

Application of polymer nanocomposite materials in food packaging

Amra Bratovčić*, Amra Odobašić, S. Ćatić, Indira Šestan

Faculty of Technology, University of Tuzla, Univerzitetska 8, 75000 Tuzla, Bosnia and Herzegovina

review paper

DOI: 10.17508/CJFST.2015.7.2.06

Summary

The term "nano" refers to nano particle size from 1 to 100 nanometers. The term "nanotechnology" was first introduced by Norio Taniguchi in 1974. Nanotechnology may be used to improve the taste and texture of food and for the production of packaging that maintain fresh product. The primary function of packaging is to maintain the quality and safety of products during transport and storage period, as well as to extend its viability by preventing unwanted effect agents such as microorganisms, chemical contaminants, oxygen, moisture and light. The aim of this paper is to point out the achievements of nanotechnology in terms of food packaging with an overview of polymers that are commonly used in food packaging, as well as strategies to improve the physical properties of polymers, including mechanical strength, thermal stability and barrier to gases. By studying of recently published literature, it was clear that nanomaterials such as nano polymers are trying to replace conventional materials in food packaging. Nanosensors can be used to prove the presence of contaminants, microtoxins and microorganisms in food.

Keywords: nanomaterials, smart packaging, nanosensors

Introduction

Nanotechnology can be generally defined as fabrication and manipulation of structures that have at least one dimension or contain components with at least one dimension that is approximately 1-100 nm in length. When particle size is reduced below this threshold, the resulting material exhibits physical and chemical properties that are significantly different from the properties of macroscale materials composed of the same substance. Research in the field of nanotechnology have risen sharply over the last decade. Nanotechnology is an interdisciplinary field and includes chemistry, physics, biology, engineering (Masciangioli and Zhang, 2003) and technology. The aim of this paper is to point out the achievements of nanotechnology in the field of food packaging. The methods based on nanotechnology can be used to improve the taste and texture of food, because it is in this way possible to save nutrients such as vitamins and reduce the concentration of fat, then the production of packaging that maintain fresh product and for making food packaging with intelligent sensors that provide information on condition that the product is in the package.

The application of polymers and biopolymers in food packaging

Currently, there are over 30 000 different natural and synthetic polymers. Knowing the species and potentially harmful impact on human health is imperative in selecting and using certain types of polymers. It must be paid special attention to the

selection of polymers in the food industry. Approximately half of all polymers that are processed in Europe is used for the production of packaging. In 2008, nanotechnology demanded over \$15 billion in worldwide research and development money (public and private) and employed over 400 000 researchers across the globe (Roco et al., 2010). In the food industry polymers are the most frequently used for packaging of food products. Their purpose is to keep the food fresh for as long as creating a controlled atmosphere and to prevent its deterioration. The polymers used for packaging because of the ease in manufacturing, chemical stability, inertness in contact with food, light sterilization, aesthetic design and low weight. Polymers which are most frequently used for food packaging include, but are not limited to, polyolefins (over 90%) as follows: polyethylene (PE) and various grades of polyethylene such as high density polyethylene (HDPE) and low density polyethylene (LDPE), polypropylene (PP) polyethylene terephthalate (PET), polystyrene (PS) and polyvinyl chloride (PVC). Though polymers have revolutionized the food industry and possess numerous advantages over conventional materials, their major drawback is an inherent permeability to gasses and other small molecules. Some polymers are better than others in this regard. PET, for example, provides a good barrier to oxygen, while HDPE fares much worse. On the other hand, HDPE offers a significantly better barrier against water vapor than PET (Finnigan, 2009). HDPE is used for packaging milk in bags and bottles. LDPE is used for making plastic bags and containers for general purposes. PP has excellent chemical resistance, is strong and has the lowest density of the plastics used

*Corresponding author: amra.bratovcic@untz.ba

as packaging materials. It has a high melting point, making it ideal for filling with hot liquids.

PET is a clear, strong and has good barrier properties to gases and moisture. The use of PET to make plastic bottles for carbonated drinks is increasing. It has good resistance to heat, mineral oils, solvents and acids. Frequently used as packaging film (mainly made of PE, PP and PVC), containers (bottles, cans, etc.) usually are made of PVC, PET and PE, a polymer foam as a protective packaging (made of PS, PE, polyurethane (PUR) and structural packaging (boxes are made of PVC and PC).

About 70% of foil packaging in the European Union are different polyethylenes. The properties of packaging materials for food packaging includes mechanical, thermal, and optical properties, then the barrier to oxygen, carbon dioxide, moisture and flavor, and antimicrobial. In recent decades, polymers replaced conventional packaging materials (metals, glass, paper) because of their functionality, they are lightweight, easy to handle and their low price. The use of synthetic polymer is present in all food packaging, they provide mechanical, chemical and microbial protection of the environment and allow the display of products.

Global production capacity for bioplastics was around 1.6 million tons in 2013, and it is predicted that the production of bioplastics will increase to around 6.7 million tonnes by 2018. The leading field is partially bio-based PET, which accounts for about 40% of global production capacity of bioplastics in 2013. Forecasts are that the application of bioplastics will expand to about 5 million tons by 2018. This would correspond to 75% of the total capacity produced bioplastic (<http://en.european-bioplastics.org/market/market-development/production-capacity/>). Engineering nanoparticles refers to metals, inorganic substances such as titanium dioxide, zinc sulfide, zinc oxide and carbon-based fullerenes and their derivatives and composites.

