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Nanocomposites in Food Packaging – A Review

Henriette Monteiro Cordeiro de Azeredo¹,
Luiz Henrique Capparelli Mattoso² and Tara Habig McHugh³

¹*Embrapa Tropical Agroindustry - CNPAT,*

²*Embrapa Agricultural Instrumentation - LNNA/CNPDI,*

³*Agricultural Research Service - ARS/WRRC/USDA,*

^{1,2}*Brazil*

³*USA*

1. Introduction

A nanocomposite is a multiphase material derived from the combination of two or more components, including a matrix (continuous phase) and a discontinuous nano-dimensional phase with at least one nano-sized dimension (i. e., with less than 100 nm). The nano-dimensional phase can be divided into three categories according to the number of nano-sized dimensions. Nanospheres or nanoparticles have the three dimensions in the nanoscale. Both nanowhiskers (nanorods) and nanotubes have two nanometric dimensions, with the difference that nanotubes are hollow, while nanowhiskers are solid. Finally, nanosheets or nanoplatelets have only one nano-sized dimension (Alexandre & Dubois, 2000).

Most nano-sized phases have a structural role, acting as reinforcements to improve mechanical properties of the matrix (usually a polymer), since the matrix transfers the tension to the nanoreinforcement through the interface. Nanoreinforcements are especially useful for biopolymers, because of their usually poor performance when compared to conventional petroleum-based polymers. The incorporation of nano-sized reinforcements to biopolymers may open new possibilities for improving not only their properties but also their cost-price-efficiency (Sorrentino et al., 2007).

Besides nanoreinforcements, whose main role is to improve mechanical and barrier properties of polymers, there are nanostructures responsible for other applications related to food packaging. For instance, when incorporated to polymer matrices, they may interact with the food and/or its surrounding environment, thus providing active or “smart” properties to packaging systems. Such properties, when present in food packaging systems, are usually related either to improvements in food safety/stability or information about the safety/stability status of a product.

The main types of nanostructures will be presented according to their primary functions/applications in food packaging systems. Some structures can have multiple applications, and sometimes applications can overlap, such as some immobilized enzymes which can act as antimicrobial components, oxygen scavengers and/or nanosensors.

2. Nanoreinforcements in food packaging materials

Polymer nanocomposites usually have much better polymer/filler interactions than conventional composites (Ludueña et al., 2007). A uniform dispersion of nanofillers into a polymer matrix results in a very large matrix/filler interfacial area, which restricts the mechanical mobility of the matrix, and improves its mechanical, thermal (especially glass transition temperature – T_g), and barrier properties.

The ratio of the largest to the smallest dimension of a filler is an important property known as aspect ratio. Fillers with higher aspect ratios have higher specific surface area, providing better reinforcing effects (Azizi Samir et al, 2005; Dalmas et al, 2007). In addition to the effects of the nanoreinforcements themselves, an interphase region of decreased mobility surrounding each nanofiller results in a percolating interphase network in the composite which plays an important role in improving the nanocomposite properties (Qiao & Brinson, 2009). For a constant filler content, a reduction in particle size increases the number of filler particles, bringing them closer to one another; thus, the interface layers from adjacent particles overlap, altering the bulk properties more significantly (Jordan et al., 2005).

2.1 Nanoclays (layered silicates)

Nanoclays have been the most studied nanofillers, due to their high availability, low cost, good performance and good processability. The first publications about applications of polymer-nanoclays composites to food packaging date from the 1990's (Ray et al., 2006). The clays for nanocomposites usually are bidimensional platelets with very tiny thicknesses (frequently around 1 nm) and several micrometers in length.

In contrast with the typical tactoid structure of microcomposites (conventional composites), in which the polymer and the clay tactoids remain immiscible (Ludueña et al., 2007; Alexandre et al., 2009), the interaction between layered silicates and polymers may produce two types of nanoscale composites (Figure 1), namely: intercalated nanocomposites, which result from penetration of polymer chains into the interlayer region of the clay, producing an ordered multilayer structure with alternating polymer/inorganic layers (Weiss et al., 2006), and exfoliated nanocomposites, which involve extensive polymer penetration, with the clay layers delaminated and randomly dispersed in the polymer matrix (Ludueña et al., 2007). Exfoliated nanocomposites have been reported to exhibit the best properties due to the optimal clay-polymer interactions (Adame & Beall, 2009; Alexandre et al., 2009).

The most studied clay is montmorillonite (MMT), whose chemical general formula is $M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$. MMT is a representative of 2:1 layered *phyllosilicates*, whose platelets have two layers of tetrahedral silica sheets filled with a central octahedral alumina sheet (Weiss et al., 2006). This kind of clay has a moderate negative surface charge that is important to define the interlayer spacing (Alexandre & Dubois, 2000). The imbalance of the surface negative charges is compensated by exchangeable cations (typically Na^+ and Ca^{2+}). The parallel layers are linked together by weak electrostatic forces (Tan et al., 2008). MMT is an excellent reinforcing filler, thanks to its high surface area and large aspect ratio, which ranges from 50 to 1000 (Uyama et al., 2003).

