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APPLICATION OF NANOTECHNOLOGY IN FOOD PACKAGING

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ABSTRACT

Nanotechnology involves the design, production and use of structures through control of the size and shape of the materials at the nanometre scale. Also, nanomaterials have been already applied in many fields of human life. Nanocomposites have already led to several innovations with potential applications in the food packaging sector. The use of nanocomposite formulations is expected to considerably enhance the shelf-life of many types of food. This improvement can lead to lower weight packages because less material is needed to obtain the same or even better barrier properties. This, in turn, can lead to reduced package cost with less packaging waste. Antimicrobial packaging is another area with high potential for applying nanocomposite technology. Nanostructured antimicrobials have a higher surface area-to-volume ratio when compared with their higher scale counterparts. Therefore, antimicrobial nanocomposite packaging systems are supposed to be particularly efficient in their activities against microbial cells. In this review, definition of nanomaterials is presented. Besides, the paper shows examples of nanocomposites and antimicrobial nanopackaging mainly with the use of nanosilver. Moreover, nanoparticles such ZnO, TiO₂, MgO and nanosensors in packaging were presented.

Keywords: Nanotechnology, nanosilver, nano-packaging

INTRODUCTION

Nanotechnology refers to the manipulation of material at the nanometric scale, that is, to a billionth of a meter. Aside from being characterized by operating at such minute dimensions (at which other disciplines such as chemistry and physics also work), nanotechnology refers specifically to the design, characterization, and production of novel nanostructures, nanodevices, and nanosystems based on controlling the form, size, and properties of matter at said scale for the purpose of using them in civil, military, and security applications (Roco 2001, Royal Society and the Royal Academy of Engineering 2004). Also, nanomaterials and nanoparticles may include any of the following nano forms: nanoparticles, nanotubes, fullerenes, nanofibres, nanowhiskers, nanosheets. Som *et al.* (2010) defined nanoparticle as a discrete entity that has three dimensions of the order of 100 nm or less.

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. Nanotechnologies are projected to impact at least \$3 trillion across the global economy by 2020, and nanotechnology industries worldwide may require at least 6 million workers to support them by the end of the decade (Roco *et al.*, 2011). As a result, scientists and industry stakeholders have already identified potential uses of nanotechnology in virtually every segment of the food industry, 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).

According to Silva *et al.* (in press), nanotechnologies are set to impact on the food industry at all stages of production from primary production at farming level, due to advances in pesticide efficacy and delivery (novel formulations and better crop adherence), to processing where emulsion creation and encapsulation have progressed to the nanoscale (Donsi *et al.*, in press; Rao & McClements, 2011). The most active area of food nanoscience research and development is packaging: the global nano-enabled food and beverage packaging market was 4,13 billion US dollars in 2008 and has been projected to grow to 7,3 billion by 2014, representing an annual growth rate of 11,65% (Industry and Market Analysis, 2009). Currently, food packaging represents the largest area of use of

nanotechnology in food industry. Also, the area of food packaging has seen much innovation in barrier improvement with the use of various nanoscale fillers and this has also resulted in reduced effects of targeted accelerating factors of spoilage and contamination (Neethirajan and Jayas, 2011). In this paper, application of nanotechnology in food packaging was discussed. Moreover, nanopackaging, nanocomposites, and nanosensors in intelligent packaging were presented. In this review, highlighted the promising approach to nanosilver in packaging food. Moreover zinc oxide, titanium dioxide, magnesium oxide nanoparticles were described.

NANO-PACKAGING IN THE FOOD INDUSTRY

The food package should hinder gain or loss of moisture, prevent microbial contamination and act as a barrier against permeation of water vapor, oxygen, carbon dioxide and other volatile compounds such as flavors and taints in addition to the basic properties of packaging materials such as mechanical, optical, and thermal properties (Rhim *et al.*, 2013). Also, the goal of food packaging system is to prevent, minimize or delay undesirable changes to the appearance, sensory characteristics like flavor, odor and texture (Pavelková, 2012).

Packaging of the future is likely to be more than just a physical container that provides food with protection from the surrounding environment. Further subdivision of nanopackaging is required; packaging from which migration into the food is purposeful and intended and packaging from which no nanoparticles migrate (in any significant amount). Using nanotechnologies to improve packaging materials is likely to be very costly and will not be introduced until methods are optimized, results are consistent and prove to weigh up favourably against costs (Cushen *et al.*, 2012). Table 1 presents potential applications of nanotechnology in the food packaging sector (Rhim *et al.*, 2013).

