

Chapter 30

**CHITOSAN EDIBLE FILMS AND
COATINGS – A REVIEW**

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ABSTRACT

The use of conventional food packaging materials is usually effective in terms of barrier. On the other hand, their non-biodegradability creates serious environmental problems, motivating researches on edible biopolymer films and coatings to at least partially replace synthetic polymers as food packaging materials. Chitosan is a biopolymer obtained by N-deacetylation of chitin, which is the second most abundant polysaccharide on nature after cellulose. Chitosan forms clean, tough and flexible films with good oxygen barrier, which may be employed as packaging, particularly as edible films or coatings, enhancing shelf life of a diversity of food products. One of the main applications of the film forming properties of chitosan is to develop coatings to decrease respiration rates and moisture loss in fresh fruits and vegetables. Chitosan has some advantages over other biomaterials because of its antimicrobial activity against a wide variety of microorganisms. The main purpose of this review is to summarize the literature on development and applications of chitosan films and coatings, and their properties/performance as affected by intrinsic factors (molecular weight and degree of deacetylation), chemical/physical treatments, and incorporation of nanoreinforcements.

INTRODUCTION

Packaging is important in post-harvest preservation of fruits and vegetables, and to extend shelf life of processed foods. The main purpose of food packaging is to act as a barrier against environmental factors, thus reducing the rates of quality changes, including microbiological, chemical, and physical deterioration. Microbiological changes are typically related to food safety, while chemical and physical changes are usually (but not only) associated with loss of sensory quality (e.g., rancidity, color changes, loss of crispiness). Regarding the barrier properties, the critical compounds that can deteriorate food quality are water vapor and oxygen.

The use of conventional food packaging materials such as synthetic polymers is usually effective in terms of barrier. On the other hand, they are non biodegradable, which create serious environmental problems. Approximately 40,000,000 tons of plastic packaging is used every year worldwide, and most of this is put to one time use and then discarded (Srinivasa and Tharanathan, 2007). This has motivated researches on edible films and coatings to at least partially replace synthetic polymers as food packaging materials. Edible films and coatings, elaborated from biopolymers (e.g., polysaccharides, proteins) can act as an adjunct to synthetic packaging for extending food stability, and possibly improving economic efficiency of packaging materials (Kester and Fennema, 1986). Moreover, edible films represent non-polluting alternative packaging options.

Chitosan is one of the most promising biomaterials to replace the synthetic ones, particularly for food and packaging applications. Chitosan is a linear polysaccharide consisting of (1,4)-linked 2-amino-deoxy- β -D-glucan, and commercially prepared by chemical alkali deacetylation of chitin, which is considered as the second most abundant polysaccharide in nature after cellulose (Dutta et al., 2009; Aranaz et al., 2010). The deacetylation is usually not complete, so chitosan is generally a copolymer comprised of D-glucosamine along with N-acetyl-D-glucosamine with various fractions of acetylated units (Aranaz et al., 2010). Chitosan is a polycation whose charge density depends on the degree of deacetylation and pH. It is soluble in diluted aqueous acidic solutions due to the protonation of $-\text{NH}_2$ groups at the C2 position (Aranaz et al., 2010). Commercially, chitosan is available from a number of suppliers in different grades of purity, molecular weight and degree of deacetylation.

ANTIMICROBIAL PROPERTIES OF CHITOSAN

Chitosan has some advantages over other biomaterials because of its antimicrobial activity against a wide variety of microorganisms including fungi, algae, and some bacteria (Tsai and Su, 1999; Entsar et al., 2003; Wu et al., 2005).

Recent data in literature has the tendency to characterize chitosan as bacteriostatic rather than bactericidal (Coma et al., 2002), although the exact mechanism is not fully understood and several other factors may contribute to the antibacterial action (Raafat et al., 2008).

Several models have been proposed, the most acceptable being the electrostatic interactions between the positively charged amino groups (NH_3^+) at pH values lower than 6.3 (the pKa of chitosan) and the negatively charged surface of bacteria. This electrostatic interaction results in twofold interference: i) by promoting changes in the properties of membrane wall permeability, thus provoking internal osmotic imbalances and consequently inhibiting the growth of microorganisms (Shahidi et al., 1999), and ii) by the hydrolysis of the peptidoglycans in the microorganism wall, leading to the leakage of intracellular electrolytes such as potassium ions and other low molecular weight proteinaceous constituents (e.g. proteins, nucleic acids, glucose, and lactate dehydrogenase) (Helander et al., 2001; Liu et al., 2004; Dutta et al., 2009). Corroborating this proposition, Fernandez-Saiz et al. (2009) recently demonstrated that only the soluble protonated glucosamine fractions that are released from the solid chitosan film have antimicrobial activity.

