Review

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Review

Shelf Life of Foods and Bioactive Materials Used in the Antimicrobial Food Packaging

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Abstract: In the food sector, packaging is one of the important steps that ensures the safe, unspoiled, minimum cost of storing, transporting and delivering the food that goes into production to the consumer. Food spoilage caused by foodborne pathogens and microorganisms is a serious problem in the food chain, reducing the shelf life of foods. Therefore, consumers' demands for more natural, disposable, biodegradable and recyclable antibacterial food packaging materials have considerably increased. This review covers a comprehensive current literature review of antibacterial food packaging, which includes with titles antibacterial agents, organic acids and other compounds, enzymes, bacteriocins, natural extracts, essential oils, application of encapsulation and antimicrobial packaging. Research findings on antimicrobial food packaging used to extend the shelf life of foods were collected from online databases such as PubMed/MedLine, Wiley Online Library, Scopus, Web of Science, and Google Scholar. In this review, the activities of different biomaterials and compounds used to extend the shelf life of foods were compared.

Keywords: the active packaging; the antimicrobial agents; shelf life of foods; biomaterials and nanomaterials

1. Introduction

The packaging material in traditional packaging systems has a barrier feature that protects food only from physical external factors. The main reason for food spoilage is microbial contamination in general. Traditional food preservation methods include freezing, cooling, fermentation, drying, thermal treatment and addition of antimicrobial agents [1]. In recent years, consumers prefer foods that are healthier, quality, less processed, less naturally damaged, fresh and long shelf life. In this way, active and smart packaging systems developed in line with consumer demands and trends in the food industry. Along with these systems, various components are added to the packaging and various polymers that will extend the shelf life of the food and prevent its spoilage. These components also provide the packaging with functions such as gas barrier properties, thermal stability, mechanical strength, and optical properties [2,3]. With the active packaging, the deterioration rate of the food reduced. The changing packaging conditions are provided to extend shelf life and maintain quality. Unlike traditional packaging, active packaging includes oxygen traps, ethylene traps, retention or release of carbon dioxide, moisture control, antimicrobial and antifungal systems. The antimicrobial packaging, which is a form of active packaging, is carried out by adding antimicrobial agents to the packaging or using antimicrobial polymer. The antimicrobial packaging is aimed at preventing microorganisms that cause food spoilage, ensuring food safety, maintaining food quality and increasing food shelf life [3–5]. The bacteria that cause food spoilage and contamination such as; *Clostridium botulinum, Campylobacter jejuni, Listeria monocytogenes, Escherichia coli, Staphylococcus aureus, Shigella spp, Salmonella spp., Yersinia enterocolitica*, viruses such as; *Hepatit A, Norovirüs* and parasites such as; *Toxoplasma gondii, Trichinella spiralis, Cyclospora cayetanensis* are foodborne

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pathogens and other microorganisms [6]. After antimicrobial functions are provided to the packaging system, the system extends the microorganism lag phase, reducing or completely stopping the microbial load at a certain rate. The first application in the food industry to combat microbial degradation was based on the direct addition of antimicrobial additives to food products as food preservatives. Food additives such as nitrates, nitrites, organic acids such as benzoic, sorbic acetic acid, chitosan, lactoferrin, and nisin are added directly to foods for antimicrobial effect. However, the added antimicrobial agent has limited effects due to rapid diffusion into food, loss of effectiveness, needing excessive amounts of additives to achieve the same antimicrobial effect, and sensory property change. Later, with the development of antimicrobial food packaging technology, antimicrobial substances were added to the food packaging material [7–9]. The advantage of this method is that packaged food can be preserved without adding edible preservatives directly to its composition. The antimicrobial packaging can control microbial growth in food by interacting with food (direct contact) or the gap (indirect contact) between packaging and food. In this way, it protects the nutritional and sensory properties of packaged foods and prolongs their shelf life. Today, antimicrobial packaging systems ensure the preservation of foods by releasing antimicrobial-containing sachets or pads to the packaging, coating or immobilizing polymers with antimicrobials and using an antimicrobial polymer.

Generally used antimicrobial agents consist of organic-inorganic nanocomposites, organic acids, organic acid salts, triclosan, antibiotics, alcohols, sulphides, nitrites, ammonium salts, bacteriocins, enzymes, biopolymers, natural extracts, essential oils, phages, metal nanoparticles. The choice of antimicrobials to be used depends on features such as the specific activity against the target microorganism, resistance development, the legal status of its use in foods, the chemical structure of the food, the properties of the packaging material to be included, and its controlled release. Therefore, not all antimicrobials are suitable for every application [10,11]. The antimicrobials such as EDTA or chitosan has also enhanced antibacterial effects in food products such as meat and fish [12]. In the another study, Researchers have synthesized an antimicrobial film by immobilizing nisin on bio-based carboxylated cellulose nanofibers (CNF). They used two methods to use in food packaging, as direct mixing of Nisin and CNF and Nisin grafted CNF [11]. Nisin graft CNF showed antimicrobial effects against various gram positive bacteria *(B.subtilis, S.aureus)*, whereas Nisin mixed CNF only inhibited *B. subtili.* Mixing Nisin and CNF is better than vaccination, but the antimicrobial activity of the vaccination has a longer effect. Divsalar et al. (2018) have synthesized a composite films containing chitosan, cellulose and nisin and used it as an antimicrobial package of ultra-filtered (UF) cheese [3]. The composite film combined with nisin showed antimicrobial activity against *L. monocytogenes*, while the pure chitosan-cellulose film did not show to antimicrobial properties. In addition, UF feta cheese packaged with composite starch film was stored at 4 ° C for 14 days and showed a significant antimicrobial effect of nisin when exposed to *L. monocytogenes*.

In this review study, antibacterial agents, organic acids and other compounds, enzymes, bacteriocins, natural extracts, essential oils, nanomaterials, biopolymers, which are used to effectively extend the shelf life of foods and ensure healthy consumption of foods, were examined in detail. By comparing the literature research findings, the most effective methods to extend the shelf life of foods were determined. This study also proposes the most effective food packaging methods and parameters that extend the shelf life of foods according to recent research. It aims to provide the components used among these parameters and the methods by which these components reach higher efficiency.

