Nanotechnology in Food Packaging Applications: Barrier Materials, Antimicrobial Agents, Sensors, and Safety Assessment

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Abstract

Nanotechnology is one of the most promising scientific fields of research in decades; it has the potential to revolutionize the global food system. Demand for safe food products represents crucial challenges for the food-packaging industry with the idea to design and produce novel packaging solutions able to maintain the safety and quality of products. In this chapter, some of the most relevant applications and challenges of nanotechnology in the field of food packaging are discussed, including nanocomposites that enhance the barrier properties of the packaging film, nanoparticles as potent antimicrobial agents, nanosystems for controlled delivery, and nanosensors and nanomaterial-based assays for the detection of food relevant analytes (gasses, small organic molecules, and food-borne pathogens). Risk assessment and safety concerns with respect to food research have also been highlighted. Being nanotechnology still a relatively new technology, there are safety concerns, which are attracting attention to international regulations to make safer the acceptance of this tool by the industry and consumers.

Introduction

Nanotechnology has developed into a multidisciplinary field of applied science and technology. Nanotechnology is the ability to work on a scale of about 1–100 nm in order to understand, create, characterize, and use material structures, devices, and systems with new properties derived from their nanostructures. Because of their size, nanoparticles have proportionally larger surface area and consequently more surface atoms than their microscale counterpart. In the nanoscale range, materials may present different electronic properties, which in turn affects its optical, catalytic, and other reactive properties [1].

Two building strategies are currently used in nanotechnology: a “top-down” approach and the “bottom-up” approach. The commercial scale production of nanomaterials currently involves basically the “top-down” approach, in which nanometric structures are obtained by size reduction of bulk materials, by using milling, nanolithography, or precision engineering. Size usually relates to functionality of food materials, smaller sizes meaning a bigger surface area, desirable for several purposes. The newer “bottom-up” approach, on the other hand, allows nanostructures to be built from individual atoms or molecules capable of self-assembling [2]. Self-assembly relies on balancing attraction and repulsion forces between a pair of molecules building blocks to form more functional supramolecular structures. Nowadays, most materials used for food packaging are practically undegradable, representing a serious global environmental problem. New bio-based materials have been exploited to develop edible and biodegradable films as a big effort to extend shelf life and improve quality of food while reducing packaging waste [3]. However, the use of edible and biodegradable polymers has been limited because of problems related to performance (such as brittleness, poor gas, and moisture barrier), processing (such as low heat distortion temperature), and cost.

Several composites have been developed by adding reinforcing compounds to polymers to enhance their thermal, mechanical, and barrier properties. Most of these reinforced materials present poor interactions at the interface of both components. Macroscopic reinforcing components usually contain defects, which become less important as the particles of the reinforcing component are smaller [4]. Polymer composites are mixtures of polymers with inorganic or organic fillers with certain geometries (fibers, flakes, spheres, particulates). The use of fillers which have at least one dimension in the nanometric range (nanoparticles) produces polymer nanocomposites (PNCs) [5]. Three types of fillers can be distinguished, depending on how many dimensions are in the nanometric range. Isodimensional nanoparticles, such as spherical silica nanoparticles or semiconductor nanoclusters, have three nanometric dimensions. Nanotubes or whiskers are elongated structures in which two dimensions are in the nanometer scale and the third is larger. When only one dimension is in the nanometer range, the composites are known as polymer-layered crystal nanocomposites, almost exclusively obtained by the intercalation of the polymer (or a monomer subsequently polymerized) inside the galleries of layered host crystals [5].

A uniform dispersion of nanoparticles leads to a very large matrix/filler interfacial area, which changes the molecular mobility, the relaxation behavior, and the consequent thermal and mechanical properties of the material. Fillers with a high ratio of the largest to the smallest dimension (i.e., aspect ratio) are particularly interesting because of their high specific surface area, providing better reinforcing effects [6]. In addition to the effects of the nanoreinforcements themselves, an interphase region of altered mobility surrounding each nanoparticle is induced by well-dispersed nanoparticles, resulting in a percolating interphase network in the composite and playing an important role in improving the nanocomposite properties [7].

Besides reinforcing nanoparticles, whose main role is to improve mechanical and barrier properties of the packaging materials, there are several types of nanostructures responsible for other functions, sometimes providing “active” or “smart” properties to the packaging system such as antimicrobial activity, enzyme immobilization, biosensing. Functional nanomaterials can prolong shelf life, decrease the demand of preservative materials, and provide hygienic surfaces that are easy to clean and can inhibit microbe accumulation or formation. Antimicrobial packaging is the most common use of nanomaterials. As a simple passive barrier, antimicrobial packaging can reduce the growth of harmful microbes. Incorporation of nanomaterials into capsulation packaging materials will yield lightweight, durable, and low gas-permeable nanocomposites contributing to food quality by extending shelf life, preserving flavor and aroma, and reducing contact with microorganisms. Encapsulating foods in packaging materials is necessary for transporting, protecting, labeling, and advertising. In recent years nanotechnology has found innumerable applications in food industry [8, 9]. Food encapsulation requires protection, tampering resistance, and special physical, chemical, or biological needs. The encapsulation packaging is significant in preserving the foods to make them safe and marketable. Innovations in food encapsulation packaging can lead to quality packaging and show consumers a friendly approach in determining the shelf life, biodegradable period, and other information. Nanotechnology has been employed for preparation of stronger and lighter materials, improving biodegradability or recyclability, incorporating sensors or indicators for consumer information, or for traceability or authentication (product security to avoid fraud) [10].

