NANOTECHNOLOGY IN THE FOOD INDUSTRY

NANOTECNOLOGIA NA INDÚSTRIA DE ALIMENTOS

Patrícia Campos BERNARDES[1]; Nélio Jose de ANDRADE[2]; Nilda de Fátima Ferreira SOARES[3]

1. Professora, Doutora, Departamento de Engenharia de Alimentos, Centro de Ciências Agrárias, Universidade Federal do Espirito Santo, Alegre, ES. paticbernardes@yahoo.com.br; 2. Professor, Doutor, Departamento de Tecnologia de Alimentos, Universidade Federal de Viçosa - UFV, Viçosa, MG; 3. Professora, PhD, Departamento de Tecnologia de Alimentos - UFV, Viçosa, MG, Brasil.

ABSTRACT: Nanotechnologies involve the manipulation of matter at a very small scale, generally between 1 and 100 nanometers. They exploit novel properties and functions that occur in matter at this scale. The application of nanotechnology in the areas of food and food packaging is growing rapidly, and in the area of food security, these applications include the detection of microorganisms, environmental protection, water purification, encapsulation of nutrients and food packing. Nanotechnology is opening up a world of new possibilities for the food industry, but the entry of nanoparticles into the food chain can result in a buildup of toxic contaminants in food and harm human health. This review focuses on the nanoencapsulation of bioactive compounds, nanosensor especially to detect foodborne pathogens, applications of nanotechnology in food packing and highlight some of aspects of toxicology.

KEYWORDS: Nanocompounds. Food packaging. Nanosensors. Nanoencapsulation. Nanocomposites.

INTRODUCTION

Nanotechnology is a new field that has grown rapidly and involves the production, processing, application of structures, devices and systems by controlling shape and size at the nanometer scale (BOUWMEESTER et al., 2009). The physical, chemical, and biological properties of structures and systems at nanoscale are substantially different than the macro-scale counterparts due to the interactions of individual atoms and molecules thereby offering unique and novel functional applications (NEETHIRAJAN; JAYAS, 2011).

According to the National Nanotechnology Initiative in the United States the federal funding was budgeted in $1.64 billion to be spent on the advancement of nanotechnologies in 2010 (CUSHEN et al., 2012).

Nanotechnology has been revolutionizing the entire food system from production to processing, storage, and development of innovative materials, products, and applications. Currently, the market of nanotechnology products in the food industry approaches US$1 billion (most of this on nanoparticle coatings for packaging applications, health promoting products, and beverages). The application of nanotechnology in the areas of food and food packaging is growing rapidly (EZHILARASI et al., 2013).

On the market, various terms as "nanofood" and "ultrathin food" has been used (CHAU, WU, YEN, 2007). Because of these new developments it is likely that radical changes in the way food is perceived, stored, packaged, transported, monitored, consumed and processed will come about (CUSHEN et al., 2012). Currently there are no approved nanofoods in the UK and EU. In these countries, nanoparticles in foods or food supplements are considered a novel food and therefore, require the appropriate regulation (GUTIERREZ et al., 2013).

There is no specific regulation that controls or limits the production of nanosized particles and this is mainly due to lack of knowledge about their risks. Despite of this lack of regulation and knowledge of the risk, many food products and nutritional additives that contain nanoscale particles are already being sold. As examples may be mentioned: nutritious beverages added with iron micelles which carry vitamins, minerals and phytochemicals in oils and zinc oxide in breakfast cereals and nanoclays found in plastic beer bottles. The FDA (Food and Drug Administration) requires manufacturers of food and food ingredients demonstrate that they are not harmful to health, although this regulation does not specifically cover the nanoparticles, which can be harmful only in nanoscale applications (SOZER; KOKINI, 2009).

Nanoparticles exhibit several features that make them of great potential for food industry, such as high surface/volume ratio, reassembling and self-reassembling capability, and the ability to create porous structures (PÉREZ-ESTEVE et al., 2013). However, there is an increasing feeling of rejection by the final consumers, which explains some opposition to use nanotechnology in the food industry.

In a survey conducted by Israel and the United States in March 2006 more than 200

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manufacturers were selling products labeled "nano". About 60 % of these products were health and fitness and 9 % were food and drink (CHAU, WU and YEN, 2007). Despite the lack of unified guidelines for nanotechnology, manufacturers have to deal with the existing general regulations for food products and the introduction of a new "nanoingredient" can be difficult and time consuming. (SOZER; KOKINI, 2009).

DEVELOPMENT

Applications of nanotechnology in the food

The market for nanotechnology ranges from the commercialization of products and processes to achieve the production on the field, up the steps associated with the process in the production of industrial inputs, agro-processing and food industry (RAMOS et al., 2009).