2. Antimicrobial Agents

2.1. Enzyme

The enzymes such as lysozyme, glucose oxidase, lactoferrin or lactoperoxidase are widely used in food packaging systems as antimicrobial. The lactoferrin can be used in combination with lysozyme to improve antimicrobial activity against Gram-negative bacteria. Lactoferrin, a whey protein that binds ferric ions, performs its antimicrobial activity by depriving bacteria from iron cells and interacting with LPS components [13]. Lactoperoxidase enzyme, which is widely used as natural antimicrobial, catalyzes the oxidation of thiocyanate ion (SCNy) producing oxidized products and hypothiocyanous acid (HOSCN) is formed. These oxidized products show antimicrobial function by causing irreversible oxidation of sulfhydryl (SH) groups found in microbial enzymes and other proteins [14]. The glucose oxidase enzyme performs its antimicrobial activity by catalyzing the formation of hydrogen peroxide and gluconic acid by oxidation of β-d glucose. According to the literature, this enzyme has been proven to have antimicrobial effects against various pathogenic foodborne bacteria. This enzyme has been proven to have an effective antimicrobial effect against pathogenic foodborne bacteria such as *Staphylococcus aureus, Salmonella infantis, Clostridium perfringens, Campylobacter jejuni, Bacillus cereus and Listeria monocytogens* [15] . Table 1 shows to antimicrobial agents used in the food packaging.

Table 1. Antimicrobial agents used in the food packaging.

Antimicrobial Class	*Antimicrobial Agent*	*Packaging Material*	*Main Microorganisms*	*Food*	*References*
Organic acid	Potassium sorbate - vanillin	Chitosan films	mould	Butter cake	[16]
	Citric acid and chitosan	Fish gelatin/chitosan	*Escherichia coli*	/	[17]
	Sodiumbenzoate Citric acid	Poly(vinylalcohol)	*S. aureus, E. coli, Candida albicans*	/	[18]
	Potassium sorbate	Fish collagen- polyvinil alchol	*E. coli, S. aureus*	/	[19]
	Sodium benzoate and potassium sorbate	Edible active coatings (EACs)	microbial growth (total aerobic counts, molds, yeasts)	Strawberry	[20]
	Sorbic acid butylated hydroxyanisole and butylated hydroxytoluene	polypropylene (PP) films	inhibited gram-negative and gram-positive bacteria growth.	/	[21]
Bacteriocin	Plantaricin BM-1	PE, LDPE, HDPE	*L.monocytogenes*	/	[22]
	Nisin	Chitosan-carboxymethylchitosan	*L.monocytogenes*	/	[23]
	Nisin	PLA	*L.monocytogenes*	*Skim milk and liquid egg white*	[24]
	Nisin	Starch/halloysite nanocomposite films	*L.monocytogenes*	Minas frescal cheese	[25]
	Nisin and bacteriocin-like substance (BLS) P34	Encapsulated in soybean phosphatidylcholine (PC-1) and PC-1-cholesterol (7:3) liposomes	*L.monocytogenes*	Minas frescal cheese	[26]
	Bacteriocin KU24		*S.aureus*	/	[27]
	Enterocin 416K1	Low-density polyethylene) (LDPE) film	significant decrease in	Frankfurters	[28]

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			L.monocytogenes		
	Bacteriocin-like substances	Starch	*L. monocytogene*	Cheese	[29]
	Bacteriocin-producer living bacteria	Poly(ethyleneterephthalate)-polyvinylalcohol (PVOH)	*L. monocytogenes*	Precooked chicken fillets	[30]
	Plantaricin BM-1	polyethylene terephthalate/polyvinylidene chloride, polypropylene (PPR) film	*L.monocytogenes*	meat	[31]
	Lactocin 705 and lactocin AL705	Polyethylene-based film	*L, plantarum CRL691 L, innocua 7*	/	[32]
Enzymes	Lactoperoxidase	Chitosan	*Shewanella putrefaciens Pseudomonas fluorescens Psychrotrophs*	Rainbow trout	[33]
	Lysozyme	Nonwovencellulose + graphene oxide	*Micrococcus lysodeikticus*	/	[34]
	Lysozyme	Polyamide11+halloysite nanotubes	*Pseudomonas* spp.	Chicken slices	[35]
	Lysozyme-chitosan-organic rectorite-sodium alginate	Electrospun Cellulose Acetate	*Escherichia coli and Staphylococcus aureus*	Pork	[36]
Biopolymers	Chitosan	Acrylonitrile-acrylamide grafted chitosan	*E. coli, S.aureus, P. aeruginosa*	Apple and guava	[37]
	Chitosan	Hydroxyethyl cellulose+sodium alginate	*E. coli, S. aureus*	/	[38]
	Chitosan-ZnO hybrid nanoparticles with clove essential oil	Chitosan/pullulan (CS/PL) nanocomposite films	*Pseudomonas aeruginosa, S. aureus, E. coli*	Checken meat	[39]
	Chitosan (Ch) + zinc oxide nanoparticles	Gallic acid films	*B. subtilis E. coli*	/	[40]
Bacteriophage	Bacteriophage (φIBB-PF7A)	Alginate	*P. fluorescens*	Chicken fillets	[41]
	Bacteriophage (vB_EcoMH2W)	Chitosan	*E. coli*	Tomatoes	[42]
Metal Nanoparticle (NP)	Zinc oxide (ZnO)	Gelatin-chitosan	*S. aureus* and *E. coli*	Chicken Cheese	[43]
	Titanyum oxide (TiO2) +Ag	Polylactic acid (PLA)	*E. coli, Listeria monocytogenes.*	/	[44]
	Cupper oxide (CuO)	Carbohydrate biopolymer	*Escherichia coli and Listeria monocytogenes*	/	[45]

	Cinnamon essential oil	Active paper	*Rhizopusstolonifer*	Sliced bread	[46]
	Thyme	Silk fibroin electrospun fibres	*Salmonella Typhimurium*	chicken meat	[47]
	Thymol and eugenol	Biodegradable polymer films: poly (lactic acid) , poly (butylene adipate-co-terephthalate) and poly (butylene succinate)	*E. coli, S. aureus, Bacillus tequilensis, B, subtilis and B. pumilis,*	/	[48]
	Oregano essential oil (OEO)	Resveratrol (RES) nanoemulsion loaded edible pectin coating	inhibiting microbial growth	fresh pork loin	[49]
	Citronella essential oil (CEO)	Chitosan + with ZnO and Ag nanoparticles	*S. aureus, E. coli C. albicans*	/	[50]
	Thymus vulgaris essential oil+ ethanolic extract Mediterranean propolis	Polylactic acid (PLA) film	*S. aureus and Penicillium sp Candida E. coli*	/	[51]
	Grape fruit seed extract	Agar/alginate/collagen hydrogel films	*L. monocytogenes, E coli.*	Potatoes	[52]
	Gallic acid, chitosan	Gallicacid/graftedchitosan films	/	Agaricus bisporus	[53]
	Salicylic acid (SA)	Chitosan films	*CS-SA coating inhibited chilling injury and increased the antioxidant enzyme activities*	Cucumber	[54]
Essansial oil and natural extracts	Ellagic acid	Candelilla wax matrix	significant reduction of *C. gloesporioides* and extended shlef life	Avocado	[55]
	Ferulic acid	Chitosan films	lower total counts, antioxidant and antimicrobial activities,	Pork	[56]
	Curcumin	Poly(butylene adipate-co-terephthalate) (PBAT) films	*E. coli L.monocytogenes*	/	[57]
	Cinnamaldehyde	Polylactic acid and starch films	*E. coli and L. inocua*	/	[58]
	Resveratrol and eugenol	Carboxymethyl cellulose films	*L.monocytogenes S. aureus, E. coli S.Enteritidis,*	/	[59]

