Chapter 13
Antimicrobial Activity of Nanomaterials for Food Packaging Applications

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13.1 Introduction

The main function of food packaging systems is to protect food against environmental factors such as microorganisms, chemical contaminants, oxygen and water vapor, extending food shelf stability and improving food safety. Conventional food packaging systems are designed to protect the food in a passive way, that is to say, they are supposed not to interact with the food, but rather to act exclusively as a barrier between the food and the surrounding environment.

On the other hand, active food packaging systems are supposed to perform some role other than providing an inert barrier to external conditions (Rooney 1995). The most common active packaging systems are the antimicrobial ones, which release antimicrobial agents into the food surface, where microbial growth predominates, inhibiting or retarding microbial growth and spoilage.

Nanocomposite antimicrobial systems 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 microbial molecules and cells when compared to larger-scale counterparts (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; Lin et al. 2005), or as antimicrobial carriers (Gu et al. 2003; Bi et al. 2011).

Antimicrobial food packaging systems are extremely useful to minimize the growth of post-processing contaminant microorganisms, extending food shelf life and improving food safety.

In this review, the main types of antimicrobial nanomaterials as they are applied in food packaging are discussed. The discussion has been focused on antimicrobial

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mechanisms and effectivity, as well as applications in food packaging systems, including not only conventional food packaging but also edible coatings used as primary packages which can be consumed with the food product.

13.2 Nano-Antimicrobials Materials and Applications

13.2.1 Silver Nanoparticles

Silver has long been known to have a broad spectrum of antimicrobial activities (Liau et al. 1997), besides having some processing advantages such as high temperature stability and low volatility (Kumar and Münstedt 2005).

Most nanocomposites used as antimicrobial food packaging are based on silver nanoparticles (AgNP), which are effective antimicrobials (Aymonier et al. 2002; Sondi and Salopek-Sondi 2004; Son et al. 2006; Yu et al. 2007; Tankhiwale and Bajpai 2009), even more than larger silver particles, thanks to their larger surface area available for interaction with microbial cells (An et al. 2008; Kvítek et al. 2008). Damm et al. (2008) observed that polyamide 6 filled with 0.06 wt% AgNP was able to completely eliminate a bacterial population within 24 h, while a polyamide 6/silver-microcomposite incorporated with 1.9 wt% of silver killed only about 80% of the bacteria within the same time.

The antimicrobial activity of AgNPs seems to be dependent on release of Ag^+ ions (Morones et al. 2005; Kumar and Münstedt 2005). According to findings by Kumar and Münstedt (2005), Ag^+ binds to electron donor groups in biological molecules containing sulfur, oxygen or nitrogen. Feng et al. (2000) suggested that interactions of Ag^+ ions with thiol groups in proteins may induce inactivation of bacterial enzymes; as a reaction to the protein denaturation effects of Ag^+ ions, DNA molecules may become condensed and unable to replicate. An other mechanism proposed for the antimicrobial activity of AgNP was based on adhesion to the cell surface, degradation of lipopolysaccharides and formation of "pits" in the membranes, largely increasing permeability (Sondi and Salopek-Sondi 2004).

Tankhiwale and Bajpai (2009) demonstrated that grafting of acrylamide onto filter paper, followed by incorporation of AgNPs, results in a biomaterial effective against *Escherichia coli* (*E. coli*), which can be used as an antibacterial packaging material.

Yoksan and Chirachanchai (2010) produced AgNPs by γ-ray irradiation reduction of silver nitrate in a chitosan solution, and incorporated them into chitosan–starch-based films. The AgNP-loaded films were active against both Gram-positive and Gram-negative bacteria. Gottesman et al. (2011) developed a method to coat paper with nano-sized coatings (90–150 nm in thickness) of AgNPs by using ultrasonic radiation. AgNPs penetrated the paper to more than 1 μm in depth, resulting in high stability of the coatings. The coated paper was

effective against *Escherichia coli* and *Staphylococcus aureus*, suggesting its potential application as an active food packaging material.

