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Abstract: Noteworthy progress in the area of food packaging has recently introduced in order to inhibit or prevent microbial growth as well as to keep the products from further microbial deterioration. Among the food packaging techniques, active packaging, particularity antimicrobial active packaging, has attracted much attention, considering the diverse materials used, the methods of application in the variety of food products to be protected. Direct and indirect techniques can be utilized to apply antimicrobial compounds into food packaging materials. The increasing importance of the application of antimicrobial packaging has led to in a better knowledge of materials, and the factors affecting the effectiveness of antimicrobial systems. This article is a review of the antimicrobial agents, the materials used for delivering them, antimicrobial migrating and non-migrating systems and the effects of antimicrobial agents on packaging properties. In general, the use of antimicrobial active packaging extends the stability of food products during storage and distribution. However, many challenges of the new approaches of antimicrobial active packaging still remain including the controlled release of antimicrobial agents, and the development of packaging materials (mainly the bio-based materials) with adequate barrier properties, transparency, tensile strength and other required characteristics.

Highlights:

- ✓ The mechanisms of action of the common antimicrobial agents for AAP were discussed
- ✓ The impact of incorporation antimicrobial agents on AAP were demonstrated
- ✓ The available techniques for preparation of AAP were summarized

Antimicrobial agents and packaging systems in antimicrobial food active packaging: an overview of approaches and interactions

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Running head: Antimicrobial active packaging

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ABSTRACT

Noteworthy progress in the area of food packaging has recently introduced in order to inhibit or prevent microbial growth as well as to keep the products from further microbial deterioration. Among the food packaging techniques, active packaging, particularity antimicrobial active packaging, has attracted much attention, considering the diverse materials used, the methods of application in the variety of food products to be protected. Direct and indirect techniques can be utilized to apply antimicrobial compounds into food packaging materials. The increasing importance of the application of antimicrobial packaging has led to in a better knowledge of materials, and the factors affecting the effectiveness of antimicrobial systems. This article is a review of the antimicrobial agents, the materials used for delivering them, antimicrobial migrating and non-migrating systems and the effects of antimicrobial agents on packaging properties. In general, the use of antimicrobial active packaging extends the stability of food products during storage and distribution. However, many challenges of the new approaches of antimicrobial active packaging still remain including the controlled release of antimicrobial agents, and the development of packaging materials (mainly the bio-based materials) with adequate barrier properties, transparency, tensile strength and other required characteristics.

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1. INTRODUCTION

Contamination of food can occur during harvesting, food processing, and distribution (Malhotra et al., 2015). Packaging is the main available mean to protect food products from external contaminants and can prevent chemical, physical, and biological changes (deterioration) during storage or even preparation of products. Conventional packaging materials with passive function cannot actively control reactions within the packages. The developments of material science and engineering have resulted in a novel type of packaging technique newcommonly known as active packaging (AP) to assist the maintenance of quality and enhancing the safety of foods. The primary characteristic of active packaging is to retaining and increasing the shelf-life of foodstuffs (Benito-Peña et al., 2016).

As an approved concept, active packaging can be categorized into two main groups: i) non-migratory AP, which could act without deliberate migration, and ii) active releasing packaging which, permitting a controlled migration of non-volatile compounds or a release of volatile agents into the atmosphere surrounding the food product (Hosseinnejad 2014). Controlled release packaging (CRP) is regarded as one of the most refined forms of delivering antimicrobial agents throughout the shelf-life of packaged foods. CRP works by releasing the antimicrobial agents at controlled rates over extended periods, thereby maintaining the quality and safety of foods (LaCoste et al., 2005). CRP has been widely used in the pharmaceutical industry as a drug delivery system (Mallapragada and Peppas, 1997a,b), the application of this new technique in food packaging is still limited.

Several methods were introduced to obtain efficient antimicrobial packaging systems:

i) Incorporation of sachets/pads which contain volatile antimicrobial compounds,

ii) Addition of volatile and also non-volatile antimicrobial compounds directly into the structure of polymers,

iii) Application of a coating or adsorbing antimicrobials onto the surfaces of polymers in contact with a foodstuff,

iv) Immobilization of antimicrobial agents in the polymers by some methods such as ion or covalent linkages, and

v) Application of polymers that can inherently act as antimicrobial compounds like chitosan (Limbo and Mousavi, 2015).

In the few last years, many reviewers have been published on the application of antimicrobials to packaging materials, highlighting the effectiveness of the released substance on reducing food spoilage and describing their incorporation or inclusion into packaging materials (Sung et al., 2013). However, the recent advances in the nanotechnology field, the development of biodegradable/biocompatible materials and the knowledge in stimuli-responsive materials helpful for the establishment of a new concept of the antimicrobial packaging added some positive points in the area of active packaging. Although the incorporation of antimicrobial substances into packaging materials has been widely studied, there are often discrepancies between the results of lab-scale and real-time trials regarding materials performances and antimicrobial effectiveness. Therefore, the article is an overview of recent research on materials used in antimicrobial food active packaging and also on the effects of antimicrobial agents on packaging properties.

2. MATERIALS USED FOR DELIVERY OF ANTIMICROBIALS

The incorporation of active compounds into natural and synthetic polymers or their application in the coating formulation are valuable strategies to expand the shelf-life of packaged food products. From a theoretical point of view, antimicrobial agents should be delivered in a progress rate.

Also, the concentration of released antimicrobial agent should not be too high or too low, in order to avoid the adverse effects on the sensorial and toxicological properties (Mastromatteo et al., 2010). In other words, a balance between the microbial growth kinetic and controlled release rate should be established to guarantee the proper protective function during the expected shelf-life. Therefore, one of the most stimulating challenges in the field of antimicrobial systems is the release rate of antimicrobial agents from packaging and also further transfers into the food products. The method of incorporation and the nature of the matrix where the antimicrobial agent has to be incorporated, the modulation of release and the food properties are the most critical factors. Moreover, there are several methods to incorporating of antimicrobial agents into the polymeric materials including the direct incorporation of antimicrobial agents into the polymers, coating, spraying onto the polymer surfaces, the immobilization by chemical grafting or the use of polymers that exhibit intrinsic antimicrobial properties (Shemesh et al., 2015).

Although many studies highlighted the efficacy of direct application of both natural and synthetic antimicrobial substances such as organosulfur compounds from plants (Llana-Ruiz-Cabello et al., 2015), essential oils (Valdes et al., 2015), chitosan (Dutta et al., 2009; Aider 2010), and silver-based additives (Toroghi et al., 2014), there is a growing interest in introducing of controlled releases techniques for those substances. Some of the advantages and disadvantages of synthetic and bio-based polymers as antimicrobial active packaging material were summarized in ***Table1***.

2.1. Synthetic (petroleum-based) polymers

Petroleum-based polymers are commonly used to produce plastic packaging for food application. The polymers used in packaging plastics with molecular weights typically between 50,000 and 200,000 Dalton are appropriate for shaping the polymers into bags, bottles, and trays

(Lee et al., 2008 ; Mousavi Khaneghah et al., 2014). The composition of plastics (regarding polymer type and additives) and processing conditions may affect the polymer morphology (i.e., the arrangement of polymer molecules characterized by two or more distinct regions), the chain entanglement and the intermolecular forces between polymer chains. Usually, materials for food packaging are mainly made of thermoplastic polymers that are characterized by dominant amorphous structure and fewer crystalline or semi-crystalline zones. These intrinsic properties largely influence density, diffusional mechanisms like permeability of gas and vapor through the material thickness or the leaching of additives into the foods.

