Chapter 6
Nanotechnology in Food Packaging

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Abstract Nanotechnology promises many interesting changes for better life. Nanotechnology can be used to improve health, wealth, products and quality of life. Food nanopackaging is still a rather unexplored field of nanoscience and food science. Here I review developments in nano-packaging. This chapter describes first biobased food packaging for biodegradable packaging. Biobased packaging is indeed an alternative to conventional packaging with non-degradable plastic polymers that are a threat to the environment. Biobased packaging reduces waste, extend the shelf life, and enhance food quality. The next section discusses nanomaterials that improve packaging, such as better barrier properties, mechanical strength, flexibility and stability. Active packaging refers to the use of active materials such as antimicrobials and oxygen scavenging reagents. Smart packaging is the use of nanosensors and nanodevices that detect freshness or contaminants in foods or monitor changes in packaging conditions or integrity. The last section discusses safety issues and heath concerns of nanopackaging.

Keywords Nanotechnology • Food packaging • Sensors • Nanocomposites • Nanoparticles

6.1 Introduction

Nanotechnology involves the fabrication, manipulation and characterization of structures, devices or materials at the nano size, approximately 1–100 nm in length, that have at least one dimension. When particle size of material is reduced into nano size, the resulting material exhibits physical and chemical properties that are significantly different from the properties of macroscale materials composed of the same substance. Therefore, it would seem illogical that structures in the size of 1–100 nm would not only exist but would also have implications and applications that could

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Fig. 6.1 Key functions of packaging systems, i.e. container of the product, preservation and protection of the product quality, presentation and identification of the product as sales element, facilitation for transportation and distribution of the product, and information of the product to the consumers

be essential to humankind (Sozer and Kokini 2009; Ravichandran 2010). Nanotechnology promises many interesting changes to improve health, wealth and quality of life, as well as reducing impact on the environmental.

Packaging systems are those products which are manufactured with any material in order to protect, to contain, to manipulate, to distribute, to transport and to identify each article along its supply chain, from raw materials to end users (Fig. 6.1). These functions are compulsory to define accurately any kind of packaging, however, according to the types of products which have to be packed and preserved, a wide range of requirements are also needed, such as mechanical, thermal and barrier properties. Due to the range of advanced functional properties of nanomaterials that can bring to packaging materials, therefore, nanomaterials are increasingly being used in the food packaging industry. It was reported that around 500 nanopackaging products are estimated to be in commercial use, while nanotechnology is predicted to be used in the manufacture of 25 % of all food packaging within the next decade (Reynolds 2007). In nano-packaging, it can also be designed to release antimicrobials, antioxidants, enzymes, flavors and nutraceuticals to extend shelf life (Cha and Chinnan 2004). The new nanotechnology products for food packaging were in the pipeline and some anti-microbial films to improve the shelf life of food and dairy products, have already been entered the market (El Amin 2005).

Novel food packaging technology is by far the most promising benefit of nanotechnology in the food industry in the near future, as described very recently by Dasgupta et al. (2015) regarding application of nanotechnology in the agro-food sector, as one of the fastest growing fields in nano-research. Furthermore, it showed by recent research trends in food processing, packaging, nutraceutical delivery, quality control and functional food. In this field many organizations, scientists, inventors as well as industries are coming up with new techniques, protocols and products that have a direct application of nanotechnology in agriculture and food products (Dasgupta et al. 2015). In food packaging, by applying nanotechnology, companies are already producing packaging materials that are extending the life of food and drinks and improving food safety. Food packaging and monitoring are major focus of food industry–related nanotechology research and development (Brody 2003). The leading development in food packaging is active and smart packaging that promises to improve food safety and quality and optimizes product shelf life (Kuswandi et al. 2011). In active and smart packaging, many companies and universities are developing packaging that would be able to alert if the packaged food becomes contaminated, respond to a change in environmental conditions, and self-repair holes and tears.

Currently in packaging industries, the largest part of materials used is non-degradable petroleum based plastic polymer materials. As a result, this non-degradable food packaging materials, represent a serious problem on the global environmental (Kirwan and Strawbridge 2003). Therefore, the use of bio-based packaging materials, such as edible and biodegradable films from renewable resources (Tharanathan 2003), could at least to some extent solve the waste problem by reducing packaging waste and also extend the shelf life, which in turn, enhance food quality. In this respect, by means of the correct selection of materials and packaging technologies, it is possible to keep the product quality and freshness during the time required for its commercialization and consumption (Stewart et al. 2002; Kuswandi et al. 2011).

However, the use of bio-based materials for food packaging has been very limited currently. This is due to natural polymers have the poor barrier and weak mechanical properties. Therefore, these natural polymers were frequently blended with other synthetic polymers or chemically modified with the goal of extending their applications in packaging (Petersen et al. 1999). In addition, like conventional packaging, bio-based packaging must serve a number of important functions, such as containment and protection of food, maintaining its sensory quality and safety, and communicating information to consumers (Robertson 1993). Other nanotechnology that could help to reduce waste of the packaging associated with processed foods is the application of nanocomposites in packaging. The application of nanocomposites promises to enhance the use of edible and biodegradable films in packaging (Lagaron et al. 2005; Sinha Ray and Bousmina 2005) and will support the preservation of fresh foods, which in turn, extending their shelf life (Vermeiren et al. 1999).

Nanotechnology was used to create tiny particles in the film, to improve the transportation of some gases through the plastic films to pump out unwanted carbon dioxide that would shorten the shelf life of the foods. In addition, they are also looking at whether the film could also provide barrier protection and prevent gases such as oxygen and ethylene from deteriorating foods (Silvestre et al. 2011; Duncan 2011). Nowadays, numerous food and pharmacy researchers are working to applied

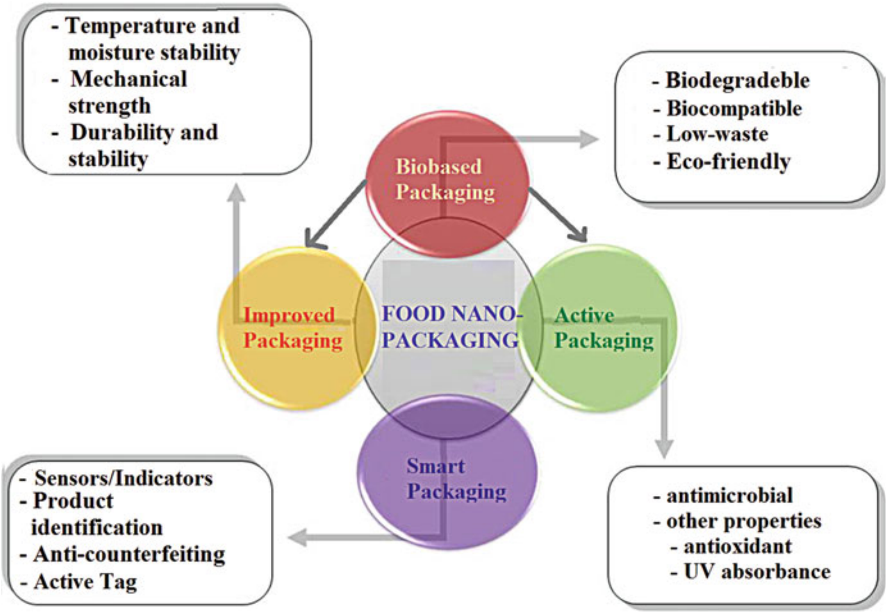

Fig. 6.2 Food nano-packaging, classification, functions and features, including: bio-based packaging for biodegradable, biocompatible, low-waste and eco-friendly; improved packaging in term of mechanical strength, durability and flexibility, and temperature and moisture stability; active packaging based nanocomposites as active material, e.g. antimicrobial and other properties, e.g. antioxidant, UV absorbance etc.; and smart packaging with nanosensors as intelligent function in packaging for the detection of food relevant analytes (gasses and small organic molecules), active tag and product identification and anticounterfeiting. Biobased packaging can also be used in improved and active packaging

nanotechnology with the aim to improve delivery of medicines, vitamins or fragile micronutrients in the daily foods by creating tiny edible capsules based nanoparticles that release their contents on demand at targeted spots in the body. Therefore, it will provide significant health benefits, such as reduced risk of heart attack, stroke, neurodegenerative diseases and cancer (Koo et al. 2005; Yan and Gilbert 2004). In addition, nanoparticles may be used to introduce multiple functionalities like color and odors but also to act as reservoirs for the controlled release functions of drugs or fungicides (Lee et al. 2003). Although promising results were obtained, the road to successful bio-nanocomposites is still long development (Sorrentino et al. 2007).

