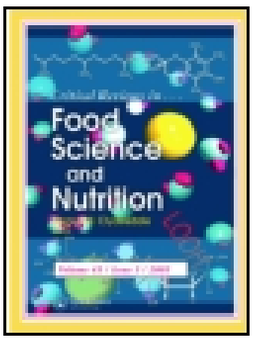

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Critical Reviews in Food Science and Nutrition

ISSN: 1040-8398 (Print) 1549-7852 (Online) Journal homepage: http://www.tandfonline.com/loi/bfsn20

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To cite this article: Nasreddine Benbettaïeb, Thomas Karbowiak & Frédéric Debeaufort (2017): Bioactive edible films for food applications:influence of the bioactive compounds on film structure and properties, Critical Reviews in Food Science and Nutrition, DOI: 10.1080/10408398.2017.1393384

To link to this article: http://dx.doi.org/10.1080/10408398.2017.1393384

Bio*active* edible films for food applications:

influence of the bioactive compounds on film structure and properties

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Abstract

Nowadays, a new generation of edible films is being especially designed for incorporating antimicrobials, antioxidants, enzymes or functional ingredients. Edible films made from natural biopolymers become the focus of many research works as an alternative to synthetic food packaging due to their edibility, biodegradability and compostability as well as to their use as active packaging. Active compounds incorporated in edible films could protect foods against

deterioration during storage and therefore extend their shelf life. These active films were mainly studied for the bioactivity, as antimicrobial or antioxidant. However, they could also improve the structure and the physicochemical properties of films through chemical linkage with reactive groups of the polymer chains for instance. Moreover, changing the film structure under cross-linking reaction may increase the cohesion between polymer chains and active compounds, and therefore their retention in the polymer network to better control their release.

This manuscript provides an overview on the effect of bio-active compounds incorporation on the film structure and functional properties. Depending on their structure, concentration, reactive groups,.., active compounds can act as plasticizer, but also as anti-plasticizer or cross-linking agents in the biopolymer matrix, and can thus ameliorate the water vapour and gas permeability. Therefore, the retention of bioactive compounds in the polymer network and their release can be better controlled. They can also provide a negative plasticizing effect on the film structure. Hence, the improvement of edible active film functionalities has been investigated to achieve suitable applications on foods.

Key words: active edible films; functional properties; plasticization; structure modification;cross-linking; controlled release.

Introduction

Over the past two decades, edible films and coatings made of natural biopolymers have received increasing attention as an alternative to synthetic food packaging due to their biodegradability and/or edibility and/or compostability as well as in their use as active packaging (Debeaufort et al., 1998; Kamper and Fennema, 1985). These biopolymers are usually extracted from biomass like plants (starch, cellulose, pectin, agar,…) or by-products from food industries (gelatin, whey protein, chitosan,…). On the one side, films prepared with polysaccharides are reasonably resistant, they have good gas barrier properties in dry conditions, but they exhibit poor oxygen barrier. On the other side, protein-based films show better mechanical and oxygen barrier properties (Khwaldia et al., 2004). They are less effective barrier to carbon dioxide (Nisperos-Carriedo, 1994). However, as they are hydrophilic biopolymers, both proteins and polysaccharides display poor water vapor barrier properties (Guilbert et al., 1995).

Several properties of polysaccharide and protein films, such as structural, thermal and mechanical properties as well as water vapour and gas permeability can be influenced by the addition of active substances (Benbettaïeb et al., 2015a; Campos et al., 2011; Silva-Weiss et al., 2013). Many investigations evaluated their possible use as a matrix to obtain active packaging materials. The incorporation of antioxidant and antimicrobial agents in these biopolymers is of key interest for food preservation. Their antioxidant and antimicrobial effects on food simulants or real product during storage were reviewed in another publication (Benbettaïeb et al., 2017). Furthermore, the active compounds could interact with the film-forming polymers and even improve the physical and functional properties of edible films via the production of cross-links between proteins and/or polysaccharides (Benbettaïeb et al., 2015b; Friesen et al., 2015; Nie et

al., 2015; Otoni et al., 2014a; Peng and Li, 2014; Vachon et al., 2000). Moreover, changing the film structure under such cross-linking reactions could modify the retention of active compounds in the polymer network and could thus tune their release, which can open new ways of applications (Benbettaïeb et al., 2015a; Cheng et al., 2015). More than 350 papers have been published in the last decade concerning the activity and efficiency of mainly antimicrobial and antioxidant films on model systems or real foods, but very little deal with the impact of the bioactive compounds incorporation on the film structure consequently on their functional properties.

The objectives of this review are then to survey the effects of active compounds introduced in edible films on their network structure and physicochemical properties. The controlled release of bioactive agents from edible films to food after cross-linking reaction is also surveyed.

1. Influence of active compounds on the mechanical and structural properties of film matrices

The interaction between the added active agents (organic acids, antimicrobial proteins, enzymes, phenolic compounds…) and the film-forming materials can subsequently affect the mechanical and structural properties of the resulting films. It can lead to either a positive or a negative effect depending on both the nature of the active compound and of the biopolymers used as matrices.

1.1. Organic acids

Ascorbic acid was reported to act as a **plasticizer** of potato starch-polyvinyl alcohol (PVA) based films with and without heat curing (Yoon, 2014).The existence of the functional groups in ascorbic acid allow to better combine starch and PVA molecules and thus could enhance the

mechanical properties In their work, authors showed that, tensile strength (TS) of PVA based films decreased by 35% and inversely the elongation at break (EAB) increased by a factor of 5 after ascorbic acid addition at 20% (wt by dry matter). . The marked decrease of TS and increase of EAB after incorporation of ascorbic acid in potato starch-PVA films **(Table 1)** is essentially related to its plasticizing effect. Furthermore, from TGA analysis, the degree of thermal decomposition of films without ascorbic acid was higher than that of the ascorbic acid-added films because the strong interaction between potato starch and PVA was weakened by the addition of ascorbic acid acting as plasticizer. Cao, Yang, & Fu. (2009) also found that organic acids acted as a plasticizer for gelatin films. They displayed that the addition of malic acid could increase the elongation at break (EAB) of gelatin films. When the concentration of malic acid increased from 1.6 to 2.4 % wt. dry matter, the EAB of gelatin films increased by 112%, simultaneously, the TS and Young's modulus (YM) decreased respectively by 55 and 60% **(Table 1)**. . It was also found that the addition of citric acid or tartaric acid decreased the TS, EAB, and YM of gelatin films **(Table 1)**. Further addition of these organic acids made gelatin films too fragile to manipulate. Yoon, Chough, & Park. (2006) used tartaric acid and malic acid to modify starch/PVA blend films. The TS of the blend films was 3 times lower when tartaric acid and malic acid were added (at 7.5 and 6.7 % wt. by dry matter, respectively), and the EAB increased by more than 15-fold **(Table 1)**. They indicated the successful use of theses organic acids as both preservatives and plasticizer for starch and PVA films.

Conversely, some **anti-plasticizing effects** of organic acids have also been displayed. Indeed, Park et al. (2001) studied the effectiveness of ascorbic acid as a cross-linking agent for chitosan and *k*-carrageenan films. They displayed an increase of TS by 46 and 25% after incorporation of

ascorbic acid (46% wt. by dry matter) in chitosan and *k*-carrageenan films, respectively. On the contrary, the EAB decreased by 24% for the chitosan films but it did not change *k*-carrageenan films (**Table 1**). However, Choi *et al.* (2017) recently displayed that the addition of tartaric acid (at 1% wt. of dry matter) to carboxymethylcellulose films did not show any anti-plasticizing or crosslinking effect, with no enhancement of the mechanical properties of the films. This might have been due to the absence or too weak chemical bonds at such concentration of organic acids.

1.2. Antimicrobial proteins and bacteriocins

Antimicrobial proteins and bacteriocins (nisin, natamycin, cathelicidins, defensins …) were tested in several works on bioactive packaging for food decontamination or food shelf-life extension. These active compounds can also generate new interactions in the polymer matrix and can modify the functional properties of the final network by their **anti-plasticizing effect**. The incorporation of nisin into whey protein film-forming solutions may induce a rearrangement of disulfide and hydrophobic bonds or protein-protein interactions. An increase of TS by 79% was significant for whey protein films **(Table 1)**, but negligible on soy protein, wheat gluten and egg albumin films (Ko et al., 2001). The electrostatic interactions between nisin molecules and protein chains forming the film network may also have contributed to the TS increase of the whey protein films. Furthermore, soy protein films had a lower hydrophobicity than that of whey protein films. Considering nisin as a hydrophobic protein, a lower number of potential hydrophobic bonds between nisin and soy protein can explain the weak effect on the TS. Moreover, the whey protein film had the highest hydrophobicity because it is water-insoluble due to the formation of covalent disulfide bonds. The low amount of cystein in wheat gluten induces a lower level of possible covalent disulfide bonds (Krochta et al., 1994). The lower TS

when nisin was added to wheat gluten films is due to the lower hydrophobicity of wheat gluten compared to whey protein.

On the opposite, Basch, Jagus, & Flores (2013) reported a **plasticizing effect** of nisin on starch and starch-HPMC films (9:1 w/w). Similarly, nisin decreased the TS by 81 % for starch films and by 85% for the starch-HPMC films (9:1 w/w) **(Table 1)**. This behavior suggests that nisin disrupts the association of biopolymer chains by decreasing the amount of interchain hydrogen bonds. Furthermore, in a system based on starch, the presence of nisin did not significantly modify the EAB with respect to the control system. However, with the addition of nisin and HPMC simultaneously, the film suffered a greater elongation (EAB increase by 109%) indicating greater flexibility **(Table 1)**. The decrease in TS and the increase in EAB confirm the plasticizing effect of this antimicrobial protein. Similarly, Sebti, Chollet, Degraeve, Noel, & Peyrol. (2007) observed a 2 fold reduction on tensile strength of HPMC-based films with nisin **(Table 1)**,result also confirmed by Cha, Choi, Chinnan, & Park (2002) for Na-alginate-based films. Similarly, Imran, El-Fahmy, Revol-Junelles, & Desobry. (2010) displayed that the TS of HPMC films containing Nisaplin (2.5% nisin in salt and milk proteins) was significantly decreased by 32%. Nisaplin incorporation in non-plasticized HPMC films significantly reduced the YM by a factor of 2.7 and thus the film rigidity. NaCl, milk proteins and carbohydrates present in the Nisaplin preparation interact with HPMC disturbing the hydrophobic interactions involved in the HPMC network stabilisation. In addition, Nisaplin have high affinity to water, which also contributes to plasticisation. In the same study, Nisaplin weakly increases the EAB from 13 to 26% caused by random break due to the presence of salt crystals of Nisaplin once the film were dried **(Table 1).**

1.3. Enzymes

Lysozyme is the most studied enzyme for active packaging applications. The addition of lysozyme had very often a negative influence on the mechanical properties of edible films and coating because of the **degradation effect** on the polymer chains particularly for protein-based films. According to Ulbin-Figlewicz, Zimoch-Korzycka, & Jarmoluk (2014), the TS and EAB of chitosan films decrease with the increasing lysozyme concentration. The maximum TS value occurred for pure chitosan film (16.2 MPa), whereas those with 0.5 % lysozyme displayed a 25 % reduced TS value, but there was no significant difference for the concentrations of enzyme higher than 1% **(Table 1)**. The EAB of films decreased by 17 and 31% only after lysozyme addition at 22 and 44% (wt. by dry matter) compared to control films (without lysozyme). The degradation ability of lysozyme against chitosan chains weakened the film network and reduced its mechanical properties. Furthermore, the addition of lysozyme also reduced the thermal stability of films by about 15°C from TGA analysis (Ulbin-Figlewicz et al., 2014). Similarly, Park, Daeschel, & Zhao.(2004) reported for lysozyme addition to chitosan films at a concentration of 60% (wt. by dry matter) a decrease of TS and EAB respectively by 45 and 34% compared to control films **(Table 1)**. The reduction in both TS and EAB indicates that the lysozyme incorporation possibly disrupts the chitosan crystalline structure formation during the drying process and weakens intermolecular hydrogen bonding among chitosan molecules corresponding to an apparent lubrification phenomenon and not a plasticization. In the presence of water, chitosan molecules could be hydrolyzed by lysozyme ($\beta_{1\text{-}4}$ linkages between *N*-acetyl-D-glucosamine units) during film formation. This hydrolysis induces the degradation of chitosan and the formation of a less dense network structure (D-glucosamine units and small amount of

N-acetyl-D-glucosamine units) (Park et al., 2004). Decrease of TS after lysozyme incorporation (0.1% wt. by dry matter) was also reported for other type of films. Cha et al. (2002) displayed 28 and 30% TS reduction on Na-alginate and *k*-carrageenan-based films respectively **(Table 1)**. Recently, Zimoch-Korzycka et al. (2015) , reported that TS of hydroxypropyl methylcellulose and chitosan films decreased, respectively by 72 and 89%, when bioactive cystatin/lysozyme was added at a concentration of 1% (v/v) (corresponding to 0.7/192 U/g activity of cystatin/lysozyme). They demonstrated that lysozyme degrades linkages within polysaccharides and could thus hydrolyze both chitosan and hydroxypropyl methylcellulose. However, they displayed that chitosan with high deacetylation degree is less susceptible to enzymatic degradation. Therefore, the choice of enzyme incorporation must be though according the biopolymer susceptibility to enzymatic hydrolysis.

