Nanostructured bioactive polymers used in food-packaging

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Abstract

The development of effective packaging materials is crucial, because food microorganisms determine economic and public health issues. The current paper describes some of the most recent findings in regards of food preservation through novel packaging methods, using biodegradable polymers, efficient antimicrobial agents and nanocomposites with improved mechanical and oxidation stability, increased biodegradability and barrier effect comparatively with conventional polymeric matrices.

Keywords: antimicrobial agents, food-packaging, food safety, microorganisms, nanocomposites, biopolymers

Introduction

Foodborne microorganisms represent an economic burden in many parts of the world, but more importantly many studies had shown that food-borne diseases are an important public health problem, with epidemics emerging in both developed and developing countries. The main pathogenic bacteria isolated from foodstuffs are: *Salmonella sp.*, *Listeria monocytogenes*, *Bacillus cereus* and *Staphylococcus aureus*. Enterobacterial strains seem to be the most frequently encountered opportunistic bacteria. Also, food products can be contaminated with yeasts and molds, which can cause serious spoilage of stored food and important economic losses [1]. Moreover some fungal species could produce mycotoxins, causing potential health problems in animal and humans [2].

In 2012, CDC (Centers for Disease Control and Prevention) reported, through the Foodborne Diseases Active Surveillance Network (FoodNet), 19.531 laboratory-confirmed cases of infection, mostly due to six key food-borne pathogens (*Campylobacter sp.*, *Listeria sp.*, *Salmonella sp.*, *Escherichia coli* O157, *Vibrio sp.*, and *Yersinia sp.*). The incidence was not significantly different in 2012 compared to 2006–2008.

The European Food Safety Authority and the European CDC reports concerning the incidence of zoonoses and food-borne outbreaks in 2012 in 27 European Union Member States, show that *Salmonella spp.* remained the most frequently reported cause of food-borne outbreaks in EU, with a slight increase in the numbers of outbreaks compared with 2011. The second most important causative agent group was bacterial toxins, followed by *Rotavirus* and *Campylobacter spp*.

Thus, effective solutions are required for keeping food products free of pathogenic microorganisms and for restricting non-pathogenic strains multiplication in order to avoid food spoilage. There are a number of solutions for food preservation, which consist of classical methods such as drying, pasteurization, refrigeration, freezing, artificial food additives, vacuum packing, canning and bottling. However, these techniques are not applicable to all foods, or they can determine a loss in the nutritional value, texture and/or flavor. Therefore, different packaging methods have been developed. Most of the used packaging solutions include the release of antimicrobial agents on the food surface, exhibiting the highest microbial contaminations, in order to inhibit or delay the microbial growth and food spoilage [3].

Packaging systems must be continuously adapted to the various consumer demands, changes in retail practices, new technologies and materials, legislative changes, especially related to environmental concerns [4].

In the recent decades, polymers have been used more and more frequently for packaging applications, replacing conventional materials (ceramics, paper and paper) due to their light weight, ease of processing, possibility of physical surface modification by flame, radiation (UV, gamma, electron and ion beam), corona discharge, plasma, laser treatments and cost-effectiveness [5, 6].

The current paper describes some of the most recent findings regarding food preservation through intelligent packaging methods, offering a new perspective of the usage of biodegradable polymers, efficient antimicrobial agents and nanocomposites with improved mechanical and oxidation stability, and increased biodegradability and antimicrobial barrier properties for the food industry field.

Biopolymers used in food packaging systems

Polymers represented the most common food packaging materials for a long time, due to several properties (softness, lightness and transparency). However, the increased use of synthetic packaging films led to serious ecological problems due to their non-biodegradability [7]. Thus, research is increasingly being directed at development of biodegradable food packaging, based on nanocomposites obtained by using natural polymers (such as starches and proteins) or synthetic biopolymers (such as polylactic acid) [8].

Biodegradable polymers *(BDPs)* are polymeric materials that could be decomposed to simple substances (carbon dioxide, other inorganic compounds, methane, water, or biomass), under the microbial enzymatic action [9]. According to their production method or the extraction source biopolymers can be classified as:

A. Polymers directly extracted or removed from vegetal or animal biomass (polysaccharides and proteins);
B. Polymers synthesized by from renewable bio-based monomers such as polylactic acid (PLA);
C. Polymers produced by microorganisms (polyhydroxyalkanoates, cellulose, xanthan, pullulan) [10].