Tankhiwale and Bajpai (2010) loaded AgNPs into a lactic acid grafted chitosan film. The nanocomposite film showed strong antibacterial properties against *Escherichia coli* and thus has potential as an antibacterial food packaging material.

Fayaz et al. (2009) biosynthesized highly stable AgNPs using *Trichoderma viride* and incorporated them into sodium alginate for vegetable and fruit preservation. The nanobiocomposite film showed good antibacterial activity against test strains, and increased shelf life of carrot and pear when compared to uncoated controls.

An et al. (2008) coated green asparagus with a nanocomposite coating based on polyvinylpyrrolidone (PVP) incorporated with silver nanoparticles, and compared their microbial stability with that of uncoated asparagus. The coating significantly hindered the growth of total aerobic psychrotrophics, yeasts and molds, and reduced the visual changes in asparagus throughout a 25-day storage.

Emamifar et al. (2010) demonstrated the effectiveness of the application of a low-density polyethylene (LDPE) nanocomposite packaging film containing AgNP on reducing microbial growth in fresh orange juice at 4°C. The authors stated that the resulting concentration of Ag^+ ions in orange juice (migrated from the film) was less than its allowable concentration (10 ppm).

In addition to their antimicrobial activity, AgNP have been reported to absorb and decompose ethylene, which may contribute to their effects on extending shelf life of fruits and vegetables (Hu and Fu 2003; Fernández et al. 2010). Moreover, AgNP have been reported to improve thermal properties and tensile properties of polymers used for food packaging. The incorporation of AgNPs into polyvinyl alcohol (PVOH) films resulted in improved thermal stability, higher glass transition temperature, and better tensile properties (Young's modulus and tensile strength) (Mbhele et al. 2003).

13.2.1.1 Nanostructured Calcium Silicate–Ag Complexes

Nanostructured calcium silicate (NCS) was used by Johnston et al. (2008) to adsorb Ag^+ ions from a solution. The resulting NCS-Ag complex exhibited effective antimicrobial activity at desirably low levels of silver down to 10 mg kg^{-1}, and could be incorporated into food packaging as an antimicrobial agent.

13.2.1.2 AgNPs Synthesized in Polymer Matrices

Ex situ AgNP synthesis consists on synthesizing AgNPs beforehand (by chemical reduction) and then dispersing them into a polymerizable formulation. Besides the hazards related to handling dry nanoparticules, this method often involves contamination of AgNP surfaces with chemicals which raise their toxicity. Moreover, it is limited by the difficulty to control the monodispersity of the nanoparticles

(Balan and Burget 2006; Vimala et al. 2010). In the in situ approach, on the other hand, the nanoparticles are generated in a polymerizable medium from cationic precursors which exhibit better dispersion ability (Balan et al. 2010).

In situ synthesis methods involving a stabilization process by reducing Ag^+ ions in water soluble polymers have been suggested and proved efficient (Fernández et al. 2010; Valodkar et al. 2010; Vimala et al. 2010). The AgNPs become attached to the polymer, and the method provides a single-step synthesis and stabilization of AgNPs (Sanpui et al. 2008).

Cellulose is able to bind electropositive transition metal atoms such as silver by electrostatic interactions. Consequently, Ag^+ ions are adsorbed by cellulose during immersion in silver nitrate (Fernández et al. 2010). Afterwards, the nanoporous structure and the high oxygen density of cellulose fibers make them effective nanoreactors for in situ synthesis of AgNP (He et al. 2003). Fernández et al. (2010) stored fresh-cut melon pieces under modified atmosphere packaging containing cellulose absorbent pads loaded with AgNP. The lag phases of the microorganisms were incremented by the pads, and microbial loads remained about 3 log CFU/g below the control (melon cuts packed without the pads) during storage time.

Chitosan has strong affinity towards silver ions, thanks to the presence of amine and hydroxyl groups (Varma et al. 2004), and is able to reduce Ag^+ ions to AgNPs under alkaline conditions (Murugadoss and Chattopadhyay 2008). Sanpui et al. (2008) reported that the presence of a low concentration (2.15%, w/w) of AgNPs in a chitosan composite was enough to significantly enhance inactivation of *E. coli* as compared with unchanged chitosan.