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	Carvacrol	Cassava starch	*E. coli, S.Typhimurium Aeromonas, S. aureus*	Pumpkin	[60]
	Green tea extract	Chitosan film	*L. inocua and E. coli K12*	/	[61]
	Grape seed extract	Edible coatings and films based on Chitosan film	*L. inocua E. coli K12*	/	[62]
	Peony extracts (Paeonia rockii) dispersed in chitosan	Polysaccharide gels	Antifungal activity and extended shelf life,16 days	Strawberries	[63]
	Blueberry(*Vaccinium spp.)* fruit and leaf extracts	Chitosan coatings	*S. aureus, L.monocytogenes S. Typhimurium E. coli,*	fresh blueberries	[64]
	Tomato plant extract	Edible Chitosan coatings	reduced the mesophyll count during 15 days	Sierra fish fillets	[65]
	Sulphur nanoparticles	Chitosan film	*L.monocytogenes, E. coli*	/	[66]
Others	Chlorine dioxide	Polylactic acid (PLA) films	*S. aureus, E. coli*	/	[5]

2.2. The organic acids and salts

The organic acids such as benzoic acid, propionic acid, sorbic acid, lactic acid and acetic acid and their salts, which are used in antimicrobial packaging and have strong antimicrobial activity, are synthetic antimicrobial agents. For example, lactic acid salts, such as sodium lactate and potassium lactate, have greater inhibitory effects against gram-negative bacteria, while offering antifungal activity against some Aspergillus species. Potassium sorbate prevents bacterial spores from germinating. Lactic acid, sodium benzoate, citric acid or potassium sorbate, which have an active antimicrobial effect against bacteria, are included in food packaging materials or composites [13]. Morey et al. (2014), have shown that the sodium citrate compound inhibits the growth and reproduction of bacteria such as; *Listeria spp.* and *Escherichia coli O157: H7* [66]. The sorbic acid and potassium sorbate show activity against a broad spectrum of bacteria and mold [67]. Alcano et al. (2016) have found that the protective effect of sorbic acid at pH 6.0-6.5 is 5-10 times more durable than that of benzoate [68]. Many studies have shown that bacterial growth can be inhibited by organic acid-based food packaging and extend the shelf life of foods. Hu et al. (2017) have developed antimicrobial ethylene-vinyl alcohol copolymer (EVOH) films using sorbic acid-chitosan microcapsules (S-MPs) and applied them to fish fillets [69].

2.3. Bacteriocins

The bacteriocins and bacteria, the natural antimicrobial peptide produced by Archaea, have positively charged compounds and hydrophobic particles. These positively charged compounds act against the microorganisms by electrostatic interaction with negative charges of phosphate groups on microbial cell membranes. The most common bacteriocins are nisin, *pediocin PA-1, bacteriocin 7293, sakacin A, lactikin 3147A and enterocin AS-48* [13]. *Weissella hellenica BCC 7293*, isolated from Thai fermented pork sausage called Nham, produced two bacteriocin, called *bacteriocin 7293A and B*. These bacteriocins were stable in organic solvents, high pH and temperature ranges, and showed antimicrobial activity against pathogenic bacteria [70].

The bacteriocins are used in food packaging systems as adding bacteria that produce bacteriocin to food, adding bacteriocin directly to food or as bacteriocin-like substances. The bacteriocins are used in conjunction with other antimicrobials in food packaging as they are more effective against gram-positive bacteria. In recent years, Enterocin AS-48 has produced improved results in the packaging of chilled food products using bacteriocin-like substances or strains producing bacteriocin with modified atmosphere packaging. In addition, the combination of bacteriosine with other.

2.4. Natural extracts

The antimicrobial compounds extracted from various herbal sources such as onion, garlic, radish, mustard, clove, thyme, rosemary kernel and grapefruit seeds are used in packaging systems. Natural extracts and compounds in food packaging; Grapefruit seeds, kombucha and green tea extracts, gallic acid, lignin olive leaf, propolis and other plant extracts can be given as examples [71]. Research have developed multi-component antimicrobial agents, which are lysozyme, nisin, grapefruit seed extract (GFSE) and EDTA, working in different combinations. They found that GFSE-EDTA is a viable antimicrobial agent against pathogenic microorganisms in Na-alginate and K-carrageenan based films. In another study conducted with olive leaf extracts, high antimicrobial activity and antioxidant activity results were obtained. These results indicate that the extracts of food waste are suitable for synthesizing packaging [72].

Tong et al. (2018) have used alginic acid (ALG) particles and grapefruit seed extract (GFSE) as natural antibacterial agents to produce antibacterial food packaging. By incorporating ALG fragments and GFSE extract into Poly-P-caprolactone (PCL), a biodegradable polymer, they obtained a uniform and homogeneously biodegradable composite film. They proved that this film was very effective against *Pseudomonas aeruginosa*. Figure 1 shows to the natural extract samples.

Figure 1. The natural extract samples.