Despite a tremendous growth in this field, food packaging nanotechnology is still rare subfield of the nanotechnology spectrum as well as in the food science and technology. This article addresses to fill this knowledge shortage by providing a comprehensive review of current developments in nano-packaging technology as it applies to foods and food-related systems, focusing specifically on applications which are most likely to enjoy consumer acceptance and regulatory attention in the immediate future as given in Fig. 6.2. Covered topics include bio-based packaging for biodegradable packaging for environmental concern; improved packaging for improved barrier properties, mechanical strength and flexibility as well as stability; active packaging for antimicrobials, and oxygen scavenging; smart packaging for intelligent functions, such as sensors/indicators that detect freshness or contaminants in foods or monitor changes in packaging conditions or integrity. Safety issues on specific health concerns related to these various applications are also briefly discussed. The article concludes with a brief overview of the outlook of the nanopackaging materials in the future.

6.2 Biobased Packaging

Biobased packaging is biodegradable packaging films that are applied to food products to control moisture transfer and/or gas exchange in order to improve safety and preserve the nutritional and sensory quality (Siracusa et al. 2008). These packaging materials are perceived to be more environmental friendly than the other conventional packaging films. Like any kind of packaging, bio-based packaging provides a barrier between a food product and its environment, thereby protecting it against unwanted effects of microorganisms, ambient relative humidity and gas conditions. The specific characteristic that distinguishes biodegradable packaging films from other packaging solutions is that they are capable of decaying through the action of living organisms (Del Nobile et al. 2009). This packaging type is generally perceived to be more environmental friendly as the breakdown products are all completely natural, i.e. carbon dioxide, biomass and water. Bio-based packaging does not (or less) use fossil fuels to produce the materials, but uses renewable sources, upon disposal energy can be recovered by incineration.

Commonly, biodegradable plastics that used as materials in bio-based packaging, are polymeric materials in which at least one step in the degradation process via naturally occurring organism's metabolism. Under appropriate conditions of moisture, temperature and oxygen availability, this biodegradation leads to fragmentation or disintegration of the plastics with no toxic or environmentally harmful residue (Chandra and Rustgi 1998). These biodegradable polymers can be classified according to their source: (i) Polymers directly extracted from biomass, such as polysaccharides, proteins, polypeptides, polynucleotides. (ii) Polymers produced by chemical synthesis of bio-based monomers or mixed biomass and petroleum, such as polylactic acid or bio-polyester. (iii) Polymers produced by micro-organism or genetically modified bacteria, such as polyhydroxybutyrate, bacterial cellulose, xanthan, curdian and pullan.

The success concept of bio-based nanocomposite in the area of synthetic polymers has stimulated new research on nanocomposites based on biodegradable polymers for food packaging applications (Sorrentino et al. 2007). Description of biopolymers is available in literature (Kaplan 1998; Doi and Steinbuechel 2002; Steinbuchel 2003; Mohanty et al. 2005; Sorrentino et al. 2007). The problems associated with biodegradable polymers are performance, processing, and cost. This is due to "performance and processing" are common to all biodegradable polymers in

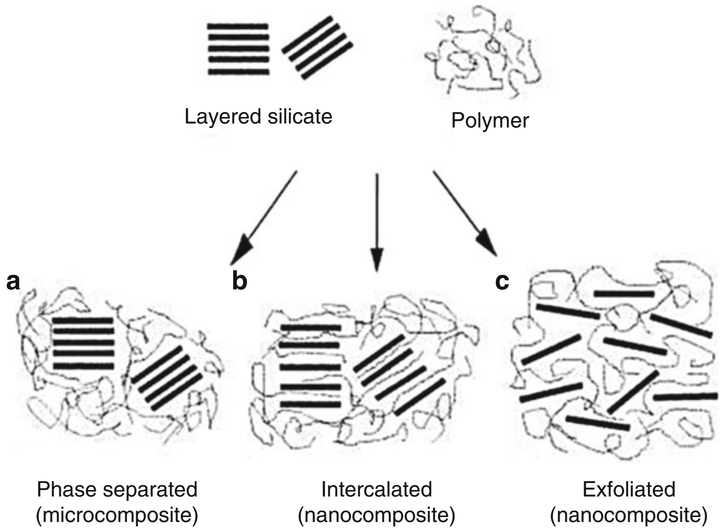

Fig. 6.3 Three types of composites when layered clays are incorporated with the polymer: (**a**) tactoid, phase-separated microcomposite; (**b**) intercalated nanocomposite and (**c**) exfoliated, polymer–clay nanocomposite (Courtesy of Alexandre and Dubois 2000)

spite of their origin (Trznadel 1995; Scott 2000). The problem particularly, brittleness, low heat distortion temperature, high gas and vapor permeability, poor resistance to protracted processing operations have strongly limited their applications. The application of nanotechnology to these polymers could open new possibilities for improving both the properties and the cost-price-efficiency.

Three main types of composites can be formed when the layered clay is incorporated with a polymer, as given in Fig. 6.3 (Alexandre and Dubois 2000). Types of composites formed mostly depend on the nature of the components used (i.e. layered silicate, organic cation and polymer matrix) and the method of preparation. Micro-composites are formed when the polymer chain is unable to intercalate into the silicate layer, which therefore phase separated polymer/clay composites are formed as shown in Fig. 6.3a. Intercalated nano-composite is obtained when the polymer chain is inserted between clay layers such that the interlayer spacing is expanded, but the layers still bear a well-defined spatial relationship to each other as shown in Fig. 6.3b. Exfoliated nano-composites are formed when the layers of the clay have been completely separated and the individual layers are distributed throughout the polymeric matrix as shown in Fig. 6.3c.

Due to nanometer-size particles obtained by dispersion, these bio-nanocomposites can remarkably improved mechanical, thermal, barrier and physico-chemical properties, when compared with the starting polymers and microscale composites. As an example, it shows great promise in providing excellent barrier properties, due to the presence of the clay layers able to delay the molecule pathway making the diffusive path more tortuous (Bharadwaj 2001). In addition, the preparation and characterization of various kinds of biodegradable polymer nanocomposites showing properties

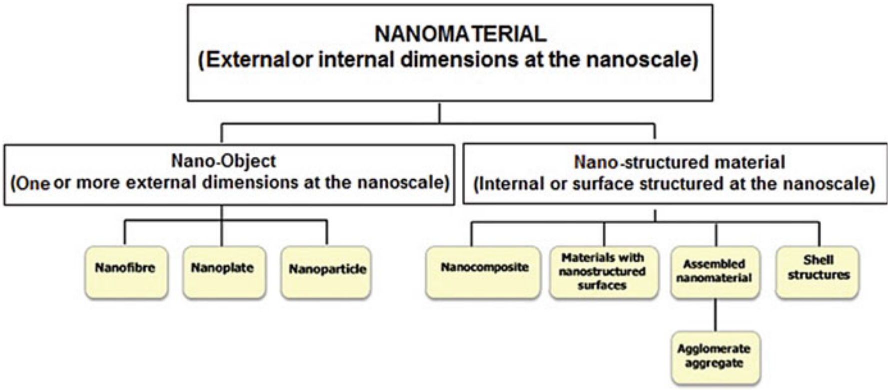

Fig. 6.4 Terminology of nanomaterial used in nano-packaging: (**a**) nano-object, and (**b**) nano-structured material. Nano-object consist of nanofibre, nanoplate and nanoparticle, while nano-structured material consist of nanocomposite, material with nanostructured surfaces, assembled nanomaterial and shell structure

suitable for a wide range of applications (Sinha Ray and Bousmina 2005). Currently, the most studied bio-nanocomposites suitable for packaging applications are starch and derivates, i.e. polylactic acid, poly(butylene succinate), polyhydroxybutyrate, and aliphatic polyester. Thus, bio-based packaging can also be used for improved packaging and active packaging.