Nanotechnology has enormous potential to revolutionize food systems. Studies show the possibility of nanoscale technologies assist in the detection of pathogens through nanosensors, identification and traceability of origin for agricultural products and animals. Most applications in the food sector are occurring in the area of packaging, but some foods and ingredients are entering in the market with a view to change the properties and increase conservation of various foods and beverages (RAMOS et al., 2009).

The application of nanotechnology in agriculture and food industry is relatively recent compared with its use in the area of drugs for controlled release of drugs. The smart release of nutrients, bioseparation of proteins, rapid detection of chemical and biological contaminants and nanoencapsulation of nutraceuticals are some emerging issues in nanotechnology for agriculture and food industry (SOZER; KOKINI, 2009). Nanotechnology also can play a vital role in controlling the size and structure of food to a greater extent. These include healthier foods (lower fat, lower salt) with desirable sensory properties; ingredients with improved properties; and the potential for removal of certain additives without loss of stability, for example in emulsions, and in smart-aids for processing foods to remove allergens such as peanut protein (NEETHIRAJAN; JAYAS, 2011). Using nanoemulsions in food products can facilitate the use of less fat without a compromise in creaminess, thus offering the consumer a healthier option. Products of this type include low fat nanostructured mayonnaise, spreads and ice creams (CHAUDHRY et al., 2008).

Edible nanolayered has potential for applications in fresh fruits, vegetables, dairy and bakery products, where they can protect food from moisture, gases, odors and off-flavors. Medeiros et al. (2013) study the preservation of ‘Coalho’ cheese by a nanolaminate coating produced by the layer-by-layer methodology. The authors observed that the edible nanolayer reduced the microrganisms’ proliferation in comparison with uncoated cheese. They conclude that gas barrier and antibacterial properties of alginate/lysozyme nanocoating can be used to extend the shelf life of ‘Coalho’ cheese.

Natural biopolymers on a nanometric scale, such as polysaccharides, can be used for encapsulation of vitamins, prebiotics and probiotics and delivery systems for drugs or nutraceuticals (SOZER; KOKINI, 2009). Other examples are the use of nanoparticles as micelles, liposomes, nanoemulsions, biopolymer nanoparticles and cubosomes. Examples of the use of nanotechnology directly in food is cooking oils containing nutraceuticals within nanocapsules, flavor enhancers and nanocoated nanoparticles that are capable of binding selectively and remove chemicals food. The main reasons for the delay in the incorporation of nanotechnology in the food sector are issues related to food labeling and consumer health aspects (SOZER; KOKINI, 2009).

Siegrist et al. (2007) evaluated the public perception of different types of food products made using nanotechnology, including an antibacterial packaging for food, a tomato nanocoating for protection from moisture and oxygen, a bread with nanocapsules of omega-3 and a juice with vitamin A nanoencapsulated in starch. The results obtained with 153 persons showed that the use of nanotechnology in packaging was considered more beneficial than application of nanotechnology directly in the food.

Chau, Wu and Yen (2007) conducted a review on the application of nanotechnology in food. These authors cite several studies developed for application of nanotechnology in food processing: food and drinks that produce interactive desired colors and flavors by adding nanocapsules that rupture at different microwave frequencies; purification of water by the application of nanotechnology in separation processes membranes focusing on disinfection, biofouling and removing contaminants; development of formulations from traditional medicinal plants for the production of nanopowders or nanoemulsions; refining frying oil using a catalytic device made of nanoceramic material aiming inhibit polymerization of frying oil and reduced off-flavors; nanotubes of milk protein with potential for use as new ingredients such as thickening agent for gelatinization, nanoencapsulament and for controlled release of certain compounds.

In the area of nutraceuticals these same authors mention the following applications: nanoparticle dispersion of some functional ingredients such as carotenoids, phytosterols and antioxidants in waters and fruit drinks to enhance bioavailability; lycopene synthetic nanoparticles, already recognized as GRAS by the FDA; micelles used as a carrier for essential oils, aroma, antioxidants, vitamins, minerals and phytochemicals for improved bioavailability; nanoparticle encapsulation of active ingredients such as polyphenols, minerals and micronutrients, to protect them from oxidation and subsequent reduction of off-flavors in the final product; liposomal nanovesicles for encapsulation of nutrients and functional ingredients such as proteins, enzymes, aromes and antimicrobial compounds. Table 1 presents examples of nanotechnology applications in different areas.

Nanoencapsulation of bioactive compounds

By reducing the size of the particles, nanotechnology can improve the properties of bioactive compounds, such as controlled release, solubility, prolonged residence time in the gastrointestinal tract and efficient absorption by the cells. Nanoencapsulation involves the incorporation, absorption or dispersion of bioactive compounds in small vesicles with diameters on the order of nanometers. The bioactive compound can be incorporated and protected from degradation, has better solubility and stability and therefore have greater bioavailability. The nanocapsules have a gastrointestinal retention time extended due to better bio-adhesive capacity in the mucus that covers the intestinal epithelium. For application in the food nanocapsules of lipid or natural polymers are the most studied and applied (CHEN, REMONDETTO; SUBIRADE, 2006).