Properties like mass transport, permeation, sorption or migration, typical of polymers, can affect the efficiency of active packaging systems (Muriel-Galet et al., 2015). The antimicrobial agents in small-size can be mixed thermally with the traditional polymers. In this case, they could be placed in the amorphous zones of the polymeric construction without significantly interfering with polymer-polymer internal (Han 2013).

LaCoste et al. (2005) developed a model using smart mixing to prepare the packaging films for the controlled release of antimicrobial agents. When two or more immiscible polymers are utilized to form a polymer mix film, the Smart blending technology may be applied to make polymer blend films with diverse morphologies like interconnected layer, multilayer, sponge and fibrous morphology. The variation in the morphologies properties can be used to control the release of active compounds, and therefore a broad range of release rates may be acquired for different food applications. At the basis of releasing mechanism, there is a complex diffusion phenomenon of active substances through the thickness of the polymer. The antimicrobial agents is a quite small molecule while compared with hosting medium (high molecular mass). Additionally, in some cases, the antimicrobial agent has a different chemical nature in comparison with hosting medium. Therefore, a high mobility is expected.

The direct incorporation of antimicrobial agents into the plastics during the thermos-mechanic transformation processes (i.e., extrusion) due to high temperatures used during the melt processing can result to reducing of their antimicrobial activity (Jones 2008). Apparently, also, the temperature of food storage can affect the release rate and the durability of the active system. For those reasons, the direct incorporation of antimicrobial organic compounds into polymers during extrusion is nowadays quite limited.

Suppakul et al. (2008) prepared LDPE-blown films containing constituents of basil essential oil. The losses in agent concentration by volatilization during extrusion resulted in a partial exhaustion of the antimicrobial activity in real tests with cheese samples. Ethylene-vinyl alcohol (EVOH) copolymers have been studied as an antimicrobial agent incorporated inside of coating films (Muriel-Galet et al., 2012, 2013). As it was stated by Muriel-Galetet al. (2015), the presence of the strong binding forces between water and EVOH while exposed to foods with high water activity can offer antimicrobial properties for the film. In this context, theoregano EO and green tea extract were impregnated with EVOH copolymers; the potential for application as antimicrobial packaging films was demonstrated due to inhibition of microbial growth in vapor phases and liquid media.

2.2. Bio-based polymers

Bio-based polymers as derived forms of lipids, polysaccharides, proteins and their composites can be produced from renewable biomass sources, such as cornstarch, vegetable fats, and oils, or even microorganisms (Hashemi & Khaneghah 2017). They can be nondegradable (for example bio-polyethylene) or biodegradable (for example polylactic acid). Biodegradable polymers are defined as materials which totally degrade when exposed to carbon dioxide (aerobic) processes, water (aerobic and anaerobic processes), methane (anaerobic processes), and

163 microorganisms. Although numerous bio-based polymers are decomposable (for example
164 polyhydroxyalkanoates and starch), not all decomposable polymers are bio-based (for instance
165 polycaprolactone) (Babu et al., 2013). Despite the poor mechanical properties and high
166 hydrophobicity, bio-based polymers usually are considered as organic matrixes which
167 antimicrobials can be incorporated.

168 Coatings and films fabricated from biodegradable polymers like protein and
169 polysaccharides-based materials as active packaging systems also have been investigated. The c
170 biodegradable polymers such as polysaccharides-based materials, soy protein, whey protein or
171 their products (Hernandez- Izquierdo and Krochta, 2008), have high hydrophilic properties and
172 crystallinity which result in some issues regarding their performance during processing. For this
173 reason, these bio-based plastics should be modified in their structure to exhibit thermoplastic
174 properties particularly when the conventional plastic conversion processes were approached.
175 Moreover, additional modifications are also might be required to provide higher moisture
176 resistance and water barrier, adequate mechanical and optical properties. In fact, as well
177 described by Han (2003), selection of the production method depends on some factors such as the
178 variety and characteristics of the antimicrobial compound (its polarity, volatility, and
179 compatibility with the polymer), their heat stability during processing as well as the remained
180 antimicrobial properties after the process. Lately, a bio-polymeric comprising a blend of two
181 biodegradables(HP-β-cyclodextrins and chitosan), and a natural volatile antimicrobial substance
182 carvacrol, was fabricated, the sorption of carvacrol was deeply affected by the glycerol content
183 and humidity (Higueras et al., 2013).

184 The introduction of nano-fillers and/or compounds in nano form into biopolymers has been
185 utilized as a remarkable plan to conquer some of the previously mentioned issues; low
186 mechanical characteristics and poor barrier property to water vapor and to control of the release.

Recently, Gorrasi (2015) explored slow releasing of rosmarinic acid from a fabricated composite with nano-hybrid compounds. Cui et al. (2017a) developed an edible film based on chitosan and *Artemisia annua* oil containing nanoliposomes as carriers of antimicrobials agents. In fact, nanoliposomes are artificial lipid vesicles that are characterized by one or multiple concentric phospholipid bilayers that entraps aqueous compartments. This kind of structure allows the volatile antimicrobial substances to be entrapped and protected from an early release. These promising results based on nanoliposomes structures as key elements for the release of antimicrobials were previously demonstrated using cinnamon oil and Salvia oil by Cui et al. (2016 a and b). Also, Makwana et al. (2014) compared antibacterial properties of free and nano-encapsulated cinnamaldehyde; their findings highlighted that the antimicrobial effect of cinnamaldehyde was enhanced by encapsulation in nanoliposomes.

Tunç and Duman (2011) studied nanocomposite films for food packaging prepared with methylcellulose and montmorillonite, a compound that can be utilized to control the release of antimicrobial compounds from film structures. The release of carvacrol as an active antimicrobial from the nanocomposite film and further inhibition of *S. aureus* and *E. coli* were evaluated.

The low water solubility can be considered as one of the leading issues associated with using essential oils in packaging. Therefore, corrective strategies could be used to improve bio-based properties as well as their interactions with incorporated antimicrobial active substances. For example, in a recently conducted research, alginate-based edible films of nanoemulsions of lemongrass, thyme, sage essential oils and sodium alginate with acceptable functional properties and antimicrobial activity against *E. coli* were fabricated *(*Acevedo-Fani et al., 2015*).*

3. ANTIMICROBIAL MIGRATING AND NON-MIGRATING SYSTEMS

Generally speaking, antimicrobial agents can inhibit the microbial growth through different approaches: a) affecting the protein structure by alteration or denaturation, as temporary or permanent effects; b) changing the cell membrane proteins or membrane lipids; c) blocking the synthesis of the cell wall formation; d) preventing replication, transcription, and translation of the nucleic acid structure; e) disturbing in the metabolism (Munoz-Bonilla et al.,2013).

Close or direct contact with the microorganism can be accounted as one of the essential requirements of involved mechanisms of action of antimicrobial agents (all above-mentioned ways), which can be achieved in two main ways: *i)* directly, if the substances, non-volatile, can diffuse and solubilize into the food surface, in which the microorganisms are mainly located or *ii)* indirectly, if the substance, volatile, acts in the headspace around the surface of the food and in the food itself after absorption.

