Nanofillers for Food Packaging: Antimicrobial Potential of Metal-based Nanoparticles

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Abstract: Background: Recently, numerous studies on the packaging of nanomaterials for foods underline the significant function of nanofillers in the manufacturing of innovative nanocomposites based on polymer or biopolymer matrices. It is evident in the literature that nanofillers exhibit effective characteristics such as antimicrobial potential, barrier, mechanical, and thermal properties. However, the exact mechanisms regulating the occurrence of the antimicrobial activity of nanofillers are only hypothesized, with the literature containing controversies regarding the mechanisms of nanofiller-induced toxicity.

Objective: The objective of this review is to highlight several types of nanofillers, especially inorganic nanofillers that can be used along with different polymers or biopolymers to form innovative food packaging materials. The antimicrobial potential of metal-based nanofillers is also discussed in the second part of the review.

Results: Even though numerous reports on polymer or biopolymer nanomaterial applications in food packaging are available, the purpose described in those reviews has not been aimed in this article, as a smaller number of reviews have approached food packaging nanomaterials in the way as done in this review article.

Conclusion: It is expected that the information contained in this paper will complement previous reports, and open new vistas for explorers to apply nanofillers in the functional food packaging area.

Keywords: Innovative food packaging, nanofillers, reinforcing, metal-based nanofillers, antimicrobials, reactive oxygen species.

1. INTRODUCTION

Food packaging is a powerful marketing tool, designed to be attractive and to provide essential information for food consumers and marketers, with its primary role being to protect food products from any possible contaminants, and to maintain the product quality and safety (safety being the first priority for consumers when they buy any foods) on its way to the final consumer [1-11]. Additionally, food packaging plays another essential role, i.e. extending the shelf life of foods. It also has to be economical, eco-friendly (lower energy consumption in manufacturing, renewable sources, lower carbon emissions, recyclability, excellent biodegradability) and user friendly [2-4, 12-16]. So far, the larger part of packaging materials tested in the food industry involves polymer materials based on petroleum with properties such as gas barrier, mechanical properties, flexible structures, chemical stability, easy sterilization, and microbial protection [3, 17-23]. In addition to petroleum-based polymer materials, the food packaging industry employs biopolymer materials to decrease the impact of petroleum-based polymer materials on the environment [13, 23-29]. Though polymers and biopolymers possess numerous advantages, the food packaging industry is currently focusing on the development of innovative packaging nanomaterials, as of today, the package is not only an inert barrier but interacts with the food product or with the headspace in the packaging-product system. Lately, polymer/biopolymer nanomaterials have been developed in order to provide desirable food packaging properties due to their superior benefits, such as improved gas barrier; UV-light (ultraviolet light), moisture, and volatile compounds barrier; mechanical strength; excellent ability to maintain the sensory quality and the nutritional value of the packaged food; improved traceability and food safety (antimicrobial active packaging), as well as providing environmental benefits and at the same time decreasing energy consumption, in comparison to conventional composites [2, 3, 17, 30-33]. Antimicrobial active packaging enhances the protection package property by embedding nanofillers into...
the matrix material or its surface (nanofillers like antimicrobial agents, oxygen absorbers, water vapor absorbers, ethylene scavengers) that are released in a controlled manner [2]. The superior effect of the active antimicrobial nanocomposites originates in the inherent features of nanofillers that are encapsulated into polymer/biopolymer matrices, even if nanofillers are in small quantities. Nanofillers (nanoparticles) display specific characteristics like nanoscale dimensions [sizes in the range of 1-100 nm (nanometer)] and a high specific surface area, having an organic/inorganic composition [3, 32, 34-38]. The nanoparticles (NPs) that are frequently used in food packaging are nanoclays, nanocellulose, nanosilver, nanogold and some metal-oxides in nanoforms, along with different polymers or biopolymers [2, 3, 39-55]. Nanoclays and nanocellulose are mainly employed to increase the properties (e.g., gas barrier, mechanical and thermal properties) of the nanostructures in which they are added [17, 23]. Ag-NPs (silver nanoparticles) are the most effective antimicrobial NPs, at exceptionally low concentrations [3, 56], while Au-NPs (gold nanoparticles) are especially used in food contaminant detection and food monitoring packaging [29, 57]. Although Ag-NPs are among the most extensively used antimicrobials [1, 3, 43, 44, 53, 56, 58], some of the metal-oxides including MgO-NPs (magnesium oxide nanoparticles), TiO₂-NPs (titanium dioxide nanoparticles), ZnO-NPs (zinc oxide nanoparticles), CuO-NPs (copper oxide nanoparticles), and Fe₃O₄-NPs (triiron tetroxide nanoparticles - magnetite) have raised great interest in food packaging owing to their properties [3, 59-65]. Generally, metal-oxides in nanoform possess more potent antimicrobial activity in comparison to metallic NPs, due to high surface area, unusual crystalline structure with more edges and corners, and the presence of high amounts of surface-active sites [66, 67]. Nevertheless, Ag-NPs have a stronger antimicrobial effect, as compared to TiO₂-NPs and ZnO-NPs [44, 56]; instead, TiO₂-NPs and ZnO-NPs exhibit advantages over Ag-NPs owing to their UV-blocking properties, ease of manufacturing, and affordability [46, 53, 68]. Even though MgO-NPs, CuO-NPs, and Fe₃O₄-NPs are less studied in comparison to TiO₂-NPs and ZnO-NPs, and the exact antimicrobial mechanism of MgO-NPs, CuO-NPs, and Fe₃O₄-NPs remains a matter of discussion [69-73], these NPs appear to have potential in food packaging. The use of metal-oxides like TiO₂-NPs, ZnO-NPs, MgO-NPs, CuO-NPs, and Fe₃O₄-NPs represents an effective tool in enhancing the mechanical and gas barrier package properties, the functional properties of packaged food (quality, flavor, color, freshness), and also the food safety due to their antimicrobial potential through the generation of higher levels of ROS (Reactive Oxygen Species), or the direct route through which the metal oxidized ions are released from NPs [3, 33, 43, 46, 53, 59, 60, 62-65, 74, 75]. The purpose of this review is to highlight several types of nanofillers, especially inorganic nanofillers that can be used along with different polymers or biopolymers to form innovative food packaging materials. The antimicrobial potential of metal-based nanofillers is also discussed in the second part of this review. Even though numerous reports on polymer or biopolymer nanomaterial applications in food packaging are available, their purpose is not similar to the one of this article, as a smaller number of reviews have approached food packaging nanomaterials in this way. It is expected that the information displayed in this paper will complement previous reports, and open new research vistas aimed at implementing metal-based nanofillers in the functional food packaging area.

2. NANOSTRUCTURES USED IN THE FOOD PACKAGING SYSTEMS

Nanocomposites generally refer to polymer or biopolymer composites (multiphase hybrid solid materials) that contain some nanofillers such as nanocellulose, nanoclay, metal nanoparticles (Au, Ag), and metal oxide nanoparticles (TiO₂, ZnO, MgO, CuO, and Fe₂O₃) providing superior or unique benefits to the packaging when compared to conventional composites [2, 3, 31, 32, 34, 76, 77].

2.1. Types of Polymer/biopolymer Matrices for Food Packaging Nanocomposites

2.1.1. Polymer Matrices for Food Packaging Nanomaterials

In most regions of the world, food products are packaged in different polymer materials such as PET (polyethylene terephthalate); PE (polyethylene); various grades of PE which consist of HDPE (high density PE), LDPE (low density PE), and LLDPE (linear low-density PE); PP (polypropylene); PA (polymamide); PC (polycarbonate); PEN (polyethylene naphthalate); PS (polystirene), and PVC (polyvinyl chloride) [2, 17, 22, 23, 43, 78, 79]. PET is particularly suitable for food packaging applications, having an exceptional propensity to substitute classical packaging materials (e.g., glass, metal) in food packaging [17, 80]. It reveals mechanical and optical properties, lower flavor scaling potential, adequate gas barrier, as well as recycling ease [2]. PET is mainly used to package beverages such as fresh-fruit-juices, carbonated soft drinks, tea, edible oils, beer, and wine [17, 75, 79, 81-83]. PE with its grades (HDPE, LDPE, LLDPE), and PP have good mechanical and barrier properties regardless of moisture. Moreover, HDPE is more resistant to moisture compared to PET [2]. HDPE, LDPE and LLDPE are used for manufacturing packaging film, plastic bags and containers (cans, bottles, etc.) for general purposes [75]. PP serves in the manufacturing of glasslike bottles, being suitable for bottling warm liquids, due to its high melting point [2]. PA shows flavor barrier properties, chemical resistance, and good impact strength, while PC possesses high impact strength, and high temperature resistance. PEN exhibits better barrier properties than PET, and it is well suited for beverage packaging due to its ability to protect against the transfer of flavors and odors [2]. PS is used to produce bottles, boxes, cartons for eggs, cups, disposable plastic tableware, food trays, lids, and plates [84]. PVC, a rigid polymer, is suitable for food containers. Though polymers possess numerous advantages, polymer packaging materials will not always provide a suitable barrier at the molecular scale (e.g., flavor molecules, gases, additives), compared to glass or metal materials [2-4, 85]. In this context, the innovative PNCs (polymer nanocomposites) are often used to provide desirable packaging properties (improved gas-barrier, UV-light, moisture, and volatile compounds barrier, mechanical strength, improved food safety) [2, 3, 17, 30-33, 47-49]. One requirement in obtaining PNCs is that the individual NPs be homogeneously dispersed in a polymer matrix. The dispersion is the key challenge to reaching the full potential of property
enhancement. The effect of NPs is attributed to polymer matrix properties, nature, type, aspect ratio, size, orientation, distribution of NPs and the concentration of the polymer and NPs [86].

