



# **Nanocarriers for Sustainable Active Packaging: An Overview during and Post COVID-19**

Mihaela Stefana Pascuta <sup>1</sup> and Dan Cristian Vodnar <sup>1,2,\*</sup>

- <sup>1</sup> Faculty of Food Science and Technology, University of Agricultural Sciences and Veterinary Medicine of Cluj-Napoca, Calea Mănăştur 3–5, 400372 Cluj-Napoca, Romania; mihaela.pascuta@usamvcluj.ro
- <sup>2</sup> Institute of Life Science, University of Agricultural Sciences and Veterinary Medicine of Cluj-Napoca, Calea Mănăştur 3–5, 400372 Cluj-Napoca, Romania
- \* Correspondence: dan.vodnar@usamvcluj.ro; Tel.: +40-747341881

Abstract: Lockdown has been installed due to the fast spread of COVID-19, and several challenges have occurred. Active packaging was considered a sustainable option for mitigating risks to food systems during COVID-19. Biopolymeric-based active packaging incorporating the release of active compounds with antimicrobial and antioxidant activity represents an innovative solution for increasing shelf life and maintaining food quality during transportation from producers to consumers. However, food packaging requires certain physical, chemical, and mechanical performances, which biopolymers such as proteins, polysaccharides, and lipids have not satisfied. In addition, active compounds have low stability and can easily burst when added directly into biopolymeric materials. Due to these drawbacks, encapsulation into lipid-based, polymeric-based, and nanoclay-based nanocarriers has currently captured increased interest. Nanocarriers can protect and control the release of active compounds and can enhance the performance of biopolymeric matrices. The aim of this manuscript is to provide an overview regarding the benefits of released active compound-loaded nanocarriers in developing sustainable biopolymeric-based active packaging with antimicrobial and antioxidant properties. Nanocarriers improve physical, chemical, and mechanical properties of the biopolymeric matrix and increase the bioactivity of released active compounds. Furthermore, challenges during the COVID-19 pandemic and a brief post-COVID-19 scenario were also mentioned.

**Keywords:** active packaging; delivery system; encapsulation; active compound; antimicrobial activity; sustainable packaging

# 1. Introduction

The highly contagious virus SARS-CoV-2 causes the clinical syndrome of COVID-19, which people worldwide are currently confronting [1]. On 11 March 2020, COVID-19 was declared by the World Health Organization as a pandemic, and lockdown occurred immediately around the world [2]. Transport restrictions and quarantine were found to be important measures in stopping COVID-19 spread [3]. Increased food loss and waste [4]; increased online shopping trends; increased demand for active compounds that boost the immune system [5]; and increased use of plastic single-use packaging for exploding home delivery systems [6] are a few challenges to face during and post-COVID-19 era. Improving packaging was mentioned as a policy response for mitigating risks to food systems during COVID-19 by the Food and Agriculture Organization of the United Nations (FAO) [4].

FAO proposed active packaging as the key technology for improving the quality of fresh foods during transportation and storage [7]. Active packaging technology is defined in the European regulation as "new types of materials and articles designed to actively maintain or improve the condition of the food" (1935/2004/EC) [8] and can "deliberately incorporate components that would release or absorb substances into or from the packaged food or the environment surrounding the food" (450/2009/EC) [9]. Active packaging



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**Copyright:** © 2022 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 (https:// creativecommons.org/licenses/by/ 4.0/). mainly consists of two basic constituents: the barrier layer (polymeric matrix) and the active layer (active compounds) [10,11]. As barrier layers, both synthetic and bio-based polymers have been studied for active packaging applications [12]. Since one of the challenges of the COVID-19 pandemic is to reduce plastic, this manuscript is focused on the biopolymeric matrix. Natural (e.g., polysaccharides, proteins, lipids, and their composites) and synthetic (e.g., polyvinyl alcohol—PVA; polylactic acid—PLA) biopolymers represent a growing focus of interest in the future with respect to commercial packaging materials [7]. They are considered ecofriendly materials for combating plastic waste [13]. However, materials for food packaging require a certain mechanical performance [14]. Therefore, unsatisfactory physico-mechanical properties are the main drawbacks for further industrial applications of biopolymeric materials [7].

Despite both scavengers (absorbers) and release (emitters) compounds being used as active layers for developing active packaging [15], release compounds are commonly incorporated into biopolymeric-based active packaging. Both organic-based releasing compounds (e.g., essential oils, phenolic compounds, vitamins, and food colorants) and inorganic-based releasing compounds (e.g., metal oxides) have been used to develop antimicrobial and antioxidant packaging with improved physico-mechanical properties. For example, zinc oxide (ZnO) nanoparticles and oregano essential oil (EO) loading Pickering emulsion-based nanocarrier was incorporated into cellulose nanofibrils film. Excellent antimicrobial (against *Listeria monocytogenes*) and antioxidant activity was obtained, while the barrier properties of the developed films against oxygen, water vapor, and visible light were improved [16]. However, the direct addition of such active compounds to biopolymeric matrices results in their burst release and unacceptable performance of the packaging materials [7]. The main disadvantages of their industrial scaleup are refer to active compounds, unpleasant flavors, and high sensitivity to environmental conditions (e.g., temperature, pH, gas, and light).

Nanoencapsulation is the technology of encasing active compounds (core material) in solid, liquid, or gaseous states in different matrices (shell materials and surrounding or wall materials) by using different methods. It offers protection and a controlled release of entrapped compounds under certain conditions [17]. Thereby, nanoencapsulation can enhance stability and increase shelf life, efficiency, and bioavailability of active compounds [18]. Based on this technology, different nanocarriers were developed. Considering wall materials, the main nanocarriers can be classified on lipid-based nanocarriers (nanoemulsions, nanoliposomes, solid lipid nanoparticles, and nano-structured lipid carriers) [17], biopolymeric-based nanocarriers (nanoparticles, nanofibres, nanogels, and cyclodextrins inclusion complexes) [19], and nanoclay-based nanocarriers (halloysite nanotubes) [7,14].

This manuscript deals with the following features: (i) an overview of the main groups of nanocarriers and their benefits for developing sustainable biopolymeric-based active packaging with antimicrobial and antioxidant properties; (ii) challenges during the COVID-19 pandemic and a brief post-COVID-19 scenario for the food packaging industry; and (iii) a brief overview of the used constituents for producing biopolymer-based active packaging with the release of antimicrobial and antioxidant compounds.

## 2. Challenges during and Post COVID-19 Era

## 2.1. Food Supply Chain

A food supply chain is the sum of all followed steps by food products to end up from the farm to the fork. Transportation was restricted during the lockdown and induced disruption in the food supply chain. Food loss and waste have increased due to the lack of transfer of ready-to-sell goods to their destination [20,21]. Perishable agricultural products were particularly affected, such as fruits and vegetables, fish, meat, and dairy products [4,22]. Active packaging was proposed by FAO as the key technology for improving the quality of fresh foods during transportation and storage [7]. Another challenge for the food supply chain was observed in the online food trade, which had an explosive increase in demand. A rapidly increased need and fast implementation for packaged food

is a warning for sustainable packaging [5]. The function of the packaging (e.g., hygiene and protection of the product) is being perceived more vigorously [6]. Moreover, consumers' concern regarding the survival of SARS-CoV-2 on packaging surfaces has resulted in an increased interest in active food packaging with antimicrobial activity [23].

The food supply chain has to face an increased demand for innovative functional food containing target active compounds such as antioxidants and vitamins [24,25]. These are considered important in boosting the immunity system and improving consumers' health [5,26]. However, antioxidants such as essential oils and vitamins have low stability in environmental conditions. On the other hand, a controlled release of active compounds into packaged food is desired for maintaining their efficiency. In this sense, nanocarriers are suitable for increasing the shelf life of active compounds and controlling their release [27,28].

#### 2.2. Consumer Behavior

Lockdown has produced a drastic change in consumer habits [3]. Online shopping and takeaway services for home delivery have exploded [5]. Due to safety concerns, instead of leaving their homes (e.g., shopping in supermarkets and restaurants), consumers immediately adopted e-commerce purchases, including food and groceries [29]. During COVID-19 lockdown, a survey conducted in SUA showed that groceries shopping had reached its highest demand (>90%) [20]. Currently, food delivery has become a global market worth more than USD 150 billion, and it has more than tripled since 2017 [30]. This form of consumer behavior results in an increase in single-use food packaging, which raises a huge amount of plastic waste [29]. As a result, the global packaging market value will increase from USD 917 billion in 2019 to USD 1.05 trillion by 2024, with a compound annual growth rate of 2,08% [3]. The packaging sector represents about 40% of the worldwide consumption of plastic material (368 million tons in 2019) [31], from which 60% represents food packaging [32].

Panic buying during the quarantine has driven consumers to try products that they have not purchased before (e.g., freeze-dry ready meals) [5,33]. Increased demand for frozen and packaged food has been registered during the COVID-19 era [3]. Moreover, the lack of cooking skills is estimated to increase food waste [34]. Consumption represents 22% of total food wastage. Total wasted food annually was estimated to be 1.3 billion metric tons [35]. Therefore, a focus on consumer education regarding food waste, packaging, and shelf-life information is important [34,36]. Another change in consumer behavior could be observed in an increased demand for healthy and immunity-boosting food compared to junk food [3]. Products that consumers consider for boosting their immune system (e.g., essential oils, vitamins) have registered a 3-fold to 4-fold increase in sales [5].

## 2.3. Plastic and Its Increased Use

Plastic is a petroleum-based material with a high molar mass, and it is very harmful for the environment due to the long period associated with its decomposition and generation of solid waste [37]. Due to its low cost, low density, flexibility, durability, strength, friendly design, and easy fabrication, plastic is for applications such as packaging [6]. Prior to the pandemic, much effort was placed into avoiding plastic use; suddenly, during the COVID-19 era, plastic was considered a protector for saving lives. Plastic has wide applications as raw materials in the production of personal protective equipment (e.g., masks and gloves) and medical supplies (e.g., vaccination residues and confirmatory COVID-19 testing) [6,31]. In the past, reusable bags were encouraged for reducing plastic waste. During the COVID-19 era, single-use plastic consumption has increased (49 million tons in 2019). Single-use plastic bags showed no evidence of bacteria being more hygienic than reusable bags (if not regularly cleaned) [6]. During the COVID-19 pandemic, food delivery services, online groceries, and demand for personal protection equipment was predicted to increase packaging materials and other materials (e.g., medical issues) by 44.8% and 13.2%, respectively. Therefore, generated plastic waste during pandemic reveals alarming records [31]. In order to reduce the plastic problem, the development of active

and biodegradable films has been observed as a viable alternative. In addition, active packaging releases active compounds, such as antimicrobials and antioxidants, that can extend the quality or shelf life of foods. Figure 1 provides an overview regarding the main challenges for food packaging during and after the COVID-19 pandemic.



Figure 1. Main challenges during and after the COVID-19 pandemic for food packaging.

