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Bio-based carrageenan composite coatings for food packaging application

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Abstract*– Biopolymers has been considered suitable materials for the development of alternative packaging; in particular, carrageenan and its composites has been explored for the development of flexible films and coatings because of its properties. The aim of this work was to develop carrageenan-based coatings for food packaging applications using anthocyanin from purple corn and oregano oil as additives. Samples of strawberries, swordfish, chicken breast and sausage were coated and evaluated for 30 days. In addition, biodegradability and characterization tests were performed by using spectroscopy and thermal analysis. Samples coated with coatings containing 5% w/w oregano oil demonstrated to inhibit the growth of mold fungus until for 15 days, while composites with 1% and 3% oregano oil presented mold after 5 days. Anthocyanin was added as a pH-indicator in films and films turn darker, indicating a degradation process form meats. Biodegradability tests showed that all formulations degrade following three stages, achieving a weight loss of 35% after 30 days. In conclusion, carrageenan-based coatings could be considered in packaging systems to increase the shelf-life of food. Oregano oil provides antifungal activity and anthocyanin give pH-responsiveness. The coatings demonstrated biodegradability and characterization demonstrated that the main structure of carrageenan in coatings was not altered.

Keywords*— Carrageenan, film, packaging, shelf life, anthocyanin.

I. INTRODUCTION

In the last years, pollution due to synthetic polymers has been increasing and one of the main causes is the poor disposal of single-use plastics, such as bottles and food packaging materials. The market of plastic has increased exponentially according to different sources (~335 million tonnes in 2017 and ~380 million tonnes in 2018) [1], and the global plastic leakage is estimated among 4.8 to 12.2 million tonnes per years between 2015-2018 [2]. The principal sources of wasted plastics are packaging, transportation,, textiles, building and construction, and the main polymers present in waste are polyethylene, polystyrene, polyvinylchloride, polyurethane, polyethylene terephthalate, polyester and fibers (polyamide and acrylic) [3]. Few amounts of this materials remain in landfills or could be incinerated. However, great amounts of plastic materials are disposed in oceans or rivers, affecting the environment. Faced with this problem, new alternative materials are being researched and developed to replace those petroleum-derived polymers. In this context, natural polymers are being considered as good alternatives with potential applications in the pharmaceutical, biomedical, cosmetic and food industries because of their properties such as biodegradability, hygroscopicity and low-toxicity [1].

Currently, biodegradable materials are trend in food packaging systems, those materials are used in food coating, food packaging materials and encapsulation matrices for functional foods [4]. Most of the systems must achieve enhanced properties; therefore, biopolymeric materials can be mixed with other constituents to elaborate "active packaging". This term refers to a "packaging" with special properties such as O_2 scavengers, CO_2 scavengers, moisture and ethylene gas regulators, the ability of release/absorb flavors and odors, and the capacity of releasing antimicrobial or antioxidant agents. Moreover, this packaging can be modified to detect environmental changes and can be able to provide information by sensing, detecting, colorimetric pH indicator capacity among others, those are considered such as "intelligent packaging". [5]. According to Rhim & Ng [6], the main benefits of using biopolymeric materials are their edibility, biodegradability, enhanced organoleptic characteristics, low cost and renewability. However, biopolymers have some drawbacks such as low barrier properties, mechanical properties, processing properties and high prices compared with synthetic polymers [7]. For that reason, several modifications, including chemical structure modifications and addition of organic/inorganic compounds, have been reported to enhance the properties.

Biopolymeric materials for smart packaging films have employed different additives, but the most important are dyes as pH-indicators and essential oils as antimicrobial agents. One of the dyes used in film packaging are anthocyanins. Anthocyanins are natural pigments found in flowers, fruits and vegetables and these dyes are able to change the color depending up the pH of medium (pH-sensitivity), making them suitable for incorporation into biodegradable matrices as pH-indicator. For example, Zhang et al. Zhang et al. (2019) incorporated anthocyanin from *Roselle calyx* into chitosan/PVA films, turning red into acid mediums, purple into neutral pH and yellow under basic mediums. Rawdkuen et al. [9] extracted anthocyanins form sweet potatoes, roselle, husk, red dragon fruit and butterfly pea and incorporate them into gelatin films, concluding that butterfly pea anthocyanins demonstrated better sensibility due to the wide range of color variation. Weston et al. [10] incorporated anthocyanins from red cabbage into PVA films to elaborate pH sensors, showing a blue-to-red colorimetric response to lactic acid, making the films suitable for use-by date indicator milk. Moreover, several studies have demonstrated that the addition of anthocyanins in films add antioxidant activity because of the

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presence of active phenolic components (ferulic acid, tannic acid, etc.) [11]–[13].

