

Potential perspectives of bio-nanocomposites for food packaging applications

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Research and development of bio-nanocomposite materials for food applications such as packaging and other food contact surfaces is expected to grow in the next decade with the advent of new polymeric materials and composites with inorganic nano-particles. This article reviews different types of new bio-based materials, such as edible and biodegradable nanocomposite films, their commercial applications as packaging materials, regulations and future trends. Special emphasis is given to the advantages of nanotechnology application in order to improve the mechanical and oxidation stability, the barrier properties, and eventually the biodegradability of conventional polymeric matrices.

Introduction

The use of protective coatings and suitable packaging by the food industry has become a topic of great interest because of their potentiality for increasing the shelf life of many food products (Ahvenainen, 2003; Coles, McDowell, & Kirwan, 2003; Giles & Bain, 2001; Hernandez, Selke, & Cultler, 2000). By means of the correct selection of

materials and packaging technologies, it is possible to keep the product quality and freshness during the time required for its commercialization and consumption (Brown, 1992; Stewart, Tompkin, & Cole, 2002).

Nowadays, the largest part of materials used in packaging industries are produced from fossil fuels and are practically *un-degradable*. For this, packaging materials for foodstuff, like any other short-term storage packaging material, represent a serious global environmental problem (Kirwan & Strawbridge, 2003). A big effort to extend the shelf life and enhance food quality while reducing packaging waste has encouraged the exploration of new bio-based packaging materials, such as edible and biodegradable films from renewable resources (Tharanathan, 2003). The use of these materials, due to their biodegradable nature, could at least to some extent solve the waste problem.

However, like conventional packaging, bio-based packaging must serve a number of important functions, including containment and protection of food, maintaining its sensory quality and safety, and communicating information to consumers (Robertson, 1993).

Unfortunately, so far the use of biodegradable films for food packaging has been strongly limited because of the poor barrier properties and weak mechanical properties shown by natural polymers. For this reason natural polymers were frequently blended with other synthetic polymers or, less frequently, chemically modified with the aim of extending their applications in more special or severe circumstances (Guilbert, Cuq, & Gontard, 1997; Petersen *et al.*, 1999).

Great attention has recently emerged around the hybrid organic–inorganic systems and, in particular to those in which layered silicates are dispersed at a nanometric level in a polymeric matrix (Giannelis, 1996). Such nano-hybrid composites possess very unusual properties, very different from their microscale counterparts. They often show improved mechanical and oxidation stability, decreased solvent uptake, self-extinguishing behaviour and, eventually, tuneable biodegradability (Alexandre & Dubois, 2000; Sinha Ray & Bousmina, 2005; Sinha Ray & Okamoto, 2003).

The application of nanocomposites promises to expand the use of edible and biodegradable films (Lagarón *et al.*, 2005; Sinha Ray & Bousmina, 2005). It will help to reduce the packaging waste associated with processed foods and will support the preservation of fresh foods, extending their

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shelf life (Labuza & Breene, 1988; Vermeiren, Devlieghere, Van Beest, de Kruijf, & Debevere, 1999).

In addition, inorganic particles may be used to introduce multiple functionalities like colour and odours but also to act as reservoirs for the controlled release functions of drugs or fungicides (Lee, An, Park, & Lee, 2003; Lee & Fu, 2003; Li, He, Evans, & Duan, 2004a; Li, He, Evans, & Duan, 2004b).

Numerous food researchers are working with the aim to improve delivery of medicines or fragile micronutrients in the everyday foods by creating tiny edible capsules, or nano-particles that release their contents on demand at targeted spots in the body. It is thought to provide significant health benefits, such as reduced risk of heart attack, stroke, neurodegenerative diseases and cancer (Koo, Rubinstein, & Onyuksel, 2005; Yan & Gilbert, 2004).

Although promising results were obtained, the road to successful bio-nanocomposites is still long. Nanotechnologies promise many stimulating changes to enhance health, wealth and quality of life, while reducing the environmental impact.

This paper highlights some recent results on the use of nanocomposites for bio-based packaging. The various biodegradable nanocomposites reported, the analysis of their potentiality and the problems associated with this new emerging area are discussed.

Nanocomposite properties and applications

Polymer composites are mixtures of polymers with inorganic or organic additives having certain geometries (fibres, flakes, spheres, particulates). The use of nanoscale fillers is leading to the development of polymer nanocomposites and represents a radical alternative to these conventional polymer composites (Alexandre & Dubois, 2000; Giannelis, 1996; Sinha Ray & Okamoto, 2003). This new generation of composites exhibits significant improvements in modulus, dimensional stability and solvent or gas resistance with respect to the pristine polymer. Nanocomposites also offer extra benefits like low density, transparency, good flow, better surface properties and recyclability. It is worth recalling that all these improvements are obtained at very low filler contents (generally lower than 5%).