La Coste and coworkers in 2005 (LaCoste et al.,2005) coined the term "controlled release packaging" (CRP) defining it as a new form of active packaging or, better, a new trait of active packaging. On the basis of that definition, a CRP is a particular solution that is designed to control the release of specific substances over extended periods of time, maintaining the quality and the safety of foods. Even if this concept has been well accepted and sounds good from a theoretical point of view, the control of the release of an active substance into food represents a challenge even now, and few works deepen this critical point. Generally, a CRP is based on passive diffusion of a molecule or initial package modifications.

A new recent concept is the responsive active packaging that refers to those solutions based on specific trigger mechanisms. In this case, an antimicrobial packaging could be triggered by some changes in the food product or package environment. For example, a biodegradable polymer embedded with an antimicrobial can be considered responsive if the release of the active substance is triggered by the biological activity of selected microorganisms (Brockgreitens and

Abbas, 2016). Therefore, the release of a substance into the packaged food can be activated by the chemical, biochemical or biological changes. These two concepts, i.e., the CRP and the responsive packaging are strictly related, and their synergism can represent the future of active packaging applications.

3.1. Flushing and gas/vapor emission

Some of the gasses like CO_2 and O_2 are primarily used for vegetables and fruits to control the respiration phenomenon and the quality decay. Despite this, modifications in the flavor and the increase of unwanted reactions in fresh fruit was noted as a result high concentrations of CO_2. In the same direction, the high level of O_2 can lead to oxidative deteriorations in addition to further microbial spoilage.

In modified atmosphere packaging (MAP) the application of carbon dioxide (10%) mixed with nitrogen and/or high or low oxygen is a conventional approach to avoid aerobic microorganism's growth. However, the higher levels of CO_2 (more than 30) can be resulted in organoleptic defects and increase the risk of packaging collapsing. Once CO_2 penetrated, as result of CO_2 solubilizing, the carbonic acid is produced which reduces the pH of the cell. Moreover, CO_2 can interfere with several enzymatic and biochemical pathways, inhibiting microbial growth (Floros and Matsos, 2005).

Concerning the oxygen, under hypobaric conditions, the O_2 in low concentration was considered as a successful approach to control of spoilage (Burg 2004). However, the effect of super-atmospheric O_2 (>21 KPa) on pathogenic microbes can differ with the species treated; generally, it is less efficient than CO_2. Packaged red meats are typical products using atmospheres at high (about 70%) and low (<0.5%) oxygen concentrations combined with carbon

dioxide and nitrogen as inert filler. In these cases, high oxygen and carbon dioxide contribute to reducing microbial growth. Furthermore, the nitrogen and argon combined with carbon dioxide are used to eliminate oxygen to inhibit the oxidative reactions as well as microbiological spoilage (Spencer and Humphreys, 2002).

The modification of the atmosphere by gas flushings like oxygen scavengers and chlorine dioxide, carbon dioxide, sulfur dioxide and ethanol emitters can be implemented by active packaging. Due to the gaseous characteristic of the agent, the antimicrobial activity reaches every corner of the package and protects the full product surface (López-Carballo et al., 2012). In this way, due to releasing in the headspace the efficacy of the agent can be improved; consequently, the required concentrations to exhibit the desired function might be reduced. After incorporation of volatiles substances like essential oils, spices, organic acids into plastic films or sachets and pads, they can be released in the headspace in vaporized form, then reach to the surface (Han 2005; Hashemi et al., 2017). Their release in the packaging headspace may represent an alternative and/or complementary strategy to reduce contamination and growth of both pathogenic as well as spoilage microorganisms during storage (Burt et al., 2007; López et al., 2007b). In general, the release rate of an antimicrobial substance in the headspace depends on the volatility and, the chemical interaction between the packaging materials and the volatile agent (Han 2005). The effectiveness also can be correlated with the solubility of the substance in food, thus the rate and the absorption capacity that are related to the food composition. In fact, their hydrophobicity could allow them to penetrate into the lipids of the bacterial mitochondria and cell membrane. However, the hydrophobicity of an essential oil or their constituents may be a disadvantage in food systems with high lipid fractions, as they are diluted in the lipids whereas microorganisms grow on the water-rich fractions (López-Carballo et al., 2012).

3.2. Coating and films with antimicrobial agents

In the last years, the coating technologies widely were used to offer new properties for packaging materials. A coating can be defined as "deposed thin layers of materials, usually lower than 1 micron, onto a plastic or cellulosic substrate" with different functions like the improvement of adhesion between two layers, the improvement of water and oxygen barrier also the enhancement of surface proprieties like wettability. The examples of traditional coatings are synthetic polymers like polyvinylidene chloride (PVDC), polyvinyl alcohol (PVOH) or ethylene vinyl alcohol (EVOH). Recently introduced coatings produced from food-grade additives and edible biopolymers can be classified as biodegradable. Flexo, gravure, and printing technologies are extensively used on an industrial scale to deposit a coating onto a plastic surface, offering excellent adhesion and uniformity.

In fact, in order to incorporate the antimicrobial agents into the coating and to avoid the further issues due to the thermal and mechanical stress, several methods, such as microencapsulation and employing polymer nanocomposites were introduced (Shemesh et al., 2015).

The design of an antimicrobial coating requires an extended knowledge regarding the interaction between the active substance/coating/substrate/food. There are some requirements for an antimicrobial coating to be used in food packaging applications:

1) The active coating should present good adherence to the film substrate and should be innert for direct food contact

2) The concentration of the release agent should be adjusted to produce an effective antimicrobial activity

3) The final active coated structure should complete the necessities of the food products, which basically can be provided by conventional passive packaging (López-Carballo et al.,

2012). To obtain the controlled release of the antimicrobial substance, the partition behavior, the diffusion phenomenon through the coating, the volatilization into the headspace (if the substance is volatile) and the solubility into foods especially if a direct interaction with the food should be calculated. The behavior of the active substances regarding partition (expressed as coefficient of partition, K) between coating (C), the substrate (S) and food (F) has to be well known to optimize the controlled release. Ideally, materials should be selected to reduce the loss of the active compound by retention in the substrate layer (high $K_{C/S}$) and to increase the concentration in the food (low $K_{C/F}$) (López-Carballo et al., 2012). If the substance is volatile, the diffusion in the headspace should be fostered, assuring a low partition coefficient K between coating and headspace ($K_{C/HS}$) to favor the antimicrobial activity of the substance on the food surface and a low K between food and headspace ($K_{F/HS}$) to avoid sensorial deterioration of the food itself.

In order to modulate the release of the active substance from the coating, the addition of polymer plasticizers is a good strategy. Usually, plasticizers increase the void volume of the polymer, accelerating the diffusion processes. On the contrary, to slow down the process of release, the inclusion into the matrix of nanoparticles can enhance the tortuosity of the diffusion order or the reduction of chain mobility by the polymer (Hernández-Muñoz et al., 2005).