The hydrophilicity of the surface of most clays make their dispersion in organic matrices difficult (Kim et al., 2003). Organoclays, produced by interactions of clays and organic compounds, have found an important application in polymer nanocomposites. An adequate organophilization is essential for successful exfoliation of clays in most polymeric matrices, since organophilization reduces the energy of clays and improves their compatibility with

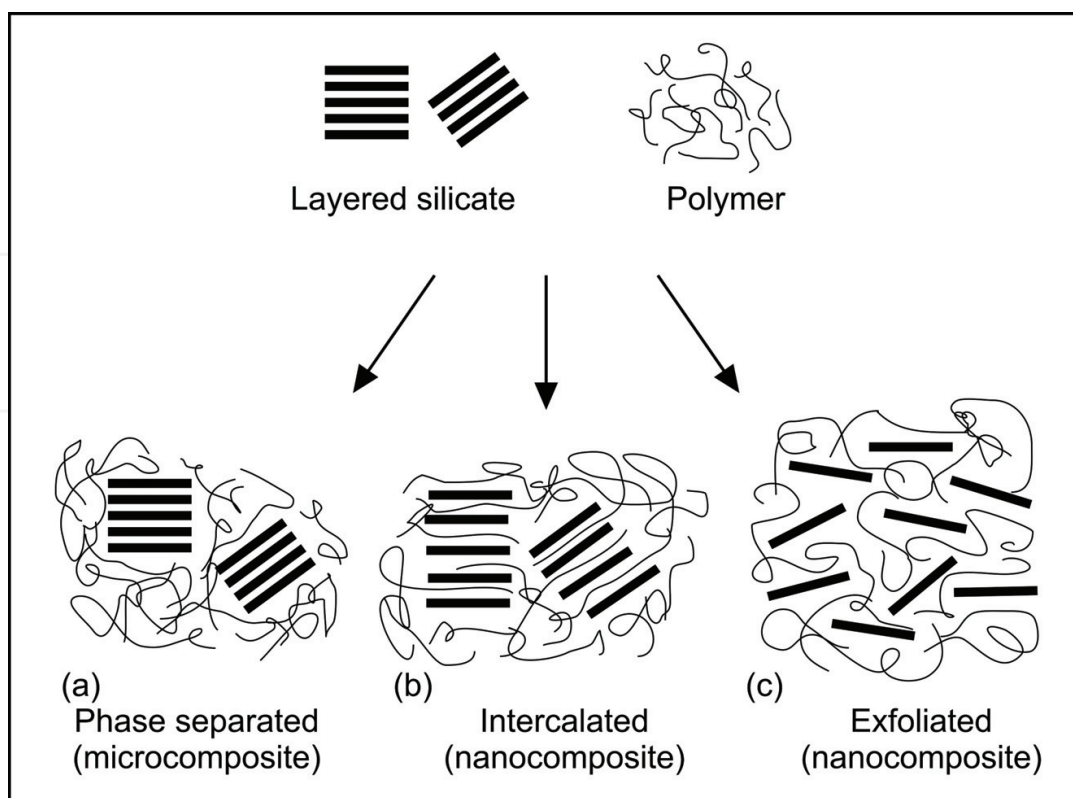


Fig. 1. Types of composites from polymer-clay interactions (Alexandre & Dubois, 2000).

organic polymers (Paiva et al., 2008). Organomontmorillonite (oMMT) have been produced, for example, by exchanging inorganic cations of MMT with organic ammonium ions, improving compatibility of MMT with organic polymers (Osman et al., 2003; Paul et al., 2003), leading to a more regular organization of the layers, and decreasing the water uptake by the resulting nanocomposite (Picard et al., 2007).

The improved barrier properties of polymer-clay nanocomposites seem to be due to a increased tortuosity of the diffusive path for permeants (Figure 2), forcing them to travel a longer path to diffuse through the film. This theory was developed by Nielsen (1967) and was further corroborated by other authors (Mirzadeh & Kokabi, 2007; Adame & Beall, 2009). The increase in path length is a function of the aspect ratio of the clay and the volume fraction of the filler in the composite. Nielsen's model has been used effectively to predict permeability of systems at clay loadings of less than 1%, but some experimental data have reported much lower permeabilities than predicted at higher loadings (Adame & Beall, 2009). Beall (2000) proposed a new model to predict permeability of nanocomposites focused on the polymer-clay interface as an additional governing factor to the tortuous path, thus providing a correction factor to Nielsen's model.

Clays have been also reported to improve the mechanical strength of biopolymers (Chen & Evans, 2005; Russo et al., 2007; Cyras et al., 2008), although they may decrease polymer elongation (Petersson & Oksman, 2006).

2.2 Cellulose nanoreinforcements

Cellulose nanoreinforcements (CNRs) are interesting materials for the preoperation of low cost, lightweight, and high-strength nanocomposites (Helbert et al., 1996; Podsiadlo et al., 2005).

