



Polysaccharide-Based Packaging Functionalized with Inorganic Nanoparticles for Food Preservation

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Abstract: Functionalization of polysaccharide-based packaging incorporating inorganic nanoparticles for food preservation is an active research area. This review summarizes the use of polysaccharidebased materials functionalized with inorganic nanoparticles (TiO₂, ZnO, Ag, SiO₂, Al₂O₃, Fe₂O₃, Zr, MgO, halloysite, and montmorillonite) to develop hybrid packaging for fruit, vegetables, meat (lamb, minced, pork, and poultry), mushrooms, cheese, eggs, and Ginkgo biloba seeds preservation. Their effects on quality parameters and shelf life are also discussed. In general, treated fruit, vegetables, mushrooms, and G. biloba seeds markedly increased their shelf life without significant changes in their sensory attributes, associated with a slowdown effect in the ripening process (respiration rate) due to the excellent gas exchange and barrier properties that effectively prevented dehydration, weight loss, enzymatic browning, microbial infections by spoilage and foodborne pathogenic bacteria, and mildew apparition in comparison with uncoated or polysaccharide-coated samples. Similarly, hybrid packaging showed protective effects to preserve meat products, cheese, and eggs by preventing microbial infections and lipid peroxidation, extending the food product's shelf life without changes in their sensory attributes. According to the evidence, polysaccharide-hybrid packaging can preserve the quality parameters of different food products. However, further studies are needed to guarantee the safe implementation of these organic-inorganic packaging materials in the food industry.

Keywords: polysaccharide; inorganic nanoparticles; functionalization; hybrid materials; active packaging; food preservation

1. Introduction

Currently, the development of eco-friendly and functional biopolymer-based materials for food packaging is a fast-growing area as an alternative to reduce the use of non-biodegradable and synthetic polymers, particularly polysaccharide-based materials [1], which could be functionalized with organic or inorganic compounds to fabricate hybrid



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Copyright: © 2021 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/). composites with advanced properties [2,3]. Hybrid composites comprise a combination of inorganic-inorganic (e.g., metal-non-metal), organic-organic (e.g., polysaccharide-protein), and organic–inorganic (e.g., polysaccharide-metal oxide) compounds made by covalent and non-covalent methods [1], being hybrid composites made up of organic polymers and inorganic nanoparticles, a class of biomaterials with a reinforced matrix for diverse applications [4].

The use of inorganic nanoparticles has exploded during recent years [1], applying them in various fields, such as textile, cosmetic, optics, agriculture, medicine, pharmaceutics, and food packaging [5]. The wide use of inorganic nanoparticles is supported by their physical, chemical, antimicrobial, optical, magnetic, electrical, and mechanical properties, thermal stability, reactivity, low-cost production, safe use, and compatibility with organic compounds such as polysaccharides [2,6,7]. Currently, inorganic nanoparticles such as zinc oxide (ZnO), silver (Ag), titanium dioxide (TiO₂), silicon dioxide (SiO₂), and iron (III) oxide (Fe₃O₄) have been used as cross-link agents to enhance the mechanical, physicochemical, water-related, and antimicrobial properties of polysaccharide-based materials for food active packaging development [8–12].

During the last decade, polysaccharide-based materials functionalized with inorganic nanoparticles have been used as packaging to preserve food products such as cheese, meat, shrimps, fruit, and vegetables. El-Sayed et al. [13] manufactured a chitosan/guar gum/ZnO coating for Ras cheese preservation, reporting no changes in its sensorial properties, and it was microbiologically stable for up to three months. In another work, starch-halloysite-nisin hybrid films have effectively inhibited *Listeria monocytogenes* growth in soft cheese [14]. Osman et al. [15] found that chicken fillets coated with a hydroxypropyl-methylcellulose packaging combined with SiO₂ and aluminum oxide (Al₂O₃) nanoparticles showed good quality attributes and microbial safety after 15 days stored at 4 °C. Meanwhile, Kaewklin et al. [11] informed that chitosan-TiO₂ films effectively extend the shelf life of tomatoes under cold storage without significant changes in quality parameters. Similarly, a sodium alginate film combined with silver nanoparticles is suitable for carrot and pears preservation with minimal changes in their sensory and quality parameters [16].

This review summarizes the advantages and limitations of polysaccharide-based materials functionalized with inorganic nanoparticles for food packaging material and their effect on quality parameters and shelf life of different food products.

2. Polysaccharides as Food Packaging Materials

Food packaging against spoilage is based on reducing the growth of undesirable and spoilage-related microorganisms, preventing, or slowing down other processes that may induce undesirable modifications in the food matrix [17]. Biopolymers traditionally used to formulate biodegradable packaging materials are obtained from proteins, lipids, polysaccharides extracted from renewable agriculture by-products, waste of food processing industry, and other natural resources (animals, plants, microorganisms, and algae) [1]. Presently, the development of new packaging materials that maintain the quality, safety, and sensorial properties of several food products, extending their shelf life, facilitating their handling and storage, with an excellent cost-benefit relation is an active research area.

In this context, polysaccharides are considered a viable alternative to fabricate food packaging materials because they are abundant, non-toxic, biodegradable, low-cost, and biocompatible [1], exhibiting an excellent film-forming ability and potential to be used in the food industry as packaging. On the other hand, the qualities of polysaccharide-based materials are still the reason to continue using them for food packaging purposes, where diverse polysaccharide sources (plant, animal, algae, and yeast) have been explored. Moreover, most of the used polysaccharides in the formulations of food packaging materials include chitosan, cellulose and its derivates, starch, gums, alginate, and pectin [18]. Remarkably, polysaccharides-based packaging has exhibited good performance as a barrier for food protection. However, some limitations related to water vapor resistance and mechanical strength have been reported for these kinds of materials [19–21].

The current trend in developing polysaccharide-based packaging was estimated using a stratified search to understand the tendency to use biopolymers as packaging material and their importance in the food industry [22]. Figure 1 describes the use of polysaccharides for biodegradable packaging materials development with or without incorporating additives (plasticized agents) or functional agents (organic or inorganic compounds) for diverse applications, particularly for food preservation.

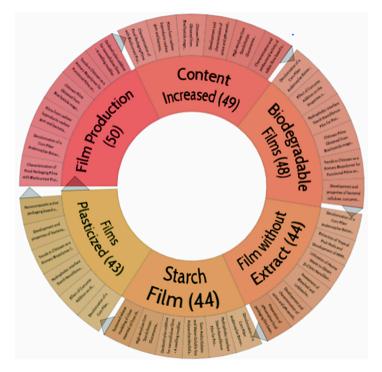


Figure 1. Stratified search clustering for the use of polysaccharides as packaging materials. Figure created using the Carrot2 software and data obtained from PubMed database using the search pattern "Polysaccharides" AND "Film packaging". Available in https://search.carrot2.org/#/search/pubmed/(Polysaccharides)%20AND%20(film%20packaging)/pie-chart (accessed on 16 May 2021).

3. Functionalization of Polysaccharide-Based Materials for Food Packaging

Most of the potential applications of polysaccharide-based materials for food packaging purposes are restricted by their poor gas permeability, low water-barrier ability, low thermal stability, high solubility, and mechanical resistance, which are limiting factors in the food preservation process [1,23]. Therefore, to reduce these limitations, polysaccharidebased materials have been combined with organic and inorganic compounds to improve their technological and functional properties [24]. The functionalization or hybridization of polysaccharide-based materials adding organic and inorganic nanoparticles is a technological strategy to fabricate hybrid composites with new functionalities for food packaging development [25,26]. Applications of some polysaccharide-based materials functionalized with organic and inorganic compounds and microorganisms for food preservation are listed in Table 1.

According to the literature, the functionalization of polysaccharide-based materials by adding organic and inorganic compounds and microorganisms (alone or combined) enhanced the thermal and water resistance, gas permeability, tensile strength, elongation at break, and elastic modulus properties and in some cases provide antimicrobial activity, which are suitable characteristic for food packaging, associated with their chemical and physical interactions with the functional group (e.g., NH₂ in chitosan, and OH in starch and cellulose) present at second carbon (C2) of polysaccharide structure [1].

Polysaccharide	Functional Agent	Presentation	Food Product	Ref.
Starch	arch Ascorbic acid		Guava fruit	[27]
Carboxymethyl cellulose	Guar gum	Edible film	Strawberry fruit	[28]
Cellulose	Allyl isothiocyanate	isothiocyanate Edible film		[29]
Chitosan	Cryptococcus laurentii	Edible film	Grapefruit fruit	[30]
Guar gum	Thyme oil	Edible film	Tilapia fillets	[31]
Sodium alginate	<i>Rosmarinus officinalis</i> essential oil	Edible film	Soft cheese	[32]
K-Carrageenan Olive leaf extract		Edible film	Lamb meat	[33]
Pectin	Oregano essential oil	Edible film	Pork loin	[34]

Table 1. Application of some functionalized polysaccharide-based materials for food preservation.

4. Food Preservation Using Polysaccharide Packaging Functionalized with Inorganic Nanoparticles

One of the essential tools for food preservation is the use of packaging materials [35]. At present, most food packaging materials are based on non-biodegradable and hard-to-recycle petrochemical polymers [36]. In this context, the potential use of food polysaccharide-based packaging has been widely explored during recent years. Figure 2 shows the distribution of searching terms on recently published papers (2016–2021) using functionalized polysaccharide-based materials with inorganic nanoparticles, where the most common keywords were polysaccharides, nanoparticles, nanocomposites, and chitosan. It is also noted that the terms' distribution is focused on four clusters, where the first one (green color) comprised the intrinsic characteristics of polysaccharides and inorganic nanoparticles, while their combination is in the second cluster (yellow color). The third cluster (blue color) explained the development of nanocomposites as packaging material, while the fourth (red color) is distinguished for the application of organic–inorganic composites for food preservation.

