



Smart Food Packaging Designed by Nanotechnological and Drug Delivery Approaches

Ludmila Motelica¹, Denisa Ficai^{1,*}, Ovidiu Cristian Oprea¹, Anton Ficai^{1,2}, and Ecaterina Andronescu^{1,2}

- ¹ Faculty of Applied Chemistry and Material Science, University POLITEHNICA of Bucharest, Spl. Independentei 313, 060042 Bucharest, Romania; motelica_ludmila@yahoo.com (L.M.); ovidiu.oprea@upb.ro (O.C.O.); anton.ficai@upb.ro (A.F.); ecaterina.andronescu@upb.ro (E.A.)
- ² Academy of Romanian Scientists, Ilfov st. 3, 050045 Bucharest, Romania
- * Correspondence: denisa.ficai@upb.ro

Received: 13 July 2020; Accepted: 13 August 2020; Published: 20 August 2020



Abstract: This paper offers a general view of the solutions that are able to confer bioactivity to the packaging materials, especially antimicrobial and antioxidant activity. These properties can be induced by the nature of the polymers blend or due to the addition of ternary components from natural agents (essential oils or other extracts) to synthetic organic and inorganic agents, including nanoparticles with a broad antimicrobial activity such as metals (e.g., *Ag*, *Au*, *Cu*) or metal oxide (e.g., TiO₂, ZnO) nanoparticles, and even bacterial cells such as probiotics. Many times, these components are synergistically used, each of them assuring a specific role or potentiating the role of the other components. The antimicrobial activity can be induced due to the applied coatings or due to the whole bulk material. Along with an increasing food stability which means a longer shelf-life some smart packaging can be exploited in order to highlight the freshness of the food. These act as a sensor (usually pH sensitive but also other mechanisms can be exploited such as aggregation/agglomeration of AuNPs leading to color change or even aldehyde-specific reactions such as the Cannizzaro reaction), and thus, consumers can be confident about the freshness of the food, especially perishable food such as seafood or fish.

Keywords: polymeric nanocomposite; food packaging; antimicrobial packaging; food freshness monitoring; smart packaging

1. Introduction

Worldwide, approximately 33% of the food production made for human consumption gets lost or wasted. Food losses are about the same regardless of country. While in developing countries more than 40% of food losses occur after harvest and at the processing level, in developed countries more than 40% of losses are at the retail and consumer level.

Currently, nanocomposites are used in many medical and industrial applications, but also increasingly used in food packaging. An extensive research on the use of nanocomposite materials has been conducted in the food industry with a main purpose of increasing the shelf life of food and minimizing the losses, being known as highly susceptible to bacterial/fungal contamination. The main purpose for the use of polymeric materials in the food industry is the production of packaging that protects food from adverse environmental conditions (dust, gas, light, and moisture), pathogenic micro-organisms, or chemical contamination during storage and distribution. Food packaging should be able to ensure the quality and safety of food throughout the distribution chain, but also during storage, including the shelf storage. In order to be used as food packaging polymeric materials must be safe to have a low production cost, to be inert, easy to dispose of, and reuse. Unfortunately, the bulk of

packages used today are not bio-degradable and this presents an increasing unacceptable environmental hazard. In addition, the mechanical, electrical, thermal, optical, and electrochemical properties of these nanostructured materials will differ significantly from those of the component materials. These are essential for assuring the expected shelf life, food quality, and safety parameters [1,2].

Food packaging is used as a protective barrier in the food industry. In addition, the demand for packaging materials is constantly growing according to the specific requirements request to each type of food. In this sense, the food packaging industry is dynamic and futuristic, which gives rise to the expansion or evolution of new processes and technologies for obtaining superior quality packaging materials.

According to the European Regulation (EC) —No. 1935/2004, good packaging must have a set of functions such as protection of food from a number of destructive or harmful substances (dirt or dust, oxygen, light, pathogenic microorganisms, moisture), to be inert, cheap to produce, easy to remove, or reuse. An optimal packaging must withstand extreme conditions during processing or filling, impervious to a lot of storage and transport conditions in the environment [3]. Many times, these functions are obtained by using natural or synthetic polymers loaded with nanoparticles and biological active agents.

Nanomaterials applied in packaging and food safety are in various forms, from bioactive bulk to bioactive coatings. The bioactivity is usually conferred using different active agents: Natural or synthetic biocides including essential oils and natural extracts; nanoparticles including metallic and metal oxide nanoparticles, etc. The antimicrobial activity can be assured by various mechanisms, by contact, or by release. Nanoparticles encapsulation is one of the mechanisms employed and can confer new properties to the surface, such as inducing antimicrobial or even antibiofilm capacity. Due to the excellent physico-chemical properties but also the antimicrobial potential of these nanomaterials, they are widely used against various pathogens (most of the microorganisms, viruses, or fungi) in medicine, water treatment, crop protection, food safety, and food preservation [3–9]. Usually, the antimicrobial activity of these nanoparticles is considered to be caused by the damage of the microbial membranes, oxidative stress, or the denaturation of the proteins [10]. It is also important to mention that a wide range of biological active agents, synthetic and natural agents (essential oils and natural extracts) are increasingly used in order to develop drug delivery systems or antimicrobial surfaces, and this technology is slowly directed also to create bioactive food packaging materials [3,5,11–15].

The current review is intended to highlight the main advances in the field of smart food packaging. We will discuss the polymeric supports used in developing food packaging and the obtaining of nanocomposites loaded with nanoparticles and biological active agents (natural and synthetic agents) in order to induce specific properties and performances. Moreover, we will identify and discuss further perspectives in this field. The main presented solutions will take into account the advances provided by the use of nanotechnology, as well as the drug loading and delivering in assuring a longer shelf life and safer food (limiting the risk of infections) and sensor development in order to monitor the freshness of the food. A current trend in the field is related to combining two antimicrobial mechanisms such as exploiting the synergism of the use of nanoparticles and the use of biological active agents (such as natural extracts or essential oils) to potentiate the activity. Furthermore, the antimicrobial activity can be combined with the antioxidant activity, and on top of them a sensorial evaluation can be added (usually based on colorimetric change) of the freshness of the food. From the point of view of the antimicrobial activity, four main classes will be discussed according to the mechanism of inducing bioactivity.

2. Native Bioactive Polymers as Packaging Materials

As the literature data show, polymeric food packaging is divided into two classes: Biodegradable and non-biodegradable. Although non-biodegradable polymers are the most widely used, they cause a great deal of environmental pollution, in the long term, and therefore, biodegradable polymers are more promising as they are green, renewable, and environmentally friendly. It is well known that,

worldwide, the use of non-biodegradable polymers was drastically reduced and additional limitations will be imposed in the near future [16,17].

There are several bioactive polymers which can be used in developing food packaging. According to the literature, these bioactive polymers can act as antimicrobial, antioxidant, water and oxygen barriers/scavengers, and thus increase the shelf life with limited food degradation. Along with the native activity, the performances can be improved by loading additional components. These food packaging materials are developed for contact with food according to the existing regulations [18–20].

Chitosan is a promising biopolymer with increasing applicability in many applications, especially in medicine but also in food packaging. This high interest for chitosan is given by several characteristics such as biocompatibility and no toxicity; abundant and natural origin, being a derivative of chitin, a polysaccharide backbone with a polycationic structure (Figure 1); the ammonium groups being responsible for the antimicrobial activity of the polymer; high water adsorbing capacity; biodegradability; etc. Due to these properties, chitosan is used in many medical and non-medical applications, as presented in Figure 1. In food industries, chitosan is used because of its native antimicrobial activity which makes it suitable for the developing food packaging materials to be able to extend the shelf life of both vegetables and fruits, as well as meats and many other food up to tens of days [19,21–31].



Figure 1. Chitosan protonation and its derived applications.

The antimicrobial activity can be even potentiated by chemical modification because the polycationic structure of the chitosan is only present if the pH is slightly acidic [32–41] or by blending it with other polymers [42–44]. By alkylation, the chitosan can be transformed in its derived ammonium salt which is active (antimicrobial) in most biological conditions (such as pH and ionic strength). For instance, Belalia et al. [33] reported the chemical modification of chitosan in order to improve the antimicrobial activity by alkylation with alkyl iodide to the NNN-trialkylchitosan. This support was tested against *Listeria monocytogenes* and *Salmonella typhimurium* and the conclusion was evident, the antimicrobial activity being well improved. Therefore, starting from this quaternized chitosan, polymeric blends were also obtained [37,38] and proved to have some important advantages because of the composite nature of the blends. Usually some mechanical properties, water vapor and oxygen permeability, water resistance, transparency, and especially the shelf life can be improved. The last property is, in fact, a consequence of the previous properties.

Recent studies [45–47] revealed that exopolysaccharides (EPS) from lactic acid bacteria are also suitable for developing active food packaging. These EPS are beneficial in improving food

texture, increasing health benefits, and especially inhibiting the growth of common pathogens from food [48]. The most important representatives of this class are dextrans, levans, kefirans, and hyaluronic acid. For instance, Kefiran and EPS extracted from the *Lactococcus lactis F-mou* strain exhibit strong antibacterial activity against several common pathogens and spoilage microorganisms while mannan EPS produced by *Weissella confusa MD1* and *Lact. fermentum S1* highlight a strong anti-biofilm capacity [45,47,49,50].

Starch, citric pectin, and feijoa peel flour (Acca sellowiana waste by-product) were used in order to develop bioactive food packaging, the antimicrobial and antioxidant behaviors being induced by the presence of the flavonoids and phenolic compounds. The addition of the feijoa peel flour is also beneficial up to 1% leading to improved mechanical properties, while starting from this composition the antimicrobial activity against *E. Coli* is already evident. By increasing the content of feijoa peel flour, the antimicrobial activity can be highlighted also against Salmonella typhimurium (above 2%) and against P. aeruginosa (above 3%) [51].

K-carrageenan can be used alone or in association with several biopolymers such as lignin [52], cellulose [53,54], and egg white protein [55] in order to develop bioactive food packaging. The K-carrageenan/lignin reveals improved thermal and mechanical properties, almost 100% UV protection, but a limited water vapor barrier. Due to the presence of lignin, a promising radical scavenging effect can be highlighted along with important anti-biofilm properties against *S. Aureus* and *S. Epidermis*. Based on these properties, the as obtained food packaging can be efficient in biomedical applications, but also in food packaging [52]. Egg white protein/k-carrageenan composite film [56] was proposed for oil packaging having suitable mechanical properties, but limited water vapor permeability and especially water solubility. Due to the improved oxygen permeability (10.85%) and especially the light transmission (53.3%) these edible films can delay the rancidity of oils during storage. Reinforcing K-carrageenan with cellulose nanocrystals (up to 9%) improved the mechanical properties, the water vapor and UV barrier can be enhanced, and these properties recommend these composite films for food packaging [54].

Starch—K-carrageenan blends were used in order to develop edible coatings on the grapes. The performances of the coatings/films are dependent on the composition while based on the analyses it can be concluded that the use of these systems can lead to an improved quality of the grapes, namely the vitamin C content is higher while the mass loss is lower (improved barrier properties) but also the sensory evaluation (color and texture) indicates significant improvements, which recommend the use of these blends as edible coating [57].