2.1.2. Biopolymer Matrices for Food Packaging Nanomaterials

In contrast to conventional polymers that still dominate the food packaging area, biopolymers are an ideal solution to be exploited and developed into food packaging materials that can reduce the environmental impact of conventional polymers [2, 3, 13, 14, 17, 22-24, 26-29, 43, 75, 78, 79, 87-90]. PHB [poly (3-hydroxybutyrate)], PHBV [poly (3-hydroxybutyrate-co-3-hydroxyvalerate)], and PLA (polylactic acid) can provide a promising alternative, having the potential to create a sustainable food packaging industry [3, 26, 27, 91]. PHB and PHBV are long-term sustainable alternatives, showing equal performance to conventional synthetic plastics, being the only fully biodegradable biopolymers with a complete green life cycle [92]. They have raised interest in food packaging applications due to their considerable hydrophobicity in comparison to natural biopolymers (e.g. polysaccharide-based biopolymers), showing promise in the competition with conventional petroleum-based polymers [3, 29, 93, 94]. PHB has properties which are very similar to many petroleum-based polymers (e.g. high crystallinity, good gas and water vapor barrier performance), being a good candidate to substituting the petrochemical opponents PE and PET [3, 14, 29, 90, 93-97]. PHB exhibits flavor barrier performance, being comparable to PET. Its water vapor barrier and CO$_2$ permeability value are very close to those of the PET and non-plasticized PVC [29]. The PHB biopolymer is more rigid and less flexible than PP, but at higher temperatures, it performs even better than PP [93, 94]. PLA has a high flexibility, lower molecular weights and lower melting temperatures when compared to PHB, which is characterised by a high degree of crystallinity, and resistance to UV-light [93, 98, 99]. PLA offers exceptional mechanical and optical properties, high molecular weight, good processability, monomer renewability, ability to be easily composted, low carbon footprint, and recycling possibility [29, 100-103]. Its mechanical properties and flavor barrier are comparable to those of PET, PE, and PVC [29]. The water permeability of PLA is still higher than that of conventional polyolefins and PET [102]. PLA is able to substitute HDPE, LDPE, PET and PS as packaging materials [101]. Although the PHB, PHBV and PLA biopolymers possess desirable characteristics as food/beverage packaging materials, they still possess certain limitations (Table 1).

To address these limitations, PHB, PHBV and PLA have been modified with different types of NPs, [13, 14, 23, 24, 27, 28, 46, 53, 75, 86-89, 99, 104, 105].

### Table 1. Limitations of PHB, PHBV and PLA biopolymers as food packaging material.

<table>
<thead>
<tr>
<th>Biopolymer</th>
<th>Refs.</th>
<th>Limitations</th>
</tr>
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<tbody>
<tr>
<td>PHB</td>
<td>[87, 93]</td>
<td>Highly crystalline, relatively brittle and stiff, low elongation to break, low thermal stability in the molten state</td>
</tr>
<tr>
<td>PHBV</td>
<td>Inferior thermal stability, inferior barrier performance against CO$_2$ permeation, and high value for flavor permeability in comparison to PET</td>
<td>[93, 94, 99]</td>
</tr>
<tr>
<td>PLA</td>
<td>Rather brittle character, reduced gas and vapor barrier characteristics, inferior thermal stability, inferior resistance to humidity, low flexibility</td>
<td>[17, 27, 29, 94, 95, 100, 101, 102, 104]</td>
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2.2. Nanofillers for Food Packaging

2.2.1. Nanocellulose

Nanocellulose is an organic nanofiller extracted from cellulose that can be adapted to different surface properties owing to the reactive surface of its hydroxyl groups [87, 106], and a promising method for enhancing the mechanical and barrier properties of biopolymers [23]. There are three types of nanocellulose, i.e. CNC (cellulose nanocrystalline), CNF (cellulose nanofibers), and BC (bacterial nanocellulose) that are grouped according to sources and the various extraction methods [23, 106-108]. CNC (cellulose nanocrystals or cellulose nanowhiskers), CNF (cellulose nanofibers), and BC are good candidates for developing and manufacturing biodegradable packages in the food industry; CNC displays superior mechanical properties due to its high crystallinity and high Young's modulus [109], while CNF offers excellent rigidity, tensile and flexural characteristics [110].

2.2.2. Nanoclays

Nanoclays are relatively inexpensive and quite reasonable to be employed as functional materials for food/beverage packaging. Nanoclays come in different types. Out of these types, the most commonly used are MMT (montmorillonite), MMTNa$^+$ (sodium montmorillonite), and organically modified MMT, due to their characteristics (e.g. huge surface area and good compatibility with most polymers) [17, 111]. Moreover, MMT has an exceptional reinforcement potential and acts as a crucial filler in biodegradation, being eco-friendly and safe to use in the food/beverage packaging [3, 17, 43, 53, 75, 112, 113]. MMT is a major component of bentonite and has been permitted for use by the EU (European Union) since May 2017.

2.2.3. Metallic-NPs

The encapsulation of these nanofillers into the polymer or biopolymer matrices enhances the performance of polymers/biopolymers, providing them with antimicrobial properties through the generation of higher levels of ROS, or direct route i.e. through metal oxidized ions release from NPs, also giving functional properties to packaged food [2, 3, 13, 17, 27, 30, 33, 43, 46, 53, 58-60, 62-65, 74, 75, 89, 114]. Metallic NPs for food packaging mainly include Ag-NPs and Au-NPs. Ag-NPs (10 nm in size) have higher stability in water, while the acid environment leads to a complete dissolution of Ag$^+$ within several hours at room temperature [40]. The applications of Ag-NPs in food packaging systems include antimicrobial and antioxidant activities. Au-NPs have been used in various areas like biological tagging, biomedical imaging, catalysis, cancer therapy, food packaging and food monitoring, scattering based imaging, and biosensors [29, 115, 116]. Au-NPs have proven to be an attractive biocidal candidate in food packaging, being a very
promising alternative in the preparation of active packaging nanostructures [117-121].

2.2.4. Metal-oxide NPs

A wide range of metal-oxide NPs are frequently used as nanofillers for food packaging including TiO2-NPs, ZnO-NPs, MgO-NPs, CuO-NPs, and Fe3O4-NPs [3, 33, 43, 46, 53, 58-65, 75, 122-138]. TiO2-NPs and ZnO-NPs are among the most commonly used metal-oxide materials along with different polymers or biopolymers, as they are known for their properties, such as being nanoscale ethylene and oxygen scavengers, as well as UV-light blockers (they protect the packed foods, and delay the aging and degradation of the nanocomposites), having antimicrobial activity (due to their dimensions of a few nanometers, TiO2-NPs having 12-17 nm, and ZnO-NPs having 12 nm), enhancing the matrices characteristics, all of which recommend them to be used in nanomaterials for food packaging [3, 33, 44, 46, 53, 58, 75, 105, 139-146]. TiO2 is a top nanofiller, extensively used in foods, cosmetics, and medicines [147], and food packaging, due to its inertia and thermostability [3]. TiO2-NPs can be used to develop UV-protective and food safety polymer packaging and to maintain food stability, as they degrade easily when exposed to light. TiO2-NPs also have the ability to modify the properties of biopolymer nanocomposites [3]. TiO2-NPs enhance the characteristics of polymer and biopolymer matrices (antimicrobial and mechanical potential, thermal stability, UV resistance, and the degradation rate of biopolymer matrices in which they are embedded [3, 99, 139, 148-154]. TiO2 may be used as a color food additive [155], but is not yet permitted in the EU. TiO2-NPs are cheap, nontoxic, photo-stable and reusable [63, 156, 157]. ZnO-NPs have distinctive physico-chemical characteristics, like excellent catalytic efficacity and physico-chemical stability [158]. The ZnO-NPs’ use in packaging focuses on antimicrobial and UV absorption, and improving the PNCs’ stability [3, 44, 46, 58, 61, 156, 159, 160]. ZnO-NPs dispersed into the biopolymer matrices produce bioanomaterials with superior stiffness, strength, toughness, significantly better thermal stability, optical and antimicrobial actions [3, 140, 144, 145, 161-165]. ZnO-NPs are generally recognised as safe materials [166], and have been permitted in the EU since 2016. MgO-NPs have a low positive surface charge [167, 168]. Under sub-band-gap UV-excitation, MgO-NPs exhibit luminescence, the band-gap of MgO-NPs being large (>7 eV [electron volt]) [168]. MgO-NPs exhibit excellent antimicrobial activity [71, 167-172] that may be based on different MgO-NPs sizes [71, 172]. Different sizes have been reported such as: 38 nm [173], 15-60 nm [174], 16-19 nm [175], 22 nm [176]. When the size is below 15 nm, MgO-NPs have a very huge surface energy, and antimicrobial efficacy becomes higher [170]. MgO-NPs own better antimicrobial action, similar to the Ag-NPs [172]. Nanostructured MgO is also a polymer reinforcement agent [167, 171]. MgO-NPs are generally recognised as safe as a direct human food ingredient, and may also be used in infant formula [177]. Nano-sized CuO is used due to its antibacterial, antiviral and antifungal activity. CuO-NPs have a huge surface area which leads to a good interaction with the cell’s microbial plasma membrane [59]. Consequently, their antimicrobial action has been generally applied in the food packaging sector, the biological activity depending on the nanoparticle synthesis method [3, 59, 60, 141, 178-182]. CuO is considered to be a good reinforcing agent [63, 182]. Fe3O4-NPs are a particular type of NPs that have recently enjoyed increased interest, due to their magnetic properties [183, 184]. Fe3O4 has superior properties compared to Fe2O3, and thus it is promising for use in food packaging [3, 64, 185]. Fe3O4-NPs are important in food packaging due to their antibacterial potential [64, 70, 138].