Essential oils (EO's) in bioplastic films have been reported to enhance antimicrobial and antifungal properties in bioplastic films for food packaging [14]. EO's are organic volatile compounds consisting of hydrocarbons and oxygenated compounds (tryacylglycerols, diacyl glycerols, fatty acids, phospholipids, fat soluble vitamins, free sterols and sterol esters) that are produced as secondary metabolites in plants and seeds [14]. The main function of EO's in packaging is to minimize or eradicate the pathogenic microbes and/or decrease the phenomenon of lipid oxidation. Additionally, EO's enhance the preservation of food due to the interruption of bacterial membranes integrity caused by the penetration in lipidic layers [15]. Several biopolymers have been mixed with EO's and the most important techniques are-casting and extrusion. method is the main strategy for the development of films, but the first is preferred for research because its low cost and ease. For example, starch is one of the main polysaccharides that have been combined with EO's. such as oregano oil [16]–[18], cinnamon oil [19], [20] or soy oil [21], [22] with potential application for meat and vegetable preservation. Other examples of polysaccharides combined with EO's are cellulose [23], chitosan [24], alginates and proteins [25]. In addition, EO's have demonstrated to add other characteristics such as oxygen/moisture barrier properties [24] and better handleability despite of the decrease in mechanical properties [16], [18]. So, there are many benefits of employing EO's in the properties of materials oriented for film packaging; however, the content of EO's vary depending on the biopolymer, ranging from 0.025% to 100% weight (based on the mass of biopolymer).

Carrageenan is a water-soluble polysaccharide extracted from red algae that has been used for the development of biopolymeric-based coatings. Several studies have demonstrated that carrageenan (kappa-carrageenan, iota carrageenan and semi-refined carrageenan) are able to form thin films in presence of plasticizers. In addition, the presence of plasticizers, such as glycerol and sorbitol, could increase the moisture content and, consequently, increase the interstitial spacing between carrageenan chains, making the films thicker and stronger [26], [27]. Moreover, carrageenans can be mixed with some fillers such as nano-clays [28], polymeric nanoparticles [29], anthocyanin [30] and oils [31] in aqueous suspensions. However, few studies have explored the application of carrageenan based coatings on food. Ribeiro et al. (2007) prepared carrageenan-chitosan based coatings enriched with calcium to protect strawberries by decreasing the microbial growth. Hamzah et al. (2013) prepared edible coatings of carrageenan using glycerol as a plasticizer for surface coating of papaya. The coatings demonstrated to delay ripening and to extend the shelf life. Zhou et al. [30] prepared carrageenan-based edible coating mixed with konjac glucomannan with camellia oil to enhance the shelf-life of chicken meat by restraining the oxidation of lipid and protein and retarding the microbial growth. Zhou, Yu, et al.[34] added bilberry anthocyanin to konjac glucomannan-carrageenan films to develop pH-responsiveness films. According to the literature described above, it's possible to elaborate carrageenan-based film with improved properties and pH-responsive characteristics. This could be suitable for the design of smart packaging for preservation of food.

Hence, the aim of the study is to develop biopolymeric coatings based on native carrageenan extracted from red algae. Moreover, anthocyanin powder, extracted from purple corn, and oregano oil were used as additives to develop pH-responsiveness coatings with conservative properties. Chemical structure and biodegradability of each formulation were evaluated and coatings were tested for different food samples to evaluate its physical-chemical properties.

II. Materials and Methods

A. Materials

Red algae *Chondracanthus chamissoi* was obtained from the peruvian coast (Ventanilla, Lima). Red algae were washed with distilled water and stored at 4°C. Purple corn was purchased from a local market, washed and stored at room temperature. Oregano oil purchased from EOP PERU. All chemicals utilized (HCl, NaOH, glycerin) were of analytical grade. To evaluate the applicability of carrageenan-based coatings, samples of strawberries, chicken breast, sausage and swordfish steak were obtained from a local market.