1.4. Phenolic compounds

Besides the use of simple phenols, polyphenols, plant extracts, essentials oils, tocopherols,… natural antioxidants based on phenolic compounds (tannins, flavonoids, phenolic acids, coumarins and volatile phenols,…) were also encapsulated in edible films or directly incorporated into food in order to extend the shelf life of food products and to prevent their oxidization, but also used for improving the functional properties of films.

1.4.1. Simple phenols

Phenolic acids, beside their use as antioxidant agents, can also covalently bind to polysaccharides or proteins by ester bonds, hydrophobic interactions; etc, and consequently can enhance some film functional properties by **cross-linking or anti-plasticizing effects**. Arabestani et al. (2016) recently indicate that oxidized ferulic acid addition (50 mg/100 g of

polymer) to bitter vetch protein-based film forming solution significantly increases both TS (about 35%) and EAB (about 20%) of the resulting film **(Table 1)**. No further increase was observed for higher concentrations (100 or 150 mg/100 g). Moreover, covalent crosslinking between ferulic acid and some reactive protein side chain were responsible for the significant changes in the mechanical properties of the films. Indeed, phenolic compounds, under oxidizing conditions, could be converted to quinone able to form covalent crosslinks with amino and thiol groups. The free radical deriving from ferulic acid could also react with tyrosyl protein residues and with itself to form diferulic acid by producing a molecular bridge between protein chains. Therefore, this induced a more rigid and stable protein film network. Mathew & Abraham. (2008) displayed that the incorporation of ferulic acid at 4% (wt. by dry matter of the film-forming solution) enhanced mechanical properties (TS increased from 45 to 62 MPa) of starch–chitosan films. The same effect was observed on gelatin films which the TS increased by 13% (Cao et al., 2007a) **(Table 1)** related to the loss of fibrillar orientation of gelatin with an apparent decrease in free volume after ferulic acid addition. A discontinuous zone, characterized by cracks, randomly distributed along the length of the network, was also observed. Recently, Benbettaïeb, Karbowiak, Brachais, et al. (2015b), in the case of chitosan-fish gelatin films (1:1 w:w), found a 43.8% increase of TS after the incorporation of 4.5% ferulic acid (wt. by dry matter) **(Table 1)**. This can be explainedby the phenol acids interaction with several sites of proteins, which led to cross-link the proteins between themselves. Proteins have positive groups due to primary ammonium group ($–NH_3^+$) and they can interact with the negative charge of the carboxylate ($–COO^-$) groups of the phenol acid. The ammonium group exists at the N-terminus of each polypeptide chain and in the side chain of lysine residues and are positively charged at

the pH used to prepare the film (5.5). The carboxyl groups of the acid phenol at the pH of film preparation (5.5) are negatively charged. The charge-charge interactions between phenolic acid and proteins and or chitosan could explain the stronger impact of ferulic acid on the properties of chitosan-gelatin film. In contrast, tyrosol (phenol, without carboxylate $–COO^-$ groups), is not able induce charge-charge interaction and thus to strengthen the films (Benbettaïeb et al., 2015b). Prodpran, Benjakul, & Phatcharat. (2012) noticed an increase of TS of myofibrillar proteins by 8 and 18% respectively for film containing ferulic acid and caffeic acid at a concentration of 4.5% wt. by dry matter. Cross-linking and/or anti-plasticizing effect of phenolic acids was also reported by Sun, Wang, Kudoh, & Zhou. (2014), who revealed a significant increase on TS of chitosan films by 76% after gallic acid addition at 27 % (wt. by dry matter). This can be attributed to the formation of ester and amide linkages between chitosan and gallic acid as proved by FTIR spectra (new peaks detected at 1700 and 1640 cm^{-1} after gallic acid addition). Sun, et al. (2011) also reported the formation of intermolecular hydrogen bonding between the NH_3^+ of the chitosan backbone and the OH^- of gallic acid which decreases the molecular mobility and the free volume in final network. However, at higher concentration of gallic acid (81% wt. by dry matter), Sun, Wang, Kadouh, & Zhou. (2014), observed an opposite tendency on chitosan films (TS and EAB decrease by 30 and 68%, respectively). It is possible that the excessive gallic acid scattered the film crack and interrupted the inner network structure as confirmed by the formation of obvious pores observed from SEM cross-section micrographs. Depending on polyphenol structure and degree of hydroxylation, the interaction may produce single or multiple hydrogen bonds that influence strength of the formed complexes. This dipole-

dipole interactions between phenolic hydroxyl group of polyphenol with polar group of protein was also reported by Cao et al. (2007b) for gelatin films containing ferulic acid.

This is in agreement with the work recently reported by Limpisophon and Schleining. (2017) on gallic acid-fish gelatin films **(Table 1)**. Film forming solution composed of gelatin and gallic acid in the range 1% to 3% (w/w of protein) was at pH 4.8 to 5.1. According to the pK*a* of gallic acid, para OH (*p*-OH), meta OH (*m*-OH) would play the role of a hydrogen bond donor/acceptor at pH 5. The hydroxyl groups of gallic acid interact with serin groups via a hydrogen bond due to the geometry of the gallic acid–collagen peptide complex. Gallic acid can also stabilize the collagen peptide through the electrostatic force of glutamic acid and serin due to the strong presence of electrons in the aromatic ring of gallic acid. In addition to hydrogen bonds (dipole-dipole interaction) that involve polar groups, proteins and polyphenols may interact via hydrophobic bonds, or stacking between non-polar aromatic rings of polyphenols and aromatic amino acids (prolin, phenylalanin, tyrosin, tryptophan, histidin) (Benbettaïeb et al., 2018; Charlton et al., 2002). Hydrophobic bonds influence the structure of the complex by stacking of aromatic rings of polyphenols against those of aromatic amino acids of protein (Brudzynski and Maldonado-Alvarez, 2015).

Literature rarely reports about the **plasticizing effect** of pure phenolic acids on biobased films. Ou et al. (2005) reported high increase of EAB (by 55%) for soy protein films with addition of ferulic acid at 0.62% (wt. by dry matter) and Arcan & Yemenicioğlu. (2011) a 40 times increase of EAB for zein films when ferulic acid, gallic acid or p-hydroxy benzoic acid were added (10% wt. by dry matter) **(Table 1)**. The increased flexibility and deformability of zein films due to phenolic compounds seemed to occur by binding of phenolic compounds on zein protein and

resulted in an increase of free volume of film matrix. Furthermore, the hydrophilic groups of phenolic compounds also decreased the hydrophobic interaction among zein chains, favoring tune absorption and contributed to higher mobility and flexibility.

1.4.2. Polyphenols and natural plant extracts

1.4.2.1. Hydrolysable and non-hydrolysable tannins

The molecular weight and structure of polyphenolic compounds present great variations and they contain a great number of hydroxyl groups able to form H-bonding with carbonyl groups of proteins. Most of the plasticizers owe their positive effects on film flexibility to their hydroxyl groups, which form hydrogen bonds with polymers. However, in the literature, reports about the plasticizing effect of pure polyphenolic compounds on biobased films are very scarce. Emmambux, Stading, & Taylor (2004) incorporated **hydrolysable tannins** like tannic acid into films of sorghum kafirin and zein prolamins. They reported an **anti-plasticizing effect** of this phenolic compound proved by a reduced elongation, and an increase of TS and YM of the films. This is due to the molecular properties of tannic acid, because this phenolic compound contains too many hydroxyl groups favoring the bind between the proteins. According to Tammineni, Rasco, Powers, Nindo, & Ünlü. (2014), the TS increased by 15% and the EAB decreased by 23% after tannic acid incorporation in bovine gelatin films at a concentration of 12% (wt. by dry matter). In the case of fish gelatin films containing tannic acid, there was only a significant EAB decrease of 31%. The increase of TS can be due to the cross-linkers stabilizing the film matrix. The same authors confirmed the improvement of the mechanical properties from the results of

thermal analysis, which display an increase in the glass transition temperature of approximately 12 and 6 °C, respectively for bovine and fish gelatin films with 12% (wt. by dry matter) tannic acid. Cross-linkers change the physical properties to varying degrees. However, the direct comparison of data among different gelatin samples is not reliable due to different formulations, test conditions and gelatin composition. The increase in TS and the decrease in EAB following the incorporation of tannic acid has been reported by several author : Rivero, García, & Pinotti. (2010) for chitosan film at 2.6 % wt. by dry matter, Cao, Fu, & He. (2007a) for gelatin films at 3.8% wt. by dry matter, Nuthong, Benjakul et al. (2009) for porcine plasma protein-based films at 5% wt. by dry matter, Prodpran, Benjakul, & Phatcharat. (2012) for myofibrillar proteins at 4.5% wt. by dry matter, and recently Vate et al. (2017) for sardine myofibrillar protein films at 5% wt. by dry matter **(Table 1**). Peña, de la Caba, Eceiza, Ruseckaite, & Mondragon.(2010) used tannins in gelatin film. They showed that TS and EAB decreased respectively from 105 MPa to 70 MPa and from 3.2 ± 0.1% to 2.5 ± 0.5%, when the tannins content on gelatin film rose from 9% to 23% wt. by dry matter **(Table 1)**. It is also worth noting that the glass transition temperature (Tg) increased from 197°C (for pure gelatin films) to 202 and 212°C, respectively after tannin addition at 9 and 23 % (wt. by dry matter), even though polyphenolic tannin has lower Tg (170°C) than gelatin. Furthermore, the authors showed by X-Ray Diffraction (XRD), that the higher tannin content, the intensity of crystal peaks of gelatin (2θ = 8.1° and 10.1°) decreased. This is due to the enlarged intermolecular interactions between hydroxyl groups in tannins and NH_2 side-chain groups in gelatin, which limit the molecular movements and thus prevent crystallization.

Non-hydrolysable tannins that include catechin and epicatechin polymers, green tea extract, grape seed procyanidins and green tea polyphenols were also studied for their **anti-plasticizing and/or cross-linking effect**. According to Wu et al. (2013), the incorporation of green tea extract in silver carp skin gelatin films, improved the antioxidant activity and directly affected the physical properties, most likely due to the interactions between the protein chains and these phenolic compounds. Green tea extract content of 12% (wt. by dry matter) in gelatin films induced significant increase of the TS by 44% and decrease of the EAB by 14% **(Table 1)**. Moreover, the thermal stability of gelatin-green tea extract films was improved and raised by 10°C when the 0.7% concentration of extract was added. This indicated that phenolic compounds bonded to gelatin and yielded to a stronger film network. The mechanism of interaction could be explained by the hydrophobic interactions between polyphenolic compounds and the hydrophobic region of gelatin. Hydroxyl groups of polyphenolic compounds were also able to combine with hydrogen acceptors of gelatin molecules by hydrogen bonds (Hoque et al., 2011). Recently, Nie et al. (2015) reported a significant increase of TS (by 26 and 23%) and a decrease of EAB (by 63 and 64%) of myofibrillar protein-based films incorporating respectively 3.5% (wt. by dry matter) of grape seed procyanidins and green tea polyphenol extract **(Table 1)**.. A thermal degradation was observed around 136 °C and 315 °C for the control films, 158 °C and 331 °C for grape seed procyanidins-incorporated films, and 150 °C and 326 °C for green tea polyphenol-incorporated films, respectively. They thus confirmed, from thermal analysis, the formation of cross-linking between phenols and proteins, which would reduce the inter-chain space of protein polymer. It is obvious that these compounds have a pronounced impact on

thermal stability of myofibrillar protein-based films via phenol-protein interaction, especially covalent cross-linking.