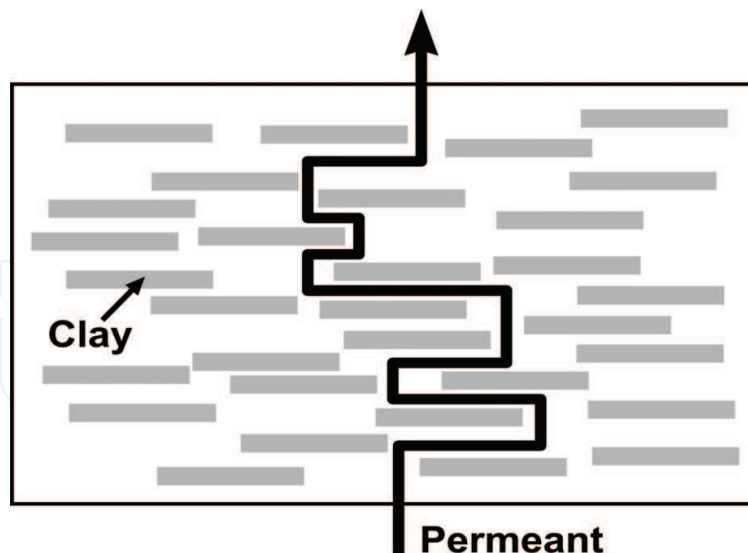


Fig. 2. Tortuous path for a permeant through a polymer-clay nanocomposite, according to Nielsen's model. (Adapted from Adame & Beall, 2009).

Cellulose chains are synthesized in living organisms (mainly plants) as microfibrils (or nanofibers), which are bundles of elongated molecules (with 2-20 nm in diameter and micrometric in length) stabilized by hydrogen bonds (Azizi Samir et al., 2005; Oksman et al., 2006; Mattoso et al., 2009). Each microfibril, formed by elementary fibrils, have crystalline and amorphous regions. The crystalline parts, which may be isolated by procedures such as acid hydrolysis, are the nanocrystals or nanowhiskers (Dujardin et al., 2003; Azizi Samir et al., 2004), whose aspect ratios are related to the origin of the cellulose and processing conditions (Azizi Samir et al., 2005). Thus, a microfibril can be considered as a string of whiskers linked by amorphous domains, which are taken as structural defects.

Our group has studied the influence of cellulose nanofibers on the physical properties of mango puree edible films (Azeredo et al., 2009) and chitosan films (Azeredo et al., 2010).

In our first study (Azeredo et al., 2009), different concentrations of cellulose nanofibers (Novacel® PH-101, provided by FMC BioPolymer, Philadelphia, PA, USA) were added to mango puree edible films. The nanofiller was homogenized with the mango puree at 6500 rpm for 30 minutes, by using a Polytron PT 3000 (Brinkmann, Westbury, NY, USA). A control film was prepared with non-reinforced mango puree. The film-forming dispersions were vacuum degassed, and films were cast on leveled glass plates and allowed to dry for 16 h at 22°C and 42% RH. Samples of the dried films were cut and peeled from the casting surface for analyses. Tensile properties were measured according to standard method D882-97 (ASTM, 1997), by using an Instron Model 55R4502 (Instron, Canton, MA) with a 100 N load cell. The gravimetric Modified Cup Method (McHugh et al., 1993) based on standard method E96-80 (ASTM, 1989) was used to determine water vapor permeability (WVP).

Table 1 presents physical properties of mango puree films containing different CNR concentrations. The addition of at least 10% CNRs was effective to decrease water vapor permeability (WVP) of the films (Table 1), similarly to results reported by Paralikar et al. (2008) and Sanchez-Garcia et al. (2008). The interactions of CNRs with mango polysaccharides may have favored water vapor barrier. The nanofillers were also effective to increase tensile strength and (especially) Young's modulus. The elongation was slightly impaired, but only at nanofiller concentrations above 10%. Several other studies have reported positive effects of CNRs on tensile properties - especially on modulus - of

polymers (Helbert et al., 1996; Bhatnagar & Sain, 2005; Wu et al., 2007), although they tend to decrease elongation (Freire et al., 2008; Tang & Liu, 2008; Kim et al., 2009). According to Helbert et al. (1996), the great effect of CNRs on modulus is ascribed not only to the geometry and stiffness of the fillers, but also to the formation of a fibrillar network within the polymer matrix, the CNRs being probably linked through hydrogen bonds.