The solubility of the antimicrobial agents in the food matrix is another main issue. In the case of high solubility, the release may happen quickly, rapidly declining the antimicrobial concentration on the surface of the food. In contrast, in the case of low solubility, the antimicrobial might be collected on the surface of food products and migrate deliberately throughout the food medium (Bastarrachea et al., 2011). In fact, the knowledge diffusion characteristics of antimicrobials can be approached to determine the necessary amount to keep the concentration levels above the minimum inhibitory concentration.

Muriel-Galet et al. (2013) developed the incorporated oregano essential oil into active EVOH-coated polypropylene (PP) films. The results indicated that the addition of the active EVOH coating did not significantly modify the functional properties of the packaging film (mechanical and barrier properties). Nonetheless, the developed packaging did not result in enhancement of inhibition of psychrotrophic bacteria, *Enterobacteria*, lactic acid bacteria, and molds and yeasts at the beginning of storage.

3.3. Impregnating polymers with antimicrobial agents

According to Munoz-Bonilla et al. (2013), different types of polymeric systems with antimicrobial activity can be divided into four main groups:

a) The polymers with an intrinsic polymeric activity

b) The polymers that are chemically or physically modified to incorporate in a covalent way the antimicrobial function

c) The polymers containing organic antimicrobial substances non-covalently linked to the matrix

d) The polymers containing inorganic antimicrobial substances non-covalently linked to the matrix.

3.3.1. Polymers with intrinsic antimicrobial activity

The inherent ability of some polymers in inhibiting microbial growth is well documented (Cho et al., 2009). Chitosan as natural antimicrobial polysaccharide has some special physicochemical characteristics conveyed by the polysaccharide backbone. Chitosan has been known as a natural substitute for chemically manufactured antimicrobial polymers. However, the

structure of chitosan is highly acetylated which provide an insoluble polymer in water and most of the conventional acidic aqueous solutions; it can quickly be dissolved in acidic solutions with pH below 6.3 (van den Broek et al., 2015). Chitosan can potentially be applied as an additive in food packaging systems since chitosan has an excellent film-forming ability combined with antimicrobial properties (Dutta et al., 2009). The antimicrobial activity of chitosan against bacteria, molds, and yeasts have been confirmed by the previous studies (Friedman and Juneja, 2010; van den Broek et al., 2015). The antimicrobial effectiveness of chitosan is affected by several factors such as the kind of chitosan, the host, the chemical composition of the substrates or both, and the environmental conditions (Aider 2010). It is commonly known that molds and yeasts are the most vulnerable microorganisms to antimicrobial effect of chitosan, followed by bacteria. Renuka et al. (2016) reported the edible chitosan coating used in ribbonfish, caused a decrease in the growth of *Pseudomonas* spp., H_2S forming bacteria and Enterobacteriaceae.

Chitosan has an intrinsic antimicrobial activity due to its positively charged amino group that reacts with negatively charged microbial cell membranes. As a result, there is an outflow of proteinaceous and other intracellular components of the microbial cells (Dutta et al., 2009). Chitosan exhibits an excellent chelating capacity for transition and heavy metals due to the high nitrogen content, which can be increased at the basic pH since the electron pair on the amine groups is available for donation to metal. Besides, the hydroxyl groups are also unprotonated at higher pH (7-9), and the complexation also occurs via hydroxyl groups (Munoz-Bonilla et al., 2013). Therefore, in this mechanism, the chitosan molecules may make a complex with the metals surrounding of bacteria, preventing the flow of essential nutrients. The intrinsic antimicrobial activity of chitosan requires intact and close contact with the food surface, in another word; the proposed product should have a smooth structure without holes, pores, air gaps. Also, the food composition influences the activity of chitosan for instance; the higher

antimicrobial activity of chitosan was recorded in low NaCl and protein content like vegetables and fruits (Devlieghere et al., 2004).

From an environmental view, it is biodegradable, biocompatible, renewable and, non-toxic, which is the typical concern of packaging materials (van den Broek et al., 2015). Furthermore, chitosan is an inexpensive biopolymer that is commercially available. All these advantageous features together combined with its low price, have made chitosan a suitable packaging material.

3.3.2. Chemical or physical incorporation through covalent bonds

Chemical or physical modifications of the matrix allow the inclusion of antimicrobial moieties covalently, resulting in the second group of polymers with antimicrobial activity. Theoretically, this goal can be achieved in different ways, like the creation of a link between the polymer and the active substance exploiting some labile bonds (carbonate, ester, urethane, orthoester, amide, ether, and anhydride) or through the grafting to conventional polymers. A possible solution to increase the release of the antimicrobial agent into foods is to immobilize the agent onto biodegradable or compostable polymers. These polymers are measured to be extremely attractive because they can go through hydrolysis to generate non-toxic compounds metabolized *in vivo* and the environment. Furthermore, they show exceptional kinetics of antimicrobial release, effectiveness, and distribution. The discharge of the active particle from the degradable delivery systems can be managed by numerous methods that can also be combined: pure peptide dispersion throughout the polymer medium, deterioration of the polymer (erosion) and power of the osmotic pressure (Sobczak et al., 2013).

The immobilization exploits the availability of functional groups on both the polymer and the antimicrobial the polymer and the formation of ionic or covalent bonds. Enzymes, peptides,

organic acids and polyamines can be mentioned as examples of antimicrobials with functional groups. Also, the immobilization of peptides and enzymes can be considered as one of the most studied applications in food packaging (Perez Espitia et al. 2012). As an example, short peptides (1-50 amino acids) with hydrophobic and cationic properties are recognized as effective defenses of the host organism, resulting in inactivity against a broad range of microorganisms such as Gram-positive and Gram-negative bacteria, fungi, parasites, and viruses (Hancock and Sahl, 2006). Peptides can be immobilized or attached to solid materials by chemical techniques, such as covalent bonding or by physical techniques, such as layer-by-layer assembly. In the first case, the peptide is sandwiched between two polyionic polymers and the number of peptides and polymers is flexible; in the second case, the antimicrobial peptide will chemically interact with a particular surface after functionalization to produce a permanent bond that leads to the development of an antimicrobial coating on the surface of the polymer. In the former system, the immobilized peptide in the layers close to the solid basis will not be in direct connection with the target surface, therefore decreasing peptide activity (Perez Espitia et al., 2012). The latter seems to be more advantageous than to the most constant attachment amongst the polymer surface and the peptide (Goddard and Hotchkiss, 2007). However, the dispersion of attached peptides into the product surface is limited due to the covalent bonding. In this case, the diffusion of the food can take place in severe conditions. Some of the packaging materials such as high-methacrylate (PMMA) and polyvinyl chloride or flexible spacers like polyethylene glycol (PEG) offer a higher peptide-relative surface availability, increasing peptide-bacteria interactions at levels that could be enough for peptide bioactivity (Costa et al.,2011). Due to the immobilization, the activity of peptides may be less efficient in the case of solid foods in comparison to liquid foods.