1.4.2.2. Flavonoids

The improvement of the mechanical properties of films was also achieved when flavonoids were added regarding to their **cross-linking and anti-plasticizing effect**. Friesen et al. (2015), recently demonstrated that TS of soy protein films containing rutin was 4 times higher than the control films though EAB was 1.6 times reduced **(Table 1).** The addition of rutin leads to increase the film strength and reduce the film flexibility because of protein–phenolic interactions. Indeed, hydrogen bonding between the hydroxyl groups of the phenolic compound and the $–NH_3^+$ groups of soy protein amino acids are predominant. Covalent linkages may also occur in a minor amount between the oxidised quinone rings of rutin and the free amino groups of the soy protein. Similarly, Benbettaïeb, Karbowiak, Brachais, et al. (2015b) demonstrated that TS values tend to increase by 14% with the incorporation of quercetin on chitosan–fish gelatin films **(Table 1)**. However, the addition of this antioxidant involved a higher thermal degradation temperatures (+15°C). This suggests that the interactions between quercetin and chitosan–gelatin molecules yield to a stronger film network, thus leading to the higher heat resistance of the films.

1.4.2.3. Natural plant extracts

Natural plant extracts were also added to biobased films. They mainly have an **anti-plasticizing and a cross-linking** effect on film structure. Hoque, Benjakul, & Prodpran (2011) displayed a significant increase on TS (by 19%) and a significant decrease on EAB (by more than 20%) of cuttlefish skin gelatin films containing cinnamon, clove and star anise extracts at 0.82% (wt. by dry matter). This behavior was explained by both hydrophobic interaction and hydrogen bonds

between polyphenol and protein.. The presence of cross-links between gelatin and active compounds involved the amide-A group interactions in films containing star anise extracts. This active extract also induced interaction between phenolic compounds and NH_2 groups of gelatin.Moreover a greater increase in TS was obtained when oxidized herb extracts were incorporated compared to fresh herb extracts (Hoque et al., 2011). With the addition of oxidized herb extracts (0.82% wt. by dry matter), TS of gelatin film increased by 34.4, 31.5 and 43.2%, respectively for cinnamon, clove extracts and star anise extracts **(Table 1)**. Oxidized phenolic compounds contribute to the formation of non-disulfide covalent bonds whichcontribute to a more compact structure.

In contrast to their anti-plasticizing effect, plant extracts did not show a clear plasticizing effect on film network structure, as for oregano and rosemary aqueous extracts in gelatin films (Gómez-Estaca et al., 2009) **(Table 1).** Other researchers have reported a significant decrease in TS by 53% and breaking deformation by 73% **(Table 1)** after murta extracts addition at a concentration of 75% (wt. by dry matter) to gelatin films (Gómez-Guillén et al., 2007). This behavior was explained by a weakening of the interactions that stabilize the protein matrix especially with higher-molecular-weight polyphenols and such high concentration (Gómez-Guillén et al., 2007).

1.4.3. Volatile phenol compounds

Beside their uses as antimicrobial and antioxidants agents, volatile phenols can also affect structural and functional properties of biobased films by their **anti-plasticizing effects** or **tensioactive properties**, which favours the **emulsification.**.. Peng & Li. (2014) displayed 19% increase of TS and 60% decrease of EAB of chitosan film after lemon-cinnamon essential oil

addition at 25% (wt. by dry matter) **(Table 1)**. They confirmed from SEM micrographs that the essential oil droplets were homogenously distributed across the film cross section. An emulsification was observed in chitosan/lemon/cinnamon essential oils composite films due to the electrostatic interaction of limonene and cinnamaldehyde. Good emulsification had a positive effect on the mechanical properties of the films. Similarly, Ojagh, Rezaei, Razavi, & Hosseini. (2010) reported that the TS of chitosan films increased from 10.9 to 29.2 MPa when cinnamon essential oil was added at a level of 47% (wt. by dry matter), and the EAB decreased by 85%. In that case, cinnamon oil seems to act as an anti-plasticizing agent. Otoni et al. (2014a) displayed an important increase of TS by 72% of pectin-papaya films after cinnamaldehyde addition at 15 % (wt. by dry matter) by an anti-plasticizing effect **(Table 1)**.. Furthermore, Elsabee and Abdou.(2013) explained the increase in TS, EAB and YM of chitosan films after olive oil (rosemary) addition (0.03% (v/v), revealing a lubrification process between lipid and carbohydrate phases. Literature also reports **plasticizing effects** of essential oils (anise, basil, coriander, and oregano) in edible chitosan films demonstrated by a reduced resistance and rigidity while increasing the EAB (Zivanovic et al., 2005). Similarly, Kavoosi, Rahmatollahi, Mohammad Mahdi Dadfar, & Mohammadi Purfard (2014) added Zataria multiflora essential oil at 6% (wt. by dry matter) in gelatin film-forming solutions before casting and drying. They found that EAB increased from 125 to 172% and logically TS and YM significantly decreased respectively from 4.4 to 2.7 MPa and from 8.8 to 5.7 MPa **(Table 1)**. Moreover, from Pranoto, Rakshit, & Salokhe. (2005a) the noticeable decrease of TS by 42% of alginate-based films containing garlic oil at 20% (wt. by dry matter) is caused by the increase of the intermolecular interactions of the structural matrix in alginate films and the decrease of the cohesion forces

within the structure. More generally, several reports have mentioned that oil addition to film formulation tends to weaken the film by decreasing network cohesion forces (Espitia et al., 2014; Klangmuang and Sothornvit, 2016; Pelissari et al., 2009; Pranoto et al., 2005b) **(Table 1)**. Klangmuang and Sothornvit recently confirm this finding. (2016), who displayed same behaviour for HPMC films. This effect could primarily be explained by the partial replacement of stronger polymer-polymer interactions by weaker polymer-oil interactions in the film network in the presence of essentials oil.. Others works have also indicated the plasticizing effect of essential oils such as basil and thyme in chitosan-based films (Bonilla et al., 2012), cinnamon, oregano or lemongrass in cellulose based films (Espitia et al., 2011), oregano oil in methylcellulose films (Otoni et al., 2014b), sunflower oil in hydroxyl-methylcellulose films (Zuniga et al., 2012), allspice, cinnamon, and clove bud oils in apple films (Du et al., 2009). The effect of oil as a plasticizer agent on film mechanical properties depends on the structure of these compounds. Recently, Acevedo-Fani et al. (2015) displayed that alginate films made with thyme, lemongrass, or sage oils at a concentration of 9.3% (wt. by dry matter) maintain their mechanical resistance. In the same study, edible films prepared from sage essential oil were the most stretchable ones (EAB= 78 ± 5%), whereas films containing lemongrass and thyme-essential oil (EAB= 32 ± 9% and 41 ± 12%, respectively) did not show significant differences regarding control films (EAB=38 ± 7%) **(Table 1)**. These variations in film flexibility could be partially explained by the influence of the electrical charge of nanoemulsions in the film structure. The repulsive forces among molecules of the same charge can increase the distance between polymers, resulting in a plasticizing effect in the case of charged polymeric film structure. The of the electrical charge difference between sage-essential oil nanoemulsions (-70 mV) and thyme or

lemongrass-essential oil nanoemulsions (-44 mV and -41 mV, respectively) could led to different level electrostatic interactions between the biopolymers and thus led to various grades of films flexibility. . Because the TS and EAB are usually related to the film network microstructure and the intermolecular forces (Atarés et al., 2010), the contradictory results may be related to the nature, the concentration, the reactive site and the groups of bioactive agents. Moreover, Jahed et al. (2017) recently displayed that the addition of oregano essential oil to chitosan films did not affect mechanical properties of network **(Table 1).** The findings of Otoni et al. (2016) on soy protein films containing carvacrol and cinnamaldehyde are in agreement with this later and in contradiction with the works mentioned before concerning the anti-plasticizing and plasticizing effects of essentials oils on hydrocolloids films. Therefore, it could be concluded that different essentials oil have shown different effects on mechanical properties of films. Depending on the type of biopolymers (molecular weight, isoelectric point (pI) and solvent) and the interactions, which are affected by relative humidity, the presence of surfactants, temperature, etc. **2.**

Influence of active compound incorporation on the barrier properties of films

2.1. Organic acids

Organic acids added to edible and biobased films, can enhance the water barrier properties when they act as **anti-plasticizer or cross-linker**. Park et al. (2001) showed a decrease of water vapor permeability (WVP) of chitosan and *k*-carrageenan films by 17 and 15%, respectively, after the incorporation of ascorbic acid at 46% (wt. by dry matter) (**Table 1**).

2.2. Antimicrobial proteins and bacteriocins

Regardless of the ever-increasing interest of the incorporation of antimicrobial proteins in edible films, the literature is rather scarce on findings about their effect on modifying film transfer

properties. Ko et al. (2001) displayed that when nisin was added up to 0.046% (wt. by dry matter), no significant effect was observed on the WVP of whey protein films, soy protein films, wheat gluten films and egg albumin films **(Table 1)**. Theoretically, the addition of nisin is expected to improve the water barrier property of films by **hydrophobic interactions** with proteins because nisin itself is a hydrophobic proteic enzyme (Klaenhammer, 1993). Therefore, this result may be due to the low concentration of nisin incorporated into the film forming solutions, which had no effect on WVP.

A plasticizing effect of nisin was reported by recent study for starch and starch-HPMC films (9:1 w/w) (Basch et al., 2013). The authors observed that the WVP increases (up to 18%) after nisin addition in both films **(Table 1).** However, the presence of HPMC in starch films increased the solubility and WVP. An increase of the WVP could be consequence of the greater disruption of the biopolymer matrix produced by the antimicrobial acting as plasticizer. Likewise, it has been reported that the addition of nisin in the starch-edible films causes an increase of the amorphous regions (Flores et al., 2010), increasing the interaction with water, which in turn can increase the solubility and WVP. Furthermore, Imran et al. (2010) using Nisaplin added at 0.66% (wt. by dry matter) as active agent in HPMC films showed that WVP for active films increased only by 16% **(Table 1)**. The re-structuring of biopolymer inside the film matrix due to active agent incorporation could affect WVP, which may explain the relative increase of WVP in the composite active films.

2.3. Enzymes

Contrarily to the effect of lysozyme on mechanical properties, water vapor permeability is usually not significantly affected by lysozyme incorporation as demonstrated by Ulbin-Figlewicz

et al. (2014) or Park, et al. (2004) for chitosan films by Zimoch-Korzycka et al. (2015) for hydroxypropyl methylcellulose and chitosan films.. On the contrary, Manab et al. (2016) displayed that the addition of modified lysozyme to whey protein films decreased the WVP, which is attributed to the increasing interaction between this enzyme and proteins chains. Because lysozyme contains hydrophobic amino acid residues, the hydrophilicity of lysozyme–chitosan composite films may decrease with lysozyme addition and thus the WVP should decrease. However, the compact structure of the crystalline parts of chitosan may be disrupted by lysozyme activity resulting in an increased WVP. These two contradicting effects with the addition of lysozyme may counterbalance the differences in WVP characteristic of lysozyme–chitosan films.

2.4. Phenolic compounds

2.4.1. Simple phenols

The incorporation of phenolic acid, the most used and studied among simple phenols, has recognized anti-plasticizing or plasticizing effect on the structure of the films. Hydroxycinnamic acids have usually a **cross-linking** effect on film network. The incorporation of ferulic acid at 4.7% (wt. by dry matter) improved the water barrier properties by 22% of starch–chitosan films (Mathew and Abraham, 2008). Fabra, Hambleton, Talens, Debeaufort, & Chiralt. (2011) showed a decrease of oxygen permeability (PO_2) by 32 % and WVP by 26% of sodium caseinate film due to ferulic acid addition at a concentration of 4.4% (wt. by dry matter) **(Table 1)**. This was explained by the cross-linking between ferulic acid and amino acid residues of the protein, which makes the matrix tighter as displayed from atomic force microscopy images and thus limits oxygen and water transfer. However, no significant effect was displayed for

concentrations lower than 1.5%. Recently, in the case of chitosan-fish gelatin film (1:1 w:w), Benbettaïeb, Karbowiak, Brachais, et al. (2015b) showed an enhancement of water barrier properties by 44%, after 4.5% ferulic acid addition. Similarly, Araghi et al. (2015) observed a decrease of WVP by 21% after 6.6% caffeic acid addition in fish gelatin films, and Masamba et al. (2016) a 33% decrease of WVP after addition of gallic acid at 27% (wt. by dry matter) on zein-oleic acid composite films **(Table 1)**. This reduction can be attributed to the formation of cross-linkages induced by the gallic acid and resulting into a more compact structure restricting water mobility. On the contrary, there is no effect of ferulic acid on the WVP of soy protein films (Ou et al., 2005) or gelatin films (Cao et al., 2007a), with ferulic acid at 0.62 and 3.8%. The opposite behaviors observed on WVP of protein films containing phenolic acid could be firstly related to the chemical structure of phenolic compounds (especially the number of OH groups) and secondly to the difference in the protein composition (polypeptides chains and the amino-acid side chains), especially primary ammonium ($–NH_3^+$) and carboxylate ($–COO^-$) groups. This is related to the modification of the mechanical properties, as previously discussed. The addition of phenolic acid having benzene ring group have an anti-plasticizing effect involving another mechanism. Indeed, the addition of 27% gallic acid decreased the WVP and the oxygen permeability of chitosan films, respectively by 12 and 58% (Sun et al., 2014). This is attributed to the large benzene ring group of gallic acid that obstructs the inter- and intra-molecular hydrogen bond network of chitosan. The film structure thus became more rigid and less permeable.