2.3. Innovative Nanostructures for Food Packaging

2.3.1. Nanostructures with Nanocellulose

Nanocellulose is a strong competitor among biomonomaterials with beneficial properties and a high potential to reinforce food packages [186]. Numerous studies reported endeavors to fabricate nanocellulose-based films for food packaging. For instance, Fortunati et al. [187] explored the influence of un-modified and surfactant modified CNCs on the PLA barrier properties, and reported a good O2 barrier for both nanostructures, and a decrease in water vapor permeability for surfactant modified CNC, emphasizing an enhancement given by CNC. Siddaramaiah [188] reported that the use of BC as reinforcement to the PLA biopolymer is a solution because the BC is capable to enhance the characteristics of the biopolymer matrix, also reducing the production cost since less material is necessary to obtain the desired properties. CNC can enhance only an exclusive characteristic of polymer matrix (e.g. mechanical property), and it cannot provide new functional properties to polymers (e.g. antimicrobial function) [189]. Yu et al. [189] reported the obtention of synthesized CNC-Ag nanofillers, resulting in nanohybrids that were used to reinforce PHBV. They showed that CNC-Ag is a bifunctional nanofiller, enhancing both the mechanical and thermal characteristics, as well as the antimicrobial property of PHBV. Their study showed that the high-performance PHBV/CNC-Ag nanostructure makes this material feasible for implementation in the food/beverage packaging area. Another group of researchers noticed an enhancement in O2 barrier, stretchability, thermal stability and UV-light blocking effect of PLA/PHB/CNC/ATBC (ATBC - acetyl tributyl citrate) biodegradable nanomaterial with 5 % of CNC (or modified CNC) and 15 % ATBC [190]. PHB reinforcement with CNC has further improved the gas barrier of the PHB matrix [191]. Fortunati et al. [192] developed a biomonomaterial that consisted of PLA, unmodified CNC and surfactant modified CNC, and showed that the surfactant leads to the CNC dispersal in the PLA matrix, notably improving the nucleation result for matrix crystallization, causing the biopolymer plasticization. George et al. [193] manufactured and characterized nano-based thin films using PLA for food packaging applications using a combination of CNC, and either Ag-NPs or a peptide-based antimicrobial agent was selected. They found that the dispersion of the CNC or the antimicrobial agents within the film significantly affected the thermal and mechanical properties. PLA with 5 % CNC and the Ag-NPs were characterized by significant improvements in mechanical properties and thermal resistance. These are very attractive properties in producing films for packaging materials. Nevertheless, in cases where more than 0.75 % of the peptide was introduced, reductions in the above values were observed. Finally, most films with
CNC and antimicrobial agents were characterized by significantly improved O₂ and water permeability properties, making them competitive with the olefin-based plastics currently dominating the market [193]. Another collection of studies in the literature that aimed at enhancing the PLA biopolymer found that reinforcing PLA with nanocellulose raised much interest as an alternative to reinforcements in bionanomaterials [104]. Salari et al. [194] synthesized BC using *Gluconsaccharobacter xylinus* in order to obtain BCNCs (bacterial cellulose nanocrystals). Then they obtained an innovative nanostructure that consisted of CH (chitosan), Ag-NPs and BCNCs. They found that the embedding of BCNCs and Ag-NPs into the CH film considerably influenced the antibacterial activity, color, transparency, sensibility to water, water vapor permeability, mechanical properties, and thermal stability properties of the film. Very recently, Marin-Silva et al. [195] have reported that CNC is a satisfactory reinforcing agent in CH-based nanocomposite packaging.

### 2.3.2. Nanostructures with Nanoclays

Polymer/clay nanomaterials. Several studies on the innovative polymer/clay nanostructures have been conducted to improve the original properties of polymers as mentioned below. In a study, Dini et al. [196] suggested an inventive method for manufacturing PET/organoclay film using melt mixing and water-assisted melt mixing, while compensating the decreasing polymer molecular weight with subsequent solid-state polymerization. The film obtained by Dini et al. using this method showed greater tensile modulus and elongation at break, and lower O₂ permeability after solid-state polymerization [196]. Vidotti et al. [197] investigated PET/organically modified MMT material obtained via melt intercalation in a twin-screw extruder using PETi (polyethylene terephthalate ionomer) as compatibilizer. Their research revealed that the PETi can contribute to enhancing the dispersion of nanofilbers in the PET matrix, leading to the improvement in PNC properties (e.g. CO₂ and water vapor barrier) [197]. The hydrophobic polymer matrices like PE with its grades (HDPE, LDPE, LLDPE), and PP are common polylefins which are employed in the production of flexible film, pouches, food bags, retail bags, sachets, shrink wraps, general-purpose containers (cans, bottles, boxes, etc.), caps, closure, and lids [2, 17, 75]. Even though these polymers have significant mechanical and moisture barrier characteristics, they display inadequate gas barrier and grease resistance characteristics [2, 17]. To improve the dispersion of a small amount of organically modified MMT in the PE, HDPE, LLDPE, LDPE, and PP, various researches have been conducted in order to increase the organic-inorganic interaction [17, 198-201]. For instance, some researchers obtained an LDPE/organically modified MMT nanomaterial with clay-improved moisture barrier [202]. Nevertheless, the moisture barrier might be diminished if the amount of organically modified MMT exceeded a critical value [17].

Biopolymer/clay nanomaterials. The nanostructures with clay nanofilbers can also be designed using biopolymers like starch-based films, PLA, PHAs, and so on. The influence of clay on the biopolymer characteristics is discussed. Nanoclays are primarily used to reinforce the biopolymer matrices from the point of structural, mechanical and barrier properties, thermal behavior, and antimicrobial potential [17, 43, 75]. The successful development of biopolymer/clay nanomaterial is aimed at achieving a uniform dispersion of exfoliated or intercalated layered silicate clay nanofilbers into the biopolymer matrix, as it is essential to choose the proper type of nanofilbers being compatible with the specific biopolymer, and then decide the optimum amount of nanofilbers in order to prepare well-developed bionanocomposites [16, 112, 203]. A lot of research has been conducted on testing clays as potential reinforcement to enhance the PLA matrix features, and to increase the clay accession in the foods packaging field [17, 204-206]. Ayana et al. [204] developed S/PLA/MMTNa⁺ as an innovative biodegradable bionanocomposite using an eco-friendly procedure, and noticed an enhancement in mechanical/thermomechanical properties, and moisture barrier (the latter being attributed to the blending of hydrophobic PLA to S). Dadashi et al. [205] also demonstrated that the water vapor permeability of PLA/clay nanomaterials was greatly enhanced. A significant increase in tensile strength and elastic modulus, and an extraordinary decrease in elongation were also noticed [205]. The content of nanoclay in the PHBV matrix is essential to improving the performance of the pure PHBV matrix (e.g. increase of the Young’s modulus, crystallinity, thermal and dynamic mechanical properties) [93, 207, 208]. However, the nanoclay encapsulation into PHBV has a lower impact on the tensile strength [209]. In a very recent study, García-Quiles et al. [210] developed PHAs/nanoclay bionanostructures with excellent mechanical improvements. In a very recent work, Pattarasirirjo et al. [211] developed an active food packaging material through the insertion of nanoclay into rice-flour-gelatine biopolymer film, and showed a decrease in the film moisture content and transparency. Their research also showed that the innovative nanostructure could inhibit the microbial growth and efficaciously prevent lipid oxidation.

