

Potentials Nanocomposites in Food Packaging

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The interest in producing renewable polymers from natural resources is considerably increased as the need for the reduction of the amount of plastic waste in the environment becomes urgent. Biopolymers are considered as an alternative raw material for the development of biodegradable packaging to plastic produced from petroleum. Starch, a renewable biopolymer consisting of amylose and amylopectin, is the most commonly used agricultural raw material for edible film manufacturing because it has low cost, easy to handle and totally biodegradable. In order to maintain the quality of foods, it is necessary to select the correct materials and appropriate technologies for the production of the packaging. Current trends include the development of packaging that interacts with food, called active biofilms or active packaging. Nanocomposites with antimicrobial function are highly useful for the minimization of the growth of contaminant microorganisms during the processing or storage of food and thereby the extension of shelf-life and improvement of food safety. Thus, this work aims to review the literature to identify the main components used in packaging with nanoparticles and the results in food preservation. For this purpose, a bibliographic survey of the last 5 years was carried out in the databases of Scielo, Science direct, Google academic and Periodicals CAPES, with the following indexers: nanocomposites, nanotechnology, active packaging, and antimicrobial packaging. Some studies demonstrated that metal oxide nanocomposites in packaging provide enhances polymer barrier properties, making the material stronger, more flame resistant, with better thermal properties and having favorable surface wettability and hydrophobicity. Studies have shown that silver nanoparticles have antimicrobial activity against Gram-negative and Gram-positive bacteria and fungi. Also, chitosan nanostructures, a natural composite, have wide antimicrobial effects. Some studies have focused on antimicrobial effects of nanostructures combining chitosan and other antimicrobial agents as carvacrol, oregano and thyme essential oil. It was observed that chitosan nanocomposites combined with layered silicate were significantly more effective against *Staphylococcus aureus* and *Escherichia coli* than both pure. Packaging that increases the shelf-life of perishable food while reducing food waste is a sustainable opportunity for innovative technology.

1. Introduction

Food contamination can occur during harvesting, food processing and even in distribution (Malhotra et al., 2015). For this reason, new technologies have been studied in order to provide safer food products. Food packaging function has changed from a passive protective system to one that plays an active role in food to preserve quality and stability (Azeredo et al., 2018). Besides the interest in creating a package that protects food from contamination, recent researches are seeking for producing plastic material from natural resources as the need for the reduction of the amount of plastic waste in the environment (Shirai et al., 2016). Biopolymers are defined as polymers formed under natural conditions during the growth of cycles of all organisms. They are formed within cells by complex metabolic processes, thus, when degraded, biopolymers release organic compounds. Thus, biopolymers are considered as an alternative raw material for the development of biodegradable packaging to plastic produced from petroleum (Fakhouri et al., 2013).

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Starch is one of the biopolymers with the highest potential to produce biodegradable materials, especially disposable food packaging, where the time of use is relatively short. However, starch-based materials have demonstrated only limited commercial impact due to weakening mechanical properties as moisture content increases. Several studies have shown that addition of nanocomposites with antimicrobial function is highly useful for the minimization of the growth of contaminant microorganisms during the processing or storage of food and thereby the extension of shelf-life and improvement of food safety, besides to increase mechanical properties to starch package (Pagno, 2016; Marcet et al., 2018; Viacava et al., 2018).

Therefore, this review aims to analyze recent developments in food packaging systems with natural antimicrobial properties, and identify the main components used in packaging with nanoparticles and the results in food preservation.