With several exceptions, peptides and proteins are not antimicrobial or antioxidant but can form suitable films able to prevent the loss of moisture and flavors to control the gas exchange (including oxygen carbon dioxide and ethylene) and certainly, can be loaded with most bioactive agents (for instance, antimicrobials, antioxidants, or nutraceutical). Just for comparison, protein films act as an oxygen barrier, having the oxygen permeability of 260, 500, 540, and 670 times lower than that of low-density methyl cellulose, polyethylene, starch, and pectin, respectively [58].

Proteins and a special gelatin of different origin can be used in developing food packaging. Fish gelatin is especially used because it can be a good alternative for the synthetic polymers as well as for all the consumers, including vegetarians. Gelatin is a bioactive material that is able to maintain food in proper conditions because of its excellent oxygen and fragrance barrier, but limited water barrier features, while the mechanical properties are usually lower compared with the mostly used synthetic polymers [42]. Starting from these characteristics, gelatin is often blended with other polymers (such as chitosan, poly(lactic acid), cellulose) or loaded with different reinforcing agents (such as nanoclays, ZnO, TiO₂, MgO, Ag NPs) or different biological active agents (especially essential oils and natural extracts). It is important to mention that gelatin, alone or in association with other polymers, can be also used in developing coatings on different food such as fish (trout, golden pomfret) fillet [43,44].

Bioactive packaging materials can be also obtained by using fish derived peptides (fraction with molecular weight of 3–10 kDa) and chitosan-polyvinyl alcohol as a film forming material,

by electrospinning. The presence of fish-derived peptides induces an antioxidant activity proportional with the release rate of the antioxidant peptides.

Sodium alginate is a film forming polysaccharide which is extensively used in the food industry. The alginate films reveal some specific properties that recommend them as food packaging, including the barrier properties against water vapor and oxygen, no toxicity, tasteless, and odorless, that is being extensively used in meat packaging preventing mass and color loss as well as gas exchanges. It is compatible with most of the antimicrobial agents and thus can prevent the contamination with the most common bacterial strains [59].

Waxes are exploited in the food industry because they are mixtures of compounds strongly dependent on the origin (usually containing esters, but also alcohols, fatty acids, hydrocarbons) revealing low water solubility, good barrier properties (both oxygen and water vapor), and thus are being used in bioactive food coatings. Depending on the composition, some of these waxes can bear antimicrobial activity and one of the most representative is the beeswax, its antimicrobial activity is being assigned to propolis. Pinto et al. [60] presented the antimicrobial activity of Abeego food wrap (a beeswax based product along with tree resin and oils, both as minor components), the coating is being realized using a propolis-rich fraction of the beeswax. According to their study, Abeego food wrap exhibited a strong antibacterial activity against some representative Gram-positive and Gram-negative bacteria (*Salmonella entritidis* and *Staphyloccocus aureus*) but not against fungal or viral strains.

Carnauba wax is extracted from the leaves of the carnauba (*Copernicia prunifera*), a Brazilian palm being one of the hardest waxes and having the highest melting point of any commercial natural wax, being approved for food applications by FDA, FAO, and EU. The main components of the wax are the aliphatic esters and diesters of cinnamic acid that possess both antioxidant and antimicrobial activity as well as an important UV barrier capacity. According to the CODEX *Alimentarius*, it is allowed for use in the food industry, including the surface treatment of fresh vegetables (such as mushrooms and fungi, roots and tubers, legumes, and aloe vera) but also for seaweeds, nuts, or seeds—up to 400 mg/kg of food. In EU, carnauba wax is allowed up to 200 mg/kg of food as coating for food supplements, snacks, nuts, coffee beans as well as for the surface treatment of the fresh citrus, melons, apples and pears, peaches, and pineapple [61].

Synthetic materials can be also exploited as an active film forming material for food packaging. For instance, polyesters obtained by homopolymerization of eugenol-bearing L-malic acid-derived carboxyanhydride or co-polymerizations with lactic acid can reveal biological activity if proper groups are linked. It is already well known that the ammonium moieties from chitosan are responsible for the antimicrobial activity, and its activity can be improved by alkylation—the quaternized ammonium salts are stable over a wide range of pH [33]. The as obtained homopolymer with a molecular weight of about 3200 g/mol (determined against the polystyrene calibration curve) exhibit antibacterial activity against *S. aureus* and *B. cereus*, and at a minor extent, against *P. aeruginosa* but no activity against *E. coli*. [62].

3. Nanostructured Polymers as Packaging Materials

Polymer nanocomposites (PNCs) are of real interest because along with the bioactivity induced by the components (or by the polymer itself), these materials due to the composite nature can exhibit some improved physical, chemical, biological, mechanical, electrical, and optical properties compared to individual components [63]. Due to the innovative properties such as maintaining the quality and safety of food but also increasing the shelf-life of the food, nanocomposite packaging has great potential as an innovative food packaging technology. The polymer nanocomposites used in developing food packaging materials are mainly composed of the polymer matrix, nanofillers, plasticizers, and compatibilizers.

One of the most practical uses of nanocomposites in food packaging is the addition of nanosized components to traditional packaging materials, such as metals and metal oxides nanoparticles, zeolites, glass, but also organic polymers cellulose, various synthetic plastics such as PE, PP, PS, PVC, etc.

The use of nanofillers in the preparation of bioactive packaging films has also been the subject of

numerous recent studies [12,64–74]. Several types of nanoparticles are exploited in food packaging materials because these can induce some advantages, especially, antimicrobial activity, but also can tailor the mechanical properties, gas and water vapor barrier, etc. [65–72]. These properties are strongly correlated with the nature and content of the nanoparticles.

Kumar et al. [75] used silver nanoparticles in order to obtain biodegradable hybrid nanocomposites based on a chitosan/gelatin/PEG blend. It is important to mention that the proposed composition can be used in protective packaging materials that are able to extend the shelf life of the red grapes by 14 days because of the antimicrobial activity and control of the gas and moisture barrier.

You et al. [73,76] studied the influence of silver addition in cellulose based materials using a chemical reduction method with NaBH₄ and an ultraviolet reduction method. Regardless of the reduction method and consequently regardless of the characteristics of the nanoparticles (28 nm for the UV-reduction method and ~11 nm for the chemical reduction method) these films highlight the antimicrobial activity against *E. coli* or *L. Monocytogenes* without affecting the toxicity against Caco-2 and FHC colon cells. It is important to mention that due to the low level of Ag (usually up to 1000 ppm), there are only marginal changes of the other properties of the films, but the slight color change and the important antimicrobial activity lead to an improved shelf life.

Nano-TiO₂ can be also used in obtaining nanostructured food packaging materials based on hydroxypropyl methylcellulose with the antimicrobial activity. It is important to mention that the best results were obtained by adding bovine bone collagen, perhaps due to the compatibilizing effect between nano-TiO₂ and hydroxypropyl methylcellulose. Due to the higher loading of the nano-TiO₂ compared to AgNPs, the addition of the oxide induces also a reinforcing role and thus some mechanical properties, thermal stability, color as well as barrier properties are improved when bovine collagen is used [65].

Copper oxide is also used to induce bioactivity to the food packaging materials. Starting from sodium alginate, cellulose nanowhiskers and embedding CuO nanoparticles antimicrobial packaging materials can be obtained against a wide range of pathogens such as: *S. aureus*, *E. coli*, *Salmonella* sp., *C. albicans*, and *Trichoderma* spp., the inhibition diameter being significant 27.49 \pm 0.91, 12.12 \pm 0.58, 25.21 \pm 1.05, 23.35 \pm 0.45, or 5.31 \pm 1.16 mm, respectively [66].

ZnO is extensively used in many applications involving biomaterials and food packaging materials because ZnO is nontoxic at a level that can confer an antimicrobial effect [77,78], the released Zn²⁺ being even beneficial as an oligoelement that can act as a cofactor for several enzymes. Different polymers or polymer blends were associated with ZnO in order to improve the shelf life of vegetables, fruits, cakes, or other food [67,79]. Again, the higher content of ZnO (1%–5%) usually leads to the change of the moisture balance, oxygen, and water permeability but also mechanical properties of the films. ZnO can be also associated with graphene oxide and the final composite food package membrane exhibits strong antibacterial activity against foodborne pathogenic and spoilage bacteria, leading to safer food products and improved shelf-life [80].

When considering the food packaging loaded with nanoparticles, it is important to consider the potential associated risks. This is why increasing attention is paid to the safety issues, and in the last years regulations were released in order to protect the consumers against these risks. For instance, the EU regulation 2016/1416 imposes a maximal limit of 5–25 mg Zn/kg food. Moreover, this value should be correlated with the tolerable upper intake limit of 40 mg/day Zn for the human body [81,82]. Taking into account these values, the amount of ZnO added as a food additive or as an antimicrobial agent in food packaging should be well below these values. For instance, alginate based nanocomposites commonly used as food packaging containing up to 0.5 g/L ZnO NPs can be used without a risking of overpassing this limit [83]. When LDPE-ZnO nanocomposite films are used for food packaging, the migration of Zn²⁺ is much lower so, even 3.5 mg Zn/L can be used without inducing any risks over the human health [84]. Unfortunately, these values are relative because many factors affect the release rate. Some factors are related to the packaging materials themselves, others are related

to the food while also the environmental conditions can change the release behavior. For instance, Heydari-Majd et al. [85] highlighted the influence of the presence of essential oils over the migration rate of Zn^{2+} for the polylactic acid/ZnO systems, the release rate being enhanced. Similar conclusions can be found also for several other nanomaterials usually loaded into the food packaging such as TiO₂, Ag NPs, carbon nanoparticles/nanotubes, etc., which after reaching the blood circulation, can be accumulated selectively and induce diseases at the brain, testes, and foetuses (in utero) level [86].

4. Drug Delivery Systems as Packaging Materials

The antimicrobial abilities of food packaging depend on many factors including the nature of the material as well as the use of antimicrobial agents. A wide range of natural and synthetic antimicrobial agents are known, some of them being used in developing food packaging. Along over 50 years of use a wide range of antimicrobial agents have been extracted from natural sources (polyphenols, glycopeptides, aminglycosides, macrolides, quinolones and flouroquinolones, natural antibiotics, etc.) because they are relatively safe and easy to obtain [87,88]. Several extraction methods can be employed such as solvent extraction, distillation, pressing and sublimation, solvent extraction being one of the most used. In certain cases, the conventional solvent extraction methods such as maceration, percolation, or reflux extraction are not efficient, and more complex and eco-friendly methods should be used, such as super critical fluid extraction, pressurized liquid extraction, subcritical water extraction, and microwave assisted extraction or ultrasound assisted extraction [89–97]. It is important to mention that along with the increasing use of the antimicrobial agents, the amount of the natural agents tend to be insufficient. Thus, synthetic organic or inorganic alternates have been developed. Synthetic organic materials including EDTA but also fungicides, parabens, and other chemicals, some of them being not well received by the consumers, have been developed [18,88]. Antimicrobial agents can act according to more mechanisms, depending on the nature of the pathogenic microorganisms, inducing death or only a severe limitation of the growth and multiplication and thus, exhibiting a microbicide or microbiostatic effect [98,99]. These agents can be integrated either directly into food or into the packaging material. For instance, propolis is extensively used due to its inhibitory activity against a broad spectrum of bacterial and fungal pathogens being added in meat products [99,100] but also in the food packaging, for instance, a chitosan based coating containing ethanolic propolis extract [101–103]. The efficiency is assured by the protective activity of these packaging materials against microbial/fungal infection by limiting the penetration of these microorganisms into the food, or these agents can be released over a period of time to maintain the quality of the products, as well as its safety, leading to an extended shelf life [101,102]. The nature of the microorganisms, and especially the nature of the cell wall composition (Gram-negative and Gram-positive), oxygen requirements (aerobes and anaerobes), growth stage (spores and vegetative cells), acid/osmosis resistance, optimal growth temperatures (mesophilic, thermophilic, psychotropic) are essential in choosing the proper antimicrobial agent [104]. The concentration of the active agents should be above the minimal inhibitory level but not exceeding the toxic level—especially if these agents are in contact with the food. The most common agents used in bioactive food packaging are antioxidants, antimicrobials, essential oils, and nanoparticles [18]. Starting from these considerations, a wide range of antimicrobial agents were used and due to their release, bioactivity is conferred to these packaging materials. Several aspects are considered as being very important. The most important characteristics induced by the use of these drug delivery systems are antioxidant, antifungal, and antibacterial as presented in Table 1. It is also important to mention that most of the natural extracts or essential oils have specific organoleptic characteristics and this is why the selection should be based on these characteristics. There are incompatible flavors and tastes with certain food as presented in Table 2.