Extra features of nanoclays. In addition to being used as an agent to improve the mechanical and barrier properties of either polymer or biopolymer matrices [17, 43, 53], nanoclays offer many extra features which are applicable for active and smart food packages. In their study, Darie et al. [212] showed that the PLA/nanoclays exhibit an acceptable antimicrobial action against Gram-positive and Gram-negative bacteria. Other researchers revealed that a small amount of organically modified MMT embedded in PCL (polycaprolactone) might be enough to stop the growth of *C. albicans* yeast [213]. Nanoclays also play the role of biocide carriers for inorganic biocides such as Ag, Cu, Mg, Zn [17, 43, 75]. Gutierrez et al. [214] examined a promising nanoclay use as a colorimetric marker for smart food packages. They introduced blueberry extract into clay interlayers and showed that the clay/blueberry extract nanopowder shared intelligent characteristics with the nanoclay, with regard to changes in pH. Some authors designed a smart S/nanoclay bionanocomposite to observe the spoilage of milk by examining the color modification [215]. Bid deci et al. [216] examined the use of active halloysite nanoclay dispersed in a pectin solution for active food packaging. Their bionanocomposite exhibited high antioxidant and antibacterial effects. Shemesh et al. [217] tested the antimicrobial capacity of LDPE / organically modified MMT / carvacrol, and suggested that this innovative nanostructure had a high
antimicrobial action against *E. coli*, *L. innocua*, and *A. alternata*. A study conducted by Tornuk et al. [218] showed that incorporating halloysite and MMT nanoclays (grafted with carvacrol, eugenol, and thymol) into the LLDPE matrix contributed to impressive antibacterial and antioxidation activities of the nanocomposite. The nanoclays enhanced the photo-oxidative degradation of polymers through improving the UV absorption capacity of PNCs [17, 219]. Other researchers developed and examined (in terms of biodegradability, mechanical and thermal characteristics) a series of nanostructures such as PBAT/bentonite, PBAT/Cloisite 20A, PBAT/ Cloisite 30B, and PBAT/Na-MMT (Cloisite 20A being organically modified MMT with dimethyl, dihydrogenated tallow, quaternary ammonium; and Cloisite 30B being organically modified MMT with methyl tallow bis-2-hydroxy ethyl quaternary ammonium). Concerning degradability, these authors showed that the degradation of the PBAT/MMT Na⁺ nanostructure was faster than that of neat PBAT and PBAT/organically modified MMT, due to the MMT Na⁺ hydrophilicity [220]. In a recent study, Castro-Aguirre et al. [221] tested three types of nanostructures with different clays like PLA/organically modified MMT with dimethyl, dihydrogenated tallow, quaternary ammonium; and Cloisite 30B being organically modified MMT with methyl tallow bis-2-hydroxy ethyl quaternary ammonium). Concerning degradability, these authors showed that the degradation of the PBAT/MMT Na⁺ nanostructure was faster than that of neat PBAT and PBAT/organically modified MMT, due to the MMT Na⁺ hydrophilicity [220]. In a recent study, Castro-Aguirre et al. [221] tested three types of nanostructures with different clays like PLA/organically modified MMT with quaternary ammonium compounds, PLA/Laponite, and PLA/halloysite nanotubes. They concluded that the embedding of nanofillers greatly increased the biodegradability of the PLA biopolymer. Girdthep et al. [222] showed that the Ag-loaded kaolinite embedded into bionanocomposite resulted in a high-performance food package with considerable degradability. In their study, Memiş et al. [223] designed FSG with active nanoclays (a mixture of MMT Na⁺, halloysite, and nanomer in different sizes), the term FSG standing for fenugreek seed gum. Their nanostructure showed encouraging antimicrobial action and mechanical characteristics. Koosha and Hamedi [224] developed an innovative nanostructure like CH/PVA/bentonite (PVA - polyvinyl alcohol) with black carrot anthocyanins in order to obtain a pH-nanosensor.

### 2.3.3. Nanostructures with Metallic-NPs

Inorganic NPs (metals and metal-oxides) came into notice as nanofillers due to their nanoscale dimension and specific surface area. Some examples of polymers (PE, PVC, LDPE, HDPE) or biopolymers (PLA, PHB, CH, S) employed after incorporation with Ag-NPs and Au-NPs for packaging of different foods are included in Table 2.

Nanostuctures with Ag-NPs. Generally, metallic-NPs possess potent antimicrobial activity. For instance, some authors obtained a PVC/Ag film and explored the antibacterial action of this in relation with minced meat, under refrigeration conditions. They noticed the inhibitive action of Ag-NPs on *E. coli* and *S. aureus* [225-233]. Alternatives so far reported include combining Ag-NPs with other NPs that can reinforce the bionanomaterial structure [234]. Another researcher manufactured an LDPE/Ag/ZnO package and used it for bottling an orange juice. The microbiological stability of orange juice was studied on certain days, throughout the storage period, and it was noticed that the package with Ag-NPs showed a more noticeable antimicrobial action than the package with ZnO-NPs during the storage period [44]. Fortunati et al. [234] explored the antimicrobial potential of PLA/Ag-NPs/cellulose film for use in food packaging, and found antimicrobial action against *S. aureus* and *E. coli* bacteria. Further studies by Pana et al. [227] showed the antibacterial influence of LDPE/Ag/ZnO film on chicken breast. Becaro et al. [235] also manufactured LDPE/Ag nanostructure for fresh-cut carrots packaging, and noticed the powerful antibacterial action of the nanostructure against *S. aureus* and *E. coli* bacteria. Their nanocomposite also preserved the ascorbic acid amount of carrots with very little weight loss.

### Table 2. Applications of metal-NPs in food packages.

<table>
<thead>
<tr>
<th>NPs</th>
<th>NCs</th>
<th>Applications</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PVC/Ag</td>
<td>Antimicrobial actions in minced beef</td>
<td>[225]</td>
</tr>
<tr>
<td></td>
<td>PE/Ag</td>
<td>Food packaging</td>
<td>[226]</td>
</tr>
<tr>
<td></td>
<td>LDPE/Ag/ZnO</td>
<td>Antimicrobial actions in cooked chicken breast</td>
<td>[227]</td>
</tr>
<tr>
<td></td>
<td>LDPE/Ag</td>
<td>Antimicrobial actions in fresh pork sirloin</td>
<td>[228]</td>
</tr>
<tr>
<td></td>
<td>LDPE/Ag/CuO/ZnO</td>
<td>Antimicrobial actions in ultra-filtrated cheese</td>
<td>[60]</td>
</tr>
<tr>
<td></td>
<td>PVC/Ag</td>
<td>Antimicrobial actions in walnut, hazelnut, pistachio, almond</td>
<td>[229]</td>
</tr>
<tr>
<td></td>
<td>PHB/Ag</td>
<td>Antimicrobial actions</td>
<td>[142]</td>
</tr>
<tr>
<td></td>
<td>LDPE/Ag</td>
<td>Food packaging</td>
<td>[230]</td>
</tr>
<tr>
<td></td>
<td>PLA/BergamotEOs/Ag/TiO₂</td>
<td>Antimicrobial actions in mangoes</td>
<td>[231]</td>
</tr>
<tr>
<td></td>
<td>PVA/MMT/Ag</td>
<td>Antimicrobial packaging</td>
<td>[232]</td>
</tr>
<tr>
<td></td>
<td>CH/Au/Ag</td>
<td>Antimicrobial packaging</td>
<td>[233]</td>
</tr>
<tr>
<td></td>
<td>S/Au</td>
<td>Antimicrobial packaging</td>
<td>[118]</td>
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<tr>
<td></td>
<td></td>
<td>Sensors for food contaminant detection</td>
<td>[57]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Food monitoring packaging</td>
<td>[29]</td>
</tr>
</tbody>
</table>
Beigmohammadi et al. [60] developed LDPE/Ag/CuO/ZnO nanocomposite material. These authors observed a decrease in the number of coliforms from cheese kept under refrigeration conditions for a period of four weeks. Castro-Mayorga et al. [140] revealed a high capacity of PHBV/ZnO as an antibacterial nanomaterial. They demonstrated that the ZnO-NPs’ antibacterial influence was considerably enhanced when the specific surface area of ZnO-NPs increased; the hexagonal-pyramid NPs showing the highest antimicrobial action, even when NPs were embedded in the PHBV coating matrix. Moreover, ZnO-NPs added certain benefits to the optical and thermal features of the nanostructure [140]. Tavakoli et al. [229] manufactured a PE/Ag nanostructure, and assessed the effect of Ag-NPs on the shelf life of packaged nuts, including almonds, hazelnuts, pistachios, and walnuts. They reported the efficiency of PE/Ag package in increasing the shelf life of nuts. Although Ag-NPs are an interesting candidate among the metal NPs, their addition to the PLA matrix resulted in the decrease of mechanical features. Castro-Mayorga et al. [142] explored the Ag-NPs’ influence on the antibacterial potential of PHB/Ag. In their study, the authors reported a significant antibacterial effect, without observing any significant change in thermal stability or biodegradability. Very recently, Brito et al. [230] noticed that the LDPE/Ag nanostructure has a significant antimicrobial effect due to the special features of Ag-NPs like huge thermal stability and chemical fitting with conventional polymers. Other researchers evaluated the effects of PLA, PLABergamotEO films, and PLA/BergamotEO/TiO2 and PLABergamotEOs/Ag/TiO2 (as nanostructures) on the attributes (e.g. fruit firmness, color, ascorbic acid content) of mango fruits stored at room temperature for 15 days [231]. They observed that the nanostructures preserve the freshness of mangoes and augment their postharvest viability up to 15 days [231].

2.3.4. Au-NPs as a Nanofiller and Smart Sensor in Food Packaging

Smart packaging is a promising sector, including the manufacture of nanoswitches (to release antimicrobials, antifungals, and antioxidants in packaged food products) and nanosensors (which point out to food quality) [75]. Yousef et al. [233] synthesized CH/Au/Ag nanostructures, having a considerable effect against S. aureus and P. aeruginosa bacteria, and A. niger and C. albicans fungi. Moreover, CH/Au/Ag nanostructures can be used for edible food packaging applications, as well as biomedical, pharmaceutical, and biosensor purposes [233]. Pagni et al. [118] prepared active biofilms of quinoa starch incorporating Au-NPs. The presence of Au-NPs enhances nanocomposite characteristics. Besides, the nanocomposite showed a powerful antimicrobial effect against E. coli and S. aureus [118]. Chowdhury et al. [236] obtained a PVA/glyoxal/Au-NPs nanocomposite, and showed that the Au-NPs played a considerable role in the swelling resistance behavior of the nanocomposite, due to the constitution of complex molecular structure with low permeability that destroys the passageway for water vapor. Their nanostructure revealed a maximum preservative impact on banana, thus qualifying as a promising material for food packaging. Au-NPs are especially used in food contaminant detection and in food packaging monitoring [29, 57], being the most suitable material to produce smart sensors, due to their intrinsic properties [57]. Au-NPs are extensively used in the detection of mercury, lead, chromium, mycotoxins, pesticide, veterinary drugs, and the monitoring of these substances in drinking water and food products [57]. With respect to food monitoring, Au-NPs have an incredible impact, as nanosensors, in sensing the food spoiling factors like bacteria, and chemical species like oxygen or ethanol, toxins (e.g. aflatoxin B1 in milk) [237-239]. Au-NPs are also used as time-temperature integrators, and alert the food consumers regarding the quality of the food by means of color modifications [77].