The antimicrobial activity varies with several factors concerning the type of chitosan, such as degree of deacetylation (DD) and molecular weight (MW). Chitosans with lower MW have been reported to have greater antimicrobial activity than native chitosans with high MW (Liu et al., 2006; Dutta et al., 2009), because of their higher water solubility, favoring the reaction with the active sites of the microorganisms (Aider and de Halleux, 2010). On the other hand, Zheng and Zhu (2003) reported different effects of chitosan MW on *Staphylococcus aureus* (Gram-positive) and *Escherichia coli* (Gram-negative). For the former, the antimicrobial activity increased on increasing chitosan MW, while for the latter it was the other way around. Antimicrobial effectiveness is also favored by a highly DD, since it increases chitosan solubility and charge density, which improve chitosan adhesion to the microbial cells (Aider and de Halleux, 2010).

The antimicrobial activity is also affected by the conditions of the medium. At low pH values, the higher solubility and protonation of chitosan enhances its effectiveness. Some solutes of the medium can react with chitosan cations, thus blocking the reactivity of the amine groups and decreasing antimicrobial activity (Aider and de Halleux, 2010).

The target microorganisms have also an important role on chitosan antimicrobial effectiveness. The charge density on the microorganism cell surface is a determinant factor to establish the amount of adsorbed chitosan. More adsorbed chitosan would evidently result in greater changes in the structure and in the permeability of the cell membrane. Yeasts and moulds are generally most sensitive, followed by Gram-positive and Gram-negative bacteria (Aider and de Halleux, 2010).

Moreover, chitosan is effective in chelating transition metal ions (Chen et al., 2002), since the $-\text{NH}_2$ groups are involved in interactions with metals (Rinaudo, 2006). It is well known that some ions such as Ag^+ , Cu^{2+} , and Zn^{2+} are antimicrobial agents. Wang et al. (2004, 2005) have reported a wide spectrum antimicrobial activity of chitosan-metal complexes. When compared with free chitosan and metal salts, the complexes showed much better antimicrobial activities. According to Wang et al. (2005), it was concluded that the higher antimicrobial activities of chitosan-metal complexes were due to the stronger positive charge after complexation. The antimicrobial activities were affected by the chelate ratio, being favored by increasing content of metal ions. The complexes were more effective against

bacteria than fungi. Additionally, it is supposed that chitosan molecules in bacteria surrounds might complex metals and blockage some essential nutrients to flow, also contributing to cell death (Kumar et al., 2005). Nevertheless, this is, evidently, not a determinant antimicrobial action since the sites available for interaction are limited and the complexation reaches saturation in function of metal concentration.

Chitosan can be combined with other compounds in order to enhance its antimicrobial activity. Indeed, the combination of chitosan or its derivatives with essential oils (Wilson et al., 2003) or diluted solution of organic acids such as acetic, sorbic, propionic, lactic, and glutamic acid (Wilson and El-Ghaouth, 2002) have been demonstrated to improve the antimicrobial effect and may represent an actual alternative to the use of synthetic fungicides such as thiabendazole.

CHITOSAN FILMS AND COATINGS

Like most polysaccharide based films, the strongly hydrophilic character of chitosan films provides them with good barrier properties against gases and lipids but a poor barrier against water vapor (Bordenave et al., 2007; Sebtì et al., 2005), which limits chitosan films uses (Caner et al., 1998), since an effective control of moisture transfer is desirable in most food packaging applications. The water vapor barrier can be improved by incorporating lipid compounds such as waxes and fatty acids into chitosan-based films. Increased resistance to water vapor transmission through chitosan films has been obtained by addition of saturated (Wong et al., 1992; Srinivasa et al., 2007) or unsaturated fatty acids (Vargas et al., 2009), and tocopherols (Park and Zhao, 2004). on the other hand, the incorporation of lipid compounds usually impairs the mechanical properties of chitosan films (Park and Zhao, 2004; Vargas et al., 2009).