Food	Natural Active Agents	References
Meat	Antioxidant agents:Ascorbic Acid, Phenols and Polyphenols, Ferulic Acid, a-Tocopherol, PhycocyaninMeatAntimicrobial agents:Thymol, Cinnamaldehyde, Gallic Acid, Curcumin, Carvacrol, Essential Oils Antifungal agents:Curcumin, essential oils	
Fruits and vegetables	Curcumin, rosemary extract, oregano essential oil, Asian spice essential oil	[106-109]
Bread	Carvacrol	[106–108]
Cheese	Antimicrobial agents: Ginger Essential Oil, Moringa Essential Oil, Lisin	[106,110,111]

Table 1. Compatibilities between different sorts of food and biological active agents designed to be loaded into food packaging materials for improving food safety and extending shelf-life.

Gelatin based electrospun films are exploited in the development of food packaging materials, their loading with essential oils, such as angelica essential oil are very useful because they induce antimicrobial activity, reduce the wettability, and enhance the water vapor barrier, which, overall means a safer food packaging film and extended shelf-life [112].

Chitosan/gelatin based food packaging materials are also exploited as drug delivery support for improving the shelf-life of several food. Zhang et al. [105], for instance, developed some chitosan/gelatin drug delivery packaging materials designed for the preservation of pork slices. The incorporation of nano-encapsulated tarragon essential oils (TEO) assured improved antioxidant, antibacterial, and sensory properties leading to a safe storage period for 16 days at 4 °C.

The antioxidant and antimicrobial activity can be also achieved by loading with curcumin [113]. The curcumin loaded microspheres and nanoparticles formed in situ in bacterial cellulose nanofiber/chitin nanofiber films can be also exploited in order to highlight the acidification of the food, which is correlated with food degradation.

More complex systems formed by biodegradable whey protein isolate based films incorporating chitosan nanofibers and further loaded with cinnamon essential oils were developed and the antimicrobial activity was proved against *Escherichia coli, Staphylococcus aureus,* and *Pseudomonas aeruginosa* [114,115]. It is important to mention that the reinforcing effect of chitosan nanofibers is significant, while the overall permeability of these films against water, light, and UV also improve the performances of these nanocomposite systems in food packaging applications.

Starch is a cheap, biodegradable material, extensively used as food packaging. Due to the limited performances, especially for some applications, these materials are reinforced with natural or synthetic compounds, including octaphenyl-polyhedral oligomeric silsesquioxane, as presented by Baysal and Dogan [116]. By loading these food packaging materials with turmeric and garlic extracts, the antimicrobial activity is induced but also important mechanical improvements can be observed especially when garlic extract is added. According to the migration studies, these food packaging materials can be used for milk products, fatty foods, liquids, acidic and dry foods. Another biological active agent which can be exploited in tuning the performances of the food packaging materials is orange-peel oil which induces important antioxidant properties, but also improved mechanical and moisture barrier compared with the reference film, without orange-peel oil [117].

Alginate based edible coatings loaded with thyme and oregano essential oils was proved to be efficient in maintaining the freshness of the fruits for a longer period of time. The evaluation was done over a period of 12 days, using freshly cut papaya cubes taking into account the following aspects: Gas exchange, microbial stability, and sensory quality. It was concluded that by increasing the content of essential oils, the shelf-life is increased but the sensorial performance decreased to an unacceptable level because of the strong and penetrating odor when 2% (v/v) of thyme essential oils are used in the 2% (w/v) alginate solution but an acceptable score is obtained when 1% (v/v) of thyme or oregano essential oils are used [118].

Lipid based delivery systems loaded with antimicrobial agents can be suitable for a wide range of food packaging materials such as vegetables, fruits, milk, meat, etc. A broad range of biological active agents were exploited in inducing the antimicrobial activity of the food packaging materials. Usually the antimicrobial agent is encapsulated to assure a longer efficiency as well as a limited food contamination. *Allium sativum* L. essential oil, gentamicin, piperine, epigallocatechin gallate, eugenol, bacteriocin, and nisin are just some of these biological active agents. Solid lipid nanoparticles can be also used as a carrier for a large number of antibiotics such as Rifampin, Amikacin, Ofloxacin, ciprofloxacin hydrochloride, clotrimazole silver complex, gentamicin, levofloxacin, cefuroxime axetil, or colistin sulfate [119].

Polymer Support	Bioactive Agent/activity	References					
Native Bioactive Polymers as Packaging Materials							
Chitosan	Chitosan/Antimicrobial activity	[19,128]					
Chitosan, ammonium salt	Chitosan, ammonium salt/Antimicrobial activity	[33]					
Chitosan or quaternized chitosan/other polymers	Chitosan or chitosan, ammonium salt/Antimicrobial activity	[33,37,38]					
Nanostructured Polymers as Packaging Materials							
Chitosan/gelatine	AgNPs/antimicrobial activity	[75]					
Cellulose nanofibril	AgNPs/antimicrobial	[73]					
Hydroxypropyl methylcellulose (HPMC)/Bovine collagen	TiO ₂ /antibacterial activity	[65]					
cellulose, sodium alginate	CuO/antioxidant and antimicrobial activity	[66]					
Bovine Gelatine	ZnO/antifungal activity	[67]					
Bionanocomposite films of agar	ZnO/antifungal activity	[79]					
Polyvinyl alcohol (PVA)	Graphene oxide (GO), and zinc oxide nanoparticles (ZnO NPs)/antibacterial activity against foodborne pathogenic and spoilage bacteria	[80]					
Drug delivery systems as packaging materials							
Gelatin	Angelica Essential Oil/antioxidant activity and inhibitory effect against both Gram-negative and Gram-positive bacteria	[112]					
Chitosan/gelatin	Tarragon essential oil/Antioxidant, Antibacterial activity	[105]					
Bacterial cellulose nanofiber (BCNF)/chitin nanofiber (CNF)	Curcumin/Antibacterial and Antioxidant activity	[113]					
Chitosan-whey protein/zein	Cinnamon oil/antibacterial activity	[114,115]					
Lipid nanostructures/?	Antibiotic loaded lipid-based nanostructures/antimicrobial	[119]					
Biodegradable starch-based nanofilms	Garlic extracts/antibacterial activity against <i>salmonella</i> and <i>S. aureus</i> bacteria	[116]					
Corn Starch Bio-Active Edible Packaging Films based on Zein	Orange-Peel Oil/antioxidant activity	[117]					
Chitosan/PEO	Natural extracts and essential oils with antioxidant, antibacterial, and antifungal activity	[106]					
Bioactive packaging materials with multiple mechanisms of activity							
Nano-cellulose composite films	Grape seed extracts and immobilized silver nanoparticles/antimicrobial activity against <i>E. coli</i> and <i>S. aureus</i>	[126]					
Cellulose acetate based nano-biocomposite films	AgNPs-organoclay and/or thymol/combined antimicrobial/antioxidant properties	[127]					
Sago starch films	Cinnamon essential oil and nano-Ti O_2 on antimicrobial and functional properties	[72]					

Table 2. Classification of the food packaging materials according to activity and composition. [112–128].

5. Probiotic Loaded Food Packaging

Probiotics can be also loaded inside the films assuring several functionalities to the developed food packaging. An extensive review in the field was published by Pavli et al. in 2018 and it concluded that most of the biopolymers can host probiotics while the derived food packaging could be used in several applications such as yogurt, cheese, juice, and chocolate protection [120]. For instance, Namratha et al. [121] developed some composite films based on pectin, alginate, and casein and loaded them with a probiotic, namely *Enterococcus faecium Rp1*. Glycerol was used as a plasticizer and the quaternary systems exhibited significant improvements in the antimicrobial and antioxidant performances along with enhanced structural, optical, and thermal properties while the viability of the probiotics was maintained up to 30 days at 4 $^{\circ}$ C.

Another composite system was also used in hosting living *Lactococcus lactis* subsp. *Lactis* that is able to assure antimicrobial activity. The antimicrobial activity is assured by *Lactococcus lactis* subsp. *Lactis* through releasing nisin which is a potent anti-listerial agent. The film forming material has to assure the characteristics required by a food packaging but also the conditions required by the bacterial strain to survive. This is the reason why along with the polyvinyl alcohol, a series of substances should be included, namely yeast extract, gelatin, sodium caseinate, or casein hydrolysates. These films were tested from the point of view of the viability of *Lactococcus lactis* subsp. *Lactis*, and it was found that at both conditions (37 °C for 1 day and 4 °C for 21 days) the viability was good but the antimicrobial activity decreased with the increased temperature. The as obtained food packaging, in the presence of nutrients (protein hydrolysate or sodium caseinate) can host the desired *Lactococcus lactis* subsp. *Lactis*, and thus can be used for safer storage of the refrigerated dairy beverages and sauces, for instance [122,123].

6. Bioactive Packaging Materials with Multiple Mechanisms of Activity

Innovative food packaging materials are developed by combining the activity of two or more biological active agents and in this way the biological activity is induced by two or even more mechanisms. In fact, the same can be mentioned to many other characteristics such as the mechanical or barrier capacity which can be improved by the addition of nanostructured reinforcing agents. Sometimes, these nanostructures such as TiO_2 and ZnO can have an intrinsic antimicrobial activity, as well. In this way, a synergic effect is obtained, without inducing toxicity due to a very high content of antimicrobial agent, where each component is below the level when the induced toxicity is concerned. Moreover, there are situations presented in the literature when due to the synergy the overall antimicrobial activity is much higher than the sum of the individual antimicrobial activity of the components, because of the potentiating effect of one component over the other [124,125].

Advanced packaging films based on nano-cellulose, silver nanoparticles, and grape seed extracts were reported by Wu et al. [126]. They used nano-cellulose as a support material that is able to form films but, in order to obtain the desired performances, the nano-cellulose support was oxidized by using 2,2,6,6-tetramethylpiperidine-1-oxyl. As a consequence, the mechanical water vapor and oxygen permeability, thermal stability, as well as the antimicrobial and antioxidant activity were significantly improved.