According to the literature [1,3,17,37,38], dipping food products in a film-forming aqueous solution is the most common method to apply organic–inorganic hybrid films (Figure 3a), followed by developing hybrid materials by the evaporative casting method and then applying them as a coating (Figure 3b).

Figure 4 is a proposal diagram to develop polysaccharide-based materials functionalized with inorganic nanoparticles based on the information discussed throughout this work. This kind of hybrid materials are recognized as a promising alternative to fabricate food packaging because they are non-toxic, eco-friendly, low-cost, available, biodegradable, and simple to prepare [1,3,11,12,37,38]. Additionally, the most reported inorganic nanoparticles used as nanofillers for the functionalization of polysaccharide-based packaging used for food preservation are zinc oxide, titanium dioxide, silver, silicon dioxide, iron oxide, zirconium, halloysite, montmorillonite, and magnesium oxide, as discussed below.

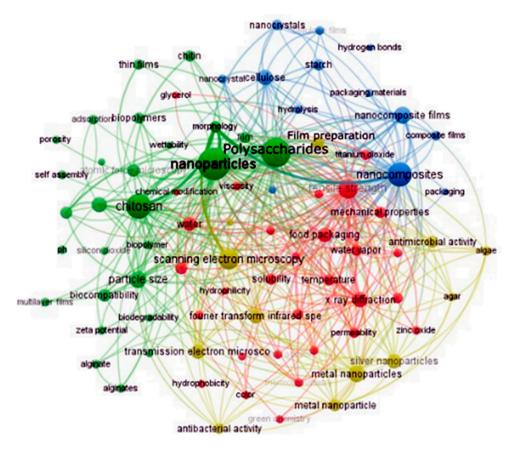


Figure 2. 2016–2021 terms occurrence network on polysaccharide-hybrid materials. (Figure created using the VOSviewer v.1.6.16 software using the term occurrence from year 2016 to 2021. The results are based on the threshold of 157 terms with four clusters, where each circle or node in the map represent a term occurrence at least ten times and the size of the circle or node of a term is proportional to the number of occurrences of that term, data obtained from SCOPUS database).

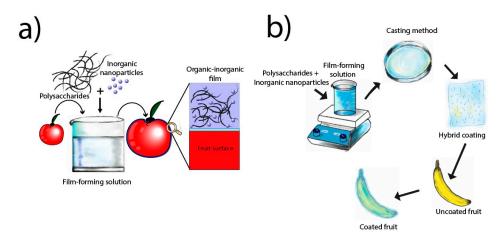


Figure 3. Application of organic–inorganic hybrid film for food preservation by dipping (**a**) and coating (**b**) methods (adapted from Tunma [37] and Anugrah et al. [39]).

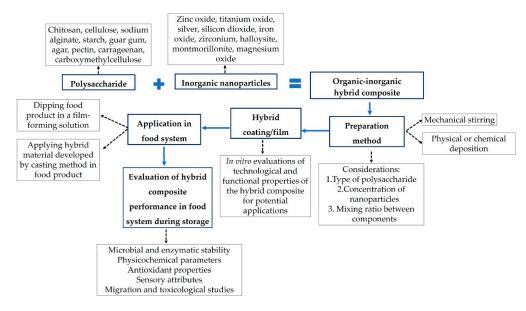


Figure 4. Suggested flow chart to develop polysaccharide-inorganic nanoparticles hybrid materials for fruit preservation [1–3,17,37–39].

4.1. Zinc Oxide (ZnO)

Zinc oxide is a multifunctional material with electrical, photocatalytic, ultravioletblocking, and antimicrobial properties; it is thermally and chemically stable and exhibit a high surface area and strong adsorption ability for diverse applications such as cosmetics, pharmaceutical, water treatment, and food packaging [40,41]. ZnO is an available and low-cost material with excellent compatibility and easy incorporation into polysaccharidebased matrix [42]. Furthermore, ZnO nanoparticles have improved the physicochemical, mechanical, antimicrobial, and water-related properties of some polysaccharide-based materials with potential for food packaging development due to its ability to interact with the hydroxyl (-OH) groups in the polysaccharide chains [39]. Table 2 summarizes the application of polysaccharide-ZnO packaging and their effects on quality parameters of various food products.

In general, polysaccharide compounds such as chitosan, carboxymethylcellulose, starch, sodium alginate, carrageenan, and pectin have been functionalized with zinc oxide nanoparticles for fruit, vegetable, and mushroom preservation (Table 2). Lavinia et al. [43] developed a hybrid film composed of chitosan and zinc oxide nanoparticles with antimicrobial properties for fresh-cut papaya preservation. They reported that after storage (12 days at 10 °C), the hybrid film significantly suppressed the microbial growth (total viable count 4.11 log colony-forming unit per gram (CFU/g)) than the uncoated sample (total viable count 7.36 log CFU/g), associated with a synergistic effect between individual components and their interactions with the cell wall, leading to cell death. Arroyo et al. [44] informed that a chitosan-sodium alginate-zinc oxide film effectively protected guava fruit against weight loss and retarded physicochemical changes (color, pH, total soluble solids, and titratable acidity) related to the ripening process without apparent mildew lesions after 20 days of storage at 21 °C. The authors highlighted the reduction of the fruit maturation rate when the hybrid film was applied, mentioning that it is a viable alternative for guava fruit preservation. Moreover, it has been reported that chitosan-zinc oxide coatings effectively extended the shelf life of okra up to 12 days at 25 $^\circ\text{C}$ without significant changes in its quality parameters (pH, total soluble solids, weight loss, and moisture content), which was associated with a reduction in microbial infections. According to the authors, the barrier properties of chitosan film and the antimicrobial properties of zinc oxide have a great impact in okra preservation.

Polysaccharide	ZnO Specifications	Other Additives	Coating Method/ Presentation	Food Product	Storage Conditions	Observed Results	Ref.
Chitosan (3 g in 300 mL)	Conc.: 0.027% w/w Commercial Size: 600 nm	Acetic acid (1 mL/100 mL)	Dipping for 10–20 s and drained at 25 °C/film	Fresh-cut papaya	10 °C for 12 days	Treated fruit showed a reduced microbial growth.	[43]
Chitosan (5% w/v)	Conc.: 1% Commercial	Sodium alginate (10% w/w in chitosan weight) Glycerol (2% v/v)	Dipping/film	Guava	21 °C for 20 days at 80% RH	The composite delayed the ripening process without apparent lesions.	[44]
Chitosan (2%)	Commercial Size: 35–45 nm	NI	Evaporative cast- ing/coating	Okra	25 °C for 12 days	The treated product showed reduced the fungal and bacterial growth.	[45]
Chitosan (1.4 <i>w</i> / <i>v</i> , DD 80–95%)	Commercial Size: 30 nm	Linseed oil 1:2 ratio on a potato protein solution (1.2%) glycerol (1.5%)	Evaporative cast- ing/coating	Raw meat	4 °C for 7 days	Threated meat preserved its sensory properties.	[46]
Chitosan (0.4 g in 100 mL)	Conc.: 0.2% <i>w/v</i>	The betanin-loaded NLPs (10%) gelatin (4 g/100 mL) glycerol (1 g/100 mL)	Evaporative cast- ing/coating	Fresh beef	4 °C for 16 days	Treated meat exhibited a reduced physicochemical changes during storage.	[47]
Chitosan $(10\% w/v)$	Commercial Size: 30 nm	Gelatin (4% w/v), glycerol (25%)	Evaporative cast- ing/coating	Chicken fillet	4 °C for 12 days at 80% RH	The hybrid film did not promote changes in the quality parameters.	[48]
Chitosan (10% w/v)	Commercial Size: 30 nm	Gelatin (4% <i>w/v</i>), glycerol (25%)	Evaporative cast- ing/coating	White cheese	4 °C for 12 days at 80% RH	The hybrid coating protected the physical and chemical quality, reduced the weight loss and inhibited bacterial growth.	[48]
Chitosan (3% w/v)	Conc. 3%	Roselle calyx extracts (2.8 g) guar gum (3% w/v)	Evaporative cast- ing/coating	Ras cheese	12 °C for three months at 80% RH	Nanocomposite films enhanced the shelf life of cheese without changes in its sensorial properties.	[13]
Chitosan $(2\% w/v)$	Conc.: 2–8% Commercial	CMC (1% <i>w</i> / <i>v</i>)	Evaporative cast- ing/coating	White cheese from buffalo milk	7 °C for 30 days	Cheese was microbiological stable during storage.	[49]
CMC (1% <i>w</i> / <i>v</i>)	Commercial	Cinnamaldehyde (100 mg/100 mL)	Evaporative cast- ing/coating	Cherry tomato	25 °C for 10 days at 45% RH	Nanocomposite film reduced changes in weight and firmness.	[50]
CMC (0.5% <i>w</i> / <i>v</i>)	Conc.: 0.2% (w/v) Commercial Size: 30-100 nm	NR	Evaporative cast- ing/coating	Pomegranate	4 °C for 12 days at 90% RH	The composite delayed the fruit ripening process.	[51]
Buckwheat starch (30 g/L)	Conc.: 3% Commercial Size: <50 nm	Sorbitol (15 g/L)	Evaporative cast- ing/coating	Mushrooms	4 °C for 6 days	Treated mushrooms exhibited reduced dehydration.	[52]

Table 2. Effects of polysaccharide-zinc oxide (ZnO) composites application on food quality.