Polymer Nanocomposites

A nanocomposite is a multiphase material derived from the combination of two or more components, including a matrix (continuous phase) and a discontinuous nano-dimensional phase with at least one nano-sized dimension (i. e., with less than 100 nm). Mechanical, thermal, and properties of nanocomposites often differ markedly from those of their component materials. Polymer nanocomposites promise a new crop of stronger, more heat resistant, and high barrier materials (Ludueña et al., 2007). Nanocomposites represent a new alternative to conventional technologies for improving polymer properties. Nanocomposites exhibit increased barrier properties, increased mechanical strength, and

improved heat resistance compared to their neat polymers and conventional composites.

Nanostructures can be classified according to the number of dimensions at the nanometer level. Nanospheres or nanoparticles have the three dimensions in the nanoscale. Both nanowhiskers (nanorods) and nanotubes have two nanometric dimensions, with the difference that nanotubes are hollow, while nanowhiskers are solid. Finally, nanosheets or nanoplatelets have only one nano-sized dimension (Alexandre and Dubois, 2000). Some types of nanostructures can have multiple applications, and sometimes applications can overlap, such as some immobilized enzymes which can act as antimicrobial components, oxygen scavengers and/or nanosensors. Uniform dispersion of the filler in the polymer matrix results in a very large interfacial area matrix/filler, which reduces the mechanical movement of the matrix and improves the mechanical, thermal (particularly the glass transition temperature, T_g) and barrier properties.

Barrier applications of polymer nanocomposites

Development of nano-composites (inserting nanomaterials in polymers) is a new strategy to improve the physical properties of polymers, including mechanical strength, thermal stability, barrier properties to gases and biodegradation.

The most frequently used strategies to enhance barrier properties are the use of polymer blends, coating articles with high barrier materials, and the use of multilayered films containing a high barrier film. An effective high barrier material is aluminum foil. Thin coatings of aluminum can be applied to films and containers by several vapor deposition technologies. Multilayers are formed by embedding a thin layer of a high barrier material within layers of structural polymers. Coatings and multilayers are effective but their application is limited by the level of adherence between the materials involved. Polymers can also be added with suitable fillers to form composites of enhanced barrier properties.

The most promising nano fillers are clay, montmorillonite and kaolinite. Graphite nanosheets are currently studied. The main emphasis is on the development of high barrier properties to oxygen, carbon dioxide, and water vapor for food packaging. Reducing the water vapor permeability is a critical issue in the development of biopolymer materials as a sustainable packaging. No material is completely impermeable to atmospheric gasses, water vapor, or natural substances contained within the food being packaged or even the packaging material itself. In some applications, high barriers to migration or gas diffusion are undesirable, such as in packages for

fresh fruits and vegetables whose shelf life is dependent on access to a continual supply of oxygen for sustained cellular respiration. Plastics utilized for carbonated beverage containers, on the other hand, must have high oxygen and carbon dioxide barriers in order to prevent oxidation and decarbonation of the beverage contents (Finnigan, 2009).

Nanocomposites formation

Nanoclay technology relies on the high surface area of clay platelets, in excess of $750 \text{ m}^2/\text{g}$, and high aspect ratio (100 to 500). There are 3 types of polymer-clay formations, namely tactoid, intercalated, and exfoliated. (Fig. 1). Tactoid structures remain in a polymer when the interlayer space of the clay gallery does not expand, usually due to its poor affinity with the polymer. No true nanocomposites are formed this way. Intercalated structures are obtained at moderate expansion of the clay interlayer. In this case, interlayer spaces expand slightly as polymer chains penetrate the basal spacing of clay, but the shape of the layered stack remains. This is the result of moderate affinity between polymer and clay.

In the case of exfoliated structures, clay clusters lose their layered identity and are well separated into single sheets within the continuous polymer phase. This is due to a high affinity between polymer and clay.

Nano additives in materials for food packing

Nano additives in food packaging materials are nanoparticles, nanotubes, nano-clay and nanofibers. Nanoclay (layered silicates) are the most studied nano additives/fillers, due to high availability, low cost and good performance. The first publications on the application of the composite polymer-nanoclay food packaging dating back to 1990 (Ray et al., 2006).

Typically clay for nanocomposites are usually two-dimensional plate, a very thin (typically about 1 nm) and several micrometers in length. The most studied clay is montmorillonite (MMT) which has a general chemical formula $(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$, a soft 2:1 layered phyllosilicate clay comprised of highly anisotropic platelets separated by thin layers of water (Weiss et al., 2006). The platelets have an average thickness of about 1 nm and average lateral dimensions ranging between a few tens of nm to several μm . Each platelet contains a layer of aluminum or magnesiumhydroxide octahedra sandwiched between two layers of silicon oxide tetrahedra.