However, at a higher concentration of gallic acid (higher than 54%), the WVP of the film increased by more than 40%, but the PO_2 was not affected (Sun et al., 2014). This behaviour

observed on mass transfer properties at high concentration of gallic acids may be related to the excessive gallic acid dispersed in the film that subsequently decreased the intermolecular forces between polymer chains probably by its **plasticizing effect.** Therefore, the free volume and segmental motions increased. Moreover, as carboxyl groups and hydroxyl groups of gallic acid are hydrophilic groups, they might promote water transfer in the matrix and therefore increasing WVP.

2.4.2. Polyphenols and natural plant extracts

2.4.2.1. Hydrolysable and non-hydrolysable tannins

The incorporation of hydrolysable and non-hydrolysable tannins had usually a positive effect on water barrier properties. For **hydrolysable tannins**, cross-linked bovine gelatin films with 2% tannic acid resulted in 80% reduction of the film solubility (Zhang et al., 2010). According to Tammineni, Rasco, Powers, Nindo, & Ünlü. (2014), the water solubility and WVP were reduced after 12% tannic acid incorporation in bovine gelatin films but did not vary significantly when added in fish gelatin films (**Table 1**). Similarly, Rivero et al. (2010) displayed a 18% decrease on the WVP of chitosan film after tannic acid incorporation at low concentration (2.6%). This tendency was even more pronounced during the storage, which would be an indicator of the reorganization of the film matrix with time. According to Ou et al. (2005), cross-linking restricts the molecular motion leading to lower WVP. Recently, Vate et al. (2017) displayed an increase of the compactness of the sardine myofibrillar protein films structure by high protein cross-linking, after tannic acid addition (at 5%) which reduced the permeability of moisture vapour through the films. The cross-linked proteins mediated by tannic acid could reduce the hydrophilic moieties in the matrix of film, resulting in a decreased film hydrophilicity and thus a

decreased WVP of the film. Similar behavior was observed for **non-hydrolysable tannins**. Indeed, Wu et al. (2013) displayed that the incorporation of green tea extract at 12% (wt. by dry matter) in silver carp skin gelatin films, induced a 17% decrease of the water solubility and of 20% for the WVP. Nie et al. (2015) reported also a significant decrease on WVP by 45 and 31% after grape seed procyanidins and green tea polyphenol, respectively when incorporated (at 3.5% wt. by dry matter) to myofibrillar protein-based film **(Table 1)**. The reason might be that polyphenolic compounds could entrapped into gelatin matrix structure and established cross-links through hydrogen bond or hydrophobic interactions. The free volume of the polymeric matrix decreased and therefore WVP is lowered (Cao et al., 2007a; Kaewprachu et al., 2017; Nagarajan et al., 2017; Nie et al., 2015; Wu et al., 2013).

2.4.2.2. Flavonoids

The addition of flavonoids seems to decrease the WVP of biobased films by their **cross-linking effect**. Friesen et al. (2015) showed a 31% decrease on WVP of soy protein isolate after rutin addition at a concentration of 4.65% **(Table 1)**. Similarly, Benbettaïeb, Karbowiak, Brachais, et al. (2015b) displayed that WVP of chitosan-fish gelatin films decrease by 25% after quercetin addition (at 4.5% wt. by dry matter) but this decreases was not significant.

2.4.2.3. Natural plant extracts

The incorporation of plant and fruit extracts reduced the WVP of edible films by their **cross-linking effect**. Hoque et al. (2011) found a significant decrease of WVP by 10% and 19% of cuttlefish gelatin films after addition of oxidized clove extracts and clove extracts at 0.82% respectively (**Table 1**). Regardless of oxidation, phenolic compounds are known to cross-link the amino or sulfhydryl groups in the protein molecules (Ozdal et al., 2013). Phenol-protein

interchain interactions may also reduce the effect of the other plasticizers within the film, thus leading to decrease water permeability. Rattaya, Benjakul, & Prodpran. (2009) reported for seaweed extract introduced in fish skin gelatin film (4.16 % wt. by dry mater) a significant decrease of WVP by 30% and of film solubility by 51%. Gelatin-murta leaves extracts films also significantly lowered WVP (Gómez-Guillén et al., 2007) **(Table 1)**. Talón et al. (2017) reported that the addition of thyme extract significantly decreased the WVP around 14% (g water/100 g film) of the pure starch and starch-chitosan blends films, having lower water content **(Table 1)**. No effect was observed at high water content (around 22%) and at low concentration of thyme extract incorporated (ratio of chitosan: thyme extract was 1:0.15). Furthermore, the addition of thyme extract improved the oxygen barrier property of starch and blend starch-chitosan films, which is consistent with the development of a tighter more closed structure. Similarly, Ciannamea et al. (2016), displayed that the addition of red grape extract at 3% induced a reduction in WVP of soy protein concentrate by approximately 45%**(Table 1)**. This could be due to the interaction between polyphenols and polar groups of protein chains. These groups will then not be available to associate with water molecules, reducing the transfer rate of water molecules through the matrix. However, Gómez-Estaca, Montero, et al. (2009) reported that adding oregano or rosemary extract, respectively at 6 and 20%, did not significantly alter the WVP of both bovine-hide gelatin films and tuna-skin gelatin films.

2.4.3. Volatile phenolic compounds

The addition of volatile phenols in biobased films decrease the WVP by their hydrophobic character when they are added into film matrix and by their anti-plasticizing properties. Sometimes, they can also increase WVP.

Regarding the **hydrophobic character of essential oils**, they could enhance the water barrier properties of films. Indeed, Peng & Li. (2014) reported that WVP of chitosan films decreases from 9.4 to 7.5x10^{-11} g/m.s.Pa when lemon, thyme or cinnamon essentials oils were added at 25% to the dry matter (**Table 1).** Peretto et al. (2014) also demonstrated that the addition of essential oil compounds (carvacrol and methyl cinnamate at only 2.8%) reduced by 36% the WVP of strawberry puree films. The water vapor transfer occurs preferentially through the more hydrophilic phase of the film, and permeability depends on the hydrophilic-lipophilic ratio. Therefore, the presence of oil compounds induced greater tortuosity that creates a resistance to the water vapor through the films. Similarly, Bahram et al. (2014) displayed a decrease of WVP by 20.9% for whey protein films after incorporation of cinnamon essential oil at 14.5% concentration **(Table 1)**. The incorporation of essentials oil into a polymeric matrix can decrease moisture transfers of the films by increasing the hydrophobicity of the film (Sánchez-González et al., 2011). Furthermore, the improvement of water barrier properties was also observed by Acevedo-Fani, Salvia-Trujillo, Rojas-Graü, & Martín-Belloso. (2015) in the case of alginate-based edible films incorporating sage oil (at 9.3%) and by Jahed et al. (2017) in the case of chitosan films containing oregano oil (at 10.5%) **(Table 1)**. They mentioned that essential oils are known to decrease WVP of polysaccharide-based films due to their hydrophobic characters. Otoni et al. (2014a) explained the significant decrease of WVP of pectin/papaya puree films after cinnamaldehyde addition (15%) by the **anti-plasticizing effect** (cross-linking) of the essential oils according to the change in mechanical properties **(Table 1)**. An opposite trend was observed for water barrier properties when Zataria multiflora essential oil was added (at 3 or 6%) in gelatin film-forming solutions before casting and drying (Kavoosi et al., 2014). They found that

Zataria multiflora essential oil favorably interacts with hydrophobic groups of gelatin and may hinder polymer chain-to-chain interactions. This **plasticizing effect** raised the film solubility and WVP by 22 and 40% respectively **(Table 1)**. Furthermore, Pranoto, Rakshit, & Salokhe. (2005a) showed a marked increase of WVP by 50% for alginate-based films containing 20% garlic oil (wt. by dry matter). Garlic oil might contribute to extend intermolecular interactions of the structural matrix in alginate films. It therefore, enhanced the moisture passing through the edible film. Moreover, as essential oils are mainly composed of phenolic compounds and alcohols, their chemical nature also plays an important role in the barrier properties of edible films. Phenolic compound containing -OH group in its chemical structure (e.g., carvacrol) seems to provide better barrier efficacy than aldehyde compounds (e.g., cinnamaldehyde, citral) because the hydroxyl group has less affinity for water than for the carbonyl groups.

Most of the effects on the barrier properties, displayed in the cited works and Table 1, remains relatively weak compared to the requirements for a significant increase of shelf life of food.

3. Towards a better controlled release of the active compounds from edible films by cross-linking

As previously displayed, incorporation of antioxidant or antimicrobial agents into edible films and coatings could modify both the structure and the barrier properties. These consequences induce an improvement or a loss of functional properties such as mechanical and barrier. Such modifications also affect the release and the activity of the compounds. However, additional treatments could be envisaged to modify the structure by cross-linking. Indeed, chemical and physical processes have been extensively studied to strengthen the structure and mechanical

properties by cross-linking. Moreover, the cross-linking could also provide a much better controlled release necessary for active packaging applications.

3.1. Chemical cross-linking

Controlled release systems have been developed and used extensively for pharmaceutical applications (Brayden, 2003). Different strategies for achieving the controlled release of drugs, the preparation and the modeling of drug delivery systems have been reported (Arifin et al., 2006; Siepmann and Peppas, 2012). However, studies in the field of food packaging are limited although controlled release of active agents from food packaging materials is an essential feature to provide desired concentrations on food surfaces. Guilbert et al. (1995) and Han & Floros. (1998) were the first researchers who developed the concept of controlled release for food packaging applications. They suggested the control of the release kinetics of antimicrobials by the use of multilayer structures. Ozdemir & Floros. (2003) formed a controlled release system by dispersing hydrophobic beeswax particles within a whey protein network by increasing the hydrophobicity and tortuosity in the films and therefore limiting the diffusion of incorporated antimicrobial agents. Buonocore, Conte, Corbo, Sinigaglia, & Del Nobile. (2005) encapsulated lysozyme in a polymer matrix (PVOH films) and tried to control the release rates by changing the concentration of cross-linking agents added in the matrix. They displayed that, changing the film structure under cross-linking reaction allowed to increase the retention of lysozyme in the polymer network and thus to control its release. In addition, Berger et al. (2004) showed that the release of the antioxidant from the films might also be related to the film microstructure densification by cross-linking or grafting. Chen, Remondetto, Rouabhia, & Subirade. (2008) used formaldehyde as a cross-linker in soy protein films in order to control the release of

rifampicin into aqueous media at different pHs. The drug release rate strongly depended on the concentration of formaldehyde used in the film. Higher degree of cross-linking reduces the degradation of the stiffer protein network, which hence retains the drugs for longer times. Nevertheless, more than 70% of the loaded compound remained in soy protein film after 6 h compared to non-treated films (100% release in simulated gastric and intestinal fluids). Therefore, cross-linking density appears to offer effective means of tuning the release rate of compounds from soy protein films. The ability of glutaraldehyde to cross-link and to reduce the release rate of theophylline from whey protein-based microcapsules in water media was also demonstrated by Lee & Rosenberg. (1999). In the same way, Latha & Jayakrishnan. (1994) indicated that glutaraldehyde cross-linked casein based microcapsules exhibited a better-controlled release. They showed that the complete release of theophylline (model of drug) from the casein spheres, cross-linked with 10 mL glutaraldehyde-saturated toluene, was achieved after 7h, in simulated gastric and intestinal fluids. But, it only took about 2 h for complete release from spheres cross-linked with 6 mL glutaraldehyde. Thus, it is possible to modulate the release of drugs from the protein matrix by changing the surface cross-linking density. From Oussalah, Caillet, Stéphane, Saucier, & Lacroix. (2006) cross-linking the alginate-based films with 2 or 20% (w/w) $CaCl_2$ allowed to control the release of essentials oils (oregano, cinnamon, or savory) from films to be applied onto meat products (bologna and ham). The release of active compounds from oregano and savory-alginate based films pretreated with 20% $CaCl_2$ was faster than that in the same respective films pretreated with 2% $CaCl_2$ regardless of the meat type. Cinnamon-alginate based films pretreated by immersion in a 20% $CaCl_2$ solution were most efficient against both pathogens bacteria (*Salmonella* Typhimurium or *Listeria monocytogenes)*.