Brittleness is an inherent quality attributed to the complex/branched primary structure and weak intermolecular forces of natural polymers (Srinivasa et al., 2007). Chitosan films are brittle (Suyatma et al., 2004), which is attributed to the high glass transition temperature (T_g) of the polymer (203°C, according to Sakurai et al., 2000). Due to the stiffness of the backbone and the molecule configuration, the glass transition (T_g) of chitosan was attributed by Quijada-Garrido et al. (2008) to torsional oscillations between two glucosamine rings across glucosidic oxygen and a cooperative reordering of hydrogen bonds. By reducing intermolecular forces and thus increasing the mobility of the polymer chains, plasticizers such as glycerol, sorbitol and polyethylene glycol lower the glass transition temperature of films and improve film flexibility, elongation and toughness (Banker, 1966; Domjan et al., 2009). Suyatma et al. (2005) reported that a glycerol concentration of 20% (w/w) was sufficient to improve flexibility of chitosan films. Some theories have been proposed to explain mechanisms of plasticization action (Di Gioia and Guilbert, 1999). According to the lubrication theory, interspersions of plasticizers make them act as internal lubricants by reducing frictional forces between polymer chains. The gel theory postulates that the rigidity of polymers comes from 3-dimensional structures, and plasticizers act by breaking polymer-polymer interactions, causing adjacent chains to move apart and so increasing flexibility. On

the other hand, the main drawback of plasticizers is the increasing permeability rates resulting from decreased film cohesion (Gontard et al., 1993). The most effective plasticizers are those whose structure is similar to that of the polymer, so hydrophilic plasticizers such as polyols are best suited to polysaccharide films (Sothornvit and Krochta, 2005). As expected, the presence of glycerol have been reported to result in chitosan films with higher elongation, but decreased strength and modulus, and increases permeability rates (for both oxygen and water vapor) of chitosan films (Caner et al., 1998; Lazaridou and Biliaderis, 2002; Ziani et al., 2008; Azeredo et al., 2010).

Chitosan coatings have been demonstrated to be effective in enhancing shelf life of a variety of foods, such as carrots (Cheah et al., 1997), mangoes (Srinivasa, et al., 2002), strawberries (Park et al., 2005) and apples (Assis, 2004). The effects of chitosan have been reported to be related to reduced rates of several changes such as weight/water loss (Jeon et al., 2002; Bhale et al., 2003; Dong et al., 2004; Hernández-Muñoz et al., 2006, 2008; Chien et al., 2007a, b, c), respiration/ripening (Jiang and Li, 2001; Hernández-Muñoz et al., 2008), lipid oxidation (Jeo et al., 2002), pigment degradation (Jiang et al., 2005), decline in sensory quality (Dong et al., 2004), ascorbic acid losses (Chien et al., 2007a, b, c), and enzyme activity (Jiang and Li, 2001; Pen and Jiang, 2003; Dong et al., 2004; Jiang et al., 2005).

Film formation as a coating is dependent not only on cohesion (attractive forces between film polymer molecules), but also on adhesion (attractive forces between film and substrate) (Sothornvit and Krochta, 2005). A coating process involves wetting of the food by the coating solution, followed by a possible adhesion between them (Casariego et al., 2008). The amino groups of chitosan backbone, when protonated in acid solution, plays important role when adsorption and adhesion is dominantly governed by ionic attraction between oppositely charged surfaces. In any case, the wettability of the coating solution is a key factor to the effectiveness of edible coatings, since it affects the thickness and uniformity (Hong et al., 2004). Sometimes a surfactant is necessary to reduce the surface tension of the coating solution and enhance its wettability (Choi et al., 2002; Casariego et al., 2008). Choi et al. (2002) used Tween 80 as a surfactant to reduce the surface tension of a chitosan coating solution and enhanced its wettability on apple skin. Casariego et al. (2008) reported that the wettability and adhesion coefficients of chitosan coatings in tomato and carrot surfaces was decreased by increasing concentrations of chitosan and hydrophilic plasticizers.

Characteristics of the chitosan, mainly MW and DD, can affect the film properties. Films from high MW chitosans tend to present higher tensile strength (Chen and Hwa, 1996; Hwang et al., 2003) and better barrier properties (Chen and Hwa, 1996) than those from low MW. Moreover, the higher the DD, the higher the tensile strength of chitosan films (Chen et al., 1994; Hwang et al., 2003), since chitosans of higher DD are more flexible and have a higher tendency to form inter- or intra-chain hydrogen bonds (Chen et al., 1994).

The nature of acidic solvent can also influence the properties of chitosan films. The solutions of choice have usually been based on aqueous acetic acid at 1%, but it imparts a strong acidic flavor to the foods (Casariego et al., 2008), then some studies have been conducted to compare its effectiveness with those of other acids. Caner et al. (1998) studied the effects of four acids (propionic, lactic, formic, and acetic) on mechanical and barrier properties of chitosan films, and reported films elaborated with lactic acid presented the best

oxygen barrier, while acetic acid produced the lowest water vapor permeability. The highest elongation was obtained with lactic acid, while formic and acetic acids resulted in higher tensile strength.