Dairi et al. [127] developed some active food packaging materials with both antimicrobial/antioxidant properties by using a hybrid formulation based on plasticized cellulose acetate/triethyl citrate reinforced with silver nanoparticles/gelatine-modified montmorillonite nanofiller and loaded with thymol. The complex, composite formulation is very important because most of the properties are improved as follows: Gelatin-modified montmorillonite nanofiller induces a mechanical and thermal improvement and an oxygen UV-barrier but also the porous nature can assist in the delivery rate of the thymol; silver nanoparticles are responsible for inducing antimicrobial activity (potentiated by the presence of some active components of the Curcuma longa tuber extract which was used for the green synthesis), while thymol is mainly responsible for the antioxidant activity.

Titanium dioxide, in nanometric form, was used in order to reinforce the sago starch-based film at different compositions (1%, 3%, and 5%) and further loaded with 0–3% of cinnamon essential oils. At these concentrations, the oxygen and water vapor permeability increased while the moisture decreased significantly from 12.96% to 8.04% and at the same time the solubility in water decreased from 25% to 13.7% [72]. The as obtained films showed excellent antimicrobial activity against *Escherichia coli, Salmonella typhimurium*, and *Staphylococcus aureus* being potential candidates for fresh pistachio packaging. The advantage of the use of titanium dioxide compared with other antimicrobial agents is related to the long term stability (higher physico-chemical stability), lower leakage because of the low solubility while due to the higher content added to reach the desired antimicrobial activity, it is able to induce improved mechanical properties.

7. Active Food Packaging Materials and Their Sensorial Activity

Food safety is an important issue of our daily life and more and more researches are devoted to this issue (Table 3). It is worth mentioning that along with safer packaging technology, including active packaging materials, an important concern related to highlighting the freshness of the food, is usually based on a visual determination—color change. As we already mentioned before, some active food packaging materials can be also exploited as sensors for the evaluation of the freshness of the food [113]. Usually, the color change takes place as a consequence of the chemical changes which occur in the food. The slow degradation in time of the food leads to a pH change or a specific compound release, but also these changes can occur as a consequence of thermal changes in a short interval. In both cases, the color change can be easily observed by the consumers. Such smart, sensitive food packaging materials can be extremely attractive for the consumers, if the price is reasonable.

Ding et al. [129], for instance, developed a polyvinyl alcohol/cellulose packaging material able to monitor the pH change due to the incorporation of acidochromic dye (170.4 μ mol/g) able to change its color from yellow (pH = 7) to brick red (pH = 10) or purple (pH = 12). It is worth mentioning that the dye is well adsorbed onto the cellulose support and assures a visual, real-time monitoring element for shrimp, for instance.

The incorporation of alizarin into the starch-cellulose packaging material can be exploited as a pH-indicator of the freshness of food, such as rainbow trout fillet [130]. The ternary alizarin-starch-cellulose as well as the binary alizarin-cellulose systems are able to indicate the freshness of the rainbow trout fillet over a wide range of pH, while if the pH is in the range of 7–9, a direct visual evaluation is suitable, with the ternary system being stable enough for use for over two months between 4 and 2 °C. Based on the color change, the freshness can be assessed from fresh to spoiled. Certainly, an intermediate stage can be defined, warning about the necessity of consuming before spoilage. Similar results can be obtained by using alginate—the red cabbage extract when a color change occurs from red to green and brown over 12 days at refrigeration temperature.

A 4 × 4 array based on 7 pH sensitive dyes, namely dimethyl yellow, methyl red, chlorophenol red, methyl orange, phenol red, thymol blue, and m-cresol purple was obtained. For a more specific result, these dyes were used as they are or as a salt with acidic (hydrochloric acid) or alkaline agent (tetrabutylammonium hydroxide) [131]. The release of CO_2 or NH₃ or even a mixture of both gases can lead to a pH change and consequently the 16 spots change accordingly and the multivariate analysis can be exploited to discriminate the content of CO_2 and NH₃ from air samples. Improvements are also expected by using ink-jet printing on variable substrates—even multiplexing several dyes into the same element to reduce the size followed by a smart-phone based real-time evaluation of the freshness of the food. Kerry et al. [132] have demonstrated that the carbon dioxide produced during microbial growth can also be used as an indicator of food altering.

A chromatic visualization of food freshness is possible to be monitored by incorporating polydiacetylene into the cellulose acetate membrane in the presence of triethyl citrate as a plasticizer. Based on the results reported by Ardilla-Diaz et al. [133], the optimal processing involves the use of 3 wt.% and 2.5 g cellulose acetate, 10% plasticizer, as well as 50.48 mg polydiacetylene while

polymerization was achieved by UV curing for 18 min at 100 ± 2 °C. These materials can be exploited as smart food packaging materials that are able to highlight extreme processing/storage conditions (the color change from blue to red being proof of such events) which can cause food degradation and food quality loss.

Ethylene-vinyl alcohol copolymer loaded with methylene blue can be used for monitoring the oxygen presence, as described by Lopez-Carballo et al. [134]. In this regard, the chromatic sensor can be manufactured by conventional printing and lamination technology. Along with the above mentioned components, glycerol (as a sacrificial electron donor) and TiO_2 (as a photocatalyst) were used. The active layer is incorporated between an external, transparent layer and an internal opaque layer just for an easy reading being permeable for oxygen. If the inner area does not contain oxygen, after 1 min of irradiation with a UV-halogen lamp (60 s), it became white, otherwise being blue, the sensor was able to detect even 0.5% of oxygen. All the components are allowed to be in contact with food, except methylene blue but, no trace of migration was identified for methylene blue.

There are also many other ways of visualizing such as that proposed by Kim et al. [134] who used the Cannizzaro reaction in order to induce color change from yellow to orange and then to red due to the specific reactions of the evolved aldehydes.

Chitosan and gold nanoparticles can be used as food packaging materials able to highlight the "memory effect" which is very important especially for fresh food such as seafood, fish, and other meats. The synthesis of the chitosan/AuNPs can be used as a frozen detector, even for one day the color change being sharp (pink => dark grey). By optimization, even the thermal history can be assessed based on the color intensity [50,135]. The integration of these "sensors" into actually used packaging can help in tracking and ensure the quality of the perishable foods, but also can be extended to pharmaceuticals and other biomaterials.

Temperature is one of the most important environmental factors that impacts the food preservation. The fluctuation of temperature during shelf-life can have a major impact on the safety and preservation of perishable food such as meat-based products. Time temperature indicators (TTIs) are efficient instruments specially designed for continuous monitoring of time-temperature history for refrigerated and frozen products during processing and commercial flux [136]. TTIs provide a visual indication which changes as time passes since the product was packed, the process being accelerated if the temperature is rising [137]. Such indicators allow continuous monitoring of the storage conditions. Therefore, they can provide information regarding a possible temperature change in the storage conditions and can be used as indirect indicators for food freshness. The basic working principle of TTIs is the visualization of the irreversible response of an enzymatic, chemical, electronic system, changes that are triggered by biological modifications that appear when food is subjected to higher temperatures [138].

Controlling the storage temperature history provides vital information to customers on the quality and food safety during the economic chain. Although TTIs are indirect indicators they are currently employed in the food industry because they are small, cheap, and easy to use comparatively with other temperature monitoring devices [139].

TTIs are usually attached to the package or containers and can be classified in three types:

- a. Critical indicators for temperature which indicate only if a product has been exposed to a higher temperature (or sometimes a lower one) than the reference value;
- b. Critical TTIs which indicate the cumulative effect of the temperature change and time passed with such higher temperature;
- c. Indicators with complete history which can accomplish a continuous monitoring of the temperature change in time [137].

The chemical based TTIs (nanoparticles, enzymes, biochemical systems) usually indicate by color change the thermal history of a product and they are applied or incorporated in the package by printing or sticking. The main advantage is the low cost and the fact that they are easy to read.

One example is the TTI VITSAB produced in Sweden (Figure 2) which are based on an enzymatic reaction that will induce pH changes inside the active label [140]. The VITSAB indicator is activated by removing the seal which is separating a lipolytic enzyme solution from the lipidic substrate. The reaction can be visualized with the help of an included solution which has its color changed by pH from green to red. When the product is packed the seal is removed and the solutions are mixed. If the temperature is near or higher than the enzyme activation temperature, then the reaction between the substrate and enzyme takes place, generating fatty acids. Therefore, the pH will change and the indicator will change the color from green to orange then to red [141].



Figure 2. VITSAB TTI label: (A) Inactive; (B) after removing seal; (C) 100% expired; (D) 120% expired.

Another example of TTI based on activation with UV light comes from BASF in the form of the $OnVu^{TM}$ label (Figure 3). The indicator is a colorless organic molecule which by irradiation for a few seconds with UV light changes its structure into an excited state, becoming dark blue. As long as the temperature is kept under -18 °C the excited form of the molecule is stable. Increasing the temperature will promote its return to the colorless ground state [142]. A small increase in temperature over a short period of time will only induce a slight fade of color while increasing the time or a big change in temperature will speed up the discoloration process.



Figure 3. OnVu TTI label. The indicator is activated by UV light in the excited form (dark blue) and slowly decays back to the ground state (colorless).

The number of commercial freshness indicators is still limited but a series of TTIs are presented in the literature. These are capable of monitoring the chemical changes during the shelf-life of food. Yoshida et al. developed a colorimetric indicator base that monitors the pH change, made from a chitosan film with anthocyanins [143]. This type of indicator can detect the metabolites obtained during microbial proliferation such as lactic acid, butyrate, and acetic acid.

There are also studies on biosensors capable of detecting xanthine production, which appears when adenine from animal tissues is metabolized [144,145]. Even the glucose level can be used as an indicator of meat alteration [146].

The TTIs can be used also as indicators of freshness for fruits (Figure 4). In this case, they monitor the level of natural volatile compounds released during the ripening process [147].



Figure 4. RipeSense TTI label for fruits. Red—Crisp; Orange—Firm; Yellow—Juicy; Green—Expired.

	Table 3. Real-time	e monitoring by	y using smar	t food p	ackaging.
--	--------------------	-----------------	--------------	----------	-----------

Support	Active Agent	Mechanism and Use	Ref.
Polyvinyl Alcohol/Cellulose	acidochromic dye	pH-induced color change for shrimp freshness monitoring	[129]
Starch-Cellulose	alizarin	pH sensitive indicator for monitoring the freshness of rainbow trout fillet	[130]
Ethylcellulose	pH sensitive dyes (dimethyl yellow, methyl red, chlorophenol red, methyl orange, phenol red, thymol blue, m-cresol purple) at acidic (hydrochloric acid) and alkaline (tetrabutylammonium hydroxide) pH	A colorimetric array based on the before presented pH sensitive dyes was developed and according to the color change of the 16 spots, assessments related to the freshness of the foods can be achieved	[131]
Cellulose Acetate	polydiacetylene	Color change from blue to red can be achieved as a consequence of extreme processing/storage conditions (pH and temperature)	[133]
Ethylene-Vinyl Alcohol copolymer	methylene blue	Oxygen sensor based on methylene blue ⇔ its leuco form	[134]
Chitosan	gold nanoparticles	Color change occurs as a consequence of the growth and aggregation or agglomeration of AuNPs due to their localized surface plasmon resonance	[135]
VITSAB indicator *	lipolytic enzyme solution /lipids	Temperature induced activation of the enzyme which catalyses the color change from green to red because a pH change occurred with the generation of fatty acids	[140,141]
OnVu TM label *	Photochromic	UV activation of the photochromic indicator which is discolored similarly with the degradation of the chilled boneless chicken breast	[142]
Paper	Methyl red	The color change (from yellow to orange and red) is a consequence of the Cannizzaro reaction of the evolved aldehydes in both liquid or gaseous form, in alkaline pH.	[148]

* Commercial available indicators which can be applied on different food.