Nanotechnology may also present new risks as a result of their novel properties, using a wide variety of nanomaterials (NM), and many of these may well prove to be harmless; however, others may present a risk to human health. Many countries recognize the need of food safety assurance of nanomaterials, existing limited data and information of their possible human health effects [11]. For this reason, many nanotechnology initiatives, commissions, or centers have been launched by governments, academia, private sectors around the world to ensure rapid development of nanotechnology, promoting economic growth, maintaining global competitiveness, and improving the innovative capability [12].

Overall though, these new technologies, if managed and regulated correctly, can play an important role in the improvement of the global food system to the benefit of human health and wellbeing [13]. This chapter will provide an up-to-date, comprehensive evaluation of the existing and upcoming applications of nanotechnology in the food packaging sector.

Nanoresearch in Food Packaging

Nanostructured materials exhibit unique physicochemical properties that open windows of opportunities for the creation of new and high performance materials, which will have a critical impact on food packaging and storage.

The most studied nanoparticles will be presented according to their primary functions/applications in food packaging systems. Some particles can have multiple applications, and sometimes the applications can overlap, such as some immobilized enzymes which can act as antimicrobial components, oxygen scavengers, and/or biosensors. Though, trends in food packaging fall into the following main applications (Fig. 1): (1) “Nanoreinforcement”: the presence of nanoparticles in the polymer matrix could considerably enhance the packaging properties (flexibility, gas barrier properties, temperature/moisture stability) and thus improve the shelf life of packaged foods; (2) “Active food nanosystem packaging”: the presence of nanoparticles allows packages to interact with food and the environment and play a dynamic role in food preservation; (3) “Smart food nanosystem packaging”: involves the presence of nanodevices in the polymer matrix designed for sensing biochemical or microbial changes in the food and/or monitoring the environment surrounding the food. They can also act as a guard against fraudulent imitation.

Nanoreinforcement

The possibility to improve the performances of polymers for food packaging by adding nanoparticles has led to the development of a variety of polymer

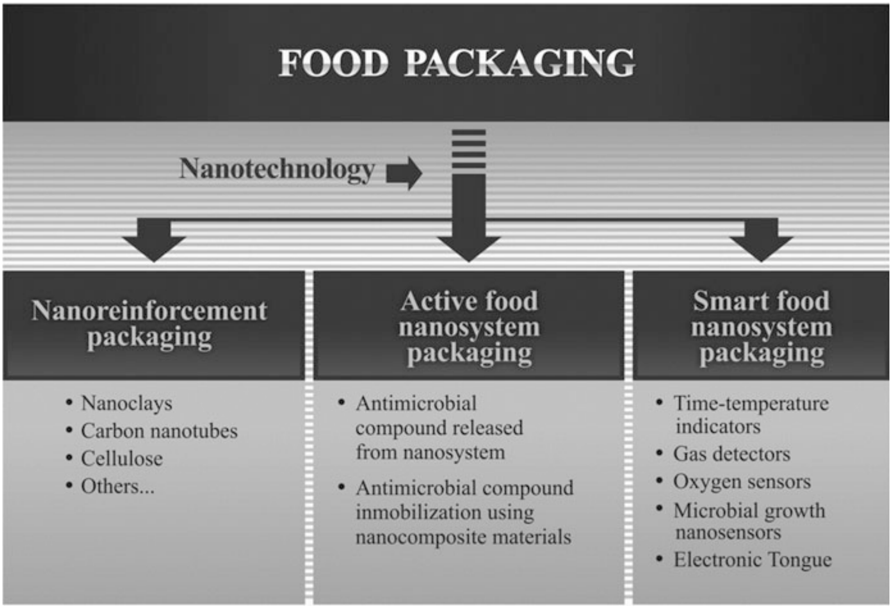

Fig. 1 Trends in food packaging with the help of nanotechnology

nanomaterials [8]. Nanoreinforcement techniques are used to increase viability and tensile strength by filling the gaps of packaging materials. This has led to the development of a variety of nanoparticle-reinforced polymers, also termed as “nanocomposites,” which typically contain up to 5% w/w nanoparticles. The enhanced barrier properties of most polymer-based nanocomposites take advantage of the improved tortuosity of the diffusion or permeation path for gases. These wall-like nanocomposites force gases to travel longer paths to diffuse through the coatings. The presence of nanoparticles with high aspect ratios in the packaging dramatically decreases the transfer rate of gases such as oxygen, carbon dioxide, and water vapor crossing the packages [14]. The nanoparticles inside polymeric nanocomposites could also bring lots of active zones with better reinforcing effects. Furthermore, variety or change in the size and number of nanoparticles per unit volume of polymers will result a significant impact on the properties of the polymers [15].

Although several nanoparticles have been recognized as possible additives to enhance polymer performance, the packaging industry has focused its attention mainly on layered inorganic solids like clays and silicates, due to their availability, low cost, significant enhancements, and relative simple processability.