Montmorillonite is a 2:1 layered phyllosilicates, whose boards have double-layer sheets of tetrahedral silica filled with a central octahedral sheet of aluminum. This type of clay has a moderately negative charge on the surface of which is important for defining

interlayer space. The imbalance of the surface negative charge is compensated by exchangeable cations (Na^+ and Ca^{2+}). Parallel layers bind together a weak electrostatic forces (Tan et al., 2008).

Hydrophilic surfaces of most of the clay makes it difficult to disperse in organic matrices. Organoclay produced by the interaction of clay and organic compounds are important applications in polymer nanocomposites. Organo-montmorillonite have been produced by exchanging inorganic cations of montmorillonite with organic ammonium ions, improving compatibility of montmorillonite with organic polymers, (Osman et al., 2003) leading to a more regular organization of the layers and decreasing the water uptake by the resulting nanocomposite (Picard et al., 2007).

By adding of less than 5% improves the mechanical, thermal properties (modulus of elasticity, rigidity, dimensional stability), thermal stability, barrier properties, and additional functional properties, UV protection, controlled release components. The particles can decrease the permeability of the clay and up to 75%.

Examples of polymer nanocomposites with montmorillonite with improved barrier properties are made of polymer matrix: polyamide, polystyrene, polyolefins, polyethylene terephthalate, epoxy resins, polyurethanes. Examples of these polymer composites are: - Imperm® (Color Matrix Europe) - used in multi-layer PET bottles and sheets for food and beverage packaging to minimise permeation of O_2 and loss of CO_2 from beverages.

- Duretham® KU 2-2601 (LANXESS Deutschland GmbH) - nanocomposite films based on polyamides with improved properties when required better barrier properties in packaging juices.

- Aegis® OX (Honeywell Polymers) a polymerised nanocomposite film contains a blend of active and passive nylon that incorporate active O_2 scavengers and passive nanocomposite clay particles to enhance barrier properties.

In contrast to the nano composite tactoid structures (conventional compositions), in which the tactoids of polymer and the clay remain immiscible, by interaction of layered silicates and polymer can form two types of nanocomposites, a) exchangeable nanocomposites that forms by penetration of the polymer chains in the interlayer region of clay, producing a multi-layer furnished structure with alternating polymer/inorganic layers (Weiss et al., 2006) and b) stratified (exfoliated) nanocomposites that involve penetration of extensive polymer with clay layers delaminated and randomly dispersed in a polymer matrix. Exfoliated nanocomposites show the best performance for optimal interaction of clay-polymer (Adame and Beall, 2009; Alexandre et al., 2009).

Cellulose filler are interesting materials for the preparation of low-cost, lightweight and very strong

nanocomposites (Helbert et al., 1996; Podsiadlo et al., 2005). Cellulose chains are synthesized in living organisms (many plants) as microfibrils or nanofibrils and they are bundles of elongated molecules (with a 2-20 nm in diameter and micrometers in length) stabilized by hydrogen bonds. Each microfibril formed from the elementary fibrils has crystalline and amorphous regions. The crystal parts are nanocrystals or nanosheets which can be isolated by methods such as acid hydrolysis. Microfibril can be seen as a series of sheets related by amorphous domains that are taken as structural defects. Similarly nanoclay, the presence of cellulosic filler reduces the permeability of the polymer. In several works it is experimentally obtained improvement barrier properties of polymers with the addition of cellulosic filler (Paralikar et al., 2008; Sanchez-Garcia et al., 2008). Barrier properties are further increased if the filler is less porous, well-dispersed in the matrix and the high ratio of filler. Due to the hydrophilic surface of cellulose, interaction between cellulose nanofiller and hydrophilic matrices are generally satisfactory (Bondeson and Oksman, 2007). On the other hand, the incorporation of cellulosic nanofiller in the hydrophobic matrix usually results in a weak interactions filler-matrix (Hubbe et al., 2008) and filler aggregate by hydrogen bonds (Freire et al., 2008).

Another disadvantage of the hydrophilic nature of cellulosic nanofiller is a high absorption capacity of water, which is undesirable in most applications. Such problems can be minimized by various modifications (hydrophobization) on the surface of the cellulose by several reactions with hydroxyl groups such as esterification (Mohanty et al., 2001) and acylation with a fatty acid. The nanoparticles of silica improve tension properties of polypropylene, starch, starch/polyvinyl alcohol, except that the starch reduces the water absorption and improves the barrier to oxygen for polypropylene.

Biopolymers

Biopolymers have attracted great attention as a potential replacement for conventional materials, plastic packaging due to the increased interest in sustainable development. Biopolymers are polymeric materials which are biodegradable or have a composition of bio-based. The carbon content in biopolymers derived from the biological material in relation to the polymers in which the carbon contents derived from the fossil resource. Biopolymers include materials produced based on plants (starch, cellulose, other polysaccharides, protein), animal products (proteins, polysaccharides), microbial products (polyhydroxybutyrate), and polymers synthesized chemically from monomers of natural origin (polylactic acid). Biopolymers are biodegradable materials, because

at least one step in the process of degradation appeared as a result of metabolism of microorganisms that occur naturally in the environment. Under certain conditions of humidity, temperature and exposure to oxygen, biodegradation leads to the decomposition and degradation of the polymeric material to a non-toxic and environmentally acceptable residue. Biopolymers as packaging material is relatively poor material because of its mechanical and barrier properties which currently limits its industrial use. A particular challenge is the development of moisture barrier properties because of the hydrophilic nature of biopolymers. However, it has been shown that the disadvantages of packaging materials based on biopolymers can be reduced by application of nanocomposites technology.

