Use of Antimicrobial Edible Films and Coatings as Packaging Materials for Food Safety

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1 Introduction

The quality of food products depends on the changes of physical, chemical, and microbiological parameters that occur during storage. Various methods are used such as heating or cooling temperature variation, reduction of water activity, curing, salting, pH control, the addition of antimicrobial agent, controlled atmosphere storage and packaging technologies to extend shelf life and to achieve better quality food products. Packaging technologies are used for protecting food products from some influences such as chemical, air, light, heat, microorganism, and environmental impacts. Packaging also facilitates the transport of food products and offers the consumer that necessary information about the product (Üçüncü 2007; Ayana and Turhan 2010; Mehmetoğlu 2010).

In recent years, due to the increased interest in minimal processed foods depending on consumer demand, use of new technologies and approaches started in the packaging industry. The active packaging technique is the most prominent of these technologies. It can be considered as an emerging technology that could have a significant effect on the shelf life extension and food safety (Perez-Perez et al. 2006). Active packaging takes place engagement of the various active components inside the packaging material. The active components, antimicrobial and become active in various architectures such as the synthetic polymers and the edible films and coatings (Ayana 2007). Organic acids, bacteriocins, antibiotics, fungicides,

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chelating agents, and parabens may show antimicrobial activity within the food packaging materials (Khairruddin 2005). Use of antimicrobial agents in food packaging can control the microbial population and growth of target specific microorganisms to provide higher safety and quality products (Perez-Perez et al. 2006).

Antimicrobial packaging is a suitable protection method especially for raw meat, processed meat products, poultry, dairy products, and seafood (Suppakul et al. 2003; Karagöz and Candoğan 2007). Controlled release of antimicrobial compounds carried out on these systems can inhibit both of the initial microorganisms and the current microbial growth during storage. These systems form a barrier mechanism for pathogens and/or spoilage microorganism for ensure food safety (Cooksey 2005).

Nowadays, the widespread use of traditional packaging material has synthetic structure. These synthetic materials are safe, convenient, and economical but they aren't biodegradable so they are one of the main factors of environmental pollution. For this reason, researchers have focused on the use of protein, lipid, and polysaccharide polymers as packaging materials which are biologically degradable and also can be consumed with food offering more environmental friendly alternatives. In this context, the use of edible films and coatings containing antimicrobial components is increasingly widespread and adopted (Ayana 2007).

We aimed to review; history of antimicrobial edible films and coatings, evaluation of edible packaging performance, characteristics of biopolymers and antimicrobial substances which are used for preparation of antimicrobial edible film and coatings, functional properties, legal and economic aspects, some food applications, and the place and importance of antimicrobial edible films and coatings in future within this chapter.

2 Edible Films and Coatings

2.1 Definition and Historical Background

Edible films and coatings are defined as continuous matrices prepared from proteins, lipids, and polysaccharides (Çağrı 2002). They become popular in the food industry, due to producing less waste, and being cost effective (Cha and Chinnan 2004). These are thin layers of edible materials and are formed on the surface of a food as coating or between food components. They can control oxygen, moisture, carbon dioxide, flavor, and aroma transfer between food components or the atmosphere surrounding the food (Wen-Xian et al. 2011). They can also carry a wide range of food additives including antioxidants, flavors, preservatives, and antimicrobial agents. If they are prepared properly they could serve all the functional properties as a packaging material (Ko et al. 2001; Skurtys et al. 2010).

Historically, during twelfth and thirteenth century, citrus fruits were dipped in wax in order to slow water loss (Yener 2007). During the fifteenth century, Yuba, the first freestanding edible film, was developed in Japan from soymilk (Çağrı 2002). In order to reduce of the loss of moisture, the surface of the meat coated with oil in sixteenth century in Europe. The introduction of the oil with gelatin coatings had been realized in nineteenth century (Kester and Fennema 1986). In the nineteenth century, almonds, nuts and hazelnuts were coated with sucrose to prevent rancidness and oxidation during storage (Debeaufort et al. 1998). Currently, edible films and coatings are used in variety of applications, including casing for sausages, and chocolate coatings for nuts hazelnuts, almonds, and some fruits (Çağrı 2002).

In order to avoid a negative impact on consumption edible films and coatings, they should be tasteless, odorless, colorless, and transparent as possible. And they should be chosen adaptable with food. Edible films and coatings which are in good property must bear the following conditions: (1) The raw materials which are used to prepare edible films and coating material to be generally recognized as safe (GRAS); (2) Slow, but they should allow controlled ventilation of the product; (3) The structural integrity must provide an appropriate mechanical processing; (4) They reduce of pathogenic and/or saprophyte microorganism without causing deterioration on the surface of product during long-protected storage (Quntavalla and Vicini 2002; Dursun and Erkan 2009).

2.2 Classification of Edible Films and Coatings

Edible films can be produced from materials with film forming ability. During manufacturing, film materials must be dispersed and dissolved in a solvent such as water, alcohol, or mixture of water and alcohol, or a mixture of other solvents. Plasticizers such as generally sorbitol or glycerol, antimicrobial agents, colors, or flavors can be added in this process. Adjusting the pH and/or heating the solutions may be done for the specific polymer to facilitate dispersion. Film solution is then casted and dried at a desired temperature and relative humidity to obtain freestanding films. In food applications, film solutions could be applied to food by several methods such as dipping, spraying, brushing, and panning followed by drying (Bourtoom 2008).

According to their components, edible films and coatings can be divided into three categories: hydrocolloids, lipids, and composites. Hydrocolloids include proteins and polysaccharides. Lipids include waxes, acylglycerols, and fatty acids. Composites contain both hydrocolloid components and lipids (Valencia-Chamorro et al. 2011a, b). Several other compounds such as plasticizers and emulsifiers may be added to edible films and coatings to improve their mechanical properties and form stable emulsions when lipids and hydrocolloids are combined. In addition, edible coatings and films can also act as carriers of food additives, including antioxidants, colorants, flavoring agents, and antimicrobial compounds (Cuppet 1994; Baldwin 1999; Franssen and Krochta 2000; Cha and Chinnan 2004; Han and Gennadious 2005).

2.2.1 Polysaccharides

Polysaccharides used for edible films or coatings include cellulose, starch derivatives, pectin derivatives, seaweed extracts, exudate gums, microbial fermentation gums, and chitosan (Bourtoom 2008) Polysaccharides are nontoxic and widely available. They have also selective permeability to carbon dioxide and oxygen, and thus retard the respiration and ripening of many fruits and vegetables by limiting the availability of oxygen. Polysaccharide-based films have a hydrophilic nature. For this reason, they are a poor barrier to water vapor. The poor water vapor barrier property allows for the movement of water vapor across the film, thus, preventing water condensation that can be a potential source of microbial spoilage in horticulture commodities (Yener 2007).

Cellulose and Derivatives

Cellulose is composed of repeating D-glucose units linked through ß-1, 4 glycosidic bonds (Çağrı 2002). It is the most abundant organic compound on earth owing to it is the principal component of plant cell. In esterification process, cellulose is reacted with aqueous caustic, then with methyl chloride, propylene oxide, or sodium monochloroacetate to yield methylcellulose (MC), hydroxypropyl methylcellulose (HPMC), and sodium carboxymethylcellulose (CMC), respectively (Çağrı 2002). These are widely reported as edible films and coatings in the scientific literature and in patents (Debeaufort et al. 1994).

Cellulose derivatives are interesting film-forming compounds, as they are odorless, tasteless, and biodegradable. In addition, their cost of application is low. HPMC is a water-soluble polymer used in the food industry as a gelling and stabilizing agent. It presents excellent film-forming properties with very efficient oxygen, carbon dioxide, and lipid barriers (De Moura et al. 2008; Sanchez-Gonzalez et al. 2009). But HPMC films are highly permeable to water vapor and this condition limits its application. HPMC is approved for food uses by the FDA (21 CFR 172.874) and the EU; its safety in food use has been affirmed by the JECFA (Imran et al. 2010). Another cellulose derivative is methyl cellulose (MC) is of interest to researches because they are able to form a continuous matrix. MC is cellulose that exhibits thermal gelation, forms excellent films, and is used in pharmaceutical and food industries (Turhan and Şahbaz 2004).

However, cellulose derivative films are poor water vapor barriers because of the inherent hydrophilic nature of polysaccharides and they possess poor mechanical properties. A way to improve the moisture barrier would be the incorporation of hydrophobic compounds, such as fatty acids, into the cellulose ether matrix to develop a composite film (Skurtys et al. 2010). In order to improve water barrier properties, lipid compounds such as fatty acids, natural waxes, surfactants, and resins are frequently incorporated in to hydrocolloid-based films (Sanchez-Gonzalez et al. 2009).

Edible coatings made of CMC, MC, HPC, and HPMC have been applied to some fruits and vegetables for providing barriers to oxygen, oil, or moisture transfer (Skurtys et al. 2010).