## 3. Active Packaging Constituents

# 3.1. Biopolymeric-Based Barrier Layer

Biopolymers have attracted attention in the food packaging industry as ecofriendly packaging, and they have relatively fast degradability, without any environmental issues [38]. They are renewable, non-toxic, and environmentally safe [39]. The global market scale of biopolymers is expected to increase, reaching USD 27.9 billion by 2025 at a compound annual growth rate of 21.7% [40]. However, the main disadvantages of these biopolymers are their high prices compared to conventional polymers, low mechanical properties, and high permeability to gases [39]. Examples of biopolymers used for producing active food packaging include polysaccharides, proteins, lipids (natural biopolymers), and PVA and PLA (synthetic biopolymers [41]). Polysaccharide-based matrices have poor water resistance, even though they have suitable gas barriers [42]. Protein-based matrices have lower moisture resistance with good mechanical strength. Lipid-based matrices have poor mechanical and optical properties but have relatively good resistance to water vapors. Lipids cannot be used alone for making active films and can only be used in combination with polysaccharides and protein-based matrices (composite-based matrices). Lipid-based coatings are often opaque, waxy, slippery, relatively tick, and easily breakable. A composite-based matrix is a combination of two or more biopolymers for reducing the weakness of individual materials [43,44]. On the other hand, PVA-based matrices have excellent thermal and mechanical properties, superior transparency, and reasonable prices [45]. Moreover, PVA-based matrices have unique characteristics, being water soluble and providing good film-forming material. Therefore, it is mainly used as a biodegradable film material [11]. In order to use biopolymers for packaging purposes, their drawbacks such as brittleness, heat stability, high gas, and water permeability should be improved [46]. Different strategies, including chemical structure modification; the addition of organic and inorganic compounds, plasticizers, and composite blending; and the incorporation of nanomaterials, were used to enhance the physical, chemical, and mechanical properties of biopolymeric matrices. Nanoscale reinforcements promote a larger interface surface area that results in quantitative enhancement in the performance of the obtained biopolymeric matrices [39]. Nanocarriers are nanomaterials that enhance biopolymeric matrices

performance. For example, nanoparticles improve active films' mechanical, physical, and barrier properties. Nanofibers possess high surface-to-volume ratios with high efficiency for releasing active compounds. Nanoemulsions increase bioavailability and stability while properly delivering active compounds from packaging into the food [43].

## 3.2. Active Layer

3.2.1. Organic-Based Releasing Compounds

EOs are natural and complex liquid mixtures that can be synthesized in several plant parts (leaves, seeds, and roots) [47]. They received much attention due to their remarkable bioactivity and health-promoting benefits. EOs have antimicrobial and antioxidant properties (benefic for increasing the shelf life of food products) due to their content of phenolic compounds. EOs are considered more effective against foodborne pathogens [48] instead of synthetic preservatives, for which their safety is ambiguous [47]. EOs use can offer clean label products and are generally recognized as safe (GRAS) by regulatory authorities [13]. However, EOs are hydrophobic compounds with high volatility, strong flavor and aroma, and are chemical instability to light, heat, moisture, and oxygen [18,49]. Table 1 presents a few examples of recent active compounds loaded with nanocarriers and nanocarrier benefits.

 Table 1. Recent examples of active compounds loaded nanocarriers.

Nanocarrier	Active Compounds Benefits		Reference
	Laurel EO	Increased bactericidal activity against <i>Pseudomonas luteola</i> compared to EO	[50]
Nanoemulsion	Ginger EO	Improved solubility, stability, and bacterial inhibition (against <i>S. aureus</i> and <i>P. aeruginosa</i> ) of EO	[51]
Pickering nanoemulsion and starch NPs	Carotenoids	Stable relative to heat and freeze-thaw treatments; better oxidative and physical stability at 6 °C and 25 °C	[52]
Pickering nanoemulsion	Black cumin seed oil	Black cumin seed oil Black cum	
Nanoliposomes	Cumin EO Reduced the rate of diffusion and increased antimicrobial and antioxidar activity of EO		[54]
	Polyphenols from bamboo leaf extract	Improved solubility and bioavailability	[55]
NPs	Nettle EO	Higher antioxidant activity and antimicrobial inhibition of <i>S. aureus</i> and <i>E. coli</i> than free EO	[56]
Nanofibers	Vitamin D3	Controlled release and improved physico-mechanical properties of nanocarrier	[57]
	Curcumin and anthocyanins	Stronger antioxidant and antimicrobial activity	[58]
SLN	Lutein	Increased bioavailability of lutein	[59]
	β-Carotene	Increased the bioaccessibility of β-carotene	[60]
NLC	Cola hispida extract	NLC offered stability and significant $(p < 0.05)$ antioxidant activity to extract	[61]
Nanogel	Curcumin	Desirable storage stability during 30 d	[62]
β-Cyclodextrin	Thyme EO	Enhanced aqueous solubility by 15 folds; minimum inhibitory concentration of EO decreased up to 29.4 folds	[63]
. ,	Rosemary EO	Exhibited prolonged activity against <i>S. aureus</i> of EO	[64]

SLN—solid lipid nanoparticles; NLC-nanostructured lipid carriers; EO—essential oil; NPs—nanoparticles; d—days.

Phenolic compounds are secondary metabolites that exist in all vascular plants and have one or several benzenic cycles. The main classes of plant phenolics are phenolic acids and coumarins, flavonoids, and lignans. These compounds possess antioxidant activity by scavenging radical oxygen species [19]. Moreover, they can inhibit microbial growth. Their incorporation in active packaging is one of the most effective methods for enhancing safety and maintaining the quality of packaged foods [39]. However, these hydrophobic compounds are unstable in the presence of heat and light, have poor solubility, and have low bioavailability [19].

Vitamins are bioactive molecules that have a crucial role in maintaining health and wellbeing [65,66]. They can combat chronic diseases (e.g., coronary heart disease, cancer, diabetes, and macular degeneration) [67], improve the immunity system, combat aging, decrease cholesterol, avoid neurological disorders, etc. [19]. Despite knowledge of their critical role in human health, vitamin deficiency is still dominant in both developed and poorly developed countries [67]. Vitamins are classified as hydrophilic (e.g., vitamin B and vitamin C) and lipophilic (e.g., vitamin A, D, E, and K). In particular, the bioavailability of liposoluble vitamins is reduced due to their low solubility in water. However, both water-soluble and oil-soluble vitamins are sensitive to heat and oxidation, and their they lose efficiency significantly during processing, transportation, and storage [19].

Food colorants are other valuable active compounds for human health, especially natural colors. They are extensively available from several sources such as plants (stems, leaves, flowers, and fruits) and microorganisms (e.g., insects). They have strong advantages such as low cost, simple extraction methods, high relative abundance, and sustainability [68]. They constitute a wide range of colorants with different stability and solubility [19]. The main classes of natural pigments are anthocyanins, betalains (hydrophilic compounds), carotenoids, and chlorophylls (lipophilic compounds) [69,70]. These are very sensitive to process and environmental conditions (heat, light, and oxygen), possessing low stability and poor bioavailability [71].

#### 3.2.2. Inorganic-Based Releasing Compounds

Bionanocomposites containing biopolymers and inorganic nanomaterials are intensively studied as an ecofriendly alternative to plastic [72]. The incorporation of metal oxides nanoparticles can enhance thermal stability, optical properties, tensile strength, and antibacterial properties of biopolymeric matrices [39]. ZnO and titanium dioxide (TiO<sub>2</sub>) are metal oxides most commonly used as antimicrobial compounds in active food packaging [15]. Moreover, other metal oxides such as magnesium oxide (MgO) have shown increased potential as an antibacterial compound [73].

 $TiO_2$  is a well-known low-cost metal oxide with high chemical stability [15]. It is a commonly used food ingredient that has been approved by the United States Food and Drug Administration (FDA) for use in human food. The incorporation of  $TiO_2$  into biopolymer-based packaging may increase tensile strength, improve heat resistance, reduce permeability, and enhance antimicrobial activity. It is a photocatalyst that acts as an oxygen and water scavenger and preservative [74]. Since 2016, the European Food Safety Agency (EFSA) has considered TiO<sub>2</sub> unsafe as a food additive due to its genotoxicity and highlighted the need for more research. However,  $TiO_2$  is not banned in the food industry. Furthermore, biosynthesis (a "green" synthesis method) using plant extracts is a recent synthesis strategy for obtaining TiO<sub>2</sub> nanoparticles with good antibacterial activity [15]. ZnO has a strong antibacterial activity, is non-toxic, has high stability, and is also recognized by FDA [75]. ZnO nanoparticles exhibit a large surface-to-volume ratio, highly crystalline structure, improved mechanical properties, high thermal conductivity, and high optical absorption (UV-VIS region). ZnO is used as an antibacterial and antifungal agent in the food industry [15], having low-cost synthesis and ease of handling [76]. It displays good antimicrobial activity against foodborne bacteria such as *Escherichia coli* and L. monocytogenes [16]. In addition, ZnO nanoparticles show excellent antioxidant and photocatalytic properties [77]. Due to a high surface area and hydrophilic surface, ZnO nanoparticles could aggregate. However, their surface modifications can hinder their aggregation and ensure better compatibility between nanoparticles and biopolymeric matrices [76]. MgO has gained a significant interest as an active compound for active packaging. MgO nanoparticles can enhance packaging polymers' antimicrobial, physico-mechanical, and thermal properties. In addition, it can be synthetized from relatively inexpensive raw materials [73].

## 4. Nanocarriers for Sustainable Active Packaging

One of the biopolymeric-based active packaging drawbacks is the changeable properties of materials during time, especially of incorporated active compounds into the biopolymer matrix [78]. Active compounds are unstable during processing and storage. Extrinsic (e.g., pH, high temperatures, light, and oxygen) and intrinsic (such as interactions with other constituents) conditions have degradative effects and reduce the shelf life of active compounds. Biopolymeric matrices should be improved since their physical, chemical, and mechanical properties are unsatisfactory for protecting packaged food [79]. The main roles of nanocarriers are to protect active compounds from damaging factors for increasing their shelf life and effectiveness and to offer controlled release. Encapsulated active compounds in biopolymeric matrices undergo two processes before they are active: migration from nanocarrier to biopolymeric matrices, followed by further diffusion and release from biopolymeric films to the food system. The particle size of nanocarriers has the largest effect on the release rate of active agents. The lower the nanocarrier size, the higher the release rate [12]. On the other hand, biopolymeric matrices can be enhanced by adding active compounds-loaded nanocarriers. Thermal stability [80], water and gas permeability, UV-VIS light transmittance [77], and mechanical strength [81] are a few examples of improved biopolymeric matrices properties by adding nanocarriers. Classification of the most common nanocarriers for producing sustainable active packaging is shown in Figure 2. This section aims to provide a brief overview of nanocarriers that improved biopolymeric matrices properties for obtaining sustainable active packaging.



**Figure 2.** Classification of main nanocarriers used for active packaging development. SLN—solid lipid nanoparticles; NLC—nano-structured lipid carriers.

## 4.1. Lipid-Based Nanocarriers

## 4.1.1. Nanoemulsions

Nanoemulsions are composed of two immiscible phases (oil and water) stabilized by a surfactant/emulsifier [17] or biopolymers (polysaccharides and proteins), normally possessing a diameter size between 10 to 200 nm [13]. Nanoemulsions are nanocarriers for both hydrophilic and lipophilic active compounds for improving their stability, aqueous solubility, and bioavailability [18]. Lipophilic compounds are entrapped in o/w emulsion, while hydrophobic compounds are incorporated in water-in-oil (w/o) or water-in-oil-in-water (w/o/w) emulsion [17]. Nanoemulsions are kinetically stable (but thermodynamically unstable) with a transparent or, sometimes, milky aspect. Their stability depends on pH,

ionic strength, and storage temperature. Moreover, the prevention of creaming, aggregation, or flocculation can be avoided by the optimization of the conditions and composition of nanoemulsion [18]. There are two techniques used for nanoemulsion production: high energy methods (top-down methods, such as high-pressure homogenization, ultrasonication, high shear homogenizer, microfluidization, and membrane emulsification) and low energy methods (bottom-up methods, such as membrane emulsification and microfluidics) [13]. Table 2 presents recent examples of improved active packaging by lipid-based nanocarriers use.

