Packaging applications of nanomaterials

Remya, S*., Mohan, C. O., Sreelakshmi, K. R. & Bindu, J.
*Scientist, QAM Division
ICAR-Central Institute of Fisheries Technology, Cochin
remya03cof@gmail.com

Food and beverage industry is in search of novel technologies to enhance the quality, safety and storage life of their products. Nanotechnology became immediately popular in the food sector, because of its potential to develop materials with improved properties that can be used as food contact materials. Currently, many large food companies in the world are reportedly exploring the potential of nanomaterials for using in food or food packaging (Chaudhry *et al*., 2008). Undoubtedly, the most active area of food nanoscience research and development is packaging. The very purpose of food packaging was considered as protecting and preserving the food inside while maintaining its quality and safety. Of late, in response to the advancement of nano technology as well as the changing consumers' demand, the food industry is attempting to develop functional packaging systems with enhanced end use convenience features, which also provides essential product information to consumers to facilitate the promotion and advertisement of the product. As a result, packaging represents about 2 % of Gross National Product (GNP) in developed countries and has become the third largest industry in the world (Mihindukulasuriya and Lim, 2014). Globally, the nano-enabled food and beverage packaging market was 4.13 billion US dollars in 2008 (Duncan, 2011).

Nanotechnology

The idea of nanotechnology was presented by Richard Feynman in 1959 and the term "nano technology" was first used by Norio Taniguchi in 1974. The word 'nano' denotes nanometer (10^{-9} m) and nanotechnology involves manufacture and use of materials in the size range of up to about 100 nm in one or more dimensions. European Commission (2009) has defined nanomaterial as an insoluble or bio-persistent and intentionally manufactured material with one or more external dimensions, or an internal structure, on a scale from 1 to 100 nm. Nanomaterials are abundant in nature and many methods are available to produce nanomaterials. Nanoparticles can be produced top down from larger structures by grinding, use of lasers, and vaporization followed by cooling. Alternately, bottom-up methods are commonly used for the synthesis of complex nanoparticles. These methods include solvent extraction/ evaporation, crystallization, self-assembly, layer-by-layer deposition, microbial synthesis, and biomass reactions (Brody *et al*., 2006). All of these are being researched for potential application in food packages.

Applications of nanomaterials in packaging

Insufficient mechanical and barrier properties, non-sustainable production, lack of recyclability, high cost, difficulty in recycling of polymer blends and multilayered composite structure, and achieving adequate shelf-life while maintaining the optimal quality and safety of the product are some of the challenges presently faced by the food and packaging industries. Presently, the incorporation of nanomaterials into plastics and bioplastics is gaining a lot of research interest, since it positively modifies the food packaging by improving barrier and mechanical properties, which also provide the ability to destroy and detect pathogens and make the packages active and intelligent.

The following are the different ways of incorporating nanomaterials in packaging (Bradley *et al*., 2011).

1. *Nanocomposites*: Incorporating nanomaterials into the packaging to improve its physical performance, durability, barrier properties, and biodegradation.
2. *Nano coatings*: Incorporating nanomaterials onto the packaging surface to improve especially the barrier properties.
3. *Surface biocides*: Incorporating nanomaterials with antimicrobial properties acting on the packaging surface.
4. *Active packaging*: Incorporating nanomaterials with antimicrobial or other properties with intentional release into the packaged food.
5. *Intelligent packaging*: Incorporating nanosensors to monitor and report on the condition of the food

Nanocomposites

The nano enabled system, which has gained the highest popularity in food packaging development, is nanocomposites. A composite material is a combination of two or more phases. One phase is the continuous phase and the other is the disperse phase. Generally, the continuous phase is a polymer, which surrounds the disperse phase and the disperse phase is the filler or reinforcing material. When the dispersed phase is nanostructured, the composite is known as nanocomposite. The concept of nanocomposites was developed in the late 1980s and firstly commercialized by Toyota. The research on the use of nanocomposites for food packaging applications started in the 1990s.

Table 1. Different types of nano-fillers for composite making

Classification	Type of nano-filler	Example
Organic	*Clay*	*Montmorillonite (MMT)*
	Natural biopolymers	*Chitosan, Cellulose*
	Natural antimicrobial agents	*Nisin*
Inorganic	*Metal*	*Silver, Copper, Gold*
	Metal oxide	*ZnO, TiO_2, MgO*

Clay is the most common filler that has been modified as nano-composite materials for food packaging applications. Amounts of nano clays, which are being incorporated, vary from 1 % to 5 % by weight. The most extensively studied clay was montmorillonite (MMT), due to the high surface area and aspect ratio. The most common type of metal studied is silver, due to the antimicrobial properties as well as stability and low volatility at high temperature. ZnO is the common type of metal oxide used, due to the deodorizing and antibacterial properties.