CNR (%) [*]	TS (MPa)	EB (%)	YM (MPa)	WVP (g.mm/ kPa.h.m ²)
0	(4.09 ± 0.12) ^d	(44.07 ± 0.98) ^a	(19.85 ± 0.51) ^e	(2.66 ± 0.06) ^a
5	(4.58 ± 0.21) ^c	(41.79 ± 0.44) ^b	(30.93 ± 1.27) ^d	(2.16 ± 0.05) ^b
10	(4.91 ± 0.13) ^c	(43.19 ± 1.73) ^{ab}	(40.88 ± 1.41) ^c	(2.03 ± 0.11) ^b
18	(5.54 ± 0.07) ^b	(39.8 ± 0.53) ^b	(78.82 ± 5.00) ^b	(1.90 ± 0.06) ^{bc}
36	(8.76 ± 0.11) ^a	(31.54 ± 2.29) ^c	(322.05 ± 19.43) ^a	(1.67 ± 0.11) ^c

^{*}On a dry basis. TS: tensile strength (MPa); EB: elongation at break (%); YM: Young’s Modulus (MPa); WVP: water vapor permeability (g.mm/kPa.h.m²). Means in same column with different letters are significantly different at p<0.05.

Table 1. Physical properties of mango puree films with different concentrations of CNRs.

In our second study (Azeredo et al., 2010), nanocomposite films were also obtained from a chitosan matrix with CNRs (Avicel® PH, also provided by FMC BioPolymer). The experiment was conducted according to a central composite design, with two variables: concentrations (on a dry basis) of CNRs (0-20%) and glycerol (0-30%). A dilute chitosan solution was made by preparing a 3% chitosan (71.3 kDa, 94% deacetylation, from *Polymer Ciência e Nutrição S/A*, Fortaleza, Brazil) in 1.5% acetic acid solution. CNRs and glycerol were added to the chitosan solution, and the dispersions were homogenized at 4500 rpm for 30 minutes, with a Polytron PT 3000. The procedure for degassing, casting, drying and analyses were the same as for the mango puree films. The glass transition temperatures (T_g) of the films were measured by differential scanning calorimetry (DSC) with an mDSC 2910 (TA Instruments, New Castle, DE), from 30°C to 200°C, at a heating rate of 10°C/min.

Figure 3 presents the contour plots for the physical properties of the nanocomposite chitosan films as functions of the CNR and glycerol concentrations. The nanofillers increased the overall tensile properties of the films, but decreased their elongation. The water vapor barrier was improved, as indicated by the decreased water vapor permeability (WVP) with increasing CNR concentrations. Moreover, T_g of the films was increased by CNRs. Thus, most responses (except by elongation) were favored by high CNR concentrations and low glycerol contents.

Several studies have been focused on CNR effects on starch systems, indicating that CNRs reduce the water sensitivity of starch (Dufresne & Vignon, 1998; Dufresne et al., 2000; Lima & Borsali, 2004; Lu et al., 2005), and reduce starch brittleness (Dufresne & Vignon, 1998). The effect of CNRs on starch brittleness is consistent with the transcrystallization phenomenon, i.e., orientation of crystals of a semicrystalline matrix perpendicularly to the cellulose microfibrils, as described by Helbert & Chanzy (1994) and Hulleman et al. (1996). Moreover, some studies have reported that the incorporation of CNRs increases T_g of starch (Anglès & Dufresne, 2000; Alemdar & Sain, 2008). However, Mathew & Dufresne (2002) found inconsistent effects of cellulose whiskers on T_g of a starch matrix. They observed that the T_g of the nanocomposite first increased up to a whisker content of around 10-15 wt % and then