Polymers incorporating clay nanoparticles are among the first polymer nanomaterials to emerge on the market as improved materials for food packaging. Several different polymers and clay fillers can be used for obtaining clay-polymer nanomaterials. The nanoclay generally used is the montmorillonite (MMT), which is relatively cheap and widely available natural clay derived volcanic ash/rocks. When well dispersed in the matrix the clay limits the permeation of gases and provides substantial improvements mainly in the gas barrier properties of nanocomposites. The homogeneous dispersion of most clays in organic polymers is not easy due to the hydrophilicity of its surface [16]. Organoclays, products from interactions between clay minerals and organic compounds, have found an important application in polymer nanocomposites. Organoclays are cheaper than most other nanomaterials, since they come from readily available natural sources and are produced in existing, full-scale production facilities. Organomontmorillonite (oMMT) have been produced, for example, by exchanging inorganic cations of MMT with organic ammonium ions, improving compatibility of MMT with organic polymers, leading to a more regular organization of the layers in the structures, and decreasing the water uptake by the nanocomposite [17].

These improvements have led to the development of nanoclay–polymer nanomaterials for potential use in a variety of food packaging applications, such as processed meats, cheese, confectionery, cereals, boil-in-the-bag foods, as well as in extrusion-coating applications for fruit juices and dairy products, or co-extrusion processes for the manufacture of bottles for beer and carbonated drinks. Many studies have reported the effectiveness of nanoclays in decreasing oxygen and water vapor permeabilities of several polymers [18].

Silica nanoparticles ($nSiO_2$) have been reported to improve mechanical and/or barrier properties of several polymer matrices. Wu et al. [19] observed that the addition of $nSiO_2$ into a polypropylene (PP) matrix improved tensile properties of the material – not only strength and modulus, but also elongation [20]. Improvements in tensile properties, again including elongation, as resulting from $nSiO_2$ addition were also reported for a starch matrix and for a starch/polyvinyl alcohol matrix [21].

It was found that SiO_2 can form a twisting path for gases when used as nanofillers in food packaging. The SiO_2 nanofillers can also improve the tensile property of nanocomposite films.

Carbon nanotubes (CNTs) may consist of a one-atom-thick single-wall nanotube (SWNT), or a number of concentric tubes called multiwalled nanotubes (MWNT), having extraordinarily high aspect ratios and elastic modulus. Kim et al. [22] modified CNTs by introducing carboxylic acid groups on their surfaces in order to enhance their intermolecular interactions with the poly(ethylene-2,6-naphtalene) (PEN) matrix. CNTs, even in concentrations as low as 0.1 wt.%, greatly improved thermal stability as well as tensile strength and modulus of PEN. Other polymers have been found to have their tensile strength/modulus improved by addition of CNTs, such as PVOH [23], polypropylene [24], and polyamide [25].

Cellulose, the building material of long fibrous cells, is a highly strong natural polymer. Cellulose nanofibers are inherently a low cost and widely available material. Moreover, they are environmentally friendly and easy of recycling by combustion and require low energy consumption in manufacturing. All of this makes cellulose nanofibers an attractive class of nanomaterials for elaboration of low cost, lightweight, and high-strength nanocomposites [26]. Cellulose nanoreinforcements have been reported to have a great effect in improving modulus of polymer matrices [27, 28].

Currently, clay at the nanoscale is the most common commercial application of nanoparticles and accounts for nearly 70% of the market volume. The industrial applications of nanoclay in multilayer film packaging include beer bottles, carbonated drinks, and thermoformed containers. Nanoclays embedded in plastic bottles and nylon food films stiffen packaging and reduce gas permeability keeping oxygen-sensitive foods fresher and extend shelf life. Bayer polymers have created a low cost nanoclay composite interior coating for paperboard cartons to keep juice fresher. PET beer bottles using nanoclays produced by NanocorR are distributed by ColorMatrix. The storage time of beer in normal PET bottles is about 11 weeks and it increases to about 30 weeks, when a nanoclay barrier is used.

Nanocomposite films enriched with silicate nanoparticles or nanocrystals exhibiting increased barrier properties can be used for plastic beer bottles (e.g., Nanocor®) [86] which have been reported in the USA, but so far not in the EU. Also cellulose nanoreinforcements have been found to be an alternative for the preparation of low cost, lightweight, and high-strength nanocomposites [26].

Active Food Nanosystem Packaging

Active packaging is designed to deliberately incorporate components that would release or absorb substances into or from the packaged food or the environment surrounding the food. Unlike conventional food packaging, an active food packaging may not only act as a passive barrier but also interact with the food in some desirable way like by releasing desirable compounds such as antimicrobial or antioxidant agents, or by removing some detrimental factor (such as oxygen or water vapor). The consequences of such interactions are usually related to improvements in shelf life or sensory characteristics of food. Antimicrobial nanosystems can be divided in two groups according to their mechanism of action: where the antimicrobial is released from nanocapsules to the headspace of the package in order to interact with the product surface (Fig. 2a); and where the antimicrobial compound is immobilized in the surface of the package using nanocomposite materials (Fig. 2b) [29].

Nanosystems to Release Antimicrobial Compounds

These systems are used to design active packaging in the form of sachets or active plastic films containing the nanocapsules that are enclosed in the interior of the package. They can be divided into two groups: indirect and direct antimicrobial activity. Nanosystems with indirect antimicrobial activity include oxygen and moisture scavengers, ethylene removers, and carbon dioxide absorbers/emitters. They are considered indirect antimicrobial agents because, even though their primary activity is to decrease spoilage due to enzymatic deteriorative reactions and alter the internal atmosphere (decrease of oxygen and moisture), they inhibit the growth of aerobic bacteria. Several nanoparticles, including TiO_2 nanoparticles, were used to produce oxygen scavenger films [30]. Some nanoparticles based on silver that have antimicrobial activity are also able to absorb and decompose ethylene [31]. Removing ethylene from a package environment helps extend the shelf life of fresh produce like fruits and vegetables.

