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## Nanotechnology for safe food packaging-review

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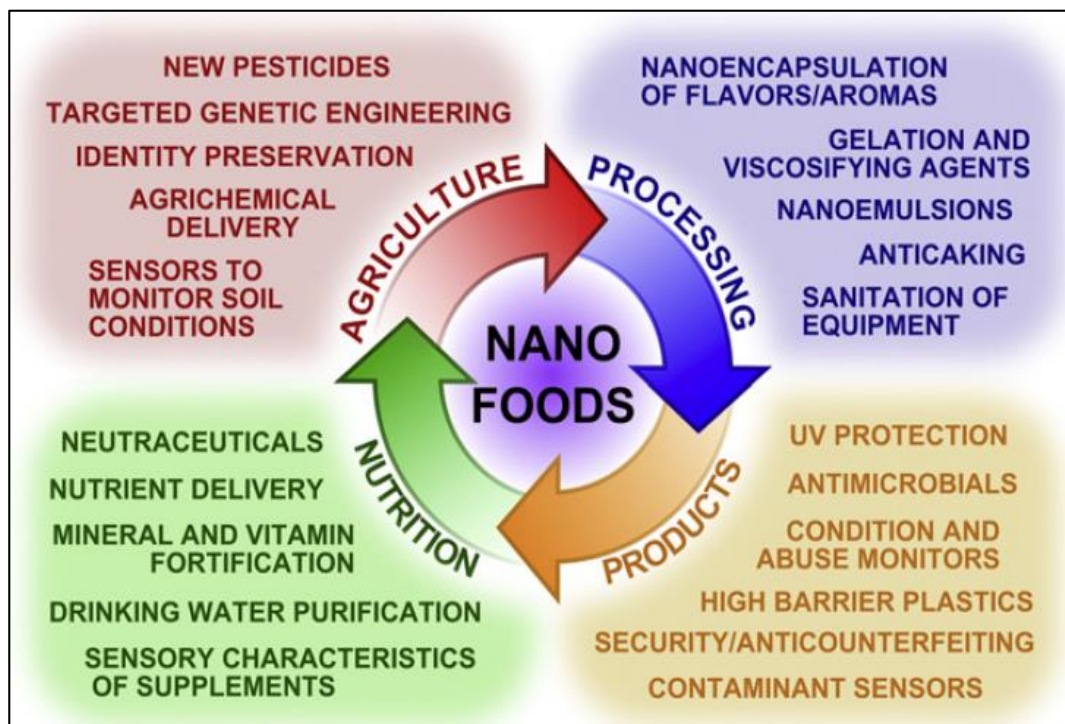
**Abstract**

Nanotechnology can be used to improve health, wealth, products and quality of life. Food nano-packaging is still a rather unexplored field of nanoscience and food science. Here I review developments in nano-packaging. This chapter describes first bio-based food packaging for biodegradable packaging. Bio-based packaging is indeed an alternative to conventional packaging with non-degradable plastic polymers that are a threat to the environment. Bio-based packaging reduces waste, extend the shelf life, and enhance food quality. The next section discusses nano-materials 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 nano-sensors and nano-devices that detect freshness or contaminants in foods or monitor changes in packaging conditions or integrity. The last section discusses safety issues and health concerns of nano-packaging.