Polysaccharide	ZnO Specifications	Other Additives	Coating Method/ Presentation	Food Product	Storage Conditions	Observed Results	Ref.
Sodium alginate (1.5% w/v)	Conc.: 1.25 g/L Commercial Size: 30–50 nm	Glycerol (1%)	Dipping/film	Strawberries	1 °C for 20 days at 95% RH	The hybrid films reduced microbial infections and activated the antioxidant system of the fruit.	[53]
Sodium alginate (1.67 g in 50 mL)	Conc.: 1 mg/mL Size: 5 to 10 nm	Calcium chloride (5% w/w) Glycerol (1.5 mL)	Evaporative cast- ing/coating	Smoked salmon	4 °C for 4 days	Treated salmon was microbiologically stable during storage.	[42]
Calcium alginate (0.7 g in 30 mL)	Conc.: 3 mg/mL Size: 50 nm	NI	Evaporative cast- ing/coating	Poultry meat	4 °C for 10 days	Hybrid coating provide microbial control during storage.	[54]
Carrageenan (8×10^{-4} kg)	Conc.: $1\% w/v$ Commercial Size: 20×10^{-9} m	Glycerol $(5 \times 10^{-4} \text{ L})$	Evaporative casting/film	Mango	20 °C at 60% RH	Treated fruit retained firmness and retarded the ripening process.	[55]
Pectin (10 g)	Concentration (100 mg/L) Size: 43.1 nm	Glycerol (1 mL)	Dipping/film	Starfruit	8 days	Treated fruit showed minimal moldy infections and preserved quality attributes during storage.	[56]
Agar	Conc.: 1%	Glycerol (1% v/v)	Evaporative cast- ing/Coating	Smoked salmon	4 °C for 8 days	Hybrid coating provide microbial control and reduced lipid oxidation during storage.	[57]

Table 2. Cont.

NI: No information; DD: deacetylated degree; Conc: nanoparticles concentration; RH: relative humidity; CMC: carboxymethylcellulose; NLPs: nanoliposomes.

Guo et al. [50] evaluated the effect of carboxymethylcellulose-zinc oxide-cinnamaldehyde films in the postharvest quality of cherry tomatoes. They found that after 10 days of storage at 25 °C, the coated tomato preserved its firmness (2.54 N) and reduced its weight loss (6.09%) compared to uncoated (1.66 N and 11.10%, respectively) or carboxymethylcellulosecoated (1.96 N and 8.64%, respectively) cherry tomatoes, suggesting that the hybrid film prevented dehydration of tomato fruit, suppressing some physiological activities. Koushesh-Saba and Amini [51] reported that carboxymethylcellulose functionalized with zinc oxide nanoparticles effectively extended the shelf life of ready-to-eat pomegranates up to 12 days under cold storage (4 °C). In general, the coated pomegranate was microbiologically stable (yeast and molds of $1.2 \log CFU/g$ and total viable count of $2 \log CFU/g$) without significant weight loss (0.6%) and changes in physicochemical parameters (pH, titratable acidity, and total soluble solids) than the control sample (yeast and molds of $2.5 \log CFU/g$ and total viable count of 2.7 log CFU/g with a weight loss of 2%). According to the authors, zinc oxide enhanced the barrier properties of the carboxymethylcellulose coating, reducing the moisture diffusion of the fruit to the surrounding atmosphere, and slowed down some physiological processes in the pomegranates, also, zinc oxide decreased the microbial load, extending the ready-to-eat fruit shelf life.

Emamifar and Bavaisi [53] fabricated a sodium alginate film functionalized with zinc oxide nanoparticles to extend the shelf life of strawberries. They reported that coated fruit exhibited a reduced population level of yeast and molds (4.11 log CFU/g) and total aerobic bacteria counts (2.98 log CFU/g) than the uncoated sample (>7 log CFU/g in all evaluated microorganisms) after 20 days of storage at 1 °C. Moreover, treated fruit preserved their quality parameters (minimal weight loss, firmness, total soluble solids,

titratable acidity, ascorbic acid, anthocyanins, and phenol content) and sensory attributes. These results were associated with a reduction in peroxidase activity (1.25 U/mg protein) followed by an increase in the activity of superoxide dismutase (1.5 U/mg protein) in comparison with uncoated fruit that showed a higher peroxidase activity, and lower SOD activity (2.75 and 0.5 U/mg protein, respectively), delaying the senescence of strawberries. According to the authors, the hybrid film exhibited significant effects on the postharvest life of strawberries due to the prevented microbial infections and fruit deterioration associated with the activation of the antioxidant system of the fruit.

Meindrawan et al. [55] evaluated the effect of a carrageenan–zinc oxide hybrid film on the postharvest quality of mangoes. They found that the hybrid-coated fruit exhibited lower weight losses (15%) and acidity content (94.11%) with a decrease in the carbon dioxide production peak (3.19 mg/kg s) than carrageenan-coated mangoes (20%, 69.91%, and 4.03 mg/kg s, respectively) after 12 days of storage at 20 °C, delaying the ripening process and preserving a good appearance without mildew infection. These results were attributed to the gas barrier properties of the hybrid film that extends the shelf life of mangoes.

Romadhan and Pujilestari [56] reported that the application of pectin–zinc oxide hybrid film effectively decreased weight loss of starfruit without significant changes in color attributes, preventing mildew apparition during 8 days of storage at 30 °C, associated with a good exchangeability of the film, preventing fruit dehydration.

Kim and Song [52] developed an active packaging with antimicrobial properties composed of buckwheat starch and zinc oxide nanoparticles for fresh-cut mushrooms preservation. They reported that hybrid films containing 3% of zinc oxide reduced the growth of *L. monocytogenes* (0.86 log CFU/g) after six days of storage at 4 °C. Moreover, the treated mushrooms exhibited lower browning index values (9) and weight loss (0.3%) than uncoated samples (16% and 1.8%, respectively) during storage. These results were attributed to the adequate gas exchangeability and ultraviolet-blocking properties of the hybrid film; reducing the oxygen content between the sample and film, consequently diminishing the oxidative stress that delayed the ripening process and prevented microbial infections, enzymatic and non-enzymatic browning, and dehydration.

Additionally, chitosan, sodium alginate, calcium alginate, and agar-based coatings combined with zinc oxide have been applied to extend the shelf life of fresh beef, chicken fillets, and smoked salmon (Table 2). Wang et al. [46] evaluated the effect of chitosan-potato protein-linseed oil-zinc oxide coating on raw meat quality parameters. They reported that treated meat preserved its sensory attributes after seven days under cold storage (4 $^{\circ}$ C). Those results were associated with the ability of the hybrid film to inhibit the microbial growth (total viable count of $4 \log (CFU/g)$ and maintain the pH values (5.8) in the meat product than the uncoated sample (total viable count $>7 \log CFU/g$ and pH of 7.5), retarding the raw meat deterioration. Similarly, Amjadi et al. [47] informed that fresh beef coated with a gelatin-chitosan-zinc oxide-betanin liposome hybrid composite was microbiological (S. aureus 2.63 log CFU/g and E. coli 3.83 log CFU/g) stable and reduced changes from lipidic oxidation (0.71 mg malondialdehyde/kg (MDA)), pH (6.27), and color attributes during 16 days at 4 °C than uncoated beef (S. aureus 5.26 log CFU/g, E. coli 6.76 log CFU/g, 1.23 mg of MDA/kg and pH of 7.20, respectively) or chitosancoated samples (S. aureus 5.76 log CFU/g, E. coli 6.13 log CFU/g, 1.50 mg of MDA/kg and pH of 7.51, respectively). These results were attributed to the antimicrobial and antioxidant properties of the hybrid film that prevented the myoglobin oxidation and accumulation of metmyoglobin, associated with the zinc oxide and betanin liposomes. Furthermore, it has been reported that a film composed of gelatin, chitosan, and zinc oxide nanoparticles effectively extended the shelf life of chicken fillets up to 12 days stored at 4 °C without significant changes in pH values, weight loss, or color attributes. Additionally, the coated samples were microbiological stable during the storage time. According to the authors, the hybrid film can prevent dehydration of chicken fillets, exhibiting antimicrobial properties [48].

Vizzini et al. [42] developed an active packaging composed of sodium alginate and zinc oxide previously doped with magnesium oxide nanoparticles to protect cold-smoked salmon against *L. monocytogenes*. They reported that coated salmon (previously inoculated with *L. monocytogenes* at 10^3 cells per gram) did not show plate counts after 4 days of storage at 4 °C than uncoated samples that exhibited a visible deterioration. Moreover, coated samples showed a reduced microbial growth from the purchasing day to the end of storage time in total viable count (from 4.4 to 6.5 log CFU/g), Enterbacteriaceae (<0.7 log CFU/g), lactic acid bacteria (from 4.4 to 5.95 log CFU/g), and yeasts (from 1.57 to 5.75 log CFU/g). These results were attributed to the barrier properties of the hybrid film and to the antimicrobial activity of zinc oxide nanoparticles that effectively prevented microbial proliferation in cold-smoke salmon.

Akbar and Anal [54] reported that an active calcium alginate–zinc oxide hybrid coating effectively extended the shelf life of ready-to-eat poultry meat up to 10 days stored at 8 °C. They found that treated meat (previously inoculated with *Salmonella typhimurium* and *Staphylococcus aureus*) exhibited a significant reduction in the viable counts of both pathogenic bacteria after the storage time. After 6 days, inoculated *S. aureus* counts decreased from 10^7 to $10^1 \log CFU/g$, while *S. typhimurium* decreased from 10^7 to $10^3 \log CFU/g$ after 8 days of storage. These results were associated with the antimicrobial properties of the zinc oxide nanoparticles, leading to bacterial cell damage, suggesting that the hybrid packaging could be used for poultry meat preservation.