Chitin and Chitosan

Chitin is the second most abundant naturally occurring biopolymer (after cellulose) and is found in the exoskeleton of crustaceans, in fungal cell walls, and other biological materials. Chitosan is a natural carbohydrate polymer derived by deacetylation of chitin [poly-β-(1 → 4)-*N*-acetyl-D-glucose-amine] which is a major component of the shells of crustacean such as crab, shrimp, and crawfish. Chitosan has been reviewed for commercial application in biomedical, food, and chemical industries. It is natural polymer which is nontoxic, biodegradable, and biocompatible. It is insoluble in water, but soluble in various acidic solvent such as dilute hydrochloric, formic, and acetic acids. It is a high molecular weight cationic polysaccharide that exhibits antibacterial and antifungal activity as well as film-forming properties (Beverlya et al. 2008; Ye et al. 2008a, b; Ferreira et al. 2009; Campos et al. 2011). Chitosan antimicrobial activity against bacteria could be due to the polycationic nature of the molecule, which allows interaction and formation of polyelectrolyte complexes with polymers produced at the bacteria cell surface (Moreira et al. 2011). Chitosan is a good choice for antimicrobial films because of its superior film-forming properties, ability to absorb nutrients used by bacteria, and capacity to bind water and inhibit various bacterial enzyme systems (Ye et al. 2008a, b).

Chitosan has been widely used for the production of edible films and coatings (Souza et al. 2010). Chitosan-based films are excellent oxygen barriers; but, due to their hydrophilic nature, they have poor moisture barrier properties (Ojagh et al. 2010). Similarly, the chitosan coatings creates a semi-permeable barrier that controls gas exchange and reduce water loss, thereby maintaining tissue firmness and reducing microbial decay of harvested vegetables for extended periods (Alvarez et al. 2013). Chitosan coatings are usually used on fruit and vegetable products such as strawberries, cucumbers, and bell peppers as antimicrobial coating and on apples, pears, peaches, and plums as gas barrier (Bourtoom 2008).

Starch

Starches are renewable resources widely available and can be obtained from different byproducts of harvesting and industrialization (Sanjurjo et al. 2006). Starches consist of approximately 25 % amylase and 75 % amylopectin (Çağrı 2002; Bourtoom 2008) Amylase is responsible for the film-forming capacity of starch. The largest source of starch is corn (maize) with other commonly used sources being wheat, potato, tapioca, and rice. Starch is used to produce biodegradable films to partially or entirely replace plastic polymer. Starch films are transparent or translucent, flavorless, tasteless, and colorless (Skurtys et al. 2010). Despite starch is the most used agriculture raw material for biodegradable films, few reports are published about starch-based coatings. Amylase is responsible for the film-forming capacity of starches and it is required for film forming and preparation of strong gels. Starches containing 55 or 75 % amylase content are commercially available, with 70 % amylase content; starch is producing stronger, tougher, and more flexible films. In addition, another important component of starch edible films and coatings is the plasticizer, which must be compatible with the film forming polymer. Plasticizers such as glycerol are frequently added to enhance flexibility; they lower glass transition temperature of system and modify the barrier properties of the films (Garcia et al. 1999; Çağrı et al. 2002).

Alginate

Alginate, a polysaccharide derived from marine brown algae (*Phaeophyceae*) and gellan, a microbial polysaccharide secreted by bacterium *Sphingomonas elodea* (formerly referred to as *Pseudomonas elodea*) is finding increasing use in the food industry as texturizing and gelling agents (Rojas-Graü et al. 2007a, b). In molecular terms, alginates are linear water-soluble polysaccharides comprising (1–4)-linked units of R-D-mannuronate (M) and â-L-guluronate (G) at different properties and different distributions in the chain. The chemical composition and sequence of the M and G residues depend on the biological source and the state of maturation of the plant. The hardness of the three blocks decreases in order to GG > MM > MG. The physical properties of alginates depend on the relative proportion of the three types of blocks. For example, formation of gels, by addition of calcium ions, involves the G block so higher the proportion of these, the greater the gel strength; solubility of alginate in acid depends on the proportion of MG blocks present (Cha et al. 2002; Hambleton et al. 2009a, b; Albert et al. 2010; Galus and Lenart 2013).

Alginate films potentially a good option for same fruit such as cut apple, since these films become stronger when cross-linked with Ca, and at the same time, stick to the cut apple surface through this cross-linking (alginate-Ca-pectin). Such biopolymer-based films and coatings can keep good quality and prolong shelf life of foods by increasing water barrier, preventing microbial contamination, maintaining the flavor, reducing the degree of shrinkage distortion, and retarding fat oxidation. Moreover, the coatings may serve as carriers for antimicrobial compounds and antioxidant in order to maintain high concentration of preservatives on the surface of foods (Olivas et al. 2007; Song et al. 2011).

Pectin

Pectin is an ingredient used in food industry with no limitation other than current good manufacturing practice. It is considered as generally recognize as safe (GRAS) by the FDA and it has been used in food mainly as gelling, stabilizing or thickening agent in products such as jams, yoghurt drinks, fruity milk drinks, and ice-cream

(Espitia et al. 2013). Pectin is an anionic polysaccharide, mostly derived from citrus fruits. The main structural features of pectin include a backbone of (1 → 4)-linked α-D-galacturonic acid units. According to their degree of methylation, pectin is divided into two categories. These are low-methoxyl pectin (LMPs) and high methoxyl pectins (HMPs), with a degree of methylation respectively lower and higher than 50 %. The degree of methylation has a decisive effect on the mechanisms of gelation (Kang et al. 2007; Piazza et al. 2009; Altenhofen Da Silva et al. 2009; Bierhalz et al. 2012). The hydrocolloidal and polyelectrolytic properties of pectin determine its unique abilities, such as strong water retention in colloidal systems together with their stabilization; easy plasticization with glycerol; due to its hydrophobic groups, ability to absorb organic lipoid substance; an expressive cation-exchange ability forming its curative action. The investigation of many authors present the structural and mechanical properties of edible films and coatings containing citric acid and apple pectin in the form of aqueous solutions with concentration up to 1 % (Baeva and Panchev 2005).

Carrageenan

Carrageenans are water-soluble polymers with a linear chain or partially sulfated galactans, which present high potential as film-forming material (Karbowiak et al. 2006). They are extensively used in food, dairy, and pharmaceutical industry as gelling, emulsifying, and stabilizing agents (Seol et al. 2009a, b). The number and position of sulfate groups on the disaccharide repeating unit determine classification in the major types: κ, ι and λ. The κ-, ι- and λ- carrageenans exhibit sulfate contents of 20 %, 33 % and 41 % (w/w), respectively (Fabra et al. 2009). κ-carrageenan has one negative charge per disaccharide with a tendency to form excellent gel and film–forming properties. Films from κ-carrageenan exhibit, therefore, the highest tensile strength when compared with that of λ- and ι-carrageenan films (Seol et al. 2009a, b). Park (1996) reported that κ-carrageenan has excellent film-forming properties with water vapor permeability (WVP) of 1.87×10^{-10} ngm/m^{2}sPa and tensile strength of 22–32 MPa, which has higher than that polyethylene films (Park 1996). And Choi et al. (2005) reported that κ-carrageenan film containing potassium sorbate has great possibility to extend the shelf life or increase the safety of foods when it is used as packaging or coating material (Choi et al. 2005). Iota-carrageenan is a hydrocolloid widely used in the dairy industry as it present significant reactivity with milk proteins (Karbowiak et al. 2006). Iota-carrageenan, a water-soluble polymer with a linear chain mainly composed of alternated (1,3)-D-galactose-4 sulfate and (1,4)-3,6-anhydro-D-galactose-2-sulfate units, is promising as a film-forming material (Hambleton et al. 2009a, b). Edible films made of ι-carrageenans display interesting advantages such as good mechanical properties, stabilization of emulsions, and reduction of oxygen transfer. But, the highly hydrophilic nature of ι-carrageenan films limits their ability to provide a significant moisture barrier. One way to improve barrier properties is to include lipidic materials in their formulation, such as fatty acids or waxes (Seol et al. 2009a, b).

The use of carregeenan as edible films and coating already covers various fields of the food industry such as application on fresh and frozen meat, poultry and fish to prevent superficial dehydration, ham or sausage-casings, granulated-coated powders, dry solids foods, oily foods, etc., but also manufacturing soft capsules, and especially non-gelatin capsules (Karbowiak et al. 2006).

2.2.2 Protein Films

With their availability, different molecular properties and chemical functional proteins are very suitable sources to obtain edible films (Güçbilmez 2005). Several globular proteins, including wheat gluten, corn zein, soy protein, and whey protein, have been investigated for their film properties (Bourtoom 2008). The edible films composed of proteins generally have good gas barrier properties and suitable mechanical and optical properties. However, they are highly sensitive to moisture and show poor water vapor barrier properties than other biopolymers (Güçbilmez 2005). Several protein edible films described and discussed in following section.

Zein

Zein is the most important protein in corn. It is a prolamine protein and for this reason dissolves in 70–80 % ethanol (Guo et al. 2012). Zein is located in small round particles, 1–2 μm in diameter, called protein bodies in maize endosperm. Three distinct fractions, a, b, and g zein, have been identified by differential solubility in aqueous alcohol solutions. Commercial zein is a mixture of proteins with different molecular sizes, solubility, and charge. Commercial preparations usually contain only the fraction of zein (Lai and Padua 1997). Zein is a relatively hydrophobic and thermoplastic material, and has excellent film-forming properties, so it can be used for fabrication of biodegradable films. These film-forming properties have attracted attention in the field of edible film and coating materials. However the characteristic brittleness of zein diminishes its usefulness as a film; some modifications are needed to improve their flexibility. In addition, preparation conditions also affect the properties of zein films (Guo et al. 2012). Zein coatings have been used to coat nuts and candy for increased gloss, and prevention of oxidation and development of off-odors. Zein coatings offer a reasonable alternative to shellac and carnauba wax. The coating can serve as a carrier for antimicrobial compounds and/or antioxidants compounds in order to maintain high concentrations of preservatives on the food surfaces. Performance of zein films as barrier packaging for popcorn, tomatoes, cooked turkey, and shell eggs has been evaluated. In addition, use of zein-based coatings for reducing oil uptake by deep-fried foods, for obtaining controlled release of active ingredients in pharmaceutical tablets, and for masking the taste of bitter orally administered drugs has been discussed in recently awarded patents (Baysal et al. 2009).