The use of biopolymer/biodegradable plastics is still limited. The three main problems are: lower mechanical, thermal and barrier properties, processability and price. Other problems are the degree of degradation under certain conditions, changes in the mechanical properties during the disposal, the potential growth of microorganisms and the release of harmful substances. However, the application of nanotechnology, i.e. by incorporation of nanoparticles or preparing polymer nanocomposites can help to overcome these problems. The nanoparticles have a high specific surface, and the advantage of ultra large contact area per unit volume between the polymer matrix and nanoelements, greater functionality per unit weight and the lack of high surface energy which results in agglomeration of the particles.

In order to benefit from the nanoparticles and obtain specific functional properties of polymer nanocomposites requires a good dispersion of nanoparticles. The final properties of polymer nanocomposites depend on the uniform dispersion of nanoparticles (no agglomeration). Uniform dispersion of the nanoparticles depends on the type nanoparticles (size, specific surface area), the concentration of nanoparticles and polymer matrix type, the interaction between the nanoparticles and polymer matrix, and the manner of production (in solvent evaporation, in situ polymerization, blending in the melt). The challenge in obtaining new materials is the structure of polymer nanocomposites with desired properties. The application of nanotechnology in food packaging is still in the development phase.

Bio-nanofibers such as chitosan, cellulose and collagen have high specific surface area per unit of weight and 1000-times relative to the microfibrils, excellent mechanical properties and are lightweight. The fibers may in some cases have superior properties compared to traditional polymers and can be used in both cases, either as a packaging material or as an additive to be injected into the polymer matrix in order to achieve additional functional properties.

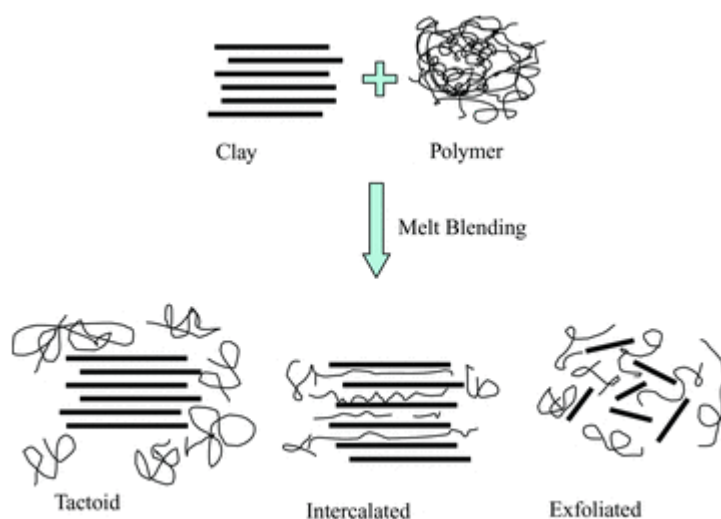


Fig. 1. Polymer clay morphologies (Arora and Padua, 2010)

Nano coating

Coatings based on nano-silica, nano-titanium, nano-aluminum may be: high barrier coatings that prevent the permeability of gases, hydrophobic coatings that enable self-cleaning, antimicrobial coatings for hygiene areas. Edible films based on polysaccharides are water soluble, inexpensive, reducing moisture resistance, while based proteins have good mechanical properties, good barrier properties to oxygen, but a reduced resistance to moisture and lipid-based show good resistance to moisture and poor barrier properties for oxygen.

Poly(lactide) (PLA) is a thermoplastic polyester which is obtained from lactic acid by fermentation of corn starch. This is a polymer with a high molecular weight, transparent, brittle, well-processed, has a high cost and can be recycled and composted. Combining nanoclay and biopolymers such as proteins and sugars can create potentially non-toxic biodegradable and biocompatible material called "green nanocomposite".

Metal nanoparticles such as silver, gold, zinc, iron, nickel, titanium, palladium, iridium and platinum (Özkar and Finke, 2005; Zhang et al., 2003), sometimes are used as catalysts, the most inert metals are studied for use in medicine, for example in the thermal treatment of tumors. Inorganic nanoparticles of metal oxides TiO_2 , ZnO and ZnS , and carbon nanotubes improves the mechanical and barrier properties, enabling thermal and electrical conductivity, additional functional properties such as antimicrobial and UV protection (already present in the market in sunscreen and cosmetic products) and photocatalytic properties.

Antimicrobial systems

Antimicrobial food packaging systems have received considerable attention since they help control the growth of pathogenic and spoilage microorganisms on food surfaces, where microbial growth predominates. Antimicrobial nanocomposite systems are particularly interesting, since materials in the nanoscale range have a higher surface-to-volume ratio when compared with their microscale counterparts. Nanomaterials are thus more efficient, since they are able to attach more copies of microbial molecules and cells (Luo and Stutzenberger, 2008).

Nanoscale materials have been investigated for antimicrobial activity as growth inhibitors (Cioffi et al., 2005), killing agents (Stoimenov et al., 2002; Qi et al., 2004; Huang et al., 2005; Kumar and Münstedt, 2005), or antibiotic carriers (Gu et al., 2003).