Baek and Song [57] developed an agar coating functionalized with zinc oxide nanoparticles for smoked salmon preservation. They found that treated salmon (previously inoculated with 5.86 log CFU/g of *L. monocytogenes* and *S. typhimurium*) showed a reduced microbial growth after 5 days of storage at 4 °C. Moreover, the hybrid film prevented lipid oxidation (1.2 mg MDA/kg) compared to the uncoated sample (0.16 mg MDA/kg); moreover, no significant changes in the visual color of salmon were detected. These results were associated with the UV-blocking ability of the zinc oxide nanoparticles, retarding the lipid oxidation process.

Similarly, a hybrid coating composed of chitosan and zinc oxide nanoparticles has been investigated to preserve white, Ras, and buffalo milk cheeses (Table 2). Amjadi et al. [48] functionalized a gelatin-chitosan coating with zinc oxide nanoparticles for cheese preservation. They reported that after 12 days of storage at 4 °C, coated cheese showed lower weight loss (36%) than the chitosan-coated (49.60%) samples. Additionally, the hybrid-coated cheese was microbiologically stable (total bacteria count $< 2 \log CFU/g$) without significant changes in its pH values (4.7) and color attributes, which were lower than the control group (total bacteria count 3.2 log CFU/g and pH of 4.5). These results were associated with the hybrid film's ability to prevent cheese dehydration and rancidity. El-Sayed et al. [13] reported that chitosan-guar gum-zinc oxide-roselle extract hybrid coating effectively extended the shelf life of Ras cheese up to three months at 12 °C, finding that coated cheeses were microbiologically stable (total bacteria count, mold, and yeast were $<5 \log (FU/g)$ without significant changes in pH values and sensory attributes than the control sample, which was infested by a green mold. Moreover, the application of the hybrid film did not promote changes in the Ras cheese nutritional composition. According to the authors, these results were attributed to the gas exchangeability and antimicrobial properties of the hybrid film that preserves the quality parameters of Ras cheese. Similar trends were reported in an Egyptian soft cheese coated with a chitosan-carboxymethylcellulose-zinc oxide composite, which was microbiologically stable (total viable and coliform counts, yeast and mold) without significant changes in pH values, titratable acidity, moisture content, color parameters, and sensory attributes after 30 days of storage at 7 °C. The authors argue that the hybrid film's adequate physicochemical (contact angle) and antimicrobial properties are responsible for the cheese shelf life extension.

According to the evidence, functionalization of chitosan, carboxymethylcellulose, starch, carrageenan, sodium alginate, calcium alginate, pectin, and agar-based packaging by adding zinc oxide nanoparticles is a viable alternative to fabricate active packaging

for fruit, vegetables, mushrooms, fresh beef, chicken fillets, smoked salmon, and white, Ras, and buffalo milk cheeses, maintaining their quality parameters without affecting their sensory attributes during storage.

4.2. Titanium Dioxide (TiO₂)

Titanium dioxide is one of the most studied inorganic nanoparticles due to their versatility for diverse research areas (materials, physics, gas sensor, energy production, wastewater treatment, cosmetics, and food science) [6,58,59]. The wide use of titanium dioxide is supported by its photocatalytic performance, antimicrobial, electrical, ultravioletblocking, and adsorptive properties, biocompatibility, chemical stability, high surface area, low-cost, and safe production [60,61]. In recent years, titanium dioxide has been explored as a nanofiller of polysaccharide-based matrices such as chitosan, starch, and cellulose to develop food packaging with improved technological and functional properties [62]. Table 3 summarizes the application of polysaccharide–titanium dioxide packaging and their effects on quality parameters of some fruit, mushrooms, seeds, and meat products.

Polysaccharide	TiO ₂ Specifica- tions	Other Additives	Coating Method/ Presentation	Food Product	Storage Conditions	Observed Results	Ref.
Chitosan (1% <i>w/w,</i> DD 85%)	Conc.: 1% w/w Commercial Size: 15 nm	Thymol (0.5%); tween-80 (0.25%) Acetic acid (1 mL/100 mL)	Dipping for 1 min and air-dried at 25 °C/film	Cantaloupe fruit	25 °C for 8 days	Treated fruit showed microbial safety and maintain quality parameters during storage.	[63]
Chitosan (1% <i>w/w,</i> DD >95%)	Conc.: 0.3% w/w Commercial Size: 30 nm	Glycerol (1% w/w) Acetic acid (1 mL/100 mL)	Dipping for 3 min and air- dried/film	Mango fruit	13 °C for 20 days	The hybrid film preserved the quality parameters of mangoes.	[64]
Chitosan (1% <i>w/w,</i> DD >99%)	Commercial	Graphene oxide (1 mg/mL) Acetic acid (0.5 mL/100 mL) Glutaraldehyde solution (2 mL)	NI/NI	Mangoes	25 °C for 14 days	Coated fruit maintained their color attributes.	[65]
Chitosan (1% <i>w/w,</i> DD >99%)	Commercial	Graphene oxide (1 mg/mL) Acetic acid (0.5 mL/100 mL) Glutaraldehyde solution (2 mL)	NI/NI	Strawberries	25 °C for 14 days	Coated fruit maintained their color attributes.	[65]
Chitosan (2% <i>w/w,</i> DD >85%)	Conc.: 1% w/w Commercial Size: 21 nm	Glycerol (30% w/w of chitosan) Acetic acid (1 mL/100 mL)	Dipping/film	Tomatoes	20 °C for 15 days	Treated fruit showed minimal changes in quality parameters and delayed the ripening process.	[11]
Chitosan (1% w/w, DD 90%)	Conc.: 0.05 g Size: 50–80 nm	Acetic acid (2.5% v/v)	Dipping/film	Red grapefruit	37 °C for 22 days	Hybrid film prevented microbial infection and extended the shelf life of fruit.	[62]
Chitosan (1% <i>w/w,</i> DD >90%)	Conc.: 0.03% w/w Anatase phase Size: <200 nm	Glycerol (6.5% v/v) Acetic acid (1 mL/100 mL)	NI/film	Stauntonvine fruit	25 °C for 45 days	Fruit treated with hybrid film showed good CO_2 transmission without significant changes in quality parameters.	[66]
Chitosan (1% w/w, DD 85%)	Conc.: 1% <i>w/w</i> Size: 15 nm	Thymol (0.5%); tween-80 (0.25%) Acetic acid (1 mL/100 mL)	NI/film	Mushroom	4 °C for 12 days	Hybrid films reduced the PPO activity and inhibited the microbial pollution growth.	[67]

Table 3. Effect on the application of polysaccharide-titanium dioxide (TiO₂) composite on the food quality.

Polysaccharide	TiO ₂ Specifica- tions	Other Additives	Coating Method/ Presentation	Food Product	Storage Conditions	Observed Results	Ref.
Chitosan (1% <i>w/w,</i> DD >75%)	Conc.: 0.02% w/v Size: 18 nm Commercial	NI	Dipping for 1 min and air- dried/film	<i>Ginko biloba</i> seeds	1 °C for 180 days	Hybrid films prevented mildew apparition.	[68]
Chitosan $(2\% w/w)$	Conc.: 1% w/w Commercial	Tween-80 (0.25%) Glycerol (0.75 mL/g chitosan) Acetic acid (1 mL/100 mL) CCEO (1.5% v/v)	Evaporative cast- ing/coating	Minced meat	4 °C for 7 days	Meat was microbially stable during storage.	[69]
Cellulose $(1\% w/v)$	Conc.: 1% w/w Commercial Size: 10–25 nm Phase: anatase	WPI (10% <i>w/v</i>) Glycerol (6% <i>w/v</i>) REO (2% <i>w/v</i>)	Evaporative casting at 30 °C/coating	Lamb meat	4 °C for 15 days	Meat was microbially stable during storage.	[70]
Cellulose $(1\% w/v)$	Conc.: 1% w/w Commercial Size: 10–25 nm Phase: anatase	WPI (10% <i>w/v</i>) Glycerol (6% <i>w/v</i>) REO (2% <i>w/v</i>)	Evaporative casting at 30 °C/coating	Lamb meat	4 °C for 15 days	Hybrid films reduced lipid peroxidation.	[71]
Starch	0.01% <i>w/w</i>	Glycerol Distilled vinegar (5%)	Evaporative casting at 35 °C/coating	Bananas	Ambient temp. for 14 days	Hybrid films extended the shelf life compared to uncoated fruit.	[37]
Starch	0.01% <i>w/w</i>	Glycerol Distilled vinegar (5%)	Evaporative casting at 35 °C/coating	Tomatoes	Ambient temp. for 21 days	Hybrid films extended the shelf life compared to uncoated fruit.	[37]
Guar gum	NI	NI	Dipping for 1 min and air- dried/film	Dates	0 °C for 60 days	Treated fruit preserved quality parameters during storage.	[72]

Table 3. Cont.

NI: No information; DD: deacetylated degree; Conc: nanoparticles concentration; CCEO: *Cymbopogon citratus* essential oil; REO: rosemary essential oil; WPI: whey protein isolate; PPO: polyphenol oxidase.