The enhancement of many properties resides in the fundamental length scales dominating the morphology and properties of these materials. The inorganic particles have at least one dimension in the nanometer (from 1 to 100 nm) range. It means that a uniform dispersion of these particles can lead to ultra-large interfacial area between the constituents. The very large organic/inorganic interface alters the molecular mobility, the relaxation behaviour and the consequent thermal and mechanical properties of the resulting nanocomposite material.

Various inorganic nano-particles have been recognized as possible additives to enhance the polymer performance. Some examples of these particles are represented by the solid layered, the synthetic polymer nano-fibres, the

cellulose nano-whiskers and the carbon nanotube. Among these, up to now only the layered inorganic solids like clay have attracted some attention by the packaging industry. This is not only due to their availability and low cost but also due to their significant enhancements and relative simple processability.

The first successful example of a polymer–clay hybrid, developed at Toyota Central Research Laboratories in 1986 (Kawasumi, 2004), was a nylon–clay hybrid. The characteristic feature of clay minerals is the stacked arrangement of negatively charged silicate layers with a thickness of about 1 nm and lateral extensions of about 100 μm . The negative surface charge results from isomorphous substitution of Si^{4+} for Al^{3+} or Al^{3+} for Mg^{2+} in the silicate layer and it is compensated by inorganic cations, such as Na^+ located in the domains between adjacent layers (Fig. 1). An organophilic clay (OMLS) is obtained if the sodium ions are replaced by long-chain organic cations, such as alkylammonium ions, alkylphosphonium ions or protonated amino acids. Synthetic layered silicates, such as hectorite, fluoromica, saponite or magadiite, can also be used as the starting material for the preparation of these organo-clays.

Layered double hydroxides (LDHs) represent another interesting class of capable nano-fillers for polymers (Fischer, Gielgens, & Koster, 1999; Wei, Shi, Wang, Li, & Duan, 2004). LDH particles are constituted by magnesium–aluminium hydroxide layers. In contrast to layered silicates the hydroxide layers display a positive surface charge which is counterbalanced by anions located in the domains between adjacent layers (De Roy, 1998; Labajos, Rives, & Ulibarri, 1992).

Two major steps are involved in solid layered dispersion in polymers: intercalation and exfoliation. In the intercalation step, the spacing between individual layers, called *d*-spacing, increases from its intrinsic value as polymer chains or monomer molecules diffuse into the clay galleries.

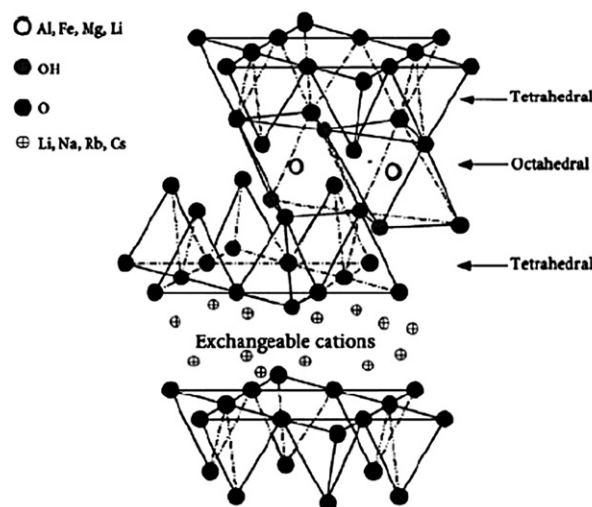


Fig. 1. The structure of 2:1 layered silicates.

In an intercalated state, the inorganic layers remain parallel to each other; in exfoliation, the individual clay particles are separated from the intercalated tactoids and are dispersed in the matrix polymer with no apparent inter-particle interactions. Whether a mixture of polymer and organic modified nano-particles produces an exfoliated or intercalated nanocomposite critically depends on the characteristics of the polymer matrix and the organic modifiers. These characteristics include the nature of the polymer as well as the type, packing density, and the size of the organic modifiers on the inorganic surface (Alexandre & Dubois, 2000; Pantoustier *et al.*, 2001). The organic component of the organo-clay or modified hydrotalcite, in fact, increases significantly the compatibility between the polymer and the filler. The surface of the silicate or hydrotalcite layers, therefore, becomes accessible to the polymer chains and intercalation or full delamination (exfoliation) of the filler particles can occur during the mixing of the filler with the polymer.

Generally, intercalation of polymer chains into the inorganic galleries is done by using one of the following two approaches: insertion of suitable monomers in the galleries and subsequent polymerization or direct insertion of polymer chains into the galleries from either solution or the melt (Fig. 2).

In the first approach, also identified as “*in situ* polymerization”, the nano-filler is swollen within the liquid monomer so as the polymer formation can occur between the intercalated sheets. Polymerization can be initiated by heat or radiation, by the diffusion of a suitable initiator, or by an organic initiator or catalyst fixed through cationic exchange inside the interlayer before the swelling step by the monomer (Sinha Ray & Okamoto, 2003; Lepoittevin *et al.*, 2002).