Table 1 Potential applications of nanotechnology in the food packaging sector (Rhim *et al.*, 2013)

1. Improved packaging properties: mechanical, thermal, barrier properties
2. Biodegradability: enhanced biodegradation
3. Active packaging: shelf life extension, oxygen scavenger, antimicrobial
4. Intelligent packaging: interaction with the environment, self-cleaning, self-healing, indication of deterioration
5. Delivery and controlled release: nutraceuticals, bioactive compounds
6. Monitoring product conditions: time temperature indicator (TTI), freshness indicator, leakage indicator, gas detector
7. Nanosensor: indication of food quality, growth of microorganisms
8. Nanocoating
9. Antimicrobial
10. Information on product: RFID, nano-barcode, product authenticity

NANOCOMPOSITIES

Traditional materials for food packaging include metal, ceramic (glass), and paper (cardboard). While these materials are still used the light weight, low cost, ease of processing and formability, and remarkable diversity in physical properties of organic polymeric materials makes plastics attractive alternatives for the packaging of foods. Polymers which are most frequently used for food packaging include, but are not limited to, polyolefins such as polypropylene (PP) and various grades of polyethylene (HDPE, LDPE, etc.), 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 (Finnigan, 2009).

Nanocomposites have already led to several innovations with potential applications in the food packaging sector. The dominant property improvement is a higher quality shelf life. This improvement can lead to lower weight packages because less material is needed to obtain the same or even better barrier properties (Rhim *et al.*, 2013). Antimicrobial activity of nanocomposites depends largely on the microbial species, organoclay types and polymer matrix used for nanocomposite formation (Hong and Rhim, 2008). For example, nanocomposites such polymer nanocomposites (PNCs) are created by dispersing an inert, nanoscale filler throughout a polymeric matrix. PNCs are stronger, more flame resistant and possess better thermal properties (e.g., melting points, degradation and glass transition temperatures) than control polymers which contain no nanoscale filler; alterations in surface wettability and hydrophobicity have also been reported. Besides, PNCs should offer the food packaging industry better down gauging opportunities, in addition to cost savings and waste reductions, due to the smaller amounts of polymer that need to be used to attain packaging materials with identical or even better mechanical attributes (Dunkan, 2011). Qi *et al.* (2013) used the poly(butylene succinate) (PBS) and 3 wt% attapulgite (ATP) reinforced branched PBS/ATP nanocomposites using a two-step in situ polymerization as potential packing materials. The introduction of 1,2-octanediol (1,2-OD) improved the thermal stability and the break elongation of PBS, but decreased the tensile strength, crystallization temperature, and crystallization rate. On the contrary, the ATP can effectively act as a nucleating agent, which enhanced the crystallization temperature of PBS matrix. Thus, the potential packing materials with various chemical physical properties could be prepared by different contents of ATP and 1,2-OD units.

Conventional packaging polymers are begun to be questioned due to increasing environmental concerns and their petroleum based sources. Research on sustainable alternative materials for food packaging is a hot topic for over a decade (Cutter, 2006). Özcalik and Tihminlioglu (2013) studied corn zein nanocomposite (CZNC) coatings as an alternative to synthetic polymer barrier layer on polypropylene (PP) films. The study was focused on the investigation of oxygen and water vapor barrier of coated films due to organomodified montmorillonite (OMMT) delamination in corn zein coatings. The final films showed good compatibility between ZNC coating and PP in terms of appearance and adhesion. Also, this is a promising eco-friendly alternative to conventional barrier packaging systems. Kumar *et al.* (2010) prepared bio-nanocomposite films based on soy protein isolate and montmorillonite. The results showed the feasibility of using bio-nanocomposite technology to improve the properties of biopolymer films based on SPI. These bio nanocomposite films could potentially be used for packaging of high moisture foods such as fresh fruits and vegetables to replace some of the existing plastics such as low density polyethylene (LDPE) and polyvinylidene chloride (PVDC).

Mechanical and thermomechanical properties are of key importance for the applicability of polymer nanocomposites. A number of researchers have investigated ways to improve the properties of starch-based materials using nanocomposites (Chen and Evans, 2005; Dimoni *et al.*, 2008; Fischer, 2003; Huang *et al.*, 2004; Park *et al.*, 2002; Park *et al.*, 2003). Katerinopoulou *et al.* (2014) prepared of thermoplastic acetylated corn starch/Na- montmorillonite (MMT) nanocomposite films with or without polyvinyl alcohol (PVOH). Enhancement in water barrier properties was observed for all nanocomposite films.