13.2.2 Metal Oxides

Metal oxide materials such as TiO_2, ZnO and MgO have been recognized as antibacterial agents. Generation of reactive oxygen species (ROS) seems to be one of the mechanisms of their antibacterial activity (Dong et al. 2010b). A great advantage of metal oxides over organic-based antimicrobial agents is their much higher stability (Zhang et al. 2010).

13.2.2.1 Titanium Dioxide (TiO_2)

TiO_2 has been widely applied 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 (Maness et al. 1999), has been used to inactivate food-related pathogenic bacteria (Kim et al. 2005; Robertson et al. 2005). Chawengkijwanich and Hayata (2008) developed a TiO_2 powder-coated packaging film able to reduce *E. coli* contamination on food

surfaces. Gelover et al. (2006) demonstrated the efficacy of TiO_2-coated films exposed to sunlight to inactivate fecal coliforms in water.

Metal doping improves visible light absorbance of TiO_2 (Anpo et al. 2001), and increases its photocatalytic activity under UV irradiation (Choi et al. 1994). It has been demonstrated that doping TiO_2 with silver greatly improved photocatalytic bacterial inactivation (Page et al. 2007; Reddy et al. 2007). This combination was explored by Cheng et al. (2006), who have obtained effective antibacterial activity from a polyvinyl chloride (PVC) nanocomposite with TiO_2/Ag^+ nanoparticles. Li et al. (2009) observed that the same combination was effective in reducing physicochemical and sensory changes in Chinese jujubes.

However, TiO_2 nanoparticles, combined or not to Ag^+, are incompatible with organic matrices, and may agglomerate. Although such drawbacks decrease their antimicrobial properties, they can be suppressed by surface modification of the nanoparticles. Cheng et al. (2006) modified TiO_2/Ag^+ nanoparticles by grafting γ-aminopropyltriethoxy-silane (APS), which resulted in improved dispersion of the nanoparticles in a PVC matrix.

13.2.2.2 Zinc Oxide (ZnO)

ZnO has been reported to present antibacterial activity against bacteria, including thermo-resistant spores (Sawai et al. 1996), which has been at least partly attributed to generation of hydrogen peroxide (H_2O_2) (Sawai et al. 1998). The antibacterial activity of ZnO powder has been reported to increase with decreasing particle size (Sawai et al. 1996; Yamamoto 2001).

ZnO nanoparticles deposited on a glass surface exhibited antibacterial activities against both *E. coli* (Gram-negative) and *S. aureus* (Gram-positive) cultures (Applerot et al. 2009b).

Emamifar et al. (2010) demonstrated that the application of LDPE packages containing nano-ZnO prolonged the microbial shelf life of fresh orange juice, without any negative effects on sensory attributes, although nano-ZnO had presented a lower antimicrobial activity on yeast and molds when compared to AgNPs. In another study, the same authors (Emamifar et al. 2011) observed that orange juice sterilized and inoculated with *Lactobacillus plantarum* presented reduced numbers of the inoculated bacteria when packed in LDPE films containing silver or ZnO nanoparticles.

Li et al. (2011a) reported that PVC films coated with ZnO nanoparticles presented excellent bacteriostatic and bactericidal effects against *E. coli*. In an in vitro test, the efficiency of ZnO-coated film was proved to be relatively constant within the pH range of 4.5–8.0. In an actual test, the number of *E. coli* cells from cut apple stored in a ZnO-coated bag was reduced in about 30% in 1 day. Moreover, fruit decay was reduced in nano-coated apples, the growth of aerobic psychrophilic microorganisms was inhibited, and the yeast and mold growth was lower than in uncoated fruit (Li et al. 2011b).

Li et al. (2010) produced chitosan/Ag/ZnO blend films via sol-cast transformation. Ag and ZnO nanoparticles were uniformly distributed within the chitosan polymer. Chitosan/Ag/ZnO blend films presented higher antimicrobial activities than nanocomposite films containing only Ag or ZnO nanoparticles. The blend films showed a wide spectrum of effective antimicrobial activities.