In general, the application of the nanotechnology in polymer based packaging that used nanoparticles can be divided into two categories: (i) nano-object materials (materials with nanoscale dimensions less than 100 nm) and (ii) nano-structured materials as shown in Fig. 6.4. In nano-objects, mostly nanomaterials used as a filler (nano-reinforcement), which involves the use of nanoplate, nanoparticles and nano-fibers (such as metal oxides nanoparticles, nanoclays, carbon nanotubes and other fillers like metallic nanoparticles). While in nano-structured materials, the nanomaterials are dispersed into a polymer matrix as nanocomposites.

Actually, the applications of nanomaterial materials in packaging are developed mainly into three applications: (i) improved packaging, such as barrier performance pertaining to gases such as oxygen, carbon dioxide, and ultraviolet rays, as well as to add strength, stiffness, dimensional stability, and heat resistance; (ii) active packaging, such as antimicrobial or other properties (e.g. antioxidant, UV absorbance) with intentional release into- and consequent effect on the packaged food in term of taste, freshness and self life; (ii) smart/intelligent packaging, such as oxygen indicators, freshness indicators and pathogen. The three main applications of nanomaterial in food packaging was also described as the research trends of food packaging with the help of nanotechnology (Ranjan et al. 2014), where in food packaging mainly related with nano-reinforcement, nanocomposite active packaging and nanocomposite smart packaging. Table 6.1 gives an overview of these potential applications of the nanotechnology in food packaging. In improved packaging, the presence of nanoparticles in the polymer matrix materials improves the properties

Table 6.1 Packaging applications of nanomaterials: (a) improved packaging, (b) active packaging and (c) smart packaging

Applications	Descriptions	Key nanomaterials
Improved packaging	Incorporation of nanomaterials into the packaging to improve physical performance, durability, barrier properties, biodegradation, biocompatibility and environmental friendly	Clays, SiO2
Active packaging	Incorporation of nanomaterials with antimicrobial or other properties (e.g. antioxidant, UV absorbance) with intentional release into- and consequent effect on the packaged food in terms of taste, freshness and self life	Ag, TiO_2
Smart packaging	Incorporation of nanosensors to monitor and report on the condition of the food (e.g. oxygen indicators, freshness indicators and pathogen)	High variability

of the material. Besides barrier properties, strength, stiffness, dimensional stability and heat resistance of materials can be improved due to nanoclays or SiO_2 nanoparticles addition. In active packaging, nanoparticles as active agents are being developed specially for antimicrobial packaging applications; silver, gold and metal oxide nanoparticles are the most studied nanoparticles with antimicrobial function, with silver nanoparticles already found in several commercial applications. Moreover, they can be suitable for other active packaging fields such as ethylene removers. In intelligent packaging, nanoparticles can be applied as reactive particles in packaging materials to inform about the state of the packaged product. The so-called nanosensors are able to respond to external stimuli change in order to communicate, inform and identify the product with the aim to assure its quality and safety. The recent developments for polymer nanomaterials for smart food packaging include oxygen indicators, freshness indicators and pathogen.

6.2.1 Starch

Starch is a potential raw material and renewable source, due to its cyclic availability from many plants and excessive production related to current needs and its low cost (Smits et al. 1998; Gonera and Cornillon 2002). There are many ways to using starch as packaging material (Kim and Pometto 1994). Starch alone does not form films with appropriate mechanical properties without chemically modification or plasticized. If starch is treated in an extruder by both thermal and mechanical energy, it can be converted to a thermoplastic material. In the thermoplastic starches production, plasticizers are used to reduce intra-molecular hydrogen bonds and to provide stability to product properties. Corn is the primary source of starch for bioplastics, although more recent global research is evaluating the potential use in bioplastics for starches from potato, wheat, rice, barley, oat and soy sources.

Since its hygroscopic nature, starch-based absorbent pads are used as a potential alternative to conventional absorbent for meat exudation (Smith et al. 1995). Films based starch, could be employed as packaging for perishable foods (such as fruits and vegetables, snacks or dry products). However, in these applications, efficient mechanical, oxygen and moisture protection is needed. Thermoplastic starch (TPS) alone often cannot meet all these requirements. Due to its hydrophilicity, its performance changes during and after processing, due to changes in the water content. To overcome this drawback, the used of clay as filler have been reported as follows.

Clay, as potential filler, has been used for improving the properties of TPS in such applications (De Carvalho et al. 2001; McGlashan and Halley 2003; Wilhelm et al. 2003; Chen and Evans 2005; Yoon and Deng 2006). Starch/clay nanocomposite films have been obtained by dispersing montmorillonite nanoparticles via polymer melt processing techniques. It has been shown that both the tensile strength and the elongation at break of TPS were increased with the presence of small amounts (>5 %) of sodium montmorillonite. Furthermore, the temperature of decomposition was increased, while the relative diffusion coefficient of water vapor was decreased (Park et al. 2003). Mechanical characterization results also show an increase of modulus and tensile strength. In addition, the conformity of the resulting material samples with actual regulations and European directives on biodegradable materials was verified by migration tests (Avella et al. 2005).

6.2.2 Polylactic Acid

The conventional chemical synthesis used for the production of polymers gives a wide variety of biopolyesters. Polylactic acid is thermoplastic aliphatic polyester, biodegradable and the polymer with the highest potential for a commercial major scale production of renewable packaging materials. Polylactic acid is derived from renewable resources by means of a fermentation process using sugar from corn, followed by either ring-opening polymerization or by condensation polymerization of lactic acid. It is one of the most important biocompatible and biodegradable polymers in a group of degradable plastics. Polylactic acid represents a good candidate to produce disposable packaging due to its good mechanical properties and process ability (Murariu et al. 2008).

The properties of the polylactic acid material are highly related to the ratio between the two forms (L or D) of the lactic acid monomer. L- polylactic acid is a material with a very high melting point and high crystallinity, whereas a mixture of D- and L- polylactic acid results in an amorphous polymer with a low glass transition temperature. Although polylactic acid is an eco-friendly boiplastic with good biocompatibility, poor hardiness, slow degradation, hydrophobicity, and lack of reactive side-chain groups limit its application (Rasal et al. 2010). Therefore, the tailoring of its properties to reach end-users demands is required. In addition, mechanical properties being better than or comparable to conventional plastics, controlled surface properties such as hydrophilicity, roughness, and reactive functionalities are the successful implementation of polylactic acid as material in food packaging. Many has been reported for the preparation of polylactic acid/clay nanocomposite materials (Choi et al. 1997; Ogata et al. 1997; Bandyopadhyay et al. 1999; Pluta et al. 2002; Sinha Ray et al. 2002a, b, 2003; Chang et al. 2003; Paul et al. 2003).