3.3.3. Polymers containing organic and inorganic antimicrobial substances non-covalently

linked to the matrix

The embedding and mixing of the polymers with antimicrobials substance have been investigated thought recent years. However, the extrusion process is a promising technique for the incorporation of antimicrobial in traditional melted polymers, some issues should be highlighted such as thermal resistance of the substance as the critical issue in addition, the aggressive thermo-mechanical treatment, especially for organic substances like essential oils and their derivatives, organic acids and other organic compounds while for inorganic substances (salts, metals) also in nano form the resistance to the extrusion process. After extrusion, the antimicrobial is not covalent bonded; thus it is free and able to transfer through the medium of polymer to be released from the packing surface and enter over the membrane of the microbial cell. The incorporation through extrusion of antimicrobials substances into the matrix of the polymer may alter the film's barrier, mechanical, and optical properties; thus, it is crucial to explore the performances of active films after extrusion. Generally, in a monolayer film, the activity of system is controlled by the extent and kinetics of the agent release to the food and to the internal and external atmospheres, which are characterized by the partition coefficient ($K_{i/j}$) and solubility ($S_{i/j}$) coefficients at the diverse interphases (i and j represent the active layer, A, the headspace, HS, the food, F, and the external environment, E) and by the diffusion coefficients in the diverse phases (D_i) (López-Carballo et al.,2012). Kuplennik et al. (2015) studied the antimicrobial activity of linear low-density polyethylene compounded with potassium sorbate. In this work, linear low-density polyethylene (LLDPE) and its mix with ethylene vinyl acetate (EVA) were compounded with potassium sorbate to examine the correlation between various compounding. Glycerol monooleate (GMO) was used as a dispersant. The results highlighted that the existence of potassium sorbate in the polymer matrix considerably increases the thermal stability of the blends in comparison to the neat matrices. From a microbiological viewpoint,

reference films, i.e., LLDPE or LLDPE/EVA blended with 5% GMO and potassium sorbate between 2-5.5% reduced the growth of yeast by 1-2 log values, suggesting that GMO itself has a particular antimicrobial activity. These results are not by those obtained by Devlieghere et al. (2000a). These authors discovered that ethylene vinyl alcohol/linear low-density polyethylene (EVOH/LLDPE) film (70 mm thick) compounded with 5.0% w/w potassium sorbate is incapable of reducing the microbial development on cheese and therefore to increase its shelf life possibly due to the restricted transfer of the antimicrobial compound from the polymer. The high barrier characteristics of the EVOH layer reduced the migration of the active compound, and this has been a limitation also in the experiment of Cerisuelo et al. (2010 a, b) that prepared by extrusion EVOH films containing carvacrol; the release of the agent during dry storage was impeded. On the contrary, while it exposed to humid environments, the agent is quickly released with high antimicrobial activity against *L. innocua, Salmonella* spp. Moreover, *E. coli*. In recent studies, the use of oregano-modified montmorillonite clays (MMT) as filler during melt compounding has been investigated to keep heat-sensitive and volatile essential oils during extrusion of LDPE Shemesh et al., 2015). The presence of clay/carvacrol combination exhibited superior and prolonged antibacterial activity against *Escherichia coli* and *Listeria*. Also, biodegradable and/or compostable polymers are used in extrusion or blending processes with antimicrobial substances. For example, Liu et al. (2009) prepared PLA films containing nisin by extrusion. Unfortunately, the high processing temperature of PLA (160°C) resulted in a loss of activity of the molecule due to its decomposition at 120°C.

Other inorganic compounds that can be added to the polymeric matrix during extrusion or blending are metal oxides like TiO_2, a photocatalytic substance. This compound under UV light produces energy-rich electron-hole pairs that can increase reactivity with the surface-absorbed molecules leading to the making of active radicals like hydroxyl radicals (•OH) and reactive

474 oxygen species (ROS) that are responsible for polyunsaturated phospholipids oxidation of
475 microorganism cell membrane. Bodaghi et al. (2013) studied the incorporation of anatase and
476 rutile titanium dioxide into a low density. The in vitro experiment highlighted that *Pseudomonas*
477 spp. was reduced by 4 and 1.35 log CFU/mL after 3 h of UVA light on TiO_2 nanocomposite thin
478 film and LDPE thin film, respectively, while the concentration of cells of *R. mucilaginosa*
479 decreased by 2 and 0.64 log CFU/mL on TiO_2 super-atmospheric thin film and LDPE thin film,
480 respectively.
481
482 *3.4. Electrospun nanofibers prepared by electrospinning technology*

483 Electrospinning technology is an efficient electrohydrodynamic process with high-cost
484 effectiveness in order to manufacture fibers in both micro and nanoscale. In particular,
485 electrospinning creates an electrically charged jet of the polymer solution by using a high voltage
486 to form nanofiber (Croisier et al., 2015). This technique recently was applied in food coatings for
487 active packaging. One of the main advantages of this system is facilitating the size control of the
488 polymer that will be employed for coating since the system allows manipulation of several
489 parameters associated with instrumental, physical and solution properties (Bhushani and
490 Anandharamakrishnan, 2014). Therefore, it becomes possible to produce polymer-based coating
491 systems with controlled release properties while maintaining its antimicrobial activities. Cui et al.
492 (2017b) demonstrated the technological advantages in using electrospinning to enhance the
493 stability of nisin-loaded poly-g-glutamic acid/chitosan (NGC) nanoparticles on polyethylene
494 oxide nanofibers in order to increase the antibacterial activity against *Listeria monocytogenes*.
495 The results of this study showed a satisfactory antibacterial effect on this kind of bacterium and
496 negligible impact on the sensory quality of cheese, suggesting a potential application in food

packaging. Neo et al. (2013) used zein nanofibers to produce packaging materials with nanoscale features embedded in antioxidants and antimicrobials. Torres-Giner et al. (2007) produced antimicrobial fiber based chitosan nanostructures with adequate nanoporous structures. Torres-Giner et al. (2008) used electrospinning fibers of zein was utilized to produce zein/chitosan films with ultrathin properties and with high antimicrobial characteristics. The use of this technique was useful in creating fibrous materials with diameters in the submicron range and different morphologies that can be exploited to tailor specific active solutions. However, intense investigations should be continuously conducted to explore the efficiency of this technique to adapt to food packaging systems.

4. EFFECTS OF ANTIMICROBIAL AGENTS ON PACKAGING PROPERTIES

The antimicrobial agents incorporated into packaging material significantly contribute to the improvement of microbial safety, shelf-life, and quality especially in the case of perishable foods (Bastarrachea et al., 2011). Nonetheless, these agents mostly serve as an additional hurdle in the packaging material and, depending on the type of antimicrobial agents, they may lead to rigorous modifications on critical properties of packaging material such as their mechanical strength, permeability, volatility, optical and thermal characteristics and even physical appearance (Bastarrachea et al.,2011; Kuorwel et al.,2014) (***Table 2***).

4.1. Effects of antimicrobial compounds on packaging systems properties

Incorporation of antimicrobial agents into packaging material could affect the structure and their engineering properties, such as the permeability to gas, the tensile strength, optical, thermal, morphological and physical properties of these materials (Bastarrachea et al.,2011; Kuorwel et

al., 2014). Among all properties, mechanical characteristics and water vapor permeability can be easily influenced by the addition of antimicrobial agents.

4.2. Effect on mechanical properties

Elongation at break (capacity for stretching) and tensile strength (resistance to elongation) are practical measures used for prediction of the ability of materials to retain their cohesion (Shojaee-Aliabadiet al., 2014). Mechanical properties of materials are mainly changed to the type of antimicrobials agents and polymers.