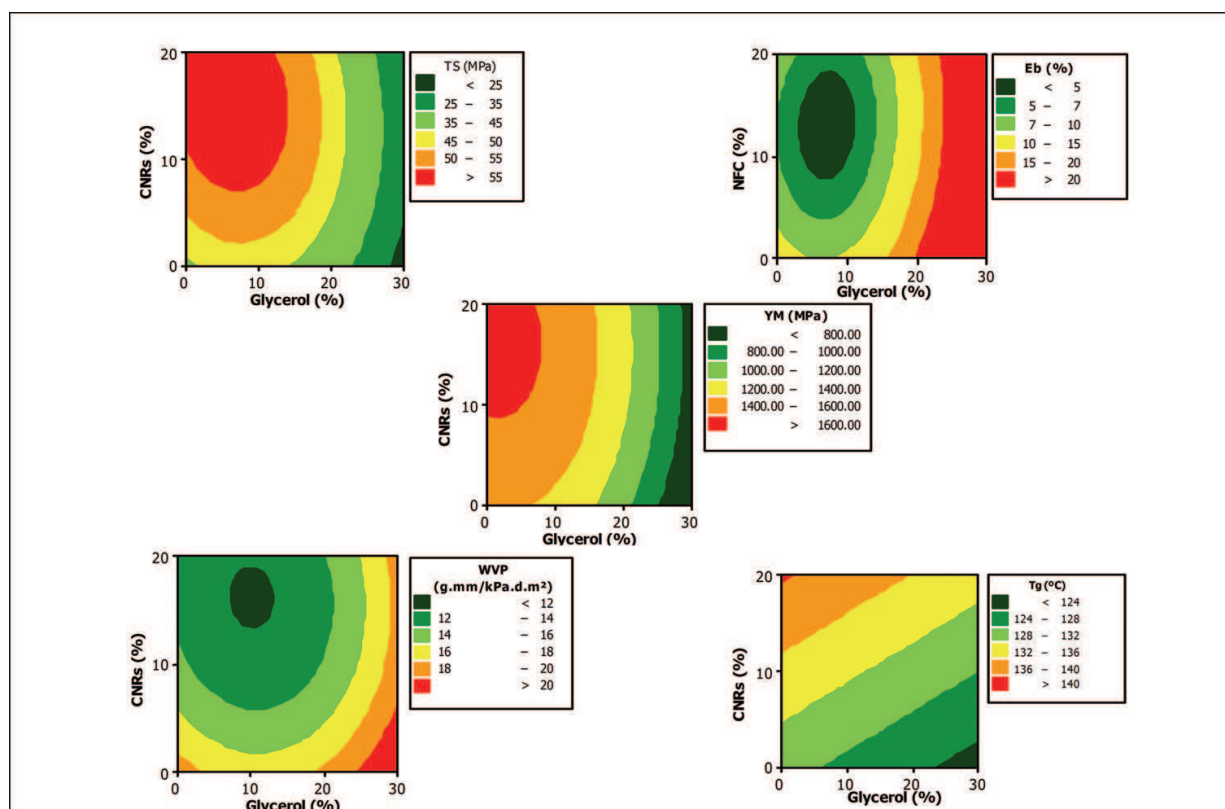


Fig. 3. Physical properties of chitosan films added with cellulose nanofibers and glycerol. TS: tensile strength (MPa); Eb: elongation at break (%); YM: Young's Modulus (MPa); WVP: water vapor permeability (g.mm/kPa.h.m²); T_g: glass transition temperature (°C).

decreased. The increase of T_g up to 15 wt % of whiskers was ascribed to the increase in the crystallinity of the matrix, the restricted mobility of amorphous amylopectin chains resulting from the physical cross-links induced by the crystallization. For the decrease of T_g above 15 wt % whiskers, a possible explanation is that sorbitol may have been partially ejected from the crystalline domains of the matrix during crystallization, its concentration increasing in the amorphous domains. This phenomenon should compete with the T_g increasing effect of the whiskers themselves, being probably predominant at high loading level inducing a decrease of T_g.

Similarly to nanoclays, the presence of cellulose nanoreinforcements is believed to increase the tortuosity of the diffusivity path for the permeants, lowering the polymer permeability (Sanchez-Garcia et al., 2008). In fact, several studies have reported improvements in barrier properties of polymers by addition of cellulose nanoreinforcements (Paralika et al., 2008; Sanchez-Garcia et al., 2008; Svagan et al., 2009). The barrier properties are further enhanced if the filler is less permeable, well dispersed in the matrix, and with a high aspect ratio (Lagaron et al., 2004).

The resulting overall properties of polymer composites with cellulose nanoreinforcements have been reported to be strongly related to the dimensions and consequent aspect ratio of the fillers (Chen et al., 2009) as well as to orientation of the nanostructures (Kvien & Oksman, 2007).

Because of the hydrophilic cellulose surface, interactions between CNRs and hydrophilic matrices are usually satisfactory (Bondeson & Oksman, 2007). On the other hand, incorporation of cellulose nanoreinforcements to hydrophobic matrices results frequently in

weak filler-matrix interactions (Hubbe et al., 2008) and filler aggregation by hydrogen bonding (Freire et al., 2008). Another limitation to the hydrophilic character of cellulose nanoreinforcements is the high water absorption capacity, which is undesirable in many potential applications (Hubbe et al., 2008). Such problems can be reduced by a variety of modifications (hydrophobization) on cellulose surfaces by several reactions involving hydroxyl groups, such as esterifications (Mohanty et al., 2001) and acylation with fatty acids (Freire et al., 2008).

2.3 Other nanoreinforcements

Carbon nanotubes may consist of a one-atom thick single-wall nanotube, or a number of concentric tubes called multiwalled nanotubes, having extraordinarily high aspect ratios and elastic modulus (Zhou et al., 2004). Several polymers have been found to have their tensile strength/modulus improved by addition of carbon nanotubes, such as polyethylene naphthalate (Kim et al., 2008), polyvinyl alcohol (Chen et al., 2005), polypropylene (López Manchado et al., 2005; Prashantha et al., 2009), and a polyamide (Zeng et al., 2006). According to Brody (2006), researches from Natick indicated that polylactic acid not only had its tensile properties improved by carbon nanotubes, but also had its water vapor transmission rate decreased in 200%.