B. Extraction of native carrageenan and anthocyanin from purple corn

Native carrageenan were extracted using an alkali treatment previous reported in literature [35], [36]. Briefly, 100g of red algae were refluxed in 700 ml of NaOH solution (1M) for 4 hours at 90°C under magnetic stirring. Then, the suspension was precipitated with 2-propanol and the extracted were resuspended and washed by three times using the same alcohol. Finally, the native carrageenan was dried until constant mass at 40°C and stored under desiccation conditions.

Anthocyanin powder was extracted from purple corn with the method reported by Chen et al. [23] Approximately 50g of purple corn were chopped and placed in 500 ml of ethanol (50% v/v) and magnetic stirred at 60°C for 24h in dark. The suspension was filtered and the supernatant were recovered and evaporated under stirring at 50°C in dark. The final powder was dried in an oven at 60°C for 48h. The anthocyanin powder was placed in a brown glass bottle under desiccation conditions.

C. Preparation of coating formulations

For this research, eight formulations were prepared, combining carrageenan, glycerin as plasticizer, anthocyanin

powder and oregano oil. Carrageenan-based coatings were prepared using a solution-casting method. Firstly, carrageenan and additives (described in Table 1) were diluted in 100 ml of distilled water and heated at 80°C for 1 h under magnetic stirring. For coating applications, suspensions were cooled until 40°C and stored in brown glasses. Moreover, some volume of carrageenan suspensions were poured onto Petri dishes and placed in a oven at 60°C in order to form thin films for thermal characterization. For control, carrageenan-glycerin films were prepared.

Table 1. Details of each carrageenan-based coating formulation.

Formulation	Formulation
CAR	1g of carrageenan, 0,3g of glycerine in 100 ml of water
CAR-1AO	1g of carrageenan, 0,3g of glycerine and 0,01g of oregan oil in 100 ml of water
CAR-3AO	1g of carrageenan, 0,3g of glycerine and 0,03g of oregan oil in 100 ml of water
CAR-5AO	1g of carrageenan, 0,3g of glycerine and 0,05g of oregan oil in 100 ml of water
CAR-M	1g of carrageenan, 0,3g of glycerine and 0,1g of anthocyanin powder in 100 ml of water
CAR-1AO-M	1g of carrageenan, 0,3g of glycerine, 0,1g of anthocyanin powder and 0,01g of oregan oil in 100 ml of water
CAR-3AO-M	1g of carrageenan, 0,3g of glycerine, 0,1g of anthocyanin powder and 0,03g of oregan oil in 100 ml of water
CAR-5AO-M	1g of carrageenan, 0,3g of glycerine, 0,1g of anthocyanin powder and 0,05g of oregan oil in 100 ml of water

D. Coating applications

Samples of strawberries, chicken breast, sausage and swordfish steak were used in order to evaluate the effectiveness of the coatings. All the samples were washed with distilled water and dried with a paper towel sheet. Firstly, food samples were cut in cubes of side 1cm approximately. Then, samples were dipped into the carrageenan-based coating suspensions for 3 min and then drained. Coated samples were allowed to dry for 3h at ambient conditions (21°C). Additionally, some food samples were immersed in distilled water and served as control. For 30 days, coated and uncoated samples were evaluated at laboratory conditions (18-22°C) in order to analyze the changes in firmness and surface color, associated with decomposition or putrefaction. Throughout 30 days, samples were inspected visually and photographed in order to compare color changes or the presence of mold.

E. Characterization

i. Fourier transform infrared spectroscopy (FTIR-ATR)

For structural analysis of carrageenan-based coatings, attenuated total reflection Fourier transform infrared spectroscopy testing was performed with a Bruker Tensor 27 IR spectrophotometer equipped with a universal ATR sampling accessory, averaging 32 scans at a resolution of 4 cm^{-1} in the range from 4000 cm^{-1} to 400 cm^{-1}. The data were analyzed by means of the software.

ii. UV-vis spectroscopy

Absorption spectra of anthocyanin solutions (10 mg/ml) at different pH values (1-10) were recorded by a UV/VIS UNICO 2802SE spectrophotometer using quartz cells in a wavelength range of 450-700 nm.

iii. Differential Scanning Calorimetry (DSC) and thermogravimetric Analysis

Approximately 5 mg of carrageenan-based film coatings were loaded into a crucible. DSC and TGA tests were performed simultaneously in a NETZSCH STA 449F3 Jupiter® thermal analyzer. Nitrogen was used as the purging gas and the flow rate was controlled at 50 ml/min. For each run, samples were heated from 30 °C to 700 °C at a heating rate of 10 °C/min.