Besides the mechanical and barrier properties of chitosan, which are important in any material intended to be used to elaborate edible films, its antimicrobial properties are those which differentiates it from most other biopolymers. The application of films and coatings based on an antimicrobial polymer is one promising approach to prevent both contamination of pathogens and growth of spoilage microorganisms on the surface of food, where the antimicrobial effects are most needed (Ouattara et al., 2000). Coating a food surface with an antimicrobial film has important advantages over the alternative ways of adding antimicrobial agents to food, i.e., their incorporation into food formulations or their direct application on food surfaces without a polymer matrix. The incorporation of antimicrobial agents into food formulations may result in partial inactivation of the agent by food components, being expected to have only limited effect on surface. Also, a direct application of the antimicrobial by coating the food surface without a polymer matrix has little effect because of its rapid diffusion within the bulk of food (Torres et al., 1985; Siragusa and Dickinson, 1992).

The antimicrobial activity of chitosan has motivated its use as edible films or coatings. Direct application of chitosan formulations onto food surfaces can be attained by spraying or dipping, rendering tough, flexible and transparent films (Tharanathan, 2003). Several studies have proved the antimicrobial effectiveness of chitosan films in different culture media (Coma et al., 2002, 2003; Möller et al., 2004; Sebti et al., 2005). Indeed, chitosan coatings have proved to control microbial growth in fresh fruits and vegetables (Chien et al., 2007a; Liu et al., 2007; Badawy and Rabea, 2009), minimally processed fruits and vegetables (Devlieghere et al., 2004; Durango et al., 2006; Hernández-Muñoz et al., 2006; Chien et al., 2007b, c; Campaniello et al., 2008; Geraldine et al., 2008), seafood (Jeon et al., 2002), cheeses (Coma et al., 2003), and meats (Ouattara et al., 2000; Zivanovic et al., 2005; Beverly et al., 2008).

CHEMICAL AND PHYSICAL TREATMENTS TO IMPROVE PROPERTIES OF CHITOSAN FILMS

Some chemical modifications have been made in order to improve mechanical and gas barrier properties of chitosan films, as well as their water solubility. Although chitosan has been confirmed as attractive biomacromolecules with relevant antimicrobial properties, applications are somewhat limited due to its pH-dependent solubility. Moreover, the low pH required of the solvent to form chitosan gel plays an important role on food surface reactions. During coating, the acidic degree of chitosan solutions directly affects fruit color as result of fast oxidation, mainly over fruit cut surfaces (Assis and Pessoa, 2004). Quaternization of the nitrogen atoms of amino groups is a modification whose objective is to introduce permanent positive charges along the polymer chains, providing the molecule with a cationic character independent on the aqueous medium pH (Curti et al., 2003; Aranaz et al., 2010). Quaternization is usually carried out by *N*-methylation, producing a trimethylated quaternary

salt, *N,N,N*-trimethylchitosan (TMCh) (Britto and Campana-Filho, 2004; Britto and Assis, 2007). Films obtained from *N*-methylated chitosan have been reported to present higher plasticity, but lower strength and elastic modulus (Britto et al., 2005; Britto and Assis, 2007). Moreover, quaternization has been associated with improvements in antimicrobial effects (Jia et al., 2001; Guo et al., 2007), because the groups usually grafted to chitosan are electronegative, strengthening the charge density of the cation (Guo et al., 2007).

Alkylation can be a good strategy to improve mechanical properties (especially elongation) and to change the hydrophilic character of chitosan (Desbrières et al., 1996). The alkyl moiety may reduce inter- and intra-chain hydrogen bonds, plasticizing the molecule, and improve its water vapor barrier (Muzzarelli and Muzzarelli, 2005). Moreover, chitosan antimicrobial activity increases with increasing the chain length of the alkyl substitute (Jia et al., 2001; Rabea et al., 2003), because of the increased lipophilic properties of the derivatives (Kenawy et al., 2007).