Silica nanoparticles ($n\text{SiO}_2$) have been reported to improve tensile properties of polypropylene (Wu et al., 2002; Vladimirov et al., 2006), starch (Xiong et al., 2008), starch/polyvinyl alcohol (Tang et al., 2008), besides decreasing water absorption by starch (Tang et al., 2008; Xiong et al., 2008) and improving oxygen barrier of polypropylene (Vladimirov et al., 2006). Jia et al. (2007) prepared nanocomposites of polyvinyl alcohol with $n\text{SiO}_2$ by radical copolymerization of vinyl silica nanoparticles and vinyl acetate. The nanocomposites had improved thermal and mechanical properties when compared to the pure polyvinyl alcohol, due to strong interactions between $n\text{SiO}_2$ and the polymer matrix via covalent bonding.

Some studies have been conducted on effects of chitin or chitosan nanostructures on polymer properties. Incorporation of chitin whiskers have greatly improved the tensile properties as well as the water resistance of soy protein isolate thermoplastics (Lu et al., 2004). De Moura et al. (2009) incorporated chitosan-tripolyphosphate nanoparticles into hydroxypropyl methylcellulose films, and observed that they significantly improved tensile and barrier properties of the films.

Other nanostructures have also been reported as good reinforcing agents, such as starch nanocrystals (SNCs), which have increased tensile strength, modulus, and T_g of pullulan films, but decreased their elongation (Kristo & Biliaderis, 2007).

3. Nanocomposite active food packaging

Conventional food packaging systems are supposed to passively protect the food, that is to say, to act as a barrier between the food and the surrounding environment. On the other hand, an active food packaging may be defined as a system that not only acts as a passive barrier but also interacts with the food in some desirable way, e. g. by releasing desirable compounds (antimicrobial or antioxidant agents, for instance), or by removing some detrimental factor (such as oxygen or water vapor). The consequences of such interactions are usually related to improvements in food stability. Some examples of nanocomposite active food packaging systems are presented in this section.

3.1 Antimicrobial systems

Antimicrobial food packaging systems have received considerable attention since they help control the growth of pathogenic and spoilage microorganisms on food surfaces, where microbial growth predominates. Antimicrobial nanocomposite systems are particularly interesting, since materials in the nanoscale range have a higher surface-to-volume ratio when compared with their microscale counterparts. Nanomaterials are thus more efficient, since they are able to attach more copies of microbial molecules and cells (Luo & 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 & Münstedt, 2005; Lin et al., 2005), or antibiotic carriers (Gu et al., 2003).

Silver is well known for its strong toxicity to a wide range of microorganisms (Liau et al., 1997), besides some processing advantages such as high temperature stability and low volatility (Kumar & Münstedt, 2005). Silver nanoparticles have been shown to be effective antimicrobials (Aymonier et al., 2002; Sondi & Salopek-Sondi, 2004; Son et al., 2006; Yu et al., 2007; Tankhiwale & Bajpai, 2009), even more effective than larger silver particles, thanks to their larger surface area available for interaction with microbial cells (An et al., 2008; Kvítek et al., 2008). In fact, the most common nanocomposites used as antimicrobial films for food packaging are based on silver nanoparticles, whose antimicrobial activity has been ascribed to different mechanisms, namely: (a) adhesion to the cell surface, degradation of lipopolysaccharides and formation of “pits” in the membranes, largely increasing permeability (Sondi & Salopek-Sondi, 2004); (b) penetration inside bacterial cell, damaging DNA (Li et al., 2008); and (c) releasing antimicrobial Ag^+ ions by dissolution of silver nanoparticles (Morones et al., 2005). The latter mechanism is consistent with findings by Kumar & Münstedt (2005), who have concluded that the antimicrobial activity of silver-based systems depends on releasing of Ag^+ , which binds to electron donor groups in biological molecules containing sulphur, oxygen or nitrogen. Besides the antimicrobial activity, silver nanoparticles have been reported to absorb and decompose ethylene, which may contribute to their effects on extending shelf life of fruits and vegetables (Li et al., 2009). 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.

Titanium dioxide (TiO_2) is widely used 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 & 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 nanocomposite with TiO_2/Ag^+ nanoparticles.

Qi et al. (2004) have reported antibacterial activity from chitosan nanoparticles, which 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. This is consistent with the observation by the same authors (Qi et al., 2004) that both chitosan and its engineered nanoparticles are ineffective at pH lower than 6, which is probably due to the absence of protonated amino groups. Another two antimicrobial mechanisms were proposed by Rabea et al. (2003), namely: chelation of trace metals by chitosan, inhibiting microbial enzyme activities; and (in fungal cells) penetration through the cell wall and membranes to bind DNA and inhibit RNA synthesis.

Carbon nanotubes have also been reported to have antibacterial properties. Direct contact with aggregates of carbon nanotubes have been demonstrated to kill *E. coli*, possibly because the long and thin nanotubes puncture microbial cells, causing irreversible damages and leakage of intracellular material (Kang et al., 2007). On the other hand, there are studies suggesting that carbon nanotubes may also 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. Anyway, once present in the food packaging material, the nanotubes might eventually migrate into food. Then, it is mandatory to know any eventual health effects of ingested carbon nanotubes.

