Nanotechnological Smart Food Packaging

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Polymer nanocomposites (PNCs) are of real interest because along with the bioactivity induced by the components (or by the polymer itself), these materials due to the composite nature can exhibit some improved physical, chemical, biological, mechanical, electrical, and optical properties compared to individual components [1]. Due to the innovative properties such as maintaining the quality and safety of food but also increasing the shelf-life of the food, nanocomposite packaging has great potential as an innovative food packaging technology. The polymer nanocomposites used in developing food packaging materials are mainly composed of the polymer matrix, nanofillers, plasticizers, and compatibilizers.

Keywords: Bioactive food packaging materials ; nanoparticles ; drug delivery ; food safety

1. Introduction

Currently, nanocomposites are used in many medical and industrial applications, but also increasingly used in food packaging. An extensive research on the use of nanocomposite materials has been conducted in the food industry with a main purpose of increasing the shelf life of food and minimizing the losses, being known as highly susceptible to bacterial/fungal contamination. The main purpose for the use of polymeric materials in the food industry is the production of packaging that protects food from adverse environmental conditions (dust, gas, light, and moisture), pathogenic micro-organisms, or chemical contamination during storage and distribution. Food packaging should be able to ensure the quality and safety of food throughout the distribution chain, but also during storage, including the shelf storage. In order to be used as food packaging polymeric materials must be safe to have a low production cost, to be inert, easy to dispose of, and reuse. Unfortunately, the bulk of packages used today are not bio-degradable and this presents an increasing unacceptable environmental hazard. In addition, the mechanical, electrical, thermal, optical, and electrochemical properties of these nanostructured materials will differ significantly from those of the component materials. These are essential for assuring the expected shelf life, food quality, and safety parameters [2][3].

Food packaging is used as a protective barrier in the food industry. In addition, the demand for packaging materials is constantly growing according to the specific requirements request to each type of food. In this sense, the food packaging industry is dynamic and futuristic, which gives rise to the expansion or evolution of new processes and technologies for obtaining superior quality packaging materials.

According to the European Regulation (EC) —No. 1935/2004, good packaging must have a set of functions such as protection of food from a number of destructive or harmful substances (dirt or dust, oxygen, light, pathogenic microorganisms, moisture), to be inert, cheap to produce, easy to remove, or reuse. An optimal packaging must withstand extreme conditions during processing or filling, impervious to a lot of storage and transport conditions in the environment [4]. Many times, these functions are obtained by using natural or synthetic polymers loaded with nanoparticles and biological active agents.

Nanomaterials applied in packaging and food safety are in various forms, from bioactive bulk to bioactive coatings. The bioactivity is usually conferred using different active agents: Natural or synthetic biocides including essential oils and natural extracts; nanoparticles including metallic and metal oxide nanoparticles, etc. The antimicrobial activity can be assured by various mechanisms, by contact, or by release. Nanoparticles encapsulation is one of the mechanisms employed and can confer new properties to the surface, such as inducing antimicrobial or even antibiofilm capacity. Due to the excellent physico-chemical properties but also the antimicrobial potential of these nanomaterials, they are widely used against various pathogens (most of the microorganisms, viruses, or fungi) in medicine, water treatment, crop protection, food safety, and food preservation [4][5][6][7][8][9][10]. Usually, the antimicrobial activity of these nanoparticles is considered to be caused by the damage of the microbial membranes, oxidative stress, or the denaturation of the proteins [11]. It is also important to mention that a wide range of biological active agents, synthetic and natural agents (essential oils and natural extracts) are increasingly used in order to develop drug delivery systems or antimicrobial surfaces, and this technology is slowly directed also to create bioactive food packaging materials [4][6][12][13][14][15][16].

2. Nanostructured Polymers as Packaging Materials

One of the most practical uses of nanocomposites in food packaging is the addition of nanosized components to traditional packaging materials, such as metals and metal oxides nanoparticles, zeolites, glass, but also organic polymers cellulose, various synthetic plastics such as PE, PP, PS, PVC, etc. The use of nanofillers in the preparation of bioactive packaging films has also been the subject of numerous recent studies [13][17][18][19][20][21][22][23][24][25][26][27]. Several types of nanoparticles are exploited in food packaging materials because these can induce some advantages, especially, antimicrobial activity, but also can tailor the mechanical properties, gas and water vapor barrier, etc. [18][19][20][21][22][23][24][25]. These properties are strongly correlated with the nature and content of the nanoparticles.