In the second approach, the layered inorganic is mixed with the polymer matrix in either the molten state or a solvent in which the polymer is soluble. Under these conditions, and if the layer surfaces are sufficiently compatible with the chosen polymer, the polymer can crawl into the interlayer space and form either an intercalated or an exfoliated nanocomposite.

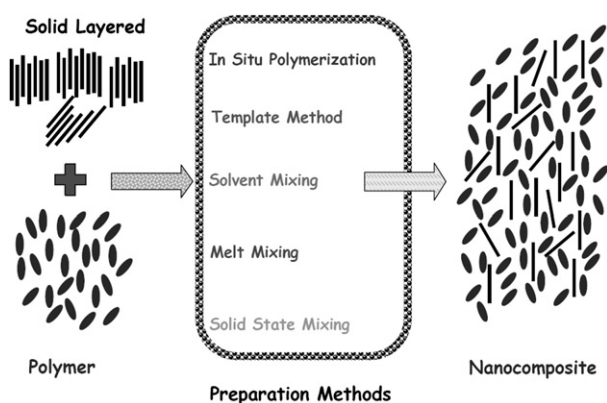


Fig. 2. Preparation methods of polymer nanocomposites.

An alternative route is represented by the template method, widely used for the synthesis of double-layer hydroxide-based nanocomposites (De Roy, 1998; Oriakhi, Farr, & Lerner, 1997; Wilson *et al.*, 1999). However it is less developed for layered silicates.

In the case of the natural polymers the choice of the suitable method for the preparation of nanocomposites is limited by the processing possibilities of the natural materials. Since nature itself produces the possible matrix polymers, only blending/compounding with suitable inorganic particles, either in the melt or in solution is an accessible manufacturing possibility. Recently, a new alternative method for the preparation of nanocomposites, which involves a solid-state mixing at room temperature (ball milling) (Mangiacapra, Gorrasi, Sorrentino, & Vittoria, 2005; Sorrentino *et al.*, 2005) was proposed. In this case, solid layered dispersion was promoted by the energy transfer between milling tools (generally balls) and polymer/inorganic particles mixture, which in turn results grinded and intimately mixed. Among the available techniques used for nanocomposites preparation, ball milling has the considerable advantage of not requiring the use of high temperature or solvent treatments.

Biodegradable nanocomposites

The extraordinary success of the nanocomposite concept in the area of synthetic polymers has stimulated new research on nanocomposites based on biodegradable polymers as matrix.

Biodegradable plastics are polymeric materials in which at least one step in the degradation process is through metabolism in the presence of naturally occurring organisms. Under appropriate conditions of moisture, temperature and oxygen availability, biodegradation leads to fragmentation or disintegration of the plastics with no toxic or environmentally harmful residue (Chandra & Rustgi, 1998).

Biodegradable polymers can be classified according to their source:

- 1 Polymers directly extracted or removed from biomass (i.e. polysaccharides, proteins, polypeptides, polynucleotides).
- 2 Polymers produced by classical chemical synthesis using renewable bio-based monomers or mixed sources of biomass and petroleum (i.e. polylactic acid or bio-polyester)
- 3 Polymers produced by micro-organism or genetically modified bacteria (polyhydroxybutyrate, bacterial cellulose, xanthan, curdian, pullan).

Detailed description of biopolymers may be found in numerous review papers and books (Doi & Steinbuechel, 2002; Kaplan, 1998; Mohanty, Misra, & Drzal, 2005; Steinbuechel, 2003). In the following, we will refer to the common bio-based polymers of potential interest for packaging industry. Several applications of bio-based packaging

as well as edible films and coatings are reported in literature. However, producers of packaging materials and manufacturers of food products have not yet demonstrated their interest because of the problems related with the application of these materials (Krochta & De Mulder-Johnston, 1997).

The problems associated with biodegradable polymers are threefold: performance, processing, and cost. Although these factors are somewhat interrelated, problems due to “performance and processing” are common to all biodegradable polymers in spite of their origin (Scott, 2000; Trznadel, 1995). In particular, brittleness, low heat distortion temperature, high gas and vapour permeability, poor resistance to protracted processing operations have strongly limited their applications.

The application of nanotechnology to these polymers may open new possibilities for improving not only the properties but also the same time the cost-price-efficiency.

Owing to the nanometer-size particles obtained by dispersion, these nanocomposites can exhibit markedly improved mechanical, thermal, barrier and physico-chemical properties, when compared with the starting polymers and conventional (microscale) composites. In particular, they show great promise in providing excellent barrier properties, due to the presence of the clay layers able to delay the molecule pathway making the diffusive path more tortuous (Bharadwaj, 2001; Neilsen, 1967; Sorrentino, Gorrasi, Tortora, & Vittoria, 2006; Sorrentino, Gorrasi, Tortora, Vittoria, & Costantino, 2006) (Fig. 3).