Other natural fillers like cellulose nanoparticles (CNP), can be incorporated into various biopolymers to prepare different bio-based nanocomposites with improved physical and mechanical properties (Paula *et al.*, 2011). Ghaderi *et al.* (2014) prepared all-cellulose nanocomposite (ACNC) film from sugarcane bagasse nanofibers 26 using N,N-dimethylacetamide/lithium chloride solvent. This study demonstrated that a very low-value agricultural waste product can be converted to a high performance nanocomposite (tensile strength: 140 MPa). Based on this study, it is also predictable that all-cellulose nanocomposite has potential for the development of barrier and protective film in food packaging industries. Besides, the tensile properties of all-cellulose nanocomposite (ACNC) film are at least comparable to better than those of other biodegradable or non-biodegradable film. Mahmoudian *et al.* (2012) prepared regenerated cellulose/montmorillonite (RC/MMT) nanocomposite films in ionic liquid, 1-butyl-3-methylimidazolium chloride (BMIMCl) using solution casting method. The results revealed improved thermal stability, mechanical and gas barrier properties by incorporation of montmorillonite (MMT) in to regenerated cellulose (RC) matrix. Also, the development of regenerated cellulose/montmorillonite (RC/MMT) nanocomposites is expected to play an important role in membrane technology and packaging. Soheilmoğhaddam *et al.* (2014) prepared novel regenerated cellulose/sepiolite bionanocomposite films using a low cost and "green" pathway. The ionic liquid 1-butyl-3-methylimidazolium chloride (BMIMCl) was used as a cellulose solvent and also a dispersion medium for sepiolite. Also, regenerated cellulose/sepiolite (RC/SEP) nanocomposites are expected to be applied in the area of biomaterials, membranes and food packaging. Another research group prepared nanocrystalline cellulose (NCC) reinforced chitosan-based biodegradable films (Khan *et al.*, 2012). Nanocrystalline cellulose (NCC) reinforced nanocomposite films due to their excellent mechanical and barrier properties should have a promising impact in food packaging over the coming years. Yang *et al.* (2014) prepared transparent and flexible cellulose-clay (montmorillonite, MTM) nanocomposite films prepared from cellulose/LiOH/urea solutions. George and Siddaramaiah (2012) demonstrated the use of bacterial cellulose nanocrystals (BNCs) in the fabrication of edible, biodegradable and high-performance nanocomposite films for food packaging applications at relatively low cost.

ANTIMICROBIAL NANOPACKAGING

According to Llorens *et al.* (2012), nanocomposite systems with antimicrobial function are particularly effective because of the high surface-to-volume ratio and enhanced surface reactivity of the nano-sized antimicrobial agents, making them able to inactivate more microorganisms when compared to higher scale counterparts. Moreover, this type of nanocomposites is useful to minimize the growth of post-processing contaminant microorganisms, extending shelf life of food and improving food safety.

Nano food packaging with antimicrobial properties represents a new generation of packaging. Commonly used or tested antimicrobial materials to prepare nanocomposite materials with antimicrobial function include metal ions (silver, copper, gold, platinum), metal oxide (TiO₂, ZnO, MgO), organically modified nanoclay (quaternary ammonium modified MMT, Ag-zeolite), natural biopolymers (chitosan), natural antimicrobial agents (nisin, thymol, carvacrol, isothiocyanate, antibiotics), enzymes (peroxidase, lysozyme), and synthetic antimicrobial agents (quaternary ammonium salts, EDTA, propionic, benzoic, sorbic acids). Combinations of more than one antimicrobials incorporated into packaging materials have also been investigated (Rhim, 2013). Inorganic materials such as metals and metal oxides have been the focus of nanotechnology research (Panea, 2014).