2.3.5. Nanostructures with Metal-oxide-NPs

Metal-oxides are employed in both food processing and packaging. As nanofillers, metal-oxides provide food packages with several favorable properties (e.g. enzyme immobilization, O2 scavenging, and antibacterial potential) [240]. A selected list of citations on the applications of metal nano-oxides (TiO2, ZnO, MgO, CuO, and Fe2O3) in food packaging are shown in Table 3.

Nanostructures with TiO2-NPs. TiO2, one of the most widely used photoactive nanomaterials, exists in several distinct forms: anatase, rutile, brookite or a combination of the three. Out of these forms, the pure crystalline anatase is the most photoactive phase of TiO2 [105]. Bodaghi et al. [123] prepared LDPE/TiO2 film using a mixture of rutile and anatase TiO2 by a melt blending technique. With this film, they packaged pears, which they then exposed to UVA-light (ultraviolet A light, wavelength 315-400 nm) treatment. The authors concluded that LDPE/TiO2 without UVA-light treatment and LDPE film with treatment contained a greater number of microorganisms than the LDPE/TiO2 treated with UVA-light. Fonseca et al. [148] produced PLA/TiO2 bi-onanocomposite through the melting technique, with TiO2-NPs in varying amounts (5% and 8% respectively), and then treated the film with UVA-light. They highlighted the extra antimicrobial potential (94% of the bacteria and 99.99 % fungi being killed under UVA-light procedure) for the film embedded with 8% nanoparticles. In addition, the researchers noticed that the addition of 5 % TiO2-NPs resulted in an enhancement of the elastic modulus by 54%, compared to the pure biopolymer. Nevertheless, bionanocomposites revealed lower shear viscosity than neat PLA, possibly considering the biopolymer degradation on account of the nanoparticles [148]. Soluble soybean polysaccharide is a biopolymer that derives from soybean cotyledons. It has attracted considerable interest like all natural biopolymers due to its availability, biodegradability, renewable sources, and cost [133]. Some researchers developed an innovative SP/TiO2 nanostructure with varying amounts of TiO2-NPs into soluble SP (soybean polysaccharide). They observed that embedding TiO2 into the SP biopolymer resulted in reduced water vapor and oxygen permeability, and moisture content. On the other hand, the SP mechanical properties were enhanced, with the bionanocomposite also showing a significant antibacterial action [133]. Zhang et al. [120] prepared PLA/TiO2 (0.5 or 1%) and showed that embedded nanoparticles enhanced the bionanomaterial characteristics. Oleyaei et al. [131] manufactured S/TiO2 nanocomposite with reduced water solubility, moisture uptake, and water vapor permeability, enhanced Young modulus and tensile
strength, and significant UV-light absorbance even with very small amounts of nanoparticles (1 %). Moreover, the melting point and glass transition temperature of the nanostructure augmented with the augmentation of nanoparticles content, and the authors considered it as helpful for the packaging area [131]. Goudarzi et al. [124] obtained an ecofriendly UV-protective S/TiO₂ bionanocomposite, and showed that the nanoparticles amount considerably influenced the biopolymer properties (e.g. sensitivity to UVA-light and moisture, thermal and mechanical characteristics). Krehula et al. [126] developed a PVC/TiO₂ nanostructure using TiO₂ adapted with copper nitrate and silver nitrate, in order to improve the polymer characteristics. They concluded that TiO₂ adapted with silver particles enhanced the UV-light sensitivity, antibacterial potential and thermal stability of the PVC matrix. Zhang et al. [134] showed that the CH/TiO₂ nanostructure, manufactured for packaging red grapes in order to extend their shelf life, revealed effective biocidal action against bacteria (e.g. S. aureus and E. coli), yeasts (e.g. C. albicans), and molds (e.g. A. niger). Segura Gonzalez et al. [241] manufactured polymer nanocomposite materials based on PLA filled with various contents of TiO₂-NPs, and investigated the antimicrobial potential of nanoparticles averse to E. Coli bacteria, which showed a considerable antibacterial action at very small amounts of nanoparticles (1 %), while no notable differences were achieved for higher amounts (20 %) of nanoparticles [241]. CH is an advantageous biopolymer due to its numerous characteristics, like mechanical strength, forming ability, and flexibility. However, CH materials have inferior mechanical characteristics compared to petroleum polymers [127]. Kaewklin et al. [125] manufactured CH/TiO₂ and used it for the packaging of cherry tomatoes, showing that the packed tomatoes generally preserved their sensory attributes. Others researchers have also synthesized a nanostructure consisting of CH and TiO₂-NPs, and highlighted that the bionanocomposite has applications that are more valuable when compared to the CH matrix [127]. Very recently, some authors manufactured PLA/TiO₂ nanocomposites with different amounts of TiO₂-NPs (0 %, 5 %, 10 %, 15 %, and 20 %), and showed an enhancement in the biopolymer crystallization with nanoparticles embedding. They also noted that the biopolymer crystallization process decreased when the quantity of nanoparticles went above 15 %, which may be accounted for TiO₂-NPs gathering into the biopolymer [242].

Nanostructures with ZnO-NPs. Rescek et al. [132] obtained PE/PCL/ZnO or casein/ZnO. They concluded that the addition of ZnO into the polymer blend improved the polymer characteristics (greater thermal stability, reduced water vapour permeability, and superior antimicrobial potential). Al-Naamani et al. [122] prepared a CH/ZnO/PE nanocomposite, and revealed that the embedding of nanoparticles into the CH/PE blend enhanced its affinity with water, whereas the CH/PE coating showed an efficient antibacterial influence. Marcous et al. [128] showed that the LDPE/ZnO/TiO₂ nanocomposite exhibits a significant antimicrobial influence on E. Coli bacteria under UV-light treatment. The authors consider that ZnO-NPs could have strong biocidal action even in the UV-light absence, whilst the biocidal efficacy of TiO₂-NPs is associated with UV-light treatment [128]. Other researchers reinforced PLA with ZnO-NPs, obtaining a tri-layered nanostructure (PLA/ZnO//PLA//PLA/ZnO) [243]. They subjected the multi-structure film to UV-A and Q-SUN treatment, and experienced the

| Table 3. Uses of nano-metal oxides as food packaging materials. |
|------------------|------------------|------------------|------------------|
| Metal-oxides     | NCs              | Applications / properties | References |
| TiO₂-NPs         | LDPE/TiO₂        | Antimicrobial actions in fruits and vegetables [123] | |
|                  | SP/TiO₂          | Biocidal potential, foods packing [133] | |
|                  | S/TiO₂           | Improvement of nanostructure properties, food packing [131] | |
|                  | S/TiO₂           | UV-protective food packaging [124] | |
|                  | PVC/TiO₂         | Food packaging [126] | |
|                  | CH/TiO₂          | Red grapes packing [134] | |
|                  | CH/TiO₂          | Tomatoes packing [125] | |
|                  | CH/TiO₂          | Food packing [127] | |
| ZnO-NPs          | PE/PCL/ZnO       | Antimicrobial activity [132] | |
|                  | CH/ZnO/PE        | Antimicrobial activity [122] | |
|                  | LDPE/ZnO/TiO₂    | Antimicrobial action [128] | |
|                  | CMC/CH/OL/ZnO    | Antifungal action [129] | |
| MgO-NPs          | CH/MgO           | Food packaging [136] | |
|                  | PLA/MgO          | Food packaging [65] | |
| CuO-NPs          | LDPE/CuO         | Food packaging [135] | |
|                  | LDPE/Ag/CuO/ZnO  | Cheese packaging [148] | |
|                  | S/Ag/ZnO/CuO     | Food packaging [137] | |
| Fe₃O₄-NPs        | S/CH/cyclophosphamide/glycerin/Fe₃O₄ | Antibacterial coating [64] | |
|                  | CH/Fe₃O₄        | Antibacterial action [138] | |
impact of these irradiations on the mechanical characteristics and antimicrobial potential of the film. To test the antimicrobial potential, they used the following microorganisms: *B. cereus*, *B. atrophaeus*, *E. coli*, *S. aureus*, and *C. albicans*. Their research showed that the PLA/ZnO layers reduced the microbial number, while the PLA layer did not stop the microbial growth. Moreover, Q-SUN treatment had an impact on the action of the PLA/ZnO against Gram-negative bacteria and *C. albicans* yeast. On the other hand, this treatment had no negative influence on the action against Gram-positive microorganisms. They also observed that the UV-A and Q-UV treatment did not affect the mechanical characteristics of PLA/ZnO [243]. Noshirvani et al. [129] proposed the CMC/CH/OL/ZnO nanocomposite as suitable packaging for sliced bread. They noticed that the water vapor permeability of the nanocomposite was greatly reduced, the bread preserving its sensory attributes. The same authors prepared and characterized CMC/CH/OL/ZnO (0.5-2 % ZnO-NPs), and suggested that the nanostructure had greater UV blocking potential and a notable potential effect against *A. niger* in the case of nanostructure with 2 % ZnO-NPs [130]. Very recently, some authors manufactured various hydroxyethylcellulose / citric acid / ZnO nanostructures with good swelling abilities, hydrophilicity, and antimicrobial properties against *S. aureus* and *E. coli* bacteria [244].