2. Nanocomposites in food packaging

Due to the great need to create packaging materials from renewable sources and with superior properties (mechanical, thermal and barrier properties, for example), new materials, as nanocomposites, have been studied (Durán and Marcato, 2013). Nanocomposites are physical combinations between two chemically distinct phases, separated by an interface. One phase is the matrix, while the other is the dispersed nanomaterial phase in the matrix (Azeredo, 2013). Two approaches are frequently used to produce nanomaterials, "top-down" and "bottom-up". In the first approach, nanometric structures are obtained by size reduction of bulk materials, involving grinding, chemical and laser abrasion. In contrast, the second allows nanostructures to be built from individual atoms or molecules capable of self-assembling, which consists on chemical reactions of reducing the metal ion of salt through a reducing agent (Huang et al., 2015). In food packaging, nanocomposites can be used to enhance physical and mechanical properties and act against biological deterioration. Some of the main properties acquired and nanocomposites are presented in Figure 1. These attributes supplied by nanocomposites offer protection and preservation to food packaging. Also, reduce the food products loss due to their increase in shelf-life (Huang et al., 2018).

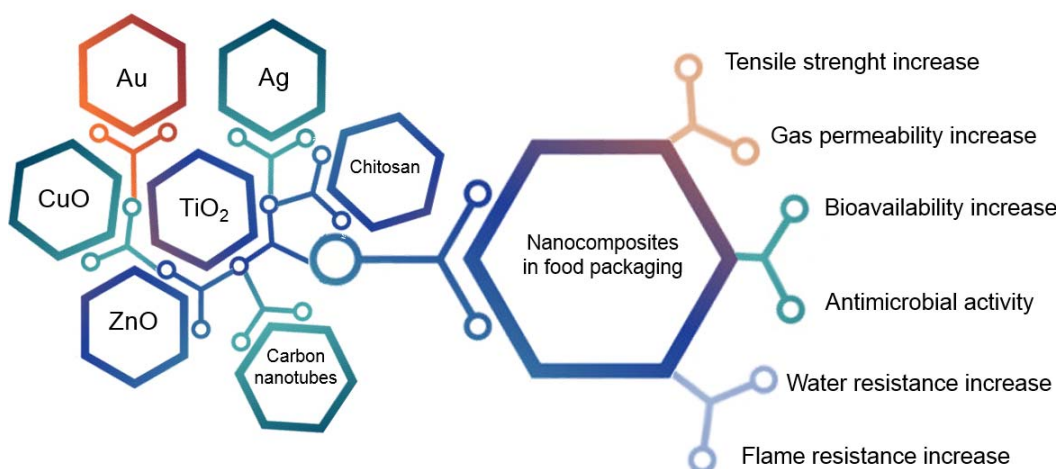


Figure 1: Nanocomposites in food packaging examples and main properties acquired

2.1 Silver

Huang et al. (2015) quotes that nanosized particle of silver (Ag) has emerged as a promising substance in a wide range of applications, including food packaging. Stable Ag nanoparticles can be *ex situ* synthesized via the regular borohydride reduction of Ag⁺ ions and then dispersed into a polymerizable formulation. In other words, nanoparticles can be *in situ* produced in a polymerizable medium from precursors with better dispersion ability. Ag has strong antimicrobial activity against many bacterial as *Enterococcus faecalis*, *Staphylococcus aureus* (*S. aureus*), *Vibrio cholerae*; besides fungi as *Candida albicans* and *Aspergillus niger* (Almeida, 2015). In addition to the antimicrobial activity, Ag nanoparticles can catalyze the absorption and

decomposition of ethylene emitted from fruit metabolism, which has been postulated as an ethylene blocker. Fruit and vegetable ripening and rotting caused by ethylene gas can, therefore, be retarded with the extension of product shelf life (Huang et al., 2015).

Mastromatteo et al. (2015) studied the synergetic effect of Ag with modified atmosphere packaging with 50% of CO₂ and 50% N₂ to extend shelf-life of Fiordilatte packaged with and without the traditional covering liquid. The results suggested that the synergistic effect of Ag nanoparticles in the coating could represent a valid preservation strategy to boost the diffusion of this dairy product beyond the local market, due to the strong antimicrobial effect against *Pseudomonas spp.*, *Enterobacteriaceae* and *Escherichia Coli (E. coli)*.