Gelatin Films

Collagen is a biopolymeric fiber and the most abundant mammalian and fish protein (Diop 2009). Gelatin versatility and functionality reflects the fact that it is the only food protein that undergoes a thermally reversible helix coil partial transition to resemble its original parent protein structure, collagen (Avena-Bustillos et al. 2006). Gelatin is a protein that is widely used in the pharmaceutical and food industries, and it is produced on a large scale at relatively low prices (De Carvalho and Grosso 2006). Gelatin is an edible biodegradable and biocompatible polymer that is produced by the thermal or physical and chemical degradation of collagen. There are two types of gelatin. These are Type A and Type B. The type of gelatin that is formed from collagen is dependent on whether the collagen is pretreated with an alkaline or an acid. Type A is prepared through acid pretreatment and has an isotonic point between 7 and 9. Gelatin Type B is prepared by alkaline pretreatment of collagen and has an isotonic point between 4.7 and 5.2 (Diop 2009). The use of gelatin in elaboration of edible films or coatings was very well studied until the 1960s, which resulted in many patents, mainly in pharmaceutical area. As a result, these materials characteristics are not easily available in the literature. But gelatin has return to attention of several researches on edible films for food application. Some researches elaborated edible films from bovine hide gelatin and determined their mechanical properties by puncture test, as function of pH and gelatin and sorbitol concentrations in the filmogenic solution, using surface-response methodology. Same researchers studied the drying of films of gelatin plasticized with sorbitol, with special interest in effect of drying conditions on the quality of the formed film in their another investigation. Those recent interest are justified by the ready availability and the low cost of gelatin. However, there is a lack of more detailed works on the plasticizer effect on the thermal and functional properties of gelatin edible films. Therefore, researches focused on to study the WVP and the mechanical and thermal properties of edible films based on bovine hide and pigskin gelatins as functions of sorbitol content (Sobral et al. 2001).

Wheat Gluten Films

Wheat gluten is a general term for water-insoluble proteins of wheat flour which is composed of a mixture of polypeptide molecules, considered to be globular proteins (Bourtoom 2008). Film production from what gluten a mixture of proteins accounting for about 80–85 % of wheat flour proteins, has also been studied (Gennadios et al. 1993). Wheat gluten protein, a renewable resource, is capable of forming a fibrous network which lends strength, elasticity, and plasticity when formed into a film with glycerol. Research on the preparation and properties of wheat gluten films arose owing to the excellent viscoelastic properties of wheat gluten. The two general methods used to prepare wheat gluten films are dry processing or solvent casting. Wheat gluten films have excellent oxygen and carbon dioxide barrier properties compared to plastic films but have low water vapor barrier properties compared to plastic films. A linear relationship between gluten film thickness and film barrier properties for oxygen and carbon dioxide gas was observed by Park and Chinnan (1995). Upwards, Olabarrieta et al. (2006) reported that an increase in oxygen permeability for pH4 wheat gluten films compared to pH11 wheat gluten films, which could be attributed to reduced protein aggregation and a more heterogeneous wheat gluten film structure at pH4 (Olabarrieta et al. 2006). Significant decrease of the WVP for wheat gluten films has proven quite challenging to achieve and represents a major limitation in the application of wheat gluten films for food packaging materials (Cousineau 2012).

Soy Protein Films

The protein content of soybeans (38–44 %) is much higher than the protein content of cereal grain (8–15 %) (Bourtoom 2008). Soy protein is extracted from soybeans used to obtain soy oil. During this process, soy flour is obtained as a secondary product and it can be purified to obtain soy protein concentrate (SPC) and soy protein isolate (SPI), which would add value to agricultural by-products. Soy proteins are composed of a mixture of albumins and globulins. Globulins are protein fractions in which the subunits are associated via hydrophobic and hydrogen bonding (Guerrero et al. 2011). Soy protein is globular in nature and is further classified into 2S, 7S, 11S and 15S fractions; the main components being conglycinin (7S) and glycinin (11S). While both of these fractions are tightly folded, alkaline conditions and heating cause dissociation and subsequent unfolding due to deamination, since soy protein is high in asparagine and glutamine residues (Skudlarek 2012). Soy protein-based edible films have received considerable attention due to their excellent film-forming abilities, low cost, and barrier properties against oxygen, lipid and aroma permeation under low to intermediate humidity conditions. This type of proteins produces smoother, clearer and more flexible films compared to those from other sources. However, due to its inherent hydrophilic nature, this material presents two major disadvantages such as fragility in the wet state and poor properties of moisture barrier. These effects can be minimized using physical, chemical or enzymatic treatments including: blending with hydrophobic additives such as neutral lipids, fatty acids or waxes; changing drying conditions; enzymatic treatment with horseradish peroxidase; heat curing; UV irradiation; and cross-linking (Gonzales et al. 2011).

Collagen Casings

Collagen is a fibrous, structural protein in animal tissue, particularly skin, bones, and tendons and represents about 30 % of the total mass of the body (Yener 2007; Alizadeh and Behfar 2013). Collagen is the most commercially successful edible protein film. Film-forming collagen has been traditionally used in the meat industry, for the production of edible sausage casings. This protein has largely replaced natural gut casings for sausages. Collagen is readily available, non-toxic and provides an excellent basis for biomaterials. Collagen edible films and coatings from animal origin proteins can be dissolved in dilute acid or alkali solutions, and in neutral solutions. Two major components are identified; α (MW 100 000 Da) and β (MW 200 000 Da), and consist of two different types of covalent cross-linked chain pairs α1-α1 and α2-α2. Hydrolysis of collagen results in gelatin. The molecular weight of gelatin covers a broad range, from 3,000 to 200 000 Da, depending on the raw material employed during gelatin production and handling conditions. Edible coatings made with gelatin reduce the migration of moisture, oxygen, and oil. Collagen films are not as strong and tough as cellophane, but have good mechanical properties. Collagen films have an excellent oxygen barrier at 0 % relative humidity; however, the oxygen permeability increases rapidly with increasing relative humidity in a manner similar to cellophane. Different cross-linking chemical agents have been used to improve the mechanical properties, to reduce the solubility, and to improve the thermal stability of these films. Carbodimide, microbial transglutaminase, and glutaraldehyde are usually used as cross-linking agents (Alizadeh and Behfar 2013).

Whey Protein Isolate

Whey proteins are byproducts of the cheese-making industry and have generally been disposed of as animal feed or used in infant formulas and sports food (Zinoviadou et al. 2009). There are several individual proteins within the mixture of whey protein, with 5-lactoglobulin, 3-lactoalbumin, Bovine Serum Albumin (BSA), and immunoglobins being the main proteins. Among them, the most abundant and important protein for film formation is 5-lactoglobulin and the second most abundant whey protein is 3-lactalbumin (Jooyandeh 2011). Whey proteins have exceptional nutritional value and functional properties (Ozdemir and Floros 2008). They have been successfully employed as raw material for biodegradable packaging because they come from a renewable source and are a byproduct of cheese making industry; hence, they are widely available, relatively easy to handle and essentially inexpensive (Ramos et al. 2012a, b). The formation of edible films and coatings from whey proteins can increase the utilization of whey, improve the nutritional value of foods and prolong shelf life (Ozdemir and Floros 2008). Manab et al. (2011) reported that the whey protein-based edible films is usually prepared using whey protein with incorporation of plasticizer, cross linking agent and lipid, before heat denaturation at 90 °C for 30 min, the pH was adjusted to 5,2 and cooled to room temperature before it was template on Teflon plate and semi-vacuum oven for 24 h. The produced edible film had a soft, transparent, and good aroma as well as oxygen-resistant characteristics at low humidity (Manab et al. 2011). Whey protein isolates (WPI) represent the purer form of such whey proteins, and shown promising mechanical features, as well as moderate moisture permeability and good oxygen barrier properties comparable to those exhibited by the best synthetic polymer-based films available, e.g., low-density polyethylene (LDPE), high density polyethylene, ethylene vinyl alcohol, polyvinylidene chloride (PVDC), cellophane, and polyester. Furthermore, those films proved excellent biomaterials for use as carriers of such food additives as antioxidants, antimicrobials, colorants, flavors, fortifying nutrients and spices; the additives improve the functionality of the packaging by bringing about novel (or extra) features (Ramos et al. 2012a, b).

2.2.3 Lipid Films

Lipid compounds utilized as protective coating consist of acetylated monoglycerides, natural wax, and surfactants. The most effective lipid substances are paraffin wax and beeswax. The primarily function of a lipid coating is to block transport of moisture due to their relative low polarity. In contrast, the hydrophobic characteristic of lipid forms thicker and more brittle films. As a result, they must be associated with film forming agents such as proteins or cellulose derivatives. Generally, WVP decrease when the concentration of hydrophobicity phase increases. Lipid-based films are often supported on a polymer structure matrix, usually a polysaccharide, to provide mechanical strength (Bourtoom 2008).