NANOSILVER IN FOOD PACKAGING

One of the most widely studied nanocomposites used as antimicrobial food packaging is based on silver nanoparticles (AgNPs) incorporated into polymeric films (Incoronato *et al.*, 2010; Llorens *et al.*, 2012; Rhim *et al.*, 2006; Sanpui *et al.*, 2008; Yoksan and Chirachanchai, 2010). Silver and silver ions have been known as effective antimicrobial agents for a long time. Nanosilver particles have extremely large surface area to contact with bacteria or fungi. They could bind to microbial DNA and the sulphhydryl groups of the metabolic enzymes in bacterial electron transport chain. The former will prevent the replication of bacteria, and the latter will inactivate them (Maki and Tambyah 2001; Thomas *et al.*, 2007). The silver nanoparticles have been exploited for the preparation of antimicrobial packaging films due to their strong antimicrobial activity with high stability (Emamifar *et al.*, 2011; Llorens *et al.*, 2012). Also, many researchers have conducted studies on the use of nanosilver in antibacterial packaging films.

Panea *et al.* (2014) studied antimicrobial capacity, nanoparticle migration properties and the influence on some meat quality traits of a packaging based on a low density polyethylene (LDPE) blended with a nano-antimicrobial master batch composed of Ag and ZnO. They observed adding ZnO + Ag nanoparticles to LDPE packaging had an antimicrobial effect both in vitro and on meat. Sensorial attributes were slightly affected by packaging and no differences were seen between packaging type in terms of meat color or visual appearance score. The addition of ZnO + Ag nanoparticles to LDPE packaging delayed breast

spoilage and lipid oxidation. In another study by **Emamifar et al. (2011)**, application of LDPE nanocomposite packaging materials containing Ag and ZnO is a new approach for inactivating *Lactobacillus plantarum* in orange juice at 4°C. Good dispersion without agglomeration of nanomaterials in the polymer matrix was shown to be very effective on the antimicrobial effects of these packaging materials. Nanosilver had a higher antimicrobial activity on *Lactobacillus plantarum* compared with ZnO nanoparticles, especially for longer storage times. In 2008, **Damm et al.** compared efficacy of polyamide 6/silver-nano- and microcomposites. They reported that nanocomposites with a low silver content presented a better increased efficacy against *Escherichia coli* than microcomposites with a much higher silver content.

Chitosan has been reported as an antibacterial agent against a wide variety of microorganisms (**Entsar et al., 2003; Wu et al., 2005**). According to **Rabea et al. (2003)**, chitosan exhibits greater antimicrobial activity than chitin, due to the greater number of free amino groups, which respond for the antimicrobial activity upon protonation. In literature there are results showed that silver-nanoparticle loaded chitosan and other biopolymerbased films exhibited excellent antibacterial ability, which have high potential to be used for food packaging materials to extend the shelf life and maintain the food safety.

Another research group demonstrated the effectiveness of chitosan-based nanocomposites containing silver nanoparticles against *Escherichia coli*, *Staphylococcus aureus* and *Listeria monocytogenes* (**Rhim et al., 2006**). **Ali et al. (2011)** generated 165 nm chitosan-silver nanoparticles by ionic gelation with tripoliphosphate, and after the subsequent loading with silver ions, they showed antimicrobial activity against *Staphylococcus aureus*. In 2012, **Zhou et al.** prepared nanosilver/gelatin/carboxymethyl chitosan hydrogel. Nanosilver/gelatin/CM-chitosan composite hydrogels were synthesized by a green and simple fabrication method, i.e. radiation-induced reduction and crosslinking. The hydrogels were found to have sound antibacterial effect on *Escherichia coli*. The results of this study suggest that nanosilver/gelatin/CM-chitosan hydrogels have potential as an antibacterial properties. **Yoksan and Chirachanchai (2010)** prepared silver nanoparticles (AgNPs) by γ -ray irradiation reduction of silver nitrate in a chitosan solution that has been incorporated into chitosan-starch based films. They found the composite films exhibited enhanced antimicrobial activity against *Escherichia coli*, *Staphylococcus aureus* and *Bacillus cereus* suggesting that the AgNP loaded chitosan-starch based films can be used as antimicrobial food packaging materials. In another study by (**Li et al., 2010**), three component films, i.e., chitosan/Ag/ZnO (CS/Ag/ZnO) blend films, by a one step sol-cast transformation method, in which AgNPs were generated by using chitosan as the reducing agent under hot alkaline condition and at the same time ZnO NPs formed in the composite. The AgNPs and ZnO were uniformly distributed within chitosan polymer and the CS/Ag/ZnO blend film had excellent antimicrobial activities against wide spectrum of microorganisms such as *Bacillus subtilis*, *Escherichia coli*, *Staphylococcus aureus*, *Penicillium*, *Aspergillus*, *Rhizopus*, and yeast. The blend film had higher antimicrobial activities than CS/Ag and CS/ZnO blend films.