The incorporation of clays in the polylactic acid to produce a polylactic acid-clay nano-composite to improve polylactic acid's mechanical and properties as well as to accelerate its degradation rate have been developed (Bandyopadhyay et al. 1999). Solvent casting of mixtures of polylactic acid and organophilic clay in chloroform resulted in materials with an enhanced crystallization tendency and increased Young's modulus (Ogata et al. 1997). However, the glass transition temperature increases only slightly with increasing clay content. This may be due to the microcomposite structure rather than nanocomposite structure. As a matter of fact, a strong tendency of tactoids formation was observed. The polylactic acid/layered silicate nanocomposites, prepared by simple melt extrusion, exhibited remarkable improvement of material properties in both solid and melt states compared to the matrix without clay (Sinha Ray et al. 2002a).

The combination of polylactic acid and clays, at the nano-scale, often results in remarkably improved mechanical and functional properties compared with pure polylactic acid or conventional composites (Okamoto et al. 2001). Different polylactic acid/silicate nano-composites have been explored: montmorillonites and fluorohectorites clays, were blended with the polylactic acid (Oliva et al. 2007; Aguzzi et al. 2007). Nanocomposites of the polylactic acid and polylactic acid/polycaprolactone blends were obtained by melt-mixing with a properly modified kaolinite (Cabedo et al. 2006). In this case, all nanocomposites showed an improvement in the gas barrier, mechanical and thermal properties with regard to the polymers and blends without clay.

6.2.3 Polyhydroxybutyrate

Polyhydrobutyrate has been the subject of extensive studies as an environmentally friendly polymeric material which is the most popular polyhydroxyalkanoate used in food-packaging. Polyhydrobutyrate is a polymer belonging to the polyesters class that are of interest as bio-derived and biodegradable plastics (Frieder 2010). Polyhydrobutyrate is produced by microorganisms (such as *Ralstonia eutrophus* or *Bacillus megaterium*) (Lenz and Marchessault 2005) and is utilized as an energy storage molecule within the microorganism's cellular structure. Due to its biodegradability and biocompatibility, this biopolyester may easily find industrial applications (Weber 2000; Lenz and Marchessault 2005). Potentially, polyhydrobutyrate offers many advantages over traditional petrochemically derived plastics in packaging applications, since it is compatible with many foods, such as dairy products, beverage, fresh meat products and ready meals. In addition to its complete biodegradability, it possesses better physical properties than polypropylene for food packaging applications and is completely non-toxic. However, as polyhydrobutyrate is a partially crystalline polymer with a high melting temperature and a high degree of crystallinity, then it is brittle and has limited applications (Hankermeyer and Tjeerdema 1999). The poor low-impact strength of polyhydrobutyrate is solved by incorporation of hydroxyvalerate monomers into the polymer to produce polyhydroxybutyrate-co-valerate (Liu et al. 2002). Polyhydroxybutyrate-co-valerate completely degrades into carbon dioxide and water under aerobic conditions (Lenz and Marchessault 2005).

Many papers report the use of polyhydrobutyrate for the preparation of polymer/clay nanocomposite materials (Park et al. 2001; Liu et al. 2002; Maiti et al. 2003; Chen et al. 2004). Instead, the formation of nanocomposite materials from polyhydrobutyrate seems to be difficult, and rather moderate improvements in properties have been reported in the case of polyhydrobutyrate as matrix material (Maiti et al. 2003). These results still have low mechanical properties with a low extension at break, which limits its range of applications. If the properties of the polyhydrobutyrate can be further improved by the addition of a small quantity of an environmentally benign material, this polymer will find numerous applications in packaging.

6.2.4 Polycaprolactone

Polycaprolactone is linear polyester prepared by either ring opening polymerization of 3-caprolactone using a variety of anionic, cationic and co-ordination catalysts or via free radical ring-opening polymerization of 2-methylene-1-3-dioxepane (Pitt 1990). It is a semicrystalline polymer with a high degree of crystallinity (around 50 %). Polycaprolactone exhibits high elongation at break and low modulus. Its physical properties and commercial availability make it very attractive as a material for packaging applications. Polycaprolactone is also interesting for applications in the biomedical (Chandra and Rustgi 1998; Okada 2002; Nair and Laurencin 2007) and agricultural areas (Nakayama et al. 1997).

Because of its low melting point, in conventional applications it must be blended with other polymers (Ishiaku et al. 2002; Lee et al. 2002; Lim et al. 2002). The blended of polycaprolactone with the fillers nanocomposites have been reported literature. The nanocomposites based on polycaprolactone/organically modified layered silicate with better physical properties have been developed (Bharadwaj et al. 2002; Di et al. 2003; Gorrasi et al. 2002, 2004; Tortora et al. 2002).

6.3 Improved Packaging

In improved packaging development, nanomaterials are mixed into the polymer matrix to improve the gas barrier properties, as well as temperature and humidity resistance of the packaging. A variety of nanoparticle reinforced polymers, also termed as nanocomposites have been developed, which typically contain up to 5 % w/w nanoparticles with clay nanoparticle composites with improved barrier properties (80–90 % reduction) for the manufacture of bottles for beer, edible oils and carbonated drinks and films (Chaudhry et al. 2008; Brody 2007). United States Food and Drug Administration (USFDA) have approved the use of nanocomposite in contact with foods (Sozer and Kokini 2009).

6.3.1 Nanocoatings

Coating in food can be defined as thin/film of edible material placed between food components to provide a barrier to mass transfer (Guilbert et al. 1997). These coatings could serve as moisture, lipid, and gas barriers. Coatings are applied and formed directly on the food product either by addition of a liquid film forming solution or by molten compounds (Baldwin et al. 1996). Components of edible coatings can be divided into two categories: water-soluble polysaccharides (hydrocolloids) and lipids. Suitable polysaccharides include cellulose derivatives, alginates, pectins, starches, chitosan and other polysaccharides (El Ghaouth et al. 1991). Many lipid compounds such as animal and vegetable fats have been used to make edible films and coatings. Suitable lipids include waxes, acylglycerols, and fatty acids. Lipid films have excellent moisture barrier properties or as coating agents for adding gloss to confectionery products. Waxes are commonly used for coating fruits and vegetables to retard respiration and lessen moisture loss (Avena-Bustillos et al. 1997).

Edible coatings are currently extensively used on a wide variety of foods, including fruits, vegetables, meats, chocolate, cheese, candies, bakery products, and French fries (Morillon et al. 2002; Cagri et al. 2004; Rhim 2004). However, until now only few research works reported the incorporation nano-particles toward coating films, in order to improve their physical properties. In order to lower the diffusion of oxygen, clay montmorillonite has been added into pectins (Mangiacapra et al. 2005). Similarly, a nanocomposites prepared by gelatin and montmorillonite has been used for considerable improvement of the physical properties (Zheng et al. 2002). An appreciable increase in stability of chitosan/layered nanocomposites was also developed (Darder et al. 2003).

Despite the lack of specific literature data, there is sufficient evidence to establish the beneficial effects of inorganic nanofiller on these materials, among which there are improved retention of flavor, sugars, acids, texture and color, increased stability during shipping and storage, improved appearance and reduced spoilage. Nanoparticles can be used as carrier of antimicrobials and additive. It can also be used to stabilize the additives and efficiently control their diffusion into the food and in the different regions, i.e., surface vs. bulk of a food system. This control can be interesting for long-term storage of foods or for imparting specific desirable characteristics, such as flavor to a food system. In this regards, an edible antibacterial nanocoating, which can be applied directly to bakery goods has also been developed by the U.S. Company Sono-Tec Corporation (El Amin 2007).