Functionalization of chitosan, starch, and guar gum-based packaging by incorporating TiO₂ nanoparticles for fruit preservation has been explored in recent years (Table 3). Qiao et al. [63] developed a hybrid film with chitosan–titanium dioxide-thymol (CS-TiO₂thymol) to enlarge the shelf life of ready-to-eat cantaloupe fruit. They reported that cantaloupe packaged in the CS-TiO₂-thymol film showed major yeast and mold counts (1.6 log CFU/g) and polyphenol oxidase stability (PPO activity decreased from 0.65 to 0.35 U/min g) compared to the chitosan control group (yeast and molds 2.6 log CFU/g, PPO decreased from 0.65 to 0.15 U/min g) after 8 days of storage at 25 °C. Furthermore, minimal changes in quality parameters (pH, titratable acidity, total soluble solids, color attributes, water activity, and ascorbic acid) of the treated fruit during storage were observed. These results were attributed to the antimicrobial activity of the hybrid film and to the ability to reduce the oxygen between the film and the fruit, influencing the polyphenol oxidase activity and preserving the quality parameters of the ready-to-eat cantaloupe fruit.

Xing et al. [64] monitored changes on the postharvest quality parameters of mangoes coated with a chitosan–titanium dioxide hybrid film during 8 days at 13 °C, reporting that coated fruit exhibited retarded decay effects (19.73% after 15 days) than those observed in control groups (without coating 36% and chitosan-coated 28%); nonetheless, treated fruit maintained their firmness without significant changes on the total soluble solids content. Similar results were reported by Xu et al. [65], who coated mangoes and strawberries treated with a self-assembly film composed of graphene oxide and chitosan embedded with titanium dioxide nanoparticles, reporting that after 14 days of storage at room temperature, treated fruit showed 5% less of weight loss. Furthermore, treated fruit exhibited a reduction in the polyphenol oxidase activity (45%) and enhanced antioxidant enzyme activity via superoxide dismutase activation (from 25 to 330 U mg protein⁻¹) in comparison with uncoated and plastic-coated samples; suggesting that chitosan–titanium dioxide hybrid films may be a potential method for fruit preservation.

Additionally, it has been reported that CS–titanium dioxide film exhibited ethylene photo-degradation (from C_2H_4 to CO_2 and H_2O) under ultraviolet-light irradiation (320 nm during 3 h), extending the shelf life of tomatoes for 15 days stored at 20 °C without significant changes in their quality parameters (weight loss, firmness, total soluble solids, color attributes, ascorbic acid, and lycopene content). This behavior was associated with a delay effect in the ripening process of the fruit in comparison with chitosan-coated fruit [11]. Likewise, Zhang et al. [62] found that chitosan–titanium dioxide hybrid films effectively extended the shelf life of red grape fruit (22 days at 37 °C) without leakage of the juice and mildew apparition compared to plastic-coated fruit that exhibited several moldy spots and sticky juice leaked to the surface after 15 days of storage, associated with the antimicrobial properties of chitosan and titanium dioxide that prevented the mildew apparition, improving chitosan film wettability and hydrophilicity by the presence of the inorganic nanoparticles.

Yuan et al. [66] developed a chitosan–titanium dioxide hybrid coating to enlarge the shelf life of Stauntonvine fruit, finding that the physicochemical (titratable acidity, total soluble solids, and ascorbic acid) properties of the hybrid-coated fruit were preserved after storage (45 days at 25 °C). These effects were attributed to an internal atmosphere modification that slow some metabolic processes (respiration and transpiration) due to the reduction in the carbon dioxide transmission coefficient (27 g d⁻¹) compared to the chitosan-coated fruit (35 g d⁻¹). Furthermore, it has been reported a reduced respiration rate effect (oxygen concentration of 5%) in mushrooms coated with a chitosan–titanium dioxide-thymol film, with a decrease in microbial counts (20% of oxygen, yeast, and molds of 4.27 log CFU/g) and polyphenol oxidase activity (17 U/mg protein) after 12 days of storage at 4 °C, compared to those observed in CS-coated (yeast and molds of 6.17 log CFU/g and PPO of 45 U/mg protein) without significant changes in physicochemical parameters such as pH, color attributes, total soluble solids, weight losses, and firmness, which were associated with the inhibition of microbial growth and antioxidant properties of the film, maintaining the mushrooms postharvest quality [67].

Tunma [37] reported that a cassava starch–titanium dioxide hybrid film effectively extends the shelf life of bananas (14 days) and tomatoes (21 days) compared to those packaged with plastic films (5 and 10 days, respectively). Furthermore, Abdel-Baky et al. [72] informed that guar-gum films functionalized with TiO_2 can preserve quality parameters of dates for eight weeks stored at 0 °C without minimal changes in the fruit weight, color attributes, total soluble solids, acidity, and phenol and flavonoid contents. Moreover, treated fruit maintained an adequate microbial safety (yeast and molds) compared with guar-xanthan-lemongrass essential oil coat. According to the authors, these behaviors were attributed to the low oxygen/high carbon dioxide microclimate generated by the guar gum–titanium dioxide hybrid film that directly slow some metabolic processes, preventing dehydration and microbial deterioration of dates [37,72].

Furthermore, Tian et al. [68] preserved *Ginkgo biloba* seeds up to 180 days (1 °C) by coating them with chitosan–titanium dioxide films. They reported no significant changes in firmness and antioxidant capacity after storage time. Additionally, seeds did not show signs of mildew apparition, which were associated with the protective effect of the hybrid film and their ability to delay the senescence of *Ginkgo biloba* seeds due to the slowdown of the respiration rate (15 ng/kg s) and ethylene production (1.22 pg/kg s) compared to the uncoated (25 ng/kg s and 3.69 pg/kg s, respectively) and CS-coated (23 ng/kg s and 4.70 pg/kg s, respectively) seeds.

Additionally, chitosan and cellulose-based packaging has been functionalized with titanium dioxide for meat preservation (Table 3). Hosseinzadeh et al. [69] informed that the hybrid film composed of chitosan, TiO₂, and Cymbopogon citratus essential oil effectively preserved minced meat quality during storage (7 days at 4 °C). They found that treated meat is safe for consumption (total viable count of $<7 \log CFU/g$) and exhibited no significant changes in sensory attributes (odor, taste, and color) after the storage period compared to those obtained in the uncoated (>9 log CFU/g) and CS-coated (>9 log CFU/g) meat. Results were attributed to the antimicrobial properties of each component of the hybrid film and its synergistic effect. Similar trends were reported by Alizadeh-Sani et al. [70], who informed that lamb meat treated with a whey protein-cellulose nanofiber film functionalized with TiO₂ and rosemary essential oil maintained the microbial quality under safety criterion (total viable count of 4.1 log CFU/g) after six days of cold storage (4 $^{\circ}$ C) without changes in sensory attributes (odor, color, texture, and overall acceptability). Nonetheless, the chitosan-titanium dioxide-rosemary essential oil hybrid film prevented the lipid oxidation of meat during storage [71]. According to the authors, these results were associated with the antimicrobial activity and antioxidant capacity of the film (mainly by the presence of bioactive compounds in rosemary essential oil).

In general, functionalization of polysaccharides such as chitosan, starch, and cellulose by incorporating titanium dioxide nanoparticles is a technological strategy to develop packaging materials for fruit, vegetables, and meat preservation due to the antimicrobial and antioxidant properties of the hybrid film that maintain the quality parameters of the treated food products during storage.

4.3. Silver (Ag)

According to the literature, the main applications of silver nanoparticles are related to their antimicrobial properties [73,74]. They exhibited high surface area, thermal and chemical stability, and were not toxic [74]. Silver nanoparticles have been used in catalysis, sensors, textile, cosmetics, biomedical, and pharmaceutical and cosmetics applications. Furthermore, Ag nanoparticles have been explored as nanofillers for the development of antimicrobial packaging materials for food preservation [75,76]. Table 4 summarizes the application of polysaccharide–silver packaging and their effects on quality parameters of some fruit and meat products.

Polysaccharide	Ag Specifica- tions	Other Additives	Coating Method/ Presentation	Food Product	Storage Conditions	Observed Results	Ref.
Chitosan $(1\% w/w)$	Commercial Size: 200 nm	Phosphatidylcholine and cholesterol (50 mg at molar ratio of 5:1)	Evaporative casting/films	Pork meat	4 °C for 15 days	Hybrid films preserved the meat quality during.	[77]
Bacterial cellulose Piece (2 cm \times 2.5 cm \times 0.3 cm)	Conc.: 1% <i>w/w</i> Size: 10 nm	NI	Evaporative cast- ing/plasmonic nanopaper	Fish	60 h	Color change suggested a food decomposition process.	[78]
Bacterial cellulose Piece (2 cm \times 2.5 cm \times 0.3 cm)	Conc.: 1% <i>w/w</i> Size: 10 nm	NI	Evaporative cast- ing/plasmonic nanopaper	Meat	60 h	Color change suggested a food decomposition process.	[78]
Cellulose acetate (1% w/w)	Conc.: 0.05 g Size: ~7 to 40 nm	Triethyl citrate (0.2 g) thymol (0.08 g)	Evaporative casting/films	Ethanol (as fatty food simulant)	NI	Hybrid films exhibited antioxidant properties.	[79]
Sodium alginate (10% w/w)	Conc.: 80 µg/mL Size: Size of 5–40 nm	Glycerol (1 mL)	Evaporative casting/films	Carrots	4 °C for 10 days	Hybrid films enhanced the shelf life of carrots.	[16]
Sodium alginate (10% w/w)	Conc.: 80 µg/mL Size: Size of 5–40 nm	Glycerol (1 mL)	Evaporative casting/films	Pears	4 °C for 10 days	Hybrid films enhanced the shelf life of pears.	[16]

Table 4. Effect on the application of polysaccharide–silver (Ag) composite on the food quality.