2.5. Essential oils

The essential oils and their components (EO) are substances with antimicrobial activity obtained from mixtures of volatile compounds from spices and herbs. It consists of a mixture of compounds such as terpenoids, esters, aldehydes, ketones, acids and alcohols, 85% of the basic components of EOs are oil and 15% are trace components. Especially, many packaging materials containing essential oil EO have been developed using bioactive substances, lemon grass, ginger, thyme, chamomile, tea tree, thymol, terpineol, carvacrol, and geraniol [73]. Encapsulating essential oils into nanoparticles and combining these nanoparticles with bio-based film to produce film nanocomposite is an effective strategy to control the release of essential oils [74]. Lee et al. (2016) have added antimicrobial thyme essential oil (TEO) to biodegradable skate skin gelatin (SSG) film [75]. While the tensile strength (TS) of the film decreased, elongation at break (E) increased with the addition of TEO. They found that SSG film containing 1% TEO inhibition of *L. monocytogenes* and *E. coli O157: H7* in packaging of chicken tenderloin samples. Issa et al. (2017) have synthesized potato starch/montmorillonite (MMT)

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activated with thyme essential oil (TEO) as nanocomposite film [76]. MMT was added to improve the mechanical properties of starch films. *E. coli* and *S. Typhi* volumes in spinach packaged with the resulting nanocomposite film decreased to detectable levels within 5 days after the EOs were included. Hager et al. (2019) have stored mixtures of nisin and lemongrass essential oil (LG) (8%), edible corn zein-based coatings and cold smoked smoke, polyvinyl chlorine (PVC) for 14 days and vacuum packaging at 42 days at 4 °C [77]. Samples treated with LG showed an antimicrobial effect in *L. monocytogenes* cell count by reducing 1.7-log in vacuum-packed samples and 2.5 log in polyvinyl chlorine. Boyacı et al. (2019) have targeted to prevent pathogenic bacterial contamination in fruit peels by covering eugenol (EUG), carvacrol (CAR) and thymol (THY) essential oil (EU) mixtures with zein edible films. By coating melons with zein-2 % EUG mixtures, it resulted in a marked and similar reduction in both L. innocua and *E. coli* counts on the melon surface during storage at 4 °C for 10 days [78].

2.6. The metal nanoparticles

The metal nanoparticles are used as antimicrobial agents because of their high thermal stability, long life and wide antifungal and antibacterial activity. The most commonly used nanoparticles include metal oxides (zinc oxide, titanium dioxide, aluminum oxide and magnesium oxide), metal ions (silver, gold, copper and platinum) and modified nanoclay [79]. These nanoparticles are used as active agents alone, as well as bacteriocins, essential oils and as a combination of several metal nanoparticles [80–83]. The safety assessment of the material, such as the migration limits of the nanoparticles in the nanocomposite packaging material, must comply with the legislation on materials in contact with food [84,85]. The antimicrobial effects of some metal nanoparticles in food packaging are shown in Table 2.

Gold et al. (2018) have tested the antimicrobial potential of triple biocomposite film based on hydroxypropyl methylcellulose/beeswax/tragacanth with pre-synthesized silver nanoparticles [80]. The nanocomposite film inhibited the growth of various pathogens such as *B. cereus, S. aureus, S. pneumonia, L. monocytogenes, E. coli, S. Typhimurium, P. aeruginosa* and *K. pneumonia*. Ebrahimi et al. (2019) have used silver (Ag), zinc oxide (ZnO) and copper oxide (CuO) metallic nanoparticles in the preparation of carboxymethyl cellulose (CMC) nanobiocomposite film. It was determined that the CMC nanobiocomposite films obtained had a roughness deviation level, the presence of Ag, ZnO and CuO nanoparticles in biopolymer tissue, reduced water vapor permeability (WVP) and increased absorption rate compared to pure CMC film [86]. Also, the addition of nanoparticles increased the tensile strength of the films, and nanobiocomposite films exhibited higher resistance than pure CMC film. Figure 2 shows the mechanisms of antibiotic resistance [87].

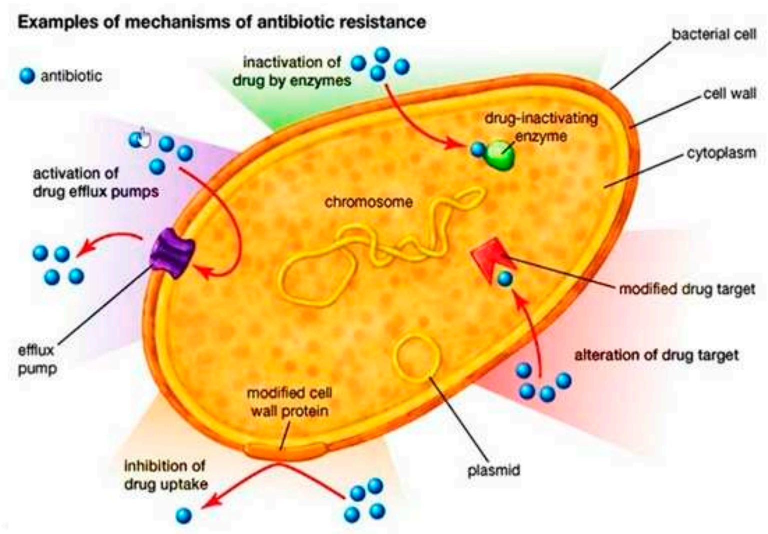

Figure 2. The mechanisms of antibiotic resistance.

Zare et al., (2019) have synthesized zinc oxide-silver (ZnO-Ag) nanocomposite (NCs) by biohydrothermal method using Thymus vulgaris (T. vulgaris) leaf extract [88]. The new degradable biopolymer (BP) nanocomposite was produced by using the solvent casting method to poly (3-hydroxybutyrateco-3-hydroxypyrate) -Citosan (PHBV-CS) without using surfactants or binders. In the analysis, morphology, physical, mechanical, barrier, antibacterial and migration properties of nanocrystals were evaluated. As a result, this bio-based nanocomposite extended food shelf life and maintained the safety and quality of poultry products, limiting the development of foodborne pathogenic bacteria.

Vishnuvarthanan & Rajeswari (2019) have prepared a carrageenan/silver nanoparticle (AgNP)/ Laponite nano composites and coated on an oxygen plasma surface modified polypropylene (PP) film to improve barrier and adhesion properties [89]. The carrageenan nanocomposites containing AgNP showed excellent antimicrobial activity against both Gram negative *E. coli* and Gram-positive *S. aureus*.