Polysaccharides and proteins

Numerous proteins of vegetal (corn zein, soy proteins, wheat gluten) and animal (milk proteins, collagen, gelatin, keratin, myofibrillar proteins) origin, as well as polysaccharide-based biopolymers (starch, pullulan, chitosan), have been investigated as packaging films [11].

In a recent study, zein protein resulted from corn processing industry, was used in combination with natural phenolic compounds to obtain packaging films with antioxidant and emulsifier activity [12]. The turkey breast wrapped in corn zein film had a lower hexanal content than samples packaged in PVDC (Poly-Vinylidene Dichloride Copolymers) [13].

Wheat gluten based bioplastics, where tested for biodegradability and results showed that they were totally degraded in aerobic fermentation performed for 36 days and after 50 days in farmland soil. No toxic effects of the modified gluten or of its metabolites have been revealed [14].

Soy protein is a biodegradable, thermoplastic polymer, but with poor response to moisture and high rigidity [5].

According to recent studies, the whey protein is one of the most promising, in regards of food packaging field, exhibiting superior barrier effect comparatively with other bioplastics and similar to synthetic layers, such as ethylene vinyl alcohol [15]. It also improves the shelf life of packed products, such as peanuts, by delaying the lipid oxidation responsible of rancidity [16] and do not modify the sensory attributes and the aspect of the coated good, while providing some health benefits [17].

Collagen is the most commercially used protein film in the meat industry, for the production of edible sausage casings [18].

Keratin is the cheapest protein, extracted from waste cornified tissues (hair, nails and feathers), although difficult to process due to its structure and high cysteine content. After processing, a fully biodegradable, water-insoluble-plastic poor mechanical properties [19, 20].

Fish myofibrillar proteins were also used to obtain biopackaging materials, which were slightly better than those determined for known protein-based films, with tensile strength close to those of low density polyethylene films [21].

Transparent and flexible edible/biodegradable films were obtained from blue marlin meat myofibrillar proteins. Their water vapor permeability was slightly lower than that of other protein-based edible films and higher than that of synthetic films. The blue marlin muscle protein films prepared at acid (2-3) or alkaline (11-12) pH led to more stable protein networks, with superior transparency. Also, another study carried out on edibile films developed from different protein extracts from *Dosidicus gigas* muscle had shown that, although every film exhibited high transparency, this property was enhanced when they were prepared at acid or alkaline pH, than in water and salt [22, 23].

Starch and starch-based biodegradable polymers have a high potential for packaging applications because of their renewability, biodegradability and low cost [24, 25, 26]. Plasticized wheat starch blending with biodegradable polyesters improved its water resistance. The problem of using conventional starch-based polymers for packaging materials remains the possible migration of hazardous substances into the food [27].

Chitosan is a natural polysaccharide biopolymer resulted from the deacetylation of chitin, a major component of the crustacean shells, with biological activities (antimicrobial activity) and functional properties (film-forming) that recommend it for use in food industry, as a food preservative or coating material [28]. Due to the positive surface charges at acidic condition, chitosan interacts with anionic components on bacteria surface, such as negatively charged lipopolysaccharide in outer membrane of Gram-negative bacteria and peptidoglycan and teichoic acid in cell wall of Gram-positive bacteria. This electrostatic interaction causes release of major proportion of proteinaceous materials from the cells [29]. In a recent study [30], chitosan coatings with acidic pH 5.0 prevented the growth of Gram-positive bacterial strains, such as *L. monocytogenes* and *S. aureus* on cheese, but not that of Gram-negative ones, such as *Pseudomonas aeruginosa*.

Polylactic acid (PLA)

The lactic acid (2-hydroxy propionic acid) monomer is produced via fermentation or chemical synthesis. The two L(+) and D(−) stereoisomers are produced industrially by bacterial (homofermentative and heterofermentative) lactic fermentation. The synthetic routes are avoided due to their limitations, represented by the dependence on a by-product of another process, impossibility to obtain only the desirable L-lactic acid stereoisomer, and high manufacturing costs [31, 32].