Nanocarrier Core Material Wall Material **Active Packaging Matrix** Effects on Packaging Matrix Effects on Food Reference Increased roughness with oil concentration, gradual reduction in elastic modulus Copaiba oil Pectin film and tensile strength, [82] increased elongation at break, Nanoand antimicrobial activity emulsion against S. aureus and E. coli Improved physicochemical properties and antibacterial Cinnamon EO Pullulan film [83] activity against S. aureus and E. coli Improved physical properties of films (e.g., mechanical, Extended storage Anthocyanidin/chitosan water vapor permeability time by 6–8 d of fish Cinnamon-perilla EO Collagen [84] nano-composite film and thermal stability), fillets hydrophobicity, and Pickering antioxidant activity nanoemulsion Exhibited good mechanical and water barrier properties Whey protein Pickering emulsion had a Marjoran EO Pectin film [85] isolate, inulin slow release of EO and a lower antioxidant activity than nanoemulsion Additional benefits Saffron extract [86] Rapeseed lecithin Pullulan film due to unique flavor Enhanced oxygen barrier components and color of saffron High antimicrobial and antioxidant activity; controlled Gelatin/chitosan Satisfactory mechanical the growth of Nano-Betanin nanofibers/ZnO NPs properties and high surface inoculated bacteria [75] liposomes nanocomposite film lipid oxidation, and hydrophobicity changes in the pH and color quality of beef meat Improved mechanical Phospholipid and Extended the shelf Garlic EO Chitosan film properties and water resistance [87] cholesterol life of chicken fillet Sova lecithin. Decreased crystallinity and Compritol<sup>®®</sup> 888 CG ATO SLN PVA film [80,88] a-Tocopherol increased antioxidant capacity Decreased tensile strength, elastic modulus, swelling ratio; increased thermal stability, water vapor NLC Calcium/alginate film [89] permeability, and contact angle by increasing NLC concentration; improved UV-absorbing properties

Table 2. Recent examples of improved active packaging by lipid-based nanocarriers use.

SLN—solid lipid nanoparticles; NLC-nanostructured lipid carriers; EO—essential oil; NPs—nanoparticles; d—days; PVA-polyvinyl alcohol; ZnO—zinc oxide.

Active packaging was produced by using nanoemulsion nanocarriers as such [83,90] or as Pickering nanoemulsions [84,85]. For example, copaiba oil nanoemulsion was incorporated into pectin films, and chemical, morphological, thermal, mechanical, and antimicrobial properties were tested. These results showed great potential for active food packaging and are a promising alternative for reducing environmental impact [82]. Cinnamon essential oil nanoemulsion was prepared by ultrasound treatment at various acoustic energy inputs. It was incorporated into pullulan-based active films for investigating the effects on structure and properties. Cinnamon nanoemulsion containing 6% Tween 80 under 10 min

of ultrasound treatment decreased water vapor permeability and increased elongation at the break of pullulan films. The smallest size (60 nm) and uniformity distribution of oil droplets in the film matrix owned the greatest cinnamon retention and bacteriostasis ability. Meanwhile, increasing the concentration of cinnamon nanoemulsion improved antibacterial activity against *E. coli* and *Staphylococcus aureus* [83]. Pickering nanoemulsion of cinnamon-perilla EO was used to improve the properties of anthocyanidin/chitosan nano-composite films. The addition of Pickering nanoemulsion did not damage the original structure of the films. Furthermore, it improved physical properties, hydrophobicity, and antioxidant activity and increased the storage time of fish fillets by 6–8 days [84]. Great potential for improving the quality and shelf life of food by using a new active food packaging system was also reported by Almasi et al. 2020 [81]. Pectin films containing marjoram essential oil-loaded Pickering emulsion had good mechanical and water barrier properties due to their highly dense and less permeable structure. In addition, encapsulated EO into Pickering emulsion nanocarrier provided significantly (p < 0.05) slower release profile and lower antioxidant activity in the film samples compared to EO-loaded nanoemulsion nanocarrier.

## 4.1.2. Nanoliposomes

Nanoliposomes are vesicles similar to natural cell membranes, smaller than 200 nm, formed by an aqueous core inside and one or more bilayers (primarily of phospholipids) outside, with amphipathic properties [17,91]. Due to their structure, these nanocarriers can deliver both hydrophilic and lipophilic (or amphiphilic) active compounds, even at the same time [91,92]. There are three types of nanoliposomes: unilamellar vesicles (one layer), multilamellar vesicles (more concentric bilayers), or multivesicular vesicles (non-concentric bilayers). Nanoliposomes are one of the most widely studied colloidal nanocarriers [93]. The great advantage of nanoliposomes nanocarriers is their controlled release of active compounds directly to a specific target location [92], preventing unnecessary interactions with other substances. In addition, nanoliposomes improve the performance of encapsulated active compounds by increasing their solubility and bioavailability and present high biocompatibility and biodegradability. However, nanoliposomes also have some disadvantages, such as chemical and physical instability [47], having the tendency to aggregate or fuse, thus increasing in size [79]. As production techniques for these nanocarriers, mechanical agitation was used (sonication, extrusion, high-pressure homogenization, and microfluidization) [93], as well as thin-film hydration, reversed-phase evaporation, solvent-injection, detergent depletion, and calcium-induced fusion [92]. The incorporation of nanoliposomes into the films may enhance the long-term stability of nanoliposomes and can provide higher protection of active compounds. For example, incorporation of saffron extract components-loaded rapeseed lecithin nanoliposomes into pullulan films caused better protection of core material during release compared to free incorporation. Free saffron extracts immediately degraded during the same conditions in phosphate-buffered saline solution. In addition, incorporated nanoliposomes reduced oxygen permeability while not affecting water vapor permeability of films significantly. The utilization of saffron extract components can provide health benefits due to its antioxidant properties [86]. Active packaging loading nanoliposomes could result in a longer food shelf life, particularly for meat products. Betanin nanoliposomes incorporating gelatin/chitosan nanofiber/ZnO nanoparticles bionanocomposite film controlled the changes in physicochemical and color properties during fresh beef meat storage time by providing high antibacterial and antioxidant activities. Furthermore, films exhibited satisfactory mechanical properties and high surface hydrophobicity [75]. Moreover, garlic EO nanoliposomes incorporating chitosan film increased the shelf life of chicken fillet at least two to three times more than the usual shelf life, which has been regulated for 3 days at 4 °C. The higher the liposome incorporation into film matrix, the stronger the inhibitory effects of total viable count, coliforms, S. aureus, and psychrotroph bacteria. Regarding garlic EO nanoliposomes effects in the chitosan film matrix, the thickness, water solubility, elongation at break, and some microstructural properties and antioxidant activity of films have been improved. Considering

the increasing demands for consumption of natural compounds, the use of such films subjected to different EO is recommended [87].

## 4.1.3. Solid Lipid Nanoparticles and Nano-Structured Lipid Carriers

Solid lipid nanoparticles (SLN) are nanoscale-sized vesicles, generally in the range of 50 nm to 1000 nm, similar to o/w crystallized nanoemulsions, produced by lipids that remain solid at room and/or body temperature (liquid lipid oil is replaced by solid lipid), which are dispersed in water and stabilized by emulsifiers/surfactants [93]. These nanocarriers are considered second generation nanoemulsions [94]. Despite the fact that SLN found applications mainly for lipophilic compounds [91], they are also suitable for both hydrophilic and hydrophobic compounds [47]. SLN was developed to avoid the drawbacks of the above-mentioned lipid-based nanocarriers and to gather all their advantages in its structure [17]. SLN is a very promising nanocarrier for active compounds used in active packaging production since the use of crystallized lipids prolong and control their release and protect active compounds from external conditions (such as extreme pH levels, high temperatures, enzymes, or oxidation) [47,92]. Moreover, SLN presents low toxicity, excellent biodegradability, sterilization and bioavailability, low cost, avoiding organic solvent [47], good mixture stability [92], and large-scale production [93]. However, SLN also has some disadvantages such as low loading efficiency and expulsion of active compounds at unexpected temperature fluctuations during transport, storage, and application due to its perfect crystalline structure. In addition, SLN is thermodynamically unstable (similarly to nanoemulsions and nanoliposomes) and can form large aggregations under acidic conditions [47,92]. SLN stability can be improved by using various shell materials [92]. The selection of proper materials (lipids and surfactants) is crucial for the loading capacity and release of active compounds and for size and stability [47]. Biopolymers were successfully used to stabilize SLN. For example, SLN prepared with pectin as a natural emulsifier and stabilizer, respectively, exhibited improved physico-chemical properties than when prepared with organic solvents (acetone and ethanol at 1:1 v:v ration) [95]. SLN nanocarriers are obtained by high-pressure/high-shear/hot/cold homogenization and/or ultrasonication, followed by cooling to induce droplet crystallization [92]. Moreover, SLN could be produced by using organic solvents emulsification (emulsification–solvent evaporation, emulsification-solvent diffusion, and solvent injection) and low energy methods (microemulsion, double emulsion, phase inversion temperature, and membrane contactor) [94].  $\alpha$ -Tocopherol-loaded SLN incorporating PVA films confirmed the possibility of its use as active packaging for food conservation. Films containing SLN showed higher thermal stability compared to pure PVA films and has changed film structure by decreasing crystallinity. Furthermore, it demonstrated a higher antioxidant capacity and a controlled release of  $\alpha$ -tocopherol [80].

Nano-structured lipid carriers (NLC) represent the next generation of SLN containing both liquid and solid lipids (oil) ranging from 4:1 to 1:4, which are dispersed in water and stabilized by emulsifiers/surfactants (also similar to *o/w* nanoemulsion) [47]. NLC is appropriate for both lipophilic and hydrophilic compounds [92], such as antimicrobials, antioxidants, nutraceuticals, pigments, or drugs [89]. Due to their imperfect crystalline structure, NLC has a higher loading efficiency, higher encapsulation efficiency, higher bioavailability, and prevents expulsion of entrapped active compounds compared to SLN [17]. However, NLC cannot offer good release control and protection of the core material and reduces its leakage compared to SLN [96]. NLC can be obtained by using methods employed for SLN [47,94]. Different amounts of NLC nanocarriers incorporating calcium/alginate films could modulate the physico-chemical and functional properties of films [89].

## 4.2. Biopolymeric-Based Nanocarriers

### 4.2.1. Nanoparticles

Nanoparticles (also known as nanocapsules) are nano vehicles with solid spherical particles less than 100 nm, obtained from biopolymers as shell materials and active com-

pounds as core materials [13,18]. Both natural (polysaccharides, proteins, and lipids) and synthetic (e.g., PLA and PVA) biopolymers are used as nanocarriers for active compounds with antioxidant and antimicrobial activity for active packaging [91]. Biopolymers can carry both hydrophilic and hydrophobic bioactive ingredients and nutraceuticals, as well as metal oxides. Nanoparticles obtained from individual biopolymers and their mixture have received significant interest as nanocarriers for sensitive active compounds due to their encapsulation efficiency, preservation, targeted delivery, and biocompatibility. Furthermore, biopolymers are considered GRAS ingredients, and their use for producing nanoparticles does not involve destructive chemicals and organic solvents, which is an interesting option for green industrial application [17]. However, full industrial scaleups of polysaccharides and proteins-based nanoparticles are more difficult compared to lipid-based nanoparticles due to a more complicated process during production [93]. Nanoparticles can be produced by using several methods such as spray-drying, freeze-drying, coacervation, ionic gelation, layer-by-layer deposition, fluidized bed coating, and supercritical fluid method [97]. Table 3 presents recent examples of improved active packaging by using biopolymeric-based nanocarriers and clay-based nanocarriers.

**Table 3.** Recent examples of improved active packaging by biopolymeric-based nanocarriers and clay-based nanocarriers use.