NI: No information; Conc: nanoparticles concentration.

Most of the reported polysaccharide-based packaging functionalized with silver nanoparticles for food preservation are focused on meat and fruit (Table 4). Wu et al. [77] functionalized a chitosan-based coating incorporating laurel essential oil and silver nanoparticles for pork meat preservation. They reported that after 15 days of cold storage at 4 °C, treated meat maintained its sensory quality (color, flavor, elasticity, viscosity, and good leakage) compared to those obtained in the uncoated samples that exhibited perceptible changes, mainly associated with changes in pH values, which were lower in the treated meat (from 5.5 to 6.5) than the uncoated meat (from 5.5 to 7.1). According to the authors, pH values >6.7 suggest a meat deterioration process. Furthermore, the total volatile base nitrogen content in treated meat was under legislative specifications following Chinese food safety standards (<15 mg/100 g) after 15 days of storage in comparison with uncoated sample (25 mg/100 g), which were attributed to the antimicrobial properties, antioxidant capacity, and oxygen blocking ability of the film. Moreover, these facts could be associated with the antioxidant properties of the hybrid film, as reported by Dairi et al. [79], who evaluated the antioxidant capacity (by the 2,2-diphenyl-1-picrylhydrazyl radical scavenging test) of a cellulose-silver-thymol hybrid film using 95% ethanol as fatty food simulant. They found that the hybrid film exhibited higher radical inhibition (94%) compared to those obtained with a cellulose-thymol film (90%) due to the synergistic effect between individual components and because the simulated system, promoting the release of silver-thymol compounds from the film to the medium, influencing the antioxidant capacity of the film.

Heli et al. [78] developed a plasmonic nanopaper through silver ion attraction into a cellulose network for fish and meat spoilage monitoring. They reported that the nanopaper suffered color changes from amber to gray in fish, or from amber to taupe in meat in a time-

dependent response, indicating a deterioration process in the food products. Nonetheless, during the detection process, there were changes detected in the population density of silver nanoparticles per μ m² of the nanopaper in fish (~1213) and meat (~1376) compared to the control (~1473). The authors argue that ammonia and other volatile compounds are released during the food degradation process that may promote the exposure to the corrosive vapors partially or entirely etched to the silver nanoparticles of the cellulose nanopaper.

Additionally, Fayaz et al. [16] developed a sodium alginate film functionalized with silver nanoparticles for carrots and pears preservation at 27 °C. They reported that the hybrid film did not promote changes in the soluble protein content of the treated samples, similar to those observed in the sodium alginate-coated carrots (0.531 mg/g); however, after ten days of storage, all samples showed a decrease in this parameter (0.45 mg/g). Furthermore, carrots and pears did not show significant weight losses and changes in their sensory attributes than the control group that exhibited a perceptible spoilage process after 6 days of storage. These results were attributed to the antimicrobial properties and gas exchangeability of the functionalized film.

According to these data, the functionalization of polysaccharide-based packaging with silver nanoparticles has been widely used for their antimicrobial properties, an important characteristic for food preservation. However, further studies are needed to evaluate the potential migration risk of Ag nanoparticles from the polysaccharide-based material in real food systems.

4.4. Silicon Dioxide (SiO_2)

Silica nanoparticles (SiO₂) are white and amorphous, they are a promising material due to their intrinsic characteristics such as non-toxicity, thermal stability, chemical inertia, low density, high surface area, porosity, biocompatibility, and biodegradability, and exhibiting antimicrobial properties [80,81]. Furthermore, it is cheap and commercially available [82]. Functionalization of polysaccharide using silicon dioxide nanoparticles have received attention due to their high number of silanol groups, and to the ability to form hydrogen bonds with the biopolymer enhancing their technological and functional properties, suitable for food preservation [83–85]. Table 5 summarizes the application of polysaccharide–silicon dioxide packaging and their effects on quality parameters of some food products.

Silicon dioxide has been used as a functional agent to develop polysaccharide-based food packaging capable of preserving fruit, mushrooms, and chicken fillets (Table 5). Yu et al. [86] developed a biodegradable polyvinyl alcohol-chitosan-silicon dioxide (PVA-CS-SiO₂) film for cherries fruit preservation. They informed that coated fruit with PVA-CS-SiO₂ exhibited lower weight losses (8.30%) and browning index (97) compared with uncoated (27.28% and 312, respectively) and polyvinyl alcohol–chitosan-coated (19.28% and 123, respectively), which were associated with enhanced oxygen and moisture barrier permeability of the hybrid film by the silicon dioxide functionalization, reducing fruit dehydration, lipid oxidation, and rancidity degree.

Eldib et al. [87] evaluated the effect of chitosan–nisin–silicon dioxide film on the quality parameters on blueberries during 8 days of storage at 28 °C. They reported that coated fruit helped to control shrinking (38.5%) and decay rates (8.61%) with a weight loss of 4% than uncoated fruit (60%, 35%, and 10%, respectively). Moreover, treated fruit suffered minimal changes in their physicochemical parameters (pH, total soluble solids, titratable acidity, and color) and sensory (hardness, chewiness, springiness, and cohesiveness) attributes during storage; associated with the inhibition of microbial growth (total viable count of 2.5 log CFU/g, and yeast and molds 3.5 log CFU/g), polyphenol oxidase inhibition (600 U/min g), and preservation of vitamin C (8 mg/100 g) and total anthocyanin (80 mg/100 g) content. Moreover, the coated fruit also had better appearance than the uncoated fruit. These results were attributed to the antimicrobial properties and gas exchangeability of the functionalized film.

Polysaccharide	SiO ₂ Specifica- tions	Other Additives	Coating Method/ Presentation	Food Product	Storage Conditions	Observed Results	Ref.
Chitosan (2% w/w)	NI	PVA (1% <i>w</i> / <i>w</i>)	Evaporative casting/film	Cherries	NI	Hybrid film prevented loss weight and enzymatic browning.	[86]
Chitosan (1% <i>w/w,</i> DD 85%)	Size: 15 nm	Nisin (1% w/w) Glycerol (0.5%) Acetic acid (1 mL/100 mL)	NI/film	Blueberries	28 °C for 8 days	Hybrid films prevented fruit decay and preserved their quality parameters.	[87]
Potato starch (5% w/w)	Conc.: 0.3% w/w Commercial	Glycerin (5% w/w)	Evaporative casting/ film	White mushroom	4 °C for 12 days	Hybrid films did not promote changes in the quality parameters during storage.	[85]
Hydroxy propyl methyl cellulose (4% <i>w/w</i>)	Conc.: 80 ppm Size: ~80 nm	Glycerol at 30% w/w	Evaporative cast- ing/coating	Chicken fillets	4 °C for 15 days	Hybrid films prevented microbial infection of foodborne pathogens.	[15]

Table 5. Effect on the application of polysaccharide-silicon dioxide (SiO₂) composite on food quality.

NI: no information; DD: deacetylated degree; Conc: nanoparticles concentration; PVA: poly vinyl alcohol.

Zhang et al. [85] monitored changes in quality parameters in white mushrooms coated with a potato starch–silicon dioxide hybrid film. In general, firmness (800 N), membrane permeability (40%), weight loss (3%), and color attributes of mushrooms changed during storage, associated with a deterioration of the metabolic process. However, mushrooms coated with the hybrid film exhibited lower delayed effects by storage than the uncoated samples (500 N, 55%, and 5%, respectively), attributed to a reduced exchange of water and oxygen permeability.

Osman et al. [15] fabricated a hydroxy propyl methyl cellulose coating functionalized with silicon dioxide nanoparticles to extend the shelf life of chicken fillets. They informed that the hybrid film is active against *Bacillus cereus* (2.5 log CFU/cm²), *Salmonella* Typhimurium (3.5 log CFU/cm²), and *Staphylococcus aureus* (3.2 log CFU/cm²) preserving raw chicken fillets up to 15 days at 4 °C (uncoated samples showed >7 log CFU/cm² in all tested bacteria).

According to these data, the functionalization of polysaccharides using silicon dioxide nanoparticles can be applied as packaging material to extend the shelf life of different food products. However, further studies must evaluate the hybrid film's behavior in foods with high water content.

4.5. Other Inorganic Nanomaterials Used to Develop Polysaccharide-Hybrid Packaging for Food Preservation

Additionally, other inorganic nanoparticles such as halloysite, aluminum oxide, montmorillonite, iron oxide, zirconium, and magnesium oxide have been incorporated to polysaccharide-based materials to develop hybrid packaging for food preservation (Table 6).

Table 6. Functionalization of polysaccharide packaging with halloysite, aluminum oxide, montmorillonite, iron(III) oxide, zirconium, and magnesium oxide nanoparticles for food preservation.