3.2 Oxygen scavengers

Oxygen (O_2) participates in several forms of food deterioration. Direct oxidation reactions result in browning reactions and rancid flavors, to name only a few examples. Food deterioration by indirect action of O_2 includes food spoilage by aerobic microorganisms. The incorporation of O_2 scavengers into food packaging systems can maintain very low O_2 levels, which is useful for several applications.

Oxygen scavenger films were successfully developed by Xiao-e et al. (2004) by adding TiO_2 nanoparticles to different polymers. The nanocomposite materials could be used as packaging films for a variety of oxygen-sensitive food products. Since TiO_2 acts by a photocatalytic mechanism, its major drawback would be the requirement of UVA light (Mills et al., 2006).

3.3 Enzyme immobilization systems

Enzymes have a variety of applications in food industry. However, their sensitivity to processing conditions and/or to enzyme inhibitors can sometimes restrict the applicability of the direct enzyme addition to foods. Immobilization is usually an effective way to improve enzyme stability to pH and temperature, resistance to proteases and other denaturing compounds, as well as to provide an adequate environment for their repeated use or controlled release (Kandimalla et al., 2006; Lopez-Rubio et al., 2006).

Enzyme immobilization has been considered for packaging applications (Appendini & Hotchkiss, 1997; Soares & Hotchkiss, 1998). The incorporation of enzymes like lactase or cholesterol reductase to packaging materials could increase the value of food products and answer the needs of consumers with enzyme deficiencies (Fernández et al., 2008). Nanoscale enzyme immobilization systems would have enhanced performance when compared to conventional ones, because of their much higher surface contact area and mass transfer rate, which are probably the most important factors affecting the effectiveness of such systems (Fernández et al., 2008). Approaches might be expected dealing with enzyme adsorption

into nanoclays incorporated to polymers (Rhim & Ng, 2007), since nanoclays have a high affinity for protein adsorption, and have been reported to be efficient enzyme carriers (Sinegani et al., 2005; Gopinath & Sugunan, 2007). Conductive polymers may also be used as immobilizing matrices for biomolecules (Ahuja et al., 2007), as reported by Sharma et al. (2004), who immobilized glucose oxidase onto films of poly(aniline-co-fluoroaniline). SiO₂ nanoparticles have been modified to immobilize glutamate dehydrogenase and lactate dehydrogenase (Qhobosheane et al., 2001), which have shown excellent enzyme activity upon immobilized.

4. Nanocomposite smart food packaging

A smart food packaging system may be defined as a system that “perceives” some property of the packaged food and uses some mechanism to register and transmit information about the current quality or safety status of the food. In this context, nanostructures can be applied as reactive particles in packaging materials. The so-called nanosensors may be able to respond to environmental changes during storage (e.g., temperature, relative humidity, oxygen exposure), degradation products or microbial contamination (Bouwmeester et al., 2009).

Food expiration dates are estimated by considering distribution and storage conditions which the food product is supposed to be exposed to. However, such conditions are frequently not the real ones. For instance, foods which require a cold chain are often exposed to temperature abuse; micropores or sealing defects in packaging systems can lead food products to an unexpectedly high exposure to oxygen. Nanosensors integrated into food packaging systems may detect spoilage-related changes, pathogens and chemical contaminants, being then useful to eliminate the need for inaccurate expiration dates, providing real-time status of food freshness (Liao et al., 2005). Below are some examples of applications of nanocomposites as smart packaging systems.

4.1 Time-temperature integrators

Time- temperature indicators or integrators (TTIs) are designed to monitor, record and translate whether a certain food product is safe to be consumed, in terms of its temperature history. This is particularly important when food is stored in conditions other than the optimal ones. For instance, if a product is supposed to be frozen, a TTI can indicate whether it had been inadequately exposed to higher temperatures and the time of exposure.

The TTIs are categorized into three basic types, namely, abuse indicators, partial temperature history indicators, and full temperature history indicators. Abuse indicators, or critical temperature indicators, merely indicate whether a reference temperature has been achieved. Partial temperature history indicators integrate the time-temperature history only when the temperature exceeds a critical predetermined value. Finally, full temperature history indicators provide a continuous register of temperature changes with time (Shing, 2000).

The communication is usually manifested by a color development (related to a temperature dependent migration of a dye through a porous material) or a color change (using a temperature dependent chemical reaction or physical change). Timestrip® has developed a system (iStrip) for chilled foods, based on gold nanoparticles, which is red at temperatures above freezing. Accidental freezing leads to irreversible agglomeration of the gold nanoparticles resulting in loss of the red color (Robinson & Morrison, 2010).

4.2 Detection of gases produced by food spoilage

Food spoilage is caused by microorganisms whose metabolism produces gases which may be detected by several types of gas sensors which have been developed to translate chemical interactions between particles on a surface into response signals.

Nanosensors to detect gases are usually based on metal oxides or, more recently, conducting polymer nanocomposites, which are able to quantify and/or identify microorganisms based on their gas emissions.