In general, there are three possible arrangements for layered silicate clay nanocomposite materials (three different modes of dispersed phase).

- **Tactoids/Nonintercalated:** Silicate layers are not delaminated (Microcomposites)
- **Intercalated:** Polymer chains are inserted into the galleries of the silicate layers
- **Exfoliated/Delaminated:** Silicate layers are completely delaminated and homogenously dispersed in the polymer. This is the ideal nanocomposite arrangement, but is hard to achieve.

Improvement of mechanical properties

Food packages should have good physical properties to protect the food from damage. The mechanical properties of the packaging materials can be enhanced by incorporation of nanomaterials such as nano fibres and rods for nanocomposite formation. The nanocomposites, thus prepared by nano reinforcement of polymers, will have excellent physical properties. Especially, fibres with a high aspect ratio (the ratio of length to width, e.g. >300) can confer useful physical characteristics to the package. Compared to traditionally used fillers like glass fibres and talc, nanomaterials are required in very less quantity to enhance the physical performance of the package. The strength and stiffness of nanocomposites prepared by materials like carbon nanotubes and cellulose nanofibres (also called cellulose nano whiskers/nanocrystals) are much better than the conventionally used materials (Siro and Plackett, 2010). Kvien *et al*. (2005) reported that biopolymers strengthened with dispersed cellulose nanowhiskers (CNW) had improved mechanical properties and thermal stability.

Enhanced barrier properties

One of the major limitations of biopolymers is their weaker barrier properties as compared to the petroleum-based counterparts. Nanocomposite formation is a proven technology for enhancing the barrier properties of biopolymer, as well as synthetic thermoplastics. The incorporation of fillers, such as nanoplatelets with high surface to thickness ratio into the polymer, enhances the barrier properties for the diffusion of permeant molecules. The presence of these fillers, which are impermeable or less permeable to gases and water vapour than the polymer matrices, results in a longer diffusion path taken by the permeant molecules as compared to their diffusion path taken in the pristine polymer matrix. This results in enhancement of overall barrier properties of a nanocomposite against vapours and gases. Clay/polymer nanocomposite is the most studied nanocomposite for food packaging applications (Lagaron *et al*., 2005). RodrIguez *et al.* (2012) have reported that oxygen transmission rate (OTR) and water vapour transmission rate (WVTR) of cellulose acetate reduced by 50 and 10 %, respectively by organic montmorillonite (OMMT). Another study showed that oxygen barrier properties of low density polyethylene (LDPE) improved by seven times after incorporating organic montmorillonite (Xie *et al*., 2012).

Nano-coatings

Nano-coatings, due to its antimicrobial efficiency and superior barrier property over multilayer films, have gained popularity in food packaging sector. In nano-structured coatings, nanosized materials are incorporated onto the packaging surface (either the inside or the outside surface, or a sandwiched as a layer in a laminate). Compared to multilayer films, reduced material usage and simpler film conversion process are advantages of nano-coatings. In a previous study by Hirvikorpi *et al*. (2010), barrier performance of the biopolymer PLA was improved after coating with aluminum oxide and antimicrobial efficiency of PVC film was enhanced by ZnO coating (Li *et al*., 2010)

Surface biocides

Biocides, which are generally using to bring down the number of microbes in food and food contact materials, have many applications in the food processing sector. Based on their application, biocides are grouped into process biocides, surface biocides and food preservatives. Surface biocides, which are incorporated into the food contact materials for reducing the number of microorganisms attached to it, will not be released from the material. Similarly, nanoenabled biocidal agents help to maintain the hygienic condition of the food contact surface by preventing or reducing microbial growth. It is different from active packaging and has no preservative effect on the food (Bradley *et al*., 2011). They are useful in food processing equipment and food handling equipment (e.g. conveyor belts) that are difficult to clean in place

Active packaging

According to the European Union Guidance to the Commission Regulation (EUGCR) No 450/2009 (EU, 2009), active food packaging systems, incorporated with active compounds such as antimicrobial compounds, oxygen absorbers, water vapour absorbers, ethylene scavengers, etc., are supposed to perform some role in addition to providing an inert barrier to external conditions. It is a novel packaging system/technology, which permits the product and the surrounding environment to interact for enhancing the product's storage life and microbial safety, while maintaining the quality of the food packaged inside (Ahvenainen, 2003).