Silver is well known for its strong toxicity to a wide range of microorganisms (Liao et al., 1997), besides some processing advantages such as high temperature stability and low volatility (Kumar and Münstedt, 2005). Silver nanoparticles have been shown to be effective antimicrobials, even more effective than larger silver particles, thanks to their larger surface area available for interaction with microbial cells (An et al., 2008). In fact, the most common nanocomposites used as antimicrobial films for food packaging are based on silver nanoparticles, whose antimicrobial activity has been ascribed to different mechanisms, namely: (a) adhesion to the cell surface, degradation of lipopolysaccharides and formation of "pits" in the membranes, largely increasing permeability (Sondi and Salopek-Sondi, 2004), b) penetration inside bacterial cell, damaging DNA (Li, Q. et al., 2008) and releasing

antimicrobial Ag^+ ions by dissolution of silver nanoparticles (Morones et al., 2005).

The antimicrobial activity of silver based systems depends on releasing of Ag^+ , which binds to electron donor groups in biological molecules containing sulphur, oxygen or nitrogen. Besides the antimicrobial activity, silver nanoparticles have been reported to absorb and decompose ethylene, which may contribute to their effects on extending shelf life of fruits and vegetables (Li, H. et al., 2009).

Titanium dioxide (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 phospholipids present in microbial cell membranes has been used to inactivate food-related pathogenic bacteria.

Metal doping improves visible light absorbance of TiO_2 (Anpo et al., 2001) and increases its photocatalytic activity under UV irradiation. It has been demonstrated that doping TiO_2 with silver greatly improved photocatalytic bacterial inactivation (Page et al., 2007). This is explained by Chen and coworkers who have received effective antibacterial activity of polyvinylchloride nanocomposites with TiO_2/Ag^+ nanoparticles (Cheng et al., 2006).

Carbon nanotubes have also been reported to have antibacterial properties. Direct contact with aggregates of carbon nanotubes have been demonstrated to kill *E. coli*, possibly because the long and thin nanotubes puncture microbial cells, causing irreversible damages and leakage of intracellular material (Kang et al. 2007). On the other hand, there are studies suggesting that carbon nanotubes may also be cytotoxic to human cells, at least when in contact to skin or lungs, which would affect people manipulating the nanotubes in processing stages rather than consumers. Anyway, once present in the food packaging material, the nanotubes might eventually migrate into food. Then, it is mandatory to know any eventual health effects of ingested carbon nanotubes.

Intelligent packaging

Intelligent packaging interacts with the environment, indicates on a condition of packaged food, freshness, presence of gases, controlled release of bioactive compounds. A smart food packaging system may be defined as a system that “perceives” some property of the packaged food and uses some mechanism to register and transmit information about the current quality or safety status of the food. In this context, nanostructures can be applied as reactive particles in packaging materials. The so-called nanosensors may be able to respond to environmental changes during storage (e.g., temperature, relative humidity, oxygen exposure), degradation products or microbial contamination. Nanosensors are an indicator of the quality of food (Bouwmeester et al., 2009).

Time-temperature integrators

Time- temperature indicators or integrators (TTIs) are designed to monitor, record and translate whether a certain food product is safe to be consumed, in terms of its temperature history. This is particularly important when food is stored in conditions other than the optimal ones. For instance, if a product is supposed to be frozen, a TTI can indicate whether it had been inadequately exposed to higher temperatures and the time of exposure. The communication is usually manifested by a color development (related to a temperature dependent migration of a dye through a porous material) or a color change (using a temperature dependent chemical reaction or physical change) (Fig. 2) Timestrip® has developed a system (iStrip) for chilled foods, based on gold nanoparticles, which is red at temperatures above freezing. Accidental freezing leads to irreversible agglomeration of the gold nanoparticles resulting in loss of the red color.



Fig. 2. Intelligent inks that change color with the temperature

(<https://www.interempresas.net/Alimentaria/Articulos/30555-Envases-inteligentes-envases-que-comunican.html>)