Nanoparticles Specifications	Polysaccharide	Other Additives	Coating Method/ Presentation	Food Product	Storage Conditions	Observed Results	Ref.
Halloysite Conc.: 6 g Commercial	Starch (25% w/w)	Glycerol (25 g) Nisin (6 g)	Extrusion/film	Minas Frescal cheese	4 °C for 14 days	Inhibited <i>Listeria</i> <i>monocytogenes</i> proliferation.	[14]
Aluminum oxide Conc.: 80 ppm Size of ~80 nm	Hydroxy propyl methyl cellulose (4% w/w)	Glycerol (30% w/w)	Evaporative casting/film	Chicken fillets	4 °C for 15 days	Coated meat was microbially stable during storage.	[15]
Montmorillonite Conc.: 2.5% <i>w/w</i> Commercial	Chitosan (1.5% w/w)	Glacial acid (1% v/v) glycerol (30% w/w), REO or GEO (2% v/v) Tween 80 (0.2% w/v)	Evaporative casting/film	Poultry meat	5 °C for 15 days	Hybrid films preserved the quality parameters during storage.	[88]
Iron(III) oxide	Sodium alginate	NI	NI/coating	Apples, carrots, and brinjal	25 °C	Hybrid films retarded decay in coated products.	[89]
Iron(III) oxide	Cellulose	NI	NI/coating	Apples, carrots, and brinjal	25 °C	Hybrid films retarded decay in coated products.	[89]
Zirconium Conc.: 4 mmol Commercial	Chitosan (3% w/v)	Glacial acid (3% v/v)	Co- precipitation method/film	Tomatoes	25 °C for 7 days	Hybrid films prevented fungal infection.	[90]
Magnesium oxide Conc.: 0.2% w/w Commercial Size of 20 nm	Chitosan (2% w/w)	BSM (2% <i>w/w</i>), glycerol (0.75% <i>w/w</i>) ZEO (2% <i>w/w</i>), Tween 80 (0.25% <i>w/v</i>)	Evaporative cast- ing/coating	Rainbow trout fillets	4 °C for 18 days	Coated fillets showed extended shelf life without changes in sensory attributes.	[91]
Magnesium oxide Conc.: 0.05% w/v Commercial Size of 20 nm	Cellulose (5% v/v)	Gelatin (20%, <i>w</i> /v) glycerin (3%, <i>v</i> /v)	Evaporative cast- ing/coating	Processed Eggs	25 °C for 112 days	Hybrid films extended the food shelf life.	[92]

NI: no information; Conc.: concentration; REO: rosemary essential oil; GEO: ginger essential oil; BSM: basil seed mucilage; ZEO: Ziziphora clinopodioides essential oil.

4.5.1. Halloysite (Hal)

Halloysite is a natural aluminum-silicate ($Al_2Si_2O_5(OH)_4nH_2O$) with tubular-shape nanotubes [93]. It possesses high surface reactivity, good mechanical strength, and thermal stability properties [94–96]. Moreover, halloysite is a biocompatible and non-toxic material that showed good dispersion in biopolymeric matrices [97,98], mainly by its positive alumina and negative silica surface charges and its selective functionalization [99], which could be used as a functional agent to develop packaging materials for food preservation [100,101].

Meira et al. [14] fabricated a starch-halloysite antimicrobial hybrid film to preserve soft cheese at 4 °C (Table 6). They reported that inoculated cheese with *Listeria monocytogenes*

(5 log CFU/g) showed a complete inhibition (under the detection limit of the method) of microbial counts after 4 days of storage, and no counts were detected after 15 days, similar to those observed in the starch-nisin film (after 1 day of storage). According to the authors, electrostatic charges between nanoparticles and cell wall could disrupt cell integrity causing bacterial death. Lee et al. [102] studied the antioxidant properties of a chitosan film functionalized with halloysite and clove essential oil in a fatty food simulant (alcohol at 95% at 25 °C). They found that hybrid films showed antioxidant activity (55 to 65% of DPPH radical scavenging) in a halloysite concentration-dependent response. According to the authors, the presence of halloysite stabilized the clove essential oil in the chitosan film, increasing its antioxidant response.

4.5.2. Aluminum Oxide (Al₂O₃)

Aluminum dioxide nanoparticles exhibited good hydrothermal stability, optical, and antimicrobial properties; they have a high surface area and porosity and are widely used in cosmetics, paints, semiconductor materials, and active packaging [103,104]. It has been reported that chicken fillets coated with a hydroxy propyl methyl cellulose-aluminum dioxide hybrid film was microbiological stable during 15 days of storage at 4 °C compared to the uncoated sample (Table 6). Nonetheless, the hybrid film was active against different foodborne pathogenic bacteria such as *Bacillus cereus* (3.5 log CFU/cm²), *Salmonella* Typhimurium (4 log CFU/cm²), and *Staphylococcus aureus* (4.5 log CFU/cm²) that permits the preservation of raw chicken fillets up to 15 days at 4 °C (uncoated samples exhibited >7 log CFU/cm² in all tested bacteria) [15].

4.5.3. Montmorillonite (MMT)

Montmorillonite is a member of the smectite mineral group with a single crystal structure, irregularly shaped particles, and a high surface area [105,106]. It is eco-friendly, commercially available, and low-cost [107]. Moreover, montmorillonite is commonly used as a nanofiller of polysaccharide-based packaging to enhance their physicochemical properties [108,109].

Pires et al. [88] functionalized a chitosan-based film with montmorillonite nanoparticles for poultry meat preservation (Table 6). In general, hybrid films effectively extended the shelf life of fresh poultry meat up to 15 days at 4 °C. The moisture content of coated meat was lower (70.8%) than uncoated samples (77.6%) with lower changes in color parameters during storage (total color change, 4.7, compared to 7.2, from red to brownish), associated with the myoglobin loss and accumulation of metmyoglobin. Moreover, pH values in coated meat decreased from 6.3 to 5.9 during the first three days, compared to 6.5 after storage, which was lower than the observed in unwrapped meat (pH 7.1 after 15 days). Likewise, the use of the hybrid film prevents lipidic oxidation via malonaldehyde (MDA of 0.20 mg/kg) and microbial deterioration (total coliforms of 2.8 log CFU/g) in comparison with uncoated meat (MDA of 1.71 mg/kg and 5.68 log CFU/g, respectively). These results were attributed to the antioxidant and antimicrobial properties of the hybrid film.

4.5.4. Iron(III) Oxide (Fe₂O₃)

Iron(III) oxide magnetic nanoparticles have been used in recent years due to their low toxicity, biocompatibility, and antimicrobial properties [110]. It has been incorporated into polysaccharide matrices to develop drug-delivery systems [111], enzyme immobilization to syrup production [112], and packaging materials with antimicrobial properties [10] suitable for food preservation [89]. Alagu et al. [89] fabricated two hybrid films (cellulose or sodium alginate) functionalized with iron(III) oxide nanoparticles to extend the shelf life of apple fruit, carrots, and brinjal (Table 6). In general, coated fruit did not show changes in protein content and weight loss compared to the control sample after storage at 25 °C. Moreover, no significant changes in the sensory attributes (color, appearance, and texture) were observed in treated fruit during the first 8 days of storage. According to Saedi and Rhim [10], the polysaccharide-iron(III) oxide hybrid film exhibited potent antimicrobial

activity against foodborne pathogenic bacteria, which could effectively extend the shelf life of diverse food products. Moreover, it has been reported that iron oxide can act as an oxygen scavenger, a suitable characteristic to preserve packaged foods [110].

4.5.5. Zirconium (Zr^{4+})

Zirconium nanoparticles have interesting industrial applications (biomedicine, sensors, catalysis, cosmetic, and food technology) due to their thermal, optical, mechanical, and catalytic properties [113]. It also exhibited good biocompatibility with biopolymers to fabricate hybrid films [114]. Ejeromedoghene et al. [90] developed a chitosan-zirconium(IV) complex as an antifungal spraying agent to control infected tomatoes with *Aspergillus niger* (Table 6). They reported that the hybrid complex effectively inhibited the fungal growth (tomatoes looked fresh) and reduced the weight loss (1.91%) after seven days of storage at room temperature in a zirconium dose-dependent response than the observed in control groups (uncoated fruit looks rotten with a weight loss of 3.2%). These results were attributed to the antimicrobial properties of the film that extends the shelf life of postharvest tomatoes.

4.5.6. Magnesium Oxide (MgO)

Magnesium oxide nanoparticles are a non-toxic white to gray powder, soluble in water with ionic properties, suitable for diverse applications [115,116]. It has been used in pharmaceutical, cosmetics, and catalysis, mainly by its high surface area, thermal stability, low coordinate sites, structural defects on their surface, and antimicrobial properties [117,118].

Naeeji et al. [91] developed a basil seed mucilage-chitosan film functionalized with Ziziphora clinopodioides essential oil and magnesium oxide nanoparticles activated via gamma irradiation to rainbow trout fillets preservation (Table 6). They reported that the coated fillets exhibited a maximum shelf life of 18 days at 4 °C. Additionally, all purchased rainbow trout fillets showed safe microbial quality at the beginning of the study. In general, coated fillets exhibited lower counts in total viable counts (5 log CFU/g), psychotropic bacteria (4.5 log CFU/g), Pseudomonas spp. (4.5 log CFU/g), Pseudomonas fluorescens (4 log CFU/g), hydrogen sulfide producing bacteria (2 log CFU/g), and Enterobacteriaceae (4 log CFU/g) after the storage period than those observed in the control group (>7 log CFU/g) after 4 days). These results were attributed to the antimicrobial properties of the hybrid film, mainly by the presence of Ziziphora clinopodioides essential oil and magnesium oxide that suppress the bacterial growth altering the surface of the cell membrane leading to microbial cell dead. Furthermore, the coated fillets showed a total volatile base nitrogen content (19.99 mg N/100 g) below to the recommended limit stipulated by the European Commission (25 mg N/100 g) with a peroxide value of 0.99 meq peroxide per 100 g of lipid; suggesting that coated fillets preserved their freshness and sensory attributes (odor, color, and overall acceptability) during storage, associated with a retarded microbial growth and reduced lipid oxidation (control group showed 2.67 meq peroxide/100 g lipid).