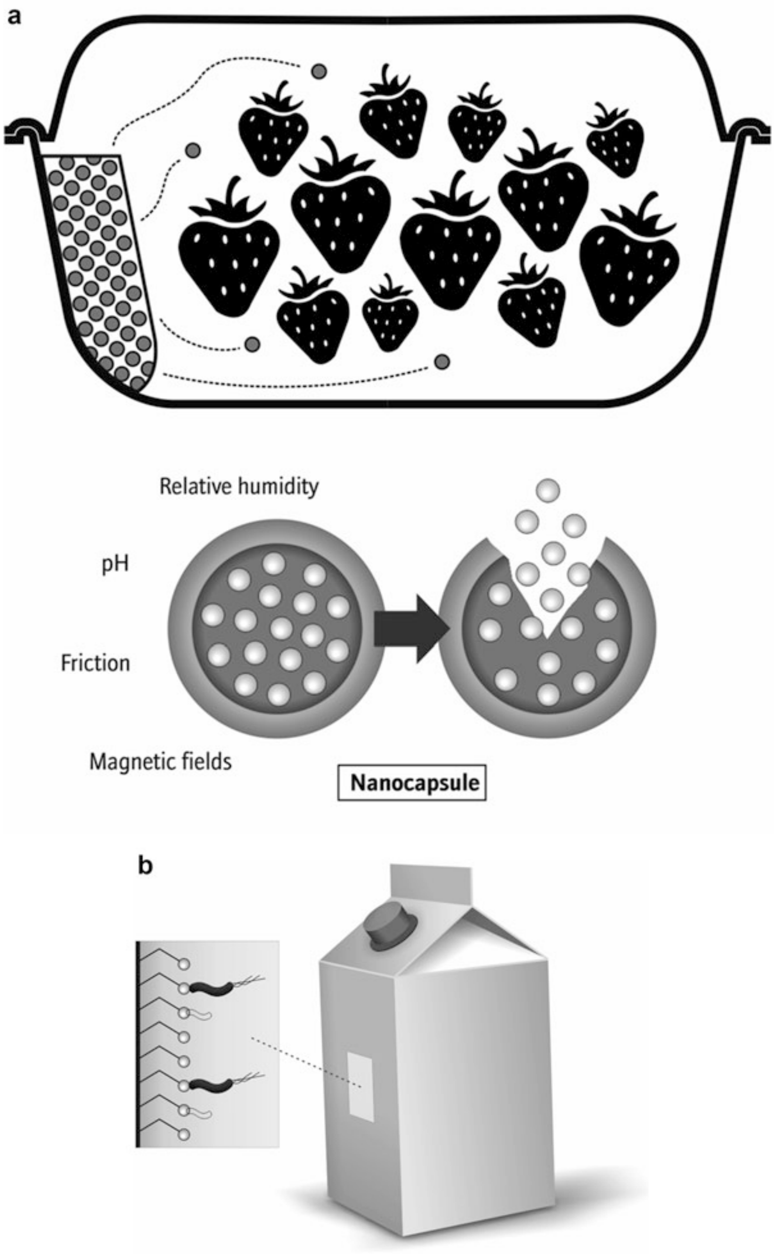

Fig. 2 (**a**) Controlled release nanosystems of antimicrobial compounds triggered using different stimuli and incorporated into the food package. (**b**) In-package immobilized antimicrobial agents using nanocomposite materials; direct contact between pathogens and nanosystem is required for action

Headspace artifacts with direct antimicrobial activity include antimicrobial volatile compounds such as metals and essential oils [32]. A cyclodextrin-essential oil nanocapsule that was used as a headspace nanosystem to increase the shelf-life of fresh-cut produce was described by Ayala-Zavala et al. [33]. In this study, it was hypothesized that internal moisture can be the driving force that releases the antimicrobial compound from the molecular complex among the cyclodextrin and the volatile essential oil constituents.

Another type of antimicrobial active packaging artifact is that in which the antimicrobial compound is embedded in the bulk polymer within nanocavities and has to migrate to the surface in order to interact with the microorganism. Different natural and synthetic polymers have been used as carriers; several reviews on this subject have been recently published [34]. Mono and multilayer antimicrobial packages using this technology have been developed [8]. Typical multilayer films consist of four layers: outer layer, barrier layer, matrix layer (in which the antimicrobial is embedded), and control layer. Several organic and inorganic compounds have been used as antimicrobials, including silver zeolites, organic acids and their derivatives, peptides, enzymes, EOs, parabens, bacterocins, and volatile compounds, among others [8, 35]. One of the main disadvantages of this kind of package is that heat-sensitive compounds cannot be used because they are inactivated during the processing of the package. An interesting option is the use of nanoencapsulation of active compounds in the case of heat-sensitive additives before incorporation into the polymer extrusion process. Controlled release of the active compound into the headspace of the package is regulated by several factors that include heat, pH, relatively humidity (RH), enzymatic activity, and physical modifications of the host, guest, or package, among others [36]. The effect of these factors is due to chemical interactions between both host and guest such as hydrogen bonding, Van der Walls interactions, and other noncovalent interactions which depend mainly on the polarity, molecular weight, polydispersity, and cross-linking of the host molecule [8] as well as its ability to undergo a reversible phase transition [37]. Among these factors, relative humidity seems to be the most important in the release of antimicrobial compounds [26, 38].