2.7. Bacteriophages

The phages or the bacteriophages, which are viruses that reproduce in bacteria, are widely found in different types of food. Lytic phages are viruses that can infect and lyse bacterial cells. Since they are specific to each host cell, they do not interact with other microorganisms or eukaryotic cells in the environment and therefore they do not cause disease in either animals or humans. The phages are used to prevent disease in farm animals, to remove fresh products such as fruits and vegetables from bacteria and to extend the shelf life of foods as a natural preservative [90]. Since phages are specific to a particular type of bacteria, their use in food packaging is chosen based on the main food-borne pathogen found in that food. Besides, instead of adding a single phage to the packaging material, phage cocktails are preferred [91]. Packaging materials containing bacteriophage in food packaging have been shown to effectively control pathogens such as *L.monocytogenes, S. enterica*, and *E. coli (Table 1)*. Due to polymer-antimicrobial chemical incompatibility, and, also antimicrobial instability problems, Bacteriocins, natural extracts, essential oils, phages, and some other antimicrobial agents have some difficulties with their incorporation into packaging films [92]. Figure 3 shows the mechanism of biosynthesis of NPs using algae [93].

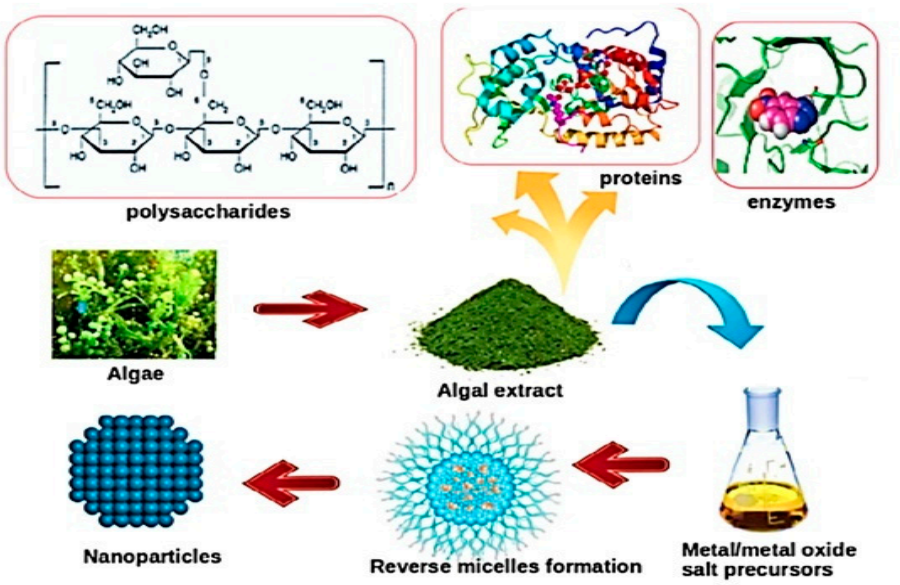

Figure 3. The mechanism of biosynthesis of NPs using algae.

Figure 4 shows the mechanisms of NP molecules in the bacteria cell [94]. In a study, the active ingredient of essential thyme oil with tubular clay nanoparticles, halloysite nanotubes (HNTs), was encapsulated for continuous release of carvacrol in packaging [95]. Wu et al. (2019) have used microscopic spherical vesicular phosphatidyl choline and cholesterol liposomes to control the release of laurel essential oil (LEO) and silver nanoparticles (AgNP) in the packaging [96]. The liposomes were mixed with chitosan, covered with polyethylene (PE) film and used to pack pork. Analysis results showed that only 29.30% of LEO and 11.79% of AgNPs were released from the liposome after 7 days at 25 °C. In addition, the liposome EO-AgNP coating showed good antioxidant and antimicrobial properties. According to another research, It was produced pectin films activated by antimicrobial marjoram essential oil charged nanoemulsions (NE) and pickering emulsions (PE). Tween 80's low molecular surfactant, whey protein isolate and inulin mixture were used for stabilization of solid particles in the preparation of emulsions. The obtained nanocarriers were added to the pectin film formulation and the morphological, physical and functional properties of the active films were analyzed. Shin & Lee (2018) encapsulated Phytoncide, a volatile, antibacterial compounds released from plants to the poly (vinyl alcohol) core with the emulsion electrospinning technique, thereby developing an environmentally friendly, antimicrobial nanofiber material with sustained release [97]. The core / sheathed phytoncide / poly (vinyl alcohol) nanofibers exhibited a well-aligned core / sheath structure with fiber diameters of 250-350 nm. They found that phytoncide was released from the core of nanofibers continuously for 14 days. The core/ sheath structured nanofibers were found to provide a 99. 9% bacterial reduction against *Staphylococcus aureus*, *Escherichia coli*. Abdou et al. (2018) investigated the extension of the shelf life of chilled chicken fillet using the nanoemulsion coating method [98]. Curcumin-cinnamon essential oil, curcumin-garlic essential oil and curcumin-sunflower oil were prepared as three different nanoemilions and pectin was added to the obtained coatings. Rheological properties of nanoemulsified pectin coatings showed shear thinning behavior. Curcumin nanoemulsion pectin coatings observed that the total number of bacteria in chickens, psychrophilic bacteria, yeast and mold growth decreased. In another research, curcumin, garlic, apple cider vinegar, pollen and chitosan were encapsulated and high antimicrobial and antioxidant activity was detected [99–101].

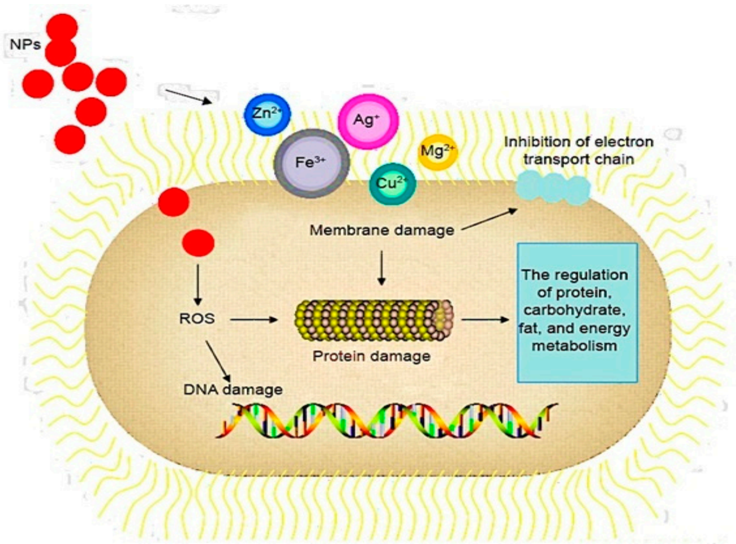

Figure 4. The mechanisms of NP molecules in the bacteria cell.