Recently, several research groups started the preparation and characterization of various kinds of biodegradable polymer nanocomposites showing properties suitable for a wide range of applications (Sinha Ray & Bousmina, 2005). So far, the most studied biodegradable nanocomposites suitable for packaging applications are starch and derivatives, polylactic acid (PLA), poly(butylene succinate) (PBS), polyhydroxybutyrate (PHB), and aliphatic polyester as PCL.

Starch and derivatives

Starch is a promising raw material because of its cyclic availability from many plants, its rather excessive

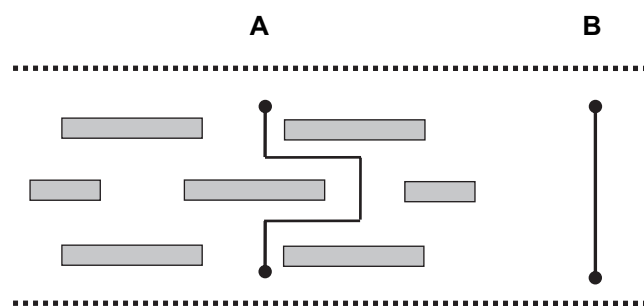


Fig. 3. Schematic illustration of the tortuosity for a diffusing penetrant introduced on exfoliating solid layered in a polymer matrix. (A) Filled polymer and (B) Unfilled polymer.

production with regard to current needs and its low cost (Gonera & Cornillon, 2002; Smits, Ruhnau, & Vliegenhart, 1998). It is known to be completely degradable in soil and water and can promote the biodegradability of a non-biodegradable plastic when blended. As a packaging material, starch alone does not form films with appropriate mechanical properties unless it is first plasticized, or chemically modified. Common plasticizers for hydrophilic polymers, such as starch, are glycerol and other low molecular weight polyhydroxy compounds, polyethers, urea and water. When starch is treated in an extruder by application of both thermal and mechanical energy, it is converted to a thermoplastic material. In the production of thermoplastic starches, plasticizers are expected to efficiently reduce intra-molecular hydrogen bonds and to provide stability to product properties. There are many opportunities for using starch as packaging material (Kim & Pometto, 1994). Due to its hygroscopic nature, starch-based absorbent pads are expected to provide a potential alternative to conventional absorbent for meat exudation (Smith, Hoshino, & Abe, 1995). As films or bag, starch could be employed as packaging for fruits and vegetables, snacks or dry products. In these applications, however, efficient mechanical, oxygen and moisture protection is needed. Thermoplastic starch (TPS) alone often cannot meet all these requirements. In particular, because of the hydrophilicity of the starch the performance changes during and after processing, due to the water content changes. To overcome this drawback, many different routes have been reported.

Clay, as potential filler, has been chosen for improving the properties of TPS in such applications (Chen & Evans, 2005; De Carvalho, Curvelo, & Agnelli, 2001; McGlashan & Halley, 2003; Park *et al.*, 2002; Wilhelm, Sierakowski, Souza, & Wypych, 2003; Yoon & Deng, 2006). It has been shown that both the tensile strength and the elongation at break of TPS were increased with the presence of small amounts (less than 5%) of sodium montmorillonite (Park *et al.*, 2002). In addition, the decomposition temperature was increased while the relative water vapour diffusion coefficient of TPS was decreased (Park, Lee, Park, Cho, & Ha, 2003).

Recently, starch/clay nanocomposite films were obtained by dispersing montmorillonite nano-particles via polymer melt processing techniques (Avella *et al.*, 2005). Mechanical characterization results show an increase of modulus and tensile strength. In addition, the conformity of the resulting material samples with actual (2005) regulations and European directives on biodegradable materials was verified by migration tests (Avella *et al.*, 2005).

PLA and PHB

The use of conventional chemical synthesis for the production of polymers gives a wide spectrum of possible biopolyesters. To date, polylactic acid is the polymer with the highest potential for a commercial major scale production of renewable packaging materials. Lactic acid, the

monomer of polylactic acid (PLA), may easily be produced by fermentation of carbohydrate feedstock. The carbohydrate feedstock may be agricultural products such as maize, wheat, molasses, whey. The properties of the PLA material are highly related to the ratio between the two forms (L or D) of the lactic acid monomer. L-PLA is a material with a very high melting point and high crystallinity, whereas a mixture of D- and L-PLA results in an amorphous polymer with a low glass transition temperature.

Polyhydroxybutyrate (PHB) is accumulated by a large number of bacteria as energy and carbon reserves. Due to its biodegradability and biocompatibility this bio-polyester may easily find industrial applications (Van der Walle, Buisman, Weshuis, & Eggink, 2000). PHB is a typical highly crystalline thermoplastic with a very low water vapour permeability which is close to that of low density polyethylene (LDPE). The major drawback for the commercial use of the PHB homopolymer is represented by an unfavorable ageing process.

Potentially, PLA and PHB offer numerous opportunities in packaging applications. They can be formed into films or used to make moulded objects. In addition, they are compatible with many foods, such as dairy products, beverage, fresh meat products and ready meals.