Controlled release of antimicrobial compounds (volatiles) into the headspace can be analyzed considering a zero-order or first-order kinetic model. There are two mathematical models used to describe these kinetic processes. The first is the Power Law (Eq. 1) and the second is Avrami's equation (Eq. 2), defined:

$$X = kt^{n\mathrm{P}} \tag{1}$$

$$X = 1 - e-^{ktn\mathrm{A}} \tag{2}$$

where X is the release fraction of nanoencapsulated antimicrobial compound at time t; k is the release rate constant; n_{P} is the diffusive release parameter; and n_{A} is the Avrami parameter or release mechanism. In both models, when $n \sim 0.5$ the active agent is released by a Fickian diffusion mechanism. However, when $n \sim 1$, it describes a zero-order release model using the Power Law model (release independent of concentration) or first-order release model when analyzed by the Avrami's model. Recently, Ho et al. [36] reported that at low RH both models were able to describe the release of ethylene from beta-cyclodextrin; however, at high RH (93%), Avrami's model better described the system. These authors reported a 20-fold release of ethylene at this RH compared to 53% humidity. Similar results were observed for essential oils [39] and isothiocyanate encapsulated in cyclodextrins [40].

When the antimicrobial compound is released from the encapsulating material to the food by direct contact, the release mechanism is explained by considering a migration process which follows a Fick's Law diffusion process. The release of an active ingredient from the packing material is regulated by three different mechanisms: (1) diffusion of the active ingredient through the polymeric material of the packaging; (2) erosion of the polymeric material causing the dispersion of the active ingredient into the food; and (3) swelling or hydration of the polymeric material [9, 38].

The most commonly used equation for the analysis of the controlled release through a diffusion process is the Higuchi equation (Eq. 3) which describes a square root of time-release kinetics [9]:

$$X = \sqrt{DC_m(2C_i - C_s)t} \tag{3}$$

where D is the diffusion coefficient of the active ingredient; C_m is the solubility of the active ingredient in the encapsulant matrix; C_i is the initial active ingredient concentration; and C_s is solubility of the active ingredient in the exterior. The limiting condition necessary to use this equation is that a pseudo-steady-state is achieved, which is only obtained when the initial concentration is much higher than the exterior concentration. For hydrophilic active ingredients where swelling and erosion plays an important role, the Power Law model (Eq. 1) is used to describe the release of antimicrobial compounds into the food matrixes [9, 38].

Immobilization of Antimicrobial Compounds Using Nanocomposite Materials

There are few examples of antimicrobial packages in which the antimicrobial compound has been immobilized with nanoassemblies into the polymer by ionic or covalent bonds. In order to attach the antimicrobial, the presence of functional groups in both the polymer and antimicrobial is necessary [41]. The presence of a flexible linking group is also desirable, in order to give more flexibility to the antimicrobial and consequently increase its antimicrobial effect [8, 42].

Metal nanoparticles, metal oxide nanomaterials, and carbon nanotubes are the most used nanoparticles to develop antimicrobial active food packaging. These particles function on direct contact, but they can also migrate slowly and react preferentially with the food matrix. Silver, gold, and zinc nanoparticles are the most studied metal nanoparticles with antimicrobial function, with silver nanoparticles already found in several commercial applications (Table 1). Silver that has high temperature stability and low volatility at the nanoscale is known to be an

Table 1 Representative examples of nanocomposite application in food packaging (Copyright © 2015 Elsevier Ltd. [44])

Source	Nanomaterial incorporated	Carrier	Food items	Observation/Conclusion on developed nanocomposite
[45]	Ag	Polyvinylpyrrolidone	Asparagus	Hindered growth of aerobic psychrotrophics, yeasts and molds, less weight loss, greener color, tenderer texture
[46]	Ag, ZnO	Low-density polyethylene (LDPE)	Orange juice	Significantly decreased yeast and mold counts without impairing juice relevant quality attribute
[47]	Ag, ZnO	LDPE	Orange juice	Significant reduction in lactobacillus plantarum growth rate
[48]	Ag	Absorbent pad	Poultry meat	Confirmed antimicrobial effect against Escherichia coli and Staphylococcus aureus
[49]	Ag	Cellulose pad	Fresh-cut melon	Lower microbial loads remained, longer microbial growth lag time
[50]	Ag	Cellulose pad	Beef meat exudates	Reduce microbial levels
[51]	ZnO	Allyl isothiocyanate, nisin	Liquid egg albumen	Effective inactivation in salmonella
[52]	Ag, TiO_2, kaolin	PE	Chinese jujube	Firmer, heavier, less decay, less browning, slower ripening, decrease in senescence and climacteric evolution
[53]	ZnO	Polyvinyl chloride (PVC)	Fuji apple cuts	Better preservation of quality, lower counts of Escherichia Coli cells
[54]	Cu	Cellulose absorber	Melon and pineapple juices	Excellent antifungal activity, reducing spoilage-related yeasts and molds
[55]	Ag	Absorber	Kiwi and melon juices	Reduced counts of total viable microorganisms, yeasts and molds
[56]	Ag	PE	Apple juice	High bactericide capacity against Alicyclobacillus acidoterrestris
[57]	Ag, TiO_2, kaolin	LDPE		Strawberry decelerated decay rate
[58]	Ag_2O	LDPE	Apple slice	Decreased microbial spoilage, delayed browning and weight loss