6.3.2 *Nanolaminates*

Nanotechnology provides food scientists with a number of ways to create novel nanolaminate films that suitable to be used in the food industry. Generallay, a nanolaminate consists of two or more layers of materials with nanometer dimensions that are physically or chemically bonded to each other. One of the most powerful methods in nanolaminated, is based on the layer by layer deposition technique, in which the charged surfaces are coated with interfacial films consisting of multiple nanolayers of different materials (Decher and Schlenoff 2003). Nanolaminates offer some advantages for the preparation of edible coatings and films over conventional technologies and may thus have a number of important applications within the food and dairy industry (Weiss et al. 2006).

A variety of different adsorbing substances could be used to create the different layers, including natural polyelectrolytes (proteins, polysaccharides), charged lipids (phospholipids, surfactants), and colloidal particles (micelles, vesicles, droplets) (Dasgupta et al. 2016a). It would be possible to incorporate active functional agents such as antimicrobials, anti browning agents, antioxidants, enzymes, flavors, and colors into the films. These functional agents would increase the shelf life and quality of coated foods. The basic functional properties of laminated films depend on the characteristics of the film-forming materials used for their preparation. Like nanocoating, these nanolaminated coatings could be created entirely from edible materials ingredients (proteins, polysaccharides, lipids) by using simple processing operations such as dipping and washing. The composition, thickness, structure, and properties of the multilayered laminate formed around the object could be controlled in a number of ways, including changing of the type of adsorbing substances in the dipping solutions, the total number of dipping steps used, the order that the object is introduced into the various dipping solutions, the solution and environmental conditions used, such as pH, ionic strength, dielectric constant, temperature, etc (Dasgupta et al. 2016b, c; Ranjan et al. 2015, 2016; Maddineni et al. 2015).

6.3.3 *Clay Nanoparticles and Nanocristals*

Nanoclays can be used to improved barrier properties of the food packaging materials by incorporating and embedding inside them. The layered silicates commonly used in nanocomposites consist of two-dimensional layers, which are 1 nm thick and several microns long depending on the particular silicate. Its presence in polymer formulations increases the tortuosity of the diffusive path for a penetrated molecule (Fig. 6.5), which in turn, providing excellent barrier properties (Bharadwaj et al. 2002; Cabedo et al. 2004; Mirzadeh and Kokabi 2007). The interaction between layered silicates and polymer chains may produce two types of ideal nanoscale composites as shown in Fig. 6.3. The intercalated nanocomposites result from the penetration of polymers chains into the interlayer region of the clay,

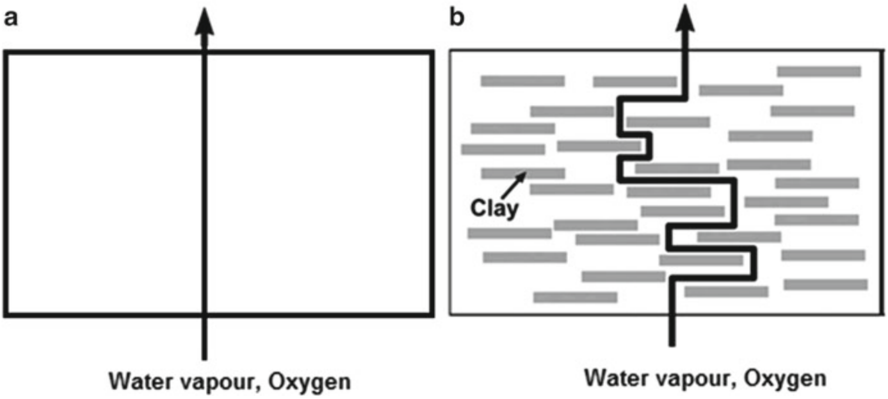

Fig. 6.5 Illustration of the "tortuous pathway" created by incorporation of exfoliated clay nanoplatelets into a polymer matrix film. In a film composed only of polymer (**a**), diffusing gas molecules on average migrate via a pathway that is perpendicular to the film orientation. In a nanocomposite (**b**), diffusing molecules must navigate around impenetrable particles/platelets and through interfacial zones which have different permeability characteristics than those of the virgin polymer. The tortuous pathway increases the mean gas diffusion length and, thus, the shelf-life of spoilable foods (Adapted from Adame and Beall 2009)

resulting in an ordered multilayer structure, with alternating polymer/inorganic layers at a repeated distance of a few nanometers (Weiss et al. 2006). The exfoliated nanocomposites involve extensive polymer penetration, with the clay layers delaminated and randomly dispersed in the polymer matrix (Luduena et al. 2007). Exfoliated nanocomposites were the best properties due to the optimal interaction between clay and polymer (Adame and Beall 2009; Alexandre et al. 2009).

The most widely studied type of clay fillers is montmorillonite, an hydrated alumina-silicate layered clay consisting of an edge-shared octahedral sheet of aluminum hydroxide between two silica tetrahedral layers (Weiss et al. 2006). The imbalance of the surface negative charges is compensated by exchangeable cations (typically Na^+ and Ca^{2+}). The parallel layers are linked together by weak electrostatic forces (Tan et al. 2008). This type of clay is characterized by a moderate negative surface charge, which is an important factor to define the equilibrium layer spacing. The charge of the layer is not locally constant as it varies from layer to layer and must rather be considered as an average value over the whole crystal (Alexandre and Dubois 2000). Montmorillonite is an effective reinforcement filler, due to its high surface area and large aspect ratio (50–1000) (Uyama et al. 2003).

Mostly nanoclays have been reported to improve the mechanical strength of several polymers (Avella et al. 2005; Chen and Evans 2005; Jawahar and Balasubramanian 2006; Mangiacapra et al. 2006; Russo et al. 2007; Cyras et al. 2008; Yu et al. 2003) and also of biopolymers, making their use feasible as packaging materials (Dean et al. 2007; Marras et al. 2008: Park et al. 2003; Petersson and Oksman 2006; Weiss et al. 2006; Xu et al. 2006). Other benefits have been reported on the performance of a diversity of polymers as resulting from using clay nanoparticles, including increased glass transition (Cabedo et al. 2004; Petersson and Oksman 2006; Yu et al. 2003) and thermal degradation temperatures (Bertini et al. 2006; Cabedo et al. 2004; Cyras et al. 2008; Paul et al. 2003; Yu et al. 2003). Furthermore, the advantage of clay nanocomposite in the packaging material offers improved shelf life, shutter proof, light in weight and heat resistant (Ravichandran 2010).

The minor disadvantages of nanoclays on polymers were decreased transparency (Yu et al. 2003). Some companies in the USA (e.g. Nanocor Inc. and Southern Clay Products, Inc.) was making plastics lighter, stronger, more heat-resistant and with improved barrier against gases, moisture and volatiles by incorporating montmorillonite in nanocomposite production (Moraru et al. 2003). Some industries have incorporated clays in nylon- 6, which is fluid and easily penetrates small spaces between layers. Nylon-6 nanocomposites can achieve oxygen transmission rates almost four times lower than that of neat nylon-6 (Brody 2003). Nanocor and Mitsubishi Gas Chemical (New York) have developed Imperm, a nanocomposite nylon MXD6 with much improved barrier properties, to be used in films and polyethylene terephthalate bottles (Brody 2006, 2007). The nanocomposite material can be used as an oxygen barrier layer in the extrusion manufacturing of bottles for fruit juices, dairy foods, beer and carbonated drinks, or as nanocomposite layers in multilayer films to enhance the shelf life of a variety of foods such as processed meats, cheese, confectionery, cereals, and boil-in-bag foods (Brody 2007; Moraru et al. 2003).