2.2 Gold

Gold nanoparticles have shown to be a potential agent in food packaging. The proposal for the synthesis of gold nanoparticles is based on the reduction of gold salts in the solution containing the ionic silsesquioxane as a stabilizer. This stabilizer is essential for the nanoparticle synthesis additionally it contains quaternary ammonium groups that promote water solubility and are known for their inhibitory and antimicrobial effect making this system very promising in the preparation of bioactive films (Pagno et al., 2015).

Pagno et al. (2015), prepared active biofilms of quinoa (*Chenopodium quinoa*) starch incorporating gold nanoparticles. The results show that the presence of gold nanoparticles produces an improvement in the mechanical, optical and morphological properties of biofilm. Besides the active biofilms exhibited strong antibacterial activity against food-borne pathogens with inhibition percentages of 99% against *E. coli* and 98% against *S. aureus*.

2.3 Metal oxide

Metal oxide nanoparticles are attractive for a large variety of applications. Their successful application depends on controlled synthesis, and solution-phase techniques allow a large degree of control over products. Metal oxide nanoparticles are often synthesized by the sol-gel method where the reaction is interrupted before gelation. The nanoparticle properties are determined by the nucleation, growth, and aging mechanisms. The most commonly used metal oxides in food packaging are metal oxide materials such as titanium dioxide (TiO₂), zinc oxide (ZnO), magnesium oxide (MgO) and Copper oxide (CuO) (Azeredo, 2013). Sarojini et al. (2019) have studied the application of ZnO in mahua oil-based polyurethane (PU) and chitosan and the findings indicated enhanced hydrophobicity, antibacterial (against *S. aureus* and *E. coli*) and barrier properties of the film.

2.4 Titanium dioxide

Nano-sized Titanium dioxide (TiO₂) particles are synthesized by various methods, in which sol-gel processing is the most common one. TiO₂ is a widely studied oxide nanoparticle for its UV blocking property as it is an efficient short-wavelength light absorber with high photostability.

Different from other nanoparticles, the antimicrobial activity of TiO₂ occurs via photocatalysts and, therefore, the antimicrobial activity is only available in the presence of UV light. TiO₂ nanoparticles are effective against foodborne pathogens, such as *Salmonella choleraesuis*, *Vibrio parahaemolyticus*, and *Listeria monocytogenes* under UV radiation (Almeida, 2015).

Xie and Hung (2018) studied the addition of TiO₂ in three biodegradable polymers (cellulose acetate - CA, polycaprolactone - PCL and polylactic acid - PLA) and analyze photocatalytic bactericidal property. Results show that TiO₂ embedded in PCL and PLA composite films did not show a significant bactericidal property against *E. coli*. On the other hand, TiO₂ embedded CA film had a remarkable potential to be used as antimicrobial food packaging. Metak (2015) studied the combination of TiO₂ with Ag for application in several types of fresh food and found an antibacterial activity against *S. aureus*, Coliforms, *E. coli* and *L. monocytogenes*.

2.5 Cooper Oxide

Copper oxide (CuO) characteristics increase with the reduction of size, then it is expected that finely dispersed bioactive Cu nanoparticles have an improved disinfectant effect. Because this short size provides greater mobility of released Cu ions, allowing them to interact closely with bacterial membranes (Conte et al. 2013). CuO oxidation by the reduction of borohydride indicates antimicrobial effect in ammonia-contained media (Huang, 2015).

Lomate et al. (2018) developed a packaging with CuO nanoparticles for extended shelf-life of Peda (Indian sweet dairy product). It was found that Cu nanoparticles uniformly dispersed into the low-density polyethylene (LDPE) matrix and provided improved mechanical properties. Nanocomposites film also shows a superior antimicrobial effect against Gram-positive and Gram-negative food deteriorating microorganisms.