Indeed, the migration of active compounds was higher from cinnamon-alginate based films than from oregano-alginate and savory-alginate based films. In another study, Oussalah et al. (2006) studied the availability of total phenolic compounds or aldehydes after addition of $CaCl_2$ in alginate films during meat (beef muscle slices) storage. A better insolubilization treatment of films (20 versus 2% $CaCl_2$) provides a higher level of availability of active compounds in alginate-based films. Furthermore, the active compounds were better retained in the films treated with 2% $CaCl_2$. Thus, the treatment of the films in 2% $CaCl_2$ changed the structure to form perfect obstructions that delay the release of the active compounds into the beef muscle during storage.

3.2. Physical cross-linking

Very few studies have established the effects of irradiation on the retention and release properties of antioxidants encapsulated in biopolymers films. Irradiation technology can be employed in the design of solid dosage forms for controlled-release application without the use of toxic chemical agents (Caillet et al., 2006). Wong & Nurjaya. (2008) worked on the influence of microwave irradiation (80 W for 5, 10, 21 and 40 min) on the drug release properties of polysaccharides beads, and showed that the extent of drug released at 4 h was reduced from 14 % of the untreated pectinate–chitosonium beads to 8% and 10% in samples treated by microwave for 5 and 10 min, respectively. Gamma-irradiation was also shown to be efficient for inducing cross-links in calcium caseinate edible films and thus can been used to immobilize enzyme or active compounds and to control their release (Lacroix et al., 2002). Recently, Benbettaïeb, Karbowiak, Assifaoui, et al. (2015a) worked on the release of antioxidants (ferulic acid and tyrosol) from electron beam treated chitosan-gelatin film into aqueous medium (at pH=7). The apparent

diffusion coefficient of tyrosol twice decreased from $67x10^{-11}$ to $39x10^{-11}$ $m^2.s^{-1}$ after a 60 kGy irradiation. Tyrosol is only sterically entrapped by the network. Thus, irradiation allows the modulation of this physical trapping and slows down its release. The same authors showed that irradiation treatment favors the interaction between coumarin and biopolymer (chitosan and gelatin) via free radical mediated mechanisms. Hence, coumarin is more linked and consequently less mobile (Benbettaïeb et al., 2016). For the non-irradiated films, the structure is less dense, water can easily enter into the network and favour the polymeric chain mobility and thus the diffusion of coumarin was greater. Irradiation allows to delay by 50% the release time. So, film irradiation after optimization, would be an effective process for controlled release of active natural antioxidants in aqueous foods or even for cosmetic, pharmaceutical and medical applications (Benbettaïeb et al., 2016).

Conclusion and future trends

The production of plastics in food packaging has increased markedly over the last 50 years. However, the current levels of their usage and disposal generate several environmental and ecological problems. Up to now, the use of alternative biodegradable materials became the best solution. In order to obtain a smarter packaging for extending the shelf life of food without ecological problems, biomaterials with active properties have been now considered. This new generation of functional biomaterials could produce a successful durable and active packaging in the future. However, for the future active packaging it is necessary to understand the effect of active compounds addition on the biopolymers properties as they would interact with polymers chains and would improve the physical and functional properties of the final films via the production of new linkages. Their mechanisms of action depends on their structure, and

concentration, the nature of biopolymers, the pH of film forming solution, and of interactions involved between matrix and bioactive compounds. In general, organic acid and antimicrobial proteins have a plasticizing effect rather than anti-plasticizing effect on film structure. Enzymes like lysozyme have a degradation effect on film structure and their addition decrease the WVP and TS of final network. Phenolic compounds may interact and form complexes with protein, usually resulting from multiple cooperative hydrophobic (pi-pi stacking), hydrogen binding (dipole-dipole) interaction and charge-charge interaction (only for phenolic acid) and thus may lead to films properties improvement. In contrast, a plasticizing effect has been observed especially in the case of volatile phenols. They might contribute to extend the intermolecular interaction of the structural matrix and decrease the cohesion forces within the network, and thus weaken the films mechanical and barrier properties. Finally, active materials have proved to work by releasing antioxidant and/or antimicrobial agents to the surface of food product. These developments should be optimized and designed for each specific product before to be implemented by the food industry. Moreover, in order to achieve a controlled release of active compounds from edible films, different techniques of cross-linking of polymers chains can be investigated. We anticipate that future efforts on the delivery of active agents in foodstuffs will increasingly incorporate interdisciplinary scientific developments at the interfaces between biomaterials science, physical chemistry of biopolymers, biophysics and encapsulation technology.

References

Acevedo-Fani, A., Salvia-Trujillo, L., Rojas-Graü, M. A., and Martín-Belloso, O. (2015). Edible films from essential-oil-loaded nanoemulsions: Physicochemical characterization and antimicrobial properties. *Food Hydrocolloids*. **47**: 168-177.

Arabestani, A., Kadivar, M., Shahedi, M., Goli, S. A. H., and Porta, R. (2016). The effect of oxidized ferulic acid on physicochemical properties of bitter vetch (Vicia ervilia) protein-based films. *Journal of Applied Polymer Science*. **133**.

Araghi, M., Moslehi, Z., Mohammadi Nafchi, A., Mostahsan, A., Salamat, N., and Daraei Garmakhany, A. (2015). Cold water fish gelatin modification by a natural phenolic cross-linker (ferulic acid and caffeic acid). *Food Science & Nutrition*. **3**: 370-375.

Arcan, I., and Yemenicioğlu, A. (2011). Incorporating phenolic compounds opens a new perspective to use zein films as flexible bioactive packaging materials. *Food Research International*. **44**: 550-556.

Arifin, D. Y., Lee, L. Y., and Wang, C.-H. (2006). Mathematical modeling and simulation of drug release from microspheres: Implications to drug delivery systems. *Advanced Drug Delivery Reviews*. **58**: 1274-1325.

Atarés, L., De Jesús, C., Talens, P., and Chiralt, A. (2010). Characterization of SPI-based edible films incorporated with cinnamon or ginger essential oils. *Journal of Food Engineering*. **99**: 384-391.

Bahram, S., Rezaei, M., Soltani, M., Kamali, A., Ojagh, S. M., and Abdollahi, M. (2014). Whey protein concentrate edible film activated with cinnamon essential oil. *Journal of Food Processing and Preservation*. **38**: 1251-1258.

Basch, C. Y., Jagus, R. J., and Flores, S. K. (2013). Physical and antimicrobial properties of tapioca starch-HPMC edible films incorporated with nisin and/or potassium sorbate. *Food and Bioprocess Technology*. **6**: 2419-2428.

Benbettaïeb, N., Chambin, O., Assifaoui, A., Al-Assaf, S., Karbowiak, T., and Debeaufort, F. (2016). Release of coumarin incorporated into chitosan-gelatin irradiated films. *Food Hydrocolloids*. **56**: 266-276.

Benbettaïeb, N., Debeaufort, F., and Karbowiak, T. (2017). Bio-active edible films for food applications - Part 1: mechanisms of antimicrobial and antioxidant activities. *Trends in Food Science & Technology*.

Benbettaïeb, N., Karbowiak, T., Assifaoui, A., Debeaufort, F., and Chambin, O. (2015a). Controlled release of tyrosol and ferulic acid encapsulated in chitosan-gelatin films after electron beam irradiation *Journal of Radiation Physics and Chemistry*. **118**: 81-86.

Benbettaïeb, N., Karbowiak, T., Brachais, C.-H., and Debeaufort, F. (2015b). Coupling tyrosol, quercetin or ferulic acid and electron beam irradiation to cross-link chitosan–gelatin films: A structure–function approach. *European Polymer Journal*. **67**: 113-127.

Benbettaïeb, N., Tanner, C., Cayot, P., Karbowiak, T., and Debeaufort, F. (2018). Impact of functional properties and release kinetics on antioxidant activity of biopolymer active films and coatings. *Food Chemistry*. **242**: 369-377.

Berger, J., Reist, M., Mayer, J. M., Felt, O., Peppas, N., and Gurny, R. (2004). Structure and interactions in covalently and ionically crosslinked chitosan hydrogels for biomedical applications. *European Journal of Pharmaceutics and Biopharmaceutics*. **57**: 19-34.

Bonilla, J., Atarés, L., Vargas, M., and Chiralt, A. (2012). Effect of essential oils and homogenization conditions on properties of chitosan-based films. *Food Hydrocolloids*. **26**: 9-16.

Brayden, D. J. (2003). Controlled release technologies for drug delivery. *Drug Discovery Today*. **8**: 976-978.

Brudzynski, K., and Maldonado-Alvarez, L. (2015). Polyphenol-protein complexes and their consequences for the redox activity, structure and function of honey. A current view and new hypothesis – a Review. pp. 71-80. Polish Journal of Food and Nutrition Sciences

Buonocore, G. G., Conte, A., Corbo, M. R., Sinigaglia, M., and Del Nobile, M. A. (2005). Mono- and multilayer active films containing lysozyme as antimicrobial agent. *Innovative Food Science & Emerging Technologies*. **6**: 459-464.

Caillet, S., Salmiéri, S., and Lacroix, M. (2006). Evaluation of free radical-scavenging properties of commercial grape phenol extracts by a fast colorimetric method. *Food Chemistry*. **95**: 1-8.

Campos, C. A., Gerschenson, L. N., and Flores, S. K. (2011). Development of edible films and coatings with antimicrobial activity. *Food and Bioprocess Technology*. **4**: 849-875.

Cao, N., Fu, Y., and He, J. (2007a). Mechanical properties of gelatin films cross-linked, respectively, by ferulic acid and tannin acid. *Food Hydrocolloids*. **21**: 575-584.

Cao, N., Fu, Y., and He, J. (2007b). Preparation and physical properties of soy protein isolate and gelatin composite films. *Food Hydrocolloids*. **21**: 1153-1162.

Cao, N., Yang, X., and Fu, Y. (2009). Effects of various plasticizers on mechanical and water vapor barrier properties of gelatin films. *Food Hydrocolloids*. **23**: 729-735.

Cha, D. S., Choi, J. H., Chinnan, M. S., and Park, H. J. (2002). Antimicrobial films based on Na-alginate and κ-carrageenan. *LWT-Food Science and Technology*. **35**: 715-719.

Charlton, A. J., Baxter, N. J., Khan, M. L., Moir, A. J., Haslam, E., Davies, A. P., and Williamson, M. P. (2002). Polyphenol/peptide binding and precipitation. *Journal of Agricultural and Food Chemistry*. **50**: 1593-1601.

Chen, L., Remondetto, G., Rouabhia, M., and Subirade, M. (2008). Kinetics of the breakdown of cross-linked soy protein films for drug delivery. *Biomaterials*. **29**: 3750-3756.

Cheng, S.-Y., Wang, B.-J., and Weng, Y.-M. (2015). Antioxidant and antimicrobial edible zein/chitosan composite films fabricated by incorporation of phenolic compounds and dicarboxylic acids. *LWT - Food Science and Technology*. **63**: 115-121.

Choi, I., Chang, Y., Shin, S.-H., Joo, E., Song, H., Eom, H., and Han, J. (2017). Development of biopolymer composite films using a microfluidization technique for carboxymethylcellulose and apple skin particles. *International Journal of Molecular Sciences*. **18**: 1278.

Ciannamea, E. M., Stefani, P. M., and Ruseckaite, R. A. (2016). Properties and antioxidant activity of soy protein concentrate films incorporated with red grape extract processed by casting and compression molding. *LWT - Food Science and Technology*. **74**: 353-362.

Debeaufort, F., Quezada-Gallo, J.-A., and Voilley, A. (1998). Edible films and coatings: Tomorrow's Packagings: A Review. *Critical Reviews in Food Science and Nutrition*. **38**: 299-313.