Nanocarrier	Core Material	Wall Material	Active Packaging Matrix	Effects on Packaging Matrix	Effects on Food	Reference
Nano- particles	ZnO loaded Gallic acid	-	Chitosan film	Remarkably improved mechanical and physical properties	-	[77]
	ZnO-loaded clove EO	Chitosan	Chitosan/ pullulan nano-composite film	Enhanced tensile strength, film hydrophobicity, water vapor and oxygen barrier, and UV light blocking ability	Extend shelf life of chicken meat by up $5 \text{ d}$ at $8 \pm 2 \degree \text{C}$	[76]
	ZnO	-	Chitosan/ bamboo leaves film	High UV barrier and strong antioxidant and antibacterial activity against <i>E. coli</i> and <i>S. aureus</i>	-	[98]
	TiO <sub>2</sub>	-	Chitosan/ red apple pomace film	Considerable mechanical properties	Antimicrobial and antioxidant activity, indicator for the freshness of salmon fillets	[99]
	TiO <sub>2</sub>	-	Cellulose nanofiber/whey protein film	-	Increased shelf life of lamb meat from around 6 to 15 d	[74]
Nanofibers	<i>Mentha spicata</i> L. EO and MgO NPs	Sodium caseinate/ gelatin	-	-	Improved sensory attributes and increased shelf life of fresh trout fillets up to 13 d	[73]
	Cinnam- aldehyde	Pullulan/ ethyl cellulose	-	Improved hydrophobicity and flexibility; inhibited E <i>coli</i> and <i>S. aureus</i> growth	-	[100]
	1,8-cineole from spice EO	Zein	-	The higher the storage time, the higher the inhibitory effects against <i>L.</i> monocytogenes and <i>S. aureus</i>	Inhibited the growth of mesophilic bacteria counts in cheese slices	[101]
Nanogels	Rosemary EO	Chitosan/ benzoic acid	Starch/ carboxy- methyl cellulose film	Improved tensile strength and transparency, increased water vapor permeability, and inhibited <i>S. aureus</i>	-	[102]
	Clove EO	Chitosan/ myristic acid	-	-	Increased antioxidant and antimicrobial activity against <i>S.</i> <i>enteritica</i> in beef meat	[103]
	Rosemary EO	Chitosan/ benzoic acid	-	-	Inhibited microbial growth of <i>S.</i> <i>typhimurium,</i> preserved color values during storage, and increased the shelf life of beef meat	[104]

Nanocarrier	Core Material	Wall Material	Active Packaging Matrix	Effects on Packaging Matrix	Effects on Food	Reference
Cyclodextrins	Cinnam- aldehyde	-	High amylose corn starch/konjac glucomannan composite film	Decreased crystallinity; improved compatibility between the two polysaccharides and enhanced film physico-mechanical properties and thermal ability; inhibited <i>S. aureus</i> and <i>E. coli</i> growth	-	[105]
	Satureja montana L. EO	-	Soy soluble polysaccharide hydrogel	More compact structure; improved hardness, adhesiveness, and springiness of hydrogel	Reduces the visible count of <i>S. aureus</i> in meat; retained freshness and extended the shelf life of chilled pork	[106]
	Carvacrol	-	Pectin coating	Nanocarriers improved aqueous solubility and thermal stability of carvacrol and showed strong antifungal activity against <i>B.</i> <i>cinerea</i> and <i>A. alternata.</i> In pectin films, nanocarriers decreased viscosity and increased thermal stability; inhibited above pathogens in vitro	-	[107]
Halloysite nanotubes	Tea polyphenol	-	Chitosan film	Improved water vapor permeability; had antioxidant and certain antibacterial activity against <i>E. coli</i> and <i>S. aureus</i> growth; 3D printing properties	-	[108]
	Salicylic acid	-	Alginate and pectin film	Cumulative release and antimicrobial activity were higher for alginate films	-	[72]
	Silver ions	APTMS	Carrageenan film	Silver ions-loaded APTMS modified halloysite nanotubes exhibited increased water contact angle, water vapor permeability, UV-light barrier, and antibacterial activity	-	[109]

Table 3. Cont.

EO—essential oil; NPs—nanoparticles; d—days; ZnO—zinc oxide; TiO<sub>2</sub>—titanium dioxide; MgO—magnesium oxide; APTMS—(3-aminopropyl)-trimethoxysilane.

Since nanoparticle-based nanocarriers have exploded during the last years based on a simple search on Google Scholar for "active packaging and nanoparticles," a few examples of recent studies of nanoparticles incorporating active packaging will be provided. ZnO nanoparticles loaded Gallic acid into chitosan films may be considered for active food packaging application and better for black grape, apple, mango, fruits, and tomato. The incorporation of nanoparticles remarkably enhanced the desired mechanical property of the chitosan film. Physical properties such as oxygen and water permeability, swelling, water solubility, and UV-vis light transmittance were also positively improved [77]. Ecofriendly active nano-composite films were successfully obtained by incorporating ZnO and clove EO-loaded chitosan hybrid nanoparticles into chitosan/pullulan composite films. The author reported enhanced UV-blocking capacity, hydrophobicity, mechanical strength, water vapor, and oxygen barrier. The enhanced bioactivity of the composite film was proved by high antioxidant activity and highly sensitive antibacterial activity for Pseudomonas aeruginosa, S. aureus, and E. coli. Furthermore, these films extended the shelf life of chicken meat to 5 days at 8  $\pm$  2 °C [76]. Incorporating TiO<sub>2</sub> nanoparticles and red apple pomace into chitosan film results in obtaining a multifunctional food packaging material. TiO<sub>2</sub> nanoparticles remarkably improved water vapor and UV-VIS light barrier properties, mechanical strength, and thermal stability of chitosan-red apple pomace films. TiO<sub>2</sub> nanoparticles and red apple pomace showed a synergistic enhancement of the antimicrobial activity in the chitosan matrix and developed a pH-responsive colorchanging property, being a successful indicator for monitoring the freshness of salmon fillets [99]. When TiO<sub>2</sub> nanoparticles and rosemary EO were added into the cellulose/whey

protein matrix, the shelf life of lamb meat increased from around 6 days to 15 days under refrigeration conditions. This active packaging significantly reduced microbial growth, lipid oxidation, and lipolysis of meat [74].

## 4.2.2. Nanofibers

Nanofibers are nanocarriers with particle sizes <100 nm obtained from the conversion of a polymer solution into solid fibers by application of high voltage electric field through spun or spray, respectively [91]. Both hydrophilic and hydrophobic active compounds can be incorporated into nanofibers, protecting them against deterioration and increasing their shelf life and bioavailability [110]. These nanocarriers help advance food packaging techniques and are facile, cost-effective, and practicable techniques for large-scale fabrication [111]. In addition, nanofibers nanocarriers do not require heat treatment, which is an advantage for preserving the original properties of heat-sensitive active compounds. As a drawback of these nanocarriers, attention should be given to biopolymeric solution properties, environmental parameters, and processing variables to optimize the characteristics of formed nanofibers [96,110]. Nanofibers are obtained by electrospinning (for high biopolymer concentrations) and electrospraying (for low biopolymer concentrations) methods [18]. For example, a desirable material for active food packaging was developed from cinnamaldehyde-loaded pullulan/ethylcellulose nanofiber films via electrospinning. The obtained film has improved flexibility and hydrophobicity and antimicrobial activity against E. coli and S. aureus [100]. Mentha spicata L. and MgO nanoparticles were incorporated into sodium caseinate/gelatin nanofibers via electrospinning. Nanofibers gently inhibited the growth of S. aureus and L. monocytogenes under in vitro conditions. In addition, these nanofibers could improve sensory qualities and extend the shelf life of fresh trout fillets up to 13 days. Therefore, developed nanofibers could open new opportunities in practical applications as a new method for enhancing the implementation of antimicrobial compounds in active food packaging [73]. Active packaging using laurel and rosemary EO-loaded nanofibers in zein films was developed via electrospinning. The antibacterial effectiveness of the active films was tested against S. aureus and L. monocytogenes increased through storage time. Compared to control, inhibition rate increased during storage time, showing a significant reduction of ~2 logarithm units after 28 days at 4 °C compared to control. Furthermore, mesophilic bacteria were also inhibited in cheese slices coated with EO-loaded zein nanofibers-based films [101].

## 4.2.3. Nanogels

Nanogels are formed by hydrophilic or amphiphilic biopolymers, which form tridimensional networks via physical or chemical cross linking or by shelf assembly process, with particle sizes in the range of 1–200 nm [112]. These nanocarriers have a good swelling ability in suitable solvents. When water solvent is used for nanogels, they are known as "hydrogels" [96]. Hydrogels are soft nanocarriers with high water content, contributing to their biocompatibility [113]. Conversely, nanoorganogels (micelle nanogels) are insoluble in water and have a high affinity for oily substances [17]. Hydrogels-based nanocarriers are used for hydrophilic compounds, while nanoorganogels-based nanocarriers are used for hydrophobic compounds [17]. Nanogels are considered very promising nanocarriers due to their high loading capacity, high stability, better compatibility, sustainable release of active compounds, good water distribution [18], tunable size, ease of preparation, and stimuli responsiveness (e.g., temperature, pH, light, and biological agent) [114]. Nanogels can be produced from natural biopolymers (e.g., alginate, chitosan, whey proteins, and soy proteins) by using appropriate cross-linking agents [96,115]. Moreover, synthetic polymers such as PVA, polyethylene oxide, polyethylene mine, polyvinylpyrrolidone, and poly-N-izopropylacrylamide could be used for producing nanogels, especially for drug delivery [96]. Cross linking provides the swelling property instead of dissolving nanogels [116]. Spherical nanogels are produced using bottom-up methods (e.g., antisolvent precipitation, coacervation, and fluid gel particle formation), while nanogels with

different shapes are produced by top-down methods (e.g., homogenization and surface modification) [112]. Currently, the interest of consumers for natural compounds and healthy food free of synthetic additives is increasing [103]. EOs have high volatility and instability when exposed to environmental factors. Nanogel-based nanocarriers can improve EOs performance. For example, the performance of clove EO was improved when it was encapsulated into chitosan/myristic acid nanogel. This nanocarrier system was applied as an active coating to preserve beef meat under refrigeration conditions. It was found that encapsulated EO into nanogel-based nanocarrier had higher antioxidant activity and inhibitory effects against Salmonella enterica Serovar Enteritidis compared to non-encapsulated EO at only 2 mg/g beef. Moreover, encapsulated EO resulted in minimal unfavorable impacts on meat color values through prolonged storage [103]. Rosemary EO-loaded chitosan/benzoic acid nanogel using the self-assembly method was used and then it was incorporated into the starch/carboxymethyl cellulose film. Encapsulation of rosemary EO into nanogel-based nanocarrier increased inhibitory effects against *S. aureus*. Furthermore, the addition of rosemary EO-loaded nanogel into film matrix improved tensile strength and transparency [102]. In another study, rosemary EO-loaded chitosan/benzoic acid nanogel also revealed improved antimicrobial activity against Salmonella typhimurium on inoculated beef cutlet samples during refrigeration storage and increased the sample's shelf life [104].