So far, the large-scale use of biodegradable polyesters (PHB, PLA) as packaging material is hampered by their high cost as well as their low performances.

Also, in this case, the use of nanometric filler promises to expand its application. Many papers (Chang, Uk-An, & Sur, 2003; Chen, Hao, Guo, Song, & Zhang, 2004; Choi, Kim, & Kim, 1997; Liu, Yang, Wang, Dong, & Liu, 2002; Maiti, Batt, & Giannelis, 2003; Ogata, Jimenez, Kawai, & Ogihara, 1997; Park, Choi, Lim, Shin, & Jhon, 2001; Paul et al., 2003; Pluta, Galeski, Alexandre, Paul, & Dubois, 2002; Sinha Ray, Maiti, Okamoto, Yamada, & Ueda, 2002; Sinha Ray, Okamoto, Maiti, & Okamoto, 2002; Sinha Ray, Okamoto, & Okamoto, 2003; Sinha Ray, Yamada, Ogami, Okamoto, & Ueda, 2002; Sinha Ray, Yamada, Okamoto, Ogami, & Ueda, 2003; Sinha Ray, Yamada, Okamoto, & Ueda, 2002) report the use of PHB and PLA for the preparation of polymer/clay nanocomposite materials.

Bandyopadhyay, Chen, and Giannelis (1999) reported the preparation of PLA–clay nanocomposites with much improved mechanical and thermal properties. Instead, the formation of nanocomposite materials from PHB seems to be difficult, and rather moderate improvements in properties have been reported in the case of PHB as matrix material (Maiti et al., 2003).

Solvent casting of mixtures of PLA and organophilic clay in chloroform resulted in materials with an enhanced crystallization tendency and increased Young's modulus (Ogata et al., 1997). However, the glass transition temperature increases only slightly with increasing clay content. This may be due to the micro-composite structure rather than nanocomposite structure. As a matter of fact, a strong tendency of tactoids formation was observed.

The PLA/layered silicate nanocomposites, prepared by simple melt extrusion, exhibited remarkable improvement of material properties in both solid and melt states compared to the matrix without clay (Sinha Ray, Okamoto, et al., 2002).

Nanocomposites of the aPLA and aPLA/PCL blends were obtained by melt-mixing with a properly modified kaolinite (Cabedo, Feijoo, Villanueva, Lagaron, & Gimenez, 2006). Also, in this case, all nanocomposites showed an improvement in the gas barrier, mechanical and thermal properties with regard to the polymers and blends without clay.

Polycaprolactone

Polycaprolactone (PCL) is linear polyester manufactured by ring-opening polymerization of ϵ -caprolactone. It is a semicrystalline polymer with a high degree of crystallinity (around 50%). PCL exhibits high elongation at break and low modulus. Its physical properties and commercial availability make it very attractive as a material for commodity applications. PCL is also interesting for applications in the medical and agricultural areas (Nakayama et al., 1997). Due to its low melting point, in conventional applications it must be blended with other polymers (Ishaku, Pang, Lee, & Ishak, 2002; Lee et al., 2002; Lim, Hyun, Choi, & Jhon, 2002; Kesel, Wauven, & David, 1997). Many research groups worked on the preparation of PCL/organically modified layered silicate (OMLS) nanocomposites with better physical properties (Gorrasi, Tortora, Vittoria, Galli, & Chiellini, 2002; Gorrasi et al., 2004; Messersmith & Giannelis, 1993; Messersmith & Giannelis, 1995; Kojima et al., 1993; Utracki, Simha, & Garcia-Rejon, 2003; Tortora, Vittoria, Galli, Ritrovati, & Chiellini, 2002; Usuki et al., 1993; Bharadwaj et al., 2002). Di, Iannace, Di Maio, and Nicolais (2003) reported the preparation of melt PCL/OMLS nanocomposites using two different types of OMLS. The thermal and rheological behaviour of the prepared nanocomposites was investigated and analyzed in terms of processing conditions and types of OMLS.

Gorrasi et al. (2002, 2003) reported studies on the correlation between morphology and vapour barrier properties of PCL/montmorillonite (MMT) composites. They prepared different compositions of PCL/OMLS nanocomposites by melt blending or catalyzed ring-opening polymerization of caprolactone. Micro-composites were obtained by direct melt blending of PCL and pristine MMT. Exfoliated nanocomposites were obtained by *in situ* ring-opening polymerization of CL with an OMLS by using dibutyltin dimethoxide as an initiator/catalyst. Intercalated nanocomposites were formed either by melt blending with OMLS or *in situ* polymerization within pristine MMT. The barrier properties were studied for water vapour and dichloromethane as an organic solvent. The sorption (S) and the zero concentration diffusion coefficients (D_0) were evaluated for both vapours. The water sorption increases with increasing the MMT content, particularly for the micro-composites containing the unmodified MMT. The thermodynamic diffusion

parameters, D_0 , were compared to the value of the parent PCL: both micro-composites and intercalated nanocomposites show diffusion parameters very near to PCL. At variance, exfoliated nanocomposites show much lower values, even for small MMT content. In the case of organic vapour, the value of sorption at low relative pressure is mainly dominated by the amorphous fraction present in the samples, not showing any preferential adsorption on the inorganic component. At high relative pressure the isotherms showed an exponential increase of sorption, due to plasticization the polyester matrix. The D_0 parameters were also compared to those of the unfilled PCL; in this case, both exfoliated and intercalated samples showed lower values, due to a more tortuous path for the penetrating molecules (Fig. 4).