iv. Biodegradation test of carrageenan-based coatings

In order to evaluate biodegradability of carrageenan-based coatings, organic compost was used, based in a previous research for organic coatings [37]. The moisture content of the compost was fixed to 50% to achieve aerobic conditions. The pH of compost was stabilized within a range of 70.0-8.0. Carrageenan-based films were cut into 25mm x 25 mm squares (thickness about 40-80 μm), the mass of each sample was about 50-100 mg. Previously, the samples were washed in ethanol (96%) for 2 min and dried at 40°C overnight. Dried samples were weighted for the first time and placed in an opaque vessel containing 50 g of compost at room temperature. The incubation time was 32 days and the samples were weighted in selected days to evaluate the weight lost during biodegradation.

v. Statistical analysis

Biodegradability experiment were carried out in triplicate. The results are expressed as mean ± standard deviation and the degradation curve was assessed with Microsoft excel. Statistical significance was determined by one-way ANOVA test.

III. Results and Discussion

Carrageenan film coatings were prepared by mixing carrageenan with essential oils an anthocyanin. As described in section 2.3, eight formulations were prepared by using native carrageenan and anthocyanin powder extracted from

purple corn. Native carrageenan from *Chondracanthus chamissoi* has been reported as hybrid κ/i carrageenan [36, 38] and, approximately, 6.44 g of neat carrageenan has been obtained from 100g of dried algae. Further, anthocyanin powder was extracted using an ethanolic method, obtaining 0.152 g of anthocyanin powder per gram of purple corn cob.

The UV-Vis spectrum and color change of anthocyanins is showed in Fig. 1. In Fig. 1a, the colors of anthocyanins solutions reveal different colors depending up the pH. At - lower pH (1-6) the solutions turn red, at pH=7-9 the solution turns purple, and at higher pH values, the solutions turn yellow-brown. Analyzing the color change, the maximum absorption peak of the anthocyanin solutions shifted towards the longer wavelength, as shown in Fig. 1b. The maximum absorption peak, which was obtained around 516 nm at pH 2, shifted from 508 to 520 nm when the pH increased from 3 to 6, while the absorbance decreased. As the pH increased from 7 to 10, the maximum absorption peak shifted from 551nm to 571 nm, and accompanied with a decrease in absorbance. The curves at pH 11 and 12 do not show any peak. The color change, accompanied with a variation in absorbance, occurred because of the transformation of the anthocyanin structure. Color at pH 2-3 are dominated by flavylium cation, at neutral pH the color is dominated by the formation of quinonoidal bases at a higher pH, the yellow color occurs due to the form of yellow chalcone [5; 23].

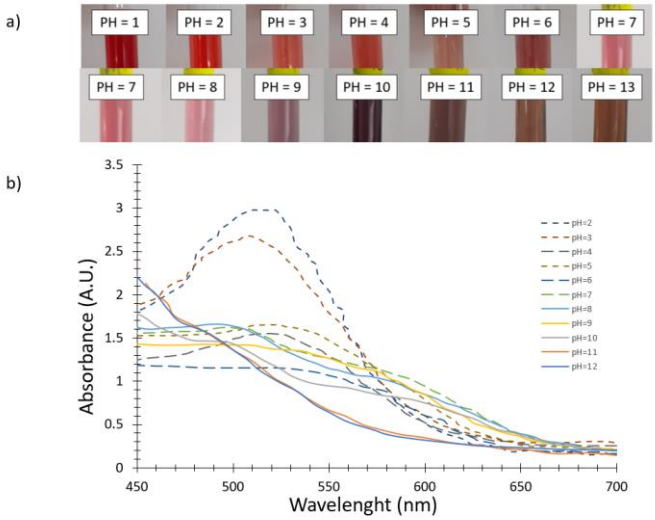

Fig. 1. a) Color spectrum of anthocyanin solutions in different pH solutions. b) UV-Vis spectrum of anthocyanin solutions.

