Emerging Nanomaterials Applications for Food Packaging and Preservation. Safety Issues and Risk Assessment [†]

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[†] Presented at the 1st International Electronic Conference on Food Science and Functional Foods, 10–25 November 2020; Available online: https://foods_2020.sciforum.net/.

Abstract: The contribution of nanomaterials to the development of food packaging systems has been enormous in last years. Nanomaterial, defined as material having one or more dimensions in the range 1–100 nm. Nano-sized materials change their optical, magnetic, electrical, and other properties and for this reason are widely used in food packaging. Nanoparticles (NPs), nanocomposites (NCs), nanoclays (NCs), nanoemulsions (NEs), nanosensors (NSs), and nanostructures (NSTs) are some of the important nanomaterials that have been used in food packaging and preservation. Nanomaterials can offer solutions in food packaging and preservation, through active and smart packaging, edible coatings and the development of a wide range of capable nanosystems. Therefore, nanomaterials can be considered as important tools and efficient options for controlling, limiting and improving safety parameters and food quality that are highly desirable in food technology. Innovative nanomaterials even achieve real-time food quality monitoring, providing an efficient option in food preservation applications. The toxicological risk posed by the use of nanomaterials in food packaging and particularly the case of edible nano-packaging, is significantly linked to the migration phenomenon as well as the occurrence of toxic effects on the exposed human body.

Keywords: nanomaterials; food preservation; food packaging; edible coatings; safety; risk

1. Introduction

Nanotechnology or "nanoscience" uses materials and structures, in the nanoscale range, usually 100 nm or less in at least one dimension, with a nanometer being 10^{-9} m [1,2]. Nanomaterial, defined as material having one or more dimensions in the range 1–100 nm [3]. Nano-sized materials are widely used in many scientific fields for the reason that they change their electrical, magnetic, optical and other properties. Many nanomaterials are naturally produced, and some are artificially synthesized [4]. In addition, particles on the nanometer scale cause surface changes and solubility [5]. According to the European Commission Recommendation: "Nanomaterial means a natural, random or manufactured material containing particles, in the unbound state or as an inert or agglomerate and where, for 50% or more of the particles in the number size distribution, one or more most external dimensions are in the size range 1–100 nm" [6]. Although these materials have the same chemical

composition as conventional ones, they have different physical and chemical properties due to their very small size [7]. In fact, these nanoscale materials have a high surface to volume ratio and surface activity [8].

The key role of food packaging is to preserve and protect food from unfavorable conditions, throughout the supply chain [9]. The materials used in food packaging are intended to reduce or delay the deterioration of food quality, preventing the transportation of gases such as oxygen from the external environment to foods, for a specific period of time until it is used by the consumer [10,11]. Research on food packaging materials aims to produce materials that will primarily protect the food but can also extend the self-life by keeping away pathogenic microorganisms [8]. The materials that are mainly used in food packaging today are paper, plastic, glass and metals. Conventional plastic like, polyethylene terephthalate (PET), poly (vinyl chloride) (PVC), polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyamide (PA) are the common plastic food packaging materials, that are derived from petroleum [12]. All these materials although they have strong mechanical and physical characteristics they are non-biodegradable materials with many waste management issues [13].

The purpose of this work is to provide recent advances in the development of efficient nano-preservatives, multifunctional devices and systems that could be used to maintain food quality as well as contribute to extending the shelf life through food packaging as well as risk and safety issues.

2. Classification of Nanomaterials and Molecular Basis of Application

2.1. Nanoparticles

Nanoparticles NPs can be separated into metalic NPs, polymeric NPs, magnetic NPs, lipid-based NPs, carbon-based NPs, semiconductor NPs and ceramic NPs, based on physical and chemical characteristics [15]. The hydrophobic or hydrophilic character of the nanoparticles is the determining factor for their applications. Metal oxide nanoparticles (MONPs) due to their high stability and durability, their low toxicity, have been extensively studied in science and technology. Among them, zinc oxide (ZnO), copper oxide (CuO) and silver (AgNPs), have been used for their antimicrobial properties and NPs such as Ag, Au, iron oxide (Fe_3O_4), ZnO, titanium dioxide (TiO_2), magnesium oxide (MgO), and CuO act antimicrobially by inhibiting biofilm formation. Metallic nanoparticles, like gold (AuNPs), AgNPs, and platinum (PtNPs), are easily synthesized, are stable and have been used for food preservation and food packaging applications [16,17]. Carbon based nanoparticles have attracted great attention because of their unique physicochemical properties and relatively higher biosecurity [18]. Nanoparticles have also been used to bind and remove mycotoxins in food [19].