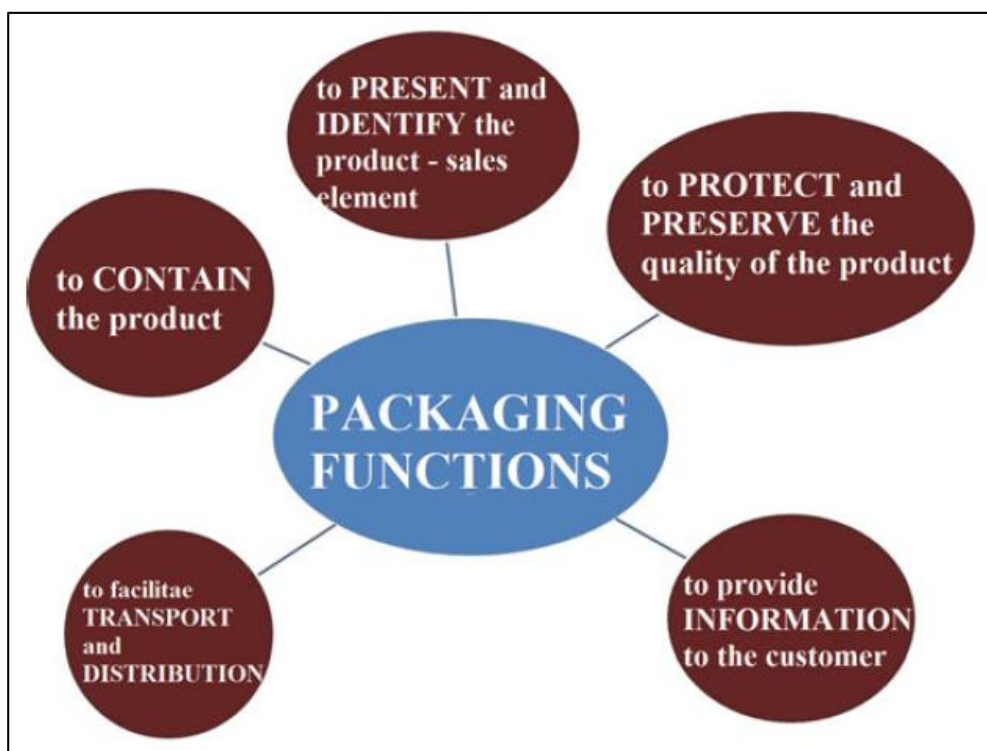
**Keywords:** Nanotechnology, food packaging, sensors, nanocomposites, nanoparticles

**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. It would also have implications and applications that could be essential to mankind (Ravichandran, 2010). Nanotechnology promises many interesting changes to improve health, wealth and quality of life, as well as reducing impact on the environment. Scientists and industry stakeholders have already identified potential uses of nanotechnology in virtually every segment of the food industry (Fig. 1), from agriculture (e.g., pesticide, fertilizer or vaccine delivery; animal and plant pathogen detection; and targeted genetic engineering) to food processing (e.g., encapsulation of flavor or odor enhancers; food textural or quality improvement; new gelation or viscosifying agents) to food packaging (e.g., pathogen, gas or abuse sensors; anticounterfeiting devices, UV-protection, and stronger, more impermeable polymer films) to nutrient supplements (e.g., nutraceuticals with higher stability and bioavailability) (Duncan, 2011) [26]. 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.2). 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 nano-materials that can bring to packaging materials, therefore, nano-materials are increasingly being used in the food packaging industry. It was reported that around 500 nano-packaging 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) [63]. In nano-packaging, it can also be designed to release antimicrobials, antioxidants, enzymes, flavors and nutraceuticals to extend shelf life (Cha and Chinnan, 2004) [16]. 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) [28].



**Fig 1:** Nanotechnology has applications in all areas of food science, from agriculture to food processing to security to packaging to nutrition and nutraceuticals. Some potential applications are shown here. The applications which will be reviewed in this article are those in the orange quadrant, which are the most likely to be marketed in the near term.



