – with the first weight loss of 20% between 40-150 °C, corresponding the loss of moisture in the films; the following weight loss (47%), between 130-360 °C, corresponding to the degradation of Q and P, where the maximum degradation occurs at 256 °C, and the last weight loss (5%) between 360 °C and 570 °C, referring to residue degradation. At 600 °C, a residue of 25% of the initial weight remains. Also, it is evident that the film containing the crosslinker has better thermal stability, which is attributed to its more complex structure, as discussed above. In Figure 6b showing the DTG curve, it is more evident that the quotient of Q-P 0.35 $CaCl_2$ is lower than that of the film without crosslinking agent, indicating that its susceptibility to decomposition is lower, due to a crosslinked polysaccharide structure. The same behavior was observed for films Q-P 0.5 and QP-05 $CaCl_2$, with similar weight losses in three stages, and the derivative curve quotient for Q-P $CaCl_2$ being higher than for Q-P 0.5. This can suggest that crosslinking is carried out mainly in the P structure, and due to the increasing concentration of pectin in the film, the quotient is lower, which indicates that it is less susceptible to weight loss at that temperature, compared to the reference films, where P and Q have higher ratios, which indicates that they degrade more quickly and lose more weight.

Dynamic mechanical analysis (DMA)

DMA analysis was performed to determine the effect of the crosslinking agent, $CaCl_2$, on the properties of the Q-P polymeric matrix. The storage modulus measures the absorbed energy and the ability of a material to withstand loads or stress (elastic behavior), while tan δ provides information related to changes associated with the movement of the polymer chains and also helps to determine the glass transition temperature (Tg) and the viscoelastic behaviour. In the present work, the properties of the films were evaluated at lower temperature with the aim to find out their suitability for a possible application as primary packaging in climacteric foods, such as fruits and vegetables.[12] DMA has been reported as a useful tool for examining the mechanical properties of biomaterials,[24,32] as it allows to identify primary and secondary relaxations.

Figures 8, 9 and 10 allow a comparison of the storage modulus of the Q-P films for each of the established formulations, those containing the crosslinking agent and those that did not. The DMA thermogram of storage modulus for Q-P 0.1 and Q-P 0.1 $CaCl_2$ (Fig. 8) shows a typical decrease of storage modulus for Q with temperature, followed by an increase at higher temperatures, which is associated with the release of water and glycerol, the latter of which acts as plasticizer. The decrease with temperature reached a minimum value approximately around 90 °C for the films without crosslinking agent and 110 °C for the film with $CaCl_2$, and is associated with a softening of the films with temperature, related to the thermal transition of molecular chains of polysaccharides.[34] Guerrero *et al*.[18] reported that this decrease in storage modulus of Q films crosslinked with citric acid by thermo-compression is around 20-30 °C, a much lower temperature, compared with the values obtained in this work. It can be observed that the storage modulus for the films with $CaCl_2$ shows a lower value, compared with the films without crosslinker.[18] When these compounds are mixed, P acts as a thinner for the Q film, and this is reflected in the decrease of the storage modulus in the films that did not contain the crosslinking agent. The crosslinking agent was added into the film composition to improve the mechanical properties, which is related to the role of the crosslinking agent in the formation of a more stable structure, due to a physical bonding between the components, without a chemical reaction taking place. In the viscosity analysis of the film-forming solutions, without the crosslinking agent ($CaCl_2$), it was noted that Q had high viscosity, while P had lower values, which corroborates the results of DMA.

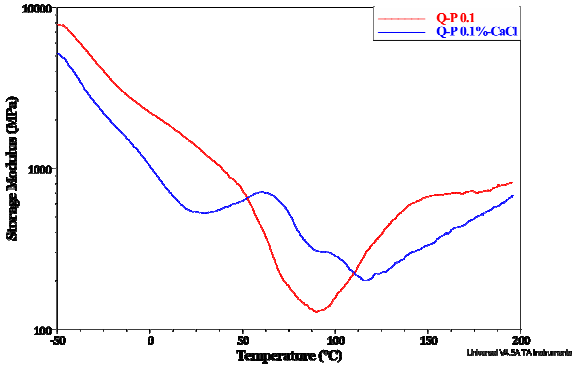

Figure 8: DMA thermogram of storage modulus for films Q-P 0.1 and Q-P 0.1 $CaCl_2$