In exfoliated nanocomposites filled with layered silicates of high aspect ratio, generally all the mechanical properties (resistance to impact, Young's modulus, flexural modulus and heat distortion temperature) appear to be substantially enhanced. The creation of a three-dimensional network of interconnected long silicate layers could be a possible explanation for such improvement. This behaviour was also constantly observed in all the bio-based nanocomposites analyzed up to now (Sinha Ray & Bousmina, 2005; Sinha Ray & Okamoto, 2003; Jimenez, Ogata, Kawai, & Ogihara, 1997). It suggests that this material can replace the conventional supporting matrix in applications where the mechanical resistance is required.

The bio-based packaging should efficiently biodegrade after a defined period without changes in mechanical and/or barrier properties.

The incorporation of inorganic particles into biopolymeric matrix is not only suitable for significant improvement of the physical properties of the virgin polymers, but also suitable to enhance their rate of biodegradation. The biodegradability of a biopolymer in nanocomposites completely depends on both the nature of pristine layered silicates and surfactants used for the modification of layered silicate, so it is possible to control the biodegradability of several biopolymers via judicious choice of organically modified layered silicate. Details regarding the mechanism of

biodegradability in nanocomposites can be found in relevant literature (Ishiaku *et al.*, 2002; Sinha Ray, Maiti, *et al.*, 2002; Sinha Ray & Okamoto, 2003; Pandey, Reddy, Kumar, & Singh, 2005).

Antimicrobial packaging is gaining interest from researchers and industry due to its potential to provide quality and safety benefits (Cha & Chinnan, 2004; De Jong *et al.*, 2005). The rationale for incorporating antimicrobials into the packaging is to prevent surface growth in foods where a large portion of spoilage and contamination occurs (Appendini & Hotchkiss, 2002; LaCoste, Schaich, Zumbrunnen, & Yam, 2005). This approach can reduce the addition of larger quantities of antimicrobials that are usually incorporated into the bulk of the food. A controlled release from packaging film to the food surface has numerous advantages over dipping and spraying. In the latter processes, in fact, antimicrobial activity may be rapidly lost due to inactivation of the antimicrobials by food components or dilution below active concentration due to migration into the bulk food matrix (Halek & Garg, 1989; Han & Floros, 1997; Ming, Weber, Ayres, & Sandine, 1997; Padgett, Han, & Dawson, 1998; Vermeiren, Devlieghere, & Debevere, 2002; Weng & Chen, 1997). In recent years, layered materials have received considerable attention as drug delivery vehicle. Because the release of drugs in drug-intercalated layered materials is potentially controllable, these new materials have a great potential as a delivery host in the pharmaceutical field (Costantino & Nocchetti, 2001; Khan, Lei, Norquist, & O'Hare, 2001; Lavan, McGuire, & Langer, 2003; Suzuki, Nakamura, Watanabe, & Kanzaki, 2001; Tajima, Suzuki, Watanabe, & Kanzaki, 2005; Donga & Feng, 2005).

An innovative procedure was proposed by Barra, Gorrasi, and Vittoria (2006). In particular, they anchored an antimicrobial molecule, benzoic acid, on an Mg/Al layered double hydroxide, through ionic bonds, followed by incorporation into a PCL matrix. Fig. 5 shows the release kinetics of the sodium benzoate directly incorporated into

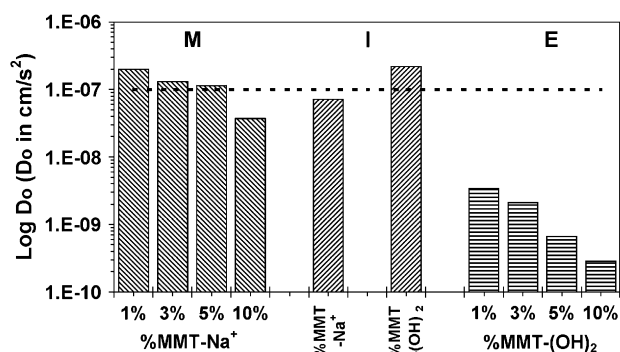


Fig. 4. Diffusivity of water vapour, as function of clay content, for the PCL micro-composite (M), the PCL exfoliated nanocomposites (E) and the 3 wt% PCL intercalated nanocomposites (I) (from Gorrasi *et al.*, 2003).