The addition of essential oils and extracts to film matrices has been mostly shown to decrease the tensile strength (TS) and increase the elongation (E) of edible films in a concentration-dependent manner; the resulting films are softer but more extensible. Impregnation of 0.5 and 1.5% thyme essential oil into chitosan-based film caused a significant reduction in TS and enhancement in E in comparison to control film (Hosseini et al., 2009). The same results also have been reported for rosemary essential oil (0.5 to 1.5%) added to alginate film and thymol and carvacrol to polypropylene film (Ramos et al.,2012). Pranoto et al. (2005) showed that changes in mechanical properties of alginate films containing garlic oil (0.2 to 0.4%) were significant when more than 0.2% garlic oil was added to alginate film.

Rhim et al. (2006) investigated the properties of four different types of chitosan-based nanocomposite films. Based on their findings some properties such as mechanical and barrier of were affected by intercalation of nanoparticles. Consequently, an increase of 7-16% was observed for, tensile strength whereas, although, the vapor permeability decreased by 25-30% depending on the used material for the preparation of nanoparticle.

In one of the recently conducted studies, antimicrobial bio-nanocomposite films based on gelatin were prepared with silver nanoparticles (AgNPs) and organoclay (Cloisite 30B).

According to the reported results by the authors, the transparency of proposed films was decreased while the UV barrier, hydrophobicity, and water vapor barrier properties were improved. In the term of mechanical properties, the incorporation of AgNPs or clay into the gelatin film could cause increasing in Tensile strength (TS); however, it resulted in a decrease in elongation at break (EAB). Moreover, considering the EDX and XRD results, the homogenous compact surface structure of the composite films was noted (Kanmani, and Rhim, 2014 a, b). In another investigation, the 50 and 100% (w/w, protein) basil leaf essential oil (BEO) in the absence and presence of 3% (w/w, protein) ZnO nanoparticles (ZnONP) were incorporated into composite films based on fish protein isolate (FPI) and fish skin gelatin (FSG) blends. As consequence of increment in BEO levels, which cause a development of heterogeneous film matrix, leading to discontinuity of film network, a significant decline in TS and increase in EAB was reported the due to progress of heterogeneous film matrix, leading to discontinuity of film network, while ZnONP incorporation resulted in higher TS but lower EAB. Based on their findings, due to the addition of BEO, as nonpolar or hydrophobic materials, the hydrophobicity of films was increased, thereby resulted in lowering the adsorptivity as well as diffusivity of water vapor through the film as indicated by lower WVP in the fabricated film with 100% BEO and 3% ZnONP. Also, the transparency of films was decreased as result of BEO and ZnONP incorporation which can be addressed to hindering of light passage or light scattering by the nanoparticles dispersed in the film matrix. Additionally, the hydrophobicity of BEO added films was improved. Moreover, the thermal stability prepared filmed with BEO and ZnONP was higher in comparison with control films. Regarding the microstructure of introduced films, the presence of ZnONP could prevent bilayer formation of a film containing 100% BEO. The author claimed that the increase in thickness of BEO incorporated films regardless of ZnONP concentration can

be correlated to the interaction between chemical components present in BEO and protein matrix (Arfat et al., 2014).

The propolis extract (PE) (high in polyphenols) in 0, 2.5, 5, 10 and 20% w/w were added to chitosan films and some of the film properties such as water vapor permeability and oxygen permeability, tensile strength, elongation at break of prepared films were investigated by Siripatrawan and Vitchayakitti (2016). Based on the reported results, the addition of propolis reduced the WVP and also WVTR, but this change was not significantly correlated with increases in amounts of propolis. The limitations in availability of hydrogen groups to form hydrophilic bonding with water as result of covalent interactions between chitosan network and polyphenolic compounds can be considered as possible reasons, which can cause a decrease in the affinity of chitosan films toward water and consequently lower WVTR. Also, due to complex chemical nature of propolis, (consists of various organic compounds, waxes, phenolic acids flavonoids and essential oils), a decline in WVP was forecasted. At same direction, due to interactions between propolis phenolic compounds and chitosan polymer matrix, the oxygen permeability was decreased. As it was expected, the tensile strength increased with increase in PE concentration from 0 to 20% which can be associated with interactions between the propolis components with the hydrophilic groups of the chitosan molecules. In the case of elongation, however, there was an increment when the concentration of propolis was increased from 0 to 10%, a significant decreased was noted while 20% propolis was added. This decrement in elongation can be associated with the formation of crystalline consequently a decline in the flexibility of film was observed (Siripatrawan and Vitchayakitti, 2016).

According to Dehnad et al. (2014), the moving chitosan chains towards their glass transition temperatures can be stimulated by the incorporation of nanoparticles (up to 2%), which resulted in an improvement in polymer functionality of thermo-sealing aspects. In this context,

high Tg range of 115–124 ◦C was reported for Chitosan–nanocellulose nanocomposites and consequently they were able to keep their solid state until the temperature (Tm) range of 97–99 ◦C.

The evaluation of physical properties of prepared films by the incorporation of Articoat DLP 02 (AR), Artemix Consa 152/NL (AX), Auranta FV (AFV) and sodium octanoate (SO) as antimicrobial agents into gelatin based films was the subject of conducted study by Calrk et al. (2016). The recorded thickness, color, and transparency of introduced films were significantly higher as compared to control films. The presence of 1, 2 and 3% of ZEO and MEO in carrageenan film negatively affected the TS of films by a factor of 2.5 and 1.5, respectively, but it made films more extensible. This effect could primarily be attributed to the ability of polymers to interact with other components such as essential oils via ionic or hydrogen bonds. These interactions may cause the limited substitution of stronger polymer-polymer interfaces by weaker polymer-oil interactions in the film matrix which may result in the loss of film cohesion, and therefore the tensile strength of the emulsified films (Shojaee-Aliabadi et al., 2014).

However, when cinnamon essential oil is used at a concentration of 0.5 to 2% in chitosan-based films, TS increases due to the significant interaction between the cinnamon essential oil and biopolymer which leads to reducing the molecular mobility of the polymer and forms a rigid structure with less stretchability (Omagh et al.,2010). It should be noted that this effect could be varied based on essential oil concentration; in CMC-based films, the existence of 1 and 2% of *Zataria multiflora* essential oil improved TS of films while using 3% of *Zataria multiflora* oil made the film structure looser because of discontinuities in the biopolymers network by oil droplets (Dashipour et al.,2015).

Besides essential oils, some of the nano-clays show good antimicrobial activities (Martins et al.,2013; de Azeredo 2013), depend on nature of nano-clay and polymer, TS and E of

615 nanocomposite tend to change; compatibility of hydrophobic nano-clay with polymer leads to
616 fully dispersion of nanoparticles into the polymer matrix and results in uniform with enhanced
617 mechanical properties of films. TS of whey protein isolate film decreased in the presence of
618 Cloisite 30B at a concentration higher than 5%, while E increased slightly (Sothornvit et
619 al.,2010). However, thermoplastic starch/Cloisite 30B nanocomposite had higher TS and lowered
620 E compared to neat thermoplastic starch film (Müller et al., 2011). On the other hand, when
621 Cloisite 30B or Cloisite 20A nano-clays were added to whey protein isolate film, both TS, and E
622 of the film was significantly reduced by Cloisite 20A nano-clay. However, there was no
623 significant effect of Cloisite 30B compared to pure film on TS and E properties (Sothornvit et
624 al.,2009).