Nanoencapsulated compounds for food application should be non-toxic and biodegradable in the human body and must use excipients that are generally regarded as safe. They need to undergo a careful toxicological safety evaluation before they can be used for human consumption. The testing of nanoparticles (NPs) is currently not fully regulated and common toxicity tests may not be suitable for NPs. The effectiveness of nanoencapsulated compounds must also be tested to assure that the process is actually improving the characteristic of non-encapsulated compounds, but few methods have been developed (GUTIERREZ et al., 2013).

The bioactive compounds that can be found naturally in certain foods have physiological benefits and can help reduce the risk of certain diseases, including cancer. Omega-3 and omega-6, probiotics, β-carotene, prebiotics, vitamins and minerals find applications in nanotechnology in foods such as bioactive compounds (WATANABE, IWAMOTO; ICHIKAWA, 2005; GUTIÉRREZ et al., 2013).

Nanocapsules have been used to mask the taste and odor of tuna fish oil (source of omega-3 fatty acids) which is integrated into bread. The nanocapsules break open only when they reach the stomach and hence the unpleasant fish oil taste can be avoided (NEETHIRAJAN; JAYAS, 2011). The viability of probiotic organisms including *Lactobacillus acidophilus*, *Lactobacillus casei, Lactobacillus rhamnosus*, and *Bifidobacterium* spp. within freeze dried yogurt can be improved by nanoencapsulation with calciumalginate (KAILASAPATHY; RYBKA 1997). Nanoencapsulated *Bifidobacteria* with starch by spray coating exhibited an affordable and industrially convenient encapsulation process (O'RIORDAN et al., 2001). The bioavailability of lycopene can be increased by fortifying nanoparticles of lycopene in tomato juice, pasta sauce, and jam (AUWETER et al., 1999). Milk protein, casein, was used to make nanosized micelles and has been employed as a vehicle for delivering sensitive health promoting ingredients including vitamin D2 (SEMO et al., 2007). De Paz et al. (2012) encapsulated β-carotene in nanosuspensions using modified n-octenyl succinate starch improving dispersibility, coloring strength and bioavailability of this compound.

In these applications packaging materials must be capable of maintaining bioactive compounds such as prebiotics, probiotics, encapsulated vitamins or bioavailable flavonoids in optimum conditions until they are released in a controlled manner to the food product. These materials can help control oxidation of foods, preventing the formation of off-flavors and undesirable textures in the foods. Various additives have been approved for nanoencapsulation may be used, including carrageenan, chitosan, gelatine, polylactic acid, polyglycolic acid and alginate (LOPEZ-RUBIO, GAVARA; LAGARON, 2006).

Table 1. Examples of nanotechnology applications in different areas.

Area	Examples	Reference
Nanoencapsulation and nanoparticles of food constituents	Nutritious beverages added with iron micelles which carry vitamins, minerals and phytochemicals in oils	Sozer and Kokini, 2009
	Nanocapsules to mask the taste and odor of tuna fish oil (source of omega-3 fatty acids) which is integrated into bread	Neethirajan and Jayas, 2011
	Nanoencapsulation of *Lactobacillus acidophilus*, *Lactobacillus casei, Lactobacillus rhamnosus*, and *Bifidobacterium* spp. with calciumalginate in freeze dried yogurt	kailasapathy and Rybka, 1997
	Nanoencapsulated *Bifidobacteria* with starch	O'Riordan et al., 2001
	Encapsulated β-carotene in nanosuspensions using modified n-octenyl succinate starch	Paz et al., 2012
	Nanoparticles of lycopene in tomato juice, pasta sauce, and jam	Auweter et al., 1999
	Nanosized micelles of casein as a vehicle for delivering vitamin D2	Semo et al., 2007
	Low fat nanostructured mayonnaise, spreads and ice creams	Chaudhry et al., 2008
Nanosensors	Fluorescent nanoparticles to sensing pathogens and toxins in foods and crops	Burris and Stewart Jr., 2012
	Functionalized quantum dots coupled with immunomagnetic separation in milk and apple juice to detect foodborne pathogenic bacteria	Zhao et al., 2009
	Sensor for detecting *Escherichia coli* in a food sample	Horner et al., 2006
	Biosensor to detect *Salmonella* antibodies on a silicon/gold nanorod array	Fu et al., 2008
Packing	Nanoclays in plastic beer bottles	Sozer and Kokini, 2009
	Preservation of 'Coalho' cheese by a nanolaminate	Medeiros et al., 2013
	Nanocomposite film of montmorillonite nanoparticles and starch/clay used for packaging vegetables	Avella et al., 2005
	Nanocomposite of polyethylene and organophilic clay	Araújo et al., 2008
	Silver nanoparticles incorporated into cellulose acetate, polyimide, polyamide and poly (2-ethyl-2-oxazoline)	Chou et al., 2005; Deng et al., 2008; Damm et al., 2007; Kang et al., 2006
	Silver–polyvinyl alcohol nanocomposites	Mbhele et al., 2003
	Nanocomposites with nanoparticles of TiO_2/Ag^+ in PVC	Cheng et al., 2006
	NiO/TiO_2 composite nanofibers with antibacterial activity	Amna et al., 2013
	Chitosan–poly(ethylene oxide) blend nanofibers	Kriegel et al., (2009
	Zein prolamine nanostructures	Torres-Giner, Gimenez and Lagaron, 2008
	Biodegradable thermoplastic starch/nanoclay	Park et al., 2002
	Biodegradable nanocomposites based on a PLA/PCL	Cabedo et al., 2006
	Multilayer of complexes polyelectrolyte/nanoclay in paper	Ou et al., 2007
	Composite nano-strutured of calcium silicate	Johnston et al., 2008
	Polypropylene/carbon nanotube nanocomposites	Bao and Tjong, 2008