Waxes belong to the non-polar lipid class. Their hydrophobicity is high. They have differences in permeability of wax films. These differences are owing to their chemical composition and crystal type. The waxy skin of fresh fruit and vegetables are applied to reduce dehydration and control the exchange of gases to prolong preservation period. There are some examples of waxes used for coating, including paraffin wax, carnauba wax, beeswax, candelilla wax, polyethylene wax (Yener 2007). Paraffin wax is permitted for use on raw fruit and vegetable and cheese. Carnauba wax is an exudate from palm tree leaves. Mineral oil consists of a mixture of liquid paraffin and naphtheric hydrocarbon. If applied as a thick layer, they must be removed before consumption (certain cheese); when used in thin layers, they are considered edible. Waxes (notably paraffin, carnauba, candellila, and bee wax) are the most efficient edible compounds providing a humidity barrier (Bourtoom 2008).

Monoglycerides are used in edible films as emulsifiers, especially for stabilizing emulsified film and increasing adhesion between two components with different hydrophobicity. Triglycerides are insoluble in bulk water, but will spread at the interface to form a stable monolayer. Water affinity or hydrophobicity of triglyceride depends on its structure. By adding palmitic, stearic, lauric acids, and stearyl alcohols to edible films, the moisture barrier properties are greatly enhanced (Yener 2007).

2.2.4 Composite Films

Edible films and coatings may be heterogeneous in nature, consisting of a blend of polysaccharides, protein, and/or lipids. This approach enables one to utilize the distinct functional characteristics of each class of film former (Bourtoom 2008). Composite films can be designed by combining lipid and hydrocolloid elements. By this way, it can decrease the disadvantages of each film. When a barrier to water vapor is desired, the lipid component can serve this function, while hydrocolloid component provides the necessary durability. Composite films consisting of a conglomerate of casein and acetylated monoglycerides have been studied in many investigations. These films can be used as coatings for processed fruit and vegetables (Yener 2007).

3 Antimicrobial Edible Films and Coatings

Nowadays, studies dealing with edible films with antimicrobial properties are on the increase. These films could prolong the shelf life and safety of foods by preventing growth of pathogenic and spoilage microorganisms as a result of their lag-phage extension and/or their growth rate reduction. Moreover, antimicrobials containing in films can be gradually released on the food surface, therefore, requiring smaller amounts to achieve the target shelf life (Ponce et al. 2008).

3.1 Properties of Antimicrobial Edible Films and Coatings

Microbial contamination in foods occurs due to post-processing to be traded manually on the surface of the food primarily and while reducing the shelf life of foods, may increase the risk of food borne illness. Antimicrobial agents applied to the surface of food directly to prevent or delay the decay of the surface by processes such as spraying or dipping. However, surface application of antimicrobial agents, antimicrobial substances transition to food quickly or neutralize in food. This case is limited the usefulness of what you did in food (Coma et al. 2002). All of these disadvantages and increasing consumer demands have led to the emergence of new food packaging systems for provide longer shelf life of foods and improve food safety. These systems limit the passage of flours, oxygen, and moisture and increase the shelf life of foods by providing antimicrobial activity (Quntavalla and Vicini 2002; Cha and Chinnan 2004). Recently years, antimicrobial edible films which studied extensively to candidate to replace synthetic antimicrobial active packaging system with features such as be consumed with food, being biologically degraded and they are reduce to the use of synthetic materials. Researches began to the mid-1980s work on edible films and coatings containing antimicrobial agent such as sorbic acid and potassium sorbate. In those years, film materials are more commonly methyl cellulose, hydroxypropyl methyl cellulose, polysaccharides, and lipids such as fatty acids but there are few studies on proteins. In the mid 1990s antimicrobial films prepared with organic acid and chitosan. To the end of the 1990s they were used as natural antimicrobial agents in edible protein films (Gernadious et al. 1994).

The antimicrobial food packaging interact with the surface of foods provide food safety by reducing the rate of growth of specific microorganisms in foods. Food composition and the target microorganism to be considered preparation of antimicrobial films and coatings and diffusion kinetics and antimicrobial activity of diffusible substance to food packaging have to be determinate (Appendini and Hotchkiss 2002).

Packaged foods with edible film packaging immediately before or after the process unpacking can be contaminated by microorganisms. These microorganisms settle the surface of food, i.e., the space between food packaging and food. In edible coating applications, on the surface of the food coated with the coating material micro-organisms cannot develop due to the direct interaction of antimicrobial substances and lack of oxygen and microbial growth occurs on the surface of coating. Antimicrobial agent is passed to food layer which not containing antimicrobial originally from the film and coating and consequently decreasing the amount of antimicrobial agent. To reduce the consumption of antimicrobial substances depending on migration on the film and coating, antimicrobial substance migration speed must be controlled by the kinetics of diffusion rate of transition (Appendini and Hotchkiss 2002).

Edible films and coatings have different protection functions. Antimicrobial agent passes slowly to food on edible film systems. Thus, there is no high concentration of antimicrobial agent in the film and food surface and film can effect a longer time against microorganisms (Coma et al. 2002; Çağrı et al. 2002). In edible coating systems, antimicrobial agents must remain on the coating material for the protection of food from microorganisms. Thus, diffusion rate on the coatings should be lower than film for effective antimicrobial activity (Gernadious et al. 1994).

3.1.1 Antimicrobial Substances

Antimicrobial substances inhibit or inactivate of microorganisms. Antimicrobial substances are used in a wide variety such as the organic acid and its salts, fungicides, bacteriocins, antibiotics, enzymes, and alcohols to provide antimicrobial activity in synthetic packaging systems. But, security and edible features are important on edible films and coatings and also type and amount of antimicrobial agent that can be used in these systems are limited (Ayana 2007). Antimicrobial agents can be classified as chemical and natural antimicrobials (Gernadious et al. 1994).

Weak organic acids such as propionic acid, sorbic acid, benzoic acid, tartaric acid, and salts of organic acids such as sodium benzoate, potassium sorbate, and propionate are used as chemical preservatives in foods commonly. Chemical preservatives consumed with the food, thus a number of these chemicals have restriction on using and limited amounts of antimicrobial agent have been used as edible films and coatings (Gernadious et al. 1994; Cha and Chinnan 2004; Ayana 2007).

Enzymes, organic acids, fatty acids, pigments, flavones, and spice oils have antimicrobial effects which are found naturally in foods and natural preservatives. They have effective antimicrobial activity when used critical amount and over. These aspects are not like chemical preservatives. Bacteriocins are antibacterial proteins produced by bacteria to kill or inhibit the growth of other bacteria. Many lactic acid bacteria (LAB) produce a high diversity of different bacteriocins. Nisin, Pediocin, and colicin are other bacteriocins which are used in edible film and coatings. Lysozyme is obtained from various sources and it is an enzyme having the antimicrobial effect by breaking β 1-4 glucozidic bonds in peptidoglican in the gram-positive and gram-negative bacteria cell walls. Lysozyme was used as antimicrobial many studies in the literature for production edible films and coatings (Gernadious et al. 1994; Cleveland et al. 2001; Cha and Chinnan 2004).

Many antimicrobial agents containing edible film and coatings are added to polymer as molten by applying thermal treatment or dissolution in solvent components. Heat-sensitive antimicrobial agents such as enzymes or volatile components can be used by dissolution using the solvent components; this is a convenient method for production antimicrobial edible films and coatings. For instance, lysozyme is used as an antimicrobial prevents denaturation of enzyme when used in cellulose ester film with solvent components. Bacteriocins which are heat resistant antimicrobial agents but they had a higher antimicrobial activity. Antimicrobial agents and polymers are both of must dissolution in the same solvent such cases. Antimicrobial agents can be used with solvents such as water and ethanol in edible films obtained from protein, lipids, and carbohydrates biopolymers (Ayana 2007).

If the non-volatile antimicrobial agents are used in packaging materials, packaging material must be in contact with the surface of food for diffusion of antimicrobials. The multilayer films should be used for diffusion of antimicrobial substances to food slowly. In a multilayer film, the innermost layer while controlling the diffusion rate of active substances, the matrix layer contains active ingredients. Also, barrier layer prevents antimicrobial agents diffusion to out of the packaging material (Appendini and Hotchkiss 2002).

When used as volatile compounds, antimicrobial agent packaging material is not required to direct contact with the food. Porous foods such as hamburger patties and bread or air gap foods such as milk powder prevents the spread of antimicrobial agent due to uneven surface and air gap. In this case only volatile antimicrobial agents are used and they provide effective protection by spreading than heterogeneous foods (Gernadious et al. 1994).