Du, W. X., Olsen, C. W., Avena-Bustillos, R. J., McHugh, T. H., Levin, C. E., and Friedman, M. (2008). Storage stability and antibacterial activity against Escherichia coli O157:H7 of carvacrol in edible apple films made by two different casting methods. *Journal of Agricultural and Food Chemistry*. **56**: 3082-3088.

Du, W. X., Olsen, C. W., Avena-Bustillos, R. J., McHugh, T. H., Levin, C. E., and Friedman, M. (2009). Effects of allspice, cinnamon, and clove bud essential oils in edible apple films

on physical properties and antimicrobial activities. *Journal of Food Sciences*. **74**: 1750-3841.

Elsabee, M. Z., and Abdou, E. S. (2013). Chitosan based edible films and coatings: A review. *Materials Science and Engineering: C*. **33**: 1819-1841.

Emmambux, M., Stading, M., and Taylor, J. (2004). Sorghum kafirin film property modification with hydrolysable and condensed tannins. *Journal of Cereal Science*. **40**: 127-135.

Espitia, P. J. P., Avena-Bustillos, R. J., Du, W.-X., Chiou, B.-S., Williams, T. G., Wood, D., McHugh, T. H., and Soares, N. F. F. (2014). Physical and antibacterial properties of açaí edible films formulated with thyme essential oil and apple skin polyphenols. *Journal of Food Science*. **79**: M903-M910.

Espitia, P. J. P., Soares, N. D. F. F., Botti, L. C. M., and Silva, W. A. (2011). Effect of essential oils in the properties of cellulosic active packaging. *Macromolecular Symposia*. **299-300**: 199-205.

Fabra, M. J., Hambleton, A., Talens, P., Debeaufort, F., and Chiralt, A. (2011). Effect of ferulic acid and α-tocopherol antioxidants on properties of sodium caseinate edible films. *Food Hydrocolloids*. **25**: 1441-1447.

Flores, S. K., Gerschenson, L. N., Jagus, R. J., and Sanjurjo, K. J. (2010). Strategies for extending shelf life of foods using antimicrobial edible films. *In B. Siegler (Ed.), Focus in food engineering. Series food science and technology*: 69-99.

Friesen, K., Chang, C., and Nickerson, M. (2015). Incorporation of phenolic compounds, rutin and epicatechin, into soy protein isolate films: Mechanical, barrier and cross-linking properties. *Food Chemistry*: 18-23.

Gómez-Estaca, J., Montero, P., Fernández-Martín, F., Alemán, A., and Gómez-Guillén, M. C. (2009). Physical and chemical properties of tuna-skin and bovine-hide gelatin films with added aqueous oregano and rosemary extracts. *Food Hydrocolloids*. **23**: 1334-1341.

Gómez-Guillén, M. C., Ihl, M., Bifani, V., Silva, A., and Montero, P. (2007). Edible films made from tuna-fish gelatin with antioxidant extracts of two different murta ecotypes leaves (*Ugni molinae Turcz*). *Food Hydrocolloids*. **21**: 1133-1143.

Guilbert, S., Gontard, N., and Cuq, B. (1995). Technology and applications of edible protective films. *Packaging Technology and Science*. **8**: 339-346.

Han, J. H., and Floros, J. D. (1998). Simulating diffusion model and determining diffusivity of potassium sorbate through plastics to develop antimicrobial packaging films. *Journal of Food Processing and Preservation*. **22**: 107-122.

Hoque, M. S., Benjakul, S., and Prodpran, T. (2011). Properties of film from cuttlefish (*Sepia pharaonis*) skin gelatin incorporated with cinnamon, clove and star anise extracts. *Food Hydrocolloids*. **25**: 1085-1097.

Imran, M., El-Fahmy, S., Revol-Junelles, A.-M., and Desobry, S. (2010). Cellulose derivative based active coatings: Effects of nisin and plasticizer on physico-chemical and

antimicrobial properties of hydroxypropyl methylcellulose films. *Carbohydrate Polymers*. **81**: 219-225.

Jahed, E., Khaledabad, M. A., Bari, M. R., and Almasi, H. (2017). Effect of cellulose and lignocellulose nanofibers on the properties of Origanum vulgare ssp. gracile essential oil-loaded chitosan films. *Reactive and Functional Polymers*. **117**: 70-80.

Kaewprachu, P., Osako, K., Rungraeng, N., and Rawdkuen, S. (2017). Characterization of fish myofibrillar protein film incorporated with catechin-Kradon extract. *International Journal of Biological Macromolecules*. **https://doi.org/10.1016/j.ijbiomac.2017.10.011**.

Kamper, S. L., and Fennema, O. (1985). Use of an edible film to maintain water vapor gradients in foods. *Journal of Food Science*. **50**: 382-384.

Kavoosi, G., Rahmatollahi, A., Mohammad Mahdi Dadfar, S., and Mohammadi Purfard, A. (2014). Effects of essential oil on the water binding capacity, physico-mechanical properties, antioxidant and antibacterial activity of gelatin films. *LWT - Food Science and Technology*. **57**: 556-561.

Khwaldia, K., Perez, C., Banon, S., Desobry, S., and Hardy, J. (2004). Milk proteins for edible films and coatings. *Critical Reviews in Food Science and Nutrition*. **44**: 239-251.

Klaenhammer, T. R. (1993). Genetics of bacteriocins produced by lactic acid bacteria*. *FEMS Microbiology Reviews*. **12**: 39-85.

Klangmuang, P., and Sothornvit, R. (2016). Barrier properties, mechanical properties and antimicrobial activity of hydroxypropyl methylcellulose-based nanocomposite films incorporated with Thai essential oils. *Food Hydrocolloids*. **61**: 609-616.

Ko, S., Janes, M. E., Hettiarachchy, N. S., and Johnson, M. G. (2001). Physical and chemical properties of edible films containing nisin and their action against Listeria monocytogenes. *Journal of Food Science*. **66**: 1006-1011.

Krochta, J. M., Baldwin, E. A., and Nisperos-Carriedo, M. O. (1994). Edible coatings and films to improve food quality. Technomic Publ. Co.

Lacroix, M., Le, T. C., Ouattara, B., Yu, H., Letendre, M., Sabato, S. F., Mateescu, M. A., and Patterson, G. (2002). Use of γ-irradiation to produce films from whey, casein and soya proteins: structure and functionals characteristics. *Radiation Physics and Chemistry*. **63**: 827-832.

Latha, M. S., and Jayakrishnan, A. (1994). Glutaraldehyde cross-linked bovine casein microspheres as a matrix for the controlled release of theophylline: In-vitro studies. *Journal of Pharmacy and Pharmacology*. **46**: 8-13.

Lee, S. J., and Rosenberg, M. (1999). Preparation and properties of glutaraldehyde cross-linked whey protein-based microcapsules containing theophylline. *Journal of Controlled Release*. **61**: 123-136.

Limpisophon, K., and Schleining, G. (2017). Use of gallic acid to enhance the antioxidant and mechanical properties of active fish gelatin film. *Journal of Food Science*. **82**: 80-89.

Manab, A., Sawitri, M. E., Al Awwaly, K. U., Widati, A. S., and Haniyah, Y. S. (2016). Antibacterial and physical properties of composite edible film containing modified lysozyme and sodium cyanoborohydrate. *International Journal of CemTech Research*. **5**.

Masamba, K., Li, Y., Sharif, H., Ma, J., and Zhong, F. (2016). Mechanical and water barrier properties of zein–corn starch composite films as affected by gallic acid treatment, Vol 12.

Mathew, S., and Abraham, T. E. (2008). Characterisation of ferulic acid incorporated starch–chitosan blend films. *Food Hydrocolloids*. **22**: 826-835.

Nagarajan, M., Prodpran, T., Benjakul, S., and Songtipya, P. (2017). Properties and characteristics of multi-layered films from tilapia skin gelatin and poly(lactic acid). *Food Biophysics*. **12**: 222-233.

Nie, X., Gong, Y., Wang, N., and Meng, X. (2015). Preparation and characterization of edible myofibrillar protein-based film incorporated with grape seed procyanidins and green tea polyphenol. *LWT - Food Science and Technology*. **64**: 1042-1046.

Nisperos-Carriedo, M. (1994). Edible coatings and films based on polysaccharides. . *In: Krochta JM, Baldwin EA, Nisperos-Carriedo MO (Eds.). Edible Coatings and Films to Improve Food Quality. Technomic Publishing Company, Pennsylvania.*: 305-330.

Nuthong, P., Benjakul, S., and Prodpran, T. (2009). Effect of phenolic compounds on the properties of porcine plasma protein-based film. *Food Hydrocolloids*. **23**: 736-741.

Ojagh, S. M., Rezaei, M., Razavi, S. H., and Hosseini, S. M. H. (2010). Development and evaluation of a novel biodegradable film made from chitosan and cinnamon essential oil with low affinity toward water. *Food Chemistry*. **122**: 161-166.

Otoni, C. G., Avena-Bustillos, R. J., Olsen, C. W., Bilbao-Sáinz, C., and McHugh, T. H. (2016). Mechanical and water barrier properties of isolated soy protein composite edible films as affected by carvacrol and cinnamaldehyde micro and nanoemulsions. *Food Hydrocolloids*. **57**: 72-79.

Otoni, C. G., Moura, M. R. d., Aouada, F. A., Camilloto, G. P., Cruz, R. S., Lorevice, M. V., Soares, N. d. F. F., and Mattoso, L. H. C. (2014a). Antimicrobial and physical-mechanical properties of pectin/papaya puree/cinnamaldehyde nanoemulsion edible composite films. *Food Hydrocolloids*. **41**: 188-194.

Otoni, C. G., Pontes, S. F. O., Medeiros, E. A. A., and Soares, N. d. F. F. (2014b). Edible films from methylcellulose and nanoemulsions of clove bud (*Syzygium aromaticum*) and oregano (*Origanum vulgare*) essential oils as shelf life extenders for sliced bread. *Journal of Agricultural and Food Chemistry*. **62**: 5214-5219.

Ou, S., Wang, Y., Tang, S., Huang, C., and Jackson, M. G. (2005). Role of ferulic acid in preparing edible films from soy protein isolate. *Journal of Food Engineering*. **70**: 205-210.

Oussalah, M., Caillet, S., Stéphane, S., Saucier, L., and Lacroix, M. (2006). Antimicrobial effects of alginate-based film containing essential oils for the preservation of whole beef muscle. *Journal of Food Protection*. **69**: 2364-2369.

Ozdal, T., Capanoglu, E., and Altay, F. (2013). A review on protein–phenolic interactions and associated changes. *Food Research International*. **51**: 954-970.

Ozdemir, M., and Floros, J. (2003). Film composition effects on diffusion of potassium sorbate through whey protein films. *Journal of Food Science*. **68**: 511-516.

Park, S., Daeschel, M., and Zhao, Y. (2004). Functional properties of antimicrobial lysozyme-chitosan composite films. *Journal of Food Science*. **69**: M215-M221.

Park, S. Y., Lee, B. I., Jung, S. T., and Park, H. J. (2001). Biopolymer composite films based on κ-carrageenan and chitosan. *Materials Research Bulletin*. **36**: 511-519.

Pasanphan, W., and Chirachanchai, S. (2008). Conjugation of gallic acid onto chitosan: An approach for green and water-based antioxidant. *Carbohydrate Polymers*. **72**: 169-177.

Pelissari, F. M., Grossmann, M. V. E., Yamashita, F., and Pineda, E. A. G. (2009). Antimicrobial, mechanical, and barrier properties of cassava starch−chitosan films incorporated with oregano essential oil. *Journal of Agricultural and Food Chemistry*. **57**: 7499-7504.

Peña, C., de la Caba, K., Eceiza, A., Ruseckaite, R., and Mondragon, I. (2010). Enhancing water repellence and mechanical properties of gelatin films by tannin addition. *Bioresource Technology*. **101**: 6836-6842.

Peng, Y., and Li, Y. (2014). Combined effects of two kinds of essential oils on physical, mechanical and structural properties of chitosan films. *Food Hydrocolloids*. **36**: 287-293.

Peretto, G., Du, W.-X., Avena-Bustillos, R. J., Sarreal, S. B. L., Hua, S. S. T., Sambo, P., and McHugh, T. H. (2014). Increasing strawberry shelf-life with carvacrol and methyl cinnamate antimicrobial vapors released from edible films. *Postharvest Biology and Technology*. **89**: 11-18.