Sensors based on conducting polymers (or electro active conjugated polymers) consist on conducting particles embedded into an insulating polymer matrix. The resistance changes of the sensors produce a pattern corresponding to the gas under investigation (Arshak et al., 2007). Conducting polymers are very important because of their electrical, electronic, magnetic and optical properties, which are related to their conjugated π electron backbones (Retama, 2005; Ahuja et al., 2007; Wiziack et al., 2007). Polyene and polyaromatic conducting polymers such as polyaniline, polyacetylene, and polypyrrole have been widely studied (Ahuja et al., 2007). Electrochemically polymerized conducting polymers have a remarkable ability to switch between conducting oxidized (doped) and insulating reduced (undoped) states, which is the basis for several applications (Rajesh et al., 2004).

Nanosensors containing carbon black and polyaniline developed by Arshak et al. (2007) have been demonstrated to be able to detect and identify three foodborne pathogens by producing a specific response pattern for each microorganism.

4.3 O₂ sensors

There has been an increasing interest to develop non-toxic and irreversible O₂ sensors to assure O₂ absence in oxygen-free food packaging systems, such as packaging under vacuum or nitrogen.

Lee et al. (2005) developed an UV-activated colorimetric O₂ indicator which uses TiO₂ nanoparticles to photosensitize the reduction of methylene blue (MB) by triethanolamine in a polymer encapsulation medium using UVA light. Upon UV irradiation, the sensor bleaches and remains colorless until it is exposed to oxygen, when its original blue color is restored. The rate of color recovery is proportional to the level of oxygen exposure.

Gutiérrez-Tauste et al. (2007) deposited MB/TiO₂ nanocomposite thin films on glass by liquid phase deposition (LPD), a soft chemical technique which has been applied to deposition of oxides to several substrates. This technique could be used to develop an O₂ indicator packaging system for a variety of oxygen-sensitive foods.

Mills & Hazafy (2009) used nanocrystalline SnO₂ as a photosensitizer in a colorimetric O₂ indicator comprising a sacrificial electron donor (glycerol), a redox dye (MB), and an encapsulating polymer (hydroxyethyl cellulose). Exposure to UVB light led to activation (photobleaching) of the indicator and photoreduction of MB by the SnO₂ nanoparticles. The color of the films varied according to O₂ exposure - bleached when not exposed, and blue upon exposed.

5. Final considerations

Nanotechnology has demonstrated a great potential to provide important changes in the food packaging sector. Nanocomposites are promising to expand the use of biodegradable polymers, since the addition of nanoreinforcements has been related to improvements in overall performance of biopolymers, making them more competitive in a market dominated

by nonbiodegradable materials. Moreover, several nanostructures can be useful to provide active and/or “smart” properties to food packaging systems, as exemplified by antimicrobial properties, oxygen scavenging ability, enzyme immobilization, or indication of the degree of exposure to some detrimental factor such as inadequate temperatures or oxygen levels. So, nanocomposites may not only be used to passively protect foods against environmental factors, but also to incorporate desirable properties to the packaging system so it may actually enhance stability of foods, or at least to indicate their eventual inadequation to be consumed.

However, there are important safety concerns about nanotechnology applications to food contact materials. On the one hand, the properties and safety of most starting materials in their bulk form are usually well known. Nano-sized counterparts frequently exhibit different properties from those found at the macro-scale, because the very small sizes of the former, in principle, would allow them to move through the body more freely than larger particles, while their high surface area increases their reactivity, although they form large aggregates in most conditions. There is limited scientific data about migration of nanostructures from packaging materials into food, but because of their tiny dimensions it is reasonable to assume that migration may occur. Few studies have been conducted to assess the risks associated to the presence of such extremely small particles, some of them biologically active, in the human body or dispersed in the environment. Hence, significant research is still required to evaluate the potential toxicity of nanotechnology products, as well as the environmental safety of their use.

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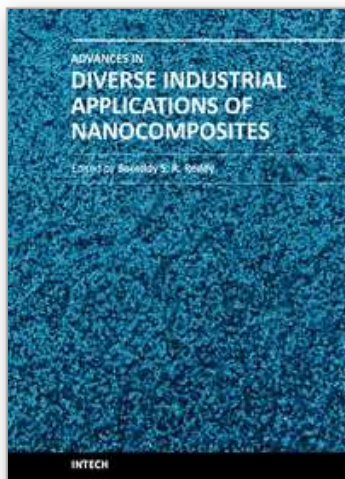
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Nanocomposites are attractive to researchers both from practical and theoretical point of view because of combination of special properties. Many efforts have been made in the last two decades using novel nanotechnology and nanoscience knowledge in order to get nanomaterials with determined functionality. This book focuses on polymer nanocomposites and their possible divergent applications. There has been enormous interest in the commercialization of nanocomposites for a variety of applications, and a number of these applications can already be found in industry. This book comprehensively deals with the divergent applications of nanocomposites comprising of 22 chapters.

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Phone: +385 (51) 770 447
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中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

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