Studies performed in Europe and North America showed that the incorporation of antimicrobial agents (bacteriocins, plant extracts) into PLA polymer could provide a possible delivery system for improving their efficacy in food applications [33, 34].

A recent study revealed that thymol (TH), which has antimicrobial effect on many food pathogens, incorporated into composite polylactic acid/poly trimethylene carbonate (PLA-PTMC) films, have a prospectively potential in antimicrobial food packaging, due to the significant inhibitory zones obtained when tested against *E. coli*, *S. aureus*, *Listeria sp*., *Bacillus subtilis*, and *Salmonella sp*. strains [35].

The limitation of using PLA as a packaging material is its brittleness, therefore requiring the improvement of its mechanical performance [36]. A series of studies have shown that PLA bioproperties can be enhanced by using different functional and ecological modifications. Huda et al. [37] showed that kenaf fiber reinforced polylactic acid (PLA) films. The crystallization and melting behavior of linear polylactic acid (PLA) treated by compressed CO_2 indicated a high plasticization effect increasing the mobility of the polymer chain, and thus accelerating the rate and broadening the crystallization window of PLA [38].

Various polymers such as thermoplastic starch, poly (ethylene oxide), poly (ethylene glycol), poly (ε-caprolactone), poly (vinyl acetate), poly (hydroxy butyrate), cellulose acetate, poly (butylene succinate), and poly (hexamethylene succinateL as well as low molecular weight compounds (oligomeric lactic acid, glycerol, triacetine, and low molecular weight citrates) have been used as plasticizers for PLA [32, 39].

Nanocomposites based on natural and synthetic biopolymers

The nanotechnological and functionalization applications for food packaging include: the improvement of plastic materials barriers, the incorporation of active components that could be released, and the sensing and signaling of relevant information [40].

Polymer nanocomposites (PNC) are polymers (thermoplastics, thermosets or elastomers) reinforced with small amounts (less than 5% of weight) of nano-sized particles [41]. A large range of nanoparticles and polymeric resins are used for food industry applications [42]. A classification of the nanoparticles based on their potential to increase the functionality of the polymer matrix is presented in Fig 1.

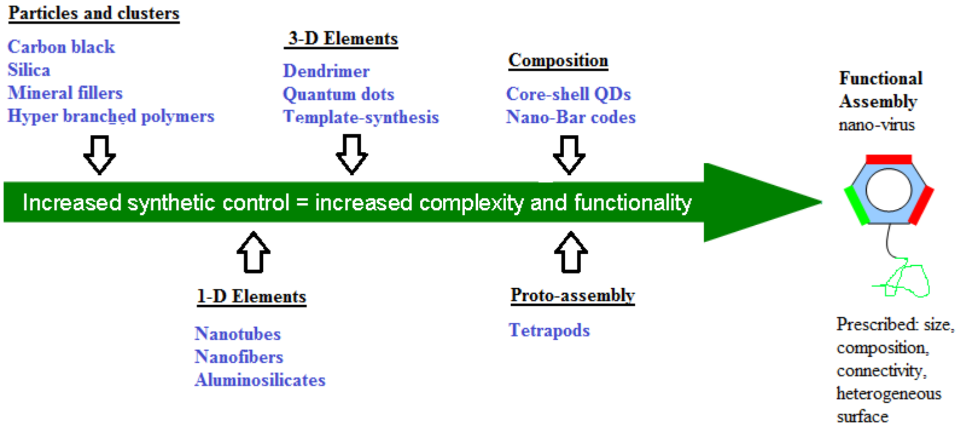

Fig 1 Classification of nanoparticles based on their potential to increase functionality of the polymer matrix

The most studied bio-nanocomposites for packaging applications are starch and cellulose derivatives, polylactic acid (PLA), polycaprolactone (PCL), poly(butylene succinate) (PBS) and polyhydroxybutyrate (PHB) [43].

In a recent study, a series of cellulose/copper nanocomposites have been prepared by varying the type of cellulose used as the matrix (vegetable or bacterial) and also the morphology of copper nanostructures (nanoparticles or nanowires) used as fillers. These composites were investigated for the first time for their antibacterial activity and provd to be active against *S. aureus*) and *Klebsiella pneumoniae* strains [44].