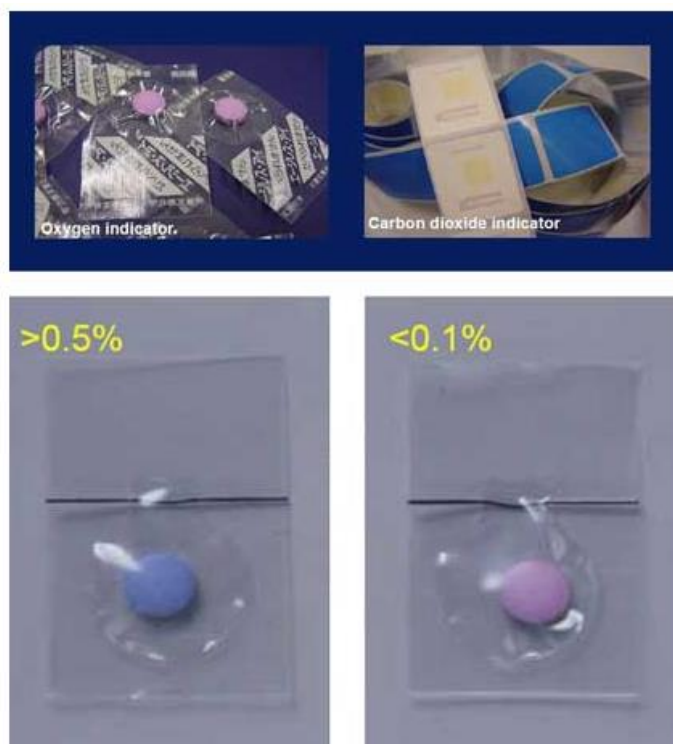


Fig. 3. Indicators of leakage O₂ and CO₂ (above). Indicator of O₂ (below)
 (<https://www.interempresas.net/Alimentaria/Articulos/30555-Envases-inteligentes-envases-que-comunican.html>)

Indicators of leaks

Leak indicators based on oxygen and carbon dioxide can be used to monitor the quality of food (Fig. 3). These indicators have a change of colour as a result of a chemical or enzymatic reaction by the presence or absence of these gases.

There has been an increasing interest to develop non-toxic and irreversible O₂ sensors to assure O₂ absence in oxygen-free food packaging systems, such as packaging under vacuum or nitrogen. Lee et al. (2005) developed an UV-activated colorimetric O₂ indicator which uses TiO₂ nanoparticles to photosensitize the reduction of methylene blue (MB) by triethanolamine in a polymer encapsulation medium using UVA light. Upon UV irradiation, the sensor bleaches and remains colorless until it is exposed to oxygen, when its original blue color is restored. The rate of color recovery is proportional to the level of oxygen exposure.

Conclusions

Applications of nanotechnology in food packaging sector are related to improve the properties of packaging and to mechanical, thermal and barrier, biodegradable, improve the durability of packed products. Polymers are one of the most widely

used material in the human environment. Polymer industry each year increase in the production of these materials, mainly in the food industry, and slightly lower growth in the rest industrial branches. The use of polymers on a global level is a very small risk to health and the environment. Harmful effect should not be neglected, but further research and development of other polymers with a much lower environmental impact. Polymers are an essential material of the future, and because of that reason their use will grow and expand it. The polymer and biopolymer nanocomposites promise competitive and eco-sustainable solutions for food packaging. Smart and intelligent packaging increases the hygienic safety and regularity of packed food, reducing waste generation by extending the shelf life of food packaged products. Greater use of polymer-nanocomposite in industry in Europe is going very slowly, and the main reasons are: the cost price of materials and processing, restrictions due to legislation, acceptance by customers in the market, lack of knowledge about the effectiveness and impact of nanoparticles on the environment and on human health, the potential risk due to migration of nanoparticles in food, and balance between the use of biomass for the production of materials or food.