Nanotubes of α-lactoalbumina

Particularly relevant to the food industry is the possibility of obtaining nanotubes of milk proteins as α-lactalbumin by partial hydrolysis. The α-lactalbumin nanotubes are capable of enhancing the viscosity due to its high surface area and stiffness, which requires less protein. Thus, these high density nanotubes of proteins can also be used as a thickener. The α-lactalbumin nanotubes have cavities of approximately 8 nm in diameter, which may allow harboring food components such as vitamins or enzymes. These cavities may also be used to encapsulate and protect nutraceuticals or to mask undesirable flavors or aromatics compounds (GRAVELAND-BIKKER; KRUIF, 2006). Because the nanotubes are composed of milk proteins, they are considered food grade materials, which should facilitate their introduction on the market and can facilitate the expansion of nutrients, supplements and pharmaceuticals nanoencapsulament applications (SOZER; KOKINI, 2009).

Nanosensors

The nanosensors are designed to respond to environmental changes, such as changes in temperature or humidity in storage places, chemical changes due to degradation of food or due to contamination by microorganisms (BOUWMEESTER et al., 2009).

Given the crucial importance of time in food microbiology, the main objective of nanosensors is to reduce the time of detection of pathogens from days to hours or even minutes. The nanosensors can be placed directly on the packaging, in order to detect chemicals released during food spoilage (BHATTACHARYA et al. 2007).

Various works have been done for development of nanosensors. Burris and Stewart Jr (2012) conducted a review about fluorescent nanoparticles to sensing pathogens and toxins in foods and crops. Zhao et al. (2009) study simultaneous detection of foodborne pathogenic bacteria (*S.* Typhimurium, *S. flexneri*, and *E. coli* O157:H7) based on functionalized quantum dots coupled with immunomagnetic separation in milk and apple juice. Horner et al. (2006) have developed a sensor for detecting *Escherichia coli* in a food sample by measuring and detecting light scattering by cell mitochondria. This sensor works on the principle that a protein of a known and characterized bacterium set on a silicon chip can bind with any other *E. coli* bacteria present in the food sample. This binding will result in a nanosized light scattering detectable by analysis of digital images. A biosensor developed by Fu et al. (2008) uses fluorescent dye particles attached to anti-*Salmonella* antibodies on a silicon/gold nanorod array. When the *Salmonella* present in the food is being tested, the nanosized dye particles on the sensor become visible. Unlike the time-consuming conventional lab tests that are based on bacterial cultures, this biosensor can detect the *Salmonella* in food instantly. Stutzenberger et al. (2007) have developed a novel strategy that employs bioactive nanoparticles in the chicken feed specifically designed to bind to the biomolecular structures on the surfaces of *Campylobacters*. The feed enriched by antibiotic-functioning nanocarbohydrate particles binds with the bacterium's surface to remove it through the bird's feces.

According Bouwmeester et al. (2009) there are no data available regarding the possible diffusion of nanoparticles (NPs) of nanosensors use in food. However, according to these authors is possible to suppose that the use of active packaging that release NPs with antimicrobial functions in foods, usually silver NPs and more rarely zinc oxide, lead to direct exposure of NPs to the consumer. Thus there is a need for information about the effects of these NPs to human health after chronic exposure. Furthermore, attention should be given to the analysis of the life cycle of these NPs and their effects on the environment.