Table 1: Nanocomposites applications in food packaging

Nanomaterial	Carrier	Food application	Findings	Source
Ag (1%) and TiO ₂ (1%)	Polyethylene	Apples, white slice of bread, carrots, soft cheese, milk powder and orange juice	Antibacterial activity against <i>S. aureus</i> , Coliforms, <i>E. coli</i> and <i>L. monocytogenes</i> .	(Metak, 2015)
Chitosan (0.2-1.0 mg/mL) and Thymol (0-0.3 mg/mL)	Polyethylene terephthalate (PET)	Blueberries and tomato cherries	Potential application as an antimicrobial and water vapour barrier.	(Medina et al., 2019)
Ag/TiO ₂ -SiO ₂	Paper-package	White Bread	Significantly increase in whiteness and water retention.	(Peter, 2016)
ZnO (5%)	Mahua oil-based polyurethane (PU) and chitosan	Carrot	Enhanced hydrophobicity, antibacterial and barrier properties of the film.	(Sarojini et al., 2019)
Cu (5 g/L)	Poly(lactic acid) (PLA)	Fiordilatte cheese	Proliferation of main spoilage microorganisms was delayed, preserving of sensory attributes.	(Conte et al., 2013)
Au (2.5 and 5% v/v)	Quinoa (<i>Chenopodium quinoa</i>) Starch	-	Produces an improvement in the mechanical, optical and morphological properties, besides exhibited strong antibacterial activity against food-borne pathogens.	(Pagno et al., 2015)
ZnO (1%) and essential oil of oregano and rosemary (1-2%)	Pullan films	Meat and poultry products	Antibacterial activity against <i>S. aureus</i> and <i>L. monocytogenes</i> .	(Morsy et al., 2014)
Carbon nanotubes (1-10 wt.%)	PHBV	-	Enhance tensile strength and increase thermal stability.	(Yu et al., 2014)
Chitosan (3mg/mL)	Gelatin nanofibers	Cheese	High antibacterial activity against <i>S. aureus</i> and <i>L. monocytogenes</i> .	(Lin et al., 2019)
ZnO (1-2% based on carrier)	Carrageenan	-	Increased mechanical and water vapor barrier properties. Strong antibacterial activity against Gram-negative microorganisms.	(Roy and Rhim, 2019)

2.6 Zinc Oxide

Zinc oxide (ZnO) nanoparticles can be produced by various techniques such as precipitation, sonochemical, thermal decomposition, and micro-emulsion method (Roy and Rhim, 2019). Once ZnO nanoparticles are formed, they tend to bind to each other to form agglomerated, which reduces their functional properties. It is therefore important to stabilize these nanoparticles using capping or stabilizing agents. As one stabilizing agent, melanin is an interesting multifunctional biologically active compound (Solano, 2017).

Nanoparticles of ZnO has presented antibacterial activity against *S. aureus* and *L. monocytogenes*, through the investigation of their inhibition and inactivation of cell development. (Morsy et al., 2014). Besides antibacterial activity, ZnO could enhance barrier properties and hydrophobicity of the film as Sarojini et al. (2019) demonstrated in carrots.

2.7 Carbon Nanotubes

Carbon nanotubes are cylinders with nanoscale diameters which may consist of one-atom thick single-wall nanotube, or several concentric tubes which is called multi-wall nanotube. They can not only be used in food packaging to enhance the mechanical properties of polymeric matrices, but also to exert powerful antimicrobial effects, because the long and thin carbon nanotubes puncture the microbial cells, causing irreversible damages (Huang, 2015). Yu et al. (2014) have carried poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PVHB) with carbon nanotubes and shown that the presence of carbon nanotubes can enhance tensile strength and increase the thermal stability of the polymer. With improved properties, packaging has great potential in food and beverage applications.