Chitosan-based nanocomposite films containing different types of nanoparticles i.e. unmodified montmorillonite, an organically modified montmorillonite, Cloisite 30B, Nano-silver and Ag-zeolite (Ag-Ion), revealed beised an antimicrobial effect, an increased tensile strength (7−16%) and decreased permeability (25−30%) [45].

Bionanocomposites containing silver nanoparticles (Ag-NPs) obtained by green physical synthesis and incorporated into the lamellar space of montmorillonite (MMT)/chitosan (Cts) by the UV irradiation reduction method showed an increased antibacterial activity [46]. Also, biodegradable starch/clay nanocomposite films have been developed, to be used as food packaging, and this material showed improved mechanical parameters, such as modulus and tensile strength [47].

Silver/poly (lactic acid) nanocomposite (Ag/PLA-NC) films have been developed, and they were also shown to have a large spectrum of antibacterial activity [48].

The incorporation of TiO_2 nanoparticles of 10 nm into a biodegradable polycaprolactone polymer in different amounts, ranging from 0.5 to 5 wt.% exhibited an antibacterial activity against *E. coli* and *S. aureus*, extremely enhanced under UV irradiation [49].

Different antimicrobial agents (AM) such as natural or chemical antimicrobials, antioxidants, biotechnology products and gases may also be incorporated in the packaging systems [50].

Systems based on natural antimicrobial agents

Volatile oils have been shown to exhibit considerable inhibitory effects against 25 different genera of bacteria [51]. They can be incorporated into polymers or into carriers used for packaging materials [52]. Garlic oil incorporated in alginate-based edible film in a concentration of 0.1% v/v garlic oil inhibited the growth of *E. coli*, *S. typhimurium*, *S. aureus* and *B. cereus* by up to 5 logs, after 24 h incubation.

In a recent study, thymol, carvacrol and linalool were incorporated into or coated onto starch-based films. The high retention of AM agent in the coatings was obtained at low temperature, while the AM diffusion rates were increased with the temperature [54].

Carvacrol was incorporated into an active package used for the preservation of fresh farmed salmon in cubes or slices. The package polymer consisted of a rigid polypropylene (PP)/ethylene–vinyl alcohol copolymer (EVOH)/PP tray heat-sealed with an active PP/EVOH/PP film lid. The carvacrol was incorporated in a concentration of 6.5% in the EVOH kernel [55]. The release of carvacrol in the fish muscle is depending on temperature and atmospheric relative humidity, the carvacrol being more easily released in the air in highly humid conditions reaching therefore a low concentration in the food matrix (Fig 2).

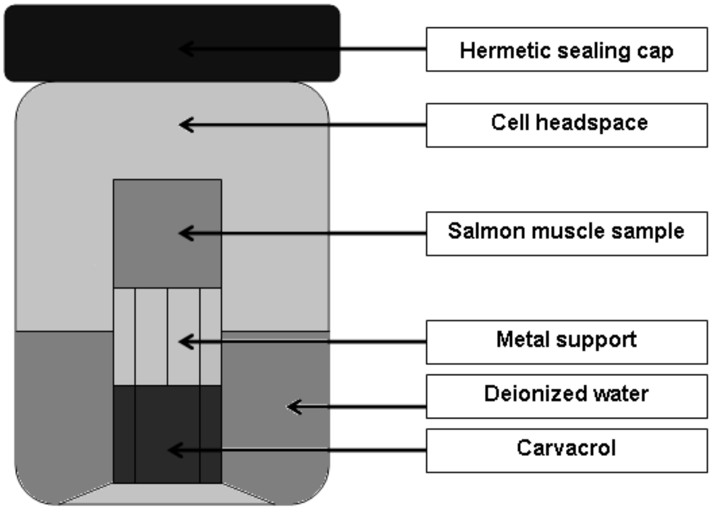

Fig 2 Scheme of the diffusion device used for evaluation of carvacrol diffusivity (J.P. Cerisuelo et al, 2013)

Trans-2-hexenal is a naturally occurring plant volatile compound with antimicrobial activity approved as food additive. Trans-2-hexenal was encapsulated into ß-cyclodextrins (ß-CDs), rendering them effective against food spoilage microorganisms (*Alternaria solani*, *Aspergillus niger*, *Botrytis cinerea*, *Colletotrichum acutatum*, *Penicillium sp*) [56].