Moreover, antibacterial properties presented nanosilver with cellulose. Cellulose-based materials are being widely used as they offer advantages including edibility, biocompatibility, barrier properties, attractive appearance, non-toxicity, non-polluting and low cost (**Imran et al., 2010**). Cellulose acetate phthalate films filled with nanosized silver particles were effective against *Escherichia coli* and *Staphylococcus aureus* (**Necula et al., 2010**). **Pinto et al. (2009)** and **Fernandez et al. (2009)** studied the antimicrobial activity of silver loaded cellulose materials. Fluff pulp cellulose, bacterial cellulose and nanostructured cellulose showed different nanoparticle size and physical properties, but a good antimicrobial activity against foodborne pathogens in protein rich cultivation media and during meat storage. Cellulose/silver nanocomposites fabricated by physical (UV and heat) or chemical methods (sodium borohydride) released a sufficient quantity of silver ions to achieve excellent antimicrobial activity against *Escherichia coli* (**Fernandez et al., 2009**) or *Klebsiella pneumoniae* (**Pinto et al., 2009**) in absorbent materials. In another study by **Moura et al. (2012)**, used nanomaterials, including metallic as active fillers in polymeric nanocomposites for food packaging. Silver nanoparticles were incorporated into a hydroxypropyl methylcellulose (HPMC) matrix for applications as food packaging materials. The antibacterial properties of HPMC/AgNPs thin films were evaluated based on the diameter of inhibition zone in a disk diffusion test against *Escherichia coli* and *Staphylococcus aureus*. They observed that the HPMC/AgNPs nanocomposites can be used in food packaging as active antimicrobial internal coatings. **Aila-Suárez et al. (2013)** studied choyotextle starch films reinforced with cellulose (C) and cellulose nanoparticle (CN) (at concentrations of 0,3%, 0,5%, 0,8% and 1,2%), using thermal, mechanical, physicochemical, permeability, and water solubility tests. Cellulose was acid-treated to obtain cellulose nanoparticle. The films were prepared by casting; potato starch and cellulose were used as the control. The solubility of the starch films decreased with the addition of cellulose and cellulose nanoparticle compared with its respective film without cellulose and cellulose nanoparticle.

In literature there are examples of use of nanosilver for packaging food. **Del Nobile et al. (2004)** reported the antimicrobial activity against *Alicyclobacillus acidoterrestris* of a silver containing polyethyleneoxide-like coating on a

polyethylene layer packing apple juice. In another study by **An et al. (2008)**, prolonged the shelf-life of asparagus coated with AgNPs dispersed in polyvinylpyrrolidone. The shelf-life of orange juice packed in nanocomposites of low density polyethylene filled with a powder containing titanium dioxide and nanosilver was extended (**Emamifar et al., 2010**). Nanostructured LDPE/Ag₂O film bags developed by **Zhou et al. (2011)** have decreased microbial spoilage in apple slices. The quality of apple slices stored at 5°C in LDPE/Ag₂O bag was acceptable after 12 days, while those packaged in conventional LDPE bag showed visible deterioration after 6 days.

ZINC OXIDE NANOPARTICLES

Zinc oxide nanoparticles as functional filler have been widely used as UV-absorbers in cosmetics, coating materials, pigments, and barrier enhancer in a number of industrial products (**Kumar and Singh, 2008; Li et al., 2009; Yu et al., 2004**). In addition, zinc oxide nanoparticles have been reported to exhibit antimicrobial effects (**Li et al., 2009; Li et al., 2010; Zhang et al., 2008**). Compared to other inorganic antimicrobial compounds – like silver (Ag) and gold (Au) nanoparticles, ZnO has several advantages, such as inexpensive cost, non-toxicities, and biocompatibilities (**Paisoonsin, 2013**). **Tankhiwale and Bajpai (2012)** prepared ZnO nanoparticles onto starch-coated polyethylene film and investigated antimicrobial action of film against *Escherichia coli*. **Li et al. (2009)** coated poly (vinyl chloride) films with zinc oxide nanoparticles, and reported antimicrobial activities against *Escherichia coli* and *Staphylococcus aureus*. **Akbar and Anal (2014)** used zinc oxide nanoparticles against two pathogens, *Salmonella typhimurium* and *Staphylococcus aureus* and were found highly effective against both of them. Zinc oxide nanoparticles loaded active film of calcium alginate was prepared for active packaging against the same foodborne pathogens. The film was used as an active packaging (a challenge study) in ready-to-eat poultry meat against the same pathogens, and reduced the number of inoculated target bacteria from log seven to zero within 10 days of its incubation at 8 ± 1 °C.

