

Application of Nanotechnology in Food packaging: A review

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Abstract: *Nanotechnology is used in food packaging to improve packaging properties such as gas leakage, heat and moisture resistance during packaging. Nanoparticles provide antimicrobial features through the development of innovative packaging systems to sense biochemical or microbial changes in food and detect the causes of food contamination and diseases to be used as a product monitoring tool for food safety and to avoid food fraud. Recently, nanoshells have been produced consisting of templates of polymers, where the dimensions of the pore holes are controlled, enabling them to prevent the exchange of moisture and gases with the external medium, which affects the distribution and use of coloring materials, flavoring materials, antioxidants, enzymes and anti-brown coloring materials. In packaging fresh food products such as meat, cheese, vegetables, fruits and others and preserving them even after opening the package by treating the surfaces of the outer packages with a thin transparent anti-oxidant layer.*

Keywords: *Nanotechnology, Nanocomposites, Food Packaging, improved, active packaging*

1. INTRODUCTION

Nano unit is the most accurate metric unit known to this point (nanometer) and it measures one billionth of a meter, that is ten times the unit of an atom known as the angstrom, and the size of the nano is about 80,000 times smaller than the diameter of a hair, and the word nanotechnology is the manufacture and use of materials and structures on the nanometer scale. It provides a wide range of opportunities to develop innovative products and applications in the diet [1].

Nanotechnology with its micro-properties is suitable for all areas of life, including those related to food. By changing the molecular structure of specific products, you can increase their nutritional value, change the taste or texture, extend shelf life for a longer time, and even reduce fat levels, in short, create a customized nutrition [2]. The potential benefits of food produced using nanotechnology are surprising. This technology promises a lot of improvement in feeding and packaging. Nanotechnology applications in food packaging are one of the most advanced technological outputs in the food industry, and to date hundreds of food products are packaged and preserved by the technology [3]. Nanocomposites technology provides a new class of composite materials in which polymers used for packaging are "weaponized" by "vaccinating" them with lightweight, high-durability Nanotubes. This improves the mechanical properties of the packaging and increases its strength and endurance of external loads and stresses during transport and storage operations ([4], [5]). Figure (1) displays the main uses of nanotechnology packaging systems, such as product container, product quality preservation and protection,

product presentation and product recognition as a sales item, facilitation of product transportation and distribution, and product information for consumers [6].



Fig. 1: main uses of nanotechnology packaging systems.

During the period from 2003–2009, food packaging sector was one of the most fast-growing areas according to a study by [7]. Results of the study demonstrated that about 54% of plastic packaging were intended to be used for food and beverages sectors. Nanotechnology applications can include many food conservation departments such as developing the properties of food packaging materials, protecting food from microbial and chemical injuries, prolonging the life span of food as well as improving certain nutrient properties such as surfactants ([8], [9]). There are some statistics that estimated the potential future effects of nanotechnology uses, as studies by ([10], [11]) indicated that these effects may, by 2020, reach hundreds of billions of dollars from the global economy and that these increasing industries will may need millions of manpower (fig. 2).

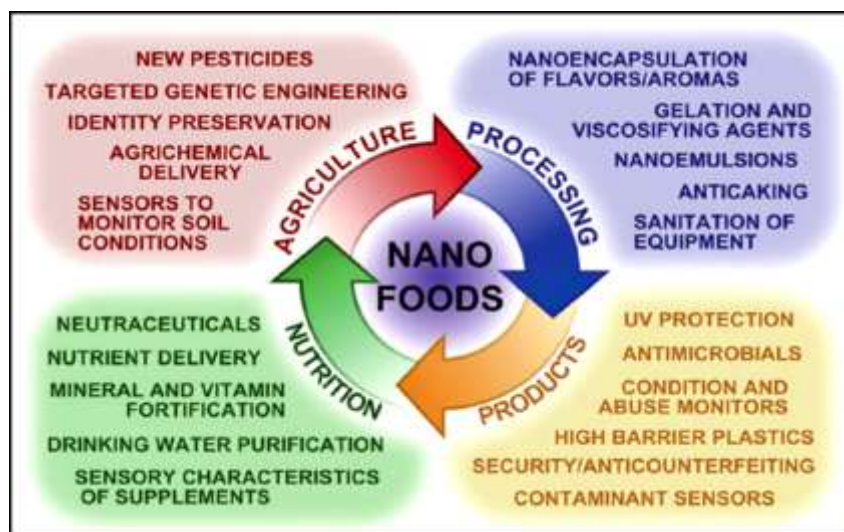


Fig. 2: Nanotechnology applications in different food sectors.