3.2 The Methods Used to Test the Antimicrobial Activity of Antimicrobial Packages

Different methods are used to test the antimicrobial activity of the antimicrobial packaging. These methods are minimum inhibitory concentration test (MIC), agar diffusion test and the rocking flask test. MIC test, which is one of the most widely, compared to antimicrobial activity of polymers and their separate effects. This method based on the principle of incubated different amounts of the antimicrobial agent containing polymers and antimicrobial agents with the target microorganism growth medium and until hold on microbial growth is observed. The lowest concentration of antimicrobial agent is determined for inhibition of microorganisms by MIC test. The agar diffusion method is based on the principle of antimicrobial films after replacing into the solid medium containing the microorganism to be tested and then incubated until the release is observed on the microbial growth medium. The presence of the microorganism to be tested or the presence of antimicrobial any ambient can be determined using this method. During incubation, a zone of inhibition has been observed around the medium by diffusion antimicrobial agent in film to medium. The zone of inhibition that exposes prevented the development of microorganisms. Measuring the diameter of the zone around the film can be expressed the effectiveness of an antimicrobial agent by quantitative terms. Swinging flask test provides detailed information on the kinetics of antimicrobial agents. The target microorganism and containing antimicrobial polymer is placed into the liquid medium such as buffer, growth medium or food and incubated in the stirred medium. Reduction in the rate of growth of microorganisms is measured by this method. Also test provides information about the antimicrobial activities of polymers in buffer (Temiz 2000; Appendini and Hotchkiss 2002).

3.3 Characteristic Properties of Antimicrobial Edible Films and Coatings

Edible films and coatings have mechanical properties such as tensile and tear resistance, physical properties such as oxygen, water vapor, flavor permeability, and optical characteristics as well as gloss, haze, transparency. The films and coatings properties can change due to increased heterogeneity in the structure of the film and coating as a result of the addition of antimicrobial substances (Quntavalla and Vicini 2002).

The films optical properties can change due to adding antimicrobial agents to plastic films but the physical strength of these films is not change. The addition of potassium sorbate did not affect the mechanical properties of the films made of polyethylene. However, the addition of water-soluble antimicrobial agent in hydrophobic plastic film caused reduction of film transparency. Film transparency and tensile are not affected when film solution prepared whey protein and antimicrobial substances such as lysozyme because protein and lysozyme compatible with each other and have the high water solubility. But the addition of antimicrobial substances in film solutions prepared such as corn zein protein which soluble in alcohol solutions, the physical resistance of films can reduce. Hence antimicrobial film must be incorporate antimicrobial agents compatible with the film-forming substance. A substance that are used as antimicrobial agents does not affect the film's taste and smell because they used low concentrations in film solutions (Gernadious et al. 1994).

When examine the literature we can see that natural antimicrobial especially essential oils are being used for the preparation of antimicrobial edible films and coatings. The major advantages of using essential oils in film and coatings is that the diffusion rate of the antimicrobial agent can be slowed down, thereby keeping high concentration of active compounds on the product surface for extended periods of time. However, further efforts must be made to control diffusion rate of these active compounds to the product surface during storage. On the other hand, the nature and amount of the essential oils, the essential oils/polymer ratio in the film and the possible interactions between the polymer and the active compounds of essential oils play important role in the film's antimicrobial activity (Sanchez-Gonzalez et al. 2011a, b).

In addition to conferring antimicrobial properties to edible films, the incorporation of essential oils leads to modifications in terms of physical film properties. These modifications are usually similar to those presented when adding more simple lipids to the film matrix. Again, the interactions established between essential oil components and the polymeric matrix become more complex, and it is important to take them into account when optimizing the composition of bioactive coatings (Sanchez-Gonzalez et al. 2011a, b).

Determination of WVP is strongly dependent on measurement conditions, such as temperature and the gradient of water vapor pressure. Coated biomaterials, such as fruits and vegetables, are characterized by irregular shapes and high water contents that make WVP measurements difficult (Garcia et al. 2009). Low WVP values are desirable in order to minimize weight losses in the coated product which, in turn, also directly affects products firmness and appearance. The incorporation of essential oils into polymeric matrices leads to an improvement in the film WVP because of the increment in the hydrophobic compound fraction in the film. Usually, WVP values fall linearly with the increase in essential oils concentration. For example, Sanchez-Gonzalez et al. (2011a, b) reported that pure chitosan films without hydrophobic compounds have poor moisture barrier properties at 20 °C, but the incorporation of bergamot oil (3 %) induces a significant reduction in WVP of nearly 50 % (Sanchez-Gonzalez et al. 2011a, b).

Propionic acid, polylactic acid (PLA), and stearic acids, natural lactoperoxidase system, natamycin, and nisin used in the edible films and coatings production as natural antimicrobials as well as essential oils. Also chemical preservatives such as sodium benzoate and potassium sorbate are widely used in production antimicrobial edible films. Ramos et al. 2012a, b reported that lactic acid, propionic acid, and natamycin incorporated WPI films have lower than those reported elsewhere for edible films manufactured from other materials. In their study WVP values 109 ± 0,75 for lactic acid, 12,8 ± 0,22 for propionic acid, 11,1 ± 1,04 for natamycin (Ramos et al. 2012a, b). Ko et al. (2001) reported that nisin at the amounts added had no significant effect on the WVP values of WPI. They found that WVP value is 2,20 ± 0,24 when the added nisin in whey protein isolate but if is not added nisin in film solution WVP value is 2,41 ± 0,18 (Ko et al. 2001). Bierhalz et al. (2012) reported that the addition of natamycin caused a significant increase of the permeability coefficient in pectin, pectin and alginate, and only alginate film formulations (WVP values are 2,13–4,11 g mm/d m^2kPa) Researchers reported that this result may be associated to al looser packing of the film macromolecules increasing the free volume of the polymeric structure, which enhances permeability. According to the same study pectin films showed lower WVP values than the respective composite films and alginate films, probably due to observed differences in thickness (Bierhalz et al. 2012). Another study used lactoperoxidase system as antimicrobial Mohamed et al. (2013) low values of WVP (5,61 ± 0,31–8,42 ± 0,91) were due to the fact that chitosan films, like many other protein or polysaccharide edible films,

Table 1 Effects of essential oils on water vapor permeability (WVP) of edible films

Essential oil and oil compounds (% w/v)	Film polymers	WVP (g mm/ kPa h m2)	References
Oregano oil (0.1)	Alginate/apple puree	5.25 ± 0.33	Rojos-Graü et al. (2007)
Carvacrol oil (0.1)	Alginate/apple puree	5.02 ± 0.22	Rojos-Graü et al. (2007)
Lemongrass oil (0.5)	Alginate/apple puree	4.91 ± 0.40	Rojos-Graü et al. (2007)
Citral (0.5)	Alginate/apple puree	5.12 ± 0.13	Rojos-Graü et al. (2007)
Cinnamon oil (0.5)	Alginate/apple puree	4.90 ± 0.27	Rojos-Graü et al. (2007)
Cinnamaldehyde (0.5)	Alginate/apple puree	4.37 ± 0.54	Rojos-Graü et al. (2007)
Oregano oil (0.1)	Cassava Starch-Chitosan	0.99 ± 0.04	Pelissari et al. (2009)
Oregano oil (0.5)	Cassava Starch-Chitosan	0.74 ± 0.08	Pelissari et al. (2009)
Oregano oil (1.0)	Cassava Starch-Chitosan	0.62 ± 0.15	Pelissari et al. (2009)
Cinnamon oil (0.4)	Chitosan	2.25 ± 0.074	Ojagh et al. (2010)
Cinnamon oil (0.8)	Chitosan	1.352 ± 0.152	Ojagh et al. (2010)
Cinnamon oil (1.5)	Chitosan	1.014 ± 0.040	Ojagh et al. (2010)
Cinnamon oil (2.0)	Chitosan	1.003 ± 0.067	Ojagh et al. (2010)
Citronella (0.25)	Hake protein	4.12 ± 0.50	Pires et al. (2013)
Tarragon (0.25)	Hake protein	4.2 ± 0.04	Pires et al. (2013)
Thyme (0.25)	Hake protein	3.57 ± 0.11	Pires et al. (2013)
Coriander (0.25)	Hake protein	3.77 ± 0.00	Pires et al. (2013)
Oregano oil (1.0)	Triticale flour protein	0.35 ± 0.04	Aquirre et al. (2013)
Oregano oil (2.0)	Triticale flour protein	0.40 ± 0.05	Aquirre et al. (2013)
Carvacrol oil (3.2)	Chitosan	2.51 ± 0.0003	Rubiler et al. (2013)
Carvacrol oil (20)	Chitosan	1.58 ± 0.0004	Rubiler et al. (2013)
Carvacrol oil (30)	Chitosan	1.69 ± 0.0002	Rubiler et al. (2013)
Satureja hortensis oil (1.0)	κ-carrageenan	1.591 ± 0.112	Shojaee-Aliabadi et al. (2013)
Satureja hortensis oil (2.0)	κ-carrageenan	0.840 ± 0.093	Shojaee-Aliabadi et al. (2013)
Satureja hortensis oil (3.0)	κ-carrageenan	0.556 ± 0.032	Shojaee-Aliabadi et al. (2013)

exhibited relatively low water barrier characteristics due to their high hydrophilic nature (Mohamed et al. 2013). Effects of essential oils on WVP of edible films are summarized in Table 1.

The important study about bio-active edible films carried out by Sanchez-Gonzalez et al. (2013). In this study researches LAB were added directly to the sodium caseinate, pea protein, and methylcellulose and hydroxypropylmethylcellulose film-forming solutions. WVP values were range of 7–34,4 g mm kPa^{-1} h^{-1} m^{-2}. Researchers reported that differences can be attributed to some changes in the experimental conditions; temperature, RH gradient, kind, and amount of plasticizer. It was verified that polymer films are highly permeable to water vapor, which is coherent with the hydrophilic nature of the protein and polysaccharides (Sanchez-Gonzalez et al. 2013).