Nanostructures with MgO-NPs. De Silva et al. [136] prepared CH/MgO (5 % and 10 % Mg-NPs) nanostructures in order to produce an improved food packaging material. They observed excellent mechanical characteristics in the case of the nanostructure with 5 % nanoparticles, and notable moisture barrier and thermal stability in both nanostructures [136]. Swaroop and Shukla [65, 245] produced a PLA/MgO innovative nanostructure and noticed an enhancement in the biopolymers characteristics (e.g. mechanical, barrier and antimicrobial potential) in the case of adding MgO nanoparticles. Zhang et al. [246] explored the influence of the MgO-NPs / Ag-NPs mixture on the mechanical and barrier properties and antimicrobial capacity of a nanocomposite based on poly (butylene adipate-co-terephthalate) biopolymer. The nanostructure shows promise for use in the food packaging industry. Wang et al. [247] introduced MgO-NPs into carbomethyl chitosan biopolymer and showed that the MgO-NPs enhanced the thermal stability, UV shielding performance, water-insolubility, and antimicrobial activity against *L. monocytogenes* and *S. baltica*. They proposed this nanostructure for the packaging of water-rich foods.

Nanostructures with CuO-NPs. Dehghani et al. [135] embedded three types of metallic-NPs (e.g. Ag, ZnO, and CuO) with different weight percentages into LDPE matrices by the melt extrusion method, and showed that the film containing ZnO-NPs showed the highest UV absorption. Some researchers explored the antimicrobial potential of the LDPE/Ag/CuO/ZnO nanocomposite produced by melting extrusion, and observed that the nanocomposite showed better antibacterial property than neat LDPE [60]. Another group of researchers studied different S-based bionanocomposites containing Ag-NPs, ZnO-NPs and CuO-NPs, alone or in mixture. The bionanocomposite with ZnO-NPs had the highest tensile strength and UV absorbance, and the lowest solubility in water, while the bionanocomposites with Ag-NPs and CuO-NPs respectively showed the highest antimicrobial potential. The bionanocomposite with mixtures of Ag-NPs, ZnO-NPs and CuO-NPs and CuO-NPs displayed a synergistic effect regarding the improvement of antimicrobial and mechanical characteristics [137]. Some researchers developed an antimicrobial nanostructure based on different combinations of sodium alginate and cellulose nanowhiskers incorporated with CuO-NPs. The cellulose nanowhisker enhances the barrier capacity of the nanostructure, thus restricting moisture penetration into the food, while the CuO-NPs prevent the microbial contamination of foods. Their innovative material showed good antibacterial activity against *S. aureus*, *E. coli*, *Salmonella* spp., *C. albicans* and the *Trichoderma* spp. [248].

Nanostructures with Fe3O4-NPs. Shariatinia and Fazli [64] developed innovative nanostructures consisting of S/CH/cyclophosphamide/glycerin/Fe3O4 (2-10% Fe3O4) for applications as antibacterial coatings. They observed that the film that consisted of 2 % Fe3O4-NPs exhibited the highest elongation, the lowest tensile strength and Young’s modulus; the highest Young’s modulus being found in the nanocomposite with 10 % Fe3O4-NPs [64]. Shrifian-Esfahni et al. [136] developed CH/Fe3O4 bionanocomposite with improved antimicrobial potential. Recently, Yadav [249] successfully synthesized a cellulose/iron oxide bionanocomposite with enhanced mechanical properties and suggested that the innovative nanostructure can be used as a food packaging material.

3. ANTIMICROBIAL POTENTIAL OF METAL AND METAL-OXIDES NPS

This section of the review deals with the antimicrobial potential of NPs, especially the ROS induction, as one of the most important antimicrobial mechanisms of NPs. The essential mechanism of nanotoxicity derives from the production of higher levels of ROS by nanomaterials [34, 250]. The ROS induction by NPs is dependent on numerous pivotal factors related to the nanoparticle, such as size, shape, morphology, surface coating, surface reactivity, specific surface area, solubility, bonded surface species, oxidation status, and the agglomeration and aggregation degrees of NPs (Fig. 1) [34, 37, 250-254].

The size, shape and morphology are key factors that significantly influence the toxicity of NPs. In comparison with microparticles, the NPs possess unique physical and chemical properties that are related to their potential for ROS induction. The toxicity of NPs is primarily size-dependent. The smaller NPs have a considerable antimicrobial action [255-257]. In general, small-sized Ag-NPs (5-13.5 nm), Au-NPs (8.4 nm), TiO2-NPs (12-17 nm), and ZnO-NPs (12 nm) have a high antimicrobial activity [146, 258].

3.1. Antimicrobial Potential of Metallic-NPs

3.1.1. Ag-NPs - Antimicrobial Activity

Ag-NPs have a strong antimicrobial activity at exceptionally low concentrations, the antimicrobial action being significantly affected by the size and shape of particle, and also by the colloidal status [3, 258]. However, their overall toxicity is not very well determined, and the toxic effects of
Ag-NPs may possibly be related to (i) the release of Ag⁺ ions formed by oxidative dissolution, (ii) direct damage of microbial cell membranes, (iii) ROS generation potentially including \( \cdot \text{O}_2^- \) (superoxide anion radical), \( \cdot \text{OH} \) (hydroxyl radical), and \( \cdot \text{O}_2 \) (singlet oxygen), which may explain the antimicrobial mechanism of Ag-NPs [43, 44, 53, 58, 259-265]. Ag-NPs enter the cells as Ag⁺, the Ag⁺ delivery being recognized as a critical determinant of Ag-NPs toxicity [259, 266]. Ag⁺ ions bind to the cell membrane and act on proteins, resulting in microbial death [43, 44, 160]. However, the generation of ROS by Ag-NPs is indubitably a principal mechanism of its toxicity [267, 268]. Ag-NPs produce highly reactive \( \cdot \text{OH} \), one of the most important biologically-active ROS [267]. The \( \cdot \text{OH} \) only acts on adjacent cells due to its diffusion-limited reactivity, as it is not expected to shift far away from its production site [269, 270]. This leads to a hypothesis, viz. the improvement of Ag-NPs adsorption on the microbial membrane will culminate in the production of a larger quantity of \( \cdot \text{OH} \) around the microbial cells, thus increasing the biocidal action [270]. Ag-NPs stimulate the production of ROS by mitochondria, and microbial cell death through intrinsic apoptotic pathways, Ag-NPs being more effective against microbes than other NPs [271]. Ag-NPs may be more toxic in lower pH environments [266]. The combined effects of the generation of \( \cdot \text{OH} \) and the release of Ag⁺ from Ag-NPs under acidic conditions might be expected to be particularly deleterious to the viability of microbial cells [266].

3.1.2. Au-NPs - Antimicrobial Activity

Controversial results regarding the involvement of Au-NPs in ROS production have been reported [272-277]. Calixto et al. [273], Her and Jaffray [274], Ngwa et al. [275], Zharov and Mercer [276], and Silvero and Becerra [277] found that Au-NPs activated by light may induce a photothermal microbial inactivation as an additional effect in parallel to the ROS production, the activity of Au-NPs becoming higher under light-emitting diodes. Moreover, Zhang et al. [265] reported that Au-NPs produced only one ROS like \( \cdot \text{O}_2 \) with antimicrobial influence. The Au⁺ ions have antibacterial action, but their antimicrobial mechanism has scarcely been studied. This is related to the long-wavelength shift of the plasmon band after Au-NPs excitation, and the corresponding short-wavelength shift of the bleaching band. The dissolution of Au-NPs from the surface of nanocomposites occurs concomitantly with the transfer of e⁻ generated by the Au plasmon. Under visible light, the \( \text{h}^+(vb) \) (valence band holes) of Au-NPs give rise to Au⁺ ions [152]. The mechanism of the biocidal activity of Ag⁺ and Au⁺ ions on microbial cells is substantially different, as it is considered that the antimicrobial effect of Au⁺ ions is mainly due to the binding of the DNA bases, which can be explained by efficient internalization of Au-NPs. In addition, in contrast to the easily-soluble NPs of Ag or Cu, Au does not dissolve easily [278]. The porins are not involved or only partially involved in the Au⁺ ions transport into the cells, unlike the transport of Ag⁺ ions, which suggests that other mechanisms may take place during the Au⁺ ions’ penetration into the cells. The binding of Au⁺ ions to the cell plasma membrane is also possible, similar to the binding of other M⁺ (metal) ions [152, 279]. Au⁺ ions appear to have less effect on microbial cell viability than Au-NPs [278]. The biocidal potential of Au-NPs has been less explored than the microbial activity of Ag-NPs. The antimicrobial Au-NPs, like all NPs, are dependent on their shape (nanoflowers, nanoprisms, nanospheres, nanorods, nanostars), size, and surface chemistry [29, 115, 116, 280, 281]. Nanospheres (10 nm) and nanorods (41 nm) are more toxic than nanoprisms (160 nm), nanostars (240 nm), and nanoflowers (370 nm) [282].