2. CLASSIFICATION OF NANO-PACKAGING SYSTEMS

Lab researches, market applications, and development trends suggest the existing of various categories of nanotechnology applications in the food packaging industry: improved packaging, intelligent packaging, active packaging ([12], [13]).

2.1 Improved packaging

Improved packaging can be achieved using materials for instance clay, silica, cellulose and chitosan, carbon nanotubes, and starch, as these materials provide flexibility, gaseous exchange and maintain temperature and humidity [14]. Improved packaging provides several features, which involve remarkable antimicrobial spectrum and novel properties to the packaging material with low cost for food packaging [15].

2.1.1 Clay and silicate nanoplatelets

Clay is one of the most widely studied materials in the food packaging industry, where different nanocomposites were developed using synthetic polymers to improve food packaging properties [16]. In addition, the combination of silicates and polymers gives preferred properties such as an excellent barrier ([17], [18]). It has been pointed out that the silicate content of polymer formulation layers can contribute to improved diffusive path and to the development of a tortuosity molecular-penetration path as shown in fig. (3) [19].

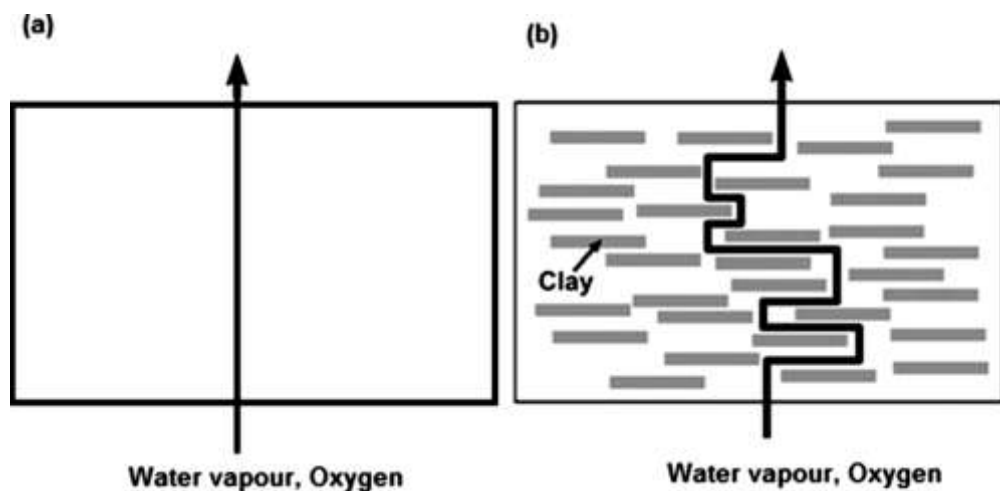


Fig. 3: devious pathway formed by integration of clay nanoplatelets into a polymer matrix.

Three types of composites (tactoid, intercalated, and exfoliated) were reported as polymer-clay formations fig. (4) [20]. An example of clay use in food packaging is the utilization of low-density polyethylene (LDPE), which enhanced oxygen barrier properties several times, especially after mixing with organic montmorillonite (OMMT) [21]. In addition, the addition of sodium montmorillonite nanomaterial to poly(vinyl alcohol) and poly(vinyl pyrrolidone) (PVP) lowers the moisture absorption capacity by 12% as a result of the hydrogen bonds between the polymer molecules [22].