Rezvani et al. (2013) were prepared edible films using sodium caseniate (6–8 g/100 g) and stearic acid (0–2 g/100 g). WVP values were determined range of 1,368 ± 0,124–1,896 ± 0,047 g mm m^2 h kPa in this study. As shown this values, any increase in ratio of stearic acid to water, decreases the WVP. The effect of stearic acid on decreasing these parameters is mainly due to the addition of hydrophobic groups in formulations (Rezvani et al. 2013). In another study, Bonilla et al. (2013) were prepared films based on PLA and different amounts of chitosan powder (CH). The effects of CH particle size (715 and 180 μm) and the amount of chitosan incorporated in the PLA matrix (5 % or 10 % on PLA basis) were investigated in terms of physicochemical characteristics. In this study, WVP values were determined range of 4–74 (g s^{-1} m^{-1} Pa^{-1}) × 10^{11}. Researchers reported that PLA films showed lower WVP than composite films, which can be due to the greater water affinity of CH could favor the transport of water molecules through the film. According to researchers, water barrier properties of PLA:CH films increased as PLA content was higher as a result of the well-known hydrophobicity of PLA (Bonilla et al. 2013).

Many antimicrobial edible films examples utilized of chemical preservatives in the literature. Potassium sorbate is the one of the chemicals most widely used. Ozdemir and Floros (2008) examined the effect of protein, sorbitol, beewax, and potassium sorbate concentrations in whey protein films on their WVP in a study. According to researches all factor influenced WVP. They reported that mixture proportions of protein 0.53, sorbitol 0.38, beewax 0,08 and potassium sorbate 0.01 would yield an edible film with minimum stickiness and WVP < 9 g mm m^{-2} h^{-1} kPa^{-1}. They stated that the addition of protein and beewax decreased WVP, while the increase in sorbitol increased WVP. Potassium sorbate was the most effective factor that adversely affected WVP (Ozdemir and Floros 2008). Another study potassium sorbate is used as antimicrobial by Arismendi et al. (2013). Xanthan gum and tapioca starch were used as film polymers. In this study WVP values were determined range of 1.7–2.3 × 10^{-9} g/m s Pa. Researchers reported that it was not observed a clear trend concerning the effect of xanthan gum and tapioca starch on WVP (Arismendi et al. 2013).

The packaging material's gases such as carbon dioxide and oxygen, transfer rates and aroma such as volatile compounds are also factors that affect the stability during storage of the food except water vapor. Oxidation of fats in foods due to food rancidity as a result of the presence of oxygen and this situation can cause reduced the acceptability of food. In addition it leads to loss of light-sensitive vitamins. Also, oxygen is important for many different organisms which cause deterioration on foods. Oxygen concentration is effect on microbial growth rate. Out of them volatile compounds that make up the taste and aroma of foods not required out of the transport packaging. The losses will occur in these compounds negatively affect the quality of the food (Ayana 2007). The oxygen barrier is quantified by the oxygen permeability coefficients (OPC) which indicate the amount of oxygen that permeates per unit of area and time in a packaging materials [kg m m^{-2} s^{-1} Pa^{-1}]. So, when a polymer film packaging has a low oxygen permeability coefficient, the oxygen pressure inside the container drops to the point where the oxidation is retarded, extending the shelf life of the product. Generally the biodegradable polymers present a value one or more order of magnitude below the synthetic polymer used in the same field like PET and OPS. Several authors reported in literature the OPC of one of the most commercialized biodegradable polymer like the PLA (Siracusa et al. 2008).

Composite films with essential oil seem to be a better barrier to gases, but little information has been found in the literature. For example, a slight decrease in oxygen permeability of the films based on alginate-apple puree with lemongrass oil (Sanchez-Gonzalez et al. 2011a, b). Altiok et al. 2010 reported that oxygen transmission rate of the films increased with an increasing oil concentration due to the microstructural changes in the film becoming porous with the addition of oil. Oxygen transmission rate of the pure chitosan film was 1.24 cc per m^2 per day. The highest oxygen permeability was obtained as 4.61 cc per m^2 per day for 1.2 % (v/v) thyme oil incorporation which suggests the promising applications of thyme oil loaded chitosan film as a wound dressing (Altiok et al. 2010).

The protection of structural integrity and having a certain impact resistance based on the location to be used are at the beginning of expected properties of a packaging material. Therefore, knowing mechanical properties of packaging materials are important for troubleshooting problems and that may arise from use areas. In general, the mechanical properties of polymeric materials are defined as the elongation, ductility, tensile deformation under the influence of external forces. Commonly used to determine the mechanical properties of polymer films was measured tensile strength and elongation. Tensile strength is the material response which applied on packaging material an external force. Elongation of the material is expressed as geometric change state by the effect of the external forces (Ayana 2007).

The mechanical properties of edible coatings depend on several factors, as the interactions between their components and the polymer matrix are strongly affected by the physical, chemical and temperature conditions, which in turn influence film stability and flexibility. The incorporation of essential oil into a continuous polymeric matrix decreases its mechanical resistance to fracture because of the structural discontinuities caused by the oil-dispersed phage. Elongation at break of pure chitosan films was, for instance, reduced when cinnamon, tea tree, or bergamot oil was incorporated (Sanchez-Gonzalez et al. 2011a, b). Effects of natural antimicrobial compounds on Tensile Strength (TS), Elongation break (E) and Young Module (YM) of antimicrobial edible films are summarized in Table 2.

Optical properties, especially color, are essential in packaging applications since they affect the appearance of the product and make consumers accept or reject the product packaged, so becoming an important quality factor to be taken into account (Ramos et al. 2013; Leceta et al. 2013). Generally, the use of essential oils induces modifications in terms of film transparency, gloss, and color. Addition of essential oils in edible films may change the native color of edible films. The appearances of the coatings are of relevance since their commercial acceptance depends mainly on this attribute. Usually, the incorporation of essential oils into films decreases their gloss and transparency due to the increase in the surface roughness of the composite films as a consequence of the migration of droplets or aggregates to the top the film during film drying, which leads to surface irregularities. Nevertheless, observed differences in terms of color are not significant when low concentrations of essential oils are used

Table 2 Effects of natural antimicrobial compounds on Tensile strength (TS), Elongation break (E), and Young Module (YM) of antimicrobial edible films

Antimcirobial compounds	Film polymers	E (%)	TS (Mpa)	YM (Mpa)	References
Nisin	Whey protein isolate	–	3.50 ± 0.34	–	Ko et al. (2001)
Nisin	Soy protein isolate	–	10.43 ± 2.53	–	Ko et al. (2001)
Nisin	Egg albumin	–	1.53 ± 0.10	–	Ko et al. (2001)
Nisin	Wheat gluten	–	1.96 ± 0.76	–	Ko et al. (2001)
Stearic acid	Hydroxypropyl methylcellulose	6.63 ± 1.28	336 ± 63	191 ± 61	Sebti et al. (2002)
Oregano oil	Alginate/apple puree	56.96 ± 3.86	2.47 ± 0.37	5.75 ± 0.96	Rojos-Graü et al. (2007)
Carvacrol oil	Alginate/apple puree	58.33 ± 4.66	2.58 ± 0.37	5.96 ± 1.12	Rojos-Graü et al. (2007)
Lemongrass oil	Alginate/apple puree	55.95 ± 5.55	2.56 ± 0.46	6.02 ± 1.07	Rojos-Graü et al. (2007)
Citral	Alginate/apple puree	57.38 ± 5.71	2.52 ± 0.44	6.46 ± 1.27	Rojos-Graü et al. (2007)
Cinnamon oil	Alginate/apple puree	57.88 ± 5.37	2.84 ± 0.48	6.86 ± 1.16	Rojos-Graü et al. (2007)
Cinnamaldehyde	Alginate/apple puree	55.50 ± 7.40	2.75 ± 0.42	6.77 ± 0.87	Rojos-Graü et al. (2007)
Grape seed extract	Soy protein isolate	–	10.74 ± 0.88	–	Sivarooban et al. (2008)
Nisin	Soy protein isolate	–	5.11 ± 0.30	–	Sivarooban et al. (2008)
EDTA	Soy protein isolate	–	9.29 ± 0.29	–	Sivarooban et al. (2008)
Grape seed extract + Nisin	Soy protein isolate	–	9.78 ± 0.12	–	Sivarooban et al. (2008)
Grape seed extract + EDTA	Soy protein isolate	–	8.34 ± 0.44	–	Sivarooban et al. (2008)
Nisin + EDTA	Soy protein isolate	–	4.72 ± 0.40	–	Sivarooban et al. (2008)
Grape seed extract + Nisin + EDTA	Soy protein isolate	–	7.78 ± 0.33	–	Sivarooban et al. (2008)
Tea tree essential oil	Hydroxypropyl methylcellulose	0.09	55	1.289	Sanchez-Gonzalez et al. (2009)
Oregano oil	Cassava Starch-Chitosan	27.18 ± 2.85	1.96 ± 0.44	67.72 ± 4.26	Pelissari et al. (2009)
Cinnamon oil	Chitosan	16.57 ± 0.77	13.35 ± 1.23	–	Ojagh et al. (2010)

(continued)

Table 2 (continued)