Nanocantilevers are another class of novel biosensors. Its detection principle is based on its ability to detect biological interactions, such as between antigen and antibody, enzyme and substrate or cofactor and receptor and ligand, through physical or electromechanical signaling (HALL, 2002). They consist of small pieces of silicon-based materials that have the ability to recognize proteins and detect pathogenic bacteria and viruses. These devices have already a great success in studies of molecular interactions and detection of chemical contaminants, toxins and antibiotic residues in food (FRÓMETA, 2006). The detection of pathogens is based on its ability to vibrate at different frequencies depending on the biomass of microorganisms. A project funded by the European Union developed a nanocantilever that can be used for diagnosis of cancer and to detect pathogens in food and water based on the detection of receptor-ligand interactions.

Food Packing

Applications of nanotechnology in food packaging area are considered highly promising, because they can improve the safety and quality of food. This includes intelligent packaging, which are reactive to environment and active packaging, which are capable of interacting with food (SOZER; KOKINI, 2009).

For packaging area Chau, Wu and Yen (2007) gives as an example the following applications: adding nanoparticles or nanocomposites, for example, silver, titanium dioxide, silicon dioxide, and nanoclays, to ensure better protection of foods by modification permeation behavior, deodorization, increased barrier properties, blocking of UV light, improved mechanical properties and heat resistance, development of antimicrobial surfaces and nylon nanocomposites with barrier properties to oxygen and carbon dioxide used in bottles for alcoholic beverages such as beer. The nanoclays embedded in the plastic bottles stiffen the packaging, reducing gas permeability, and minimizes the loss of carbon dioxide from the beer and the ingress of oxygen to the bottle, keeping the beer fresher and increases the shelf life to more than six months.

Nanoparticles are incorporated into packaging materials to improve their barrier properties, as an example can be cited NPs of silicate, silver, magnesium and zinc oxide. When NPs are incorporated into the packaging material direct contact with food is possible only after the diffusion of NPs. Avella et al. (2005) evaluated the diffusion of montmorillonite nanoparticles (MMT) of starch/clay nanocomposite film used for packaging vegetables and found that diffusion was minimal. In addition, there was improvement in mechanical properties such as tensile strength. However, more studies are needed for a definitive conclusion about the diffusion.

Nanocomposites

Polymer composites are mixtures of polymers with inorganic materials or organic fillers with certain geometries (fibers, spheres, particles) (AZEREDO, 2009). Nanocomposites are a class of materials formed by hybrids of organic and inorganic materials, where the inorganic phase is dispersed at the nanometer level in a polymeric matrix. The inorganic phase further used to prepare polymer nanocomposites is montmorillonite clay (MMT) of natural origin. This shows good lamination capacity coupled with high solvent resistance and thermal stability required for polymerization processes and extrusion, factors that led to its popularization as filler for nanocomposites with proven efficacy. Generally, conventional composites involving a high amount of inorganic filler, greater than 10 % w/w, and could have as a consequence an increase of losses in stiffness and elongation properties and toughness. Already nanocomposites show an improved in mechanical and thermal, using small amounts of clays (OKAMOTO; RAY, 2003). This is due to the fact that while in polymers containing conventional fillers, clays particles with dimensions in order of micrometers are encapsulated in the polymeric matrix the nanocomposite particles are finely divided in smaller anisotropic nanolayers. The uniform dispersion of the nanoparticles leads to a large interfacial area, which changes the molecular mobility, relaxation behavior and thus the thermal and mechanical properties of the material (AZEREDO, 2009).

Various polymers have been used for the preparation of nanocomposite polymer/clay, among which, one of the most used is polyethylene (PE) due to its excellent properties: low weight, low cost and good processability. The nanocomposite polymer/clay generally exhibit attractive properties in terms of optical, electrical and barrier, and reduced flammability of resins in which that are employed (ARAÚJO et al., 2008).

Various inorganic nanoparticles have been recognized as additives to improve performance of polymers. Some examples of such particles are represented by nanoclays, polymer synthetic nanofibers, carbon nanotubes and nanocelulose. Among these, so far inorganic solids such as clay have attracted some attention in the packaging industry. This fact is not only due to its availability and low cost, but also due to its significant improvements and relative ease of processing (SORRENTINO, GORRASI; VITTORIA, 2007).

The main role of some nanoparticles is to improve the mechanical and barrier properties of polymers for packaging materials, but there are other structures responsible for different functions such as antimicrobial properties, immobilization of enzymes and biosensors (AZEREDO, 2009).