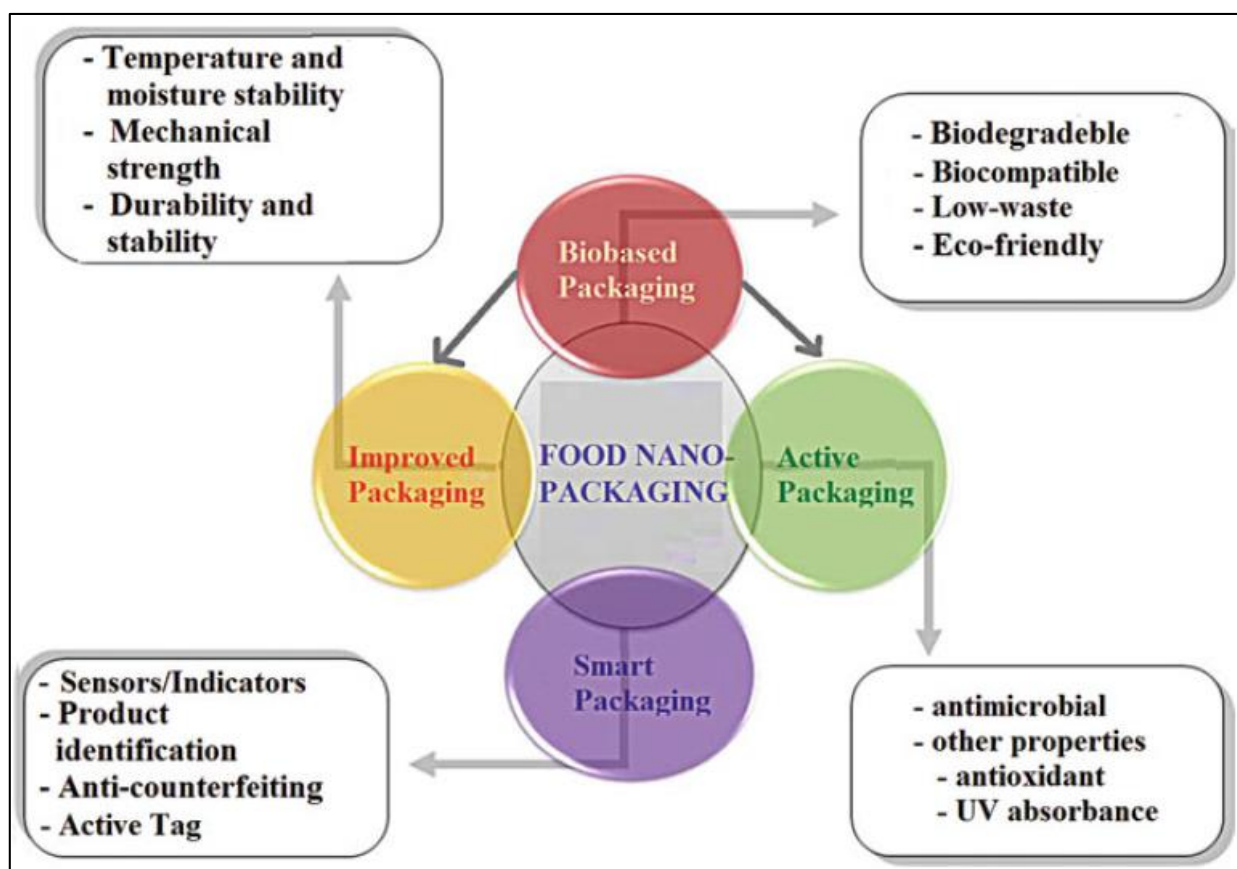
**Fig 2:** Key functions of packaging systems, i.e. container of the product, preservation and protection of the product quality, presentation and identification of the product as sales element, facilitation for transportation and distribution of the product, and information of the product to the consumers.

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) <sup>[22]</sup> 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) <sup>[22]</sup>. 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 nanotechnology research and development (Brody, 2003) <sup>[13]</sup>. 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) [42]. 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 environment (Kirwan and Strawbridge, 2003) [39]. Therefore, the use of bio-based packaging materials, such as edible and biodegradable films from renewable resources (Tharanathan, 2003) [72], 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.

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. 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. 3. 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 of the nano-packaging materials in the future.



**Fig 3:** 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 nano-composites as active material, e.g. antimicrobial and other properties, e.g. antioxidant, UV absorbance etc.; and smart packaging with nano-sensors as intelligent function in packaging for the detection of food relevant analyses (gasses and small organic molecules), active tag and product identification and anti-counterfeiting. Bio-based packaging can also be used in improved and active packaging.