#### 4.2.4. Cyclodextrin-Based Inclusion Complex Nanocarriers

Cyclodextrins are cyclic oligosaccharides of  $\alpha$ -d-glucopyranose obtained from the enzymatic processing of starch by certain bacteria such as Bacillus macerans [93]. α-cyclodextrins,  $\beta$ -cyclodextrins, and  $\gamma$ -cyclodextrins, which consist of six, seven, and eight D-glucose units, respectively, are the main types of natural cyclodextrins [117].  $\alpha$ -cyclodextrins have the smallest inner diameter (0.50–0.57 nm), followed by  $\beta$ -cyclodextrins (0.62–0.78 nm) and  $\gamma$ -cyclodextrins (0.80–0.95 nm), respectively [117,118]. Cyclodextrin has a toroid three-dimensional shape [117] with rigid lipophilic cavities and a hydrophilic outer membrane [93]. Their cavity is less polar than water [96]. In an aqueous environment, cyclodextrins can entrap either an entire highly hydrophobic molecule [93], such as EOs and vitamins, or a lipophilic moiety [91]. Cyclodextrins ("host") entrap active compounds ("guest") with the help of hydrogen bonds, van der Waals forces, or of hydrophobic effects, during simple mixing, kneading, coprecipitation, and nanoprecipitation, respectively, to form inclusion complexes [91]. Cyclodextrins are useful for converting active compounds (e.g., liquid EOs) into crystalline powder forms for better packaging and storage costs. Cyclodextrins nanocarriers increase the bioavailability and bioefficacy of active compounds by increasing water solubility, dissolution, and release rates of the active compounds. Furthermore, cyclodextrins improve the molecular stability of their guests by delaying the crystal growth of dry powders (physical stability) and by deceleration of chemical reactivity, such as dehydration, oxidation, and thermal decomposition (chemical stability) [93]. However, cyclodextrin can cause severe diarrhea symptoms and nephrotoxicity at certain limits. More studies for improving the applicability of cyclodextrin nanocarriers in food packaging are requested [119]. Most studies have only investigated the inclusion mechanism and host-guest interaction of a few compounds [118]. Due to their benefits, cyclodextrin-based nanocarriers present interest in developing sustainable active packaging materials. For example, cinnamaldehyde-loaded ß-cyclodextrin nanocarriers increased the compatibility between two polysaccharides of high amylose corn starch/konjac glucomannan composite films, resulting in improved thermal ability, mechanical strength, moisture content, and water vapor resistance. In addition, composite films with loaded nanocarrier showed obvious inhibition activity to S. aureus and E. coli, displaying a promising application in food active packaging [105]. Incorporation of Satureja montana L. EO-loaded methyl-β-cyclodextrin into soy soluble polysaccharide hydrogel exhibited a more compact structure, improved physical characteristics of nanogel, and exhibited antimicrobial activity against S. aureus in chilled pork meat. This packaging material can be used as safe and effective active packaging for increasing chilled meat shelf life and maintains its freshness [106]. In another

study, 2-hydroxypropyl-β-cyclodextrin nanocarrier increased thermal stability and aqueous stability of carvacrol as a core material. This inclusion complex exhibited strong antifungal activity against *Botrytis cinerea* and *Alternaria alternate* pathogens. When carvacrol-loaded-2-hydroxypropyl-β-cyclodextrin was added into pectin films, the apparent viscosity was decreased and thermal stability was increased. Moreover, carvacrol/cyclodextrin-loaded pectin films suppressed the colony growth of the above-mentioned pathogens in vitro; therefore, it could be a promising coating material for food preservation as well [107]. Hydroxypropyl has been noted to have increased levels and optimized biocompatibility profile compared to typical cyclodextrins [17].

## 4.3. Halloysite Nanotubes

Halloysite nanotubes are one of the most used nanoclays for producing sustainable active packaging. They have a unique tubular structure with a double role: (i) nanocarrier for active compounds and (II) nano-filler for occupying the gap in the molecular chains of film structure to improve the performance [7]. Halloysite nanotubes are aluminosilicate-clay mineral (1:1) nanotubes from the kaolin groups, in which an octahedral alumina layer alternates with a tetrahedral silica layer [14]. Halloysite is a natural tubular nanocarrier with a hollow cavity, large nanoencapsulation surface, and negatively charged exterior [7,14]. These normally have a length of  $0.2-1.5 \,\mu$ m, an inner diameter of  $10-30 \,$  nm, and an outer diameter of 40–70 nm, respectively [14]. Halloysite nanotube-based nanocarriers can entrap active compounds inside nanotube through vacuum operation or outside nanotube by electrostatic force [7]. These are non-toxic, inexpensive, and biocompatible materials, with widespread availability and tunable surface chemistry. Encapsulation of active compounds into halloysite nanotube-based nanocarriers improve thermal stability, antimicrobial activity, and sustained release [7,14]. A simple approach to construct promising active packaging with natural antioxidants and antibacterial activity was obtained by incorporation of tea polyphenol-loaded halloysite nanotubes into chitosan films [120]. This loaded nanocarrier improved water vapor permeability due to the tortuous channels formed by the nanotube. If not added in excess, which results in agglomeration, halloysite nanotubes significantly improved the mechanical properties of chitosan films [121]. The formation of a three-dimensional network enhanced the stability of nano-composite films. These films had antioxidant activity and certain inhibitory effects against S. aureus and E. coli. Furthermore, this packaging film was suitable for 3D printing as a new idea and solution of preparation [108]. Inorganic nanomaterials based on natural origin were also loaded into halloysite nanotubes for obtaining ecofriendly material for active packaging. For example, salicylic acid-loaded halloysite nanotubes were incorporated into alginate and pectin films. Cumulative release in 50% ethanol mimicking fatty food was more controlled and prolonged with alginate films. Furthermore, alginate films had a greater ability to inhibit the growth of four bacteria strains responsible for food spoilage (E. coli, P. aeruginosa, S. aureus, S. typhimurium) compared to pectin films [72]. For improving silver ion loading capacity, (3-aminopropyl)-trimethoxysilane (APTMS) was used to modify halloysite nanotubes. Then, modified and unmodified halloysite nanotubes-nanocarriers were used as nanofillers for carrageenan films. The incorporation of silver ions-loaded APTMS-modified halloysite nanotubes increased UV-light barrier, water vapor permeability, water contact angle, and antibacterial activity compared to their unmodified counterparts [109].

#### 5. Future Perspective and Post COVID Scenario

Active packaging has promising potential to combat the challenges of the COVID-19 pandemic, such as increased use of plastic and consumers' need for healthy and safe food with increased shelf life to combat food loss and waste during unstable transportation through the food supply chain. The COVID-19 pandemic has changed the pattern of consumers' habits. Considering a survey of 23,000 European shoppers, 72% of them would change their eating habits in the post-COVID-19 era to follow healthier patterns [5]. Therefore, the food industry had to adapt immediately to new strategies to comply with

consumers' demands [122]. The demand for healthy food containing active compounds has increased during COVID-19. For example, active compounds such as EOs, phenolic compounds, vitamins, and food colorants are considered essential for human health and wellbeing due to their properties to boost the immune system. However, such compounds have low availability being highly sensitive to environmental conditions, and some of them have low water solubility (hydrophobic compounds). Biopolymers-based nanocarriers are the most versatile methods of the 21st century that have revolutionized the food industry [18]. They can enhance bioavailability and bioactivity and increase the shelf life of active compounds by protecting them from direct exposure to processing, transport, and storage conditions. In addition, nanocarriers offer controlled and targeted release.

Changes in consumer demand and new lifestyles are the main issues behind the evolution of new food packaging [123–125]. This new packaging should be environmentally friendly and innovative/active (antimicrobial and antioxidant properties) [126]. Since online shopping and delivery systems have currently exploded, plastic-based single-use packaging represents the cheapest and safest solution for the individual package. In addition, plastic consumption in the medical field and for individual protection has increased. Due to the harmful effects of plastic on the environment, increased efforts to combat plastic use before the pandemic occurred. Therefore, all efforts to combat plastic fell off, and new strategies should be discovered as soon as possible. Biopolymers are suitable materials for offering ecofriendly food packaging. For example, the use of EOs-loaded biopolymeric nanocarrier as active compounds in active packaging has become an attractive trend due to their antimicrobial and antioxidant properties and are considered more effective against foodborne pathogens [13]. Antimicrobial and antioxidant activity also resulted in increased food shelf life due to delayed oxidative reactions and microorganisms' growth [127–129]. Developing active packaging with antimicrobial and antioxidant properties can be a good strategy for decreasing food loss and waste during unstable transportation inside the food supply chain. However, both active compounds and biopolymeric matrices have some drawbacks for complying with performant food packaging [130]. Nanocarriers have shown their potential to improve the disadvantages of active packaging materials. They can increase the stability and bioactivity of active compounds by a controlled release. In addition, nanocarriers can improve the physical, chemical, and mechanical properties of biopolymeric films.

## 6. Conclusions

The development of biopolymeric-based active packaging incorporating released active compounds-loaded nanocarriers represents a promising strategy for the food pack-aging sector. Active compounds-loaded nanocarriers are able to increase the shelf life and durability of biopolymeric-based active packaging by improving physical, mechanical, and chemical properties. At the same time, nanocarriers contribute to the strong antimicrobial and antioxidant properties of packaging. Nanocarriers can offer protection, stability, and controlled and targeted release of active compounds that improve their efficiency. This manuscript is focused on the benefits of the main groups of nanocarriers loading active compounds that are used for developing sustainable biopolymeric-based active packaging with antimicrobial and antioxidant properties. In addition, challenges during and post COVID-19 pandemic are briefly discussed for sustaining their commercial exploitation.

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# References

- Vodnar, D.C.; Mitrea, L.; Teleky, B.E.; Szabo, K.; Călinoiu, L.F.; Nemeş, S.A.; Martău, G.A. Coronavirus Disease (COVID-19) Caused by (SARS-CoV-2) Infections: A Real Challenge for Human Gut Microbiota. *Front. Cell. Infect. Microbiol.* 2020, 10, 786. [CrossRef] [PubMed]
- WHO. WHO Director-General's Opening Remarks at the Media Briefing on COVID-19-11 March 2020. WHO Director-General Speeches No. 4 March 2020. Available online: https://www.who.int/director-general/speeches/detail/who-director-general-sopening-remarks-at-the-media-briefing-on-covid-19---11-march-2020 (accessed on 24 November 2021).
- Kumar, P.; Singh, R.K. Strategic framework for developing resilience in Agri-Food Supply Chains during COVID 19 pandemic. Int. J. Logist. Res. Appl. 2021, 1–24. [CrossRef]
- Food and Agriculture Organization of the United Nations. Mitigating Risks to Food Systems during COVID-19: Reducing Food Loss and Waste. 2020. Available online: https://www.fao.org/3/ca9056en/ca9056en.pdf (accessed on 23 November 2021). [CrossRef]
- Galanakis, C.M.; Rizou, M.; Aldawoud, T.M.S.; Ucak, I.; Rowan, N.J. Innovations and technology disruptions in the food sector within the COVID-19 pandemic and post-lockdown era. *Trends Food Sci. Technol.* 2021, 110, 193–200. [CrossRef]
- 6. De Sousa, F.D.B. Pros and Cons of Plastic during the COVID-19 Pandemic. Recycling 2020, 5, 27. [CrossRef]
- Li, Q.; Ren, T.; Perkins, P.; Hu, X.; Wang, X. Applications of halloysite nanotubes in food packaging for improving film performance and food preservation. *Food Control* 2021, 124, 107876. [CrossRef]
- Regulation (EC) No 1932/2004 on Materials and Articles Intended to Come into Contact with Food and Repealing Directives 80/590/EEC and 89/109/EEC. 2004. Available online: https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=celex%3A32004 R1935 (accessed on 1 December 2021).
- Commision Regulation (EC) No 450/2009 on Active and Intelligent Materials and Articles Intended to Come into Contact with Food. 2009. Available online: https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=CELEX%3A32009R0450 (accessed on 1 December 2021).
- Szabo, K.; Teleky, B.E.; Mitrea, L.; Călinoiu, L.F.; Martău, G.A.; Simon, E.; Varvara, R.A.; Vodnar, D.C. Active Packaging—poly (Vinyl Alcohol) Films Enriched with Tomato By-Products Extract. *Coatings* 2020, 10, 141. [CrossRef]
- Mitrea, L.; Călinoiu, L.-F.F.; Martău, G.-A.; Szabo, K.; Teleky, B.-E.E.; Mureșan, V.; Rusu, A.-V.V.; Socol, C.-T.T.; Vodnar, D.-C.C.; Mărtau, G.A. Poly(vinyl alcohol)-Based Biofilms Plasticized with Polyols and Colored with Pigments Extracted from Tomato By-Products. *Polymers* 2020, *12*, 532. [CrossRef]
- 12. Kuai, L.; Liu, F.; Chiou, B.-S.; Avena-Bustillos, R.J.; McHugh, T.H.; Zhong, F. Controlled release of antioxidants from active food packaging: A Review. *Food Hydrocoll.* **2021**, *120*, 106992. [CrossRef]
- 13. Rehman, A.; Jafari, S.M.; Aadil, R.M.; Assadpour, E.; Randhawa, M.A.; Mahmood, S. Development of active food packaging via incorporation of biopolymeric nanocarriers containing essential oils. *Trends Food Sci. Technol.* **2020**, *101*, 106–121. [CrossRef]
- VBertolino, V.; Cavallaro, G.; Milioto, S.; Lazzara, G. Polysaccharides/Halloysite nanotubes for smart bionanocomposite materials. *Carbohydr. Polym.* 2020, 245, 116502. [CrossRef] [PubMed]
- 15. Nikolic, M.V.; Vasiljevic, Z.Z.; Auger, S.; Vidic, J. Metal oxide nanoparticles for safe active and intelligent food packaging. *Trends Food Sci. Technol.* **2021**, *116*, 655–668. [CrossRef]
- Wu, M.; Zhou, Z.; Yang, J.; Zhang, M.; Cai, F.; Lu, P. ZnO nanoparticles stabilized oregano essential oil Pickering emulsion for functional cellulose nanofibrils packaging films with antimicrobial and antioxidant activity. *Int. J. Biol. Macromol.* 2021, 190, 433–440. [CrossRef]
- Jafari, S.M. Nanoencapsulation Technologies for the Food and Nutraceutical Industries; Academic Press: Cambridge, MA, USA, 2017; pp. 1–34. [CrossRef]
- Chaudhari, A.K.; Singh, V.K.; Das, S.; Dubey, N.K. Nanoencapsulation of essential oils and their bioactive constituents: A novel strategy to control mycotoxin contamination in food system. *Food Chem. Toxicol.* 2021, 149, 112019. [CrossRef]
- 19. ARezaei, A.; Fathi, M.; Jafari, S.M. Nanoencapsulation of hydrophobic and low-soluble food bioactive compounds within different nanocarriers. *Food Hydrocoll.* **2019**, *88*, 146–162. [CrossRef]
- Chitrakar, B.; Zhang, M.; Bhandari, B. Improvement strategies of food supply chain through novel food processing technologies during COVID-19 pandemic. *Food Control.* 2021, 125, 108010. [CrossRef]
- Precup, G.; Mitrea, L.; Nemes, A.; Călinoiu, L.-F.; Martău, G.-A.; Teleky, B.E.; Coman, V.; Vodnar, D.C. Food processing by-products and molecular gastronomy. In *Gastronomy and Food Science*; Academic Press: Cambridge, MA, USA, 2021; pp. 137–164.
- Coman, V.; Teleky, B.-E.; Mitrea, L.; Martău, G.A.; Szabo, K.; Călinoiu, L.-F.; Vodnar, D.C. Bioactive potential of fruit and vegetable wastes. In *Advances in Food and Nutrition Research*; Academic Press: Cambridge, MA, USA, 2019; p. 69.