Antimicrobial nanomaterials

Antimicrobial packaging is the most promising form of active packaging, where an antimicrobial nanomaterial is added into the packaging material for releasing onto the food surface. Thus, the storage life of food can be improved using antimicrobial nanoparticles and nanocomposites. Nano particles, due to their small dimension and surface reactivity, provide antimicrobial activity to packaging materials for preventing the proliferation of spoilage and pathogenic microorganisms. Metal nanoparticles such as silver, gold, zinc, or metal oxides are widely using in various active packaging applications. Rhim *et al*. (2014) reported that silver nanoparticles, when added in agar films, exhibited antimicrobial activity against both gram positive (*Listeria monocytogenes)* and gram negative (*Escherichia coli* O157:H7) pathogens. In the same way, PLA/silver-OMMT antimicrobial nanocomposite showed strong antimicrobial efficiency against gram-negative *Salmonella sp.* (Busolo *et al*., 2010) and sodium alginate film loaded with silver nanoparticle exhibited antibacterial activity against *Staphylococcus aureus* and *Escherichia coli* (Fayaz *et al*., 2009).

Oxygen scavengers

Presence of oxygen in food package can reduce product shelf-life because of various degradation reactions such as rancidity, growth of aerobic microorganisms, browning, depletion of vitamins, loss of essential flavour compounds etc. Hence, oxygen within the package should be eliminated or reduced to a level acceptable. Packaging substrates coated or incorporated with nanomaterials have been investigated for their oxygen scavenging ability. Packaging substrates that have been coated with TiO_2 have been examined for their oxygen scavenging ability. High density polyethylene (HDPE) packaging films with oxygen absorbing efficiency was developed by incorporating with iron containing kaolinite (Busolo and Lagaron, 2012). The oxygen scavenging capacity of this altered HDPE film was attributed to oxygen trapping and increased tortuous diffusion path.

Intelligent packaging

Intelligent packaging systems can monitor the condition of packaged foods to give information regarding the quality of the packaged food during transport and storage. It can be basically divided into sensors and indicators. The nanotechnology enabled indicator/sensor, interacts with internal factors (food components and headspace species) and/or external environmental factors and generates a response (e.g., visual cue, electrical signal), that correlates with the state of the food product. For example, a UV activated oxygen indicator has been fabricated using TiO_2 nanoparticles (Mills and Hazafy, 2008). Smolander *et al*. (2004) prepared a freshness indicator by coating transition metal (silver and/or copper) on plastic film or paper, which upon reacting with sulphide volatiles, produced as fresh meats undergo spoilage, turns into distinctive dark colour. Triangular Ag nanoplates were employed as colorimetric indicators (Zeng *et al*., 2010), which keep track of time-temperature histories to which a perishable product is exposed from the point of manufacture to the retail outlet or end-consumer. Antibodies conjugated to nanomaterials, such as quantum dots, have been developed to detect bacteria. Yang and Li (2006) studied the use of quantum dots for simultaneous detection of *Escherichia coli* O157:H7 and *Salmonella Typhimurium*.

Conclusion

Nanomaterials can not only passively protect the food against environmental factors, but also incorporate properties to the packaging material so it may actually enhance stability of foods, or at least to indicate their eventual inadequation to be consumed. Moreover, nanotechnology derived packaging was perceived by public as being more beneficial than the nanotechnology engineered foods, which means nanotechnology inside a food is perceived as less acceptable than being on the outside (i.e. in the food packaging). However, there are many safety concerns about nanomaterials. There is limited scientific data about migration of most types of nanoparticles from the packaging material into food, as well as their eventual toxicological effects. So, precautions should be taken and more research is required on the migration behaviours of nanomaterials in food and its potential impacts on health/safety, as well as the environment.