625 The sealability properties of packaging material such as pouches and sachets carry great
626 importance. This property is strictly associated with the mechanical strength of the material since
627 the package should have the high durability to hold the primary product inside the package and
628 block its release during storage. In food packaging, sealing by heating is commonly employed to
629 merge two polymers in order to formulate packaging material with higher mechanical strength.
630 Films containing starch exhibit excellent elasticity, however, these materials are most fragile, and
631 their mechanical resistances can be significantly increased by the addition of plasticizers. The
632 incorporation of sorbitol as plasticizer could drastically improve the heat sealability of the edible
633 films. In some cases, using the combination of more than one plasticizer at optimum molar ratio
634 could give even a better seal strength to the film. The use of sorbitol in combination with glycerol
635 at 3:1 ratio could give a very high seal strength to the film compared to only starch-based film
636 without plasticizers (Abdorreza et al. 2011). Moreover, some films do not show thermoplastic
637 characteristics, hence, cannot be stretched or heat-sealed. Chitosan film is a common example for

this and even though its numerous advantages in the packaging industry, their use consequently increase the cost of the film (van den Broek et al. 2014).

Optical properties associated with the transparency of the packaging material are a highly desirable as one of the primary requirements. Recently, the use of polymers in nanocomposite form instead of pure form gained great importance. Due to their high transparency, low density and favorable surface properties, they are widely used as the packaging material of beverages (Ahmed and Varshney, 2011). Polylactides, which are lactic acid-based polymers with excellent biocompatibility and biodegradability, have been widely studied in nanocomposite form to produce high transparent packaging material. These nanocomposites can be incorporated with organic layered silicate as packaging filler (Rhim et al. 2013). Beside these polymer/nanocomposites, the design of PLA films layer-by-layer with the addition of different antimicrobial agents can provide desirable transparent films as well as improve its oxygen permeability. The addition of an extremely thin layer of chitosan and negatively charged montmorillonite (MMT) clays into PLA films could result in high optical clarity PLA films without altering other important properties (Svagan et al. 2012). Further studies should be investigated in order to obtain same optical transparency of the film using fewer layers for the economic viability of the packaging material.

4.3. Effect on Permeability

Previous studies have been indicated that the addition of antimicrobials agents to a polymer matrix can alter gas barrier properties in the dried films (Baestarrachea et al., 2011). Although changes in water vapor permeability (WVP) of polymer-based films as influenced by antimicrobials has been widely studied in the literature, there are not many reports about the impact of different antimicrobial agents on gas permeability of polymeric films (Shojaee-

662 Aliabadi et al., 2013). In most studies (***Table 3***), incorporation of essential oils usually tends to
663 reduce WVP of films due to increasing the hydrophobic: hydrophilic ratio of the film matrix and
664 interrupt in the hydrophilic network, therefore enhancing the tortuosity factor for mass transfer in
665 the continuous matrix (Benavides et al.,2 012; Shojaee-Aliabadi et al., 2013; Lee et al.,2015).
666 However, this decrease is related to essential oil concentration; at a higher concentration of
667 essential oil, at which mechanical properties of films deteriorated, the loss of structure
668 compactness overcame the hydrophobicity and tortuosity factor of the film, therefore assist water
669 vapor transfer through the film (Bonilla et al., 2012). Furthermore, it has been shown that some
670 polymers tend to interact with polyphenolic compounds of essential oils, which may diminish the
671 readiness of the hydrophilic groups to form hydrophilic bonds; this, in turn, decrease their
672 interactions with water, resulting in reduction in the films of water vapor transmission rate
673 (Ojagh et al., 2010). Contrary, incorporation of aqueous extract to film usually increases WVP
674 because of plasticizing effect of water, which diminishes intermolecular interaction between the
675 polymer-polymer chains, thus raise the films' WVP. However, in some cases polyphenolic
676 molecules of plant extracts are able to be cross-linked to increase interaction among adjacent
677 polymer chains or to act as filler to decrease the porosity of film, resulting in a decline of WVP of
678 films (Erdohan et al., 2013; Peng et al., 2013).

679 Incorporation of essential oils or plant extracts in film matrix can modify functionalities of
680 films. Shojaee-Aliabadi et al. (2014) reported that addition of Zataria multiflora Boiss and
681 Menthapulegium essential oils in Κ-carrageenan films could improve water vapor permeability of
682 these composite films. On the other hand, the antimicrobial activity of films over B. cereus, S.
683 aureus, and E. coli bacteria was increased through the incorporation of essential oils.

684 Besides water vapor permeability, some antimicrobial agents have been reported to
685 decrease the permeability of gases like oxygen through polymers used as packaging material. The

use of nano-clays in combination with polymeric material is known to improve the gas barrier characteristics of the packaging system. The addition of clays mainly alters the path that gas molecules pass through the material since they result in a tortuous path (Nielsen, 1967) where gas molecules have to travel the long path in order to diffuse through the film. In this case, the concentration of the clay added into material has a significant influence on the distance of this path that each gas molecule has to travel (Silvestre et al. 2011).

5. CONCLUSIONS

Active packaging is gaining more importance, and a rapid progress and applications have been observed due to consumer preferences for natural and minimally processed preserved foods. Active packaging with antimicrobial properties remains a significant challenge even with the enormous developments made in the last years. The main difficulties are related to the controlled released of antimicrobial agents, developments in packaging materials (mainly the bio-based materials) that possess adequate barrier properties, transparency, tensile strength, coefficient, and stiffness of friction. However, the gap between commercial applications and research is not filled since in vitro tests performed in laboratory conditions, unfortunately, do not represent real storage and distribution conditions.

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DECLARATION OF CONFLICT OF INTEREST

There is no conflict of interest.

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Tables

Table 1. Advantages and disadvantages of synthetic and bio-based polymers as antimicrobial active packaging material

Polymers	*Advantages*	*Disadvantages*
Synthetic	High industrial availability Cheap Easy manufacturing Light-weight	Mostly limited for plastic material production Petroleum-based Long degradation times (years) Environmental problems
Bio-based	Renewable resources Edible Biodegradable and biocompatible Significant reduction in packaging volume Controlled release of active agents Controllable shelf-life Excellent mechanical properties Environmental-friendly characteristic Nontoxic	Hydrophilic polymers show poor water vapor and moisture barrier Expensive manufacturing

Table 2. Mechanical properties of polymer-based films containing antimicrobial agents