ZnO nanoparticles in aqueous media tend to agglomerate into large flocculates, due to their hydrophobicity, and thus do not interact effectively with microorganisms (Applerot et al. 2009a). Gordon et al. (2011) combined ZnO with FeO to produce magnetic composite nanoparticles with improved colloidal stability. The effectivity of the nanoparticles was reported to be increased by higher Zn/Fe weight ratios; moreover, the antibacterial activity was higher for Gram-positive than for Gram-negative bacteria.

13.2.3 Metal Hydroxides

$Ca(OH)_2$ has been reported as an effective antibacterial agent (Mendonça et al. 1994), its efficiency being highly dependent on the release of OH^- ions (Beltes et al. 1997).

$Mg(OH)_2$ is an approved drug and food additive (Dong et al. 2010b). Dong et al. (2010a, b) demonstrated the effectiveness of $Mg(OH)_2$ nanoparticles and nanoplatelets against *E. Coli*. Their antibacterial effect was attributed to two possible mechanisms (Dong et al. 2010a). The first is related to a direct penetration of $Mg(OH)_2$ nanoparticles into cell walls and damages to membrane proteins, leading to cell death. The second is adsorption of water on the nanoparticle surfaces, forming a thin layer of highly concentrated in OH^- ions, which, in contact with bacteria, could damage the membranes.

13.2.4 Chitosan Nanostructures

Chitosan is a linear polysaccharide consisting of (1,4)-linked 2-amino-deoxy-β-D-glucan units, prepared by alkali deacetylation of chitin. Since the deacetylation is usually incomplete, chitosan is a copolymer comprised of deacetylated and acetylated units (Dutta et al. 2009; Aranaz et al. 2010), as shown in Fig. 13.1. It is a polycation whose charge density depends on the degree of deacetylation and pH

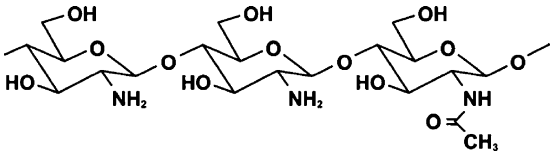

Fig. 13.1 Scheme of the chemical structure of chitosan

(Aranaz et al. 2010). Chitosan has long been reported as an antibacterial agent against a wide variety of microorganisms (Tsai and Su 1999; Entsar et al. 2003; Wu et al. 2005).

Nano-scale chitosan and its derivatives have antimicrobial effects towards bacteria (No et al. 2002; Qi et al. 2004), viruses (Chirkov 2002) and fungi (Badawy et al. 2005). The minimum inhibitory concentrations (MIC) depend on the organism, pH, molecular weight, degree of polymerization, and the presence of lipids and proteins (No et al. 2002). Antimicrobial activity of chitosan may be attributed to interactions between the positively charged chitosan and the negatively charged cell membranes, increasing membrane permeability and eventually causing rupture and leakage of the intracellular material. Indeed, it has been reported that both bulk chitosan and its nanoparticles are ineffective at pH lower than six, probably because of the absence of protonated amino groups (Qi et al. 2004). According to Shi et al. (2006), chitosan nanoparticles (CSN) exhibit higher antibacterial activity than bulk chitosan because of their higher surface area and charge density, favoring a higher interaction with the negatively charged surfaces of bacterial cells. Results by Xing et al. (2009) indicate that oleoyl–chitosan nanoparticles act by damaging cell membrane and putative binding to extracellular (such as phosphate groups) or intracellular (such as DNA and RNA) targets.

Keawchaoon and Yoksan (2011) produced carvacrol-loaded CSN, which presented higher antibacterial activity when compared to unloaded chitosan nanoparticles. Carvacrol is a major component of essential oil fractions of oregano and thyme, which has been known for its bactericidal effects (Ultee et al. 1999).

Ali et al. (2011) synthesized CSN by ionic gelation with sodium tripolyphosphate (TPP) and loaded them with Ag+ ions to produce silver loaded chitosan nanoparticles (Ag-CSN). The minimum inhibitory concentrations of CSN and Ag-CSN against *S. aureus* were reported to be respectively 50 and 500 times lower than that of bulk chitosan.