Azeredo (2009) has reviewed the use of various nanoparticles that are capable of improving the mechanical and barrier properties of packaging materials. Among them we can highlight: bentonite, organoclays, montmorillonite and silica. Some industries have incorporated nanoclays in nylon-6 to improve the barrier properties (BRODY, 2007). Other authors have reported other benefits such as increased glass transition temperature and temperature of degradation of the polymers, on the other hand, a small disadvantage of the nanoclays is the decrease of transparency (AZEREDO, 2009).

Another advantage of the incorporation of nanoparticles into polymers is the formation of nanocomposites with antimicrobial property. The nanocomposites most commonly used as antimicrobial film for food packaging using silver nanoparticles. Silver nanoparticles have been incorporated into polymeric materials as cellulose acetate (CHOU et al., 2005), polyimide (DENG et al., 2008), polyamide (DAMM et al., 2007) and poly (2-ethyl-2-oxazoline) (KANG et al., 2006). Besides the antimicrobial properties Mbhele et al. (2003) reported the ability of silver nanoparticles in improving mechanical and thermal properties, increasing stability, and the glass transition temperature of polyvinyl alcohol matrices.

Azeredo (2009) cites studies that report the antimicrobial activity of chitosan nanoscale and also the use of nisin for developing antimicrobial films.

Titanium dioxide (TiO_2) is another compound which has antimicrobial capacity and can be used alone or in combination with silver. Cheng et al. (2006) obtained good antimicrobial properties of nanocomposites with nanoparticles of TiO_2/Ag^+ in PVC. Amna et al. (2013) made a characterization of NiO/TiO_2 composite nanofibers and their antibacterial activity. TEM analysis demonstrated that the exposure of the selected microbial strains (*Staphylococcus aureus, Escherichia coli, Salmonella* Typhimurium and *Klebsiella pneumoniae*) to the composite nanofibers led to disruption of cell membranes and depressed the activity of some membranous enzymes, which caused bacteria to die eventually. These researches stated that surface modification using NiO and TiO2 composite nanostructures is an innovative combination to enhance food safety.

Bionanocomposites

The use of bionanocomposites for food packaging not only protects the food and increases its lifetime but it can also be considered a more environmentally friendly solution, because it reduces the requirement of plastics use as packaging materials. Most traditional packing materials are made from non-degradable materials, which increases environmental pollution, in addition to consume fossil fuels for its production. However, the present biodegradable films exhibit poor mechanical and barrier properties, these properties must be improved before they can substantially replace traditional plastics (THARANATHAN, 2003; SUYATMA et al., 2004) and thus help manage worldwide waste problem (SORRENTINO, GORRASI; VITTORIA, 2007). The main natural polymers that can be used in the manufacture of bionanocomposites are starch, cellulose, polylactic acid, gelatin, collagen and chitosan. Regarding plasticizers may be used glycerol, vegetable oils and triethylcitrate. These bioplastics has the major advantage that they are easily degraded by microorganisms resulting in natural products.

Cellulose is a polymer strong, cheap widely available in addition to being environmentally friendly is easy to recycling and required low power consumption for their manufacture. Cellulose nanofibers can be used for making composites of low cost, lightweight and with high strength. Its barrier property to water vapor can be improved by the addition of nanoparticles. Cellulose nanofibers have been reported as capable of improving the thermal properties of polymers (AZEREDO, 2009) .

Kriegel et al. (2009) have developed a methodology using electrospinning technique for making biodegradable green food packaging from chitin. These strong and naturally antimicrobial nanofibers were used for developing the green food packaging.

Nanoparticles of zein can be used as carriers for compounds of edible flavor or for the encapsulation of nutraceuticals as well to improve the resistance of plastics and bioactive food packaging (TORRES-GINER, GIMENEZ; LAGARON, 2008). Control of uniformity and organization of zein films at the nanoscale is crucial in terms of mechanical and traction properties. Park et al. (2002) prepared films from blends of thermoplastic starch with nanoclay and the resulting properties were investigated. They found that the strong interaction between the thermoplastic starch and nanoclay improved the tensile strength and reduced permeability to water vapor compared with the thermoplastic starch without the addition of nanoclay.

Biopolyesters are another important class of biodegradable polymers formed from biologic monomers, including polylactic acid (PLA) and polixidroxibutirato (PHB). Biopolyesters are biodegradable and biocompatible and can form films or be molded into objects (THARANATHAN, 2003). However, applications of biopolyesters for food packaging have some major limitations which are due to its gas barrier properties relatively poor and fragility. In an attempt to overcome these limitations, nanoclays have been used as fillers in the matrix of biopolyester forming nanocomposites structures (CHEN et al., 2003). Cabedo et al. (2006) demonstrated that addition of nanoclay (kaolinite), into polylactic acid films improved thermal stability without decreasing mechanical and barrier properties of the nanocomposite. With these positive results it is expected that potential applications in food packaging of these polymers increase.