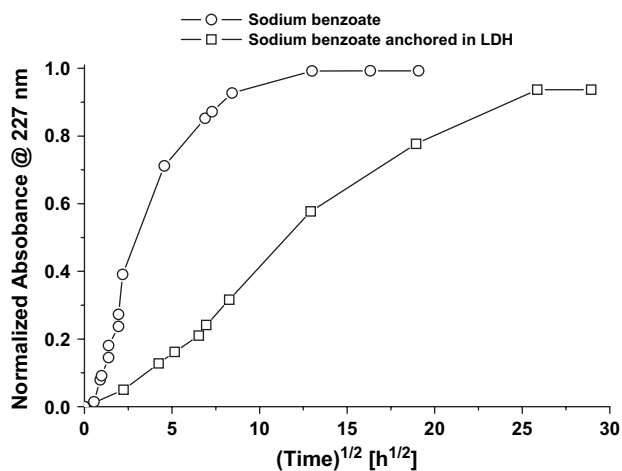


Fig. 5. Diffusion profiles for Benzoate into water.

the polycaprolactone (PCL) by solvent casting method, and the release of the benzoate ionically bonded to magnesium–aluminium hydroxalate (LDH) and blended with the PCL. It is clearly evident that the release of the molecule (chosen as model antimicrobial molecule) from the lamellar solid incorporated into the polymeric matrix is very much slower than the release of the same simply blended to the PCL. As consequence of this, such systems are very promising in the active packaging field.

Edible nanocomposite-based material

Edible films and coatings are defined as thin, continuous layers of edible material used as a coating or as a film placed between food components to provide a barrier to mass transfer (Balasubramaniam, Chinnan, Mallikarjunan, & Philips, 1997; Guilbert *et al.*, 1997). They essentially differ in the mode of formation and application to foods. Edible coatings are applied and formed directly on the food product either by addition of a liquid film-forming solution or by molten compounds. They may be applied with a paintbrush, by spraying, dipping or fluidizing. In other words, edible coatings form an integral part of the food product and hence should not impact the sensory characteristics of the food (Baldwin, Nisperos, Chen, & Hagenmaier, 1996; Banks, 1985; Bender, Brecht, Sargent, Navarro, & Campbell, 1993). Edible films, in contrast, are freestanding structures, formed and then applied to foods. They are formed by casting or by traditional plastic processing techniques, such as extrusion (Baldwin, 1994; Park, Testin, Vergano, Park, & Weller, 1996).

Components of edible films and coatings can be divided into two categories: water-soluble polysaccharides (hydrocolloids) and lipids. Suitable polysaccharides include cellulose derivatives, alginates, pectins, starches, chitosan and other polysaccharides (Ayranci & Tunc, 1997; El Ghaouth, Arul, Ponnampalam, & Boulet, 1991). It should be noted, however, that great differences exist in how easily these substances can form films of good integrity (Park, Chinnan, & Shewfelt, 1994).

Because of the diverse capabilities and the huge chemistry, technology and applications of the water-soluble polysaccharides, often referred to as gums or hydrocolloids, the reader is referred to the books written by Aspinall (1970), Glicksman (1984) and Wurzburg (1986).

Hydrocolloids serve numerous diverse roles such as providing hardness, crispness, compactness, thickening quality, viscosity, adhesiveness, gel-forming ability and mouth-feel (Whistler & Daniel, 1990).

Many lipid compounds such as animal and vegetable fats have been used to make edible films and coatings. Suitable lipids include waxes, acylglycerols, and fatty acids. Lipid films have excellent moisture barrier properties or as coating agents for adding gloss to confectionery

products. Waxes are commonly used for coating fruits and vegetables to retard respiration and lessen moisture loss (Avena-Bustillos, Cisneros-Zevallos, Krochta, & Saltveit, 1994; Avena-Bustillos, Krochta, Saltveit, Rojas-Villegas, & Saucedo-Perez, 1994).

Acetylated monoglycerides are frequently added to wax formulations to add pliability to the coating (Avena-Bustillos, Krochta, & Saltveit, 1997). Coatings to sucrose fatty acid esters are effective moisture barriers for maintaining the crispness of snack foods (Kester & Fennema, 1989) and for extending the shelf life of apples (Drake, Fellman, & Nelson, 1987).

Many lipids exist in a crystalline form and their individual crystals are highly impervious to gases and water vapour (Greener & Fennema, 1989b; Kamper & Fennema, 1984). Since the permeant can pass between crystals, the barrier properties of crystalline lipids are highly dependent on the intercrystalline packing arrangement. Although fatty acids and fatty alcohols are effective barriers to water vapour, their fragility requires their use in conjunction with a supporting matrix.

Sometimes, composite films can be formulated to combine the advantages of the lipid and hydrocolloid components and lessen the disadvantages of each (Greener & Fennema, 1989a; Kamper & Fennema, 1984).