Chitosan nanostructures have been demonstrated to disperse well in biopolymers such as starch (Chang et al. 2010) and hydroxypropyl methylcellulose (De Moura et al. 2009), having the potential to be used as antimicrobial agents in edible or biodegradable food packaging systems.

Watthanaphanit et al. (2010) observed that the incorporation of chitosan whiskers into alginate imparted antibacterial activity against both Gram-positive and Gram-negative bacteria to the nanocomposite material.

13.2.5 Carbon Nanotubes

Carbon nanotubes (CNTs) are arrangements of carbon hexagons into tube-like fullerenes, having diameters of a few nanometers with lengths up to centimeters. They may consist of a one-atom-thick single-wall nanotube (SWNT), or a number of concentric tubes called multi-walled nanotubes (MWNT) (Zhou et al. 2004). They have received much attention because of their very interesting mechanical,

electrical and thermal properties (Mi et al. 2007), and have been incorporated into polymer matrices such as PVOH (Chen et al. 2005), polypropylene (López Manchado et al. 2005; Prashantha et al. 2009), polyamide (Zeng et al. 2006), and PLA (Brody 2006).

CNTs have also been reported to have antibacterial properties. Direct contact with aggregates of CNTs have been demonstrated to kill *E. coli* (Kang et al. 2007). The antibacterial activity of CNTs has been related not only to their adsorption ability (Upadhyayula et al. 2009) but mainly to puncture of microbial cells by their needle-like structure, causing irreversible damage and leakage of intracellular material (Narayan et al. 2005; Kang et al. 2007). Indeed, Kang et al. (2008) have demonstrated that single-walled carbon nanotubes (SWNTs) are much more toxic to bacteria than multi-walled carbon nanotubes (MWNTs), thus providing evidence that the diameter of CNTs is a key factor governing their antibacterial effects.

13.2.6 Nanoclays

Layered silicates or nanoclays typically have a stacked arrangement of negatively charged silicate layers (nanoplatelets) which are 1 nm thick and several microns long depending on the particular silicate (Sorrentino et al. 2007). Layered silicates have been incorporated into polymer matrices in order to enhance polymer mechanical and barrier properties (Bharadwaj et al. 2002; Uyama et al. 2003).

13.2.6.1 Organically Modified Nanoclays as Antimicrobials

Hong and Rhim (2008) have reported antibacterial activity from two organically modified montmorillonites (OMMT), namely Cloisite 30B and Closite 20A, while an unmodified montmorillonite (Cloisite Na^+) has not shown any antibacterial activity, even though the three nanoclays have the same basic montmorillonite (MMT) structure. The OMMT ruptured cell membranes and inactivated both Gram-positive and -negative bacteria. The contrast between the antimicrobial activity of the OMMT and the inefficacy of the unmodified MMT may be attributed to the presence of quaternary ammonium groups in the OMMT (Rhim et al. 2006; Hong and Rhim 2008). When comparing the effects of the two organoclays, the authors of the study (Hong and Rhim 2008) reported that Cloisite 30B showed significantly higher antimicrobial activity than Cloisite 20A, which were partly attributed to their degrees of hydrophobicity. Since Cloisite 20A is more hydrophobic, it may keep bacteria from being adsorbed into the clay surface, thus reducing clay antimicrobial activity.

Other studies (Rhim et al. 2009; Sothornvit et al. 2009) reported Cloisite 20A not to present any antibacterial activity, and Closite 30B to provide films only with some bacteriostatic activity. However, even those results were not very consistent with one another. While Sothornvit et al. (2009) observed that Cloisite 30B provided whey protein isolate (WPI) films with bacteriostatic effects against

Gram-negative bacteria, Rhim et al. (2009) observed that poly-(lactic acid) (PLA) films with Cloisite 30B presented bacteriostatic effect against *Listeria monocytogenes*, a Gram-positive bacteria, but not against the Gram-negative bacteria tested.