effective antifungal and antimicrobial and is known for its toxicity towards an array of microorganisms [43]. The antimicrobial activity of silver nanocomposite has been associated with several actions, including adhesion and rupture of cell surface; degradation of lipopolysaccharides; increase in permeability; and binding of silver to electron donor groups in biological molecules containing sulfur, oxygen, or nitrogen. Silver nanocomposites have been obtained by several researchers and their antimicrobial effectiveness has been reported [59, 60].

Silver nanoparticles are also used in conjunction with zeolites minerals and gold nanoparticles. The use of the combination silver/zeolite and silver/gold produces a greater antibacterial effect than silver alone, although no commercial application has been found at the moment. It is also important to highlight that titanium dioxide (TiO_2), zinc oxide (ZnO), silicon oxide (SiO_2), and magnesium oxide (MgO) are among the most studied oxide nanoparticles for their ability to be UV blockers and photo-catalytic disinfecting agents [61].

Nanoscale chitosan has been reported to demonstrate antimicrobial activity due to the electrostatic interactions between positively charged chitosan molecules and negatively charged cell membrane molecules, increasing membrane permeability. However, due to its possible cytotoxicity, incorporation of chitosan in food packaging materials is still not recommended [62].

Carbon nanotubes have also been reported to have antibacterial properties; direct contact with aggregates of these structures has been demonstrated to affect the survival of *Escherichia coli*, possibly because the long and thin nanotubes puncture microbial cells, causing irreversible damages and leakage of intracellular material. On the other hand, there are studies suggesting that carbon nanotubes may also be cytotoxic to human cells, at least when in contact to skin [63]. Once present in the food packaging material, the nanotubes might eventually migrate into food. Thus, it is mandatory to know any eventual health effects of ingested carbon nanotubes.

The main inconvenience of this kind of active packaging is that, in order to inhibit the microorganism growth, direct contact between the fresh produce and the polymer is necessary. Moreover, in active packaging, nanomaterials may migrate into food once present in the food packaging materials. Because of poor packaging performance and subsequent migration of nanomaterials from the packaging, ingestion of foods previously in contact with nano-packaging can be an exposure route.

Smart Food Nanosystem Packaging

Technology in terms of smart packaging has been explored for the possibility of preserving food for as long as possible. Smart food packaging are mainly intended to monitor the condition of packaged food or the environment surrounding the food [64]. Nanotechnology has benefited the area of food safety mostly through the development of highly sensitive and low-cost nanosensors. The nanosensors may be able to respond to environmental changes during storage (e.g., temperature, relative humidity, and oxygen exposure), degradation products or microbial contamination. Nanosensors integrated into food packaging systems may detect spoilage-related changes, pathogens, and chemical contaminants, thus eliminating the need for inaccurate expiration dates, and thereby providing real-time status of food freshness [65]. This is not only useful for quality control to ensure that consumers are able to purchase products which are at their peak of freshness and flavor, but also has the potential to improve food safety and reduce the frequency of foodborne illnesses. Recent progress shows that the current smart packaging segment is dominated by oxygen scavengers, moisture absorbers, and barrier packaging products, accounting for about 80% of the market [10]. Nanosensors can assist in the case of temperature increases or in the presence of micropores or sealing defects in packaging systems that can expose food products to a unexpected levels of oxygen, which will result in undesirable changes. In fact due to the short quality guarantee period, bakery and meat products have used the most nano-enabled smart packaging technology to date. Some of the most commonly used nanosensors in the food sector are described in the following sections.

Time-Temperature Indicators (TTIs)

Time-temperature indicators (TTIs) are designed to monitor, record, and translate the safety of food. This is particularly important when food is stored in conditions other than the optimal ones. They fall into two categories: one relies on the migration of a dye through a porous material, which is temperature and time dependent, and the second uses a chemical reaction (initiated when the label is applied to the packaging) which results in a color change. These indicators allow consumers to feel confident about what they are purchasing and manufacturers to trace their foods along the supply line. Timestrip® has developed a system (iStrip) for chilled foods, based on gold nanoparticles, which is red at temperatures above freezing. Accidental freezing leads to irreversible agglomeration of the gold nanoparticles resulting in loss of the red color [66].

Gas Detectors

Several types of gas sensors have been developed, which can be used for quantification and/or identification of microorganisms based on their gas emissions. Metal oxides gas nanosensor is one of the most popular types of sensors because of their high sensitivity and stability [67]. More recently, nanosensors based on conducting polymers, which can quantify and/or identify microorganisms based on their gas emissions, are being used [68]. These materials contain conducting particles embedded in insulating polymeric matrices. The sensors will respond to the gases from microorganisms by resistance changes [69]. A typical example is the use of gold nanoparticles that incorporated enzymes for microbe's detection [10]. Nanofibrils of perylene-based fluorophores have the ability to indicate fish and meat spoilage by detection of gaseous amines. ZnO and TiO_2 nanocomposites can also be used for the detection of volatile organic compounds [10].