Suggested Readings

- Ahvenainen, R. (2003). Active and intelligent packaging: An introduction. In R. Ahvenainen (Ed.), *Novel food packaging techniques* (pp. 5-21). Cambridge, UK: Woodhead Publishing Ltd.
- Busolo, M. A., Fernandez, P., Ocio, M. J., & Lagaron, J. M. (2010). Novel silver-based nanoclay as an antimicrobial in polylactic acid food packaging coatings. *Food Additives and Contaminants*, 27, 1617-1626.
- Busolo, M. A., & Lagaron, J. M. (2012). Oxygen scavenging polyolefin nanocomposite films containing an iron modified kaolinite of interest in active food packaging applications. *Innovative Food Science & Emerging Technologies*, 16, 211-217.
- Bradley, E. L., Castle, L., & Chaudhry, Q. (2011). Applications of nanomaterials in food packaging with a consideration of opportunities for developing countries. *Trends in Food Science and Technology*, 22, 604-610.
- Brody, A. L., Bugusu, B., Han, J. H., Sand, C. K., & McHugh, T. H. (2008). Innovative Food Packaging Solutions. *Journal of Food Science*, 73(8), R107-R116.
- Chaudhry, Q., Scotter, M., Blackburn, J., Ross, B., Boxall, A., Castle, L., et al. (2008). Applications and implications of nanotechnologies for the food sector. *Food Additives and Contaminants*, 25, 241-258.
- Duncan, T.V. (2011). Applications of nanotechnology in food packaging and food safety: Barrier materials, antimicrobials and sensors. *Journal of Colloid and Interface Science*, 363 (1), 1-24.
- European Commission (2009). Regulation (EC) No 1223/2009 of the European Parliament and of the Council of 30 November 2009 on cosmetic products (recast). *Official Journal L* 342, 22.12.2009, p. 59.
- EU (2009). Guidance to the commission regulation (EC) No 450/2009 of 29 May 2009 on active and intelligent materials and articles intended to come into contact with food. Version 10. European Commission Health and Consumers Directorate- General Directorate E-Safety of the Food chain. E6- Innovation and sustainability.
- Hirvikorpi, T., Vaha-Nissi, M., Harlin, A., & Karppinen, M. (2010). Comparison of some coating techniques to fabricate barrier layers on packaging materials. *Thin Solid Films*, 518, 5463-5466.
- Fayaz, A. M., Balaji, K., Girilal, M., Kalaichelvant, P. T., & Venkatesan, R. (2009). Mycobased synthesis of silver nanoparticles and their incorporation into sodium alginate films for vegetable and fruit preservation. *Journal of Agricultural and Food Chemistry*, 57(14), 6246-6252.
- Lagaron, J. M., Cabedo, L., Cava, D., Feijoo, J. L., Gavara, R., & Gimenez, E. (2005). Improving packaged food quality and safety. Part 2: nanocomposites. *Food Additives and Contaminants*, 22, 994-998.

- Li, X. H., Xing, Y. G., Li, W. L., Jiang, Y. H., & Ding, Y. L. (2010). Antibacterial and physical properties of poly (vinyl chloride)-based film coated with ZnO nanoparticles. *Food Science and Technology International*, 16, 225-232.
- Mihindukulasuriya, S. D. F., & Lim, L. T. (2014). Nanotechnology development in food packaging: A review. *Trends in Food Science & Technology*, 40, 149-167.
- Mills, A., & Hazafy, D. (2008). A solvent-based intelligence ink for oxygen. *Analyst*, 133, 213-218.
- Rhim, J. W., Wang, L. F., Lee, Y., & Hong, S. I. (2014). Preparation and characterization of bio-nanocomposite films of agar and silver nanoparticles: laser ablation method. *Carbohydrate Polymers*, 103, 456-465.
- RodrIguez, F. J., Galotto, M. J., Guarda, A., & Bruna, J. E. (2012). Modification of cellulose acetate films using nanofillers based on organoclays. *Journal of Food Engineering*, 110, 262-268.
- Siro, I., & Plackett, D. (2010). Microfibrillated cellulose and new nanocomposite materials: a review. *Cellulose*, 17, 459-494.
- Smolander, M., Hurme, E., Koivisto, M., & Kivinen, S. (2004). Indicator. In (Vol. *International Patent* WO2004/102185 A1).
- Xie, L., Lv, X. Y., Han, Z. J., Ci, J. H., Fang, C. Q., & Ren, P. G. (2012). Preparation and performance of high-barrier low density polyethylene/organic montmorillonite nanocomposite. *Polymer-Plastics Technology and Engineering*, 51, 1251-1257.
- Yang, L., & Li, Y. (2006). Simultaneous detection of *Escherichia coli* O157:H7 and *Salmonella Typhimurium* using quantum dots as fluorescence labels. *Analyst*, 131, 394-401.
- Zeng, J., Roberts, S., & Xia, Y. (2010). Nanocrystal-based time-temperature indicators. *Chemistry e A European Journal*, 16, 12559-12563.