According to **Silvestre et al. (2011)**, the incorporation of micro- and nanoscale particles into polymeric matrix is related with the improvement of barrier (oxygen, carbon dioxide and ultraviolet rays) and mechanical properties, dimensional stability and heat resistance of packages. Also, **Patino et al. (2013)** assessed the manufacture of polyamide (PA-6) composite casings based on silver-zinc crystals with potential application in sausages packaging. PA-6 films were prepared as a multilayer film by bubble film sheet co-extrusion (130 8C–14,000 kPa), identified according to the layers distribution as control and active casings by adding 3% (w/w) of silver-zinc crystals to obtain a film with good barrier and mechanical properties. **Paisoons (2013)** prepared ZnO-deposited DBD plasma-treated PP packaging film with antibacterial activities against gram-positive *Staphylococcus aureus* and gram-negative *Escherichia coli*. **Nafchi et al. (2013)** prepared of bionanocomposite films filled with nanorod rich zinc oxide. The films exhibited UV absorption and displayed an excellent antimicrobial activity against the *Escherichia coli*. These properties suggest that bionanocomposites based on ZnO-nr have the potential as an active packaging material for food.

TITANIUM DIOXIDE NANOPARTICLES

Titanium dioxide (TiO₂) is an inert, non-toxic and inexpensive material, whose high refractive index and high capability to absorb UV light make it an interesting white pigment and environmentally friendly catalyst (**Zhao and Yang, 2003**). The photocatalyst reaction of TiO₂ leads to generation of hydroxyl radicals (-OH) and reactive oxygen species (ROS) on the TiO₂ surface, resulting in the oxidation of polyunsaturated phospholipids of cell membranes of microorganisms. As a consequence, the microorganism is inactivated (**Cho et al. 2004; Kuhn et al., 2003**).

Several authors (**Chawengkijwanich and Hayata, 2008; Zhou et al., 2009**) reported the incorporation of TiO₂ into polymers could be conceivably an effective approach to obtain useful photoactive filmable materials for food packaging applications. **Yu et al., (2011)** developed a thin film containing TiO₂ and silver nanoparticles by the template sol-gel method. The authors reported that better inactivation of *Escherichia coli* was obtained with increasing silver content under UV illumination. **Long et al. (2014)** studied effects of UV exposure time, nano-TiO₂ concentrations, and initial bacteria populations on nano-TiO₂ photocatalytic disinfection against Gram-negative pathogen bacteria *Salmonella typhimurium* and Gram-positive bacteria *Listeria monocytogenes*, the two most typical pathogens found in meat products. **Bodaghi et al. (2013)** evaluated of the photocatalytic antimicrobial effects of a TiO₂ nanocomposite food packaging film by in vitro and in vivo tests. The film caused inactivation of *Pseudomonas spp.*, *Rothia mucilaginosa* and mesophilic bacteria in saline solution and on pearls when exposed to UVA light. The number of microorganisms on LDPE-TiO₂ nanocomposite film plus UVA light was lower than that on LDPE-TiO₂ nanocomposite film without UVA light and LDPE film exposed to UVA light. **Gumiero et al. (2013)** prepared a new composite polymeric film for food packaging applications prepared from high density polyethylene (HDPE), CaCO₃ and TiO₂ micro-particles, and evaluation of its

effects by real packaging of a short-ripened cheese. These composite films can represent sustainable, mass-producible, cost-effective and highly shapeable photoactive materials which appear to be well suitable for food packaging. **Maneerat and Hayata (2006)** have investigated the antifungal activity of TiO₂-coated plastic film against *Penicillium expansum*. Another research group synthesized polyethylene with nano-powder (nano-Ag, kaolin, anatase TiO₂, rutile TiO₂) (**Li et al. 2009**). **Xing et al. (2012)** observed antibacterial activity of the TiO₂-PE film to inactivate *Escherichia coli* or *Staphylococcus aureus*. The TiO₂-incorporated PE film exhibited more effective antibacterial activity for *Staphylococcus aureus*. The photocatalytic degradation of methylene blue (MB) and inactivation of Gram-negative bacteria *Escherichia coli* (generic) and *Pseudomonas aeruginosa* by TiO₂ nanoparticles in aqueous suspension were studied by **Wang et al. (2013)**.