Antimcirobial compounds	Film polymers	E (%)	TS (Mpa)	YM (Mpa)	References
Natamycin	Alginate	6.84 ± 1.09	106.73 ± 4.99	–	Bierhalz et al. (2012)
Natamycin	Pectin	4.75 ± 0.37	48.46 ± 5.93	–	Bierhalz et al. (2012)
Natamycin	Pectin/Alginate	4.81 ± 0.45	80.87 ± 7.08	–	Bierhalz et al. (2012)
Thyme oil	Hake protein	129.8 ± 51.2	6.67 ± 2.41	–	Pires et al. (2013)
Lactoperoxidase system	Chitosan	24.68 ± 2.21	279.26 ± 46	–	Mohamed et al. (2013)
Lactic acid bacteria (LAB)	Sodium caseinate	5.8 ± 0.6	10.47 ± 0.16	269 ± 77	Sanchez-Gonzalez et al. (2013)
Lactic acid bacteria (LAB)	Pea protein	15 ± 2	5.2 ± 1.2	90 ± 44	Sanchez-Gonzalez et al. (2013)
Lactic acid bacteria (LAB)	Hydroxypropyl methylcellulose	33 ± 2	30.1 ± 1.2	381 ± 115	Sanchez-Gonzalez et al. (2013)
Lactic acid bacteria (LAB)	Methylcellulose	34 ± 2	28.2 ± 1.2	388 ± 92	Sanchez-Gonzalez et al. (2013)
Citronella oil	Hake protein	181.9 ± 31.0	7.06 ± 1.64	–	Pires et al. (2013)
Tarragon oil	Hake protein	161.8 ± 31.0	2.99 ± 1.63	–	Pires et al. (2013)
Thyme oil	Hake protein	111.2 ± 44.8	4.33 ± 0.94	–	Pires et al. (2013)
Coriander oil	Hake protein	178.2 ± 25.5	4.70 ± 1.60	–	Pires et al. (2013)
Oregano oil	Triticale flour protein	12.10 ± 0.26	2.08 ± 0.19	82.53 ± 11.22	Aquirre et al. (2013)
Carvacrol oil	Chitosan	26.79 ± 21.93	37.86 ± 12.07	–	Rubiler et al. (2013)
Resveratrol	Chitosan	6.00 ± 2.00	78 ± 2.00	2.585 ± 151.00	Pastor et al. (2013)
Resveratrol	Methylcellulose	10.00 ± 3.00	65 ± 7.00	1.871 ± 132.00	Pastor et al. (2013)
Satureja hortensis oil	κ-carrageenan	35.82 ± 2.02	19.88 ± 2.37	–	Shojaee-Aliabadi et al. (2013)

in bioactive films (Du et al. 2009; Sanchez-Gonzalez et al. 2011a, b). In reviewing the literature, Rhim et al. (2000) reported that the addition of various compounds that structurally bind with the film-forming solutions changed the native color of the soy protein film (Rhim et al. 2000). Sivarooban et al. (2008) also reported that the incorporation of 1 % grape seed extract into SPI films significantly influenced the L^*, a^* and b^* values (Sivarooban et al. 2008). Du et al. (2009) reported that darker films were produced with the addition of cinnamon, allspice and clove bud oils into apple film-forming solutions, and the $L,^*$ b^* values as well as the whitish index of apple solutions increased as the concentration of the oils increased (Du et al. 2009).

3.4 Applications of Antimicrobial Edible Films and Coatings

In the literature, there are a lot of investigations in vivo and in vitro on edible antimicrobial films and coatings based on natural polymer or polymers mixed in different proportions.

The successes obtained in vitro studies guided the development of edible film and coating applications. Ko et al. (2001) were investigated the effects of hydrophobicity/hydrophilicity of edible films against *Listeria monocytogenes* strain V7 by various nisin concentrations (4.0–160 IU/film disk) and pH values ranging from 2.0 to 8.0. According to these study results, as the nisin concentration increased, the amount of inhibition progressively increased in all tested film. Using nisin, edible films with higher hydrophobicity values of 280–450 units under an acidic environment exerted a greater inhibitory effect against *L. monocytogenes*. Dawson et al. (2005) were examined the antimicrobial activity of nisin-absorbed silica and corn starch powders against *Lactobacillus plantarum* and *Listeria monocytogenes*. And nisin-absorbed powders were highly efficient at both adsorption and release of antimicrobial activity. Zivanovic et al. (2005) were determined the antimicrobial activity of chitosan films enriched with essential oils such as oregano, coriander, basil, and anise against *Listeria monocytogenes* and *Escherichia coli* O157:H7 by an agar diffusion test. The chitosan films and chitosan-oregano essential oil films were applied on inoculated bologna samples and stored 5 days at 10 °C. Pure chitosan films reduced *L. monocytogenes* by 2 logs, whereas the films with 1 % and 2 % oregano essential oil decreased the numbers of *L. monocytogenes* by 3.6 to 4 logs and *E. coli* by 3 logs. These films have the potential to be used as active biodegradable films with strong antimicrobial effects. Seydim and Sarıkuş (2006), in their study, antimicrobial properties of WPI films containing 1.0–4.0 % (wt/vol) ratios of oregano, rosemary, and garlic essential oils were test by in vitro against *Escherichia coli* O157:H7 (ATCC 35218), *Staphylococcus aureus* (ATCC 43300), *Salmonella enteridis* (ATCC 13076), *Listeria monocytogenes* (NCTC 2167), and *Lactobacillus plantarum* (DSM 20174). According to results of these studies, the film containing oregano essential oil was the most effective against these bacteria at 2 % level than those containing garlic and rosemary extracts. The use of rosemary essential oil incorporated into

WPI films did not exhibit any antimicrobial activity, whereas inhibitory effect of WPIs film containing garlic essential oil was observed only 3 % and 4 % level. Sanjurjo et al. (2006) studied the antimicrobial activity of nisin supported in edible films prepared with suspensions of tapioca starch containing glycerol. Studied were performed with *L. innocua*, after equilibration of edible films at a relative humidity (RH) of 57.5 % and at 25 °C. Results obtained showed that nisin supported in starch-based films in active and that the film is a useful barrier to further product contamination. Du et al. (2008)'s study's main objective was to evaluate the antimicrobial activities against *E. coli* O157:H7, storage stabilities of novel edible films made from tomatoes containing carvacrol, the main constituent of oregano oil by two different casting methods. Antimicrobial assays of tomato films indicated that optimum antimicrobial effects occurred with carvacrol levels of approximately 0.75 % added to tomato purees before film preparation.

Applications (Table 3) of antimicrobial edible films and coatings to meat, fish, poultry, fresh fruits, and vegetables, and tree nuts have received increasing interest because films and coatings can serve carriers for various antimicrobials that can maintain fresh quality, extend product shelf life, and reduce the risk of pathogen growth. Edible films with antimicrobial properties could prolong shelf life and safety of foods by preventing growth of pathogenic and spoilage microorganisms as a result of their lag-phage extension and/or their growth rate reduction (Quntavalla and Vicini 2002). Moreover, antimicrobials imbedded in films can be gradually released on the food surface, therefore requiring smaller amounts to achieve the target shelf life (Min and Krochta 2005).

Edible films and coatings have long been known to protect perishable fruits and vegetables from deterioration by retarding dehydration, suppressing respiration, improving textural quality, helping to retain volatile flavor compounds, and reducing microbial growth. The technology for using edible films and coatings as carriers of additives to extend the shelf life has been widely explored. Similarly, edible films and coatings carrying antimicrobials are a promising tool for decreasing the risk of pathogenic bacteria and also for extending minimally processed ready to eat meats shelf life. Minimally processed ready to eat meats and seafood products are a potential source of food-borne pathogenic bacteria such as *Salmonella typhimurim*, *Listeria monocytogenes*, and *E. coli* O157:H7 and studies about antimicrobial edible films and coatings focus on these pathogens mainly. In meats products, application of films and coatings not only is useful as a carrier of the antimicrobial but it can also prevent moisture loss during storage of fresh or frozen meats, reduce the rate of rancidity, and restrict volatile flavors loss. Dairy products, especially cheeses are complex food products that contain casein, fat, and water. In the case of fresh and semi-fresh cheese microbial stability and product safety must be controlled. Antimicrobial edible films and coatings are used mainly controlled microbial growth in the surface and also diminish the risk of pathogens such as *Listeria monocytogenes* and some yeasts and molds (Campos et al. 2011). Table 3 summarizes relevant application of antimicrobial external edible films and coatings to prevent microbial spoilage.