Carbon nanotubes

Carbon nanotubes can be incorporated into polymer structures to increase their mechanical properties in terms of tensile strength and elasticity (ELKIN et al., 2005). A carbon nanotube (CNT) is characterized by winding one or more graphene sheets concentrically with diameter in nanometer dimensions, with hollow inner cavity (ZARBIN, 2007) indicating the possibility to accommodate active substances such as volatile antimicrobial which must be encapsulated for use.

Some research made with polypropylene and polyethylene show that the addition of carbon nanotube in the polymer matrix increases the elasticity and mechanical strength of nanocomposite (BAO; TJONG, 2008; LIANG et al., 2008).

Carbon nanotubes also exhibit antimicrobial properties. Direct contact with aggregates of carbon nanotubes is fatal for *Escherichia coli*, possibly due to cell disruption by nanotubes causing irreversible damage (KANG et al., 2007). On the other hand, there are studies that suggest that carbon nanotubes would be cytotoxic to human cells when in contact with skin and lungs. Thus, it is necessary to know the effects of carbon nanotubes on health when ingested because of the possibility of diffusion of nanotubes present in packaging for food (AZEREDO, 2009).

The toxicity of carbon nanotubes is related to its geometric structure. It has been demonstrated that they cause necrosis, cell degeneration and apoptosis in cell lines of macrophages (BYSTRZEJEWSKA-PIOTROWSKA, GOLIMOWSKI; URBAN, 2009). Regarding the diffusion of these compounds, further studies are needed to reach a conclusive statement. There is an obstacle in determining the diffusion of nanoparticles into food mainly due to the lack of methods for the detection of nanoparticles in food matrices (BOUWMEESTER et al., 2009).

Carbon nanotubes are also used for removing various toxic compounds from water, among them we can cite: arsenic, lead, copper, cadmium and bisphenol A (BYSTRZEJEWSKA-PIOTROWSKA, GOLIMOWSKI; URBAN, 2009).

Nanocomposites for paper production

One area of the paper industry that can benefit from advances in nanotechnology is the development of high value-added coatings constructed from highly organized structures at the nanoscale. Self-organization of layer-by-layer (LBL) aqueous solutions is a versatile and relatively simple strategy for the construction of an organized structure on a solid substrate. The driving force for the synthesis of multi-layer is the electrostatic attraction between oppositely charged molecules. Polyelectrolyte multilayer structures, polyelectrolytes and nanostructures (nanospheres and clays), polyelectrolytes and carbon nanotubes have been reported. The technique of self-organization of LBL is used to enhance the strength of dry paper by constructing multilayers of polyelectrolytes on wood fibers. Besides the strength of dry paper, wet paper strength is important in certain products in the area of hygiene and paper packaging, which require strength when they are wet (OU et al., 2007)

Ou et al. (2007) evaluated the use of LBL technique in the construction of multilayer of complexes polyelectrolyte/nanoclay in paper to modify their water repelling properties and increase the strength of wet paper. These authors justify the use of clay for to be a cheap source of polyanionic material. The modified paper contained 16 bilayer of the complex poly(allylamine hydrochloride)/ kaolinite on the surface. The paper sheets modified by multilayer complex polyelectrolyte/nanoclay changed wetting characteristics of hydrophilic to hydrophobic. The wet paper strength increased by over 270 % compared with the unmodified paper. The average particle size of the clay suspension used was 235.7 nm. The authors found that the greater the number of layers deposited more hydrophobic paper became. The increase of wet paper strength reported in this study is in part due to increased hydrophobicity of the surface of the paper sheet which slows down the attack by water and partly because of the presence of the polyelectrolyte used which is considered as a reinforcing additive for forming crosslinks.

Johnston et al. (2008) developed a composite material of nano-strutured calcium silicato (NCS) to provide effective thermal buffering for paperboard packages during the transport and temporary storage of chilled perishable food from the supplier to the market. The boxes produced with the composite NCS provide thermal protection adequate to maintain the temperature within the box at 10 ° C for 5 h after external temperature has increased to 23 °C. The composite therefore provides sufficient thermal buffering to ensure perishable food in a paperboard container remains below 10 °C during transport and temporary storage en route from the supplier to the market.

Toxicology

It is not yet known whether consumption of foods containing nanomaterials poses a significant health risk. This will depend on the toxicity of the nanomaterial used, the rate of diffusion and the consumption rate of the particular food (CUSHEN et al., 2012).

Nanoparticles (NPs) may be present in foods as suspensions (most solid in liquid) or emulsion (two liquid phases); major NPs used in food chain are the metals or oxides of metals such as silver, copper, zinc oxide and titanium oxide. These particles are known to have various structures and shapes: spherical, tubular, irregular, non-spherical or may exist in clusters. These characteristics are important in relation to the potential risks to health and environment, and determine their fate and behavior in the environment, humans and in other organisms (BOUWMEESTER et al., 2009).