### 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) [68]. 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

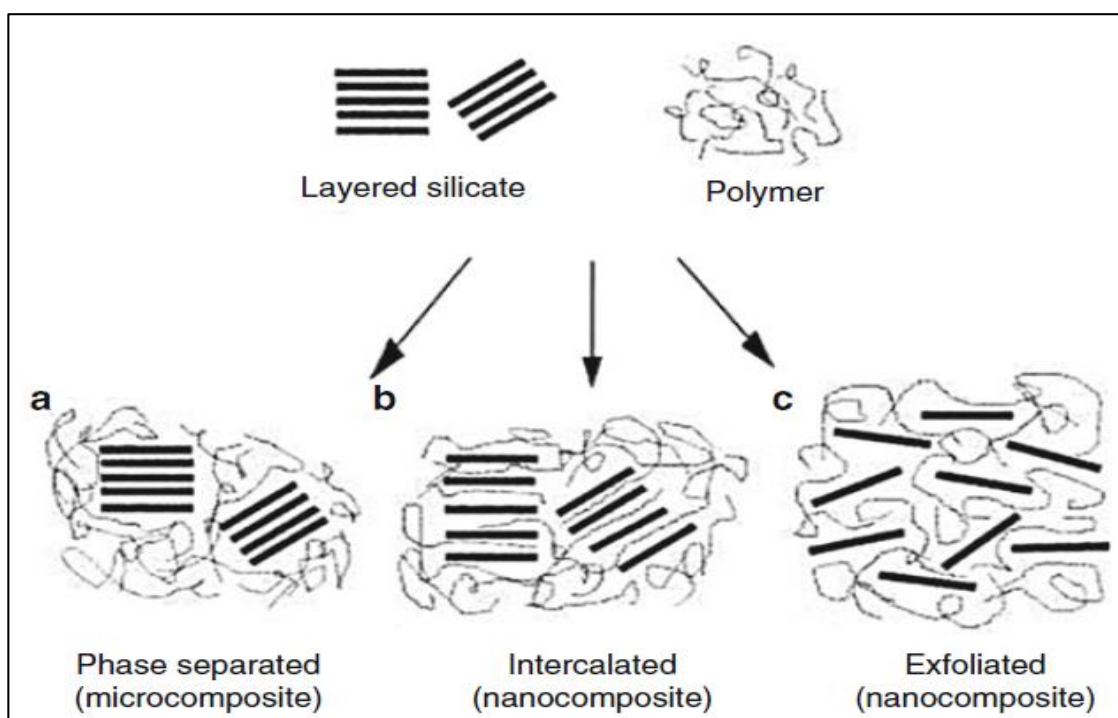
biodegradable packaging films from other packaging solutions is that they are capable of decaying through the action of living organisms (Del Nobile *et al.*, 2009) [24]. This packaging type is generally perceived to be more environmental friendly as the breakdown products are all completely natural, 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 steps in the degradation process via naturally occurring

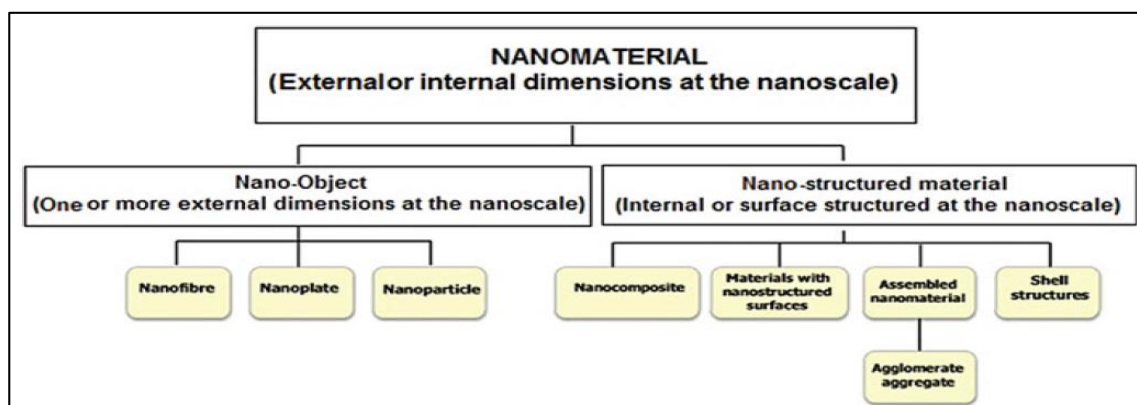
organism's metabolism. Under appropriate conditions of moisture, temperature and oxygen availability, this biodegradation leads to fragmentation or disintegration of the plastics with no toxic or environmentally harmful residue (Chandra and Rustgi, 1998) [17]. These biodegradable polymers can be classified 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.

Three main types of composites can be formed when the layered clay is incorporated with a polymer, as given in Fig. 4

(Alexandre and Dubois, 2000) [6]. 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. 4a. 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. 4b. 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.4c.



**Fig 4:** Three types of composites when layered clays are incorporated with the polymer: (a) tactoid, phase-separated micro-composite; (b) intercalated nano-composite and (c) exfoliated, polymer– clay nano-composite (Courtesy of Alexandre and Dubois, 2000) [6].



**Fig 5:** Terminology of nanomaterial used in nano-packaging: (a) nano-object, and (b) nanostructured material. Nano-object consist of nanofibre, nanoplate and nanoparticle, while nanostructured material consist of nano-composite, material with nanostructured surfaces, assembled nanomaterial and shell structure.