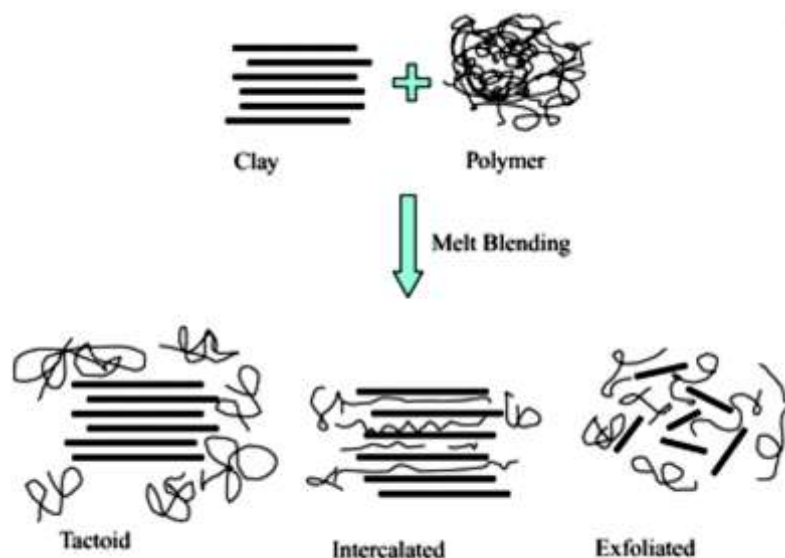


Fig. 4. Polymer clay morphologies.

Montmorillonite, another type of nanoclay fillers, is considered as the most common nanoclay combined with two layers of hydrated alumina-silicate [23]. A study by [24] demonstrated that the linkage between the two silica layers exhibits weak electrostatic forces which cause a medium negative surface charge essential to establish the layer spacing equilibrium. Another benefits of using clay in food packaging is prolonging shelf life, heat and fracture resisting [25].

2.1.2 Cellulose

Another natural biopolymer is cellulose which is widely used for food packaging due to the numerous advantages, they provide such as enhanced thermo mechanical properties, biodegradability and low cost alongside with its light weight, low density and high strength ([26], [27]). Cellulose is acid hydrolyzed to produce whiskers as a packaging material in combination with starch ([26], [28]). Moreover, (HPMC), which is an integration of chitin with hydroxypropyl methyl cellulose provided an enhanced systematic and barrier properties [29]. Plants, animals, bacteria and algae are rich sources of nanocellulose ([30], [31]). Cellulose chains are synthesized in the form of elongated molecule nanofibers or microfibrils (2-20 nm in diameter and micrometers in length) and have crystalline and amorphous regions [32].

2.1.3 Chitin (chitosan)

Next to cellulose, chitin (chitosan) is a natural polysaccharide and it is the second most abundant semi-crystalline biopolymer. The most known sources of chitin are crab, shellfish, shrimp, insects, fungus and yeast as reported by ([33], [34]). The main structural unit of chitin is the filaments, which is a chitin fiber, are entrenched in protein matrix with diameters of 2.5 to 2.8 nm, which are firmly bonded with hydrogen bonds and in the form of crystalline and shapeless domains ([33], [34]). Chitin nanowhiskers can be obtained by breaking the amorphous domains, which split the chitin crystallites ([35], [36]). Chitosan is mostly used for its antimicrobial capability through the antimicrobial film synthesis through chitosan / alcohol combination, which function against food-borne pathogens, and has the potential to sustain pH, color and firmness of food samples ([37], [38]).

2.1.4 Carbon nanotubes

Carbon nanotube was discovered by the Japanese scientist Ijima Sumio in 1991 during his research on carbon products in the process of electric discharge between two carbon electrodes [39]. Graphite (a carbon nanotube), interconnected rope shape as a result of atomic forces (Van Der Waals forces), where the atoms at the ends of the slide are connected to each other, to close the tube fig. (5) ([40], [41]).

Recently, the use of carbon nanotubes (organic and inorganic) in food sector has increased as a packaging material due to its desirable properties such as elastic and tensile strength, especially in combination with polymeric compounds such as polyethylene, polyamide, polypropylene, polyvinyl alcohol and naphthalene [42]. Additionally, [43] reported that carbon nanotubes exhibit an antimicrobial property during their study on *Salmonella* species. Moreover, carbon nanotubes have also showed an antifungal activity when they were combined with polyethylene films and used for dates packaging [43].

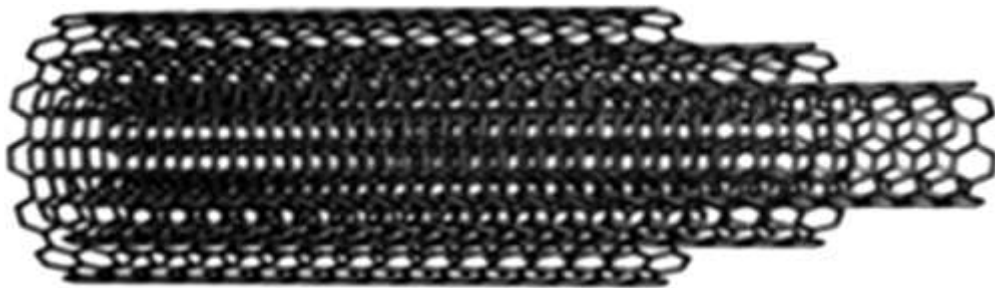


Fig. 5: structure of carbon nanotubes (MWCNT).