Samples of foods (strawberries, jam, sword fish and chicken breast) were coated by immersion and drying process (Fig. 2-5, more images can be found in Appendix section) and analyzed for 30 days under room conditions. Samples of uncoated strawberry (Fig. 2) showed (control) get dried and turn darker with small appreciation of mold. On the other hand, coated samples shows more zones with mold after 5 days, with the exception of samples with 5% of oregano oil. However, after 30 days, the samples coated with CAR-5AO-M presented lower presence of mold, similar to uncoated sample. After this evaluation, it can be concluded that carrageenan-based film does not promote the conservation of strawberry because of the coatings do not avoid the moisture evaporation. Additionally, the organic charge of anthocyanin powder would promote the proliferation of fungi, excepting the samples with higher content of oregano oil. In the case of sausage samples (Fig. 3), all the samples showed the presence of mold fungi after 30 days. However, samples containing 3% of oregano oil presented mold fungi after the fifth day, and sample coated with CAR-5AO-M presented mold after the day 10. It can be concluded that, for sausage, carrageenan-based coatings offer a low protection. For swordfish samples (Fig. 4), all the samples presented low content of mold fungi and samples with anthocyanin powder turn darker, probably due to the releasing of putrescine (amine basis) from fish decomposition [39]. In the case of chicken breast (Fig. 5), samples coated with formulations with 5% of oregano oil did not present mold fungi until the day fifteen, then all the samples presented fungi proliferation. Samples coated with formulations containing anthocyanin powders turn darker, probably due to the releasing of cadaverine [40], an amine from decomposition, similar to fish decomposition. After this evaluation, carrageenan-based coatings with oregano oil (with at least 5% of oregano oil) could be used for the packaging of meat, and formulations with anthocyanin powder presented good sensibility in color change when a basis compound is released.

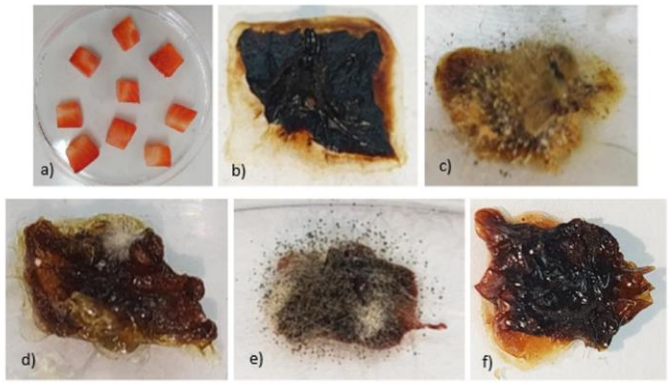

Fig. 2. Samples of strawberry: a) sample of fresh strawberry; and samples after 30days b) uncoated sample, c) samples coated with CARR, d) sample coated with CAR-5AO, e) sample coated with CAR-M, f) sample coated with CAR-5AO-M.

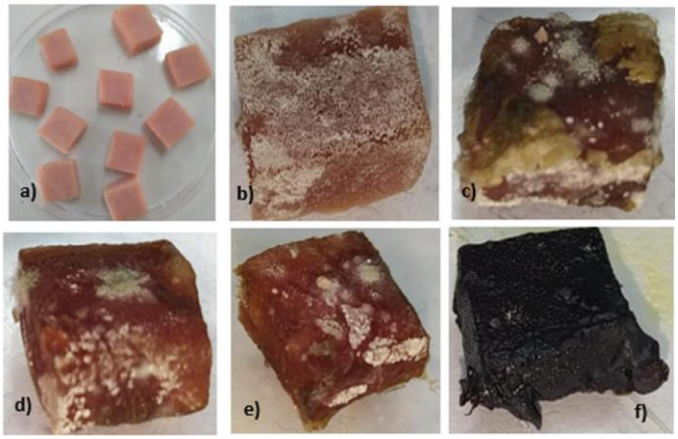

Fig. 3. Samples of sausage: a) sample of sausage; and samples after 30days b) uncoated sample, c) samples coated with CARR, d) sample coated with CAR-5AO, e) sample coated with CAR-M, f) sample coated with CAR-5AO-M.