8. Conclusions

In conclusion, the increasing standards of the humanity along with the important technical advances are making possible the development of more complex materials at a reasonable price and this trend can be easily observed also in the food packaging field. It is important to mention that from a historical point of view, the food packaging materials evolved very much, from a non-active, pure barrier to active (loaded with nanostructures or biological active agents including cells such as probiotics) and even hybrid food packaging materials with multiple functions and multiple mechanisms of action.

The use of these new technologies will not come without raising some questions, at which the producers must find the answers. The prolonging of the shelf-life by using antimicrobial packages raises the concern about safety as well as about how the consumer can judge the freshness of a product as usual when only the expiring information is marked. The additional substances from the packaging may lead to unwanted and unpleasant changes of organoleptic properties of food.

Nowadays, important advances are obtained by co-loading nanomaterials and biological active agents to especially enhance shelf-life and food safety. The use of various natural or synthetic substances or nanoparticles, that come in close and prolonged contact with the food can lead to some migration into the food, and from there into the human body. While the actual level from one meal can be extremely low, during the years the accumulation can lead to dangerous levels and this is why there are regulations with the maximal admitted level of these agents.

The use of smart packaging materials is also beneficial and can be exploited in monitoring the freshness of the food, including fruits and vegetables, but also perishable food such as seafood and fish, but, along with the technological advance these smart packaging materials will be accessible for a larger range of food. These sensor-based packaging materials become more and more attractive as being easy to use and can confer confidence to the consumer at a reasonable price. As a perspective, it is expected to develop new, smarter, packaging materials that are able to assure safer foods, improved shelf-life, and real time monitoring of the food. Most probably, these functionalities will be optimized by combining the use of nanomaterials and the delivery capacity of these nanocomposites.

Funding: This work was supported by a grant of the Romanian Ministry of Research and Innovation, CCCDI—UEFISCDI, project No. PN-III-P1-1.2-PCCDI-2017-0689 /P1. *"Lib2Life—Revitalizarea bibliotecilor şi a patrimoniului cultural prin tehnologii avansate"* within PNCDI III.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Marsh, K.; Bugusu, B. Food packaging-Roles, materials, and environmental issues. J. Food Sci. 2007, 72, R39–R55. [CrossRef] [PubMed]
- Rhim, J.W.; Park, H.M.; Ha, C.S. Bio-nanocomposites for food packaging applications. *Prog. Polym. Sci.* 2013, 38, 1629–1652. [CrossRef]
- Oprea, O.; Andronescu, E.; Ficai, D.; Ficai, A.; Oktar, F.N.; Yetmez, M. ZnO Applications and Challenges. *Curr. Org. Chem.* 2014, 18, 192–203. [CrossRef]
- 4. Ficai, A.; Sonmez, M.; Ficai, D.; Andronescu, E. Graphene based materials for environmental applications. *Adv. Mater. Technol. Environ. Appl.* **2017**, *1*, 79–85.
- 5. Kamran, F.; Reddy, N. Bioactive Peptides from Legumes: Functional and Nutraceutical Potential. *Recent Adv. Food Sci.* **2018**, *1*, 134–149.
- 6. Nedelcu, I.A.; Ficai, A.; Sonmez, M.; Ficai, D.; Oprea, O.; Andronescu, E. Silver Based Materials for Biomedical Applications. *Curr. Org. Chem.* **2014**, *18*, 173–184. [CrossRef]
- 7. Spoiala, A.; Ficai, D.; Gunduz, O.; Ficai, A.; Andronescu, E. Silver nanoparticles used for water purification. *Adv. Mater. Technol. Environ. Appl.* **2018**, *2*, 220–234.
- 8. Fu, P.P. Introduction to the Special Issue: Nanomaterials-Toxicology and medical applications. *J. Food Drug. Anal.* **2014**, 22, 1–2. [CrossRef]

- 9. Baranwal, A.; Srivastava, A.; Kumar, P.; Bajpai, V.K.; Maurya, P.K.; Chandra, P. Prospects of Nanostructure Materials and Their Composites as Antimicrobial Agents. *Front. Microbiol.* **2018**, *9*, 422. [CrossRef]
- 10. Brandelli, A. The interaction of nanostructured antimicrobials with biological systems: Cellular uptake, trafficking and potential toxicity. *Food Sci. Hum. Wellness* **2020**, *9*, 8–20. [CrossRef]
- 11. Vasile, C. Polymeric Nanocomposites and Nanocoatings for Food Packaging: A Review. *Materials* **2018**, *11*, 1834. [CrossRef]
- 12. Krasniewska, K.; Galus, S.; Gniewosz, M. Biopolymers-Based Materials Containing Silver Nanoparticles as Active Packaging for Food Applications-A Review. *Int. J. Mol. Sci.* **2020**, *21*, 698. [CrossRef] [PubMed]
- 13. Jamroz, E.; Kopel, P. Polysaccharide and Protein Films with Antimicrobial/Antioxidant Activity in the Food Industry: A Review. *Polymers* **2020**, *12*, 1289. [CrossRef] [PubMed]
- 14. Otles, S.; Tetik, I.; Dudys, E. Nanotechnology and its applications in the food industry. *Recent Adv. Food Sci.* **2020**, *3*, 247–258.
- Bajpai, V.K.; Kamle, M.; Shukla, S.; Mahato, D.K.; Chandra, P.; Hwang, S.K.; Kumar, P.; Huh, Y.S.; Han, Y.K. Prospects of using nanotechnology for food preservation, safety, and security. *J. Food Drug. Anal.* 2018, 26, 1201–1214. [CrossRef] [PubMed]
- 16. European Parliament and Council. *Directive 94/62/EC of 20 December 1994 on Packaging and Packaging Waste;* European Parliament and Council: Brussels, Belgium, 2018.
- 17. IETC. Plastic Shopping Bags Ban. In *Primary Industries Water and Environment;* International Environmental Technology Centre: Osaka, Japan, 2013.
- 18. Malhotra, B.; Keshwani, A.; Kharkwal, H. Antimicrobial food packaging: Potential and pitfalls. *Front. Microbiol.* **2015**, *6*, 611. [CrossRef] [PubMed]
- 19. Tripathi, S.; Mehrotra, G.K.; Dutta, P.K. Chitosan based antimicrobial films for food packaging applications. *E Polym.* **2008**, *8*. [CrossRef]
- 20. Dutta, J.; Tripathi, S.; Dutta, P.K. Progress in antimicrobial activities of chitin, chitosan and its oligosaccharides: A systematic study needs for food applications. *Food Sci. Technol. Int.* **2012**, *18*, 3–34. [CrossRef]
- 21. Kumar, S.; Mukherjee, A.; Dutta, J. Chitosan based nanocomposite films and coatings: Emerging antimicrobial food packaging alternatives. *Trends Food Sci. Technol.* **2020**, *97*, 196–209. [CrossRef]
- 22. Mehdizadeh, T.; Mojaddar Langroodi, A. Chitosan coatings incorporated with propolis extract and Zataria multiflora Boiss oil for active packaging of chicken breast meat. *Int. J. Biol. Macromol.* **2019**, 141, 401–409. [CrossRef]
- 23. Hosseinzadeh, S.; Partovi, R.; Talebi, F.; Babaei, A. Chitosan/TiO2 nanoparticle/Cymbopogon citratus essential oil film as food packaging material: Physico-mechanical properties and its effects on microbial, chemical, and organoleptic quality of minced meat during refrigeration. *J. Food Process. Pres.* **2020**, *44*. [CrossRef]
- 24. Zheng, K.; Xiao, S.; Li, W.; Wang, W.; Chen, H.; Yang, F.; Qin, C. Chitosan-acorn starch-eugenol edible film: Physico-chemical, barrier, antimicrobial, antioxidant and structural properties. *Int. J. Biol. Macromol.* **2019**, *135*, 344–352. [CrossRef] [PubMed]
- 25. Perinelli, D.R.; Fagioli, L.; Campana, R.; Lam, J.K.W.; Baffone, W.; Palmieri, G.F.; Casettari, L.; Bonacucina, G. Chitosan-based nanosystems and their exploited antimicrobial activity. *Eur. J. Pharm. Sci.* **2018**, *117*, 8–20. [CrossRef] [PubMed]
- Sahin, Y.M.; Yetmez, M.; Oktar, F.N.; Gunduz, O.; Agathopoulos, S.; Andronescu, E.; Ficai, D.; Sonmez, M.; Ficai, A. Nanostructured Biomaterials with Antimicrobial Properties. *Curr. Med. Chem.* 2014, *21*, 3391–3404. [CrossRef] [PubMed]
- 27. Fundueanu, G.; Constantin, M.; Bucatariu, S.; Nicolescu, A.; Ascenzi, P.; Moise, L.G.; Tudor, L.; Trusca, V.G.; Gafencu, A.V.; Ficai, D.; et al. Simple and dual cross-linked chitosan millicapsules as a particulate support for cell culture. *Int. J. Biol. Macromol.* **2020**, *143*, 200–212. [CrossRef]
- Mutlu, E.C.; Ficai, A.; Ficai, D.; Yildirim, A.B.; Yildirim, M.; Oktar, F.N.; Demir, A. Chitosan/poly(ethylene glycol)/hyaluronic acid biocompatible patches obtained by electrospraying. *Biomed. Mater.* 2018, *13*, 055011. [CrossRef]
- 29. Injorhor, P.; Ruksakulpiwat, Y.; Ruksakulpiwat, C. Effect of shrimp shell chitosan loading on antimicrobial, absorption and morphological properties of natural rubber composites reinforced with silica-chitosan hybrid filler. *Biointerface Res. Appl. Chem.* **2020**, *10*, 5656–5659.