2.1.5 Starch nanomaterial

Starch, a polysaccharide, was extensively studied as a promising and renewable natural material for food packaging due to its characters such as affordability, non-toxicity, biodegradability, and abundance [44]. Reference [45] was the first to report starch nanocrystals during the acid hydrolysis of potato starch, which produced microcrystals of diameter tens of nanometers [45]. Starch combined with clay represents a favorable nanocomposite for food packaging material ([45], [46]). A study by [47] demonstrated that integration of minerals such as (Ag, Ti, Zn, Mg) and other synthetic polymers to food packaging can enhance starch water resistance, hence, make it an excellent food packaging material. Similar to cellulose, starch application as the food packing material improves flexibility and decreases elastic property [48].

2.2 Smart (Intelligent) packaging

Intelligent packaging is one of the solutions offered to reduce food waste, detecting microbial and chemical changes in food and aims for the monitoring of food products and factors surrounding and affecting it. Moreover, these novel food packaging systems provide the consumer with greater convenience in terms of (quality, distribution, methods of preparation) [49]. In this packaging system, new and innovative methods and systems are used, such as nanosensors, time and temperature indicators, O₂ sensors, freshness indicators ([14], [50]). Recently, the use of nanotechnology in smart food packaging has been studied and this has been the goal of various food production companies around the world [51]. The application of nanotechnology in intelligent packaging involves different nanosensors systems such as

oxygen indicators, time-temperature integrators (TTIs) and freshness and spoilage indicators [14].

2.2.1 O_2 indicators

Gas nanosensors are among the most promising applications in the future of intelligent food packaging, as the key purpose of their use is the early detection of gases ([6], [52]). O_2 is among the main gases that became of special concern due to its potential to enhance aerobic microorganism development during storage [6]. Therefore, vacuuming food packages beside incorporation of O_2 sensors is used to with the purpose of extending food shelf-life [14]. References ([53], [54]) reported the use of UV based colorimetric O_2 indicator which is created with Titania (TiO_2) nanoparticles. The used of TiO_2 is based on bleaching the reduction of methylene blue by triethanolamine in a polymer encapsulation medium [53]. This O_2 sensor is created in the form of coating film which contain a polymer carrier consisting of TiO_2 , redox dye, and sacrificial electron donor ([54], [55]). The mechanism of TiO_2 sensors involves O_2 bleaching until absence of color is achieved followed by the appearance of blue color. Color change is an indicator of the O_2 exposure level (fig. 6).

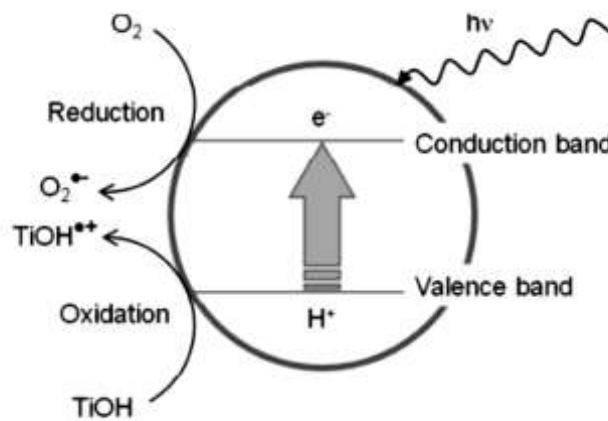


Fig. 6: TiO_2 sensor mechanism.

2.2.2 Time-Temperature Indicators

Temperatures is considered as a crucial factor that may negatively affect food and reduces food shelf life especially if stored, distributed or manufactured in poor conditions. These indicators are usually come in the form of a small badge fixed on the outer surface of food package. (TTIs) are applied to trace thermal changes [56]. Ag^+ nanoplates, a colorimetric indicator for time-temperature tracking was first used by (Zeng et al., 2010) due to their thermodynamic instability. The basis of (TTIs) mode of action is the change in color depending on the food exposure to different temperatures (fig. 7) [32].



Fig. 7: Time-temperature indicators (TTIs) change in color.