2.8 Chitosan nanostructures

Chitosan is a linear polysaccharide and copolymer that have been reported as an antibacterial agent against a wide variety of microorganisms. Chitosan nanoparticles are usually prepared by interaction of oppositely charged macromolecules. The formation mechanism is based on electrostatic interaction between amine groups of chitosan and the negatively charged groups of a polyanion, such as tripolyphosphate (TPP) (Zhao et al., 2011).

Chitosan nanostructures have been demonstrated to disperse well in biopolymers, having the potential to be used as antimicrobial agents in edible or biodegradable food packaging systems. Some studies have focused on antimicrobial effects of nanostructures combining chitosan and other antimicrobial agents (Peng et al., 2013; Medina et al., 2019), as in the research of Wang et al. (2012), where composite chitosan-ZnO were supported by polyvinyl acetate (PVA) and verified against *E. coli* and *Candida albicans* in different composite concentrations and showed to be a powerful antimicrobial agent (Wang et al., 2012).

2.9 Food packaging applications

Several nanocomposites applications have been already studied. Table 1 summarizes some of the implementations of engineered nanomaterials into food packaging systems and the most important findings on their performance in enhancing properties from packaging.

3. Conclusions

Nanotechnology is a trend in food packaging that can significantly extend food shelf-life, by improving performance properties, quality, safety and feasibility of packaging. The advantages of this new technology are indisputable, although there are still risks associated with the toxicity of nanomaterials that need to be fully understood. None the less, nanocomposites packaging materials appear to have many advantages and a very bright future for a wide range of applications in food industry.

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References

- Almeida A.C.S., Franco E.A.N., Peixoto F.M., Pessanha K.L.F., Melo N.R., 2015, Aplicação de nanotecnologia em embalagens de alimentos, *Polímeros*, 25, 89–97.
- Azeredo H.M.C., 2013, Antimicrobial nanostructures in food packaging, *Trends in Food Science and Technology*, 30, 56–69.
- Azeredo H.M.C., Otoni C.G., Assis O.B.G., Corrêa D.S., Moura M.R., Mattoso L.H., 2018, Nanoparticles and antimicrobial Food Packaging, Reference Module in Food Science.
- Conte A., Longano D., Costa C., Ditaranto N., Ancona A., Cioffi N., Scrocco C., Sabbatini L., Contò F., Nobile M. A. D., 2013, A novel preservation technique applied to fiordilatte cheese, *Innovative Food Science and Emerging Technologies*, 19, 158–165.
- Durán N., Marcato P.D., 2013, Nanobiotechnology perspectives. Role of nanotechnology in the food industry: a review, *International Journal of Food Science and Technology*, 48, 1127–1134.
- Huang J.-Y., Li X., Zhou W., 2015, Safety assessment of nanocomposite for food packaging application, *Trends in Food Science and Technology*, 45, 187–199.
- Huang Y., Mei L., Chen X., 2018, Recent Developments in Food Packaging Based on Nanomaterials, *Nanomaterials*, 8, 830–859.
- Lin L., Gu Y., Cui H., 2019, Moringa oil/chitosan nanoparticles embedded gelatin nanofibers for food packaging against *Listeria monocytogenes* and *Staphylococcus aureus* on cheese, *Food Packaging and Shelf Life*, 19, 86–93.
- Lomate G.B., Dandi B., Mishra S., 2018, Development of antimicrobial LDPE/Cu nanocomposite food packaging film for extended shelf life of peda, *Food Packaging and Shelf Life*, 16, 211–219.
- Malthotra B., Keshwani A., Kharkwal H., 2015, Antimicrobial food packaging: potential and pitfalls, *Frontiers in Microbiology*, 6, 1–9.
- Mastromatteo M., Conte A., Lucera A., Saccotelli M.A., Buonocore G.G., Zambrini A.V., Nobile M.A.D., 2015, Packaging solutions to prolong the shelf life of Fiordilatte cheese: Bio-based nanocomposite coating and modified atmosphere packaging, *LWT - Food Science and Technology*, 60, 230–237.