The quaternary salts of chitosan were tested against several bacteria such as *Escherichia coli* and *Staphylococcus aureus* (Kim et al., 1997; Jia et al., 2001; Sun et al., 2006). The most important finding is that the antibacterial activity of quaternary ammonium chitosan was stronger in acetic acid medium than in pure water. Indeed, its antibacterial activity increased as the concentration of acetic acid increases (Jia et al., 2001). It was also found that the antibacterial activities of the chitosan derivatives, mainly those containing quaternary ammonium sites, increased with increasing chain length of the alkyl substituent in acetate buffer (pH = 6.0). From these findings it is evident that the number of positive sites along the polymer chain, which are higher in acid than in a neutral medium, strongly affects the antibacterial activity. There is no published data regarding the action of chitosan quaternary salt against fungal action, but other derivatives such as *N,O*-carboximethyl chitosan (El-Ghaouth et al., 1992) and glycolchitosan (El-Ghaouth et al., 2000a,b) have been tested. It was discovered that the *N,O*-carboximethylchitosan, a water soluble derivative, was less effective than chitosan in reducing the radial growth of the fungi *B. cinerea* and *Rhizopus stolonifer*, while glycolchitosan, an acid soluble derivative, was more effective than chitosan against the fungi *B. cinerea* and *P. expansum*. Thus, as already mentioned, it would appear that the fungicide effect depends on the charge density of the derivative chain.

The application of electric fields has been suggested to improve properties of chitosan films. The application of electric fields resulted in decreased permeability of chitosan films to water vapor (García et al., 2009; Souza et al., 2009), oxygen and carbon dioxide (Souza et al., 2009), as well as increased tensile strength and elongation at break (García et al., 2009; Souza et al., 2010). Images from atomic force microscopy (AFM) suggested that the application of electric fields improved the uniformity of the film surfaces, which was attributed to a more uniform gel structure leading to the improvements in barrier properties (Souza et al., 2009).

ADDITION OF NANOREINFORCEMENTS TO CHITOSAN FILMS

The addition of reinforcing fillers to biopolymers such as chitosan has been reported to enhance their thermal, mechanical, and barrier properties. The smaller the filler particles, the

better is the filler-matrix interaction (Ludueña et al., 2007). Fillers with at least one dimension in the nanometric range (< 100 nm) are called nanoreinforcements, and their composites with polymers are nanocomposites (Alexandre and Dubois, 2000). A uniform dispersion of nanofillers leads to a very large matrix/filler interfacial area, which changes the molecular mobility, and favors the thermal and mechanical properties of the material (Vaia and Wagner, 2004).

Azeredo et al. (2010) reinforced chitosan films with cellulose nanofibers, which increased the T_g of the films and improved their tensile strength and water vapor barrier, although the elongation was decreased. A nanocomposite film with 15% cellulose nanofibers was comparable to some synthetic polymers in terms of strength and stiffness.

Han et al. (2010) prepared chitosan-clay nanocomposites by an ion exchange reaction between oligomeric chitosan and a Na^+ -montmorillonite (NaMMT). The thermal stability of chitosan was improved by combination with NaMMT, which was attributed to a thermal insulation effect of the clay and strong electrostatic interactions between cationic chitosan molecules and anionic silicate layers. The antimicrobial activity was also enhanced by the clay, which seems contradictory, since the anionic silicate layers tend to neutralize the positive charges of chitosan. The authors attributed this effect to a synergy between the components of the nanocomposite, because of the high dispersion of the chitosan molecules through the inorganic matrix.

CHITOSAN NANOPARTICLES IN FILMS

De Moura et al. (2009) incorporated chitosan/tripolyphosphate nanoparticles (CsN) to hydroxypropyl methylcellulose (HPMC) films, and observed improvements in mechanical properties and water vapor barrier of the films. The water vapor permeability was affected by the size of the CsN – the smaller the particles, the lower the permeability. According to the authors, CsN tended to occupy the empty spaces in the pores of the HPMC matrix, thereby improving tensile and barrier properties. The thermal stability of the films was also favored by addition of CsN.

Chang et al. (2010) added CsN to a glycerol plasticized starch matrix. The tensile strength, storage modulus, glass transition temperature, water vapor barrier and thermal stability were improved by low contents of CsN, when the particles were well dispersed in the matrix. Such effects were attributed to close interactions between CsN and the matrix, due to their chemical similarities. However, higher CsN loads (8%, w/w) resulted in aggregation of CsN in the nanocomposites.

FINAL CONSIDERATIONS

Considering the problems related to disposal of non-biodegradable materials, the use of biopolymers as food packaging materials is an important tendency. Among the known biopolymers, chitosan is especially promising because of its antimicrobial properties. The

antimicrobial activity is related to the cationic character of chitosan, and has been successfully explored to extend shelf life of a variety of foods. Introducing alkyl chain and promoting the quaternization of chitosan it is possible to obtain water soluble films with different hydrophilic character, having potential application for minimally processed food industry. The beneficial use of water soluble quaternary salt of chitosan is devoted to its improvement on decreasing browning effect, increasing the fungicidal action and represents an advance in overcoming consumer acceptance.

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