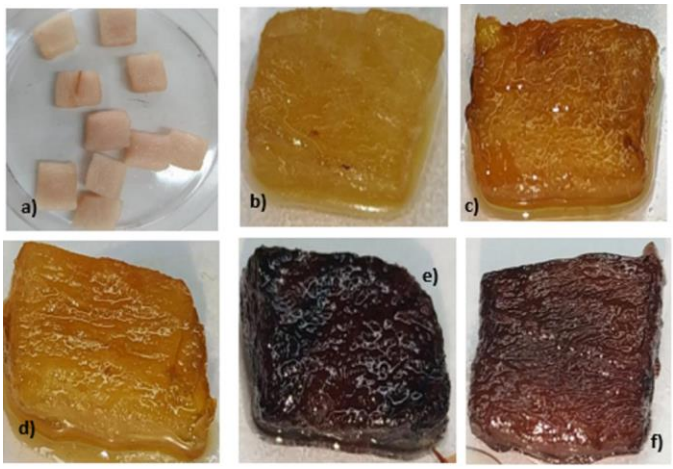

Fig. 4. Samples of swordfish: a) sample of swordfish; and samples after 30days b) uncoated sample, c) samples coated with CARR, d) sample coated with CAR-5AO, e) sample coated with CAR-M, f) sample coated with CAR-5AO-M.

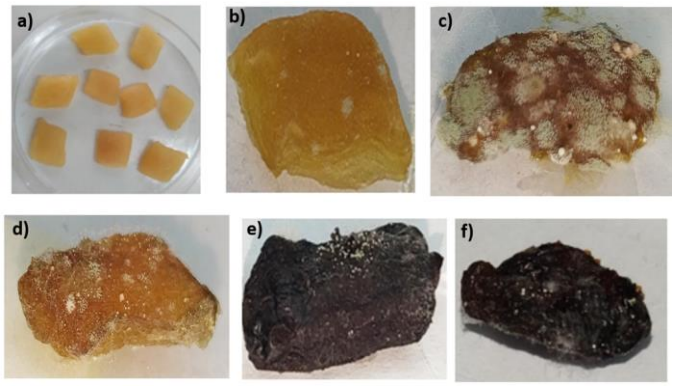

Fig. 5. Samples of chicken breast: a) sample of fresh chicken breast; and samples after 30days b) uncoated sample, c) samples coated with CARR, d) sample coated with CAR-5AO, e) sample coated with CAR-M, f) sample coated with CAR-5AO-M.

Biodegradation tests of carrageenan film coatings (Fig. 6a and 6b) reported the weight loss during degradation and three stages can be distinguished: the first stage corresponds to the absorption of moisture from the compost (up to day 5). The second stage corresponds to a rapid loss of mass typical of the diffusion of the absorbed moisture; and the third degradation (slightly slower) corresponds to the disintegration and depolymerization of the carrageenan films. In Fig. 6a it can be seen that the films suffer a loss of shape. Especially, the deformation suffered by the films with anthocyanin can be appreciated. In this case, it can be seen that films carrageenan films are more susceptible to degradation due to the higher organic load. Additionally, the presence of oregano oil increases the deformation of the film, although this does not necessarily affect the loss of mass in the test. It could be concluded that the films present a stable mass until day 10 on average. Carrageenan presented an initial stage of moisture absorption, caused by the hydrophilicity of changes and the capacity of carrageenan to form three dimensional networks (hydrogels) [41], [42]. Then, according to Torres et al. [37] these stages are usual promoted by the leaching of plasticizers and the break of glycosidic linkage in polysaccharides.