Kumar et al. [28] used silver nanoparticles in order to obtain biodegradable hybrid nanocomposites based on a chitosan/gelatin/PEG blend. It is important to mention that the proposed composition can be used in protective packaging materials that are able to extend the shelf life of the red grapes by 14 days because of the antimicrobial activity and control of the gas and moisture barrier.

You et al. [26][29] studied the influence of silver addition in cellulose based materials using a chemical reduction method with $NaBH_4$ and an ultraviolet reduction method. Regardless of the reduction method and consequently regardless of the characteristics of the nanoparticles (28 nm for the UV-reduction method and ~11 nm for the chemical reduction method) these films highlight the antimicrobial activity against *E. coli* or *l. Monocytogenes* without affecting the toxicity against Caco-2 and FHC colon cells. It is important to mention that due to the low level of Ag (usually up to 1000 ppm), there are only marginal changes of the other properties of the films, but the slight color change and the important antimicrobial activity lead to an improved shelf life.

Nano-TiO_2 can be also used in obtaining nanostructured food packaging materials based on hydroxypropyl methylcellulose with the antimicrobial activity. It is important to mention that the best results were obtained by adding bovine bone collagen, perhaps due to the compatibilizing effect between nano-TiO_2 and hydroxypropyl methylcellulose. Due to the higher loading of the nano-TiO_2 compared to AgNPs, the addition of the oxide induces also a reinforcing role and thus some mechanical properties, thermal stability, color as well as barrier properties are improved when bovine collagen is used [18].

Copper oxide is also used to induce bioactivity to the food packaging materials. Starting from sodium alginate, cellulose nanowhiskers and embedding CuO nanoparticles antimicrobial packaging materials can be obtained against a wide range of pathogens such as: *S. aureus*, *E. coli*, *Salmonella sp.*, *C. albicans,* and *Trichoderma spp.*, the inhibition diameter being significant 27.49 ± 0.91, 12.12 ± 0.58, 25.21 ± 1.05, 23.35 ± 0.45, or 5.31 ± 1.16 mm, respectively [19].

ZnO is extensively used in many applications involving biomaterials and food packaging materials because ZnO is nontoxic at a level that can confer an antimicrobial effect [30][31], the released Zn^{2+} being even beneficial as an oligoelement that can act as a cofactor for several enzymes. Different polymers or polymer blends were associated with ZnO in order to improve the shelf life of vegetables, fruits, cakes, or other food [20][32]. Again, the higher content of ZnO (1%–5%) usually leads to the change of the moisture balance, oxygen, and water permeability but also mechanical properties of the films. ZnO can be also associated with graphene oxide and the final composite food package membrane exhibits strong antibacterial activity against foodborne pathogenic and spoilage bacteria, leading to safer food products and improved shelf-life [33].

When considering the food packaging loaded with nanoparticles, it is important to consider the potential associated risks. This is why increasing attention is paid to the safety issues, and in the last years regulations were released in order to protect the consumers against these risks. For instance, the EU regulation 2016/1416 imposes a maximal limit of 5–25 mg Zn/kg food. Moreover, this value should be correlated with the tolerable upper intake limit of 40 mg/day Zn for the human body [34][35]. Taking into account these values, the amount of ZnO added as a food additive or as an antimicrobial agent in food packaging should be well below these values. For instance, alginate based nanocomposites commonly used as food packaging containing up to 0.5 g/L ZnO NPs can be used without a risking of overpassing this limit [36]. When LDPE-ZnO nanocomposite films are used for food packaging, the migration of Zn^{2+} is much lower so, even 3.5 mg Zn/L can be used without inducing any risks over the human health [37]. Unfortunately, these values are relative because many factors affect the release rate. Some factors are related to the packaging materials themselves, others are related to the food while also the environmental conditions can change the release behavior. For instance, Heydari-Majd et al. [38] highlighted the influence of the presence of essential oils over the migration rate of Zn^{2+} for the polylactic acid/ZnO systems, the release rate being enhanced. Similar conclusions can be found also for several other nanomaterials usually loaded into the food packaging such as TiO_2, Ag NPs, carbon nanoparticles/nanotubes, etc., which after reaching the blood circulation, can be accumulated selectively and induce diseases at the brain, testes, and foetuses (in utero) level [39].

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