- Mallakpour, S.; Azadi, E.; Hussain, C.M. Recent breakthroughs of antibacterial and antiviral protective polymeric materials during COVID-19 pandemic and after pandemic: Coating, packaging, and textile applications. *Curr. Opin. Colloid Interface Sci.* 2021, 55, 101480. [CrossRef] [PubMed]
- Ştefănescu, B.E.; Călinoiu, L.F.; Ranga, F.; Fetea, F.; Mocan, A.; Vodnar, D.C.; Crisan, G. The Chemical and Biological Profiles of Leaves from Commercial Blueberry Varieties. *Plants* 2020, 9, 1193. [CrossRef]
- Ştefănescu, B.E.; Călinoiu, L.F.; Ranga, F.; Fetea, F.; Mocan, A.; Vodnar, D.C.; Crișan, G. Chemical Composition and Biological Activities of the Nord-West Romanian Wild Bilberry (*Vaccinium myrtillus* L.) and Lingonberry (*Vaccinium vitis-idaea* L.) Leaves. *Antioxidants* 2020, 9, 495. [CrossRef] [PubMed]
- Simon, E.; Călinoiu, L.; Mitrea, L.; Vodnar, D. Probiotics, Prebiotics, and Synbiotics: Implications and Beneficial Effects against Irritable Bowel Syndrome. *Nutrients* 2021, 13, 2112. [CrossRef]
- Hamedi, H.; Kargozari, M.; Shotorbani, P.M.; Babolanimogadam, N.; Fahimdanesh, M. A novel bioactive edible coating based on sodium alginate and galbanum gum incorporated with essential oil of *Ziziphora persica*: The antioxidant and antimicrobial activity, and application in food model. *Food Hydrocoll.* 2017, 72, 35–46. [CrossRef]
- Socaciu, M.-I.; Semeniuc, C.A.; Vodnar, D.C. Edible Films and Coatings for Fresh Fish Packaging: Focus on Quality Changes and Shelf-life Extension. *Coatings* 2018, *8*, 366. [CrossRef]
- Barone, A.S.; Matheus, J.R.V.; de Souza, T.S.P.; Moreira, R.F.A.; Fai, A.E.C. Green-based active packaging: Opportunities beyond COVID-19, food applications, and perspectives in circular economy—A brief review. *Compr. Rev. Food Sci. Food Saf.* 2021, 20, 4881–4905. [CrossRef] [PubMed]
- Kabir Ahuja, C.P.; Chandra, V.; Lord, V. Ordering in: The Rapid Evolution of Food Delivery; McKinsey Co.: Atlanta, GA, USA, 2021; Volume 148, pp. 148–162.
- 31. De Sousa, F.D.B. Plastic and its consequences during the COVID-19 pandemic. *Environ. Sci. Pollut. Res.* **2021**, *28*, 46067–46078. [CrossRef] [PubMed]
- Nemes, S.A.; Szabo, K.; Vodnar, D.C. Applicability of Agro-Industrial By-Products in Intelligent Food Packaging. *Coatings* 2020, 10, 550. [CrossRef]
- Mitrea, L.; Teleky, B.-E.; Leopold, L.-F.; Nemes, S.-A.; Plamada, D.; Dulf, F.V.; Pop, I.-D.; Vodnar, D.C. The physicochemical properties of five vegetable oils exposed at high temperature for a short-time-interval. *J. Food Compos. Anal.* 2022, 106, 104305. [CrossRef]
- Kahramanoğlu, İ.; Rengasamy, K.R.; Usanmaz, S.; Alas, T.; Helvacı, M.; Okatan, V.; Aşkın, M.A.; Wan, C. Improving the safety and security of fruits and vegetables during COVID-19 pandemic with postharvest handling. *Crit. Rev. Food Sci. Nutr.* 2021, 1–11. [CrossRef]
- 35. Food and Ariculture Organizaion of the United States. Food Wastage Footprint & Climate Change Global Food Loss and Waste. 2011. Available online: https://www.fao.org/3/bb144e/bb144e.pdf (accessed on 23 November 2021).
- Mitrea, L.; Ranga, F.; Fetea, F.; Dulf, F.V.; Rusu, A.; Trif, M.; Vodnar, D.C. Biodiesel-Derived Glycerol Obtained from Renewable Biomass-A Suitable Substrate for the Growth of *Candida zeylanoides* Yeast Strain ATCC 20367. *Microorganisms* 2019, 7, 265. [CrossRef]
- 37. Martau, G.-A.; Unger, P.; Schneider, R.; Venus, J.; Vodnar, D.C.; Pablo, L.-G. Integration of Solid State and Submerged Fermentations for the Valorization of Organic Municipal Solid Waste. *J. Fungi* **2021**, *7*, 766. [CrossRef] [PubMed]
- Teleky, B.-E.; Vodnar, D.C. Biomass-Derived Production of Itaconic Acid as a Building Block in Specialty Polymers. *Polymers* 2019, 11, 1035. [CrossRef]
- 39. Taherimehr, M.; YousefniaPasha, H.; Tabatabaeekoloor, R.; Pesaranhajiabbas, E. Trends and challenges of biopolymer-based nanocomposites in food packaging. *Compr. Rev. Food Sci. Food Saf.* **2021**, *20*, 5321–5344. [CrossRef]
- 40. Kumar, A.N.; Kim, G.-B.; Muhorakeye, A.; Varjani, S.; Kim, S.-H. Biopolymer production using volatile fatty acids as resource: Effect of feast-famine strategy and lignin reinforcement. *Bioresour. Technol.* **2021**, *326*, 124736. [CrossRef] [PubMed]
- Alizadeh, A.M.; Masoomian, M.; Shakooie, M.; Khajavi, M.Z.; Farhoodi, M. Trends and applications of intelligent packaging in dairy products: A review. *Crit. Rev. Food Sci. Nutr.* 2020, 62, 383–397. [CrossRef] [PubMed]
- 42. Mitrea, L.; Vodnar, D.C. Klebsiella pneumoniae—A Useful Pathogenic Strain for Biotechnological Purposes: Diols Biosynthesis under Controlled and Uncontrolled pH Levels. *Pathogens* **2019**, *8*, 293. [CrossRef] [PubMed]
- Petkoska, A.T.; Daniloski, D.; D'Cunha, N.M.; Naumovski, N.; Broach, A.T. Edible packaging: Sustainable solutions and novel trends in food packaging. *Food Res. Int.* 2020, 140, 109981. [CrossRef]
- Jeevahan, J.J.; Chandrasekaran, M.; Venkatesan, S.P.; Sriram, V.; Britto Joseph, G.; Mageshwaran, G.; Durairaj, R.B. Scaling up difficulties and commercial aspects of edible films for food packaging: A review. *Trends Food Sci. Technol.* 2020, 100, 210–222. [CrossRef]
- Rezaeigolestani, M.; Misaghi, A.; Khanjari, A.; Basti, A.A.; Abdulkhani, A.; Fayazfar, S. Antimicrobial evaluation of novel poly-lactic acid based nanocomposites incorporated with bioactive compounds in-vitro and in refrigerated vacuum-packed cooked sausages. *Int. J. Food Microbiol.* 2017, 260, 1–10. [CrossRef]
- Mitrea, L.; Călinoiu, L.-F.; Precup, G.; Bindea, M.; Rusu, B.; Trif, M.; Ştefănescu, B.-E.; Pop, I.-D.; Vodnar, D.-C. Isolated Microorganisms for Bioconversion of Biodiesel-Derived Glycerol Into 1,3-Propanediol. Bull. Univ. Agric. Sci. Vet. Med. Cluj-Napoca Food Sci. Technol. 2017, 74, 43–49. [CrossRef]