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. 5. In nano-objects, mostly nano-materials used as filler (nano-reinforcement), which involves the use of nanoplate, nanoparticles and nanofibers (such as metal oxides nanoparticles, nanoclays,

carbon nanotubes and other fillers like metallic nanoparticles). While in nano-structured materials, the nano-materials are dispersed into a polymer matrix as nano-composites. Actually, the applications of nanomaterial 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; (iii) 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) [60], where in food packaging mainly related with nano-reinforcement, nano-composite active packaging and nano-composite smart packaging.

#### a) 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) [69, 31]. There are many ways to using starch as packaging material (Kim and Pometto, 1994) [38]. 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 bio-plastics, although more recent global research is evaluating the potential use in bio-plastics for starches from potato, wheat, rice, barley, oat and soy sources.

#### b) Polylactic Acid

The conventional chemical synthesis used for the production of polymers gives a wide variety of bio-polyesters. 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) [52].

#### c) Polyhydroxybutyrate

Polyhydroxybutyrate has been the subject of extensive studies as an environmental friendly polymeric material which is the most popular polyhydroxyalkanoate used in food-packaging. Polyhydroxybutyrate is a polymer belonging to the polyesters class that are of interest as bio derived and biodegradable plastics. Polyhydroxybutyrate is produced by microorganisms (such as *Ralstonia eutrophus* or *Bacillus megaterium*) (Lenz and Marchessault, 2005) [44] and is utilized as an energy storage molecule within the microorganism's cellular structure. Due to its biodegradability and biocompatibility,

this bio-polyester may easily find industrial applications (Weber *et al.*, 2002; Lenz and Marchessault, 2005) [73, 44]. Potentially, polyhydroxybutyrate 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 nontoxic. However, as polyhydroxybutyrate 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) [35]. The poor low-impact strength of polyhydroxybutyrate is solved by incorporation of hydroxyvalerate monomers into the polymer to produce polyhydroxybutyrate-co-valerate (Liu *et al.*, 2002) [46]. Polyhydroxybutyrate-co-valerate completely degrades into carbon dioxide and water under aerobic conditions (Lenz and Marchessault, 2005) [44].

#### d) 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) [57]. It is a semi-crystalline 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) [17, 55, 53] and agricultural areas (Nakayama *et al.*, 1997) [54].

#### 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 nano-composites 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) [18, 14]. United States Food and Drug Administration (USFDA) have approved the use of nano-composite in contact with foods (Sozer and Kokini, 2009) [70].

#### a) 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) [33]. 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) [10]. Components of edible coatings can be divided into two categories: water-soluble polysaccharides (hydrocolloids) and lipids. Suitable polysaccharides include cellulose derivatives, alginates, pectin's, starches, chitosan and other polysaccharides (El Ghaouth *et al.*, 1991) [29]. 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)<sup>[9]</sup>.

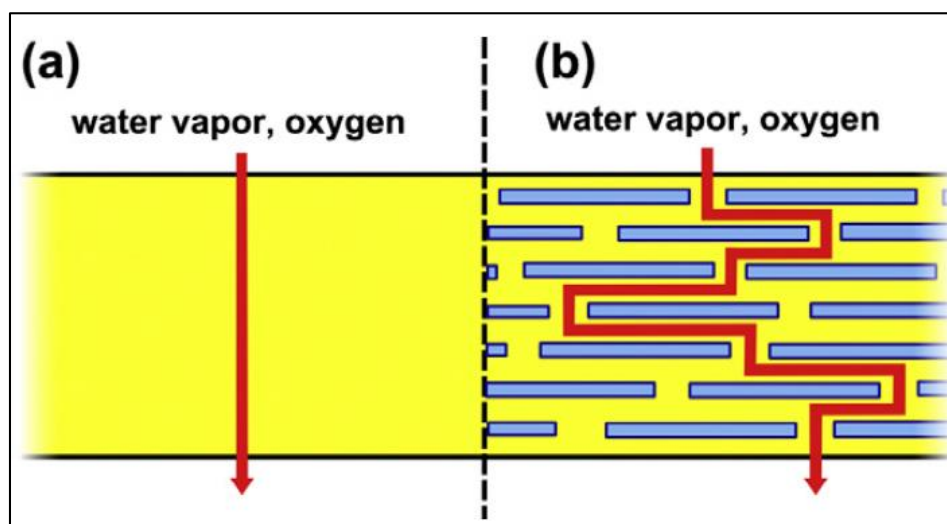
### b) Nanolaminates

Nanotechnology provides food scientists with a number of ways to create novel nanolaminate films that suitable to be used in the food industry. Generally, 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)<sup>[23]</sup>. 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)<sup>[74]</sup>.