Cui et al. (2018) have encapsulated the tea tree oil (TTO) and beta-cyclodextrin (β-CD) inclusion complex into the poly (ethylene oxide) (PEO) matrix, using the electrospinning method to produce antimicrobial food packages [102]. The encapsulation efficiency of TTO in the inclusion complex reached 73.23% at 60 °C. As a result, they determined TTO antibacterial activity against *E. coli* at different temperatures for 7 days on beef. They found that TTO achieved an inhibition yield of 99.99% at 4 or 12 ° C, indicating that it can prolong shelf life on beef. Figure 5 shows types of antimicrobial agents used in edible packaging such as organic acids, essential oils, enzymes, and bacteriocins for protection of foods against microbial growth [103]. Table 2 shows to antimicrobial effects of metal nanoparticles in antimicrobial food packaging. Figure 5 shows to Types of antimicrobial agents used

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in edible packaging such as organic acids, essential oils, enzymes, and bacteriocins for protection of foods against microbial growth.

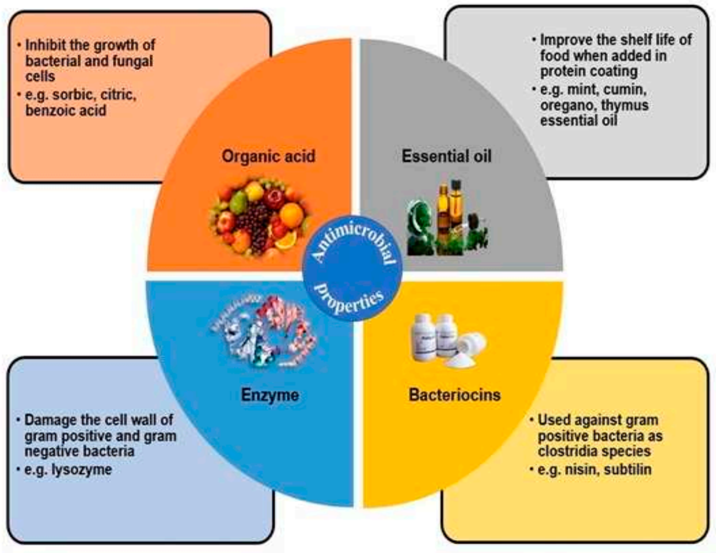

Figure 5. Types of antimicrobial agents used in edible packaging such as organic acids, essential oils, enzymes, and bacteriocins for protection of foods against microbial growth.

Table 2. Antimicrobial effects of metal nanoparticles in antimicrobial food packaging.

Metal Nanoparticle	*Packaging Material*	*Food product*	*Antimicrobial Results*	*References*
Silver (Ag) nanoparticle (NP) Ag NP's	Poly(acrylic acid) (PAA) nanofibers	Culture media	The PAA-silver nanofibers achieved Zones of growth inhibition of C. *albicans* fungi and Methicillin-resistant *Staphylococcus aureus* (MRSA) bacteria indicating their antimicrobial activity against both fungi and bacteria	[104]
	Agar hydrogel	Latte cheese	Ag-based nanoparticle packaging system inhibited the growth of *Pseudomonas* spp.	[105]
	Polystyrene (PS) matrix	Culture media	The PS/Ag nanocomposites exhibred antimicrobial effect against gram pozitive, gram negative, yeast and fungal test microbe	[106]
	Chitosans/montmorillonite nanocomposite films	Culture media	The nanocomposite-AgNPs films inhibited the growth of *Escherichia coli* and *Bacillus subtilis*.	[107]
	Carboxymethyl Chitosan	Culture media	The prepared antibacterial membranes were effective and killed all bacteria	[108]
	PVC-based film		PVC based films containing silver nanoparticle and quercetin confirmed to be higly effective in	[109]

Silver (Ag) nanoparticle+ quercetin		Culture media	inhibiting bacterial growth of food *pathogens (L. monocytogenes, E. coli, S. Typhimurium)*	
Gold nanoparticles (AuNP's)	Poly(vinyl) alcohol (PVA) crosslinked composite films	Banana	Banana shelf life has improved with PVA-glyoxal-AuNPs composite film	[110]
Silver nanoparticles (Ag-NP) and gold nanoparticles (Au-NP)	Chitosan nanocomposite films (CS)	Culture media	The prepared films were good antibacterial activity against *Staphylococcus aureus, Pseudomonas aeruginosa, Aspergillus niger, Candida albicans*	[111]
Titanium dioxide (TiO_2)	Poly(vinylpyrrolidone) (PVP) coated with alumina and titanium dioxide, hollow calcined titanium dioxide nanospheres (CSTiO2)	Culture media	Developed CSTiO2 hollow nanospheres exhibited higher antibacterial capacity against resistant *E. coli* strains, than S. *aureus* strains. when compared to commercial TiO2 nanoparticles, CSTiO2 nanospheres exhibited superior performance. In addition, the positive effect of UV irradiation on the antimicrobial activity was demonstrated.	[112]
TiO_2–ZnO nanoparticle	Low-density polyethylene (LDPE) films	Fresh calf minced meat	ZnO-coated LDPE film and TiO2 coated LDPE film showed an excellent antibacterial effect on *E. coli*. But Mixed TiO2/ZnO-coated LDPE films are not suitable option to inhibit *E. coli*growth.	[113]
Ag + organoclay NPs	Starch from yellow dent corn	Culture media	Bio-nanocomposite films was significantly inhibited the growth of *Escherichia coli* and *Staphylococcus aureus*.	[83]
Ag+TiO_2 + Attapulgite +SiO_2 NP's	Polyethylene (PE) based nanocomposite master batch	Rice	Nano packaging material was exhibrit antimicrobial effects and maintained low O2 and high CO2 content in the packages. The packages inhibited the growth of molds and the production of fatty acids and reduced the oxidation of fats and proteins.	[114]
Zinc oxide (ZnO) NPs	Starch-PVA composite films	Culture media	ZnO NPs were showed promising activity against *S. typhimurium.*	[7]
	Olive flounder bone gelatin (OBG)	Spinach	OBG–ZnO film was showed antimicrobial activity against *L. monocytogenes* inoculated on spinach without affecting the quality of spinach, such as vitamin C content and color.	[115]