13.2.6.2 Nanoclays in Chitosan Films

Although unmodified nanoclays themselves do not have antimicrobial activity, they may adsorb bacteria from a solution enabling a better interaction with antimicrobial polymers such as chitosan (Wang et al. 2006). Indeed, some studies reported antimicrobial properties from the combination between chitosan and unmodified nanoclays.

Han et al. (2010) observed that chitosan–MMT nanocomposites exhibited significantly higher antimicrobial activity against *S. aureus* and *E. coli* than pure chitosan and Na-MMT. Since the antimicrobial activity of chitosan has been ascribed to its cationic character, the increased antimicrobial activity of the nanocomposites seems contradictory, because the positive charges of chitosan are neutralized via electrostatic interactions with anionic silicate layers. The authors concluded that the nanocomposites exhibited synergistic effects between the components, because the chitosan molecules were evenly distributed through the inorganic matrix.

Wang et al. (2006, 2007, 2009) have carried out a series of studies on chitosan/rectorite intercalated nanocomposites with antimicrobial properties. In their first study (Wang et al. 2006), using unmodified Ca^{2+}-rectorite and organic rectorite, they observed that, although pristine rectorite by itself had not inhibited bacterial growth, the chitosan/rectorite nanocomposites presented stronger antibacterial activity than pure chitosan, particularly against Gram-positive bacteria. In a further study (Wang et al. 2007), the authors suggested that the antibacterial mechanism of the nanocomposites were divided into two stages: the first being the adsorption of the bacteria from solution and immobilization on the clay surface, and the second being related to chitosan accumulation on the clay surface, inhibiting bacterial growth. Finally, in a more recent study, the authors (Wang et al. 2009) prepared nanocomposites of quaternized chitosan and OREC, which presented strong inhibition against bacteria (both Gram-positive and -negative) and fungi, but mainly against Gram-positive bacteria. The excellent antimicrobial activity of the nanocomposites was attributed to the high affinity and strong interaction between quaternized chitosan and OREC, combining the adsorption and immobilization capacity of OREC with the antimicrobial activity of quaternized chitosan. In the three studies of the group (Wang et al. 2006, 2007, 2009), the authors observed that the antimicrobial activity was directly proportional to the amount or the interlayer distance of the nanoclay, thanks to an increase in effective layers per unit weight, causing more bacteria to be adsorbed and immobilized on the clay surface.

13.2.6.3 Nanoclays with Ag^+ Ions

Incoronato et al. (2010) obtained Ag-MMT antimicrobial nanoparticles by bringing Na-MMT in contact with AgNO3 solutions at various concentrations in order to replace exchangeable Na+ ions of Na-MMT with Ag+ ions. The nanoparticles were incorporated into three different polymeric matrices (agar, zein, and polycaprolactone), but only the agar nanocomposites presented antimicrobial activity, which was ascribed to the highest water content (and thus the highest level of macromolecular mobility) of the agar hydrogel. The release kinetics of Ag+ ions was controlled because of the weak electrostatic interactions established with surface platelets of MMT. In a further study (Incoronato et al. 2011), the authors evaluated the effectiveness of an active packaging system of agar with Ag-MMT nanoparticles on the stability of Fior di Latte cheese. The nanocomposite packaging system markedly increased the shelf life of the cheese, without affecting the functional dairy microbiota and the sensory quality of the product.

Costa et al. (2011) obtained Ag-MMT nanoparticles by replacing the Na+ ions of natural MMT by Ag+ ions from nitrate solutions. The nanoparticles were used to extend stability of a fruit salad. Sensory and microbiological tests indicated that the Ag-MMT nanoparticles were effective in inhibiting microbial growth.

Busolo et al. (2010) studied the antimicrobial performance of polylactic acid (PLA) containing a silver-based nanoclay for use in food packaging applications. The nanobiocomposite showed strong activity against *Salmonella* spp. In addition to the strong biocidal properties, the films exhibited enhanced water vapour barrier. A silver migration study using a slightly acidified water medium as a food simulant suggested that migration levels were within levels specified by the European Food Safety Agency (EFSA).