Polymer	Antimicrobial compound	Antimicrobial content	TS (MPa)		E (%)		Y (MPa)		Temperature (°C)/RH (%)	References
			Without AM	With AM	Without AM	With AM	Without AM	With AM		
Carrageenan κ	*Satureja hortensis* EO	1%	26.29	19.88	36.46	35.82	-	-	25/54	Shojaee-Aliabadi and others 2013
		2%		11.44		41.46				
		3%		9.52		44.77				
Agar/nanocellulose	Savory EO	0.5%	31.21	28.26	50.73	46.17	55.76	62.99	-	Atef and others 2015
		1%		28.13		49.38		57.02		
		1.5%		20.38		51.67		46.50		
Kafirin	Citral	2.5%	3.48	1.89	79.7	141	-	-	-	Giteru and others 2015
	Quercetin	2%		3.25		46.7				
Chitosan	Cinnamon EO	0.4%	10.97	13.35	24.73	16.57	-	-	25/51	Ojagh and others 2010
		0.8%		17.43		11.26				
		1.5%		24.10		6.42				
		2%		29.23		3.58				
Alginate-apple puree		0.5%	2.90	2.84	51.06	57.88	7.07	6.86	23/50	Rojas-Graü and others 2007
Alginate	Red ginseng extract	0.5 g/ml	22.20	13.81	19.32	27.95	203.0	64.86	-	Norajit and others 2010
	White ginseng extract			8.05		24.39		63.63		
Polypropylene	Thymol	4%	30	28	19	23	851	593	-	Ramos and others 2012
		6%		28		24		680		
		8%		28		25		585		
Whey protein isolate	Lactoperoxidase system	0.03%	2.31	2.09	140.31	129.50	25.80	23.57	23/50	Harris and Krochta 2005
		0.06%		2.09		135.60		23.21		
		0.15%		1.09		119.52		17.16		
		0.25%		0.96		91.99		14.47		
	Lactic acid	1.5%	-	1.85	-	1.21	-	-	23/50	Pintado and others 2009
		3%		1.32		3.10				
	Malic acid	1.5%		1.89		2.08				
		3%		1.19		9.03				

Table 2. Continued

Polymer	Antimicrobial compound	Antimicrobial content	TS (MPa)		E (%)		Y (MPa)		Temperature (°C)/RH (%)	References
			Without AM	With AM	Without AM	With AM	Without AM	With AM		
Chitosan	Nisin	51 (10^3 IU/g chitosan)	37.03	23.70	3.45	14.13	-	-	-	Pranoto and others 2005
		102 (10^3 IU/g chitosan)		16.57		16.00				
		153 (10^3 IU/g chitosan)		17.53		28.78				
		204 (10^3 IU/g chitosan)		13.58		30.72				
	Lysozyme	20%	17.4	14.4	60.3	53.8	-	-	-	Park and others 2004
		60%		9.5		39.3				
		100%		7.4		29.1				
Gelidiumcorneum	Nanoclay (Cloisite 30B)	1%	19.59	23.25	15	28.05	-	-	25/50	Lim and others 2010
		3%		26.40		33.21				
		5%		24.18		27.84				
		7%		18.52		22.50				
κ-Carrageenan/ Locust bean gum		1%	26.88	28.73	18.8	22.64			20/0	Martins and others 2013
		2%		29.27		25.06				
		4%		28.38		26.23				
		8%		29.79		26.82				
		16%		33.82		29.82				
Gelatin	Silver nanoparticle	10 mg	35	27.5	49.9	60.5	697.8	448.5	-	Kanmani and Rhim 2014
		20 mg		26.3		45.6		546.7		
		30 mg		28.6		48.8		609.6		
		40 mg		26.9		51.4		529.8		
Polypropylene/EVOH	Oregano EO	7.5%	303.76	274.44	658.48	-	-	-	-	Muriel-Galet and others 2013
	Citral			281.51						
Polylactic acid	Olive leaf extract	0.5%	32.60	32.50	27.82	11.79	-	-	-	Erdohan and others 2013
		1%		30.77		24.54				
		2.5%		27.69		26.99				
		2%		25.64		19.70				
		3%		22.39		30.53				

Table 2. Continued

Polymer	Antimicrobial compound	Antimicrobial content	TS (MPa)		E (%)		Y (MPa)		Temperature (°C)/RH (%)	References
			Without AM	With AM	Without AM	With AM	Without AM	With AM		
Polyethylene-co-vinylacetate	Carvacrol	3.5%	24.8	19.7	590	650	46.8	47.1	-	Nostro and others 2012
		7%		16.4		680		39.9		
	Cinnamaldehyde	3.5%		20.7		610		47.3		
		7%		17.1		680		40.6		
	Eugenol	3.5%	-	20.0		600		45.3		Nostro and others 2013
		7%		16.5		630		39.2		

AM: Antimicrobial; TS: Tensile strength; E: Elongation at break; Y: ; RH: Relative humidity; EO: Essential oil; EVOH: Ethylene vinyl alcohol.

Table 3. Water vapour permeability of polymer-based films containing antimicrobial agents

Polymer	Antimicrobial	AM content	WVP		Unit	Temperature (°C)/ RH (%)	References
			Without AM	With AM			
k-carrageenan	*SaturejaHortensis* EO	1%	2.383	1.591	(g/m s Pa 10^{-10})	25/75	Shojaee-Aliabadi and others 2013
		2%		0.840			
		3%		0.556			
Agar/nanocellulose	Savory EO	0.5%	1.60	1.53	(g/m s Pa10^{-10})	-	Atef and others 2015
		1%		1.82			
		1.5%		2.34			
Kafirin	Quercetin	2%	0.66	0.74	(g mm/m^2 h kPa)	-	Giteru and others 2015
	Citral	2.5%		0.69			
Chitosan	Cinnamon EO	0.4%	2.250	1.352	(g/m s Pa 10^{-10})	25/75	Ojagh and others 2010
		0.8%		1.234			
		1.5%		1.014			
		2%		1.003			
	Nisin	51 (10^3 IU/g chitosan)	0.02309	0.02397	(g m/m^2 day kPa)	-	Pranoto and others 2005
		102 (10^3 IU/g chitosan)		0.02525			
		153 (10^3 IU/g chitosan)		0.02762			
		204 (10^3 IU/g chitosan)		0.03420			
	Lysozyme	20%	177.2	157.4	(g mm/m^2 h kPa)	25/50	Park and others 2004
		60%		160.0			
		100%		166.2			
	Green tea extract	0.5%	13.39	8.34	(g/msPa10^{-11})	-	Peng and others 2013
		1%		6.68			
		2%		5.07			
	Black tea extracts	0.5%		11.51			
		1%		7.81			
		2%		5.82			
Alginate-apple puree	Cinnamon EO	0.5%	4.95	4.90	(g mm/m^2 h kPa)	-	Rojas-Graü and others 2007
Ethylene Vinyl Alcohol Copolymer	Green tea extract	5%	8.9	2.5	(kg m/m^2 s Pa10^{-16})	23/75	López de Dicastillo and others 2011
Gelidiumcorneum	Nanoclay (Cloisite 30B)	1%	1.59	1.50	(g m/m^2 s Pa 10^{-9})	25/50	Lim and others 2010
		3%		1.42			

		5%		1.43			
		7%		1.37			
Gelatin	Silver nanoparticle	10 mg	3.02	2.92		-	Kanmani and Rhim 2014
		20 mg		2.97			
		30 mg		2.99			
		40 mg		2.97			
Polylactic acid	Olive leaf extract	0.5%	0.054	0.042	(g mm/m^2 h kPa)	-	Erdohan and others 2013
		1%		0.046			
		2.5%		0.044			
		2%		0.048			
		3%		0.047			
Sweet potato starch	Potassium sorbate	5%	1.970	2.535	g/(s m Pa10^{-10})	23/75	Shen and others 2010
		10%		3.769			
		15%		9.937			

WVP: Water vapour permeability; AM: Antimicrobial; RH: Relative Humidity; EO: Essential oil