2.2.3 Freshness and spoilage indicators

During storage, distribution and displaying, it is highly important to monitor any change in the food product quality. Information regarding any sign of spoilage or microbial metabolites caused by microorganisms are crucial to guarantee the quality of the food product ([14], [52]). Polymer nanocomposites or metal oxides are applied for the quantification and/or identification of gas emissions produced by microorganisms. In a study by [57], (1–10 nm thickness) silver and/or copper coating was applied in preference to plastic or paper packaging. This type of coating change in color upon spoilage that may take place in fresh meats which react with sulfide volatiles. Moreover, poly(thiophene) was used by [58] to create highly accurate colorimetric reactions to 22 amines.

2.3 Active packaging

Active food packaging can be defined as the packaging that changes the conditions of the packed food product for the purpose of increasing the product's validity or improving safety and sensory properties and then maintaining the quality of the packaged product or can be defined as the type of packaging that is used to give an additional function and a protective barrier against external influences, and it is a phenomenon (that enables interaction, control or influence) that occurs inside the packaging [59]. Active food packaging may involve incorporating of antioxidant, antimicrobial, pigment, nutrients and nanoparticles into food packaging material [60]. Table (1) shows different active packaging types applied in food packaging. Nanomaterials (such as silver nanoparticles) are incorporated in such packaging systems to directly interact with food or environment, thus, provide enhanced protection against internal and/or external factors ([61], [62]).

2.3.1 Oxygen Scavengers

O₂ is a main factor for food deterioration, therefore, access of O₂ reduce food product shelf life and may cause several negative impacts such as rancidity, microorganisms' growth, loss of color, and vitamins and flavor loss ([52], [63]). Therefore, elimination or reduction of access O₂ to an acceptable level might help in preventing these negative effects. Currently, O₂ scavengers are developed and incorporated in food packaging systems to reduce O₂ effects ([64], [65]). TiO₂ nanoparticles and various polymers nanocomposite material ((PET, PP, FEP, LLDPE, and nylon) were explored to be used in packaging materials as O₂ scavengers [66]. The principle that stands behind using TiO₂ is that by using UV radiation to photoinduce TiO₂,

electrons are accumulated on the TiO₂ surface, hence, electrons are transferred to O₂ which is a rate determining step that can act as O₂ scavengers [67].

Table I: different active packaging types applied in food packaging.

Type of application	Foods
Oxygen scavengers	Ground coffee, tea, roasted nuts, potato chips, chocolate, fat powdered milk, powdered drinks, bread, tortillas, pizza, pizza crust, refrigerated fresh pasta, fruit tortes, cakes, cookies, beer, deli meats, smoke and cured meats, fish, cheese
Carbon dioxide absorbers	Ground coffee
Carbon dioxide emitters	Meat, fish
Moisture absorbers	Dry and dehydrated products, meat, poultry, fish
Ethylene scavengers	Kiwifruit, banana, avocados, persimmons
Ethanol emitters	Bread, cakes, fish
Antimicrobial releasing films	Dry apricots
Antioxidant releasing films	Cereals
Flavor absorbing films	Navel orange juice
Flavor releasing films	Ground coffee
Color containing films	Surimi
Anti-fogging films	Some fresh fruit and vegetable packages
Anti-sticking films	Soft candies, cheese slices
Light absorbers	Pizza, milk
Time-temperature indicators	Microwaveable pancake syrup, refrigerated pasta, deli items

2.3.2 Antimicrobial active packaging

Silver, titanium, copper and zinc are examples of nanocomposites used in numerous active packaging applications ([68], [69]). Because of their small dimensions and surface activity, adding these particles to the packaging materials gives them anti-microbial activity against disease-causing and spoilage microorganisms ([32], [61]). Reference [70] reported that antimicrobial packaging can be categorized into basic categories; the incorporation of antimicrobial nanoparticles into a sachet attached to the stored food package, the incorporation of antimicrobial nanoparticles into a packaging film, and using the antimicrobial nanoparticles as a carrier (packaging coating) (table. 2). Silver nanoparticles, among other nanocomposites, are the most effective against both Gram-positive and Gram-negative bacteria ([71], [72]). In addition, [73] reported that Ag⁺ nanoparticles demonstrate temperature stability in addition to their high toxicity against wide range of microorganisms.

Table II: Incorporation of antimicrobial nanoparticles in different food packaging systems.