Pranoto, Y., Rakshit, S. K., and Salokhe, V. M. (2005a). Enhancing antimicrobial activity of chitosan films by incorporating garlic oil, potassium sorbate and nisin. *LWT - Food Science and Technology*. **38**: 859-865.

Pranoto, Y., Salokhe, V. M., and Rakshit, S. K. (2005b). Physical and antibacte rial properties of alginate-based edible film incorporated with garlic oil. *Food Research International*. **38**: 267-272.

Prodpran, T., Benjakul, S., and Phatcharat, S. (2012). Effect of phenolic compounds on protein cross-linking and properties of film from fish myofibrillar protein. *International Journal of Biological Macromolecules*. **51**: 774-782.

Rattaya, S., Benjakul, S., and Prodpran, T. (2009). Properties of fish skin gelatin film incorporated with seaweed extract. *Journal of Food Engineering*. **95**: 151-157.

Rivero, S., García, M., and Pinotti, A. (2010). Crosslinking capacity of tannic acid in plasticized chitosan films. *Carbohydrate Polymers*. **82**: 270-276.

Sánchez-González, L., Vargas, M., González-Martínez, C., Chiralt, A., and Cháfer, M. (2011). Use of essential oils in bioactive edible coatings: A Review. *Food Engineering Reviews*. **3**: 1-16.

Sebti, I., Chollet, E., Degraeve, P., Noel, C., and Peyrol, E. (2007). Water sensitivity, antimicrobial, and physicochemical analyses of edible films based on HPMC and/or chitosan. *Journal of Agricultural and Food Chemistry*. **55**: 693-699.

Siepmann, J., and Peppas, N. A. (2012). Modeling of drug release from delivery systems based on hydroxypropyl methylcellulose (HPMC). *Advanced Drug Delivery Reviews*. **64**: 163-174.

Silva-Weiss, A., Ihl, M., Sobral, P. J. A., Gómez-Guillén, M. C., and Bifani, V. (2013). Natural additives in bioactive edible films and coatings: functionality and applications in foods. *Food Engineering Reviews*. **5**: 200-216.

Sun, X., Wang, Z., Kadouh, H., and Zhou, K. (2014). The antimicrobial, mechanical, physical and structural properties of chitosan–gallic acid films. *LWT - Food Science and Technology*. **57**: 83-89.

Sun, Y., Liu, Y., Li, Y., Lv, M., Li, P., Xu, H., and Wang, L. (2011). Preparation and characterization of novel curdlan/chitosan blending membranes for antibacterial applications. *Carbohydrate Polymers*. **84**: 952-959.

Talón, E., Trifkovic, K. T., Nedovic, V. A., Bugarski, B. M., Vargas, M., Chiralt, A., and González-Martínez, C. (2017). Antioxidant edible films based on chitosan and starch containing polyphenols from thyme extracts. *Carbohydrate Polymers*. **157**: 1153-1161.

Tammineni, N., Rasco, B., Powers, J., Nindo, C., and Ünlü, G. (2014). Bovine and fish gelatin coatings incorporating tannins: effect on physical properties and oxidative stability of salmon fillets. *Journal of Food Chemistry and Nutrition*. **2**: 10.

Ulbin-Figlewicz, N., Zimoch-Korzycka, A., and Jarmoluk, A. (2014). Antibacterial activity and physical properties of edible chitosan films exposed to low-pressure plasma. *Food and Bioprocess Technology*. **7**: 3646-3654.

Vachon, C., Yu, H. L., Yefsah, R., Alain, R., St-Gelais, D., and Lacroix, M. (2000). Mechanical and structural properties of milk protein edible films cross-linked by heating and γ-irradiation. *Journal of Agricultural and Food Chemistry*. **48**: 3202-3209.

Vate, N. K., Benjakul, S., and Prodpran, T. (2017). Improvement of properties of sardine myofibrillar protein films using squid Ink tyrosinasein combination with tannic acid. *Turkish Journal of Fisheries and Aquatic Sciences*. **17**: 853-861.

Wong, T. W., and Nurjaya, S. (2008). Drug release property of chitosan–pectinate beads and its changes under the influence of microwave. *European Journal of Pharmaceutics and Biopharmaceutics*. **69**: 176-188.

Wu, J., Chen, S., Ge, S., Miao, J., Li, J., and Zhang, Q. (2013). Preparation, properties and antioxidant activity of an active film from silver carp (Hypophthalmichthys molitrix) skin gelatin incorporated with green tea extract. *Food Hydrocolloids*. **32**: 42-51.

Yoon, S.-D. (2014). Cross-linked potato starch-based blend films using ascorbic acid as a plasticizer. *Journal of Agricultural and Food Chemistry*. **62**: 1755-1764.

Yoon, S. D., Chough, S. H., and Park, H. R. (2006). Effects of additives with different functional groups on the physical properties of starch/PVA blend film. *Journal of Applied Polymer Science*. **100**: 3733-3740.

Zimoch-Korzycka, A., Rouilly, A., Bobak, #x141, ukasz, Jarmoluk, A., Korzycki, M., and #x142 (2015). Chitosan and cystatin/lysozyme preparation as protective edible films components. *International Journal of Polymer Science*. **2015**: 10.

Zivanovic, S., Chi, S., and Draughon, A. F. (2005). Antimicrobial activity of chitosan films enriched with essential oils. *Journal of Food Science*. **70**: M45-M51.

Zuniga, R. N., Skurtys, O., Osorio, F., Aguilera, J. M., and Pedreschi, F. (2012). Physical properties of emulsion-based hydroxypropyl methylcellulose films: effect of their microstructure. *Carbohydrate Polymers*. **90**: 1147-1158.

Table 1. Effect of active compounds on the mechanical and water barrier properties of edible films

Class and nature of active compounds		Polymer matrix	wt % of dry matter	TS (MPa)	E (%)	WVP (10^{-11} g/m.s.Pa)	PO2 (10^{-15} g/m.s.Pa)	References
Organic acids	Ascorbic acid	*k*-carrageenan	0	30.2±1.3**a**	5±3.2 **a**	190± 3**a**	-	(Park et al., 2001)
			46	37.8±0.8 **b**	5.6±0.6 **a**	160± 2**b**	-	
		chitosan	0	3.2±0.7 **a**	82.2±9.7 **a**	360± 20 **a**	-	
			46	4.7±0.8 **b**	62.7±9.5 **b**	300± 20 **b**	-	
		potato starch / PVA blend films	0	70±5 **a**	10±3 **a**	-	-	(Yoon, 2014)
			20	45±2 **b**	50±4 **b**	-	-	
	Tartaric acid	gelatin	0	90±2 **a**	3.6±0.3 **a**	-	-	(Cao et al., 2009)
			1.6	70±4 **b**	3±0.1 **b**	-	-	
		starch/PVA blend	0	60	20	-	-	(Yoon et al., 2006)
			7.5	20	420	-	-	
		CMC/apple skin	0	3.8±1 **a**	22±5 **a**	13.8±1.14 **a**	-	(Choi et al., 2017)
			1	3±0.5 **a**	20±3 **a**	10±2.16 **a,b**	-	
	Citric acid	gelatin	0	90±2 **a**	3.6±0.3 **a**	-	-	(Cao et al., 2009)
			1.6	62±4 **b**	2±0.3 **b**	-	-	
		pectin	0	5.5±1.2 **a**	0.8±0.02 **a**	-	-	(Da Róz et al., 2016)
			1.5	3.8±1 **a**	0.73±0.01 **b**	-	-	
	Malic acid	gelatin	0	90±2 **a**	3.6±0.3 **a**	-	-	(Cao et al.,

			1.6	65±3 **b**	4±0.2 **b**	-	-	2009)
			2.4	28±7 **c**	8.5±0.4 **c**	-	-	
		starch/PVA blend	0	60	20	-	-	(Yoon et al., 2006)
			6.7	17	310	-	-	
Bacteriocins	Nisin	whey protein isolate	0	1.95±0.39 **a**	-	39100±1350 **a**	-	(Ko et al., 2001)
			0.02	3.5±0.34 **b**	-	42930±3240 **a**	-	
		soy protein isolate	0	8.59±0.94 **a**	-	46440±1890 **a**	-	
			0.04	10.43±2.53 **a**	-	47790±540 **a**	-	
		wheat gluten	0	1.80±0.60 **a**	-	71280±8370 **a**	-	
			0.04	1.96±0.76 **a**	-	58050±6210 **a**	-	
		egg albumin	0	1.79±0.21 **a**	-	65070±4860 **a**	-	
			0.03	1.39±0.18 **a**	-	59400±6480 **a**	-	
		starch	0	2.7±0.2 **a**	2.4±0.2 **a**	135±10 **a**	-	(Basch et al., 2013)
			0.1	0.5±0.01 **b**	2.2±0.3 **a**	145±10 **a**	-	
		starch-HPMC	0	5.5±0.3 **a**	1.1±0.3 **a**	142±1 **a**	-	
			0.1	0.8±0.01 **b**	2.3±0.02 **b**	168±1 **b**	-	
		HPMC	0	60±1 **a**	3.3 **a**	5.6±0.23 **a**	-	(Sebti et al., 2007)
			0.7	35±3 **b**	3.1±0.7 **a**	11.1±0.5 **a**	-	
		Na-alginate	0	27.5±1 **a**	17±2 **a**	-	-	(Cha et al., 2002)
			0.2	12.5±5 **b**	4±1.5 **b**	-	-	
		pullulan	0	8 ±1 **a**	9±2 **a**	-	-	(Pattanayaiying et al., 2015)
			0.02	5±0.5 **b**	16±1 **b**	-	-	

	Nisaplin	HPMC	0	63±8 **a**	13±1 **a**	42±1 **a**	-	(Imran et al., 2010)
			0.66	43±9 **b**	26±14 **a**	49±1 **a**	-	
Enzymes	Lysozyme	chitosan	0	16.19±5.95 **a**	9.69 ±4.37 **a**	13.4 ±2.5 **a**	-	(Ulbin-Figlewicz et al., 2014)
			22	12.08±4.7 **b**	8.08±2.7 **b**	14.7±3.6 **a**	-	
			44	10.92±3.4 **b**	6.65±1.9 **c**	14.5±2.4 **a**	-	
			0	17.4±4.6 **a**	60.3±16.2 **a**	203.8± 54.5**a**	-	(Park et al., 2004)
			20	14.4±3.4 **b**	53.8±9 **b**	181±30.5 **a**	-	
			60	9.5±2.3 **c**	39.3±11.7 **c**	184±27.5 **a**	-	
		Na-alginate	0	27±0.7 **a**	17.5±2.4 **a**	-	-	(Cha et al., 2002)
			0.1	19±4 **b**	9±2.5 **b**	-	-	
		k-carrageenan	0	18±4 **a**	36±8 **a**	-	-	
			0.1	13±1 **a**	22.5±2.5 **b**	-	-	
		potato starch	0	37±1 **a**	5±2 **a**	208±20 **a**	-	(Moreno et al., 2015)
			0.1	23±2 **b**	2.5±1.5 **a**	161±18 **b**	-	
Phenolic compounds	Tannin	pigskin gelatin	0	95±5 **a**	3.2±0.1 **a**	-	-	(Peña et al., 2010)
			9	105±8 **a**	3.4±0.3 **a**	-	-	
			23	70±4 **b**	2.5±0.5 **a**	-	-	
	Tannic acid	bovine gelatin	0	48±1.8 **a**	4.5±0.4 **a**	56700±4050 **a**	-	(Tamminen i et al., 2014)
			12	55±2 **b**	3.5±0.2 **b**	43200±3520 **b**	-	
		fish gelatin	0	21±1.8 **a**	4.7±0.4 **a**	48600±3240 **a**	-	
			12	16±2 **a,b**	3.2±1**b**	45900±4050 **a**	-	
		chitosan	0	73.8±5.4 **a**	-	10.14±0.4 **a**	-	(Rivero et al., 2010)
			2.6	95±4.2	-	8.35±0.7	-	