Wang et al. [92] evaluated the effect of gelatin–bacterial cellulose–magnesium oxide hybrid coating on the quality parameters of preserved eggs during 110 days of storage at 25 °C with 55% of relative humidity. They reported that the coated preserved eggs showed a reduced weight loss (2%) than those observed in the control group (4.5%), associated with the barrier properties of the hybrid coating to prevent a dehydration process. Moreover, coated eggs (pH from 11 to 10) showed lower pH values after storage (control group pH from 11 to 9.5). According to the authors, the hybrid coating blocked the eggshell pores that prevented the oxidation process and avoided the loss of volatile alkaline nitrogencontaining substances. Furthermore, sensory attributes (hardness, springiness, chewiness, and color) of the coated preserved eggs were less affected during storage than the uncoated samples, demonstrating a protective effect on the quality parameters of preserved eggs.

According to the evidence, the functionalization of polysaccharide-based packaging incorporating inorganic nanoparticles such as halloysite, aluminum oxide, montmorillonite, iron oxide, zirconium, and magnesium oxide is an interesting strategy applied for food

preservation. However, further studies are required to validate their potential uses as food packaging, mainly in foods with high amounts of water.

5. Disadvantages of Polysaccharide-Based Food Packaging Functionalized with Inorganic Nanoparticles and Perspectives

Despite the observation that the functionalization of polysaccharide-based packaging incorporating inorganic nanoparticles provides beneficial effects on food preservation, it is necessary to evaluate the safe application of this kind of organic–inorganic food packaging due to the presence of inorganic nanoparticles such as titanium dioxide, zinc oxide, silver, silicon dioxide, halloysite, aluminum oxide, montmorillonite, iron oxide, zirconium, and magnesium oxide in their composition and their interaction with the food product.

In this context, it is crucial to control or minimize the potential migration of nanoparticles from packaging to food products [23]. Al-Naamani et al. [45] informed that the migration of zinc oxide nanoparticles incorporated in a chitosan–zinc oxide hybrid film to okra preservation might occur. They reported 1.8% of the total zinc oxide (0.08 mg/cm^2) in the coating released by a zinc ionization (Zn^{2+}) after 12 days of storage at 25 °C. However, the concentration was under the safe recommended dosage. Similarly, Vizzini et al. [42] informed that zinc oxide doped with magnesium oxide used as functional agent of alginate film did not show cytotoxic effects in U937 and HL-60 cell lines at concentration below of 1 mg/mL, which may be safely used as reinforcement agent of polysaccharide-based packaging for food preservation.

Recently, Enescu et al. [119] evaluated the specific migration according to the European normative legislation (1130–1:2004) of titanium dioxide from a chitosan–titanium dioxide hybrid film using ethanol at 95% and olive oil as food simulants under microwave and dry ash digestions over 10 days. They concluded that a negligible amount of titanium dioxide ($<5.44 \times 10^{-4}$ % of the total titanium dioxide in the chitosan film) migrated from the polymeric matrix to the simulated food model, but most of the titanium dioxide content is chemically bonded in the chitosan matrix. Furthermore, they reported that the chitosan–titanium dioxide hybrid complex did not show cell toxicity on in vitro tests (resazurin and CCK8, and Caco-2 cells), suggesting that chitosan–titanium dioxide could be used as food packaging material. Moreover, Alizadeh-Sani et al. [71] detected a low content of titanium dioxide nanoparticles in a meat product coated with a whey protein-cellulose nanofiber film functionalized with titanium dioxide but were <1% w/w and complied the Food and Drug Administration specifications.

Similar trends were reported by Fortunati et al. [120], where the migration rate of silver nanoparticles in a cellulose-Ag film immersed in ethanol solution at 10% did not exceed the limit specifications established by the European Food Safety Authority in a time-dependent storage response but mentioned that after 10 days, the number of liberated nanoparticles increased due to moisture absorption into the polymer, suggesting their use in food with low water content. Likewise, Abdullah and Dong [96] reported that the presence of halloysite in a starch film showed minimal migration content, depending on the hydrophilic, lipophilic, and acidic characteristics of the food products. Moreover, nanoparticles migration can occur due to dissolution, diffusion, and abrasion of the packaging material [121].

García et al. [121] mentioned that a negligible number of migrated nanoparticles to the food system occur when organic–inorganic packaging is used, particularly for those ionizable nanoparticles such as zinc or magnesium oxides; conversely to other nanoparticles such as titanium dioxide that remain in the biopolymeric matrix, and thus do not easily migrate. On the other hand, an inorganic nanofiller as a functional agent of polysaccharide packaging for food preservation should be following the recommended safe dosages, according to the international regulations [121]. Therefore, further studies are needed to evaluate the migration of inorganic nanoparticles from the biopolymeric matrix to food systems and their potential human health risks on the usage of this kind of hybrid packaging for food preservation that permits the establishment of policies about the use of inorganic nanoparticles as a functional agent of polysaccharide-based materials. Additionally, some limitations have been reported during the functionalization of polysaccharide-based materials adding inorganic nanoparticles. The main reported limitations include the interaction between polysaccharides and inorganic nanoparticles, as well as their proper mixing ratio, and those associated with the concentration and dispersion of the inorganic fillers that strongly influence (negatively or positively) the functional and technological properties of the hybrid material [122–125]. For example, the physicochemical properties of the hybrid materials are influenced by their preparation method (mechanical stirring and evaporative casting, electrospinning, dip-, spin-, and spray-coating, and spray-drying) and the type of polysaccharide used, which are associated with chemical and physical interactions between polysaccharides and inorganic nanoparticles [1]. Moreover, the improper mixing ratio among components can affect the technological properties of the hybrid materials due to a saturation of the available functional groups in the polysaccharide structure; nonetheless, there are not standardized protocols to prepare polysaccharide-inorganic nanoparticles hybrid materials with desirable characteristics.

Another reported limitation is the concentration of nanoparticles added and their effect on the physicochemical and structural characteristics of hybrid materials. According to the evidence, the technological properties of the functionalized polysaccharide-based materials are negatively affected by higher concentrations of nanoparticles, because of the formation of agglomerates associated with an excessive and non-homogeneous dispersion into the biopolymeric matrix, limiting their potential applications [126].

In general, the development of suitable protocols to fabricate polysaccharide-based materials functionalized with inorganic nanoparticles that permits solving these limitations is an area of opportunity for the food packaging industry.

6. Concluding Remarks

Significant evidence indicated that the functionalization of polysaccharide-based packaging by incorporating inorganic nanoparticles is a suitable approach for food preservation. The most studied polysaccharide includes chitosan, cellulose, and starch, while inorganic nanoparticles are titanium dioxide, zinc oxide, silver, and silicon dioxide in a concentration ranged from 0.01 to 80 mg per 100 mL of film-forming solution. Moreover, films (by dipping) and coatings (evaporative casting) are the most common methods to use polysaccharide-hybrid packaging for food preservation.

In general, polysaccharide-hybrid packaging can preserve the quality parameters of different food products. For example, treated fruit, vegetables, mushrooms, and *Gingko biloba* seeds markedly increased their shelf life without significant changes in their quality attributes, associated with a reduction in the deterioration process of the food products due to the prevention of the water loss, non-enzymatic and enzymatic oxidation, and microbial infections, mainly by the presence of inorganic nanoparticles. Similarly, hybrid packaging showed protective effects to preserve meat products, cheese, and preserved eggs by preventing microbial infections and lipid peroxidation, extending the food product's shelf life without changes in their sensory attributes.

As for the future fabrication of polysaccharide-hybrid food packaging is necessary to evaluate the migration rate of inorganic nanoparticles from the polymeric matrix to the food system and their possible human health risk. Moreover, there is no information about the stability and structural changes in the hybrid food packaging, promoted by the time and storage conditions when interacting with the food product. Therefore, further studies are needed to guarantee the safe implementation of these organic–inorganic packaging materials in the food industry. Author Contributions: Conceptualization, L.M.A.-E., Z.V.-d.I.M., A.P.-L., and E.M.-G.; methodology, L.M.A.-E., Z.V.-d.I.M., N.R.-B., J.M.R.-G., L.E.I.-M., C.I.M.-V., A.P.-L., and E.M.-G.; investigation, L.M.A.-E., Z.V.-d.I.M., N.R.-B., J.M.R.-G., L.E.I.-M., C.I.M.-V., A.P.-L., and E.M.-G.; writing—original draft preparation, L.M.A.-E., Z.V.-d.I.M., N.R.-B., J.M.R.-G., L.E.I.-M., C.I.M.-V., A.P.-L., and E.M.-G.; writing—original draft preparation, L.M.A.-E., Z.V.-d.I.M., N.R.-B., J.M.R.-G., L.E.I.-M., C.I.M.-V., A.P.-L., and E.M.-G.; writing—original draft preparation, L.M.A.-E., Z.V.-d.I.M., N.R.-B., J.M.R.-G., L.E.I.-M., C.I.M.-V., A.P.-L., and E.M.-G.; writing—original draft preparation, L.M.A.-E., Z.V.-d.I.M., N.R.-B., J.M.R.-G., L.E.I.-M., C.I.M.-V., A.P.-L., and E.M.-G.; writing—review and editing, L.M.A.-E., Z.V.-d.I.M., C.I.M.-V., A.P.-L., and E.M.-G.; supervision, L.M.A.-E., Z.V.-d.I.M., C.I.M.-V., A.P.-L., and E.M.-G.; supervision, L.M.A.-E., Z.V.-d.I.M., C.I.M.-V., A.P.-L., and E.M.-G. All authors have read and agreed to the published version of the manuscript.

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