In the year of 2006 a report by the Institute of Food Science and Technology (IFST, 2006) recommended the use of nanoparticles in food sector only after its safety has been proven through rigorous testing. Governments should consider the appropriate labeling and should also define and set standards that will help to increase consumer acceptability (SOZER; KOKINI, 2009).

Bouwmeester et al. (2009) notes that little is known about the safety of using nanotechnology in the agro-food area. Although the potential beneficial effects of nanotechnology are well described, the toxicological effects of nanoparticles and their impacts are still poorly understood. These authors cite some research topics that may contribute to a risk assessment of nanotechnology and nanoparticles in food: establish a definition for nanoparticles to facilitate discussions, prioritize research and exchange of study results; develop analytical tools for nanoparticle characterization in complex biological matrices such as food; evaluate the effects of nanoparticle toxicity and assess the validity of the test systems used today after oral exposure; estimate consumer exposure to nanoparticles. Some studies have shown that in fact there are reasons to suspect that nanoparticles may exhibit toxic effects in biological systems (NEL et al., 2006; OBERDÖRSTER et al., 2005; DONALDSON; SEATON, 2007).

Commercially available food storage bags containing Ag nanoparticles were filled with four kinds of food simulating solutions to test for diffusion (HUANG et al., 2011). Results indicated that diffusion of Ag nanoparticles from the polyethylene bags into the food simulating solutions had occurred and that the amount of diffusion increased with storage time and temperature. This result may impact negatively on the progress of such packaging materials.

Many researchers have found that for high doses of different nanoparticles cytotoxic effects are dose and time dependent. Regarding the toxicity potential of the nanoparticles to the reproductive system, experimental data suggest that the NP cross the blood testicles barrier and are deposited there and probably has adverse effects on sperm (MCAULIFFE; PERRY, 2007). A study from Monteiller et al. (2007) shows that toxicities of nanoparticles and large particles were similar when the dose was expressed in surface area.

Although nanomaterials can be toxic and cause harm some research indicates that depending on processing, nanomaterials products without harmful effects can be obtained (ZHANG et al., 2003). For example, the toxicity of selenium is significantly reduced as their size is reduced to nanoscale. It was also reported that administration of carbon nanotubes in the trachea of mice can cause death and that the doping of carbon nanotubes with nitrogen reduced its toxicity and the risk of death, preparing the way for the use of this technology in food packaging. More research on the toxicity of nanoparticles in contact with food, however, should be taken to dissipate doubts. Although most studies were generally about nanotoxicity of materials or non-food consumer products, the relevant results of these studies can be used for understanding the potential toxicity of foods using nanotechnology (CHAU, WU; Yen, 2007).

CONCLUSION

In order nanotechnology to be used to their full potential, they must be accepted by consumers. Nowadays, the potential risks of nanomaterials to human health and the environment are poorly understood. Thus, further studies on the applications of nanotechnology in food processing and packaging, toxicity, analysis of risk and benefit are needed to address the lack of knowledge, sustaining the growth of nanotechnology in the food industry and packaging and avoid any danger to consumer health. Based on current knowledge about the effects of the use of nanotechnology in the food industry and packaging, the discussion about the benefits and risks are still long. Other issue related to the use of nanotechnology not only in the food industry as in other areas is the release of these nanomaterials into the environment and the disposal of such materials. These nanoparticles have already has been called "nanowaste". Nanoparticles released into the environment can reach water, soil and air may persist for long periods or be ingested by organisms may lead to contamination of the environment and humans.

RESUMO: A nanotecnologia envolve a manipulação da matéria em uma escala muito pequena, geralmente entre 1 e 100 nanômetros. Ela explora novas propriedades e funções que ocorrem na matéria nesta escala nanometrica. A aplicação da nanotecnologia nas áreas de alimentos, embalagens para alimentos e segurança alimentar têm crescido rapidamente. Estas aplicações incluem a detecção de microrganismos, proteção ambiental, purificação de água, encapsulamento de nutrientes e embalagem para alimentos. A nanotecnologia está abrindo novas possibilidades para a indústria de alimentos, mas, a entrada de nanopartículas na cadeia alimentar pode resultar em um acúmulo de contaminantes que podem ser tóxicos e prejudicar a saúde humana. Esta revisão enfoca a nanoencapsulação de compostos bioativos, nanosensores, especialmente para detecção de patógenos em alimentos, aplicação da nanotecnologia na área de embalagens para alimentos e destaca alguns aspectos sobre toxicologia.

PALAVRAS-CHAVE: Nanocompostos. Embalagens de alimentos. Nanosensores. Nanoencapsulação. Nanocompósitos.

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