- 30. Ullah, F.; Javed, F.; Zakaria, M.R.; Jamila, N.; Khattak, R.; Khan, A.N.; Akil, H.M. Determining the molecular-weight and interfacial properties of chitosan built nanohydrogel for controlled drug delivery applications. *Biointerface Res. Appl. Chem.* **2019**, *9*, 4452–4457.
- 31. Ullah, F.; Javed, F.; Khan, A.N.; Kudus, M.H.A.; Jamila, N.; Minhaz, A.; Akil, H.M. Synthesis and surface modification of chitosan built nanohydrogel with antiviral and antimicrobial agent for controlled drug delivery. *Biointerface Res. Appl. Chem.* **2019**, *9*, 4439–4445.
- 32. Arkoun, M.; Ardila, N.; Heuzey, M.C.; Ajji, A. Chitosan-Based Structures/Coatings with Antibacterial Properties. *Handb. Antimicrob. Coat.* 2018, 357–389. [CrossRef]
- 33. Belalia, R.; Grelier, S.; Benaissa, M.; Coma, V. New bioactive biomaterials based on quaternized chitosan. *J. Agric. Food Chem.* **2008**, *56*, 1582–1588. [CrossRef] [PubMed]
- 34. Li, J.J.; Cha, R.T.; Mou, K.W.; Zhao, X.H.; Long, K.Y.; Luo, H.Z.; Zhou, F.S.; Jiang, X.Y. Nanocellulose-Based Antibacterial Materials. *Adv. Healthc. Mater.* **2018**, *7*, 1800334. [CrossRef] [PubMed]
- Liu, Y.; Li, M.; Qiao, M.Y.; Ren, X.H.; Huang, T.S.; Buschle-Diller, G. Antibacterial membranes based on chitosan and quaternary ammonium salts modified nanocrystalline cellulose. *Polym. Adv. Technol.* 2017, 28, 1629–1635. [CrossRef]
- 36. Nechita, P.; Bobu, E.; Parfene, G.; Dinica, R.M.; Balan, T. Antimicrobial Coatings Based on Chitosan Derivatives and Quaternary Ammonium Salts for Packaging Paper Applications. *Cell. Chem. Technol.* **2015**, *49*, 625–632.
- 37. Hu, D.Y.; Wang, H.X.; Wang, L.J. Physical properties and antibacterial activity of quaternized chitosan/carboxymethyl cellulose blend films. *LWT Food Sci. Technol.* **2016**, *65*, 398–405. [CrossRef]
- 38. Hu, D.Y.; Wang, L.J. Fabrication of antibacterial blend film from poly (vinyl alcohol) and quaternized chitosan for packaging. *Mater. Res. Bull.* **2016**, *78*, 46–52. [CrossRef]
- 39. Saini, S.; Falco, C.Y.; Belgacem, M.N.; Bras, J. Surface cationized cellulose nanofibrils for the production of contact active antimicrobial surfaces. *Carbohydr. Polym.* **2016**, *135*, 239–247. [CrossRef]
- 40. Pour, Z.S.; Makvandi, P.; Ghaemy, M. Performance properties and antibacterial activity of crosslinked films of quaternary ammonium modified starch and poly(vinyl alcohol). *Int. J. Biol. Macromol.* **2015**, *80*, 596–604. [CrossRef]
- Wang, B.B.; Yang, X.D.; Qiao, C.D.; Li, Y.; Li, T.D.; Xu, C.L. Effects of chitosan quaternary ammonium salt on the physicochemical properties of sodium carboxymethyl cellulose-based films. *Carbohydr. Polym.* 2018, 184, 37–46. [CrossRef]
- 42. Hosseini, S.F.; Gómez-Guillén, M.C. A state-of-the-art review on the elaboration of fish gelatin as bioactive packaging: Special emphasis on nanotechnology-based approaches. *Trends Food Sci. Technol.* **2018**, *79*, 125–135. [CrossRef]
- 43. Nowzari, F.; Shabanpour, B.; Ojagh, S.M. Comparison of chitosan-gelatin composite and bilayer coating and film effect on the quality of refrigerated rainbow trout. *Food Chem.* **2013**, *141*, 1667–1672. [CrossRef] [PubMed]
- Feng, X.; Bansal, N.; Yang, H.S. Fish gelatin combined with chitosan coating inhibits myofibril degradation of golden pomfret (Trachinotus blochii) fillet during cold storage. *Food Chem.* 2016, 200, 283–292. [CrossRef] [PubMed]
- 45. Hasheminya, S.M.; Dehghannya, J. Novel ultrasound-assisted extraction of kefiran biomaterial, a prebiotic exopolysaccharide, and investigation of its physicochemical, antioxidant and antimicrobial properties. *Mater. Chem. Phys.* **2020**, 243, 122645. [CrossRef]
- Wang, K.; Niu, M.; Song, D.; Song, X.; Zhao, J.; Wu, Y.; Lu, B.; Niu, G. Preparation, partial characterization and biological activity of exopolysaccharides produced from Lactobacillus fermentum S1. *J. Biosci. Bioeng.* 2020, 129, 206–214. [CrossRef] [PubMed]
- 47. Lakra, A.K.; Domdi, L.; Tilwani, Y.M.; Arul, V. Physicochemical and functional characterization of mannan exopolysaccharide from Weissella confusa MD1 with bioactivities. *Int. J. Biol. Macromol.* **2020**, *143*, 797–805. [CrossRef]
- 48. Moradi, M.; Guimarães, J.T.; Sahin, S. Current applications of exopolysaccharides from lactic acid bacteria in the development of food active edible packaging. *Curr. Opin. Food Sci.* **2020**, *40*, 33–39. [CrossRef]
- Nehal, F.; Sahnoun, M.; Smaoui, S.; Jaouadi, B.; Bejar, S.; Mohammed, S. Characterization, high production and antimicrobial activity of exopolysaccharides from Lactococcus lactis F-mou. *Microb. Pathog.* 2019, 132, 10–19. [CrossRef]

- 50. Wang, Y.C.; Mohan, C.O.; Guan, J.; Ravishankar, C.N.; Gunasekaran, S. Chitosan and gold nanoparticles-based thermal history indicators and frozen indicators for perishable and temperature-sensitive products. *Food Control* **2018**, *85*, 186–193. [CrossRef]
- 51. Sganzerla, W.G.; Rosa, G.B.; Ferreira, A.L.A.; da Rosa, C.G.; Beling, P.C.; Xavier, L.O.; Hansen, C.M.; Ferrareze, J.P.; Nunes, M.R.; Barreto, P.L.M.; et al. Bioactive food packaging based on starch, citric pectin and functionalized with Acca sellowiana waste by-product: Characterization and application in the postharvest conservation of apple. *Int. J. Biol. Macromol.* 2020, 147, 295–303. [CrossRef]
- 52. Rukmanikrishnan, B.; Rajasekharan, S.K.; Lee, J.; Ramalingam, S.; Lee, J. K-Carrageenan/lignin composite films: Biofilm inhibition, antioxidant activity, cytocompatibility, UV and water barrier properties. *Mater. Today Commun.* **2020**, *24*, 101346. [CrossRef]
- 53. Sedayu, B.B.; Cran, M.J.; Bigger, S.W. Reinforcement of refined and semi-refined carrageenan film with nanocellulose. *Polymers* **2020**, *12*, 1145. [CrossRef] [PubMed]
- 54. Yadav, M.; Chiu, F.C. Cellulose nanocrystals reinforced κ-carrageenan based UV resistant transparent bionanocomposite films for sustainable packaging applications. *Carbohydr. Polym.* **2019**, *211*, 181–194. [CrossRef] [PubMed]
- Huang, X.; Luo, X.; Liu, L.; Dong, K.; Yang, R.; Lin, C.; Song, H.; Li, S.; Huang, Q. Formation mechanism of egg white protein/κ-Carrageenan composite film and its application to oil packaging. *Food Hydrocoll.* 2020, 105, 105780. [CrossRef]
- 56. Farhan, A.; Hani, N.M. Active edible films based on semi-refined κ-carrageenan: Antioxidant and color properties and application in chicken breast packaging. *Food Packag. Shelf* **2020**, *24*, 100476. [CrossRef]
- 57. Wahjuningsih, S.B.; Rohadi Susanti, S.; Setyanto, H.Y. The effect of k-carrageenan addition to the characteristics of jicama starch-based edible coating and its potential application on the grapevine. *Int. J. Adv. Sci. Eng. Inf. Technol.* **2019**, *9*, 405–410. [CrossRef]
- 58. Chen, H.; Wang, J.; Cheng, Y.; Wang, C.; Liu, H.; Bian, H.; Pan, Y.; Sun, J.; Han, W. Application of protein-based films and coatings for food packaging: A review. *Polymers* **2019**, *11*, 2039. [CrossRef]
- 59. Puscaselu, R.; Gutt, G.; Amariei, S. The use of edible films based on sodium alginate in meat product packaging: An eco-friendly alternative to conventional plastic materials. *Coatings* **2020**, *10*, 166. [CrossRef]
- 60. Pinto, C.T.; Pankowski, J.A.; Nano, F.E. The anti-microbial effect of food wrap containing beeswax products. *J. Microbiol. Biotechnol. Food Sci.* **2017**, *7*, 145–148. [CrossRef]
- 61. De Freitas, C.A.S.; de Sousa, P.H.M.; Soares, D.J.; da Silva, J.Y.G.; Benjamin, S.R.; Guedes, M.I.F. Carnauba wax uses in foo—A review. *Food Chem.* **2019**, *291*, 38–48. [CrossRef]
- 62. Gazzotti, S.; Todisco, S.A.; Picozzi, C.; Ortenzi, M.A.; Farina, H.; Lesma, G.; Silvani, A. Eugenol-grafted aliphatic polyesters: Towards inherently antimicrobial PLA-based materials exploiting OCAs chemistry. *Eur. Polym. J.* **2019**, *114*, 369–379. [CrossRef]
- 63. Ray, S.S.; Bousmina, M. Biodegradable polymers and their layered silicate nanocomposites: In greening the 21st century materials world. *Prog. Mater. Sci.* 2005, *50*, 962–1079. [CrossRef]
- 64. Ramos, Ó.L.; Pereira, R.N.; Cerqueira, M.A.; Martins, J.R.; Teixeira, J.A.; Malcata, F.X.; Vicente, A.A. Bio-Based Nanocomposites for Food Packaging and Their Effect in Food Quality and Safety. In *Food Packaging and Preservation*; Grumezescu, A.M., Holban, A.M., Eds.; Academic Press: Cambridge, MA, USA, 2018; pp. 271–306.
- Shao, X.; Sun, H.; Zhou, R.; Zhao, B.; Shi, J.; Jiang, R.; Dong, Y. Effect of bovine bone collagen and nano-TiO₂ on the properties of hydroxypropyl methylcellulose films. *Int. J. Biol. Macromol.* 2020, *158*, 937–944. [CrossRef] [PubMed]
- 66. Saravanakumar, K.; Sathiyaseelan, A.; Mariadoss, A.V.A.; Xiaowen, H.; Wang, M.H. Physical and bioactivities of biopolymeric films incorporated with cellulose, sodium alginate and copper oxide nanoparticles for food packaging application. *Int. J. Biol. Macromol.* **2020**, *153*, 207–214. [CrossRef]
- 67. Sahraee, S.; Milani, J.M.; Ghanbarzadeh, B.; Hamishehkar, H. Development of emulsion films based on bovine gelatin-nano chitin-nano ZnO for cake packaging. *Food Sci. Nutr.* **2020**, *8*, 1303–1312. [CrossRef]
- Saadat, S.; Pandey, G.; Tharmavaram, M.; Braganza, V.; Rawtani, D. Nano-interfacial decoration of Halloysite Nanotubes for the development of antimicrobial nanocomposites. *Adv. Colloid Interface Sci.* 2020, 275, 102063. [CrossRef]
- 69. Oun, A.A.; Shankar, S.; Rhim, J.W. Multifunctional nanocellulose/metal and metal oxide nanoparticle hybrid nanomaterials. *Crit. Rev. Food Sci. Nutr.* **2020**, *60*, 435–460. [CrossRef]