6.4 Active Packaging

In active packaging development, nanomaterials are used to interact directly with the food or the environment to allow better protection of the product. For example, silver nanoparticles and silver coatings can provide anti-microbial properties, with other materials being used as oxygen or UV scavengers. Nano silver, Nano magnesium oxide, nanocopper oxide, nano titanium dioxide and carbon nanotubes are also predicted for future use in antimicrobial food packaging (Chaudhry et al. 2008; Doyle 2006, Miller and Senjen 2008). Antimicrobial packaging for food products which absorbs oxygen has been developed and commercialized by Kodak company (Asadi and Mousavi 2006). Oxygen scavenging packaging using enzymes between polyethylene films have also been developed (Lopez-Rubio et al. 2006). An active packaging application could also be designed to stop microbial growth once the package is opened by the consumer and rewrapped with an active-film portion of the package (Brody 2007).

6.4.1 Antimicrobial Films

The incorporation of antimicrobial compounds (e.g. silver nanoparticles and silver coatings) into food packaging materials has received considerable attention currently. The films with antimicrobial activity could help control the growth of pathogenic and spoilage microorganisms. An antimicrobial film is particularly desirable due to its acceptable structural integrity and barrier properties imparted by the nanomaterial, and the antimicrobial properties contributed by the antimicrobial agents impregnated within the film (Rhim and Ng 2007). Here, the film allows nanomaterials to be able to attach more copies of biological molecules, which confers greater efficiency (Luo and Stutzenberger 2008).

Nanomaterials have been studied for antimicrobial activity so that they can be used as growth inhibitors (Cioffi et al. 2005), killing agents (Huang et al. 2005; Kumar and Munstedt 2005; Lin et al. 2005; Qi et al. 2004; Stoimenov et al. 2002), or antibiotic carriers (Gu et al. 2003). The most common antimicrobial films for food packaging are based on silver nanoparticles, which are well known for its strong toxicity to a wide range of microorganisms, with high temperature stability and low volatility (Kumar and Munstedt 2005). Film based on silver nanoparticles has been produced and their antimicrobial affectivity has been reported.

Nanocomposites with low silver nanoparticles content presented a better increased efficacy against *E. coli* than microcomposites with much higher silver in polyamide 6/silver-nano- and microcomposites (Damm et al. 2007, 2008). Moreover, silver nanoparticles absorbs and decomposes ethylene (Hu and Fu 2003), which may contribute to its effects on extending shelf life of fruits and vegetables. Indeed, nanocomposite polyethylene film with silver nanoparticles retarded the senescence of jujube, a Chinese fruit (Li et al. 2009). A coating containing silver nanoparticles was effective in decreasing microbial growth and increasing shelf life of asparagus (An et al. 2008). Silver nanoparticles increased modulus and strength of a poly(vinyl alcohol) matrix, and improved its thermal properties, enhancing its stability and increasing its Tg (Mbhele et al. 2003). Nanostructured calcium silicate has also been used that adsorb Ag^+ from solution down to the 1 mg/kg level (Johnston et al. 2008) as antimrobial film.

Other materials that have been used as antimicrobial materials are titanium dioxide (TiO_2), carbon nanotubes, nisin and chitosan. TiO_2 is widely used as a photocatalytic disinfecting material for surface coatings (Fujishima et al. 2000). TiO_2 photocatalysis, which promotes peroxidation of the polyunsaturated phospholipids of microbial cell membranes (Maness et al. 1999), has been used to inactivate several food-related pathogenic bacteria (Kim et al. 2003, 2005; Robertson et al. 2005). A TiO_2 powder-coated packaging film has been verified its ability to reduce E. coli contamination on food surfaces, suggesting that the film could be used for fresh cut produce (Chawengkijwanich and Hayata 2008).

Carbon nanotubes have also been reported to have antibacterial properties. Direct contact with aggregates of carbon nanotubes was demonstrated to be fatal for *E. coli*, possibly because the long and thin carbon nanotubes puncture microbial cells, causing irreversible damages (Kang et al. 2007). On the other hand, there are studies suggesting that carbon nanotubes are cytotoxic to human cells, at least when in contact to skin (Monteiro-Riviere et al. 2005) and lungs (Warheit et al. 2004), which would affect people working directly with carbon nanotubes in processing stages rather than consumers. Nevertheless, it is mandatory to know eventual health effects of carbon nanotubes when ingested, since the risk of ingestion of particles incorporated to a food packaging material must be taken into account because of the possibility of migration to food.

Antimicrobial peptides, such as nisin, could also be integrated with layer by layer structures to develop antimicrobial films (Haynie et al. 2006). Nisin acts as a depolarization agent on bacterial membranes and creates pores in lipid bilayers (Sahl et al. 1987). Multilayer peptide nanofilms, which intercalated different peptides designed to be oppositely charged at neutral pH which was much more stable than when the peptide film was stabilized only by electrostatic interactions (Li et al. 2006).

Antibacterial activity of nanoscale chitosan has also been reported (Qi et al. 2004). One possible antimicrobial mechanism involves interactions between positively charged chitosan and negatively charged cell membranes, increasing membrane permeability and eventually causing rupture and leakage of intracellular material. This is consistent with the observation that both raw chitosan and engineered nanoparticles are ineffective at pH values above 6, which would be due to the absence of protonated amino groups (Qi et al. 2004).

6.4.2 Oxygen Scavenging Film

Oxygen (O_2) is responsible for the deterioration of many foods either directly or indirectly. For example, direct oxidation reactions result in browning of fruits and rancidity of vegetable oils. Food deterioration by indirect action of O_2 includes food spoilage by aerobic microorganisms. Therefore, the incorporation of O_2 scavengers into food package can maintain very low O_2 levels, which is useful for several applications, since it will enhance self-life of the food.

Oxygen scavenger films were successfully developed by adding titania nanoparticles (TiO_2) to different polymers (Xiao-e et al. 2004). So that they can be used for packaging a wide variety of oxygen-sensitive products. Attention has particularly focused on the photocatalytic activity of nanocrystalline titania under ultraviolet radiation. Since TiO_2 act by a photocatalytic mechanism, and its major drawback is the requirement of UVA light (Mills et al. 2006).

6.4.3 UV Absorbing Films

Commonly used material as UV absorbing is film based on nanocrystalline titania (TiO_2). The efficacy of TiO_2-coated films exposed to sunlight to inactivate fecal coli forms in water has been demonstrated (Gelover et al. 2006). Metal doping improves visible light absorbance of TiO_2 and increases its photo catalytic activity under UV irradiation (Anpo et al. 2001). It has been reported that doping TiO_2 with silver greatly improved photo catalytic bacterial inactivation (Page et al. 2007; Reddy et al. 2007). This combination was resulted good antibacterial properties of TiO_2/Ag+ nanoparticles in a nanocomposite with PVC (Cheng et al. 2006).

6.5 Smart Packaging

In smart/intelligent, nanomaterials are used for sensing biochemical or microbial changes in the food, for example detecting specific pathogens developing in the food, or specific gases from food spoiling (Kuswandi et al. 2011). In terms of smart packaging, nanoparticles can be applied as reactive particles in packaging materials to inform about the state of the packaged product. The so-called nanosensors are able to respond to external stimuli change in order to communicate, inform and identify the product with the aim to assure its quality and safety. The recent developments for polymer nanomaterials for smart food packaging include spoilage indicators, oxygen indicators, product identification and traceability.

6.5.1 Nanosensors

Packaging equipped with nanosensors is also designed to track either the internal or external conditions of food products, pellets and containers, throughout the supply chain. For example, such packaging can monitor temperature or humidity over time and then provide relevant information of these conditions, for example by changing color. Nanosensors in plastic packaging can detect gases given off by food when it spoils and the packaging itself changes color to alert you. The so-called nanosensors are able to respond to environmental changes (e.g., temperature or humidity in storage rooms, levels of oxygen exposure), degradation products or microbial contamination (Bouwmeester et al. 2009).