References

- Adame, D., Beall, G.W. (2009): Direct measurement of the constrained polymer region in polyamide/clay nanocomposites and the implications for gas diffusion, *Applied Clay Science*, 42, 545-552. doi: 10.1016/j.clay.2008.03.005.
- Alexandre, B., Langevin, D., Médéric, P., Aubry, T., Couderc, H., Nguyen, Q. T., Saiter, A., Marais, S. (2009): Water barrier properties of polyamide 12/montmorillonite nanocomposite membranes: structure and volume fraction effects, *Journal of Membrane Science* 328 (1-2), 186-204. doi: 10.1016/j.memsci.2008.12.004.
- Alexandre, M., Dubois, P. (2000): Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials. *Materials Science and Engineering, R: Reports* 28, 1-63. doi: 10.1016/S0927-796X(00)00012-7.
- Arora A., Padua G.W. (2010): Nanocomposites in Food Packaging Review, *Journal of Food science* 75 (1), 43-49. doi: 10.1111/j.1750-3841.2009.01456.x.
- An, J., Zhang, M., Wang, S., Tang, J. (2008): Physical, chemical and microbiological changes in stored green asparagus spears as affected by coating of silver nanoparticles-PVP, *LWT-Food Science and Technology* 41 (6), 1100-1107. doi: 10.1016/j.lwt.2007.06.019.
- Anpo, M., Kishiguchi, S., Ichihashi, Y., Takeuchi, M., Yamashita, H., Ikeue, K., Morin, B., Davidson, A., Che, M. (2001): The design and development of second-generation titanium oxide photocatalysts able to operate under visible light irradiation by applying a metal ion-implantation method, *Research on Chemical Intermediates* 27 (4-5), 459-467. doi: 10.1163/156856701104202101.
- Finnigan, B. (2009): Barrier polymers, in: K.L. Yam (Ed.), *The Wiley Encyclopedia of Packaging Technology*, John Wiley and Sons, Inc., New York, pp. 103-109. doi: 10.1002/9780470541395.
- Bondeson, D. and Oksman, K. (2007): Polylactic acid/cellulose whisker nanocomposites modified by polyvinyl alcohol, *Composites: Part A* 38, 2486-2492. doi: 10.1016/j.compositesa.2007.08.001.
- Bouwmeester, H., Dekkers, S., Noordam, M.Y., Hagens, W.I., Bulder, A.S., De Heer, C., Ten Voorde, S.E.C.G., Wijnhoven, S.W.P., Marvin, H.J.P. and Sips, A.J.A.M. (2009): Review of health safety aspects of nanotechnologies in food production, *Regulatory Toxicology and Pharmacology* 53, 52-62. doi: 10.1016/j.yrtph.2008.10.008.
- Cheng, Q., Li, C., Pavlinek, V., Saha, P., Wang, H. (2006): Surface-modified antibacterial TiO₂/Ag⁺ nanoparticles: Preparation and properties, *Applied Surface Science* 252, 4154-4160. doi: 10.1016/j.apsusc.2005.06.022.
- Cioffi, N., Torsi, L., Ditaranto, N., Tantillo, G., Ghibelli, L., Sabbatini, L., Blevè-zacheo, T.; D'alessio, M., Zambonin, P.G., Traversa, E. (2005): Copper nanoparticle/polymer composites with antifungal and bacteriostatic properties, *Chemistry of Materials* 17, 5255-5262. doi: 10.1021/cm0505244.
- Freire, C.S.R.; Silvestre, A.J.D.; Pascoal Neto, C.; Gandini, A.; Martin, L., Mondragon, I. (2008): Composites based on acylated cellulose fibers and low-density polyethylene: Effect of the fiber content, degree of substitution and fatty acid chain length on final properties, *Composites Science and Technology* 68 (15-16), 3358-3364. doi: 10.1016/j.compscitech.2008.09.008.
- Fujishima, A., Rao, T.N., Tryk, D.A. (2000): Titanium dioxide photocatalysis, *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 1 (1), 1-21. doi: 10.1016/S1389-5567(00)00002-2.
- Gu, H.W., Ho, P.L., Tong, E., Wang, L., Xu, B. (2003): Presenting vancomycin on nanoparticles to enhance antimicrobial activities, *Nano Letters* 3, 1261-1263. doi: 10.1021/nl034396z.
- Helbert, W., Cavaillé, C.Y., Dufresne, A. (1996): Thermoplastic nanocomposites filled with wheat straw cellulose whiskers. Part I: Processing and mechanical behaviour, *Polymer Composites* (17) 4, 604-611. doi: 10.1002/pc.10650.
- <http://en.european-bioplastics.org/market/market-development/production-capacity/>
- <https://www.interempresas.net/Alimentaria/Articulos/30555-Envases-inteligentes-envases-que-comunican.html>
- Huang, L., Li, D.Q., Lin, Y.J., Wei, M., Evans, D.G., Duan, X. (2005): Controllable preparation of nano-MgO and investigation of its bactericidal properties, *Journal of Inorganic Biochemistry* 99, 986-993. doi: 10.1016/j.jinorgbio.2004.12.022.
- Hubbe, M.A., Rojas, O.J., Lucia, L.A., Sain, M. (2008): Cellulosic nanocomposites: A review. *Bioresources* 3 (3), 929-980. doi: http://ojs.cnr.ncsu.edu/index.php/BioRes/article/view/BioRes_03_3_0929_Hubbe_RLS_Cellulosic_Nanocomposites_Rev274.
- Kang, S., Pinault, M., Pfefferle, L.D., Elimelech, M. (2007): Single-walled carbon nanotubes exhibit strong antimicrobial activity, *Langmuir* 23, 8670-8673. doi: 10.1021/la701067r.
- Kumar, R., Münstedt, H. (2005): Silver ion release from antimicrobial polyamide/silver composites, *Biomaterials* 26, 2081-2088. doi: 10.1016/j.biomaterials.2004.05.030.
- Li, H., Li, F., Wang, L., Sheng, J., Xin, Z., Zhao, L., Xiao, H., Zheng, Y., Hu, Q. (2009): Effect of nano-packing on preservation quality of Chinese jujube (*Ziziphus jujuba* Mill. var. *inermis* (Bunge) Rehd), *Food Chemistry* 114 (2), 547-552. doi: 10.1016/j.foodchem.2008.09.085.
- Li, Q., Mahendra, S., Lyon, D.Y.; Brunet, L., Liga, M.V., Li, D., Alvarez, P.J.J. (2008): Antimicrobial nanomaterials for water disinfection and microbial control: Potential applications and implications, *Water Research* 42 (18), 4591-4602. doi: 10.1016/j.watres.2008.08.015.
- Liau, S.Y., Read, D.C., Pugh, W.J., Furr, J.R., Russell, A.D. (1997): Interaction of silver nitrate with readily identifiable groups: Relationship to the antibacterial action of silver ions, *Letters in Applied Microbiology* 25, 279-283. doi: 10.1046/j.1472-765X.1997.00219.x.