Nanoparticles	Polymer matrix	Tested microorganisms
Ag/Chitosan	PLA ¹	<i>Staphylococcus aureus</i> (ATCC6538) <i>Escherichia coli</i> (DSMZ 30083)
Ag	Agar banana powder	<i>Escherichia coli</i> <i>Lysteria monocytogenes</i>
TiO ₂ /Ag/Cu	PVC ²	Mixed microorganism culture media
ZnO/Ag/Cu	PLA ¹ /PEG ³	<i>Lysteria monocytogenes</i> <i>Salmonella typhimurium</i>
Ag	PE ⁴	<i>Escherichia coli</i>
Ag/Cu	Guar Gum	<i>Lysteria monocytogenes</i> <i>Salmonella typhimurium</i>
Ag/TiO ₂	PE	<i>Aspergillus flavus</i>
Ag/Cu	Fish skin Gelatin	<i>Lysteria monocytogenes</i> <i>Salmonella enterica</i> sv Typhimurium
Ag	Starch/PVA ⁵	<i>Lysteria innocua</i> ; <i>Escherichia coli</i> <i>Aspergillus niger</i> , <i>Penicillium, expansum</i>
Ag/SiO ₂ /TiO ₂	LDPE ⁶	<i>Escherichia coli</i>
Ag	PHBV ³	<i>Salmonella enterica</i> <i>Lysteria monocytogenes</i>
SiO ₂	PBAT ⁸	<i>Escherichia coli</i> ; <i>Staphylococcus aureus</i>
ZnO	LDPE	<i>Bacillus subtilis</i> ; <i>Enterobacter aerogenes</i>
ZnO	MC ⁹	<i>Staphylococcus aureus</i> ; <i>Lysteria monocytogenes</i>
Nanoclay (NaMMT, OrgMMT)	PVOH/chitosan	<i>Escherichia coli</i>

3. SAFETY AND REGULATION CONCERNS

Despite the tremendous and rapid development in the nanotechnology applications in food packaging, there are still concerns about the potential risks that these materials could cause to human health and environment [74]. Therefore, comprehensive data concerning the use of nanoparticles in food packaging is strongly needed. As a result of the application of nanoparticles in food packaging, it has become necessary to study the possibility of nanoparticle migration from food packaging to the human body or to the environment. Currently, there are insufficient studies and regulations that are concerned with determining the risks of the migration of these materials to humans and the environment [5]. On the other hand, some previous studies showed the toxicity of some nanoparticles to plants that are consumed by humans, and consequently, the arrival of these nanoparticles (such as silver nanoparticles) to the digestive system and their toxic effects on various cells [75].

Different governments set regulations regarding the applications of food packaging containing nanoparticles. In the USA, Food and Drug Administration (FDA), established Nanotechnology Task Force (NTF) to regulate the use of nanotechnology in food contact materials [76], [77]). In 2011, a report by (FDA) stated that the assessing of safety and effectiveness of food products or their impact on public health (especially those containing nanomaterials) depends on the behaviors shown by these nanomaterials [78]. In 2012, the FDA in their Draft Guidance for Industries stated that there is a deep debate about the type of test that can be conducted to ensure the safety of the food product that nanotechnology has been applied in during its production or packaging [79]. On the other hand, the European Food Safety Association (EFSA) Scientific Committee published its opinion regarding application of nanotechnologies in relation to food and feed safety [80]. Thus, nanotechnology applications related to food safety should meet with three main required regulations; (i) food, (ii) health and (iii) environment (fig. 8). These three regulations are to ensure the maximum benefit from the application of nanotechnology in food packaging with an emphasis on providing the maximum health conditions for humans, animals and the environment [6].



Fig. 8: main regulations required for the application of nanotechnology in food packaging.

4. CONCLUSIONS

Nanotechnology is defined as the science that studies the processing of matter on the atomic and molecular scale through the development of new techniques and methods to measure, form, and manipulate matter of around 1 to 100 nanometers. The application of nanotechnology in food packaging is one of the most important advanced technical outputs in the food industry sector. To this day, hundreds of food products are packaged, and preserved using Nanotechnology. However, with regard to consumer safety of nanomaterials interacting with food, it is very important to evaluate and study the potential risks, knowing that there are few studies linked to the effects of nanomaterials on the human body. Additionally, previous studies indicated the potential for nanomaterials to migrate into foodstuffs, with the migration rate potentially related to the proportion of nanoparticles present in the composites. Further migration and toxicity studies are still needed in order to ensure the safe development of nanotechnologies in the food packaging industry.

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