Usually, producers estimated the expiration date of food by considering distribution and storage conditions, especially temperature to which the food product is predicted to be exposed. However, such conditions are not always known, and foods are frequently exposed to temperature abuse; this is particularly worrying for products which require a cold chain. Furthermore, sealing defects in packaging systems can lead food products to an unexpected high exposure to oxygen, which can result in undesirable changes. Nanosensors, when integrated into food packaging, can detect certain chemical compounds, pathogens, and toxins in food, being then useful to eliminate the need for inaccurate expiration dates, providing real-time status of food freshness (Liao et al. 2005).

They have also been reported that nano-biosensors already have been developed and commercialized to detect pathogens, spoilage, chemical contaminants, or product tampering, or to track ingredients or products through the processing chain (Nachay 2007). Nanosensors based on carbon nanotubes have also been pointed out to have several advantages over conventional detection methods such as high performance liquid chromatography. Carbon nanotubes based nanosensor is rapid and high-throughput detection; simplicity and cost effectiveness; reduced power requirements and easier recycling; and the un-necessity of exogenous molecules or labels. Furthermore, a multiwalled carbon nanotubes based biosensor have also been developed that can detect microorganisms, toxic proteins, and degraded products in food and beverages (Nachay 2007).

Engineered nanosensors have also been developed in packages to change color to warn the consumer if a food is beginning to spoil, or has been contaminated by pathogens using electronic "noses" and "tongues" to "taste" or "smell" scents and flavors (Joseph and Morrison 2006, Asadi and Mousavi 2006; Scrinis and Lyons 2007; Sozer and Kokini 2009). In real market applications, Nestlé, British Airways, MonoPrix Supermarkets are using chemical nanosensors that can detect color change (Pehanich 2006).

6.5.2 Freshness and Spoilage Indicators

Based on applied studies of the surface properties of materials, several types of gas sensors have been developed, which translates chemical interactions between particles on the surfaces into a response signal. Conducting polymers or electro active conjugated polymers, which can be synthesized either by chemical or electrochemical oxidation, are very important because of their electrical, electronic, magnetic and optical properties, which are related to their conjugated p electron backbones (Ahuja et al. 2007; Kuswandi et al. 2012). Polyene and polyaromatic conducting polymers such as polyaniline, polyacetylene, polypyrrole have been widely studied (Ahuja et al. 2007; Kuswandi et al. 2012). Electrochemically polymerized conducting polymers have a remarkable ability to switch between conducting oxidized (doped) and insulating reduced (undoped) state, which is the basis of many applications (Rajesh and Kaneto 2004). On-package indicator contains polyaniline film, that responds through visible color change to a variety of basic volatile amines released during fish spoilage period has been developed (Fig. 6.6) (Kuswandi et al. 2012). Color changes, in terms of total color difference of polyaniline, correlated well with total volatile amine levels and microbial growth patterns in fish samples (milkfish). These responses enabled the real-time monitoring of fish spoilage either at various constant temperatures or with temperature fluctuations.

Food spoilage is caused by microorganisms, whose metabolism produces gases which can be detected by conducting polymer nanocomposites or metal oxides, which can be used for quantification and/or identification of microorganisms based on their gas emissions as well as for food freshness detection. Sensors based on conducting polymer nanocomposites consist on conducting particles embedded into an insulating polymer matrix. The resistance changes of the sensors produce a

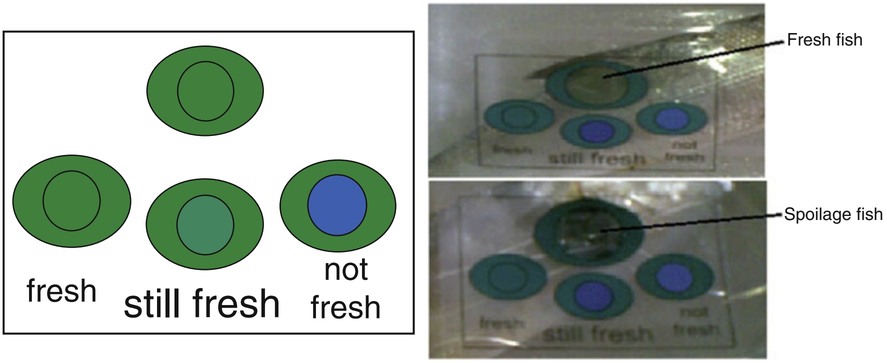

Fig. 6.6 Freshness sensor for smart packaging based on nanofibre of polyaniline. Left is sensor reference color change for detection of fish freshness, and right is sensor response towards fresh fish and spoilage fish (Courtesy of Kuswandi et al. 2012)

pattern that corresponds to the gas under investigation (Arshak et al. 2007; Kuswandi et al. 2012). Conducting polymer nanocomposites sensors containing carbon black and polyaniline have been developed to detect and identify food borne pathogens by producing a specific response pattern for each microorganism. Three bacteria, such as Bacillus cereus, Vibrio parahemolyticus and Salmmonella spp. could be identified from the response pattern produced by the sensors (Arshak et al. 2007). Chicken meat freshness was evaluated based on the smell when the output data of metal, such as tin and indium oxide gas sensors were processed with a neural network (Galdikas et al. 2000). An "electronic tongue" incorporated in food packaging have also been developed (Joseph and Morrison 2006). 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.

6.5.3 O_2 Indicators

Oxygen allows aerobic microorganism to grow during food storage. There has been an increasing interest to develop non-toxic and irreversible oxygen sensors to assure oxygen absence in oxygen free food packaging systems, such as packaging under vacuum or nitrogen. An UV-activated colorimetric oxygen indicator using UVA light has been developed, which uses nanoparticles of titania (TiO_2) to photosensitize the reduction of methylene blue by triethanolamine in a polymer encapsulation medium (Lee et al. 2005). 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. Nanocomposite thin films deposited methylene blue/TiO_2 on glass by liquid phase deposition, a soft chemical technique which has been applied to deposition of oxides to several substrates have been developed for oxygen indicator packaging systems in a variety of oxygen-sensitive foods (Gutierrez-Tauste et al. 2007).

Nanocrystalline SnO_2 has been used as a photo sensitizer in a colorimetric O_2 indicator comprising a sacrificial electron donor (glycerol), a redox dye (methylene blue), and an encapsulating polymer (hydroxyethyl cellulose) (Mills and Hazafy 2009). Exposure to UVB light led to activation (photo bleaching) of the indicator and photo reduction of methylene blue by the SnO_2 nanoparticles. The color of the films varied according to O_2 exposure – bleached when not exposed, and blue upon exposed.

6.5.4 Product Identification and Anti-counterfeiting

Some smart packaging has also been developed to be used as a tracking device for food safety or to avoid counterfeit. BioMerieux have developed a multi-detection test – Food Expert ID® for nano surveillance response to food scares. The nanotech company pSiNutria are also developing nano-based tracking technologies, including an ingestible BioSilicon which could be placed in foods for monitoring purposes and pathogen detection, but could also be eaten by consumers (Scrinis and Lyons 2007; Miller and Sejnon 2008). A United States company Oxonica Inc, has been developed nano-barcodes to be used for individual items or pellets, which must be read with a modified microscope for anti-counterfeiting purposes (Roberts 2007). Commercially available Nanobarcodes® manufactured by electroplating inert metals-such as gold, nickel, platinum, or silver- into templates that define the particle diameter, and then releasing the resulting striped nanorods from the templates (www.nanoplextech.com).