Even if edible films have been extensively studied and applied, up to now only few research works indicate the possibility of incorporation nano-particles in order to improve the physical properties of these materials. The paper of Mangiacapra *et al.* (2005) demonstrated the possibility to lower the diffusion of oxygen by adding clay montmorillonite into pectins. Similarly, Zheng, Li, Ma, and Yao (2002) reported a considerable improvement of the physical properties in nanocomposites prepared by gelatine and montmorillonite. An appreciable increase in stability of chitosan/layered nanocomposites was also reported (Darder, Colilla, & Ruiz-Hitzky, 2003).

Despite the lack of specific literature data, there is sufficient evidence to establish the beneficial effects of inorganic nano-filler on these materials, among which there are improved retention of flavour, acids, sugars, texture and colour, increased stability during shipping and storage, improved appearance and reduced spoilage.

Additionally, edible coatings and films are a viable means for incorporating food additives and other substances to enhance product colour, flavour, and texture and to control microbial growth (Siragusa & Dickson, 1992).

To this purpose, nano-particles can be used as carrier of antimicrobials and additive. Recent studies have demonstrated their ability to stabilize the additives and efficiently control their diffusion into the food as well as between different regions, i.e., surface vs. bulk of a food system. This control can be especially important for long-term storage of foods or for imparting specific desirable characteristics, such as flavour, to a food system.

Legal and ethical barriers and controversies

Nanotechnology has an extremely high potential to benefit society through applications in food packaging. It can make the products cheaper and the production more efficient. Producing less waste and using less energy. However, any new technology carries an ethical responsibility for wise application and the recognition that there are potential unforeseen risks that may come with the tremendous positive potential. In parallel to the technical evolution of nanotechnologies, it is expected that there will be new regulatory directives and guidelines to accommodate nanotechnology-based products.

At present no government has developed any regulatory regime, specifically referring to the production and application of nano-particles. Also in the frame of chemical legislation, particle size does not play a role for the registration of new substances. A lot of new knowledge has to be generated on how nano-material based processes and products may interfere with human health before any regulation in this field can be established (Borm *et al.*, 2006; Derfus, Chan, & Bhatia, 2004; Hoet, Nemmar, & Nemery, 2004; Oberdörster, 2004; Oberdörster, Oberdörster, & Oberdörster, 2005). In addition, limited eco-toxicological data for nano-materials precludes a systematic assessment of the impact of nano-particles on ecosystems (Colvin, 2003).

The ability to assess the toxicity of intentionally produced nano-materials by extrapolating from the current particle toxicological database was examined by several reports (Dreher, 2004; Swiss Report, 2004; United Kingdom Royal Society, 2004; European NanoSafe, 2004; European Commission, 2004). Their findings indicate a high degree of uncertainty in the prediction of the toxicity of such nano-materials.

Despite this lack in knowledge, a handful of food and nutrition products containing invisible and un-labeled nanoscale additives are already on supermarket shelves (Mazzola, 2003; Gaskell *et al.*, 2004). In addition, a number of pesticides containing nanoscale materials have been released in the environment and are commercially available (Moore, 2004; Paull, Wolfe, Hebert, & Sinkula, 2003).

With respect to nano-fillers discussed in this work, it is important to point out that the majority of the works present in literature make use of additives and surfactants in order to increase the compatibility between the polymer and the filler. Except for specific product developed by few companies around the world, these additives are not food contact approved as yet.

However, as stated by Lagarón *et al.* (2005): at the moment “*there is no reason to believe that material nanocomposites making use of substances in positive lists can impose any immediate risk threat for food contact applications*”.

The actual knowledge does not suggest any justification for imposing a ban on the production of nano-clays or LDHs based nanocomposites for food packaging

applications (Cole & Bergeson, 2006). However, a better knowledge of the effects of these nano-particles on the human health and environment is necessary for an adequate regulation of their use for food contact applications.

Summary

Nanocomposites concept represents a stimulating route for creating new and innovative materials, also in the area of natural polymers. Materials with a large variety of properties have been realized, and even more are due to be realized. The nanocomposite materials obtained by mixing natural polymers and sheets of crystalline solid layered (clays or LDHs), offer a great variety of property profiles. They are even able to compete, both in price and in performance, with synthetic polymeric materials in packaging.

In spite of the great possibilities existing for packaging in bio-based nanocomposite materials, the future scenario is difficult to predict. At this stage, we can only imagine that simple traditional packing will be replaced with multi-functional intelligent packaging. The next generation of packaging materials will be able to fit the requirements of preserving fruit, vegetable, beverage, wine and other foods. By adding appropriate nano-particles, it will be possible to produce packages with stronger mechanical, barrier and thermal performance. To food safety, nano-structured materials will prevent the invasion of bacteria and micro-organisms. Embedded nano-sensors in the packaging will alert the consumer if a food has gone bad.

However, it is clear that the enthusiasm for such nano-material systems must be placed against the backdrop of the proper considerations of safety for the consumers and the health-care workers, and in the context of stringent regulatory approval perspectives.

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