3.2. Antimicrobial Potential of Metal-oxides NPs

Metal-oxides induce ROS [\( \cdot \text{O}_2^- \), \( \cdot \text{OH} \), and \( \cdot \text{O}_2 \)] generation, which explains their antimicrobial mechanism [258, 263, 264, 283]. The possible paths for ROS induction by NPs are the internalization and dissolution of the NPs in microbial cells that result in an increase in the amount of M⁺ responsible for antimicrobial action by direct binding to the microbial plasma membrane [283]. ROS exhibit different levels of dynamics and activity [284]. \( \cdot \text{O}_2^- \) is a strong oxidiz-
ing compound, while \( \cdot \text{OH} \) is the most reactive, since it accepts one more electron than \( \text{H}_2\text{O}_2 \), giving rise to a water molecule [263, 284]. ROS produce DNA disruption (critical cellular target of ROS) [263, 284].

**3.2.1. TiO\(_2\)-NPs and ZnO-NPs - Antimicrobial Activity**

When TiO\(_2\)-NPs and ZnO-NPs are irradiated by UV-light or activated by visible light, many highly reactive reagents (e\(^-\)/h\(^+\)) are produced [3, 152, 154, 157, 284, 285] (Eq. 1).

\[
\text{Metal oxide} \xrightarrow{h^\nu} \text{Metal oxide}(e^-/h^+) \quad (1)
\]

The term \( h^\nu \) refers to solar light with photonic energy, \( e^-/h^+ \) refers to the conduction band electron and the term \( h^\nu \) is the energy for hydrogen bond formation. (e\(^-\)/h\(^+\)) pairs have a high potential to generate ROS [66]. Photocatalytic systems with antimicrobial effects under visible light have not been widely reported and their mechanism of microbial inactivation is only partially understood [152]. The oxidative reactions can affect microbial cell integrity, and the chemical arrangement of surface structures is the main mechanism of their photocatalytic antibacterial activities [70, 154, 286].

TiO\(_2\)-NPs - antimicrobial activity. Despite the fact that other metal-oxides like ZnO-NPs, MgO-NPs, CuO-NPs, and Fe\(_{2}O_{3}\)-NPs, TiO\(_2\)-NPs do not release M\(^+\) ions, the toxicity of these NPs could be attributed to the size-dependent interaction between NPs and intracellular biomolecules adsorbed onto NPs. So, TiO\(_2\) nanotoxicity refers to cytotoxicity, phototoxicity, and its potential to adsorb intracellular biomolecules [283]. TiO\(_2\) photocatalysts need UV-light photons with energies \( \geq 3.2 \text{ eV} \) [152, 287]. TiO\(_2\) (e\(^-\)/h\(^+\)) are generated in TiO\(_2\) due to the interband transition induced by the UV-quanta absorption. The photogenerated charges react with adsorbed \( \text{O}_2 \) and \( \text{H}_2\text{O} \), and generate ROS able to damage bacteria [152, 288]. The mechanism of photocatalytic bacterial inactivation under low-intensity solar irradiation for TiO\(_2\) is shown in Equations 2-6 [289].

\[
\text{bacteria} + [\text{TiO}_2 - \text{PNC}] \xrightarrow{\text{light}} [\text{TiO}_2^* - \text{PNC}] \xrightarrow{\text{bacteria}} \text{bacteria}^* \rightarrow \text{TiO}_2 - \text{PNC}[e^-/h^+] \quad (2)
\]

\[
\text{TiO}_2[e^-(cb)] - \text{PNC} + \text{O}_2 \xrightarrow{\text{ads}} \cdot \text{O}_2^- \xrightarrow{\text{ads}} \text{E}_0 - 0.16 \text{NHE} \quad (3)
\]

\[
\text{TiO}_2[e^-(cb)] - \text{PNC} + \text{O}_2 + \text{H}^+ \rightarrow \text{HO}_2^- \xrightarrow{\text{ads}} \text{E}_0 - 0.05 \text{NHE} \quad (4)
\]

\[
\text{TiO}_2[h^+(cb)] - \text{PNC} + \text{OH}^- \xrightarrow{\text{ads}} \cdot \text{OH} \xrightarrow{\text{ads}} \text{E}_0 - 1.90 \text{NHE} \quad (5)
\]

\[
\text{TiO}_2[h^+(cb)] - \text{PNC} + \text{H}_2\text{O}_2 \xrightarrow{\text{ads}} \cdot \text{OH} \xrightarrow{\text{ads}} \text{E}^+ \quad (6)
\]

The suffix ‘ads’ designates adsorption, and NHE is Normal Hydrogen Electrode. The photocatalytic reaction can be justified by the following processes. Firstly, light absorption takes place, followed by excitation of e\(^-\) (in a few nano seconds) to generate (e\(^-\)/h\(^+\)) [290, 291]. Secondly, the redox reactions triggering takes place with the h\(^+\) of the valence reacting with H\(_2\)O or OH\(^-\) (hydroxyl anions), which are adsorbed onto the surface and lead to the formation of ‘OH, as well as ‘O\(_2^-\) [290, 291]. These ‘OH ions are very powerful and are indiscriminate oxidizing agents against the bacteria. The metal-oxides consist of a positive charge, while the microorganisms exhibit a negative charge, which is the reason for the electromagnetic effect between the microorganisms and metals, leading to the oxidation of the microorganisms, ultimately resulting in their death [290, 291].

ZnO-NPs - antimicrobial activity. The suggested biocidal mechanisms of ZnO-NPs refer to the microbial cell damage through contact between NPs and cell membranes, ROS formation, and the antimicrobial Zn\(^{2+}\) deliverance (once internalized ZnO-NPs) [46, 263]. ZnO is an oxide semiconductor with direct band-gap energy (3.37 eV) and high excitation binding energy, which provides more effective excitation emissions at higher temperatures [292]. Upon light exposure, the (e\(^-\)/h\(^+\)) are produced inside and on the ZnO-NPs. Electrons (e\(^-\)) interact with O\(_2\) and produce ‘O\(_2^-\)’, while holes (h\(^+\)) interact with OH\(^-\) or H\(_2\)O and generate ‘OH radicals [284], ZnO-NPs have the potential to induce ROS with both their photocatalytic characteristics and photo corrosion under UV-light exposure [283]. To date, the mechanisms of ZnO-NPs toxicity have not been fully clarified, and thus are still controversial [293].

**3.2.2. MgO-NPs - Antimicrobial Activity**

A general assessment of MgO-NPs toxicity is not yet possible [71], with nano-MgO being less studied in comparison with nano-TiO\(_2\) and nano-ZnO. The exact antimicrobial mechanism of MgO-NPs is still unknown, as the literature contains controversies on the mechanisms of the toxicity of MgO-NPs. Induction of ROS was suggested as one of the leading theories for the antimicrobial activity of MgO-NPs [294]. A number of mechanisms, such as the generation of ‘O\(_2^-\) [168, 172, 284], oxidative stress as a major toxicity mechanism [71], strong electrostatic interaction of NPs (positively charged) with bacteria (negatively charged) which is subsequently damaging to the bacterial cell [172], alkaline effect [168, 172], and possible biofilm destruction effect [294] have been proposed to account for the antibacterial mechanism of MgO-NPs. Furthermore, whilst it was appreciated that MgO-NPs deliver a notable quantity of Mg\(^{2+}\), Mg\(^{2+}\) ions did not yield any important nanotoxicity; this behavior being different from other metal-oxides, like Zn\(^{2+}\) ion release from ZnO [168, 295]. Some researchers stated that the MgO-NPs have a strong antimicrobial action even in the absence of any ROS induction, as the cell membrane impairment takes place through the combination of the MgO-NPs bound to the cell membrane with the results of pH change, Mg\(^{2+}\) deliverance, and UV irradiation (if there is irradiation) [168, 295]. On the other hand, the rise in pH and Mg\(^{2+}\) amount produced through the dissociation of MgO-NPs is not the principal mechanism of bacterial death. The MgO-NP interactions with the microbial membrane could be the crucial mechanism of bacterial destruction [294].

**3.2.3. CuO-NPs and Fe\(_{3}O_{4}\)-NPs - Antimicrobial Activity**

The ROS induction by transition metals, including Cu and Fe, takes place through Haber-Weiss mechanisms (oxidized M\(^+\) ions interact with H\(_2\)O\(_2\) and produce ‘OH) and Fenton-type mechanisms (to induce oxidative stress: ‘O\(_2^-\) and ‘OH) reactions. The Fenton Reaction typically implies the transition of M\(^+\) (like zero-valent Cu\(^{0}\) and Fe\(^{2+}\)) which interacts with H\(_2\)O\(_2\) to give an oxidized M\(^+\) and ‘OH [37, 296]. The Fenton Reaction can go further by dissolving Fe\(^{2+}\) and
Cu+ ions as pointed out in Eq. 7, Fe2+ and Cu+ possess lower redox potentials than that of H2O2/H2O (1.77 V) (ECu+/Cu = +0.52 V; EFe2+/Fe = -0.44 V) which are favourable to initiate the Fenton Reaction, as seen in Eq. 8 [297].

\[ \text{M}^2+ + \text{H}_2\text{O}_2 \rightarrow \text{M}^{n+1} + \cdot \text{OH} + \cdot \text{OH}^- \quad (7) \]

\[ \text{M} \text{(NPs)} + \text{H}_2\text{O}_2 + n\text{H}^+ \rightarrow \text{M}^{n+} + \cdot \text{OH} + \text{H}_2\text{O} \quad (8) \]

Thus, H2O2 reacts with nano-oxides in the presence of transport H+ as shown in Eq. 7, which leads to the production of ·OH. In this way, the cascade ROS generation is initiated [297].