- Azizi-Lalabadi, M.; Ehsani, A.; Ghanbarzadeh, B.; Divband, B. Polyvinyl alcohol/gelatin nanocomposite containing ZnO, TiO₂ or ZnO/TiO₂ nanoparticles doped on 4A zeolite: Microbial and sensory qualities of packaged white shrimp during refrigeration. *Int. J. Food Microbiol.* 2020, *312*, 108375. [CrossRef]
- Arroyo, B.J.; Bezerra, A.C.; Oliveira, L.L.; Arroyo, S.J.; Melo, E.A.; Santos, A.M.P. Antimicrobial active edible coating of alginate and chitosan add ZnO nanoparticles applied in guavas (*Psidium guajava* L.). *Food Chem.* 2020, 309, 125566. [CrossRef]
- Arezoo, E.; Mohammadreza, E.; Maryam, M.; Abdorreza, M.N. The synergistic effects of cinnamon essential oil and nano TiO₂ on antimicrobial and functional properties of sago starch films. *Int. J. Biol. Macromol.* 2020, 157, 743–751. [CrossRef]
- Yu, Z.; Wang, W.; Kong, F.; Lin, M.; Mustapha, A. Cellulose nanofibril/silver nanoparticle composite as an active food packaging system and its toxicity to human colon cells. *Int. J. Biol. Macromol.* 2019, 129, 887–894.
 [CrossRef] [PubMed]
- 74. Lee, J.H.; Jeong, D.; Kanmani, P. Study on physical and mechanical properties of the biopolymer/silver based active nanocomposite films with antimicrobial activity. *Carbohydr. Polym.* **2019**, 224, 115159. [CrossRef] [PubMed]
- Kumar, S.; Shukla, A.; Baul, P.P.; Mitra, A.; Halder, D. Biodegradable hybrid nanocomposites of chitosan/gelatin and silver nanoparticles for active food packaging applications. *Food Packag. Shelf* 2018, 16, 178–184. [CrossRef]
- 76. Yu, Z.; Wang, W.; Dhital, R.; Kong, F.; Lin, M.; Mustapha, A. Antimicrobial effect and toxicity of cellulose nanofibril/silver nanoparticle nanocomposites prepared by an ultraviolet irradiation method. *Colloids Surf. B Biointerfaces* **2019**, *180*, 212–220. [CrossRef]
- 77. Neacsu, I.A.; Melente, A.E.; Holban, A.M.; Ficai, A.; Ditu, L.M.; Kamerzan, C.M.; Tihauan, B.M.; Nicoara, A.I.; Bezirtzoglou, E.; Chifiriuc, M.C.; et al. Novel hydrogels based on collagen and ZnO nanoparticles with antibacterial activity for improved wound dressings. *Rom. Biotech. Lett.* **2019**, *24*, 317–323. [CrossRef]
- 78. Lungu, I.I.; Holban, A.M.; Ficai, A.; Grumezescu, A.M. Zinc oxide nanostrucures: New trends in antimicrobial therapy. In *Nanostructures for Antimicrobial Therapy*; Elsevier: Amsterdam, The Netherlands, 2017; pp. 503–514.
- 79. Kumar, S.; Boro, J.C.; Ray, D.; Mukherjee, A.; Dutta, J. Bionanocomposite films of agar incorporated with ZnO nanoparticles as an active packaging material for shelf life extension of green grape. *Heliyon* 2019, *5*, e01867. [CrossRef]
- Zhang, R.; Wang, Y.; Ma, D.; Ahmed, S.; Qin, W.; Liu, Y. Effects of ultrasonication duration and graphene oxide and nano-zinc oxide contents on the properties of polyvinyl alcohol nanocomposites. *Ultrason. Sonochem.* 2019, 59, 104731. [CrossRef]
- 81. Halder, S.; Schneller, T.; Waser, R. Enhanced stability of platinized silicon substrates using an unconventional adhesion layer deposited by CSD for high temperature dielectric thin film deposition. *Appl. Phys. Mater. Sci. Process.* **2007**, *87*, 705–708. [CrossRef]
- 82. Institute of Medicine, Food and Nutrition Board. *Dietary Reference Intakes for Vitamin A, Vitamin K, Arsenic, Boron, Chromium, Copper, Iodine, Iron, Manganese, Molybdenum, Nickel, Silicon, Vanadium, and Zincexternal Link Disclaimer;* National Academy Press: Washington, DC, USA, 2001.
- 83. Aristizabal-Gil, M.V.; Santiago-Toro, S.; Sanchez, L.T.; Pinzon, M.I.; Gutierrez, J.A.; Villa, C.C. ZnO and ZnO/CaO nanoparticles in alginate films. Synthesis, mechanical characterization, barrier properties and release kinetics. *LWT* **2019**, *112*, 108217. [CrossRef]
- 84. Bumbudsanpharoke, N.; Ko, S. Nano-Food Packaging: An Overview of Market, Migration Research, and Safety Regulations. *J. Food Sci.* **2015**, *80*, R910–R923. [CrossRef]
- 85. Heydari-Majd, M.; Ghanbarzadeh, B.; Shahidi-Noghabi, M.; Najafi, M.A.; Hosseini, M. A new active nanocomposite film based on PLA/ZnO nanoparticle/essential oils for the preservation of refrigerated Otolithes ruber fillets. *Food Packag. Shelf* **2019**, *19*, 94–103. [CrossRef]
- 86. Sharma, D.; Rajput, J.; Kaith, B.S.; Kaur, M.; Sharma, S. Synthesis of ZnO nanoparticles and study of their antibacterial and antifungal properties. *Thin Solid Films* **2010**, *519*, 1224–1229. [CrossRef]
- 87. Suhr, K.I.; Nielsen, P.V. Antifungal activity of essential oils evaluated by two different application techniques against rye bread spoilage fungi. *J. Appl. Microbiol.* **2003**, *94*, 665–674. [CrossRef] [PubMed]
- Huang, T.; Qian, Y.; Wei, J.; Zhou, C. Polymeric Antimicrobial Food Packaging and Its Applications. *Polymers* 2019, 11, 560. [CrossRef]

- Danila, E.; Kaya, D.A.; Patrascu, M.; Kaya, M.A.; Kumbakisaka, S. Comparative study of Lavandula Angustifolia essential oils obtained by microwave and classical hydrodistillation. *Rev. Chim. (Bucharest)* 2018, 69, 2240–2244. [CrossRef]
- 90. Ullah, H.; Ali, S. Classification of anti-bacterial agents and their functions. In *Antibacterial Agents;* Kumavath, R.N., Ed.; Intech: London, UK, 2017; pp. 1–16.
- 91. Zhang, Q.W.; Lin, L.G.; Ye, W.C. Techniques for extraction and isolation of natural products: A comprehensive review. *Chin. Med.* **2018**, *13*. [CrossRef]
- 92. Yahya, N.A.; Attana, N.; Wahab, R.A. An overview of cosmeceutically relevant plant extracts and strategies for extraction of plant-based bioactive compounds. *Food Bioprod. Process.* **2018**, *112*, 69–85. [CrossRef]
- 93. Lozano-Grande, M.A.; Gorinstein, S.; Espitia-Rangel, E.; Davila-Ortiz, G.; Martinez-Ayala, A.L. Plant Sources, Extraction Methods, and Uses of Squalene. *Int. J. Agron.* **2018**, 2018, 5–13. [CrossRef]
- Kumari, B.; Tiwari, B.K.; Hossain, M.B.; Brunton, N.P.; Rai, D.K. Recent Advances on Application of Ultrasound and Pulsed Electric Field Technologies in the Extraction of Bioactives from Agro-Industrial By-products. *Food Bioprocess Technol.* 2018, *11*, 223–241. [CrossRef]
- Gavahian, M.; Chu, Y.H.; Sastry, S. Extraction from Food and Natural Products by Moderate Electric Field: Mechanisms, Benefits, and Potential Industrial Applications. *Compr. Rev. Food Sci. Food* 2018, 17, 1040–1052. [CrossRef]
- 96. Xu, C.C.; Wang, B.; Pu, Y.Q.; Tao, J.S.; Zhang, T. Advances in extraction and analysis of phenolic compounds from plant materials. *Chin. J. Nat. Med.* **2017**, *15*, 721–731. [CrossRef]
- Vinatoru, M.; Mason, T.J.; Calinescu, I. Ultrasonically assisted extraction (UAE) and microwave assisted extraction (MAE) of functional compounds from plant materials. *TrAC Trend Anal. Chem.* 2017, 97, 159–178. [CrossRef]
- Welsch, T.T.; Gillock, E.T. Triclosan-resistant bacteria isolated from feedlot and residential soils. J. Environ. Sci. Health A 2011, 46, 436–440. [CrossRef] [PubMed]
- Netikova, L.; Bogusch, P.; Heneberg, P. Czech Ethanol-Free Propolis Extract Displays Inhibitory Activity against a Broad Spectrum of Bacterial and Fungal Pathogens. *J. Food Sci.* 2013, 78, M1421–M1429. [CrossRef] [PubMed]
- 100. Pateiro, M.; Barba, F.J.; Dominguez, R.; Sant'Ana, A.S.; Khaneghah, A.M.; Gavahian, M.; Gomez, B.; Lorenzo, J.M. Essential oils as natural additives to prevent oxidation reactions in meat and meat products: A review. *Food Res. Int.* 2018, 113, 156–166. [CrossRef]
- 101. Shahbazi, Y.; Shavisi, N. A novel active food packaging film for shelf-life extension of minced beef meat. *J. Food Saf.* **2018**, *38*. [CrossRef]
- 102. Rollini, M.; Mascheroni, E.; Capretti, G.; Coma, V.; Musatti, A.; Piergiovanni, L. Propolis and chitosan as antimicrobial and polyphenols retainer for the development of paper based active packaging materials. *Food Packag. Shelf* 2017, 14, 75–82. [CrossRef]
- 103. Jafari, N.J.; Kargozari, M.; Ranjbar, R.; Rostami, H.; Hamedi, H. The effect of chitosan coating incorporated with ethanolic extract of propolis on the quality of refrigerated chicken fillet. *J. Food Process. Pres.* 2018, 42. [CrossRef]
- 104. Formosa-Dague, C.; Duval, R.E.; Dague, E. Cell biology of microbes and pharmacology of antimicrobial drugs explored by Atomic Force Microscopy. *Semin. Cell Dev. Biol.* **2018**, *73*, 165–176. [CrossRef]
- 105. Zhang, H.; Liang, Y.; Li, X.; Kang, H. Effect of chitosan-gelatin coating containing nano-encapsulated tarragon essential oil on the preservation of pork slices. *Meat Sci.* **2020**, *166*, 108137. [CrossRef]
- 106. Topuz, F.; Uyar, T. Antioxidant, antibacterial and antifungal electrospun nanofibers for food packaging applications. *Food Res. Int.* **2020**, *130*, 108927. [CrossRef] [PubMed]
- 107. Aziz, M.; Karboune, S. Natural antimicrobial/antioxidant agents in meat and poultry products as well as fruits and vegetables: A review. *Crit. Rev. Food Sci.* **2018**, *58*, 486–511. [CrossRef] [PubMed]
- 108. Khalil, H.P.S.A.; Banerjee, A.; Saurabh, C.K.; Tye, Y.Y.; Suriani, A.B.; Mohamed, A.; Karim, A.A.; Rizal, S.; Paridah, M.T. Biodegradable Films for Fruits and Vegetables Packaging Application: Preparation and Properties. *Food Eng. Rev.* 2018, 10, 139–153. [CrossRef]
- Kwon, S.J.; Chang, Y.; Han, J. Oregano essential oil-based natural antimicrobial packaging film to inactivate Salmonella enterica and yeasts/molds in the atmosphere surrounding cherry tomatoes. *Food Microbiol.* 2017, 65, 114–121. [CrossRef] [PubMed]