	Polylactic Acid (PLA)	Culture media	decreased in *E. coli* growth by 3.14 log for 0.5% ZnO loading in the PLA coating layer	[116]
Silver (Ag)-Cupper(Cu) NP	Polylactide with cinnamon essentiol oil	Chicken meat	PLA composite films showed strong antimicrobial activity against *Salmonella Typhimurium, Campylobacter jejuni* and *Listeria monocytogenes* on contaminated chicken meat samples during 21 days at 4 °	[117]
MgO NP's	Carboxymethyl (CM)-Chitosan CS	Culture media	CM-CS/MgO nanocomposite films exhibited antimicrobial activity against *L. monocytogenes* and *Shewanella baltica*	[118]
Selenium nanoparticles (SeNPs)	Potato starch film	Culture media	The SeNPs/potato starch nanofilm inhibited growth of *Salmonella Typhimurium* and *E. coli*, slightly inhibited *B. cereus*, but no inhibition occurred with *L. innocua.*	[119]
Silica nanoparticles (SiO2)	Poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)	Culture media	The antibacterial activity of PHBV/SiO2 (2.0%) nanocomposites ,94.7% growth inhibition for *E. coli* and 92% for *S. aureus*	[120]
Aluminu+ doped zinc oxide (AZO)	Polylactic Acid (PLA)	Culture media	Great antibacterial activity against *E. coli*	[121]
Zinc oxide–silver nanocomposites (ZnO–Ag NCs).	Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)-chitosan (PHBV-CS)	Culture media	The nanocomposites PHBV/Ag–ZnO (10%) showed great antimicrobial activity potent against *S. aureus* and *E. coli* if compared with nanocomposites Ag-ZnO 5%, 3% and 1%	[122]

3. The Antimicrobial Packaging Methods

The homogeneous distribution of the antimicrobial agent into the film or coating, improving the mechanical and barrier properties of the films, and the good antimicrobial activity of the film are the main features expected from the packaging films. Today, as antimicrobial packaging methods, systems such as adding pouches or pads containing antimicrobial agents into the packaging, coating or adsorbing of volatile / non-volatile antimicrobial agents to the polymers, coating or adsorbing antimicrobials to the polymer surface, and using polymers with antimicrobial properties are used.

3.1. Adding sachets or pads containing antimicrobial agents to packages

The oxygen absorbers, moisture absorbers and ethanol vapor generating vesicles or pads are most commonly used commercially in antimicrobial packaging. Antimicrobial sac or pads can be loosely or closedly attached to the packaging [123]. In the packaging of freshly cut tomatoes; Antimicrobial vesicles were successfully applied by adding different types of essential oils to vesicles to prevent deterioration and growth of pathogenic bacteria [124]. In the study of Agrimonti et al.,

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(2019), they examined the antimicrobial effects of cellulosic pads prepared with emulsions containing thyme and oregano essential oils and the effect of packaged meat on shelf life [125]. Marques et al. (2019) aimed to obtain antimicrobial vesicles that can be used as preservatives for foods. Basil (BEO) and Pimenta dioica (PDEO) essential oils (EO) and food-borne pathogen *S. aureus, E. coli, L. monocytogenes, P. aeruginosa, S. Enteritidis* bacteria and degrading agent were tested against *B. nivea* [126].

3.2. Addition of antimicrobial agents directly into the polymer

The antimicrobial agents are used directly or by adsorbing with different solvents and by incorporating into edible film, polyethlene or polymers such as various polyolefins. It is used with polymers such as 1-3% silver-added zeolites that disrupt the enzymatic activity of microbial cells, polypropylene, polyethylene, butadiene styrene and nylon. The antimicrobial enzymes such as lactoferrin and lactoperoxidase, magainins, kropin natural phenols, antioxidants, metals such as copper and antimicrobial peptides have a wide application in polymer application. Edible films combined with niacin or lysozyme cause inhibition of *E. coli* when combined with chelating agents such as EDTA [127]. Yu et al. (2018) have synthesized a biodegradable composite film containing polyvinyl alcohol (PVA) / chitosan (CS) in their study. However, this film has poor mechanical properties and new film has been developed by adding sodium metasilicate to the solution of silicon oxide (SiO_2), PVA and CS [128].

3.3. The coating of antimicrobial agent on polymer surface

If the antimicrobial substance is heat sensitive, the polymer may lose its activity at high temperature in shaping. Therefore, the antimicrobial agent is incorporated by coating the previously shaped polymer surface [129]. The edible coating is a thin layer of edible material that is applied to the surface of food to control the exchange of food, gas, moisture, and dissolved substances with the environment [130]. High antimicrobial activity of chitosan nanoparticle coatings against mold, yeast, mesophilic and psychotrophic bacteria in the apple slice was observed. Nabifarkhani et al. (2015) have found that the development of mushrooms was delayed in sweet cherries coated with thyme oil and nano composite coatings [131]. Vishnuvarthanan and Rajeswari (2019) have prepared carrageenan/silver nanoparticle (AgNP) / Laponite nano composites and coated on oxygen plasma surface modified polypropylene (PP) film to improve barrier and adhesion properties [88]. Mechanical, barrier, adhesion and antimicrobial properties were also investigated for use in food packaging applications. The carrageenan nanocomposites with AgNP showed excellent antimicrobial activity against both Gram negative *E. coli* and Gram-positive *S. aureus bacteria*. In another study, In vitro cytotoxicity analysis and synthesis of biocidal Allen/Mt/Mma/Peg/Poss Nanocomposites for food packaging was performed and high surface activity results against bacteria were obtained [82].

3.4. Addition of the antimicrobial agent to the polymers

In order for the antimicrobial agents to be immobilized to the packaging polymer, both antimicrobial and polymer must have functional groups. Antimicrobial agents that have functional groups are peptides, some enzymes, organic acids and polyamines. The polymers with functional groups are ethylene methyl acrylate, ethylene vinyl acetate, ethylene acrylic acid, nylon, polystyrene, ionomer, etc. These materials do not migrate to antimicrobial food by immobilization of antimicrobial and their activity is limited only by the food contact surface. It is suitable for the packaging of liquid foods, as packaging with the food provides good contact [132]. Conte et al. (2008) have incorporated the antimicrobial enzyme lysozyme into a plasma-treated polyethlene (PE) film by chemical immobilization [133]. The films treated with lysozyme-loaded plasma exhibited antimicrobial action against *Micrococcus lysodeikticus*. Figure 6 shows the schematic to Show antimicrobial mechanism of action according to the literature [134].