2.2. Nanocomposites

A nanocomposite is a hybrid material, consists of many phases of different solid materials with at least one phase and one dimension in the nanoscale and it is usually enhanced by up to 5% by weight of nanoparticles. Nanocomposites are applicable to a variety of materials suitable for food packaging [3] with antimicrobial activity against various microorganisms such as Gram-positive and Gram negative bacteria, filamentous fungi and yeast [20–22], lower permeability to O_2 and CO_2 and antimicrobial activity in *Escherichia coli* [23,24].

2.3. Nanoemulsions

Nanoemulsions have been used to carry antimicrobial, antioxidant, anti-brown, aromatic and coloring agents in food products, causing positive effects on food quality and affecting consumer acceptance related to nutritional and health benefits [25]. Nanoemulsions combine with naturally occurring antimicrobial agents such as essential oils (EOs) and interact more with microbial cell membranes causing the death of microorganisms [26].

2.4. Nanoclays

The incorporation of nanoclays into biopolymers has enhanced their mechanical properties, and resistance to moisture and gases, allowing them to be used as alternative biodegradable and environmentally friendly food packaging nanocomposites [27]. Microstructure of polycaprolactone/clay nanocomposite film, was used for food preservation purposes with good mechanical properties [28].

2.5. Nanosensors

Nanosensors incorporated in food packaging materials can monitor any physical, chemical or biological changes during food processing. In addition, smart packaging with specialized nanosensors and nanotechnologies are capable of detecting toxins, pathogenic bacteria and chemicals [29,30]. Various biosensors have been designed to detect mycotoxins in foods. Aflatoxins produced by *Aspergillus flavus* and *Aspergillus parasiticus* contaminating food could be detected using a magnetic nano-gold immunosensor. In addition, in smart packaging, various nanobiosensors are used to the detection of pathogens, e.g., *Listeria monocytogenes*, *E. coli* and *Salmonella* spp. [29].

2.6. Nanostructures

Nanostructures are attractive carriers to delivery antimicrobial compounds that have been used to control spoilage and pathogenic microorganisms during food production and storage [31]. Nanoliposomes, nanospheres, nanocapsules, nanotubes and nanofibers are some common nanostructures.

3. Nanomaterials and Active and Intelligent Food Packaging Applications

3.1. Active Packaging

Novel nanomaterials or nanostructures (NSM) have been synthesized and their properties have been investigated [32]. Active packaging is a system of interaction of the packaging with the food and the inside of the packaging, so that the quality of the food can be maintained or even improved [33]. Comparing the active with the conventional packaging, the active packaging contributes significantly to the preservation of food through both the antioxidants and the antimicrobial compounds it releases into the packaging as well as through the capture of oxygen and water vapor which are degrading factors of quality [34]. Some recent studies of the use of nanomaterials in active food packaging applications are presented in Table 1.

Table 1. Recent studies of the use of nanomaterials in active food packaging applications.

Food Matrix	Category	Nanomaterials	Effect	Reference
Grapes	Active food packaging	Nanocomposites of chitosan/gelatin and silver nanoparticles	Extend the shelf life for two weeks	[35]
Fresh-cut apple	Active food packaging	Poly-lactic acid film incorporated with ZnO nanoparticle	Maintain the quality for two weeks	[36]
Peach	Biodegradable packaging films	Chitosan-rice starch/Nano-ZnO nanocomposites	Control the microbial growth and spoilage	[37]
Lamb meat	Active films	Cellulose nanofiber/whey protein/containing TiO_2 nanoparticles and rosemary essential oil	Reduced microbial growth, extend the shelf life for 6 to 15 days	[38]