CuO-NPs - antimicrobial activity. Nano CuO is an antimicrobial metal-oxide [283], but its antimicrobial mechanism is not quite known [3, 63]. Some authors consider that CuO-NPs have the potential to induce all types of ROS [284]. The CuO-NPs dissolution is the pivotal factor that leads to ·O2− and H2O2 formation, and DNA damage [283]. The Cu+ catalyzes Fenton, Fenton-like, and Haber-Weiss reactions (Equations 9 -11) [37, 34, 283].

\[ \text{Cu}^2+ + \cdot \text{O}_2^- \rightarrow \text{Cu}^+ + \text{O}_2 \quad (9) \]  

(Fenton-like Reaction)

\[ \text{Cu}^+ + \text{H}_2\text{O}_2 \rightarrow \text{Cu}^{2+} + \cdot \text{OH} + \cdot \text{OH}^- \quad (10) \]  

(Fenton Reaction)

\[ \cdot \text{O}_2^- + \text{H}_2\text{O}_2 \rightarrow \cdot \text{OH} + \cdot \text{OH}^- \quad (11) \]  

(Haber-Weiss Reaction)

Inside the microbial cells, Cu2+ is reduced to Cu+, triggering oxidative stress through Cu+ -driven ROS. However, the precise antimicrobial activity of CuO-NPs has not been clarified [296].

Fe3O4-NPs - antimicrobial activity. Nano Fe3O4 exhibits improved catalytic activity [298-305]. Fe3O4-NPs have been widely reported as suitable Fenton-like reagents due to their magnetic and redox properties. Costa et al. [306] showed that the Fe2+ ions in the Fe3O4-NPs structure are essential for an active heterogeneous Fenton-like system. Fe3O4-NPs could produce oxidative stress by a direct route through Fe2+ and Fe3+ ions release from NPs, by a surface catalytic reaction with H2O2, producing OH and ·OH as highly reactive species, and the ·O2−, Fe2+ and Fe3+ ions released from Fe3O4-NPs catalyze Fenton (classic Fenton reagent - mixture of H2O2 + Fe2+, Fenton-like reagent - mixture of H2O2 + Fe3+) and Haber-Weiss reactions with a significant role in ROS induction [70, 73, 307-309]. The steps involved in the Fenton and Haber-Weiss reactions are described below (Equations 12 -21).

\[ \text{Fe}(s) + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + 2\text{H}_2\text{O} \quad (12) \]

\[ \text{Fe}^{2+} + \cdot \text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot \text{O}_2 \quad (13) \]

\[ \text{Fe}^{3+} + \cdot \text{O}_2^- + 2\text{H}^+ \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O}_2 \quad (14) \]

\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot \text{OH}^- + \cdot \text{OH} \quad (15) \]  

(Fenton Reaction)

\[ \text{Fe}^{3+} + \cdot \text{OH} \rightarrow \text{FeOOH}^{2+} + \text{H}^+ \quad (16) \]  

(Fenton-like Reaction)

\[ \text{FeOOH}^{2+} \rightarrow \text{Fe}^{3+} \cdot \text{O}_2\text{H} \quad (17) \]

\[ \text{Fe}^{3+} \cdot \text{O}_2\text{H} \rightarrow \text{Fe}^{2+} + \cdot \text{O}_2 + \text{H}^+ \quad (18) \]

\[ \text{Fe}^{2+} + \cdot \text{OH} \rightarrow \text{Fe}^{3+} + \cdot \text{OH}^- \quad (19) \]

\[ \cdot \text{O}_2^- + \text{H}_2\text{O}_2 \rightarrow \cdot \text{OH} + \cdot \text{OH}^- \quad (20) \]

\[ \text{H}_2\text{O}_2 \rightarrow \cdot \text{OH} + \cdot \text{OH}^- \quad (21) \]  

(Haber-Weiss Reaction)

Microorganisms + ·OH → Microorganisms damage

The ·OH radical induction takes place in acidic conditions, the pH 3 value being the optimum condition for triggering the Fenton Reaction [310]. The redox couple Fe3+/Fe2+ due to its catalytic behavior propagates the Fenton process (Equations 12-14). Generally, the Fenton Reaction is initiated by ·OH radical formation (Eq. 15) [311-313]. Only a small amount of Fe2+ is necessary because it can be regenerated by reaction (16), called a Fenton-like Reaction. The Fenton-like Reaction produces FeOOH2+ and the protonated superoxide species converts to the deprotonated species (·O2H) (Eq. 17). Then ·OH is produced again by the reaction of H2O2 in the presence of Fe3+/Fe2+ via the Haber-Weiss Reaction (21). Although Fe2+ ions are essential in the Fenton process, it is well known that the reaction rate of Fe2+ ions regenerates from Fe3+. The presence of Fe3+ ions at the end of the reaction (13) produces new reactions involved in ROS production, reintroducing the Fe2+ (active species) to the chain of reactions, which leads to the increase in the ROS amounts. Fe2+ ions appear at the end of the reaction (18), and these ions might enter reactions (13) and (14), giving rise to an endless circle of reactions. The mechanism of the Fenton Reaction is still not fully understood, and the cytotoxicity of Fe3O4-NPs remains a matter of discussion [69, 70, 72, 73].

Although the innovative food packaging materials based on inorganic NPs possess antimicrobial properties among many other benefits (enhanced thermal properties; improved gas, moisture and volatile compounds barriers; enhanced UV-light barrier; reinforced polymer/biopolymer matrices, smart packaging) [2, 3, 17, 314], NPs may pose serious threats to human health due to their cytotoxic effects [315]. NPs are added to food packaging to intentionally interact with the food or its surroundings (antimicrobial active packaging), or they may penetrate into the food matrix through a migration process from the packaging material [314]. The release of NPs or their migration/ dispersion into the food matrix must be carefully considered since they can have potentially negative consequences in terms of food safety. The molecular volume of NPs is a decisive factor for their migration; NPs with a diameter greater than 5 nm are quasi-fixed in the nanocomposite material, and the diffusion rate is significantly small even for large amounts of NPs in the nanocomposite [34]. Also, the NPs which are entirely inserted in the packaging material, and that are fully covered do not migrate into the food. Nevertheless, in the case of package surface abrasion or cut edge areas, the food constituents easily enter the nanocomposite material, and NPs will be dissolved by the food constituents or even physically released, depending on the food storage conditions, and the chemical nature of the food [31]. Upon reaching into the foods, the migrated NPs from the nanopackages can be ingested, and may bioaccumulate to potentially unsafe levels into the human body, exhibiting either acute or chronic toxicity [316, 317]. The chronic nanotoxicity is the most significant, since NPs in small amounts are likely to be consumed.
over a long time [316]. Upon reaching the intestine, NPs may get access to vital organs through the blood flow and deteriorate the tissues and cells [317, 318]. NPs may deteriorate the cell membranes and enter into cells through diffusion, endocytosis and membrane receptor proteins. Their nanotoxicity is predominantly due to an increase in ROS, the resultant oxidative stress leading to cell death [318]. Furthermore, NPs could indirectly alter human health by disturbing the microbiota that normally lives within the gastrointestinal tract [318]. There is also the risk for potential environmental contamination by NPs due to their release from the polymer/biopolymer bulk following their degradation [319].

CONCLUSION

The innovative polymer/biopolymer nanocomposites have brought numerous advantages in the food packaging industry, owing to their properties, i.e. enhancement of the gas, moisture, and volatile compounds barrier; UV-light barrier; mechanical and thermal properties; as well as other benefits, like excellent ability to ensure the traceability and food safety in comparison to conventional composites. Thanks to their antimicrobial capability and incredible impact as biosensors, nanomaterials are a promising strategy in the management of the food spoiling factors. The antimicrobial packages extend the product shelf life and make foods safer by fighting off harmful microorganisms, while the smart nanosensors read the consumer a more reasonable read on the freshness indicators of foods. Moreover, the biopolymer nanocomposites can provide an encouraging alternative, exhibiting eco-friendly characteristics (renewable sources, lower carbon emissions, recyclability, excellent biodegradability), and the potential to create a long-term sustainable food packaging industry. This review has highlighted in detail the nanoparticles that can be used, in surprisingly small amounts, along with different polymers/biopolymers to produce innovative food packaging materials, and has also provided some examples of innovative nanostructures for food packaging. For instance, the innovative nanostructure based on carboxymethyl chitosan biopolymer and magnesium oxide nanoparticles has been proposed for packaging water-rich foods, while another nanostructure based on polyvinyl alcohol, glyxol and gold nanoparticles has been developed to improve the swelling resistance of the nanocomposite by destroying the passageway for water vapor. The review paper has also contributed an overview of antimicrobial packaging containing metal-oxide nanoparticles, with a focus on antimicrobial mechanisms, the generation of reactive oxygen species being the primary antimicrobial mechanism. The exact mechanisms through which this antimicrobial activity occurs are only hypothesized, as in the literature, there exist controversies regarding the mechanisms of nanoparticle-induced toxicity and therefore, this aspect needs to be researched further. Although the diffusion rate is significantly small even for large nanoparticles amounts in the nanocomposite, the release of nanoparticles or their migration into the food matrix must be carefully considered, since they can have potentially negative influences on human health. The nanoparticles can also be released from the polymer/biopolymer bulk following their degradation into the environment, as they have the potential to contaminate the environment. Although the nanofillers can generate active and smart food packaging systems; their release into the food matrix and environment must be a priority in designing nanostructures for food packaging.

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CONFLICT OF INTEREST

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Nanofillers for Food Packaging

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