### c) Clay Nanoparticles and Nanocrystals

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 nano-composites 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), which in turn, providing excellent barrier properties (Bharadwaj *et al.*, 2002; Cabedo *et al.*, 2004; Mirzadeh and Kokabi, 2007)<sup>[11, 51]</sup>. The interaction between layered silicates and polymer chains may produce two types of ideal nanoscale composites as shown in Fig. 4. The intercalated nano-composites result from the penetration of polymers chains into the interlayer region of the clay, resulting in an ordered multilayer structure, with alternating polymer/inorganic layers at a repeated distance of a few nanometers (Weiss *et al.*, 2006)<sup>[74]</sup>. The exfoliated nano-composites involve extensive polymer penetration, with the clay layers delaminated and randomly dispersed in the polymer matrix (Ludueno *et al.*, 2007)<sup>[48]</sup>. Exfoliated nano-composites were the best properties due to the optimal interaction between clay and polymer (Adame and Beall, 2009; Alexandre *et al.*, 2009)<sup>[3, 5]</sup>.



**Fig 6:** 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 (Adame and Beall, 2009)<sup>[3]</sup>.

### 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)<sup>[18, 25, 50]</sup>. 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)<sup>[14]</sup>

### a) 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)<sup>[64]</sup>. Here, the film allows nanomaterials to be able to attach more copies of biological molecules, which confers greater efficiency (Luo and Stutzenberger, 2008)<sup>[49]</sup>. 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; Yan-Jun *et al.*, 2005; Qi *et al.*, 2004; Stoimenov *et al.*, 2002)<sup>[36, 40, 45, 58, 71]</sup>, or antibiotic carriers (Gu *et al.*, 2003)<sup>[32]</sup>. 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) [40]. Film based on silver nanoparticles has been produced and their antimicrobial affectivity has been reported.

### b) Oxygen Scavenging Film

Oxygen (O<sub>2</sub>) 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<sub>2</sub> includes food spoilage by aerobic microorganisms. Therefore, the incorporation of O<sub>2</sub> scavengers into food package can maintain very low O<sub>2</sub> 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<sub>2</sub>) to different polymers (Xiao-e *et al.*, 2004) [75]. So that they can be used for packaging a wide variety of oxygen-sensitive products.

### c) UV Absorbing Films

Commonly used material as UV absorbing is film based on nanocrystalline Titania (TiO<sub>2</sub>). The efficacy of TiO<sub>2</sub> 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<sub>2</sub> and increases its photo catalytic activity under UV irradiation (Anpo *et al.*, 2001) [7]. It has been reported that doping TiO<sub>2</sub> with silver greatly improved photo catalytic bacterial inactivation (Page *et al.*, 2007; Reddy *et al.*, 2007) [56, 62]. This combination was resulted good antibacterial properties of TiO<sub>2</sub> / Ag<sup>+</sup> nanoparticles in a nano-composite with PVC (Cheng *et al.*, 2006) [19].