MAGNESIUM OXIDE NANOPARTICLES

Nano-structured MgO is an essential minerals for human health and is an exceptionally important materials that has a unique ability to destructively adsorb different gases (**Lei et al., 2005; Lei et al., 2005**), including chemical warfare agents, surrogates, catalysis, additive in refractory, toxic waste remediation, paint, flame retardants, polymer reinforcement agents, and superconductor product and antibacterial materials (**Sasaki et al., 2006; Makhluף et al., 2005; Gordon et al., 2011**). The biocidal action occurs because MgO nanoparticles have an opposite electrical charge from bacteria. When the bacteria are drawn to the MgO nanoparticles, the nanoparticles sharp edge penetrates the bacteria's tough outer shell, causing them to die within about 5 min (**Trapalis et al., 2003; Mishra et al., 1995; Gao et al., 1995**).

It is well known that nanoparticles of magnesium oxide (MgO) effectively kill bacteria, including *E. coli* form and anthrax (**Richards et al., 2000**). **Haldorai et al. (2013)** prepared a novel multi-functional magnesium oxide (MgO) immobilized chitosan (CS) composite. The composite exhibited a superior antibacterial efficacy of 93% within 24 h against *Escherichia coli* as measured by colony forming units. **Al-Hazmi et al. (2012)** prepared magnesium oxide (MgO) nanowires with diameters of 6 nm and lengths of 10 μm. Reaction was performed via a microwave hydrothermal approach at low temperature growth of 180 °C for 30 min. The antibacterial behavior of MgO nanowires concentration in solid media against Gram negative and Gram positive for different bacteria were tested. Prepared MgO nanowires have bacteriostatic activity against *Escherichia coli* and *Bacillus sp.* **Ma et al. (2005)** prepared of MgO and Fe nanostructure in Mg matrix composite by reaction sintering. These new in situ formed Fe nanoparticles and MgO nanowire contain valuable antiseptic and antibacterial properties which creates a vast potential for materials which could induce biocidal actions. Moreover, MgO nanowire and Mg₂Cu–Mg nanoeutectic were presented.

NANOSENSORS IN INTELLIGENT PACKAGING

Nanosensors are nanotechnology-enabled sensors characterized by a range of variations (**Bowles and Lu, 2008**). Generally, nanosensors can be applied as labels or coatings to add an intelligent function to food packaging in terms of ensuring the integrity of the package through the detection of leaks (for foodstuffs packed in a vacuum or inert atmosphere), indications of time-temperature variations (e.g., freeze–thaw–refreeze), or microbial safety (the deterioration of foodstuffs) (**FAO/WHO, 2010; Mahalik and Nambiar, 2010; Watson et al., 2011**). Nanosensors can detect certain chemical compounds, pathogens, and toxins in food, being then useful to eliminate the need for inaccurate expiration dates, providing real-time status of food freshness. Also, intelligent packaging is the area where nanotechnology is expected to have a large impact. The recent developments for smart PNEP include oxygen indicators, freshness indicators and pathogen sensors. 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 (**Silvestre et al., 2011**).

A principal prerequisite in the development of food spoilage indicators is knowledge of the quality indicating metabolites. Carbon dioxide (CO₂) is generally known to be produced during microbial growth. Also, CO₂ sensors have high potential application. **Nopwinyuwong et al. (2010)** prepared novel colorimetric indicator label for monitoring freshness of intermediate-moisture dessert spoilage. Color changes, in terms of total color difference of a mixed pH dye-based indicator, correlated well with CO₂ levels of intermediate-moisture dessert. This colorimetric mixed-dye-based food spoilage indicator allows the food product to have an effective shelf life by permitting dynamic freshness to be monitored visually along side the best-before date, consequently decreasing margins of error. **Borchert et al. (2013)** described an optochemical CO₂ sensor which uses a phosphorescent reporter dye phosphorescent Pt-porphyrin PtTFPP and a colourimetric pH indicator -naphtholphthalein incorporated in plastic matrix together with a phase transfer agent tetraoctyl- or cetyltrimethylammonium hydroxide. The sensor material was optimized for food packaging applications and underwent detailed characterization with respect to its

CO₂ sensitivity, response and recovery times, stability, cross-sensitivity to oxygen and temperature. **Jung et al. (2012)** presented chitosan-based carbon dioxide (CO₂) indicator to monitor freshness or quality of packaged foods during their storage. For the enhancement of signal strength of indicator, 2-amino-2-methyl-1-propanol (AMP) was used as an additive to the chitosan solution. The indicator solution of chitosan and AMP can be conveniently packed into sachets, which are permeable to gaseous CO₂, inside food packs. They therefore have great potential to be used as sensors for monitoring the fermentation process and spoilage of foods.