Oxygen Sensors

There has been an increasing interest to develop nontoxic and irreversible oxygen sensors to assure oxygen absence in oxygen free food packaging systems, such as packaging under vacuum or nitrogen. Lee et al. [70] developed an UV-activated colorimetric oxygen indicator, which uses nanoparticles of TiO_2 to photosensitize the reduction of methylene blue (MB) in a polymer encapsulation medium, using UV-A light. Upon UV irradiation, the sensor bleaches and remains colorless, until it is exposed by oxygen, when its original blue color is restored. The rate of color recovery is proportional to the level of oxygen exposure. Another sensor for detecting O_2 is nanocrystalline SnO_2 used as a photosensitizer [71]. The color of these detectors gradually changes in response to a small amount of oxygen.

Microbial Growth Nanosensors

The ability to determine whether food products are contaminated by various bacteria, fungi, viruses, or toxins that can cause foodborne illnesses remains an important research objective. Taking advantage of the unique electrical, magnetic, luminescent, and catalytic properties of nanomaterials, pathogen detection strategies are increasingly abandoning conventional microbiological analysis methods in preference of a reliance on nanomaterials themselves as the means of detection [72]. In this sense, faster, sensitive, and more economical diagnostic assays are being developed to assist in the battle against microbial growth. Apart from striving for sensitivity and speed, nanotechnologists have geared their efforts towards the development of nanotechnology-based systems that are affordable, robust, and reproducible, making them suitable for applications. A review on microbial growth nanosensors has been recently published by Ayala-Zavala et al. [29].

Electronic Tongue

“Electronic Tongue” technology is made up of sensor arrays to signal condition of the food. The device consists of an array of nanosensors extremely sensitive to gases released by spoiling microorganisms, producing a color change which indicates whether the food is deteriorated. Such nanosensors could be placed directly into the packaging material, where they would serve as an “electronic tongue” or “nose” by detecting chemicals released during microbial growth in food. Conducting polymers have been used as detectors in electronic nose nanosystems. When gas is adsorbed by the nanosensor, conducting organic polymer sensors exhibit a change in resistance which is sensed and delivered as the output [69]. Kraft Foods Company has developed an electronic microdevice like a tongue that can be embedded in food packages. This novel device can change color to indicate whether the food has deteriorated because of spoiling microorganisms, with an array of nanosensors sensitive to gases released from these microorganisms [73].

Self-Heating and Cooling Packaging

Self-cooling packaging, which makes use of a chemical or physical process, such as evaporation of gases, to keep the temperature inside the packaging cool, thus keeping the food fresh, has been developed by the assistance of nanotechnology. Furthermore, the microsized powered systems could make use of a flexible or thin-film photovoltaic cell for food cooling by using thermoelectric materials.

The same principle can be used for self-heating packaging. This technology will reduce the need for large-scale and long-time refrigeration in the supply chain, although it may generate a higher cost in this case. Recently fullerene nanotubes have been found to improve the self-cooling efficiency. Carbon dioxide and nitrogen can be used as the refrigerants held by fullerene nanotubes at a pressure slightly higher than atmospheric pressure. Self-cooling beverage and food container have adopted this technology conditioned by fullerene nanotubes (World patent number 0073718).

Some companies have made efforts in developing smart packaging in the self-heating and self-cooling fields. Nestlé has focused its research on coffee cans that self-heat by simply shaking. Caldo Caldo, an Italian branch, is pursuing similar technology for products such as coffee, cappuccino, chocolate, and tea. Self-cooling technology has been successfully used in the market for cooling beer kegs by zeolite heat pumps and endothermic reactions between sodium thiosulfate pentahydrate and water (www.idspackaging.com).

Enzyme Inmobilization Systems

Smart packaging containing immobilized enzymes such as lactase or cholesterol reductase can be employed for designing food products that require certain enzyme treatments for customers suffering from high cholesterol levels or lactose intolerance [74]. Nanoscale immobilization systems would have strongly enhanced performance, since they would increase the available surface contact area and modify the mass transfer, probably the most important factors affecting the effectiveness of such systems [75].

Current Status of Regulation of Nanomaterials in Food

As with any new technology that offers significant benefits to humankind, there are risks of adverse and unintended consequences with nanotechnology. The small size and subsequent larger surface area of nanoparticles result in novel and specific properties, but it also renders them biologically more active, leading to unexpected consequences on interaction with biological systems. Smaller size also imparts a different biokinetic behavior and ability to reach more distal regions of the body [76]. Moreover, environmental contamination is another concern. These apprehensions have generated concerns about the potential adverse effects of nanotechnology on human health and the environment. Many countries recognize the need of food safety assurance of nanomaterials, existing limited data and information of their possible human health effects [11].

Nowadays, there are no internationally agreed research protocols or standards. The provision of data has not been required on particle size, and some common nanomaterials, such as nanoclays and metal oxides, may thus be authorized although not precisely in nano-sized forms [77]. The USA and the EU are examples of administrative authorities first to adapt to regulating nanotechnologies in the area of food.