				b		3 **b**		
			0	11±3 **a**	70±4 **a**	313±47.2 **a**	3319±316 **a**	(Talón et al., 2017)
			4	15±3 **b**	64±4 **b**	333±55.5 **a**	2389±111 **b**	
		myofibrillar protein films (sardine)	0	7.12±0.2 **a**	38.17±2.75 **a**	2.98±0.07 **a**	-	(Vate et al., 2017)
			5	7.83±0.1 **b**	32.46±1.92 **b**	2.56±0.09 **b**	-	
	Proanthocyanidin	chitosan-gelatin	0	44.1±5.5 **a**	9.4±4.9 **a**	-	-	(Kim et al., 2005)
			0.9	68.5±8.6 **b**	11.9±3.5 **a**	-	-	
	Green tea extract	silver carp skin gelatin	0	25.25±1.17 **a**	48±6**a**	11±0.36 **a**	-	(Wu et al., 2013)
			12	36.88±1.22 **b**	42.5±2**b**	9±1 **b**	-	
	Green tea polyphenol	myofibrillar protein	0	3.78±0.4 **a**	176±0 **a**	15.7±5.5 **a**	-	(Nie et al., 2015)
			3.5	4.65±0.47 **b**	65±0 **b**	10.7±2.6 **b**	-	
	Thyme extract	chitosan-starch	0	9.5±1.7 **a**	90±11 **a**	266.6±8.3 **a**	1833±528 **a**	(Talón et al., 2017)
			4	8.2±1.2 **a,b**	47±6 **b**	244.4±36.1 **b**	1194±472 **b**	
	Grape seed procyanidin	myofibrillar protein	0	3.78±0.4 **a**	176±0 **a**	15.7±5.5 **a**	-	(Nie et al., 2015)
			3.5	4.8±0.7 **b**	62±0 **b**	8.6±1.5**b**	-	
	Red grappe extract	soy protein concentrate	0	2.27±0.2 **a**	48.1±7.3 **a**	31±3 **a**	-	(Ciannamea et al., 2016)
			3	2.35±0.3 **a**	48.2±11.5 **a**	18±1 **b**	-	
	Quercetin	chitosan-fish gelatin	0	25.9±3.9 **a**	2.2±0.4**a**	5.2±1.1 **a**	36900±5600 **a**	(Benbettaïeb et al., 2015)
			4.5	29.4±1 **a**	4.2±1.8 **a**	3.9±0.3 **a**	19200±200 **b**	
	Rutin	soy protein	0	9±0.05 **a**	115±5**a**	48.6±1.38 **a**	-	(Friesen et al., 2015)

		isolate	4.6	37.3±3 **b**	73.5±0.5 **b**	33.3±2.2 **b**	-	
	Ferulic acid	sodium caseinate	0	27.1±1.6 **a**	3.1±0.1 **a**	16470±270 **a**	-	(Fabra et al., 2011)
			4.4	23±0.8 **b**	2.9±0.2 **a**	12150±1350 **b**	-	
		chitosan-fish gelatin	0	25.9±3.9 **a**	2.2±0.4**a**	5.2±1.1 **a**	36900±5600 **a**	(Benbettaïeb et al., 2015)
			4.5	37.1±2.1 **b**	4.2±0.3**b**	2.9±0.1 **b**	45200±22000 **a,b**	
		soy protein isolate	0	1.47±0.044 **a**	61.7±7.8 **a**	2656±69 **a**	-	(Ou et al., 2005)
			0.6	1.68±0.13 **b**	94.7±3.9 **b**	2610±57 **a**	-	
		gelatin	0	85.2±2**a**	4.7±1**a**	0.057±0.01 **a**	-	(Cao et al., 2007)
			3.8	96±3**b**	3±0.2**b**	0.055±0.008**a**	-	
		zein	0	10.2±0.8 **a**	3.3±0.6 **a**	-	-	(Arcan and Yemenicioğlu, 2011)
			10	0.7±0.05 **b**	135±50 **b**	-	-	
		bitter vetch (Vicia ervilia) protein-based films	0	5±0.8 **a**	120±18 **a**	20±0.27 **a**	-	(Arabestani et al., 2016)
			4.5	7.8±0.5 **b**	150±10 **b**	13.88±0.55 **b**	-	
	Gallic acid	fish gelatin	0	14.06±0.26 **a**	4.53±0.88 **a**	6.4±0.33 **a**	-	(Limpisophon and Schleining, 2017)
			3	17.46±0.85 **b**	78.83±5.97 **b**	5.18±0.41 **b**	-	
		zein	0	17.5±0.2 **a**	3.7±0.5 **a**	15.2±2.7 **a**	-	(Masamba et al., 2016)
			27	21±1.2 **b**	5±0.8 **a**	9.3±2.2 **b**	-	
		chitosan	0	13.87±0.6 **a**	32.36±1.18 **a**	25.2±0.3 **a**	0.043±0.001 **a**	(Sun et al., 2014)
			27	23.77±0.45 **b**	33.15±2.53 **a**	22.4±0.5 **b**	0.018±0.002 **b**	
			54	18.4±1.	25.6±0.6	22.3±0.4	0.028±0.0	

				46 **c**	**b**	**b**	01 **c**	
			81	9.2±0.6 **d**	10.9±0.9 **c**	37.1±0.7 **a**	0.044±0.002 **a**	
		zein	0	10.2±0.8 **a**	3.3±0.6 **a**	-	-	(Arcan and Yemenicioğlu, 2011)
			10	0.48±0.12 **b**	182.4±23.6 **b**	-	-	
	p-hydroxy benzoic acid	zein	0	10.2±0.8 **a**	3.3±0.6 **a**	-	-	
			10	0.45±0.02 **b**	188.6±25 **b**	-	-	
	Coumarine	chitosan-fish gelatin	0	25.9±3.9 **a**	2.2 ±0.4 **a**	5.2±1.1 **a**	-	(Benbettaïeb et al., 2016)
			4.5	30.9±0.8 **a,b**	4.7 ±0.5 **b**	4.7±0.3 **a**	-	
	Tyrosol	chitosan-fish gelatin	0	25.9±3.9 **a**	-	5.2±1.1 **a**	36900±5600**a**	(Benbettaïeb et al., 2015)
			4.5	29.3±3.7 **a**	-	2.8±0.17 **b**	21500±800 **b**	
	Cinnamon essential oil	whey protein	0	0.82±0.09 **a**	36.6 ± 0.05**a**	25.6±2.4 **a**	-	(Bahram et al., 2014)
			14.5	0.56±0.04 **b**	34.9 ± 0.05**a**	20.3±1.23 **b**	-	
	Lemon and cinnamon oil	chitosan	0	41.5 ±2.5 **a**	20±1 **a**	9.3±0.2 **a**	-	(Peng and Li, 2014)
			25	50±2 **b**	8±3 **a**	7.5±0.5 **b**	-	
	Carvacrol and methyl cinnamate	strawberry puree-pectine	0	2.38±0.89 **a**	56.7±6.9 **a**	25.5±4.7 **a**	-	(Peretto et al., 2014)
			2.8	2.07±0.41 **a**	56.2±7.5 **a**	16.9±1.3 **b**	-	
	Cinnamaldehyde	high methylester pectin-papaya	0	4.84± 0.29**a**	191.6±39.4 **a**	90.5±0.5 **a**	-	(Otoni et al., 2014)
			15	8.36±0.15 **b**	180.3±13.75 **a**	81.9±0.5 **b**	-	
	Cinnamaldehyde	soy protein isolate/tween 60 and acetem	0	2.15±0.18 **a**	342.4±25.2 **a**	78±3.61 **a**	-	(Otoni et al., 2016)
			6.7	2.1±0.18 **a**	376±50.4 **a**	83±2.5 **a**	-	
	Carvacrol	soy	0	2.15±0.	342.4±25	78±3.61	-	

		protein isolate/tween 60 and acetem		18 **a**	.2 **a**	**a**		
			6.7	1.91±0.11**a**	359.8±31.1 **a**	82.2±4.7 **a**	-	
	Thyme oil	alginate	0	5.5±1.1 **a**	38±7 **a**	23.6±2.1 **a**	-	(Acevedo-Fani et al., 2015)
			9.3	5.4±1 **a**	41±12 **a**	21.8±2.3 **a,b**	-	
		Açai	0	1.43±0.35 **a**	99.13±42.5 **a**	71.1±12.2 **a**	-	(Espitia et al., 2014)
			5.6	0.59±0.11 **b**	89.2±9.2 **a**	86.9±14.7 **a,b**	-	
	Lemongrass oil	alginate	0	5.5±1.1 **a**	38±7 **a**	23.6±2.1 **a**	-	(Acevedo-Fani et al., 2015)
			9.3	6.5±1.7 **a,b**	32±9 **a**	21.2±2.4 **a,b**	-	
	Sage oil	alginate	0	5.5±1.1 **a**	38±7 **a**	23.6±2.1 **a**	-	(Acevedo-Fani et al., 2015)
			9.3	5±1.2 **a**	78±5 **b**	19±4 **b**	-	
	Garlic oil	alginate	0	66.12 **a**	4.05 **a**	22653 **a**	-	(Pranoto et al., 2005)
			19	38.67 **b**	2.73 **a,b**	34442 **a**	-	
	Zataria multiflora essential oil	bovine gelatin	0	4.4±0.26 **a**	125±7 **a**	5900±370 **a**	-	(Kavoosi et al., 2014)
			3	3.4±0.23 **b**	144±6 **b**	6750±590 **a,b**	-	
	Thai ginger essential oils	HPMC	0	14±1.5 **a**	58±12 **a**	65.2±9.8 **a**	-	(Klangmuang and Sothornvit, 2016)
			0.7	7.5±1 **b**	65±5 **a,b**	77.31±5.28 **a**	-	
	Origanum vulgare essential oil	chitosan	0	21.56±0.95 **a**	52.2±1.06 **a**	750±13 **a**	-	(Jahed et al., 2017)
			10.5	20.94±1.2 **a**	53.2±1.27 **a**	500± 14 **b**	-	
	Cinnamon extract	cuttlefish skin gelatin	0	32.78±3.10 **a**	5.92±0.7 **a**	9.6±0.3 **a**	-	(Hoque et al., 2011)
			0.8	39.11±1.73 **b**	4.31±0.41 **b**	8±0.6 **b**	-	
	Oxidized cinnamon extract		0	32.78±3.10 **a**	5.92±0.7 **a**	9.6±0.3 **a**	-	
			0.8	44.06±1	4.82±0.2	8.8±0.5 **c**	-	

				.96 **c**	2 **b**			
	Clove extract	cuttlefish skin gelatin	0	32.78±3.10 **a**	5.92±0.7 **a**	9.6±0.3 **a**	-	
			0.82	39.04±1.43 **b**	4.08±0.39 **b**	7.7±0.7 **b**	-	
	Oxidized clove extract		0	32.78±3.10 **a**	5.92±0.7 **a**	9.6±0.3 **a**	-	
			0.82	43.13±1.82 **c**	4.69±0.26 **b**	8.8±0.5 **c**	-	
	Star anise extract	cuttlefish skin gelatin	0	32.78±3.10 **a**	5.92±0.7 **a**	9.6±0.3 **a**	-	
			0.82	38.09±1.9 **b**	4.73±0.28 **b**	7.9±0.6 **b**	-	
	Oxidized star anise extracts		0	32.78±3.10 **a**	5.92±0.7 **a**	9.6±0.3 **a**	-	
			0.82	46.96±2.03 **d**	4.28±0.3 **b**	9±0.2 **c**	-	
	Oregano extract	bovine-hide gelatin	0	10.7±2.2 **a**	14.1±5 **a**	6.1±0.3 **a**	-	(Gómez-Estaca et al., 2009)
			6	10.2±1.3 **a**	14.1±4.7 **a**	5.91±0.22 **a**	-	
	Rosemary extract	bovine-hide gelatin	0	10.7±2.2 **a**	14.1±5 **a**	6.1±0.3 **a**		
			20	9.9±1.3 **a**	14.2±6.9 **a**	6.6±0.08 **a**	-	
	Rosemary extract	gelatin	0	2.4±1.8 **a**	4.4±0.14 **a**	20.3±2.8 **a**	-	(Bonilla and Sobral, 2016)
			1	3.3±0.5 **a**	65±0.1 **b**	26.8 **a**	-	
	Cinnamon extract		0	2.4±1.8 **a**	4.4±0.14 **a**	20.3±2.8 **a**	-	
			1	3.3±0.6 **a**	51±0.1 **b**	19.9 **a**	-	
	Soloyo Chico murta extract	tuna-fish gelatin	0	5.91±1.5 **a**	13.7±0.3 **a**	6 ± 0.52 **a**	-	(Gómez-Guillén et al., 2007)
			75	2.75±1 **b**	3.61±0.03 **b**	5.08±0.3 **b**	-	

Value in same column and type of film, with different superscript letter are significantly different

($p < 0.05$