13.2.6.4 Effects of Nanoclays on Solubility, Release and Stability of Antimicrobials

Besides the direct or indirect antimicrobial effects of some nanoclays by themselves, Sánchez-García et al. (2008) reported that mica clay has been reported to enhance the solubility of the antimicrobial thymol in a polycaprolactone (PCL) matrix, by retention of the apolar thymol on the surface of the clay nanoplatelets. On the other hand, the thymol diffusion coefficient has decreased with the addition of mica clay to the biocomposite, probably because of the increased tortuosity effect (Fig. 13.2) imposed to thymol diffusion by the dispersed nanoclay. Thus, it was possible to control the release of thymol from the matrix.

Tunç and Duman (2011) observed that the release of the antimicrobial carvacrol from cellulose/carvacrol/MMT nanocomposite films was controlled by MMT concentration in the films.

An OMMT was reported by Konwar et al. (2010) to act as a supporting material for the stabilization of AgNPs in polyester/clay silver nanocomposites, preventing their aggregation.

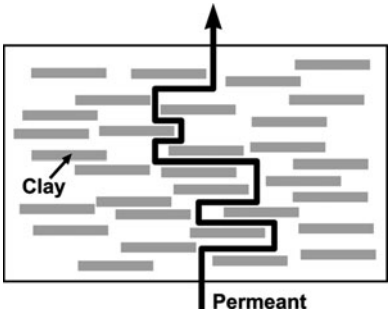

Fig. 13.2 Tortuosity effect imposed by a nanoclay to diffusion of a permeant such as thymol through a polymer matrix (Adapted from Ray and Okamoto 2003)

13.2.7 Tourmaline Nanocrystals

Tourmaline is a naturally complex group of hydrous silicate minerals containing Li, Al, B, and Si and various quantities of alkalis (K and Na) and metals (Fe, Mg, and Mn) (Rhim and Ng 2007). Nanoparticles like tourmaline are classified as isodimensional nanoparticles, since their three dimensions are nanometric, while the layered silicate nanoplatelets have only one dimension in the nanometer range (Rhim and Ng 2007; Sorrentino et al. 2007).

Ruan et al. (2003) incorporated tourmaline nanocrystals into cellulose films and the resulting material presented antimicrobial action against *S. aureus*.

13.2.8 Nano-Hybrid Systems with Antimicrobial Properties

Hybrid organic–inorganic systems have aroused great attention, particularly those in which fillers are dispersed at a nanometric level in a polymeric matrix, forming nano-hybrid composite systems.

Marini et al. (2007) coated polyethylene (PE) films with antibacterial nano-hybrid coatings prepared by a sol–gel process from tetraethoxysilane (TEOS), triethoxysilane terminated poly(ethylene glycol)-block-poly(ethylene) (PE-PEG-Si), and triethoxysilane terminated quaternary ammonium salt (QAS-Si). The objective of bonding the quaternary ammonium salt (QAS) to the organic–inorganic network was to reduce QAS diffusivity and to enhance its stability. The coated PE films showed good activity against both Gram-negative and Gram-positive bacteria.

Layered double hydroxides (LDHs), also known as "anionic clays", act as ion delivery vehicles, because of their anion exchange properties. They are cheap, eco-friendly, and can be organically modified with several organic anions, generally much more numerous than organic cations commonly involved in modification of cationic clays (Bugatti et al. 2010). Intercalation compounds of ZnAl-LDH with benzoate and derivatives (antimicrobial agents) were elaborated by Bugatti et al. (2010), and the resulting nano-hybrids were incorporated into polycaprolactone