- Ludueña, L.N., Alvarez, V.A., Vasquez, A. (2007): Processing and microstructure of PCL/clay nanocomposites. *Materials Science and Engineering: A* 460-461, 121-129. doi: 10.1016/j.msea.2007.01.104.
- Luo, P.G., Stutzenberger, F. J. (2008): Nanotechnology in the detection and control of microorganisms, *Advances in Applied Microbiology* 63, 145-181. doi: 10.1016/S0065-2164(07)00004-4.
- Masciaglioli, T., Zhang, W. (2003): Environmental Technologies at the Nanoscale, *Environ. Sci. Technol.* 37, 102A-108A. doi: 10.1021/es0323998.
- Mohanty, A.K., Misra, M., Drzal, L. T. (2001): Surface modifications of natural fibers and performance of the resulting biocomposites: An overview, *Composite Interfaces* 8 (5), 313-343. doi: 10.1163/156855401753255422.
- Morones, J.R., Elechiguerra, J.L., Camacho, A., Holt, K., Kouri, J.B., Ramirez, J.T., Yacaman, M. J. (2005): The bactericidal effect of silver nanoparticles, *Nanotechnology* 16, 2346-2353. doi: 10.1088/0957-4484/16/10/059.
- Osman, M.A., Ploetze, M., Suter, U.W. (2003): Surface treatment of clay minerals - thermal stability, basal-plane spacing and surface coverage, *Journal of Materials Science* 13, 2359-2366. doi: 10.1039/B302331A.
- Özkar S., Finke R.G. (2005): Iridium (0) Nanocluster, Acid-Assisted Catalysis of Neat Acetone Hydrogenation at Room Temperature: Exceptional Activity, Catalyst Lifetime, and Selectivity at Complete Conversion, *J. Am. Chem. Soc.* 127, 4800-4808. doi: 10.1021/ja0437813.
- Page, K., Palgrave, R.G., Parkin, I.P., Wilson, M., Savin, S.L.P., Chadwick, A.V. (2007): Titania and silver-titania composite films on glass-potent antimicrobial coatings, *Journal of Materials Chemistry* 17 (1), 95-104. doi: 10.1039/B611740F.
- Paralikar, S.A., Simonsen, J., Lombardi, J. (2008): Poly(vinyl alcohol)/cellulose nanocrystal barrier membranes. *Journal of Membrane Science* 320 (1-2), 248-258. doi: 10.1016/j.memsci.2008.04.009.
- Picard, E., Gauthier, H., Gérard, J.F., Espuche, E. (2007): Influence of the intercalated cations on the surface energy of montmorillonites: Consequences for the morphology and gas barrier properties of polyethylene/montmorillonites nanocomposites, *Journal of Colloid and Interface Science* 307, 364-376. doi: 10.1016/j.jcis.2006.12.006.
- Podsiadlo, P., Choi, S.Y., Shim, B., Lee, J., Cuddihy, M., Kotov, N.A. (2005): Molecularly engineered nanocomposites: Layer-by-layer assembly of cellulose nanocrystals, *Biomacromolecules* 6, 2914-2918. doi: 10.1021/bm050333u.
- Qi, L.F., Xu, Z.R.; Jiang, X., Hu, C., Zou, X. (2004): Preparation and antibacterial activity of chitosan nanoparticles, *Carbohydrate Research* 339, 2693-2700. doi: 10.1016/j.carres.2004.09.007.
- Ray, S., Easteal, A., Quek, S.Y., Chen, X.D. (2006): The potential use of polymer-clay nanocomposites in food packaging. *International Journal of Food Engineering* 2 (4), artigo 5. doi: 10.2202/1556-3758.1149.
- Roco M.C., Mirkin C.A., Hersam M.C. (Eds.) (2010): Nanotechnology Research Directions for Societal Needs in 2020: Retrospective and Outlook, World Technology Evaluation Center (WTEC) and the National Science Foundation (NSF), *J Nanopart Res.* doi: 10.1007/s11051-011-0275-5.
- Sanchez-Garcia, M.D., Gimenez, E., Lagaron, J.M. (2008): Morphology and barrier properties of solvent cast composites of thermoplastic biopolymers and purified cellulose fibers, *Carbohydrate Polymers* 71, 235-244. doi: 10.1016/j.carbpol.2007.05.041.
- Sondi, I., Salopek-Sondi, B. (2004): Silver nanoparticles as antimicrobial agent: a case study on E. coli as a model for Gram-negative bacteria, *Journal of Colloid and Interface Science* 275, 177-182. doi: 10.1016/j.jcis.2004.02.012.
- Stoimenov, P., Klinger, R.L., Marchin, G.L., Klabunde, K.J. (2002): Metal oxide nanoparticles as bactericidal agents, *Langmuir* 18, 6679-6686. doi: 10.1021/la0202374.
- Tan, W., Zhang, Y., Szeto, Y.S., Liao, L. (2008): A novel method to prepare chitosan/montmorillonite nanocomposites in the presence of hydroxyl-aluminum oligomeric cations, *Composites Science and Technology* 68 (14), 2917-2921. doi: 10.1016/j.compscitech.2007.10.007.
- Weiss, J., Takhistov, P., McClements, D.J. (2006): Functional materials in food nanotechnology, *Journal of Food Science* 71 (9), R107-116. doi: 10.1111/j.1750-3841.2006.00195.x.
- Zhang, Q., Kusaka, Y., Zhu, X., Sato, K., Mo, Y., Kluz, T., Donaldson, K. (2003): Comparative toxicity of standard nickel and ultrafine nickel in lung after intratracheal instillation, *J. Occup. Health* 45, 23-30. doi: <http://doi.org/10.1539/joh.45.23>.

Received: October 13, 2015

Accepted: December 1, 2015

Published online: December 9, 2015