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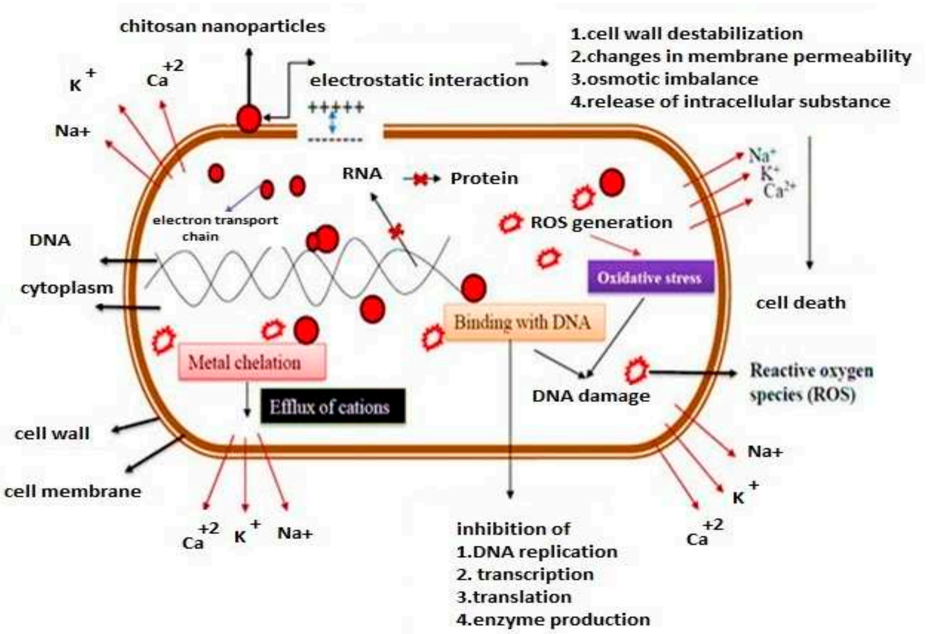

Figure 6. The schematic to show antimicrobial mechanism of action.

3.5. The natural antimicrobial polymer

The polymers such as chitosan and poly-L-lysine cationic polymers that are naturally antimicrobials are used in films and coatings. The antimicrobial effect, on the other hand, cationic charges in chitosan compete with calcium in the electronegative regions on the cell membrane surface of the bacteria and inhibit the bacterial cell. The calcium alginate films show antimicrobial activity due to the calcium chloride in its structure. It also has antimicrobial properties of polyelectrolytes (polycations and polyanions), which are some bio-based polymers [135–137]. Electrospinning chitosan in the form of nanofibers is a promising process that has been widely researched. Arkoun et al. (2017) have produced chitosan and poly (ethelen oxide) based nanofibers by electrospinning to prevent spoilage of meat and growth of pathogenic bacteria such as *E. coli, S. enterica serovar Typhimurium, S. aureus and L. innocua* [138]. Yadav et al., (2020) developed chitosan-gelatin (Ch-ge) biocomposite films (Ch-ge-Q) containing Quercetin-starch (Q) according to the solution casting method [139]. Pavoni et al. (2019) determined the effect of the acid type used for chitosan solubility and the starch: chitosan ratio on the properties of corn starch-chitosan based films. In another study, zataria multiflora essential oil (ZEO) enriched propolis extract (PE) was coated with chitosan (CH) to determine the effect on the chemical, microbial and organoleptic properties of poultry meat [140].

4. Conclusions

Nowadays, consumers prefer healthier, fresh and minimally processed, high-quality, safe and long-lasting foods. The purpose of antimicrobial packaging, which has emerged as an active packaging technology, is to achieve controlled release of the antimicrobial substance added to the packaging material or atmosphere into the foods. Thus, it will be possible to ensure food safety by inhibiting microorganisms that affect food deterioration, and to protect food longer and more actively by preserving quality and sensory properties. In antimicrobial food packaging, methods such as adding vesicles / pads containing antimicrobial agents into the packaging, adding antimicrobial agents to packaging films and coatings, and using antimicrobial polymers are used. In recent years, great efforts have been made to develop more efficient, long-lasting and environmentally friendly antimicrobial packaging materials by increasing the performance of antimicrobial agents. For this purpose, more effective antimicrobial compounds of natural origin such as essential oils, natural extracts, bacteriocins and biopolymers are preferred instead of chemical antimicrobials such as organic acids, nitrates, sulfites. The current studies such as the antimicrobial agents are resolutely incorporated into the packaging materials, providing continuous antimicrobial effect to the food with a more controlled release and protecting these antimicrobials from deterioration or evaporation. This review includes current research on the different types of antimicrobial agents that can be included in food packaging systems and their antimicrobial effects in foods and antimicrobial packaging methods. According to the literature research findings, one of the most effective methods used to extend the shelf life of foods is that bioactive components, metals and other active ingredients show higher antimicrobial and antioxidant effects on nanosurfaces by encapsulation methods. The techniques used in this sense have a very important place in extending the shelf life of foods and synthesizing antimicrobial food packaging. It is observed that there is a significant increase in the in vitro, biocompatibility and antimicrobial effects of packaging films. However, as it is known, there are many encapsulation techniques. Among these methods, electrospinning methods are considered to be quite efficient. This review shows that the biomaterials used in packaging can extend the shelf life of foods and offer healthier foods to the consumer. In particular, packaging films synthesized as a result of encapsulation of biodegradable polymers and biomaterials give the consumer the chance to consume much healthier food. This review offers many suggestions to improve the awareness of consumers. The most important of these suggestions is to be more selective in consumer perception, which affects health in the packaging as well as the consumed foods.

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Abbreviations

EDTA:Ethylenediaminetetraacetic acid; CNF: cellulose nanofibers; UF: ultra-filtered; LPS: Lipopolysaccharides; HOSCN: hypothiocyanous acid; SH: sulfhydryl; PE: poly ethylene; LDPE: low density poly ethylene; HDPE: high density poly ethylene; PVOH: polyvinylalcohol; PLA: Polylactic acid; EVOH: ethylene-vinyl alcohol; S-MPs: sorbic acid-chitosan microcapsules; GFSE: grapefruit seed extract; ALG: alginic acid; PLC: Poly-P-caprolactone; EO: essential oils; TEO: thyme essential oil; SSG: skate skin gelatin; LG: lemongrass; MMT: montmorillonite; TS: tensile strength; EUG: eugenol; CAR: carvacrol; THY: thymol; CMC: carboxymethyl cellulose; ZnO-Ag: zinc oxide-silver; NC: nanocomposite; PHBV-CS: poly (3-hydroxybutyrateco-3-hydroxypyrate) –Citosan; HNTs: halloysite nanotubes; PEO: poly (ethylene oxide) ;TTO: tea tree oil; β-CD: beta-cyclodextrin; PAA: poly(acrylic acid); MRSA: Methicillin-resistant; CSTiO2: calcined titanium dioxide nanospheres; OBG: Olive flounder bone gelatin; PDEO: Pimenta dioica

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