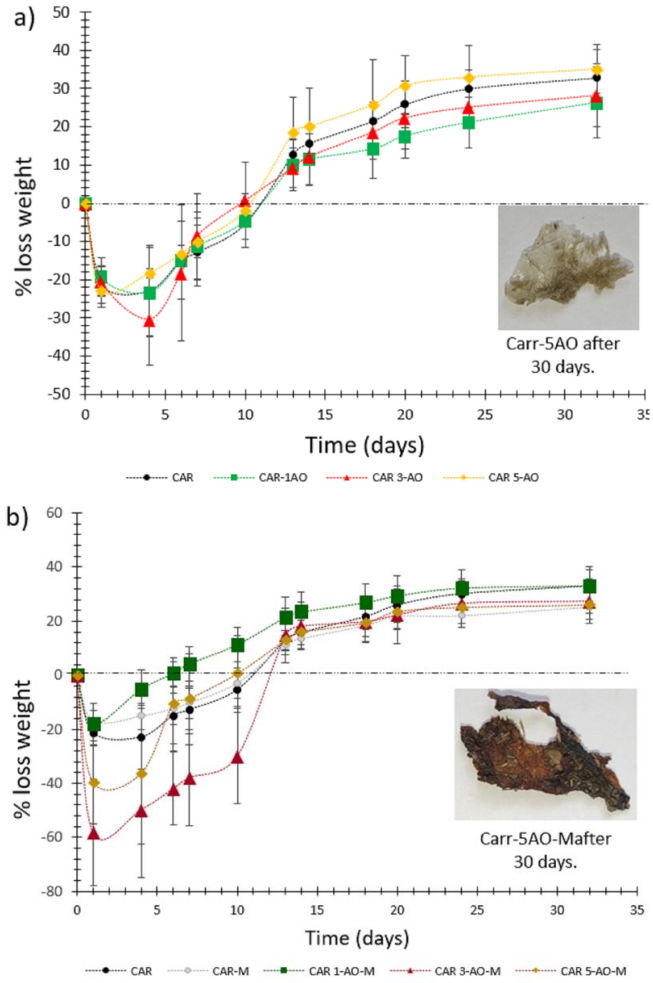

Fig. 6. Representative weight loss curves for carrageenan-based coatings. Images of samples after 30 days is showed.

Carrageenan film coating were characterized using infrared spectroscopy and thermogravimetric analysis. Fig. 7 shows the infrared spectrum obtained for carrageenan films and oregano oil. A broad signal is observed between 3000 and 3500 cm^{-1} corresponding to the presence of hydroxyl groups associated with the presence of moisture. Carrageenan chains are quite hygroscopic, so they can easily absorb humidity from the environment [38]. A weak signal is also observed at 2916 cm^{-1}, corresponding to carbon and hydrogen (C-H) bonds present in the polymer chains [43], [44]. The characteristic peaks of carrageenan are observed at 1219 cm^{-1} corresponding to sulfate ester, 920 cm^{-1} corresponding to 3,6-anhydro-D-galactose (Velde et al., 2004), 830-860 cm^{-1} and 808 cm-1 corresponding to the D-galactose group characteristic of kappa and iota carrageenan [38] demonstrating that it is a hybrid carrageenan. The presence of oregano oil cannot be clearly seen, since the characteristic bands (around 1200 cm^{-1}) overlap with the carrageenan bands [45]. In the same way, the presence of anthocyanin (Fig. 7b) does not alter the structure of the films, being well integrated into the carrageenan-based-coatings.

Fig. 8 show the thermograms where, in general terms, a decomposition in 4 stages can be seen: a first stage of loss of absorbed moisture (up to 150°C); a stage at 258°C, corresponding to a first degradation due to the disappearance of sulfate ester groups (Othman, 2014). Between 250 and 400°C, a gradual degradation of the polymer chains is observed [46], [47]. Above 400°C, total degradation begins, until finally at 600°C the carbonization of the material is observed. The percentage of ash obtained is close to 49% by weight in all cases, due to the fact that the carrageenan molecules have a high carbon load. The presence of oil and anthocyanin increase the organic load, which increases the mass loss between 200 and 400°C. Insert in Fig. 8, DSC thermograms, shows that, although the oregano oil load does not affect the chemical structure, it can influence the displacement of the degradation temperature, probably associated with the higher organic load and the temperature above the smoke point.