Allyl isothiocyanate is acolorless, volatile sulphur compound responsible for the pungent taste of mustard, radish, horseradish, and wasabi. Besides having a wide spectrum of antimicrobial activity, this phytochemical was shown to have anticancer activity [57]. Dias et al. [58], have developed an antimicrobial packaging incorporating allyl isothiocyanate (AIT) and carbon nanotubes (CNT), used for the packaging of cooked chicken meat contaminated with *Salmonella choleraesuis*. The diffusion of AIT into the meat reduced the microbial contamination, oxidation processes and color changes.

Bacteriocins produced by lactic acid bacteria also have strong antimicrobial activity against closely related bacteria, this is why their use in food preservation was received with increased interest [59]. Mauriello et al. incorporated the bacteriocin 32Y into the polythene films and showed their efficacy against *L. monocytogenes* during meat products storage.

Systems based on synthetic antimicrobial agents and organic acids

Lauric arginate (LAE), a food-grade cationic surfactant synthesized by esterifying arginine with ethanol, followed by reacting the ester with lauroyl chloride, that exhibits a wide range of antimicrobial activities against food pathogens and spoilage molds [61, 62]. The incorporation of LAE into EVOH 29 and EVOH 44 allowed to obtain active materials with very similar functional properties in packaging design to conventional food packaging [63].

Han and Floros [64] incorporated 1.0% w/w potassium sorbate in low-density polyethylene films of 0.4-mm thick they demonstrating an inhibitory effect on yeast growth and a longer lag period of mold growth [65].

Ethylenediaminetetraacetic acid (EDTA) is one of the most commonly used antimicrobial agents due to its capacity to disrupt the lipopolysacharide structure of Gram-negative bacteria [66]. The incorporation of sodium-EDTA into soy and whey proteins has been reported to reduce the growth of *L. monocytogenes*, *E. coli* O157:H7 and *S. typhimurium* strains [67].

Benzoic anhydride has been added to low-density polyethylene (LDPE) films exhibiting antimycotic activity against *Rhizopus stolonifer*, *Penicillium spp.* and *Aspergillus toxicarius* grown on cheese [68].

Organic acids (e.g., acetic and propionic acid) incorporated into a thin chitosan film were completely released 5 - 10 min after immersion in buffer. However, the release mechanism seems to be controlled by the contact of the matrix with water, therefore the acid diffusion rate onto the meat surface will be probably lower [69].

Araujo et al. [70], obtained polyamide 6 nanocomposites with improved mechanical resistance and organophilization, containing clay organically modified with three quaternary ammonium salts (hexadecyltrimethyl ammonium bromide, hexadecyltrimethylammonium chloride and alkyl dimethyl benzyl ammonium chloride).

Antimicrobial packaging films containing sorbic acid showed a significant inhibitory effect on *E .coli* growth [71].

The incorporation of benzoic acid and sorbic acid in poly(ethylene-co-methacrylic acid) promoted the occurrence of anti-fungal properties, probably due to the high diffusion rate of preservatives from the films [72].

Conclusions and future perspectives

Although there are many promising available methods for food packaging, which were shown to exhibit both efficient antimicrobial properties and eco-friendly properties, future studies are required in order to select the most harmless materials to the consumer’s health. In terms of the latest innovation in food packaging, many scientists have suggested that nanotechnology has the potential to completely revolutionize the food packaging industry.

Thus, based on the studies, carried out by researchers from around the world, we can speculate that in the near future, solutions for the conservation of fresh food products with the aid of "smart" packaging, with antimicrobial properties and without any negative effect on consumers, will be developed and used in the food industry. This would bring great advantages to both consumers and producers, as the inhibition of microbial growth and multiplication, would lead to a longer self life of the products and also to fewer risks for the consumers health. However, before adopting such a method at the industrial level, rigorous testing should be carried out, in order to minimize the long-term, harmful effects on the human health.

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