- 110. Cui, H.; Wu, J.; Li, C.; Lin, L. Improving anti-listeria activity of cheese packaging via nanofiber containing nisin-loaded nanoparticles. *LWT Food Sci. Technol.* **2017**, *81*, 233–242. [CrossRef]
- Lin, L.; Gu, Y.; Cui, H. Moringa oil/chitosan nanoparticles embedded gelatin nanofibers for food packaging against Listeria monocytogenes and Staphylococcus aureus on cheese. *Food Packag. Shelf* 2019, *19*, 86–93. [CrossRef]
- 112. Zhou, Y.; Miao, X.; Lan, X.; Luo, J.; Luo, T.; Zhong, Z.; Gao, X.; Mafang, Z.; Ji, J.; Wang, H.; et al. Angelica Essential Oil Loaded Electrospun Gelatin Nanofibers for Active Food Packaging Application. *Polymers* 2020, 12, 299. [CrossRef]
- Yang, Y.N.; Lu, K.Y.; Wang, P.; Ho, Y.C.; Tsai, M.L.; Mi, F.L. Development of bacterial cellulose/chitin multi-nano fi bers based smart films containing natural active microspheres and nanoparticles formed in situ. *Carbohydr. Polym.* 2020, 228, 115370. [CrossRef]
- 114. Mohammadi, M.; Mirabzadeh, S.; Shahvalizadeh, R.; Hamishehkar, H. Development of novel active packaging films based on whey protein isolate incorporated with chitosan nanofiber and nano-formulated cinnamon oil. *Int. J. Biol. Macromol.* **2020**, *149*, 11–20. [CrossRef]
- 115. Vahedikia, N.; Garavand, F.; Tajeddin, B.; Cacciotti, I.; Jafari, S.M.; Omidi, T.; Zahedi, Z. Biodegradable zein film composites reinforced with chitosan nanoparticles and cinnamon essential oil: Physical. mechanical, structural and antimicrobial attributes. *Colloids Surf B Biointerfaces* **2019**, 177, 25–32. [CrossRef]
- 116. Baysal, G.; Dogan, F. Investigation and preparation of biodegradable starch-based nanofilms for potential use of curcumin and garlic in food packaging applications. *J. Biomater. Sci. Polym. Ed.* 2020, *31*, 1127–1143. [CrossRef] [PubMed]
- 117. Wang, Y.; Zhang, R.; Ahmed, S.; Qin, W.; Liu, Y. Preparation and Characterization of Corn Starch Bio-Active Edible Packaging Films Based on Zein Incorporated with Orange-Peel Oil. *Antioxidants* 2019, *8*, 391. [CrossRef] [PubMed]
- 118. Tabassum, N.; Khan, M.A. Modified atmosphere packaging of fresh-cut papaya using alginate based edible coating: Quality evaluation and shelf life study. *Sci. Hortic.* **2020**, 259, 108853. [CrossRef]
- 119. Yousefi, M.; Ehsani, A.; Jafari, S.M. Lipid-based nano delivery of antimicrobials to control food-borne bacteria. *Adv. Colloid Interface Sci.* **2019**, 270, 263–277. [CrossRef]
- 120. Pavli, F.; Tassou, C.; Nychas, G.J.E.; Chorianopoulos, N. Probiotic incorporation in edible films and coatings: Bioactive solution for functional foods. *Int. J. Mol. Sci.* **2018**, *19*, 150. [CrossRef]
- Namratha, S.; Sreejit, V.; Preetha, R. Fabrication and evaluation of physicochemical properties of probiotic edible film based on pectin–alginate–casein composite. *Int. J. Food Sci. Technol.* 2020, 55, 1497–1505. [CrossRef]
- Settier-Ramírez, L.; López-Carballo, G.; Gavara, R.; Hernández-Muñoz, P. Antilisterial properties of PVOH-based films embedded with Lactococcus lactis subsp. lactis. *Food Hydrocoll.* 2019, 87, 214–220. [CrossRef]
- Settier-Ramírez, L.; López-Carballo, G.; Gavara, R.; Hernández-Muñoz, P. PVOH/protein blend films embedded with lactic acid bacteria and their antilisterial activity in pasteurized milk. *Int. J. Food Microbiol.* 2020, 322, 108545. [CrossRef]
- 124. Holban, A.M.; Grumezescu, V.; Ficai, A.; Grumezescu, A.M.; Chifiriuc, M.C.; Iordache, F.; Andronescu, E. Highly Biocompatible Magnetite Nanoparticles Functionalized with Chitosan for Improving the Efficiency of Antibiotics. *Univ. Politeh. Buchar.* 2016, 78, 47–58.
- 125. Danila, E.; Moldovan, Z.; Popa, M.; Chifiriuc, M.C.; Kaya, A.D.; Kaya, M.A. Chemical composition, antimicrobial and antibiofilm efficacy of limon and L. angustifolia EOs and of their mixtures against Staphylococcus epidermidis clinical strains. *Ind. Crops Prod.* **2018**, *122*, 483–492. [CrossRef]
- 126. Wu, Z.; Deng, W.; Luo, J.; Deng, D. Multifunctional nano-cellulose composite films with grape seed extracts and immobilized silver nanoparticles. *Carbohydr. Polym.* **2019**, 205, 447–455. [CrossRef] [PubMed]
- 127. Dairi, N.; Ferfera-Harrar, H.; Ramos, M.; Garrigos, M.C. Cellulose acetate/AgNPs-organoclay and/or thymol nano-biocomposite films with combined antimicrobial/antioxidant properties for active food packaging use. *Int. J. Biol. Macromol.* **2019**, *121*, 508–523. [CrossRef] [PubMed]
- Dutta, J.; Dutta, P.K. Antimicrobial Activity of Chitin, Chitosan, and Their Oligosaccharides, Chitin, Chitosan, Oligosaccharides and Their Derivatives: Biological Activities and Applications; CRC Press: Boca Raton, FL, USA, 2010; pp. 195–210.

- 129. Ding, L.; Li, X.; Hu, L.; Zhang, Y.; Jiang, Y.; Mao, Z.; Xu, H.; Wang, B.; Feng, X.; Sui, X. A naked-eye detection polyvinyl alcohol/cellulose-based pH sensor for intelligent packaging. *Carbohydr. Polym.* 2020, 233, 115859. [CrossRef] [PubMed]
- 130. Ezati, P.; Tajik, H.; Moradi, M.; Molaei, R. Intelligent pH-sensitive indicator based on starch-cellulose and alizarin dye to track freshness of rainbow trout fillet. *Int. J. Biol. Macromol.* **2019**, *132*, 157–165. [CrossRef]
- Zhang, Y.N.; Lim, L.T. Colorimetric array indicator for NH₃ and CO₂ detection. *Sens. Actuators B Chem.* 2018, 255, 3216–3226. [CrossRef]
- 132. Safarik, I.; Pospiskova, K.; Horska, K.; Safarikova, M. Potential of magnetically responsive (nano)biocomposites. *Soft. Matter.* **2012**, *8*, 5407–5413. [CrossRef]
- Ardila-Diaz, L.D.; Oliveira, T.V.; Soares, N.F.F. Development and Evaluation of the Chromatic Behavior of an Intelligent Packaging Material Based on Cellulose Acetate Incorporated with Polydiacetylene for an Efficient Packaging. *Biosensors* 2020, 10, 59. [CrossRef]
- 134. Lopez-Carballo, G.; Muriel-Galet, V.; Hernandez-Munoz, P.; Gavara, R. Chromatic Sensor to Determine Oxygen Presence for Applications in Intelligent Packaging. *Sensors* **2019**, *19*, 4684. [CrossRef]
- 135. Mohan, C.O.; Gunasekaran, S.; Ravishankar, C.N. Chitosan-capped gold nanoparticles for indicating temperature abuse in frozen stored products. *Npj Sci. Food.* **2019**, *2*, 3. [CrossRef]
- Lee, S.J.; Rahman, A.T.M.M. Intelligent Packaging for Food Products. *Innov. Food Packag.* 2014, 171–209. [CrossRef]
- 137. Galagan, Y.; Su, W.F. Fadable ink for time-temperature control of food freshness: Novel new time-temperature indicator. *Food Res. Int.* **2008**, *41*, 653–657. [CrossRef]
- Kerry, J.P.; O'Grady, M.N.; Hogan, S.A. Past, current and potential utilisation of active and intelligent packaging systems for meat and muscle-based products: A review. *Meat Sci.* 2006, 74, 113–130. [CrossRef] [PubMed]
- 139. Taoukis, P.S.; Labuza, T.P. Applicability of Time-Temperature Indicators as Shelf-Life Monitors of Food-Products. J. Food Sci. 1989, 54, 783–788. [CrossRef]
- 140. Fang, Z.X.; Zhao, Y.Y.; Warner, R.D.; Johnson, S.K. Active and intelligent packaging in meat industry. *Trends Food Sci. Technol.* **2017**, *61*, 60–71. [CrossRef]
- 141. Wang, S.D.; Liu, X.H.; Yang, M.; Zhang, Y.; Xiang, K.Y.; Tang, R. Review of Time Temperature Indicators as Quality Monitors in Food Packaging. *Packag. Technol. Sci.* **2015**, *28*, 839–867. [CrossRef]
- 142. Brizio, A.P.D.R.; Prentice, C. Use of smart photochromic indicator for dynamic monitoring of the shelf life of chilled chicken based products. *Meat Sci.* 2014, *96*, 1219–1226. [CrossRef]
- 143. Yoshida, C.M.P.; Maciel, V.B.V.; Mendonca, M.E.D.; Franco, T.T. Chitosan biobased and intelligent films: Monitoring pH variations. *LWT Food Sci. Technol.* **2014**, *55*, 83–89. [CrossRef]
- 144. Arvanitoyannis, I.S.; Stratakos, A.C. Fresh and Processed Meat and Meat Products. *Contemp. Food Eng.* **2012**, 223–259.
- 145. Arvanitoyannis, I.S.; Stratakos, A.C. Application of Modified Atmosphere Packaging and Active/Smart Technologies to Red Meat and Poultry: A Review. *Food Bioprocess. Technol.* **2012**, *5*, 1423–1446. [CrossRef]
- 146. Umuhumuza, L.C.; Sun, X.L. Rapid detection of pork meat freshness by using L-cysteine-modified gold electrode. *Eur. Food Res. Technol.* **2011**, *232*, 425–431. [CrossRef]
- 147. Fuertes, G.; Soto, I.; Carrasco, R.; Vargas, M.; Sabattin, J.; Lagos, C. Intelligent Packaging Systems: Sensors and Nanosensors to Monitor Food Quality and Safety. *J. Sens.* **2016**, 2016, 1–8. [CrossRef]
- 148. Kim, Y.H.; Yang, Y.J.; Kim, J.S.; Choi, D.S.; Park, S.H.; Jin, S.Y.; Park, J.S. Non-destructive monitoring of apple ripeness using an aldehyde sensitive colorimetric sensor. *Food Chem.* 2018, 267, 149–156. [CrossRef] [PubMed]



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).