- Katopodi, A.; Detsi, A. Solid Lipid Nanoparticles and Nanostructured Lipid Carriers of natural products as promising systems for their bioactivity enhancement: The case of essential oils and flavonoids. *Colloids Surf. A Physicochem. Eng. Asp.* 2021, 630, 127529. [CrossRef]
- Salmas, C.; Giannakas, A.; Katapodis, P.; Leontiou, A.; Moschovas, D.; Karydis-Messinis, A. Development of ZnO/Na-Montmorillonite Hybrid Nanostructures Used for PVOH/ZnO/Na-Montmorillonite Active Packaging Films Preparation via a Melt-Extrusion Process. *Nanomaterials* 2020, 10, 1079. [CrossRef]
- Martău, G.A.; Călinoiu, L.-F.; Vodnar, D.C. Bio-vanillin: Towards a sustainable industrial production. *Trends Food Sci. Technol.* 2021, 109, 579–592. [CrossRef]
- Özogul, Y.; El Abed, N.; Özogul, F. Antimicrobial effect of laurel essential oil nanoemulsion on food-borne pathogens and fish spoilage bacteria. *Food Chem.* 2021, 368, 130831. [CrossRef] [PubMed]
- Tang, M.; Liu, F.; Wang, Q.; Wang, D.; Wang, D.; Zhu, Y.; Sun, Z.; Xu, W. Physicochemical characteristics of ginger essential oil nanoemulsion encapsulated by zein/NaCas and antimicrobial control on chilled chicken. *Food Chem.* 2021, 374, 131624. [CrossRef]
- Chutia, H.; Mahanta, C.L. Properties of starch nanoparticle obtained by ultrasonication and high pressure homogenization for developing carotenoids-enriched powder and Pickering nanoemulsion. *Innov. Food Sci. Emerg. Technol.* 2021, 74, 102822. [CrossRef]
- Foo, M.L.; Ooi, C.W.; Tan, K.W.; Chew, I.M. Preparation of black cumin seed oil Pickering nanoemulsion with enhanced stability and antioxidant potential using nanocrystalline cellulose from oil palm empty fruit bunch. *Chemosphere* 2021, 287, 132108. [CrossRef]
- 54. Homayonpour, P.; Jalali, H.; Shariatifar, N.; Amanlou, M. Effects of nano-chitosan coatings incorporating with free/nanoencapsulated cumin (*Cuminum cyminum* L.) essential oil on quality characteristics of sardine fillet. *Int. J. Food Microbiol.* **2021**, 341, 109047. [CrossRef]
- Chen, L.; Zhao, H.; Zi, Y.; Zhang, Y. Fabrication, characterization, and in vitro digestion of bamboo leaf extract loaded liposomes. Food Struct. 2021, 30, 100238. [CrossRef]
- 56. Bagheri, R.; Ariaii, P.; Motamedzadegan, A. Characterization, antioxidant and antibacterial activities of chitosan nanoparticles loaded with nettle essential oil. *J. Food Meas. Charact.* **2020**, *15*, 1395–1402. [CrossRef]
- Wsoo, M.A.; Razak, S.I.A.; Bohari, S.P.M.; Shahir, S.; Salihu, R.; Kadir, M.R.A.; Nayan, N.H.M. Vitamin D3-loaded electrospun cellulose acetate/polycaprolactone nanofibers: Characterization, in-vitro drug release and cytotoxicity studies. *Int. J. Biol. Macromol.* 2021, 181, 82–98. [CrossRef]
- 58. Duan, M.; Yu, S.; Sun, J.; Jiang, H.; Zhao, J.; Tong, C.; Hu, Y.; Pang, J.; Wu, C. Development and characterization of electrospun nanofibers based on pullulan/chitin nanofibers containing curcumin and anthocyanins for active-intelligent food packaging. *Int. J. Biol. Macromol.* **2021**, *187*, 332–340. [CrossRef]
- Liu, M.; Wang, F.; Pu, C.; Tang, W.; Sun, Q. Nanoencapsulation of lutein within lipid-based delivery systems: Characterization and comparison of zein peptide stabilized nano-emulsion, solid lipid nanoparticle, and nano-structured lipid carrier. *Food Chem.* 2021, 358, 129840. [CrossRef]
- De Abreu-Martins, H.H.; Artiga-Artigas, M.; Piccoli, R.H.; Martín-Belloso, O.; Salvia-Trujillo, L. The lipid type affects the in vitro digestibility and β-carotene bioaccessibility of liquid or solid lipid nanoparticles. *Food Chem.* 2019, 311, 126024. [CrossRef] [PubMed]
- 61. Ajala, T.O.; Abraham, A.; Keck, C.M.; Odeku, O.A.; Elufioye, T.O.; Olopade, J.O. Shea butter (*Vitellaria paradoxa*) and *Pentaclethra macrophylla* oil as lipids in the formulation of Nanostructured lipid carriers. *Sci. Afr.* **2021**, *13*, e00965. [CrossRef]
- Zeng, Q.; Zeng, W.; Jin, Y.; Sheng, L. Construction and evaluation of ovalbumin-pullulan nanogels as a potential delivery carrier for curcumin. *Food Chem.* 2021, 367, 130716. [CrossRef] [PubMed]
- 63. Rezaei, A.; Khavari, S.; Sami, M. Incorporation of thyme essential oil into the β-cyclodextrin nanosponges: Preparation, characterization and antibacterial activity. *J. Mol. Struct.* **2021**, *1241*, 130610. [CrossRef]
- 64. Halahlah, A.; Kavetsou, E.; Pitterou, I.; Grigorakis, S.; Loupassaki, S.; Tziveleka, L.A.; Kikionis, S.; Ioannou, E.; Detsi, A. Synthesis and characterization of inclusion complexes of rosemary essential oil with various β-cyclodextrins and evaluation of their antibacterial activity against Staphylococcus aureus. *J. Drug Deliv. Sci. Technol.* 2021, 65, 102660. [CrossRef]
- 65. Szabo, K.; Dulf, F.V.; Diaconeasa, Z.; Vodnar, D.C. Antimicrobial and antioxidant properties of tomato processing byproducts and their correlation with the biochemical composition. *LWT* **2019**, *116*, 108558. [CrossRef]
- Szabo, K.; Dulf, F.V.; Teleky, B.-E.; Eleni, P.; Boukouvalas, C.; Krokida, M.; Kapsalis, N.; Rusu, A.V.; Socol, C.T.; Vodnar, D.C. Evaluation of the Bioactive Compounds Found in Tomato Seed Oil and Tomato Peels Influenced by Industrial Heat Treatments. *Foods* 2021, 10, 110. [CrossRef]
- 67. Tan, Y.; McClements, D.J. Improving the bioavailability of oil-soluble vitamins by optimizing food matrix effects: A review. *Food Chem.* **2021**, *348*, 129148. [CrossRef]
- Orona-Navar, A.; Aguilar-Hernández, I.; Nigam, K.; Cerdán-Pasarán, A.; Ornelas-Soto, N. Alternative sources of natural pigments for dye-sensitized solar cells: Algae, cyanobacteria, bacteria, archaea and fungi. J. Biotechnol. 2021, 332, 29–53. [CrossRef]
- Szabo, K.; Teleky, B.E.; Ranga, F.; Simon, E.; Pop, O.L.; Babalau-Fuss, V.; Kapsalis, N.; Vodnar, D.C. Bioaccessibility of microencapsulated carotenoids, recovered from tomato processing industrial by-products, using in vitro digestion model. *LWT* 2021, 152, 112285. [CrossRef]

- 70. Sharma, M.; Usmani, Z.; Gupta, V.K.; Bhat, R. Valorization of fruits and vegetable wastes and by-products to produce natural pigments. *Crit. Rev. Biotechnol.* 2021, 41, 535–563. [CrossRef] [PubMed]
- Ghosh, S.; Sarkar, T.; Das, A.; Chakraborty, R. Micro and Nanoencapsulation of Natural Colors: A Holistic View. *Appl. Biochem. Biotechnol.* 2021, 193, 3787–3811. [CrossRef]
- 72. Kurczewska, J.; Ratajczak, M.; Gajecka, M. Alginate and pectin films covering halloysite with encapsulated salicylic acid as food packaging components. *Appl. Clay Sci.* 2021, 214, 106270. [CrossRef]
- 73. Eghbalian, M.; Shavisi, N.; Shahbazi, Y.; Dabirian, F. Active packaging based on sodium caseinate-gelatin nanofiber mats encapsulated with Mentha spicata L. essential oil and MgO nanoparticles: Preparation, properties, and food application. *Food Packag. Shelf Life* **2021**, *29*, 100737. [CrossRef]
- Alizadeh-Sani, M.; Mohammadian, E.; McClements, D.J. Eco-friendly active packaging consisting of nanostructured biopolymer matrix reinforced with TiO<sub>2</sub> and essential oil: Application for preservation of refrigerated meat. *Food Chem.* 2020, 322, 126782. [CrossRef]
- 75. Amjadi, S.; Nazari, M.; Alizadeh, S.A.; Hamishehkar, H. Multifunctional betanin nanoliposomes-incorporated gelatin/chitosan nanofiber/ZnO nanoparticles nanocomposite film for fresh beef preservation. *Meat Sci.* 2020, *167*, 108161. [CrossRef] [PubMed]
- Gasti, T.; Dixit, S.; Hiremani, V.D.; Chougale, R.B.; Masti, S.P.; Vootla, S.K.; Mudigoudra, B.S. Chitosan/pullulan based films incorporated with clove essential oil loaded chitosan-ZnO hybrid nanoparticles for active food packaging. *Carbohydr. Polym.* 2021, 277, 118866. [CrossRef] [PubMed]
- Yadav, S.; Mehrotra, G.; Dutta, P. Chitosan based ZnO nanoparticles loaded gallic-acid films for active food packaging. *Food Chem.* 2020, 334, 127605. [CrossRef]
- Firouz, M.S.; Mohi-Alden, K.; Omid, M. A critical review on intelligent and active packaging in the food industry: Research and development. *Food Res. Int.* 2021, 141, 110113. [CrossRef]
- 79. Zhang, L.; Yu, D.; Regenstein, J.M.; Xia, W.; Dong, J. A comprehensive review on natural bioactive films with controlled release characteristics and their applications in foods and pharmaceuticals. *Trends Food Sci. Technol.* **2021**, *112*, 690–707. [CrossRef]
- De Carvalho, S.M.; Noronha, C.M.; da Rosa, C.G.; Sganzerla, W.G.; Bellettini, I.C.; Nunes, M.R.; Bertoldi, F.C.; Manique Barreto, P.L. PVA antioxidant nanocomposite films functionalized with alpha-tocopherol loaded solid lipid nanoparticles. *Colloids Surf. A Physicochem. Eng. Asp.* 2019, 581, 123793. [CrossRef]
- 81. Almasi, H.; Azizi, S.; Amjadi, S. Development and characterization of pectin films activated by nanoemulsion and Pickering emulsion stabilized marjoram (*Origanum majorana* L.) essential oil. *Food Hydrocoll.* **2019**, *99*, 105338. [CrossRef]
- Norcino, L.; Mendes, J.; Natarelli, C.; Manrich, A.; Oliveira, J.; Mattoso, L. Pectin films loaded with copaiba oil nanoemulsions for potential use as bio-based active packaging. *Food Hydrocoll.* 2020, 106, 105862. [CrossRef]
- Chu, Y.; Cheng, W.; Feng, X.; Gao, C.; Wu, D.; Meng, L.; Zhang, Y.; Tang, X. Fabrication, structure and properties of pullulan-based active films incorporated with ultrasound-assisted cinnamon essential oil nanoemulsions. *Food Packag. Shelf Life* 2020, 25, 100547. [CrossRef]
- Zhao, R.; Guan, W.; Zhou, X.; Lao, M.; Cai, L. The physiochemical and preservation properties of anthocyanidin/chitosan nanocomposite-based edible films containing cinnamon-perilla essential oil pickering nanoemulsions. *LWT* 2022, 153, 112506. [CrossRef]
- 85. Mohamed, H.M.; Mansour, H.A. Incorporating essential oils of marjoram and rosemary in the formulation of beef patties manufactured with mechanically deboned poultry meat to improve the lipid stability and sensory attributes. *LWT* **2012**, *45*, 79–87. [CrossRef]
- 86. Najafi, Z.; Kahn, C.J.; Bildik, F.; Arab-Tehrany, E.; Şahin-Yeşilçubuk, N. Pullulan films loading saffron extract encapsulated in nanoliposomes; preparation and characterization. *Int. J. Biol. Macromol.* **2021**, *188*, 62–71. [CrossRef]
- Kamkar, A.; Molaee-aghaee, E.; Khanjari, A.; Akhondzadeh-basti, A.; Noudoost, B.; Shariatifar, N.; Alizadeh Sani, M.; Soleimani, M. Nanocomposite active packaging based on chitosan biopolymer loaded with nano-liposomal essential oil: Its characterizations and effects on microbial, and chemical properties of refrigerated chicken breast fillet. *Int. J. Food Microbiol.* 2021, 342, 109071. [CrossRef] [PubMed]
- De Carvalho, S.M.; Noronha, C.M.; Floriani, C.L.; Lino, R.C.; Rocha, G.; Bellettini, I.C.; Ogliari, P.J.; Barreto, P.L.M. Optimization of α-tocopherol loaded solid lipid nanoparticles by central composite design. *Ind. Crop. Prod.* 2013, 49, 278–285. [CrossRef]
- 89. Khorrami, N.K.; Radi, M.; Amiri, S.; McClements, D.J. Fabrication and characterization of alginate-based films functionalized with nanostructured lipid carriers. *Int. J. Biol. Macromol.* **2021**, *182*, 373–384. [CrossRef]
- 90. Martău, G.A.; Teleky, B.-E.; Ranga, F.; Pop, I.D.; Vodnar, D.C. Apple pomace as a sustainable substrate in sourdough fermentation. *Front. Microbiol.* **2021**, *12*, 1–16. [CrossRef] [PubMed]
- Pisoschi, A.M.; Pop, A.; Cimpeanu, C.; Turcuş, V.; Predoi, G.; Iordache, F. Nanoencapsulation techniques for compounds and products with antioxidant and antimicrobial activity—A critical view. *Eur. J. Med. Chem.* 2018, 157, 1326–1345. [CrossRef] [PubMed]
- 92. Wang, P.; Wu, Y. A review on colloidal delivery vehicles using carvacrol as a model bioactive compound. *Food Hydrocoll.* **2021**, 120, 106922. [CrossRef]
- 93. Gupta, S.; Variyar, P.S. Nanoencapsulation of Essential Oils for Sustained Release: Application as Therapeutics and Antimicrobials; Elsevier Inc.: Amsterdam, The Netherlands, 2016.