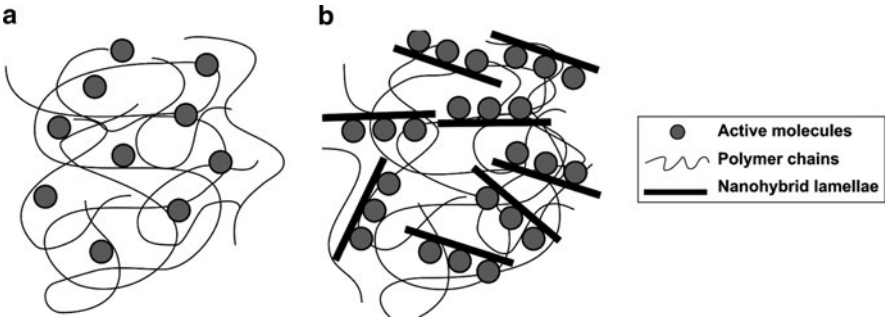

Fig. 13.3 Schematic picture of active molecules into a polymeric matrix: (**a**) free dispersed; (**b**) fixed on inorganic lamellae and dispersed as exfoliated filler (Source: Bugatti et al. 2011)

(PCL) films. The benzoate anions in the nano-hybrids exhibited much slower and controlled release when compared to those directly dispersed in PCL. According to Bugatti et al. (2011), the release of active molecules directly dispersed into a polymeric matrix (Fig. 13.3a) is only driven by diffusion, whereas when they are fixed on the inorganic lamellae of a clay by ionic bonds (Fig. 13.3b) the release depends on many factors, such as diffusion of water molecules carrying counter-anions inside the matrix.

13.3 Nanocarriers of Antimicrobials

Some nanoparticles, although not having antimicrobial properties themselves, may be used as carriers of antimicrobials, deserve mentioning in this review.

Bi et al. (2011) elaborated phytoglycogen-based nanoparticles to prolong the efficacy of an antimicrobial peptide (nisin) against *Listeria monocytogenes*, a food-related pathogen, in order to minimize nisin loss during storage and meanwhile provide an effective release in the presence of bacteria. Phytoglycogen was subjected to β-amylolysis as well as subsequent succinate or octenyl succinate substitutions. Nisin loading and retention were favored by nanoparticles, especially by those subjected to β-amylolysis, with a high degree of substitution with hydrophobic octenyl succinate moieties.

13.4 Toxicological Aspects and Final Considerations

The food packaging sector can benefit from antimicrobial nanocomposites, which can be used to reduce microbial growth on food surfaces. However, safety concerns have to be considered, since nano-sized materials frequently exhibit different properties than those of the corresponding starting materials. The much larger surface area of nanoparticles allows a greater contact with cell membranes,

as well as a greater capacity for absorption and migration (Li and Huang 2008). Hence, their toxicity profiles cannot be extrapolated from those of their non-nano-sized counterparts (Restuccia et al. 2010). Moreover, nanostructures can have more free movement through the body when compared to their larger-scale counterparts (Brayner 2008).

Exposure to nanoparticles present in food packaging can occur through dermal contact, inhalation, or ingestion of nanoparticles which have migrated to food (Carlson et al. 2008; Li and Huang 2008; Restuccia et al. 2010). Moreover, nanoparticles may eventually be released into the environment and enter the food chain indirectly (Hoet et al. 2004).

Several studies have already been conducted on toxicological aspects of the nano-antimicrobial materials indicated in this study. Carbon nanotubes may be cytotoxic to human cells, at least when in contact to skin (Shvedova et al. 2003; Monteiro-Riviere et al. 2005) or lungs (Warheit et al. 2004), which would affect people manipulating the nanotubes in processing stages rather than consumers. Although bulk ZnO is non-toxic (Li et al. 2011a), Sharma et al. (2009) demonstrated that ZnO nanoparticles have a genotoxic potential in human epidermal cells. Some nanoparticles cause more inflammation than larger respirable particles elaborated from the same material at the same mass dose (Brayner 2008).

Although there are limited scientific data available about the migration of nanostructures from packaging materials into food, it is prudent to consider that, once present in the food packaging material, nanoparticles might eventually migrate into food. Thus, it is mandatory to know about any eventual health effects from ingestion of nanoparticles. The toxicity issue is even more important when edible coatings are concerned, since edible coatings must be considered as part of the food itself, and not just as a food contact material. Hence, actual applications of nanocomposite packaging requires further studies focused on the potential toxicity of nanotechnology products.

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