Table 3 Applications of antimicrobial compounds in food system to control pathogens and spoilage micro flora

Antimicrobial compounds	Film polymers	Target Microorganisms	Food Application	References
Propionic acid, Acetic acid, Lauric acid, Cinnamaldehyde	Chitosan	Enterobacteriaceae spp. *Lc. sakei Serratia liquefaciens*	Vacuum-packaged meats processed	Quattara et al. (2000)
Chitosan	Starch/Chitosan	*S. aureus E. coli* Mesophilic aerobes Mold and yeast Psychrotrophic bacteria	Minimally processed carrot	Durango et al. (2006)
Lemongrass oil, Oregano oil, Vanillin	Apple puree-alginate	*L. innocua*	Fuji apples	Rojas-Graü et al. (2007a, b)
Chitosan	Chitosan	Total microorganisms	Sliced mango fruit	Chien et al. (2007)
Oleoresins (olive, rosemary, onion, capsicum, cranberry, garlic, oreganum, and oreganum + carvacrol)	Chitosan Carboxymethyl cellulose Casein	*L. monocytogenes*	Butternut squash	Ponce et al. (2008)
Nisin, Sodium lactate, Sodium diacetate, Potassium sorbate, Sodium benzoate	Chitosan-coated plastic films	*L. monocytogenes*	Ham steaks	Ye et al. (2008a, b)
Acetic acid, Lactic acid	Chitosan	*L. monocytogenes*	Ready-to-eat (RTE) roast beef	Beverlya et al. (2008)
Nisin, Sodium lactate, Sodium diacetate, Potassium sorbate, Sodium benzoate	Chitosan-coated plastic films	*L. monocytogenes*	Smoked-salmon	Ye et al. (2008a, b)
Nisin, Natamycin	Cellulose	Staphylococcus sp. Psychrotrophic bacteria	Sliced mozzarella cheese	Dos Santos Pires et al. (2008)
Ovotransferrin	κ-carrageenan	*Escherichia coli S. typhimurium Staphylococcus aureus Candida albicans*	Chicken breast	Seol et al. (2009a, b)
Oregano oil, Clove oil	Chitosan	*L. monocytogenes*	Kasar cheese	Torlak and Nizamlıoğlu (2009)
Olive leaf extract	Methylcellulose	*S. aureus*	Kasar cheese	Ayana and Turhan (2009)
Oregano oil, Thyme oil	Soy protein	*E. coli* O157:H7	Fresh ground beef patties	Emiroğlu et al. (2010)
		S. aureus		
		P. aeruginosa		
		Lac. plantarum		
Nisin	Sodium caseinate	*L. innocua*	Semi-soft cheese	Cao-Hoang et al. (2010)
Sodium lactate, Sodium diacetate	Alginate	*L. monocytogenes*	Smoked salmon	Neetoo et al. (2010)

(continued)

Table 3 (continued)

Antimicrobial compounds	Film polymers	Target Microorganisms	Food Application	References
Bergamot oil, Lemon oil, Tea tree oil	Chitosan Hydroxypropylmethylcellulose	*L. monocytogenes E. coli S. aureus*	A model solid food system	Sanchez-Gonzalez et al. (2011a, b)
Chitosan	Chitosan Sodium caseinate/ Chitosan	Mezophilic and psychrotrophic bacteria Yeast and Molds	Carrot Cheese Salami	Del Rosario Moreira et al. (2010)
Sodium lactate, Sodium diacetate	Starch Chitosan Alginate Pectin	*L.monocytogenes*	Roasted turkey	Jiang et al. (2011)
Chitosan	Chitosan	Mesophilic and psychrotrophic bacteria Yeast and Moulds Lactic acid bacteria Coliforms *E.coli* O157:H7	Fresh cut broccoli	Del Rosario Moreira et al. (2011)
Sodium benzoate, Sodium propionate, Potassium sorbate	Hydroxypropylmethylcellulose/ lipid	*Penicillium digitatum Penicillium italicum*	Clemenules mandarins	Valencia-Chamorro et al. (2011)
Sodium benzoate, Lactic acid, Chitooligosaccharide	Whey protein isolate	Spoilage microflora	Cheese	Ramos et al. (2012a, b)
Rosmarinic acid extract, Asian essential oil mixture, Italian essential oil mixture	Methylcellulose/ polycaprolactone	*E.coli, S. typhimurium*	Fresh broccoli	Takala et al. (2013a, b)
Tea tree oil, Rosemary oil, Clove oil, Lemon oil, Oreganum oil, Calendula oil, Aloe vera oil, Bee pollen, Ethanolic extract of propolis, Pomegranate extract Resveratrol	Chitosan	*E.coli, L. monocytogenes*	Fresh cut broccoli	Alvarez et al. (2013)
Ethyl-N-dodecanoly-L-arginate	Chitosan	Mesophilic and psychrotrophic bacteria Yeast and Moulds Lactic acid bacteria Coliforms Hydrogen sulfide-producing bacteria Pseudomonas spp.	Chicken breast fillets	Higueras et al. (2013)
Organic acid mixture, Rosemary extract, Asian spice essential oil, Italian spice essential oil	Methylcellulose Polycaprolactone/alginate	*E.coli, S. typhimurium, L. monocytogenes*	Fresh broccoli	Takala et al. (2013a, b)

4 Legal and Economic Aspects of Antimicrobial Edible Films and Coatings

Edible films, including all of its components must be safe to eat or must have the GRAS status. Moreover, edible films when incorporated with antimicrobials are considered as active food packaging (Espitia et al. 2013). Definitions stated in Regulation 1935/2004/EC and in Regulation 450/2009/EC consider that "active materials and articles are intended to extend the shelf life or maintain or improve the condition of packaged food." They are designed to deliberately incorporate components that would release or absorb substance into or from the packaged food or the environmental surrounding the food (Campos et al. 2011).

Edible films can be classified as food products, food ingredients, food additives, food contact substances, or food packaging materials. Thus, their elaboration should follow all required regulations pertinent to food ingredients, since they are an integral part of the edible portion of food products. Moreover, besides the GRAS status of all ingredients used, production of pectin, and other biodegradable polymers, edible films should be done in food processing facilities following with good manufacturing practice (Bierhalz et al. 2012).

According to legislation and labeling in the USA, edible coatings and films are considered part of the food; as a consequence, their ingredients must comply with the Code of Federal Regulations and be declared on the label under the Federal Food, drug, and Cosmetic Act (Frassen and Krochta 2003). The EU considers that an edible film is a special active part of the food and, seen from a legal point of view, it is to be regarded as a foodstuff, along with the food packed in the film, having to fulfill the general requirements for food. Another important topic within regulatory status is the presence of allergens because many edible films and coatings are made with or can contain ingredients that could cause allergic reactions such as wheat protein (gluten) or peanut protein. Therefore, the presence of known allergen on a film or coating on a food must be also stated in the label (Campos et al. 2011).

As is known in each country has clear regulations regarding the addition of preservatives to food, which often include purity requirements, analytical methodology, labeling, and maximum allowed levels. Therefore, at the moment, under such legislation must be ruled the application of edible films containing preservatives. As a consequence, it is important to remark that the edible film formulation proposed must be adapted in order to ensure a content of preservative in the food that is in accordance with maximum values allowed by food legislation of the country of application (Campos et al. 2011).

5 Future Trends of Antimicrobial Edible Films and Coatings

Synthetic polymers are gradually being replaced by biodegradable materials especially those derived from replenishable, natural resources. More than the origin, the chemical structural of biopolymer that determines its biodegradability. Use of such biopackaging will open up potential economic benefits to farmers and agricultural processors.

For example, once considered a waste product in the cheese manufacturing process, whey and whey protein products are "green" alternatives to traditional plastics as edible films. Based on its excellent oxygen barrier properties, whey protein films can be competitive materials replacing EVOH (Ethylene vinyl alcohol), nylon or polyesters, which are typically used as oxygen barriers. Innovative techniques of preserving food safety and structural nutritional integrity as well as complete biodegradability must be adopted. Eventually biopackaging constitutes a niche market and that will be our future. Biodegradable packaging is estimated to grow 20 % over the next few years, taking up a larger share of the packaging market (Tharanathan 2003; Jooyandeh 2011).

The incorporation of essential oils into edible films and coatings allows us to reduce the quantities required to guarantee food safety. However, during the drying stage of the film, significant losses of volatile compounds occur. Micro- and nanoencapsulation of essential oils could be a solution to minimize this problem and improve the effectiveness of active coatings enriched with essential oils (Sanchez-Gonzalez et al. 2011a, b).

Moreover, researches related to the application of nanotechnology to edible films and coatings are scarce. However, when more toxicological studies are published in the coming years, the application of nanotechnology may lead research toward the incorporation of nanoscale materials in edible films and study their potential synergistic effects on films antimicrobial activity as well as their contribution to the improvement of physical-mechanical properties of edible films and coatings (Espitia et al. 2013).

6 Conclusions

The use of edible films and coatings for a variety of foods widespread continue. Edible films and coatings provide benefits as a carrier of antimicrobial agents, flavors, antioxidants, coloring agents, vitamins and probiotics in the field of active packaging. Antimicrobial edible films and coatings can provide effectively inactivation or inhibition of pathogens and spoilage microorganism. These active films and coatings are capable of natural and biodegradable polymers so have competitive offers with synthetic materials both environmentally and economically. But still food packaging industry needs to improve the physical and mechanical properties of edible films and coatings for food applications. A very large part of the studies on the subject laboratory are scale. Many studies have focused on trade are need to provide a more realistic information. Despite limiting factors they use on foods, edible films and coatings particularly containing antimicrobial active substances add value to the food products by extending shelf life of products. Antimicrobial films and coatings applications should be regarded as a hurdle technology such as pulse light, high pressure, and irradiation. But it should be noted that the active ingredients affect to sensory and functional properties of edible films and coatings. Studies about the effects of active edible films and coatings on the sensory properties of the products are very limited. Edible films and coatings formulations providing high-sensory performance and functionality with a long shelf life should develop necessary. Cooperation with regulatory agencies such as government, industry, and research groups will play a key role successfully in application of innovative food packaging technologies such as edible films and coatings.

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