- Araujo, V.H.S.; Delello Di Filippo, L.; Duarte, J.L.; Spósito, L.; de Camargo, B.A.F.; da Silva, P.B.; Chorilli, M. Exploiting solid lipid nanoparticles and nanostructured lipid carriers for drug delivery against cutaneous fungal infections. *Crit. Rev. Microbiol.* 2021, 47, 79–90. [CrossRef] [PubMed]
- 95. Xue, J.; Wang, T.; Hu, Q.; Zhou, M.; Luo, Y. A novel and organic solvent-free preparation of solid lipid nanoparticles using natural biopolymers as emulsifier and stabilizer. *Int. J. Pharm.* **2017**, *531*, 59–66. [CrossRef]
- 96. Assadpour, E.; Jafari, S.M. Nanoencapsulation. In *Nanomaterials for Food Applications*; Elsevier: Amsterdam, The Netherlands, 2019; pp. 35–61. [CrossRef]
- 97. Ghosh, T.; Mahansaria, R.; Katiyar, V. Nanoencapsulation: Prospects in Edible Food Packaging. In *Nanotechnology in Edible Food Packaging*; Springer: Singapore, 2021; pp. 259–272. [CrossRef]
- Liu, J.; Huang, J.; Hu, Z.; Li, G.; Hu, L.; Chen, X.; Hu, Y. Chitosan-based films with antioxidant of bamboo leaves and ZnO nanoparticles for application in active food packaging. *Int. J. Biol. Macromol.* 2021, 189, 363–369. [CrossRef]
- 99. Lan, W.; Wang, S.; Zhang, Z.; Liang, X.; Liu, X.; Zhang, J. Development of red apple pomace extract/chitosan-based films reinforced by TiO2 nanoparticles as a multifunctional packaging material. *Int. J. Biol. Macromol.* **2021**, *168*, 105–115. [CrossRef]
- Yang, Y.; Zheng, S.; Liu, Q.; Kong, B.; Wang, H. Fabrication and characterization of cinnamaldehyde loaded polysaccharide composite nanofiber film as potential antimicrobial packaging material. *Food Packag. Shelf Life* 2020, 26, 100600. [CrossRef]
- 101. Göksen, G.; Fabra, M.J.; Ekiz, H.I.; López-Rubio, A. Phytochemical-loaded electrospun nanofibers as novel active edible films: Characterization and antibacterial efficiency in cheese slices. *Food Control.* **2020**, *112*, 107133. [CrossRef]
- Mohsenabadi, N.; Rajaei, A.; Tabatabaei, M.; Mohsenifar, A. Physical and antimicrobial properties of starch-carboxy methyl cellulose film containing rosemary essential oils encapsulated in chitosan nanogel. *Int. J. Biol. Macromol.* 2018, 112, 148–155. [CrossRef]
- 103. Rajaei, A.; Hadian, M.; Mohsenifar, A.; Rahmani-Cherati, T.; Tabatabaei, M. A coating based on clove essential oils encapsulated by chitosan-myristic acid nanogel efficiently enhanced the shelf-life of beef cutlets. *Food Packag. Shelf Life* 2017, 14, 137–145. [CrossRef]
- Hadian, M.; Rajaei, A.; Mohsenifar, A.; Tabatabaei, M. Encapsulation of *Rosmarinus officinalis* essential oils in chitosan-benzoic acid nanogel with enhanced antibacterial activity in beef cutlet against *Salmonella typhimurium* during refrigerated storage. *LWT* 2017, 84, 394–401. [CrossRef]
- 105. Zou, Y.; Yuan, C.; Cui, B.; Wang, J.; Yu, B.; Guo, L.; Dong, D. Mechanical and antimicrobial properties of high amylose corn starch/konjac glucomannan composite film enhanced by cinnamaldehyde/β-cyclodextrin complex. *Ind. Crop. Prod.* 2021, 170, 113781. [CrossRef]
- 106. Cui, H.; Wang, Y.; Li, C.; Chen, X.; Lin, L. Antibacterial efficacy of *Satureja montana* L. essential oil encapsulated in methyl-β-cyclodextrin/soy soluble polysaccharide hydrogel and its assessment as meat preservative. *LWT* **2021**, *152*, 112427. [CrossRef]
- 107. Sun, C.; Cao, J.; Wang, Y.; Huang, L.; Chen, J.; Wu, J.; Zhang, H.; Chen, Y.; Sun, C. Preparation and characterization of pectin-based edible coating agent encapsulating carvacrol/HPβCD inclusion complex for inhibiting fungi. *Food Hydrocoll.* 2021, 125, 107374. [CrossRef]
- 108. Wang, Y.; Yi, S.; Lu, R.; Sameen, D.E.; Ahmed, S.; Dai, J.; Qin, W.; Li, S.; Liu, Y. Preparation, characterization, and 3D printing verification of chitosan/halloysite nanotubes/tea polyphenol nanocomposite films. *Int. J. Biol. Macromol.* 2020, 166, 32–44. [CrossRef] [PubMed]
- 109. Saedi, S.; Shokri, M.; Roy, S.; Rhim, J.-W. Silver loaded aminosilane modified halloysite for the preparation of carrageenan-based functional films. *Appl. Clay Sci.* 2021, 211, 106170. [CrossRef]
- 110. Coelho, S.C.; Estevinho, B.N.; Rocha, F. Encapsulation in food industry with emerging electrohydrodynamic techniques: Electrospinning and electrospraying—A review. *Food Chem.* **2020**, *339*, 127850. [CrossRef] [PubMed]
- 111. Sameen, D.E.; Ahmed, S.; Lu, R.; Li, R.; Dai, J.; Qin, W.; Zhang, Q.; Li, S.; Liu, Y. Electrospun nanofibers food packaging: Trends and applications in food systems. *Crit. Rev. Food Sci. Nutr.* **2021**, *16*, 1–14. [CrossRef]
- 112. Zhang, Z.; Hao, G.; Liu, C.; Fu, J.; Hu, D.; Rong, J.; Yang, X. Recent progress in the preparation, chemical interactions and applications of biocompatible polysaccharide-protein nanogel carriers. *Food Res. Int.* **2021**, *147*, 110564. [CrossRef]
- 113. Keskin, D.; Zu, G.; Forson, A.M.; Tromp, L.; Sjollema, J.; van Rijn, P. Nanogels: A novel approach in antimicrobial delivery systems and antimicrobial coatings. *Bioact. Mater.* 2021, *6*, 3634–3657. [CrossRef] [PubMed]
- Shah, S.; Rangaraj, N.; Laxmikeshav, K.; Sampathi, S. Nanogels as drug carriers–Introduction, chemical aspects, release mechanisms and potential applications. *Int. J. Pharm.* 2020, 581, 119268. [CrossRef] [PubMed]
- Coman, V.; Oprea, I.; Leopold, L.F.; Vodnar, D.C.; Coman, C. Soybean Interaction with Engineered Nanomaterials: A Literature Review of Recent Data. *Nanomaterials* 2019, *9*, 1248. [CrossRef] [PubMed]
- 116. Maqsoudlou, A.; Assadpour, E.; Mohebodini, H.; Jafari, S.M. Improving the efficiency of natural antioxidant compounds via different nanocarriers. *Adv. Colloid Interface Sci.* **2020**, 278, 102122. [CrossRef]
- Liu, Z.; Ye, L.; Xi, J.; Wang, J.; Feng, Z.-G. Cyclodextrin Polymers: Structure, Synthesis, and Use as Drug Carriers. *Prog. Polym. Sci.* 2021, 118, 101408. [CrossRef]
- Xiao, Z.; Zhang, Y.; Niu, Y.; Ke, Q.; Kou, X. Cyclodextrins as carriers for volatile aroma compounds: A review. *Carbohydr. Polym.* 2021, 269, 118292. [CrossRef]
- Liu, Y.; Sameen, D.E.; Ahmed, S.; Wang, Y.; Lu, R.; Dai, J.; Li, S.; Qin, W. Recent advances in cyclodextrin-based films for food packaging. *Food Chem.* 2022, 370, 131026. [CrossRef] [PubMed]

- 120. Plamada, D.; Vodnar, D.C. Polyphenols—Gut Microbiota Interrelationship: A Transition to a New Generation of Prebiotics. *Nutrients* **2022**, *14*, 137. [CrossRef]
- 121. Martău, G.A.; Mihai, M.; Vodnar, D.C. The Use of Chitosan, Alginate, and Pectin in the Biomedical and Food Sector—Biocompatibility, Bioadhesiveness, and Biodegradability. *Polymers* **2019**, *11*, 1837. [CrossRef] [PubMed]
- 122. Varvara, R.-A.; Szabo, K.; Vodnar, D.C. 3D Food Printing: Principles of Obtaining Digitally-Designed Nourishment. *Nutrients* **2021**, *13*, 3617. [CrossRef]
- 123. Călinoiu, L.F.; Mitrea, L.; Precup, G.; Bindea, M.; Rusu, B.; Szabo, K.; Dulf, F.V.; Ştefănescu, B.E.; Vodnar, D.C. Sustainable Use of Agro-Industrial Wastes for Feeding 10 Billion People by 2050; Wageningen Academic Publishers: Wageningen, The Netherlands, 2018; pp. 482–486. [CrossRef]
- 124. Precup, G.; Vodnar, D.-C. Pasteurization in the kitchen. In *Handbook of Molecular Gastronomy*; CRC Press: Boca Raton, FL, USA, 2021; pp. 451–458.
- Konai, M.M.; Bhattacharjee, B.; Ghosh, S.; Haldar, J. Recent Progress in Polymer Research to Tackle Infections and Antimicrobial Resistance. *Biomacromolecules* 2018, 19, 1888–1917. [CrossRef]
- 126. Teleky, B.-E.; Vodnar, D.C. Recent Advances in Biotechnological Itaconic Acid Production, and Application for a Sustainable Approach. *Polymers* **2021**, *13*, 3574. [CrossRef] [PubMed]
- 127. Cottet, C.; Salvay, G.; Peltzer, M.A. Incorporation of Poly (Itaconic Acid) with Quaternized Thiazole Groups on Gelatin-Based Films for Antimicrobial-Active Food Packaging. *Polymers* **2021**, *13*, 200. [CrossRef] [PubMed]
- 128. Teleky, B.-E.; Martău, G.-A.; Vodnar, D.-C. Physicochemical Effects of *Lactobacillus plantarum* and *Lactobacillus casei* Cocultures on Soy–Wheat Flour Dough Fermentation. *Foods* **2020**, *9*, 1894. [CrossRef]
- Mitrea, L.; Călinoiu, L.-F.; Precup, G.; Bindea, M.; Rusu, B.; Trif, M.; Ferenczi, L.-J.; Ştefănescu, B.-E.; Vodnar, D.C. Inhibitory Potential of *Lactobacillus plantarum* on *Escherichia coli*. *Bull. Univ. Agric. Sci. Vet. Med. Cluj-Napoca. Food Sci. Technol.* 2017, 74, 99. [CrossRef]
- 130. Cheng, H.; Xu, H.; Julian McClements, D.; Chen, L.; Jiao, A.; Tian, Y.; Miao, M.; Jin, Z. Recent advances in intelligent food packaging materials: Principles, preparation and applications. *Food Chem.* **2021**, *375*, 131738. [CrossRef]