6.5.5 Active Tags and Traceability

Generally, active tags in packaging are radiofrequency identification. The tags are electronic information-based systems that uses radio frequency to transfer data from a tag attached to an object to trace and identify the object automatically. Radiofrequency identification is an improvement to the previous manual tracking systems or barcodes. Furthermore, it has a longer reading range, it is very strong and can work under extreme temperatures and different pressures, it can be detected at distances of more than 100 m, and many tags can be read simultaneously (Abad et al. 2007, 2009). Nanotechnology is also enabling sensor packaging to incorporate cheap radio frequency identification tags. The nano-enabled radiofrequency identification tags are much smaller, flexible and can be printed on thin labels. This increases the tags versatility and thus enables much cheaper production (www.thefreelibrary.com/).

6.6 Safety Issues

In terms of consumer safety, it is important to evaluate the potential migration of packaging constituents into food and to assess their potential hazard for a comprehensive risk assessment. However, to date very few studies have been published regarding the effects of nanomaterials upon ingestion, or the potential interaction of nanomaterial-based food contact materials with food components (Silvestre et al. 2011; Jain et al. 2016). In Europe, the legislation currently applies an overall migration limit of 10 mg constituent per dm^2 surface area to all substances that can migrate from food contact materials to foodstuffs (Commission Regulation (EU) No. 10/2011). For a liter cubic packaging containing 1 kg of food, this equates to a migration of 60 mg of substance per kg of food. However, with the exception of a few materials specifically listed in Annex 1 of the legislation, nanomaterial risk assessment has to be performed on a case-by-case basis (Silvestre et al. 2011; Commission Regulation (EU) No. 10/2011).

The migration of silver from three different types of nanocomposites into food stimulants, including an analysis of the form of silver migrating (ions or particles) has been studied (Echegoyen and Nerín 2013). Their results showed that silver migrated into food stimulants and that acidic food presented the highest level of migration. Moreover, heating was observed to increase migration, with microwave heating inducing more migration than a classical oven. The authors suggest that migration of silver could occur through two different mechanisms: the detachment of silver nanoparticles from the composites, or the oxidative dissolution of silver ions.

The migration of silver and copper from nanocomposites, used for their antimicrobial properties in food packaging has also been studied (Cushen et al. 2014). The study showed that the percentage of nanofiller in the nanocomposites was one of the most critical parameters driving migration, more so than particle size, temperature or contact time. A model to study migration of particles from food packaging has also been developed in this study. This model was a good predictor of the level of migration of nanosilver and to a lesser extent of nanocopper into food stuff and, when further developed and validated, could potentially be of benefit to industry by reducing the time and costs usually associated with migration studies.

More recently, the migration and toxicological profile of an organo-modified clay polylactic acid nanocomposite to be used as a food contact materials was evaluated. Migration studies indicated that less than 10 mg per dm^2 of the nanocomposite migrated in water, under the conditions of the experiment (Maisanaba et al. 2014a). Further analysis of the food stimulant indicated that the levels of metals measured were below the permitted values. In addition, the authors evaluated the potential toxicity of migration extracts both in vitro and in vivo. Assessment of the potential cytotoxicity of the migration extracts in vitro, on two cell types representative of the digestive system and their ability to induce DNA mutations, did not reveal any evidence of in vitro toxicity compared to control (Maisanaba et al. 2014a). Furthermore, exposure of rats to the same migration extracts for 90 days in drinking water did

Fig. 6.7 Relevant regulation for nano-packaging, including food product legislation and product safety directive, chemical safety regulation, and environmental regulation

not show evidence of toxicity in terms of oxidative stress, inflammation, clinical biomarkers and histopathological analysis (Maisanaba et al. 2014b).

These studies indicate the potential for nanomaterials to migrate from food contact materials into foodstuffs, with the rate of migration potentially associated with the percentage of nanofiller present in the composite material. There remains is a need for further migration and toxicological studies in order to ensure safe development of nanotechnologies in the food packaging industry. Thus, safe and successful implementation of nano-packaging applications need to fulfill three regulations, i.e. (i) food regulation, (ii) health regulation and (iii) environmental regulation as shown in Fig. 6.7. These are needed to ensure that society can benefit from novel applications of nano-packaging, whilst a high level of protection of health, safety and the environment is maintained. Furthermore, these are needed to ensure the safety use of these nano-packaging, with special emphasis in the enhancement of knowledge regarding their eventual toxicological effects, migration potential and levels of exposure for both workers and consumers, with special emphasis on the effects on the selected nanomaterials to human health following chronic exposure. In addition, it is necessary for the producers not only to assure product quality ensuring regulatory compliance but also to involve the consumer providing clear information in regard to benefits/possible risks balance and protection of the environment. If all regulation fulfils, then the fruitful of incorporation of nanomaterial into food packaging would play an important role in making the world's food supply healthier, safer, and tastier and more nutritious as well as environmental friendly.

6.7 Conclusion

Based on all the research conducted during last decade, clearly nanotechnology offers tremendous opportunities for innovative developments in food packaging that can benefit both consumers and industry. The application of nanotechnology shows considerable advantages in improving the properties of packaging materials, even in the early stages and will require continued investments to fund the research and development to better understand the advantages and disadvantages of nanotechnology use in packaging materials. The use of nanotechnology to fabricate food packaging can give numerous benefits in the range of advanced functional properties. They can bring to packaging materials with enhanced processing, health and packaging functionalities, shelf-life, transportability, and reduced costs.

Nanotechnology has the potential to improve foods, making them tastier, healthier, and more nutritious, to generate new food packaging functions, new food packaging, and storage. However, many of the applications are currently at an elementary stage, and most are aimed at high-value products, at least in the short term. In addition to this, nanomaterials can be used to make packaging that keeps the product inside fresher for longer extending the life of food and improving food safety. Smart packaging, incorporating nanosensors, could even provide consumers with information on the state of the food inside. Food packages are embedded with nanosensors that alert consumers when a product is no longer safe to eat. Sensors can warn before the food goes spoil or can inform consumers the exact nutritional status contained in the contents. In fact, nanotechnology will be change the fabrication of the entire packaging industry.

In spite of the great possibilities existing for food packaging based on nanomaterials, it is hoped that simple traditional packaging will be replaced with multi-functional smart packaging. The next generation of packaging materials will be able to fit the requirements of preserving perishable foods and other food products. By adding appropriate nanoparticles, it will be possible to produce packages with stronger mechanical, barrier and thermal performance. Nano-structured materials will prevent the invasion of bacteria and microorganisms as a concern for food safety. The nanosensors embedded in the packaging may alert the consumer if a food has deteriorated and cannot be consumed any more.

Regardless of how applications of nanotechnology in the food packaging sector are ultimately marketed, governed, or perceived by the public, it seems clear that the integrating of nanoscale material in packaging will continue to yield exciting and unforeseen packaging products. However, the potential dangers and ethical questions, that the use of this new technology should be responded wisely with more research and development regarding these issues. Therefore, successful and safe implementation of nanotechnology applications will require constant dialogue between the scientists and companies who invent them and the consumers who purchase them. If it succeeds, then the fruitful of incorporation of nanomaterial into food packaging may play an important role in making the world's food supply healthier, safer, tastier, more nutritious and plentiful as well as environmental friendly.

Regulatory bodies, should author guidance with respect to the criteria to be followed in evaluating the safety of food packaging, uses of nanomaterials with novel properties and functions. Novel methods, approaches and standardized test procedures to study the effects of nanomaterials upon ingestion, or the potential interaction of nanomaterial-based food contact materials with food components are urgently needed for the evaluation of potential hazards relating to human exposure to nanoparticles. Even though, it is widely expected that nanotechnology-derived food packaging will be available increasingly to consumers worldwide in the coming years.

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