- Marcet I., Weng S., Sáez-Orviz S., Rendueles M., Díaz M., 2018, Production and characterisation of biodegradable PLA nanoparticles loaded with thymol to improve its antimicrobial effect, *Journal of Food Engineering*, 239, 26–32.
- Medina E., Caro N., Abugoch L., Gamboa A., Díaz-Dosque M., Tapia C., 2019, Chitosan thymol nanoparticles improve the antimicrobial effect and the water vapour barrier of chitosan-quinoa protein films, *Journal of Food Engineering*, 240, 191–198.
- Metak A.M., 2015, Effects of nanocomposites based nano-silver and nano-titanium dioxide on food packaging materials, *International Journal of Applied Science and Technology*, 5, 26–40.
- Morsy M.K., Khalaf H.H., Sharoba A.M., El-Tanahi H.H., Cutter C.N., 2014, Incorporation of essential oils and nanoparticles in pullulan films to control foodborne pathogens on meat and poultry products, *Journal of Food Science*, 79, 675–682.
- Pagno C.H., Costa T.M.H., Menezes E.W., Benvenuti E.V., Hertz P.F., Matte C.R., Tosati J.V., Monteiro A.R., Rios A.O., Flôres S.H., 2015, Development of active biofilms of quinoa (*Chenopodium quinoa* W.) starch containing gold nanoparticles and evaluation of antimicrobial activity, *Food Chemistry*, 173, 755–762.
- Peng Y., Wu Y., Li Y., 2013, Development of tea extracts and chitosan composite films for active packaging materials, *International Journal of Biological Macromolecules*, 59, 282–289.
- Peter A., Mihaly-Cozmuta L., Mihaly-Cozmuta A., Nicula C., Ziemkowska W., Basiak D., Danciu V., Vulpoi A., Baia L., Falup A., Craciun G., Ciric A., Begea M., Kiss C., Vatuiu D., 2016, Changes in the microbiological and chemical characteristics of white bread during storage in paper packages modified with Ag/TiO₂-SiO₂, Ag/N-TiO₂ or Au/TiO₂, *Food Chemistry*, 197, 790–798.
- Roy S., Rhim J.-W., 2019, Carrageenan-based antimicrobial bionanocomposite films incorporated with ZnO nanoparticles stabilized by melanin, *Food Hydrocolloids*, 90, 500–507.
- Sarojini K.S., Indumathi M.P., Rajarajeswari G.R., 2019, Mahua oil-based polyurethane/chitosan/nano ZnO composite films for biodegradable food packaging applications, *International Journal of Biological Macromolecules*, 124, 163–174.
- Viacava G.E., Ayala-Zavalab J.F., González-Aguilarb G.A., Ansorena M.R., 2018, Effect of free and microencapsulated thyme essential oil on quality attributes of minimally processed lettuce, *Postharvest Biology and Technology*, 145, 125–133.
- Wang Y., Zhang Q., Zhang C., Li P., 2012, Characterisation and cooperative antimicrobial properties of chitosan/nano-ZnO composite nanofibrous membranes, *Food Chemistry*, 132, 419–427.
- Xie J., Hung Y.-C., 2018, UV-A activated TiO₂ embedded biodegradable polymer film for antimicrobial food packaging application. *LWT – Food Science and Technology*, 96, 307–314.
- Yu H.-Y., Qin Z.-Y., Sun B., Yang X.-G., Yao J.-M., 2014, Reinforcement of transparent poly(3-hydroxybutyrate-co-3-hydroxyvalerate) by incorporation of functionalized carbon nanotubes as a novel bionanocomposite for food packaging, *Composites Science and Technology*, 94, 96–104.
- Zhao L.-M., Shi L.-E., Zhang Z.-L., Chen J.-M., Shi D.-D., Yang J., Tang Z.-X., 2011, Preparation and application of chitosan nanoparticles and nanofibers, *Brazilian Journal of Chemical Engineering*, 28, 353–362.