### 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) [42]. 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

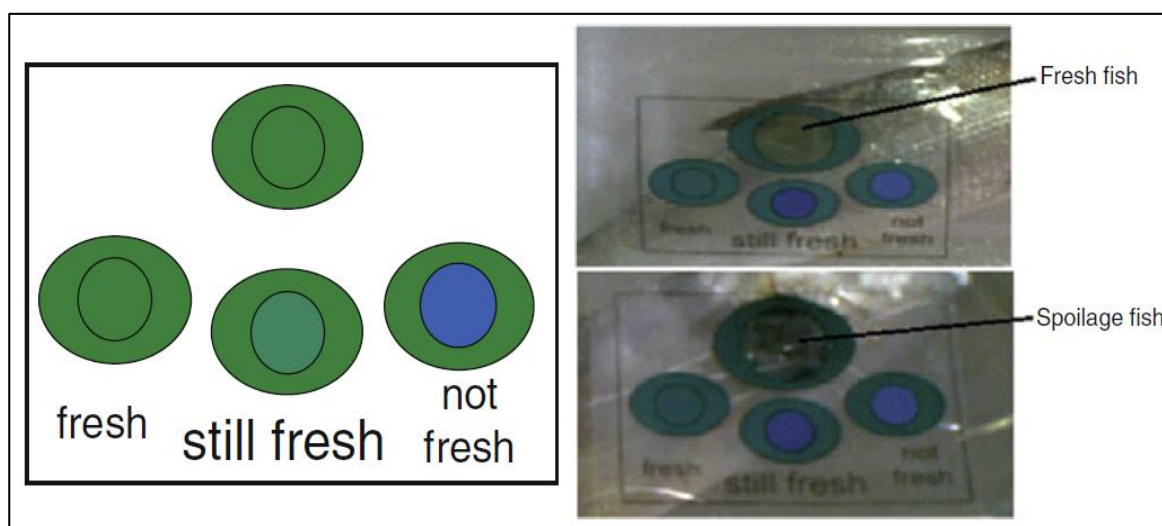
polymer nanomaterials for smart food packaging include spoilage indicators, oxygen indicators, product identification and traceability.

### a) 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) [12].

### b) 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) [4, 41]. Polyene and polyaromatic conducting polymers such as polyaniline, polyacetylene, polypyrrole have been widely studied (Ahuja *et al.*, 2007; Kuswandi *et al.*, 2012) [4, 41]. 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 (Takashima and Kaneto, 2004) [59]. 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.7) (Kuswandi *et al.*, 2012) [41]. Color changes, in terms of total color difference of polyaniline, correlated well with total volatile amine levels and microbial growth patterns in fish samples (milk, fish). These responses enabled the real-time monitoring of fish spoilage either at various constant temperatures or with temperature fluctuations.



**Fig 7:** Freshness sensor for smart packaging based on nano fibre of polyaniline. Left is sensor reference color change for detection of fish freshness, and right is sensor response towards fresh fish and spoilage fish (Kuswandi *et al.*, 2012) [41].

### c) O<sub>2</sub> 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<sub>2</sub>) to photosensitize the reduction of methylene blue by triethanolamine in a polymer encapsulation medium (Lee *et al.*, 2005) [43]. 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. Nano-composite thin films deposited methylene blue/TiO<sub>2</sub> 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) [34].

### d) 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 (Scriner and Lyons, 2007; Miller and Sejnou, 2008) [6, 50]. 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) [65]. 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.

### e) 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) [1]. 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.

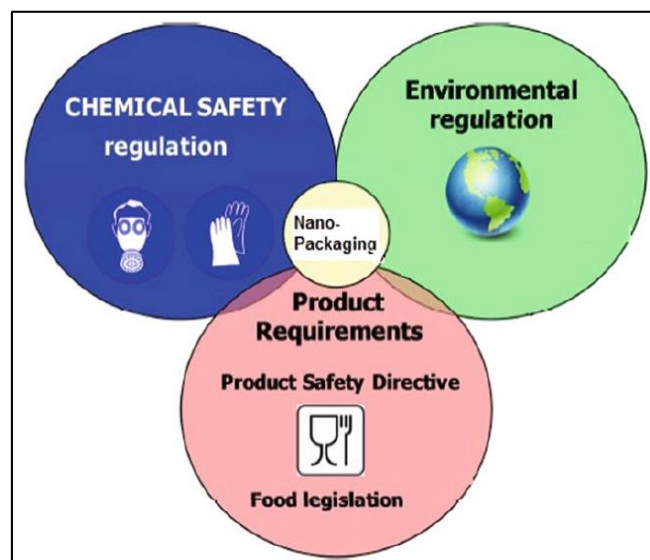
### Safety Issues

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.*, 2018) [67, 37]. In Europe, the legislation currently applies an overall migration limit of 10 mg constituent per dm<sup>2</sup> 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.

The migration of silver from three different types of nano-composites into food stimulants, including an analysis of the form of silver migrating (ions or particles) has been studied (Echegoyen and Nerín, 2013) [27]. 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.

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 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 implementations 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. 8 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. If all regulation fulfills, 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.



**Fig 8:** Relevant regulation for nano-packaging, including food product legislation and product safety directive, chemical safety regulation, and environmental regulation.

### 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.

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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