European Union

Regarding to nanomaterials, on October 2011 the European Commission adopted the “Recommendation on the definition of a nanomaterial” based on the published opinion “Scientific basis for the definition of the term nanomaterial” of the Scientific Committee on Emerging and Newly Identified Health Risks [78]. Also, in 2011 the Scientific Network for Risk Assessment of Nanotechnologies in Food and Feed (Nano Network) was launched, with the main goals of facilitating harmonization of assessment practices, methodologies, and also achieving synergies in risk assessment activities [79]. At the 2014 meeting, the Nano Network focused on updates of research results from toxicological studies relevant for the oral route of exposure [79]. In addition, in order to inform consumers of the presence of engineered nanomaterials in food, The EU is the only identified region that has adopted a new legislation that states “All ingredients present in the form of engineered nanomaterials shall be clearly indicated in the list of ingredients. The names of such ingredients shall be followed by the word ‘nano’ in brackets.” This regulation is being applied from 13 December 2014 and the obligation to provide nutrition information will apply from 13 December 2016 (Article 18 of Regulation (EU) No. 1169/2011).

USA

The US Food and Drug Administration (FDA) is among the first government agencies around the world having a definition of nanotechnology and nanoproducts. However, the FDA has not adopted a regulatory definition, but it has identified points to consider in deciding whether an FDA-regulated product contains nanomaterials or otherwise involves the application of nanotechnology: (1) whether an engineered material or end product has at least one dimension in the nanoscale (approximately 1 nm to 100 nm) or (2) whether an engineered material or end product exhibits properties or phenomena, including physical or chemical properties or biological effects, which are attributable to its dimension (s), even if these dimensions fall outside the nanoscale range, up to one micrometer.

In 2014, the FDA issued a final guidance document addressing the use of nanotechnology in the area of foods. The final foods guidance alerts manufacturers to the potential impact of any significant manufacturing process change, including changes involving nanotechnology, on the safety and regulatory status of food substances. This guidance also does not establish regulatory definitions. Rather, it is intended to help industry and others identify when they should consider potential implications for regulatory status, safety, effectiveness, or public health impact that may arise with the application of nanotechnology in FDA-regulated products [80]. FDA has been working to develop information needed to help it regulate nanomaterials in all its programs effectively. The FDA Nanotechnology Task Force, formed in August 2006, is charged with determining regulatory approaches that encourage the continued development of innovative, safe, and effective FDA-regulated products that use nanotechnology materials [81].

Latin America

Brazil, Mexico, and Argentina are the main countries in development of nanotechnologies in Latin America, according to the number of research institutions, infrastructure created, the number of academic and scientific publications, international conventions, and quantity of human resources working in this area [82]. Regarding to regulatory status, in Brazil there is an emerging standardization through ordinances, under the Ministry of Science and Technology (MCT), with objectives of creating the administration and the National Nanotechnology system, as well as provide other interaction with countries on the subject. Nothing looks on security. The objectives are especially to disclose Brazilian achievements in the field, partnership with other countries, and little is addresses in aspects of environment and social impacts [83].

In the case of Mexico, the Federal Government established in 2011 a Working Group on Regulations for Nanotechnology, conformed by policy makers, academics and industry representatives. The Group considered that the Mexican legal framework already includes a number of regulations useful as a first approximation for nanotechnologies. However, some specific issues that still needed further discussion and procedures were identified and consequently a set of guidelines were prepared and finally adopted by the Federal Government [84]. However, any concrete legal change is underway since the Guidelines are nonbinding and there are no implementation mechanisms currently being developed. The challenges ahead are then enormous.

In Argentina, the Ministry of Science and Technology established the nanotechnologies as priority areas for funding from 2003. In 2005 was created the Argentinean Nanotechnology Foundation (FAN) with a federal budget of $10 million for the next 5 years. In addition, The National Agency for Science and Technology Promotion (ANPCyT) through its sectorial fund started a new line of funding in three areas of nanotechnology in 2010: nanomaterials, nanointermediaries, and nanosensors. Despite these initiatives for the development of nanotechnologies, there are no current regulations in this matter [85].

Conclusions

Nano-food packaging is a new generation of packaging technology based on nanomaterials, which has become one of the most developed areas in nanotechnology and represents a radical alternative to the conventional food packaging. Utilization of nanocomposites in food packaging has become the most developed area in the food industry. Nanocomposites promise to expand the use of edible and biodegradable films, since the addition of nanoreinforcements has been related to improvements in overall performance of biopolymers, enhancing their mechanical, thermal, and barrier properties, usually even at very low contents. Thus, nanoparticles have an important role to improve feasibility of use of biopolymers for several application, including food packaging.

Moreover, several nanoparticles can provide active and/or “smart” properties to food packaging materials, such as antimicrobial properties, oxygen scavenging ability, enzyme immobilization, or indication of the degree of exposure to some degradation-related factor. So nanocomposites cannot only passively protect the food against environmental factors, but also incorporate properties to the packaging material so it may actually enhance stability of foods, or at least to indicate their eventual inadequation to be consumed.

However, there are many safety concerns about nanomaterials, as their size may allow them to penetrate into cells and eventually remain in the system. There is no consensus about categorizing nanomaterials as new (or unnatural) materials. On one hand, the properties and safety of the materials in its bulk form are usually well known, but the nano-sized counterparts frequently exhibit different properties from those found at the macroscale. There are limited scientific data about migration of most types of nanoparticles (NPs) from the packaging material into food, as well as their eventual toxicological effects. It is reasonable to assume that migration may occur; hence, the need for accurate information on the effects of NPs to human health following chronic exposure is imperative.

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