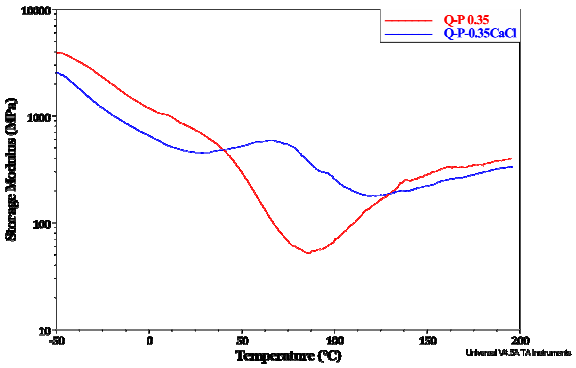

Figure 9: DMA thermogram of storage modulus for films Q-P 0.35 and Q-P 0.35 $CaCl_2$

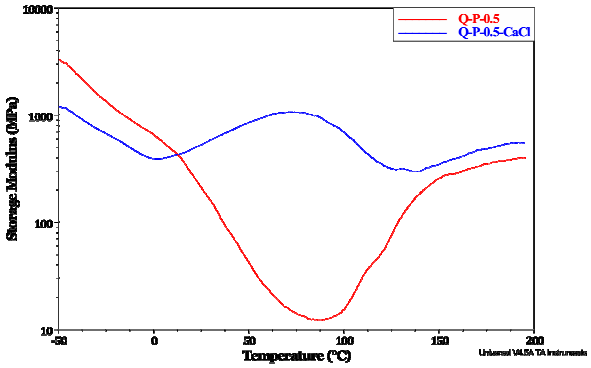

Figure 10: DMA thermogram of storage modulus for films Q-P 0.5 and Q-P 0.5 $CaCl_2$

Norcino *et al.*[14] reported that Q films show a lower storage modulus than P films, which is attributed to the relaxation of polysaccharide chains. This suggests a lower capacity to absorb energy as the film is more rigid. Similar behavior was reported for Q films crosslinked with silver nanoparticles.[35]

It is evident that, with a rising P content in the films (Figs. 9 and 10), the variation of storage modulus of the films with and without and $CaCl_2$ is more pronounced, which can confirm the presence of a crosslinked structure, confirming the previous discussion regarding thermal stability. This is associated with interactions between polymer chains, such as hydrogen bonding, crosslinks and ionic interactions within the polysaccharide structure of P.[36]

CONCLUSION

In the present work, the preparation of films based on Q and P, with the addition of a crosslinking agent, $CaCl_2$, is reported. The solutions of P before film formation showed low dynamic viscosity values, and, when combined with Q, there was an increasing trend in dynamic viscosity as the concentration of P increased, which is attributed to the thickening effect on this polysaccharide. On the other hand, when adding $CaCl_2$ to the solution, an opposite effect was remarked, since the highest value of dynamic viscosity was exhibited by the solution with low P content (Q-P 0.1 $CaCl_2$), which indicates that P content has a limited role in the value of dynamic viscosity. FTIR analysis showed evidence of ionic crosslinking between Q and P, due to variations in the peaks attributed to the carboxylate, amine, alkyl and glycosidic functional groups of both polysaccharides. The TGA results also confirmed a certain degree of crosslinking in the films, because both the decomposition temperature and the material residue at the end of the analysis (600 °C) increased in the films with $CaCl_2$. The DTG curves corroborated the greater thermal stability of the Q-P films, since the quotient of the curve is lower, which can be associated with lower susceptibility to decomposition of a more stable crosslinked structure. Finally, the DMA results corroborated that there is crosslinking between Q and P, as the storage modulus is higher in the films with $CaCl_2$, especially in the region between 90 and 110 °C, where the polysaccharides presented a softening related to the molecular

transition of Q and P. Thus, the results obtained in the present investigation revealed that the addition of $CaCl_2$ as a crosslinking agent to Q-P formulations has a positive effect on the properties of Q-P films.

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