Fruits and vegetables	Active food packaging	Silver nanoparticles	Absorption and decomposition of ethylene emitted	[39]
Chicken meat	Active food packaging	Polylactide films and bimetallic Ag-Cu nanoparticles and and essential oil	Maximum antibacterial action during 21 days at 4 °C	[40]
Salmon	Active films	chitosan/montmorillonite/α-tocopherol film	Inhibition of oxidation reactions	[41]
Bread	Active food packaging	Carboxymethyl cellulose-chitosan-ZnO NPs nanocomposite	Extend the shelf life by 15 days	[42]
Meat and poultry products	Active food packaging	Essential oils and nanoparticles in pullulan films	Control foodborne pathogens	[43]
Lamb meat	Active food packaging	Nano-composite films containing TiO_2 nanoparticles and rosemary essential oil	Extend the shelf life by 12–15 days	[44]

3.2. Intelligent ("Smart") Packaging

The smart food packaging checks the status of the packaging and informs the consumer of the quality and safety of the packaged product as well as of the integrity of the container and any breach. A smart packaging could provide accurate information on the remaining shelf life of the particular food, and nutritional information, associated with the air intake in a vacuum package, with the development of microorganisms, with the leaking gases from the packaging, or with the existence chemical compounds. In the detection of gases produced by spoilage, smart packaging can detect hydrogen, hydrogen sulphide, nitrogen oxides, sulfur dioxide and ammonia through nanosensors at surprisingly low levels [45,46].

4. Edible Coatings and Films in Food Packaging

In recent years, there has been a growing interest in the use of edible materials in food packaging [47]. An edible packaging should consist of materials that are edible as it can be consumed with the packaged foods. All ingredients used to form edible packaging should be classified as GRAS (generally recognized as safe) [48]. The use of edible coatings in the post-harvest management of fruits and vegetables is an emerging technology that significantly contributes to extend the preservation time. Especially in the post-harvest storage of fresh cut fruits, extending shelf life through edible coatings is achieved by reducing moisture, respiration, and gas exchange as well as with the reduction or even suppression of physiological disorders [49,50].

5. Regulations and Safety Issues-Risk Assessment

Regulatory systems are necessary to manage the potential risks posed by the use of nanotechnology in the food sector [51]. In the United States, Regulation 258/97 stipulates that if a nanomaterial is used as a primary ingredient, then it must be considered as "fresh food" [52]. When the term "food additive" is used in accordance with Regulation No. 1333/2008 of the European Commission, even if its composition has been approved as a raw material, it is not necessarily apply to the nano form and the nanosystem requires examination as a different additive; It must therefore be evaluated as a new, safe material before being placed on the market [53]. According to European Commission Regulation no. 2015/2283, EFSA must verify that for the involvement of mechanically engineered nanoparticles in food production, their safety assessment was performed using the latest generation of analytical techniques [54].

EFSA has recently published its Risk Assessment Guidelines for the Application of Nanosciences and Nanotechnologies in the Food Chain [55]. While providing an organized way to conduct nanomaterial safety assessment in food/feed, it also stresses that additional research is needed to assess the safety of nanomaterials, to characterize them and to measure their reactivity.

The toxicological risk involved in the use of nanomaterials in food packaging, is significantly linked to the phenomenon of migration as well as to the occurrence of toxic effects on the exposed human body [56]. Limited information on potential toxicity, behavior, bioavailability, biodistribution and bioaccumulation of NM has not yet allowed the adoption of international regulations [57]. Long-term exposure to nanoparticles can cause oxidative stress in human cells, kidney and liver damage, and DNA damage [58]. Inhalation and penetration through the dermal tissue into individuals working in nanotechnology plants is considered to be extremely common [59]. The way nanoparticles migrate into the food system is characterized by a diffusion process similar to that described by Fick's second law. Therefore, the development of innovative packaging materials containing nanomaterials should be complemented by corresponding migration surveys, which will identify both global and specific migration data [60].

6. Conclusions

Nanotechnology is recognized as one of the key technologies affecting all industries, including the food industry. The mechanism of action of most nanomaterials used in food preservation is not fully understood. Innovative NMs achieve preserving quality and minimizing food spoilage providing an efficient option in applications in food preservation. The use of these materials in food preservation is an emerging trend that creates significant inconvenience, as some of them, through ingestion, inhalation and exposure end up in the human body.

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