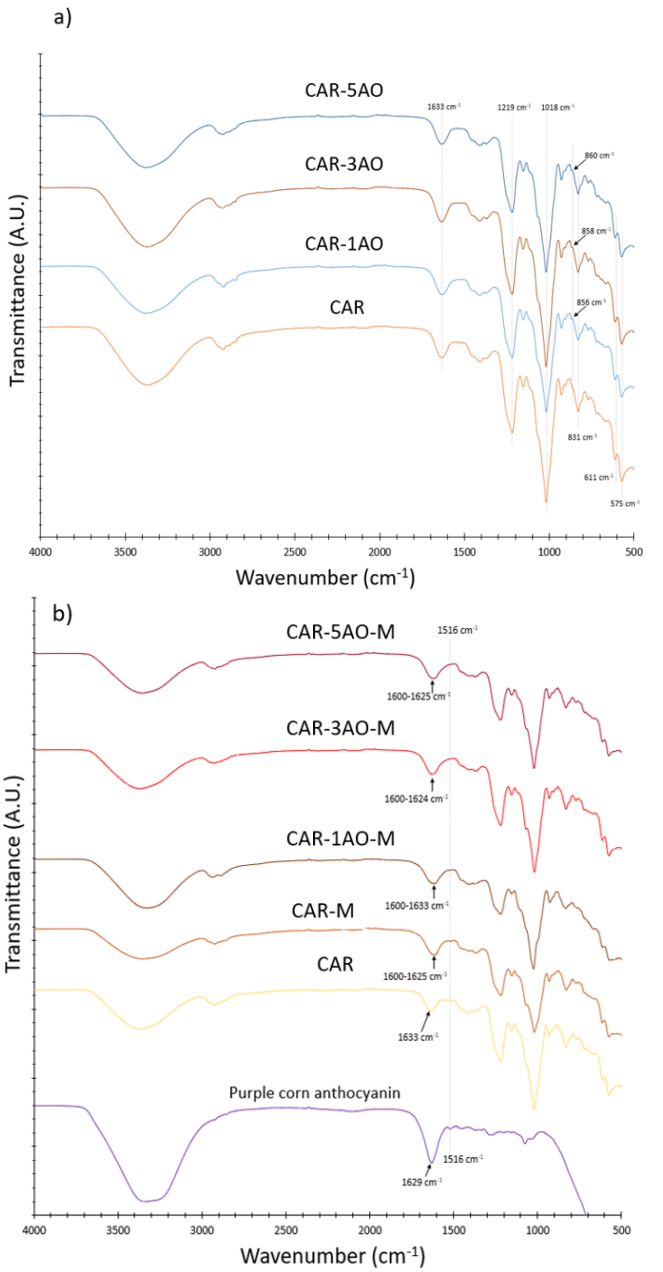

Fig. 7. FTIR spectra of carrageenan-based coatings and anthocyanin powder.

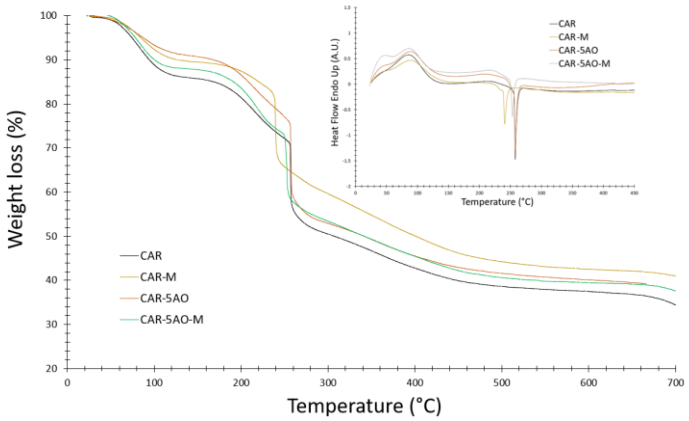

Fig. 8. TGA thermogram and DSC thermogram (insert) of carrageenan-based coatings CARR, CARR-M, CARR-5AO, CARR-5AO-M.

IV. Conclusions

Carrageenan-based coatings were prepared by a solution technique in aqueous suspensions, employing oregano oil and anthocyanin powder (from purple corn) as additives. Eight formulations were prepared by varying the content of oregano oil and examining the use of anthocyanin powder. Samples of strawberries, sausage, sword fish and chicken breast were coated by immersion and tested for 30 days under room conditions. Only the samples of swordfish and chicken breast coated with formulations containing 5% of oregano oil demonstrated inhibition of the growth of mold fungi after 15 days, compared with other formulations; however, after 30 days, all the samples presented mold. This indicates that the addition of oregano oil with concentrations higher or similar than 5% of oregano oil could be considered for the development of coatings for preservation and these coatings could extend the shelf-life. The addition of anthocyanin powder in coatings were used as indicator of the state of foods. In samples fish and chicken, the samples turn purple and dark purple, probably associated to the release of amines of decomposition.

Moreover, the films demonstrated to be biodegradable in compost conditions. The weight loss of films was around 20-35% after 30 days and three stages of degradation can be distinguished. The first stage corresponds to a water absorption due to the hydrophilicity of carrageenan chains. The second stage correspond to a desorption of water due to chains degradation, and the final stage corresponds a degradation of the integrity of coatings with a less weight loss rate. Characterization of FT-IR demonstrated that the additions of oregano oil and anthocyanin powder do not affect the chemical structure of carrageenan. Therefore, carrageenan serves as a good substrate for the elaboration of coatings for packaging.

Carrageenan-based coatings have demonstrated to be great alternatives for the development of films and coatings for food preservation and they can be considered as good alternative of synthetic plastic films. Despite of the main advantages of using biopolymers, further studies will be needed in order to evaluate the impact of coatings in food characteristics such as flavor and odors or to improve film properties such as barrier properties.

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