An interesting solution is optoelectronic nose prepared by **Salinas et al. (2014)**. This new optoelectronic nose composed of seven sensing materials prepared by the incorporation of pH indicators and chromogenic reagents selective to metabolites into inorganic materials (UVM-7 and alumina). The nose has been applied to monitor fresh pork sausage ageing. The results strongly suggest the potential feasibility of the use of colorimetric arrays as systems for easy, rapid and effective meat freshness assessment able to inform retailers and consumers about the safety state of the fresh pork sausages.

Oxygen indicators are used in intelligent food packaging, which monitors the condition of packaged food to give information on the food quality during transport and storage (**Ahvenainen, 2003**). In recent years, many works on UV-activated colorimetric oxygen indicators have been reported (**Lee et al., 2004; Lee et al., 2005; Mills and Hazafy, 2008; Roberts et al., 2011**). **Vu and Wo (2013)** presented water-resistant UV-activated oxygen indicators. The UV-activated visual oxygen indicator films were fabricated using thionine, glycerol, P₂₅ TiO₂, and zein as a redox dye, a sacrificial electron donor, UV-absorbing semiconducting photocatalyst, and an encapsulation polymer. This oxygen indicator was successfully photo-bleached and regained colour fast in the presence of oxygen. **Mills and Hazafy (2009)** prepared nanocrystalline SnO₂-based, UVB-activated, colourimetric oxygen indicator. The use of ncSnO₂ as a photocatalyst in the UV activated oxygen-sensitive inks opens up many possible avenues of application as it allows for a much more controllable UV-activation step.

A printing ink with oxygen indicative properties incorporated into the packaging has been suggested as a cheap method of producing an oxygen indicator suitable for food packaging (**Pascall et al., 2008**). Also, **Lawrie et al. (2013)** described simple inkjet-printed, UV-activated oxygen indicator. They reported a series of UV-activated O₂ indicator films consisting of: a redox dye – methylene blue (MB), a sacrificial electron donor (SED) – glycerol, and nanoparticles of a UV-sensitive semiconducting photocatalyst (SC) – TiO₂, all encapsulated within a polymer – in the case of a water-based system, hydroxyethyl cellulose (HEC). Another sensor presented **Marek et al. (2013)**. Researchers developed time-monitoring sensor based on the oxidation of leuco methylene blue (LMB) to methylene blue (MB). The sensor changes its color from yellow to green in the presence of oxygen. For better handling, the indicator was also integrated into a mechanically stable polymer matrix. This makes the sensor widely applicable and compatible with current polymer processing technologies. The diffusion of the oxygen in the polymer matrix as well as the oxygen uptake due to the oxidation reaction determines the time monitoring of the sensor. **Wanhsuksombat et al. (2010)** prepared the lactic acid-based TTI prototype based on the vapor diffusion of lactic acid. Four lactic acid-based TTIs were made in different substrate concentrations. Color changes associated with the diffusion of lactic acid were monitored. In the vapor diffusion of lactic acid, an irreversible color change of a chemical chromatic indicator (from green to red) clearly and progressively occurred due to the pH reduction.

CONCLUSION

Food packaging must protect the food from physical damage and from dirt and insects etc. Food packs must also be easy to handle, be used to dispense the food, and have many other attributes linked to the physical characteristics of the packaging material. Also, in this study presented novel and efficient polymer materials for food packaging based on nanotechnology. The use of polymer nanotechnology can in fact extend and implement all the principal functions of the package (containment, protection and preservation, marketing and communication). This is the reason why many of the world's largest food packaging companies are actively exploring the potential of polymer nanotechnology in order to obtain new food packaging materials with improved mechanical, barrier and antimicrobial properties and also able to trace and monitor the condition of food during transport and storage.

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